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Structures of Linear Multisulphur Systems. VI. The Crystal and Molecular Structure of 2-*p*-Methoxyphenyl-4,5-[1-(1,3-dithiolane-2-ylidene)-tetramethylene]-1,6,6a-thiathiophthene, $C_{19}H_{18}OS_5$

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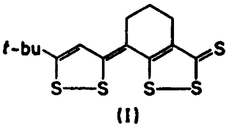
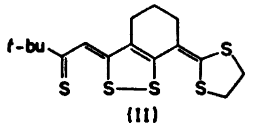
An X-ray crystallographic investigation of the title compound, $C_{19}H_{18}OS_5$, has been carried out. The crystals are triclinic, space group $P\bar{1}$ with four molecules in the unit cell. The cell dimensions are $a = 14.167(5)$ Å, $b = 11.623(5)$ Å, $c = 12.947(4)$ Å, $\alpha = 63.67(4)°$, $\beta = 101.78(5)°$, $\gamma = 100.95(6)°$. 7228 independent reflections with $2\theta \leq 52°$ (Mo$K\alpha$-radiation) were measured on an off-line diffractometer. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares to an R of 0.052. There are significant differences in bond lengths and angles between the two independent molecules in the asymmetric unit. In each molecule four sulphur atoms are lying on an approximately linear row, the interatomic distances in molecules a and b being S(1)−S(2) = 2.429(1) Å [2.563(1) Å], S(2)−S(3) = 2.225(1) Å, [2.165(1) Å], S(3)−S(4) = 2.920(1) Å, [2.974(1) Å], the numbers in brackets referring to molecule b.

A number of structure investigations of compounds with four and five collinear sulphur atoms have been undertaken.[1-8] Examples of these types of compounds are shown in formulas I−III.

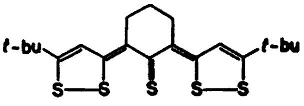
In these molecules S−S distances have been found to lie in the range between a single S−S bond length and van der Waals distance. Because the bonds are weak, they are easily perturbed by the influence of different substituents and by the intermolecular environment.



(I)



(II)



(III)

EXPERIMENTAL

The compound was synthesized by Stavaux and Lozac'h.[9] Deep red crystals grew from a toluene solution by slow evaporation at room temperature. The crystal used throughout the data collection had dimensions 0.40 × 0.40 × 0.10 mm^3, and was mounted with the [100] vector along the goniometer head axis. Weissenberg and precession photographs indicated a triclinic space group. Unit cell dimensions were derived from diffractometer measurements of 2θ values for 15 reflections using Mo$K\alpha$ radiation ($\lambda_{\alpha_1+\alpha_2} = 0.71069$ Å).

7228 unique reflections with $2\theta \leq 52°$ were recorded on an off-line four-circle diffractometer employing the $\theta - 2\theta$ scan technique and using niobium filtered MoK radiation. Scan ranges were calculated according to the tangent relationship of Alexander and Smith [10] using constants evaluated by scanning a number of reflections manually. Two reference reflections were monitored throughout the data collection; the repeated measurements were used for scaling the data. 1933 of the reflections were less than twice the estimated error in measurement;

Table 1. Atomic coordinates. The numbers in parentheses are standard deviations, referring to the last decimal places.

