Ergebnisse

Die Struktur des Na-Kurrol *A* ist weitgehend der Struktur des $(AgPO_3)_x$ (Jost, 1960) analog und hat also folgendes Bauprinzip. Anion: Spiralig gewundene parallel *y* laufende PO_4-Tetraederketten (Fig. 1), 4 Tetraeder pro Windung, Ganghöhe der Spirale gleich der Gitterkonstanten *b*. Na^+-Ionen: Von 5 Sauerstoffatomen umgeben (Fig. 3), von diesen gehören 3 zur einen Nachbar-Kette, die beiden anderen zu je einer der beiden anderen Nachbar-Ketten. Der spiralige Bau der PO_4-Ketten bestätigt eine Vermutung von Thilo, Schulz & Wichmann (1953).

Alle P–O-Bindungen (Fig. 2) sind beim Na-Kurrol *A* um etwa 0,02 Å länger als beim $(AgPO_3)_x$. In der Kette der –P–O–P–... Bindungen wechseln lange und kurze Bindungen ab. Die Unterschiede in der Länge sind verglichen mit dem mittleren Fehler σ der Bindungslänge hinreichend gross, um sie als reell anzusehen (Lipson & Cochran, 1953, p. 309). Das Alternieren langer und kurzer Bindungen wurde auch beim $(AgPO_3)_x$ beobachtet, nur war dort der mittlere Fehler der Bindungslänge zu gross, um diese Beobachtung als gesichert anzusehen. Kantenlängen der PO_4-Tetraeder siehe Tabelle 3. Die Volumina der Maxima von P und O unter Berücksichtigung von $F(000)$, deuten darauf hin, dass beide Atome mindestens in guter Näherung neutral sind. Der kleinste Na^+–Na^+-Abstand beträgt 3,51 Å.

Tabelle 3. *Kantenlängen der* PO_4*-Tetraeder (vgl. Fig.* 3)

Tetraeder um P_1		Tetraeder um P_2	
$O'_{21}O_{12}$	2,46 Å	$O_{12}O_{21}$	2,44 Å
$O_{11}O'_{21}$	2,43	$O_{22}O_{21}$	2,49
$O_{13}O'_{21}$	2,54	$O_{23}O_{21}$	2,53
$O_{11}O_{12}$	2,57	$O_{22}O_{12}$	2,52
$O_{13}O_{12}$	2,60	$O_{23}O_{12}$	2,50
$O_{11}O_{13}$	2,49	$O_{22}O_{23}$	2,50

Die Arbeit wurde durch Herrn Prof. E. Thilo angeregt, dem ich ebenso wie Frau Prof. Boll-Dornberger für Diskussionen herzlich danke.

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Literatur

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Bertaut, E. F. (1958). *Fortschr. Min.* **36**, 119.

Corbridge, D. E. C. (1955). *Acta Cryst.* **8**, 520.

Dornberger-Schiff, K., Liebau, F. & Thilo, E. (1955). *Acta Cryst.* **8**, 752.

Dornberger-Schiff, K. (1956). *Ang. Chem.* **68**, 755.

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

Hartree, B. R. & Hartree, W. (1948). *Proc. Roy. Soc.* A, **193**, 299.

Hartree, B. R., Hartree, W. & Swirles, B. (1939). *Philos. Trans.* A, **238**, 229.

Jost, K. H. (1960). *Acta Cryst.* (Im Druck.)

Lipson, H. & Cochran, W. (1953). *The Determination of Crystal Structures.* London: MacMillan.

Plieth, H. & Wurster, Chr. (1951). *Z. anorg. Chem.* **267**, 49.

Thilo, E., Schulz, G. & Wichmann, E. M. (1953). *Z. anorg. Chem.* **272**, 182.

Tomiic, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Acta Cryst. (1961). **14**, 847

The Molecular and Crystal Structure of 2-Benzoylimino-3-Methylthiazolid-5-One

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It is established that the compound obtained from acid-catalyzed cyclisation of the derivatives of N-benzoylthiocarbamoylsarcosine is 2-benzoylimino-3-methylthiazolid-5-one and that the molecules, although not strictly planar, are arranged substantially in layers which are parallel to the $(10\bar{1})$ planes. The crystal, the structure of which is obtained by direct methods, is monoclinic with space group $P2_1/c$, having a unit-cell with

$$a=7{\cdot}45,\ b=12{\cdot}10,\ c=12{\cdot}10\ \text{Å},\ \beta=95°.$$

Introduction

From one of a series of degradative studies on peptides and proteins Elmore & Toseland (1956) concluded that N-benzoylthiocarbamoyl-N-phenylglycine and its derivatives were cyclised by trifluoroacetic acid to 3-benzoyl-1-phenyl-2-thiohydantoin, a compound which had been described previously by Douglass & Dains (1934). There is, however, an alternative mechanism of ring closure which leads to 2-benzoylimino-3-phenylthiazolid-5-one, but a choice of the former was first made because, in part, of supporting data from infra-red spectra (Elmore, 1959). In this later paper Elmore (1959) reports the outcome of a re-examination of the problem in which, in view of the similarity between the derivatives from both N-phenylglycine and sarcosine, he replaced acid–catalysed cyclisation of the derivatives of N-benzoylthiocarbamoyl-N-phenylglycine by acid–catalysed cyclisation of the derivatives of N-benzoylthiocarbamoylsarcosine. Had the mechanism of cyclisation been as previously postulated, namely that of ring closure on the nitrogen, then the process would have led to 3-benzoyl-1-methyl-2-thiohydantoin (Fig. 1(*a*)). However, the supporting evidence for this structure from the infrared investigation was now lacking and the only chemical evidence available indicated rather that the compound was 2-benzoylimino-3-methylthiazolid-5-one (Fig. 1(*b*)).

