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X-RAY STUDIES OF SOME SULPHUR-CONTAINING ORGANIC COMPOUNDS.

by

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A thesis submitted to the University of Keele in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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June 1968.

F O R E W A R D.

In presenting this thesis I would like to record my gratitude to the following,

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and all other friends and colleagues who have contributed to this work in any way.

A B S T R A C T.

In this thesis, X-ray crystal structure analyses of the desaurin from acetophenone, 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole) and the 1,2,4-trithiacyclopentane from pinacolone, are described.

The X-ray analysis of the desaurin from acetophenone confirms the desaurin structure and shows that the molecule is the trans isomer. The 1,3-dithiete ring is planar, with carbon-sulphur bond lengths of 1.766 and 1.764Å, and a carbon-sulphur-carbon bond angle of 82.0°.

The structure of 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole) was determined employing the symbolic addition procedure, using one symbolic assignment. The sulphur-(sp^2-)carbon bond lengths are 1.748 and 1.745Å, and the sulphur-carbon-sulphur bond angle is 115.1°.

The diffraction study of the 1,2,4-trithiacyclopentane from pinacolone confirms the thrithiacyclopentane structure and shows that the molecule is a cis isomer. The heterocyclic system is non-planar; the sulphur-sulphur bond length is 2.103Å and the mean carbon-sulphur bond length is 1.740Å.

In each molecule, the α,β-unsaturated carbonyl systems adopt an s-cis conformation and this system and the sulphur atoms are approximately coplanar. The intramolecular sulphur-oxygen distances in the three molecules are considerably less than the sum of the van der Waals radii of sulphur and oxygen; similar observations in related systems have been taken as evidence of sulphur-oxygen interaction and this interpretation is discussed.

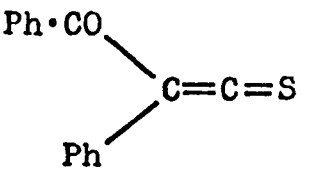
CONTENTS.

CHAPTER 1.

INTRODUCTION.

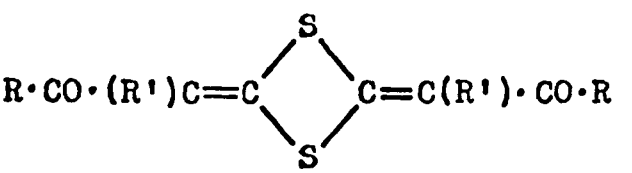
The desaurins and 1,2,4-trithiacyclopentanes.

Bergreen (1) found that when deoxybenzoin was treated with thiophosgene in the presence of sodium ethoxide, an insoluble yellow product was obtained, which he suggested was phenylbenzoylthioketen I. However Meyer (2), after a molecular weight



I

determination, proposed the dimeric structure II_a, and termed compounds of this type "desaurins" on account of their yellow



II a, R = R' = Ph.

colour. Eleven other desaurins, including the desaurin from acetophenone III, were prepared by early German workers (3,4,5,6),

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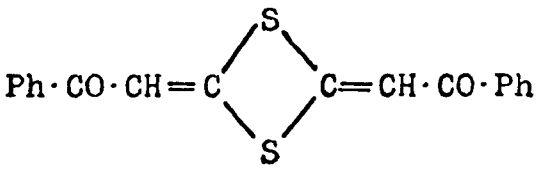
(1) H. Bergreen, Ber., 21, 337 (1888).
(2) V. Meyer, ibid., 23, 1571 (1890).
(3) Idem., ibid., 21, 353 (1888).
(4) P. Petrenko-Kritschenko, ibid., 25, 2239 (1892).
(5) C. Kelber and A. Schwarz, ibid., 45, 137 (1912).
(6) C. Kelber, ibid., 43, 1252 (1910).

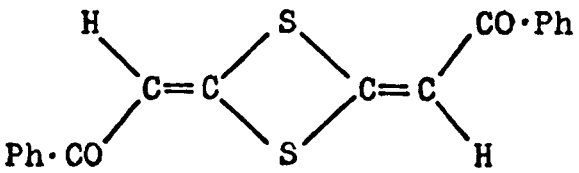
whilst a number of other such compounds have more recently been prepared by Gompper and Töpfl (7). The few original degradations



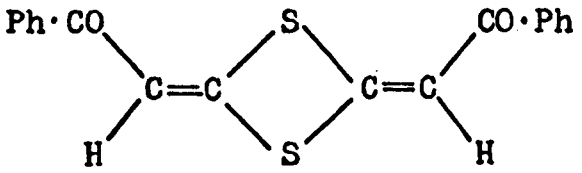
III

or other studies on the desaurins (8) provide little proof for such a novel heterocyclic system and it was not until a more recent re-examination of these compounds by Yates and Moore (9) that Meyer's structural proposal was shown to be correct.

It is evident that in the desaurins two geometrical isomers, cis and trans, are possible; thus for the desaurin from acetophenone III, the two isomers possible are IV and V. In the preparation



IV



V

of each desaurin only one geometrical isomer has been isolated; the nature of the isomer formed in each case cannot be easily ascertained except from a crystal structure analysis.

Kelber (6) and later Gompper (7) showed that oxidation

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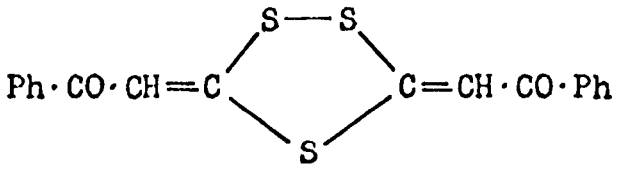
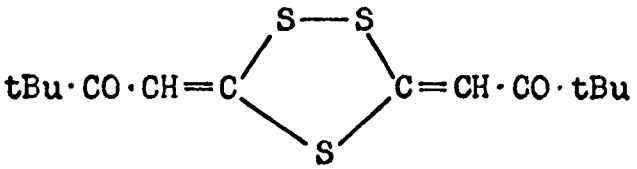
(7) R. Gompper and W. Töpfl, ibid., 95, 2871 (1962).
(8) W. Wachter, ibid., 25, 1727 (1892).
(9) P. Yates and D. R. Moore, J. Am. Chem. Soc., 80, 5577 (1958).

of benzoyldithioacetic acid with bromine or ammonium peroxydisulphate yields a yellow product, for which Gompper proposed the 1,2,4-trithiacyclopentane structure VI. By using suitable alternative ketones, various 1,2,4-trithiacyclopentanes,

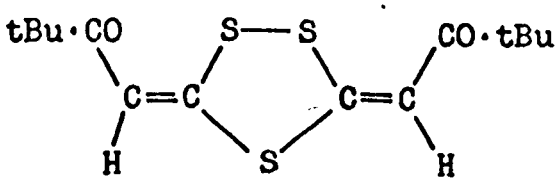


VI

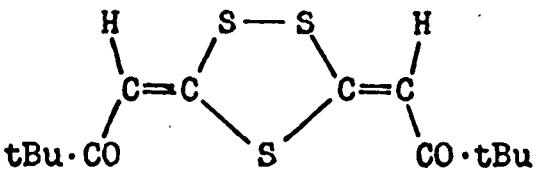


VII

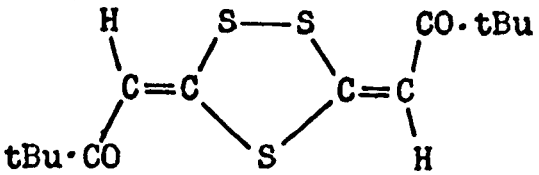
including that from pinacolone VII, have been prepared utilising the method of Gompper. For each trithiacyclopentane, three geometrical isomers, (two cis and one trans), are possible; thus for the 1,2,4-trithiacyclopentane from pinacolone VII, the three isomers are VII_a, VII_b and VII_c.



VII_a



VII_b

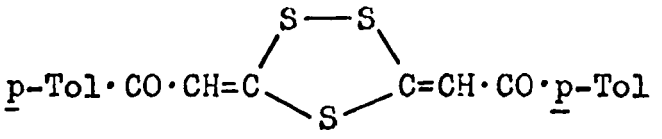


VII_c

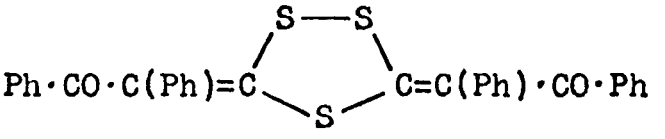
A recent extensive examination of the desaurins and 1,2,4-trithiacyclopentanes by Lynch (10), has shown that certain

(10) T. R. Lynch, Ph.D. Thesis, University of Toronto, 1966.

trithiacyclopentanes, notably those from acetophenone VI, p-methylacetophenone VIII and deoxybenzoin IX, when prepared using the



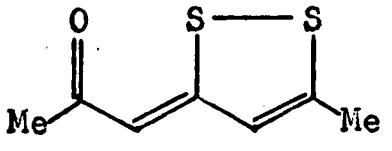
VIII



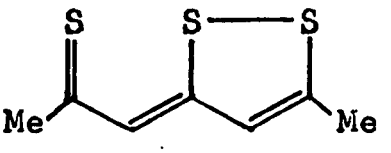
IX

method of Gompper, yield two isomeric forms, separable by fractional crystallisation. However, the preparation of the trithiacyclopentane from pinacolone yielded a single isomer, which was identified as one of the cis forms, VII_a or VII_b, on the basis of its n.m.r. spectrum.

Lynch (10) also noted that the desaurins and trithiacyclopentanes exhibit unusually weak carbonyl absorption in their infra red spectra. It is evident that if the α,β-unsaturated carbonyl systems of these compounds exist in an s-cis conformation, the possibility of sulphur-oxygen interaction arises which could account for the unusual spectral properties found. Examples of close intramolecular approach of oxygen and sulphur atoms have been previously reported. An X-ray diffraction study of 2,5-dimethyl-dithiofurophthene, X (11), showed that in spite of a remarkably short



X



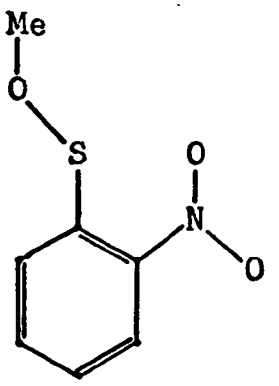
XI

sulphur-oxygen distance of 2.41Å, (the sum of the van der Waals

(11) M. Mammi, R. Bardi, G. Traverso and S. Bezzi, Nature, 192, 1282 (1961).

radii of oxygen and sulphur is taken to be 3.05Å), the molecular skeleton was planar. Attention was also drawn (11) to the close structural similarity between X and dimethyl-thiothiophthene XI, (the structure analysis of which had been previously reported (12)), and the existence of a partial sulphur-oxygen bond was proposed.

A study of the methyl ester of o-nitrobenzenesulfenic acid, XII (13), showed a non-bonded sulphur-oxygen distance of 2.44Å,



XII

which together with the planarity of the molecule, (except for the methyl group), was taken to indicate the existence of an attractive interaction between oxygen and sulphur.

X-ray diffraction studies on two compounds having some structural similarity to the desaurins and trithiacyclopentanes have recently been published≠. The structure analysis of the

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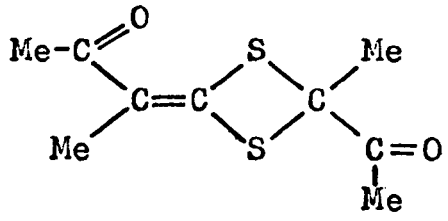
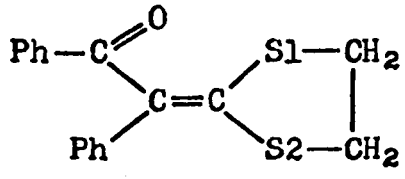
(12) S. Bezzi, M. Mammi and C. Garbulio, Nature, 182, 247 (1958).
(13) W. C. Hamilton and S. J. Laplaca, J. Am. Chem. Soc., 86, 2289 (1964).
≠ These studies were published after the structure of the desaurin from acetophenone had been reported in short note form, and we are grateful to the authors for supplying us with structural details prior to publication.

2-methylene-1,3-dithiacyclobutane derivative, XIII (14), showed



XIII

the α,β-unsaturated carbonyl system to adopt the s-cis conformation. In addition this system and the sulphur atoms were found to be approximately coplanar, (the mean deviation from the plane being 0.04Å), which resulted in a short sulphur-oxygen distance of 2.63Å. An X-ray diffraction study of 2-desylidene-1,3-dithiolane, XIV (15,16), yielded a somewhat similar result. The



XIV

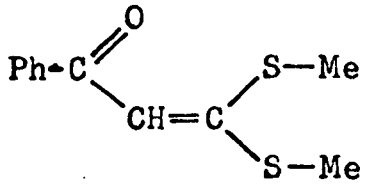
S1-C=C-C=O system is again planar and the sulphur-oxygen distance is correspondingly short at 2.70Å. In this molecule, however, the second sulphur atom, S2, is out of the least squares plane by 0.24Å.

The aims of the present work.

This thesis describes the crystal structure determinations, by single crystal X-ray diffraction methods, of the desaurin from

(14) J. A. Kapecki, J. E. Baldwin and I. C. Paul, Tetrahedron Letters, 5307 (1967).
(15) A. Tulinsky, private communication.
(16) W. H. Schmidt and A. Tulinsky, Tetrahedron Letters, 5311 (1967).

acetophenone III, the 1,2,4-trithiacyclopentane from pinacolone VII and of 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole) XV.



XV

The main purpose of the work is to confirm the desaurin and 1,2,4-trithiacyclopentane structures, to establish their stereochemistry and obtain dimensional details of the heterocyclic systems. A secondary purpose is to determine whether sulphur-oxygen interaction, which had been hypothesized from spectral data, is present. 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole) bears a structural similarity to 'half' of the molecule of the desaurin from acetophenone, and consequently it was hoped that the structure analysis would provide some interesting comparisons to be made with the desaurin structure.

CHAPTER 2.

INTRODUCTION TO THE X-RAY CRYSTALLOGRAPHIC WORK.

Since a crystal can be considered as a continuous periodic electron density distribution in three-dimensions, this density can be represented by a three-dimensional Fourier series in which the structure factors, (F_{hkl}'s), are the Fourier coefficients. The electron density at a point (x,y,z)* in the unit cell is given by,

$$\rho(x,y,z) = \frac{1}{V}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} F_{hkl}.\exp\left[-2\pi i(hx + ky + lz)\right], \qquad (2.1)$$

where V is the volume of the unit cell. The structure factor is, however, a complex quantity requiring both an amplitude and a phase to express it fully. Although the amplitude of each structure factor can be determined experimentally, the phase cannot, and therefore it is not possible to compute the electron density summation, (2.1) , solely from experimental data.

The Patterson function.

Perhaps the most widely-used method of overcoming the phase problem is by use of the Patterson function. Patterson (17,18) showed that if a Fourier summation is carried out using $|F_{hkl}|^2$ as coefficients, (which are phaseless), the resulting synthesis reveals information of the orientation and magnitudes

(17) A. L. Patterson, Phys. Rev., 46, 372 (1934).
(18) Idem., Z. Krist., 90, 517 (1935).
* Where (x,y,z) are fractional coordinates.

of interatomic vectors. The Patterson function,

$$P(u,v,w) = \sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \cos 2\pi(hu + kv + lw) \qquad (2.2)$$

exhibits peaks at vector distances, $\left[(u,v,w)\right]$, from the origin equal to vector distances between pairs of maxima in the electron density. Although it appears that the structure of any crystal can be easily solved from the Patterson function, the number of peaks in the vector map rises rapidly with the number of atoms in the unit cell; with N atoms in the unit cell there are N(N-1) interatomic vectors, each of which will contribute a peak in the vector map. The height of each Patterson peak is dependent upon the product of the scattering powers of the two atoms involved. In a multi light-atom problem, the Patterson function will therefore consist of a large number of vector peaks, each of approximately the same height. If the experimentally determined $|F_{hkl}|^2$ are used as coefficients in (2.2), these peaks are diffuse and many will coalesce making it extremely difficult to identify individual interatomic vectors. It is possible, however, to transform, (or 'sharpen'), the $|F_{hkl}|^2$ and thereby increase the resolving power of the Patterson synthesis. A simple sharpening technique (19) is to transform the experimental $|F_{hkl}|^2$ to the theoretical values, $(|{}^sF_{hkl}|^2)$, they would have been if the crystal was composed of point atoms having no thermal motion,

$$|{}^sF_{hkl}|^2 = \frac{|F_{hkl}|^2}{\sum_{i=1}^{N} f_i^2 \cdot \exp(-2B_{ov} \cdot \sin^2\theta/\lambda^2)} \qquad (2.3)$$

(19) M. J. Buerger, "Vector Space", Wiley and Sons, New York, (1959), p. 64.

where, f_i = the scattering factor of the ith atom in a unit cell containing N atoms,

B_{ov} = the overall isotropic temperature factor.

By using the sharpened coefficients, $|^s F_{hkl}|^2$, in the Patterson synthesis, the electrons of the normal peak are concentrated into a 'sharp' peak, which leads not only to better resolution but also makes the weaker peaks more prominent. One disadvantage of using sharpened coefficients in the Patterson synthesis is that the Fourier series ceases to be convergent, which can result in spurious detail being produced in the background of the synthesis. Even with the superior resolution of a sharpened Patterson function, the solution of a multi light-atom problem from its Patterson is still extremely difficult. The problem can be simplified, however, if some features of the molecular structure are known. If the molecule contains a rigid group of atoms, and the dimensions of the rigid group are known, (for example a benzene ring), the complete structure analysis can be carried out by a systematic search in the Patterson function (20,21).

Although many light atom structures have been solved in the past by either interpreting a suitable sharpened Patterson function, or by using both the Patterson and a search technique, at the present time many structures of this type are subjected to direct phase determination methods, (see later).

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(20) C. E. Nordman, Acta Cryst., 15, 18 (1962).
(21) C. E. Nordman and K. Nakatsu, J. Am. Chem. Soc., 85, 353 (1963).

The Patterson 'heavy-atom' method.

The greatest use of the Patterson synthesis is made when a small number of atoms in the unit cell are of relatively high atomic number, ('heavy'), compared with the majority. It is then possible to locate the heavy atoms easily from the Patterson function, since the vector peaks between different heavy atoms stand out predominently against the background of light atom interactions.

Having located the positions of the heavy atoms in this manner, there are then two main courses that may be followed to locate the remaining light atoms in the structure. The choice between the two methods depends upon the size of the contribution made by the heavy atoms to the structure factors. With one heavy atom per unit cell, the structure factor can be sub-divided into heavy atom, (H), and light atom, (L) contributions,

$$F_{hkl} = f_H \exp 2\pi i(hx_H + ky_H + lz_H) + \sum_{i=1}^{N-1} f_{L_i} \exp 2\pi i(hx_{L_i} + ky_{L_i} + lz_{L_i}), \quad (2.4)$$

where f_H and f_{L_i} are the scattering factor of the heavy and ith light atoms respectively.

If f_H is very much greater than f_L, the heavy atom contribution will tend to dominate the right hand side of equation (2.4), except in the relatively rare cases when all the light atoms of the residue scatter in phase to give a contribution greater than that of the heavy atom. In the case of a centrosymmetrical crystal, where all structure factors are real, the result is especially useful, as the signs of a high proportion of F_{hkl} are determined

solely from the heavy atom contribution. Allocating the phases so determined to the observed structure amplitudes allows an initial electron density synthesis to be computed. Because the $|F_{hkl}|$ data contain a light atom contribution, this synthesis, in favourable cases, will reveal light atom locations in addition to returning the heavy atom positions. Lipson and Cochran (22) suggest that the heavy atom method is most powerful, (in a centrosymmetrical structure), when the sum of the squares of the atomic numbers of the heavy and light atoms are equal. Under these conditions approximately three quarters of the signs determined solely from the heavy atom contribution are correct; half the signs are correct, on average, because the two contributions will have the same sign, and half of the remainder, on average, will be correct because the contributions of the light atoms are opposite in sign to, but less than, the contribution from the heavy atoms. In any particular example the fraction of structure factors having the same sign as the heavy atom contribution can be assessed using the more exact relationships of Sim (23).

The application of the heavy atom method to non-centrosymmetrical structures is not as straightforward as in the centrosymmetrical case, but the basic principles outlined above remain the same. In this case each structure factor is complex, posessing a phase which can assume any value between 0 and 2π, and not merely 0 or π as in the centrosymmetrical case. There

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(22) H. Lipson and W. Cochran, "The Determination of Crystal Structures", G. Bell and Sons Ltd., London, (1953), p.207.
(23) G. A. Sim, Acta Cryst., 10, 177 (1957).

is therefore a range of errors between the correct phases of the structure factors, and the phases calculated from the heavy atom positions. However for a proportion of the structure factors, the 'heavy atom phases' so determined will be sufficiently close to their correct value that an initial electron density synthesis will show some, if not all, of the light atom locations. For any specific example, the fraction of the structure factors, $N(\Delta)$, for which the phase calculated from the heavy atom contribution is within $\pm\Delta$ of its true value has been calculated by Sim (24).

When the heavy atom contribution does not greatly dominate the right hand side of equation (2.4), a higher fraction of the structure factors will have a phase different from that determined solely from the heavy atom locations. An initial electron density synthesis, based on the heavy atom phases, will therefore contain much spurious detail and unambiguous identification of the light atoms may be impossible. When this is the case, information about the positions of the light atoms can often be found by reverting back to the sharpened Patterson function and using the vector convergence method (25), or computing the Buerger minimum function (26).

The heavy atom method was employed in the structure analyses of the desaurin from acetophenone, (Chapter 5), and the 1,2,4-trithiacyclopentane from pinacolone, (Chapter 12).

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(24) G. A. Sim, ibid., 10, 536 (1957).
(25) C. A. Beevers and J. H. Robertson, ibid., 3, 164 (1950).
(26) M. J. Buerger, ibid., 4, 531 (1951).

Phase determination by direct methods.

Direct methods are those in which an attempt is made to derive the phases of the structure factors without previously postulating any atomic positions.

The first contribution in this field was made by Harker and Kasper (27), who showed that relationships could be formulated between certain $F_{\vec{h}}$ and $|F_{\vec{h}}|^2$ which imposed limitations on the phase of some structure factors. The relationships, in the form of inequalities which vary with the symmetry of the crystal under consideration, were applied in practice by Gillis (28), who succeeded in determining the signs of about forty structure factors for the oxalic acid dihydrate crystal, and by Kasper et al. (29), who used them to solve the structure of decaborane. Karle and Hauptman (30), using the criterion that the electron density must be everywhere non-negative, derived a set of inequality relationships which are valid for all the space groups, and showed that the introduction of specific symmetry elements to the set produced the Harker-Kasper inequalities which had been previously formulated.

A major impetus to the development of direct methods was initiated by Sayre (31), who examined relationships between the $F_{\vec{h}}$'s of a structure and those of the same structure in which the atoms were replaced by 'squared atoms'. If the structure

(27) D. Harker and J. S. Kasper, ibid., 1, 70 (1948).
(28) J. Gillis, ibid., 1, 174 (1948)
(29) J. S. Kasper, C. M. Lucht and D. Harker, ibid., 3, 436 (1950).
(30) J. Karle and H. Hauptman, ibid., 3, 181 (1950).
(31) D. Sayre, ibid., 5, 60 (1952).

consists of equal, resolved atoms, (so that the electron density and the squared density have an identical distribution of peaks and differ only in peak shape), Sayre showed, for a centro-symmetrical crystal, that the sign relation,

$$sF_{\vec{h}} = s\sum_{\vec{k}} F_{\vec{k}} \cdot F_{\vec{h}-\vec{k}} \qquad (2.5)$$

could be formulated, (s is an abbreviation for 'sign of'). Sayre illustrated the value of (2.5) by solution of the centric 0kl projection of hydroxyproline (31), which he achieved by finding a consistent set of signs for some of the larger $F_{\vec{h}}$ which satisfied the equation. Relationship (2.5) is true when the summation extends over all $\vec{k}$ and the atoms are equal and resolved; however Sayre, by his work on hydroxyproline, and Zachariasen (32), showed in practice that (2.5) remained valid when only structure factors of large magnitude are used in the summation and the atoms of the molecule are of more than one chemical type.

Hauptman and Karle (33) derived, by mathematical analysis, a number of relationships between structure factors which led them to the conclusion that the phase problem was soluble if sufficient data were available. Since $|F_{\vec{h}}|$ decrease as the Bragg angle increases, (because of the decline of scattering factor with increasing θ), Hauptman and Karle in their work sharpened $|F_{\vec{h}}|$ to normalised structure amplitudes $|E_{\vec{h}}|$,

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(32) W. H. Zachariasen, ibid., 5, 68 (1952).
(33) H. Hauptman and J. Karle, "Solution of the Phase Problem, I, The Centrosymmetric Crystal", A. C. A. Monograph No. 3, The Letter Shop, Wilmington, (1953).

$$|E_{\vec{h}}|^2 = \frac{|{}''F_{\vec{h}}|^2}{\varepsilon_{\vec{h}} \sum_{i=1}^{N} f_i^2 \; \vec{h}} \qquad (2.6).$$

where, $|{}''F_{\vec{h}}|$ = the observed structure amplitude, placed on an absolute scale and suitably corrected for atomic thermal motion,

$\varepsilon_{\vec{h}}$ = an integer which corrects for space group extinctions,

f_i = the scattering factor of the ith atom in a unit cell containing N atoms.

The 'probability equivalent' of the Sayre equation derived by Hauptman and Karle is,

$$\Sigma_2 : \qquad sE_{\vec{h}} \sim s\sum_{\vec{k}_r} E_{\vec{k}} \cdot E_{\vec{h}-\vec{k}} \quad , \qquad (2.7)$$

where the symbol $\vec{k}_r$ implies that $\vec{k}$ ranges only over those vectors associated with large $|E|$ values. Probability formulae for evaluating the reliability of a sign determined by application of Σ_2 were derived by Hauptman and Karle (33) and also by Cochran and Woolfson (34,35). For Σ_2 the associated probability function, $P+(\vec{h})$, which determines the probability that the sign of $E_{\vec{h}}$ be positive, is given by (34,35),

$$P+(\vec{h}) = 1/2 + 1/2\tanh\left[\frac{\sigma_3}{\sigma_2^{3/2}}|E_{\vec{h}}|\sum_{\vec{k}} E_{\vec{k}} \cdot E_{\vec{h}-\vec{k}}\right], \qquad (2.8)$$

where $\sigma_n = \sum_{i=1}^{N} Z_i^n$; Z_i being the atomic number of the ith atom.

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(34) M. M. Woolfson, Acta Cryst., 7, 61 (1954).
(35) W. Cochran and M. M. Woolfson, ibid., 8, 1 (1955).

It is evident, for a centrosymmetrical crystal, that the signs of normalised structure factors can be determined by using the Σ_2 relationship (2.7), and that a probability assessment of each generated sign may be made by employing the probability function (2.8). Application of Σ_2 is initialised employing certain large $|E_{\vec{k}}|$'s whose phases may be assigned arbitrarily to specify the origin, (c.f. Chapter 9), and is supplemented, in the symbolic addition procedure (36,37), by additional larger $|E_{\vec{k}}|$'s whose phases are denoted by symbols. After repeated Σ_2 application the signs of numerous $E_{\vec{h}}$ are generated, (either absolutely or in terms of the assigned symbols), and the normalised structure factors are then used as Fourier coefficients to generate an 'E-map' (38). Karle et al. (37,38) have illustrated that in general the atomic positions are readily obtained from a three-dimensional E-map computed with about ten normalised structure factors, (of larger $|E|$), per atom of the asymmetric unit. If p symbols have been assigned, there will be theoretically 2^p possible sign combinations to consider; however relationships amongst the symbols frequently occur as the phase determination proceeds and generally the number of E-maps it is necessary to compute is considerably reduced.

The symbolic addition procedure was employed in the structure analysis of 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole), and the practical aspects of the procedure are described in Chapter 9.

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(36) I. L. Karle and J. Karle, ibid., 16, 969 (1963).
(37) I. L. Karle, K. Britts and P. Gum, ibid., 17, 496 (1964).
(38) I. L. Karle, H. Hauptman, J. Karle and A. B. Wing, ibid., 11, 257 (1958).

Least squares refinement of structure parameters.

The method of least squares can be used in structure refinement (39) by minimising some function of the observed and calculated structure amplitudes with respect to the atomic parameters. The function most commonly minimised is,

$$R' = \sum_q w(hkl)\left[|F_o(hkl)| - |F_c(hkl)|\right]^2, \qquad (2.9)$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, q is the total number of independent $|F_o|$ data and w(hkl) is a weight applied to each term which depends upon the reliability of the $|F_o(hkl)|$ datum. Although strictly w(hkl) is proportional to $1/(\sigma|F_o(hkl)|)^2$, (where $\sigma|F_o|$ is the standard deviation of the observed structure amplitude), frequently, in crystal structure refinement, only relative weights can be estimated and it is often assumed that $\sigma|F_o|$ depends only on $|F_o|$.

The trial set of n atomic parameters, $(p_1, p_2 \ldots p_n)$, require corrections to be applied, (Δp_i), to adjust them to their 'most probable' values, $(p_1+\Delta p_1, \ldots p_n+\Delta p_n)$, which will result in the required minimisation of (2.9). If the parameter shifts required are small, (so that Taylor's expansion to first order may be employed), (2.9) can be re-written as,

$$R' = \sum_q w\left[|F_o| - |F_c'| + \frac{\partial F_c'}{\partial p_1}.\Delta p_1 + \frac{\partial F_c'}{\partial p_2}.\Delta p_2 \ldots\ldots + \frac{\partial F_c'}{\partial p_n}.\Delta p_n\right]^2 \qquad (2.10)$$

where F_c' is the value calculated using the trial set of parameters.

(39) E. W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941).

Function (2.10) will be minimum when the partial derivatives with respect to each of the n parameters vanish, i.e.,

$$\frac{\partial R'}{\partial p_1} = 0; \quad \frac{\partial R'}{\partial p_2} = 0 \;\ldots\ldots\; \frac{\partial R'}{\partial p_n} = 0 \tag{2.11}$$

Therefore the n conditions of type (2.11) may be written as a series of n equations, (the "normal equations"),

$$\sum_q w\left[\left(\frac{\partial F_c'}{\partial p_1}\right)\left(\frac{\partial F_c'}{\partial p_1}\right)\Delta p_1 + \left(\frac{\partial F_c'}{\partial p_1}\right)\left(\frac{\partial F_c'}{\partial p_2}\right)\Delta p_2 + \;\ldots\; \left(\frac{\partial F_c'}{\partial p_1}\right)\left(\frac{\partial F_c'}{\partial p_n}\right)\Delta p_n\right]$$

$$= -\sum_q w(|F_o| - |F_c'|)\left(\frac{\partial F_c'}{\partial p_1}\right)$$

. . . . . .

$$\sum_q w\left[\left(\frac{\partial F_c'}{\partial p_n}\right)\left(\frac{\partial F_c'}{\partial p_1}\right)\Delta p_1 + \left(\frac{\partial F_c'}{\partial p_n}\right)\left(\frac{\partial F_c'}{\partial p_2}\right)\Delta p_2 + \;\ldots\; \left(\frac{\partial F_c'}{\partial p_n}\right)\left(\frac{\partial F_c'}{\partial p_n}\right)\Delta p_n\right]$$

$$= -\sum_q w(|F_o| - |F_c'|)\left(\frac{\partial F_c'}{\partial p_n}\right)$$

The normal equations represent a set of n simultaneous equations in n unknowns and may therefore be solved for Δp_1, Δp_2 .. Δp_n. Since (2.10) is an approximation, the required minimisation of the function (2.9) is not normally achieved by a single cycle of least squares refinement. However, by applying the calculated Δp_i and repeating the procedure, additional improvement in the parameters can be obtained. The standard deviation of each atomic parameter is calculable from the least squares residuals, and

in practice refinement is continued until the parameter shifts calculated represent only a fraction of their standard deviation.

Computational work.

All computations were carried out on the I.B.M. 7094 at the University of Toronto.

The program used for structure factor calculations and full matrix least squares refinement was a modified version of OR-FLS (40,41). One modification, due to Shiono, was that reflection data were read into the program one at a time from magnetic tape; consequently there was no restriction on the number of observations. In the original version of OR-FLS the value of the atomic scattering factor for each reflection was obtained by linear interpolation from a stored table of 32 values for ($\sin\theta/\lambda$) from 0.0 to 1.55 in 0.05 intervals. Because of the coarse mesh of this table, values interpolated at low angles could be significantly in error, and a second Shiono modification was to replace the original 'f' table with the 51 scattering factor values for $\sin\theta$ from 0.0 to 1.0 in intervals of 0.02. The 51 unit table for sulphur, carbon and oxygen were prepared using the Aitken polynomial method (42) on the scattering factor values listed in International Tables (43)‡. To the scattering curve for sulphur 0.3 electrons were added over the whole $\sin\theta$

(40) W. R. Busing, K. O. Martin and H. A Levy, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (1962).
(41) R. Shiono, Crystallography Laboratory, University of Pittsburgh, Pittsburgh, (1963).
(42) See, for example, T. A. Bak and J. Lichtenberg, "Mathematics for Scientists", Benjamin, (1966), p. 459.
(43) International Tables for X-Ray Crystallography, Volume III, The Kynoch Press, Birmingham, (1962), p. 201; (a) p. 214.
‡ A listing of the interpolation program is given in Appendix V.

range to allow for the real part of the anomalous scattering (43_a). Patterson, electron density, difference and the E-map syntheses were computed employing "A three-dimensional Fourier synthesis program" written by Shiono (41).

EXPERIMENTAL - PART I

THE X-RAY STRUCTURE ANALYSIS OF THE DESAURIN FROM ACETOPHENONE.

CHAPTER 3.

PRELIMINARY X-RAY WORK.

The desaurin from acetophenone, prepared by the method of Kelber and Schwarz (5), crystallises from nitrobenzene as small plates (44). The major face exhibited is (001), using the axial description given below.

X-ray equipment.

This portion of the work was carried out using a Norelco X-ray generator, operated at 45 kV and approximately 14 mA; nickel filtered copper radiation was used throughout. The recording device used was a Stoe integrating Weissenberg goniometer. Ilford industrial G X-ray film was used, being processed at 20°C with Kodak D19B developer and Kodak F-5 acid-hardening fixer.

Crystal density.

The density of the crystals was determined by flotation in a benzene and carbon tetrachloride mixture at room temperature, the density of the liquid mixture in which the crystals remained suspended being found by use of a specific gravity bottle. The average value of the crystal density was found to be 1.45 $g.cc^{-1}$.

Unit cell dimensions and space group.

Unit cell dimensions were originally estimated from zero level Weissenberg photographs and were later determined more accurately from new sets of zero level photographs calibrated

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(44) We are grateful to Dr. T. R. Lynch for providing crystals of the desaurin from acetophenone.

with aluminium powder lines. A least squares refinement procedure was used.

System monoclinic (y axis unique)

$a = 5.470$ Å ($\sigma = 0.008$)

$b = 4.848$ Å ($\sigma = 0.012$)

$c = 28.299$ Å ($\sigma = 0.008$)

$\beta = 96.9^{o}$ ($\sigma = 0.1$)

$V = 745.0$ Å^3

The following systematic absences were noted on zero level and equi-inclination Weissenberg photographs;

hkl : no general absences,

hOl : absent for $l = 2N + 1$,

OkO : absent for $k = 2N + 1$.

The space group is therefore $P2_1/c$.

<u>The number of molecules per unit cell</u>.

The number of molecules per unit cell can be expressed by the formula,

$$n = \frac{d_{meas} \cdot V}{1.66 \cdot M}$$

where, d_{meas} = the crystal density,

V = the volume of the unit cell, (in Å^3),

M = the molecular weight of the compound.

Using $d_{meas} = 1.45$ g.cc^{-1}, $M = 324$ and $V = 745.0$ Å^3, the calculated value of n is 2.01. Thus Z, the number of molecules per unit cell, is 2.

CHAPTER 4.

COLLECTION OF THREE-DIMENSIONAL INTENSITY DATA.

Optimum crystal size.

The linear absorption coefficient, μ, is defined by,

$$\mu = d\sum\rho\mu_m,$$

where, d = the crystal density,

ρ = the fractional weight of each element,

μ_m = the mass absorption coefficient for each element.

Using the mass absorption coefficients listed in International Tables (45), the calculated value of μ is 33.15 cm^{-1}. Buerger (46) showed that the X-ray reflections with the longest path through the crystal reach their maximum intensity when the crystal diameter is $2/\mu$, and suggested that this value be taken as the optimum thickness, t, for crystals used in X-ray diffraction work. For the desaurin, t is 0.61 mms. The crystals from which intensity data were collected were much smaller than this optimum size, (the approximate dimensions of the largest crystal used were $0.2_0 \times 0.2_0 \times 0.0_2$ mms), and no absorption corrections were applied.

Collection of three-dimensional intensity data.

Three-dimensional intensity data were collected utilising

(45) International Tables for X-ray Crystallography, Volume III, The Kynoch Press, Birmingham, (1962), p.162.
(46) M. J. Buerger, "X-ray Crystallography", Wiley and Sons Inc., New York, N.Y., (1940), p.180.

the equi-inclination Weissenberg method. To ensure that the intensity data recorded came within the range where they could be estimated easily by eye, the multi-film technique was employed (47); thus a pack of four films, interleaved with aluminium foil (0.001 inches thick), was used for each exposure. The intensity of each reflection was measured by visual comparison with an intensity wedge consisting of twenty-eight 'spots' whose relative intensities were known. This wedge was generated by allowing a reflection from the crystal to pass through its reflecting position for varying numbers of times, the translational motion of the film-holder being retained. The crystal used to prepare the wedge was that from which intensity data were collected, so that the shape of the spots on the wedge were typical of the shape of the reflections on the films to be measured.

Initially, recrystallisation of the desaurin from nitrobenzene produced crystals which were generally multiple, together with some very small crystals which were used for data collection. Crystals were mounted about the a and b axes and two series of photographs were recorded, h0l through h3l, and 0kl through 4kl. For each layer the intensity of each reflection was measured on all four films of the pack (48), an average film factor determined, and the average intensity for each plane calculated. The intensity data were corrected for Lorentz and polarisation factors employing the graphical method devised by Cochran (49). The Lp corrected

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(47) J. M. Robertson, J. Sci. Instr., 20, 175 (1943).
(48) We are grateful to Dr. T. R. Lynch for these initial measurements.
(49) W. Cochran, J. Sci. Instr., 25, 253 (1948).

intensities, measured on different photographs, were placed on the same arbitary scale by comparing $|F_{hkl}|^2$ of common reflections, the 0kl film being taken as the arbitary reference standard. The routes by which this inter-scaling was achieved is shown in Figure 4.1.

Absolute scaling and overall temperature factor.

The intensity data for the crystal, (now on an arbitary scale), were placed on an approximately absolute scale by the method due to Wilson (50). The theory depends on the approximation that,

$$\langle |F|^2 \rangle = \langle \sum_{i=1}^{N} {}'f_i^2 \rangle \quad ,$$

where $\langle |F|^2 \rangle$ is the average absolute intensity and $'f_i$ is the scattering factor of the ith atom.

Since $$|F_o|^2 = K.|F|^2,$$

then $\langle |F_o|^2 \rangle = K \langle |F|^2 \rangle$ and $\langle |F_o|^2 \rangle = K.\langle \sum {}'f_i^2 \rangle$

where $|F_o|^2$ are the corrected observed intensities, on some arbitary scale, and K is a scaling factor with respect to the absolute data. Since under the conditions of observation the atoms possess thermal motion, a temperature factor, B_{ov}, must be introduced to modify the theoretical scattering factors accordingly, i.e.,

$$'f_i = f_i \exp(-B_{ov} \cdot RHO),$$

where $RHO = (\sin\theta/\lambda)^2$.

and f_i = the scattering factor for a non-vibrating atom.

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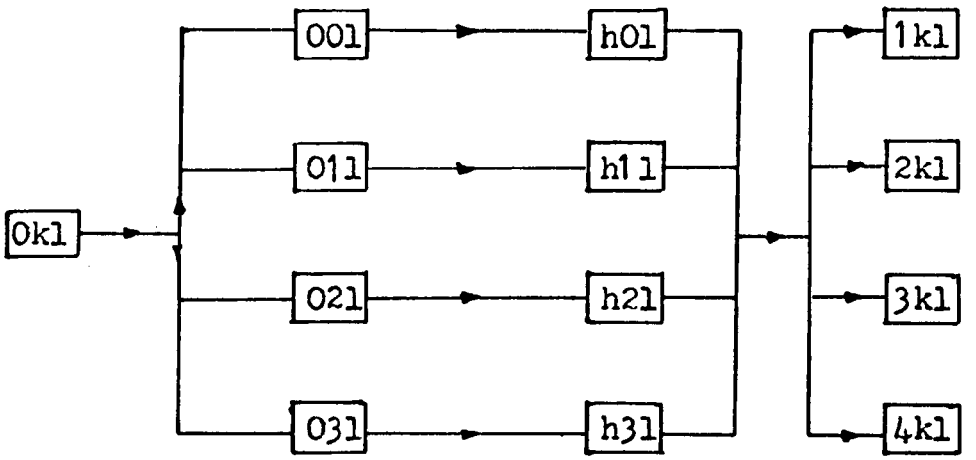
(50) A. J. C. Wilson, Nature, 150, 152 (1942).



Layer	K'	Layer	K'
h01	2.51	0kl	1.00
h11	2.15	1kl	1.11
h21	0.85	2kl	1.03
h31	2.29	3kl	2.30
		4kl	1.08

The routes by which inter-film scaling was achieved and the scaling factors determined (K').

Figure 4.1

Therefore, $$\langle |F_o|^2 \rangle = K.\langle \sum_{i=1}^{N} f_i^2 \rangle.\exp(-2B_{ov}.RHO),$$

and $$\ln\left[\frac{\langle |F_o|^2 \rangle}{\langle \sum_i f_i^2 \rangle}\right] = \ln(K) - 2B_{ov}.RHO \quad .$$

The hOl zone was divided into five ranges, each containing approximately an equal number of reflections, and the value of $\ln\left[\frac{\langle |F_o|^2 \rangle}{\langle \sum_i f_i \rangle}\right]$ was calculated and plotted against the average RHO for each range. The resultant plot is shown in Figure 4.2, and yielded values of 14.8 for the scale factor, (with respect to $|F_o|^2$, $[\equiv 1/K]$), and 5.0A^2 for the overall temperature factor, B_{ov}.

It was noted that almost all reflections for which $2\theta(\underline{CuK\alpha}) > 80^o$ had immeasurably small intensities; consequently it was decided to exclude these data for initial stages of the structure analysis. Data Set 1, ($2\theta(CuK\alpha) \leq 80^o$), comprising 430 independent reflections of which 334 had measurable intensities, were used for the identification of atomic locations using Patterson and electron density syntheses. Further recrystallisations of the desaurin, (from nitrobenzene), yielded a few larger crystals and at a later stage in the structure analysis layers hOl through h4l were re-collected, (Data Set 2). Intensity data, measured on these photographs, were corrected for Lorentz and polarisation factors using a program written for the I.B.M. 7094*, and were elevated to the absolute scale by comparing $|F_{hkl}|^2$ common to Data Set 1. Of the 1493 independent reflections recorded in Data Set 2, 1020 had measurable intensities.

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* A listing of the Lp program is given in Appendix V.

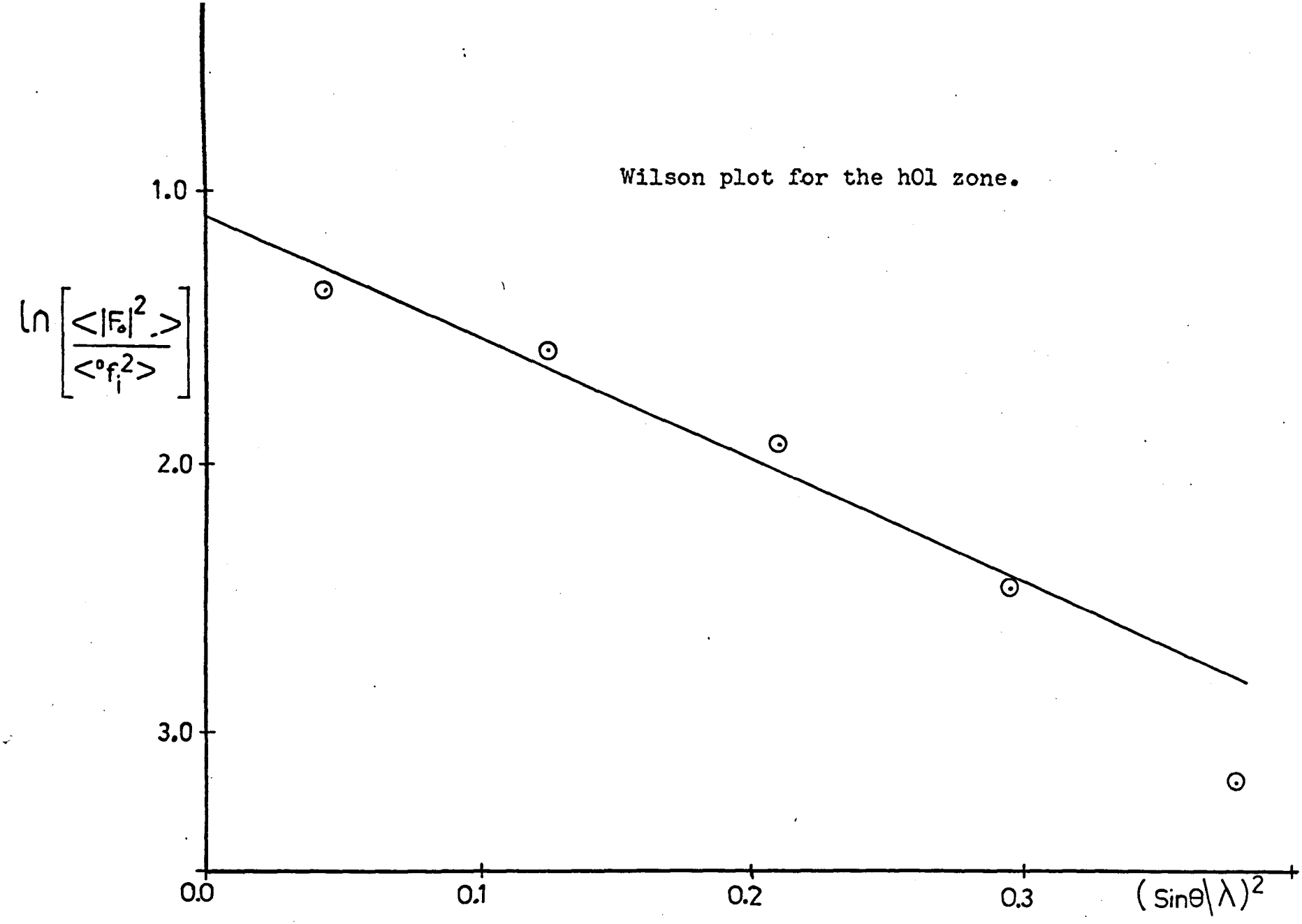

Wilson plot for the h01 zone.
1.0
2.0
3.0
$\ln\left[\frac{\langle|F_o|^2\rangle}{\langle {}^of_i^2\rangle}\right]$
0.0
0.1
0.2
0.3
$(\sin\theta/\lambda)^2$

FIGURE 4.2

CHAPTER 5.

THREE-DIMENSIONAL PATTERSON AND FOURIER SYNTHESES.

The three-dimensional Patterson function.

The Patterson function was computed for a quarter of the unit cell defined by $-0.5 \leqslant u \leqslant 0.5$, $0.0 \leqslant v \leqslant 0.5$ and $0.0 \leqslant w \leqslant 0.5$, in intervals of 0.05 in u and v, and 0.01 in w. The $|F_{hkl}|^2$ of Data Set 1 were used as the Fourier coefficients and the computation was carried out using the general Fourier program. $|F_{000}|^2$ was omitted from the calculation.

As stated in Chapter 3, the desaurin from acetophenone crystallises in space group $P2_1/c$ with two molecules, (four sulphur atoms), per unit cell. If one sulphur atom is situated at the general position (x,y,z) in the unit cell, the remaining three sulphur atoms must be located at space group equivalent positions $(\bar{x},\bar{y},\bar{z})$, $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$. Peaks in the Patterson function which represent sulphur-sulphur vectors will therefore be located at,

1.	$\pm(2x, 2y, 2z)$	single fold weight.	Table 5.1
2.	$\pm(2x, \overline{2y}, 2z)$		
3.	$\pm(0, \frac{1}{2}-2y, \frac{1}{2})$	two fold weight	
4.	$\pm(2x, \frac{1}{2}, \frac{1}{2}+2z)$		

In reported structures of six-membered sulphur-containing heterocyclics, where a divalent sulphur atom is bonded to an

sp^2-hybridised carbon atom, sulphur-carbon bond lengths in the order 1.76-1.78Å and sulphur-carbon-sulphur bond angles of approximately 100° have been found (80,81). By applying these dimensions to the 1,3-dithiete ring of the desaurin, it is therefore expected that the sulphur-sulphur inversion peaks, (#'s 1 and 2), will be of the order 2.4Å to 2.8Å distant from the origin.

Inspection of the Patterson function revealed a prominent peak about 2.6Å from the origin, which obviously represented the intramolecular sulphur-sulphur vector. This peak and the corresponding peaks on the Harker line, (0,v,1/2), and the Harker section, (u,1/2,w), which complete the sulphur-sulphur vector set, are listed below. The numbering of the peaks below is in keeping with the system used in Table 5.1; the peak heights listed were measured from the lowest negative trough in the computed function.

	U	V	W	Peak height.
1,(2)	-0.380	0.000	0.046	300
3.	0.000	0.500	0.500	650
4.	0.380	0.500	0.454	280

By referring to Table 5.1 it is seen that these vector peaks correspond to an asymmetric sulphur atom situated at (-0.190, 0.000, 0.023) in the unit cell. Since the sulphur atom has a 'pseudo-special' location, (x,0,z), some of the sulphur-sulphur vectors have a weight different from those given in

Table 5.1. In this special case the two inversion peaks coalesce into a single peak on the mirror plane at V = 0 having two fold weight, whilst the peak on the Harker line becomes four-fold at (0,1/2,1/2). Thus it is evident that the vector set identified has relative peak heights which are consistent with the theoretical weights of the interactions.

Structure factor calculations and three-dimensional electron density syntheses.

For space group $P2_1/c$, the calculated structure factors, F_c, are given by,

$$(k+l) = 2n \quad ; \quad F_c = 4\sum_{i=1}^{N} f_i \cos 2\pi(hX_i + lZ_i).\cos 2\pi kY_i \ ,$$
$$(k+l) = 2n+1 \quad ; \quad F_c = -4\sum_{i=1}^{N} f_i \sin 2\pi(hX_i + lZ_i).\sin 2\pi kY_i \ , \qquad (5.1)$$

where f_i and (X_i,Y_i,Z_i) are the scattering factor and the fractional coordinates pertaining to the ith atom of an asymmetric unit containing N atoms.

Structure factors were calculated employing a modified version of OR-FLS and the general Fourier program was used to compute electron density syntheses. The two programs were run sequentially, the input data for the Fourier being prepared by OR-FLS and stored out-of-core between programs. The reflection data used in this portion of the work were those of Data Set 1 and each electron density synthesis was computed within the bounds $-0.5 \leqslant x \leqslant 0.5$, $-0.5 \leqslant y \leqslant 0.5$ and $0.0 \leqslant z \leqslant 0.5$, in intervals of 0.025 in x and y and 0.005 in z. The synthesis was calculated for twice the asymmetric volume required by the space group as

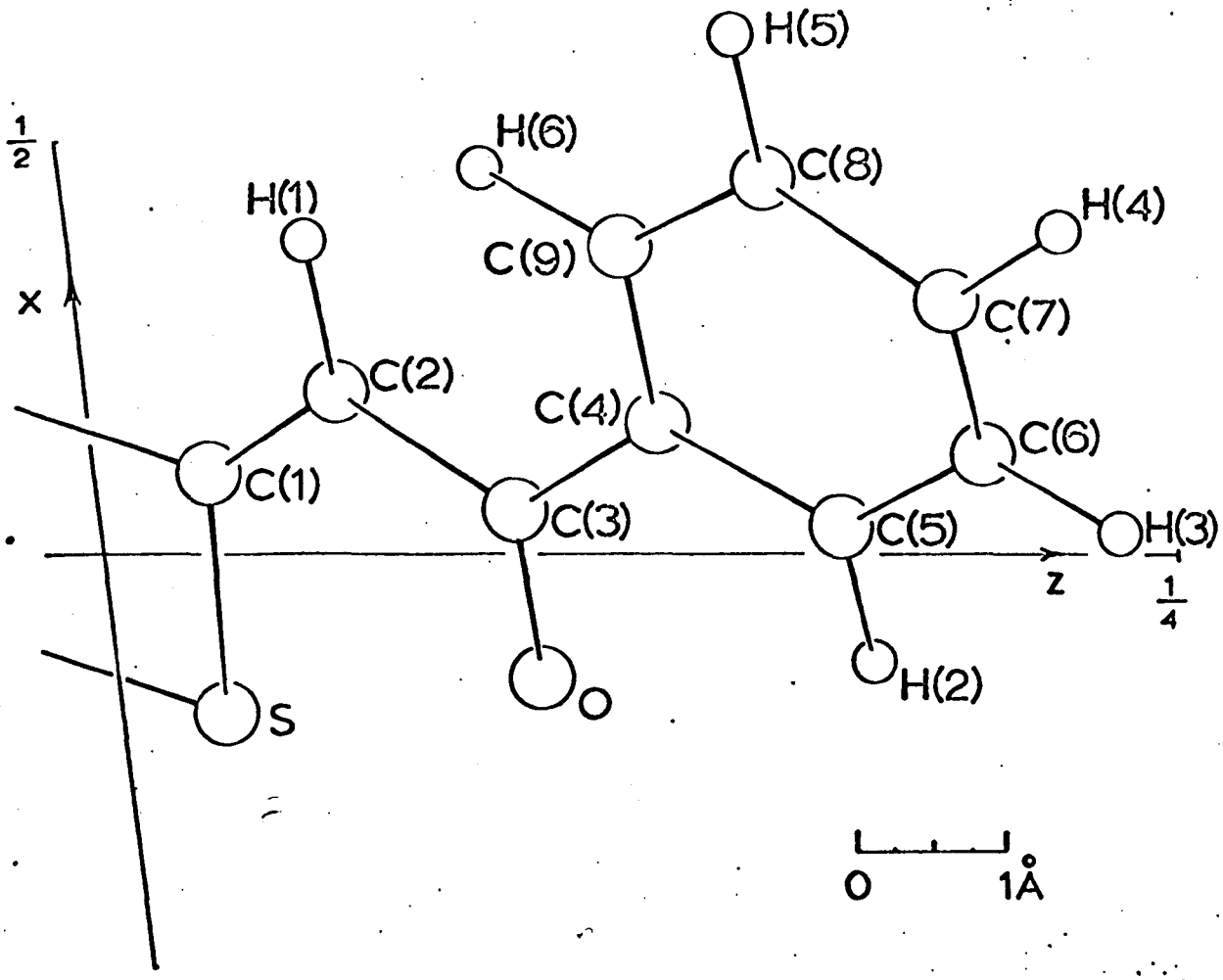
this enabled an easier comparison to be made between 'true' and 'false' electron density peaks, (discussed below). Isotropic temperature factors used in the structure factor calculations were $4.0\mathring{A}^2$ for the sulphur atom and $5.0\mathring{A}^2$ for the light atoms. The residual index,

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} ,$$

has reflections of zero measured intensity included with $|F_o| = 0.0$.

