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Structures of Linear Multisulfur Systems. XI. The Crystal and Molecular Structure of 2-(5-Phenyl-1,2-dithiole-3-ylidene)-6-(5-*t*-butyl-1,2-dithiole-3-ylidene)-cyclohexanethione, $C_{22}H_{22}S_5$

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Crystals of the title compound, $C_{22}H_{22}S_6$, are monoclinic, space group $P2_1/c$, with $Z=4$ in a unit cell of dimensions $a=11.289(3)$, $b=23.952(6)$, $c=9.614(2)$ Å, $\beta=126.65(1)°$. 3286 unique reflections were recorded on a four-circle diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares technique to a final R of 0.082. The five sulfur atoms are approximately collinear, all S—S bond lengths being intermediate between a single bond and van der Waals distance; S(1)—S(2) = 2.179(3), S(2)—S(3) = 2.554(3), S(3)—S(4) = 2.582(3), and S(4)—S(5) = 2.149(3) Å. The structure of another modification of this compound has previously been solved. There are only minor differences between the two molecular structures, while the packing of the molecules in the crystal differs appreciably.

A structure investigation of the title compound was first carried out in 1970, and the results were reported in a short note.[1] The crystals originally obtained were of poor quality and the atomic parameters arrived at had low accuracy. In order to improve these results a reinvestigation was planned. It was difficult to get suitable crystals of the original modification (later referred to as mod. 1). However, adequate crystals of another modification (mod. 2) were obtained and used for X-ray investigation.

EXPERIMENTAL

The compound has been synthesized by Stavaux and Lozac'h.[2] Various crystallization procedures were tried. The crystals used in this investigation grew by slow evaporation from a carbon disulfide solution at approximately 5 °C, while crystals of mod. 1 were obtained from DMSO at room temperature.[1] A crystal of dimensions $0.43 \times 0.06 \times 0.32$ mm was chosen for data collection. The space group was derived from photographic Weissenberg and precession data, and unit cell dimensions from diffractometer measurement of 2θ values for 16 reflections with $2\theta > 30°$ [$\lambda_{(MoK\alpha_1)} = 0.70926$ Å]. These measurements were performed with an ω-scan procedure.[3] 3286 unique reflections with $2\theta \leqslant 48°$ were recorded according to the experimental procedure described elsewhere.[4] The intensities of 1100 of the reflections were less than the estimated error in measurements; these reflections were given the threshold value of σ_I and were included in the refinement only if $|F_c| > |F_{threshold}|$. Standard deviations in intensities were calculated as $\sigma_I = k[\sigma_c^2 + (0.01N_{net})^2]^{\frac{1}{2}}$, where k is the appropriate scale factor, σ_c is the estimated error due to counting statistics, N_{net} is the net count of the reflection. The data were corrected for Lorentz and polarization effects and for absorption. Standard deviations in the structure factors were calculated as $\sigma_F = \sigma_I/2(ILp)^{\frac{1}{2}}$.

CRYSTAL DATA

Mod. 2 (present work)	Mod. 1.[1]
$C_{22}H_{22}S_5$; M.W. = 446.74	as mod. 2
Space group $P2_1/c$	as mod. 2
a = 11.289(3) Å	a = 20.009(9) Å
b = 23.952(6) Å	b = 8.066(6) Å
c = 9.614(2) Å	c = 13.457(7) Å
β = 126.65(1)°	β = 103.07(2)°
V = 2085.6(9) Å^3	V = 2116(2) Å^3
Z = 4	Z = 4
$\mu(MoK\alpha) = 5.43$ cm^{-1}	$\mu(MoK\alpha) = 5.35$ cm^{-1}
$D_x = 1.423$ g cm^{-3}	$D_x = 1.403$ g cm^{-3}

D_m not measured due to lack of material.