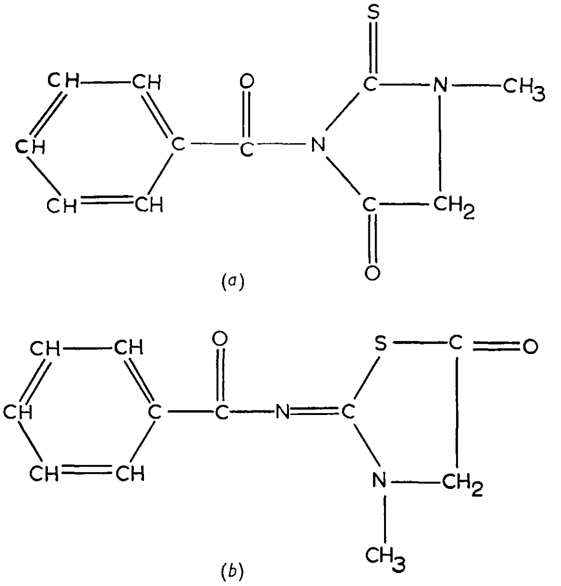


Fig. 1. Molecules obtained by alternative mechanisms of ring closure (*a*) 3-benzoyl-1-methyl-2-thiohydantoin, (*b*) 2-benzoylimino-3-methylthiazolid-5-one.

The present structure determination was undertaken in an attempt to resolve the problem.

Experimental details

It was established from oscillation and zero-layer-line Weissenberg photographs, obtained with Cu $K\alpha$ radiation, that the unit cell was monoclinic with

$$a=7\cdot45,\ b=12\cdot10,\ c=12\cdot10\ \text{Å};\ \beta=95^\circ,$$

the linear dimensions being determined to an accuracy of the order of $\pm\frac{1}{2}\%$. The space group was $P2_1/c$ and from a rough value of 1·35 g.cm.$^{-3}$ for the density of the compound it was calculated that there were four molecules in the unit cell.

Intensity data were collected by eye estimation of $0kl$ and $h0l$ Weissenberg photographs. The crystal was sufficiently small for absorption corrections to be negligible, but the Lorentz and polarization factors were applied and preliminary scaling and temperature factors were determined by Wilson's method (1942).

Determination of the trial structure

On a Patterson projection along [100] the fractional y and z coordinates of possible non-equivalent locations of the sulphur atom were (0·220, 0·033), (0·083, 0·050) and (0·058, 0·175) respectively. Further interpretation of the vector map was deferred, and subsequently found unnecessary, pending the outcome of an alternative direct method of approach described by Woolfson (1957). In applying this method those $0kl$ reflexions having suitably high unitary structure factors were selected and divided into groups (*a*), (*b*), (*c*) and (*d*) as shown in Table 1 and in addition weaker reflexions of mixed k and l indices were placed in the group (X); altogether there were fifty-nine terms whose signs were to be determined. (The reflexion 0,14,0 appears in group (X) because it made no contribution to the triple products obtained from group (*a*)). Utilizing the sign relationships that products of the type

$$S(k,l).S(k',l').S(k+k',l+l')$$

and

$$S(k,l).S(k',l').S(k-k',l-l')\,,$$

where $S(k,l)$ represents the sign of the $0kl$ reflexion, are probably positive, relationships of the kind $a_ra_sa_t$, $a_rb_sb_t$, $a_rc_sc_t$, $a_rd_sd_t$ and $b_rc_sd_t$ were determined, as also were those relating one of group (X) with two from a composite group containing all the reflexions in the groups (*a*), (*b*), (*c*) and (*d*). Seven triple products involving the structure invariants, i.e. those of type $a_ra_sa_t$, were obtained and it was assumed that five of these relationships would be satisfied; of forty-five sets of products of the non-arbitrary type $b_rc_sd_t$ it was assumed that thirty-three would hold.

