Table 10. *Neighboring atoms and interatomic distances*

(The positions given refer to the pseudo-cell.)

Each Ti at 0, 0, 0 has:
  2 Be (at 0, 0, 0·29; etc.) at 2·13 Å;
  6 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·55 Å;
  12 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·80 Å.

Each Be at 0, 0, 0·29 has:
  1 Ti at 2·13 Å;
  6 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·13 Å;
  12 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 3·34 Å.

Each Be near $\frac{1}{3}$, $\frac{2}{3}$, 0 has:
  1 or 2 Ti at 2·55 Å;
  4 or 2 Be (at 0, 0, 0·29; etc.) at 3·34 Å;
  2 or 4 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·2 Å;
  4 or 2 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·3 Å.

Each Be at $\frac{1}{2}$, 0, $\frac{1}{4}$ has:
  2 Be (at 0, 0, 0·29; etc.) at 2·13 Å;
  2 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·2 Å;
  2 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·3 Å;
  4 Be (at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{4}$; etc.) at 2·12 Å;
  2 Ti at 2·8 Å.

If the beryllium atom which is displaced is considered more carefully, it will be seen that it may exist in at least four situations, namely: surrounded at its *z* level by none, one, two or three titanium atoms. If the beryllium atom is at the center of the triangle of surrounding titanium sites, it will be too close to any corner containing a titanium atom. It is unlikely, then, that three titanium atoms will surround a beryllium, and, therefore, also unlikely that no titanium atoms will surround it. Each of these beryllium atoms is probably surrounded by one or two titanium atoms at the corners of the titanium-site triangle and must move away from the titanium atoms. The Fourier synthesis (Fig. 2) shows the beryllium atoms to lie at 2·5 Å from some of the pseudo-cell corners, and atomic radii are consistent with this being a Be–Ti distance.

Though the structure is known only roughly, even this is encouraging for a structure which involves 624 atoms. The structure seems to involve a not quite fully ordered superlattice, and it seems possible that the nature of the disorder may yet become understandable.

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The Crystal Structure of Thiophene at −55° C.*

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The crystal modification of thiophene in the range −38 to −98° C. is orthorhombic, space group either D_{2h}^{18}–*Bmab* or the non-centrosymmetric equivalent C_{2v}^{17}–*B2ab*, with no conclusive distinction possible from the data. The crystal structure has been determined on the basis of each of these possible space groups, with the use of three-dimensional Fourier sections based on visual intensity measurements from the entire reciprocal sphere. In *Bmab* each one of the four molecules occupies statistically any one of four equivalent positions related to one another by two mutually perpendicular mirror planes, both normal to the plane of the ring. In *B2ab*, these four positions reduce to two equivalent positions. These two possible structures show approximately equally good agreement with the observed data. The disorder has made it unwise to attempt determination of intramolecular bond distances, but the closest intermolecular approach of 3·7 Å indicates, as expected, that no very strong binding forces are present in the crystal. The unit-cell dimensions are $a = 9{\cdot}76$, $b = 7{\cdot}20$ and $c = 6{\cdot}67$ Å. The plane of the molecule is parallel to a, and makes an angle of 47·8° with b.

Introduction

Considerable advances have been achieved in the last decade in correlating the bond distances in polycyclic aromatic hydrocarbons, predicted from molecular-orbital and valance-bond treatments, with those experimentally measured. More recently, similar techniques have been applied to some heterocyclic molecules, and, in the case of thiophthen, the agreement between the calculated bond distances (Evans & de Heer, 1949) and the measured distances (Cox, Gillot & Jeffrey, 1949) has been most encouraging. The more simple sulfur analogue, thiophene, had been investigated by the electron-diffraction method by Schomaker & Pauling (1939), but when the molecular-orbital treatment was applied by Longuet-Higgins (1948) the agreement was not quite as good.

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It thus became desirable to examine the crystal structure of thiophene with a view to an accurate establishment of the bond distances. However, it was known from the very careful heat-capacity study of thiophene by Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith & Huffman (1949) that four crystalline modifications existed, and that the study of the highest-temperature form, just beneath the melting-point, would probably show sufficient disorder to disallow bond-distance measurements. This eventuality was found to be the case, and so the present study is a contribution to the description of molecular crystals in the region of their melting-points, rather than to the compilation of accurate bond-distance determinations. The crystal structure is shown to be of a highly disordered nature, but one in which there is not free rotation. The closest approach distances between nearest molecules are about 3·7 Å, and hence no unusual intermolecular attractions were detected.