Structure factors were calculated using the positional parameters of the sulphur atom determined from the Patterson function, (R = 0.66). Since the sulphur atoms are located at $\underline{y} = 0$, (and $\underline{y} = 1/2$), they make no contribution to structure factors having $(k+\ell)=2n+1$, (see equation (5.1)), and the initial electron density synthesis, phased by the sulphur atom, has therefore (020) as a false mirror plane. From the distribution of peaks in this synthesis and packing considerations, it was evident the <u>α,β</u>-unsaturated carbonyl system is in an <u>s-cis</u> conformation, (with the plane of the benzene ring lying approximately parallel to the long c axis). Attention was first focussed on seven peaks corresponding to atoms of the C(1)-C(2)-C(3)-O[‡] system and the false symmetry related group, (C(3) lay on the mirror plane); however an unambiguous subdivision of the seven peaks into *two* unsaturated carbonyl systems related by the false mirror plane proved difficult. Since the sulphur

‡ The atomic numbering system employed is shown in Figure 5.1.



The atomic numbering system used.

Figure 5.1.

atoms are not confined to (020) by any space group requirements, the possibility arises that these atoms are located only 'close-to' these planes, (the Patterson function having insufficient resolution to show a small finite character in the y coordinate of the atoms). The asymmetric sulphur atom was allocated y = 0.01, hoping that this would sufficiently weight the phases of structure factors for which $(k+\ell) = 2n+1$, that one set of three peaks corresponding to a molecular C(1), C(2) and O system would increase in density whilst the 'false symmetry' related set would show a reduction in peak density. However the only significant difference in the subsequent electron density synthesis was that the density at one oxygen location was noticeably greater than the density at the 'false symmetry' position. A third electron density synthesis, phased by the sulphur, (y = 0.01), and 'true' oxygen atoms, (R = 0.58), revealed unambiguously the C(1) and C(2) positions, which together with O and C(3), (still centred on y = 1/2), completed the conjugated carbonyl system of the molecule. A fourth structure factor calculation, using S, O, C(1) and C(2), (R = 0.51), and electron density synthesis revealed the locations of C(4) and C(7), and still showed C(3) centred on y = 1/2, (a location which was now accepted). These three atoms were included in a fifth structure factor calculation, (R = 0.43), and the remaining four carbon atoms, which completed the asymmetric unit, were identified from the subsequent electron density synthesis. A final electron density synthesis, phased by all eleven atoms of the asymmetric unit, (R = 0.33), was devoid of spurious detail;

the fractional coordinates of the atoms estimated from this synthesis are listed in Table 5.2. At this stage all the gross features of the molecular structure had been established and R was 0.28[‡]. Least squares refinement of the atomic parameters was now initiated.

‡ The $|F_o|$ were rescaled by equating $\Sigma|F_o|$ and $\Sigma|F_c|$.

Atom	X/a	Y/b	Z/c
S	-0.210	0.010	0.023
O	-0.175	0.345	0.097
C(1)	0.085	0.168	0.027
C(2)	0.245	0.332	0.062_5
C(3)	0.040	0.500	0.097
C(4)	0.173	0.660	0.136
C(5)	0.017_5	0.707	0.169
C(6)	0.110	0.875	0.205
C(7)	0.315	1.000	0.205
C(8)	0.465	0.992	0.162
C(9)	0.376	0.805	0.129

Atomic coordinates estimated from the final three-dimensional electron density synthesis.

Table 5.2.

CHAPTER 6.

REFINEMENT OF THE STRUCTURE.

The program employed for least squares refinement was OR-FLS, which had previously been used for basic structure factor calculations and which had now been converted into Fortran IV language. This version of OR-FLS was able to handle up to 45 atoms and a maximum of 450 parameters, of which 165 could be refined simultaneously.

The function minimised was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used throughout the refinement was that due to Hughes (39),

$$w = 1/|F_o|^2 \qquad \text{if } |F_o| \geqslant 4F_{min},$$
$$w = 1/(4F_{min})^2 \qquad \text{if } |F_o| < 4F_{min},$$
$$w = 0.0 \qquad \text{if } F_o = 0.0 \ .$$

For least squares cycles using isotropic temperature factors F_{min} was set as 1.0, however it was found that with $F_{min} = 3.0$ R reduced to its lowest value and this latter allocation for F_{min} was used for cycles in which anisotropic temperature factors were employed.

Two residual indices are quoted throughout this part of the work; R_1 is the index obtained using all experimentally recorded reflection data, (1493 for Data Set 2; the 478 reflections too faint to be measured being included, (initially), with $|F_o| = 0.0$). R_2 is the index obtained when only those reflections

which had measurable intensities are used in the summation.

Refinement employing isotropic temperature factors.

The initial positional parameters used in the refinement were those obtained from the final electron density synthesis, (Table 5.2), with isotropic temperature factors specified as $4.0A^2$ for the sulphur atom and $5.0A^2$ for oxygen and carbon atoms. Two cycles of refinement were performed using Data Set 1; in the first only positional parameters were allowed to vary, whilst in the second all 44 atomic parameters were refined. At this stage the more extensive Data Set 2 were introduced for the final phases of the refinement. Although these data had been adjusted to the absolute scale via Data Set 1, each layer h01 through h41 was assigned an individual scale factor, which were treated as variables in the least squares refinement. After a further four cycles of refinement of the 49 parameters, R_1 and R_2 had reduced to 0.193 and 0.153 respectively. The maximum shift calculated in the last cycle represented about half of the standard deviation of the parameter, and it was considered that conversion to anisotropic temperature factors could now be safely made. The atomic parameters at this stage are listed in Table 6.1.

Refinement employing anisotropic temperature factors.

The anisotropic temperature factor, $T(hkl)_i$, applied to the contribution by atom i to $F_c(hkl)$ is,

$$T(hkl)_i = \exp -1/4(h^2a^{*2}B_{11i} + k^2b^{*2}B_{22i} + l^2c^{*2}B_{33i} + 2hka^*b^*B_{12i} + 2hla^*c^*B_{13i} + 2klb^*c^*B_{23i})$$

	X/a	Y/b	Z/c	B_{iso} (Å^2).
S	-0.1965	0.0024	0.0236	3.598
O	-0.1502	0.3365	0.0980	4.757
C(1)	0.0950	0.1608	0.0263	3.460
C(2)	0.1948	0.3391	0.0583	3,586
C(3)	0.0549	0.4254	0.0959	3.371
C(4)	0.1588	0.6310	0.1326	3.319
C(5)	0.0367	0.6746	0.1727	4.320
C(6)	0.1223	0.8591	0.2071	5.182
C(7)	0.3330	1.0141	0.2020	4.964
C(8)	0.4603	0.9754	0.1628	4.949
C(9)	0.3709	0.7826	0.1283	4.161

Atomic parameters at the conclusion of the refinement using isotropic temperature factors.

Table 6.1

where a*, b* and c* are reciprocal cell parameters.

The Hughes weighting scheme was retained with F_{min} reset to 3.0, and reflections of zero measured intensity were again included with $|F_o| = 0.0$. On the initial cycle of refinement a singularity was produced in the matrix due to correlation between the B_{22} thermal parameter of the sulphur atom and the scale factors; consequently these parameters were not allowed to refine simultaneously. After four cycles of refinement R_1 and R_2 had improved to 0.164 and 0.125 respectively and the parameter shifts were insignificantly small. Reflections of zero observed intensity were now allocated the value F_{un}, suggested by Hamilton (51) as being the statistically probable value for an unobserved reflection in a centrosymmetrical space group;

$$F_{un}(hkl) = \left[\frac{I_{min}}{3} \cdot \frac{1}{Lp_{hkl}} \cdot S\right]^{1/2}$$

where, I_{min} = the minimum observed intensity on the film,

Lp_{hkl} = the Lorentz-polaristion factor,

S = the film scale factor.

After a further two cycles of refinement R_1 and R_2 improved to 0.127 and 0.111 respectively; parameter shifts calculated in the last cycle were at most 25% of the standard deviation of the parameter and refinement was considered complete. The final positional and thermal parameters and their estimated standard

(51) W. C. Hamilton, Acta Cryst., 8, 185 (1955).

deviations, calculated from the least squares residuals, are given in Tables 6.2 and 6.3.

The location of hydrogen atoms.

The observed structure amplitudes possess a small contribution from the hydrogen atoms of the molecule. As the positional and thermal parameters of the non-hydrogen atoms were now known accurately, a Fourier synthesis using (F_o-F_c) coefficients, (the difference synthesis), will show the residual electron density in the cell and should exhibit maxima at the locations of the hydrogen atoms.

Peaks attributable to the six hydrogen atoms of the asymmetric half molecule were easily identified in the computed difference synthesis. Their fractional coordinates are listed in Table 6.4, together with the 'theoretical' hydrogen positions calculated from the carbon atom locations assuming a carbon-hydrogen bond length of 1.075Å.

A final structure factor calculation was computed with the F_c's based on the parameters of all seventeen atoms of the asymmetric unit. In this calculation the hydrogen atoms, (located from the difference synthesis), were allocated the anisotropic thermal motion of the carbon atoms to which they are bonded, and the hydrogen scattering curve used was that given by McWeeny (52). The final values of R_1 and R_2 were 0.124 and

(52) R. McWeeny, ibid., 4, 513 (1951).

	X/a	σ(X/a) x10⁴	Y/b	σ(Y/b) x10⁴	Z/c	σ(Z/c) x10⁵
S	-0.1969	2	0.0022	3	0.02352	5
O	-0.1506	7	0.3345	11	0.09797	16
C(1)	0.0945	9	0.1614	13	0.02628	19
C(2)	0.1970	9	0.3399	13	0.05813	21
C(3)	0.0545	10	0.4272	14	0.09602	20
C(4)	0.1607	9	0.6315	12	0.13243	20
C(5)	0.0357	11	0.6716	14	0.17243	22
C(6)	0.1219	14	0.8600	16	0.20662	24
C(7)	0.3314	13	1.0131	15	0.20196	26
C(8)	0.4587	13	0.9748	15	0.16246	28
C(9)	0.3714	11	0.7813	14	0.12761	24

The final fractional coordinates and standard deviations of the non-hydrogen atoms.

Table 6.2

	B_{11}	σB_{11}	B_{22}	σB_{22}	B_{33}	σB_{33}	B_{12}	σB_{12}	B_{13}	σB_{13}	B_{23}	σB_{23}
S	2.82	0.06	3.83	0.07	4.20	0.07	-0.39	0.05	0.55	0.04	-0.53	0.05
O	3.38	0.17	5.73	0.28	5.81	0.22	-1.45	0.17	1.11	0.14	-1.49	0.20
C(1)	2.41	0.18	3.86	0.31	4.05	0.23	0.02	0.18	0.24	0.15	0.12	0.21
C(2)	3.05	0.20	3.52	0.31	4.68	0.25	0.07	0.19	0.18	0.17	-0.11	0.22
C(3)	3.04	0.20	3.65	0.31	4.16	0.24	0.06	0.19	0.21	0.16	-0.18	0.21
C(4)	3.15	0.20	2.55	0.27	4.33	0.23	0.33	0.18	0.19	0.16	0.22	0.20
C(5)	4.68	0.27	3.40	0.33	4.77	0.27	0.23	0.23	0.74	0.21	-0.30	0.24
C(6)	6.02	0.34	3.89	0.36	4.71	0.28	0.04	0.28	0.43	0.24	-0.28	0.26
C(7)	5.13	0.31	3.55	0.35	5.58	0.32	0.54	0.24	-0.85	0.25	-0.28	0.25
C(8)	4.37	0.27	3.66	0.35	6.49	0.36	0.14	0.23	-0.28	0.25	-0.13	0.27
C(9)	4.08	0.24	3.03	0.31	5.31	0.28	-0.41	0.21	0.41	0.20	-0.02	0.24

The final anisotropic thermal parameters, ($Å^2$), and their standard deviations.

Table 6.3

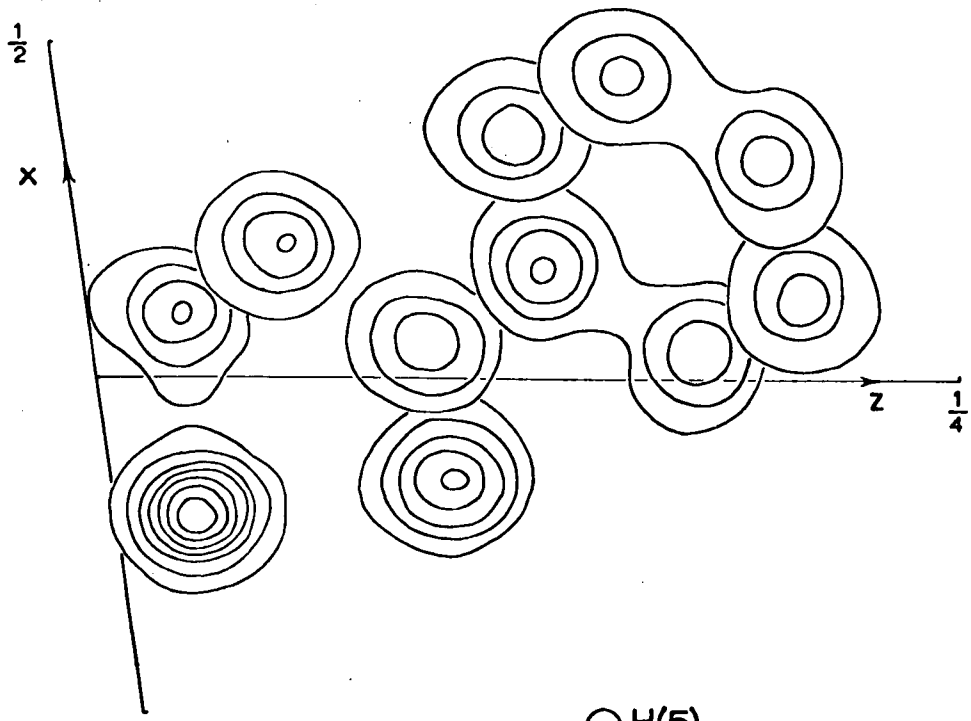
	Attached to Carbon	X/a	Y/b	Z/c	X/a	Y/b	Z/c
H(1)	C(2)	0.372	0.421	0.055	0.3793	0.4184	0.0561
H(2)	C(5)	-0.085	0.529	0.175	-0.1277	0.5546	0.1762
H(3)	C(6)	-0.058	0.914	0.221	0.0259	0.8890	0.2372
H(4)	C(7)	0.404	1.150	0.227	0.3963	1.1616	0.2289
H(5)	C(8)	0.614	1.081	0.159	0.6220	1.0925	0.1589
H(6)	C(9)	0.487	0.783	0.098	0.4683	0.7496	0.0972

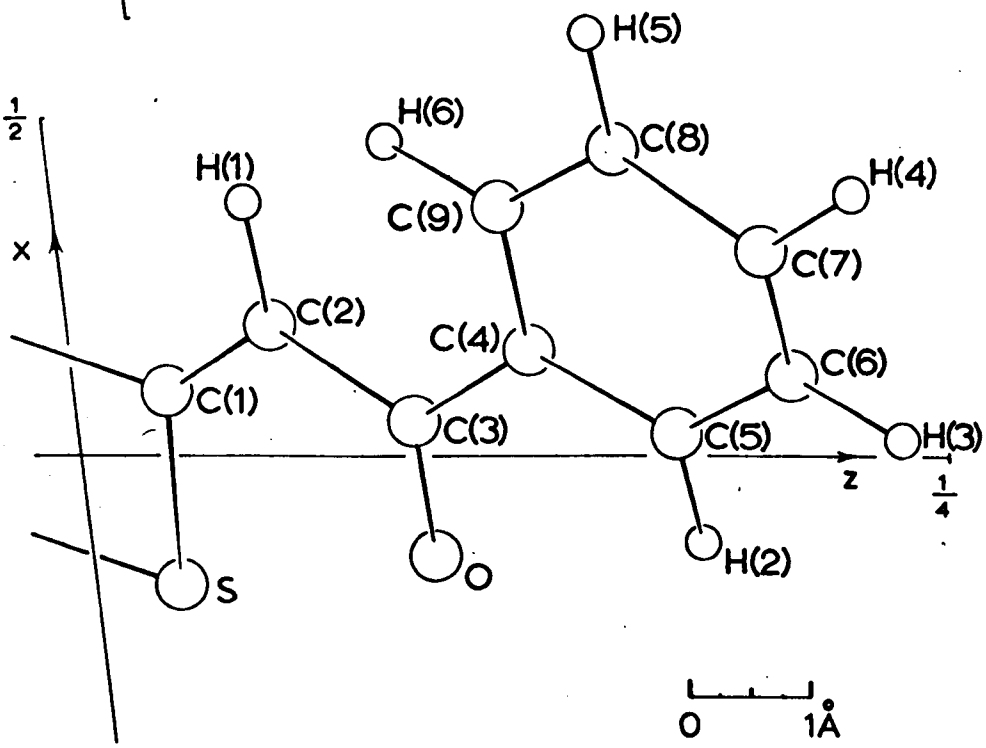
The hydrogen positions obtained from the difference synthesis.

The theoretical hydrogen positions calculated from the carbon locations.

Table 6.4

0.110 respectively. The observed and calculated structure factors are tabulated in Appendix I. Superimposed sections of a final three-dimensional electron density distribution, taken through the atomic centres parallel to (010), are shown in Figure 6.1, together with a drawing of the corresponding molecular unit.





Composite electron density normal to [010]. Contour intervals at the carbon and oxygen atoms 1.0 eÅ^{-3}, at the sulphur atom, 2.0 eÅ^{-3}, (the zero contour is omitted).

Figure 6.1.

EXPERIMENTAL - PART II

THE X-RAY STRUCTURE ANALYSIS OF 3-PHENYL-1-PROPENE-1,3-DIONE 1-(DIMETHYL MERCAPTOLE).

CHAPTER 7.

PRELIMINARY X-RAY WORK AND INTENSITY DATA COLLECTION.

3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole)*, prepared by the method of Kelber (6), crystallises from an ethyl acetate and pentane mixture as yellow needles (53). The crystals were not sufficiently well formed to study the morphology, except to note that the needle axis is parallel to b.

X-ray equipment.

Preliminary photographic work was carried out using a Philips 1009 X-ray generator and a Stoe integrating Weissenberg goniometer. Three-dimensional intensity data were collected using a Picker automated four-circle diffractometer. Nickel filtered copper radiation was used throughout the structure analysis.

Crystal density.

The density of the crystals, determined by flotation in a hexane and carbon tetrachloride mixture at room temperature, was found to be 1.26_5 g.cc^{-1}. For PDM, therefore, the linear absorption coefficient, μ, is 36.01 cm^{-1}**.

Unit cell dimensions and space group.

Cell dimensions were originally estimated from zero level Weissenberg photographs and were later refined using

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* Abbreviated throughout the text as PDM.
(53) We are grateful to Dr. P. Yates for supplying crystals of PDM.
** μ was calculated in the manner described in Chapter 4.

measurements from the diffractometer. A least squares refinement procedure was used on observed theta angles for forty-two reflections.

System monoclinic (y axis unique)

$a = 5.972$ Å ($\sigma = 0.007$)

$b = 10.382$ Å ($\sigma = 0.025$)

$c = 19.536$ Å ($\sigma = 0.011$)

$\beta = 109.42^{\circ}$ ($\sigma = 0.02$)

$V = 1142.3$ Å^3

The following systematic absences were found on zero level and equi-inclination Weissenberg photographs,

hkl - no general absences,

hOl - absent for $l = 2N + 1$,

OkO - absent for $k = 2N + 1$.

The space group is therefore identified as $P2_1/c$.

<u>The number of molecules per unit cell</u>.

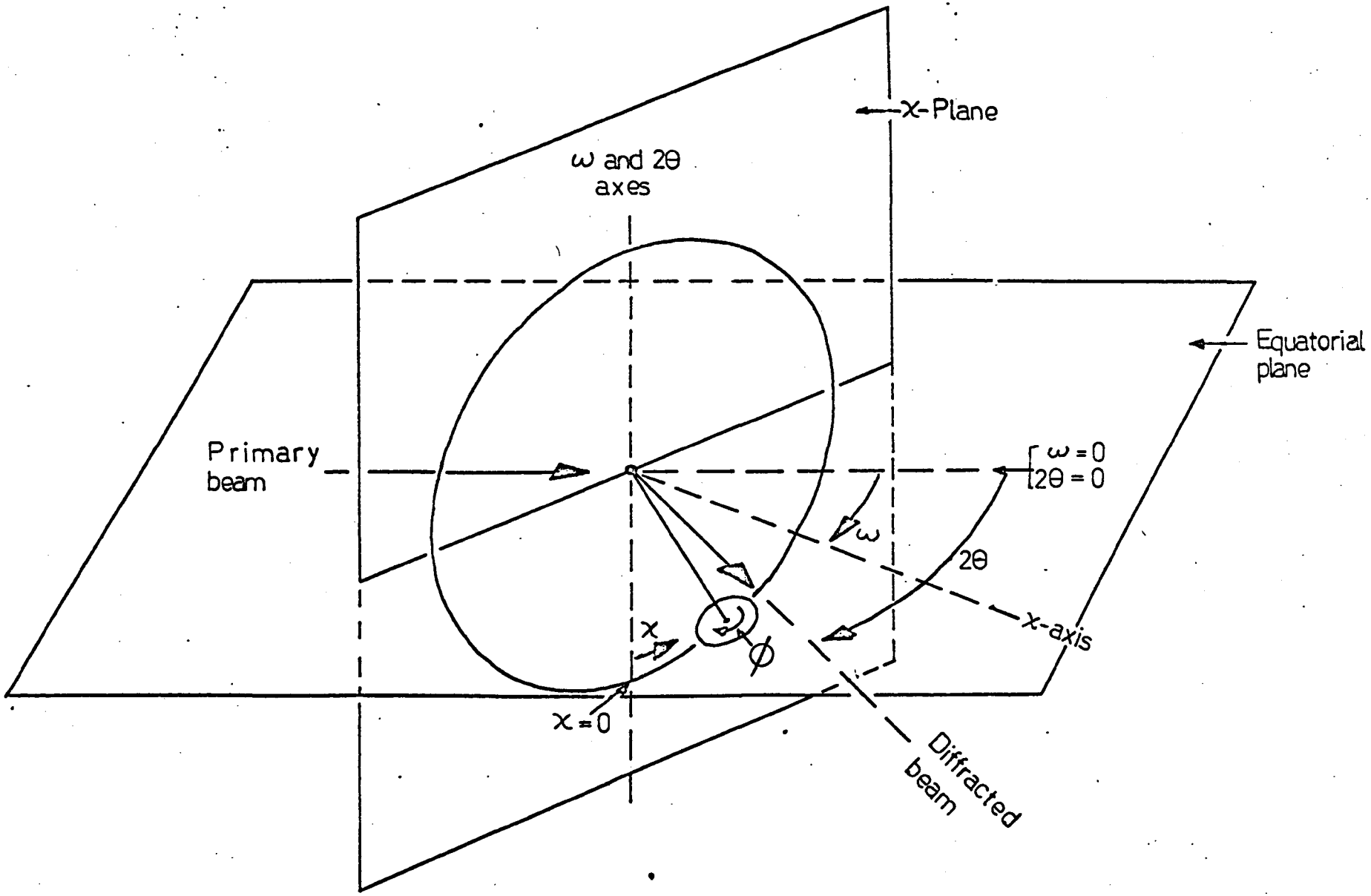
Using $d_{meas} = 1.26_5$ g.cc^{-1} , $V = 1142.3$ Å^3, and molecular weight, M, of 224.3,

$$\underline{n} = \frac{d_{meas} \cdot V}{1.66 \cdot M} = 3.89.$$

Thus there are four molecules of PDM per unit cell.

<u>The Picker four circle diffractometer</u>.

A diagramatic representation of the four angles of the diffractometer is shown in Figure 7.1, which also defines the senses of 2θ, χ and ω. The zero position for ϕ is chosen



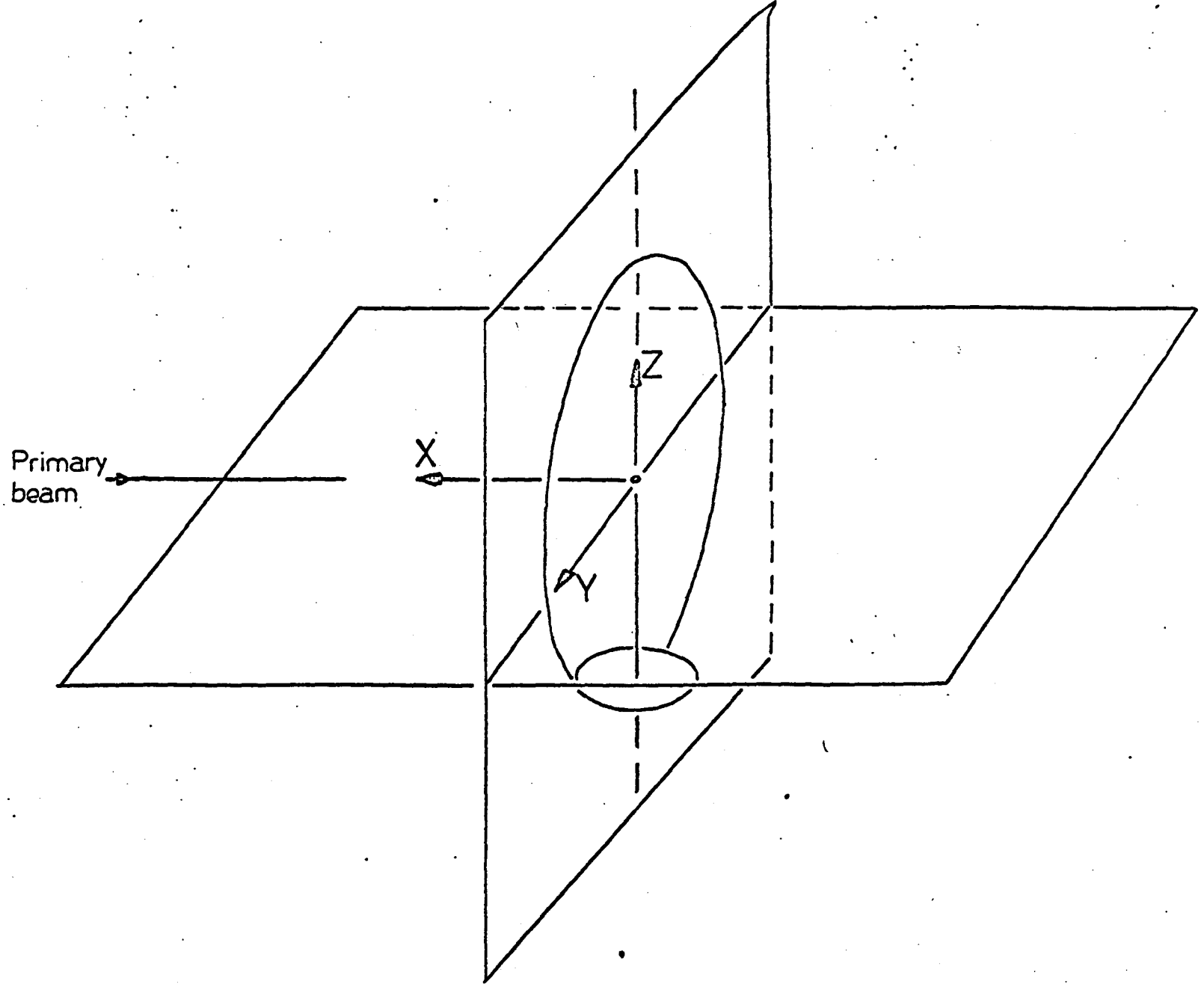
Schematic representation of a four-circle diffractometer.

Figure 7.1.

arbitrarily and the figure shows the direction of rotation which increases this angle. The diffractometer with all angles set to zero is shown schematically in Figure 7.2, which also defines the laboratory orthogonal axes system employed.

The intensity measurement for each reflection is carried out by moving the crystal through the Bragg reflecting position by motion about the ω-axis. The detector rotates about the 2θ-axis, (which is coincident with the ω-axis), its motion being restricted to the equatorial plane. This diffraction geometry is the commonly used normal-beam equatorial set-up.

The symmetrical-A setting, ($\omega = \theta$), was used in all data collection. How the angular settings bring a reciprocal lattice point to the reflecting position on the surface of the Ewald sphere is shown in Figure 7.3. Figure 7.3_1 shows the Ewald sphere and a smaller sphere drawn through the reciprocal lattice point P with its centre at the origin of the reciprocal lattice. A ϕ rotation brings P to position Q in the χ-plane, and a χ rotation moves it to position R on the Y orthogonal axis. Figure 7.3_2 is a plan view on to the equatorial plane. The reciprocal lattice point, now at R, is brought to the surface of the Ewald sphere by rotating ω through the angle θ, the detector being positioned at 2θ to receive the diffracted beam. With the Picker instrument in the symmetrical-A type mode, the ω and 2θ movements are linked in a 1:2 ratio, and the positioning of the crystal and detector for measurement of intensity



The diffractometer with all angles set to zero, showing the laboratory orthogonal axes system employed.

Figure 7.2.

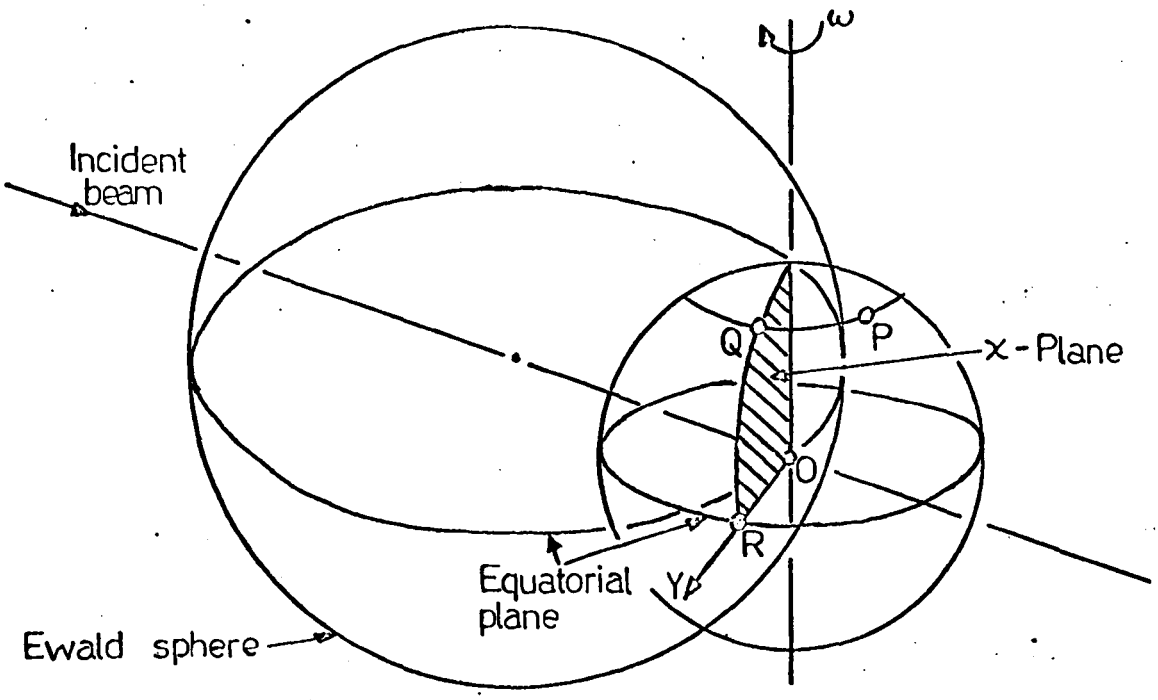


Figure 7.3_1: Normal-beam equatorial geometry.

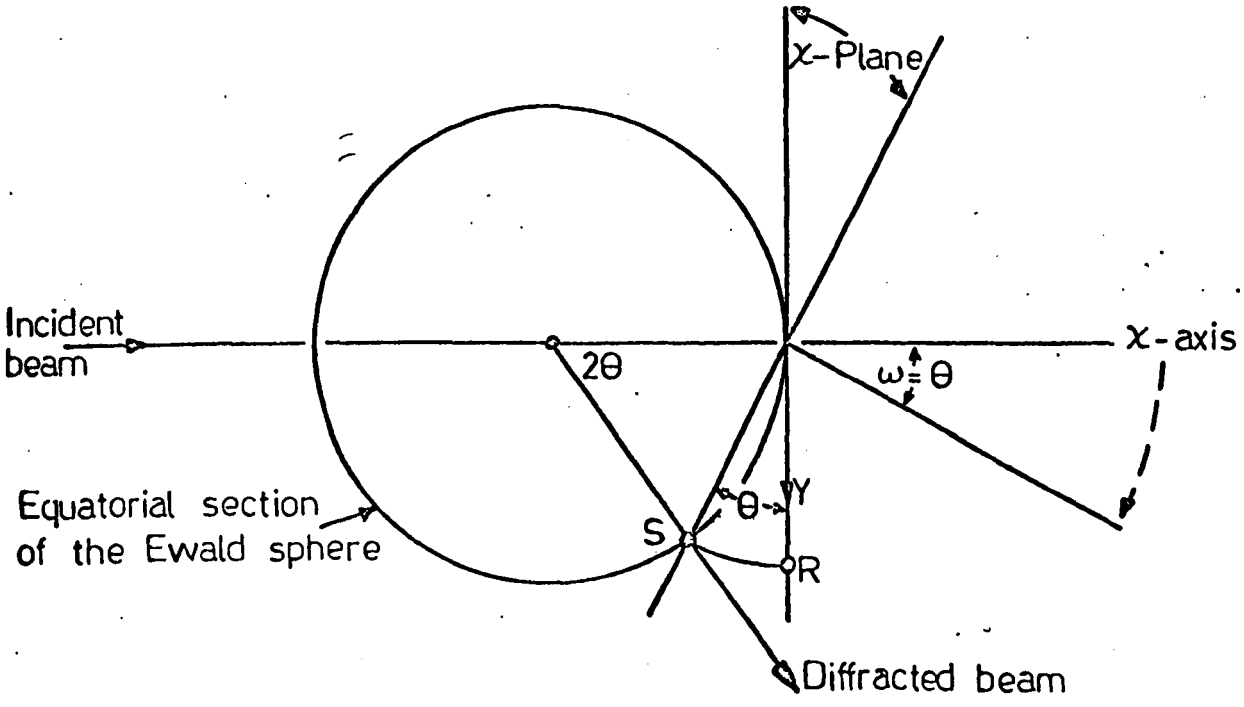


Figure 7.3_2.: The symmetrical-A setting.

The sequence of angular movements which bring the reciprocal lattice point P to the reflecting position.

Figure 7.3.

datum for each reflection is achieved by three angular settings, χ , ϕ and 2θ.

The detector used for intensity measurement was a Picker 2811B scintillation counter, consisting of a thallium activated sodium iodide crystal and a photomultiplier tube, The diffracted X-radiation was filtered by a nickel slide, (0.001 inches thick), placed in front of the detector window. To guarantee that the scintillation counter was being used in the range where quanta entering and counts recorded have a linear relationship, a threshold point of 10,000 counts per second was used with the detector. If the count rate for any diffracted beam was greater than 10,000 c.p.s. attenuators were automatically introduced into the beam to reduce the count rate to below the threshold level. These attenuators were prepared using aluminium foil of different thicknesses. The attenuator factor for each was determined by positioning the detector to receive a moderately strong diffracted beam from the crystal, and counting for a fixed time period with and without the attenuator in position, (the crystal and detector remaining stationary). The attenuator factors so determined are given in the following Table, (CuK_{α}).

Attenuator	Attenuator factor, (A_t).
1	1.35228
2	1.82866
3	2.47286
4	3.34400
5	4.52203

Collection of intensity data.

All intensity data were collected on the diffractometer employing the ω-2θ scan mode, (moving-crystal, moving-counter). A variable scan range was used during the collection to allow for the increasing angular separation of the $K\alpha_1$ and $K\alpha_2$ components of the diffracted X-ray spectrum. The scan range, $\Delta 2\theta$, for each reflection was calculated using the formulation of Alexander and Smith (54),

$$\Delta 2\theta = 1.80 + 0.86\tan\theta_m, \ (CuK\alpha), \qquad (7.1_a)$$

where θ_m is computed using the weighted mean wavelength of the $K\alpha$ radiation. Thus the scan limits for each measurement are,

$$\left.\begin{aligned} 2\theta_1 &= 2\theta_m - \Delta 2\theta/2 \\ 2\theta_2 &= 2\theta_m + \Delta 2\theta/2 \end{aligned}\right\} (7.1_b)$$

The scan rate used was one degree per minute and background counts were taken at both $2\theta_1$ and $2\theta_2$ for twenty seconds. The maximum ω angle attainable with the diffractometer is about 67°, above which the χ-circle enters into collision with the X-ray tube housing; consequently the intensity data collection was limited to reflections with $2\theta_m(CuK\alpha) \leqslant 130^o$, (which allows about 4° for scan completion).

The dimensions of the crystal used for intensity data collection were 0.3 mm in length, (parallel to b), and 0.1 x 0.1 mm in cross section. The crystal was mounted with b* parallel to the

(54) L. E. Alexander and G. S. Smith, Acta Cryst., 17, 1195 (1964).

ϕ-axis of the goniostat, and c* was labelled $\phi = 0$. Refined cell dimensions were obtained, (p.46), from which angular settings χ, ϕ, $2\theta_1$ and $2\theta_2$ were calculated (55) for all independent reflections, (hkl and $hk\bar{l}$), within the range $0 < 2\theta_m(\underline{CuK\alpha}) \leq 130^\circ$. The digital input-output unit to the diffractometer is an I.B.M. 026 printing card punch, the input card for each reflection being pre-punched with indices and the required setting angles. The following output card, (initially blank), contains a duplication of this information and also records the attenuator number used, the total count over the scan range, (PK), and the twenty second background counts at $2\theta_1$ and $2\theta_2$, (B_1 and B_2 respectively). The input cards were sorted by hand to keep the time required for angular settings to a minimum. The hkl and $hk\bar{l}$ series were run separately as the two major groups, and within each group data were collected in $h\underline{n}l$ levels. The setting cards in each $h\underline{n}l$ level were further sorted so that the l index changed more rapidly than h and such that the sum of the differences between the indices of sucessive planes was a minimum. The average time taken for the complete angular settings and count measurements for each reflection was four minutes, of which twenty seconds, on average, represented the time taken to set the required angles.

Data reduction.

With a twenty second background count at each end of the scan, the average background signal is $(B_1+B_2)/40$ counts per

(55) We are grateful to Dr. J. Trotter, University of British Columbia, for the program used to calculate setting angles.

second. By assuming that this background count rate is characteristic for the total scan, the integrated intensity, PK, is background corrected and attenuator scaled by,

$$I = \left[PK - \frac{60 \cdot \Delta 2\theta \cdot (B_1 + B_2)}{40} \right] \cdot A_t \quad ,$$

(where $60.\Delta 2\theta$ represents the scan time, in seconds). As all intensity data are measured in the equatorial plane, the Lorentz-polarisation factor applicable is,

$$Lp = \frac{1 + \cos^2 2\theta}{2\sin 2\theta} \quad .$$

No absorption corrections were applied, thus,

$$|F_{hkl}|^2 = I_{hkl} \cdot \frac{1}{Lp_{hkl}} \quad .$$

The standard deviation of each observed structure amplitude, σF_o, was calculated by employing the statistical treatment formulated by Abrahams et al. (56,57,58). With background measurements taken for a total of forty seconds and a scan rate of one degree per minute, then,

$$\sigma F_{hkl} = \frac{1}{2|F_{hkl}|} \cdot \sqrt{\sigma^2 |F_{hkl}|^2} \quad ,$$

where,

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(56) B. B. Cetlin and S. C. Abrahams, Acta Cryst., 16, 943 (1963).
(57) S. C. Abrahams, ibid., 17, 1327 (1964).
(58) S. C. Abrahams and J. L. Bernstein, ibid., 18 926, (1965).

$$\sigma^2|F_{hkl}|^2 = \left[\frac{1}{Lp_{hkl}}\right]\left[PK + \left[\frac{\Delta 2\theta.60}{40}\right]^2.(B_1+B_2)\right].A_t + C_{or}|F_{hkl}|^4$$

C_{or} incorporates many instumental features, such as the short time X-ray supply and counter circuit instability, and in this work was assigned the value 0.002, (this being the average of the values found by Abrahams).

Intensity data were reduced, in the manner described above, to observed structure amplitudes, each with a corresponding standard deviation, employing a program written for the I.B.M. 7094 (59). If the peak corrected for background, (I), was zero or negative, the reflection was allocated a background corrected intensity value of two counts, reduced in the normal manner, and termed unobserved. In cases where the observed structure amplitude was finite, but had $\sigma F_o \geq |F_o|$, the calculated values of σF_o and $|F_o|$ were retained, but the reflection was again termed unobserved.

Intensity measurements were made on 1882 independent reflections within the range $0 < 2\theta_m(\underline{CuK\alpha}) \leq 133^o$. After data reduction 322 of these reflections, (17%), were classified as unobserved. Throughout the course of the work two residual index values are used. R_1 is the residual index obtained using all 1882 reflections for which intensity measurements were made,

(59) The data reduction program was written by Mr. K. S. Dichmann, Chemistry Department, University of Toronto.

reflections classified as unobserved being treated as described above; whilst R_2 is the index obtained when reflections termed unobserved are excluded from the summation.

CHAPTER 8.

THE GENERATION OF NORMALISED STRUCTURE AMPLITUDES.

Generation of the K-curve.

The observed structure amplitudes were placed on the absolute scale using the K-curve method described by Karle and Hauptman (60) and later by Norment (61).

The magnitude of the normalised structure factor, $|E_{hkl}|$, is defined by equation (2.6), which can be extended to the form,

$$|E_{hkl}| = \left[\frac{|F_{hkl}|^2 . K(S_{hkl})}{\varepsilon_{hkl} \sum_{i=1}^{N} f_{i\ hkl}^2} \right]^{1/2} \qquad (8.1)$$

where, ε_{hkl} is a quantity which depends upon the systematic absences of the space group of the crystal; for $P2_1/c$ ε has the value two for h0l and 0k0 sets, and is otherwise unity,

$f_{i\ hkl}$ is the scattering factor of the ith atom in a unit cell containing a total of N atoms,

$|F_{hkl}|$ is the observed structure amplitude,

$K(S_{hkl})$ is a function of $\sin\theta$ which places each $|F_{hkl}|^2$ datum on the absolute scale.

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(60) J. Karle and H. Hauptman, Acta Cryst., 6, 473 (1953).
(61) H. G. Norment, U. S. Naval Research Laboratory Report 5739, Washington, D. C., (1961).

The theory of the method depends on the approximation $\langle |E|^2 \rangle = 1$. Initially the reciprocal lattice, $(0 < 2\theta_m \leq 130^\circ)$, was divided into ten ranges of equal volume so that each sub-interval contained approximately the same number of reflections. Each of the ten ranges was characterised by a minimum and maximum $\sin\theta$, (S_1 and S_2 respectively), and by a mean $\sin\theta$, S_m, where,

$$S_m = \left[\frac{S_1^3 + S_2^3}{2} \right]^{1/3}$$

The value of $K(S_m)$ was calculated for each range, where,

$$K(S_m) = \sum_{S_1}^{S_2} \frac{\varepsilon_{hkl} \sum_{i=1}^{N} f_{i\,hkl}^2}{\sum_{S_1}^{S_2} |F_{hkl}|^2} \quad . \qquad (8.2)$$

The procedure was repeated using fifteen and twenty ranges. The calculated values of $K(S_m)$ and S_m are listed in Table 8.1, and the K-curve plot of $K(S_m)$ against S_m is given in Figure 8.1, which also shows a monotonically increasing curve drawn through the experimental points.

It is assumed that the curve through the experimental points can be formulated by an exponential function of the type,

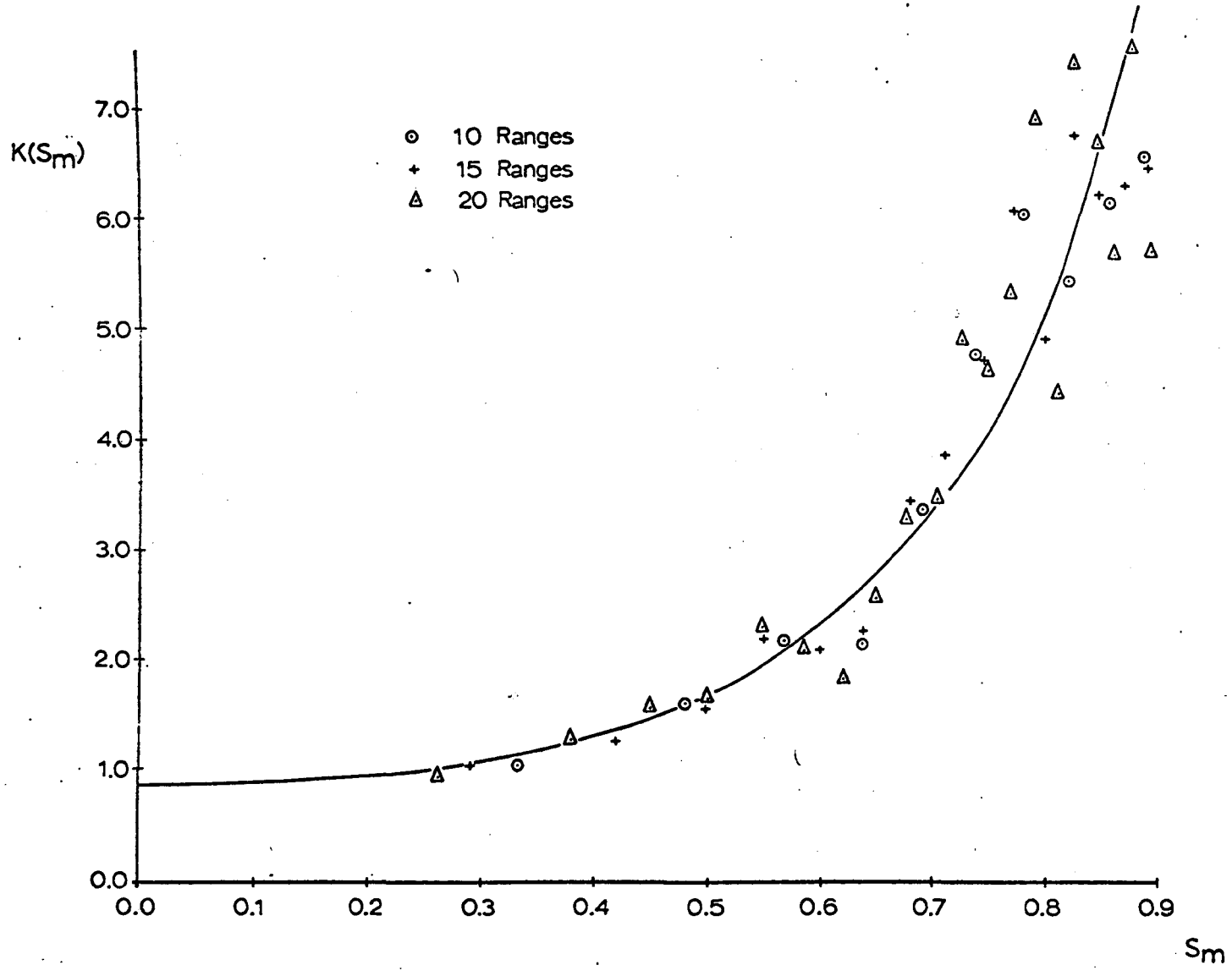
$$K(S_m) = A \exp B (S_m)^C . \qquad (8.3)$$

The 'best fit' values of A and B were calculated by a least squares method for the seven equations of type (8.3) which had the exponent C specified from 1.0 to 4.0 in intervals of 0.5. Also computed for each equation was the sum of the squares of the deviations of the forty-five experimental points from the formulated curve,

10 Ranges		15 Ranges		20 Ranges	
S_m	$K(S_m)$	S_m	$K(S_m)$	S_m	$K(S_m)$
0.3316	1.0475	0.2896	1.0433	0.2632	0.9543
0.4782	1.5979	0.4177	1.2318	0.3795	1.2713
0.5670	2.1831	0.4953	1.6330	0.4500	1.5552
0.6343	2.1418	0.5541	2.2017	0.5034	1.6500
0.6897	3.3541	0.6025	2.0707	0.5474	2.2824
0.7374	4.7696	0.6642	2.2253	0.5853	2.0813
0.7796	6.0392	0.6811	3.4261	0.6188	1.7930
0.8177	5.4467	0.7143	3.8616	0.6490	2.5529
0.8525	6.1488	0.7448	4.7001	0.6767	3.2657
0.8847	6.5652	0.7729	6.0601	0.7022	3.4617
		0.7991	4.9021	0.7260	4.9055
		0.8237	6.7563	0.7484	4.6289
		0.8469	6.2195	0.7695	5.3104
		0.8689	6.3475	0.7895	6.8578
		0.8899	6.4606	0.8085	4.4094
				0.8267	7.4067
				0.8441	6.6556
				0.8608	5.6656
				0.8769	7.5611
				0.8924	5.7065

The computed values of $K(S_m)$ and S_m.

Table 8.1.



The K-curve plot.

Table 8.1

SUM. The coefficients of the seven curves and the corresponding values of SUM are listed in Table 8.2. A minimum occurs for SUM between the two curves formulated with C = 1.5 and C = 2.0, so that the exponential functions derived with these coefficients are most representative of the experimental point distribution.

The K-curve method is essentially a modified Wilson function‡, if C is specified as two, then the relationships between the scaling quantities determined by this method and those of Wilson's original treatment are,

$$A = K',$$

$$B = \frac{2B_{ov}}{\lambda^2},$$

where K' is the absolute scaling factor, (with respect to $|F_o|^2$), and B_{ov} is the overall temperature factor of Wilson's method.

The generation of normalised structure amplitudes.

The magnitudes of the normalised structure factors, $|E_{hkl}|$, were computed using the expanded form of equation (8.1),

$$|E_{hkl}| = \left[\frac{|F_{hkl}|^2 \cdot A\exp B(\sin\theta_{hkl})^C}{\varepsilon_{hkl} \sum_{i=1}^{N} f_{i\,hkl}^2} \right]^{1/2} \qquad (8.4)$$

The program used to compute the normalised structure factor magnitudes was also coded to calculate the statistical averages, $\langle |E|^2 \rangle$, $\langle \big| |E|^2 - 1 \big| \rangle$ and $\langle |E| \rangle$; and the percentage distribution of $|E|$.

‡ Wilson's method for obtaining the absolute scaling factor and overall temperature factor is discussed in Chapter 4.

A	B	C(specified)	SUM
0.3058	3.5355	1.0	3.128
0.5918	3.0369	1.5	2.777
0.8320	2.8586	2.0	2.991
1.0295	2.8081	2.5	3.729
1.1947	2.8221	3.0	5.155
1.3356	2.8741	3.5	7.635
1.4580	2.9514	4.0	11.796

The 'best fit' coefficients A and B computed for the seven curves. SUM is the sum of the squares of the deviation of the forty-five experimental points from the formulated curve.

