BMDT-TTF$^+$ cation radicals as in the case of (TTF)ClO$_4$.

The dimers are not isolated from each other but are connected by the side-by-side S···S contacts of 3·395 (3)–3·772 (3) Å. As summarized in Table 2, some side-by-side contacts between the cation radicals in the adjacent dimers are shorter than the sum of the van der Waals radii. The side-by-side contacts are nearly parallel to the direction along the *c* axis as shown in Fig. 2. Hence a one-dimensional array of the dimers extends along the *c* axis. This makes a marked contrast to the two-dimensional network of eclipsed dimers observed in (BMDT-TTF)$_2$Au(CN)$_2$ (Nigrey *et al.*, 1986). The side-by-side coordination of BMDT-TTF$^+$ with I$_3^-$ probably intercepts the extension of the dimer network along the *b* axis as seen in Fig. 2.

The authors are indebted to Professor Gunzi Saito of the Institute for Solid State Physics for kindly providing BMDT-TTF. This work was in part supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References

HERBSTEIN, F. H., KAFTORY, M., KAPON, M. & SAENGER, W. (1981). *Z. Kristallogr.* **154**, 11–16.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KATO, R., KOBAYASHI, H. & KOBAYASHI, A. (1986). *Chem. Lett.* pp. 2013–2016.

KATO, R., KOBAYASHI, H., KOBAYASHI, A., MORIYAMA, S., NISHIO, Y., KAJITA, K. & SASAKI, W. (1987). *Chem. Lett.* pp. 507–510.

KATO, R., KOBAYASHI, H., KOBAYASHI, A. & SASAKI, Y. (1985). *Chem. Lett.* pp. 1231–1234.

KOBAYASHI, H., KATO, R., KOBAYASHI, A., NISHIO, Y., KAJITA, K. & SASAKI, Y. (1986). *Chem. Lett.* pp. 789–792.

NIGREY, P. J., DUESLER, E., WANG, H. H. & WILLIAMS, J. M. (1987). *Acta Cryst.* C**43**, 1073–1075.

NIGREY, P. J., MOROSIN, B., KWAK, J. F., VENTURINI, E. L. & BAUGHMAN, R. J. (1986). *Synth. Met.* **16**, 1–15.

SAKURAI, T. (1967). *UNICS – Universal Crystallographic Computation Program System.* The Crystallographic Society of Japan, Tokyo, Japan.

SHIBAEVA, R. P., LOBKOVSKAYA, R. M., KAMINSKII, V. F., LINDEMANN, S. V. & YAGUBSKII, E. B. (1986). *Kristallografiya,* **31**, 920–925.

SHIBAEVA, R. P., LOBKOVSKAYA, R. M., YAGUBSKII, E. B. & KOSTYUCHENKO, E. E. (1986*a*). *Kristallografiya,* **31**, 455–461.

SHIBAEVA, R. P., LOBKOVSKAYA, R. M., YAGUBSKII, E. B. & KOSTYUCHENKO, E. E. (1986*b*). *Kristallografiya,* **31**, 1110–1114.

SHIBAEVA, R. P., LOBKOVSKAYA, R. M., YAGUBSKII, E. B. & LAUKHINA, E. E. (1987). *Kristallografiya,* **32**, 901–904.

SUGANO, T. & KINOSHITA, M. (1988). In preparation.

SUGANO, T., YAKUSHI, K. & KURODA, H. (1978). *Bull. Chem. Soc. Jpn,* **51**, 1041–1046.

URAYAMA, H., YAMOCHI, H., SAITO, G., NOZAWA, K., SUGANO, T., KINOSHITA, M., SATO, S., OSHIMA, K., KAWAMOTO, A. & TANAKA, J. (1988). *Chem. Lett.* pp. 55–58.

