

The Crystal Structure of Naphthaceno[5,6-*cd*:11,12-*c'd'*]bis-(1,2-dithiolane) (Tetrathiotetracene)

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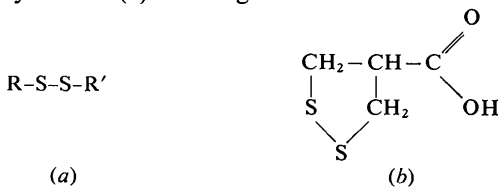
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Tetrathiotetracene crystals belong to space group $P\bar{1}$ with $a=9.890$, $b=18.226$, $c=3.968$ Å, $\alpha=87^\circ 38'$, $\beta=79^\circ 44'$, $\gamma=96^\circ 29'$ and two molecules per cell. The crystal structure has been determined by a three-dimensional X-ray diffraction analysis. Intensity data were collected on photographic film and a Stoe diffractometer. The structure was solved from the Patterson functions (001) and (100) with the help of the Fourier technique and packing considerations. Refinement by a full-matrix, least-squares method gave a final R value of 0.13 for 1100 reflexions. The S-S bond length is 2.100 Å and the average S-C distance is 1.781 Å. The molecule is nearly planar; only the S atoms are slightly out of the plane (0.021 to 0.056 Å). The C-C bond lengths are almost the same as those in the tetracene molecule.

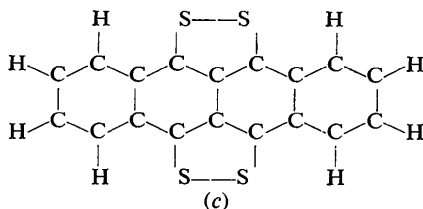
Introduction

The crystal structure analysis of tetrathiotetracene was carried out because specific knowledge concerning the dihedral angle of the disulphide bonds is of some importance to organic and theoretical chemistry. It has been established that the dihedral angle between the $3p\pi_{\perp}$ orbitals of the two sulphur atoms in a normal disulphide (*a*) is about 90° , whereas in 1,2-dithiolane-4-carboxylic acid (*b*) this angle is 26° .



In the latter case the steric requirements of the five-membered ring necessitate overlap of the $3p\pi_{\perp}$ orbitals of the two sulphurs and the resultant removal of the $3p\pi_{\perp}$ orthogonality which exists in case (*a*) leads to a destabilization of the disulphide bond in dithiolane or to an increase of the S-S bond length (0.05 Å).

When the structural studies were initiated, the structures of two unsaturated five-membered cyclic disulphides had been reported in the literature: 4-methyltrithione by Kehl & Jeffrey (1958), and thiuret hydroiodide by Foss & Tjomsland (1958). Since then many papers have been published, principally by Hordvik and coworkers. In the tetrathiotetracene molecule (*c*) the steric requirements of the five-membered ring are also present but in this case the effect of the π -delocalized system is not known.



Experimental

Dr Marschalk, who prepared (Marschalk, 1950) and has published several papers on tetrathiotetracene kindly provided us with a sample of the compound. Tetrathiotetracene was crystallized from trichlorobenzene as green dark needles.

The crystal data were obtained from Weissenberg photographs with Cu $K\alpha$ radiation. Lattice constants were refined by least-squares methods.

Crystal data

$C_{18}H_{18}S_4$ $M=256.42$
Triclinic, $a=9.890$ (6), $b=18.226$ (13), $c=3.968$ (15) Å,
 $\alpha=87^\circ 38'$, $\beta=79^\circ 44'$, $\gamma=96^\circ 29'$,
 $V=699.52$ Å³, $Z=2$, $D_c=1.65$ g cm⁻³, $D_m=1.63$ g cm⁻³
 $F(000)=304$, Cu $K\alpha$, $\lambda=1.5418$, $\mu=59.26$ cm⁻¹.
The space group is $P1$ or $P\bar{1}$.

Intensity data were collected by the multi-film equi-inclination Weissenberg technique with nickel-filtered copper radiation. Reflexion intensities for layers $hk0$, $hk1$ and $0kl$ were measured with a Nonius microdensitometer. The layers $0kl-5kl$ were collected on a Stoe diffractometer. The data were corrected for Lorentz, polarization and absorption effects.