Crystal data

Thiophene, C_4H_4S; molecular weight, 84·13; melting-point, −38·1° C.; density of liquid measured at 15° C., 1·072 g.cm.$^{-3}$ (Lumbroso, 1949); density of crystal, calculated, 1·204 g.cm.$^{-3}$; orthorhombic bipyramidal or pyramidal with

$$a = 9{\cdot}76 \pm 0{\cdot}02, \quad b = 7{\cdot}20 \pm 0{\cdot}02$$

and $$c = 6{\cdot}67 \pm 0{\cdot}02\ \text{Å};$$

(hkl) present only when $h+l=2n$, ($h0l$) only when $h=2n$ and $l=2n$, and ($hk0$) only when $h=2n$ and $k=2n$. Space group either D_{2h}^{18}–$Bmab$ or C_{2v}^{17}–$B2ab$. Pyro-electric tests gave negative and hence inconclusive results. Four molecules in the unit cell. Molecular symmetry required is C_{2h} for the centrosymmetric and C_2 for the polar space group. Volume of the unit cell, 468 Å^3. Total number of electrons per unit cell, $F(000) = 176$.

Earlier measurements were made on the powder by Bruni & Natta (1929, 1930) at −170° C. They indexed the film, of which a microphotometer trace was reproduced in the paper, on the basis of a tetragonal cell with $a = 7{\cdot}22$ and $c = 9{\cdot}54$ Å, giving a density of 1·11 g.cm.$^{-3}$. Several planes on their film remained unindexed, and so it is not certain how correct is this interpretation of the lowest-temperature crystal form of thiophene.

The crystals of thiophene are colorless and grow with a random orientation. They are denser than the liquid, small bubbles being formed on freezing the liquid, an observation which is in agreement with the higher calculated density for the crystal as compared with the measured density of the liquid.

Analysis of the structure

The initial study of this crystal structure was confined to the centrosymmetric space group, the possibility of the correctness of the non-centrosymmetric space group being deferred* until further refinement on the assumption of $Bmab$ had ceased. Thus the latter space group required the molecule to be centrosymmetric, at least statistically. It was readily seen from steric considerations that placing the four sulfur atoms at the four-fold positions of this space group led to unsatisfactory packing. These considerations led to the formulation of a simple 'head-to-tail' type of disorder,† in which each molecule is randomly oriented about a hypothetical two-fold axis normal to the plane of the ring. If any point along the molecular two-fold axis is placed at the four-fold positions, provided this axis lies in the (100) or (001) planes, this disorder would then require the sulfur atoms to lie in 8 (d) or 8 (f) (*Internationale Tabellen*, 1935, vol. 1). With these considerations in mind, Patterson F^2 projections were prepared along the a, b and c axes. Before setting up these functions, since the complete set of (hkl) data was available, the intensities were placed on the absolute scale by the methods of Wilson (1942) and Harker (1948). None of the Patterson projections resulted in any resolvable maxima, but an F^2 section in the (100) plane gave three maxima that could be located (see Fig. 1).

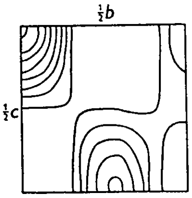

Fig. 1.

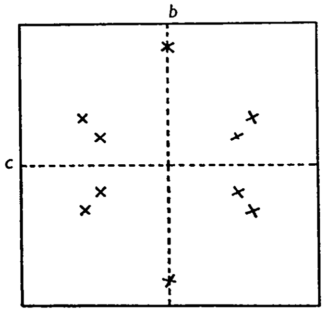

Fig. 2.

Fig. 1. Patterson F^2 section in the (100) plane. The asymmetric unit only is shown, the contours being at equal but arbitrary levels. The b and c axes in this diagram are made equal in length.

Fig. 2. Explanation of Patterson section in Fig. 1. The relations of the resolved maxima, indicated by the small crosses, throughout the whole cell are shown.

