Acta Cryst. (1991). C**47**, 1109–1111

Structure of 3,3′-Hexamethylenedithio-4,4′-di-*p*-tolyltetrathiafulvalene Hemibenzene Solvate

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(*Received* 14 *June* 1990; *accepted* 7 *September* 1990)

Abstract. $C_{26}H_{26}S_6.\frac{1}{2}C_6H_6$, $M_r = 569·94$, monoclinic, $C2/c$, $a = 28·454$ (4), $b = 10·524$ (1), $c = 19·337$ (8) Å, $\beta = 98·63$ (3)°, $V = 5725·2$ Å^3, $Z = 8$, $D_x = 1·32$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·475$ mm^{-1}, $F(000) = 2392$, room temperature, final $R = 0·039$ for 2389 observed reflections. The compound is in a *cis* configuration. The striking stereochemical molecular feature is the presence of a crown-type configuration which includes the tetrathiafulvalene (TTF) fragment. In order to adjust to this necklace configuration the latter distorts severely from planarity. Folding occurs around the sulfur–sulfur axis of each five-membered ring leaving three essentially planar moieties at dihedral angles of 46·6 and 34·4°. The two five-membered rings have an envelope conformation leading to an overall boat conformation for the TTF moiety. The conformation of the alkyl fragment of the crown is *sc*(synclinal)–*ap*(antiperiplanar)–*ap*–*sc*–*sc*–*ap*–*sc*. The shortening of the C_{sp^3}—C_{sp^3} bond distances toward the middle of the alkyl chain in the crown [range 1·473 (7)–1·545 (7) Å] is probably due to the large thermal motion of C(7) and C(8) atoms involved in the bond. There are no intermolecular contacts shorter than normal van der Waals distances.

Experimental. Yellow prismatic crystals were grown in a benzene solution. Single crystal of dimensions 0·42 × 0·35 × 0·28 mm mounted on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions and crystal orientation matrix from least-squares refinement of setting angles of 25 reflections measured in the range $12·1 < 2\theta < 28·3°$. Intensity data with maximum Bragg angle $\theta_{\max} = 25°$ (corresponding to h − 33/33, k 0/12, l 0/23) collected using ω–2θ scan mode with the following conditions: ω scan width $\Delta\omega = (1·00 + 0·35\tan\theta)°$ extended 25% on each side for background measurement, horizontal aperture $(2·0 + 0·5\tan\theta)$ mm, vertical aperture 4 mm, prescan speed 10° min^{-1}, $\sigma(I)/I = 0·010$, maximum time for final scan 60 s, orientation checked every 400 reflections and maintained within 0·12°, intensities of three reflections monitored every hour showed a decay (av. fluctuation 8·7% over 62 h of X-ray exposure) and the intensities were scaled accordingly. The data were corrected for Lorentz and polarization effects but not for absorption. 5473 reflections measured of which 5012 were unique ($R_{\rm int} = 0·012$). 2389 reflections with $I > 3\sigma(I)$ were considered observed and used in the calculations. Structure solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement (on F_o) by full-matrix least-squares calculations initially with isotropic and finally with anisotropic thermal parameters for non-H atoms. H atoms visible in difference Fourier maps but included at idealized positions (C—H = 1·0 Å, $B_{\rm iso} = 5·0$ Å^2). Expression minimized $\sum w(\Delta F)^2$ for 2389 reflections and 316 parameters. Final $R = 0·039$, $wR = 0·049$, $S = 1·346$, $w = 1/[\sigma^2(F_o) + 0·05F_o^2]$, $(\Delta/\sigma)_{\max} = 0·0$, highest peak in final difference Fourier synthesis 0·17 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography*

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0108-2701/91/051109-03$03.00