Normalized structure factors (E) were computed with *NRC-4* of Hall (1966), which establishes scale and temperature corrections for the observed structure factors. Table 1 shows the experimental values for several functions of the normalized structure factors compared with the corresponding theoretical values for centrosymmetric and non-centrosymmetric structures respectively. The overall implication of these results is that the structure is centrosymmetric.

Structure analysis

The Patterson functions (001) and (100) were computed. Since the c cell constant was relatively small the molecule was expected to lie nearly parallel to (001).

Table 1. Statistical distributions and averages, experimental and theoretical

	PT	$P1$	Experimental
$\langle E \rangle$	0.798	0.886	0.789
$\langle E ^2 \rangle$	1.000	1.000	0.990
$\langle E^2 - 1 \rangle$	0.968	0.736	0.956
$E > 3$	0.3 %	0.01 %	0.45 %
$E > 2$	5.0 %	1.8 %	3.63 %
$E > 1$	32.0 %	37.0 %	32.65 %

The trial sulphur coordinates (X, Y), obtained from the Patterson function (001), were used to initiate the cyclic Fourier process which led to the structure of the whole molecule.

Structure-factor calculations were performed with the scattering factors of Hanson, Herman, Lea & Skillman (1964) and the agreement values R were 38 %

Table 2. Atomic coordinates and temperature factors ($\times 10^{-4}$) with e.s.d.'s in parentheses

Heavy atoms	x/a	y/b	z/c	B
S(1)	-213 (4)	1781 (2)	6123 (10)	—
S(2)	-2024 (4)	1169 (2)	8904 (11)	—
S(3)	3099 (4)	4453 (2)	4978 (11)	—
S(4)	1587 (4)	3629 (2)	7645 (11)	—
C(1)	-1519 (12)	283 (5)	7799 (32)	2.36 (18)
C(2)	-262 (11)	333 (5)	5492 (29)	2.18 (18)
C(3)	560 (12)	1015 (5)	4336 (33)	2.69 (20)
C(4)	1776 (12)	1060 (5)	2160 (31)	2.74 (20)
C(5)	2613 (11)	1750 (5)	906 (31)	2.42 (19)
C(6)	3831 (13)	1757 (5)	-1191 (33)	2.79 (20)
C(7)	4377 (14)	1117 (6)	-2589 (36)	3.37 (23)
C(8)	3607 (14)	443 (6)	-1379 (34)	3.29 (23)
C(9)	2316 (11)	388 (5)	972 (31)	2.16 (18)
C(10)	154 (10)	4107 (4)	7207 (26)	1.51 (16)
C(11)	513 (11)	4767 (4)	5265 (31)	2.08 (17)
C(12)	1921 (12)	5053 (5)	3888 (30)	2.49 (19)
C(13)	2313 (11)	5697 (4)	1983 (28)	2.03 (17)
C(14)	3740 (11)	5990 (5)	519 (30)	2.19 (18)
C(15)	4019 (12)	6648 (5)	-1418 (32)	2.83 (21)
C(16)	2964 (13)	7057 (5)	-2140 (34)	3.07 (22)
C(17)	1603 (12)	6829 (5)	-717 (32)	2.55 (19)
C(18)	1216 (12)	6131 (5)	1389 (32)	2.43 (19)

Hydrogen atoms. The thermal parameters were taken to be those of the adjacent carbon atom.

	x/a	y/b	z/c
H(1)	2398 (269)	2262 (117)	1322 (657)
H(2)	4403 (269)	2389 (127)	1770 (743)
H(3)	5310 (290)	1116 (122)	-4091 (708)
H(4)	4218 (266)	191 (128)	-3959 (713)
H(5)	4569 (260)	5740 (111)	579 (664)
H(6)	5152 (269)	6992 (129)	-1074 (727)
H(7)	3261 (281)	7626 (123)	-3930 (727)
H(8)	832 (236)	7144 (101)	-1245 (588)