The relations of these maxima are shown for a complete cell in Fig. 2, and employing a model of the 'head-to-tail' type in their interpretation, it was soon possible to construct a structure that would fit their positions, as is shown in Fig. 3. The plane of this disordered molecule was tilted to make an angle of 50° with the b axis, and the distance from the sulfur atom at the 'head' or 'tail' position to the origin was found to be 1·4 Å. In the calculation of structure factors based upon this model, the molecular dimensions found in thiophene by Schomaker & Pauling (1939) were employed. The phases thus obtained were introduced

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* We are much indebted to Dr B. Post and Prof. I. Fankuchen for pointing out our earlier omission of $B2ab$.

† A similar model with symmetry reduced to $B2ab$ gave poor agreement.

into a Fourier section along the (100) plane, which upon evaluation gave a value of 48° 51′ for the tilt with respect to the *b* axis, while the distance from the 'sulfur atom' to the origin had decreased to 1·20 Å. The new phases thus found were used to sum Fourier sections along (010) and along (001) and also in evaluating half-cell projections along the *a*, *b* and *c* axes. These last five functions were summed on the X-ray Analogue Computer at Pennsylvania State College by the very kind permission of Prof. R. Pepinsky. However, on later calculation of the structure factors, the rather poor agreement among the observed and calculated data made it apparent that while the model was correct enough in essence, some very drastic change had to be made to secure better agreement.

At this point, various other types of disorder were carefully considered, including one in which the sulfur atoms remained unchanged in position, while the carbon atoms could move, or oscillate, above and below the original mean molecular plane. Another possible disorder investigated was one in which there was free rotation in the molecular plane about the approximate center of the molecule. Although the latter type of disorder did help the agreement somewhat, certain planes remained in very poor agreement, especially the axial terms (220) and (202). The disorder which gave the best agreement throughout all (*hkl*) planes was one in which the molecules remained in the original plane obtained from the (100) Fourier section, and randomly assumed any one of four possible positions. These positions are related to each other by two perpendicular mirror planes, mutually normal to the molecular plane. This disorder places all atoms in the general sixteen-fold positions of *Bmab*, which have the co-ordinates:

$$x, y, z;\quad x, \bar{y}, \bar{z};\quad x, \tfrac{1}{2}+y, \tfrac{1}{2}-z;\quad x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;$$
$$\bar{x}, \bar{y}, \bar{z};\quad \bar{x}, y, z;\quad \bar{x}, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\quad \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z;$$

to these eight positions must be added 0, 0, 0 and $\frac{1}{2}, 0, \frac{1}{2}$ in order to complete the unit cell. The appropriate fraction of each atom was chosen to give a final total of four thiophene molecules in the unit cell.

At this stage in the investigation, it became apparent that the best way to refine the structure was the construction of a Fourier section in the (011) plane in conjunction with a section in the (100) plane, since the molecule lay very nearly in the (011) plane. The (011) section was set up by forming the first summation along reciprocal-lattice rows perpendicular to the $(01\bar{1})$ plane, and then expanding the resulting sums in the usual way. The phases corresponding to the four-fold type of disorder were then introduced into a Fourier section along the (011) plane, and then this and the (100) section were refined to the diagrams reproduced in Figs. 4 and 5, at which point no further changes of sign occurred in the calculated structure factors.

At this stage, the possibility of the space group being *B2ab* was again investigated. The co-ordinates obtained from Figs. 4 and 5 were used to calculate the structure factors for the model, *B2ab*, which led to agreement between the observed and calculated structure factors only insignificantly better than before (see next section). Fourier sections in the planes (011) and (100) were then evaluated (see Figs. 6, 7), but no appreciable changes in the co-ordinates resulted from them. The agreement remained virtually unchanged.

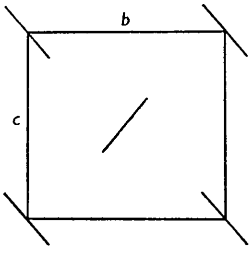

Fig. 3.

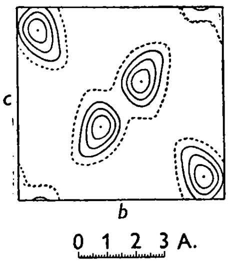

Fig. 4.

