Table 5 (cont.)

hkl	β compound $F_{obs.}$	$F_{calc.}$	α compound $F_{obs.}$	$F_{calc.}$	hkl	β compound $F_{obs.}$	$F_{calc.}$	α compound $F_{obs.}$	$F_{calc.}$
$\bar{4}04$	51	−49	<17	3	106	33	−50	20	−23
504	36	−47	21	−23	$\bar{1}06$	36	55	46	44
$\bar{5}04$	55	−57	61	−64	206	<13	−10	28	−25
604	21	19	—	—	$\bar{2}06$	20	15	24	14
$\bar{6}04$	23	22	51	−51	306	29	55	—	—
704	22	30	—	—	$\bar{3}06$	48	−58	46	−43
$\bar{7}04$	60	49	22	14	406	18	28	—	—
$\bar{8}04$	<20	−4	59	46	$\bar{4}06$	36	−48	54	−59
$\bar{9}04$	47	−38	18	19	506	13	−29	—	—
					$\bar{5}06$	19	21	<12	−14
105	35	−50	48	−49	$\bar{6}06$	36	40	27	26
$\bar{1}05$	27	41	57	50	$\bar{7}06$	<11	−5	22	35
205	33	46	19	−11	$\bar{8}06$	22	−31	—	—
$\bar{2}05$	60	46	82	79					
305	36	59	27	23	107	10	−33	—	—
$\bar{3}05$	<14	−13	14	2	$\bar{1}07$	24	37	21	19
405	<10	−6	29	31	207	14	−35	—	—
$\bar{4}05$	69	−84	46	−53	$\bar{2}07$	<12	−15	23	−20
505	34	−50	—	—	307	<8	16	—	—
$\bar{5}05$	20	−16	54	−61	$\bar{3}07$	27	−48	47	−38
605	10	−7	—	—	407	<15	32	—	—
$\bar{6}05$	45	43	<19	−17	$\bar{4}07$	<12	−7	22	−19
705	15	18	25	38	507	30	47	22	27
$\bar{8}05$	27	−29	21	19	$\bar{6}07$	19	22	37	31
$\bar{9}05$	29	−33	—	—	$\bar{7}07$	15	27	—	—

A Refinement of the Crystal Structure Analysis of β-Isoprene Sulphone

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The results of the crystal structure analysis of β-isoprene sulphone published in 1942 have been corrected for the termination-of-series errors. These corrections are considerable, producing changes in the atomic co-ordinates up to 0·06 A. and comparable amendment of the interatomic distances. The new C–C bond lengths are 1·47 A. for the two formal single bonds and 1·38 A. for the double bond. The mean C–S bond length is 1·74 A., and the S–O bond length is 1·44 A. A calculation of the standard deviation of these values indicates that with the exception of the S–O and C–C double bond lengths they are significantly different from the bond lengths associated with the normal representation of the molecule. There is some evidence to show that methylene groups are often 'activated' by adjacent sulphone groups, and the shortening of the formal single bonds may be a general feature of such molecules; but further experimental evidence is necessary.

Introduction

The crystal structure analysis of β-isoprene sulphone by Cox & Jeffrey (1942) revealed a heterocyclic ring compound in which the characters of the bonds were not adequately described by the usual representation (I). Instead of interatomic distances corresponding

(I)
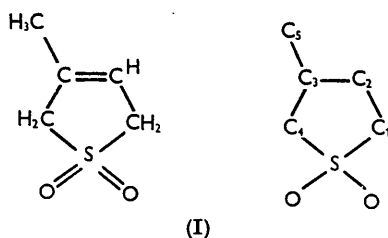
closely to integral bond orders, the values which they deduced from the Fourier synthesis of the X-ray data were

$$C_1-C_2 = C_3-C_4 = 1\cdot41, \quad C_2-C_3 = 1\cdot42, \quad C_3-C_5 = 1\cdot54 \text{ A.},$$

$$C_1-S = 1\cdot74, \quad C_4-S = 1\cdot75 \text{ A.},$$

$$S-O = 1\cdot44 \text{ A.}$$

Only the lengths of the bonds external to the ring agreed within the estimated experimental error with the standard values of 1·545 A. for a carbon single bond, 1·34 A. for a carbon double bond, and 1·43 A. for a S–O double bond. The C–C bonds in the ring showed the largest discrepancies, which amounted to a decrease of 0·13 A. in the length of the bonds represented as single, and an increase of 0·08 A. in the formal double bond. The

C–S bonds also appeared to be significantly shortened, but this was less certain since the length of the single bond of unit order was not accurately known within the limits 1·78–1·82 A.