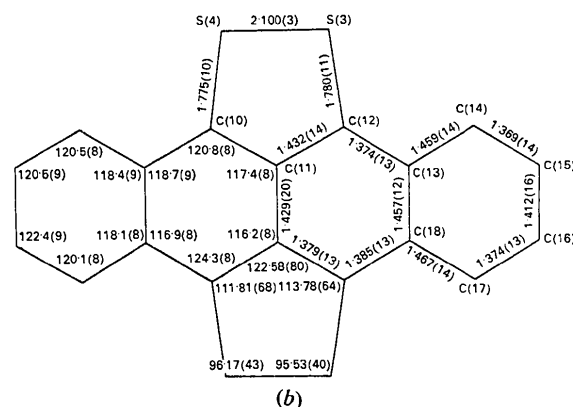
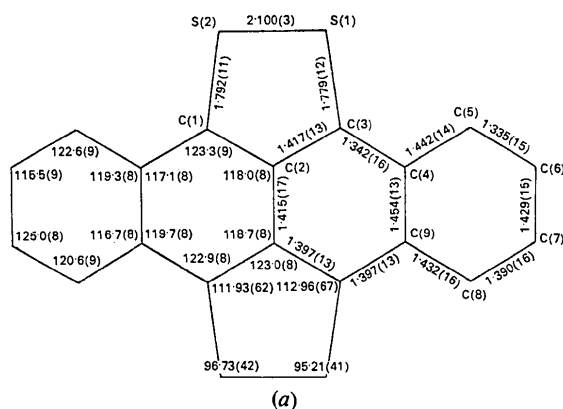


Fig. 1. Observed bond lengths and angles (a) in molecule A, (b) in molecule B.

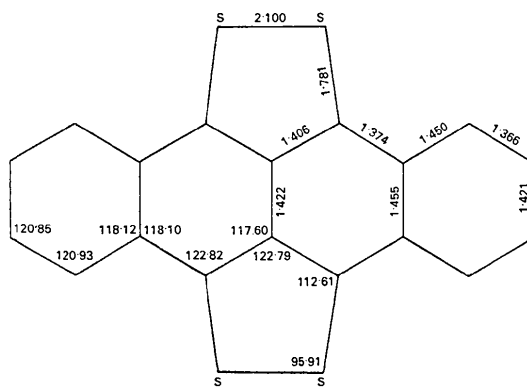


Fig. 2. Average values for chemically equivalent bond lengths and angles.

Table 2 (cont.)

Anisotropic temperature coefficients and their e.s.d.'s ($\times 10^{-6}$); $f = f_0 \exp(-\sum \beta_{ij} h k l)$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	8210 (433)	1362 (74)	44240 (2825)	979 (151)	-4435 (1501)	-2159 (403)
S(2)	8118 (449)	1896 (85)	51586 (3032)	1215 (165)	-3354 (1502)	-1924 (451)
S(3)	5988 (381)	2158 (87)	54707 (3087)	1367 (155)	-4148 (1486)	-475 (452)
S(4)	6339 (409)	1799 (83)	55192 (3197)	1232 (152)	-296 (1592)	+1691 (458)

structure factors are compared in Table 3. The final reliability index R is 0.13. Because the data were collected from several crystals, further refinement could not be expected to lead to a more reliable structure. The space group is $P\bar{1}$ and the molecular centres are situated on non-equivalent crystal centres.

The bond lengths and their e.s.d.'s for the two different molecules are given in Fig. 1(a) and (b) together with the bond angles. All equivalent bond lengths and angles in the non-equivalent molecules are equal within experimental errors, their averages being given in Fig. 2. The theoretical and experimental values for the tetracene molecule (Gleicher, 1966; Robertson, Sinclair & Trotter, 1961) are summarized in Table 4.

Table 4. Intercomparison of mean C-C bond lengths

Present analysis	Tetracene		
	Theoretical		Experimental
1.366 (7)	1.364	1.358	1.385 (14)
1.421 (12)	1.429	1.440	1.479 (20)
1.450 (7)	1.436	1.445	1.431 (14)
1.455 (12)	1.421	1.422	1.439 (20)
1.374 (7)	1.390	1.385	1.398 (14)
1.406 (7)	1.412	1.415	1.409 (24)
1.422 (12)	1.419	1.413	1.475 (20)

The equations of the best molecular least-squares planes and the distances of the atoms from their respective planes are presented in Table 5. The equations of the planes are expressed in orthogonal coordinates X, Y, Z with X parallel to \mathbf{a} , Y perpendicular to \mathbf{a} in the ab plane and Z parallel to \mathbf{c}^* .