Table 8.2

Normalised structure factor magnitudes were computed using the two 'best-fitting' K-curves, (C = 1.5 and C = 2.0, Table 8.2). The statistical averages and the |E| distribution produced are shown in Table 8.3, together with the theoretical values of these quantities for both acentric and centric space groups. From Table 8.3 it can be seen that the averages and |E| distribution are almost identical for the two K-curve formulations and a detailed inspection of the complete |E| listings showed that individual |E|'s were, in general, insignificantly different in the two sets; the only major differences apparent occur at low sinθ when $K(S_m)$ approximates to A. The symbolic addition procedure was carried out using normalised structure factor magnitudes generated with the second K-curve, (C = 2.0), as this made the thermal correction factor analogous with the normally assumed Debye form.

For application of the symbolic addition procedure, the normalised structure factor magnitudes were listed in descending order and classified by their indices into the eight groups of type ggg, gug, ugg, ggu, uuu, uug, ugu and guu, (where g = even and u = odd). There are 91 planes with $|E| \geqslant 2.0$ and 242 with $|E| \geqslant 1.5$. The fact that the distribution of the |E|'s within the eight parity groups is reasonably uniform, (shown in Table 8.4), indicates that there is no specialisation in the location of the sulphur atoms, (as had been found in the desaurin from acetophenone structure), and is a favourable indication for the success

	Experimental		Theoretical	
	K-curve 1.	K-curve 2.	Centric	Acentric
A	0.5918	0.8320		
B	3.0369	2.8586		
C	1.5	2.0		
$\langle \lvert E \rvert \rangle$	0.835	0.835	0.798	0.886
$\langle \lvert E^2-1 \rvert \rangle$	0.922	0.922	0.968	0.736
$\langle E^2 \rangle$	1.016	1.017	1.000	1.000
$\% \lvert E \rvert \geqslant 3.0$	0.2	0.2	0.3	0.0_1
$\% \lvert E \rvert \geqslant 2.0$	4.9	4.8	5.0	1.8
$\% \lvert E \rvert \geqslant 1.0$	32.1	32.2	32.0	37.0

The distribution of normalised structure factor magnitudes and statistical averages found together with the theoretical values.

Table 8.3

h k l	$\|E\| \geqslant 2.0$	$\|E\| \geqslant 1.5$
g u g	9	40
g u u	13	31
g g g	13	26
g g u	14	29
u u g	8	25
u u u	10	26
u g g	11	32
u g u	13	33
$\sum \left.\begin{matrix} g & u & g \\ g & g & u \\ u & u & g \\ u & g & u \end{matrix}\right]$	44	127
$\sum \left.\begin{matrix} g & u & u \\ g & g & g \\ u & u & u \\ u & g & g \end{matrix}\right]$	47	115

The distribution of normalised structure factor magnitudes throughout the eight sub-groups.

Table 8.4

of the symbolic addition procedure.

The program used to generate the K-curve and compute normalised structure factor magnitudes was written in Fortran IV for the I.B.M. 7094[‡].

‡ A listing of this program is given in Appendix V.

CHAPTER 9.

THE SYMBOLIC ADDITION PROCEDURE.

The practical aspects of the symbolic addition procedure follow the method outlined by Karle and Karle (62). The only phase relationship used was Σ_2, which for a centrosymmetrical crystal is formulated as,

$$sE_{\vec{h}} \sim s\sum_{\vec{k}} E_{\vec{k}} \cdot E_{\vec{h}-\vec{k}} \text{ , (where 's' means 'sign of').}$$

The hyperbolic tangent probability formula was used to evaluate the reliability of phases generated by application of the Σ_2 relationship (34,35). The probability function, $P+(\vec{h})$, which determines the probability that the sign of $E_{\vec{h}}$ be positive, is defined by,

$$P+(\vec{h}) = 1/2 + 1/2\tanh\left[\frac{\sigma_3}{\sigma_2^{3/2}}\left|E_{\vec{h}}\right| \cdot \sum_{\vec{k}} E_{\vec{k}} \cdot E_{\vec{h}-\vec{k}}\right],$$

where $\sigma_n = \sum_{i=1}^{N} Z_i^n$; Z_i being the atomic number of the ith atom in a unit cell containing N atoms. For PDM $\sigma_2 = 4013$ and $\sigma_3 = 46,284$.

The Σ_2 listing and combinational count.

A Σ_2 listing (62) of all combinations of $\vec{k}$ and $\vec{h}-\vec{k}$ for a given $\vec{h}$ was computed, considering only the 91 reflections with $|E| \geqslant 2.0$, (which were expanded to 364 $|E_{\vec{h}}|$ using symmetry related reflections). This listing facilitated a concise

(62) J. Karle and I. L. Karle, Acta Cryst., 21, 849 (1966).

means of applying the Σ_2 formula by hand for this group of reflections. Also computed were the number of times each of the reflections entered into a Σ_2 combination with other members of the set (63).

Origin specification.

Working in three-dimensions in the monoclinic system, (with a primitive unit cell), the origin is fixed by assigning phases arbitrarily to three linearly independent reflections (64,65). The three $E_{\vec{k}}$ selected to specify the origin were,

h	k	l	s	|E|	number of combinations.
2	2	-9	+	2.63	60
5	1	-2	+	2.83	33
2	3	1	+	2.90	36

These three linearly independent reflections were chosen on the basis that they have large |E| value, (hence any new phases generated by Σ_2 application will have a high associated probability), and that they form numerous Σ_2 combinations amongst themselves and with other reflections of larger |E|.

The symbolic addition procedure.

Σ_2 generation with the three origin specifying reflections

(63) The program used to compute the Σ_2 listing and combinational count was written by Mr. F. T. C. Leung, Chemistry Department, University of Toronto.
(64) H. Hauptman and J. Karle, Acta Cryst., 12, 93 (1959).
(65) K. Lonsdale and H. J. Grenville-Wells, ibid., 7, 490 (1954).

yielded signs for five additional $E_{\vec{h}}$ on the first cycle. Although each of the generated signs was the result of a single Σ_2 combination, the associated probability values were all greater than 0.99. These five normalised structure factors were added to the original three to form the input for the next cycle. After three cycles of Σ_2 application, in this manner, a total of thirteen reflections, (exclusive of those used to specify the origin), could be allocated an absolute phase, (+ or -). If the generated sign was the result of a single Σ_2 combination, a probability minimum of 0.975 was imposed; single generations of lower probability were placed to one side in the hope that further Σ_2 combinations would be formed at a later stage, which would produce a corresponding increase in the probability factor. One- and two-dimensional data were treated with great care during the procedure, as it has been previously found that exceptions to the Σ_2 relationship are much more numerous with these type of reflections.

Since no additional signs could be generated after these three cycles a symbolic assignment was necessary and by inspection of the Σ_2 listing 2.10.2 was chosen and allocated the symbol $\underline{A}$. This reflection was chosen on the basis that it would enter into many Σ_2 combinations with the sixteen reflections whose phases were already known, and that it had a large $|E|$ of 2.64. After nine additional cycles of Σ_2 all 91 reflections with $|E| \geqslant 2.0$ could be allocated phases of +, - or $\pm A$. Since A must be plus or minus, phases determined as $+A^2$ and $-A^2$ were carried through as + and - respectively. In the final three cycles of the

procedure it was noted that phases generated for a few of the reflections were of mixed absolute and symbol type, (either +A and - or -A and +), indicating that the relationship A = - was probable. Karle and Karle (62) point out that symbols are often found to be definable in terms of others or in terms of absolute values, but suggest that any relationships indicated should not be assumed until the completion of the procedure. The relationship that A was negative was therefore not accepted at this stage, and reflections for which generated phases were of mixed absolute and symbolic type were placed aside and not used in Σ_2 generation when the list was extended.

Now that phases could be allocated to all reflections with $|E| \geqslant 2.0$, the list was extended by including the 151 planes for which $2.0 > |E| \geqslant 1.5$. The input for the extended cycle were 84 $E_{\vec{k}}$ for which phases had been generated in the first part of the procedure, (seven reflections being excluded because of low probability or because phases indicated were of a mixed absolute and symbol type). As the $|E|$ values in the new list were smaller, with the result that the triple product for a single Σ_2 combination and hence the probability were lower, a criterion was adopted that there must be at least five independent Σ_2 combinations for any new reflection before the indicated phase would be accepted. On the first pass phases could be assigned to 107 $E_{\vec{h}}$ in the new list using this criterion (66). Numerous of the phases generated had both symbolic and

(66) This final Σ_2 cycle was computed using a program written by Mr. F. T. C. Leung.

absolute contributors, indicating again that A was negative, and this assignment was now accepted.

A summary of the $\sum_2$ cycles is given in Appendix II.

The E map computation.

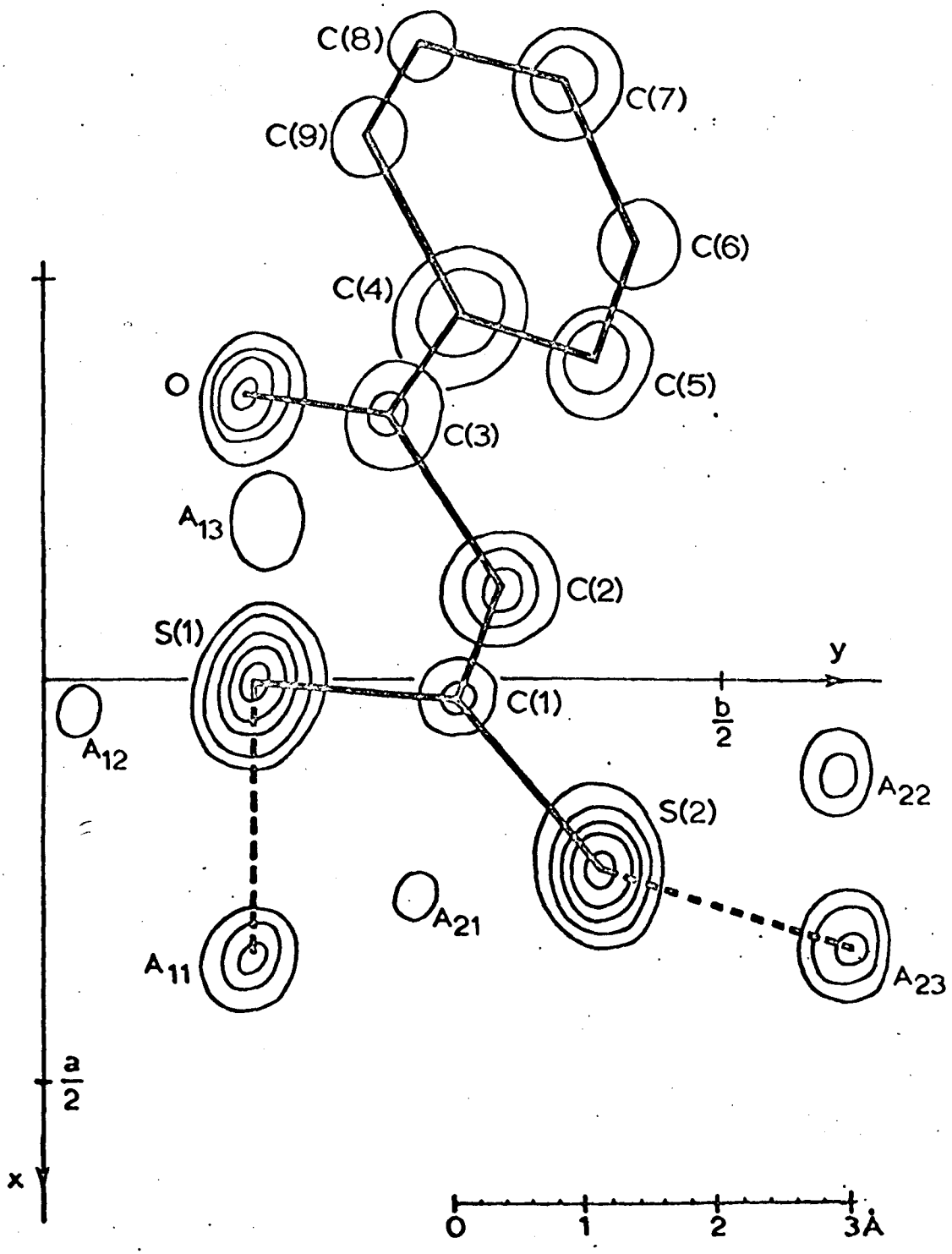
The 198 signs determined for reflections with larger |E| were already in excess of the ten to twelve normalised structure factors per atom of the asymmetric unit generally accepted as being sufficient to produce a well resolved E-map (37,38). Using the 198 normalised structure factors as Fourier coefficients, the three-dimensional E-map was computed for a quarter of the unit cell defined by $-0.5 \leq x \leq 0.5$, $0.0 \leq y \leq 0.5$ and $0.0 \leq z \leq 0.5$, in intervals of 0.05 in x, 0.025 in y and 0.015 in z. The resultant synthesis clearly revealed the location of all the atoms of the molecule, with the exception of the two carbon atoms of the methyl groups. Around the sulphur atoms there were subsiduary diffraction peaks, (in the region 1.7Å to 2.2Å distant from the sulphur atoms), similar to those found in the E-map of allylthiourea (67), and unambiguous identification of the remaining carbon atoms was not possible. The fractional coordinates of the twelve atoms whose locations could be identified from the E-map are listed in Table 9.1. A composite drawing of the E-map, formed by superimposing sections taken through the peak centres normal to c*, is shown in Figure 9.1, where also is shown the atomic numbering system employed. The

(67)K. S. Dragonette and I. L. Karle, Acta Cryst., 19, 978 (1965).

Atom	X/a	Y/b	Z/c
S(1)	0.530	0.160	0.487
S(2)	0.728	0.412	0.465
O	0.073	0.153	0.393
C(1)	0.475	0.310	0.438
C(2)	0.280	0.333	0.383
C(3)	0.075	0.258	0.360
C(4)	-0.125	0.310	0.303
C(5)	-0.110	0.404	0.250
C(6)	-0.320	0.438	0.197
C(7)	-0.535	0.383	0.184
C(8)	-0.540	0.265	0.230
C(9)	-0.370	0.237	0.275

The atomic coordinates estimated from the E-map.

Table 9.1



Composite E-map normal to c*. The contours are spaced at equal arbitary intervals.

Figure 9.1.

additional peaks around the sulphur atoms are shown in Figure 9.1 with the label A.

In the allylthiourea problem the subsiduary peaks close to the sulphur atom were removed by increasing the number of coefficients in the E-map computation. However we decided that rather than generate more phases using Σ_2, an electron density synthesis, using observed structure amplitudes phased by the twelve atoms whose positions were postulated, should unambiguously identify the carbon atoms of the methyl groups and at the same time confirm the atomic locations obtained from the E-map. Structure factors were computed using the atomic locations listed in Table 9.1 and allocating an overall temperature factor of $3.4\mathring{A}^2$, (calculated from the B coefficient of the K-curve). Reflections tagged unobserved were excluded from the calculation which yielded a residual index of 0.38. The subsequent electron density synthesis‡ clearly revealed the positions of the carbon atoms of the methyl groups. The fractional coordinates of all fourteen atoms of the molecule were assessed from the synthesis, and are listed in Table 9.2. Refinement of the atomic parameters by the method of least squares was now initiated.

‡ The electron density synthesis was computed for the quarter of the unit cell and with mesh intervals previously defined for the E-map synthesis.

Atom	X/a	Y/b	Z/c
S(1)	0.530	0.157_5	0.483
S(2)	0.732	0.405	0.468
O	0.065	0.157_5	0.390
C(1)	0.480	0.304	0.438
C(2)	0.286	0.334	0.382_5
C(3)	0.070	0.261	0.358_5
C(4)	-0.132	0.297_5	0.298_5
C(5)	-0.117	0.398_5	0.253
C(6)	-0.313	0.446	0.196_5
C(7)	-0.533	0.382_5	0.182
C(8)	-0.555	0.277_5	0.228
C(9)	-0.356	0.234	0.287
Me(10)	0.835	0.149	0.537_5
Me(11)	0.630	0.550	0.401

Atomic coordinates estimated from the three-dimensional electron density synthesis.

Table 9.2

CHAPTER 10.

REFINEMENT OF THE STRUCTURE.

The least squares program used was the same version of OR-FLS which had previously been employed in the refinement of the desaurin from acetophenone structure. All recorded reflection data were used in the refinement except in the final two cycles with anisotropic temperature factors when reflections classified as unobserved were excluded. Each observed structure amplitude was weighted using its standard deviation, σF_o, calculated in the data reduction procedure,

$$w_{F_o} = \frac{1}{(\sigma F_o)^2} .$$

An overall scale factor was treated as a variable throughout the refinement; the function minimised was $\sum w(|F_o| - |F_c|)^2$.

Refinement with isotropic temperature factors.

The initial positional parameters used in the refinement were those obtained from the electron density synthesis, (Table 9.2), and each atom was allocated an isotropic temperature factor of $3.4 Å^2$. One cycle of refinement was computed with the thermal parameters of the atoms fixed and was followed by three cycles in which all fifty-six positional and thermal parameters were refined, R_1 and R_2 improving to 0.18 and 0.16 respectively. The maximum parameter shift calculated in the last cycle represented about a quarter of the standard deviation of the parameter and

conversion of the thermal parameters into anisotropic mode was now considered in order. The atomic parameters at this stage are listed in Table 10.1.

Refinement with anisotropic temperature factors.

Four cycles of least squares refinement, performed on the one hundred twenty-seven variables using all recorded reflection data, proceeded normally. A further two cycles, computed with reflections tagged unobserved excluded, produced only small parameter shifts and illustrated that the weighting of these reflections was such that their inclusion or exclusion had little effect during the least squares refinement. The shifts calculated in the final cycle were at most 25% of the standard deviation of the parameter, and refinement was considered complete. The residual index R_2 was 0.112. The final positional and thermal parameters of the fourteen non-hydrogen atoms of the molecule, and their estimated standard deviations, calculated from the least squares residuals, are listed in Tables 10.2 and 10.3. B_{ij}, in Table 10.3, are coefficients in the anisotropic temperature expression,

$$\exp -1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})$$

Location of the hydrogen atoms.

The final atomic parameters, (Tables 10.2 and 10.3), were used to set-up coefficients for a three-dimensional difference synthesis, from which peaks attributable to the twelve hydrogen

Atom	X/a	Y/b	Z/c	B_{iso} ($Å^2$)
S(1)	0.5257	0.1589	0.4812	3.613
S(2)	0.7298	0.4106	0.4651	3.906
O	0.0653	0.1523	0.3892	4.114
C(1)	0.4831	0.3100	0.4377	3.167
C(2)	0.2740	0.3428	0.3845	3.417
C(3)	0.0733	0.2600	0.3603	3.257
C(4)	-0.1406	0.3020	0.2969	3.486
C(5)	-0.1225	0.3998	0.2512	4.359
C(6)	-0.3287	0.4342	0.1924	4.328
C(7)	-0.5451	0.3724	0.1846	4.371
C(8)	-0.5548	0.2730	0.2304	4.378
C(9)	-0.3560	0.2355	0.2879	3.487
Me(10)	0.8455	0.1558	0.5351	4.470
Me(11)	0.6412	0.5507	0.4042	4.131

Atomic parameters at the completion of the isotropic least squares refinement.

Table 10.1

Atom	X/a	σX/a $\times 10^4$	Y/b	σY/b $\times 10^4$	Z/c	σZ/c $\times 10^5$
S(1)	0.5264	5	0.1585	3	0.4812	15
S(2)	0.7300	5	0.4107	3	0.4649	15
O	0.0684	13	0.1511	7	0.3895	38
C(1)	0.4843	17	0.3079	9	0.4378	55
C(2)	0.2739	18	0.3433	10	0.3857	58
C(3)	0.0729	18	0.2580	9	0.3610	56
C(4)	-0.1386	19	0.3024	10	0.2982	55
C(5)	-0.1223	20	0.3986	11	0.2509	59
C(6)	-0.3262	21	0.4356	11	0.1934	60
C(7)	-0.5435	22	0.3732	13	0.1840	62
C(8)	-0.5569	21	0.2729	11	0.2312	63
C(9)	-0.3546	19	0.2363	11	0.2874	61
Me(10)	0.8446	19	0.1558	12	0.5355	64
Me(11)	0.6406	20	0.5491	10	0.4045	60

The final fractional coordinates and standard deviations of the non-hydrogen atoms.

Table 10.2

Atom	B_{11}	σB_{11}	B_{22}	σB_{22}	B_{33}	σB_{33}	B_{12}	σB_{12}	B_{13}	σB_{13}	B_{23}	σB_{23}
S(1)	3.34	0.15	3.03	0.12	4.03	0.14	0.06	0.11	0.15	0.11	0.96	0.11
S(2)	3.53	0.15	3.28	0.13	4.36	0.15	-0.56	0.12	0.07	0.11	0.64	0.11
O	3.56	0.39	2.84	0.33	5.24	0.39	0.15	0.30	-0.13	0.32	2.04	0.31
C(1)	2.49	0.47	2.67	0.46	2.97	0.49	-0.62	0.38	0.24	0.40	-0.51	0.39
C(2)	3.29	0.51	2.60	0.44	4.37	0.57	0.32	0.42	1.15	0.45	0.44	0.45
C(3)	3.74	0.55	2.10	0.44	3.48	0.50	0.19	0.40	0.72	0.42	-0.49	0.41
C(4)	3.65	0.56	2.39	0.47	3.01	0.49	0.76	0.42	0.97	0.43	0.00	0.40
C(5)	3.93	0.62	4.96	0.59	3.61	0.53	1.38	0.53	0.90	0.49	1.45	0.50
C(6)	3.71	0.62	4.28	0.64	4.25	0.57	0.30	0.54	0.09	0.48	-0.86	0.50
C(7)	4.03	0.67	5.63	0.79	4.13	0.60	1.32	0.58	0.39	0.51	-0.92	0.54
C(8)	3.86	0.66	3.70	0.57	4.10	0.60	-0.05	0.49	-0.25	0.52	-0.94	0.49
C(9)	2.86	0.54	4.03	0.59	4.50	0.57	-1.48	0.47	1.11	0.47	-2.79	0.50
Me(10)	2.75	0.53	3.10	0.60	6.02	0.72	0.44	0.49	-1.66	0.50	0.44	0.57
Me(11)	4.99	0.65	2.88	0.48	5.64	0.62	0.68	0.48	0.97	0.51	2.99	0.47

The final anisotropic thermal parameters, ($Å^2$), and their standard deviations.

Table 10.3

atoms of the molecule were identified. Their fractional coordinates are listed in Table 10.4, together with the theoretical values calculated from the carbon atom positions assuming a carbon-hydrogen bond length of 1.075Å. In this calculation one hydrogen atom of each methyl group was considered staggered with respect to the corresponding S-C(1) direction. The numbering system used for the hydrogen atoms is shown in Figure 10.1.

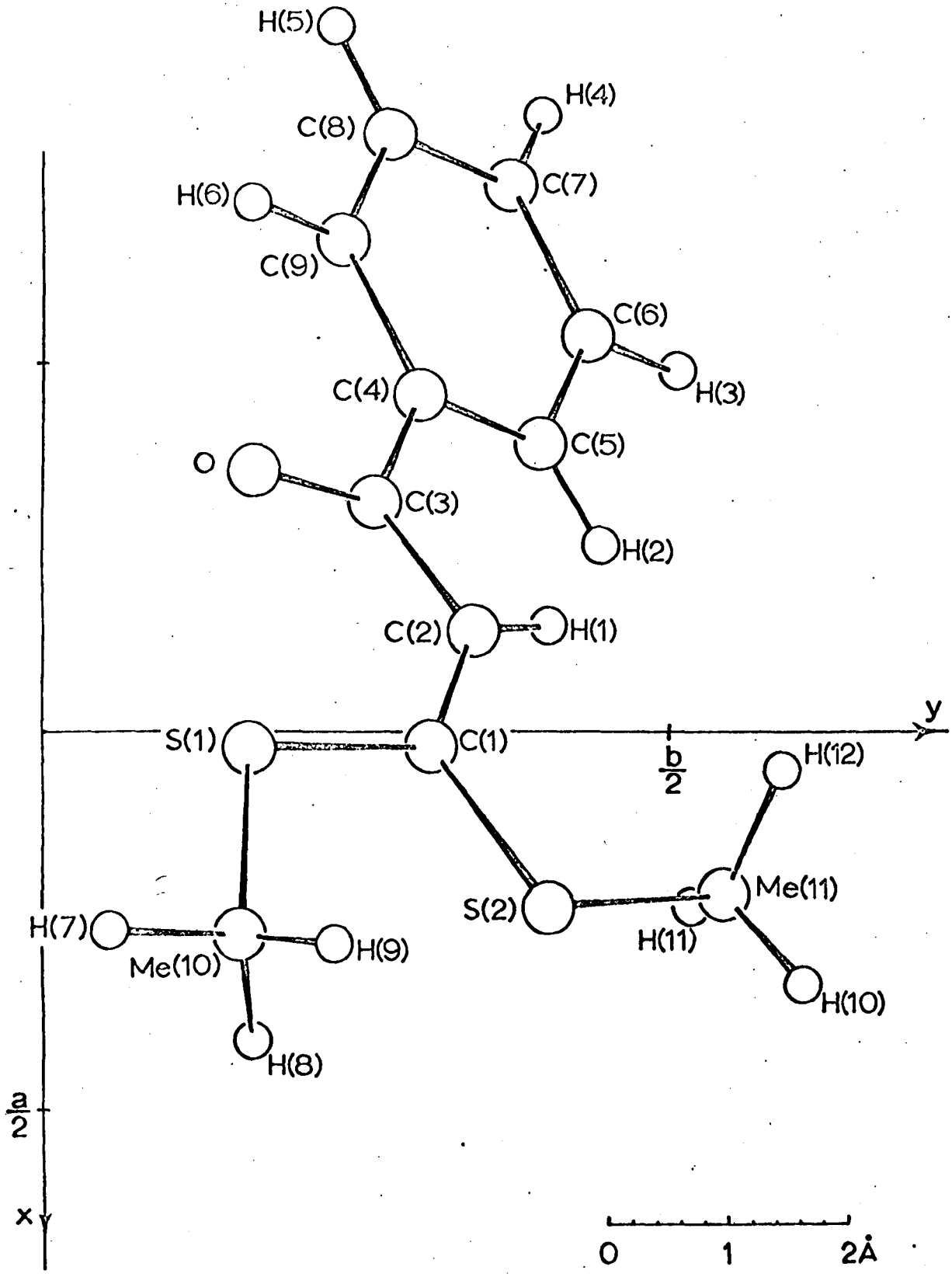
Hydrogen atoms, located from the difference synthesis and assigned the anisotropic thermal motion of the carbon atom to which they are bonded, were included in a final structure factor calculation. The hydrogen atom scattering factor used was that listed in International Tables (43). The observed and calculated structure factors are tabulated in Appendix III, and yield R_1 and R_2 of 0.119 and 0.101 respectively. Superimposed sections of a final three-dimensional electron density distribution, taken through the atomic centres normal to c*, are shown in Figure 10.2.

Analysis of the phases generated by the symbolic addition procedure.

The phases generated by the symbolic addition procedure for the 198 normalised structure factors which constituted the input of the E-map were compared with those calculated from the final atomic parameters. It was revealed that the phase of 254, ($|E| = 1.58$), was the only incorrect allocation made during the symbolic addition procedure. Since it cannot be considered that this single incorrect phase could have significantly affected the resultant E-map, the additional diffraction maxima around the sulphur atoms apparent in the synthesis appear the result of a lack of coefficients in the computation.

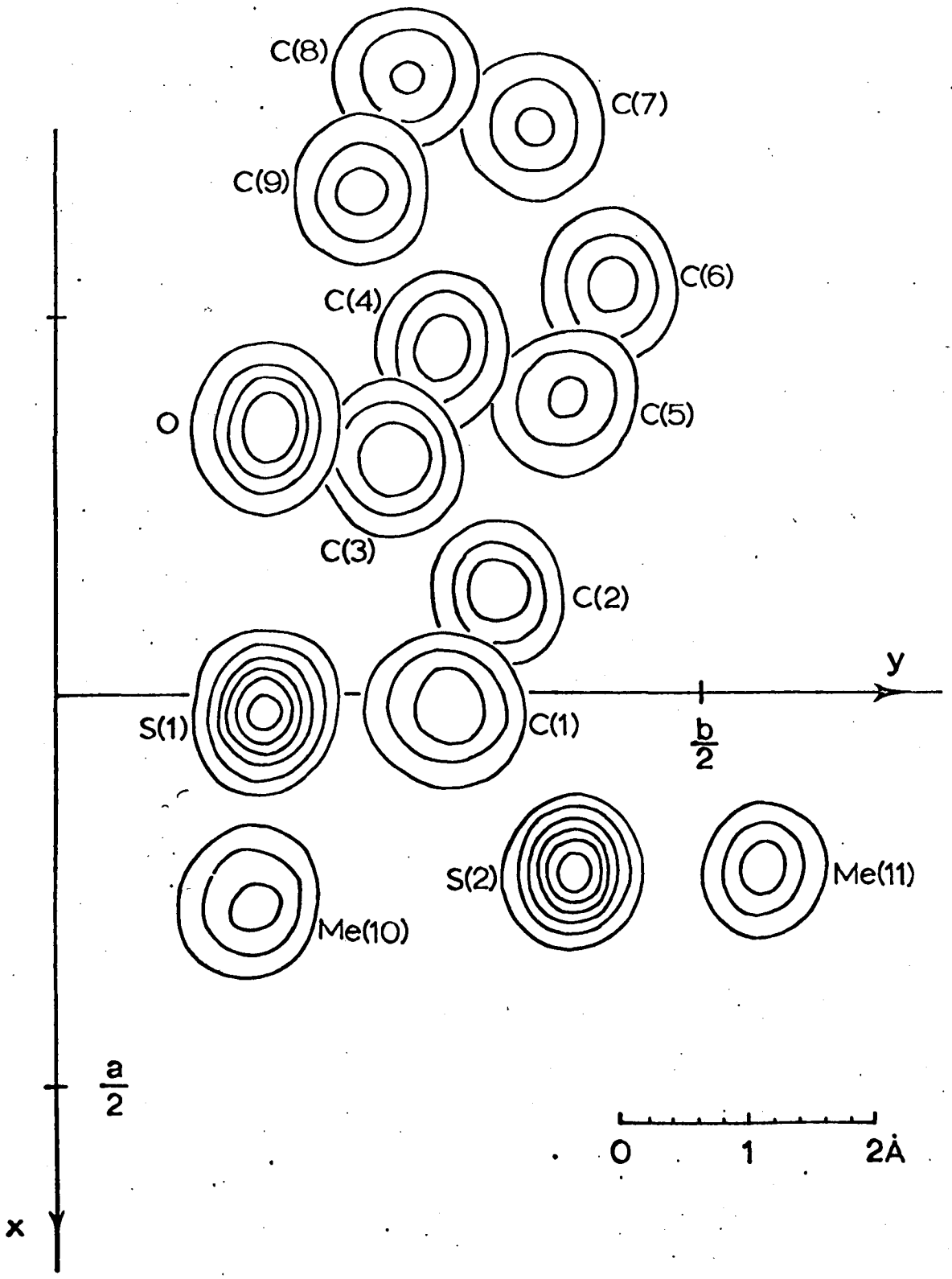
Atom	Attached to carbon	X/a	Y/b	Z/c	X/a	Y/b	Z/c
H(1)	C(2)	0.245	0.422	0.351	0.2593	0.4382	0.3626
H(2)	C(5)	0.024	0.475	0.261	0.0451	0.4447	0.2581
H(3)	C(6)	-0.390	0.483	0.149	-0.3159	0.5111	0.1569
H(4)	C(7)	-0.685	0.416	0.144	-0.7001	0.4021	0.1406
H(5)	C(8)	-0.720	0.219	0.230	-0.7230	0.2250	0.2237
H(6)	C(9)	-0.355	0.178	0.340	-0.3622	0.1580	0.3226
H(7)	Me(10)	0.852	0.068	0.533	0.8706	0.0639	0.5619
H(8)	Me(10)	0.972	0.158	0.495	0.9520	0.1645	0.5011
H(9)	Me(10)	0.885	0.217	0.570	0.8874	0.2325	0.5747
H(10)	Me(11)	0.805	0.600	0.416	0.7918	0.6121	0.4211
H(11)	Me(11)	0.600	0.490	0.354	0.6012	0.5203	0.3489
H(12)	Me(11)	0.530	0.618	0.421	0.4878	0.5954	0.4109
		Hydrogen positions obtained from the difference synthesis.			Theoretical hydrogen positions calculated from the carbon locations.		

Table 10.4



The atomic numbering system used.

Figure 10.1



Composite electron density normal to c*. Contour intervals at carbon and oxygen atoms 1.0 eÅ^{-3}, at the sulphur atoms 2.0 eÅ^{-3}. The zero contour is omitted.

Figure 10.2.

EXPERIMENTAL - PART III

THE STRUCTURE ANALYSIS OF THE 1,2,4-TRITHIACYCLOPENTANE FROM PINACOLONE.

CHAPTER 11.

PRELIMINARY X-RAY WORK AND INTENSITY DATA COLLECTION.

The 1,2,4-trithiacyclopentane from pinacolone, prepared by the method of Gompper (7), crystallises from a chloroform and hexane mixture as yellow needles (68). The crystals have a as the needle axis with (011) and (01$\bar{1}$) developed, (Figure 11.1, p.82).

X-ray equipment.

Preliminary photographic work was carried out using a Philips 1009 X-ray generator and a Stoe integrating Weissenberg goniometer. Three-dimensional intensity data were collected using a Picker automated four-circle diffractometer. Nickel filtered copper radiation was used throughout the structure analysis.

Unit cell dimensions.

Cell dimensions were originally obtained from zero level Weissenberg photographs and were later determined more accurately using measurements from the diffractometer. The crystal, (later used for intensity data collection), was mounted with b* parallel to the ϕ axis of the goniostat, and at $\chi = 0$, β^* was determined directly as the ϕ angular displacement between a* and c*. The axial lengths were calculated from average observed theta angles for two h00, three 0k0 and four 001 reflections,

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(68) We are grateful to Dr. P. Yates for supplying crystals of the 1,2,4-trithiacyclopentane from pinacolone.

System monoclinic (y axis unique)

$a = 5.93_6$ Å ($\pm 0.00_7$)‡

$b = 13.02_3$ Å ($\pm 0.01_0$)

$c = 22.73_2$ Å ($\pm 0.01_5$)

$\beta = 108.0_2{}^{\circ}$ ($\pm 0.0_2$)

$V = 1757.3$ Å^3

Because the cell dimensions were determined using relatively few measurements from the diffractometer, their accuracy were assessed by comparing observed and calculated values of 2θ and ϕ for twenty reflections of the h0l and 0kl zones. The maximum deviation found was 0.02°.

Crystal density.

The average density of the crystals, (d_{meas}), determined by flotation in an acetone and carbon tetrachloride mixture at room temperature, was found to be 1.22 $g.cc^{-1}$. Using this value for the crystal density the linear absorption coefficient, μ, is 37.5 cm^{-1} ‡‡.

Space group and number of molecules per unit cell.

The systematic absences found on zero level and equi-inclination Weissenberg photographs were,

hkl - no general absences,

h0l - absent for $l = 2N + 1$,

0k0 - absent for $k = 2N + 1$.

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‡ The errors quoted with the cell dimensions represent the the maximum deviation of the calculated quantities from the mean value.

‡‡ μ was calculated in the manner described in Chapter 4.

The space group is therefore identified as $P2_1/c$.

Using $d_{meas} = 1.22\ g.cc^{-1}$, $V = 1757.3\ \mathring{A}^3$ and molecular weight, $M_r = 316.5$,

$$n = \frac{d_{meas} \cdot V}{1.66 \cdot M} = 4.07.$$

Thus there are four molecules of the 1,2,4-trithiacyclopentane from pinacolone per unit cell.

Collection of three-dimensional intensity data.

An acicular crystal was cut into a more symmetrical shape and used for intensity data collection. The approximate dimensions of the crystal were,

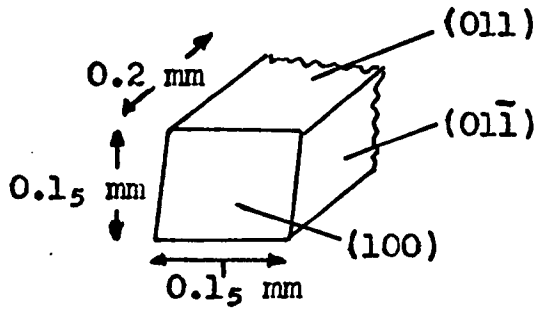

Figure 11.1

Absorption is therefore fairly low, ($\mu_{CuK\alpha} = 37.5\ cm^{-1}$), and no corrections were applied.

Three dimensional intensity data were collected using a Picker automated four-circle diffractometer‡. The crystal was mounted with b* parallel to the Ø axis of the goniostat and a* was specified as Ø = 0. All data were collected employing the ω-2θ scan mode, (moving-crystal, moving-counter), using a scan rate of one degree per minute. The scan range for each reflection

‡ The Picker diffractometer and its mode of operation for intensity data collection are described in Chapter 7, p.47.

was calculated using the standard equations of Alexander and Smith, (equations 7.1), and background measurements were taken at both $2\theta_1$ and $2\theta_2$ for twenty seconds. As previously stated in Chapter 7, the maximum value of ω safely attainable with the Picker diffractometer is 67°; consequently the intensity data collection was restricted to reflections for which $2\theta_m(CuK_\alpha) \lesssim 130^o$. The setting cards, which form the input to the diffractometer, were ordered by hand to minimise the time required for angular slew between measurements. The hkl and $hk\bar{l}$ series were run separately as the two major groups and within each data were collected in hnl levels, with the l index changing more rapidly than h. Crystal orientation and system stability were checked during the automatic phases of the collection by taking intensity measurements for twelve 'test' reflections after each hnl level was completed. The maximum deviation of a test measurement, from its mean value over the total collection, was found to be 2%.

The procedure whereby intensity data, measured using the diffractometer, were reduced to observed structure amplitudes was analogous to that employed in the structure analysis of PDM[‡]; the statistical treatment due to Abrahams being retained to calculate the standard deviation, σF_o, of each $|F_o|$ datum. The classification and treatment of unobserved reflections followed the same lines as that employed in the PDM data reduction, (page 53). Intensity measurements were made on 2778 independent

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‡ Details of the data reduction are given in Chapter 7, p.51.

reflections within the range $0 < 2\theta_m \leq 130^o$; after data reduction 530 of these reflections, (19.1%), were classified as unobserved.

Absolute scaling and overall temperature factor.

The K-curve method‡ was employed to place the observed structure amplitudes on the absolute scale and ascertain the average isotropic temperature factor.

Initially the reciprocal lattice, $(0 < 2\theta_m \leq 130^o)$, was divided into ten sub-intervals, (of equal volume), and the value of $K(S_m)$ calculated for each, $\left[K(S_m)\right.$ is defined by equation (8.2)$\left.\right]$. The procedure was repeated using fifteen and twenty ranges. The calculated values of $K(S_m)$ and the corresponding values of S_m, (the mean $\sin\theta$ for the range), are listed in Table 11.1; the resultant K-curve plot, of $K(S_m)$ against S_m, is shown in Figure 11.2. Again it was assumed that the K-curve could be fitted by the exponential function (8.3), viz,

$$K(S_m) = A\exp B(S_m)^C \qquad (11.1)$$

Seven equations of type (11.1) were formulated, having C specified from 1.0 to 4.0 in intervals of 0.5, and for each the best fit values of A and B were calculated using a least squares method. The coefficients of the seven curves and the corresponding values of SUM, (the sum of the squares of the deviations of the 45 experimental points from the formulated curve), are listed in Table 11.2.

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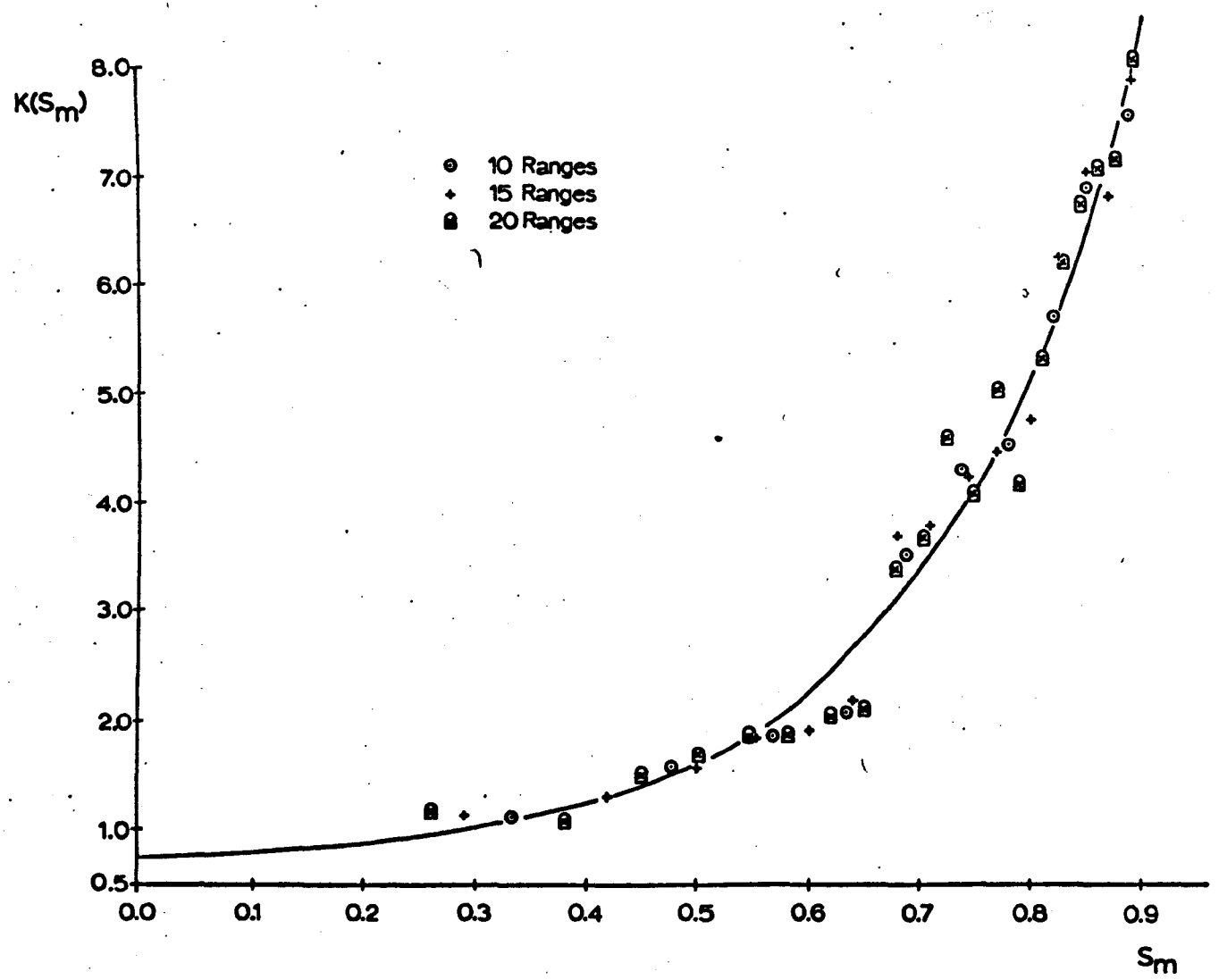
‡ The K-curve method is discussed in Chapter 8, p.55.

10 Ranges		15 Ranges		20 Ranges	
S_m	$K(S_m)$	S_m	$K(S_m)$	S_m	$K(S_m)$
0.3316	1.1115	0.2897	1.1175	0.2632	1.1477
0.4782	1.5665	0.4177	1.2829	0.3795	1.0509
0.5670	1.8403	0.4953	1.5543	0.4500	1.4947
0.6343	2.0667	0.5541	1.8439	0.5034	1.6626
0.6897	3.5055	0.6025	1.8837	0.5474	1.8259
0.7374	4.3026	0.6442	2.1470	0.5853	1.8568
0.7796	4.5198	0.6811	3.5645	0.6188	2.0326
0.8177	5.6951	0.7143	3.7734	0.6490	2.1028
0.8525	6.8810	0.7448	4.2729	0.6767	3.3627
0.8847	7.5412	0.7729	4.4546	0.7022	3.6781
		0.7991	4.7466	0.7260	4.5747
		0.8237	6.2379	0.7484	4.0572
		0.8469	7.0279	0.7695	4.9995
		0.8689	6.7931	0.7895	4.1570
		0.8899	7.8390	0.8085	5.2954
				0.8267	6.1872
				0.8441	6.7282
				0.8608	7.0533
				0.8769	7.1286
				0.8924	8.0494

Computed values of $K(S_m)$ and S_m used for the K-curve generation.

Table 11.1



The K-curve plot.

Figure 11.2

A	B	C	SUM
0.2827	3.6127	1.0	3.069
0.5468	3.1293	1.5	2.028
0.7681	2.9687	2.0	1.669
0.9498	2.9376	2.5	1.638
1.1016	2.9725	3.0	1.840
1.2311	3.0470	3.5	2.276
1.3437	3.1482	4.0	3.013

The 'best fit' coefficients A and B for the seven curves. SUM is the sum of the squares of the deviations of the forty-five experimental points from the formulated curve.

Table 11.2

Generation of normalised structure amplitudes.

Normalised structure factor magnitudes were computed* using the two 'best-fitting' K-curves, (C = 2.0 and C = 2.5; Table 11.2). The statistical averages and the percentage distribution of |E| produced are given in Table 11.3, together with the theoretical values of these quantities. As is evident from Table 11.3, the computed averages and |E| distribution for the two K-curve formulations are not significantly different and in all further work the curve with C = 2.0 was used. This K-curve therefore yields,

$$K'' = \sqrt{0.7681} = 0.876,$$

$$B_{ov} = \frac{2.9687.\lambda^2}{2} = 3.53\ \mathring{A}^2,$$

where K" is the scale factor required to place the observed structure amplitudes on the absolute scale and B_{ov} is the average isotropic temperature factor.

All reflections having $|E| \geqslant 1.5$ were classified by their indices into the eight parity groups and produced the distribution shown in Table 11.4. There are 129 reflections having $|E| \geqslant 2.0$, but only 43 of these are contained in parity groups for which (k+l) is odd. When reflections having $|E| \geqslant 1.5$ are considered, this specialisation in |E| distribution is less severe but still apparent. For the purpose of comparison a similar distribution

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* Normalised structure factor magnitudes were calculated using equation (8.4), p. 58.

	Experimental		Theoretical.	
	K-curve 1.	K-curve 2.	Centric	Acentric
A	0.7681	0.9498		
B	2.9687	2.9376		
C	2.0	2.5		
$\langle \lvert E \rvert \rangle$	0.821	0.821	0.798	0.886
$\langle \lvert E^2 - 1 \rvert \rangle$	0.944	0.944	0.968	0.736
$\langle E^2 \rangle$	1.010	1.010	1.000	1.000
$\% \lvert E \rvert \geqslant 3.0$	0.2	0.1	0.3	0.0_1
$\% \lvert E \rvert \geqslant 2.0$	4.6	4.5	5.0	1.8
$\% \lvert E \rvert \geqslant 1.0$	31.9	31.9	32.0	37.0

The distribution of normalised structure amplitudes and statistical averages found, and the theoretical values of these quantities.

Table 11.3

h k l	$\|E\| \geqslant 2.0$	$\|E\| \geqslant 1.5$
g g g	26	52
g g u	14	43
g u g	9	38
g u u	27	56
u g g	16	52
u g u	11	38
u u g	9	34
u u u	17	51
$\sum$ g g g, u g g, g u u, u u u	86	211
$\sum$ g g u, u g u, g u g, u u g	43	153

The distribution of $|E|$ within the eight sub-groups, for the trithiacyclopentane from pinacolone.

Table 11.4

of the normalised structure factor magnitudes for the desaurin from acetophenone is shown in Table 11.5*. The effect of the specialised y coordinate of the sulphur atoms of the desaurin is very apparent, in that of 73 reflections having $|E| \geqslant 2.0$ and 210 reflections having $|E| \geqslant 1.5$, only 2 and 13 respectively are contained in parity groups for which (k+l) is odd. Although the $|E|$ distribution amongst the eight parity groups is much less severely specialised for the 1,2,4-trithiacyclopentane from pinacolone, it is sufficient to indicate that one or two sulphur atoms of the molecule are probably located 'close' to (020).

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* The normalised structure factor magnitudes for the desaurin from acetophenone were computed after completion of the structure analysis.

h k l	$\|E\| \geqslant 2.0$	$\|E\| \geqslant 1.5$
u u u	18	40
u u g	1	1
u g g	17	59
u g u	0	5
g g g	16	54
g g u	1	5
g u u	20	44
g u g	0	2
$\sum$ u u g, u g u, g g u, g u g	2	13
$\sum$ u u u, u g g, g g g, g u u	71	197

The distribution of $|E|$ within the eight sub-groups, for the desaurin from acetophenone.

Table 11.5

CHAPTER 12.

THREE-DIMENSIONAL PATTERSON AND ELECTRON DENSITY SYNTHESES.

In Chapter 2 it was noted that resolution of peaks in the Patterson function is improved by employing sharpened coefficients, ($|{}^{s}F_{hkl}|^2$), formulated by equation (2.3), viz,

$$|{}^{s}F_{hkl}|^2 = \frac{|F_{hkl}|^2 \exp(2B_{ov}.RHO)}{\sum_{i=1}^{N} f_{i\,hkl}^2} , \qquad (12.1)$$

where,

$|F_{hkl}|$ = the observed structure amplitude,

RHO = $(\sin\theta/\lambda)^2$,

B_{ov} = the overall isotropic temperature factor,

$f_{i\,hkl}$ = the scattering factor of the ith atom in a unit cell containing N atoms.

By using the K-curve coefficients, A and B, (with C specified as 2.0), equation (12.1) can be re-written as,

$$|{}^{s}F_{hkl}|^2 = \frac{|F_{hkl}|^2 \,.\, A\exp\left[B(\sin\theta)^{2.0}\right]}{\sum_{i=1}^{N} f_{i\,hkl}^2} \qquad (12.2)$$

and comparison with equation (8.4) therefore yields,

$$|{}^{s}F_{hkl}|^2 = \varepsilon_{hkl}\,|E_{hkl}|^2 \quad .$$

A sharpened Patterson function can therefore be computed by employing $\varepsilon|E|^2$ coefficients in the summation.

The origin peak apparent in the Patterson function is removed (69) by employing in the synthesis coefficients of type,

$$\left[|'F_{hkl}|^2 - \sum_{i=1}^{N} f_{i\ hkl}^2 \right] \qquad (12.3)$$

where $|'F_{hkl}|$ is the observed structure amplitude adjusted to the same scale as $f_{i\ hkl}$, (usually absolute for non-vibrating atoms). By expressing $|'F_{hkl}|^2$ in the form $\{|F_{hkl}|^2.A\exp B(\sin\theta)^C\}$, and sharpening the coefficients, (by dividing through by $\sum f_{i\ hkl}^2$), the origin-removed sharpened Patterson function can therefore be computed by employing $[\varepsilon_{hkl}|E_{hkl}|^2 - 1]$ terms in the summation.

The program used to compute the K-curve and calculate normalised structure factor magnitudes, was also coded to produce a binary data tape of $(\varepsilon|E|^2 - 1)$ and $\varepsilon|E|^2$ coefficients. The prepared data tape was utilised as input by a subsequent general Fourier program whence either the sharpened Patterson function or the origin-removed sharpened Patterson function was computed.

<u>The three-dimensional Patterson function</u>.

The origin-removed sharpened Patterson function was computed for the quarter of the unit cell defined by $-0.5 \leq u \leq 0.5$, $0.0 \leq v \leq 0.5$ and $0.0 \leq w \leq 0.5$, in intervals of 0.05 in u, 0.02 in v and 0.01 in w.

The equivalent positions of space group $P2_1/c$ are $\pm(x,y,z)$ and $\pm(x, \frac{1}{2}-y, \frac{1}{2}+z)$. Peaks in the Patterson function which represent vectors between symmetry related atoms will

(69) See, for example, M. J. Buerger, "Vector Space", Wiley and Sons, New York, (1959), p. 56.

therefore be located at,

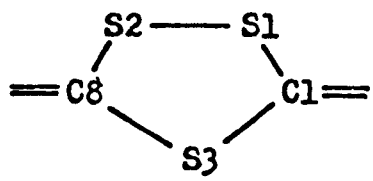
			weight	
A.	$\pm(2x, 2y, 2z)$	Inversion peaks	1x	Table 12.1
B.	$\pm(2x, \overline{2y}, 2z)$			
C.	$\pm(2x, \frac{1}{2}, \frac{1}{2} + 2z)$	Harker section	2x	
D.	$\pm(0, \frac{1}{2} - 2y, \frac{1}{2})$	Harker line	2x	

The desaurin from acetophenone crystallises in space group $P2_1/c$ with two molecules, (four sulphur atoms), per unit cell. Thus the only sulphur-sulphur peaks apparent in the Patterson function are those representing vectors between symmetry related atoms, and by using Table 5.1, (≡ Table 12.1), the real space coordinates of the sulphur atoms were easily determined.