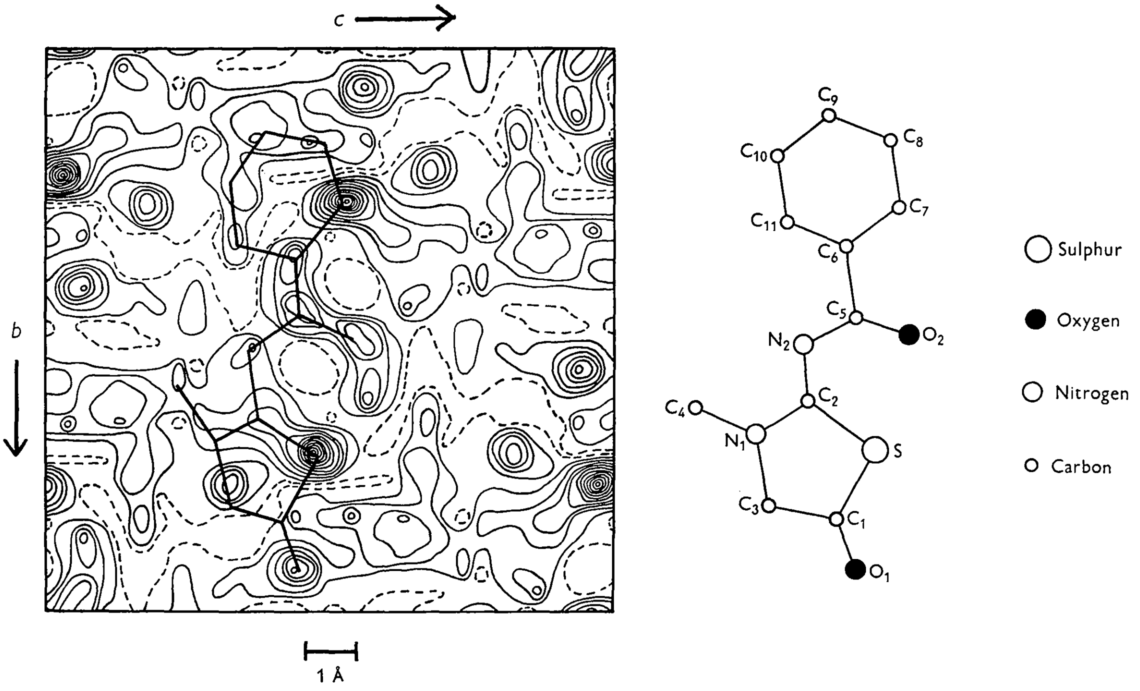
The procedure described by Woolfson (1957) for developing sets of signs from such data has been programmed by him for the Mercury computer and use of this programme produced five sets of signs for the fifty-nine reflexions considered. With the exception of one sign two of these sets were identical, so that it was necessary to plot only four electron-density maps and of these the most promising was that yielded by the two virtually identical sets (Fig. 2(*a*)). The y, z coordinates (0·225, 0·033) of the centre of the very high peak are in close agreement with the values (0·220, 0·033) derived from the Patterson projection as the coordinates of one of three probable

Table 1. *Division into groups of type* (*a*), (*b*), (*c*), (*d*) *and* (*X*) *of reflexions with suitable unitary structure factors, U*

Group (*a*)			Group (*b*)			Group (*c*)			Group (*d*)			Group (*X*)					
U	k even	*l* even	*U*	*k* odd	*l* odd	*U*	*k* odd	*l* even	*U*	*k* even	*l* odd	*U*	*k*	*l*	*U*	*k*	*l*
0·23	2	6	0·46	9	3	0·36	3	4	0·35	12	7	0·26	14	0	0·15	8	3
0·22	0	10	0·37	9	1	0·32	1	10	0·33	10	11	0·18	9	11	0·15	8	11
0·21	4	12	0·32	11	1	0·30	13	6	0·32	10	9	0·18	2	11	0·15	7	13
0·19	4	14	0·24	5	1	0·23	5	2	0·32	8	7	0·17	7	9	0·15	5	8
0·19	0	2	0·23	13	3	0·23	13	8	0·24	4	5	0·17	1	2	0·15	4	4
0·18	14	4	0·22	11	3	0·21	3	6	0·23	12	5	0·17	5	11	0·14	3	15
0·18	10	8	0·22	7	3	—	—	—	0·23	6	7	0·17	7	6	0·14	5	13
0·18	2	14	0·19	7	7	—	—	—	0·23	8	5	0·16	5	6	0·14	14	2
0·16	2	0	—	—	—	—	—	—	0·21	12	9	0·16	6	3	0·14	10	4
0·16	4	6	—	—	—	—	—	—	0·21	12	3	0·16	8	13	0·14	0	14
0·16	0	8	—	—	—	—	—	—	0·20	6	1	0·15	1	12	0·13	14	5
—	—	—	—	—	—	—	—	—	—	—	—	0·15	13	1	—	—	—

locations of the sulphur atom and, as can be seen in Fig. 2(*a*), by placing the sulphur atom on this peak it was possible to fit in projection the model of the molecule of 2-benzoylimino-3-methylthiazolid-5-one shown in Fig. 2(*b*) on to the peaks of the electron-density distribution. With this atomic arrangement, however, the value of F_c for the very strong 012 reflexion was almost zero, but this major discrepancy was removed by a 180° rotation of the molecule about an axis parallel to the C_5–C_6 direction so that both the sulphur atom and the benzene ring positions remained virtually unchanged; a Fourier synthesis calculated with the signs obtained from the coordinates of the trial structure also indicated a change of this nature.

In projection the molecule now straddled the centre of symmetry at $y=\frac{1}{2}$, $z=\frac{1}{2}$ in such a way that only atoms C4 and O2 were resolved and it was not surprising when, at this stage, it was found possible to postulate an equally plausible structure in which a projection of the molecule of 3-benzoyl-1-methyl-2-thiohydantoin also straddled the centre of symmetry. Two further stages of refinement of both structures



(*a*) (*b*)

Fig. 2. (*a*) Projection along [100] of the electron-density distribution calculated with the most plausible set of signs obtained from Woolfson's method of sign determination. Contours at arbitrary intervals with the zero contours shown as broken lines. (*b*) Model of the molecule of 2-benzoylimino-3-methylthiazolid-5-one which was constrained to fit the distribution shown in Fig. 2(*a*).