YAGUBSKII, E. B., SHCHEGOLEV, I. F., LAUKHIN, V. N., KONONOVICH, P. A., KARTSOVNIK, M. V., ZVARYKINA, A. V. & BURAVOV, L. I. (1984). *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 12–15.

YAGUBSKII, E. B., SHCHEGOLEV, I. F., PESOTSKII, S. I., LAUKHIN, V. N., KONONOVISH, P. A., KARTSOVNIK, M. V. & ZVARYKINA, A. V. (1984). *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 275–277.

YAKUSHI, K., NISHIMURA, S., SUGANO, T. & KURODA, H. (1980). *Acta Cryst.* B**36**, 358–363.

Acta Cryst. (1988). C**44**, 1767–1770

CI Pigment Yellow 10, 4-[2′,5′-(Dichlorophenyl)hydrazono]-5-methyl-2-phenyl-3*H*-pyrazol-3-one

BY A. WHITAKER

Department of Physics, Brunel University, Uxbridge, Middlesex, England

(*Received* 7 *March* 1988; *accepted* 3 *June* 1988)

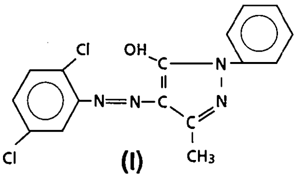
Abstract. $C_{16}H_{12}Cl_2N_4O$, $M_r = 347{\cdot}2$, triclinic, $P\bar{1}$, $a = 8{\cdot}879\ (3)$, $b = 9{\cdot}073\ (2)$, $c = 10{\cdot}021\ (2)$ Å, $\alpha = 95{\cdot}25\ (2)$, $\beta = 75{\cdot}26\ (2)$, $\gamma = 94{\cdot}09\ (2)°$, $V = 776{\cdot}5\ (5)$ Å^3, $Z = 2$, $D_m = 1{\cdot}478\ (5)$, $D_x = 1{\cdot}485\ (1)$ Mg m^{-3}, $F(000) = 356$, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 3{\cdot}70$ mm^{-1}, room temperature. $R = 6{\cdot}5\%$ for 2913 independent intensities. The molecule exists as the hydrazone tautomer and there are three intramolecular hydrogen bonds, one of which is very weak. These hydrogen bonds keep the molecule approximately planar. The molecules are linked by van der Waals forces into columns parallel to **a**.

Introduction. This paper is concerned with the crystal and molecular structure of an azo-pigment and with the long-term aim of relating colour and crystal structure in pigments.

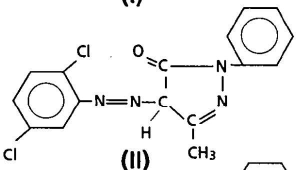
The present compound, CI Pigment Yellow 10 (CI No. 12710), is a commercially available pigment used for printing inks of all types, emulsion paints and

0108-2701/88/101767-04$03.00

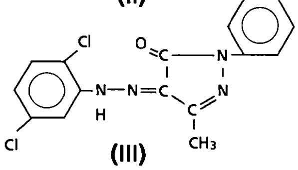
distempers, paper coating and styrene resins. It is an azo-pigment and is usually given the azo-hydroxy formula (I). For other azo-pigments of this group infrared evidence variously favours the azo-hydroxy form (I) (Pelz, Püschel, Schellenberger & Löffler, 1960), the azo-keto form (II) (Snavely, Trahanovsky & Suydam, 1962) and the hydrazone form (III) (Jones, Ryan, Sternhell & Wright, 1963; Parent, 1976). It is interesting to note that although the *Colour Index* (1971) prefers form (I), Lewis (1985) prefers form (II). On the other hand, the crystal structures of two members of this group have been determined (Golinski, Reck & Kutschabsky, 1982; Whitaker, 1988) from which it was concluded that, in the solid state, the hydrazone structure was preferred.



(I)



(II)



(III)

Experimental. The crystals were obtained by the slow cooling of a saturated hot (358 K) toluene solution of the commercial pigment Hansa Yellow R.

