

Tetracarbomethoxytetrathiofulvalene

By V. K. BELSKY

L. Ya. Karpov Physico-Chemical Institute, Moscow, U.S.S.R.

AND DONALD VOET

Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19174, U.S.A.

(Received 2 June 1975; accepted 29 August 1975)

Abstract. $C_{14}H_{12}O_8S_4$, triclinic, $P\bar{1}$, $a=6.805$ (3), $b=8.133$ (3), $c=8.542$ (4) Å, $\alpha=97.30$ (3), $\beta=100.31$ (3), $\gamma=99.03$ (3)°, $Z=1$, $D_x=1.598$ g cm⁻³. The structure was solved using the heavy-atom technique and was refined by the full-matrix least-squares method to a final R value of 7.1%. The covalent bonding parameters of the ring system appear to be insensitive to the charge of the molecule or to the substituents to the rings. The ring system is planar to within experimental error.

Introduction. Dark red prism-shaped crystals of the title compound, TCMTTF, grown from a hot methanol solution, were provided by M. V. Lakshmikantham and M. P. Cava of the Chemistry Department of the University of Pennsylvania. A crystal of approximate dimensions $0.3 \times 0.2 \times 0.1$ mm was used in all X-ray measurements. Preliminary oscillation, Weissenberg and precession measurements indicated that the crystal had triclinic lattice symmetry. All subsequent X-ray measurements were performed using a Picker FACS-I automated diffractometer employing graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). Unit-cell parameters were determined by a least-squares fit of the angular positions of twelve reflections. The X-ray reflection data were measured to the limit $2\theta=50^\circ$ using the $\theta-2\theta$ scan mode, a scan width of 1.8°

and a scan rate of $1^\circ/\text{min}$. Stationary background counts of 20s each were taken at both limits of each scan. Of the 1610 measured unique reflections, 1565 were non-zero. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The statistical distribution of the normalized structure factors together with the reasonable calculated density for one molecule of TCMTTF in the unit cell suggested that the space group of the crystal was $P\bar{1}$. The sulfur atoms were located by analysis of the Patterson map. The remaining non-hydrogen atoms were found using the heavy-atom method. The structure was refined by the full-matrix least-squares method using isotropic, followed by anisotropic, temperature factors. The atomic scattering factors were taken from Cromer & Waber (1965). The weighting scheme used was that of Stout & Jensen (1968) with an instrumental instability factor of 0.02. The refinement converged to a final R value, based on the 1565 unique non-zero reflections, of 0.071.* The six methyl H atoms were not apparent in the final

* Observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31342 (7 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional and thermal parameters for TCMTTF with standard deviations

The anisotropic temperature factors have the functional form

$$T = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-4}] .$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.5617 (2)	0.5681 (2)	0.2697 (2)	163 (4)	196 (4)	119 (3)	-34 (3)	11 (2)	61 (2)
S(2)	0.8104 (2)	0.6338 (2)	0.6035 (2)	122 (4)	183 (3)	112 (2)	-32 (2)	23 (2)	52 (2)
C(1)	0.8066 (10)	0.6805 (8)	0.3020 (8)	221 (17)	118 (10)	130 (10)	29 (10)	45 (10)	46 (8)
C(2)	0.9210 (9)	0.7137 (7)	0.4533 (7)	138 (14)	121 (10)	131 (10)	-1 (0)	29 (10)	37 (8)
C(3)	0.5778 (9)	0.5421 (8)	0.4738 (7)	147 (15)	156 (11)	123 (10)	1 (0)	52 (9)	42 (8)
C(4)	0.8737 (10)	0.7340 (9)	0.1556 (8)	183 (17)	187 (13)	141 (10)	8 (1)	62 (11)	58 (10)
C(5)	1.1405 (12)	0.7629 (12)	0.0144 (9)	234 (21)	367 (22)	139 (12)	11 (1)	92 (13)	92 (13)
C(6)	1.1218 (9)	0.8237 (8)	0.5035 (8)	166 (16)	146 (11)	138 (10)	12 (1)	82 (10)	35 (9)
C(7)	1.4169 (13)	0.8983 (11)	0.7097 (10)	256 (22)	207 (15)	202 (15)	-34 (14)	-18 (1)	20 (1)
O(1)	0.7668 (10)	0.7924 (10)	0.0584 (7)	348 (19)	472 (19)	213 (11)	153 (16)	84 (12)	209 (12)
O(2)	1.0532 (8)	0.6981 (6)	0.1415 (5)	274 (15)	262 (11)	137 (8)	59 (10)	95 (9)	80 (8)
O(3)	1.1905 (8)	0.9287 (6)	0.4289 (6)	245 (14)	202 (10)	203 (9)	-61 (9)	36 (9)	81 (8)
O(4)	1.2222 (6)	0.7940 (6)	0.6428 (5)	144 (11)	221 (10)	155 (8)	-34 (8)	34 (7)	57 (7)

difference Fourier map. This is probably due to the commonly observed rotational disorder of methyl groups.