The convergence of the C–C bond lengths towards a mean value close to the 1·39 A. of benzene suggested analogy with a conjugated system of alternate double and single bonds. It was proposed that the molecule should be described as a resonance hybrid of (I) with (II) and (III).

(II)   (III)
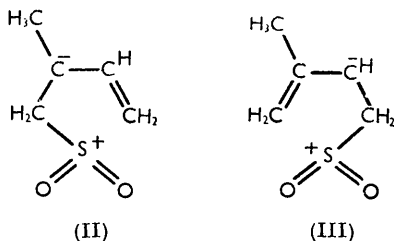
In order to account for the observed bond lengths, all three states must contribute equally. This was not entirely satisfactory, for it would be expected that (II) and (III) should be considerably less stable than (I). Furthermore, it was difficult to understand why there should be a transference of electron density from the sulphur atom to the system of carbon atoms.

Subsequent advances in the theoretical treatment of molecular structure (e.g. Coulson, 1947) indicate that this representation is unsatisfactory as a means of describing the electron distribution in the molecule, and there appeared to be no adequate explanation of the results as published in 1942.

During the last few years, however, important contributions have been made towards a better understanding of the factors which introduce systematic errors into the measurement of bond lengths by the X-ray Fourier synthesis methods (the same systematic errors will influence the results of electron diffraction measurements (Viervoll, 1947; Cruickshank & Viervoll, 1949)). It was shown by Cruickshank (1949) that in the structure analysis of the hydrocarbon dibenzyl, the systematic 'termination-of-series' errors were as large as 0·03 A., although the random errors from the uncertainty in the experimental measurements alone were estimated to be only ± 0·01 A. In a structure containing an atom heavy in comparison with its neighbours the effect may be greater and errors up to 0·05 A. may arise in locating the positions of the lighter atoms. Fortunately, it is possible to correct for these termination-of-series errors to a close approximation by a method suggested by Booth (1946), although the calculation of these corrections adds more to the already considerable amount of computational work required to obtain an accurate three-dimensional electron-density distribution in a crystal structure; this is an obstacle which has been overcome in these laboratories by the establishment of a computing section using Hollerith equipment as an auxiliary to the X-ray crystal-structure analysis. In the crystal-structure analysis by Cox, Gillot & Jeffrey (1949) of thiophthen, which resembles isoprene sulphone in that it contains a heterocyclic ring with one sulphur and four carbon atoms, these systematic errors affected some of the bond lengths to the extent of 0·03 A. Corrections of the same order were expected for the isoprene sulphone. A recent study of the accuracy of X-ray structure analysis by Cox & Cruickshank (1949) and by Cruickshank (1949) also made it possible to give some quantitative estimate of the reliability of the final results.

Method of refinement of the atomic parameters

(1) The Fourier syntheses for the electron density and its first and second differentials at points close to the maxima were calculated by the Hollerith punched-card system of Cox, Gross & Jeffrey (1949). The atomic co-ordinates used were those derived in the earlier work. Owing to the special positions of the sulphur and carbon atoms on the mirror plane at $y = \frac{1}{4}$, the computations were much simpler than for the general case. With the assumption of spherical symmetry about the peak maxima, the formulae given by Booth (1948) were used to calculate the small deviations of the peak maxima from the points at which the series were evaluated. This gave a more accurate set of atomic co-ordinates for all the atoms with the exception of the oxygen atoms.

(2) The method of estimating the 'termination-of-series' corrections to be applied to the 'observed' atomic co-ordinates is to examine the corresponding Fourier syntheses with the calculated structure factors as coefficients. The more closely the atomic scattering factors used in calculating the structure factors approximate to the 'observed' the more exact are the termination-of-series corrections.

Since there are three types of atom in the structure it was not possible to deduce experimental scattering-factor curves, as was done when calculating these corrections for the dibenzyl and thiophthen analyses. For more complicated structures this lack of information about the scattering factors and the need to assume spherical atomic symmetry may indeed impose severe limitations on the application of the method. In this analysis the best correspondence in the peak heights was obtained using the sulphur scattering factors from thiophthen and the carbon curves from dibenzyl; the thiophthen carbon values gave relatively too high maxima and tended to underestimate the corrections. The structure factors for all observed reflexions were therefore calculated from these f curves, and with 1·33 of the carbon factors for the oxygen atoms. The trigonometric data already on the Hollerith cards were used, and these were printed out into a convenient tabular form for the completion of the structure-factor calculations with the ordinary desk-type calculating machines.