Table 2. *Comparison of observed and calculated structure factors*

0	*k*	*l*	$\|F_o\|$	F_c
0	1	1	53·2	55·2
0	2	0	64·5	−58·5
0	0	2	89·3	100·7
0	2	1	13·8	15·8
0	1	2	77·1	90·1
0	2	2	21·0	−19·4
0	3	1	22·8	25·0
0	1	3	11·1	−12·6
0	3	2	27·9	29·8
0	2	3	34·4	−37·2
0	4	0	30·1	22·1
0	0	4	37·3	36·0
0	4	1	13·3	14·8
0	1	4	36·6	−35·2
0	3	3	4·2	4·1
0	4	2	24·8	26·2
0	2	4	37·3	−36·2
0	4	3	7·3	−8·6
0	3	4	95·9	92·4
0	5	1	64·1	54·4
0	1	5	2·2	0·3
0	5	2	58·0	−48·2
0	2	5	4·4	−5·4
0	4	4	36·4	33·1
0	5	3	36·8	35·1
0	3	5	10·7	−12·4
0	6	0	9·1	4·3
0	0	6	13·1	15·3
0	6	1	43·4	−35·3
0	1	6	3·3	−4·3
0	6	2	3·5	1·5
0	2	6	47·9	−42·0
0	5	4	9·9	−8·6
0	4	5	50·2	48·9
0	6	3	29·9	−25·8
0	3	6	40·5	37·9
0	5	5	10·7	6·7
0	7	1	< 2·6	−2·2
0	1	7	3·7	8·5
0	6	4	20·5	−18·1
0	4	6	26·9	26·5
0	7	2	< 2·8	−4·8
0	2	7	< 2·8	−8·0
0	7	3	35·0	−29·8
0	3	7	3·5	−2·9
0	6	5	7·3	−7·1
0	5	6	< 3·0	−0·2
0	8	0	4·0	6·8
0	0	8	22·5	−23·7
0	7	4	10·7	10·9
0	4	7	7·5	9·5
0	8	1	15·8	12·6
0	1	8	18·3	−22·4
0	8	2	16·5	18·0
0	2	8	3·6	3·9
0	8	3	19·4	16·1
0	3	8	16·1	19·5
0	7	5	7·9	−8·5
0	5	7	5·5	5·8
0	6	6	< 3·2	2·7
0	8	4	< 3·2	−4·9
0	4	8	< 3·2	−0·4
0	9	1	43·4	38·3
0	1	9	14·4	−16·4
0	9	2	< 3·6	1·5
0	2	9	7·2	−10·0
0	7	6	18·3	21·0
0	6	7	26·0	−28·4
0	8	5	24·6	22·6
0	5	8	15·8	−17·6
0	9	3	50·8	47·0
0	3	9	4·6	3·5
0	9	4	< 3·6	3·6
0	4	9	7·9	8·0
0	7	7	19·4	−19·0
0	8	6	< 3·6	−3·5
0	6	8	6·7	−4·7
0	10	0	4·8	1·2
0	0	10	22·1	−24·6
0	10	1	9·1	−10·5
0	1	10	31·3	−32·2
0	10	2	10·6	8·6
0	2	10	13·1	−13·4
0	9	5	7·9	8·8
0	5	9	5·1	−6·0
0	10	3	8·6	5·2
0	3	10	10·3	12·5
0	8	7	27·3	29·5
0	7	8	7·6	5·4
0	9	6	< 3·6	−3·9
0	6	9	9·8	−13·3
0	10	4	11·8	11·8
0	4	10	< 3·6	−8·1
0	11	1	23·4	−22·9
0	1	11	8·1	−7·4
0	11	2	< 3·9	−1·8
0	2	11	14·0	−14·0
0	10	5	4·2	2·1
0	5	10	7·7	−9·9
0	8	8	5·4	−4·8
0	9	7	< 3·6	−4·7
0	7	9	12·9	−12·1
0	11	3	17·1	−16·1
0	3	11	< 3·6	−3·4
0	10	6	5·3	−3·8
0	6	10	< 3·6	5·7
0	11	4	< 3·6	−0·3
0	4	11	6·3	9·7
0	12	0	< 3·6	−5·2
0	0	12	< 3·6	−5·7
0	12	1	< 3·6	3·7
0	1	12	10·4	−9·4
0	12	2	< 3·6	0·2
0	2	12	< 3·6	2·9
0	11	5	6·6	−6·5
0	5	11	11·1	−11·9
0	9	8	5·8	−3·3
0	8	9	6·6	8·1
0	10	7	8·5	−9·9
0	7	10	< 3·4	2·7
0	12	3	13·1	11·9
0	3	12	< 3·4	4·9
0	11	6	< 3·4	1·9
0	6	11	< 3·4	−3·3
0	12	4	6·4	3·3
0	4	12	12·6	−12·4
0	9	9	< 3·4	−4·5
0	10	8	10·2	−7·3
0	8	10	< 3·4	−3·4
0	12	5	12·9	13·1
0	5	12	< 3·4	−2·3
0	13	1	8·5	8·9
0	1	13	< 3·4	1·9
0	11	7	6·6	−5·7
0	7	11	< 3·4	3·9
0	13	2	5·3	3·6
0	2	13	< 3·4	2·3
0	13	3	11·8	11·8
0	3	13	< 3·2	2·0
0	12	6	< 3·2	−4·7
0	6	12	< 3·2	5·7
0	10	9	16·2	−14·2
0	9	10	5·0	−2·4
0	13	4	12·0	10·0
0	4	13	4·9	4·5
0	11	8	5·9	−5·3
0	8	11	7·3	8·2
0	12	7	16·2	14·8
0	7	12	5·7	6·1
0	13	5	6·0	5·0
0	5	13	6·7	−9·2
0	14	0	11·7	10·3
0	0	14	6·2	−6·3
0	14	1	< 2·7	−0·7
0	1	14	4·5	−4·3
0	14	2	6·2	6·6
0	2	14	7·7	10·0
0	10	10	< 2·6	0·7
0	11	9	< 2·6	2·3
0	9	11	7·7	−8·3
0	13	6	12·6	10·1
0	6	13	< 2·6	−1·4
0	14	3	< 2·6	−3·3
0	3	14	< 2·6	0·5
0	12	8	< 2·6	−3·8
0	8	12	< 2·6	−3·0
0	14	4	7·3	6·6
0	4	14	7·6	−7·9
0	13	7	< 2·3	0·2
0	7	13	5·8	7·7
0	11	10	< 2·3	−1·5
0	10	11	12·2	10·7
0	14	5	5·1	−6·1
0	5	14	6·8	−4·3
0	15	1	4·0	−4·1
0	1	15	< 2·1	−0·4
0	12	9	7·5	7·2
0	9	12	< 2·1	0·1
0	15	2	< 2·1	0·7
0	2	15	< 2·1	0·3
0	15	3	< 1·7	−1·7
0	3	15	5·0	6·9
0	14	6	< 1·7	0·5
0	6	14	4·8	6·3
0	13	8	7·9	7·1
0	8	13	5·4	5·7
0	15	4	3·0	− 3·7
0	4	15	< 1·2	−1·4
0	11	11	2·3	5·6

