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3,3′-Dithienyl Ketone

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Abstract. $C_9H_6OS_2$, monoclinic, $P2_1/c$, $a = 6{\cdot}168$ (5), $b = 11{\cdot}168$ (14), $c = 13{\cdot}374$ (35) Å, $\beta = 105{\cdot}33$ (16)°, $M_r = 194{\cdot}3$, $D_x = 1{\cdot}48$ g cm^{-3}. The thiophene rings make angles of 20·9 and 20·1° with the trigonal coordination plane at C(6). The bridging C—C distances of 1·463 (5) and 1·466 (6) Å indicate that there is relatively limited π delocalization between the C=O bond and the thiophene π systems. One of the thiophene rings is disordered.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions $\pm(hkl)$ on a Syntex $P2_1$ diffractometer (Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å). Intensity measurements were carried out in the θ–2θ mode ($3{\cdot}5 \le 2\theta \le 135{\cdot}0$°) with graphite-monochromated Cu $K\alpha$ radiation at scan speeds varying linearly between 2·93° min^{-1} (150 counts s^{-1} and below) and 29·30° min^{-1} (5000 counts s^{-1} and above). Scan and background times were equal. Lorentz and polarization corrections were applied but no absorption correction [μ(Cu $K\alpha$) = 4·8 cm^{-1}] was made.

After application of the acceptance criterion $I > 2{\cdot}0\sigma(I)$, 1400 unique reflexions were retained for use in the refinement. The structure was solved by direct methods (*SHELX* 76, G. M. Sheldrick) and refined by a blocked full-matrix least-squares method. After introduction of anisotropic temperature factors had led to values for R_G [$= (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] and R of 0·150 and 0·104 respectively, inspection of the difference synthesis revealed electron density peaks of 0·79 e Å^{-3} at 0·47 Å from C(10) and 0·39 e Å^{-3} at 0·45 Å from C(7). These peaks could be best interpreted in terms of a disorder of ring B as depicted in Fig. 1, *i.e.* the ring B' is related to B by rotation of ~180° about the axis C(8)—C(6). The atoms of ring B' were accordingly introduced into the refinement under the following conditions:

(1) The site occupation factors (s.o.f.) of rings B and B' were correlated so that s.o.f. (B') = 1 − s.o.f. (B).

(2) The equivalent distances in the rings B and B' were restrained to refine together with allowed standard deviations in the bond lengths of ±0·01 Å.

(3) The six H atoms of rings A and B were refined with a group isotropic temperature factor under the bond-length constraint that d(C—H) = 1·08 ± 0·01 Å.

(4) The atoms of rings B and B' were at first assigned a joint isotropic temperature factor, then at the final stage of the refinement the former ring atoms were allowed to refine anisotropically. This constrained refinement led, however, to unreasonable values for S(2)—C(10) and S(2′)—C(10′) (1·78 Å).

After inspection of the current values for the S(1)—C(2) and S(1)—C(5) distances in ring A, which should reasonably be similar to those in rings B and B', S(2)—C(7) and S(2)—C(10) and the equivalent bonds in ring B' were constrained to 1·70 ± 0·015 Å. Although this led to a significant increase in R_G (0·086 to 0·094) the

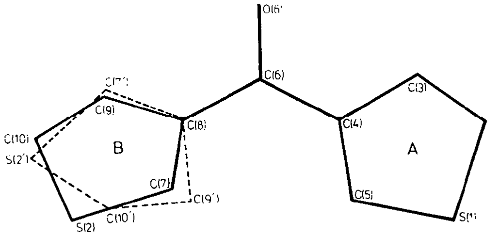
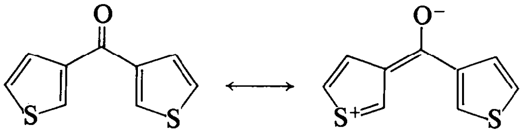


Fig. 1. The B ring disorder in (I).

refinement may be regarded as more physically meaningful in view of the fact that there are no significant differences between bond lengths in the *A* and *B* rings and that these bond lengths are in a similar range to those observed in other thiophene derivatives (Rychnovsky & Britton, 1968). The terminal value of R_w ($=\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$) was 0·086 and *R* was 0·083. The s.o.f. for the *B′* ring refined to 0·151 (5), the *B′* ring group isotropic temperature factor to 0·106 (5) Å^2, and that for the H atoms to 0·096 Å^2 (e.s.d. for *A* ring H atoms 0·009, for *B* ring 0·011 Å^2). The weights were given by $w = k/[\sigma^2(F_o) + gF_o^2]$, where *k* and *g* refined to 3·6985 and 0·000611. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Final positional parameters are in Table 1, bond lengths are listed in Table 2.* Fig. 2 is a perspective view of the molecule with the numbering system used, and Fig. 3 shows the unit-cell contents perpendicular to [100].



