Crystal and Molecular Structure of 4-(Thio-*p*-toluoyl)-5-*p*-tolyl-1,2-dithiole-3-thione

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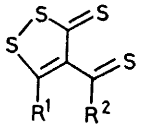
X-Ray crystal-structure analysis confirms that the 4-thioacyl-1,2-dithiole-3-thione molecule (with two *p*-tolyl substituents) is not symmetric. One pair of sulphur atoms is single-bonded and the other pair is not bonded. The conformation of the molecule is discussed. Crystals are monoclinic, *a* = 7.398(7), *b* = 13.802(10), *c* = 17.021(14)Å, β = 93.57(1)°, space group $P2_1/c$ with $Z = 4$. By use of 2478 significant reflections the structure was solved by direct methods and refined to *R* 0.067.

ATTEMPTS by Brown *et al.*[1] to prepare separable pairs of derivatives of the 4-thioacyl-1,2-dithiole-3-thione system (I) in which R^1 and R^2 are interchanged, failed, only



(I)

one product being obtained. This fact suggests that such derivatives are interconvertible (but, at room temperature, not rapidly so according to n.m.r. evidence). Extended Hückel calculations[2] on the unsubstituted parent molecule showed that (I) with S–S *ca.* 2.0 Å and S · · · S *ca.* 3.25 Å and its mirror image about the central C–C bond represent a pair of energy minima lying some 35 kcal mol^{-1} below that of the molecule having C_{2v} symmetry with both S · · · S *ca.* 3.0 Å. (There is a local, as opposed to global, energy minimum for another C_{2v} structure with both S–S *ca.* 1.9 A, but this is some 12 kcal mol^{-1} higher in energy.)

We report here the crystal structure analysis of the *p*-tolyl symmetrical derivative (I; $R^1 = R^2 = p$-tolyl). This shows the molecules to have the unsymmetric form (I) as expected, with the thiotoluoyl group twisted out of the dithiole ring plane.

EXPERIMENTAL

Crystal Data.—$C_{18}H_{14}S_4$, $M = 358$. Monoclinic, $a = 7.398(7)$, $b = 13.802(10)$, $c = 17.021(14)$ Å, $\beta = 93.57(1)°$, $U = 1\,734.6$ Å^3, $D_c = 1.37$, $Z = 4$, $D_m = 1.36(1)$ g cm^{-3}, $F(000) = 744$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 34.9 cm^{-1}. Space group $P2_1/c$ from systematic absences.

The crystal used for data collection was a thin plate, of irregular shape, of dimensions *ca.* 0.3 × 0.1 × 0.2 mm. It was mounted about the *x* axis, parallel to its longest dimension. Cell parameters and their standard deviations were obtained from diffractometer angular settings of 12 well-centred reflections by use of Cu-K_α radiation. Intensities were collected on a computer-controlled Picker four-circle diffractometer equipped with pulse-height analyser by use of filtered Cu-K_α radiation. Scanning was in the θ—2θ mode at 2° min^{-1}. Backgrounds were determined for 30 s at each end of the scan range of 1.6° adjusted for α splitting. The take-off angle was 3.0°. During the course of data collection there was a random deviation of $<5\%$ from the mean in the intensity of the standard reflection, recorded every 30 reflections. Counting statistics and an Abrahams factor[3] of 0.01 were used to calculate $\sigma(I)$. Of the 2 898 independent reflections measured, 2 478 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Absorption corrections were not applied.

Structure Determination.—The crystal structure was determined by direct methods from the 456 reflections having $|E| \geqslant 1.40$ using the program MULTAN.[4] An unique non-trivial solution was obtained, and the computed *E* map revealed the positions of all 18 non-hydrogen atoms. Refinement was by XFLS 3 using $[\sigma(F_o)]^{-2}$ as weights and Hartree–Fock scattering factors[5] with appropriate corrections for anomalous dispersion applied for sulphur. Three cycles of isotropic refinement gave a conventional unweighted *R* of 0.167 for all significant reflections. Another two cycles, with anisotropic temperature factors applied to all non-hydrogen atoms, lowered *R* to 0.082. A difference-Fourier map computed at this stage revealed all the hydrogen atom positions, and these were then included in later refinement. Two more cycles using mixed temperature factors (anisotropic for non-hydrogen atoms, isotropic otherwise) and refining all variable parameters gave a final unweighted *R* of 0.067 † and a value of 1.07 for the estimated standard deviation of a unit observation. The final difference map showed no peaks >0.3 eÅ^{-3}, the largest being situated near the sulphur atoms. Results are shown in Tables 1—5.

DISCUSSION

As expected from both experimental and theoretical studies S(1) and S(2) are single-bonded at 2.044 (3) Å, and S(3) and S(4) are non-bonded so that the molecule is without mirror symmetry. The conformation of the molecule shows how the various conflicting stereochemical requirements are reconciled. First, mutual coplanarity of rings (1) and (2) (Figure) would yield maximum π conjugation but this is prevented by the close proximity of H(9) to C(2) and to C(10) and the close proximity of H(5) to S(2). The twist of 47.7(2)° is clearly a compromise which brings these non-bonded distances to 2.89, 2.75, and 2.82 Å respectively. The double interaction of H(9) with non-bonded carbon atoms may be the reason why the *exo*-angles at C(3) are

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† Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22082 (15 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[1] E. I. G. Brown, D. Leaver, and T. J. Rawlings, *Chem. Comm.*, 1969, 83.

