Disorder in Crystals of the Dithienyls and β-Thiophenic Acid

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The crystal structures of the three isomeric dithienyls $C_8H_6S_2$ have been determined by three-dimensional X-ray methods. In all cases the molecules in the solid are planar. Crystals of 2,2′-dithienyl appeared to decompose during the X-ray exposures; those of 2,3′-dithienyl and 3,3′-dithienyl show disorder. Disorder as found in 3,3′-dithienyl may also be assumed for β-thiophenic acid. Within the rather large experimental errors the bond lengths and angles in the thiophene rings of the dithienyls are equal to those in thiophene.
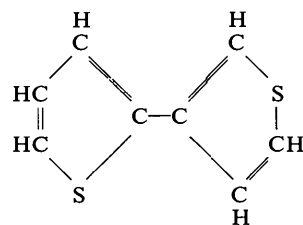
Introduction

A considerable amount of work has been done in Groningen on the synthesis, reactions and conformations of the isomeric dithienyls (I), (II) and (III) (Wynberg, Logothetis & VerPloeg, 1957; Kraak & Wynberg, 1968).
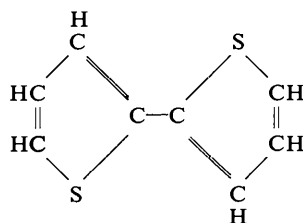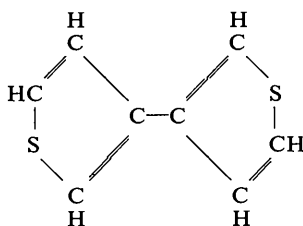

(I)

2,2′-dithienyl, m.p. 33–34 °C

(II)

2,3′-dithienyl, m.p. 63–64 °C

(III)

3,3′-dithienyl, m.p. 131–132·5 °C

This paper describes our attempts to determine the conformation of the molecules in the solid state by X-ray diffraction.

Experimental

The compounds were prepared in the Laboratory of Organic Chemistry of the University of Groningen. After many attempts suitable crystals were obtained from solutions in toluene (2,2′-dithienyl), light petroleum (2,3′-dithienyl) and benzene (3,3′-dithienyl) by slow evaporation of the solute. Crystals of 2,2′- and 2,3′-dithienyl were grown at room temperature, those of 3,3′-dithienyl at −20 °C.

The crystallographic data are listed in Table 1. The cell constants were obtained from zero layer line Weissenberg photographs calibrated with NaCl reflexion spots (λ(Cu $K\alpha$) = 1·5418 Å, λ(Cu $K\alpha_1$) = 1·54051 Å, λ(Cu $K\alpha_2$) = 1·54433 Å).

The intensities of 2,2′-dithienyl were collected at low temperature (−140 °C) with Ni-filtered Cu radiation. The multiple film Weissenberg technique was employed. Different crystals had to be used because of decomposition of the compound during the X-ray exposures. Although many attempts were made, it appeared to be impossible to obtain a consistent set of photographs. Small changes were observed in the diffraction pattern of a crystal which had been heated to room temperature in between the exposures and corresponding photographs from different crystals were not identical. We decided to confine the intensity measurements to the zero and fourth layer line about the *b* axis. The intensities were measured on integrated photographs by means of a Nonius densitometer.

For 2,3′-dithienyl the intensities were measured at room temperature by an automatic Nonius diffractometer (Zr-filtered Mo radiation), the θ–2θ scan method being used.

For 3,3′-dithienyl, two sets of intensity data (Series *A* and *B*, Table 1) were collected at room temperature from two different specimens. The intensities of both sets were measured with Zr-filtered Mo radiation on the automatic Nonius diffractometer by the ω- and $\theta/2\theta$-scanning techniques for series *A* and *B* respectively. The disagreement factor, $\Sigma \, \Delta|F|/\Sigma \, |F|$, between the two sets amounted to 0·07 for the common re-

flexions. The number of reflexions in series A was slightly higher than in B, clearly as a result of the use of a larger specimen (with approximately 10% volume increment) for data collection. Appropriate absorption corrections were applied to all the intensities in both sets with the use of a program evolved in this laboratory based on procedures suggested by Busing & Levy (1957).