Fig. 3., The arrangement of the molecules in the (100) plane.

Fig. 4. Electron density in the (100) plane. Each contour line represents a density increment of $\frac{1}{2}$ e. Å^{-3}, the half-electron line being broken. The origin is the center of symmetry.

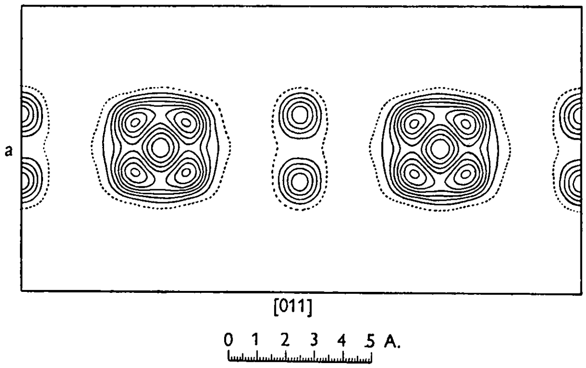

Fig. 5. Electron density in the (011) plane. Each contour line represents a density increment of $\frac{1}{2}$ e. Å^{-3}, the half-electron line being broken. The density at the origin, the center of symmetry, is 0·6 e. Å^{-3}.

A very encouraging feature during the final stages of this study was the very low-level background of electron density in the three-dimensional sections, which remained within the limits −0·6 and 0·5 Å^{-3} for both space groups. The scale factor finally obtained was found to be lower than that calculated at the beginning of the study by the methods of Wilson (1942) and Harker (1948) by a factor of 1·4 for *Bmab* and 1·1 for *B2ab*. The best value for the temperature factor was observed to be 8·5 Å^2 for *B*, in the expression

$$\exp\left[-B(\sin\theta/\lambda)^2\right].$$

This value* is considerably larger than is usually found

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* Least-squares values of scale and temperature factors (with weighting factors taken as unity except for $F_{hkl} \geqslant 13$ for which $W^{\frac{1}{2}}_{hkl} = 13/F_{hkl}$) were not significantly different from those reported herein. The sum of squares of residuals was 640 for the *Bmab* model, and 500 for the *B2ab* model. This difference is probably not significant.

in organic crystals, and it is undoubtedly principally due to the large thermal vibrations that the peaks are so smeared out.

It was not easy to determine the positions of the atomic centers from the electron-density maps in Figs. 5 and 7, but it was observed that changes in atomic positions by about 0·05 Å had no appreciable effect on the agreement between observed and calculated structure factors. Thus the final assessment of the atomic co-ordinates, based upon the Schomaker & Pauling (1939) model, is given in Table 1. It is of interest to note that the sections in Figs. 5 and 7 pass within 5° of the plane of one molecule, and nearly normally to the plane of the next. The overall shape of this disordered molecule may thus be almost complately described from the maps given in Figs. 4 and 5 for *Bmab* or the maps in Figs. 6 and 7 for *B2ab*.

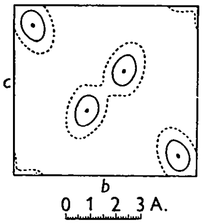

Fig. 6.

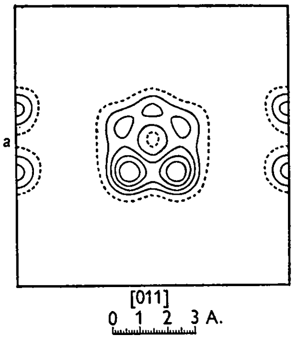

Fig. 7.

Fig. 6. Electron density in the (100) plane. Each contour line represents a density increment of 1 e.Å^{-3}, the one-electron line being broken. The same origin as in Fig. 4 is used.

Fig. 7. Electron density in the (011) plane. Each contour line represents a density increment of 1 e.Å^{-3}, the one-electron line being broken. The origin is the same as in Fig. 5, but is no longer a center of symmetry. The density at the origin is 0·9 e.Å^{-3}.