With the calculated structure factors as coefficients, a Fourier synthesis at the level $y=0\cdot250$ was computed at 60ths of the cell edges in the regions close to the maxima. The positions of the maxima were deduced graphically and comparison with the atomic parameters from which the structure factors were calculated gave the magnitude and direction of the termination-of-series errors.

(3) A Fourier synthesis at $y=0\cdot250$ in 60ths was also evaluated, using the *observed* structure factors in order to compare the graphical method of locating peak maxima with the differential method. As was expected, the results showed very close agreement.

The computations of all the Fourier syntheses were done with the Hollerith equipment at an accuracy which eliminated any significant rounding-off errors.

The oxygen parameters were examined separately by computing section and line Fourier syntheses with the observed and calculated structure factors.

Results

The results of this investigation are summarized in Tables 1, 2 and 3. The parameters of the electron-density maxima at the various stages of the analysis are given in Table 1; column A refers to the original co-ordinates of Cox & Jeffrey (1942), columns B to the new co-ordinates *without* termination-of-series corrections, column C to the new co-ordinates *with* termination-of-series corrections. The refinement of the structure is discussed below in terms of the results as shown in Table 1.

The Fourier series from which the parameters A and B were derived are not strictly comparable. The structure-factor calculations using the thiophthen and dibenzyl scattering factors introduced two sign changes, and two terms for which the intensity measurements were inconsistent (planes 461 and 46$\bar{3}$) were omitted from the new synthesis. These differences and the exclusion of rounding-off errors account for the differences of the order of 0·02 A. between the co-ordinates A and B.

Table 2. *Bond lengths and angles corresponding to the final co-ordinates of the structure refinement*

S–O	$1\cdot43_6$ A.	C_1–S–C_4	98·3°
S–C_1	$1\cdot75_9$	S–C_1–C_2	104·2°
S–C_4	$1\cdot74_4$	S–C_4–C_3	106·3°
C_1–C_2	$1\cdot47_4$	C_1–C_2–C_3	117·0°
C_2–C_3	$1\cdot37_6$	C_2–C_3–C_4	114·2°
C_3–C_4	$1\cdot47_1$	C_2–C_3–C_5	124·5°
C_3–C_5	$1\cdot52_3$	C_4–C_3–C_5	121·0°

Table 3. *Final atomic positions in fractional co-ordinates referred to monoclinic axes*

	x	y	z
C_1	0·1144	0·250	0·2042
C_2	0·2775	0·250	0·4195
C_3	0·4866	0·250	0·4316
C_4	0·5158	0·250	0·2234
C_5	0·6762	0·250	0·6392
S	0·2614	0·250	0·0311
O_1	0·2233	0·0933	−0·0940
O_2	0·2233	0·4067	−0·0940

The differential and Fourier syntheses from which B_1 and B_2 were derived are comparable, since they were calculated with identical coefficients. The largest discrepancies, 0·010 and 0·006 A., occur at those atoms where the point of summation of the differential synthesis was furthest from the maximum, i.e. 0·036 and 0·023 A. This suggests that for these particular parameters the Fourier values are more accurate, and that

Table 1. *Parameters of electron-density maxima*

$a=6\cdot703$, $b=7\cdot667$, $c=6\cdot679$ A., $\beta=110°\ 16'$.
Space group, $P2_1/m$. $Z=2$.
The atomic co-ordinates are in Ångström units referred to the a axis and c' perpendicular to a.

X	A	B_1	B_2	(B_1-B_2)	D	$(A-D)$	C
C_1	0·335	0·315	0·317	0·002	0·358	−0·023	0·294
C_2	0·906	0·898	0·899	0·001	0·916	−0·010	0·889
C_3	2·304	2·327	2·322	0·005	2·363	−0·059	2·263
C_4	2·963	2·964	2·964	0·000	2·986	−0·023	2·941
C_5	3·066	3·031	3·041	0·010	3·053	+0·013	3·054
S	1·684	1·678	1·678	0·000	1·682	+0·002	1·680
O	1·735		1·705		1·725	+0·010	1·715
Z							
C_1	1·271	1·274	1·279	0·005	1·271	0·000	1·279
C_2	2·555	2·572	2·575	0·003	2·503	+0·052	2·627
C_3	2·655	2·678	2·672	0·006	2·623	+0·032	2·704
C_4	1·415	1·412	1·408	0·004	1·424	−0·009	1·399
C_5	4·002	4·012	4·012	0·000	4·010	−0·008	4·004
S	0·195	0·196	0·197	0·001	0·197	−0·002	0·195
O	−0·595		−0·576		−0·582	−0·013	−0·589
Y							
O	0·728		0·741		0·754	−0·026	0·715