h	0	*l*	$\|F_o\|$	F_c
1	0	0	24·2	20·8
0	0	2	101·9	102·1
1	0	$\bar{2}$	28·2	22·8
1	0	2	31·1	−37·5
2	0	0	110·2	−116·9
2	0	$\bar{2}$	292	−303
2	0	2	25·4	−23·5
0	0	4	48·0	46·8
1	0	$\bar{4}$	21·1	14·7
1	0	4	36·6	38·7
3	0	0	23·9	32·2
2	0	$\bar{4}$	46·8	−38·6
3	0	$\bar{2}$	33·0	−31·8
2	0	4	29·2	−27·5
3	0	2	5·8	−12·4
0	0	6	21·7	18·2
3	0	$\bar{4}$	37·1	−35·6
1	0	$\bar{6}$	22·0	−18·8
1	0	6	7·9	−2·2
4	0	0	5·5	−7·6
3	0	4	< 5·0	−1·3
2	0	$\bar{6}$	27·1	−24·7
4	0	$\bar{2}$	62·5	64·2
4	0	2	30·2	26·9
2	0	6	10·3	11·2
4	0	$\bar{4}$	80·4	94·2
3	0	$\bar{6}$	8·2	−3·9
4	0	4	< 6·0	−7·8
0	0	8	34·7	−34·0
1	0	$\bar{8}$	6·5	−1·3
3	0	6	22·7	22·7
5	0	0	< 6·0	−9·1
5	0	$\bar{2}$	29·9	−20·4
1	0	8	24·4	−19·6
2	0	$\bar{8}$	7·2	−5·6
4	0	$\bar{6}$	10·6	−0·3
5	0	2	6·8	3·7
5	0	$\bar{4}$	24·4	20·5
2	0	8	16·2	16·8
3	0	$\bar{8}$	< 6·7	−6·6
4	0	6	9·9	8·2
5	0	4	7·9	−12·0
5	0	$\bar{6}$	18·6	17·0
3	0	8	47·5	47·9
6	0	0	20·3	−17·9
6	0	$\bar{2}$	14·8	11·3
4	0	$\bar{8}$	< 7·2	3·6
1	0	$\overline{10}$	8·2	3·2
0	0	10	34·7	−31·6
6	0	2	7·5	−9·8
6	0	$\bar{4}$	20·6	−25·8
2	0	$\overline{10}$	44·4	42·5
1	0	10	43·0	−45·0
5	0	6	29·2	−28·1
4	0	8	18·2	19·1
3	0	$\overline{10}$	11·0	9·4
2	0	10	11·3	−6·3
6	0	4	9·6	−15·3
5	0	$\bar{8}$	< 7·2	−0·9
6	0	$\bar{6}$	20·0	−21·4
7	0	0	< 7·2	−5·4
7	0	$\bar{2}$	8·6	6·0
4	0	$\overline{10}$	15·9	−8·2
3	0	10	19·3	18·7
7	0	2	< 7·2	−0·7
7	0	$\bar{4}$	19·6	15·1
5	0	8	20·3	−15·1
6	0	6	18·9	−20·6
1	0	$\overline{12}$	17·6	22·4
0	0	12	< 7·2	−4·0
6	0	$\bar{8}$	8·9	10·9
2	0	$\overline{12}$	27·1	25·8
1	0	12	9·9	−12·0
5	0	$\overline{10}$	< 7·2	10·1
7	0	$\bar{6}$	8·6	4·8
7	0	4	< 7·2	6·2
4	0	10	< 7·2	−1·0
3	0	$\overline{12}$	7·2	10·3
2	0	12	< 7·2	7·3
8	0	$\bar{2}$	< 7·2	8·9
8	0	0	< 7·2	3·0
4	0	$\overline{12}$	37·8	−34·2
6	0	8	13·4	−1·0
8	0	$\bar{4}$	12·7	−11·4
7	0	$\bar{8}$	< 7·2	0·4
6	0	$\overline{10}$	8·9	5·9
3	0	12	11·0	11·8
7	0	6	11·0	7·9