	Molecule *a*			Molecule *b*		
Atom	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
S(1)	0.86195(7)	0.17417(10)	0.63597(8)	0.44703(9)	0.26871(11)	0.50990(9)
S(2)	0.83949(7)	0.03940(9)	0.83773(8)	0.40477(8)	0.11941(10)	0.71465(9)
S(3)	0.81955(7)	−.08810(9)	1.02211(8)	0.36810(8)	−.01535(10)	0.88518(9)
S(4)	0.77973(7)	−.26494(10)	1.25736(8)	0.31310(8)	−.20552(10)	1.11570(9)
S(5)	0.91050(8)	−.46464(10)	1.37938(8)	0.42107(11)	−.42920(12)	1.22723(11)
O	1.14655(19)	0.28538(25)	0.25081(21)	0.76957(20)	0.30971(30)	0.18065(24)
C(1)	0.95757(24)	0.09966(32)	0.64697(28)	0.53456(25)	0.17686(34)	0.52931(30)
C(2)	0.98427(24)	0.00069(32)	0.75280(29)	0.54857(25)	0.07103(35)	0.63343(31)
C(3)	0.93499(23)	−.04234(31)	0.84967(27)	0.49328(24)	0.02883(33)	0.72477(29)
C(4)	0.95797(23)	−.15015(31)	0.95496(27)	0.50575(23)	−.08675(31)	0.82597(28)
C(5)	0.90672(23)	−.18398(31)	1.04644(27)	0.44848(23)	−.12153(32)	0.91173(29)
C(6)	0.92650(24)	−.29279(32)	1.15801(28)	0.45741(27)	−.24000(34)	1.01858(31)
C(7)	0.87689(25)	−.33195(31)	1.25038(28)	0.40320(26)	−.28188(34)	1.10608(30)
C(8)	0.83744(34)	−.44842(43)	1.46734(34)	0.32435(47)	−.43238(52)	1.29959(46)
C(9)	0.75205(32)	−.38428(39)	1.39843(33)	0.29975(40)	−.30868(46)	1.26401(38)
C(10)	1.00898(24)	0.14230(30)	0.54500(27)	0.59567(24)	0.21262(34)	0.43679(28)
C(11)	1.10059(26)	0.10988(34)	0.55434(29)	0.64817(28)	0.12444(36)	0.43424(31)
C(12)	1.14884(25)	0.15442(35)	0.45909(35)	0.70572(28)	0.16074(39)	0.34749(34)
C(13)	1.10516(26)	0.23250(33)	0.35162(30)	0.71156(26)	0.28487(41)	0.26203(33)
C(14)	1.23471(30)	0.24011(44)	0.25542(36)	0.76763(36)	0.43022(51)	0.08323(43)
C(15)	1.01347(27)	0.26548(34)	0.33903(29)	0.66086(28)	0.37339(37)	0.26342(32)
C(16)	0.96667(26)	0.22049(33)	0.43502(28)	0.60334(27)	0.33641(36)	0.34933(33)
C(17)	1.03638(26)	−.22807(35)	0.96555(29)	0.57880(26)	−.17172(36)	0.83734(31)
C(18)	1.02368(30)	−.36322(36)	1.05966(34)	0.56932(45)	−.30175(51)	0.93650(48)
C(19)	1.01095(29)	−.36241(36)	1.17198(31)	0.53505(46)	−.31901(52)	1.02964(45)
H(2)	1.0347(22)	−.0434(29)	0.7605(25)	0.5886(24)	0.0176(32)	0.6432(27)
H(81)	0.8827(47)	−.3759(64)	1.5079(52)			
H(82)	0.8296(38)	−.5222(51)	1.5252(42)			
H(91)	0.7059(40)	−.4522(52)	1.3740(45)			
H(92)	0.7372(40)	−.3266(53)	1.4268(45)			
H(11)	1.1291(30)	0.0528(38)	0.6199(34)	0.6481(29)	0.0252(39)	0.4900(33)
H(12)	1.2068(19)	0.1332(25)	0.4740(22)	0.7369(26)	0.0937(34)	0.3423(29)
H(141)	1.2393(31)	0.1303(43)	0.2899(37)	0.7905(45)	0.5063(62)	0.1088(49)
H(142)	1.2932(29)	0.2646(39)	0.2994(35)	0.8063(43)	0.4148(54)	0.0414(50)
H(143)	1.2445(33)	0.2819(44)	0.1654(40)	0.6945(43)	0.4455(50)	0.0397(43)
H(15)	0.9820(22)	0.3217(30)	0.2617(26)	0.6633(28)	0.4682(37)	0.2023(32)
H(16)	0.9026(29)	0.2384(38)	0.4215(32)	0.5788(24)	0.4022(31)	0.3535(27)
H(171)	1.0965(30)	−.1853(39)	0.9868(34)			
H(172)	1.0298(32)	−.2301(41)	0.8967(37)			
H(181)	0.9667(35)	−.4058(44)	1.0297(38)			
H(182)	1.0807(31)	−.4119(41)	1.0792(36)			
H(191)	1.0098(34)	−.4407(45)	1.2215(38)			
H(192)	1.0780(26)	−.3098(36)	1.1983(30)			