Co-ordinates and molecular relations

The best co-ordinates obtained by the methods already described are collected in Table 1, the origin for either space group being the same point as the center of symmetry for *Bmab*. The value of the discrepancy $\Sigma\,||F_c|-|F_o||\div\Sigma\,|F_o|$ for all possible (hkl) reflections using the co-ordinates listed above is 28 % for *Bmab* and 26 % for *B2ab*. For F_c, the atomic scattering curves for sulfur and carbon given in the *Internationale Tabellen* (1935, vol. 1), and a temperature factor of 8·5 Å^2 were used. These co-ordinates correspond to a model in which the distance of the sulfur atom from the origin is 1·22 Å, so that the center of gravity of the molecule lies on the crystallographic center. The angle made by the molecular plane with the *b* axis is 47·8°. A diagram of the disordered molecule for *Bmab* is given in Fig. 8, in which all four possible positions are shown occupied. The model based upon *B2ab* consists of two of these four positions resulting from elimination of the mirror plane normal to the *a* axis.

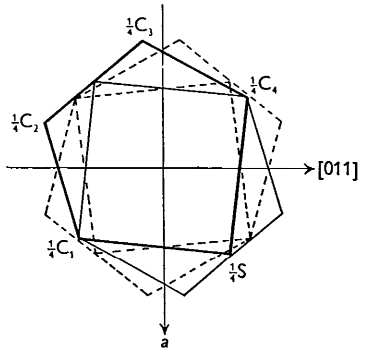

Fig. 8. The disordered thiophene molecule, with a quarter molecule occupying each of the four possible positions.

Intermolecular distances

The molecules in this crystal show no unusually close approaches, the smallest intermolecular distances being 3·68 and 3·71 Å between each sulfur atom and the two closest carbon atoms of adjacent molecules. These two approaches lie approximately in the (010) and (100) planes so that there is a complete three-dimensional network of such approaches throughout the crystal.

There are also three other distances of about 3·80 Å between the closest carbon atoms of neighboring molecules. Apart from these five distances, all others are greater than 4·00 Å.

The slope of the molecules is such, as seen from Fig. 3, that the plane of each molecule intersects very nearly the center of the next nearest molecule, since the average molecular plane lies only 5° away from the (011) plane.

Discussion

The considerable degree of disorder found in this crystalline modification of thiophene has not permitted the accurate measurement of any bond distances. The disorder is of an unusual type, whether it corresponds to the centrosymmetric space group or not, but there appears to be little doubt that one of these two descriptions is correct. It is unfortunate that the experimental data do not clearly allow a choice between the two models. The electron-density maps of

Table 1. *Co-ordinates referred to the crystal axes*

	x (Å)	x/a	y (Å)	y/b	z (Å)	z/c
$\frac{1}{4}$S	0·96	0·098	0·51	0·071	0·56	0·084
$\frac{1}{4}$C$_1$	0·76	0·078	−0·65	−0·090	−0·72	−0·108
$\frac{1}{4}$C$_2$	−0·53	−0·054	−0·89	−0·123	−0·98	−0·147
$\frac{1}{4}$C$_3$	−1·42	−0·145	−0·13	−0·018	−0·15	−0·022
$\frac{1}{4}$C$_4$	−0·76	−0·078	0·65	0·090	0·72	0·108

Figs. 5 and 7 show very definitely that there is not a random distribution around the ring, as would be found for a free rotator about its centre of inertia. The poor agreement among the observed and calculated structure factors confirmed the incorrectness of a freely rotating model.

Various types of disorder in molecular crystals have been reported, following Pauling's (1930) suggestion that certain molecules of small moment of inertia might be able to rotate in a high-temperature crystal modification. A summary of many of the investigations since that time is given in a recent paper by Ubbelohde (1950), although no disorder quite the same as that present in thiophene seems to have been observed before. It has been suggested by Andrew (1950), after a study of the nuclear resonance absorption lines of benzene crystals, that rotation or tunnelling of the molecules about their hexagonal axes, or much less probably, their diad axes, should be considered very likely. This molecular motion, together with the great similarity between the unit-cell dimensions of benzene, with $a=9{\cdot}76$, $b=7{\cdot}39$ and $c=6{\cdot}85$ Å (Cox, 1932) and thiophene, might well provide the basis on which the formation of the well-known solid solutions of thiophene and benzene depends, and of the difficulty of separation of a liquid solution.