Table 1. *Atomic parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}* (Å^2)
S(1)	0·14975 (4)	0·1534 (1)	0·07276 (6)	3·84 (3)
S(2)	0·21782 (4)	−0·0378 (1)	0·04727 (7)	3·90 (3)
S(3)	0·15471 (5)	−0·2602 (1)	0·06345 (7)	4·31 (3)
S(4)	0·21694 (5)	0·1426 (1)	−0·24714 (6)	4·35 (3)
S(5)	0·23902 (4)	0·1170 (1)	−0·09229 (6)	3·60 (3)
S(6)	0·17431 (4)	0·3161 (1)	−0·06170 (6)	3·61 (3)
C(1)	0·1930 (2)	0·1092 (4)	0·0220 (2)	3·3 (1)
C(2)	0·2021 (1)	0·1719 (4)	−0·0344 (2)	2·93 (9)
C(3)	0·1304 (2)	−0·0069 (4)	0·0799 (2)	3·3 (1)
C(4)	0·1626 (2)	−0·0951 (4)	0·0662 (2)	3·5 (1)
C(5)	0·1742 (2)	−0·2984 (5)	−0·0195 (3)	4·4 (1)
C(6)	0·1485 (2)	0·2329 (5)	−0·0831 (3)	4·9 (1)
C(7)	0·1734 (2)	−0·2605 (5)	−0·1472 (3)	6·2 (2)
C(8)	0·1511 (2)	−0·2013 (5)	−0·2131 (3)	6·4 (2)
C(9)	0·1592 (2)	−0·0591 (5)	−0·2206 (3)	4·4 (1)
C(10)	0·2078 (2)	−0·0277 (4)	−0·2385 (2)	3·9 (1)
C(11)	0·2067 (2)	0·1971 (4)	−0·1652 (2)	3·4 (1)
C(12)	0·1772 (2)	0·2886 (4)	−0·1517 (2)	3·2 (1)
C(13)	0·0833 (2)	−0·0252 (4)	0·0989 (2)	3·4 (1)
C(14)	0·0469 (2)	0·0592 (5)	0·0753 (3)	4·4 (1)
C(15)	0·0021 (2)	0·0422 (5)	0·0918 (3)	5·2 (1)
C(16)	−0·0089 (2)	−0·0581 (5)	0·1318 (3)	5·3 (1)
C(17)	0·0272 (2)	−0·1419 (5)	0·1561 (3)	4·8 (1)
C(18)	0·0726 (2)	−0·1260 (5)	0·1404 (3)	4·0 (1)
C(19)	0·1458 (2)	0·3707 (4)	−0·1999 (2)	3·3 (1)
C(20)	0·1027 (2)	0·4116 (5)	−0·1853 (3)	4·7 (1)
C(21)	0·0735 (2)	0·4908 (5)	−0·2266 (3)	5·3 (1)
C(22)	0·0860 (2)	0·5352 (5)	−0·2882 (3)	4·5 (1)
C(23)	0·1288 (2)	0·4953 (5)	−0·3048 (3)	4·9 (1)
C(24)	0·1587 (2)	0·4163 (5)	−0·2618 (2)	4·2 (1)
C(25)	−0·0585 (2)	−0·0766 (7)	0·1834 (4)	7·9 (2)
C(26)	0·0549 (2)	0·6261 (6)	−0·3338 (3)	6·4 (2)
C(30)	0·5208 (2)	0·0984 (6)	0·4704 (3)	6·5 (2)
C(40)	0·4749 (2)	0·1098 (6)	0·4838 (3)	6·8 (2)
C(50)	0·5453 (2)	−0·0107 (6)	0·4862 (3)	6·7 (2)

$$B_{eq} = 8\pi^2\textstyle\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)—C(1)	1·748 (4)	C(9)—C(10)	1·513 (6)
S(1)—C(3)	1·786 (4)	C(11)—C(12)	1·328 (5)
S(2)—C(1)	1·740 (4)	C(12)—C(19)	1·470 (6)
S(2)—C(4)	1·771 (4)	C(13)—C(14)	1·388 (6)
S(3)—C(4)	1·752 (4)	C(13)—C(18)	1·390 (5)
S(3)—C(5)	1·819 (5)	C(14)—C(15)	1·372 (6)
S(4)—C(10)	1·823 (4)	C(15)—C(16)	1·373 (7)
S(4)—C(11)	1·751 (4)	C(16)—C(17)	1·382 (6)
S(5)—C(2)	1·745 (4)	C(16)—C(25)	1·503 (7)
S(5)—C(11)	1·777 (4)	C(17)—C(18)	1·382 (6)
S(6)—C(2)	1·754 (4)	C(19)—C(20)	1·382 (6)
S(6)—C(12)	1·778 (4)	C(19)—C(24)	1·389 (5)
C(1)—C(2)	1·334 (5)	C(20)—C(21)	1·369 (6)
C(3)—C(4)	1·359 (6)	C(21)—C(22)	1·375 (7)
C(3)—C(13)	1·456 (5)	C(22)—C(23)	1·371 (6)
C(5)—C(6)	1·501 (6)	C(22)—C(26)	1·497 (7)
C(6)—C(7)	1·545 (7)	C(23)—C(24)	1·378 (6)
C(7)—C(8)	1·473 (7)	C(30)—C(40)	1·372 (8)
C(8)—C(9)	1·524 (7)	C(30)—C(50)	1·355 (8)