Table 1. Atomic coordinates and anisotropic thermal parameters with the corresponding standard deviations, referring to the last decimal places, listed in parentheses. The anisotropic temperature factors are defined by: $T_i = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$; the values are multiplied by 10^3.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	1.06411(20)	0.63622(8)	0.06342(23)	57(1)	61(1)	48(1)	−19(1)	26(1)	−9(1)
S(2)	0.98324(18)	0.57656(8)	0.16007(21)	44(1)	58(1)	37(1)	−10(1)	17(1)	−8(1)
S(3)	0.87710(21)	0.50850(8)	0.26387(21)	48(1)	68(1)	30(1)	−15(1)	16(1)	−10(1)
S(4)	0.78077(19)	0.43869(8)	0.38003(20)	46(1)	67(1)	27(1)	−6(1)	16(1)	−3(1)
S(5)	0.69818(21)	0.37966(9)	0.47117(21)	61(1)	83(2)	35(1)	−12(1)	26(1)	0(1)
C(1)	0.9600(6)	0.6104(3)	−.1443(7)	30(4)	45(4)	46(4)	5(3)	21(3)	6(3)
C(2)	0.8723(7)	0.5669(3)	−.1733(8)	43(4)	47(5)	37(4)	−6(4)	22(3)	−3(3)
C(3)	0.8598(7)	0.5458(3)	−.0448(7)	38(4)	29(4)	36(4)	2(3)	17(3)	−1(3)
C(4)	0.7574(7)	0.5058(3)	−.0760(7)	41(4)	41(4)	26(3)	5(3)	14(3)	4(3)
C(5)	0.7515(6)	0.4844(3)	0.0578(7)	32(4)	46(4)	21(3)	10(3)	7(3)	3(3)
C(6)	0.6454(7)	0.4440(3)	0.0287(8)	47(4)	45(5)	40(4)	−4(4)	22(4)	4(3)
C(7)	0.6483(7)	0.4208(3)	0.1610(7)	47(4)	41(4)	37(4)	3(4)	22(4)	−2(3)
C(8)	0.5472(7)	0.3790(3)	0.1394(7)	46(4)	53(5)	31(4)	−19(4)	15(3)	−10(3)
C(9)	0.5580(7)	0.3554(3)	0.2684(8)	43(4)	48(4)	42(4)	2(3)	27(4)	2(3)
C(10)	0.9691(7)	0.6378(3)	−.2733(8)	41(4)	39(4)	51(4)	2(4)	26(4)	0(3)
C(11)	1.0709(8)	0.6798(3)	−.2268(9)	64(5)	72(6)	54(5)	−10(5)	31(4)	−1(4)
C(12)	1.0749(9)	0.7060(3)	−.3501(13)	80(7)	65(6)	100(7)	−12(5)	53(6)	4(6)
C(13)	0.9802(10)	0.6934(3)	−.5223(11)	95(7)	61(6)	97(6)	8(5)	71(6)	28(5)
C(14)	0.8773(8)	0.6512(3)	−.5721(10)	60(5)	83(6)	61(5)	−1(4)	41(5)	15(4)
C(15)	0.8736(7)	0.6246(3)	−.4491(9)	55(5)	59(5)	57(5)	−13(4)	33(4)	1(4)
C(16)	0.6457(8)	0.4839(3)	−.2583(8)	74(6)	67(5)	36(4)	−13(4)	32(4)	−5(4)
C(171)	0.5083(20)	0.4637(10)	−.2982(25)	18(11)	140(22)	29(10)	−33(11)	−10(8)	57(11)
C(172)	0.5606(22)	0.4343(9)	−.2635(21)	48(14)	102(18)	8(9)	−38(12)	−11(9)	4(9)
C(18)	0.5258(8)	0.4254(3)	−.1568(7)	80(6)	100(7)	19(3)	−58(5)	12(4)	−16(4)
C(19)	0.4600(7)	0.3093(3)	0.2572(8)	48(4)	51(5)	49(4)	8(4)	29(4)	6(4)
C(20)	0.5479(9)	0.2543(4)	0.3236(10)	93(6)	68(6)	101(7)	−2(5)	59(6)	7(5)
C(21)	0.4065(9)	0.3233(3)	0.3642(10)	72(6)	100(7)	78(5)	5(5)	54(5)	9(5)
C(22)	0.3212(9)	0.3009(3)	0.0707(10)	81(6)	62(6)	73(5)	−10(5)	46(5)	2(4)

Table 2. Coordinates and isotropic thermal parameters for hydrogen atoms with corresponding standard deviations in parentheses. $T_i = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$. Thermal parameters are multiplied by 10^3.