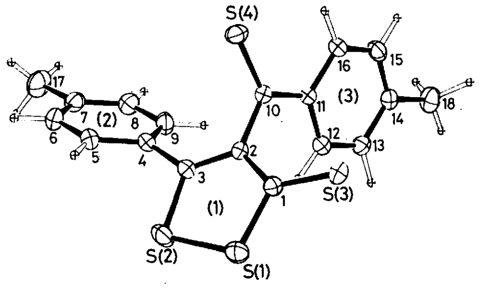
[2] G. Calzaferri and R. Gleiter, *J.C.S. Perkin II*, 1975, 559.

[3] S. C. Abrahams and J. L. Bernstein, *Acta Cryst.*, 1965, **18**, 926.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[5] D. T. Cromer and J. H. Mann, *Acta Cryst.*, 1968, **A24**, 321.

so different: 128.8(3) and 114.0(3)°. Second, coplanarity of C(10)–S(4) with ring (3) would also maximize π conjugation, as would the coplanarity of C(3), C(2), C(10), and S(4). Clearly both conditions cannot be satisfied simultaneously. If C(3)–C(2) and C(4)–C(10) were planar *s-trans*, rings (2) and (3) would badly clash; if they were planar *s-cis*, ring (3) and S(3) would badly clash. The compromise reached is that C(3)–C(2), C(10)–S(4) is twisted 73.8(4)° from the planar *s-cis* conformation and ring (3) is twisted 10.4(4)° from the plane of the three atoms about C(10). This creates close contacts between S(4) and H(16) and between C(2) and H(12) which may account for the somewhat small internal angle of 117.5(3)° at C(11). In all four cases where sp^2 carbon atoms are bonded together there is the usual correlation of torsional angle with bond length (see Table 5).



Molecular conformation, showing the atom numbering system used in the analysis

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$)

	x	y	z
S(1)	5 912(2)	2 380(1)	2 131(1)
S(2)	3 949(2)	1 365(1)	2 282(1)
S(3)	6 968(2)	3 962(1)	3 169(1)
S(4)	4 427(2)	2 640(1)	4 978(1)
C(1)	5 575(5)	3 053(3)	2 967(2)
C(2)	4 125(5)	2 701(3)	3 402(2)
C(3)	3 248(5)	1 882(3)	3 140(2)
C(4)	1 711(5)	1 378(3)	3 472(2)
C(5)	1 702(7)	366(3)	3 524(3)
C(6)	190(7)	−105(3)	3 787(3)
C(7)	−1 300(6)	401(4)	4 007(3)
C(8)	−1 269(6)	1 402(3)	3 963(3)
C(9)	220(6)	1 883(3)	3 705(3)
C(10)	3 756(5)	3 195(3)	4 160(2)
C(11)	2 876(5)	4 139(3)	4 118(2)
C(12)	2 107(6)	4 501(3)	3 407(2)
C(13)	1 269(6)	5 397(3)	3 372(2)
C(14)	1 166(5)	5 966(3)	4 040(2)
C(15)	1 948(6)	5 606(3)	4 743(2)
C(16)	2 762(5)	4 719(3)	4 791(2)
C(17)	−2 971(8)	−120(4)	4 255(4)
C(18)	281(7)	6 947(4)	4 014(3)
H(5)	257(6)	2(4)	334(3)
H(6)	21(7)	−83(5)	381(3)
H(8)	−235(6)	181(3)	413(2)
H(9)	31(5)	260(3)	367(2)
H(12)	226(5)	403(3)	294(2)
H(13)	75(7)	568(4)	382(3)
H(15)	187(5)	601(3)	521(2)
H(16)	327(6)	441(3)	530(3)
H(17A)	−271(7)	−65(4)	458(3)
H(17B)	−357(9)	−50(5)	381(4)
H(17C)	−357(9)	31(5)	452(4)
H(18A)	−66(8)	686(5)	427(4)
H(18B)	125(8)	753(4)	428(4)
H(18C)	27(8)	717(5)	355(4)

TABLE 2

Bond lengths (Å)

S(1)–S(2)	2.044(3)	C(8)–C(9)	1.381(6)
S(1)–C(1)	1.731(4)	C(9)–C(4)	1.383(6)
S(2)–C(3)	1.734(4)	C(7)–C(17)	1.513(8)
S(3)–C(1)	1.646(4)	C(2)–C(10)	1.499(5)
S(4)–C(10)	1.639(4)	C(10)–C(11)	1.456(5)
C(1)–C(2)	1.426(5)	C(11)–C(12)	1.398(5)
C(2)–C(3)	1.364(5)	C(12)–C(13)	1.383(6)
C(3)–C(4)	1.475(6)	C(13)–C(14)	1.389(6)
C(4)–C(5)	1.400(5)	C(14)–C(15)	1.388(6)
C(5)–C(6)	1.392(7)	C(15)–C(16)	1.364(6)
C(6)–C(7)	1.376(7)	C(16)–C(11)	1.405(5)
C(7)–C(8)	1.385(6)	C(14)–C(18)	1.503(6)