The intermolecular relations of this crystal are not easy to understand. There are no really significantly short approaches between molecules, and the consequent lack of powerful forces binding the molecules together is given illustration by the random manner in which the crystal grows from the melt. The reason for this molecular arrangement might be suggested by an examination of Fig. 3, in which it is seen that each molecule points very nearly towards the center of the next nearest neighbor. At the center of each disordered molecule there will be a slightly closer van der Waals approach than elsewhere, and the hydrogen atoms of neighboring molecules might be more readily accommodated at that point. It may be observed that this is the point towards which the hydrogen atoms are directed. Steric forces of this nature will not be very large, however, and would be easily overcome. The number of transitions in thiophene which occur before an ordered state is reached, at which there is no entropy at the absolute zero, does seem to indicate the need for such an explanation.

The intermolecular approaches found in the present study may be compared with those reported in thiophthen, in which Cox *et al.* (1949) observe for the shortest distances, S ... C to be 3·86 and C ... C to be 3·82 Å, the next closest approach being over 4·0 Å. It thus seems clear that somewhat similar binding forces are operative in both crystals.

The electron density at the highest peak in Fig. 5 is just over 4 e.Å^{-3}, and this represents the added contributions of one quarter sulfur atom and two quarter carbon atoms (see Fig. 8), which should be about seven electrons. The small value of this observed density must be due to the large degree of thermal vibration in the crystal, as indicated by the high temperature factor. The electron density in Fig. 4, where the section does not pass precisely through any atomic center, is 2·5 e.Å^{-3} at the highest point. This is very nearly the same value as in Fig. 5 at corresponding places between atomic centers. Similar considerations apply to the electron-density map in Fig. 7. Here, the scale factor is slightly higher than in the case of *Bmab*, and the peak electron density which represents the added contributions of one-half a sulfur atom and one-half a carbon atom is 5·8 e.Å^{-3}. The maps in Figs. 5 and 7 are not, in themselves, sufficient to decide which of the two possible space groups is correct, so both models have to be retained. An interesting observation is the very regular shape of the cross-section through the ring, shown in Figs. 5 and 7, where the section passes almost normally through the molecular plane. We therefore conclude that if an anisotropic temperature factor is required, as might well be expected of such a structure, it is not caused by vibrations normal to the molecular plane.

It is proposed to continue this study of thiophene in its other crystalline modifications at low temperatures. It is to be hoped that the elucidation of these other crystal structures assumed by thiophene will lead to a fuller understanding of the present modification.

Experimental

The sample of thiophene used in this investigation was very kindly supplied in a state of 99·95 % purity by the late Dr H. M. Huffman of the U.S. Bureau of Mines. The general experimental techniques employed have already been described in detail (Abrahams, Collin, Lipscomb & Reed, 1950). The material was introduced by capillarity into thin Pyrex tubes of less than 1 mm. in diameter, and sealed off to be about 1 cm. in length. The single crystals grow quite readily, with no preferred orientation, so that the use of a precession camera with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) allowed the entire reciprocal sphere to be explored easily. The precession angle used was 23°. All the (*hkl*) planes listed under F_m in Table 2 were recorded in this manner, at −55° C., and some Weissenberg photographs were also taken, from which it was seen that no additional data could be gleaned.

The layer-line screen used with the Weissenberg camera was of novel design. It was made sufficiently small in diameter to facilitate removal of the cylindrical film-holder, which had an arc cut out of the back-reflection area on the lower side, so that it subtended about 70° at the center. The layer-line screen could itself be easily removed from the camera without disturbing the supply of cold air, by making it in the form of two semi-cylinders, hinged along one edge and with catches on the other. The slit in the screen was 2·0 mm. in width.

Table 2. *Measured and calculated values of the structure factors of thiophene at* −55° C.