The crystal used for intensity measurements was 0·53 × 0·45 × 0·35 mm. The intensity data were collected using an Enraf–Nonius CAD-4 automatic four-circle diffractometer of the National X-ray Diffractometer Service, filtered copper radiation and $\omega/2\theta$ scans. Cell dimensions from least-squares analysis on 25 reflections with θ range 24·47 to 39·42°. Observed density by flotation.

The intensities were corrected for Lorentz–polarization and absorption factors (North, Phillips & Mathews, 1968) (maximum and minimum transmission factors 1·00 and 0·81 respectively) to give 2913 independent intensities with $0 \le h \le 10$, $-11 \le k \le 11$ and $-12 \le l \le 12$. Maximum $2\theta = 140{\cdot}0°$. Three standard reflections were measured periodically (015, 143 and $4\bar{6}0$). The variations in normalized intensities for 35 sets of measurements were 0·99 to 1·02, 1·00 to 1·02 and 0·96 to 1·02 respectively; the average normalized intensities varied from 0·990 to 1·013.

The structure was partially solved using direct methods, the remainder of the structure being obtained from a difference Fourier synthesis. The full-matrix least-squares refinement was based on F with a weighting function w such that $1/w = \sigma^2 + 0{\cdot}03F^2$; σ was obtained from counting statistics. The atomic scattering factors used were those given in *SHELX76* (Sheldrick, 1976). No corrections for anomalous dispersion.

After anisotropic refinement of the heavy atoms, the H atoms were found from two successive Fourier syntheses; their positions indicated the hydrazone tautomer. They were included in the refinement at a distance of 1·05 Å from and riding upon the appropriate heavy atom. Refinement continued until the shifts were less than one tenth the corresponding standard deviations (Mason, 1964). For the final refinement the methyl group was freed from positional restraint. $R = 6{\cdot}5\%$, $wR = 8{\cdot}3\%$. The comparatively high wR value is attributed to the use of all data, which is considered to be methodologically more satisfactory than imposing an arbitrary cut-off value (Hirschfeld & Rabinovich, 1973; Wilson, 1976, 1978). No attempt was made to refine the parameters of the other H atoms. The final coordinates, together with the isotropic temperature factors, are given in Table 1.* The maximum and minimum electron densities on the final difference Fourier synthesis were 0·50 and −0·72 e Å^{-3} respectively.

Inspection of the observed and calculated structure factors indicates that several reflections (*e.g.* 210, 212) were affected by extinction; one (212) particularly so. However, no corrections were applied for extinction and these structure factors were included in the refinement.

The following programs were used: *SHELX76* (Sheldrick, 1976) for data processing, solution of the structure, Fourier synthesis and least-squares refinements, *BONDLA* (Doherty, Stewart & Hall, 1983) for the calculation of atomic distances and angles, and *PARST* (Nardelli, 1982) for calculation of weighted least-squares planes of the molecule. Figs. 1 and 2 were drawn by *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The bond lengths and angles are given in Table 2. Comparison of the observed bond lengths with the accepted values (*International Tables for X-ray Crystallography,* 1968) confirms that the hydrazone tautomer is the better model, agreeing with previous determinations (Golinski, Reck & Kutschabsky, 1982; Whitaker, 1988). Fig. 1 gives the molecular structure

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and intermolecular distances < 3·50 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51097 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates and e.s.d.'s after anisotropic refinement, temperature factors after isotropic refinement*

The isotropic temperature factor is defined by $\exp\{[(-8\pi^2U\sin^2\theta)/\lambda^2] \times 10^{-3}\}$ (Cruickshank, 1956).