Table 2 (*cont.*)

h 0 l	$\lvert F_o\rvert$	F_c	h 0 l	$\lvert F_o\rvert$	F_c	h 0 l	$\lvert F_o\rvert$	F_c	0 k l	$\lvert F_o\rvert$	F_c
8 0 2	< 7·2	7·3	2 0 $\overline{14}$	< 6·7	10·1	9 0 $\bar{2}$	< 5·7	5·2	9 0 2	6·2	5·4
5 0 10	< 7·2	−4·5	4 0 12	8·9	10·5	9 0 0	< 5·7	2·1	4 0 $\overline{14}$	10·6	−12·0
8 0 $\bar{6}$	< 7·2	10·1	1 0 14	11·6	−10·9	2 0 14	5·7	−8·1	5 0 12	13·0	−14·4
5 0 $\overline{12}$	14·5	−15·6	3 0 $\overline{14}$	< 6·0	−3·8	8 0 $\bar{8}$	< 5·7	1·8	3 0 14	12·3	13·3
8 0 4	14·8	12·8	7 0 $\overline{10}$	< 6·0	4·6	8 0 6	11·6	−1·1	9 0 $\bar{6}$	7·5	−11·3
1 0 $\overline{14}$	< 7·2	0·1	7 0 8	< 6·0	−2·4	6 0 $\overline{12}$	12·0	12·2	9 0 4	< 3·6	1·2
0 0 14	10·6	−12·4	6 0 10	6·8	−7·3	9 0 $\bar{4}$	7·2	−9·7	5 0 $\overline{14}$	4·8	−12·3

were required before it could be established that the correct molecule was indeed that shown in Fig. 1(*b*).

Refinement of the [100] projection

Refinement was effected by two-dimensional (F_o-F_c) syntheses calculated on the Mercury computer, the atomic scattering factors being in the form published by Vand, Eiland & Pepinsky (1957). Hydrogen atoms were included as and when their coordinates were indicated by the difference maps and, in the final stages, individual temperature factors were assigned to a number of atoms. The respective values of B in the expression $\exp(-B\sin^2\theta/\lambda^2)$ for these atoms were S: 2·3; O_2: 3·3; C_4, C_5, N_2: 3·8; O_1: 4·8 Å²; for all other atoms the value of B was 4·2 Å². Excluding those reflexions for which the calculated value of the intensity was less than the minimum observed value in the appropriate range of $\sin\theta$, the agreement residual obtained from the observed and calculated structure factors listed in Table 2 was 0·14; the electron-density distribution and the corresponding atomic positions are shown in projection in Figs. 3(*a*) and 3(*b*) respectively. (By the introduction of more isotropic temperature parameters the residual was reduced to below 0·12 but the validity of this procedure with the experimental data available was questionable.)

Of the original fifty-nine signs from which the initial trial structure was obtained, fifty-five were ultimately found to be correct.

Refinement of the [010] projection

It was now established that the molecule was virtually planar and, since the $20\bar{2}$ reflexion was very strong, it could be inferred that the plane was substantially parallel to the $(10\bar{1})$ planes of the crystal. Utilizing this and the further information that the reflexions 200 and 400 were respectively very strong and very weak, preliminary values of the unknown x coordinates of the atoms in the projection along [010] were obtained with the aid of structure-factor graphs. Initially the agreement residual was 0·57, but after adjustment of the relative orientation of the two rings to correct large discrepancies between F_o and F_c for each of the reflexions 302, $40\bar{4}$ and 404 the value of the residual was reduced to 0·42.

Refinement from this point was continued by (F_o-F_c) syntheses; the hydrogen atoms of the methyl group and of the CH_2 group were included when the