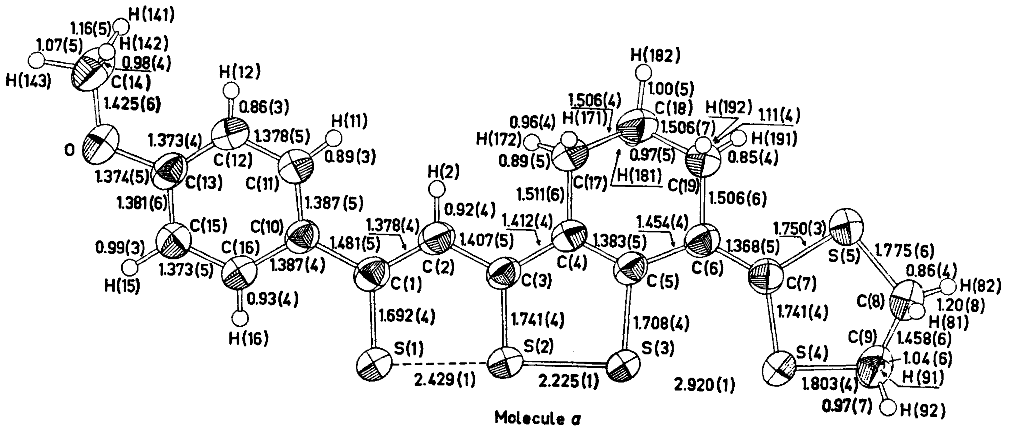
these reflections were given the threshold value of $2\sigma_c$ and were not included in the refinement unless $|F_c| > |F_{\text{threshold}}|$. Standard deviations in intensities were calculated as $\sigma_I = k[\sigma_c^2 + (0.02N_{\text{net}})^2]^{\frac{1}{2}}$, where k is the appropriate scalefactor, σ_c is the estimated error due to counting statistics and N_{net} is the net count, $(N_{\text{scan}} - N_{\text{background}})$, of the reflection. Standard deviations in structure factors were calculated as $\sigma_F = \sigma_I/2(I\ \text{Lp})^{\frac{1}{2}}$. The data were corrected for Lorentz and polarization effects according to standard procedures and for absorption using the method described by Coppens *et al.*[11] Extinction correction was not made as no evidence of extinction was detected at the end of the refinement.

Table 2. Thermal parameters with standard deviations, referring to the last decimal places, in parentheses. Anisotropic thermal parameters are of the form: $T_i = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$. The values are multiplied by 10^4.
Isotropic parameters are defined by: $T_i = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$. These values are multiplied by 10^3.