Table 5. Equations of the best molecular least-squares planes and the distances ($\times 10^{-4}$ Å) of the atoms from their respective planes

Molecule 1: $-0.3179X + 0.0710Y - 0.9455Z + 0.8741 = 0$
 Molecule 2: $-0.1748X - 0.4700Y - 0.8652Z + 0.61156 = 0$

Molecule 1		Molecule 2	
S(1)	250	S(3)	-426
S(2)	-210	S(4)	+564
C(1)	55	C(10)	261
C(2)	168	C(11)	289
C(3)	17	C(12)	-72
C(4)	26	C(13)	-79
C(5)	7	C(14)	-247
C(6)	-152	C(15)	-73
C(7)	186	C(16)	539
C(8)	81	C(17)	151
C(9)	-5	C(18)	-50

Discussion

As shown in Table 4, the C-C bond lengths do not differ significantly from equivalent bonds in the tetracene molecule and the disulphide rings do not therefore alter the π distribution. The observed S-S bond length of 2.10 Å is longer than the usually accepted values of 2.04 Å and the dihedral angle between the planes containing C-S-S and S-S-C is

$\sim 0^\circ$. According to Hordvik (1966) (Fig. 3) a relationship exists between bond length and dihedral angle. From the empirical bond length/dihedral angle curve the observed parameters are in excellent agreement with the theoretical value. This increase of the bond length has been explained in terms of a single molecular orbital theory (Bergson, 1957), by a net

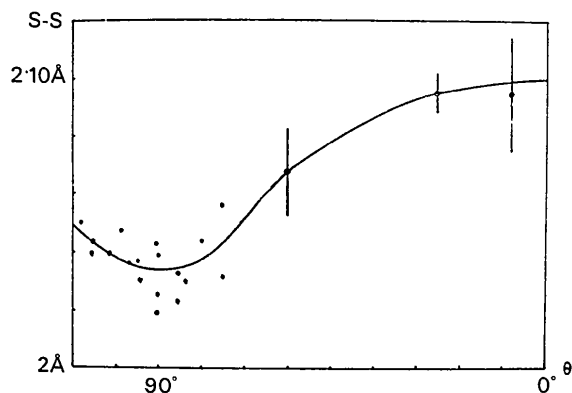


Fig. 3. Variation of sulphur-sulphur bond length with the dihedral angle.

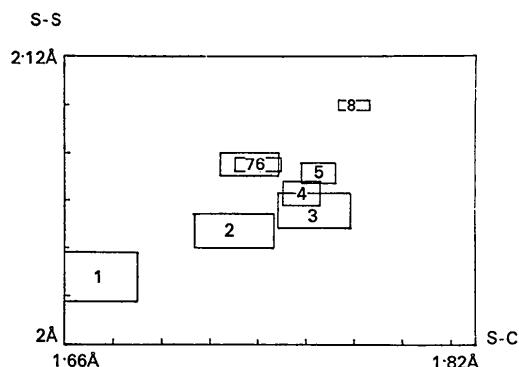


Fig. 4. Correlation between S-C and S-S bond lengths in planar groups. (1) Hordvik & Sletten (1966a, b). (2) Jeffrey & Shiono (1959). (3) Hordvik (1960). (4) Hordvik (1963). (5) Hordvik (1966). (6) Hordvik & Kjøge (1966). (7) Andreotti, Cavalca, Manfredotti & Musatti (1969). (8) Present analysis.

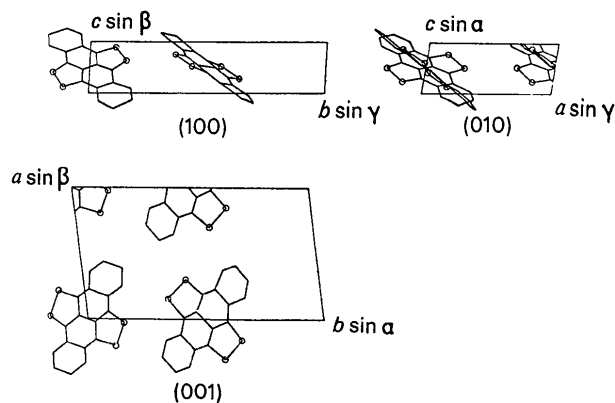


Fig. 5. Packing of molecules.