Table 1 lists the final atomic parameters. The molecular configuration of TCMTTF together with its covalent bonding parameters and the atomic numbering scheme used is illustrated in Fig. 1. The aver-

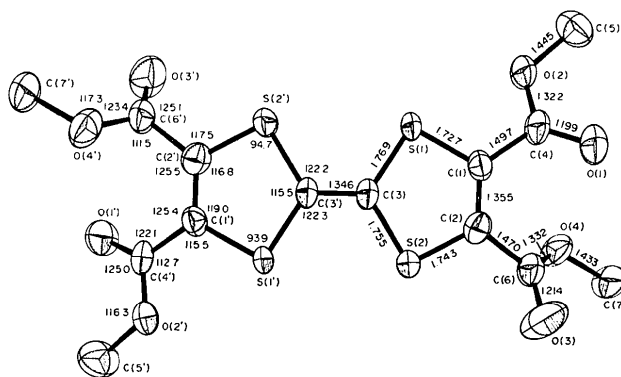


Fig. 1. An ORTEP drawing (Johnson, 1965) of a molecule of TCMTTF indicating the covalent bond distances and angles together with the atomic numbering scheme used in this report. The molecule lies across a crystallographic center of symmetry. Thermal ellipsoids are drawn at the 50% level.

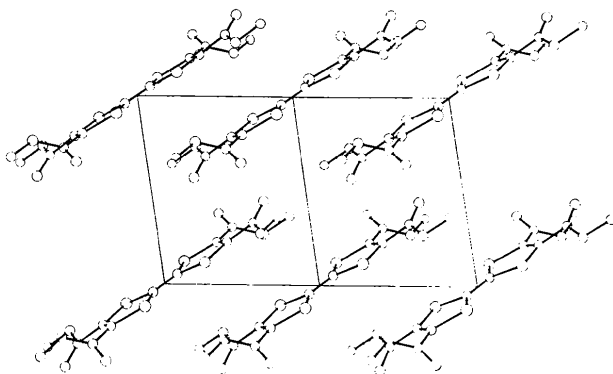


Fig. 2. A view of the crystal structure of TCMTTF illustrating the packing of the molecules in the crystal.

age standard deviations of the covalent bonding parameters, as estimated from the variance-covariance matrix of the final cycle of least-squares refinement, are 0.006 Å for S-C distances, 0.008 Å for C-C and C-O distances and 0.4° for bond angles.

Discussion. This structure determination was undertaken as part of a program to investigate the structural properties of high-conductivity organic charge-transfer salts and their components. Salts containing tetrathiofulvalene (TTF) cations in complex with tetracyanoquinodimethane (TCNQ) anions have been shown to have metallic conductance properties (Garito & Heeger, 1974). It is therefore of interest to determine the effects of chemical modifications to the TTF components of the above salts.

It can be seen from Fig. 1 that, in addition to its crystallographic center of symmetry, the twofold molecular symmetry of TCMTTF is well preserved. However, the chemically equivalent bond angles, S(1)-C(1)-C(2) and S(2)-C(2)-C(1), are significantly different. In Table 2 the covalent bonding parameters of the TCMTTF rings are compared with the corresponding quantities reported for TTF (Cooper, Kenney, Edmonds, Nagel, Wudl & Coppens, 1971) and for the TTF cation in its charge-transfer salt with the TCNQ anion (Kistenmacher, Phillips & Cowen, 1974). Because the carboxymethyl groups of TCMTTF are electron-withdrawing in character one might reasonably expect a trend of corresponding bonding parameters in the order TTF, TCMTTF and TTF⁺. However there is no such trend in the data presented in Table 2.

In all three of the TTF containing crystal structures reported to date the TTF molecules have crystallized across crystallographic centers of symmetry. Table 3 indicates that the TTF skeleton of TCMTTF is planar to within experimental error. In contrast, the five-membered rings in both TTF and TTF⁺ deviate significantly from coplanarity in a manner such that these molecules assume an overall chair conformation. Table 3 also indicates that the C atoms substituent to the rings of TCMTTF deviate significantly from the plane of the ring system.