In the 1,2,4-trithiacyclopentane from pinacolone there are three sulphur atoms per asymmetric molecule and interpretation of the Patterson function will therefore be made more difficult by sulphur 'cross-vector' peaks, (i.e. peaks representing the vectors between sulphur atoms unrelated by space group symmetry). The twelve sulphur atoms in the unit cell will give rise to one hundred and thirty-two sulphur-sulphur vector peaks in the complete Patterson function. From Table 12.1 it can be seen that of these peaks, six will occur on both the Harker section and Harker line, (each of two-fold weight), and twelve inversion peaks will occur in the body of the unit cell. The remaining forty-eight peaks, of two-fold weight, represent the cross-vector sulphur-sulphur interactions. In the quarter of the unit cell for which the

Patterson function was computed, there will be, therefore, three peaks on both the Harker section and Harker line, three single weight inversion peaks and twelve double weight cross-vector peaks. The most easily identified of the cross-vector peaks will be those representing intramolecular interactions. Although no structural details of the 1,2,4-trithiacyclopentane system were available, (at this time), it was possible to assess approximate dimensions by utilising bond distances and angles found in related sulphur-containing systems. In 1,2-dithiolane-4-carboxylic acid (70) and 1,2-dithiane-3,6-dicarboxylic acid (71), disulphide bond lengths of 2.07 and 2.09Å, (respectively), were found, with heterocyclic C-S-S angles in the order 92-99°. The structure analyses of the desaurin from acetophenone and PDM yield C(sp^2)-S bond distances of 1.75-1.77Å ; in addition the S(II)-C(sp^2)-S(II) bond angle found in PDM is 115° ‡. Structure analyses of six-membered sulphur-containing heterocyclics (80,81), have yielded C(sp^2)-S(II)-C(sp^2) angles of ~100°.

The atomic numbering system employed for the trithiacyclopentane ring is,



By applying the dimensions quoted above to this system, approximate sulphur-sulphur distances in the molecule will be,

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(70) O. Foss, A. Hordvik and J. Sletten, Acta Chem. Scand., 20, 1169 (1966)
(71) O. Foss, K. Johnson and T. Reistad, ibid., 18, 2345 (1964).
‡ Structural data for PDM and the desaurin are given in Chapter 14.

S1 - S2 ~ 2.1Å

S1 S3 } ~ 3.0Å
S2 S3

In the computed portion of the Patterson function, three prominent peaks, characteristic of intramolecular sulphur-sulphur vectors, were found, (Table 12.2).

#	U	V	W	Peak height	Distance from origin (Å)	Interpretation.
1	0.100	0.100	0.080	793	2.17	S1-S2
18	0.525	0.000	0.055	1150	2.97	S1-S3
6	-0.425	0.090	0.025	631	2.99	S2-S3

Peaks representing intramolecular S-S vectors.

Table 12.2

Peaks 1 and 6 have the normal two-fold weighing associated with the interaction, whereas peak 18, situated on the mirror plane at V = 0, will be of four-fold weight. The specialised location of peak 18 indicates that S1 and S3 must have approximately the same y coordinate. This set therefore fixes the orientation of the three sulphur atoms of the heterocyclic ring.

Three peaks were observed on the Harker section having relative positions consistent with this orientation, (Table 12.3).

#	U	V	W	Peak height	Interpretation.
12	-0.60	0.50	0.21	607	S1-S1
15	-0.40	0.50	0.37	695	S2-S2
14	0.45	0.50	0.32	751	S3-S3

Peaks on the Harker section (u, 1/2, w).

Table 12.3

Inspection of the Harker line showed only two prominent peaks, (Table 12.4).

#	U	V	W	Peak height	Interpretation.
16	0	0.28	1/2	682	S2-S2
17	0	0.47	1/2	1052	S1-S1 S3-S3

Peaks on the Harker line (0, v, 1/2)

Table 12.4

Peak 16 has the normal two-fold weight characteristic of the interaction, whilst peak 17 is formed by a superimposition of two such peaks, (the analysis of intramolecular sulphur-sulphur vectors had already indicated that S1 and S3 have approximately the same y coordinate).

By using Table 12.1, (C and D, in which the Harker peaks are expressed in terms of general, real space, coordinates of the atoms), together with the intramolecular vector set, the fractional coordinates of the sulphur atoms of the asymmetric molecule were taken as,

	X/a	Y/b	Z/c
S1	-0.300	0.010	-0.145
S2	-0.200	0.110	-0.065
S3	0.225	0.020	-0.090

Table 12.5

Prominent peaks in the Patterson function corresponding to all sulphur-sulphur cross-vectors indicated that the sulphur atoms were correctly located in the unit cell. The coordinates of the highest twenty-two peaks in the computed portion of the

Patterson function, and the sulphur-sulphur vectors to which they correspond, are given in Table 12.6. The subscript applied to the sulphur atom, in Table 12.6, indicates the equivalent position occupied, and uses the key,

S_1 ; x, y, z (the coordinates listed in Table 12.5)

S_2 : -x, -y, -z

S_3 : x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z

S_4 ; -x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z

From Table 12.6 it can be seen that the relative peak heights, (each measured from the lowest negative trough in the computed function), compare quite well with the theoretical weight. Peak 13 is 'non-Harker', and represents S1-S3 vectors; the effective four-fold weighting is again due to the y coordinates of these atoms being approximately the same. The S1 inversion peak, (#19), has double weighting due to the atom lying close to the plane at y = 0. Peak 11 is too near to the origin, ($\sim$0.7Å), to represent any interatomic vector, and must result from slight errors in the origin removal procedure.

Although the resolution in the Patterson function was remarkably good, and many peaks representing vectors between sulphur and light atoms were clearly evident, it was decided to compute electron density syntheses to locate the remaining sixteen light atoms in the molecule.

Three-dimensional electron density syntheses.

In the desaurin from acetophenone, the sulphur atoms lie very close to (020), causing pseudosymmetry in the electron

#	u	v	w	Peak height	Corresponding S - S vectors	Weight x
1.	0.10	0.10	0.08	793	S1-S2 intramolecular	2
2.	$\overline{0.05}$	0.12	0.15	693	$S3_4$-$S2_3$;$S2_4$-$S3_3$	2
3.	$\overline{0.10}$	0.38	0.42	686	$S1_3$-$S2_1$;$S3_2$-$S1_4$	2
4.	0.05	0.42	0.35	656	$S3_1$-$S2_4$;$S2_3$-$S3_2$	2
5.	0.45	0.38	0.48	632	$S3_3$-$S2_1$;$S2_2$-$S3_4$	2
6.	$\overline{0.42_5}$	0.09	0.02_5	631	S2-S3 intramolecular	2
7.	0.05	0.04	0.23	606	$S3_4$-$S1_3$;$S1_4$-$S3_3$	2
8.	0.45	0.46	0.44	563	$S3_2$-$S1_4$;$S1_3$-$S3_1$	2
9.	0.40	0.22	0.13	425	S2 inversion	1
10.	$\overline{0.45}$	0.04	0.18	422	S3 inversion	1
11.	0.00	0.04	0.02	404		
12.	0.40	0.50	0.21	607	S1 Harker (section)	2
13.	$\overline{0.05}$	0.50	0.27	1127	$\left\{\begin{matrix} S1_1\text{-}S3_4;S3_3\text{-}S1_2 \\ S3_1\text{-}S1_4;S1_3\text{-}S3_2 \end{matrix}\right\}$	4*
14.	0.45	0.50	0.32	751	S3 Harker (section)	2
15.	$\overline{0.40}$	0.50	0.37	695	S2 Harker (section)	2
16.	0.00	0.28	0.50	686	S2 Harker (line)	2
17.	0.00	0.47	0.50	1052	$\left\{\begin{matrix} S1 \\ S3 \end{matrix}\right\}$ Harker (line)	4*
18.	$\overline{0.47_5}$	0.00	0.05_5	1150	S1-S3 intramolecular	4*
19.	0.42_5	0.00	0.28_5	590	S1 inversion	2*
20.	0.35	0.00	0.30_5	490		
21.	0.50	0.12	0.21	723	$S2_4$-$S1_3$;$S1_4$-$S2_3$	2
22.	0.50	0.41	0.29	600	$S1_1$-$S2_4$;$S2_3$-$S1_2$	2

The highest peaks in the Patterson function, and the S-S vectors to which they correspond.

Table 12.6

density syntheses, which delayed the identification of the light atoms. Interpretation of the Patterson function of the 1,2,4-trithiacyclopentane from pinacolone reveals that S1 and S3 exhibit a similar specialisation in position. However, the effect in this structure will be much less severe as both S1 and S3 have a greater displacement from (020), (0.13Å and 0.26Å compared with 0.01Å in the desaurin), and in addition S2 will make a 'normal' contribution to all structure factors.

Structure factors were calculated using the sulphur positions determined from the Patterson function and assigning an overall temperature factor of 3.5Å^2; reflection data classified as unobserved were excluded from the calculation which yielded R = 0.41. The subsequent electron density synthesis* was devoid of false symmetry and the light atom locations were clearly revealed as the sixteen highest, (non-sulphur), peaks on the sections. A calculation of interatomic distances and angles showed the molecular dimensions to be reasonable for this stage of the structure analysis. Structure factors were re-calculated from the positions of all nineteen atoms and yielded a residual index of 0.25. Inspection of the second electron density synthesis showed that all the light atoms included in the structure factor calculation had increased in peak density and that there were no spurious peaks on the sections. The atomic coordinates estimated from this second electron density synthesis are listed in Table 12.7. The atomic coordinates tabulated comprise an

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* The electron density syntheses were computed for the quarter of the unit cell and with mesh intervals previously defined for the Patterson synthesis.

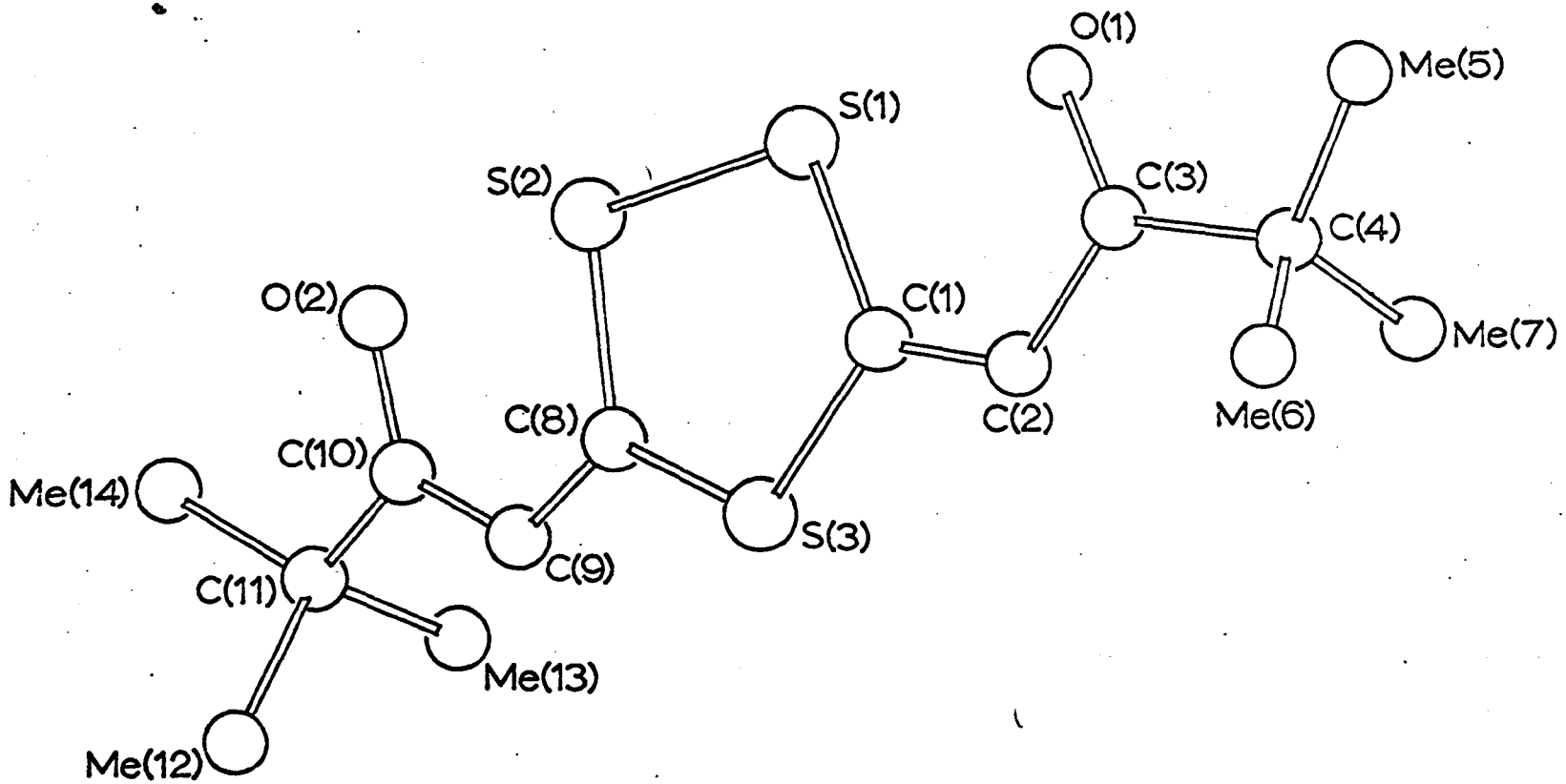
(asymmetric) molecule, (the sulphur locations listed are the invertion equivalents of the positions determined from the Patterson function). The atomic numbering system employed is shown in Figure 12.1

Refinement of the atomic parameters by the method of least squares was now initiated.

Atom	X/a	Y/b	Z/c
S(1)	0.302	-0.016	0.146_5
S(2)	0.202_5	-0.110	0.066_5
S(3)	-0.230	-0.021	0.087
O(1)	0.385	0.093	0.242
O(2)	0.067_5	-0.235_5	-0.023_5
C(1)	0.025	0.021	0.148
C(2)	-0.012_5	0.076	0.199_5
C(3)	0.190	0.113	0.247_5
C(4)	0.150	0.165	0.300
Me(5)	0.395	0.200	0.348
Me(6)	-0.020	0.257	0.278
Me(7)	0.044	0.092	0.338
C(8)	-0.115	-0.108	0.050
C(9)	-0.262_5	-0.168	0.006
C(10)	-0.160	-0.236	-0.028_5
C(11)	-0.310	-0.318	-0.071
Me(12)	-0.542_5	-0.263	-0.118
Me(13)	-0.410	-0.400	-0.0345
Me(14)	-0.185	-0.364	-0.112

Atomic coordinates estimated from the second electron density synthesis.

Table 12.7



The atomic numbering system used throughout the structure analysis.

Figure 12.1

CHAPTER 13.

REFINEMENT OF THE STRUCTURE.

The standard version of OR-FLS was employed for the initial stages of refinement, but was replaced, for cycles involving anisotropic temperature factors, by an extensively modified version able to accommodate simultaneous refinement of 172 parameters. Each observed structure amplitude was weighted using its standard deviation calculated in the data reduction procedure,

$$w_{F_o} = \frac{1}{(\sigma F_o)^2}$$

An overall scale factor was treated as a variable throughout the refinement; the function minimised was $\sum w(|F_o| - |F_c|)^2$. During the course of the refinement two residual indices are quoted; R_1 is the residual index obtained using all 2778 reflections for which intensity measurements were made, whilst R_2 is the index produced when reflections termed unobserved are excluded from the summation.

The initial positional parameters used in the refinement were those obtained from the second electron density synthesis, (Table 12.7), and each atom was allocated an isotropic temperature factor of 3.5Å^2. Two cycles of refinement were computed with the thermal parameters of the atoms fixed, followed by four cycles in which all 76 positional and thermal parameters were refined, R_1 and R_2 improving to 0.188 and 0.168 respectively.

The parameter shifts calculated in the last cycle were less than one half of the corresponding standard deviation and convertion of the temperature factors into anisotropic mode was now considered in order. The atomic parameters at this stage are listed in Table 13.1.

It was noted that the observed and calculated structure amplitudes for 011, 023 and 024 were in extremely poor agreement for such low order reflections,

	$\|F_o\|$	$\|F_c\|$
011	89.8	136.8
023	142.7	181.1
024	88.2	103.2

On re-checking the diffractometer output it was revealed that there had been insufficient attenuation available during the intensity data collection for these reflections; consequently they were excluded from all further refinement.

The modified version of OR-FLS was introduced and refinement continued employing anisotropic temperature factors. Two cycles were computed with the thermal parameters of the carbon atoms of the methyl groups fixed, followed by four cycles in which all 172 parameters were refined, R_1 and R_2 improving to 0.094 and 0.074 respectively. The maximum shift calculated in the final cycle represented about 20% of the standard deviation of the parameter and refinement was considered complete. The final positional and thermal parameters and their estimated standard deviations, calculated from the least squares residuals,

Atom	X/a	Y/b	Z/c	B_{iso}(Å^2).
S(1)	0.2938	-0.0140	0.1448	3.762
S(2)	0.1952	-0.1089	0.0655	3.480
S(3)	-0.2300	-0.0192	0.0880	3.229
O(1)	0.3834	0.0925	0.2402	5.050
O(2)	0.0541	-0.2321	-0.0223	5.087
C(1)	0.0158	0.0220	0.1494	2.650
C(2)	-0.0181	0.0774	0.1951	2.982
C(3)	0.1855	0.1113	0.2444	3.609
C(4)	0.1486	0.1680	0.3000	3.892
Me(5)	0.3885	0.1972	0.3447	6.874
Me(6)	-0.0108	0.2610	0.2777	6.561
Me(7)	0.0282	0.0938	0.3328	7.678
C(8)	-0.1110	-0.1076	0.0477	2.553
C(9)	-0.2571	-0.1659	0.0048	2.638
C(10)	-0.1593	-0.2355	-0.0298	3.114
C(11)	-0.3150	-0.3165	-0.0732	3.752
Me(12)	-0.5390	-0.2663	-0.1186	6.868
Me(13)	-0.3897	-0.3933	-0.0309	9.014
Me(14)	-0.1857	-0.3670	-0.1138	9.271

Atomic parameters at the conclusion of the refinement employing isotropic temperature factors.

Table 13.1

are listed in Tables 13.2 and 13.3. B_{ij}, in Table 13.3, are coefficients in the anisotropic temperature factor expression,

$$\exp -1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})$$

From Table 13.3 it can be seen that the thermal vibrations of the atoms are 'non-isotropic' in nature. Although the values of B_{ij} produced from a least squares refinement must be treated with caution, since they will tend to encompass systematic errors in the $|F_o|$, those of the carbon atoms of the six methyl groups, ('C(Me)'), appear especially notable. The thermal parameters of the C(Me) atoms show a high degree of anisotropy and the magnitudes of the motion of these atoms contrast with those of the fourth carbon atom of the t-butyl groups, (C(4) and C(11)). A difference synthesis computed at this point did not suggest any corrections to the C(Me) parameters. Although peaks attributable to the hydrogen atoms bonded to C(2) and C(9) were apparent in the synthesis, the regions where 't-butyl hydrogens' are theoretically expected were characterised by smears of low electron density and consequently their locations could not be fixed.

The observed and calculated structure factors, (the latter from the atomic parameters listed in Tables 13.2 and 13.3), are tabulated in Appendix IV. Superimposed sections of a final electron density distribution, taken through the atomic centres parallel to (010), are shown in Figure 13.1, together with a drawing of the corresponding molecular unit.

Atom	X/a	σ(X/a) x 10^4	Y/b	σ(Y/b) x 10^5	Z/c	σ(Z/c) x 10^5
S(1)	0.2936	3	-0.0142	13	0.1446	8
S(2)	0.1956	3	-0.1087	13	0.0657	7
S(3)	-0.2295	3	-0.0192	12	0.0882	7
O(1)	0.3849	7	0.0944	37	0.2407	21
O(2)	0.0562	8	-0.2329	35	-0.0225	22
C(1)	0.0160	8	0.0203	40	0.1491	24
C(2)	-0.0177	10	0.0752	41	0.1950	25
C(3)	0.1879	11	0.1109	45	0.2448	28
C(4)	0.1512	11	0.1664	50	0.3002	27
Me(5)	0.3902	13	0.1975	69	0.3450	36
Me(6)	-0.0125	15	0.2614	60	0.2770	35
Me(7)	0.0291	15	0.0898	69	0.3328	36
C(8)	-0.1099	9	-0.1064	39	0.0481	23
C(9)	-0.2566	9	-0.1663	40	0.0047	24
C(10)	-0.1583	10	-0.2360	43	-0.0298	26
C(11)	-0.3129	11	-0.3167	45	-0.0725	27
Me(12)	-0.5363	14	-0.2656	63	-0.1171	37
Me(13)	-0.3882	19	-0.3921	65	-0.0301	40
Me(14)	-0.1847	16	-0.3674	80	-0.1121	48

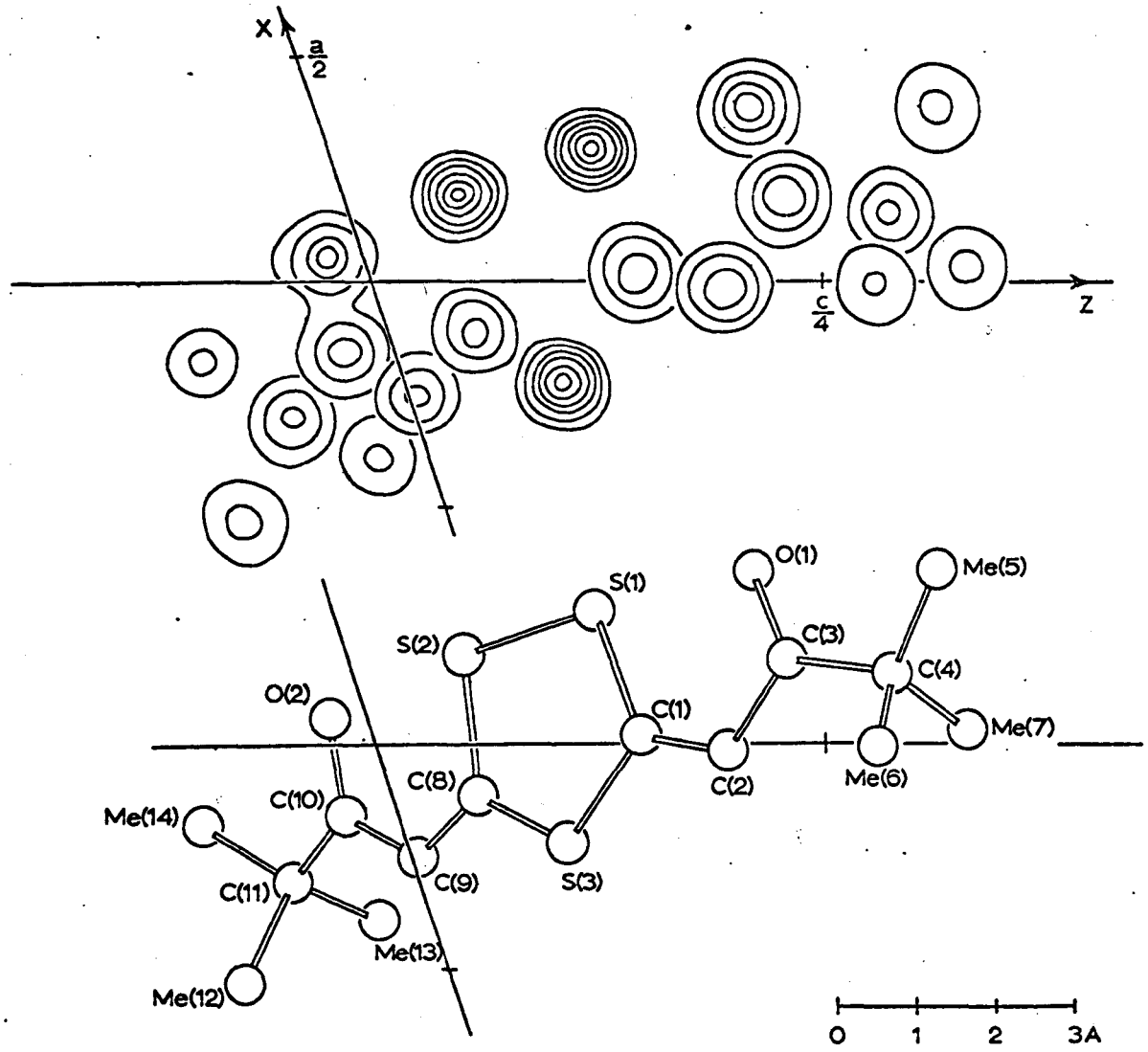
The final fractional coordinates and standard deviations of the non-hydrogen atoms.

Table 13.2

Atom	B_{11}	σB_{11}	B_{22}	σB_{22}	B_{33}	σB_{33}	B_{12}	σB_{12}	B_{13}	σB_{13}	B_{23}	σB_{23}
S(1)	2.63	0.06	5.16	0.08	5.44	0.09	-0.77	0.06	1.51	0.06	-2.34	0.07
S(2)	2.77	0.07	4.60	0.08	4.80	0.08	-0.20	0.06	1.50	0.06	-1.68	0.07
S(3)	2.82	0.06	3.71	0.07	4.16	0.08	0.57	0.06	0.70	0.05	-1.44	0.06
O(1)	3.11	0.21	7.77	0.31	7.42	0.29	-0.57	0.20	1.91	0.21	-3.59	0.25
O(2)	3.99	0.23	5.89	0.27	7.99	0.31	-0.52	0.20	2.21	0.21	-3.56	0.24
C(1)	2.34	0.23	2.47	0.24	3.26	0.25	-0.30	0.20	0.56	0.20	-0.60	0.21
C(2)	3.77	0.28	2.61	0.26	3.33	0.28	-0.42	0.22	0.61	0.23	-1.13	0.23
C(3)	4.15	0.31	2.92	0.29	4.51	0.33	-0.43	0.25	1.19	0.26	-0.66	0.26
C(4)	4.77	0.33	4.63	0.35	3.34	0.30	-0.23	0.28	1.18	0.26	-1.29	0.27
Me(5)	4.90	0.39	11.94	0.64	6.65	0.46	-1.61	0.42	0.30	0.35	-5.78	0.47
Me(6)	10.32	0.58	6.00	0.46	7.18	0.49	3.73	0.43	2.41	0.44	-1.25	0.39
Me(7)	8.39	0.53	10.37	0.60	6.73	0.47	-3.32	0.46	4.05	0.42	-0.08	0.46
C(8)	2.98	0.24	2.05	0.23	2.80	0.24	0.57	0.20	1.18	0.20	-0.19	0.20
C(9)	3.52	0.27	2.28	0.25	3.00	0.26	0.33	0.21	1.19	0.22	-0.66	0.21
C(10)	3.71	0.28	2.63	0.27	3.60	0.29	-0.08	0.23	0.89	0.24	-0.59	0.23
C(11)	4.17	0.31	3.06	0.29	4.17	0.33	-0.01	0.24	1.07	0.26	-1.29	0.25
Me(12)	5.90	0.42	7.50	0.50	8.12	0.52	0.55	0.40	-1.21	0.38	-2.16	0.44
Me(13)	15.30	0.83	6.43	0.51	8.02	0.55	-5.68	0.55	1.35	0.54	1.22	0.45
Me(14)	7.88	0.55	15.38	0.83	14.93	0.79	-2.56	0.53	5.12	0.55	-12.88	0.70

The final anisotropic thermal parameters, ($Å^2$), and their standard deviations.

Table 13.3



Composite electron density normal to [010]. Contour intervals at carbon and oxygen atoms, 1.0 eÅ^{-3}, at sulphur atoms, 2.0 eÅ^{-3}, (the zero contour is omitted).

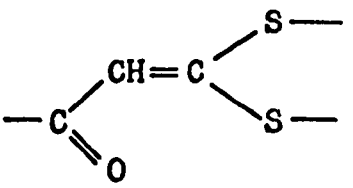
Figure 13.1

CHAPTER 14.

DISCUSSION.

Structural data were computed using the 'X-ray 63 system' (72) and a general interatomic distances and angles program (73). The standard deviations in bond lengths and angles involving sulphur, carbon and oxygen atoms, calculated for each molecule, take into account both the standard deviation in atomic position, as estimated from the least squares residuals, and the standard deviations in the cell dimensions.

The desaurin from acetophenone, PDM and the 1,2,4-trithiacyclopentane from pinacolone have a common chemical grouping of the β-dithia-α,β-unsaturated carbonyl system,



The three structure analyses thus afford a means of comparing molecular dimensions for this group, and perhaps ascertaining the effect of the different substituents on the system. Cruickshank (74) has emphasised the importance of applying proper significance tests before drawing any conclusions from a comparison of this type. If two independent experimental determinations

(72) J. M. Stewart, University of Washington, Seattle (1965).
(73) R. Shiono and S. S. C. Chu, X-Ray Crystallography Laboratory, University of Pittsburg, Pittsburg (1964).
(74) D. W. J. Cruickshank, Acta Cryst., 2, 65 (1949).

of a specific bond length yield values L_1 and L_2 with standard deviations σ_1 and σ_2 respectively, Cruickshank suggests the adoption of the following significance levels;

$P > 5\%$	$\Delta L < 1.65\sigma_A$	not significant
$5\% > P > 1\%$	$1.65\sigma_A < \Delta L < 2.33\sigma_A$	possibly significant
$1\% > P > 0.1\%$	$2.33\sigma_A < \Delta L < 3.09\sigma_A$	significant
$P < 0.1\%$	$\Delta L > 3.09\sigma_A$	highly significant

where, P = the probability that the difference between the two bond lengths is due to experimental error,

$\Delta L = (|L_1 - L_2|)$,

$\sigma_A = (\sigma_1^2 + \sigma_2^2)^{1/2}$

It is evident therefore that only differences of more than about three standard deviations may be taken as definitely significant.

To analyse the packing of the molecules in the unit cell, all intermolecular interatomic distances of less than 4.0Å were calculated for each structure. In general the interatomic contact distances between molecules should not be less than the sum of the van der Waals radii, except in cases where hydrogen bonding is present in the crystal. In this work the van der Waals radii of oxygen, carbon and the methyl group were taken as 1.4Å, 1.7Å and 1.95Å respectively (75). The van der Waals radius of sulphur quoted by Pauling (75) is 1.85-1.95Å; however there have been suggestions that this value is excessively

(75) L. Pauling, "The Nature of the Chemical Bond", 2nd Edit., Cornell University Press, Ithaca, N. Y., (1940), pp. 187-193.

high. The sulphur-sulphur contact distances in rhombic sulphur indicate a value of 1.65±0.01Å (76), whilst crystal structure analyses of other sulphur-containing organic compounds imply values ranging from 1.65-1.75Å (77,78,79). A constant value for the van der Waals radius cannot strictly be assumed for any atom, such factors as the state of hybridisation of the atom and the electronegativity of atoms attached to it will affect the value found in any specific case. In this work, however, the minimum observed value of 1.65Å was assumed for the van der Waals radius of sulphur‡.

Least squares planes were calculated for various atomic groups using the X-ray 63 system. All planes are formulated by an equation of type,

$$Px + Qy + Rz = S,$$

where x, y and z are atomic fractional coordinates with respect to the crystallographic axes. In the tables of least squares plane data, the atomic deviations from the plane are shown as the distance Δ, (in Å); an asterisk with this distance indicates that the atom so marked was not used to define the plane.

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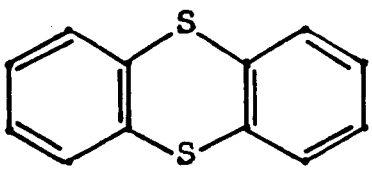
(76) B. E. Warren and J. T. Burwell, J. Chem. Phys., 3, 6 (1935).
(77) H. L. Yakel, Jn., and E. W. Hughes, Acta Cryst., 7, 291 (1954).
(78) R. E. Marsh, ibid., 8, 91 (1955).
(79) J. Donohue, J. Am. Chem. Soc., 72, 2701 (1950).
‡ The short intramolecular sulphur-oxygen distances found are therefore compared with a van der Waals contact distance of 3.05Å.

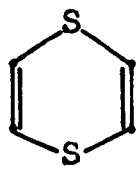
14.1 Details of the molecular and crystal structure of the desaurin from acetophenone.

Structural data were calculated from the final atomic coordinates, (and standard deviations), of the sulphur, oxygen and carbon atoms listed in Table 6.2, and the hydrogen atom locations obtained from the difference synthesis, (Table 6.4).

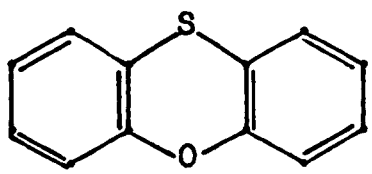
The analysis confirms the 1,3-dithiete structure proposed by Meyer (2) and supported by Yates and Moore (9). The question of the relative stereochemistry of the benzoyl substituents on the C(2) and C(2') carbons was resolved at an early stage in the diffraction study, since the space group and the presence of two molecules per unit cell require a centrosymmetrical molecule; the desaurin is therefore the trans isomer. A further implication of a molecular centre of symmetry is that the 1,3-dithiete ring is planar, in contrast to the situation found in the six-membered sulphur-containing heterocycles XVI, XVII and XVIII, in which the molecules are folded about an axis through



XVI



XVII



XVIII

the heteroatoms (80,81,82). The structure analysis of the desaurin reveals that the α,β-unsaturated carbonyl system adopts

(80) H. Lynton and E. G. Cox, J. Chem. Soc., 4886 (1956).
(81) P. A. Howell, R. M. Curtis and W. N. Lipscomb, Acta Cryst., 7, 498 (1954).
(82) S. Hosoya, ibid,, 20, 429 (1966).

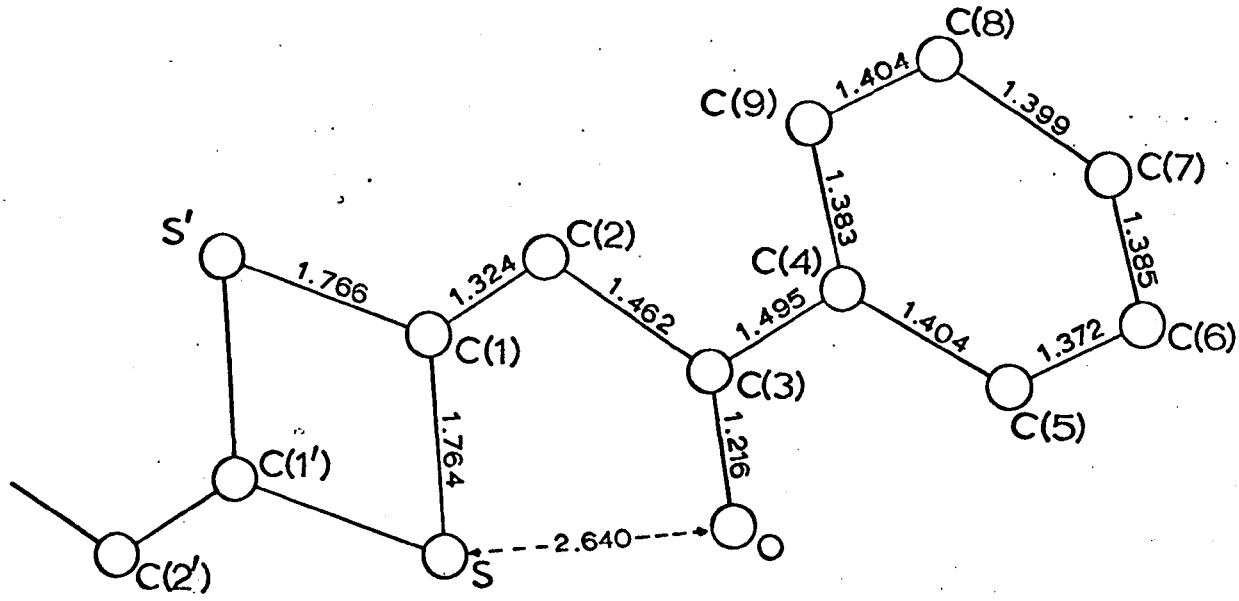
an s-cis conformation, as illustrated in Figure 14.1$_1$.

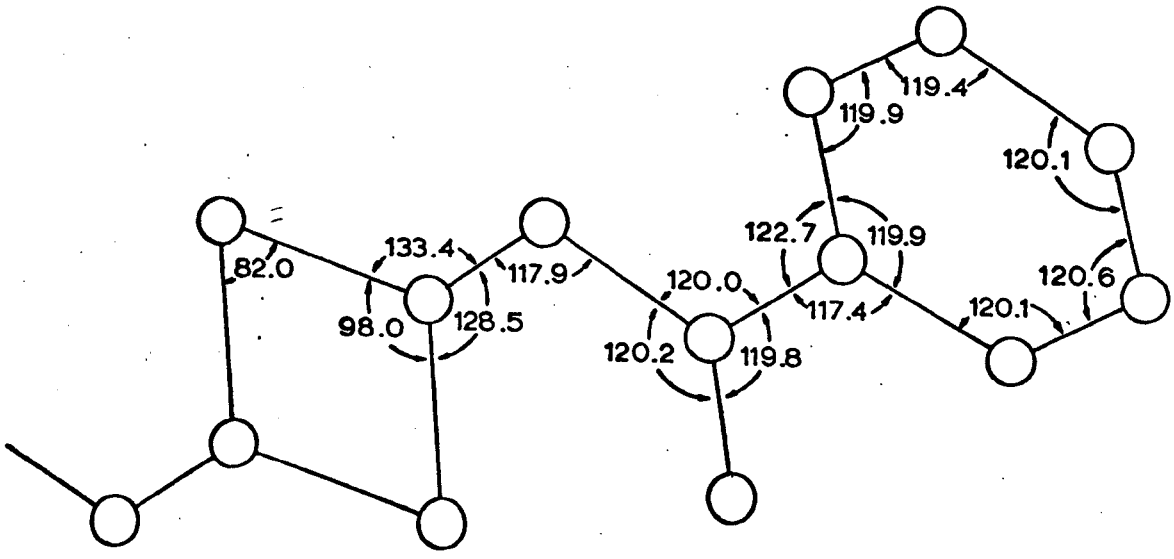
Bond lengths and angles, (involving non-hydrogen atoms), are shown in Figure 14.1$_1$, and are listed, together with their estimated standard deviations, in Tables 14.1$_1$ and 14.1$_2$.

The two independent carbon-sulphur bond lengths in the desaurin are remarkably similar, (1.766Å and 1.764Å), and are in the centre of the range of C(sp^2)-S(II) distances found in XVI, XVII and XVIII, (1.78Å, 1.76Å and 1.75Å respectively). As expected, in the dithiete ring, the C-S-C angles, (82.0°), are smaller than the S-C-S angles, (98.0°). In five- and six-membered heterocycles containing divalent sulphur, the sulphur valence angles are usually in the range 90-105° (83), so that the angle found in the 1,3-dithiete ring is significantly reduced from its normal value. However, the C-S-C angle in the desaurin is not the smallest observed; in the three-membered ring of ethylene sulphide, the angle subtended at the sulphur atom is 48.3° (84,85‡).

The bond distances and angles in the α,β-unsaturated carbonyl system are discussed in section 14.4, where a comparative study of the results of the three structure analyses is made. The C(3)-C(4) bond length, 1.495Å, is in accord with distances

(83) S. C. Abrahams, Quart. Rev., X, 407 (1956).
(84) H. Dreizler and H. D. Rudolf, Z. Natur., 17a, 712 (1962).
(85) R. Desiderato and R. L. Sass, Acta Cryst., 23, 430 (1967).
‡ Desiderato and Sass draw attention to an error in the original paper (84) where the sulphur valence angle is reported as 58.8°.





Desaurin from acetophenone:

Bond lengths and angles.

Figure 14.1.

			Distances (Å)	σ(Å)
S	–	C(1)	1.764	0.006
S'	–	C(1)	1.766	0.006
C(1)	–	C(2)	1.324	0.008
C(2)	–	C(3)	1.462	0.009
C(3)	–	C(4)	1.495	0.008
C(3)	–	O	1.216	0.007
C(4)	–	C(5)	1.404	0.009
C(5)	–	C(6)	1.372	0.010
C(6)	–	C(7)	1.385	0.011
C(7)	–	C(8)	1.399	0.011
C(8)	–	C(9)	1.404	0.010
C(9)	–	C(4)	1.383	0.009
S	–	O	2.640	0.006
S	–	S'	2.665	0.006
C(1)	–	C(1')	2.315	0.009

Desaurin from acetophenone:

Intramolecular interatomic distances and their standard deviations.

Table 14.1$_1$

					Angle (°)	σ(°)
S	–	C(1)	–	S'	98.0	0.4
C(1)	–	S	–	C(1')	82.0	0.4
S	–	C(1)	–	C(2)	128.5	0.5
S'	–	C(1)	–	C(2)	133.4	0.5
C(1)	–	C(2)	–	C(3)	117.9	0.5
C(2)	–	C(3)	–	O	120.2	0.6
C(4)	–	C(3)	–	O	119.8	0.5
C(2)	–	C(3)	–	C(4)	120.0	0.5
C(3)	–	C(4)	–	C(5)	117.4	0.5
C(3)	–	C(4)	–	C(9)	122.7	0.6
C(9)	–	C(4)	–	C(5)	119.9	0.6
C(4)	–	C(5)	–	C(6)	120.1	0.6
C(5)	–	C(6)	–	C(7)	120.6	0.7
C(6)	–	C(7)	–	C(8)	120.1	0.7
C(7)	–	C(8)	–	C(9)	119.4	0.6
C(8)	–	C(9)	–	C(4)	119.9	0.6

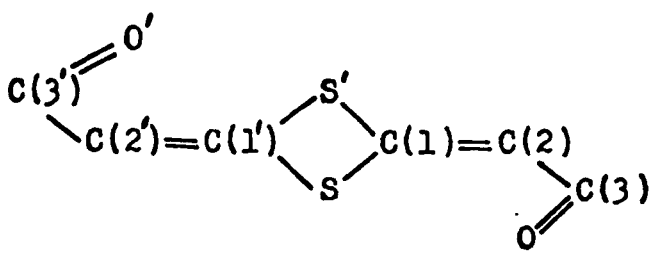
Desaurin from acetophenone:

Bond angles and their standard deviations.

Table 14.1_2

found in similarly conjugated systems (86). The bond distances and angles in the benzene ring, 1.372-1.404Å, (mean 1.391Å), and 119.4-120.6°, (mean 120.0°), are consistent with the accepted values. Deviations from the least squares plane for the benzene ring, (Table 14.1_3, plane A), are small; the maximum deviation being ±0.003Å, (C(6) and C(7)). Bond distances and angles involving hydrogen atoms are listed in Table 14.1_4, (the numbering system employed for the hydrogen atoms is shown in Figure 5.1). The C-H bond lengths range from 0.96 to 1.14Å, (mean 1.05Å), and the C-C-H angles from 100° to 132°, (mean 120°). Little significance can be attached to individual deviations of these bond lengths and angles from the normally accepted values since the hydrogen atoms were not included in the least squares refinement.

The most striking feature of the molecular structure of the desaurin, (also of PDM and the 1,2,4-trithiacyclopentane from pinacolone *vide supra*), is the close planarity of the (*s-cis*) *α,β*-unsaturated carbonyl system and the sulphur atoms, which incurs a correspondingly short intramolecular sulphur-oxygen distance. The least squares plane calculated for the central ten atoms of the molecule,



summarised in Table 14.1_3, (plane B), shows the maximum atomic

(86) "Tables of Interatomic Distances and Configurations in Molecules and Ions", Chem. Soc. Special Publication, Nos 11 and 18, London, 1958 and 1965.

Atom	Δ (Å)
C(4)	+0.0030
C(5)	+0.0001
C(6)	-0.0032
C(7)	+0.0032
C(8)	-0.0001
C(9)	-0.0029

Plane A: $2.752x - 3.443y + 12.125z = -0.1237$

Atom	Δ (Å)
(S'),S	(-), +0.0060
(O'),O	(+), -0.0012
(C(1')),C(1)	(-), +0.0168
(C(2')),C(2)	(+), -0.0021
(C(3')),C(3)	(+), -0.0036

Plane B: $1.796x - 3.621y + 15.131z = 0.0$

Desaurin from acetophenone;

Least squares plane data.

Table 14.1_3

	Distance (Å)		Angle (°)
C(2) – H(1)	1.05	C(1) – C(2) – H(1)	120.
C(5) – H(2)	0.96	C(3) – C(2) – H(1)	122.
C(6) – H(3)	1.14	C(4) – C(5) – H(2)	111.
C(7) – H(4)	1.01	C(6) – C(5) – H(2)	127.
C(8) – H(5)	1.01	C(5) – C(6) – H(3)	100.
C(9) – H(6)	1.11	C(7) – C(6) – H(3)	132.
		C(6) – C(7) – H(4)	123.
		C(8) – C(7) – H(4)	117.
		C(7) – C(8) – H(5)	122.
		C(9) – C(8) – H(5)	119.
		C(8) – C(9) – H(6)	111.
		C(4) – C(9) – H(6)	130.

Desaurin from acetophenone:

Bond distances and angles involving hydrogen atoms.

Table 14.1$_4$

Atom 'A'	Atom 'B'	Unit translation on Atom 'B'.	Distance (Å).
S	S_2	(-1, 0, 0)	3.42
S	O_1	(0,-1, 0)	3.85
S	$C(3)_1$	(0,-1, 0)	3.63
S	$C(4)_1$	(0,-1, 0)	3.89
O	$C(2)_1$	(-1, 0, 0)	3.61
O	$C(4)_1$	(0,-1, 0)	3.88
O	$C(8)_1$	(-1,-1, 0)	3.45
O	$C(9)_1$	(-1, 0, 0)	3.57
C(1)	$C(1)_2$	(0, 1, 0)	3.70
C(1)	$C(2)_2$	(0, 1, 0)	3.63
C(1)	$C(9)_1$	(0,-1, 0)	3.59
C(2)	$C(8)_1$	(0,-1, 0)	3.59
C(2)	$C(9)_1$	(0,-1, 0)	3.42
C(3)	$C(8)_1$	(0,-1, 0)	3.50
C(3)	$C(9)_1$	(0,-1, 0)	3.64
C(4)	$C(7)_1$	(0,-1, 0)	3.65
C(4)	$C(8)_1$	(0,-1, 0)	3.63
C(5)	$C(7)_1$	(0,-1, 0)	3.63
C(5)	$C(8)_1$	(-1, 0, 0)	3.46
C(5)	$C(9)_1$	(-1, 0, 0)	3.74

Atom 'B' is generated from the coordinates listed in Table 6.2 using the symmetry operation $(\ )_i$ and unit translations shown.

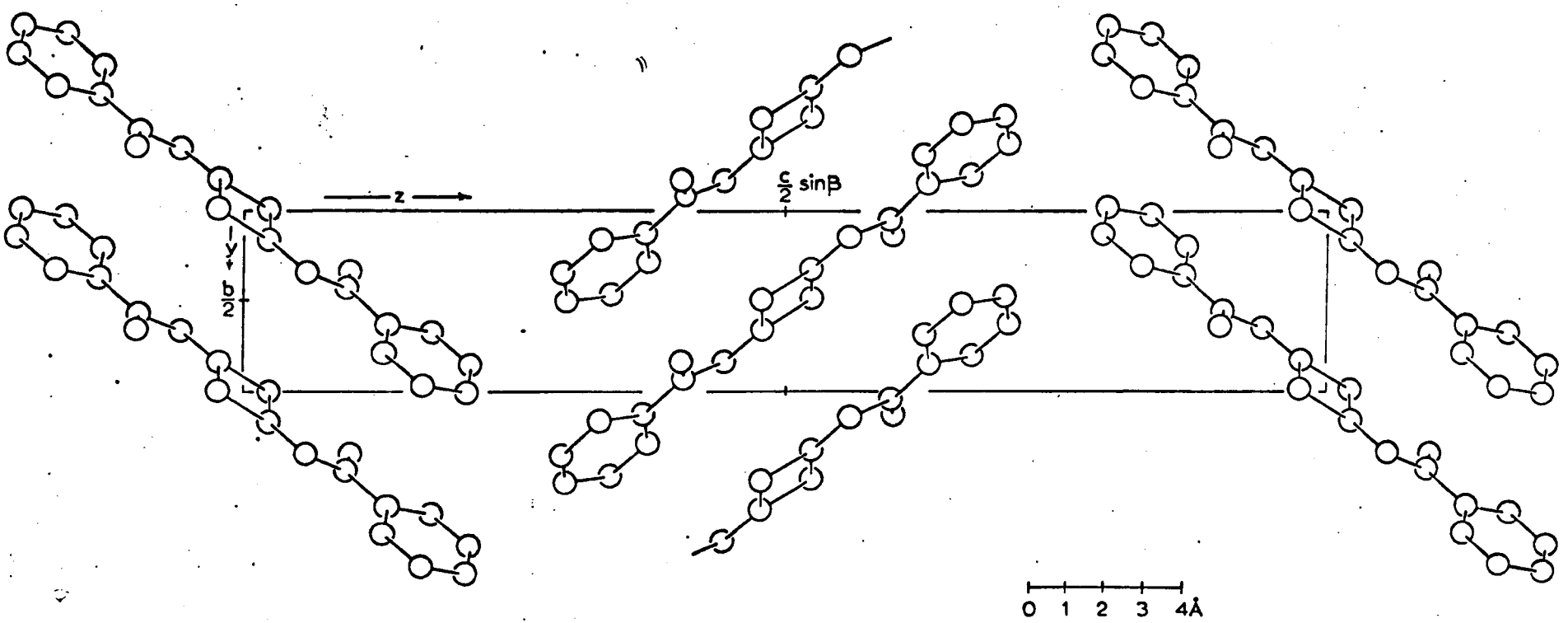
$)_1$: x, y, z

$)_2$: -x, -y, -z

Desaurin from acetophenone:

Closest contacts of neighbouring molecules.

Table 14.1.



Desaurin from acetophenone:

Projection of the structure along [100], illustrating the packing of the molecules.

Figure 14.1$_2$.

deviation from the plane is ∓0.017Å, (C(1) and C(1′)), with a mean atomic deviation of 0.006Å. However, the molecule as a whole is not planar; the plane of the benzene ring is inclined at an angle of 11.4° to that of the central ten atom system. The intramolecular sulphur-oxygen distance is 2.640Å, being 0.41Å less than the sum of the van der Waals radii of sulphur and oxygen. The approximate planarity of the central portion of the molecule and the short intramolecular sulphur-oxygen distance are further discussed in section 14.4.

Intermolecular interatomic distances of less than 3.9Å are listed in Table 14.1_5, and the molecular packing is illustrated in Figure 14.1_2. The contact distances between molecules all appear reasonable; the only interatomic separation of note is the sulphur-sulphur contact of 3.42Å, which provides additional support that the van der Waals radius of sulphur is somewhat less than the value suggested by Pauling.

14.2 Details of the molecular and crystal structure of 3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole)≠.

Structural data were calculated from the final atomic coordinates, (and standard deviations), of the sulphur, oxygen and carbon atoms, listed in Table 10.2, and the hydrogen locations obtained from the difference synthesis, (Table 10.4).

The structure analysis reveals that the α,β-unsaturated

≠ The abbreviation PDM for this molecule is retained throughout this chapter.

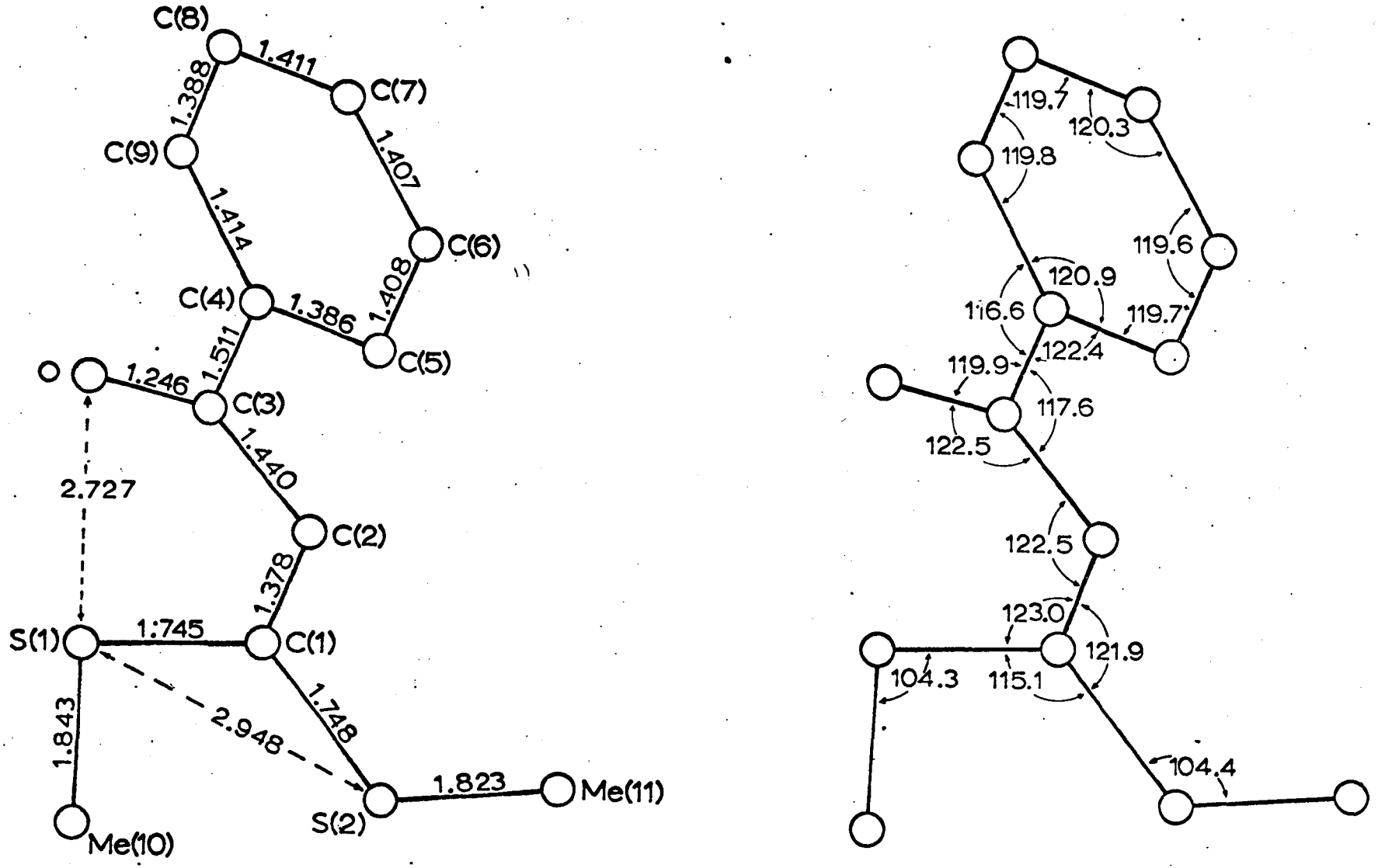
carbonyl system adopts an s-cis conformation, analogous to the situation found in the desaurin. Bond distances and angles, (involving non-hydrogen atoms), are shown in Figure 14.2_1, and are listed, together with their estimated standard deviations, in Tables 14.2_1 and 14.2_2.