C(1)—S(1)—C(3)	92·5 (2)	S(5)—C(11)—C(12)	117·1 (3)
C(1)—S(2)—C(4)	91·4 (2)	S(6)—C(12)—C(11)	115·7 (3)
C(4)—S(3)—C(5)	101·0 (2)	S(6)—C(12)—C(19)	114·3 (3)
C(10)—S(4)—C(11)	101·2 (2)	C(11)—C(12)—C(19)	130·0 (4)
C(2)—S(5)—C(11)	93·5 (2)	C(3)—C(13)—C(14)	120·1 (4)
C(2)—S(6)—C(12)	93·9 (2)	C(3)—C(13)—C(18)	122·4 (4)
S(1)—C(1)—S(2)	117·7 (2)	C(14)—C(13)—C(18)	117·5 (4)
S(1)—C(1)—C(2)	124·5 (3)	C(13)—C(14)—C(15)	120·9 (4)
S(2)—C(1)—C(2)	124·4 (3)	C(14)—C(15)—C(16)	122·0 (5)
S(5)—C(2)—S(6)	112·4 (2)	C(15)—C(16)—C(17)	117·5 (5)
S(5)—C(2)—C(1)	124·7 (3)	C(15)—C(16)—C(25)	121·3 (5)
S(6)—C(2)—C(1)	122·7 (3)	C(17)—C(16)—C(25)	121·2 (5)
S(1)—C(3)—C(4)	113·9 (3)	C(16)—C(17)—C(18)	121·4 (4)
S(1)—C(3)—C(13)	116·8 (3)	C(13)—C(18)—C(17)	120·7 (4)
C(4)—C(3)—C(13)	129·3 (4)	C(12)—C(19)—C(20)	120·8 (4)
S(2)—C(4)—S(3)	116·4 (3)	C(12)—C(19)—C(24)	122·4 (4)
S(2)—C(4)—C(3)	117·0 (3)	C(20)—C(19)—C(24)	116·7 (4)
S(3)—C(4)—C(3)	126·6 (3)	C(19)—C(20)—C(21)	121·9 (4)
S(3)—C(5)—C(6)	116·4 (3)	C(20)—C(21)—C(22)	121·5 (5)
C(5)—C(6)—C(7)	110·2 (4)	C(21)—C(22)—C(23)	117·0 (5)
C(6)—C(7)—C(8)	115·2 (5)	C(21)—C(22)—C(26)	121·4 (5)
C(7)—C(8)—C(9)	116·5 (5)	C(23)—C(22)—C(26)	121·6 (5)
C(8)—C(9)—C(10)	113·0 (4)	C(22)—C(23)—C(24)	122·2 (4)
S(4)—C(10)—C(9)	112·5 (3)	C(19)—C(24)—C(23)	120·7 (4)
S(4)—C(11)—S(5)	115·2 (2)	C(40)—C(30)—C(50)	120·3 (5)
S(4)—C(11)—C(12)	127·7 (3)		

(1974, Vol. IV). All calculations were performed on a DEC PDP 11/60 using the *Enraf–Nonius SDP* (Frenz, 1983). Table 1* gives atomic parameters and Table 2 bond lengths and angles. A drawing of the molecule with the atom-numbering scheme is presented in Fig. 1. Fig. 2 illustrates clearly the unusual ring-strain effects and the non planarity of the TTF group.

Related literature. The title compound has recently been synthesized (Bertho-Thoraval, 1988) during the course of a novel and general experimental approach to prepare tetrathiafulvalene (TTF)-type organic π donors starting from mesoionic derivatives (Bertho, Robert, Batail & Robin, 1990). The folding angle values in the TTF moiety are larger than those reported in 3-tetrathiafulvaleno 3-paracyclophanes (Staab, Ippen, Tao-pen, Krieger & Starker, 1980). The sulfur–exocyclic carbon bonds are significantly longer [1·771 (4) to 1·786 (4) Å] than those observed