Table 2. A comparison of corresponding bond lengths and angles in TTF, TCMTTF and TTF⁺

	TTF*	TCMTTF†	TTF ⁺ ‡
S(1)-C(1), S(2)-C(2)	1.723, 1.729 Å	1.727, 1.743 Å	1.740, 1.743 Å
S(1)-C(3), S(2)-C(3)	1.756, 1.758	1.769, 1.755	1.742, 1.744
C(1)-C(2)	1.314	1.355	1.323
C(3)-C(3')	1.349	1.346	1.369
C(1)-S(1)-C(3), C(2)-S(2)-C(3)	94.5, 94.3°	93.9, 94.7°	94.8, 95.1°
S(1)-C(1)-C(2), S(2)-C(2)-C(1)	118.0, 118.6	119.0, 116.8	117.1, 117.6
S(1)-C(3)-C(3'), S(2)-C(3)-C(3')	122.7, 122.8	122.3, 122.2	122.5, 122.8
S(1)-C(3)-S(2)	114.5	115.5	114.7
σ (Bond distance)	0.003 Å	0.007 Å	0.003 Å
σ (Bond angle)	0.2°	0.4°	0.3°

* Cooper *et al.* (1971).

† This study.

‡ Kistenmacher, Phillips & Cowan (1974).

Table 3. Deviations of atoms from the least-squares plane through the TTF ring system

Atom	Deviation†
S(1), S(1')	+, -0.004 Å
S(2), S(2')	-, +0.003
C(1), C(1')	-, +0.008
C(2), C(2')	+, -0.008
C(3), C(3')	0.000
C(4), C(4')	-, +0.030*
C(5), C(5')	+, -0.157*
r.m.s. deviation	0.006

* Atoms not used in calculating the least-squares plane.

† The equation of the least-squares plane of the TTF ring system is

$$-0.5258x + 0.9032y + 0.1401z = 2.4822 \text{ \AA.}$$

The crystal structure of TCMTTF is illustrated in Fig. 2. It can be seen that the molecules pack to form a layered structure but that there is little overlap between rings of neighboring molecules in adjacent layers. There are no abnormal intermolecular contacts in the structure.

Acta Cryst. (1976). **B32**, 274

(2*RS*,*SRS*)-3-Methyl-3-phenylsulphinylbutan-2-ol

BY F. H. ALLEN,* OLGA KENNARD† AND G. M. SHELDRIK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

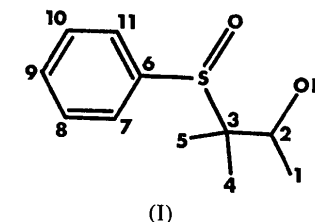
AND E. OESER

Technische Hochschule, 61 Darmstadt, Germany (BRD)

(Received 22 August 1975; accepted 10 September 1975)

Abstract. $C_{11}H_{16}O_2S$, $M = 212.31$, monoclinic, $P2_1/c$, $a = 6.104$ (4), $b = 7.952$ (5), $c = 23.057$ (8) Å, $\beta = 92.22$ (3)°, $V = 1118.3$ Å³, $Z = 4$, $D_x = 1.261$ g cm⁻³. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R_w = 0.037$ for 1282 unique reflexions measured on a diffractometer.

Introduction. As part of a continuing study of stereo-specific rearrangements (Allen, Kennard, Nassimbeni, Shepherd & Warren, 1974) we have performed an X-ray analysis of 3-methyl-3-phenylsulphinylbutan-2-ol (I) in order to establish the relative stereochemistry of the chiral centres C(2) and S.



The data were collected with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and graphite crystal monochromator on a Stoe STADI-4 four-circle diffractometer (at Darmstadt). A stationary background - θ - ω scan - stationary background technique was employed, with fixed counting times which were increased for shells of increasing θ . 3114 reflexions were measured up to $2\theta = 55^\circ$, of which 1576 with $I < 2\sigma(I)$ were accepted as observed. Equivalent reflexions were averaged to give 1282 unique observations. Unit-cell parameters were

* To whom correspondence should be addressed.

† External Staff, Medical Research Council.

We wish to thank Drs M. P. Cava and M. V. Lakshminantham for graciously providing the crystals of TCMTTF. This study was supported, in part, by NSF Grant No. DMR72-03025 and by a grant from the International Research and Exchanges Board.

References

- COOPER, W. F., KENNEY, N. C., EDMONDS, J. W., NAGEL, A., WUDL, F. & COPPENS, P. (1971). *Chem. Commun.* pp. 889-890.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- GARITO, A. F. & HEEGER, A. J. (1974). *Acc. Chem. Res.* **7**, 232-240.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763-768.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 456-458. New York: Macmillan.