In the initial stages of this investigation, the intensities from crystals of 3,3'-dithienyl were recorded at low temperature ($-140\,^\circ$C, series C) using the equi-inclination Weissenberg method and Cu $K\alpha$ radiation. Most of the intensities were measured on b-axis photographs. However, for the purpose of scaling between different levels about this axis, reflexion intensities on

a few levels about the c axis were also measured; but these scale factors were in error by as much as 10% and absorption corrections were not applied. Consequently, the intensities in series C are less reliable than those in series A and B.

Structure determinations

For 2,2'- and 3,3'-dithienyl the space groups chosen (Table 1) were indicated unambiguously from systematic absences on the photographs. In both compounds the molecules are situated at a twofold position (a centre of symmetry) so that there is only one independent thiophene ring per cell. For 2,3'-dithienyl, however, the space group can be either $P1$ or $P\bar{1}$. As no

Table 1. *Crystallographic data for the dithienyls*

Estimated standard deviations $\times 10^3$ Å are given in parentheses.

	2,2'-Dithienyl ($-140\,^\circ$C)	2,3'-Dithienyl (room temperature)	3,3'-Dithienyl (room temperature)	3,3'-Dithienyl ($-140\,^\circ$C)
a	7·76 Å	8·184 (3) Å	18·310 (2) Å	18·182 (4) Å
b	5·90	5·598 (1)	7·638 (2)	7·516 (3)
c	8·91	9·815 (5)	5·579 (2)	5·487 (2)
α	90°	99·12 (4)°	90°	90°
β	106·6	116·03 (3)	90	90
γ	90	86·09 (4)	90	90
Space group	$P2_1/c$	$P\bar{1}$ or $P1$	$Pccn$	$Pccn$
Z	2, at $\bar{1}$	2	4, at $\bar{1}$	4, at $\bar{1}$
	71 refl. $h0l$	1112 refl. hkl	507 refl. hkl (A)	566 refl. hkl (C)
	97 refl. $h4l$		453 refl. hkl (B)	

Table 2. *Final parameters*

For numbering of atoms see Figs. 6, 7 and 8.

	2,2'-Dithienyl					2,3'-Dithienyl‡			
	x	y	z	B		x	y	z	B
S	0·2500 (5)	0·1687 (9)	$-0\cdot3770$ (4)*	3·51 Å²	1	0·0937	0·0398	0·3515	8·4 Å²
C(1)	0·0760 (16)	$-0\cdot0178$ (29)	$-0\cdot4282$ (14)	3·00	2	$-0\cdot0270$	$-0\cdot1905$	0·2780	8·0
C(2)	0·0975 (15)	$-0\cdot2123$ (35)	$-0\cdot3287$ (13)	3·10	3	$-0\cdot0775$	$-0\cdot2252$	0·1026	9·3
C(3)	0·2621 (18)	$-0\cdot1833$ (42)	$-0\cdot2071$ (15)	4·13	4	0·0086	$-0\cdot0167$	0·0745	5·5
C(4)	0·3580 (19)	0·0082 (39)	$-0\cdot2159$ (15)	3·88	5	0·1217	0·1566	0·2329	6·5
H(2)†	$-0\cdot0042$	$-0\cdot3477$	$-0\cdot3404$	3·00	6	0·6222	0·4003	0·3404	10·3
H(3)	0·3038	$-0\cdot2964$	$-0\cdot1042$	4·00	7	0·5034	0·6471	0·3294	10·9
H(4)	0·4790	0·0620	$-0\cdot1243$	4·25	8	0·4426	0·7074	0·1650	8·7
					9	0·5154	0·5055	0·0787	6·1
					10	0·6255	0·3145	0·1825	8·5

3,3'-Dithienyl§
U_{ij}'s are in 10^{-4} Å²

	x	y	z	B	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0·17543	0·05049	0·05337		563	910	976	-121	-359	156
C(1)	0·09329	0·07936	$-0\cdot08612$		535	666	623	-185	-16	173
C(2)	0·03868	$-0\cdot00096$	0·03884		568	408	474	-115	-197	136
C(3)	0·06593	$-0\cdot08408$	0·25020		820	565	527	-177	119	-33
C(4)	0·14061	$-0\cdot06593$	0·28061		857	677	751	196	91	-396
H(1)†	0·08643	0·14976	$-0\cdot25196$	6·0 Å²						
H(3)	0·03090	$-0\cdot15651$	0·37767	6·1						
H(4)	0·17423	$-0\cdot11688$	0·42468	6·1						

* The numbers in parentheses are the standard deviations ($\times 10^4$) which resulted from the least-squares program.
† The numbers correspond to the carbon atoms to which the hydrogen atoms are attached.
‡ Only the parameters of the 'average' structure model are given.
§ The parameters of the 'normal' rings only are listed.

piezoelectric effect was observed, the space group $P\bar{1}$ was tentatively adopted for the structure determination.