Atom	X/a	Y/b	Z/c	U
H(2)	0.808(5)	0.548(2)	−.299(6)	6(2)
H(8)	0.492(5)	0.366(2)	0.044(5)	3(1)
H(11)	1.123(6)	0.689(2)	−.122(7)	4(2)
H(12)	1.161(7)	0.733(3)	−.314(8)	10(2)
H(13)	0.977(7)	0.711(3)	−.622(8)	10(2)
H(14)	0.803(6)	0.638(2)	−.720(8)	7(2)
H(15)	0.810(5)	0.598(2)	−.485(6)	4(1)
H(201)	0.630(5)	0.264(2)	0.448(6)	5(2)
H(202)	0.581(6)	0.249(3)	0.257(8)	9(2)
H(203)	0.488(9)	0.230(4)	0.324(10)	15(3)
H(211)	0.465(6)	0.326(2)	0.466(7)	7(2)
H(212)	0.325(6)	0.291(2)	0.367(7)	9(2)
H(213)	0.358(8)	0.358(3)	0.323(9)	10(3)
H(221)	0.254(6)	0.263(3)	0.054(8)	9(2)
H(222)	0.265(6)	0.339(2)	0.029(7)	9(2)
H(223)	0.345(6)	0.283(2)	0.007(7)	5(2)

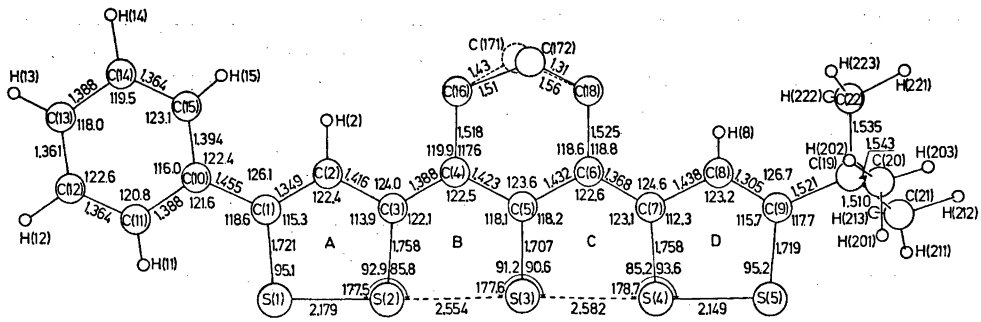


Fig. 1. Bond distances and angles. Standard deviations in S–S, S–C and C–C bonds are 0.003, 0.006 and 0.008–0.016 Å, respectively (0.03 Å in disordered region); in ∠S–S–S 0.1°, ∠S–S–C 0.3° and in angles at C 0.5–1.0°.

Table 3. Bond angles not shown in Fig. 1.

Angle	(°)	Angle	(°)
C(4)–C(16)–C(171)	116(1)	C(9)–C(19)–C(20)	109.2(7)
C(4)–C(16)–C(172)	113(9)	C(9)–C(19)–C(21)	111.3(6)
C(16)–C(171)–C(18)	114(1)	C(9)–C(19)–C(22)	111.5(6)
C(16)–C(172)–C(18)	126(2)	C(20)–C(19)–C(21)	108.8(7)
C(6)–C(18)–C(171)	114(1)	C(20)–C(19)–C(22)	109.4(6)
C(6)–C(18)–C(172)	114(1)	C(21)–C(19)–C(22)	106.5(7)

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods. An E-map based on 289 reflections with $|E| \geq 1.7$ revealed all the non-hydrogen atoms. The refinement indicated disorder in the trimethylene bridge, analogous to what has been observed in two other related structures.[5,6] Two atomic sites for C(17) were refined, C(171) and C(172), each with a population parameter of 0.5. All hydrogen atoms except those in the disordered region were localized in a difference Fourier map, and refined isotropically. No sign of secondary extinction was detected at the end of the refinement. The function minimized in the full-matrix least-squares process was $\sum w(|F_o|-|F_c|)^2$, where $w=1/\sigma_F^2$. Scattering factors were for S and C those of Cromer and Mann,[7] and for H those of Stewart *et al.*[8] The final agreement factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, is 0.082, $R_w=0.048$, and the standard deviation of an observation of unit weight, $S=\sum w(|F_o|-|F_c|)^2/(m-n)^{\frac{1}{2}}$, is 1.68 ($m$ is the number of reflections included and n the number of parameters refined on).