(I) (I′)

Discussion. This X-ray analysis of 3,3′-dithienyl ketone (I) was undertaken in order to study the importance of the mesomeric contributions of the two dipolar structures of the type (I′). The distortions of the thiophene bond lengths in three *O*-acetylthiophenecarboxylic acids (Griffe, Durant & Pieret, 1972) in comparison to those in the parent compound (Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen, 1961) have been interpreted as indicating a significant contribution from such dipolar structures. Steric contact between the H atoms on C(5) and C(7) in (I) must lead either to a widening of the C(4)—C(6)—C(8) angle or to a twisting of one or both of the thiophene rings relative to the trigonal coordination plane at C(6). The latter is, in

Table 1. *Positional parameters* (×10^4 *for the non-hydrogen atoms and* × 10^3 *for hydrogen atoms*)

	x	*y*	*z*
S(1)	4414 (2)	4313 (1)	7038 (1)
C(5)	5548 (8)	5384 (3)	7916 (3)
C(4)	7824 (7)	5284 (3)	8277 (2)
C(3)	8653 (8)	4281 (3)	7822 (3)
C(2)	6927 (8)	3639 (3)	7118 (3)
O(6)	11362 (5)	6145 (3)	8967 (2)
C(6)	9360 (8)	6115 (3)	8962 (3)
C(7)	6715 (8)	6782 (4)	10013 (3)
C(8)	8580 (6)	6929 (3)	9654 (2)
C(9)	9796 (9)	7977 (4)	10098 (3)
C(10)	8846 (10)	8611 (4)	10802 (3)
S(2)	6409 (3)	7889 (1)	10824 (1)
C(7′)	9984 (43)	7867 (23)	10037 (27)
C(9′)	6329 (34)	6863 (35)	9755 (29)
C(10′)	6556 (58)	7633 (31)	10623 (29)
S(2′)	8642 (20)	8679 (11)	10768 (9)
H(5)	434 (7)	600 (3)	807 (4)
H(3)	1034 (4)	394 (4)	809 (3)
H(2)	706 (9)	287 (3)	666 (3)
H(7)	526 (6)	620 (4)	983 (4)
H(10)	978 (9)	942 (3)	1103 (4)
H(9)	1122 (7)	834 (5)	988 (5)

Table 2. *Bond lengths* (Å)

C(5)—S(1)	1·692 (4)	C(2)—S(1)	1·701 (5)
C(4)—C(5)	1·363 (7)	C(3)—C(4)	1·431 (6)
C(6)—C(4)	1·463 (5)	C(2)—C(3)	1·416 (6)
C(6)—O(6)	1·233 (6)	C(8)—C(6)	1·466 (6)
C(7)—C(8)	1·368 (7)	C(9)—C(8)	1·432 (6)
C(7′)—C(8)	1·370 (26)	C(9′)—C(8)	1·432 (26)
S(2)—C(7)	1·688 (5)	C(10)—S(2)	1·712 (6)
C(9)—C(10)	1·422 (8)	S(2′)—C(7′)	1·701 (36)
C(10′)—S(2′)	1·710 (37)	C(9′)—C(10′)	1·422 (54)

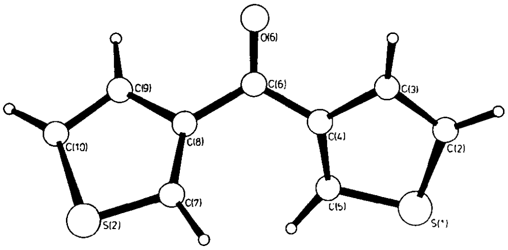


Fig. 2. The molecule in perspective with the numbering system used.