In all cases a rough model of the structures could be obtained from a Patterson map. Refinements were carried out by least-squares methods. The calculations were done on a TR4 computer with a program written by Palm & Peterse according to Cruickshank's (1961) scheme. All observed reflexions (Table 1) were given equal weights. The scattering factors of hydrogen were taken from Stewart, Davidson & Simpson (1965) and those of the heavy atoms from Moore (1963). Lists of observed and calculated structure factors can be made available from the authors on request.

2,2'-Dithienyl

Because of the decomposition of the crystals, cell constants and intensities are not very accurate. For the least-squares refinement with anisotropic thermal parameters, the $h0l$ and $h4l$ reflexions alone were used. In the few terminal cycles, hydrogen atoms at positions calculated from the known geometry of a thiophene ring were taken into account for the calculation of the structure factors. R decreased to 0·08 and the final parameters are listed in Table 2.

The existence of a disordered structure as encountered in the case of 3,3'-dithienyl (see below) was not indicated here. However, it is possible that the presence of a small amount of disorder may be obscured as a result of the inaccuracies involved in the structure determination.

2,3'-Dithienyl

For 2,3'-dithienyl, the peaks in the three-dimensional Patterson synthesis appeared to be very diffuse, thus indicating disorder in the crystals. For space group $P\bar{1}$ only the average molecular structure shown in Fig. 1(a) could be deduced from the Patterson map. The two molecules in the unit cell appeared to be independent; they are located at the inversion centres at (0,0,0) and ($\frac{1}{2},\frac{1}{2}$,0), so that the thiophene rings within a molecule are centrosymmetrically related. Only the average structure model was refined, the scattering factor of the composite atoms being taken as $\frac{1}{4}f(S)+\frac{3}{4}f(C)$. During the least-squares refinement, the index R decreased to 0·10. The final parameters are listed in Table 2. The large values of the thermal parameters show that the carbon and sulphur parts of the composite atoms do not coincide as was assumed during our refinement.

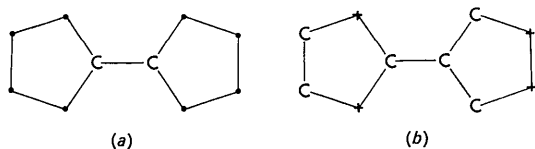It may be mentioned here that attempts were also made to refine the structure in space group $P1$. In this

space group, the sites (0,0,0) and ($\frac{1}{2},\frac{1}{2}$,0) do not correspond to inversion centres and all the four thiophene rings in the unit cell are independent. The non-centrosymmetric molecular model as represented in Fig. 1(b) was used for the refinement. It is possible to place this model in two different ways related by inversion symmetry about (0,0,0) or ($\frac{1}{2},\frac{1}{2}$,0), which results in two possibilities for the relative positions of the two molecules. Both these alternatives were considered and it was observed that the minimum R index obtained has the same value, 0·10, as for the case of the refinement in $P\bar{1}$. The isotropic temperature factor B was found to be 6·0 Å² on the average for the carbons of the central bond. For the rest of the C atoms, the average B value of 5·3 Å² was much lower than the average value of 11·7 Å² of the 'mixed' atoms, thereby indicating that the latter atoms have far less sulfur content than assumed in the molecular model. Therefore, we are led to believe that model (a) in Fig. 1 is much more predominant and hence closer to reality than model (b).

3,3'-Dithienyl

For 3,3'-dithienyl, no indication of disorder was obtained on inspection of the three-dimensional Patterson synthesis. After anisotropic least-squares refinement without assuming disorder, the structure model obtained [Fig. 2(a)] appeared to be not quite satisfactory, however, because of the following reasons: (a) the thermal parameters of S ($8\pi^2U_{ii}=7\cdot2$ Å² at room temperature) are large in comparison with those of C(4) ($8\pi^2\bar{U}_{ii}=3\cdot8$ Å²), indicating that the electron densities assumed for C(4) and S are too low and too high respectively, (b) the agreement between F_o and F_c is rather poor; the index R, 0·10 for series A, is higher than the value, 0·05, expected from a comparison of the two sets of F values measured at room temperature, (c) the difference map [Fig. 3(a)] shows anomalies in the neighbourhood of C(4) and (d) the 'double' bond C(3)–C(4) in the thiophene ring is long in comparison with the 'double' bond C(1)–C(2) and the 'single' bond C(2)–C(3).