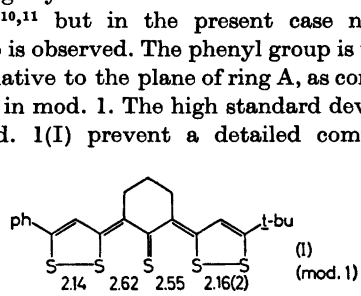
The final positional and thermal parameters with standard deviations as calculated from the inverse least-squares matrix are listed in Tables 1 and 2. Lists of observed and calculated structure factors are available from the author on request.

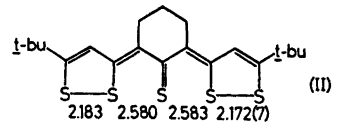
All calculations have been carried out on a UNIVAC 1110 computer. The programs concerning data collection and initial handling of the intensity data have been written by cand. real. K. Maartmann-Moe of this Department. For the other calculations the X-ray 72 system has been used.[9]

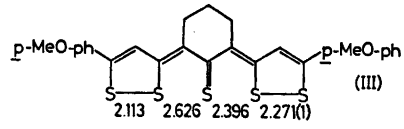
RESULTS AND DISCUSSION

Intramolecular distances and the most important angles involving sulfur and carbon are shown in Fig. 1. The remaining angles are listed in Table 3. The C–H bond lengths lie in

the range 0.79 – 1.17 Å, the mean value being 0.97 Å. Standard deviations in these bonds are 0.04 – 0.10 Å. The five-sulfur array is almost linear, and each of the five-membered rings A, B, C, D is approximately planar. The molecule is slightly twisted, mainly around C(3) – C(4) and C(6) – C(7), causing a dihedral angle between rings A and D of 10.8°. In the three other linear five-sulfur structures studied (in this paper denoted I, II, III) the molecules are slightly bent around the central S – C bond,[1,10,11] but in the present case no such feature is observed. The phenyl group is twisted 7.5° relative to the plane of ring A, as compared to 6.3° in mod. 1. The high standard deviations in mod. 1(I) prevent a detailed comparison between the two molecular structures. The relative differences between the two outer and the two inner S – S bond lengths are not the same in the two modifications. The differences are, however, hardly significant. The four S – S distances are all longer than the bonds found in cyclic dithioles, but appreciably shorter than van der Waals distance, in agreement with the observations for structures I, II and III.[1,10,11] This feature has also been reproduced in







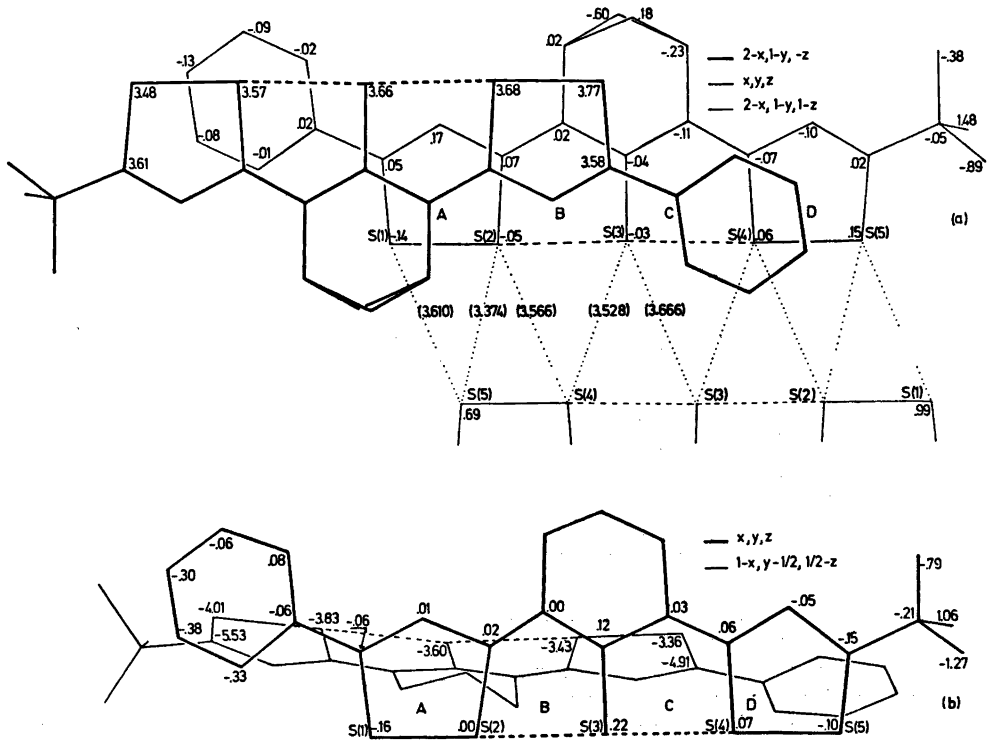


Fig. 2. (Overlap of molecules, (a) in mod. 2, and (b) in mod. 1. Distances from the least-squares plane of rings A + B + C + D of each reference molecule are shown. S···S distances shown in parentheses.