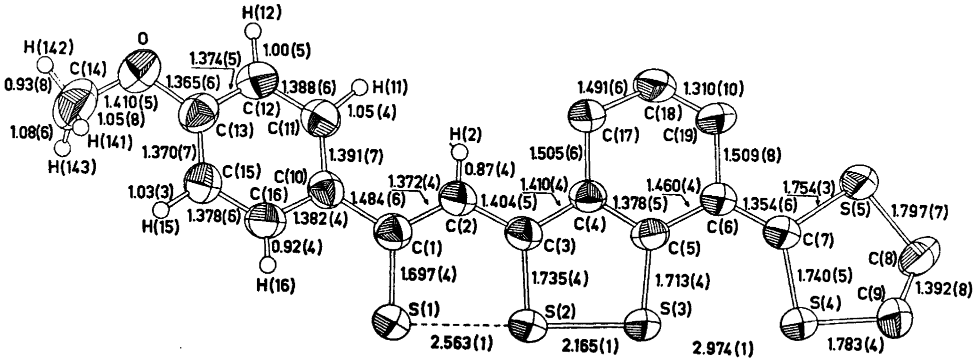
Atom	Molecule	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	*a*	663(7)	644(6)	489(5)	257(5)	−166(5)	170(5)
	b	816(8)	729(7)	628(7)	386(6)	−1(6)	239(6)
S(2)	*a*	536(6)	509(5)	479(5)	165(4)	184(4)	131(4)
	b	697(7)	559(6)	605(6)	288(5)	−88(5)	174(5)
S(3)	*a*	579(6)	560(6)	458(5)	203(5)	−146(4)	173(4)
	b	749(7)	558(6)	600(6)	300(5)	−88(5)	240(5)
S(4)	*a*	606(6)	716(7)	436(5)	227(5)	−155(5)	159(4)
	b	709(7)	637(4)	598(6)	307(5)	−84(5)	239(5)
S(5)	*a*	842(8)	594(6)	498(6)	276(6)	−52(5)	230(5)
	b	1380(11)	784(8)	871(9)	649(8)	222(7)	679(8)
O	*a*	765(18)	735(18)	553(15)	145(14)	−201(13)	292(13)
	b	700(19)	972(23)	726(19)	147(16)	−278(18)	249(15)
C(1)	*a*	507(21)	457(20)	485(20)	48(17)	−250(17)	106(16)
	b	477(21)	543(22)	552(22)	76(18)	−194(19)	62(17)
C(2)	*a*	470(20)	489(21)	518(21)	79(17)	−234(18)	126(16)
	b	487(22)	535(23)	564(23)	139(18)	−138(19)	91(18)
C(3)	*a*	451(20)	467(20)	427(19)	75(16)	−230(16)	96(15)
	b	420(20)	517(21)	512(21)	119(17)	−161(18)	34(16)
C(4)	*a*	452(20)	451(20)	470(20)	80(16)	−236(17)	94(16)
	b	382(19)	468(20)	533(21)	86(16)	−185(17)	58(16)
C(5)	*a*	452(20)	429(19)	447(19)	44(15)	−21(16)	117(15)
	b	428(20)	472(20)	582(22)	91(16)	−220(18)	108(16)
C(6)	*a*	497(21)	477(20)	479(20)	79(17)	−230(17)	112(16)
	b	604(24)	515(22)	558(22)	205(18)	−93(18)	177(19)
C(7)	*a*	536(22)	432(20)	457(20)	59(16)	−189(16)	96(16)
	b	585(24)	495(22)	557(22)	181(18)	−120(18)	142(18)
C(8)	*a*	987(33)	888(32)	553(24)	382(27)	4(23)	361(23)
	b	1894(60)	1034(40)	1099(41)	806(41)	187(32)	1039(42)
C(9)	*a*	857(31)	645(26)	601(24)	114(23)	−145(21)	326(22)
	b	1437(47)	840(33)	701(30)	601(32)	146(25)	564(30)
C(10)	*a*	486(21)	426(19)	442(19)	48(16)	−221(16)	110(16)
	b	443(20)	529(22)	469(20)	50(17)	−181(18)	20(16)
C(11)	*a*	585(23)	533(22)	462(20)	163(18)	−192(17)	91(17)
	b	648(25)	581(24)	551(23)	154(20)	−223(19)	50(19)
C(12)	*a*	499(22)	606(23)	544(22)	164(18)	−232(19)	113(17)
	b	662(27)	679(27)	666(26)	190(21)	−299(23)	104(21)
C(13)	*a*	599(24)	478(21)	523(22)	23(18)	−270(18)	194(18)
	b	468(22)	777(29)	585(23)	76(20)	−328(22)	61(18)
C(14)	*a*	665(28)	964(33)	750(28)	36(24)	−392(25)	309(22)
	b	945(36)	1002(38)	945(36)	−5(30)	−328(31)	510(29)
C(15)	*a*	651(25)	526(22)	460(20)	151(19)	−182(17)	122(18)
	b	618(25)	609(25)	606(24)	85(20)	−127(20)	191(20)
C(16)	*a*	554(23)	533(21)	473(20)	133(18)	−210(17)	123(17)
	b	564(24)	551(24)	692(25)	138(19)	−182(21)	140(20)
C(17)	*a*	617(23)	587(23)	494(21)	207(19)	−227(18)	123(18)
	b	514(22)	631(24)	568(22)	217(19)	−115(19)	139(18)
C(18)	*a*	789(28)	549(24)	708(25)	222(21)	−232(21)	252(21)
	b	1624(53)	1009(40)	1200(43)	928(39)	462(33)	933(41)
C(19)	*a*	805(27)	562(24)	532(22)	284(21)	−94(19)	219(20)
	b	1715(53)	1094(40)	1011(38)	1009(39)	314(31)	849(38)

Table 2. Continued.