These effects were assumed to be significant, as they persisted for all three sets of intensity data even though these were worked out independently. The results reported in this paper are those of series A (Table 1), as this series has more reflexions than B and is considered more accurate than C (see experimental).

The observed anomalies were tentatively explained by assuming that a minority of the thiophene rings, statistically distributed in the crystal, are rotated around the central bond over an angle of 180° [Fig. 2(b)]. The weights of the two approximately coincident rings were estimated by trial and error making use of anisotropic least-squares refinement. The weights chosen were represented by the scattering factors used for the fractional atoms. For each of the chosen weights, the (fractional) atoms of the normal rings were refined, whereas those of the rotated rings were kept fixed. The anomalies appeared to become small for approx-

Fig. 1. Models for the average molecular structure of 2,3'-dithienyl. (a) In space group $P\bar{1}$, . $=\frac{1}{4}S+\frac{3}{4}C$. (b) In space group $P1$, $+$ $=\frac{1}{2}S+\frac{1}{2}C$.

imately 15% of the rings having the reversed orientation.

In the final stages of refinement, the number of rings in the reversed orientation was kept at 15%. Hydrogen atoms at positions calculated from the known geometry of a thiophene ring were included in the structure factor calculations. The parameters of carbon and sulphur atoms in the 'normal' and 'rotated' rings were refined in turn during alternating least-squares cycles. The index R decreased to 0·055. The final difference map is shown in Fig. 3(b), and the final parameters of the 'normal' ring are listed in Table 2. The bond lengths and angles are represented in Figs. 2(c) and 4. Comparison of Figs. 2(a) and 2(c) shows that the length of the bond C(3)–C(4) changed considerably when disorder was taken into account during the refinement. In the disordered model the 'double' bonds C(1)–C(2) and C(3)–C(4) have equal lengths and the 'single' bond C(2)–C(3) is longer.

Discussion of the structures

The best models obtained for the molecules are given in Fig. 4. In spite of the difficulties encountered during the work, it can be concluded that in all cases the molecules in the crystals are planar. In the observed average structures the largest distances to the best molecular planes are 0·02 Å for 2,2′-, 0·01 Å for 2,3′-, and 0·006 Å for 3,3′-dithienyl.

For 2,2′-dithienyl, which has been investigated in the gaseous as well as in the solid state, there is a difference in conformation for the molecules in the two phases. In the gas phase, there is an angle of twist around the central bond with an average value of approximately 34° (Almenningen, Bastiansen & Svendsäs, 1958). In the solid the molecules are planar and have the *anti* conformation (Fig. 4). The bond lengths and angles observed in the solid are not very accurate because of the inaccuracies in the intensities. The estimated standard deviations are approximately 0·02 Å for C–S, 0·03 Å for C–C, 0·8° for C–S–C and 2° for C–C–C. Owing to these large standard deviations it is impossible to make a meaningful comparison of the bond lengths and angles in the two phases. In Fig. 4 the bond lengths in the solid are compared with the lengths obtained from theoretical (SCMO) calculations (Kracht & Wiebenga, 1967).

For 2,3′-dithienyl no information on the molecular conformation could be obtained because of the high degree of disorder in the crystals. Atomic distances and
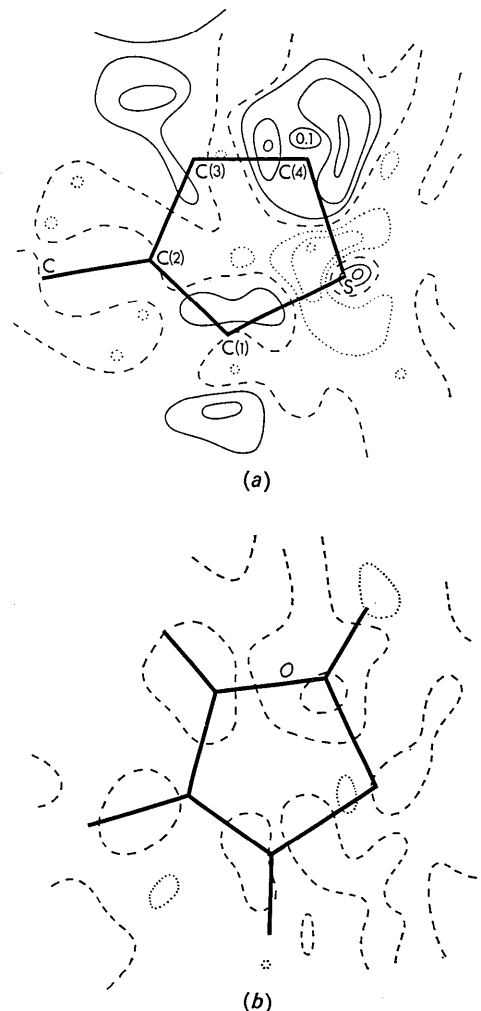