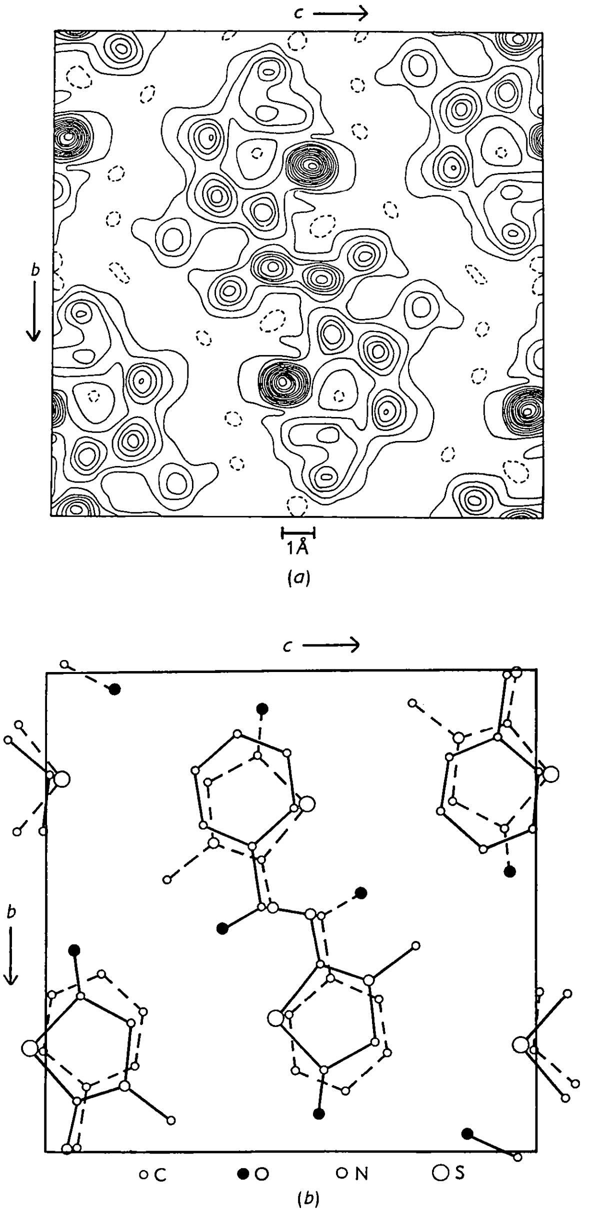


Fig. 3. (*a*) Projection of the electron-density distribution along [100]. The zero contours are broken lines; other contours are drawn at 2, 4, 6, 8, 10, 12, 14, 16, 20, 24, and 28 e.Å⁻². (*b*) Corresponding projection of the molecular arrangement.

appropriate peaks were discernible on the difference maps after which the benzene-ring hydrogen atoms were inserted by calculation. During later stages of refinement it was evident that in this projection the thermal vibration of the sulphur atom was anisotropic, the major axis of the vibration ellipse being roughly at right angles to the plane of the five-membered ring; one effect of this was to introduce into the difference map a peak in the region of two overlapping carbon atoms. In order to remove this peak it was found by the graphical method of Cochran (1954) that the most suitable value of the ratio of the maximum root-mean-square anisotropic displacement to the root-mean-square displacement of the original isotropic vibration was 1·4 and the most suitable value of the ratio for the minimum anisotropic displacement was 0·8. All other temperature factors were assumed isotropic with $B=3{\cdot}2$ Å^2 for C_4, 2·7 Å^2 for O_2 and 2·0 Å^2 for the remainder.

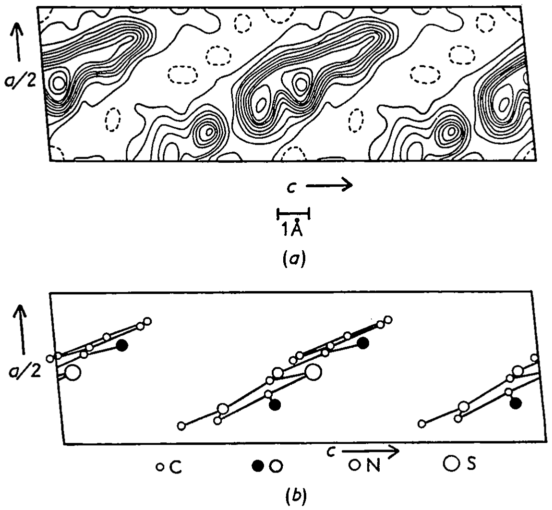


Fig. 4. (*a*) Projection of the electron-density distribution along [010]. The zero contours are shown as broken lines; other contours are drawn at 2, 4, 6, 8, 10, 12, 14, 16, 20, 24 and 28 e.Å^{-2}. (*b*) Corresponding projection of the molecular arrangement.

Lastly a correction for primary extinction (Vand, 1955) was applied to all low-order reflexions. The observed and calculated structure factors are shown in Table 2 and these give a residual of 0·15 when unobserved reflexions for which the calculated intensity is less than the minimum observed in the appropriate range of sin θ are omitted. The projected electron density along [010] and the corresponding atomic positions are shown in Figs. 4(*a*) and 4(*b*) respectively.

Discussion of the structure

Fractional coordinates of the atoms in one asymmetric unit are shown in Table 3; hydrogen atoms are included solely because account was taken of their contribution to the calculated structure factors and not because deviations from accepted bond lengths and angles involving these atoms are significant. Intramolecular bond lengths and angles are listed in Table 4, the indicated errors in bond lengths being standard deviations calculated by Cruickshank's formula (1949).

With the possible exception of C_1 and O_1, the atoms of the five-membered ring and the associated exocyclic atoms C_4 and O_1 are probably co-planar, and this

Table 3. *Final fractional coordinates of the atoms in one asymmetric unit*

Atom		*x*	*y*	*z*
O_1		0·130	0·080	0·445
C_1		0·163	0·173	0·435
S		0·235	0·276	0·533
C_2		0·210	0·390	0·441
N_1		0·104	0·355	0·338
C_3		0·069	0·231	0·326
C_4		0·053	0·429	0·246
N_2		0·237	0·489	0·458
C_5		0·302	0·513	0·562
O_2		0·335	0·460	0·643
C_6		0·326	0·639	0·577
C_7		0·394	0·681	0·681
C_8		0·412	0·794	0·697
C_9		0·364	0·868	0·612
C_{10}		0·292	0·830	0·505
C_{11}		0·276	0·718	0·494
H	CH_2	−0·008	0·218	0·283
H		0·117	0·218	0·260
H	CH_3	0·017	0·390	0·200
H		0·100	0·450	0·183
H		−0·025	0·490	0·270
H	C_6H_5	0·243	0·697	0·413
H		0·270	0·877	0·440
H		0·377	0·942	0·621
H		0·433	0·617	0·745
H		0·458	0·827	0·777