Atom	U molecule a	U molecule b	Atom	U molecule a	U molecule b
H(2)	51(9)	62(10)	H(143)	135(16)	129(20)
H(81)	209(25)		H(15)	60(9)	90(13)
H(82)	113(19)		H(16)	62(13)	62(10)
H(91)	154(21)		H(171)	85(14)	
H(92)	134(21)		H(172)	68(15)	
H(11)	73(14)	85(13)	H(181)	117(16)	
H(12)	13(7)	84(12)	H(182)	74(15)	
H(141)	79(14)	140(25)	H(191)	78(16)	
H(142)	80(13)	135(22)	H(192)	85(12)	



Molecule *a*



Molecule *b*

Fig. 1. Intramolecular distances in molecules *a* and *b* together with the standard deviations as calculated based on the least-square parameters. Thermal ellipsoids for non hydrogen atoms are drawn at the 50 % probability level, hydrogen atoms are drawn with a fixed radius. Hydrogens are not included in the disordered regions of *b*.
Figs 1 and 3 are prepared using the ORTEP program.[20]

CRYSTAL DATA

$C_{19}H_{18}OS_5$, M.W. = 422.68
Crystal system triclinic, spacegroup $P\bar{1}$ (or $P1$).
Cell dimensions: $a = 14.167(5)$ Å, $b = 11.623(5)$ Å, $c = 12.947(4)$ Å, $\alpha = 63.67(4)°$, $\beta = 101.78(5)°$, $\gamma = 100.95(6)°$.
$V = 1858(2)$ Å^3, $Z = 4$.
$D_x = 1.511$ g cm^{-3}, $D_m = 1.50$ g cm^{-3} (flotation)
$\mu_{\mathrm{Mo}K\alpha} = 6.0$ cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

The distribution of E-values clearly indicated a centrosymmetric space group, thus $P\bar{1}$ was chosen rather than $P1$. A Patterson map revealed that the linear sulphur rows of the two independent molecules in the asymmetric unit were approximately parallel, however, the position of each row was not found. In retrospect it is seen that as expected the most dominant peaks in the map are due to intermolecular sulphur-sulphur vectors between the two molecules in the asymmetric unit. Since the S – S vectors between centrosymmetrically related molecules give peaks of approximately the same size as overlapping intermolecular S – C vectors, it was difficult to choose among a number of possible solutions.

A symbolic addition procedure programmed by Long [12] was tried. Two attempts were made with different starting sets, in each case using three variable signs. The most probable set of signs, judging from the internal consistency, was identical in the two runs. The corresponding E-map was not possible to interpret in terms of the structure. Six more sets were tested, none of which gave the correct solution.

The automatic procedure was then abandoned, and the signs of 170 reflections were calculated by hand, in each step including reflections determined with multiple, consistent sign relationships. Four symbolic signs were used. One of the possible solutions had no internal inconsistencies in the sign determination and was identical with the most probable set obtained by the automatic procedure. The second most consistent set was different from any of the sets tested. An E-map based on the 170 reflections clearly revealed 47 out of the 50 non-hydrogen atoms in the asymmetric unit. A structure factor calculation gave $R = 0.49$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$), and the remaining atoms were found in the subsequent Fourier map.

The structure was refined by full-matrix least-squares. The carbon atoms C(8), C(9), C(18) and C(19) of molecule b had fairly high temperature factors, indicating disorder for these atoms. However, an attempt to refine two fractional atoms for each of the four sites were not successful. At an R of 0.07 all hydrogen atoms, except those on C(8), C(9), C(17), C(18), C(19) of molecule b, were located from a difference map. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms with isotropic temperature factors. The refinement converged, at a conventional R of 0.052, and a weighted R of 0.058. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{\frac{1}{2}}$, is 2.87.

The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. The atomic scattering factors used were for non-hydrogen atoms those of Hanson *et al.*[13] and for hydrogen those of Stewart *et al.*[14] The final positional and thermal parameters, with standard deviations estimated from the least-squares process, are given in Tables 1 and 2.

Lists of observed and calculated structure factors may be obtained from the author.

The thermal parameters of each molecule were analyzed in terms of rigid body motion using the method of Schomaker and Trueblood.[15] For both molecules the thermal motion of the atoms of rings A + B are described reasonably well by the rigid body approximation. The axis of largest oscillation amplitude is in each case nearly parallel to the S(1) – S(2) – S(3) direction. Bond length corrections according to this model are 0.002 Å for S – S bonds, 0.014 Å for S – C and 0.004 Å for C – C bonds in rings A + B. Bond lengths shown in Fig. 1 are uncorrected for thermal motion.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

In Fig. 1 the atomic labelling used in this analysis and the intramolecular distances of the two molecules are shown. The intramolecular angles are listed in Table 3.