Table 6. Distance less than 3, 3·3, 3·5, 3·6, 3·8, 4 Å for the intermolecular contacts H···H, H···C, H···S, C···C, C···S, S···S respectively (Å)

S(4) (II)····S(1) (I)	3·75	S(2) (I)····S(2) (I-c)	3·96
C(16) (II)····S(2) (I)	3·68	H(1) (I)····S(4) (II-c)	3·09
C(17) (II)····S(1) (I)	3·45	C(10) (II)····C(11) (II-c)	3·52
C(17) (II)····S(2) (I)	3·73	C(11) (II)····S(4) (II-c)	3·80
H(29) (II)····S(2) (I)	3·22	C(12) (II)····S(3) (II-c)	3·76
H(30) (II)····S(1) (I)	2·92	C(12) (II)····S(4) (II-c)	3·69
H(30) (II)····S(2) (I)	3·39	C(12) (II)····C(13) (II-c)	3·53
H(27) (II)····S(3) (II,T)	3·18	C(13) (II)····S(3) (II-c)	3·69
C(1) (II)····S(2) (I-c)	3·49	C(14) (II)····S(3) (II-c)	3·70
C(2) (I)····S(2) (I-c)	3·75	C(15) (II)····C(14) (II-c)	3·50
C(3) (I)····S(1) (I-c)	3·73	C(16) (II)····C(13) (II-c)	3·55
C(3) (I)····S(2) (I-c)	3·65	C(16) (II)····C(14) (II-c)	3·58
C(4) (I)····S(1) (I-c)	3·65	C(17) (II)····C(18) (II-c)	3·49
C(5) (I)····S(1) (I-c)	3·65	C(5) (I)····H(6) (II,T-c)	3·01
C(8) (I)····C(9) (I-c)	3·49	C(6) (I)····H(6) (II,T-c)	2·64
C(3) (I)····C(4) (I-c)	3·52	C(15) (II)····H(2) (I,T-c)	2·72
C(6) (I)····C(5) (I-c)	3·55	S(3) (II)····C(14) (II,T-c)	3·67
C(8) (I)····C(4) (I-c)	3·60	S(3) (II)····C(15) (II,T-c)	3·77
S(1) (I)····S(1) (I-c)	3·96	S(3) (II)····H(5) (II,T-c)	2·96
S(1) (I)····S(2) (I-c)	3·78	H(1) (I)····H(6) (II,T-c)	2·62
H(4) (I)····C(8) (I-c)	3·13	H(2) (I)····C(15) (II,T-c)	2·71
H(4) (I)····C(9) (I-c)	3·02	H(2) (I)····H(6) (II,T-c)	1·70
H(4) (I)····C(11) (I-c)	3·35	H(5) (I)····H(5) (II,T-c)	2·95
C(1) (I)····C(1) (I-c)	3·65	C(7) (I)····S(2) (I,T-b-c)	3·70
S(1) (I)····C(17) (II-c)	3·78	H(3) (I)····S(2) (I,T-b-c)	3·07
S(1) (I)····H(10) (II-c)	2·89		

antibonding character of the four $3\pi_{\perp}$ electrons of the two sulphurs.

The average bond angle S-S-C of 95.9° is significantly shorter than the published values 107° (Toussaint, 1945) to 103° (Lee & Bryant, 1969). A review by Abrahams (1956) states that the valency angle for two-bonded sulphur is normally tetrahedral or slightly less. In our case, the steric requirements of the five-membered ring necessitate this decrease.

The observed C-S bond length of 1.781 \AA is shorter than the usually accepted values of 1.81 \AA . Fig. 4 shows the correlation between the S-S and S-C bond lengths in planar groups.

Molecular packing

The molecules are arranged as shown in Fig. 5. Contact between molecules is exclusively due to van der Waals interactions as supported by the distances listed in Table 6.

We thank Dr C. Marschalk for providing a sample of tetrathiotetracene.

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