		Bmab	*B2ab*	
hkl	F_m	F_c	$0{\cdot}81F_c$	α (°)
200	43·0	+43·0	38·5	25
400	30·5	−34·5	29·5	158
600	12·5	−20·0	18·0	204
800	2·5	−1·0	7·5	264
020	36·0	+50·0	40·5	0
040	9·5	−10·5	8·5	180
060	4·5	−8·0	6·5	180
002	26·5	+34·0	27·5	0
004	8·5	−15·5	12·5	180
006	4·0	−5·0	4·0	180
220	4·0	+9·0	11·5	50
240	13·0	−8·0	7·5	208
260	3·0	−4·0	6·0	238
420	18·0	−18·0	17·5	147
440	3·0	+0·5	2·0	78
460	<3·0	+3·0	3·0	327
620	3·0	−7·0	6·0	198
640	5·5	+5·0	9·5	66
660	4·0	+4·0	3·0	20
820	3·0	+1·0	4·5	280
840	3·0	+2·0	1·0	7
202	4·0	+4·0	8·0	66
204	12·0	−9·5	10·5	222
206	2·5	−1·5	4·0	254
402	19·0	−14·5	14·5	142
404	4·0	+4·0	3·0	68
406	<2·0	+2·0	2·5	316
602	3·0	−4·0	3·0	193
604	5·5	+7·0	6·5	29
606	<5·0	+2·0	1·5	26
802	<5·5	+1·0	3·0	282
804	<5·0	+1·5	1·5	32
012	30·5	−34·0	27·5	180
014	2·5	−6·5	5·5	180
016	2·5	+2·0	1·0	0
022	16·0	+15·5	12·5	0
024	<2·5	−4·0	3·0	180
026	<3·0	−2·0	1·5	180
032	26·5	−33·0	27·0	180
034	2·5	−10·0	8·5	180
036	<2·5	+1·5	1·0	0
042	4·5	+1·5	1·0	0
044	2·5	+5·0	4·0	0
046	<2·0	+0·5	0·5	0
052	<2·5	−7·0	5·5	180
054	<2·5	−3·5	3·0	180
056	<2·0	−0·5	0·5	180
062	2·5	−2·0	2·0	180
064	<2·0	+1·0	1·0	0
111	81·0	+65·0	52·5	7
113	6·0	−5·0	5·0	214
115	<4·0	−1·5	1·5	217
121	57·0	−52·0	43·0	192
123	16·0	−22·0	19·5	200
125	<3·5	−0·5	0·5	225
131	<3·5	+4·0	3·0	343
133	6·5	+4·5	4·5	324
141	8·5	−10·5	9·5	204
143	8·5	−12·0	11·0	208
151	7·0	−8·5	8·0	210
153	<6·5	+3·0	2·5	350
161	<6·5	+0·5	1·0	292
163	<5·0	−1·0	1·0	222
212	18·0	−14·0	12·5	208
214	<5·0	−1·5	5·0	254
216	<5·0	+0·5	0·5	348
222	7·0	+2·0	2·5	42
224	8·0	−3·0	5·5	244
226	<5·0	−1·0	1·5	246
232	15·0	−13·5	15·0	225
234	<6·5	−3·0	7·0	258
242	<4·5	+1·0	4·0	282
244	4·5	+2·0	2·0	332
252	<4·5	−1·5	5·5	256
254	<4·5	−1·0	1·5	245
311	13·0	−13·0	18·0	124
313	<5·0	−5·0	5·0	173
321	5·0	−0·5	4·0	264
323	7·0	+3·0	9·0	290
331	9·0	−6·5	6·0	147
333	5·0	−1·5	2·5	248
341	5·0	+2·0	5·5	287
343	<5·0	+2·5	7·0	286
351	5·0	−1·5	4·0	258
353	<5·0	−0·5	1·0	244
361	<5·0	+1·0	1·5	298
412	5·5	+7·5	6·0	348
414	<5·0	+4·0	4·0	319
422	11·5	−8·0	8·0	147
424	<5·0	+1·5	1·5	326
432	5·5	+10·0	11·5	38
434	<5·0	+4·0	4·0	322
442	<5·0	−0·5	0·5	202
444	5·0	−2·0	1·0	186
452	<5·0	+2·5	3·0	315
454	<5·0	+1·5	1·0	320
511	16·0	−20·0	16·5	149
513	<5·0	+1·5	3·5	67
515	<5·0	+8·0	6·5	7
521	8·5	+10·5	8·5	1
523	10·0	+11·5	9·5	2
525	<5·0	+1·5	1·5	319
531	5·0	−2·5	4·0	168
541	<5·0	−3·0	2·5	184
612	5·0	+7·5	7·0	30
614	<5·0	+2·0	1·5	16
622	<6·5	−1·5	1·0	184
624	<6·5	+4·5	4·0	28
632	5·0	+8·0	7·5	32
634	<5·0	+5·0	6·0	20
642	<5·0	+1·0	1·0	39