TABLE 3

Bond angles (°)

S(1)–S(2)–C(3)	94.4(1)	C(5)–C(6)–C(7)	121.6(4)
S(2)–S(1)–C(1)	97.2(1)	C(6)–C(7)–C(8)	118.4(4)
S(1)–C(1)–S(3)	117.4(2)	C(6)–C(7)–C(17)	121.2(4)
S(1)–C(1)–C(2)	113.3(3)	C(8)–C(7)–C(17)	120.4(4)
S(3)–C(1)–C(2)	129.2(3)	C(7)–C(8)–C(9)	120.8(4)
S(2)–C(3)–C(2)	117.1(3)	C(8)–C(9)–C(4)	121.0(4)
S(2)–C(3)–C(4)	114.0(3)	C(2)–C(10)–C(11)	118.0(3)
S(4)–C(10)–C(2)	117.1(3)	C(10)–C(11)–C(12)	121.2(3)
S(4)–C(10)–C(11)	124.9(3)	C(10)–C(11)–C(16)	121.3(3)
C(1)–C(2)–C(3)	118.0(3)	C(12)–C(11)–C(16)	117.5(3)
C(1)–C(2)–C(10)	118.4(3)	C(11)–C(12)–C(13)	120.9(4)
C(3)–C(2)–C(10)	123.4(3)	C(12)–C(13)–C(14)	121.2(4)
C(2)–C(3)–C(4)	128.8(3)	C(13)–C(14)–C(15)	117.5(4)
C(3)–C(4)–C(5)	120.1(4)	C(13)–C(14)–C(18)	122.1(4)
C(3)–C(4)–C(9)	121.3(4)	C(15)–C(14)–C(18)	120.4(4)
C(5)–C(4)–C(9)	118.5(4)	C(14)–C(15)–C(16)	122.2(4)
C(4)–C(5)–C(6)	119.6(4)	C(15)–C(16)–C(11)	120.7(4)

TABLE 4

Best least-squares planes. Equations of planes are in the form $AX + BY + CZ = D$, where X, Y, and Z are real orthogonal co-ordinates (Å), and X is along x, z along z^*, and Y furnishes a right-handed system. Deviations (Å $\times 10^3$) of relevant atoms from the planes are given in square brackets

Plane (1): S(1)—(3), C(1)—(4), C(10) [ring (1)]

$$0.616X - 0.591Y + 0.521Z = 2.529$$

[S(1) 27(1), S(2) −28(1), S(3) −15(1), C(1) 45(4), C(2) 63(4), C(3) 11(4), C(4) 28(4), C(10) 13(4)]

Plane (2): C(4)—(9) [ring (2)]

$$0.344X + 0.046Y + 0.938Z = 5.936$$

[C(4) 8(4), C(5) −6(4), C(6) −1(5), C(7) 4(4), C(8) 1(5), C(9) −8(4), C(3) 103(4), C(17) 76(6)]

Plane (3): S(4), C(10), C(2), C(11) [:C(10):S(4)]

$$0.892X + 0.453Y - 0.006Z = 4.052$$

[S(4) 0(1), C(10) −10(4), C(2) 3(4), C(11) 4(4)]

Plane (4): C(11)—(16) [ring (3)]

$$0.884X + 0.429Y - 0.185Z = 2.652$$

[C(11) 1(4), C(12) 2(4), C(13) −1(4), C(14) −4(4), C(15) 8(4), C(16) −5(4), C(10) 1(4), C(18) 9(5)]

Angles (°) between normals to planes: (1)–(2) 47.7(2), (1)–(3) 73.8(4), (1)–(4) 78.7(4), (2)–(3) 71.2(4), (2)–(4) 81.3(4), (3)–(4) 10.4(4)

TABLE 5

Correlation of bond lengths (Å) and torsion angles (°) for C(sp^2)–C(sp^2) systems

Bond	Angle	Length
C(1)–C(2)	2.3(2)	1.426(5)
C(10)–C(11)	10.4(4)	1.456(5)
C(3)–C(4)	47.4(2)	1.475(6)
C(2)–C(10)	73.8(4)	1.499(5)

The dithiole ring is closely coplanar and C(4) and S(3) are both closely coplanar with it [plane (1), Table 4]. Although the two S–C bond lengths are virtually equal [1.731(4) and 1.734(4) Å], there is a significant difference in the internal angles at S(1) and S(2) [94.4(1) and 97.2(1)°]. This is probably associated with the difference in internal angles at C(1) and at C(3). These are consistent with the usual observation that for sp^2 carbon the angle containing a double bond is larger than that containing two single bonds.

There are no unusually short intermolecular distances.

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