A, original atomic co-ordinates.
B_1, co-ordinates from differential synthesis of observed F's.
B_2, co-ordinates from Fourier synthesis at $(x, \frac{1}{4}, z)$ in 60ths with observed F's.
D, co-ordinates from Fourier synthesis at $(x, \frac{1}{4}, z)$ in 60ths with calculated F's.
$(A-D)$, termination-of-series corrections.
C, final co-ordinates corrected for termination-of-series errors.

in general for the refinement of atomic co-ordinates by the differential method, using the simplifying assumption of spherical symmetry around the maxima, a shift of greater than 0·04 A. requires a second differential refinement. Excluding these two values, the mean difference is less than 0·002 A.

The termination-of-series errors, given by $A - D$, are considerable, with the largest value 0·060 A., and the mean 0·020 A.; they are, in fact, approximately twice as large as those found in the thiophthen structure analysis. When applied as corrections to the co-ordinates B_2, the final co-ordinates C are obtained. The corresponding final molecular dimensions are shown in Table 2.

The accuracy of the bond lengths

With the correction for the termination-of-series errors, there remain the random errors which are due to the experimental errors in the intensity measurements and to the method of correcting for the finite series. These random errors can be estimated by the method of Cox & Cruickshank (1949) from the curvature of the electron density peaks and the agreement between the observed and calculated structure factors. The values so obtained for the standard deviations of the carbon atomic co-ordinates were

$$\sigma_x = 0·016, \quad \sigma_z = 0·017 \text{ A.},$$

and for the sulphur atomic co-ordinates

$$\sigma_x = 0·0035, \quad \sigma_z = 0·0039 \text{ A.}$$

The standard deviations for the bonds are approximately

$$0·023 \text{ A. for C–C,} \quad \text{and} \quad 0·017 \text{ A. for C–S.}$$

With these figures, the conventional significance tests can be used to discuss the final results shown in Table 2 by means of the formula

$$P = 1 - \text{erf}\left(\frac{1}{\sqrt{2}} \cdot \frac{\Delta}{\sigma}\right),$$

where P is the probability that the difference Δ is due to random errors (Cruickshank, 1950). The values for P corresponding to the differences between the observed values and 'standard' values are shown in Table 4. On this basis, the C_1–C_2, C_3–C_4 bond lengths are significantly shorter than the 'standard' diamond value, whereas the C_3–C_5 is not. The difference between the length of the formal double bond C_2–C_3 and a 'standard' ethylene bond length is not significant. The C–S bonds

are not significantly different from the mean value of 1·751 A., which, is, however, *highly* significant when compared with a standard length of 1·81 A. (cf. Cox & Jeffrey, 1950). The S–O bond length of 1·436 A., with a standard deviation approximately the same as for the C–S, is in close agreement with the measurements from other molecules (see below).

Since the mirror plane of symmetry of the molecule coincides with the crystallographic mirror plane of the space group $P2_1/m$, it is not possible to use deviations from planarity as an independent means of estimating the accuracy. The angles S–C_1–C_2 and S–C_4–C_3, C_1–C_2–C_3 and C_2–C_3–C_4 are equal within $\pm 1\frac{1}{2}°$, and the almost chemically equivalent C_1–C_2 and C_3–C_4, S–C_1 and S–C_4 are within $\pm 0·01$ A. This self-consistency of the molecular dimensions lies well within the limits estimated from the standard deviations, whereby the bond-length differences corresponding to $P = 0·01$ (significant) and 0·05 (possibly significant) are 0·059 and 0·045 A. respectively for the C–C bonds.

The significant shortening of the C–C single bonds as compared with the diamond single bond might well be accompanied by a lengthening of the double bond, as is theoretically predicted for conjugated molecules. Although the results actually reveal a bond 0·036 A. longer than the standard value, these statistical estimates suggest that this may be an experimental error, and little weight should be attached to the observation.