Table 3. Bond angles with the corresponding standard deviations listed in parentheses.

Angle	Molecule *a*	Molecule *b*
S(2)–S(1)–C(1)	92.3(1)	90.3(1)
S(1)–S(2)–S(3)	178.65(6)	176.93(7)
S(1)–S(2)–C(3)	88.5(1)	86.3(1)
S(3)–S(2)–C(3)	90.5(1)	91.8(1)
S(2)–S(3)–S(4)	175.58(4)	178.09(5)
S(2)–S(3)–C(5)	95.6(1)	96.1(1)
S(4)–S(3)–C(5)	85.5(1)	83.8(1)
S(3)–S(4)–C(7)	80.6(1)	80.5(1)
S(3)–S(4)–C(9)	175.3(2)	170.0(2)
C(7)–S(4)–C(9)	97.6(2)	96.5(2)
C(7)–S(5)–C(8)	97.4(2)	97.2(2)
S(1)–C(1)–C(2)	117.4(3)	118.2(3)
S(1)–C(1)–C(10)	119.8(2)	120.5(2)
C(2)–C(1)–C(10)	122.8(3)	121.2(3)
C(1)–C(2)–C(3)	123.4(3)	125.1(3)
C(1)–C(2)–H(2)	119(2)	120(2)
C(3)–C(2)–H(2)	117(2)	114(2)
S(2)–C(3)–C(2)	118.3(2)	119.9(2)
S(2)–C(3)–C(4)	118.6(3)	117.6(3)
C(2)–C(3)–C(4)	123.1(3)	122.5(3)
C(3)–C(4)–C(5)	119.1(3)	119.0(3)
C(3)–C(4)–C(17)	119.9(3)	119.8(3)
C(5)–C(4)–C(17)	121.0(2)	121.1(3)
S(3)–C(5)–C(4)	116.1(2)	115.5(2)
S(3)–C(5)–C(6)	121.4(3)	122.6(3)
C(4)–C(5)–C(6)	122.5(3)	121.9(3)
C(5)–C(6)–C(7)	124.9(3)	125.5(3)
C(5)–C(6)–C(19)	116.2(3)	115.4(3)
C(7)–C(6)–C(19)	118.8(3)	119.0(3)
S(4)–C(7)–S(5)	113.3(2)	112.8(2)
S(4)–C(7)–C(6)	127.5(2)	127.5(2)
S(5)–C(7)–C(6)	119.2(2)	119.7(3)
S(5)–C(8)–C(9)	111.8(3)	111.3(4)
S(5)–C(8)–H(81)	108(4)	
S(5)–C(8)–H(82)	107(5)	
C(9)–C(8)–H(81)	104(3)	
C(9)–C(8)–H(82)	119(4)	
H(81)–C(8)–H(82)	106(5)	
S(4)–C(9)–C(8)	110.5(3)	113.3(4)
S(4)–C(9)–H(91)	100(3)	
S(4)–C(9)–H(92)	98(3)	
C(8)–C(9)–H(91)	105(3)	
C(8)–C(9)–H(92)	112(3)	
H(91)–C(9)–H(92)	130(5)	
C(1)–C(10)–C(11)	122.6(2)	122.0(3)
C(1)–C(10)–C(16)	120.1(3)	121.0(3)
C(11)–C(10)–C(16)	117.3(3)	117.0(3)
C(10)–C(11)–C(12)	121.8(3)	120.9(3)
C(10)–C(11)–H(11)	122(3)	128(3)
C(12)–C(11)–H(11)	116(3)	111(3)
C(11)–C(12)–C(13)	119.4(3)	120.4(4)
C(11)–C(12)–H(12)	115(2)	119(2)
C(13)–C(12)–H(12)	125(2)	120(2)
C(12)–C(13)–C(15)	120.3(3)	119.6(4)
C(12)–C(13)–O	124.9(3)	115.5(4)
C(15)–C(13)–O	114.8(3)	124.9(3)
C(13)–O–C(14)	117.0(3)	117.3(4)
O–C(14)–H(141)	120(2)	111(3)
O–C(14)–H(142)	118(3)	98(3)
O–C(14)–H(143)	102(3)	111(2)
H(141)–C(14)–H(142)	101(3)	119(5)
H(141)–C(14)–H(143)	106(4)	105(5)
H(142)–C(14)–H(143)	109(3)	113(5)
C(13)–C(15)–C(16)	119.5(3)	119.7(3)
C(13)–C(15)–H(15)	120(2)	123(3)
C(16)–C(15)–H(15)	120(2)	117(3)
C(10)–C(16)–C(15)	121.7(3)	122.5(4)
C(10)–C(16)–H(16)	121(2)	121(2)
C(15)–C(16)–H(16)	117(2)	116(2)
C(4)–C(17)–C(18)	111.5(3)	113.2(4)
C(4)–C(17)–H(171)	106(3)	
C(4)–C(17)–H(172)	105(3)	
C(18)–C(17)–H(171)	108(2)	
C(18)–C(17)–H(172)	110(3)	
H(171)–C(17)–H(172)	115(4)	
C(17)–C(18)–C(19)	111.4(3)	121.1(5)
C(17)–C(18)–H(181)	105(2)	
C(17)–C(18)–H(182)	113(2)	
C(19)–C(18)–H(181)	111(3)	
C(19)–C(18)–H(182)	105(3)	
H(181)–C(18)–H(182)	110(4)	
C(6)–C(19)–C(18)	112.3(3)	119.7(4)
C(6)–C(19)–H(191)	117(4)	
C(6)–C(19)–H(192)	108(2)	
C(18)–C(19)–H(191)	105(4)	
C(18)–C(19)–H(192)	107(2)	
H(191)–C(19)–H(192)	107(4)	