(a)

(b)

Fig. 3. Residual electron density for 3,3′-dithienyl in the plane of the molecule. (a) After anisotropic refinement without assuming disorder; hydrogen atoms were not taken into account in the structure model. (b) At the end of the refinement with a disordered structure model. Contours are at intervals of 0·15 e.Å⁻³; positive contours are represented as full lines and negative contours are dotted, the zero line being broken.

(a)

(b)

(c)
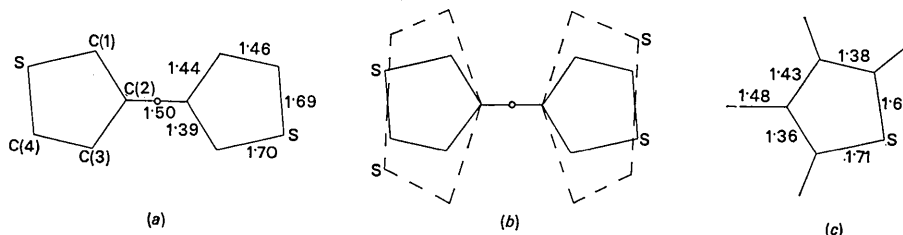
Fig. 2. Structure models for 3,3′-dithienyl. (a) After anisotropic refinement without assuming disorder; O = inversion centre. (b) Trial model for the superimposed rings with the rotated rings on twice the scale in vertical direction. (c) The final model for the non-rotated rings.

angles could be measured only in the average structure model. The mean value of corresponding distances or angles are listed in Fig.4(b). The values of 1·44 and 1·45 Å, observed for the central bond in the two molecules, show good agreement. The remaining distances (.—. = 1·52–1·61 Å and .—C = 1·53–1·62 Å) show large differences.

In 3,3′-dithienyl the 'average' molecules lie at inversion centres in the unit cell. It is impossible, however, to decide from the X-ray evidence whether this centre of symmetry, and thus the *anti* conformation, is preserved for all the individual molecules. A small proportion of the molecules, from 0 up to 30%, may have the non-centrosymmetric *syn* conformation occurring when only one of the rings has the reversed orientation.
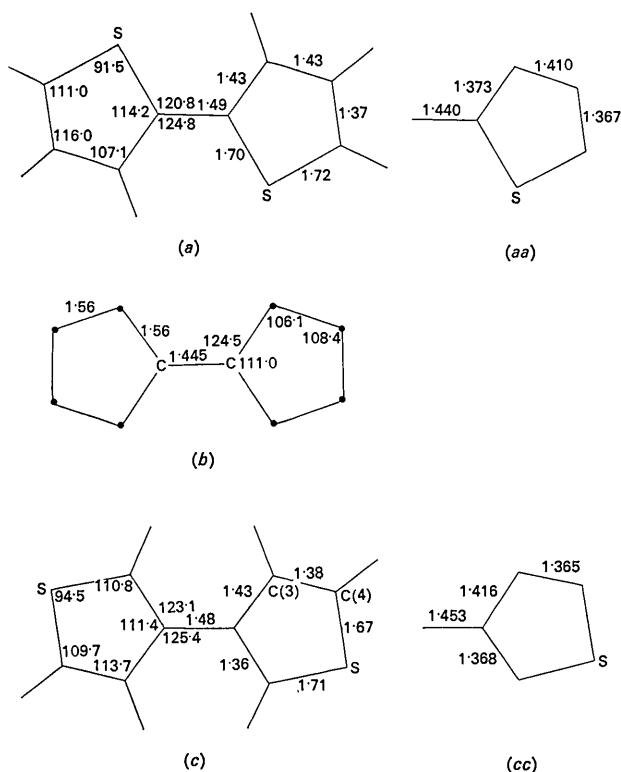
The standard deviations in the bond lengths and angles, as estimated from the least-squares residuals, are not very high, the values being nearly 0·008 Å for C–C, 0·006 Å for C–S, 0·7° for C–C–C and 0·3° for C–S–C. Quite large systematic errors may occur, however, because of an incorrect choice of the weight of the rings in the reversed orientation. The error in the distance C(3)–C(4) which is affected most by the disorder has been roughly estimated as 0·03 Å. Comparison of Figs.4(c) and 4(cc) shows that the agreement between experimental and theoretical bond lengths is good.