Table 4. *Values of bond lengths and bond angles*

Bond length		Angle	
$O_1=C_1$	1·16 ± 0·04 Å	$O_1=C_1-S$	132°
C_1-S	1·79 ± 0·03	C_1-S-C_2	97
$S-C_2$	1·78 ± 0·03	$S-C_2-N_1$	109
C_2-N_1	1·51 ± 0·04	$C_2-N_1-C_3$	116
N_1-C_3	1·53 ± 0·04	$N_1-C_3-C_1$	107
C_3-C_1	1·63 ± 0·04	C_3-C_1-S	109
N_1-C_4	1·47 ± 0·04	$C_3-C_1=O_1$	115
$C_2=N_2$	1·23 ± 0·04	$C_3-N_1-C_4$	120
N_2-C_5	1·36 ± 0·04	$C_4-N_1-C_2$	124
$C_5=O_2$	1·19 ± 0·03	$N_1-C_2=N_2$	119
C_5-C_6	1·54 ± 0·04	$S-C_2=N_2$	130
C_6-C_7	1·43 ± 0·04	$C_2=N_2-C_5$	114
C_7-C_8	1·39 ± 0·04	$N_2-C_5=O_2$	134
C_8-C_9	1·40 ± 0·04	$N_2-C_5-C_6$	111
C_9-C_{10}	1·45 ± 0·04	$O_2=C_5-C_6$	115
$C_{10}-C_{11}$	1·37 ± 0·06	$C_5-C_6-C_{11}$	124
$C_{11}-C_6$	1·42 ± 0·06	$C_5-C_6-C_7$	119
		$C_6-C_7-C_8$	120
		$C_7-C_8-C_9$	121
		$C_8-C_9-C_{10}$	121
		$C_9-C_{10}-C_{11}$	115
		$C_{10}-C_{11}-C_6$	125
		$C_{11}-C_6-C_7$	116

plane is inclined to that of the benzene ring at an angle of some 10° about the N_2–C_5 bond. The packing of the molecules is reasonable and is consistent with inter-molecular binding by Van der Waals forces, the molecules themselves being arranged substantially in layers of the order of 3·3 Å apart and parallel to the $(10\bar{1})$ planes. The shortest intermolecular contact within a layer is an $O \cdots C$ distance of length $3{\cdot}33 \pm 0{\cdot}04$ Å and the shortest contact between layers is again an $O \cdots C$ distance of length $3{\cdot}32 \pm 0{\cdot}04$ Å; the length of the intermolecular $S \cdots CH_3$ contact is $3{\cdot}87 \pm 0{\cdot}02$ Å.

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References

COCHRAN, W. (1954). *Acta Cryst.* **7**, 503.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
DOUGLASS, I. B. & DAINS, F. B. (1934). *J. Amer. Chem. Soc.* **56**, 719.
ELMORE, D. T. (1959). *J. Chem. Soc.* p. 3152.
ELMORE, D. T. & TOSELAND, P. A. (1956). *J. Chem. Soc.* p. 188.
VAND, V. (1955). *J. Appl. Phys.* **26**, 1191.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
WOOLFSON, M. M. (1957). *Acta Cryst.* **10**, 116.

Acta Cryst. (1961). **14**, 853

Effects of Bonding on Electron Diffraction Values of Bond Distances Involving Hydrogen Atoms in Solids

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The effects of bonding on the maximum of the potential of the hydrogen atom are calculated from an approximate model for various data cut-offs and thermal motions as a function of the shift of the electron cloud. It is concluded that the shift of the maximum of potential is much smaller than the shift of the electron cloud and is in the opposite direction. Hence electron diffraction determinations of bond distances involving hydrogen atoms should yield values which are slightly longer than internuclear distances. For typical conditions of data cut-off and thermal motion this lengthening is predicted to be about 0·03 Å, in good agreement with some recent data obtained by Vainshtein. These results do not negate the argument that the apparent contraction of heavy atom-hydrogen atom bond distances found in X-ray studies is the result of migration of the K electron of the hydrogen atom toward the heavy atom.

Introduction

There are now many well-established cases where X-ray studies have led to anomalously short values of bond distances involving hydrogen atoms. To cite just two examples Marsh (1958) found the C–H distance in glycine to be $0{\cdot}91 \pm 0{\cdot}06$ Å ($\sim 0{\cdot}18$ Å short); McDonald (1960) found the N–H distances in NH_4HF_2 to be $0{\cdot}88 \pm 0{\cdot}03$ Å ($\sim 0{\cdot}15$ Å short). A qualitative explanation for such apparent shortening is that the K electron of the hydrogen atom as a result of bonding migrates toward the heavy atom. The separation of the maximum electron density of the hydrogen atom from that of the heavy atom, this separation being the one determined in X-ray studies, is then less than the internuclear separation. In atoms heavier than hydrogen the K electrons are not involved in bonding and their contribution to the electron density at the origin is sufficiently great to keep the maximum electron density coincident with the nucleus. Tomiie (1958) (who gives other examples of short distances) has looked into this problem of short hydrogen distances in detail and concludes that the observed shortenings are reasonable on the basis of a valence bond calculation of bonding effects.

On the other hand bond distances involving hydrogen atoms can be determined by electron diffraction techniques to smaller limits of error than is generally possible with X-ray methods. Such distances, which are in fact the distances between maxima of the potentials of the atoms, are usually within a few hundredths of an Ångström of the internuclear distances. It seems clear then that it is necessary to show that charge migration has only a small effect on the position of the maximum of the hydrogen atom poten-