

Thus the structure of the compound is unambiguously shown to be (4), which arises from isomer (3a). All bond lengths and bond angles are fully consistent with literature values. The shortest non-hydrogen-atom intermolecular contact was 3.283 (3) Å between O(2) and C(1). There are no others shorter than 3.6 Å.

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Structure of Thiazolo[5,4-*d*]thiazole

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Abstract. C₄H₂N₂S₂, *M_r* = 142.20, monoclinic, *P*2₁/*n*, *a* = 7.847 (9), *b* = 6.606 (9), *c* = 5.517 (7) Å, β = 107.0 (1)°, *V* = 273.5 (9) Å³, *Z* = 2, *D_x* = 1.73 g cm⁻³, Mo *K*α radiation, λ = 0.71073 Å, μ = 8.09 cm⁻¹, *F*(000) = 144, *T* = 293 K, *R* = 4.9% based on 780 independent reflections. The structure consists of the packing of planar molecules placed on inversion centers. The geometric features are compared with thiazole and thiophene analogues to provide evidence for variations in 'aromaticity'. Three short contacts [S...N 3.201 (4), N...N 3.24 (1), N...H—C 2.56 (3) Å] determine the intermolecular packing.

Introduction. For a number of years polymers exhibiting electroconducting properties have been extensively studied at our institute. Recently, polyheterocyclic systems have attracted our attention with the aim of overcoming the drawbacks of polyacetylene, namely air stability and processability. Moreover, our interest has also been devoted to the elucidation of conduction models for these materials and to the prediction of potential applicative developments. In particular, we have focused our attention on the different contributions which play a decisive role in understanding the complex phenomena occurring in the conduction process. As part of our research concerning polymeric systems having an N atom in the conjugation pathway we studied polythiazole and its oligomers, *i.e.*, 4,4'-dimethyl-2,2'-bi-

thiazole as a model compound, in order to obtain precise inter- and intraring geometric parameters for *ab initio* calculations on these polymeric systems (Bolognesi, Catellani, Destri & Porzio, 1987). Here we present the crystal and molecular structure of thiazolo[5,4-*d*]thiazole with particular reference to known thiazole and thiophene analogues.

Experimental. The synthesis of thiazolo[5,4-*d*]thiazole was carried out by cyclization of dithiooxamide (Johnson, Rotenberg & Ketcham, 1970) and the product was crystallized from a solution of 50% aqueous ethanol. The experimental details and the crystal data are summarized in Table 1. Intensity data were collected on a Nonius CAD-4 computer-controlled diffractometer with a non-aligned crystal; subsequently the data were corrected for Lorentz and polarization effects, and an experimental absorption correction was applied (North, Phillips & Mathews, 1968). The absorption correction values range from 0.89 to 1.00. Unit-cell parameters and their e.s.d.'s were determined by an accurate centering of 25 strong reflections (θ range 8–15°) and then refined by least squares. The structure was solved by the Patterson method, by which the position of the S atom was determined. The positional and thermal parameters were refined using full-matrix least squares and minimizing $\sum w(F_o - KF_c)^2$, where $w = 1/\sigma^2$. After a difference Fourier map, which allowed the localization of all H atoms ($\Delta\rho$ max. and min. ±0.3 e Å⁻³), six

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Table 1. *Experimental data*

Scan mode	$\theta-2\theta$
Scan speed ($^{\circ} \text{ min}^{-1}$)	2.6
Scan width ($^{\circ}$)	$1.3 + 0.35 \tan \theta$
θ range ($^{\circ}$); d_{min} (\AA)	3–35; 0.62
Measured reflections	$h-12/12, k/0/13, l/0/8$
Number of collected reflections	1289
Number of observed reflections (with $I > 3.0\sigma$)*	780
Standard reflections (measured every 130 reflections)	$313, 31\bar{1}, 121\ddagger$
Wavelength (\AA) (Mo $K\alpha$ graphite-monochromated radiation)	0.7107
μ (Mo $K\alpha$) (cm^{-1}) \ddagger	8.09
Temperature (K)	293
Approximate crystal size (mm)	$0.15 \times 0.25 \times 0.30$

* $\sigma^2(I)$ = peak counts + total background counts.

\ddagger The intensity variation of the standard reflections during the collection was less than 2.0%.