The bond lengths and angles in the thiophene rings of the dithienyls may be compared with those in thiophene. The two models proposed for thiopene by Bak, Christensen, Rastrup-Andersen & Tannenbaum (1956) from micro-wave data are given in Fig.5. Comparison of Figs.4 and 5 shows that, within the rather large experimental errors, the values observed for the dithienyls are equal to those in thiophene.

Arrangement of the molecules

As may be seen from Table 1, all three dithienyls have a short crystal axis (5·49–5·90 Å). The projections of the structures along these axes are compared in Figs.6, 7 and 8. In all cases the central bonds of the molecules lie approximately on parallel planes, namely on (202), (200) and (020) for 2,2′-, 2,3′- and 3,3′-dithienyl respectively. In all three dithienyls the angle between the plane of the molecule and the shortest axis is approximately 30° (29·7° for 2,2′-, 31·7° and 33·2° for 2,3′- and 31·2° for 3,3′-dithienyl). In this respect, the dithienyls are analogous to α- and β-thiophenic acid, where angles of 30·4 and 31·5° with short axes of 5·67 and 5·45 Å respectively have been observed.

In 2,2′-dithienyl, all molecules have the same tilt relative to the [101] direction, 7·4°; for the c direction alternating tilts, 46·5°, are observed. For 3,3′-dithienyl (Fig.8) both for the a and for the b direction the molecules have alternating tilts, 8·6 and 57·4° respectively. In 2,3′-dithienyl the molecules within a layer are parallel. The plane of the molecule at (0,0,0) makes angles of 53·3, −31·7 and −8·2° with a, b and c respectively; for the molecule at (½,½,0) these angles are 54·5, 33·2 and −8·6°.

None of the intermolecular distances is shorter than those expected for the conventional van der Waals contacts.

Disorder in β-thiophenic acid

The structure of β-thiophenic acid as described by Hudson & Robertson (1964) appears to show the same anomalies as the structure obtained for 3,3′-dithienyl when no disorder was assumed (Fig.2). In β-thiophenic acid again one of the 'double' bonds in the thiophene ring is long [Fig.9(b)], the thermal parameters B of S and C(4) are 3·4 and 1·2 Å² respectively (low temperature data). This suggests that disorder may also occur in crystals of β-thiophenic acid. A refinement of the

Fig.4. Structure models obtained for the dithienyl molecules. (a) 2,2′-Dithienyl, (aa) theoretical values. (b) 2,3′-Dithienyl, 'average' model obtained in the space group P1̄. (c) 3,3′-Dithienyl; the *anti* conformation shown is present in 70–100% of the molecules, (cc) theoretical values.
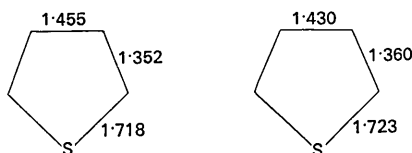