Discussion of the molecular structure

The results of this investigation show that although the molecular structure is closer to the formal representation (I) than was indicated by the results of the earlier work, nevertheless the C–C single bonds in the heterocyclic ring have lengths which are significantly shorter than the value of 1·54 A. normally associated with a single C–C bond. The C–S bonds are also significantly short as compared with a bond length of 1·81 A. They are of the same length as those in the thiophthen molecule, and if this effect is due to π bonding between the carbon and sulphur atoms the π bond order should be approximately 0·5, as shown by the theoretical calculations of Evans & de Heer (1949).

From the theoretical point of view there seems to be no obvious a priori reason to suspect that this should be so. The molecule has no conjugated double bonds as in thiophen and thiophthen, neither should the d electrons

Table 4. *Application of significance tests*

Bond	Observed length (A.)	Standard length (A.)	P	Significance levels
C_1–C_2	1·474	1·545	0·002	Significant
C_3–C_4	1·471	1·545	0·002	Significant
C_2–C_3	1·376	1·340	0·11	Not significant
C_3–C_5	1·523	1·545	0·34	Not significant
C_1–S	1·759	1·810	0·003	Significant
C_4–S	1·744	1·810	0·0001	Significant
Mean C–S	1·751	1·810	0·0005	Significant

of the sulphur atom be available for π bonding to the adjacent carbon atoms. The strain in the carbon valency angles of S–C$_1$–C$_2$ and S–C$_4$–C$_3$ from 110° to 105°, and C$_1$–C$_2$–C$_3$ and C$_2$–C$_3$–C$_4$ from 120 to 116°, seem insufficient alone to account for the shortening of the single bonds by as much as 0·07 A. There have been no experimental structure determinations either by X-rays or electron diffraction on unconjugated heterocyclic molecules with which these results can be compared.

The chemistry of these cyclic sulphones has, however, received some attention, particularly in relation to the tautomeric change into the α isomer discovered by Eigenberger (1931 *a, b*):


(I)   (II)   (III)
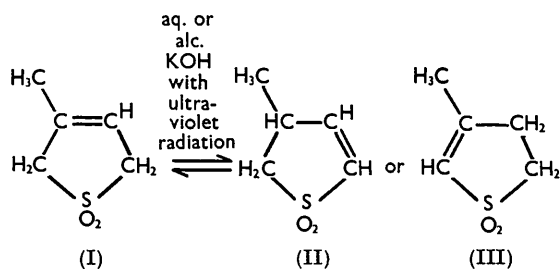
van Zuydewijn (1937) established the structure of the α isomer as either (II) or (III), probably the former, and showed that in 0·5 N-alcoholic KOH at 20–35° C. the equilibrium mixture contained 8·5 % of the β sulphone. This equilibrium can be approached from either side and the function of the ultra-violet radiation is merely to accelerate the isomerization. The same reaction takes place with β-butadiene sulphone (IV) giving (V). It

(IV)   (V)
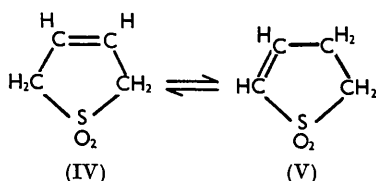
seems therefore that the cyclic sulphones of this type possess a potentially mobile hydrogen atom on the methylene group which can undergo this prototropic change.

Similar 'activation' of the methylene hydrogens by SO$_2$ groups was studied by Shriner, Struck & Jorison (1930) who showed that compounds of the type
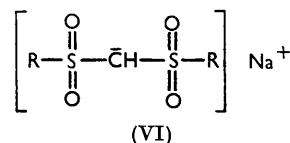
$$\phi.SO_2.CH_2.\phi, \quad \phi.CH_2.SO_2.CH_2.\phi,$$

and $$\phi.SO_2.CH_2.SO_2.\phi$$
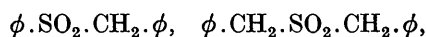
slowly reacted with sodium and sodium ethylate with

salt formation (VI) (although the corresponding sulphoxides do not):

(VI)

In this reaction the sulphones somewhat resemble diketones, but Rothstein (1937) considers that whereas in diketones the reaction takes place through enolization, in these compounds the explanation must lie in some delocalization of the C–H bonding electrons. Rothstein (1937) also investigated the equilibrium

$$CH_2.\phi.SO_2.CH=CH.CH_2.SO_2.Et$$

$$\rightleftharpoons CH_2.\phi.SO_2.CH_2.CH=CHSO_2Et,$$
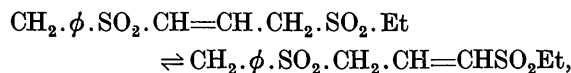
and ascribed the effect again to hyperconjugation in the three-carbon unsaturated system when terminated by sulphonyl groups.