\ddagger The variation in transmittance was estimated at +10%.

Table 2. *Atomic fractional coordinates ($\times 10^5$ for S; $\times 10^4$ for N, C; $\times 10^3$ for H) and thermal parameters (\AA^2), with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$$

	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
S	11075 (8)	25585 (8)	22035 (9)	3.151 (9)
N	913 (2)	3898 (3)	-2307 (3)	2.74 (3)
C1	-22 (2)	4779 (3)	1205 (3)	2.14 (3)
C2	1533 (3)	2447 (3)	-709 (4)	3.02 (4)
H2	216 (4)	125 (4)	-89 (6)	4.2 (6)

anisotropic least-squares cycles were carried out, refining also the positional and thermal (isotropic) parameters of H atoms, to yield a conventional R value of 0.049 and wR of 0.06 (final shift-to-e.s.d. ratio and goodness of fit were <0.05 and 1.19 respectively). Both real and imaginary components of the anomalous dispersion were included in the atomic-scattering-factor calculations (*International Tables for X-ray Crystallography*, 1974). All the computer programs are part of the Nonius package (B. A. Frenz & Associates Inc., 1982). In Table 2, the atomic fractional coordinates and the thermal parameters are given.*

Discussion. An *ORTEP* (Johnson, 1965) drawing of the molecule is shown in Fig. 1, while interatomic distances and angles are reported in Table 3. The condensed rings lie on an inversion center, at the middle point of the $C1-C1^i$ bond, and in a plane, the maximum displacement of which is 0.002 \AA . In Table 4 the bond distances for either thiophene or thiazole rings are reported for comparison. In spite of the barely significant differences, related to e.s.d.'s, a trend is evident for both thiophene and thiazole. On passing from monomer to dimer moieties, an enhanced 'quinoidic' character, *i.e.* decreased 'aromaticity', seems to

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44099 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

appear [see the increased differences in c , d , e distances for compounds (1) and (2), (4) and (5) of Table 4]. This is in good agreement with *ab initio* calculations carried out for optimizing the initial geometries of polythiophene (Bredas, Themans, Fripiat, André & Chance, 1984) and polythiazole (Bredas & Themans, 1986). Unfortunately homologues of the series are not available for this trend to be assessed definitely.

Conversely, no understandable trend of differences in bond distances for fused-ring compounds (3) and (6) can be recognized, implying that further investigations are necessary to clarify the effect. However, one cannot rule out the influence on bond distances and angles of both steric stress and variation of the electronic-charge distribution induced by fused-ring formation.

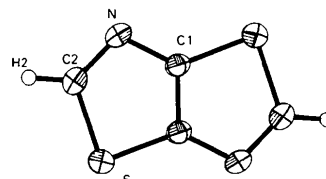


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule viewed normal to the plane of the rings, with thermal ellipsoids at the 50% probability level.

Table 3. *Selected interatomic distances (\AA) and angles ($^{\circ}$) in the molecule, with e.s.d.'s in parentheses*

S-C1	1.719 (2)	N-C2	1.296 (3)
S-C2	1.736 (2)	C1-C1 ⁱ	1.372 (3)
N-C1 ⁱ	1.368 (2)	C2-H2	0.95 (3)
C1-S-C2	87.7 (1)	C1-N-C2	108.0 (2)
S-C1-C1 ⁱ	109.6 (2)	N-C2-S	117.6 (2)
C1-C1 ⁱ -N	117.1 (2)		

Symmetry code: (i) $-x, 1-y, -z$.

Table 4. *Comparison of the interatomic distances (\AA) in structures containing thiophene or thiazole moieties*

	(1)	(2)*	(3)	(4)	(5)	(6)
a	1.714 (1)	1.717/1.721	1.718 (7)	1.724 (2)	1.718 (5)	1.736 (2)
b	1.714 (1)	1.717/1.721	1.758 (4)	1.713 (2)	1.744 (5)	1.719 (2)
c	1.370 (1)	1.357/1.346	1.356 (9)	1.367 (2)	1.334 (7)	1.372 (3)
d	1.423 (1)	1.433/1.444	1.439 (8)	1.372 (2)	1.395 (6)	1.368 (2)
e	1.370 (1)	1.357/1.346	1.374 (6)	1.304 (2)	1.332 (6)	1.296 (3)