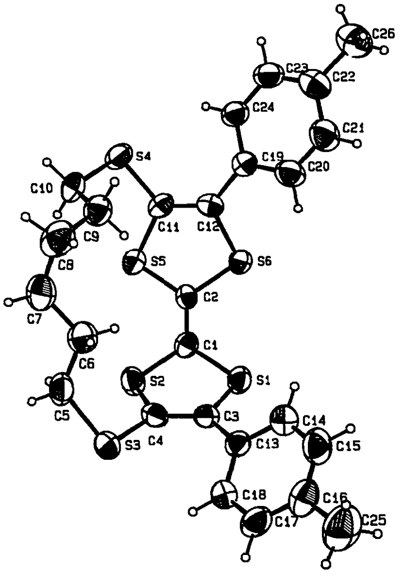

Fig. 1. Perspective view of the molecule (*ORTEP*II, Johnson, 1976). Thermal ellipsoids are drawn at the 50% probability level for C, O, S atoms; H atoms are spheres of arbitrary radii.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and bond angles involving H atoms, torsion angles and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53563 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

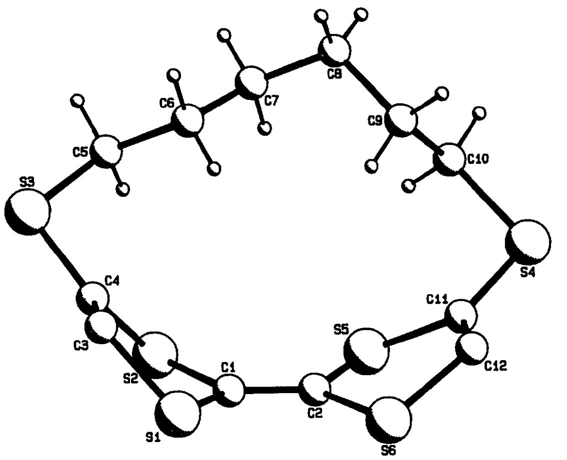

Fig. 2. Side view of the molecule (*PLUTO*; Motherwell & Clegg, 1978). The *p*-tolyl substituents have been omitted for clarity.

in the TTF molecule [1·729 (2) to 1·732 Å] (Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens, 1971). The average S—C_{sp^3} bond length of 1·821 (4) Å is in agreement with the sum of single-bond radii (1·812 Å) (Pauling, 1960) as well as with the previously reported value [1·802 (4) Å] for 3,4′-dimethyl-3′4-bis(methylthio)-2,2′,5,5′-tetrathiafulvalene (Ouahab & Batail, 1985).

References

Bertho, F., Robert, A., Batail, P. & Robin, P. (1990). *Tetrahedron*, **46**, 433–444.
Bertho-Thoraval, F. (1988). Thèse Doctorat, Univ. Rennes 1, France.
Cooper, W. F., Kenny, N. C., Edmond, W. J., Nagel, A., Wudl, F. & Coppens, P. (1971). *J. Chem. Soc. Chem. Commun.* pp. 889–890.
Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package*; *SDP Users Guide*. Version of 6 January 1983. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Ouahab, L. & Batail, P. (1985). *Acta Cryst.* C41, 928–929.
Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
Staab, H. A., Ippen, J., Tao-pen, C., Krieger, C. & Starker, B. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 66–67.

Acta Cryst. (1991). C**47**, 1111–1113

Structure of 6,7-Dimethoxy-2,2-dimethyl-2*H*-chromene, a Natural Precocene

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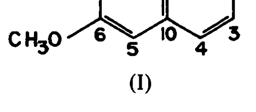
(*Received* 1 *October* 1990; *accepted* 23 *October* 1990)

Abstract. $C_{13}H_{16}O_3$, $M_r = 220{\cdot}3$, orthorhombic, $Pca2_1$, $a = 14{\cdot}358\ (2)$, $b = 9{\cdot}297\ (1)$, $c = 9{\cdot}011\ (1)$ Å, $V = 1202{\cdot}9\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}216$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}80$ mm^{-1}, $F(000) = 472$, $T = 298$ K, $R = 0{\cdot}036$ for 866 observed reflections. The heterocyclic ring is in a distorted sofa conformation, and the C—O bonds are inequivalent: C(2)—O(1) = 1·463 (4) Å and C(9)—O(1) = 1·379 (4) Å.

Experimental. Crystals of compound (I) were obtained from *n*-hexane at 277 K. The data collection and refinement parameters are summarized in Table 1.



(I)

The structure was solved using standard direct methods and difference Fourier synthesis techniques. In the final cycles of full-matrix least-squares

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