The C(1)-S bond distances in PDM, 1.745Å and 1.748Å, are identical within experimental error, but are shorter than the corresponding lengths in the desaurin, (1.766Å and 1.764Å); however the differences in these bond lengths between the two molecules are not significant, representing about $1.4\sigma_A$. The major differences between the molecular structures of PDM and the desaurin lie in the valence angles at the sulphur atoms and in the S-C(1)-S angle;

	PDM	Desaurin
S-C(1)-S	115.1°	98.0°,
$\hat{S}$	$\left\{\begin{matrix}104.4^\circ\\104.3^\circ\end{matrix}\right\}$	82.0°.

These angles in the 1,3-dithiete ring of the desaurin are, as expected, significantly smaller than the corresponding angles in PDM. Consequently the intramolecular sulphur-sulphur distance in PDM, (2.948Å), is appreciably longer than in the desaurin, (2.665Å). The S-C(sp^3) bond lengths, 1.823Å and 1.843Å, are not significantly different and are consistent with the accepted carbon-sulphur single bond length of 1.82Å (83).

Bond distances and angles in the α,β-unsaturated carbonyl system show little difference from the values found in similarly



PDM: Bond lengths and angles.

Figure 14.2

			Distance (Å)	σ(Å)
S(1)	–	C(1)	1.745	0.011
S(1)	–	Me(10)	1.843	0.011
S(2)	–	C(1)	1.748	0.010
S(2)	–	Me(11)	1.823	0.011
O	–	C(3)	1.246	0.013
C(1)	–	C(2)	1.378	0.013
C(2)	–	C(3)	1.440	0.014
C(3)	–	C(4)	1.511	0.013
C(4)	–	C(5)	1.386	0.016
C(4)	–	C(9)	1.414	0.016
C(5)	–	C(6)	1.408	0.014
C(6)	–	C(7)	1.407	0.018
C(7)	–	C(8)	1.411	0.018
C(8)	–	C(9)	1.388	0.014
S(1)	–	S(2)	2.948	0.007
S(1)	–	O	2.727	0.010

PDM:

Intramolecular interatomic distances and their standard deviations.

Table 14.2_1

					Angle (°)	σ(°)
C(1)	–	S(1)	–	Me(10)	104.3	0.5
C(1)	–	S(2)	–	Me(11)	104.4	0.5
S(1)	–	C(1)	–	S(2)	115.1	0.5
S(1)	–	C(1)	–	C(2)	123.0	0.8
S(2)	–	C(1)	–	C(2)	121.9	0.8
C(1)	–	C(2)	–	C(3)	122.5	0.9
O	–	C(3)	–	C(2)	122.5	0.8
O	–	C(3)	–	C(4)	119.9	0.9
C(2)	–	C(3)	–	C(4)	117.6	0.9
C(3)	–	C(4)	–	C(5)	122.4	1.0
C(3)	–	C(4)	–	C(9)	116.6	1.0
C(5)	–	C(4)	–	C(9)	120.9	0.9
C(4)	–	C(5)	–	C(6)	119.7	1.1
C(5)	–	C(6)	–	C(7)	119.6	1.1
C(6)	–	C(7)	–	C(8)	120.3	1.0
C(7)	–	C(8)	–	C(9)	119.7	1.1
C(4)	–	C(9)	–	C(8)	119.8	1.1

PDM:

Bond angles and their standard deviations.

Table 14.2_2

conjugated atomic groups; the dimensions of this system are discussed in detail, and compared with the analogous dimensions in the desaurin and trithiacyclopentane from pinacolone, in section 14.4. The C(3)-C(4) bond length, 1.511Å, is comparable with the analogous distance in the desaurin of 1.495Å, and the bond distances and angles in the benzene ring, 1.386-1.414Å, (mean 1.402Å), and 119.6-120.9°, (mean 120.0°) are consistent with the accepted values. Deviations from the least squares plane of the benzene ring, summarised in Table 14.2_3, (plane A), are small; the maximum atomic displacement from the plane is 0.019Å, [C(4)], and the mean atomic deviation is 0.010Å.

Bond lengths and angles involving hydrogen atoms are listed in Table 14.2_4, (the numbering system used for the hydrogen atoms is shown in Figure 10.1). As in the desaurin, little significance can be attached to any individual deviation of these distances and angles from the accepted values since the hydrogen atoms were not included in the least squares refinement. The mean values of the bond lengths and angles involving hydrogen atoms are, 1.08Å for C(sp^2)-H; 1.06Å for C(sp^3)-H; 119° for C-C(sp^2)-H; 105° for S-C(sp^3)-H and 114° for H-C(sp^3)-H.

The coplanarity of the α,β-unsaturated carbonyl system and the sulphur atoms is still much in evidence in PDM, though to a lesser degree than found in the desaurin structure. Various least squares planes were calculated, and are summarised in Table 14.2_3, (planes B, C and D). Least squares plane B, calculated for the S(1), S(2), C(1) and C(2) system, illustrates

	Plane A	Plane B	Plane C	Plane D
	Δ(Å)	Δ(Å)	Δ(Å)	Δ(Å)
S(1)		0.0004	0.0136	0.0149
S(2)		0.0004	-0.0127*	-0.0043
O		-0.0308*	-0.0275	-0.0305
C(1)		-0.0013	-0.0076	-0.0035
C(2)		0.0005	-0.0152	-0.0123
C(3)		0.0468*	0.0366	0.0358
C(4)	-0.0194			
C(5)	0.0095			
C(6)	0.0050			
C(7)	-0.0094			
C(8)	-0.0006			
C(9)	0.0148			
Me(10)		0.2125*	0.2325*	0.2366*
Me(11)		0.1635*	0.1302*	0.1407*
P	-2.6616	-3.5265	-3.5295	-3.5396
Q	6.9544	3.9428	4.0432	4.0231
R	13.836	16.955	16.854	16.858
S	6.5785	6.9277	6.9067	6.9016

PDM;

Least squares plane data.

Table 14.2_3

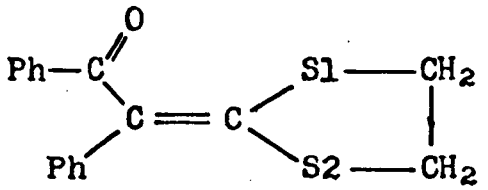
Distance (Å)		Angle (°)		Angle (°)	
C(2) – H(1)	1.04	C(1) – C(2) – H(1)	127.	S(1) – Me(10) – H(7)	93.
C(5) – H(2)	1.15	C(3) – C(2) – H(1)	109.	S(1) – Me(10) – H(8)	111.
C(6) – H(3)	0.96	C(4) – C(5) – H(2)	127.	S(1) – Me(10) – H(9)	113.
C(7) – H(4)	1.04	C(6) – C(5) – H(2)	111.	H(7) – Me(10) – H(8)	87.
C(8) – H(5)	1.12	C(5) – C(6) – H(3)	147.	H(7) – Me(10) – H(9)	138.
C(9) – H(6)	1.19	C(7) – C(6) – H(3)	93.	H(8) – Me(10) – H(9)	113.
Me(10) – H(7)	0.92	C(6) – C(7) – H(4)	112.	S(2) – Me(11) – H(10)	102.
Me(10) – H(8)	1.27	C(8) – C(7) – H(4)	127.	S(2) – Me(11) – H(11)	94.
Me(10) – H(9)	0.90	C(7) – C(8) – H(5)	126.	S(2) – Me(11) – H(12)	114.
Me(11) – H(10)	1.07	C(9) – C(8) – H(5)	114.	H(10) – Me(11) – H(11)	112.
Me(11) – H(11)	1.12	C(8) – C(9) – H(6)	125.	H(10) – Me(11) – H(12)	103.
Me(11) – H(12)	1.09	C(4) – C(9) – H(6)	112.	H(11) – Me(11) – H(12)	130.

PDM:

Bond distances and angles involving hydrogen atoms.

Table 14.2$_4$

that C(1) shows no significant deviation from the formal sp^2-hybrid state and acts as a base-line for the other calculated planes; atoms C(3) and O are displaced on either side of plane B by 0.047Å and 0.031Å respectively. The X-ray diffraction study of 2-desylidene-1,3-dithiolane, XIV, by Tulinsky (15,16),



XIV*

showed that the S1-C=C-C=O system is approximately coplanar (the mean atomic deviation being 0.034Å), but that S2, which is not involved in any sulphur-oxygen interaction, is significantly displaced from the plane by 0.24Å. Consequently least squares plane C was calculated for the analogous S(1)-C(1)=C(2)-C(3)=O system of PDM. The out-of-plane distances for plane C show a direct contrast to the findings of Tulinsky; S(2) is displaced 0.013Å from the plane and is, in fact, closer to the plane than four of the defining atoms. Least squares plane D, calculated for the S(1), S(2), C(1), C(2), C(3) and O system, is the closest comparison available to the ten atom plane of the desaurin. The maximum atomic deviation from plane D and the mean atomic deviation are 0.036Å, [C(3)], and 0.017Å respectively, (compared with 0.017Å and 0.006Å respectively for plane B of the desaurin). The intramolecular S(1)-O distance in PDM, 2.727Å, is greater

* Reproduced from chapter 1.

Atom 'A'	Atom 'B'	Unit translation on Atom 'B'.	Distance (Å).
S(1)	$S(1)_2$	(1, 0, 1)	3.41
S(1)	$Me(10)_2$	(1, 0, 1)	3.89
S(2)	$S(2)_2$	(2, 1, 1)	3.57
S(2)	$C(2)_2$	(1, 1, 1)	3.88
S(2)	$C(3)_1$	(1, 0, 0)	3.69
S(2)	$C(4)_1$	(1, 0, 0)	3.77
S(2)	$C(9)_1$	(1, 0, 0)	3.79
S(2)	$Me(11)_2$	(2, 1, 1)	3.80
O	$C(5)_4$	(0,-1, 0)	3.88
O	$C(6)_4$	(0,-1, 0)	3.41
O	$Me(10)_1$	(-1, 0, 0)	3.53
O	$Me(10)_2$	(1, 0, 1)	3.47
C(1)	$C(9)_1$	(1, 0, 0)	3.46
C(1)	$Me(11)_2$	(1, 1, 1)	3.71
C(2)	$C(8)_1$	(1, 0, 0)	3.56
C(2)	$C(9)_1$	(1, 0, 0)	3.56
C(3)	$C(8)_1$	(1, 0, 0)	3.88
C(4)	$Me(11)_1$	(-1, 0, 0)	3.80
C(6)	$C(9)_4$	(-1, 0, 0)	3.74
C(6)	$Me(10)_3$	(-1, 0,-1)	3.68
C(7)	$C(9)_4$	(-1, 0, 0)	3.89
C(7)	$Me(11)_4$	(0,-1, 0)	3.74
C(8)	$Me(11)_4$	(1,-1, 0)	3.45

Atom 'B' is generated from the coordinates listed in Table 10.2 using the symmetry operation $(\ )_i$ and unit translation shown.

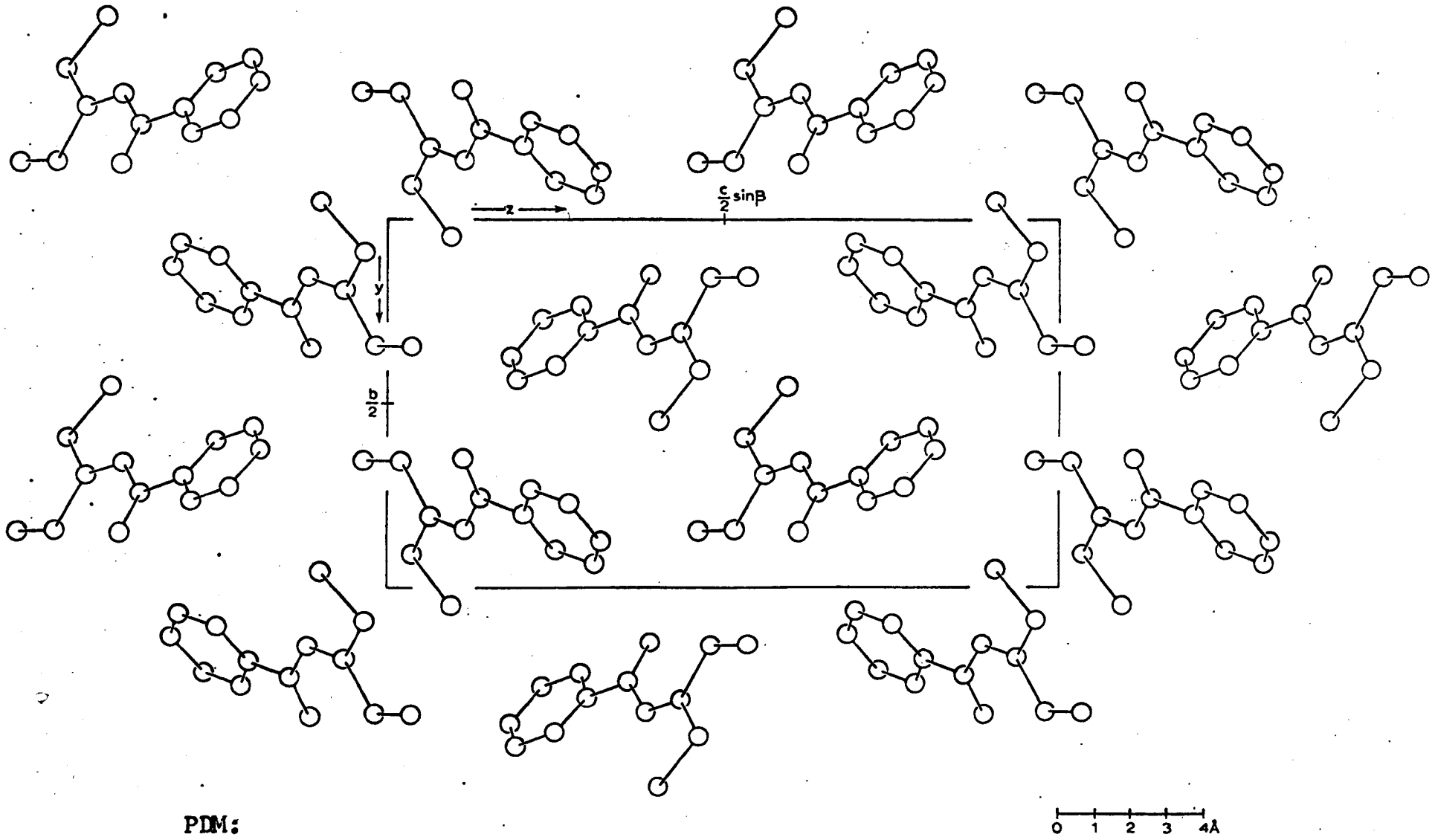
$)_1$: x, y, z. $)_3$: x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z.

$)_2$: -x, -y, -z. $)_4$: -x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z.

PDM:

Closest contacts of neighbouring molecules.

Table 14.2.



PDM:

Projection of the structure along [100], illustrating the packing of the molecules.

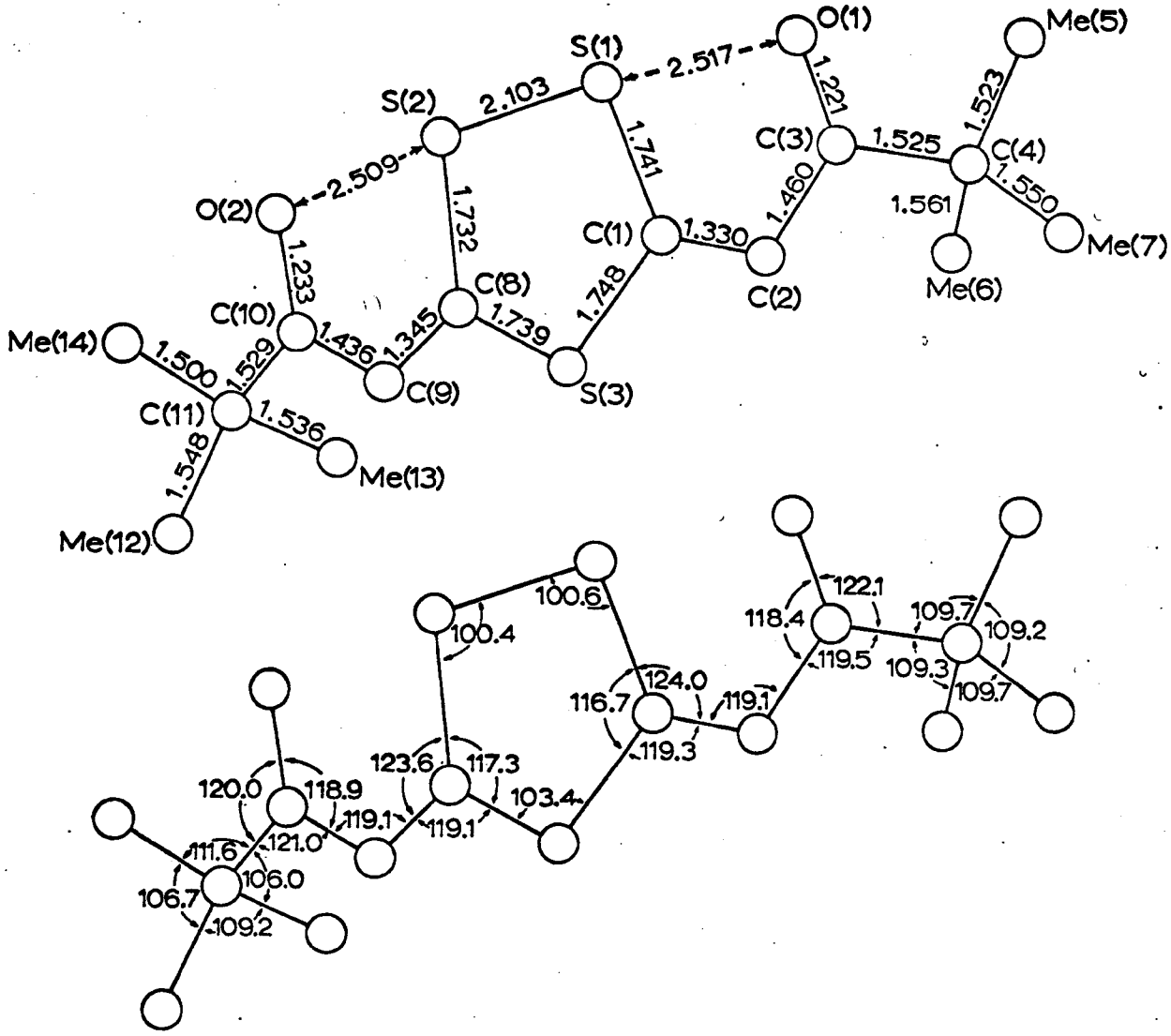
Figure 14.2$_2$.

than the corresponding length in the desaurin, (2.640Å), but is still appreciably less than the sum of the van der Waals radii of sulphur and oxygen. The approximate coplanarity of the α,β-unsaturated carbonyl system and the sulphur atoms, and the short sulphur-oxygen distance, are further discussed in section 14.4. As in the desaurin, the plane of the benzene ring is inclined to that of the sub-system, and in this molecule is rotated 19.3° from plane D.

Intermolecular interatomic distances of less than 3.9Å are listed in Table 14.2_5, and the molecular packing is illustrated in Figure 14.2_2. The contact distances between molecules range upwards from 3.41Å, (C(6)-O; S(1)-S(1)), and appear reasonable, with the exception of the C(8)-Me(11) separation of 3.45Å. This distance is less than the theoretical carbon-methyl group contact distance of 3.65Å, although it is greater than twice the van der Waals radius of a carbon atom. Examination of a three-dimensional difference synthesis in the region of S(2) revealed no density which might suggest an alternative position for Me(11). The sulphur-sulphur separation, 3.41Å, across a space group inversion centre, is very similar to the situation found in the desaurin.

14.3 The molecular and crystal structure of the 1,2,4-trithiacyclopentane from pinacolone.

Structural data were calculated from the final atomic coordinates, (and standard deviations), listed in Table 13.2. Bond lengths and angles are shown in Figure 14.3_1, and are



Trithiacyclopentane from pinacolone:

Bond lengths and angles.

Figure 14.3.1

listed, together with their estimated standard deviations, in Tables 14.3_1 and 14.3_2. The structure analysis confirms the 1,2,4-trithiacyclopentane structure forwarded by Gompper (7) and supported by Lynch (10), and reveals that the molecule is the cis isomer VII_a, with both α,β-unsaturated carbonyl systems adopting an s-cis conformation, as illustrated in Figure 14.3_1.

Hordvik (87) conducted an extensive survey of structural data for molecules containing an S(II)-S(II) bond which showed that the dihedral angle* between the valences of the sulphur atoms is correlated to the disulphide bond length. The variation in disulphide bond length with dihedral angle was assumed to be in part due to lone pair repulsion, which is most pronounced when the dihedral angle is 0°, (cis), and in part due to pi bonding, which is most pronounced at dihedral angle 90°. A plot of the dihedral angle against the S(II)-S(II) bond length, for a number of linear and unsaturated heterocyclic disulphides, resulted in a smooth curve from which Hordvik estimates the length of a single bond between two divalent sulphur atoms at dihedral angle zero is 2.10Å.

Least squares plane data for various groups of atoms in the trithiacyclopentane from pinacolone molecule are listed in Table 14.3_3. Plane A, calculated for the C(1)-S(1)-S(2)-C(8) system, shows this grouping is approximately planar, (the mean atomic deviation is 0.013Å), but that S(3) is significantly

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(87) A. Hordvik, Acta Chem. Scand., 20, 1885 (1966).
* In the disulphide system $-C_1-S_1-S_2-C_2-$, the angle between the $C_1S_1S_2$ and $S_1S_2C_2$ planes is termed the "dihedral angle".

			Distance (Å)	σ(Å)
S(1)	–	S(2)	2.103	0.003
S(1)	–	C(1)	1.741	0.006
S(2)	–	C(8)	1.732	0.006
S(3)	–	C(1)	1.748	0.005
S(3)	–	C(8)	1.739	0.006
O(1)	–	C(3)	1.221	0.008
O(2)	–	C(10)	1.233	0.008
C(1)	–	C(2)	1.330	0.008
C(2)	–	C(3)	1.460	0.007
C(3)	–	C(4)	1.525	0.010
C(8)	–	C(9)	1.345	0.007
C(9)	–	C(10)	1.436	0.009
C(10)	–	C(11)	1.529	0.008
C(4)	–	Me(5)	1.523	0.009
C(4)	–	Me(6)	1.561	0.010
C(4)	–	Me(7)	1.550	0.012
C(11)	–	Me(12)	1.548	0.009
C(11)	–	Me(13)	1.536	0.012
C(11)	–	Me(14)	1.500	0.014
S(1)	–	O(1)	2.517	0.005
S(2)	–	O(2)	2.509	0.005

Trithiacyclopentane from pinacolone:

Intramolecular interatomic distances and their standard deviations.

Table 14.3$_1$

			Angle (°)	σ(°)
S(2)	– S(1) –	C(1)	100.6	0.2
S(1)	– S(2) –	C(8)	100.4	0.2
C(1)	– S(3) –	C(8)	103.4	0.3
S(1)	– C(1) –	S(3)	116.7	0.3
S(1)	– C(1) –	C(2)	124.0	0.4
S(3)	– C(1) –	C(2)	119.3	0.4
C(1)	– C(2) –	C(3)	119.1	0.6
O(1)	– C(3) –	C(2)	118.4	0.6
O(1)	– C(3) –	C(4)	122.1	0.5
C(2)	– C(3) –	C(4)	119.5	0.6
C(3)	– C(4) –	Me(5)	109.7	0.6
C(3)	– C(4) –	Me(6)	109.3	0.5
C(3)	– C(4) –	Me(7)	107.3	0.6
Me(5)	– C(4) –	Me(6)	111.7	0.6
Me(5)	– C(4) –	Me(7)	109.2	0.6
Me(6)	– C(4) –	Me(7)	109.7	0.7
S(2)	– C(8) –	S(3)	117.3	0.3
S(2)	– C(8) –	C(9)	123.6	0.5
S(3)	– C(8) –	C(9)	119.1	0.4
C(8)	– C(9) –	C(10)	119.1	0.5
O(2)	– C(10) –	C(9)	118.9	0.5
O(2)	– C(10) –	C(11)	120.0	0.6
C(9)	– C(10) –	C(11)	121.0	0.5
C(10)	– C(11) –	Me(12)	110.2	0.5
C(10)	– C(11) –	Me(13)	106.0	0.5
C(10)	– C(11) –	Me(14)	111.6	0.6
Me(12)	– C(11) –	Me(13)	109.2	0.6
Me(12)	– C(11) –	Me(14)	106.7	0.6
Me(13)	– C(11) –	Me(14)	113.3	0.7

Trithiacyclopentane from pinacolone:

Bond angles and their standard deviations.

Table 14.3_2

	Plane A	Plane B	Plane C	Plane D
	Δ(Å)	Δ(Å)	Δ(Å)	Δ(Å)
S(1)	-0.0145	0.3170*	-0.0218	-0.2672*
S(2)	0.0145	0.3611*	-0.1474*	-0.0268
S(3)	0.2145*	0.0	0.1180*	0.1395*
O(1)	-0.1438*		0.0329	
O(2)	-0.1729*			0.0417
C(1)	0.0111	0.0	0.0206	
C(2)	-0.0938*		0.0031	
C(3)	-0.2204*		-0.0349	
C(8)	-0.0112	0.0		0.0238
C(9)	-0.1661*			0.0070
C(10)	-0.3098*			-0.0457
P	-0.9624	-2.1053	-0.9892	-0.7946
Q	-10.299	-9.6764	-10.834	-9.5099
R	13.898	14.763	12.613	15.424
S	1.8589	1.9710	1.6655	1.8649

Trithiacyclopentane from pinacolone:

Least squares plane data.

Table 14.3_3

displaced from the plane by 0.215Å. Consequently the heterocycle is most easily defined by plane A and a second plane through the C(1)-S(3)-C(8) system, (plane B), which intersect at an angle of 11.5°. The sulphur-sulphur bond length found in this cis, effectivly-planar‡ disulphide system is 2.103Å, which according to Hordvik's work (87) must be considered as an example of a S(II)-S(II) single bond with no pi character. It is evident, however, that if the short intramolecular sulphur-oxygen distances found in this molecule, PDM and the desaurin from acetophenone are interpreted as partial bonding between these atoms, the net observed effect in this molecule could be a lengthening of the disulphide bond. This point is further discussed in section 14.4.

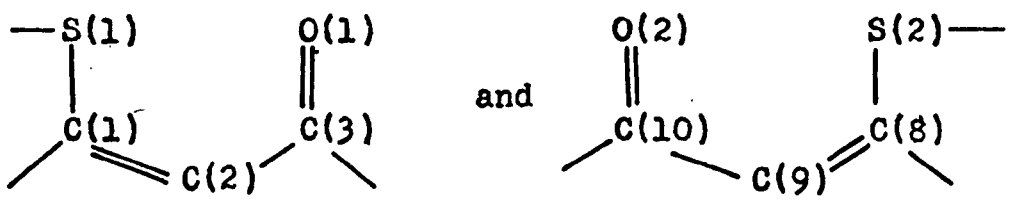
The four independent C(sp^2)-S bond lengths in the molecule, (1.741Å, 1.748Å, 1.739Å and 1.732Å), are not significantly different and the mean value of 1.740Å is consistent with the corresponding mean distance in PDM of 1.747Å. The valence angles at S(1) and S(2), 100.6° and 100.4°, are identical within experimental error, but are smaller than the angle subtended at S(3), (103.4°). The endocyclic angles at C(1) and C(8), 116.7° and 117.3°, are comparable with the analogous S-C(1)-S bond angle of 115.1° in PDM.

The molecular dimensions of the two α,β-unsaturated carbonyl systems in the molecule are not significantly different, (Figure 14.3_1). The maximum deviation between 'equivalent' bond lengths and angles in the two systems is between the

‡ The strict dihedral angle between the C(1)S(1)S(2) and S(1)S(2)C(8) planes is 2.0°.

C(2)-C(3) and C(9)-C(10) distances, (1.460Å and 1.436Å respectively), representing about $2\sigma_A$. The dimensions of the conjugated carbonyl systems are discussed in section 14.4. The C(3)-C(4) and C(10)-C(11) bond lengths, 1.525Å and 1.529Å respectively, are not significantly different and are consistent with the distance normally associated with a C($\underline{sp}^3$)-CO bond (86). Fortunately the dimensions of the t-butyl groups were of minimal interest in this study; the high thermal motion of the methyl groups is reflected in the large individual deviation in bond lengths and angles from the accepted values. However the mean C-Me distance and Me-C-Me angle, 1.545Å and 109.5° at C(4), 1.528Å and 109.5° at C(11), are reasonably consistent with the normal values.

Least squares planes were calculated for,



Plane C Plane D

which showed, (Table 14.3_3), that each atomic grouping is approximately coplanar. The maximum atomic displacement from the plane and the mean atomic deviation are 0.035Å, 0.023Å for plane C; 0.046Å, 0.029Å for plane D. However the central portion of the molecule is strictly non-planar; planes C and D intersect at an angle of 10.1°, and S(3) is significantly displaced from each plane, (0.118Å from plane C and 0.140Å from plane D). The

Atom 'A'	Atom 'B'	Unit translation on Atom 'B'	Distance (Å)
S(1)	$S(3)_1$	(1, 0, 0)	3.45
S(2)	$S(3)_1$	(1, 0, 0)	3.49
S(2)	$S(3)_2$	(0, 0, 0)	3.93
S(3)	$O(2)_2$	(0, 0, 0)	3.88
S(2)	$Me(5)_4$	(1,-1, 0)	3.67
S(2)	$C(8)_2$	(0, 0, 0)	3.74
S(2)	$C(9)_1$	(1, 0, 0)	3.98
S(2)	$C(9)_2$	(0, 0, 0)	3.98
S(3)	$C(9)_2$	(-1, 0, 0)	3.95
O(1)	$C(2)_1$	(1, 0, 0)	3.99
O(1)	$Me(7)_1$	(1, 0, 0)	3.75
O(1)	$Me(12)_2$	(0, 0, 0)	3.90
O(2)	$C(1)_2$	(0, 0, 0)	3.93
O(2)	$Me(12)_1$	(1, 0, 0)	3.72
O(2)	$Me(13)_1$	(1, 0, 0)	3.94
C(1)	$Me(6)_4$	(0,-1, 0)	3,77
Me(6)	$Me(12)_2$	(-1, 0, 0)	3.79
Me(7)	$Me(14)_3$	(0,-1, 0)	3.54
C(8)	$C(8)_2$	(0, 0, 0)	3.99

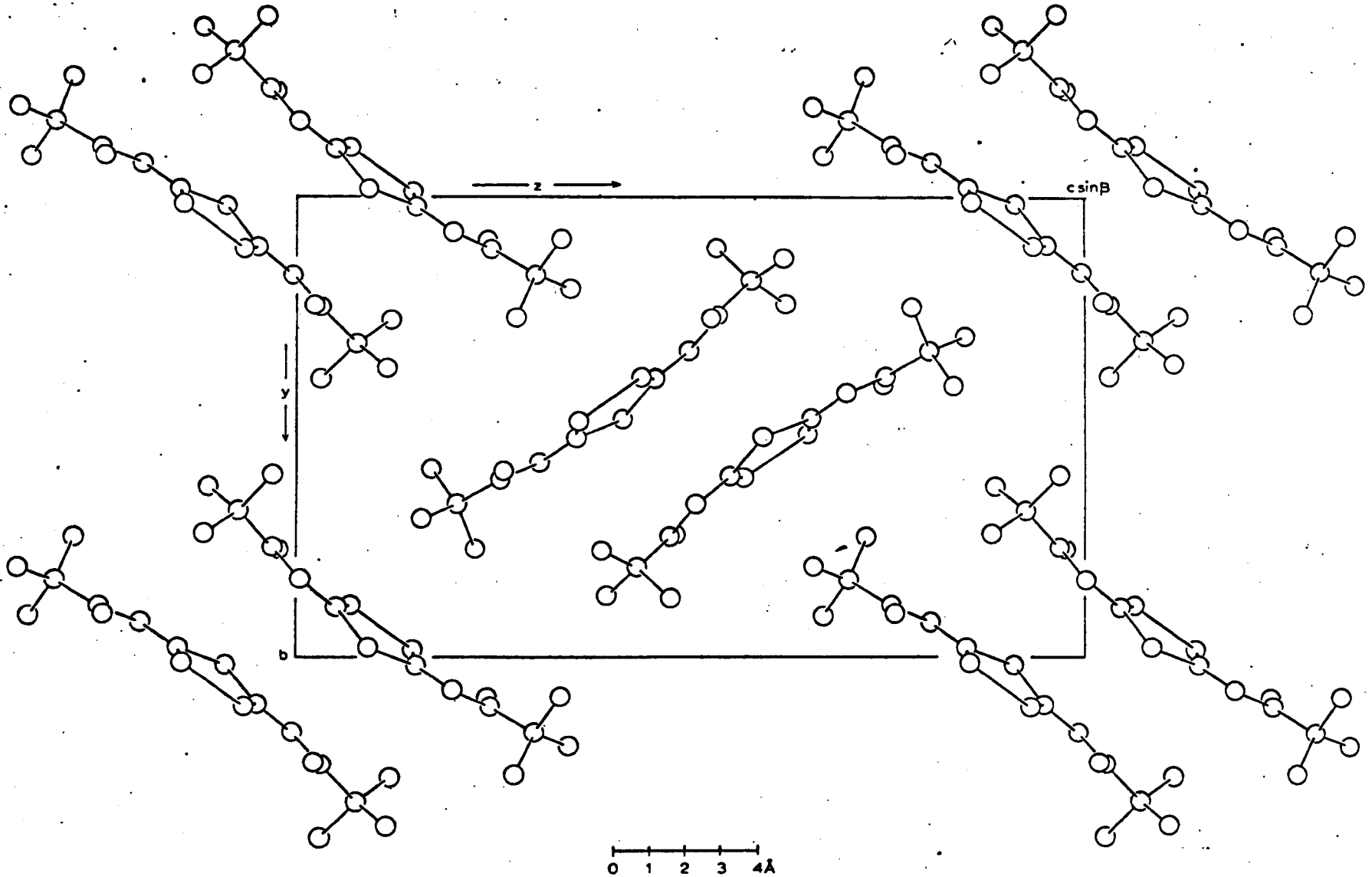
Atom 'B' is generated from the coordinates listed in Table 13.2 using the symmetry operation $(\ )_i$, and unit translations shown.

$)_1$: x, y, z
$)_2$: -x, -y, -z
$)_3$: x, ½ - y, ½ + z
$)_4$: -x, ½ + y, ½ - z

Trithiacyclopentane from pinacolone:

Closest contact of neighbouring molecules.

Table 14.3_4



Trithiacyclopentane from pinacolone:

Projection of the structure along [100], illustrating the packing of the molecules.

Figure 14.32.

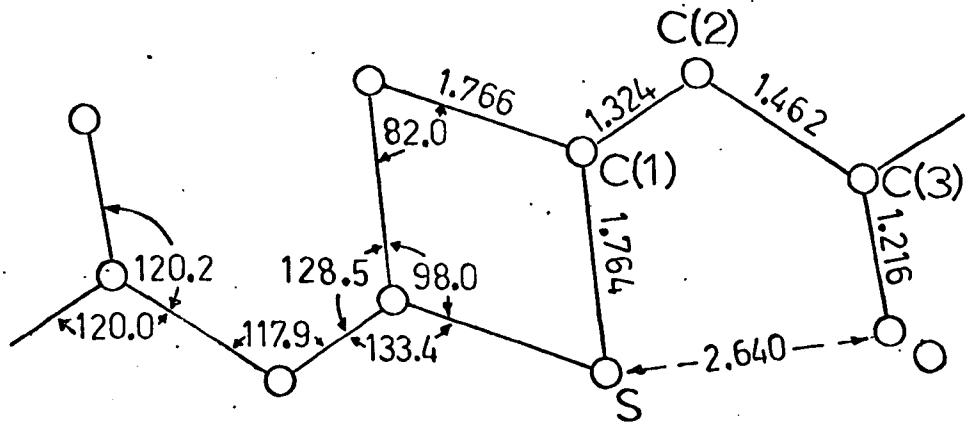
intramolecular sulphur-oxygen distances of 2.509Å and 2.517Å are the smallest observed in the three structure analyses; the mean S--O distance of 2.513Å being 0.54Å less than the sum of the van der Waals radii of sulphur and oxygen. The approximate coplanarity of the α,β-unsaturated carbonyl and sulphur sub-system, and the short sulphur-oxygen distances, are discussed in the following section.

Intermolecular interatomic distances of less than 4.0Å are listed in Table 14.3_4, and the molecular packing is illustrated in Figure 14.3_2. Two unusual contact distances are the Me(7)-Me(14) and Me(6)-Me(12) separations of 3.54Å and 3.79Å respectively. Each of these distances is shorter than the separation of 3.90Å often found between methyl groups (75), but they are greater than twice the van der Waals radius of a carbon atom. Similar observations of unusually short contact distances between two methyl groups have been reported in other crystal structures (88,89) and a careful study did not suggest any alternative positions for the C(methyl) atoms in this analysis.

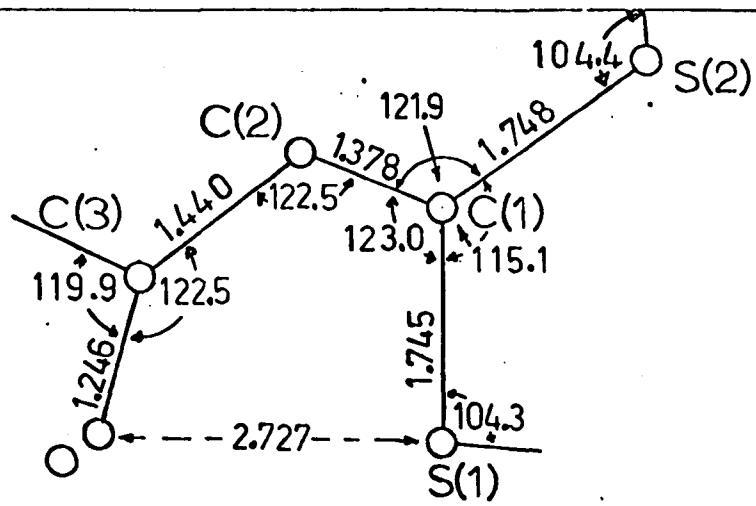
14.4 A comparison of molecular structures.

The dimensions of the β-dithia-α,β-unsaturated carbonyl systems in the three molecules are shown collectively in Figure 14.4_1. Since the dimensions of the two α,β-unsaturated carbonyl systems of the 1,2,4-trithiacyclopentane from pinacolone are not significantly different, (section 14.3), the values shown

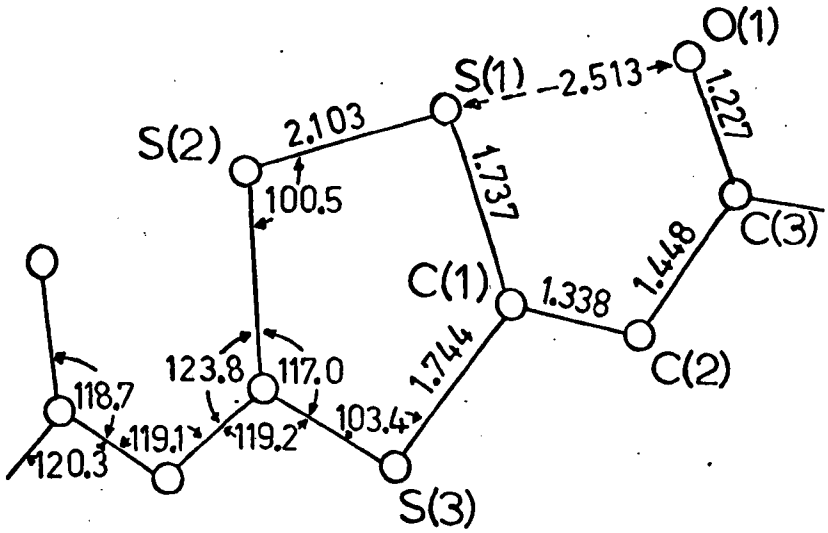
(88) A. C. Macdonald and J. Trotter, J. Chem. Soc., B, 1966, 929.
(89) H. Luth and J. Trotter, Acta Cryst., 19, 614 (1965).



Desaurin from acetophenone.



3-phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole). PDM



1,2,4-trithiacyclopentane from pinacolone, (mean dimensions).

Figure 14.4.

in Figure 14.4, are the mean dimensions of the two systems.

The C(sp^2)-S(II) bond lengths in the three molecules are,

Desaurin	: 1.766Å, 1.764Å	(±0.006Å)	; mean 1.765Å,
PDM	: 1.745Å, 1.748Å	(±0.011Å)	; mean 1.747Å,
Trithiacyclopentane from pinacolone	: 1.741Å, 1.732Å 1.748Å, 1.739Å	(±0.006Å)	; mean 1.740Å.

Data so far accumulated indicate that the length of a carbon-sulphur single bond is 1.82Å, whilst bond-order, bond-length relationships suggest a value of 1.61Å for a pure double bond (83,90). The carbon-sulphur distances found are significantly less than the single bond length, indicating that there is some interaction between the electron in the p-pi orbital of C(1) and the lone-pair electrons of the sulphur atom. The mean C(1)-S bond length in the desaurin is greater than the corresponding mean lengths in PDM and the trithiacyclopentane from pinacolone. Although the difference is not highly significant, ($\sim 2\sigma_{\bar{A}}$), it appears possible that the C(1)-S bonds in the desaurin are lengthened to relieve some steric strain in the 1,3-dithiete ring in an analogous manner to the lengthening of carbon-carbon bonds in cyclobutane systems (91,92).

The bond lengths of the conjugated carbonyl systems in the three molecules are:

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(90) E. G. Cox and G. A. Jeffrey, Proc. Roy. Soc., A, 207, 110 (1951).
(91) J. D. Dunitz, Acta Cryst., 2, 1 (1949).
(92) N. Camerman and S. C. Nyburg, Tetrahedron Letters, 4127 (1967).

	C(1)-C(2)	C(2)-C(3)	C(3)-O
Desaurin	1.324 0.008Å	1.462 0.009Å	1.216 0.007Å
PDM	1.378 0.013Å	1.440 0.014Å	1.246 0.013Å
Trithiacyclopentane	1.330 0.008Å	1.460 0.007Å	1.221 0.008Å
from pinacolone ‡	1.345 0.007Å	1.436 0.009Å	1.233 0.008Å

Application of Cruickshank's significance tests to each 'set' of bond lengths for the system, reveals that the only possibly significant difference is in the C(1)-C(2) distance. This bond in PDM is 0.054Å longer than in the desaurin, ($\sim 3.7\sigma_A$), and 0.040Å longer than the mean in the trithiacyclopentane from pinacolone, ($\sim 2.7\sigma_A$). Simple carbon-carbon double bond lengths are normally in the range 1.31-1.34Å, being lengthened in a C=C-C=O system by conjugation to around 1.36Å (86). The C(1)-C(2) bond lengths found therefore suggest that the electrons are more localised in this bond of the desaurin and 1,2,4-trithiacyclopentane from pinacolone molecules. The C(2)-C(3) bond lengths in the three molecules are not significantly different and are consistent with the distance of 1.44Å normally associated with this conjugated system (86). Values ranging from 1.17Å to 1.20Å are suggested for the length of a carbon-oxygen double bond (83), whilst in ketones and conjugated systems the carbonyl bond length normally lies in the range 1.22-1.24Å (86). The C(3)-O distances found in the three structure analyses are not significantly different, the maximum difference is 0.030Å between

‡ Bond lengths in the analogous C(8)=C(9)-C(10)=O(2) system.

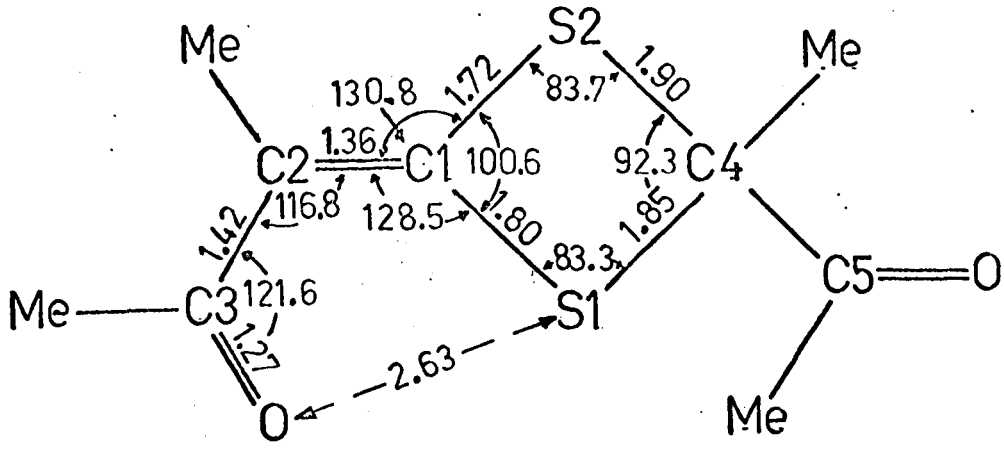
the values in PDM and the desaurin, ($\sim 2\sigma_A$). When the three bond lengths are considered overall, the distances found in PDM suggest a greater delocalisation of electrons in the system than in the desaurin and the 1,2,4-trithiacyclopentane from pinacolone.

The valence angles at C(2) and C(3) in the three molecules, (Figure 14.4_1), are reasonably consistent with the value of 120° normally associated with an sp^2-hybridised carbon atom. The magnitudes of the exocyclic angles≠ at C(1) are, of course, governed by the S-C(1)-S angle. In the desaurin this latter angle is considerably reduced from the normal value to 98.0° in the 1,3-dithiete ring and consequently the exocyclic angles in this molecule are significantly greater than those in PDM and the trithiacyclopentane from pinacolone.

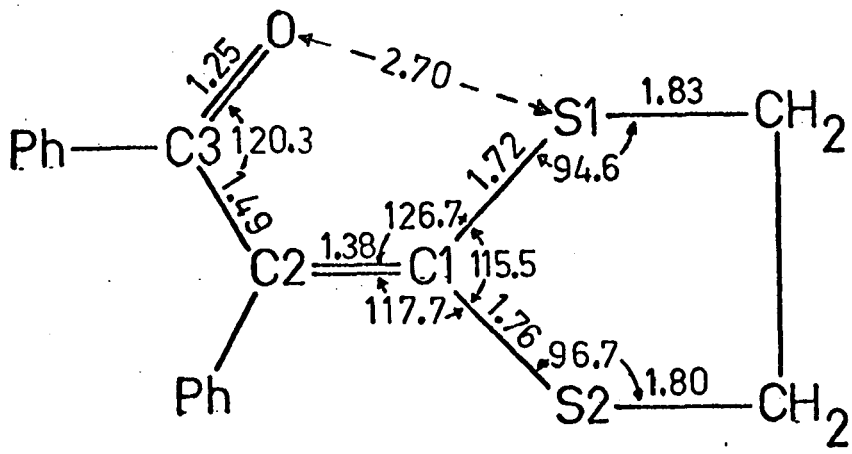
The 2-methylene-1,3-dithiacyclobutane derivative, XIII (14), and 2-desylidene-1,3-dithiolane, XIV (15,16), have some similarity to the structures reported in this thesis. Dimensional details of the comparative portions of XIII and XIV are shown in Figure 14.4_2.

The 2-methylene-1,3-dithiacyclobutane system in XIII is reported to be approximately planar and is therefore comparable with the planar 1,3-dithiete ring of the desaurin. Two notable features of XIII are the 'non-equivalence' of the C(sp^2)-S bond lengths, 1.80Å and 1.72Å, (contrasting with 1.766Å and 1.764Å in the desaurin), and the extremely long S2-C(sp^3) length of

≠ Exocyclic is used loosely to indicate the S(1)-C(1)-C(2) and S(2)-C(1)-C(2) angles in PDM.



XIII



XIV

Dimensional details of the comparative portions of the 2-methylene-1,3-dithiacyclobutane derivative XIII, and 2-desylidene-1,3-dithiolane XIV.

Figure 14.42

1.90Å. The endocyclic valence angles in the desaurin, 98.0° at C($\underline{sp}^2$) and 82.0° at S(II), are not significantly different from the analogous angles in XIII, 100.6° and the mean value of 83.5° respectively; the slightly larger values of these angles in XIII are coupled with the small valence angle of 92.3° at the $\underline{sp}^3$-hybridised carbon atom C(4).

The C($\underline{sp}^2$)-S bond lengths in XIV, 1.72Å and 1.76Å, are consistent with the corresponding distances in PDM, (mean 1.747Å), and the trithiacyclopentane from pinacolone, (mean 1.740Å). The S(1)-C(1)-S(2) angles in XIV and PDM, (115.5° and 115.1° respectively), are comparable, although the valence angles at the sulphur atoms in XIV, 94.6° and 96.7°, reflect the severe puckering in the 1,3-dithiolane system and are significantly smaller than the analogous angles in PDM of 104.3° and 104.4°. The C($\underline{sp}^3$)-S bond lengths in XIV, 1.83Å and 1.80Å, and PDM, 1.843Å and 1.823Å, are in quite good agreement.

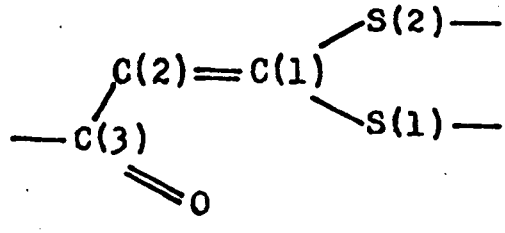
Bond lengths in the C=C-C=O systems of XIII and XIV indicate pronounced conjugation and overall appear more consistent with the distances found in PDM than those in the desaurin and trithiacyclopentane from pinacolone molecules.

Attention has already been drawn in the foregoing sections to the approximate planarity of the (s-cis) α,β-unsaturated carbonyl and sulphur atom sub-systems, in the desaurin, PDM and the 1,2,4-trithiacyclopentane from pinacolone molecules, which incur short intramolecular sulphur-oxygen distances. Similar observations in other molecules have been described in Chapter 1,

for which partial sulphur-oxygen bonding has been proposed (11, 12,13).

In the 2-methylene-1,3-dithiacyclobutane derivative XIII, (Figure 14.4_2), it is reported that the four-membered sulphur-containing ring and the α,β-unsaturated carbonyl system are approximately coplanar, (with a mean deviation of 0.04Å), as is found for the central ten atom system of the desaurin from acetophenone, (mean deviation 0.006Å). It is interesting to note that the distortions of the exocyclic angles at C(1) found in the desaurin, (Figure 14.4_1), are apparent to some extent in XIII, (Figure 14.4_2). The intramolecular sulphur-oxygen distances, 2.640Å in the desaurin and 2.63Å in XIII, are some 0.41Å less than the sum of the van der Waals radii of sulphur and oxygen. Comparison of the dimensions of the β-dithia-α,β-unsaturated carbonyl systems in the desaurin and XIII, suggest that the extremely close similarity in sulphur-oxygen distance is probably fortuitous.

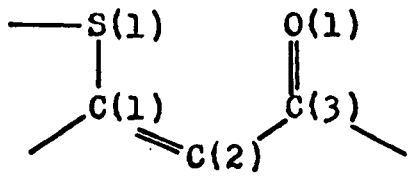
Least squares plane data for the α,β-unsaturated carbonyl and sulphur sub-system in PDM,



has been given in section 14.2, (Table 14.2_3, plane D), and showed that this group of six atoms is approximately coplanar, (with a mean atomic deviation of 0.017Å). As previously stated,

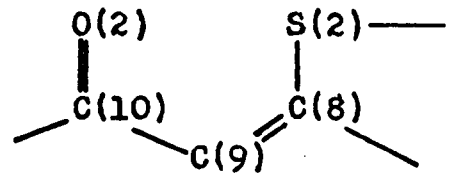
in 2-desylidene-1,3-dithiolane XIV (16), (Figure 14.4_2), it is reported that although the analogous S(1)-C(1)=C(2)-C(3)=O grouping is approximately coplanar, (mean deviation 0.034Å), S(2) is significantly out-of-plane by 0.24Å. The findings in the PDM molecule are in direct contrast to those in XIV on this point; S(2) in PDM is closely coplanar with the five atom system, (Table 14.2_3, plane C). The distortions in exocyclic angles at C(1), found in the desaurin, are not apparent in the PDM molecule, (Figure 14.4_1); however in XIV a severe 'reverse' distortion is evident, (Figure 14.4_2). The intramolecular sulphur-oxygen distances in PDM, (2.727Å), and XIV, (2.70Å), are closely similar, but it is unwise to take a distance of around 2.7Å as characteristic for the grouping on the basis of two determinations.