The two chemically equivalent molecules are shown to have markedly different sulphur-sulphur bond lengths. Corresponding S–C, O–C, and C–C distances in the two molecules are not significantly different, when bonds involving the disordered atoms C(8), C(9), C(18) of molecule *b* are excluded.

The atoms of rings A, B and C in each molecule show a small but significant deviation from planarity, the atomic deviations being essentially the same for the two molecules (Fig. 2). The atom C(18) of the trimethylene bridge is bent out of the plane in the same direction in the two molecules. In molecule *b* there is a disorder in this part of the molecule which could not be satisfactorily resolved by the refinement procedure. In a related multisulphur compound [8] a disordered structure could be for-

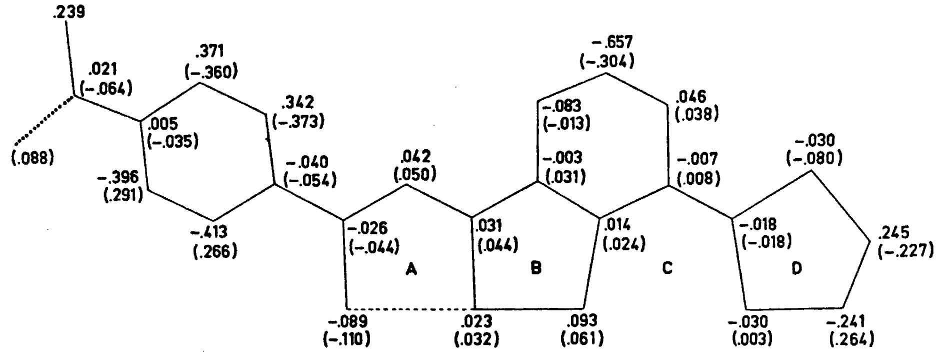


Fig. 2. Deviations (Å) from least-squares planes through the atoms of rings A + B + C for molecules *a* and *b*. Numbers referring to molecule *b* are in parentheses.

mulated in which two sites of approximately equal weight were found for C(18); the two sites being located on opposite sides of the least-squares plane. In the present case one of the configurations evidently is dominant.

The puckering of the 1,3-dithiolane rings are opposite in the two molecules. As mentioned above there are some signs of disorder in C(8) and C(9) of molecule *b*. The positions of these atoms are therefore uncertain. The $C_{sp^3}-C_{sp^3}$ bond C(8) – C(9) of 1.39 Å is clearly in error. In molecule *a* where there is apparently no disorder, the C(8) – C(9) bond of 1.458 Å is also unusually short. In other molecules containing 1,3-dithiolane rings the $C_{sp^3}-C_{sp^3}$ bonds have been found to be significantly shorter than the single bond value.[2,16] The tendency of these rings to be more or less disordered may account for this discrepancy.