The intensities were carefully estimated visually, and the multiple-film technique was used to obtain accurate correlations between strong and weak reflections, the films being interleaved with brass foil of 0·029 mm. thickness. The ratio of the strongest intensity to the weakest was not more than 1000 to 1 in any zone. The initial value for the appropriate temperature factor was arbitrarily estimated by taking the f curve at the value of $\sin\theta$ beyond which no further reflections were visible, as 3 % of its value at $\sin\theta=0$. This gave $B=8{\cdot}5$ in the expression $\exp[-B(\sin\theta/\lambda)^2]$, and it was not possible, subsequently, to obtain a better value. The plot of $\ln(F_m/F_c)$ versus $(\sin\theta/\lambda)^2$ showed sufficient scattering to give no indications of a more nearly correct B. The structure factors were derived from the intensity measurements by the usual formulae for a mosaic crystal, and the results are given in Table 2 under F_m. The calculated values of F and the phase constants (or signs) are derived from the co-ordinates in Table 1.

The numerical evaluation of the Fourier synthesis was carried out by three-figure methods (Robertson, 1948). Electron densities were sampled at 6° intervals along a, every 0·163 Å; 12° intervals along b, every

0·240 Å.; 12° intervals along c, every 0·222 Å; and 12° intervals along [011], every 0·328 Å. The positions of the contour lines were obtained from the summation totals by graphical interpolation.

A final Fourier section in (011) was constructed, based on the calculated structure factors in Table 2, for comparison with Fig. 5. The two maps were sufficiently similar to exclude any new information being yielded about the position of the atomic centers. The greatest difference found between the two sections at any point was 0·5 e.Å^{-3}, and the principal effect was to raise the level of the background from a small negative to a small positive electron density. The peak positions did not show any appreciable alteration.

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The Crystal Structure of 2-Metanilamido-5-Br-Pyrimidine*

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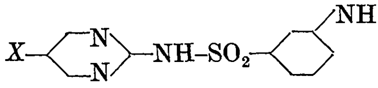
The crystal structure of 2-metanilamido-5-Br-pyrimidine, $C_{10}H_9BrN_4O_2S$, and its isomorphous iodine analog, has been determined by two-dimensional Fourier methods. These compounds are active anti-malarials. The crystals are monoclinic space group $P2_1/n$. A 'subtraction Fourier' method is described which was helpful in obtaining the signs of weak reflections. The method may prove useful in cases where a heavy scatterer, used to determine the phases of the stronger reflections, obscures the detail of the lighter atoms. The analysis is based mainly on one well-resolved projection, and on a combination of the Pauling covalent radii with the essential structural features disclosed by the second, heavily overlapped, projection of the molecule. The configuration of the –NH–SO_2– linkage between aromatic rings is given for the first time. Weak hydrogen-bonding between NH_2 and oxygen atoms of SO_2, of length 3·15 Å, is indicated, with one hydrogen of the NH_2 group of one molecule directed to one of the oxygens of an adjacent molecule.

Interest has recently been shown in the structure of pyrimidines (Clews & Cochran, 1948, 1949; Pitt, 1948). These analyses have demonstrated that the pyrimidine ring, while not a regular hexagon, is probably planar. Evidence is given that the C–N bonds are about 0·03 kX. shorter than the C–C bonds. The present analysis, of the compound (1),



, X = Br or I, (1)

is not precise enough to contribute to the knowledge of the details of the pyrimidine ring. However, some detail was obtained for the frequently encountered –NH–SO_2– linkage between the aromatic rings.

Compound (1), together with a large number of related substances, was described in a paper on anti-malarials from the Stamford Research Laboratories of the American Cyanamid Company (English, Clark, Shepherd, Marson, Krapcho & Roblin, 1946). The chlorine, bromine, and iodine analogues of compound (1) were given to us by the authors; these compounds are active anti-malarials. It was felt that there was a possibility of isomorphism in this series, which, if substantiated, could contribute to the solution of the

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