In the 1,2,4-trithiacyclopentane from pinacolone molecule, least squares planes were calculated for,



Plane C

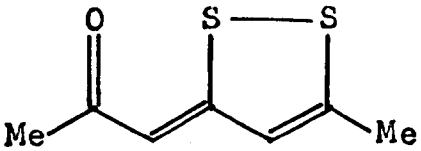
and



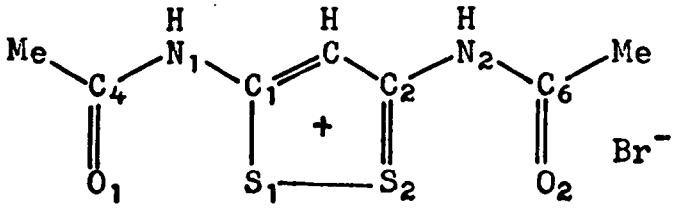
Plane D

which showed, (Table 14.3_3), that each atomic grouping is approximately coplanar. Although the mean atomic deviations, (0.023Å for plane C and 0.029Å for plane D), are greater than those found in the desaurin and PDM, the intramolecular sulphur-oxygen distances found are the shortest in the three analyses.

The unusually short S--O distances found in this molecule, which involve the sulphur atoms of a five-membered heterocyclic disulphide system, are similar to those found in 2,5-dimethyl-dithiofurophthene, X (11), and 3,5-diacetamido-1,2-dithiolium bromide, XIX (93).



X*



XIX

The molecular skeleton of 2,5-dimethyl-dithiofurophthene is reported to be essentially planar, (with a maximum atomic deviation of 0.04Å), incuring an extremely short intramolecular sulphur-oxygen distance of 2.44Å, with a disulphide bond length of 2.12Å. Mammi et. al. (11), after comparing the molecular dimensions of X with those of the previously reported isologue 2,5-dimethyl-thiothiophthene XI (12), interpreted the short S--O distance as evidence of partial bonding between these atoms.

In 3,5-diacetamido-1,2-dithiolium bromide, the 1,2-dithiolium ring is found to be planar within experimental error. Although the nitrogen atoms lie close to this plane, the exo-cyclic carbon atoms, C_4 and C_6, and the carbonyl oxygen atoms, O_1 and O_2, are out-of-plane by +0.091A, +0.094A, +0.048A and +0.130A respectively. Least squares planes through the S_1-C_1-N_1-C_4-O_1 and S_2-C_2-N_2-C_6-O_2 systems of XIX would therefore appear to be akin to the 'butterfly-wing' disposition of planes

(93) A. Hordvik and H. M. Kjoge, Acta Chem., Scand., 20, 1923 (1966).
* Reproduced from Chapter 1.

C and D about the heterocycle in the 1,2,4-trithiacyclopentane from pinacolone molecule. The intramolecular sulphur-oxygen distances in XIX, 2.571Å for S_1--O_1, and 2.515Å for S_2--O_2, are comparable with those found in trithiacyclopentane from pinacolone, (2.517Å and 2.509Å). Hordvik (93) suggests that the slight asymmetry of the sulphur-oxygen distances in XIX is due to the oxygen atom O_1 entering into a weaker contact, (3.113Å), with a second S_1 atom of a symmetry related ion, and concludes that the short S--O distances are indicative of partial bonding between these atoms. By taking the sum of the covalent radii of sulphur and oxygen as 1.71Å, the sum of the van der Waals radii as 3.25Å‡, and assuming a linear bond-order, bond-length relationship, the sulphur-oxygen contacts of 2.571Å and 2.515Å were taken as corresponding to sigma bond-orders of 0.47 and 0.44 respectively. By comparing the disulphide bond length in XIX, (2.080Å), with those found in thiuret hydrobromide, 2.081Å (94), and thiuret hydrochloride hemihydrate, 2.071Å (95,96), Hordvik concludes that the partial bonding between the sulphur and oxygen atoms does not appreciably affect the disulphide bond length. Whether the close S--O contacts in the trithiacyclopentane from pinacolone effectively lengthen the disulphide bond is not at all easy to detect without further structural data on 1,2,4-trithiacyclopentane derivatives. In this context a structure analysis

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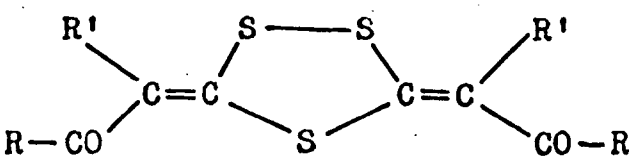
‡ Hordvik assumes the van der Waals radius of sulphur is 1.85Å.

(94) A. Hordvik and S. Joys, ibid., 19, 1539 (1965).
(95) A. Hordvik and J. Sletten, ibid., 19, 753 (1965).
(96) Idem., ibid., 20, 1907 (1966).

of the second cis isomer type,



would unequivocally test this point.

14.5 Conclusion.

The structures of the desaurin and 1,2,4-trithiacyclopentane are confirmed and dimensional details of these novel heterocyclic systems are now established. The structure analyses reveal that in each molecule the α,β-unsaturated carbonyl systems adopt an s-cis conformation and the S-C=C-C=O systems are approximately planar, incuring intramolecular sulphur-oxygen distances which are considerably less than the sum of the van der Waals radii of sulphur and oxygen. In the light of similar observations in related systems, and the conclusions drawn therefrom, the short sulphur-oxygen distances found in this work could perhaps be considered as evidence for partial bonding between the sulphur and oxygen atoms, or a strong charge interaction.

In 2,5-dimethyl-thiothiophthene XI, Giacometti and Rigatti (97) considered that the sulphur atoms use only their 3p orbitals for bonding, and viewed the sulphur-sulphur bonds as having both sigma and pi contributions. Mammi et al. (11) considered the partial bonding between the sulphur and oxygen atoms in the related 2,5-dimethyl-dithiofurophthene X to be of

(97) G. Giacometti and G. Rigatti, J. Chem. Phys., 30, 1633 (1959).

the same general nature, as did Hordvik in 3,5-diacetamido-1,2-dithiolium bromide, XIX (93). A reasonable mechanism by which partial bonding between sulphur and oxygen could occur in the three molecules studied in this work, is through overlap of a 2p orbital on oxygen with a suitably orientated 3d orbital on sulphur. If the $2p_x$ and $2p_z$ orbitals of oxygen are involved in bonding to carbon, the $2p_y$ orbital remains for bonding to the sulphur. This orbital lies in the plane of the α,β-unsaturated carbonyl system and is directed towards the sulphur atom. Consequently overlap between this orbital and a 3d orbital on the sulphur may give rise to a sigma type bond. An alternative formulation involves p-pi-d-pi bonding between the oxygen $2p_z$ orbital and a sulphur 3d orbital.

APPENDIX I

The desaurin from acetophenone.

Observed and calculated structure factors.

Unobserved reflections are marked *

H	L	$10F_o$	$10F_c$
		K=0	
0	2	627	471
0	4	227	-152
0	6	994	433
0	8	61	55
0	10	343	295
0	12	224	-218
0	14	286	-227
0	16	385	-312
0	18	253	-227
0	20	162	-157
0	22	189	-191
0	24	101	-94
0	26	294	-265
0	28	110	-113
0	30	75	68
• 0	32	12	21
0	34	30	33
1	-34	72	72
1	-32	62	63
1	-30	82	82
• 1	-28	15	16
• 1	-26	15	-17
• 1	-24	26	-34
1	-22	35	-45
1	-20	49	-43
1	-18	133	-131
1	-16	252	-238
1	-14	849	-742
1	-12	519	-449
1	-10	146	92
1	-8	294	-236
1	-6	156	-169
1	-4	368	-356
1	-2	841	826
1	0	749	770
• 1	2	6	12
1	4	648	608
1	6	65	-19
1	8	264	202
1	10	414	403
1	12	448	442
1	14	352	305
1	16	176	-156
1	18	75	-62
1	20	57	-52
• 1	22	14	18
1	24	158	-135
1	26	253	-243
• 1	28	14	0
• 1	30	13	-30
1	32	29	-46
• 2	-34	10	7
• 2	-32	12	10
2	-30	88	77
2	-28	71	60
2	-26	80	85
2	-24	151	177
2	-22	91	99
2	-20	71	75
2	-18	154	163
2	-16	60	-41
2	-14	255	-213
2	-12	28	17
2	-10	164	-162
2	-8	132	-148
2	-6	97	83
2	-4	430	-424
2	-2	547	-524
2	0	242	-237
2	2	279	-286
2	4	247	-253
2	6	25	-34
2	8	94	-83
2	10	100	101
2	12	469	443
2	14	97	102
• 2	16	13	32
2	18	164	173
2	20	76	90
2	22	91	113
2	24	36	49
2	26	40	49
2	28	34	42
• 2	30	11	-14
3	-32	63	-53
3	-30	42	-47
3	-28	47	-42
3	-26	89	81
3	-24	96	103
3	-22	34	43
3	-20	77	94
3	-18	146	163
3	-16	272	280
3	-14	260	254
3	-12	288	287
3	-10	216	237
3	-8	89	106
3	-6	90	84
3	-4	130	-138
3	-2	120	-127
3	0	381	-431
3	2	541	-607
3	4	124	-122
3	6	196	-188
3	8	319	-302
3	10	161	-146
3	12	176	-167
3	14	110	-111
3	16	30	39
3	18	51	64
3	20	72	78
3	22	147	147
3	24	122	122
3	26	93	95
3	28	94	104
4	-30	88	-87
4	-28	104	-93
4	-26	58	-61
4	-24	66	-65
4	-22	29	-35
4	-20	34	-39
4	-18	45	48
4	-16	86	101
4	-14	225	232
4	-12	474	496
4	-10	112	119
• 4	-8	14	5
4	-6	267	274
4	-4	213	290
4	-2	141	147
4	0	144	-120
4	2	76	-85
4	4	37	-45
4	6	113	-120
4	8	111	-133
4	10	223	-254
4	12	185	-205
4	14	194	-232
4	16	96	-119
4	18	36	53
• 4	20	13	-4
• 4	22	12	-4
• 4	24	10	10
5	-26	96	-92
5	-24	55	-54
• 5	-22	12	-25
5	-20	69	-94
5	-18	110	-116
5	-16	89	-89
5	-14	118	109
5	-12	71	76
5	-10	112	-122
5	-8	26	36
5	-6	58	71
5	-4	116	135
5	-2	198	224
5	0	157	164
5	2	92	109
• 5	4	15	10
5	6	47	61
5	8	39	53
5	10	25	30
5	12	85	-91
5	14	138	-154
5	16	58	59
• 5	18	10	7
5	20	59	-78
6	-22	27	20
6	-20	47	-30
6	-18	46	-53
6	-16	95	-94
6	-14	94	-88
6	-12	110	-106
6	-10	109	-118
6	-8	116	-118
6	-6	102	-102
• 6	-4	13	-25
6	-2	40	42
6	0	78	86
• 6	2	12	-3
• 6	4	12	-4
6	6	103	110
6	8	120	128
6	10	90	104
6	12	29	42
6	14	55	80
		K=1	
0	1	324	375
0	2	117	111
0	3	283	328
0	4	688	-735
0	5	921	1056
0	6	282	-227
0	7	247	234
0	8	172	158
0	9	97	69
0	10	90	81
0	11	141	-122
0	12	177	-171
0	13	145	-148
0	14	210	-202
0	15	83	-72
0	16	58	62
0	17	362	-293
0	18	117	121
0	19	178	-163
• 0	20	8	-11
0	21	299	-299
0	22	147	-154
0	23	212	-217
• 0	24	9	9
• 0	25	9	-6
0	26	72	71
0	27	39	-59
• 0	28	9	3
0	29	31	-38
0	30	52	48
0	31	20	-33
• 0	32	7	18
• 0	33	6	3
• 0	34	6	-0
1	-35	49	66
• 1	-34	6	-10
1	-33	57	56
1	-32	0	-10
1	-31	44	45
1	-30	21	-32
1	-29	49	54
• 1	-28	9	-11
1	-27	113	108
1	-26	48	-54
1	-25	27	35
1	-24	45	51
1	-23	107	-110
1	-22	93	95
1	-21	50	-62
1	-20	19	-28
1	-19	250	-238
1	-18	78	-66
1	-17	247	-241
• 1	-16	7	-13
1	-15	75	-78
1	-14	86	82
1	-13	341	-303
1	-12	86	93
1	-11	315	-304
1	-10	325	314
1	-9	418	-413
1	-8	192	171
1	-7	272	-254
1	-6	137	-134
1	-5	12	9
1	-4	66	64
1	-3	195	184
1	-2	60	-68
1	-1	25	-38
1	0	241	271
1	1	274	-256
1	2	333	-363
1	3	858	914
1	4	826	-772
1	5	558	542
1	6	197	137
1	7	344	291
1	8	371	273
1	9	635	571
1	10	76	45
1	11	48	-11
1	12	209	-143
1	13	114	120
1	14	40	-50
1	15	169	147
• 1	16	8	1
1	17	63	67
• 1	18	8	-5
• 1	19	8	5
1	20	18	18
1	21	117	-133
• 1	22	9	-3
1	23	47	-55
1	24	55	56
1	25	71	-75
• 1	26	9	-4
1	27	50	-51
• 1	28	9	9
1	29	90	-84
1	30	63	67
1	31	102	-104
• 1	32	6	-10
1	33	16	-26
1	34	26	-34
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2	-28	28	33
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2	7	150	146
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2	14	11	12
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2	23	63	70
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2	25	61	70
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• 3	-27	8	-0
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• 3	-25	9	22
• 3	-24	9	12
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3	-19	132	169
3	-18	35	49
3	-17	195	192
3	-16	129	158
3	-15	293	309
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3	-9	224	219
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3	-7	74	69
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3	-2	243	-225
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3	0	114	98
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3	5	316	-334
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3	8	34	-42
3	9	176	-154
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3	11	182	-156
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3	15	88	98
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3	23	113	125
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4	0	53	-54
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4	2	33	-38
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4	5	225	-213
4	7	143	-143
4	8	75	-80
4	9	216	-210
4	10	108	-107
4	11	192	-204
4	12	67	73
• 4	13	9	-0
4	14	109	101
4	15	114	-113
• 4	16	9	13
4	17	145	-140
4	18	22	28
4	19	44	-59
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• 4	21	7	-16
• 4	22	7	4
4	23	12	30
• 4	24	6	-5
4	25	12	25
• 4	26	4	-17
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5	-25	75	-71
• 5	-24	7	12
5	-23	93	-95
• 5	-22	7	12
5	-21	99	-95
• 5	-20	8	6
5	-19	62	-67
• 5	-18	8	11
5	-17	43	-50
• 5	-16	9	6
5	-15	77	-80
5	-14	23	-32
5	-13	63	-63
• 5	-12	9	-7
5	-11	16	-25
5	-10	96	-101
5	-9	149	149
5	-8	109	-105
5	-7	141	151
5	-6	98	95
5	-5	62	64
5	-4	90	83
5	-3	114	137
5	-2	34	-43
5	-1	68	76
5	0	64	-81
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• 5	2	9	2
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5	5	101	98
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5	7	33	37
5	8	16	-22
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• 5	14	8	18
5	15	47	-66
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5	17	58	-75
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6	-11	66	-78
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6	-9	45	-62
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6	3	98	97
• 6	4	7	3
6	5	117	111
6	6	34	45
6	7	94	85
6	8	59	62
6	9	62	70
6	10	17	26
6	11	66	79
• 6	12	5	7
0	13	60	74
		K=2	
0	0	260	295
0	1	112	135
0	2	145	169
0	3	167	184
0	4	350	381
0	5	190	175
0	6	256	276
0	7	209	-229
0	8	28	-12
0	9	312	-307
0	10	90	85
• 0	11	7	7
0	12	33	27
0	13	60	-34
0	14	76	-67
• 0	15	9	8
0	16	219	-223
0	17	151	-144
0	18	179	-176
0	19	91	-86
0	21	127	110
0	22	172	-165
0	23	45	39
0	24	82	-92
0	25	33	26
• 0	27	11	3
0	28	74	-60
• 0	29	10	-16
0	30	17	-16
• 0	31	8	-11
• 0	32	7	-5
• 0	33	7	17
1	-32	107	85
• 1	-31	9	-22
1	-30	73	61
• 1	-29	10	-20
1	-28	56	47
• 1	-27	11	-14
1	-26	40	47
• 1	-25	11	2
• 1	-24	12	-11
1	-23	74	-70
1	-22	65	66
1	-21	101	-106
1	-20	70	-79
1	-19	172	181
1	-18	268	-265
1	-17	143	135
1	-16	118	-124
1	-15	58	53
1	-14	155	-144
1	-13	40	49
1	-12	223	-232
1	-11	101	-106
1	-10	297	-291
1	-9	129	157
1	-8	208	-220
1	-7	74	58
1	-6	277	-301
1	-5	53	-56
1	-4	168	-213
1	-2	89	107
1	-1	59	-60
1	0	59	-75
1	1	32	-48
1	2	252	278
1	3	73	81
1	4	300	301
1	5	265	255
1	6	81	98
1	7	363	-317
1	8	571	550
1	9	375	-310
1	10	376	340
• 1	11	8	16
1	12	58	69
• 1	13	9	0
1	14	143	136
1	15	125	113
1	16	127	130
• 1	17	10	-19
1	18	69	70
• 1	19	11	-10
1	20	33	-33
1	21	63	60
1	22	33	-34
• 1	23	12	13
1	24	61	-62
• 1	25	11	14
1	26	94	-83
• 1	27	10	-7
1	28	89	-78
• 1	29	9	-17
1	30	100	-87
1	31	13	-22
1	32	49	-43
• 2	-33	6	-13
2	-32	83	67
2	-31	61	-37
2	-30	66	51
• 2	-29	10	-10
2	-28	79	72
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2	-22	111	132
• 2	-21	11	12
2	-20	78	90
2	-19	137	149
2	-18	97	112
• 2	-17	10	-12
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2	-14	28	-33
2	-13	27	42
2	-12	26	-31
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2	-8	258	-317
2	-7	101	-99
2	-6	579	-547
2	-5	185	186
2	-4	226	-253
2	-3	64	66
2	-2	177	-192
2	-1	147	-127
2	0	188	-181
2	1	185	-169
2	2	162	-156
• 2	3	7	3
2	4	311	-291
2	5	50	41
2	6	198	171
2	7	343	-284
2	8	207	173
• 2	9	9	-9
2	10	27	32
2	11	57	58
2	12	227	188
• 2	13	10	13
2	14	159	167
2	15	109	117
2	16	166	176
2	17	40	30
2	18	161	160
2	19	66	66
2	20	177	172
• 2	21	11	14

K=2

H	L	10F$_o$	10F$_c$
2	22	82	83
2	23	28	-22
* 2	24	11	-1
2	25	26	26
* 2	26	10	14
* 2	27	9	18
2	28	15	-28
* 2	29	7	-7
* 2	30	6	-11
* 3	-31	7	2
* 3	-30	8	-15
* 3	-29	9	6
* 3	-28	9	6
* 3	-27	10	-12
* 3	-26	10	14
3	-25	24	33
3	-24	22	36
3	-23	20	23
3	-22	115	191
3	-21	84	89
3	-20	173	204
3	-19	33	46
3	-18	83	78
3	-17	97	-112
3	-16	87	110
* 3	-15	11	16
3	-14	167	209
3	-13	63	67
3	-12	81	98
* 3	-11	10	-17
3	-10	117	124
3	-9	87	-81
3	-8	56	-55
3	-7	20	20
3	-6	144	-150
3	-5	17	24
* 3	-4	9	-16
3	-3	83	-82
3	-2	89	-102
* 3	-1	9	-2
3	0	121	-192
3	1	115	-129
3	2	222	-232
3	3	118	-92
3	4	228	-208
3	5	127	-118
3	6	276	-269
3	7	123	-99
3	8	191	-165
3	9	189	177
3	10	38	41
3	11	49	54
3	12	98	-100
3	13	33	-25
3	14	41	-39
3	15	33	32
3	16	47	44
3	17	63	51
3	18	87	78
3	19	32	39
3	20	160	127
* 3	21	10	-19
3	22	36	38
* 3	23	10	26
3	24	40	42
3	25	24	27
3	26	42	49
* 3	27	7	9
3	28	34	49
* 4	-29	6	20
4	-28	78	-71
* 4	-27	8	-3
4	-26	67	-66
4	-25	33	22
4	-24	43	-40
4	-23	36	31
* 4	-22	10	-3
4	-21	78	73
4	-20	19	-24
* 4	-19	11	-4
* 4	-18	11	4
4	-17	80	-78
4	-16	86	81
* 4	-15	12	-3
4	-14	41	50
* 4	-13	11	19
4	-12	89	122
4	-11	33	41
4	-10	186	186
4	-9	40	37
4	-8	134	160
* 4	-7	11	-19
4	-6	136	172
4	-5	123	-132
4	-4	123	111
4	-3	51	-72
4	-2	126	121
4	-1	20	34
4	0	104	119
4	1	20	-33
* 4	2	11	10
4	3	47	-61
4	4	138	-145
4	5	106	-99
4	6	136	-130
4	7	23	27
* 4	8	12	-1
4	9	144	151
4	10	140	-139
* 4	11	11	6
4	12	138	-138
* 4	13	11	-22
4	14	69	-81
* 4	15	11	-5
4	16	192	-193
* 4	17	10	-15
4	18	47	-65
* 4	19	9	-7
4	20	32	-33
4	21	30	29
4	22	23	-34
4	23	24	31
* 5	-25	6	-0
5	-24	75	-72
* 5	-23	7	1
5	-22	106	-92
5	-21	38	36
5	-20	97	-91
* 5	-19	9	-0
5	-18	94	-91
5	-17	48	-32
5	-16	93	-94
* 5	-15	10	-14
5	-14	55	-60
* 5	-13	11	-1
5	-12	19	-26
* 5	-11	11	21
5	-10	48	47
* 5	-9	11	23
5	-8	81	90
* 5	-7	11	-20
5	-6	61	60
5	-5	139	-133
5	-4	158	155
5	-3	65	-60
5	-2	169	175
5	-1	64	65
5	0	104	107
5	1	49	47
5	2	139	121
5	3	28	29
5	4	91	115
* 5	5	11	-13
5	6	118	98
5	7	46	32
5	8	26	25
5	9	72	61
* 5	10	10	6
* 5	11	10	13
* 5	12	9	1
* 5	13	9	2
5	14	78	-77
* 5	15	8	-23
5	16	75	-76
5	17	17	-26
5	18	76	-76
* 5	19	5	1
6	-14	71	-71
6	-13	49	-43
6	-12	97	-87
6	-11	19	-25
6	-10	79	-74
* 6	-9	12	13
* 6	-8	95	-86
* 6	-7	12	-24
* 6	-6	9	-8
6	-5	94	-86
6	-4	20	21
* 6	-3	9	7
6	-2	31	-30
6	-1	50	53
6	0	31	42
6	1	46	42
6	2	117	93
6	3	56	48
6	4	95	86
* 6	5	7	6
6	6	95	85
* 6	7	7	18
6	8	89	87
6	9	11	17
6	10	53	66
* 6	11	4	8

K=3

H	L	10F$_o$	10F$_c$
0	1	386	391
0	2	45	-57
0	3	18	23
0	4	102	-97
0	5	96	113
0	6	22	32
0	7	88	88
0	8	52	60
0	9	87	-71
* 0	10	6	-0
0	11	66	59
0	12	70	-60
0	13	22	-24
0	14	38	-35
0	15	119	-116
* 0	16	8	-3
0	17	44	-45
* 0	18	8	-7
0	19	53	-59
* 0	20	8	12
0	21	73	-75
0	22	28	-26
0	23	87	-76
0	24	26	-32
0	25	96	-92
* 0	26	7	-11
0	27	55	-82
* 0	28	7	3
* 0	29	6	-9
* 0	30	5	22
* 0	31	4	7
* 1	-30	6	-17
1	-29	11	47
* 1	-28	7	-7
1	-27	13	43
* 1	-26	8	-17
* 1	-25	8	1
* 1	-24	8	16
1	-23	76	56
* 1	-22	8	23
* 1	-21	8	6
* 1	-20	8	1
1	-19	68	-75
1	-18	48	-53
1	-17	20	12
1	-16	36	-42
1	-15	224	-205
1	-14	154	141
1	-13	293	-288
1	-12	46	49
1	-11	271	-267
1	-10	83	-88
1	-9	162	-185
* 1	-8	6	-9
* 1	-7	5	-18
1	-6	40	42
1	-5	232	-260
1	-4	63	74
1	-3	76	-103
1	-2	20	-14
1	-1	65	92
1	0	13	-6
1	1	74	100
1	2	15	-11
1	3	144	152
1	4	34	-21
1	5	74	73
1	6	21	24
1	7	141	154
1	8	15	14
1	9	179	185
1	10	79	82
1	11	262	273
1	12	31	-18
1	13	248	240
1	14	61	-68
1	15	109	138
1	16	20	34
1	17	95	98
1	18	25	28
1	19	44	-48
* 1	20	8	-12
* 1	21	8	-15
1	22	21	-29
* 1	23	8	-13
* 1	24	8	-12
1	25	102	-108
* 1	26	7	-6
1	27	38	-72
* 1	28	6	-3
1	29	27	-41
2	-29	62	68
2	-28	27	-29
2	-27	46	98
* 2	-26	7	-16
2	-25	124	127
2	-24	53	43
2	-23	177	146
* 2	-22	8	0
* 2	-21	8	-4
2	-20	95	-57
2	-19	129	135
2	-18	49	-55
2	-17	133	133
2	-16	57	59
2	-15	141	-156
2	-14	57	61
2	-13	103	-108
2	-12	68	-77
2	-11	156	-172
* 2	-10	7	2
2	-9	109	-122
* 2	-8	7	7
2	-7	111	-134
* 2	-6	6	-7
2	-5	201	-231
* 2	-4	6	-5
2	-3	225	-258
2	-1	336	-313
2	0	61	52
2	1	130	-143
2	2	70	-63
2	3	204	-197
2	4	64	-55
2	5	87	86
2	6	63	65
2	7	139	127
2	8	96	83
2	9	86	-79
* 2	10	8	-10
2	11	249	246
2	12	100	-92
2	13	272	256
2	14	57	65
2	15	171	150
2	16	95	73
2	17	114	104
* 2	18	8	-14
2	19	41	39
* 2	20	8	3
2	21	111	97
* 2	22	8	7
2	23	35	37
* 2	24	7	18
* 2	25	6	23
* 2	26	6	-0
* 2	27	5	6
* 2	28	4	-1
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3	-27	19	45
3	-26	16	30
3	-25	58	69
* 3	-24	7	17
3	-23	54	48
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3	-21	18	31
* 3	-20	8	-13
3	-19	137	129
* 3	-18	8	7
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3	-16	12	23
3	-15	92	106
* 3	-14	8	-4
3	-13	110	120
* 3	-12	8	-6
3	-11	29	47
* 3	-10	8	-3
3	-9	20	31
3	-8	30	-46
3	-7	11	-28
* 3	-6	8	-12
3	-5	20	23
* 3	-4	8	9
3	-3	133	-147
3	-2	49	48
3	-1	245	-245
3	0	57	-63
3	1	255	-233
3	2	143	-131
3	3	112	-116
3	4	70	61
3	5	94	73
3	6	87	72
3	7	205	-193
3	8	41	-37
3	9	93	-92
3	10	67	-79
3	11	46	45
* 3	12	8	-8
3	13	66	-72
3	14	48	51
3	15	28	30
* 3	16	8	4
3	17	21	23
* 3	18	8	18
3	19	43	38
* 3	20	7	14
3	21	43	47
* 3	22	6	6
3	23	45	50
* 3	24	5	10
3	25	38	75
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* 4	-24	6	6
4	-23	39	-38
* 4	-22	7	-1
4	-21	87	-62
* 4	-20	7	-4
* 4	-19	7	-15
* 4	-18	8	-4
4	-17	25	24
4	-16	29	30
4	-15	67	64
* 4	-14	8	22
4	-13	144	135
* 4	-12	8	-7
4	-11	112	120
4	-10	28	-27
4	-9	18	21
4	-8	15	-29
4	-7	130	123
* 4	-6	8	25
4	-5	170	162
4	-4	49	59
4	-3	36	34
* 4	-2	8	-2
4	-1	72	70
4	0	86	-76
4	1	57	59
* 4	2	8	-10
4	3	34	27
4	4	38	32
* 4	5	8	14
* 4	6	8	-5
4	7	50	-50
* 4	8	8	-11
4	9	81	-68
4	10	36	-38
4	11	111	-145
4	12	45	-35
4	13	148	-125
* 4	14	7	-7
4	15	101	-87
* 4	16	7	12
4	17	33	-40
4	18	19	15
4	19	18	-25
* 4	20	5	-11
4	21	42	-56
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* 5	-20	5	-4
5	-19	60	-62
* 5	-18	6	10
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* 5	-16	6	17
5	-15	56	-52
* 5	-14	7	-3
5	-13	12	10
* 5	-12	7	-5
5	-11	21	-26
* 5	-10	7	-9
* 5	-9	7	-9
* 5	-8	7	-6
5	-7	53	53
5	-6	36	29
5	-5	84	79
* 5	-4	8	26
5	-3	140	144
* 5	-2	8	19
5	-1	232	184
* 5	0	8	-9
5	1	155	127
5	2	27	-20
5	3	118	102
5	4	26	21
5	5	113	94
5	6	38	34
5	7	25	32
* 5	8	7	2
* 5	9	6	9
5	10	19	-23
* 5	11	6	-11
* 5	12	5	-12
5	13	88	-76
* 5	14	4	-0
5	15	41	-45
* 6	-10	6	-15
6	-9	78	-62
* 6	-8	7	-12
6	-7	15	-25
6	-6	14	12
* 6	-5	8	5
6	-4	16	21
* 6	-3	5	8
* 6	-2	7	-3
6	-1	76	81
6	0	24	-28
6	1	78	80

K=4

H	L	10F$_o$	10F$_c$
0	0	73	85
* 0	1	5	5
0	2	90	100
* 0	3	6	-12
0	4	104	135
0	5	23	-39
0	6	148	140
0	7	51	62
0	8	40	56
* 0	9	10	16
* 0	10	11	7
0	11	36	-40
* 0	12	12	-8
0	13	79	102
0	14	52	-58
0	15	25	21
0	16	71	-71
0	17	33	-41
0	18	78	-68
* 0	19	13	-10
0	20	89	-78
0	21	57	-47
0	22	105	-100
1	-21	48	43
1	-20	38	-38
* 1	-19	13	-4
1	-18	84	-76
1	-17	44	-40
1	-16	87	-95
1	-15	68	-63
1	-14	89	-100
1	-13	24	-26
1	-12	58	-65
1	-11	35	31
1	-10	157	-164
* 1	-9	10	15
1	-8	130	-144
* 1	-7	10	23
1	-6	100	-138
* 1	-5	9	4
1	-4	15	-17
1	-3	16	-18
1	-2	16	23
* 1	-1	8	-13
1	0	107	-127
1	1	61	58
1	2	117	135
1	3	38	41
1	4	174	197
1	5	30	-20
1	6	100	109
1	7	41	51
1	8	157	185
1	9	41	46
1	10	125	144
1	11	82	92
1	12	78	102
1	13	49	53
1	14	40	46
1	15	64	-69
1	16	61	57
* 1	17	13	-12
1	18	49	46
* 1	19	12	-12
* 1	20	12	-2
1	21	20	-34
2	-22	99	90
* 2	-21	12	-8
2	-20	60	50
2	-19	46	-48
2	-18	47	40
* 2	-17	13	-0
2	-16	26	-23
2	-15	45	-38
2	-14	57	62
2	-13	102	-85
2	-12	28	-39
2	-11	42	45
2	-10	160	-199
2	-9	66	76
2	-8	112	-129
* 2	-7	11	-6
2	-6	132	-163
2	-5	34	-43
2	-4	108	-130
2	-3	73	-80
2	-2	185	-231
* 2	-1	11	3
2	0	81	-88
2	1	149	139
2	2	56	48
2	3	20	23
2	4	136	-136
2	5	30	-39
* 2	6	12	10
2	7	69	69
2	8	77	68
2	9	36	45
2	10	85	86
2	11	32	25
— 2	12	104	86
2	13	22	23
2	14	54	45
2	15	22	-22
2	16	175	142
2	17	37	-37
2	18	155	104
* 2	19	11	-3
2	20	81	71
* 2	21	10	24
2	22	28	32
* 2	23	8	17
3	-22	34	60
* 3	-21	10	-18
* 3	-20	86	79
* 3	-19	11	3
3	-18	65	62
3	-17	21	25
3	-16	102	100
3	-15	54	-56
3	-14	107	112
3	-13	39	-35
3	-12	39	-37
3	-11	48	49
3	-10	50	54
* 3	-9	13	22
3	-8	57	53
* 3	-7	13	-7
3	-6	75	-69
3	-5	45	-46
3	-4	88	-71
3	-3	27	-37
3	-2	88	-81
3	-1	47	36
* 3	0	12	-11
3	1	88	65
3	2	142	-123
3	3	29	25
3	4	166	-144
* 3	5	13	8
3	6	123	-99
3	7	35	-26
3	8	100	-89
3	9	85	-73
* 3	10	12	-19
* 3	11	12	19
3	12	80	-70
3	13	30	34
3	14	65	43
3	15	53	-56
3	16	71	62
3	17	36	-31
* 3	18	9	-11
* 3	19	8	19
3	20	29	46
* 4	-18	9	16
* 4	-17	10	20
4	-16	59	36
* 4	-15	11	-9
4	-14	34	12
* 4	-13	11	-5
4	-12	29	39
* 4	-11	12	11
4	-10	89	111
* 4	-9	12	11
4	-8	99	95
* 4	-7	12	7
4	-6	107	102
4	-5	30	34
4	-4	91	73
* 4	-3	12	10
* 4	-2	62	52
* 4	-1	12	-8
4	0	92	42
4	1	107	73
* 4	2	12	-6
* 4	3	12	27
* 4	4	12	-21
4	5	79	-49
4	6	68	-52
4	7	67	-58
4	8	75	-57
4	9	59	-50
4	10	110	-92
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* 4	14	8	-1
4	15	18	-35
* 5	-13	7	-1
5	-12	34	-42
* 5	-11	8	15
5	-10	24	29
* 5	-9	8	12
5	-8	76	73
5	-7	22	26
5	-6	63	52
5	-5	40	42
5	-4	75	68
* 5	-3	9	7
5	-2	87	81
5	-1	63	55
5	0	77	63
5	1	22	29
5	2	66	68
5	3	49	-36
5	4	93	79
* 5	5	7	-8
* 5	6	61	58
* 5	7	6	-9

APPENDIX II.

3-Phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole).

A summary of the symbolic addition procedure.

* denotes reflections for which the phase generated had both absolute and symbolic contributors, indicating A = - .

** denotes reflections which were not used as input for cycle 13.

*** denotes the initial symbolic assignment A.

For cycles 1 through 12, $|E| > 2.0$.

For cycle 13, $2.0 > |E| \geq 1.5$.

cycle no.	h	k	l	|E|	s
	2	2	-9	2.63	+
	5	1	-2	2.83	+
	2	3	1	2.90	+
1.	4	1	-8	2.38	-
	0	1	10	2.37	+
	3	1	7	2.57	+
	3	3	7	2.39	-
	3	2	-3	2.33	-
2.	2	1	1	2.04	-
	1	1	-4	2.71	+
	1	1	-5	2.41	+
	1	3	-5	2.13	-
	5	0	8	2.06	-
	1	4	6	2.50	+
3.	4	0	2	2.50	+
	4	2	3	2.57	+
***	2	10	2	2.64	+A
4.	4	8	-7	2.50	-A
	1	11	5	2.20	+A
	0	7	1	3.32	+A
5.	2	6	0	2.19	-A
	2	6	2	2.11	-A
	0	8	9	2.75	+A
	3	9	-4	2.03	-A
	3	6	6	2.50	+A
	1	10	-4	2.05	-A
	4	8	-9	2.20	-A
	5	8	-3	2.01	+A
6.	2	7	11	2.11	+A
	0	11	1	2.04	-A
	0	9	1	2.04	-A
	0	6	10	2.12	-A
	2	2	-11	2.64	+
	0	4	9	2.27	-A
	1	5	5	2.05	-A

cycle no.	h	k	l	|E|	s
	5	3	7	2.08	+A
	5	0	6	2.21	-
	1	4	15	2.54	+A
	3	2	15	2.34	+
	0	10	10	2.06	+A
	3	4	-13	2.20	-A
7.	2	9	10	2.15	-A
	4	1	11	2.25	-
	2	5	11	2.10	+A
	0	4	2	2.41	-
	2	6	-2	2.27	-A
	0	8	13	2.30	+A
	1	3	14	2.00	-
	3	3	5	2.03	-
	1	2	-4	2.56	-A
	3	6	4	2.49	+A
	1	6	16	2.03	+A
	1	8	13	3.04	-A
	5	8	-5	2.43	+A
8.	0	5	12	2.13	-
	2	9	9	2.29	-A
	0	9	3	2.13	-A
	0	7	3	2.07	+A
	2	6	4	2.14	-A
	0	2	19	2.41	-
	4	4	-11	2.01	+A
	3	7	-6	2.01	-A
	3	10	4	2.62	-A
	3	10	2	2.10	-A
	3	6	2	2.31	+A
9.	0	5	3	2.15	+A
	0	12	2	2.98	+
	0	4	13	2.04	-A
	1	5	9	2.29	-A
	1	4	11	2.70	+A

cycle no.		h	k	l	|E|	s
9. cont.		1	4	-7	2.15	-A
		1	8	1	2.04	+A
		1	8	11	2.10	-A
10.		2	7	6	2.04	-A
		0	2	15	2.56	-
		0	8	5	2.32	+A
		1	3	10	2.41	-
		3	2	11	2.26	+
11.		2	1	16	2.11	+
		2	2	3	2.25	-
		3	2	9	2.12	+
		0	5	15	2.28	-A
		1	11	-6	2.03	-
12.		4	1	4	2.48	+
	*	4	3	6	2.12	+
	*	0	9	6	2.09	-
	*	0	4	14	3.04	+
	**	0	12	0	2.40	+
	**	0	10	8	2.26	+A
	*	1	1	8	2.18	-
	*	3	9	2	2.01	+
13.	*	2	5	14	1.94	-
		0	3	10	1.94	+
		2	9	-10	1.90	+A
		2	5	6	1.89	+A
		0	3	4	1.88	+
		4	9	2	1.85	+A
		2	9	-8	1.84	+A
		2	3	-8	1.84	-A
		2	7	-6	1.81	+A
		6	1	2	1.78	-
		2	5	-10	1.75	-A
	*	0	3	8	1.74	+
		4	5	0	1.70	-A
	*	0	1	2	1.69	+
		4	9	0	1.64	+A
		2	7	-4	1.64	+A
		2	7	-12	1.63	+A
		4	5	-10	1.61	+
		2	5	-12	1.60	-A
		2	5	-8	1.58	-A
		2	5	4	1.58	-A
		6	3	0	1.56	-
		4	1	13	1.94	-
	*	4	3	5	1.78	+
		2	3	11	1.76	-A
		2	9	7	1.75	+
		2	5	-9	1.72	+A
		0	3	1	1.71	-A
	*	4	9	3	1.67	+
	*	2	1	15	1.59	+
		2	7	9	1.58	+A
	*	2	9	3	1.51	+
		2	4	12	1.97	-
		2	10	0	1.84	+A
	*	4	4	-12	1.80	+
		2	0	14	1.75	+
		4	6	8	1.74	-A
		2	2	0	1.67	+A
		4	4	0	1.60	-
		0	8	11	1.99	+A
		4	8	-5	1.97	-A
		2	2	11	1.93	-
		0	8	7	1.86	+A
		6	2	-9	1.83	+
		0	4	11	1.73	-A

	h	k	l	|E|	s
	0	4	7	1.71	-A
	6	4	1	1.67	+A
	2	10	-11	1.64	-
*	0	2	1	1.56	+
	2	2	13	1.52	-
*	2	4	13	1.51	+
	4	4	-7	1.51	+A
	1	9	-14	1.92	-A
	1	1	16	1.92	-
*	1	5	10	1.91	+
	3	7	-2	1.81	-A
*	3	3	8	1.79	+
	1	5	16	1.75	+
	1	9	-12	1.74	+
*	1	9	0	1.70	-
	3	5	14	1.68	-A
	1	7	8	1.59	+A
	1	1	-6	1.58	+
	1	5	-14	1.58	+A
	1	1	18	1.58	-
	5	1	-4	1.55	+
*	3	5	-8	1.52	-
	1	1	14	1.51	-
	1	7	3	1.98	-A
	5	5	3	1.96	-A
	1	9	3	1.93	+A
*	3	5	-7	1.82	+
*	1	1	-19	1.79	-
	1	11	7	1.79	+A
*	3	9	-3	1.79	-
	1	9	5	1.70	+A
	1	7	7	1.68	-A
	5	5	5	1.56	-A
	1	6	-4	1.99	+A
	3	0	-4	1.96	-

	h	k	l	|E|	s
	5	4	6	1.95	+
	1	6	-2	1.93	+A
	1	0	6	1.92	-
	3	6	0	1.91	+A
	3	6	-8	1.91	-A
*	1	6	10	1.90	+
	5	0	0	1.90	-
	3	6	8	1.83	+A
	3	6	10	1.79	+A
	1	6	-6	1.75	+A
	1	0	20	1.59	+
	3	2	6	1.56	-A
	1	2	-15	1.95	-
	3	8	-13	1.79	+A
	5	8	-1	1.79	+A
*	5	4	-1	1.75	+
*	1	8	7	1.73	+
	1	4	3	1.73	+
	5	8	-7	1.69	+A
	1	8	-5	1.65	+A
*	1	2	-9	1.65	-
	5	2	-15	1.62	-
	5	4	-5	1.58	-A
	1	8	-3	1.58	+A
	1	8	-1	1.57	+A
	1	4	13	1.57	+A
	1	2	-13	1.57	-
*	3	2	3	1.56	-
	1	2	5	1.54	+
	1	8	-7	1.52	+A

APPENDIX III.

3-Phenyl-1-propene-1,3-dione 1-(dimethyl mercaptole).

Observed and calculated structure factors.

Reflections classified as unobserved are marked * .

H	L	$10F_o$	$10F_c$
K = 0			
0	2	497	505
0	4	724	706
0	6	97	120
0	8	174	191
0	10	114	87
0	12	383	-317
0	14	294	-269
0	16	109	-92
0	18	177	-164
0	20	49	-51
* 1	-22	21	-32
1	-20	52	53
1	-18	110	-104
1	-16	64	74
1	-14	98	101
* 1	-12	15	-18
* 1	-10	17	42
1	-8	359	369
1	-6	446	430
1	-4	552	-484
1	-2	386	-348
1	0	677	-783
1	2	361	-423
1	4	609	-712
1	6	788	-899
1	8	57	27
1	10	278	-294
1	12	116	-133
1	14	104	-128
1	16	67	29
1	18	88	87
1	20	132	152
* 2	-22	16	-7
* 2	-20	27	-31
2	-18	45	25
2	-16	160	162
* 2	-14	17	9
2	-12	236	225
2	-10	203	-207
2	-8	107	90
2	-6	54	51
2	-4	260	-222
2	-2	538	-502
2	0	216	224
2	2	471	459
2	4	367	340
2	6	167	137
2	8	309	308
2	10	377	379
2	12	288	290
2	14	293	286
2	16	96	85
* 2	18	21	34
3	-22	120	119
3	-20	130	118
3	-18	154	149
3	-16	42	-21
3	-14	94	59
3	-12	54	-51
3	-10	38	-6
3	-8	298	291
3	-6	49	-81
3	-4	816	-774
3	-2	544	-558
3	0	226	-219
3	2	133	-128
3	4	67	-50
3	6	122	-124
3	8	173	157
3	10	88	113
3	12	133	-110
3	14	91	-84
3	16	106	-92
4	-20	120	-119
4	-18	95	-94
4	-16	99	-100
4	-14	120	-131
4	-12	172	-183
4	-10	184	-178
4	-8	111	98
4	-6	317	291
4	-4	344	335
4	-2	294	290
4	0	242	214
4	2	618	603
* 4	4	18	11
4	6	85	63
4	8	47	-40
* 4	10	18	0
* 4	12	16	38
5	-20	46	-51
5	-18	97	108
5	-16	54	-28
5	-14	160	180
5	-12	176	190
5	-10	100	114
5	-8	232	242
5	-6	217	222
* 5	-4	36	25
5	-2	198	-204
5	0	355	-356
5	2	127	-139
5	4	197	-214
5	6	295	-322
5	8	234	-267
* 6	-16	20	-23
* 6	-14	31	10
6	-12	53	-53
6	-10	63	-31
6	-8	184	-213
6	-6	113	-94
6	-4	83	59
* 6	-2	66	-44
* 6	0	17	19
6	2	51	53
6	4	83	103
K = 1			
0	1	159	133
0	2	811	837
0	3	267	227
0	4	421	392
0	5	925	456
0	6	146	128
0	7	197	-199
0	8	266	266
0	9	135	-124
0	10	517	461
0	11	244	-214
0	12	216	212
0	13	57	-45
0	14	37	-3
0	15	136	-113
0	16	160	158
0	17	58	-61
0	18	41	-4
0	19	48	31
0	20	116	110
* 0	21	33	17
* 1	-22	15	-29
1	-21	50	-55
1	-20	106	137
1	-19	190	-197
* 1	-18	23	-29
1	-17	65	-71
* 1	-16	29	20
* 1	-15	17	-19
1	-14	82	87
1	-13	83	110
* 1	-12	15	-50
1	-11	215	230
1	-10	48	63
1	-9	160	161
1	-8	110	136
1	-7	399	403
1	-6	681	712
1	-5	1126	1169
1	-4	1359	1441
1	-3	241	219
1	-2	149	-110
1	-1	400	380
1	0	383	425
1	1	415	-435
1	2	349	386
1	3	215	-265
1	4	97	111
1	5	88	66
1	6	226	-234
1	7	210	-178
1	8	497	-567
1	9	182	-142
1	10	155	-171
1	11	65	-69
1	12	222	-246
1	13	58	-57
1	14	180	-188
1	15	80	80
1	16	184	-197
* 1	17	21	14
1	18	114	-144
1	19	61	58
1	20	79	-88
2	-22	87	-82
2	-21	79	84
2	-20	61	-56
2	-19	104	98
2	-18	105	113
2	-17	127	128
2	-16	120	-108
2	-15	143	145
2	-14	150	-159
2	-13	227	230
2	-12	38	33
2	-11	65	66
2	-10	92	-105
2	-9	53	44
2	-8	315	-294
2	-7	264	-267
2	-6	141	-152
2	-5	50	-67
2	-4	79	-50
2	-3	463	-447
2	-2	272	-252
2	-1	523	-522
* 2	0	25	-16
2	1	773	-723
2	2	77	-62
2	3	229	-234
2	4	390	378
2	5	240	-245
2	6	200	-184
2	7	91	-109
* 2	8	27	9
2	9	166	-169
* 2	10	17	-20
2	11	74	52
2	12	100	119
2	13	133	120
2	14	46	32
2	15	167	172
2	16	198	182
2	17	45	35
2	18	98	81
* 3	-22	15	-11
3	-21	47	39
3	-20	80	71
* 3	-19	18	-25
3	-18	103	86
3	-17	44	-38
3	-16	180	171
3	-15	175	-187
3	-14	101	98
3	-13	75	-80
3	-12	172	169
3	-11	115	-115
3	-10	123	115
3	-9	118	-99
3	-8	139	145
3	-7	320	-312
3	-6	173	166
3	-5	187	-176
3	-4	273	265
3	-3	259	234
3	-2	79	-55
3	-1	350	342
3	0	158	-153
3	1	256	224
* 3	2	3[illegible]	16
3	3	3[illegible]	323
3	4	44	51
3	5	295	281
3	6	40	-17
3	7	446	451
3	8	51	-32
3	9	160	163
3	10	123	119
3	11	88	62
* 3	12	18	-9
* 3	13	23	-4
* 3	14	31	2
3	15	81	-73
3	16	94	-95
* 4	-21	18	-12
* 4	-20	35	-19
* 4	-19	17	-4
4	-18	55	-36
* 4	-17	18	19
* 4	-16	18	19
4	-15	58	-52
4	-14	69	-85
4	-13	57	-16
4	-12	95	-98
* 4	-11	35	-28
4	-10	170	182
4	-9	87	-63
4	-8	459	-458
4	-7	97	97
4	-6	186	-194
4	-5	78	79
4	-4	232	-241
4	-3	153	138
4	-2	272	-281
4	-1	208	216
4	0	117	-113
* 4	1	35	-19
4	2	62	-77
* 4	3	37	-7
4	4	382	386
4	5	82	-82
* 4	6	33	63
4	7	144	-137
4	8	64	71
4	9	119	-124
4	10	85	67
4	11	198	-199
4	12	106	102
4	13	136	-145
5	-20	43	-18
5	-19	55	-30
* 5	-18	31	0
5	-17	70	-64
* 5	-16	35	-32
* 5	-15	18	12
* 5	-14	28	-35
* 5	-13	31	-19
5	-12	102	112
5	-11	80	73
5	-10	94	79
5	-9	126	109
5	-8	122	125
5	-7	90	54
5	-6	188	173
5	-5	65	47
5	-4	224	238
* 5	-3	34	9
5	-2	395	386
5	-1	110	-91
5	0	134	-120
5	1	69	51
5	2	117	103
5	3	86	-80
5	4	43	-19
* 5	5	18	10
5	6	39	31
* 5	7	32	21
5	8	55	-46
* 5	9	25	13
6	-11	85	57
6	-10	47	19
* 6	-9	25	-22
* 6	-8	19	-17
6	-7	68	-60
6	-6	160	-158
6	-5	144	148
6	-4	40	-30
6	-3	45	-38
6	-2	72	-76
6	-1	96	-96
6	0	110	-97
6	1	90	-98
6	2	143	-162
6	3	95	-97
6	4	97	-103
K = 2			
0	0	708	-711
0	1	696	690
0	2	210	183
0	3	245	-234
0	4	192	-173
0	5	445	373
* 0	6	18	11
0	7	429	407
0	8	145	-125
0	9	49	62
0	10	103	-81
0	11	123	-122
0	12	91	71
0	13	187	-161
0	14	218	-204
0	15	309	-268
0	16	93	-44
0	17	100	-77
0	18	59	-52
0	19	184	-163
* 0	20	32	14
0	21	81	-74
1	-22	81	-57
* 1	-21	26	-44
1	-20	91	-101
* 1	-19	18	-23
1	-18	52	39
1	-17	173	-184
1	-16	62	-54
1	-15	311	-328
1	-14	69	75
1	-13	308	-320
1	-12	124	132
1	-11	295	-302
* 1	-10	12	23
1	-9	491	-490
1	-8	289	276
1	-7	194	-215
1	-6	386	-371
1	-5	224	-212
1	-4	1164	1220
1	-3	337	331
1	-2	194	188
1	-1	179	172
1	0	98	90
1	1	58	-70
1	2	144	-159
1	3	98	129
1	4	53	22
1	5	450	494
1	6	219	107
1	7	359	179
1	8	149	156
1	9	257	203
1	10	124	-117
* 1	11	32	-26
1	12	27	31
1	13	92	70
1	14	40	6
1	15	85	95
1	16	90	83
1	17	42	51
1	18	59	78
* 1	19	15	-22
* 2	-22	15	5
* 2	-21	24	-21
2	-20	49	17
* 2	-19	38	26
2	-18	86	93
* 2	-17	18	-12
2	-16	65	47
2	-15	127	137
* 2	-14	26	53
2	-13	194	187
2	-12	57	-54
2	-11	613	625
2	-10	229	204
2	-9	724	735
* 2	-8	13	-23
2	-7	259	257
* 2	-6	23	-25
2	-5	253	248
2	-4	398	-375
2	-3	327	308
2	-2	207	-200
2	-1	319	298
2	0	612	-557
2	1	49	-35
2	2	392	-404
2	3	702	-641
* 2	4	29	-30
2	5	388	-394
2	6	148	-136
2	7	298	-304
2	8	55	-34
2	9	262	-236
2	10	64	-48
2	11	299	-281
2	12	103	82
2	13	192	-199
* 2	14	10	-7
* 2	15	18	-5
* 2	16	17	10
* 2	17	18	0
* 2	18	27	3
* 3	-22	32	4
* 3	-21	39	25
* 3	-20	15	-7
* 3	-19	34	9
3	-18	40	-42
3	-17	80	95
* 3	-16	34	29
3	-15	47	-26
3	-14	76	-80
3	-13	92	108
3	-12	84	-82
3	-11	102	-80
3	-10	104	-101
3	-9	40	-41
3	-8	110	-106
3	-7	274	-264
3	-6	253	-241
3	-5	291	-296
3	-4	167	158
3	-3	637	-622
3	-2	254	230
3	-1	95	-132
3	0	345	320
3	1	368	-355
3	2	158	148
3	3	346	-375
3	4	157	138
3	5	164	-181
3	6	283	268
3	7	109	88
* 3	8	33	-5
3	9	300	269
3	10	132	130
3	11	266	273
3	12	54	40
3	13	144	155
3	14	40	14
3	15	180	174
* 4	-19	17	2
4	-18	43	-19
4	-17	72	87
4	-16	73	-92
* 4	-15	18	20
4	-14	84	69
* 4	-13	57	58
4	-12	106	-104
4	-11	70	-58
4	-10	137	152
4	-9	95	77
* 4	-8	17	-16
4	-7	101	103
4	-6	44	15
* 4	-5	29	25
4	-4	80	103
4	-3	106	101
4	-2	44	23
4	-1	244	243
* 4	0	19	8
4	1	250	257
4	2	175	-164
4	3	406	422
* 4	4	19	-17
* 4	5	43	8
4	6	63	67
4	7	117	100
4	8	99	-94
* 4	9	18	-35
4	10	130	-124
4	11	98	-95
4	12	101	101
5	-20	38	5
5	-19	72	-62
5	-18	64	-39
* 5	-17	32	-40
5	-16	66	56
5	-15	167	-159
5	-14	59	-43
5	-13	146	-141
* 5	-12	15	-4
5	-11	99	-94
5	-10	45	33
5	-9	98	-100
5	-8	49	24
5	-7	76	-71
5	-6	44	44
* 5	-5	18	33
5	-4	97	-110
5	-3	62	-32
5	-2	124	134
5	-1	133	127
5	0	55	48
* 5	1	33	6
5	2	53	-26
5	3	53	-29
5	4	56	-4
* 5	5	25	-35
5	6	40	-19
5	7	70	-71
5	8	47	31
5	9	42	-36
6	-16	44	50
6	-15	62	65
6	-14	44	17
6	-13	71	81
6	-12	41	50
6	-11	104	86
* 6	-10	19	10
6	-9	177	167
* 6	-8	20	27
6	-7	141	132
6	-6	62	-34
6	-5	43	42
6	-4	141	-124
6	-3	89	90
6	-2	51	-58
6	-1	64	55
6	0	69	-40
6	1	50	50
6	2	91	-69
6	3	90	27
K = 3			
0	1	647	606
0	2	330	-295
0	3	428	404
0	4	618	569
0	5	321	303
0	6	202	182
0	7	340	316
0	8	405	362
0	9	281	280
0	10	368	347
0	11	136	125
0	12	78	67
* 0	13	20	-5
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0	15	166	160
0	16	174	-157
0	17	81	-48
0	18	43	-12
0	19	106	-76
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1	-18	118	-123
* 1	-17	115	136
* 1	-16	18	-18
* 1	-15	24	32
1	-14	129	-139
* 1	-13	17	18
1	-12	161	-195
1	-11	89	-79
1	-10	104	-99
1	-9	184	-179
1	-8	198	201
1	-7	297	-293
1	-6	118	127
1	-5	798	-829
1	-4	455	485
1	-3	114	-92
1	-2	219	213
1	-1	106	-102
* 1	0	373	431
1	1	239	-230
1	2	363	397
1	3	203	-222
1	4	322	367
1	5	350	-369
1	6	144	122
1	7	148	-117
1	8	157	-144
1	9	98	-88
1	10	393	-439
1	11	110	-135
1	12	115	-84
1	13	80	-65
1	14	219	-252
1	15	77	-11
1	16	109	-83
1	17	93	66
1	18	89	-98
* 1	19	15	20
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2	-21	85	-96
2	-20	55	-62
* 2	-19	27	-50
2	-18	64	-61
* 2	-17	39	-45
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2	-15	85	-76
* 2	-14	23	1
2	-13	188	-200
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2	-11	116	-127
* 2	-10	29	13
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2	-7	201	198
2	-6	56	48
2	-5	91	111
2	-4	191	186
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2	-2	82	73
2	-1	31	-2
2	0	85	71
2	1	910	855
2	2	311	293
2	3	212	251
2	4	352	-323
2	5	345	315
2	6	241	-230
2	7	257	254
2	8	173	-180
2	9	258	261
2	10	106	-94
2	11	257	264
2	12	83	91
* 2	13	18	-3
2	14	82	77
* 2	15	53	-79
2	16	68	61
* 2	17	15	6
* 3	-21	15	7
* 3	-20	17	24
3	-19	107	100
* 3	-18	32	10
3	-17	88	61
3	-16	144	143
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3	-14	187	184
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3	-12	129	141
3	-11	71	-63
3	-10	42	-40
3	-9	46	19
3	-8	45	44
* 3	-7	15	18
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3	-5	122	-123
3	-4	273	-258
3	-3	313	-307
3	-2	255	-248
3	-1	255	-248
3	0	174	-168
3	1	166	-167
3	2	239	-250
3	3	206	-199
3	4	94	96
3	5	369	-337
3	6	49	-41
3	7	377	-380
3	8	260	259
3	9	132	-132
3	10	45	-32
* 3	11	17	3
3	12	143	141
* 3	13	31	-14
3	14	87	65
* 3	15	27	3
4	-21	47	-25
4	-20	53	55
4	-19	105	-104
* 4	-18	23	12
4	-17	182	-196
* 4	-16	18	-9
* 4	-15	38	-15
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4	-13	65	-55
4	-12	150	140
* 4	-11	18	17
4	-10	221	-223
* 4	-9	29	4
4	-8	159	-196
4	-7	93	74
4	-6	74	-83
4	-5	196	190
4	-4	97	-82
4	-3	39	17
4	-2	99	-111
4	-1	39	-26
4	0	85	85
4	1	78	51
4	2	191	173
4	3	124	136
4	4	83	76
4	5	239	240
4	6	262	289
4	7	112	124
* 4	8	19	28
4	9	116	117
4	10	113	120
4	11	92	115
* 4	12	91	91
5	-19	79	88
5	-18	66	-55
5	-17	98	105
5	-16	143	-136
5	-15	62	75
5	-14	75	96
5	-13	92	90
5	-12	96	-94
5	-11	90	93
5	-10	44	43