References: (1) thiophene (Nygaard, Nielsen, Kirchheiner, Maltessen, Rastrup-Andersen & Sorensen, 1969), (2) 2,2'-thienylthiophene (Almenning, Bastiansen & Svendsen, 1958; Bredas, Themans, Fripiat, André & Chance, 1984), (3) 2,5-di-*tert*-butyl-3,6-dineopentylthieno[3,2-*b*]thiophene (McKenzie, 1975), (4) thiazole (Nygaard, Asmussen, Hog, Maheshwari, Nielsen, Petersen, Rastrup-Andersen & Sorensen, 1971), (5) 4,4'-dimethyl-2,2'-bithiazole (Bolognesi, Catellani, Destri & Porzio, 1987), (6) this work.

* The standard deviations were not given; the values after the slashes are from *ab initio* calculations.

The shortest packing contacts in the crystal involve the N atoms, namely $N \cdots \bar{N}(\bar{x}, 1-y, -1-z)$ 3.24 (1), $N \cdots S(x, y, z-1)$ 3.201 (4), $N \cdots H_2-C_2(\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z)$ 2.56 (3) Å. The last contact, already found in 4,4'-dimethyl-2,2'-bithiazole (Bolognesi *et al.*, 1987), constitutes evidence for hydrogen-bond formation between the N and C atoms [see for confirmation the range of hydrogen-bond distances (2.3–2.6 Å) in Taylor & Kennard (1982)]. Finally one can infer that H2 has some acidic character, as found in bithiazole derivatives (Bolognesi *et al.*, 1987).

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The Structure of 1,6-Dihydroxy-7,8-dimethoxyxanthone

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Abstract. $C_{15}H_{12}O_6$, $M_r = 288.3$, monoclinic, $A2/a$, $a = 14.081$ (4), $b = 12.397$ (4), $c = 16.335$ (5) Å, $\beta = 116.38$ (7)°, $V = 2554$ (1) Å³, $Z = 8$, $D_m = 1.48$ (3), $D_x = 1.50$ Mg m⁻³, $\lambda(\text{Co K}\alpha) = 1.7903$ Å, $\mu = 1.55$ mm⁻¹, $F(000) = 1200$, $T = 298$ K, $R = 0.078$, $wR = 0.076$ for 1250 independent reflections. The xanthone ring is roughly planar with normal bond lengths and angles, and the molecules in the crystal are stabilized by O–H \cdots O type hydrogen bonds. The planes of the xanthone rings are stacked alternately at distances of 3.50 (3) and 5.80 (3) Å.

Introduction. Xanthenes are heterocyclic ring systems that have many pharmacological applications. The title compound was supplied by Dr Gopalakrishna of Government Medical Stores, Madras. The present work was undertaken to study the effect of substituents on the conformation of the xanthone system.

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Experimental. D_m by flotation; yellow needles (from methanol) 0.3 × 0.5 × 0.3 mm; Picker four-circle manual diffractometer (at the Department of Crystallography and Biophysics, University of Madras); $\theta/2\theta$ scan technique; Co K α radiation. Cell parameters refined from 34 strong accurately centred reflections in the range $30 \leq 2\theta \leq 58^\circ$; Lp correction, absorption ignored; 1402 unique reflections with $2\theta \leq 130^\circ$ and with $0 \leq h \leq 14$, $0 \leq k \leq 12$, $-16 \leq l \leq 14$; 1250 observed reflections with $|F_o| > 3.0\sigma(|F_o|)$; solution using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); two standard reflections monitored for every 100 reflections; $|E| \geq 1.30$ for phase generation, E map revealed all non-H atoms except C atom of the methoxy group at position 7 whose position and all H-atom positions were subsequently located from $\Delta\rho$ map. Full-matrix refinement (Gantzel, Sparks & Trueblood, 1961); anisotropic temperature factors for non-H atoms and isotropic for H atoms. The function minimized was $\sum w(F_o - F_c)^2$, where $w = 1/|F_o|^2$ if $|F_o| \geq |F_o|_{\min}$ and $w = 1/|F_o|_{\min}^2$ if $F_o < |F_o|_{\min}$ with $|F_o|_{\min} = 15.0$; max. $(\Delta/\sigma) = 0.3$; final