Fig.5. Models proposed for thiophene from micro-wave data.
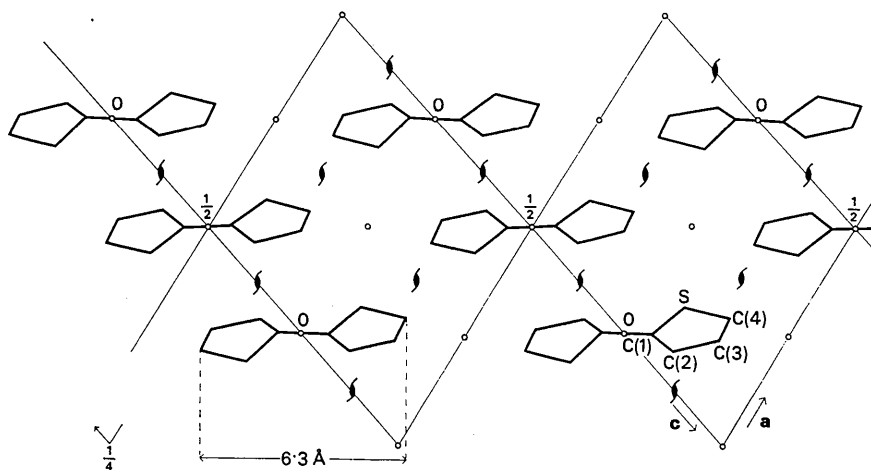
Fig. 6. Projection of the structure of 2,2'-dithienyl along the short crystal axis (b axis). The heights of the molecules in terms of b-translation are given by the numbers at the inversion centres. Thin lines indicate the unit cell chosen.

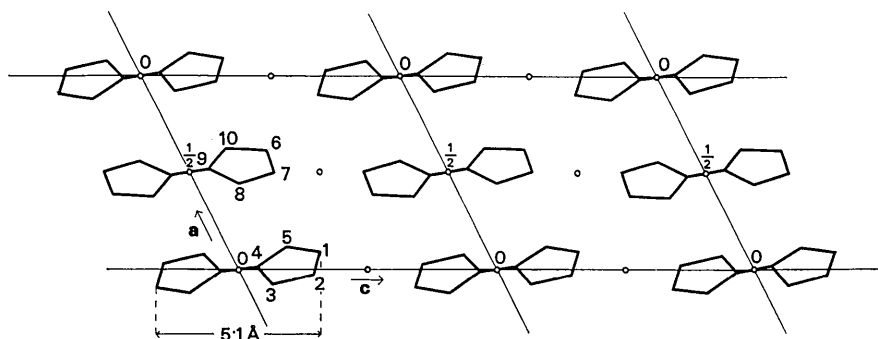Fig. 7. Projection of the average structure observed for 2,3'-dithienyl along the short crystal axis (b axis). (See also Fig. 6.)
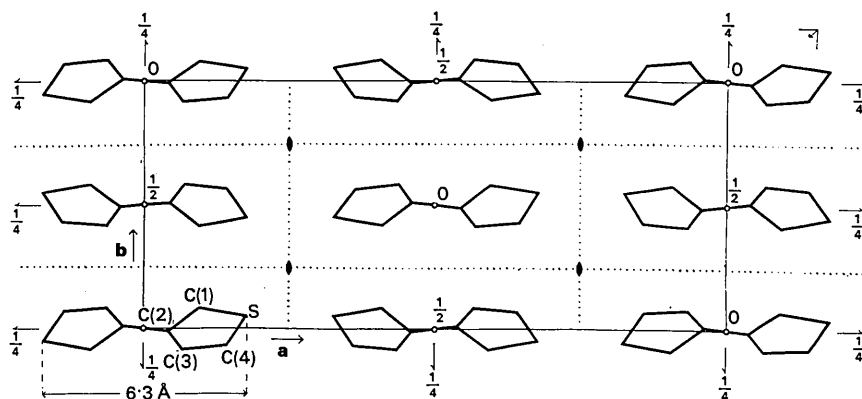

Fig. 8. Projection of the structure of 3,3'-dithienyl along the short crystal axis (c axis). All thiophene rings are tentatively drawn in the normal orientation. (See also Fig. 6.)

(a)

(b)

(c)

Fig. 9. Comparison of the structure models for β-thiophenic acid. (a) The numbering of the atoms. (b) The structure model proposed by Hudson & Robertson (1964). (c) The final model for the 'normal' molecules.

structure with Hudson & Robertson's data was carried out in the same way as described for 3,3′-dithienyl. The probability that the rings are in the reversed orientation has been estimated as 15%. The final model for the 'normal' rings is shown in Fig. 9(c). The changes in the bond lengths obtained by taking disorder into consideration are significant, minor changes in molecular geometry being due to inclusion of hydrogen atoms in the refinement procedures.

It was disappointing that introduction of disorder decreased the index R from 0·13 to 0·10 only. However, much accuracy has not been claimed for the intensities which were estimated visually on low temperature Weissenberg photographs (Robertson, 1966). This may explain why the observed bond lengths are far from satisfactory: the 'single' bond is not longer than the average value of the 'double' bonds.

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