In discussing the structure of β-isoprene sulphone, Koch (1949), basing his arguments on the unrevised bond lengths, the ultra-violet absorption spectrum and the methylenic reactivity, postulates the existence of extensive hyperconjugation, formally expressed in (VIIa) and (VIIb):

(VIIa)   (VIIb)
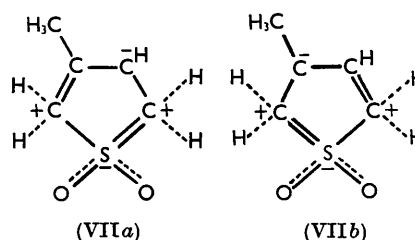
The C–C bond lengths now reported in this paper are certainly more in keeping than were the original values with the magnitude of the bond shortening to be expected for the acceptor bonds of hyperconjugation, although it still seems unlikely that this can be the complete explanation.

The S–O bond length of 1·436 A. is 0·05 A. shorter than the sum of the Pauling covalent radii for double-bonded atoms. It is consistent with the remarkably constant values reported for S–O bonds in other molecules and gives no support to a description other than a pure double bond (Table 5).

While the chemical evidence definitely shows that sulphones with unsaturated hydrocarbon systems undergo reactions which support their possessing some

Table 5. S–O *bond lengths*

1·433 A.	SO$_2$	Spectroscopy; Dailey, Golden & Wilson (1947)
1·43	SO$_3$	Electron diffraction; Palmer (1938)
1·45	SOCl$_2$	Electron diffraction; Palmer (1938)
1·43	SO$_2$Cl$_2$	Electron diffraction; Palmer (1938)
1·43	SO$_2$F$_2$	Electron diffraction; Stevenson & Russell (1939)
1·43	K.SO$_3$NH$_2$	X-rays; Brown & Cox (1940)
1·43	K$_2$SO$_3$N$_2$O$_2$	X-rays Cox; Jeffrey & Stadler (1949)

unusual features in their molecular structures, isoprene sulphone, thiophen and thiophthen are the only hetero-cyclic sulphur compounds whose molecular dimensions have hitherto been investigated in detail, and the present requirement seems to be for further structure studies of molecules of a similar type.

Crystallographic data for α-isoprene sulphone

Orthorhombic; $a = 10 \cdot 58$, $b = 7 \cdot 85$, $c = 7 \cdot 68$ A.

$$D_m = 1 \cdot 37, \quad D_X = 1 \cdot 375, \quad N = 4.$$

Absent spectra: $(0kl)$ absent for k odd, $(h0l)$ absent for $h + l$ odd.

Space group: Pbn or $Pbnm$, probably the former with no molecular symmetry.

I wish to thank Prof. E. G. Cox for his interest and criticism and for the computing facilities available in his laboratories, and Mr Greenhalgh for operating the Hollerith equipment.

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Interpretation of the Patterson Synthesis: Rubidium Benzyl Penicillin

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In substances containing a heavy atom, and suitable multiplicity in the space-group symmetry, the Patterson function may be used directly, by the 'Vector Convergence Method', to give approximate positions of the lighter atoms in the crystal structure. The method is here illustrated by application to the case of rubidium benzyl penicillin. The three-dimensional Patterson function has been calculated and the vectors to the penicillin molecule from the four Rubidium atoms in the unit cell have been studied by construction of 'Vector Convergence Density' maps in three-dimensional space. A fair degree of correlation has been found between these results and the known structure of the crystal.

Introduction

In a recent short communication (Beevers & Robertson, 1950), a technique for interpretation of the three-dimensional Patterson synthesis, the 'Vector Convergence Method', was discussed, and its use in the analysis of the structure of strychnine hydrobromide was mentioned. It was pointed out that the method was applicable when a heavy atom is present, and when the space group confers multiplicity on the crystal

structure, e.g. when, as for $P2_12_12_1$, there are four equivalent points in the unit cell.

It is interesting to note the connexions which exist between this method, which arose as a practical expedient in the course of work on an actual structure solution, and the largely theoretical approach which was the subject of a recent paper by Buerger (1950). As was pointed out very clearly in this paper, the Patterson function, or vector set, contains n images of