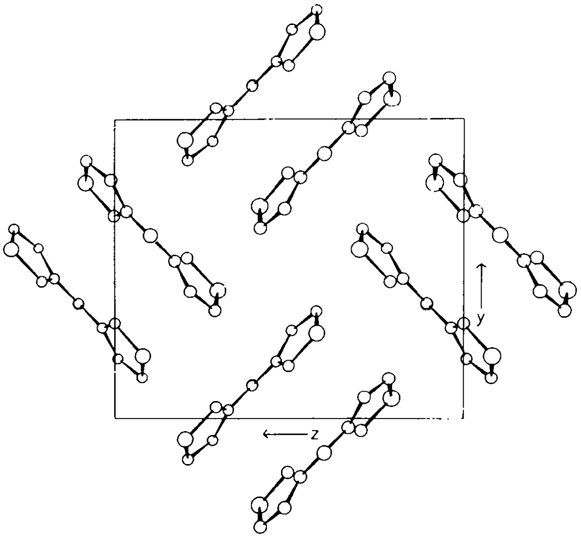


Fig. 3. Unit-cell contents perpendicular to [100].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33673 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

fact, observed with rings *A* and *B* making respective angles of 20·9 and 20·1°, whereas the C(4)—C(6)—C(8) angle of 121·5 (4)° is normal. The bond lengths and angles are similar in both thiophene systems lending the molecule an approximate C_2 symmetry. Both thiophene rings are planar [maximum deviation from their weighted least-squares planes = 0·02 Å at C(10)]. The disordered *B'* ring represents a 175·6° rotation of ring *B* about C(8)—C(6). The bond length distribution indicates that the contribution of the dipolar structures is limited. In octaethylxanthoporphinogen dihydrate (Sheldrick, 1976) bridging C—C distances of 1·440 (5) and 1·481 (5) Å were recorded, which indicated significant π-delocalization between the C=O bond and the first pyrrole ring. It is not possible to explain the short C(4)—C(5) and C(8)—C(7) distances in (I) in terms of any possible mesomeric contribution.

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5,6,7,8,15,16,17,18-Octahydrodibenzo[*e*,*o*][1,4,8,13]tetraazacyclohexadecene

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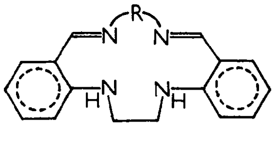
Abstract. $C_{20}H_{24}N_4$, $M_r = 320·4$, orthorhombic, *Fdd*2, $a = 40·778$ (26), $b = 34·990$ (24), $c = 4·928$ (1) Å, $V = 7031·4$ Å^3, $Z = 16$, $D_x = 1·21$ g cm^{-3}. The arrangement of N atoms is approximately planar but the geometry of the ligand shows considerable distortion from that observed in the corresponding $\mathrm{Cu^{II}}$ complex [Losman, D., Engelhardt, L. M. & Green, M. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 791–796].

Introduction. $C_{20}H_{24}N_4$ (I) was recrystallized from dichloromethane/methanol. Intensities were measured on a Philips PW1100 diffractometer using graphite-monochromated Mo *Kα* radiation and an ω–2θ scan. Unit-cell dimensions were obtained by least-squares analysis from the setting angles of 25 reflexions. Owing to poor crystal quality two octants of data were collected and equivalent reflexions were averaged. All independent reflexions *hkl* (all indices positive) were measured in the range $3·0 \leq \theta \leq 25·0°$. Reflexions $\bar{h}kl$ were measured for $3·0 \leq \theta \leq 28·0°$ but weak reflexions giving $I_t - 2\sqrt{I_t} < I_b$ on the first scan were omitted from the data set: I_t and I_b are respectively the count rates at the top of the reflexion profile and in the background. To increase the accuracy of measured reflexions a multiple-scan technique was employed; each reflexion was scanned repeatedly until 500 counts had been recorded or until a maximum of three scans had been made. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 0·40$ cm^{-1}); 932 unique reflexions with $F \geq 3\sigma(F)$ were used in the structure refinement. Space group *Fdd*2 is determined unambiguously by the systematic absences: *hkl*, $h + k$, $k + l$, $l + h \neq 2n$; $0kl$, $k + l \neq 4n$; $h0l$, $h + l \neq 4n$.



(I) R = $(CH_2)_4$

Conventional direct methods failed to give any encouraging molecular fragments so an attempt was

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