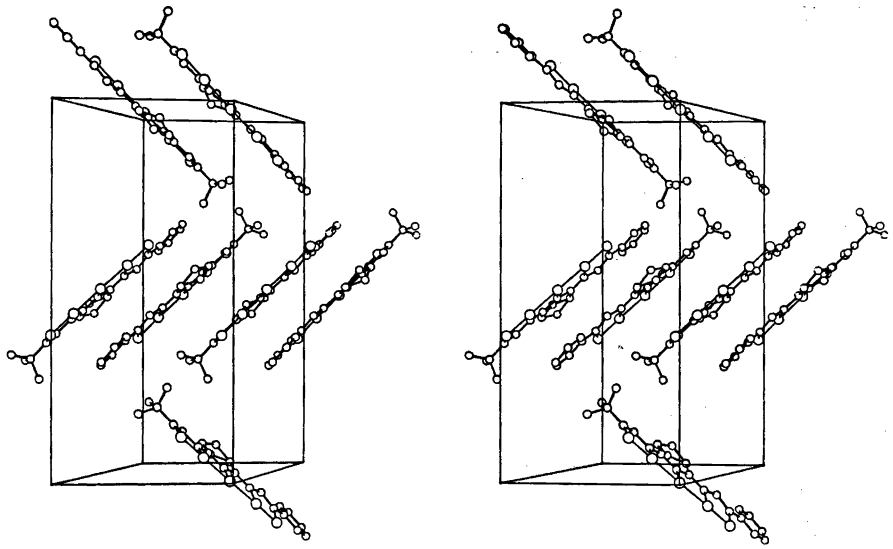


Fig. 3. Stereodrawing showing the packing of molecules in mod. 2. The a-axis runs along the interocular line, left to right, the b-axis vertically and c^* is pointing towards the viewer. Figs. 3 and 4 were drawn utilizing the ORTEP program.[13]

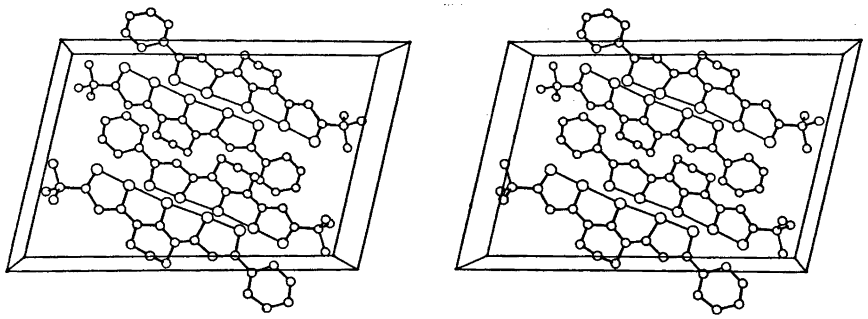


Fig. 4. The packing of molecules in mod. 1 as seen down the b-axis; the a-axis runs horizontally, left to right.

CNDO/2 calculations on model five-sulfur compounds.[12] The pronounced asymmetry in the sulfur sequence of the symmetrically substituted molecule III, together with the variation in lengths of corresponding S–S bonds in the different compounds, suggest that these bonds are easily changed by rather weak forces, intramolecular as well as intermolecular.

The major differences between mods. 1 and 2 are found in the packing of the molecules in the crystals. In the present structure pairs of centrosymmetrically related molecules overlap to a considerable extent, the distance between the molecular planes being 3.6 Å. The shortest intermolecular sulfur-sulfur contacts also occur between centrosymmetrically related molecules (Fig. 2a). In mod. 1 the overlap occurs between molecules related by a screw axis (Fig. 2b). The two molecules are inclined approximately 70° relative to one another. The two types of stacking patterns represented in mods. 1 and 2 are also found in several of the other linear four- and five-sulfur compounds studied. The crystalline packing arrangements are shown in stereodrawings Figs. 3 and 4.

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