H	L	10F$_o$	10F$_c$
4	-9	61	20
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5	-7	45	17
5	-6	79	67
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5	-4	172	189
5	-3	124	-93
5	-2	107	94
5	-1	32	5
5	0	173	180
5	1	102	-106
5	2	85	78
5	3	84	-96
5	4	59	-7
5	5	146	-162
5	6	87	-63
5	7	166	-196
5	8	81	-59
6	-12	66	61
6	-11	75	-69
6	-10	84	75
6	-9	24	-28
6	-8	26	-21
6	-7	47	28
6	-6	172	165
6	-5	19	25
6	-4	92	-67
6	-3	33	15
6	-2	23	19
6	-1	64	59
6	0	127	121
6	1	95	91
6	2	98	-120
6	3	133	131

K = 4

H	L	10F$_o$	10F$_c$
0	0	693	-658
0	1	29	45
0	2	731	-708
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0	4	283	-254
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0	6	209	-177
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0	8	104	-68
0	9	426	379
0	10	30	-8
0	11	270	263
0	12	73	59
0	13	263	258
0	14	356	314
0	15	65	63
0	16	37	28
0	17	74	63
0	18	93	82
0	19	45	-18
0	20	66	49
1	-21	17	-23
1	-20	30	27
1	-19	18	-42
1	-18	78	-93
1	-17	48	69
1	-16	32	-36
1	-15	18	17
1	-14	21	4
1	-13	17	-17
1	-12	19	-4
1	-11	52	31
1	-10	25	42
1	-9	57	68
1	-8	383	-410
1	-7	602	624
1	-6	270	-251
1	-5	65	67
1	-4	117	-112
1	-3	346	338
1	-2	360	348
1	-1	263	271
1	0	92	76
1	1	349	357
1	2	238	229
1	3	445	485
1	4	188	225
1	5	191	94
1	6	524	505
1	7	213	-238
1	8	209	232
1	9	213	-245
1	10	44	18
1	11	366	-431
1	12	31	22
1	13	176	-181
1	14	18	36
1	15	232	247
1	16	33	4
1	17	104	-130
1	18	95	-110
2	-21	15	-17
2	-20	62	34
2	-19	115	-124
2	-18	46	32
2	-17	65	-37
2	-16	64	-50
2	-15	103	-117
2	-14	40	-25
2	-13	103	-87
2	-12	54	44
2	-11	127	-122
2	-10	232	-246
2	-9	83	-72
2	-8	145	149
2	-7	164	163
2	-6	55	-62
2	-5	94	81
2	-4	111	100
2	-3	81	-65
2	-2	57	14
2	-1	70	-45
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2	1	180	-169
2	2	26	-22
2	3	61	-39
2	4	161	-173
2	5	239	-217
2	6	213	-204
2	7	196	-213
2	8	176	-174
2	9	19	-26
2	10	211	-202
2	11	132	103
2	12	242	-236
2	13	169	187
2	14	45	-26
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2	16	44	-23
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3	-19	67	62
3	-18	134	-119
3	-17	101	75
3	-16	123	-122
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3	-10	98	105
3	-9	102	85
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3	-7	49	-51
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3	-5	15	-2
3	-4	298	292
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3	3	32	-1
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3	5	86	108
3	6	18	-12
3	7	166	182
3	8	58	77
3	9	120	-126
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3	11	66	49
3	12	25	28
3	13	51	-28
3	14	25	-10
4	-20	92	99
4	-19	42	38
4	-18	58	53
4	-17	18	-29
4	-16	88	86
4	-15	121	-128
4	-14	47	48
4	-13	117	-129
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4	-11	287	-291
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4	-7	246	-244
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4	-4	66	-75
4	-3	138	-137
4	-2	129	-119
4	-1	88	-94
4	0	250	-253
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4	2	215	-186
4	3	73	46
4	4	76	-63
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4	6	88	-74
4	7	139	155
4	8	40	37
4	9	104	107
4	10	20	-36
4	11	64	69
4	18	34	17
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5	-14	89	-90
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5	-12	77	-79
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5	-10	69	-60
5	-9	108	107
5	-8	81	-85
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5	-6	172	177
5	-5	195	177
5	-4	22	48
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5	-2	43	-14
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5	0	134	144
5	1	125	124
5	2	142	137
5	3	73	80
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5	6	157	173
5	7	65	-46
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6	-7	51	-41
6	-6	48	49
6	-5	65	58
6	-4	16	13
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6	-2	39	32
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6	1	122	-145

K = 5

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0	6	112	113
0	7	111	-87
0	8	151	135
0	9	45	-22
0	10	134	-120
0	11	163	106
0	12	271	-265
0	13	32	33
0	14	124	-126
0	15	219	192
0	16	49	-25
0	17	97	87
0	18	116	-101
0	19	32	42
1	-20	15	-11
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1	-18	43	-62
1	-17	31	-39
1	-16	104	-116
1	-15	18	41
1	-14	219	-236
1	-13	41	-31
1	-12	173	-173
1	-11	109	-97
1	-10	100	-107
1	-9	86	-80
1	-8	280	298
1	-7	71	-95
1	-6	203	-176
1	-5	147	-139
1	-4	201	-209
1	-3	108	-118
1	-2	206	-180
1	-1	106	-99
1	0	120	136
1	1	130	157
1	2	27	5
1	3	148	163
1	4	104	115
1	5	396	456
1	6	237	189
1	7	201	249
1	8	174	190
1	9	332	361
1	10	255	274
1	11	59	49
1	12	131	-34
1	13	85	73
1	14	120	119
1	15	62	-24
1	16	130	135
1	17	85	-72
1	18	83	103
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2	-19	27	-42
2	-18	70	79
2	-17	62	-60
2	-16	67	45
2	-15	18	-14
2	-14	131	133
2	-13	198	-208
2	-12	259	257
2	-11	27	-4
2	-10	325	332
2	-9	339	-358
2	-8	330	346
2	-7	87	101
2	-6	170	151
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2	-4	213	204
2	-3	180	167
2	-2	184	161
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2	0	61	-54
2	1	174	177
2	2	82	89
2	3	109	100
2	4	323	-305
2	5	42	-68
2	6	343	-357
2	7	209	-210
2	8	96	-60
2	9	145	-121
2	10	178	-159
2	11	259	-252
2	12	45	-29
2	13	73	-85
2	14	177	191
2	15	91	-110
2	16	58	-66
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3	-19	86	-71
3	-18	17	20
3	-17	59	-34
3	-16	61	-58
3	-15	65	-62
3	-14	121	-109
3	-13	105	87
3	-12	30	20
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3	-10	135	-141
3	-9	142	143
3	-8	272	-278
3	-7	337	346
3	-6	283	-273
3	-5	64	51
3	-4	186	-183
3	-3	192	189
3	-2	105	-97
3	-1	55	-68
3	0	213	-195
3	1	75	-88
3	2	201	-204
3	3	131	-132
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3	5	109	-111
3	6	84	90
3	7	102	-75
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3	9	45	51
3	10	173	181
3	11	78	-78
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3	13	61	42
3	14	118	115
4	-19	75	67
4	-18	49	65
4	-17	86	86
4	-16	21	3
4	-15	87	85
4	-14	51	-40
4	-13	112	109
4	-12	33	-21
4	-11	18	-8
4	-10	217	212
4	-9	49	-42
4	-8	136	150
4	-7	140	-143
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4	-5	129	-129
4	-4	170	180
4	-3	151	-121
4	-2	169	160
4	-1	169	-186
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4	1	131	-71
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4	3	84	-88
4	4	100	105
4	5	109	112
4	6	50	-39
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4	8	17	10
4	9	16	-15
4	10	62	-70
4	-17	15	-8
4	-16	95	-1
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5	-14	122	-103
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5	-8	46	-26
5	-7	38	-52
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5	-2	25	-23
5	-1	30	17
5	0	54	-15
5	1	84	77
5	2	36	70
5	3	174	163
5	4	102	-91
5	5	123	130
5	6	44	-37
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6	-10	28	28
6	-9	40	41
6	-8	131	116
6	-7	54	-34
6	-6	70	62
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6	-3	65	79
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K = 6

H	L	10F$_o$	10F$_c$
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0	6	133	111
0	7	46	50
0	8	162	149
0	9	34	37
0	10	280	265
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0	12	103	93
0	13	47	-77
0	14	48	24
0	15	69	59
0	16	68	78
0	17	70	58
0	18	91	85
1	-19	25	27
1	-18	113	123
1	-17	30	26
1	-16	69	59
1	-15	61	49
1	-14	86	-89
1	-13	59	74
1	-12	132	137
1	-11	89	-88
1	-10	151	-141
1	-9	149	187
1	-8	235	-241
1	-7	93	89
1	-6	371	-401
1	-5	284	276
1	-4	494	-447
1	-3	21	20
1	-2	458	-451
1	-1	192	-169
1	0	135	-126
1	1	27	-22
1	2	59	-52
1	3	49	34
1	4	259	159
1	5	150	-186
1	6	157	-27
1	7	107	-59
1	8	106	-46
1	9	93	-97
1	10	222	223
1	11	63	45
1	12	55	-25
1	13	46	15
1	14	96	-28
1	15	67	-29
1	16	135	-150
1	17	27	-12
2	-19	37	9
2	-18	106	-112
2	-17	35	-10
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2	-8	45	-66
2	-7	126	-135
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2	4	378	371
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2	10	18	32
2	11	117	121
2	12	38	57
2	13	18	-34
2	14	75	-60
2	15	60	61
3	-19	38	-14
3	-18	54	51
3	-17	59	-54
3	-16	111	120
3	-15	30	26
3	-14	18	-30
3	-13	35	-32
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3	-11	25	1
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3	-7	18	-30
3	-6	21	-27
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3	-3	177	193
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3	0	312	-336
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3	2	355	-346
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3	4	349	-347
3	5	39	31
3	6	311	-272
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3	10	165	-170
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4	-14	32	18
4	-13	41	-24
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4	-2	87	-92
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4	3	48	54
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4	6	77	65
4	7	37	-10
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5	-15	33	23
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5	-8	24	-10
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5	-6	18	-6
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5	-4	20	-40
5	-3	58	63
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5	1	34	-61
5	2	16	-4
5	3	44	-48
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5	5	27	-24

K = 7

H	L	10F$_o$	10F$_c$
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0	6	41	-13
0	7	153	-120
0	8	92	-95
0	9	22	22
0	10	81	-67
0	11	52	46
0	12	84	71
0	13	130	107
0	14	63	62
0	15	109	110
0	16	61	68
0	17	116	101
1	-18	91	102
1	-17	50	-54
1	-16	123	141
1	-15	19	-24
1	-14	159	164
1	-13	57	-57
1	-12	73	57
1	-11	57	-59
1	-10	80	116
1	-9	107	-124
1	-8	162	170
1	-7	45	-59
1	-6	157	181
1	-5	17	-9
1	-4	36	17
1	-3	215	203
1	-2	55	-49
1	-1	63	37
1	0	169	-169
1	1	204	218
1	2	143	-172
1	3	298	364
1	4	154	-113
1	5	202	236
1	6	112	48
1	7	210	212
1	8	186	-204
1	9	55	-48
1	10	38	-19
1	11	144	158
1	12	116	74
1	13	90	81
1	14	81	55
1	15	53	-27
1	16	41	-5
2	-18	58	-14
2	-17	16	-33
2	-16	59	-51
2	-15	32	-73
2	-14	18	-18
2	-13	96	117
2	-12	201	239
2	-11	18	-19
2	-10	60	-65
2	-9	30	-17
2	-8	220	-211
2	-7	18	-24
2	-6	299	-298
2	-5	39	31
2	-4	289	-269
2	-3	243	254
2	-2	109	-96
2	-1	93	-73
2	0	100	83
2	1	141	-151
2	2	132	126
2	3	151	-144
2	4	97	106
2	5	18	-21
2	6	278	264
2	7	136	-134
2	8	97	84
2	9	177	-162
2	10	96	98
2	11	202	-171
2	12	17	-23
2	13	83	-71
2	14	99	108
3	-18	14	-29
3	-17	80	-88
3	-16	50	53
3	-15	18	13
3	-14	28	10
3	-13	64	-50
3	-12	49	-52
3	-11	88	94
3	-10	39	1
3	-9	115	116
3	-8	46	46
3	-7	35	-46
3	-6	286	285
3	-5	192	193
3	-4	91	92
3	-3	134	135
3	-2	265	257
3	-1	193	206
3	0	185	196
3	1	66	58
3	2	39	24
3	3	67	-83
3	4	98	97
3	5	108	141
3	6	65	7
3	7	51	29
3	8	34	11
3	9	41	-46
3	10	99	-104
3	11	23	-91
4	-16	23	10
4	-15	68	62
4	-14	16	11
4	-13	56	49
4	-12	22	-12
4	-11	81	76

	H	L	$10F_o$	$10F_c$
	4	-10	68	-67
	4	-9	40	29
	4	-8	51	20
	4	-7	74	-44
•	4	-6	99	33
	4	-5	184	195
	4	-4	70	-94
	4	-3	155	-145
	4	-2	122	-123
	4	-1	133	-131
	4	0	113	-113
	4	1	128	-127
	4	2	49	-23
	4	3	149	-148
	4	4	66	-94
	4	5	40	-35
	4	6	42	-34
•	4	7	29	-23
	4	8	55	-64
	5	-13	75	-72
	5	-12	108	104
	5	-11	105	-113
	5	-10	47	31
	5	-9	110	-109
	5	-8	55	54
	5	-7	90	-81
	5	-6	43	44
	5	-5	42	-29
	5	-4	45	27
•	5	-3	34	45
	5	-2	47	-42
	5	-1	120	124
•	5	0	30	5
	5	1	90	97
	5	2	73	-59

K = 8

	H	L	$10F_o$	$10F_c$
	0	0	96	-77
	0	1	218	-187
	0	2	156	-148
	0	3	180	-167
	0	4	74	-77
	0	5	291	-276
	0	6	43	-10
	0	7	214	-164
	0	8	108	122
	0	9	283	-278
	0	10	78	-109
	0	11	180	-177
	0	12	40	-36
	0	13	177	-168
•	0	14	16	-16
	0	15	69	-59
•	0	16	23	-3
•	1	-16	24	21
•	1	-15	16	22
•	1	-14	24	20
•	1	-13	18	14
•	1	-12	21	-7
•	1	-11	18	-3
	1	-10	42	-77
	1	-9	114	-149
	1	-8	45	32
	1	-7	217	-221
•	1	-6	17	21
	1	-5	254	273
	1	-4	106	-124
	1	-3	253	-247
	1	-2	108	85
	1	-1	256	-250
	1	0	82	90
	1	1	268	-304
	1	2	137	170
	1	3	196	-131
•	1	4	28	-7
	1	5	163	105
	1	6	52	-19
	1	7	183	167
	1	8	96	87
	1	9	134	182
•	1	10	18	9
	1	11	169	203
	1	12	50	57
	1	13	206	228
	1	14	60	75
	2	-17	91	96
	2	-16	58	-50
•	2	-15	37	-11
•	2	-14	19	15
	2	-13	65	75
	2	-12	52	-18
	2	-11	101	81
	2	-10	47	-48
	2	-9	107	105
	2	-8	71	53
•	2	-7	18	-13
•	2	-6	18	7
	2	-5	112	-122
	2	-4	100	112
	2	-3	57	59
	2	-2	141	-144
	2	-1	215	213
	2	0	69	79
	2	1	65	45
•	2	2	19	16
•	2	3	30	9
	2	4	168	-178
•	2	5	33	-47
	2	6	93	95
	2	7	153	156
•	2	8	19	-19
•	2	9	27	37
•	2	10	33	49
	2	11	85	-71
	2	12	74	-85
•	3	-16	24	-9
	3	-15	105	-101
	3	-14	113	130
	3	-13	162	-171
•	3	-12	21	-11
	3	-11	132	-124
•	3	-10	24	-11
	3	-9	86	-77

	H	L	$10F_o$	$10F_c$
•	3	-8	19	18
•	3	-7	10	-36
	3	-6	84	80
	3	-5	142	132
•	3	-4	35	37
	3	-3	60	48
•	3	-2	33	-27
	3	-1	55	51
•	3	0	29	-2
	3	1	172	165
	3	2	50	45
	3	3	59	-73
•	3	4	16	-27
•	3	5	31	-38
	3	6	78	-79
•	3	7	31	31
	3	8	37	1
•	3	9	23	-19
•	4	-14	25	-28
	4	-13	52	78
	4	-12	49	15
	4	-11	110	102
	4	-10	49	22
	4	-9	203	205
	4	-8	109	-92
	4	-7	243	248
•	4	-6	18	27
	4	-5	195	217
	4	-4	72	-73
	4	-3	103	95
	4	-2	86	-106
	4	-1	42	64
	4	0	53	-30
	4	1	53	78
•	4	2	23	25
	4	3	78	-81
•	4	4	16	2
	4	5	76	-92
	4	6	39	-13
	5	-10	55	-37
	5	-9	96	-103
	5	-8	67	-64
	5	-7	118	-113
	5	-6	53	28
	5	-5	182	-178
	5	-4	59	71
	5	-3	143	-154
	5	-2	58	32
	5	-1	116	-131

K = 9

	H	L	$10F_o$	$10F_c$
	0	1	230	224
•	0	2	33	-7
	0	3	234	219
	0	4	117	-87
	0	5	180	157
	0	6	209	-218
	0	7	130	139
	0	8	66	-70
•	0	9	31	-14
	0	10	42	45
	0	11	39	-5
•	0	12	16	-11
	0	13	58	-52
	0	14	32	36
	1	-15	46	-67
	1	-14	149	171
•	1	-13	16	-9
	1	-12	156	169
•	1	-11	24	-35
	1	-10	89	53
	1	-9	48	79
•	1	-8	35	11
	1	-7	98	114
	1	-6	104	100
	1	-5	84	-122
	1	-4	62	-54
	1	-3	159	-155
	1	-2	167	-157
	1	-1	83	-77
	1	0	186	-231
	1	1	93	-31
•	1	2	35	10
	1	3	200	-206
	1	4	68	8
	1	5	164	-179
	1	6	104	-155
	1	7	122	-136
	1	8	67	-25
	1	9	90	-110
	1	10	101	-45
	1	11	41	-29
	1	12	61	39
•	2	-15	14	0
	2	-14	113	-122
•	2	-13	24	19
	2	-12	77	-77
•	2	-11	32	41
	2	-10	188	-189
	2	-9	60	43
	2	-8	200	-217
	2	-7	85	91
	2	-6	87	-95
•	2	-5	27	17
	2	-4	107	-90
	2	-3	51	-31
•	2	-2	18	0
	2	-1	168	166
	2	0	77	-59
	2	1	58	55
	2	2	162	145
	2	3	168	179
	2	4	118	124
•	2	5	21	-0
	2	6	128	116
	2	7	161	166
	2	8	131	147
	2	9	185	202
	2	10	161	159
•	3	-14	14	14
•	3	-13	19	33
	3	-12	40	27
•	3	-11	37	-46

	H	L	$10F_o$	$10F_c$
•	3	-10	17	14
	3	-9	45	-40
	3	-8	50	65
•	3	-7	32	-15
•	3	-6	33	28
	3	-5	64	-52
	3	-4	224	204
	3	-3	185	-161
	3	-2	130	117
	3	-1	191	-209
	3	0	68	51
	3	1	68	-69
	3	2	190	200
	3	3	72	-59
	3	4	68	53
	3	5	65	-68
	3	6	40	31
	3	7	94	-86
	4	-11	43	-46
	4	-10	56	36
•	4	-9	15	20
•	4	-8	22	-2
•	4	-7	16	-16
	4	-6	49	38
	4	-5	54	60
	4	-4	51	58
	4	-3	40	72
	4	-2	81	-74
	4	-1	76	46
	4	0	129	143
	4	1	104	115
	4	2	136	-115
	4	3	117	124

K = 10

	H	L	$10F_o$	$10F_c$
	0	0	133	-148
	0	1	48	-16
	0	2	76	-72
	0	3	77	-60
	0	4	69	80
	0	5	71	-41
	0	6	79	-48
	0	7	54	-62
	0	8	170	-179
•	0	9	35	-1
	0	10	137	-130
•	0	11	28	-69
•	0	12	14	-23
	1	-12	66	81
	1	-11	78	69
	1	-10	143	154
	1	-9	52	52
	1	-8	112	116
•	1	-7	33	21
	1	-6	121	136
•	1	-5	35	-2
	1	-4	218	221
	1	-3	95	-92
	1	-2	141	137
	1	-1	41	-42
	1	0	101	75
	1	1	82	-57
	1	2	157	-95
	1	3	43	-8
	1	4	132	118
	1	5	36	-60
	1	6	81	-20
	1	7	49	-33
	1	8	103	-51
	1	9	50	-41
	1	10	46	-3
	2	-12	79	89
	2	-11	127	-132
	2	-10	83	89
	2	-9	103	-103
	2	-8	80	-93
	2	-7	93	-79
	2	-6	85	-82
	2	-5	66	-73
	2	-4	113	-117
•	2	-3	18	2
	2	-2	64	-62
	2	-1	67	-84
	2	0	180	-174
	2	1	75	60
	2	2	248	-251
	2	3	83	95
	2	4	127	-135
	2	5	72	45
	2	6	132	123
	3	-11	71	77
	3	-10	92	-91
	3	-9	42	30
•	3	-8	35	-26
	3	-7	61	59
•	3	-6	16	-24
	3	-5	112	107
•	3	-4	96	10
	3	-3	74	72
	3	-2	113	116
	3	-1	120	130
•	3	0	37	-5
•	3	1	35	13
	3	2	164	160
	3	3	90	113
	3	4	149	143

K = 11

	H	L	$10F_o$	$10F_c$
	0	1	151	138
	0	2	91	-78
	0	3	71	63
	0	4	52	-48
	0	5	104	113
•	0	6	34	65
	0	7	60	-69
	0	8	69	-62
	0	9	50	-46
	1	-9	130	137
•	1	-8	39	-73
	1	-7	111	141
	1	-6	169	-180
	1	-5	95	97

	H	L	$10F_o$	$10F_c$
	1	-4	104	-103
•	1	-3	17	9
	1	-2	49	-31
	1	-1	57	28
•	1	0	38	15
	1	1	61	-72
	1	2	77	-61
	1	3	92	-20
	1	4	125	-73
	1	5	141	-137
	1	6	77	67
	1	7	104	-65
	2	-8	91	93
	2	-7	77	-76
	2	-6	96	93
	2	-5	74	-85
	2	-4	43	31
	2	-3	67	-69
	2	-2	47	11
	2	-1	54	-61
	2	0	130	117
	2	1	64	-66
	2	2	54	-74
	2	3	78	-81
	2	4	39	14

K = 12

	H	L	$10F_o$	$10F_c$
	0	0	200	188
	0	1	59	36
	0	2	171	168
	0	3	65	69

APPENDIX IV.

The 1,2,4-trithiacyclopentane from pinacolone.

Observed and calculated structure factors.

Reflections classified as unobserved are marked *

K = 0

H	L	10F$_o$	10F$_c$
0	2	360	513
0	4	223	-194
0	6	246	-283
* 0	8	41	-41
0	10	423	-433
0	12	309	324
0	14	344	338
* 0	16	41	-55
0	18	269	-266
0	20	142	139
0	22	52	-21
0	24	65	-36
1	-26	229	-210
1	-24	156	-155
1	-22	84	56
1	-20	119	136
1	-18	204	209
* 1	-16	14	24
1	-14	197	-175
1	-12	790	-822
1	-10	285	297
1	-8	49	-36
1	-6	177	204
1	-4	691	613
1	-2	525	613
1	0	930	929
1	2	431	-353
1	4	155	153
1	6	132	132
1	8	787	-846
* 1	10	41	-49
1	12	470	511
1	14	191	177
1	16	50	-52
1	18	19	-210
1	20	76	-47
1	22	93	-71
2	-26	45	-54
2	-24	58	-56
2	-22	88	-101
2	-20	97	105
2	-18	284	310
2	-16	157	-168
2	-14	462	-483
2	-12	430	-466
2	-10	85	-100
* 2	-8	24	28
2	-6	537	505
2	-4	648	629
2	-2	716	-796
2	0	772	-803
2	2	450	-410
2	4	175	199
2	6	671	669
2	8	122	124
2	10	130	129
2	12	272	272
2	14	223	-233
* 2	16	33	55
2	18	50	29
2	20	125	-110
3	-26	152	157
* 3	-24	15	18
* 3	-22	16	-17
3	-20	86	-74
3	-18	132	-108
3	-16	219	-236
3	-14	431	452
3	-12	359	358
3	-10	292	-286
3	-8	214	-222
3	-6	682	614
* 3	-4	43	-10
3	-2	807	-762
3	0	98	13
3	2	107	-112
3	4	219	-211
3	6	492	501
3	8	549	585
3	10	86	-72
3	12	200	-197
3	14	97	-105
3	16	94	-87
* 3	18	25	-4
4	-24	66	48
4	-22	111	103
4	-20	152	-165
4	-18	120	-342
4	-16	129	103
4	-14	372	399
4	-12	143	155
4	-10	198	201
* 4	-8	48	-24
4	-6	472	-462
4	-4	741	-695
4	-2	308	283
4	0	355	340
4	2	50	-38
* 4	4	29	-44
4	6	300	311
* 4	8	16	18
4	10	101	98
4	12	152	157
4	14	53	61
5	-22	91	-72
* 5	-20	33	-43
* 5	-18	53	-40
5	-16	108	82
5	-14	241	-243
5	-12	45	68
5	-10	129	116
5	-8	102	-92
5	-6	470	-477
5	-4	129	-130
5	-2	103	-134
5	0	250	232
5	2	150	160
5	4	270	273
5	6	210	196
5	8	207	-237
* 5	10	14	17
6	-18	159	154
6	-16	65	-86
6	-14	127	-126
6	-12	164	-171
6	-10	178	-179
6	-8	193	-187
6	-6	229	238
6	-4	103	110
6	-2	188	-181
6	0	44	26
6	2	48	49
6	4	76	-72

K = 1

H	L	10F$_o$	10F$_c$
E 0	1	847	1367
0	2	64	100
0	3	329	-365
0	4	449	-430
0	5	412	-475
0	6	139	130
0	7	264	-259
0	8	149	-141
0	9	153	-181
0	10	466	-494
0	11	120	-146
0	12	348	-363
0	13	477	491
0	14	108	-87
0	15	171	168
0	16	49	23
0	17	184	-180
0	18	88	-63
0	19	74	-45
0	20	123	112
0	21	225	219
0	22	49	64
0	23	43	-15
0	24	66	61
* 0	25	38	-19
1	-26	41	-40
1	-25	147	-134
1	-24	98	-99
* 1	-23	21	-22
* 1	-22	29	-31
1	-21	232	225
1	-20	121	-116
1	-19	53	73
* 1	-18	38	34
1	-17	122	114
1	-16	164	161
* 1	-15	44	3
1	-14	238	244
1	-13	457	-503
1	-12	181	174
1	-11	513	-518
* 1	-10	18	-14
1	-9	462	485
1	-8	99	134
1	-7	61	-29
1	-6	274	233
1	-5	396	-365
1	-4	349	-356
1	-3	342	-315
1	-2	239	-182
1	-1	999	1031
1	0	879	-801
1	1	52	-108
1	2	329	300
1	3	665	673
1	4	232	-244
1	5	289	284
1	6	41	-13
1	7	329	-352
1	8	551	-557
1	9	670	-687
1	10	135	-126
1	11	331	334
1	12	193	-197
1	13	318	334
* 1	14	29	4
1	15	83	131
* 1	16	16	-13
1	17	164	-157
1	18	108	102
1	19	70	-43
* 1	20	16	-26
1	21	148	-130
1	22	56	-44
* 1	23	28	-39
* 2	-26	38	3
* 2	-25	26	-4
2	-24	80	-54
2	-23	163	-149
* 2	-22	16	39
* 2	-21	29	-5
* 2	-20	16	-37
2	-19	248	236
2	-18	79	90
2	-17	173	195
2	-16	208	213
2	-15	107	-112
2	-14	124	121
2	-13	476	-509
2	-12	319	328
2	-11	126	-122
2	-10	167	-173
2	-9	107	-119
* 2	-8	10	10
2	-7	313	307
2	-6	94	-10
2	-5	759	763
2	-4	450	366
2	-3	96	99
2	-2	319	353
2	-1	1055	-997
2	0	203	183
2	1	467	-471
2	2	96	-85
2	3	77	59
2	4	153	126
2	5	276	241
2	6	110	-121
2	7	75	-85
2	8	67	-88
2	9	231	240
2	10	73	-70
2	11	92	-89
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0	13	266	-246
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2	13	119	-111
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K = 4

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0	18	266	-261
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* 2	-14	16	-10
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2	6	263	-258
2	7	112	-92
2	8	96	-73
2	9	52	49
2	10	174	192
2	11	50	44
2	12	208	-199
2	13	63	84
2	14	51	43
2	15	46	-51
2	16	334	325
2	17	118	94
2	18	216	220
2	19	65	72
* 2	20	13	-19
* 3	-25	17	-7
3	-24	102	-102
3	-23	75	61
3	-22	131	-132
* 3	-21	31	14
3	-0	95	78
3	-19	65	-70
* 3	-18	30	-0
* 3	-17	20	6
3	-16	103	106
3	-15	131	-130
3	-14	295	278
3	-13	135	-121
3	-12	52	-42
3	-11	148	132
3	-10	734	-733
3	-9	156	-167
3	-8	404	-403
3	-7	129	-107
3	-6	184	168
3	-5	42	26
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* 3	-3	13	-23
3	-2	133	127
3	-1	117	111
3	0	433	399
3	1	233	-240
3	2	149	-191
3	3	123	-123
3	4	415	-432
3	5	355	-358
3	6	96	-103
3	7	196	-186
3	8	234	233
3	9	228	259
3	10	54	12
3	11	135	127
* 3	12	16	-14
* 3	13	28	1
3	14	149	143
* 3	15	15	-28
3	16	60	56
3	17	97	-93
3	18	30	29
* 4	-24	37	8
4	-23	60	10
4	-22	199	192
4	-21	129	115
4	-2.	68	65
4	-19	57	56
4	-18	123	116
4	-17	79	-87
* 4	-16	41	-33
4	-15	81	-83
4	-14	71	68
4	-13	65	-59
4	-12	341	-340
4	-11	153	159
4	-10	248	-257
4	-9	140	126
* 4	-8	29	0
4	-7	362	366
4	-6	284	-290
* 4	-5	27	-14
4	-4	44	-31
4	-3	295	-277
4	-2	421	417
* 4	-1	33	-35
4	0	317	336
4	1	86	-85
4	2	453	-453
4	3	130	-126
4	4	291	-282
4	5	11	133
* 4	6	27	-31

H	L	$10F_o$	$10F_c$
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* 4	9	46	19
4	10	94	75
* 4	11	46	-15
4	12	204	213
4	13	80	83
4	14	54	34
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* 5	-21	37	11
5	-20	63	75
5	-19	77	-60
5	-18	79	64
5	-17	73	62
5	-16	221	-218
5	-15	95	82
5	-14	229	-245
* 5	-13	24	28
5	-12	183	-167
* 5	-11	21	13
5	-10	244	258
5	-9	171	177
* 5	-8	36	31
5	-7	65	41
5	-6	80	-72
* 5	-5	33	15
5	-4	113	-107
5	-3	187	-186
* 5	-2	20	-9
5	-1	44	28
5	0	225	-212
5	1	84	-104
5	2	85	99
5	3	117	125
5	4	158	173
5	5	180	175
* 5	6	15	23
* 5	7	16	7
5	8	93	-96
5	9	76	-68
5	10	110	109
6	-17	86	72
* 6	-16	149	149
* 6	-15	125	110
6	-14	55	-65
* 6	-13	14	-22
6	-12	79	87
* 6	-11	19	9
* 6	-10	23	-13
* 6	-9	115	-111
* 6	-8	49	35
6	-7	131	-155
6	-6	122	119
* 6	-5	15	7
6	-4	95	-107
6	-3	105	98
6	-2	265	-296
* 6	-1	11	11
6	0	100	-82
* 6	1	55	-42
6	2	199	195
* 6	3	36	13

K = 5

H	L	$10F_o$	$10F_c$
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0	3	189	-199
0	4	58	-59
0	5	101	-100
0	6	307	-304
0	7	733	711
0	8	246	-252
0	9	239	228
0	10	151	-143
0	11	133	124
0	12	168	-171
0	13	114	112
0	14	213	207
0	15	227	-213
0	16	123	-129
0	17	425	-390
0	18	116	-106
0	19	84	-75
0	20	55	-46
0	21	115	104
* 0	22	12	-12
0	23	139	135
1	-24	2	-05
1	-23	69	67
* 1	-22	15	13
* 1	-21	36	-33
1	-20	2	99
1	-19	197	-180
1	-18	80	78
1	-17	226	-227
1	-16	253	269
1	-15	208	-223
1	-14	125	158
* 1	-13	27	-32
1	-12	49	-49
1	-11	425	411
1	-10	82	-86
1	-9	586	627
1	-8	443	451
1	-7	538	516
1	-6	602	677
1	-5	953	993
1	-4	166	136
1	-3	422	-423
1	-2	39	-29
1	-1	129	-158
1	0	156	156
1	1	181	163
1	2	293	-296
1	3	69	68
1	4	112	81
1	5	709	713
1	6	95	122
1	7	181	-158
1	8	71	-57
1	9	387	-381
1	10	60	-66
1	11	241	-250
1	12	134	-146
1	13	277	276

H	L	$10F_o$	$10F_c$
1	14	84	94
1	15	171	-148
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1	17	113	101
1	18	89	97
1	19	98	105
1	20	99	94
1	21	43	-54
1	22	67	-61
* 2	-24	37	45
2	-23	142	-144
2	-22	65	79
2	-21	224	-221
2	-20	45	-34
* 2	-19	41	19
2	-18	117	-114
2	-17	196	177
2	-16	171	168
2	-15	114	-100
* 2	-14	31	-14
* 2	-13	49	61
2	-12	50	-39
2	-11	62	12
2	-10	101	94
2	-9	392	-353
2	-	44	56
2	-7	251	-281
2	-6	268	-259
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2	-4	231	230
2	-3	85	-76
2	-2	199	220
2	-1	234	-235
2	0	55	-85
2	1	35	15
2	2	552	-500
2	3	475	480
2	4	162	175
* 2	5	44	24
2	6	201	204
2	7	138	-144
* 2	8	34	24
2	9	167	160
2	10	107	97
2	11	274	-265
2	12	80	-70
2	13	56	-43
2	14	147	-141
2	15	153	132
2	16	44	27
2	17	229	217
2	18	104	119
2	19	46	55
2	20	81	85
3	-24	54	55
3	-23	116	-109
3	-22	70	61
* 3	-21	16	6
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3	-19	98	101
3	-18	94	-102
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3	-16	129	-136
3	-15	217	201
* 3	-14	36	-49
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3	-12	117	114
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3	8	47	-29
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3	11	119	-133
3	12	78	-73
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3	14	49	-30
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* 3	16	14	-29
* 3	17	17	30
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* 4	-22	26	-8
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4	-19	55	-53
* 4	-18	34	21
* 4	-17	16	27
4	-16	97	-79
* 4	-15	16	-9
* 4	-14	24	37
4	-13	53	14
4	-12	70	73
4	-11	376	357
* 4	-10	42	-12
* 4	-9	20	26
* 4	-8	37	44
* 4	-7	15	-16
* 4	-6	29	-14
4	-5	51	-19
4	-4	113	-82
4	-3	81	79
4	-2	51	52
4	-1	473	490
4	0	210	207
* 4	1	39	-28
4	2	181	180
4	3	305	-317
4	4	89	76
4	5	121	-115
* 4	6	16	-1
4	7	91	70

H	L	$10F_o$	$10F_c$
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* 4	9	16	-12
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4	11	180	163
4	12	81	93
4	13	196	205
4	14	113	97
5	-21	46	49
* 5	-20	18	-16
5	-19	41	55
5	-18	42	14
5	-17	44	-33
5	-16	150	150
5	-15	269	-274
* 5	-14	41	1
5	-13	225	-228
5	-12	172	-167
5	-11	126	119
5	-10	102	-91
5	-9	192	197
5	-8	177	191
5	-7	54	-73
5	-6	148	121
5	-5	115	-102
5	-4	79	81
* 5	-3	46	-5
5	-2	151	149
5	-1	97	-73
* 5	0	16	-15
5	1	75	-87
* 5	2	16	-24
5	3	165	170
5	4	157	146
* 5	5	31	33
5	6	106	101
* 5	7	36	-53
5	8	63	-26
* 5	9	17	-8
6	-16	65	56
6	-15	118	-133
6	-14	58	-54
* 6	-13	28	27
* 6	-12	39	-46
6	-11	65	76
* 6	-10	14	-2
6	-9	54	-44
6	-8	37	-28
6	-7	134	157
6	-6	45	47
* 6	-5	37	-29
6	-4	130	134
6	-3	202	214
6	-2	48	55
6	-1	249	-269
6	0	117	-117
6	1	73	83
6	2	57	-64

K = 6

H	L	$10F_o$	$10F_c$
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0	1	183	163
0	2	31	25
0	3	286	-290
0	4	745	-729
0	5	245	-243
0	6	177	150
0	7	477	-485
0	8	176	157
0	9	66	-82
0	10	158	155
0	11	75	-58
0	12	195	178
0	13	221	221
0	14	399	383
0	15	118	120
0	16	155	-134
0	17	49	-40
0	18	203	-180
0	19	121	-137
0	20	80	75
0	21	44	-57
0	22	148	119
0	23	49	60
1	-24	61	54
1	-23	42	-24
* 1	-22	15	9
* 1	-21	93	91
* 1	-20	20	6
* 1	-19	41	49
1	-18	70	-62
* 1	-17	16	11
* 1	-16	46	-11
* 1	-15	26	-25
1	-14	197	-183
1	-13	99	-69
1	-12	92	-136
1	-11	270	-267
1	-10	228	215
* 1	-9	35	-27
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1	-7	468	452
1	-6	554	-550
1	-5	439	436
1	-4	546	-524
1	-3	78	48
1	-2	259	-217
1	-1	137	-140
1	0	329	-300
1	1	427	-426
1	2	14.	-98
1	3	444	433
1	4	203	223
1	5	239	264
1	6	219	229
1	7	265	246
1	8	145	-165
1	9	85	-99
1	10	128	-135
1	11	227	-220
1	12	167	177
1	13	127	129
* 1	14	41	74
1	15	62	-51
* 1	16	42	-8
* 1	17	36	-4

H	L	10F$_o$	10F$_c$
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* 1	19	37	66
* 1	20	47	5
* 1	21	19	11
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2	-23	111	124
2	-22	123	-134
* 2	-21	30	29
* 2	-20	25	-12
2	-19	246	-242
2	-18	156	162
2	-17	60	-33
* 2	-16	49	-84
2	-15	140	136
2	-14	98	-122
2	-13	81	-46
* 2	-12	29	-20
* 2	-11	54	-52
2	-10	129	-113
2	-9	180	179
* 2	-8	26	-28
2	-7	64	57
2	-6	105	-102
* 2	-5	44	10
2	-4	48	75
2	-3	247	244
2	-2	252	-238
* 2	-1	45	23
2	0	603	-606
2	1	396	-362
2	2	227	213
2	3	131	112
2	4	259	245
2	5	245	234
2	6	44	-56
2	7	100	88
2	8	163	-177
* 2	9	47	5
2	10	266	-272
* 2	11	41	-12
2	12	139	-136
2	13	295	-293
2	14	135	-135
2	15	176	173
2	16	148	115
2	17	60	70
2	18	119	127
2	19	171	172
3	-24	66	-56
* 3	-23	39	56
3	-22	56	-43
* 3	-21	25	-22
3	-20	91	81
3	-19	145	-144
3	-18	66	54
* 3	-17	16	-9
3	-16	53	46
3	-15	65	-77
3	-14	217	254
3	-13	185	181
3	-12	105	120
3	-11	283	272
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* 3	-9	44	31
3	-8	90	-71
3	-7	368	-360
3	-6	190	190
3	-5	265	-268
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3	-3	130	-115
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3	-1	150	143
3	0	161	140
3	1	272	285
3	2	80	87
3	3	252	240
3	4	380	-395
3	5	75	-37
3	6	107	-112
3	7	135	-121
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* 3	9	25	-40
3	10	124	-122
* 3	11	24	-26
3	12	135	-130
3	13	63	-69
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* 3	15	14	-7
3	16	63	29
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4	-19	87	77
4	-18	106	-95
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4	-16	118	87
* 4	-15	41	16
4	-14	99	93
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* 4	-12	13	-12
* 4	-11	26	-4
4	-10	166	-174
4	-9	101	117
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4	-6	57	22
4	-5	157	-163
4	-4	110	87
4	-3	151	-134
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4	-1	257	254
4	0	244	248
4	1	377	358
4	2	209	-203
4	3	150	132
4	4	152	-156
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4	6	102	-97
4	7	113	-101
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4	9	118	-127
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* 4	11	16	11
4	12	195	197
4	13	116	121
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5	-19	50	53

H	L	10F$_o$	10F$_c$
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5	-15	139	135
5	-14	168	-164
5	-13	221	-209
5	-12	51	23
5	-11	213	-207
5	-10	277	279
5	-9	46	-45
5	-8	133	126
5	-7	136	155
* 5	-6	30	13
* 5	-5	40	33
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5	-3	183	198
5	-2	95	99
5	-1	56	23
5	0	161	-155
5	1	137	-133
* 5	2	15	26
5	3	50	-55
5	4	82	65
5	5	143	138
5	6	50	-48
* 5	7	13	-34
5	8	96	-94
* 6	-14	22	-27
6	-13	102	-97
6	-12	116	120
* 6	-11	14	-3
* 6	-10	24	-9
* 6	-9	28	23
6	-8	46	46
6	-7	51	28
6	-6	81	88
6	-5	136	145
6	-4	92	102
6	-3	121	125
6	-2	214	-230
6	-1	103	-111
6	0	82	-81

K = 7

H	L	10F$_o$	10F$_c$
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0	3	25	-273
0	4	238	-217
0	5	395	-394
0	6	182	-190
0	7	186	160
* 0	8	14	-9
0	9	54	-55
0	10	303	305
0	11	66	76
0	12	428	367
0	13	417	408
0	14	358	347
0	15	66	56
0	16	59	83
0	17	132	-130
0	18	161	-161
0	19	46	-36
0	20	176	-162
0	21	57	46
0	22	79	53
1	-23	85	76
1	-22	56	31
* 1	-21	36	7
1	-20	106	81
1	-19	52	-25
1	-18	73	-60
1	-17	100	97
1	-16	207	197
* 1	-15	16	20
1	-14	267	-282
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1	-10	289	-301
1	-9	150	125
1	-8	433	429
1	-7	131	124
1	-6	302	309
1	-5	369	-374
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1	-3	60	-61
1	-2	156	-136
* 1	-1	65	-81
1	0	311	-298
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1	2	587	-603
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1	5	123	104
1	6	349	322
1	7	80	-62
1	8	191	186
1	9	226	-213
1	10	310	-302
1	11	51	41
1	12	90	85
1	13	316	297
1	14	184	-183
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1	16	48	-63
1	17	69	-50
1	18	57	17
* 1	19	49	36
* 1	20	24	21
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2	-22	71	97
* 2	-21	39	-32
2	-20	136	-127
2	-19	166	160
2	-18	243	-243
2	-17	197	195
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2	-15	153	-151
2	-14	137	124
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2	-11	67	-63
2	-10	75	76

H	L	10F$_o$	10F$_c$
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2	-3	136	135
2	-2	242	217
2	-1	280	-291
2	0	224	-226
2	1	332	-322
2	2	121	-110
2	3	219	203
2	4	221	198
* 2	5	35	-20
2	6	153	152
* 2	7	25	47
2	8	84	73
* 2	9	16	-10
2	10	63	-64
2	11	57	-59
2	12	101	-114
2	13	174	-174
2	14	319	-313
* 2	15	35	-37
2	16	52	-36
2	17	115	112
2	18	196	180
* 3	-23	90	-36
3	-22	39	7
* 3	-21	22	-10
3	-20	102	-86
3	-19	71	51
3	-18	52	-49
* 3	-16	16	36
3	-15	71	66
3	-14	106	101
3	-13	123	78
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3	-10	189	160
3	-9	281	-288
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3	-5	189	197
3	-4	111	-94
* 3	-3	17	-16
3	-2	215	207
* 3	-1	15	0
3	0	270	240
3	1	111	93
3	2	275	273
3	3	185	-158
3	4	108	112
3	5	111	-126
3	6	215	-204
3	7	185	193
3	8	49	-22
3	9	127	92
* 3	10	16	10
3	11	177	-173
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3	13	44	-47
3	14	59	-51
3	15	46	-16
3	16	29	13
4	-21	51	24
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4	-19	158	144
4	-18	140	113
4	-17	75	-70
* 4	-16	25	20
4	-15	111	113
4	-14	132	131
4	-13	95	94
4	-12	80	-86
* 4	-11	37	49
* 4	-10	37	-42
4	-9	139	131
4	-8	125	-127
4	-7	54	57
* 4	-6	42	3
4	-5	161	-151
4	-4	349	-353
4	-3	137	123
* 4	-2	16	13
4	-1	309	318
4	0	192	178
* 4	1	20	1
4	2	121	119
4	3	166	-167
4	4	83	-67
4	5	71	-73
4	6	101	-95
* 4	7	33	34
4	8	186	-178
4	9	66	-64
4	10	112	-115
* 4	11	36	13
4	12	74	69
5	-18	95	83
* 5	-17	14	-23
5	-16	184	182
5	-15	104	-107
* 5	-14	19	-1
* 5	-13	20	3
5	-12	270	-267
5	-11	161	178
5	-10	147	-145
5	-9	143	132
* 5	-8	29	38
5	-7	55	-54
* 5	-6	31	13
5	-5	101	-97
5	-4	33	-35
5	-3	79	48
* 5	-2	35	28
* 5	-1	34	7
5	0	169	-173
* 5	1	20	-18
5	2	159	-156
5	3	102	95
* 5	4	14	21
* 5	5	14	-16
5	6	49	45
5	7	129	-140

H	L	10F$_o$	10F$_c$
6	-12	50	-51
* 6	-11	13	20
* 6	-10	24	2
6	-9	48	-58
6	-8	49	30
6	-7	86	91
* 6	-6	23	16
6	-5	58	56
6	-4	168	185
* 6	-3	32	-66