The ring of the *p*-methoxyphenyl group is inclined at 16.5(5)° from ring A in molecule *a* and at 18.9(5)° in molecule *b*, the torsion angle in *a* being in the opposite direction to that in *b*. The methyl of the methoxy group is oriented *cis* and *trans* relative to C(12) in molecules *a* and *b*, respectively. The dihedral angle between the phenyl ring and the methoxy group is 9.2(5)° in *a* and 8.2(5)° in *b*.

The packing of molecules in the crystal is illustrated in Fig. 3. The crystal environments of the two molecules are similar, though with some noticeable differences. Pairs of centrosymmetrically related molecules overlap to a considerable extent; the interplanar spacing between molecule *a* and its inversion through (1,0,1) being 3.65 Å, and the corresponding distance between *b* and its inversion through (½,0,1) (*b*′) being 3.90 Å. Another difference between the molecular environments of *a* and *b* is that the oxygen of a *p*-methoxy group is

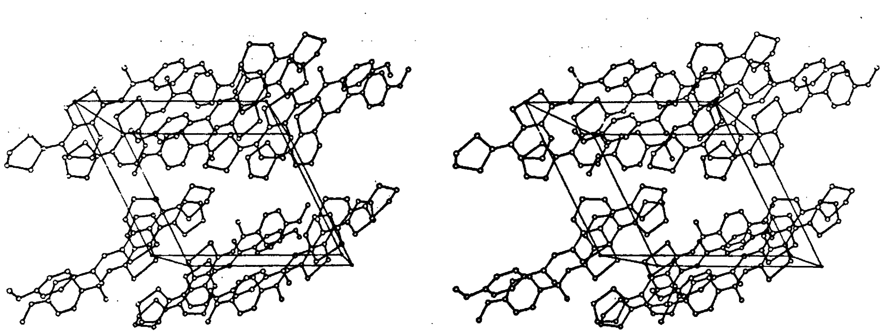
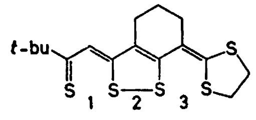
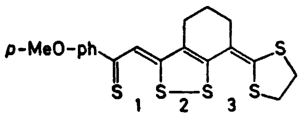


Fig. 3. Stereoscopic view of the molecular packing. The *a*-axis points towards the viewer, the *b* axis is horisontal, left to right, and *c* is vertical, top to bottom.

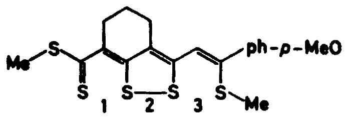
Table 4. Comparison between S – S distances (Å) in related compounds with four approximately collinear sulphur atoms.



(II)



(IV)



(V)

Molecule	Bonds					References
	1	2	3	1+2	1+2+3	
II	2.482	2.209	2.965	4.691	7.656	2
IV	2.429	2.225	2.920	4.654	7.574	present
	2.563	2.165	2.974	4.728	7.702	investigation
V	2.551	2.156	3.002	4.707	7.709	4

located 3.65 Å above ring C of molecule *b*, while no corresponding short contact is found for molecule *a*. The shortest intermolecular S···S distances occur between pairs of molecules not related by symmetry, *e.g.* between *a* and *b′* where S(2)*a*···S(4)*b′* = 3.45 Å, S(3)*a*···S(3)*b′* = 3.71 Å and S(4)*a*···S(2)*b′* = 3.53 Å.

Intramolecular distances of the collinear sulphur row in chemically related 4-sulphur compounds are given in Table 4. The variation in bonding through the chain is hard to explain in terms of substituent effects only. The large differences between chemically equivalent molecules in the present determination, clearly show that minor packing differences may exert a profound effect in the semi-covalent bonding between sulphur atoms. In a linear three-sulphur compound with two molecules in the asymmetric unit, large differences in S – S distances between chemically equivalent molecules have also been observed.[17] These findings are in agreement with the results from MO calculations on thiathiophthene, where it has been shown that the potential energy curve has a rather flat minimum when plotted as a function of the variation in S – S bond lengths.[18,19]

It is interesting to notice that a short central S – S bond length (2) corresponds to a long chain length and also to a long S(3)···S(4) distance (3). This may imply that the fourth sulphur atom exerts a small but significant influence on the thiathiophthene sulphur sequence, S(1)···S(3).

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