K = 8

H	L	10F$_o$	10F$_c$
0	0	630	646
0	1	230	234
0	2	232	225
0	3	47	-33
0	4	161	-132
0	5	125	-116
0	6	186	-183
0	7	173	-148
0	8	69	86
0	9	91	89
0	10	184	-180
* 0	11	16	-8
0	12	67	49
0	13	356	337
0	14	113	103
0	15	187	174
0	16	87	-56
* 0	17	40	9
0	18	101	-98
0	19	156	-135
0	20	61	-73
* 0	21	51	-57
1	-22	75	66
1	-21	66	65
* 1	-20	15	22
* 1	-19	15	-20
1	-18	60	69
1	-17	64	-67
* 1	-16	26	20
* 1	-15	18	7
1	-14	52	-30
1	-13	215	-231
1	-12	59	-21
1	-11	476	-488
1	-10	68	93
* 1	-9	15	-7
1	-8	216	164
1	-7	205	205
1	-6	130	-125
1	-5	226	221
1	-4	85	-60
1	-3	257	-282
1	-2	301	299
1	-1	145	-146
1	0	192	168
1	1	380	-352
1	2	62	-33
1	3	228	-202
1	4	195	201
1	5	197	193
1	6	76	-59
1	7	234	239
1	8	177	-158
1	9	51	-69
1	10	240	-247
1	11	59	-77
1	12	257	233
1	13	44	36
1	14	92	76
* 1	15	25	-36
1	16	68	-79
* 1	17	15	-0
1	18	49	-10
* 1	19	13	-3
* 2	-22	33	-45
* 2	-21	33	-44
2	-20	79	84
2	-19	171	165
2	-18	242	235
2	-17	84	-75
* 2	-16	33	-41
2	-15	168	176
2	-14	145	-129
* 2	-13	37	-62
2	-12	79	-55
* 2	-11	40	-43
* 2	-10	20	-35
2	-9	134	130
* 2	-8	39	-12
2	-7	217	-223
2	-6	281	288
* 2	-5	36	-20
2	-4	247	257
2	-3	220	211
* 2	-2	37	22
2	-1	59	79
2	0	265	-258
2	1	263	-272
* 2	2	38	2
2	3	57	-52
2	4	120	129
2	5	253	262
2	6	88	68
2	7	202	208
2	8	194	178
* 2	9	23	-20
* 2	10	130	117
2	11	30	45
2	12	94	-72
2	13	244	-225
* 2	14	41	-51
2	15	176	-189
* 2	16	14	-10
* 2	17	37	50
* 3	-22	20	4
3	-21	45	-54
* 3	-20	14	7
3	-19	45	-21
3	-18	45	-57
* 3	-17	31	24
3	-16	110	-111
3	-15	75	62

H	L	10F$_o$	10F$_c$
3	-14	161	149
3	-13	190	187
3	-12	52	-49
3	-11	237	267
3	-10	138	-136
3	-9	121	151
3	-8	64	52
3	-7	400	-400
3	-6	304	314
3	-5	162	-155
* 3	-4	41	-66
* 3	-3	41	45
3	-2	183	-190
3	-1	57	58
3	0	177	-187
3	1	303	293
3	2	127	123
3	3	170	170
3	4	63	-44
3	5	120	-122
3	6	165	158
3	7	79	-65
3	8	237	250
3	9	58	62
* 3	10	21	37
* 3	11	33	20
3	12	120	-116
3	13	74	-67
* 3	14	23	-49
4	-20	111	-139
4	-19	181	183
4	-18	187	-197
* 4	-17	15	23
* 4	-16	15	-10
* 4	-15	46	15
4	-14	140	136
4	-13	69	78
4	-12	77	73
4	-11	83	-88
* 4	-10	16	15
* 4	-9	49	-8
4	-8	68	68
4	-7	86	-104
4	-6	242	-248
4	-5	153	-158
4	-4	327	-329
4	-3	150	-179
* 4	-2	19	11
4	-1	94	80
4	0	106	119
4	1	197	176
* 4	2	38	-56
4	3	96	94
* 4	4	16	-17
4	5	85	-88
4	6	87	88
4	7	95	-65
* 4	8	38	-4
4	9	204	-202
4	10	77	-82
* 4	11	16	17
5	-17	103	89
* 5	-16	35	-14
* 5	-15	113	123
* 5	-14	17	-18
5	-13	180	-186
5	-12	93	107
5	-11	203	-207
5	-10	61	68
* 5	-9	44	5
5	-8	52	-69
5	-7	143	117
5	-6	218	-230
5	-5	47	-76
5	-4	55	-34
5	-3	84	71
5	-2	69	84
5	-1	112	100
5	0	64	68
5	1	149	-146
5	2	95	84
5	3	77	-63
5	4	81	83
5	5	72	68

K = 9

H	L	10F$_o$	10F$_c$
0	1	454	447
0	2	228	221
0	3	68	-56
* 0	4	29	19
0	5	167	-171
0	6	67	-52
0	7	278	-273
0	8	271	-277
0	9	245	-227
0	10	204	-208
0	11	247	-249
* 0	12	36	-9
0	13	174	163
0	14	135	144
0	15	132	131
0	16	127	122
0	17	46	-65
0	18	83	-74
0	19	149	-141
0	20	138	-143
* 1	-21	35	37
1	-20	42	35
1	-19	93	100
* 1	-18	15	-20
1	-17	124	134
* 1	-16	38	22
1	-15	80	-56
1	-14	182	182
1	-13	210	-183
1	-12	75	-76
1	-11	233	-230
1	-10	220	-202
1	-9	112	110
1	-8	262	250
1	-7	68	-91
1	-6	189	173
* 1	-5	39	60
1	-4	77	82
1	-3	211	212

H	L	10F$_o$	10F$_c$
1	-2	84	-97
1	-1	371	390
* 1	0	15	-12
1	1	68	57
1	2	212	-206
1	3	46	35
1	4	47	-28
* 1	5	15	-4
1	6	231	218
* 1	7	35	-35
1	8	72	-79
1	9	241	239
1	10	230	-238
1	11	130	118
1	12	69	77
1	13	96	99
1	14	49	56
* 1	15	15	-20
1	16	43	16
1	17	103	-103
* 1	18	18	13
2	-21	69	60
2	-20	136	-138
2	-19	168	193
2	-18	78	-67
2	-17	98	108
2	-16	164	160
2	-15	200	-198
2	-14	219	247
2	-13	90	-74
2	-12	64	-84
* 2	-11	28	-23
* 2	-10	43	-14
2	-9	145	167
* 2	-8	16	-5
2	-7	212	202
2	-6	192	-174
2	-5	294	315
2	-4	190	186
2	-3	124	139
2	-2	308	306
2	-1	272	-293
2	0	229	-229
2	1	159	-144
2	2	275	-285
2	3	122	118
* 2	4	16	-23
2	5	91	122
2	6	183	180
2	7	150	162
* 2	8	41	-9
2	9	93	96
2	10	175	174
2	11	89	101
* 2	12	16	21
2	13	89	-77
2	14	182	-194
2	15	94	-100
2	16	64	-68
* 3	-20	13	-15
3	-19	45	-19
* 3	-18	15	3
3	-17	104	-99
* 3	-16	12	-22
3	-15	59	-39
* 3	-14	16	9
3	-13	122	133
3	-12	153	149
3	-11	44	-64
3	-10	59	47
* 3	-9	34	-36
3	-8	75	-71
3	-7	136	113
3	-6	264	276
3	-5	106	-61
* 3	-4	40	28
* 3	-3	211	-201
* 3	-2	21	-3
3	-1	205	-223
3	0	143	141
3	1	46	-47
3	2	146	148
* 3	3	16	-11
3	4	47	-18
3	5	50	50
3	6	87	-80
3	7	276	273
3	8	55	64
3	9	195	199
3	10	132	130
3	11	78	-67
3	12	20	28
3	13	84	-82
4	-1	98	90
4	-2	61	-91
4	-3	77	-95
4	-4	141	-123
4	-5	348	-351
* 4	-6	16	-4
* 4	-7	53	-63
4	-8	95	104
4	-9	70	-54
* 4	-10	12	1
4	-11	60	55
* 4	-12	16	-22
4	-13	97	100
4	-14	63	-31
4	-15	135	121
4	-16	121	-118
4	-17	71	-84
4	-18	79	82
* 4	0	198	202
* 4	1	16	18
* 4	2	199	190
* 4	3	57	-47
* 4	4	39	16
4	5	59	56
4	6	48	22
* 4	7	35	47
4	8	89	-83
4	9	40	-42
* 5	-14	29	-28
5	-13	58	75
5	-12	216	-211
5	-11	109	111
5	-10	47	-47
* 5	-9	16	5

	H	L	$10F_o$	$10F_c$
	5	-8	188	185
	5	-7	165	-165
	5	-6	83	38
	5	-5	152	-155
*	5	-4	32	21
*	5	-3	33	37
*	5	-2	37	50
	5	-1	61	63
	5	0	66	-68
*	5	1	33	47
	5	2	71	-50
	5	3	74	74

K = 10

	H	L	$10F_o$	$10F_c$
	0	0	412	385
	0	1	272	276
	0	2	81	68
	0	3	187	190
	0	4	145	-129
	0	5	44	-48
	0	6	234	-242
	0	7	124	-133
	0	8	154	-159
	0	9	253	-258
	0	10	315	-294
	0	11	65	-70
	0	12	84	78
*	0	13	25	-1
	0	14	128	106
	0	15	109	86
	0	16	52	48
*	0	17	22	0
	0	18	87	-62
	0	19	115	-121
*	1	-19	13	22
	1	-18	120	115
	1	-17	59	61
	1	-16	75	86
	1	-15	143	161
	1	-14	116	-97
	1	-13	117	135
	1	-12	131	-120
	1	-11	109	-105
	1	-10	61	-54
	1	-9	159	171
	1	-8	70	-81
	1	-7	256	257
	1	-6	84	-64
	1	-5	52	51
	1	-4	49	-55
*	1	-3	15	34
	1	-2	196	190
	1	-1	44	-56
	1	0	44	5
*	1	1	45	-39
	1	2	88	-80
	1	3	54	-54
	1	4	83	-82
	1	5	166	173
	1	6	45	-51
	1	7	214	220
	1	8	128	-123
	1	9	318	-307
	1	10	82	-82
	1	11	74	-61
	1	12	136	128
	1	13	65	43
	1	14	79	58
	1	15	56	49
	1	16	40	-3
	1	17	77	89
	2	-19	143	-144
	2	-1	100	114
	2	-17	57	48
	2	-16	46	-42
	2	-15	254	248
	2	-14	189	186
	2	-13	62	54
	2	-12	49	-31
	2	-11	89	-105
*	2	-10	24	-31
	2	-9	49	-60
	2	-8	31	21
	2	-7	154	-159
	2	-6	183	179
	2	-5	149	-167
	2	-4	59	51
	2	-3	339	363
	2	-2	93	-95
	2	-1	67	61
	2	0	229	-231
	2	1	181	-166
*	2	2	35	-2
	2	3	174	-170
	2	4	102	96
*	2	5	16	-8
	2	6	142	146
*	2	7	17	12
	2	8	70	55
	2	9	86	64
	2	10	148	165
	2	11	143	150
*	2	12	14	-6
*	2	13	24	-20
	2	14	93	-101
	2	15	121	-116
*	3	-19	12	-15
	3	-18	51	-56
	3	-17	50	-52
	3	-16	45	-32
	3	-15	81	-87
	3	-14	44	59
	3	-13	46	-53
	3	-12	56	44
	3	-11	102	89
*	3	-10	14	-5
	3	-9	77	-91
*	3	-8	42	56
	3	-7	189	-162
	3	-6	170	165
	3	-5	49	-39
	3	-4	98	-89
	3	-3	212	244
	3	-2	156	-155
*	3	-1	16	1
*	3	0	21	-29

	H	L	$10F_o$	$10F_c$
*	3	1	36	22
	3	2	42	16
	3	3	94	-99
	3	4	56	-41
	3	5	182	-190
	3	6	142	145
	3	7	60	-65
	3	8	183	172
	3	9	157	156
*	3	10	36	28
	3	11	104	109
	3	12	114	109
	4	-16	113	109
	4	-15	149	-160
	4	-14	130	144
	4	-13	68	-64
	4	-12	75	96
	4	-11	47	-27
	4	-10	57	52
	4	-9	175	183
	4	-8	42	-8
	4	-7	171	191
	4	-6	116	-124
*	4	-5	36	-17
	4	-4	136	-150
	4	-3	176	-145
*	4	-2	15	15
	4	-1	46	-27
	4	0	65	31
	4	1	106	114
*	4	2	21	-20
	4	3	41	42
*	4	4	37	-36
	4	5	55	41
	4	6	103	97
	4	7	52	40
	5	-11	106	-102
	5	-10	71	53
	5	-9	164	176
*	5	-8	26	-13
	5	-7	98	112
	5	-6	125	-146
*	5	-5	23	-26
*	5	-4	13	20
*	5	-3	13	23
	5	-2	48	33
	5	-1	42	-11

K = 11

	H	L	$10F_o$	$10F_c$
	0	1	79	68
	0	2	307	322
	0	3	72	-70
	0	4	256	250
	0	5	84	-81
	0	6	43	13
*	0	7	34	31
	0	8	59	-23
	0	9	44	-27
	0	10	180	-181
*	0	11	28	-41
	0	12	81	-46
	0	13	42	20
*	0	14	37	24
	0	15	106	109
	0	16	93	99
	0	17	63	76
*	1	-18	44	-3
*	1	-17	24	12
	1	-16	129	134
*	1	-15	24	-34
	1	-14	201	221
	1	-13	92	101
	1	-12	122	-128
	1	-11	47	48
	1	-10	132	-119
*	1	-9	25	30
*	1	-8	43	7
	1	-7	98	-113
	1	-6	66	79
	1	-5	133	-145
	1	-4	126	-136
	1	-3	62	-49
	1	-2	50	37
	1	-1	58	51
*	1	0	26	38
	1	1	73	-70
*	1	2	37	38
*	1	3	50	55
	1	4	152	135
	1	5	56	55
	1	6	331	337
*	1	7	16	5
	1	8	79	-79
	1	9	182	-188
	1	10	144	-150
*	1	11	15	13
*	1	12	15	4
	1	13	105	97
	1	14	109	115
	1	15	108	103
	2	-18	85	-65
*	2	-17	13	-31
	2	-16	138	143
	2	-15	82	-87
	2	-14	145	150
	2	-13	88	-88
	2	-12	185	-185
	2	-11	59	73
	2	-10	93	-80
*	2	-9	37	-57
	2	-8	126	-126
*	2	-7	47	-8
	2	-6	86	-84
*	2	-5	21	35
	2	-4	187	198
*	2	-3	38	14
	2	-2	319	332
	2	-1	80	-88
	2	0	64	-37
*	2	1	41	-62
	2	2	191	-212
	2	3	46	-10
	2	4	114	-124
	2	5	46	0
*	2	6	37	53

	H	L	$10F_o$	$10F_c$
	2	7	83	-65
	2	8	65	-68
	2	9	71	48
	2	10	135	140
*	2	11	49	54
	2	12	72	97
	2	13	46	-42
	3	-17	43	-19
	3	-16	96	-88
	3	-15	82	96
	3	-14	94	102
	3	-13	59	53
*	3	-12	39	14
	3	-11	52	-33
	3	-10	100	84
*	3	-9	40	7
	3	-8	52	-62
	3	-7	94	103
	3	-6	97	-108
	3	-5	108	118
	3	-4	143	139
	3	-3	73	-87
*	3	-2	22	30
	3	-1	61	-72
	3	0	83	-85
	3	1	49	-43
	3	2	87	-98
*	3	3	16	-29
	3	4	231	-248
*	3	5	27	-4
	3	6	183	-181
	3	7	82	79
	3	8	60	29
	3	9	82	79
	3	10	135	146
	4	-14	113	-115
	4	-13	50	54
*	4	-12	13	12
	4	-11	49	49
	4	-10	80	65
	4	-9	48	38
	4	-8	259	258
*	4	-7	15	6
*	4	-6	57	57
	4	-5	60	-69
	4	-4	115	-101
*	4	-3	37	7
	4	-2	158	-169
	4	-1	65	73
*	4	0	32	3
	4	1	52	48
	4	2	41	24
	4	3	55	-36
	4	4	45	-32

K = 12

	H	L	$10F_o$	$10F_c$
	0	0	174	174
	0	1	144	142
*	0	2	33	3
	0	3	368	393
*	0	4	42	45
	0	5	179	182
	0	6	109	121
	0	7	123	130
*	0	8	30	44
	0	9	124	-126
	0	10	59	35
	0	11	91	-62
*	0	12	39	-41
*	0	13	34	-8
	0	14	89	86
	0	15	102	108
	1	-16	77	-74
	1	-15	175	177
	1	-14	56	-61
	1	-13	68	55
	1	-12	49	-28
	1	-11	198	209
	1	-10	149	175
	1	-9	101	-104
	1	-8	55	35
*	1	-7	16	20
*	1	-6	38	3
	1	-5	72	-68
*	1	-4	47	17
	1	-3	62	-74
*	1	-2	16	-13
	1	-1	71	69
	1	0	98	90
	1	1	46	49
*	1	2	24	-24
*	1	3	53	65
	1	4	68	50
	1	5	180	182
	1	6	138	140
	1	7	103	118
	1	8	143	-133
	1	9	184	-186
*	1	10	32	-31
	1	11	71	-66
*	1	12	14	15
	1	13	51	47
	2	-16	69	-84
	2	-15	167	191
	2	-14	64	-65
*	2	-13	33	-14
	2	-12	45	45
	2	-11	139	-134
	2	-10	91	87
*	2	-9	41	-59
*	2	-8	16	-12
	2	-7	113	-106
	2	-6	49	-51
*	2	-5	33	21
*	2	-4	25	-1
	2	-3	307	318
	2	-2	133	-146
	2	-1	103	103
*	2	0	31	-29
	2	1	216	-224
*	2	2	16	-25
	2	3	191	-197
*	2	4	33	-12
	2	5	55	33
	2	6	64	-56

	H	L	$10F_o$	$10F_c$
	2	7	47	-26
	2	8	84	-103
	2	9	61	69
*	2	10	13	-4
	2	11	128	134
	3	-14	81	75
*	3	-13	13	-30
*	3	-12	14	-15
	3	-11	106	103
	3	-10	53	-82
	3	-9	69	59
*	3	-8	39	-22
*	3	-7	37	-30
	3	-6	50	31
*	3	-5	15	17
*	3	-4	37	48
	3	-3	93	100
	3	-2	53	-39
*	3	-1	15	-17
	3	0	66	64
*	3	1	15	-25
*	3	2	24	8
	3	3	87	-98
	3	4	46	-48
	3	5	156	163
	3	6	71	-64
	3	7	70	-69
	4	-10	40	-15
	4	-9	169	173
	4	-8	45	-33
	4	-7	138	139
*	4	-6	33	42
	4	-5	46	-49
	4	-4	42	38
	4	-3	137	-154
	4	-2	69	78
	4	-1	62	-67
	4	0	47	53

K = 13

	H	L	$10F_o$	$10F_c$
*	0	1	39	28
	0	2	170	183
*	0	3	26	15
	0	4	87	93
	0	5	64	93
	0	6	50	28
	0	7	80	100
	0	8	72	-62
*	0	9	49	60
	0	10	65	-54
*	0	11	14	10
*	0	12	36	-25
*	0	13	12	-17
*	1	-13	13	-25
	1	-12	95	-104
	1	-11	129	149
	1	-10	138	-147
	1	-9	110	118
	1	-8	74	75
*	1	-7	24	18
*	1	-6	40	34
*	1	-5	35	-11
*	1	-3	32	5
	1	-4	94	-109
	1	-2	78	-93
*	1	-1	28	-17
	1	0	87	-113
*	1	1	39	-5
	1	2	58	-73
	1	3	99	-48
	1	4	42	9
	1	5	111	134
	1	6	192	210
*	1	7	15	-1
	1	8	62	-58
*	1	9	17	-16
	1	10	135	-154
*	1	11	73	-75
*	2	-13	38	-12
*	2	-12	32	-44
	2	-11	74	85
	2	-10	51	-54
*	2	-9	14	6
*	2	-8	27	-15
*	2	-7	57	-38
	2	-6	102	113
*	2	-5	15	-13
	2	-4	101	106
*	2	-3	28	-42
	2	-2	178	194
	2	-1	49	-30
	2	0	48	-50
	2	1	65	56
	2	2	148	-154
*	2	3	47	14
*	2	4	14	11
	2	5	60	64
*	2	6	22	30
	2	7	124	-152
*	2	8	13	-10
	3	-10	89	109
*	3	-9	21	-37
*	3	-8	33	-25
	3	-7	43	-42
	3	-6	42	-25
	3	-5	57	73
	3	-4	78	94
*	3	-3	29	-8
	3	-2	76	95
	3	-1	72	68
	3	0	39	34
	3	1	55	69
*	3	2	13	-2
	3	3	52	-50

K = 14

	H	L	$10F_o$	$10F_c$
	0	0	171	-187
*	0	1	42	45
	0	2	108	-108
	0	3	68	72
	0	4	56	-46
*	0	5	14	-18
	0	6	87	92

	H	L	$10F_o$	$10F_c$
	0	7	90	-91
	0	8	50	45
	0	9	40	-23
	1	-10	119	151
*	1	-9	33	-30
*	1	-8	34	2
	1	-7	132	157
	1	-6	74	-65
*	1	-5	20	19
	1	-4	81	-77
*	1	-3	45	-59
	1	-2	44	-60
	1	-1	53	-63
*	1	0	24	-32
	1	1	134	-142
*	1	2	29	-10
	1	3	100	-116
	1	4	60	51
	1	5	152	145
	1	6	114	114
	1	7	44	32
	2	-1	63	48
*	2	-2	10	13
	2	-3	93	102
*	2	-4	13	33
*	2	-5	13	-9
*	2	-6	37	-43
*	2	-7	34	-24
*	2	-8	33	-45
	2	0	83	97
	2	1	119	135
*	2	2	37	33
	2	3	63	-75
*	2	4	52	47

K = 15

	H	L	$10F_o$	$10F_c$
	0	0	38	0
	0	1	88	-122
	0	2	57	53
	0	3	87	-99
*	0	4	34	30
	1	-3	40	-24
*	1	-2	28	10
	1	-1	72	-73
*	1	0	12	-20

APPENDIX V.

Crystallographic programs.

```
C     INTERPOLATION PROGRAM . INPUT IS F VALUES AT SIN THETA/LAM. 0.0
C     TO 1.10 IN STEPS OF 0.05 (23 OF ). ..OUTPUT IS F VALUES FOR SIN
C     THETA FROM 0.02 TO 1.00 IN STEPS /F 0.02 ( 50 OF)..
C     DATA IS 1. SINTHETA/LAM. FVALUE.. 23 OF IN FORMAT F6.4,F5.2..
C     SINTHETA/LAM RUNS FROM 0.00 TO 1.10..
C     DATA2.  MM(FORMATI3). MM IS THE NO. OF VALUES OF SINTHETA
C     TO BE INTERPOLATED..
C     DATA 3.. MM VALUES OF SINTHETA IN FORMAT F6.4..
  103 FORMAT(1X,28H SINT        RHO       SCATT  )
  102 FORMAT(I3)
  112 FORMAT(F6.4)
  111 FORMAT(1X,F7.4,3X,F7.4,3X,F8.4)
  100 FORMAT(F6.4,F5.2)
      DIMENSION SN(23),F(23),B(4),C(3),D(2)
      DO 1 I=1,23
    1 READ(5,100) SN(I),F(I)
      READ(5,102) MM
      WRITE(6,103)
      KK=0
  420 KK=KK+1
      IF(KK-MM)421,421,422
  421 READ(5,112) X
      SX=(X/1.5418)
  150 A=0.0500
  200 A=A+0.0500
      IF(A-SX)200,201,202
  202 BI=(A/0.0500)+1.0000
      I=BI
      J=I-3
      DO 300 K=1,4
      J=J+1
  300 B(K)=(F(J)*(SN(J+1)-SX)-F(J+1)*(SN(J)-SX))/(SN(J+1)-SN(J))
      J=I-3
      K=0
      DO 301 L=1,3
      J=J+1
      K=K+1
  301 C(L)=(B(K)*(SN(J+2)-SX)-B(K+1)*(SN(J)-SX))/(SN(J+2)-SN(J))
      J=I-3
      L=0
      DO 302 M=1,2
      L=L+1
      J=J+1
  302 D(M)=(C(L)*(SN(J+3)-SX)-C(L+1)*(SN(J)-SX))/(SN(J+3)-SN(J))
      J=I-2
  303 FCAL=(D(1)*(SN(J+4)-SX)-D(2)*(SN(J)-SX))/(SN(J+4)-SN(J))
  304 WRITE(6,111) X,SX,FCAL
      GO TO 420
  201 BI=(A/0.0500)+1.0000
      I=BI
      WRITE(6,111) X,SX,F(I)
      GO TO 420
  422 RETURN
      END
```

```
$IBFTC LP103   DECK
C
C      L.P. CORRECTION FOR EQUI-INCLINATION WEISSENBERGS
C     IF ITEST IS 0 PRINT, IF = 1 THEN PUNCH, IF = 2 THEN PRINT AND PUNC
C                                 ******************
C                                 **  VERSION 103    **
C                                 ******************
    1 FORMAT(3F7.3,4F7.4)
    2 FORMAT(A5,4F8.4)
    3 FORMAT(3I3,F9.2,F5.3,I3)
    4 FORMAT(I3)
    5 FORMAT(1H$,3I9,F9.2,9X,F9.0,I5)
    6 FORMAT(1X,6H      ,F7.4,F7.2,3I4,F9.2,F8.3,F9.2)
    7 FORMAT(1H0,58H        SINT    FOBS    H   K   L    OBSI    DLP
     1 I*D  )
    8 FORMAT(1H1,15H LAYER CODE IS A5,7H,MU IS F8.4,8H DEGREES,17H,SCALE
     1 FACTOR IS F8.4)
    9 FORMAT(1X,31H MINIMUM INTENSITY MEASURED IS F8.4,9H,ZETA IS F8.4)
   10 FORMAT(1X,6H **** ,F7.4,F7.2,3I4,F9.2,F8.3,F9.2)
   11 FORMAT(1H0,12H REFLECTION 3I3,32H HAS SIN(THETA) GREATER THAN 1.0)
      DIMENSION RCP(6),PRCP(6)
      READ(5,4)ITEST
      READ(5,1) A,B,C,CAA,CBB,CCC,WAVE
      D=SQRT(1.+2.*CAA*CBB*CCC-CAA*CAA-CBB*CBB-CCC*CCC)
      D=1./(D*A*B*C)
      SAA=SQRT(1.-CAA*CAA)
      SBB=SQRT(1.-CBB*CBB)
      SCC=SQRT(1.-CCC*CCC)
      RCP(1)=D*B*C*SAA
      RCP(2)=D*A*C*SBB
      RCP(3)=D*A*B*SCC
      RCP(4)=(CBB*CCC-CAA)/(SBB*SCC)
      RCP(5)=(CAA*CCC-CBB)/(SAA*SCC)
      RCP(6)=(CAA*CBB-CCC)/(SAA*SBB)
      PRCP(1)=RCP(1)*RCP(1)*0.25
      PRCP(2)=RCP(2)*RCP(2)*0.25
      PRCP(3)=RCP(3)*RCP(3)*0.25
      PRCP(4)=RCP(1)*RCP(2)*RCP(6)*0.25
      PRCP(5)=RCP(1)*RCP(3)*RCP(5)*0.25
      PRCP(6)=RCP(2)*RCP(3)*RCP(4)*0.25
  100 CONTINUE
      READ(5,2) ICODE,AMU,SCALE,ZMINI,ETA
      WRITE(6,8) ICODE,AMU,SCALE
      WRITE(6,9) ZMINI,ETA
      IF(ITEST-1) 120,121,120
  120 CONTINUE
      WRITE(6,7)
  121 CONTINUE
  112 CONTINUE
      READ(5,3) IH,IK,IL,OBSI,Q,ID
      IF(IH-999) 102,103,102
  103 IF(IK-999) 100,104,100
  102 FH=IH
      FK=IK
      FL=IL
```

```
      RHO=FH*FH*PRCP(1)+FK*FK*PRCP(2)+FL*FL*PRCP(3)+2.*FH*FK*PRCP(4)+2.*
     1FK*FL*PRCP(6)+2.*FL*FH*PRCP(5)
      SQSINT=RHO*WAVE*WAVE
      SINT=SQRT(SQSINT)
      IF(SINT-1.) 400,400,401
  401 CONTINUE
      WRITE(6,11)  IH,IK,IL
      GO TO 112
  400 CONTINUE
      CENT=SQRT(1.-(SINT*SINT))
      XISQ=(4.*SQSINT)-(ETA*ETA)
      XI=SQRT(XISQ)
C     USING THE EQUATION GIVEN IN COCHRAN.
C     D=(XI *CENT)/(1+COSSQ(TWOTHETA))
      CTWTH=(1.-(SINT*SINT*2.))
      CSQTW=CTWTH*CTWTH
      DLP=(XI *CENT)/(1.+CSQTW)
      IF(OBSI) 200,201,200
  201 CALCID=ZMINI*DLP*SCALE
      ID=1
      GO TO 202
  200 CALCID=OBSI*DLP*SCALE
  202 IH=FH
      IK=FK
      IL=FL
      FOBS=SQRT(CALCID)
  402 CONTINUE
      IF(ITEST-1) 206,207,206
C     PRINT OUT
  206 IF(ID)209,208,209
  208 WRITE(6,6) SINT,FOBS,IH,IK,IL,OBSI,DLP,CALCID
      GO TO 250
  209 WRITE(6,10) SINT,FOBS,IH,IK,IL,OBSI,DLP,CALCID
  250 IF(ITEST-1) 112,112,207
  207 IF(ID) 220,221,220
  220 FOBS=0.
  221 CONTINUE
      WRITE(6,5) IH,IK,IL,FOBS,Q,ID
      GO TO 112
  104 RETURN
      END
$DATA
```

```
C       A PROGRAM TO GERERATE NORMALISED STRUCTURE FACTORS
C            SUBROUTINE SYSTAB SETS UP THE CORRECT EPSILON VALUES
C
    1 FORMAT(3F7.3,4F7.4)
    2 FORMAT(7F10.4)
    3 FORMAT(1H0,32H RECIPROCAL CELL PARAMETERS ARE )
    4 FORMAT(1X,6F10.5)
    5 FORMAT(I3)
    6 FORMAT( F9.6)
    7 FORMAT(3I9,2F9.2,F9.0,I5)
    8 FORMAT(1X,3I5,F9.4,F9.3,5F7.3,2F9.3,F9.4)
    9 FORMAT(1H$,3I4,F9.4)
   10 FORMAT(1H0,95H    H    K    L   SINT      OBSI   F1      F2      F3
     1    F4      F5       SIG2   EP*SIG2    E**2  )
   12 FORMAT(1H0,17H  SCALE FACTOR = F9.4///)
   13 FORMAT(1X,6H Z IS F9.4,53H ,NO OF ATOMS OF THIS TYPE IN THE
     1UNIT CELL IS I3//)
   14 FORMAT(1H0,60H    A*         B*         C*       COS(AL*)  COS(BE*)
     1COS(GA*))
   15 FORMAT(10I3)
   16 FORMAT(1H0,25X,23H NUMBER OF F CURVES IS I5)
   17 FORMAT(1H0,25X,27H DATA SET UP IS ON LOGICAL I5)
   18 FORMAT(1H0,25X,34H NO INITIAL PRINT OUT IS REQUESTED)
   19 FORMAT(1H0,25X,34H    INITIAL PRINT OUT IS REQUESTED)
  220 FORMAT(1H0,25X,29H   A K GENERATION IS REQUIRED)
  221 FORMAT(1H0,25X,29H  AN E GENERATION IS REQUIRED)
      DIMENSION  RCP(6),PRCP(6),AFM(11,51),FM(15),NOAT(10),CONT(10)
C
C       TAPE ALLOCATIONS.
C     NN IS BINY TAPE FOR EXPANDED DATA AND MM IS TAPE USED IN KGEN
C       FOR STORAGE AND LSQFIT PICK-UP.
C
      NFOUR=2
      NN=1
      MM=4
      READ(5,1) A,B,C,CAA,CBB,CCC,WAVE
      D=SQRT(1.+2.*CAA*CBB*CCC-CAA*CAA-CBB*CBB-CCC*CCC)
      D=1./(D*A*B*C)
      SAA=SQRT(1.-CAA*CAA)
      SBB=SQRT(1.-CBB*CBB)
      SCC=SQRT(1.-CCC*CCC)
      RCP(1)=D*B*C*SAA
      RCP(2)=D*A*C*SBB
      RCP(3)=D*A*B*SCC
      RCP(4)=(CBB*CCC-CAA)/(SBB*SCC)
      RCP(5)=(CAA*CCC-CBB)/(SAA*SCC)
      RCP(6)=(CAA*CBB-CCC)/(SAA*SBB)
      PRCP(1)=RCP(1)*RCP(1)*0.25
      PRCP(2)=RCP(2)*RCP(2)*0.25
      PRCP(3)=RCP(3)*RCP(3)*0.25
      PRCP(4)=RCP(1)*RCP(2)*RCP(6)*0.25
      PRCP(5)=RCP(1)*RCP(3)*RCP(5)*0.25
      PRCP(6)=RCP(2)*RCP(3)*RCP(4)*0.25
      WRITE(6,3)
      WRITE(6,14)
```

```
      WRITE(6,4) ( RCP(I),I=1,6)
      CALL FOUR1 (NFOUR,RCP)
C     READ IN SCATTERING FACTORS
      READ(5,15) NN1,NF,NOWR,KCURV,NN2
      WRITE(6,16) NF
      WRITE(6,17) NN
      IF(NOWR.EQ.0)  GO TO 230
      WRITE(6,19)
      GO TO 231
  230 WRITE(6,18)
  231 CONTINUE
      IF(KCURV .EQ.0)  GO TO 232
      WRITE(6,220)
      GO TO 233
  232 WRITE(6,221)
  233 CONTINUE
      REWIND NN
      DO 31 I=1,11
      DO 31 J=1,51
   31 AFM(I,J)=0.
      I=0
   20 I=I+1
      READ(5,2) (AFM(I,J),J=1,7)
      IF (AFM(I,1))21,21,22
   22 READ(5,2) (AFM(I,J),J=8,51)
      NATSC=I
      GO TO 20
   21 CONTINUE
C     READ IN THE NO. OF ATOMS OF EACH CHEM. TYPE IN THE ASSYMETRIC UNIT
      DO 101 L=1,NF
      READ(5,5) NOAT(L)
  101 CONTINUE
      READ(5,6) SCALE
      WRITE(6,12) SCALE
      DO 500 L=1,NF
      WRITE(6,13) AFM(L,1),NOAT(L)
  500 CONTINUE
      WRITE(6,10)
  102 READ(5,7) IH,IK,IL,FOBS,SIG,Q,ID
      FH=IH
      FK=IK
      FL=IL
      IF(IH) 25,23,25
   23 IF(IK) 25,24,25
   24 IF(IL) 25,50,25
   25 RHO=FH*FH*PRCP(1)+FK*FK*PRCP(2)+FL*FL*PRCP(3)+2.*FH*FK*PRCP(4)+2.*
     1FK*FL*PRCP(6)+2.*FL*FH*PRCP(5)
      SQSINT=RHO*WAVE*WAVE
      SINT=SQRT(SQSINT)
      OBSI=SCALE*FOBS*FOBS
      IF(SINT-1.) 26,102,102
   26 BRAG=SINT
      DO 27 I=2,51
      BRAG=BRAG-0.02
```

```
      IF(BRAG)28,28,27
   27 CONTINUE
   28 I=I-1
      FRAC=(BRAG+0.02)*50.
      DO 29 K=1,10
   29 FM(K)=0.
      DO 30 K=1,NATSC
   30 FM(K)=AFM(K,I)+(AFM(K,I+1)-AFM(K,I))*FRAC
C     IF(ID.EQ.0)   GO TO 999
C     OBSI = 0.56
  999 CONTINUE
      TOT=0.
      DO 104 L=1,NF
      FNOAT=NOAT(L)
       CONT=FNOAT*FM(L)*FM(L)
      TOT=TOT+CONT
  104 CONTINUE
      SIG2 = TOT
      CALL SYSTAB (IH,IK,IL,EPSI)
      ESIG2 = SIG2 * EPSI
      ESQ = (OBSI/ESIG2)
      WRITE(NN) IH,IK,IL,ESIG2,ESQ,OBSI,FOBS,SINT,ID,EPSI
      IF(NOWR.EQ.0)  GO TO 444
      WRITE(6,8) IH,IK,IL,SINT,OBSI,(FM(I),I=1,5),SIG2,ESIG2,ESQ
  444 CONTINUE
      GO TO 102
   50 IH = 999
      WRITE(NN) IH,IK,IL,ESIG2,ESQ,OBSI,FOBS,SINT,ID,EPSI
      END FILE NN
      REWIND NN
      IF (KCURV - 1) 777,666,666
  666 CALL KGEN (NN,MM)
      CONTINUE
      GO TO 995
  777 CALL EGEN (NN,NFOUR)
      CONTINUE
  995 RETURN
      END
```

```
$IBFTC KKK
      SUBROUTINE KGEN(NN,MM)
C
C     THIS IS USED TO CALCULATE SUMS FOR GENERATING K CURVE, SO THAT
C     AN EXPONENTIAL FIT OF THE FORM K = A*EXP(B*SINT**C)
C     CAN BE OBTAINED AND THIS USED TO PLACE
C     THE INTENSITIES ON THE TRUE SCALE
      DIMENSION S(30),TSIG(30),TIN(30),ZN(30),SM(30),CCK(30)
    1 FORMAT(3I3,F9.6)
    2 FORMAT(2F9.6)
    3 FORMAT(1H0,66H RANGE     TOT(SIG2)       TOT(INT)              K      S
     1IN(TH)M      NO//)
    4 FORMAT(1H ,I5,3F15.4,F10.6,F6.1)
```

```
    5 FORMAT(1X,3I5,2F15.4,I5,F9.6,F6.1)
    6 FORMAT(1H1,50H     H     K     L        E*SIG2              OBSI    RANGE)
    7 FORMAT(18H1KCURVE GENERATION//)
    8 FORMAT(6H0      )
    9 FORMAT(20H K CURVE SET NUMBER I3)
   10 FORMAT(12H REFLECTION 3I3,36H   IS OUTSIDE THE MAXIMUM SIN(THETA),
     115H AND IS IGNORED)
      REWIND MM
   11 CONTINUE
C
      REWIND NN
      READ(5,1) N,III,NSET,SINMAX
      WRITE(MM) N,NSET
      IF(III.EQ.0)  GO TO 100
      WRITE(6,6)
  100 CONTINUE
      DO 101 I = 1,N
      TSIG(I) = 0.0
      TIN(I) = 0.0
      ZN(I) = 0.0
      CCK(I) = 0.0
  101 CONTINUE
      CALL RANSET(N,SINMAX,S    ,SM    )
  102 CONTINUE
      READ (NN) IH,IK,IL,ESIG2,ESQ,OBSI,FOBS,SINT,ID,EPSI
      IF(IH.EQ.999) GO TO 999
      IF(SINT.LE.S(N))  GO TO 103
C     WRITE(6,10) IH,IK,IL
      GO TO 102
  103 CONTINUE
      DO 104 I = 1,N
      IF(SINT.GE.S(I))  GO TO 104
      TSIG(I) = TSIG(I) + ESIG2
      TIN(I) = TIN(I) + OBSI
      ZN(I) = ZN(I) + 1.0
      IF (III.EQ.0)  GO TO 150
      WRITE(6,5)  IH,IK,IL,ESIG2,OBSI,I,SINT,EPSI
  150 CONTINUE
      GO TO 102
  104 CONTINUE
C
C -   REACHES 999 AT THE END OF ALL DATA
  999 CONTINUE
      REWIND NN
C
C     PUT OUT THE REQUIRED SUMS
      WRITE(6,3)
      DO 110 I = 1,N
      CCK(I) = (TSIG(I)/TIN(I))
      WRITE(6,4) I,TSIG(I),TIN(I),CCK(I),SM(I),ZN(I)
      WRITE(MM ) I,TSIG(I),TIN(I),CCK(I),SM(I),ZN(I),S(I)
  110 CONTINUE
      IF(NSET.NE.0)  GO TO 11
```

```
C
C          FINAL SET OF K CURVE
      REWIND MM
      WRITE(6,7)
      WRITE(6,3)
      JK = 0
   12 CONTINUE
      JK = JK + 1
      WRITE(6,9) JK
      WRITE(6,8)
      READ(MM) N,NSET
      DO 14 I = 1,N
      READ (MM ) I,TSIG(I),TIN(I),CCK(I),SM(I),ZN(I),S(I)
      WRITE(6,4) I,TSIG(I),TIN(I),CCK(I),SM(I),ZN(I)
   14 CONTINUE
      IF(NSET.NE.0)  GO TO 12
      CALL LSQFIT(MM)
      RETURN
      END


$IBFTC ECALC
      SUBROUTINE EGEN (NN,NFOUR)
      DIMENSION FM(20)
C
C    THIS SUB READS BACK FROM BINY TAPE NN, AND SETS UP AVERAGES REQUIRED
C
C        THE SIX QUANTITES REQUIRED ARE
C
C                                          E DESIG              NUMBER TOTAL
C     AVERAGE  E                           TOTE                 NUM
C     AVERAGE(E**2 - 1)                    TESQM1               NUM
C     AVERAGE    ( E**2)                   TOTESQ               NUM
C
C     PERCENT  WITH  E . GT. 3.0                                 N3
C     PERCENT  WITH  E . GT. 2.0                                 N2
C     PERCENT  WITH  E . GT. 1.0                                 N1
C
C        THIS SUB ROUTINE ALSO OUTPUTS CARDS WITH THE REQUIRED.
C      FUNCTIONS ON.    N.B.  DATA IS SCALED USING THE EXP. FUNCTION
C     GENERATED FROM   KGEN
    1 FORMAT(1H1,17HTOTAL /E/       = F12.4,26H NUMBER OF OBSERVATIONS =
     1I5,23H ***AVERAGE /E/       = F12.4)
    2 FORMAT(1H0,17HTOTAL /E**2-1/ = F12.4,31X,23H ***AVERAGE /E**2-1/ =
     1 F12.4)
    3 FORMAT(1H0,17HTOTAL /E**2/   = F12.4,31X,23H ***AVERAGE /E**2  / =
     1 F12.4)
    4 FORMAT(1H0,6H       )
    5 FORMAT(1H0,26H NUMBER WITH /E/ GT 3.0 = I5,18H PERCENT GT 3.0 = F8
     1.4)
    6 FORMAT(1H0,26H NUMBER WITH /E/ GT 2.0 = I5,18H PERCENT GT 2.0 = F8
     1.4)
    7 FORMAT(1H0,26H NUMBER WITH /E/ GT 1.0 = I5,18H PERCENT GT 1.0 = F8
     1.4)
```

```
    8 FORMAT(1X,3I5,3F9.3)
    9 FORMAT(1H1,42H     H     K     L      E       E**2    (E**2-1))
   10 FORMAT (3F10.5,I10)
   11 FORMAT(1H$,3I4,5F9.4)
   12 FORMAT(1X,3I4,6F9.4)
   13 FORMAT(1H1,57H    H    K    L     E       E**2     E**2-1      SINT      K
     1CALC )
   14 FORMAT(1H0,50H THE AVERAGE E**2 IS OUTSIDE THE PERMISSABLE RANGE//
     1,35H AND CONSEQUENTLY THE JOB IS HALTED//,47H IF THE A COEFFICIENT
     2 IS REPLACED BY THE VALUE F10.4,28H AN AVERAGE E**2 WILL RESULT//,
     326H OR RE-ANALYSE THE K CURVE)
   15 FORMAT(1H0,51H THE K CURVE USED IS OF THE FORM K = A*(B(SINT)**C)/
     1///,32H THE COEFFICIENTS USED HERE ARE ///, 5H A = F10.4//,5H B =
     2F10.4//,5H C = F10.4//)
   16 FORMAT(I3)
   17 FORMAT(1H0,45H ONLY THE AVERAGES ARE REQUIRED NO INDIVIDUAL///,
     1 40H LISTING FOR EACH PLANE WILL BE GIVEN    )
C     READ IN PARAMETERS OF THE EXPONENTIAL FUNCTION
  778 READ (5,10) A,B,C,NAVER
      IF(A.GT.100.) GO TO 800
      IF(NAVER.EQ. )  GO TO 240
      WRITE(6,17)
      WRITE(6,13)
  240 CONTINUE
C
C     SET SCK AND NPUN TO 1 FOR INITIAL RUN
      SCK = 1.0
      NPUN = 1
      IEND = 0
C
  400 CONTINUE
      N1 = 0
      N2 = 0
      N3 = 0
      NUM = 0
      TOTE = 0.0
      TOTESQ = 0.0
      TESQM1 = 0.0
      REWIND NN
  201 CONTINUE
      READ (NN) IH,IK,IL,ESIG2,ESQ,OBSI,FOBS,SINT,ID,EPSI
      IF(IH.EQ.999)   GO TO 200
C     IF(SINT.GT.0.75)  GO TO 201
      CONK = A*EXP(B*SINT**C)
      E2 = ESQ * CONK * SCK
      E2M1 = E2 - 1.0
      E = SQRT(E2)
      NUM = NUM + 1
      TOTE = TOTE + E
      IF(E2M1.GE.0.0)   GO TO 301
      EEM1 = -E2M1
      GO TO 300
  301 EEM1 = E2M1
```

```
  300 TESQM1 = TESQM1 + EEM1
      TOTESQ = TOTESQ + E2
C
C      PRCENTAGE TOTALS
      IF(E.LT.3.0)   GO TO 220
      N1 = N1 + 1
      N2 = N2 + 1
      N3 = N3 + 1
      GO TO 555
  220 IF(E.LT.2.0)    GO TO 210
      N1 = N1 + 1
      N2 = N2 + 1
      GO TO 555
  210 IF(E.LT.1.0)   GO TO 555
      N1 = N1 + 1
  555 CONTINUE
      IF(NPUN.NE.0)  GO TO 302
      IF(NAVER.NE.0) GO TO 302
      CALL CARD          (IH,IK,IL,E,E2,E2M1,SINT,CONK)
      CONTINUE
  302 CONTINUE
      IF (IEND.NE.1) GO TO 201
C
      CALL FOUR2 (IH,IK,IL,E,E2M1,SINT,ID,FOBS,NFOUR,EPSI)
      IF(NAVER.NE.0) GO TO 201
      WRITE(6,12)     IH,IK,IL,E,E2,E2M1,SINT,CONK,ESQ
      GO TO 201
  200 CONTINUE
      ZNUM = NUM
      ZN1 = N1
      ZN2 = N2
      ZN3 = N3
      AVE        = TOTE/ZNUM
      AVESM1 = TESQM1 / ZNUM
      AVESQ = TOTESQ/ZNUM
      PERE3 = (ZN3/ZNUM) * 100.0
      PERE2 = (ZN2/ZNUM) * 100.0
      PERE1 = (ZN1/ZNUM) * 100.0
      WRITE(6,1)    TOTE,NUM,AVE
      WRITE(6,2)    TESQM1, AVESM1
      WRITE(6,3)   TOTESQ,AVESQ
      WRITE(6,4)
      WRITE(6,5)    N3, PERE3
      WRITE(6,6)   N2, PERE2
      WRITE(6,7)   N1, PERE1
      WRITE(6,15) A,B,C
      IF(IEND.EQ.1)  GO TO 311
      IF(AVESQ.LT.0.98)  GO TO 500
      IF(AVESQ.GT.1.02)  GO TO 500
      IEND = 1
      NPUN = 0
      GO TO 400
C
  500 IEND = 0
```

```
      SCK = (1.0/AVESQ)
      D = SCK * A
      WRITE(6,14) D
  311 CONTINUE
      CALL FOUR2 (IH,IK,IL,E,E2M1,SINT,ID,FOBS,NFOUR)
      REWIND NN
      GO TO 778
  800 RETURN
      END


$IBFTC KFIT
      SUBROUTINE LSQFIT (MM)
      DIMENSION Y(100),X(100,2),A(2),W(100),Z(100),ZZ(100)
      DIMENSION  TSIG(100),TIN(100),CCK(100),SM(100),ZN(100),S(100)
      REWIND MM
C   READS BACK  SINTHETA (SM)  AND K (CCK) FROM TAPE MM READY TO GO TO
C        THE LIBRARY SUBROUTINE FOR THE LEAST SQUARES FIT.
      J1 = 1
      J2 = 0
  101 CONTINUE
      READ(MM)  N,NSET
      J2 = J2 + N
      DO 104 I = J1,J2
      READ(MM)  I,TSIG(I),TIN(I),CCK(I),SM(I),ZN(I),S(I)
  104 CONTINUE
      J1 = J1 + N
      IF(NSET.NE.0)  GO TO 101
      NTOT = J2
      WRITE(6,111)  NTOT
  111 FORMAT(1H1,43H LEAST SQUARES FITTING SUBROUTINE IS CALLED,//36H TH
     1E TOTAL NUMBER OF POINTS USED IS I5)
C
C       ENTER INTO THE L.S. SUBROUTINE.
C     THIS PROGRAM USES LEAST SQUARES LIBRARY SUBROUTINE
C        TO FIT NTOT POINTS (W,Z)  TO A CURVE
      DO 106 I = 1,NTOT
      ZZ(I) = SM(I)
      W(I) = CCK(I)
  106 CONTINUE
      ON = 1.
  100 DO 1 I = 1,NTOT
      Y(I) = ALOG(W(I))
      Z(I) = ZZ(I)**XN
    1 CONTINUE
      DO 2 I = 1,NTOT
      DO 2 J = 1,2
    2 X(I,J) = Z(I)**(J-1)
      CALL LSTSQ   (Y,X,100,NTOT,2,A,S)
      WRITE (6,12) XN
   12 FORMAT (1X, 5HXN = , F10.5//)
      WRITE (6,20) S, (J, A(J), J = 1,2)
   20 FORMAT (1X, 17HSUM OF SQUARES = , E13.6// (1X,I3, E20.6))
```

```
      AA = EXP(A(1))
      SS = EXP(S)
      B = A(2)
      WRITE (6,44) AA,B,SS
   44 FORMAT (4H0A= ,F10.5,5X,4HB = ,F10.5,17HSUM OF SQUARES = ,E13.6//)
      DO 4 K = 1,5
    4 WRITE (6,30)
   30 FORMAT (4H    )
      XN = XN + 0.5
      IF (XN.GT.10.0) GO TO 110
      GO TO 100
  110 RETURN
      END


$IBFTC PUNCH
      SUBROUTINE CARD   (IH,IK,IL,E,E2,E2M1,SINT,CONK)
      IF (E.LT.1.4) GO TO 10
      W-ITE (6,11) IH,IK,IL,E,E2,E2M1,SINT,CONK
   11 FORMAT (1H$,3I4,5F9.4)
   10 RETURN
      END


$IBFTC -ANGES
      SUBROUTINE RANSET (N,SINMAX,S   ,SM   )
      DIMENSION S(30),SM(30),S3(30),S3MEAN(30)
C
C     SINMAX IS THE MAXIMUM SIN(THETA) . THIS SET UP IS FOR 3-D ONLY
    1 FORMAT(1H0,25H THE NUMBER OF RANGES IS I5//,27H THE MAXIMUM SIN(TH
     1ETA) IS F9.4////)
    2 FORMAT(1H0,5X,5HRANGE,8X,7HSINT**3,6X,8HMEANS**3,9X,4HSINT,9X,9HME
     1AN SINT//)
    3 FORMAT(1H ,I10,4(5X,F10.5))
    4 FORMAT(1H1,48H RANSET HAS BEEN CALLED FOR GENERATION OF RANGES)
      WRITE(6,4)
      ZN = N
      S3MAX = (SINMAX)**3
      S3IN1 = (S3MAX)/ZN
      S3IN2 = S3IN1/2.0
      SMIN = 0.0
      DO 100 I = 1,N
      ZI = I
      S3(I) = SMIN + (S3IN1*ZI)
      S(I) = (S3(I))**0.333333
      S3MEAN(I) = S3(I) - S3IN2
      SM(I) = (S3MEAN(I))**0.333333
  100 CONTINUE
      WRITE(6,1)  N,SINMAX
      WRITE(6,2)
      DO 101 I = 1,N
      WRITE(6,3) I,S3(I),S3MEAN(I),S(I),SM(I)
```

```
  101 CONTINUE
      RETURN
      END


$IBFTC SETUP 1
      SUBROUTINE FOUR1 (NFOUR,RCP)
C
C THIS SETS UP REC. DATA ON NFOUR -- REQUIRED FOR SHARPENED PATTERSON
C
      DIMENSION RCP(6)
      REWIND NFOUR
      WRITE(NFOUR) (RCP(I),I=1,6)
      WRITE(6,1) NFOUR
    1 FORMAT(1H0,47H*** RECIPROCAL CELL DATA IS WRITTEN ON LOGICAL I5)
      RETURN
      END


$IBFTC SETUP2
      SUBROUTINE FOUR2 (IH,IK,IL,E,E2M1,SINT,ID,FOBS,NFOUR,EPSI)
      DIMENSION FM(20)
C
C     THIS SET UP IS THE  MAIN ONE FOR DATA FOR A SUBSIQUENT SHARPENED
C           AND ORIGIN REMOVED SHARPENED PATTERSON
C
      FH=IH
      FK=IK
      FL=IL
      YC=0.0
      AC=0.0
      BO=0.0
      BC=0.0
      SIGYO=0.0
      Q=1.0
      RHO=0.0
      DO 100 I=1,10
      FM(I)=0.0
  100 CONTINUE
      QE2 = EPSI * E * E
      Q = SQRT( QE2)
      Q2M1 = QE2 - 1.0
      W-ITE(NFOUR) FH,FK,FL,Q,YC,Q2M1,AC,BO,BC,SIGYO,Q,ID,RHO,
     1 SINT,(FM(I),I=1,10)
      IF(IH.NE.999) GO TO 101
      WRITE(6,102)
  102 FORMAT(1H0,49HIH=999 IS REACHED AND TRANSFER COMPLETE TO FOUR2 )
      END FILE NFOUR
      REWIND NFOUR
  101 RETURN
      END
```

```
$IBFTC SYST
      SUBROUTINE SYSTAB (IH,IK,IL,EPSI)
C
C     P21/C
C
      IF(IK.EQ.0)  GO TO 101
      IF(IH.NE.0)  GO TO 102
      IF(IL.NE.0)  GO TO 102
  101 EPSI = 2.0
      GO TO 100
  102 EPSI = 1.0
  100 RETURN
      END
```

560*CARDS