	x	y	z	U(Å^2)
Cl(1)	0·9954 (1)	0·6123 (1)	0·6754 (1)	69 (1)
C(1)	1·0492 (2)	0·4442 (2)	0·7133 (2)	46 (1)
C(2)	1·1723 (3)	0·3735 (3)	0·6231 (2)	50 (1)
C(3)	1·2160 (2)	0·2405 (3)	0·6542 (2)	52 (1)
C(4)	1·1354 (2)	0·1798 (3)	0·7761 (2)	46 (1)
Cl(2)	1·1890 (1)	0·0122 (1)	0·8145 (1)	76 (1)
C(5)	1·0129 (2)	0·2485 (2)	0·8678 (2)	46 (1)
C(6)	0·9679 (2)	0·3837 (2)	0·8360 (2)	39 (1)
N(1)	0·8450 (2)	0·4576 (2)	0·9232 (2)	43 (1)
N(2)	0·7662 (2)	0·4006 (2)	1·0395 (2)	44 (1)
C(7)	0·6509 (2)	0·4749 (2)	1·1148 (2)	38 (1)
C(8)	0·5503 (2)	0·4347 (2)	1·2453 (2)	44 (1)
C(9)	0·5580 (3)	0·2997 (3)	1·3173 (3)	64 (1)
N(3)	0·4484 (2)	0·5332 (2)	1·2954 (2)	46 (1)
N(4)	0·4733 (2)	0·6443 (2)	1·2007 (2)	44 (1)
C(10)	0·5955 (2)	0·6161 (2)	1·0885 (2)	41 (1)
O	0·6482 (2)	0·6891 (2)	0·9876 (1)	53 (1)
C(11)	0·3814 (2)	0·7706 (2)	1·2370 (2)	39 (1)
C(12)	0·2845 (3)	0·7889 (3)	1·3698 (2)	53 (1)
C(13)	0·1970 (3)	0·9130 (3)	1·4064 (3)	63 (1)
C(14)	0·2020 (3)	1·0162 (3)	1·3123 (3)	64 (1)
C(15)	0·2960 (3)	0·9963 (3)	1·1808 (3)	59 (1)
C(16)	0·3853 (2)	0·8737 (2)	1·1414 (2)	52 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cl(1)–C(1)	1·732 (2)	N(3)–N(4)	1·415 (3)
C(1)–C(2)	1·384 (3)	N(4)–C(10)	1·369 (2)
C(2)–C(3)	1·378 (4)	C(10)–O	1·231 (2)
C(3)–C(4)	1·389 (3)	C(10)–C(7)	1·474 (3)
C(4)–Cl(2)	1·729 (3)	N(4)–C(11)	1·421 (3)
C(4)–C(5)	1·378 (3)	C(11)–C(12)	1·392 (3)
C(5)–C(6)	1·396 (3)	C(12)–C(13)	1·382 (4)
C(6)–C(1)	1·400 (3)	C(13)–C(14)	1·379 (4)
C(6)–N(1)	1·388 (2)	C(14)–C(15)	1·373 (4)
N(1)–N(2)	1·327 (2)	C(15)–C(16)	1·381 (3)
N(2)–C(7)	1·298 (2)	C(16)–C(11)	1·391 (3)
C(7)–C(8)	1·445 (3)	N(1)–Cl(1)	2·933 (2)
C(8)–C(9)	1·492 (4)	N(1)–O	2·755 (2)
C(8)–N(3)	1·293 (3)	C(16)–O	2·981 (3)

Cl(1)–C(1)–C(2)	119·8 (0·2)	C(9)–C(8)–N(3)	122·5 (0·2)
C(2)–C(1)–C(6)	121·0 (0·2)	N(3)–C(8)–C(7)	111·0 (0·2)
C(6)–C(1)–Cl(1)	119·2 (0·1)	C(8)–N(3)–N(4)	107·6 (0·2)
C(1)–C(2)–C(3)	119·7 (0·2)	N(3)–N(4)–C(11)	118·3 (0·1)
C(2)–C(3)–C(4)	119·2 (0·2)	C(11)–N(4)–C(10)	129·2 (0·2)
C(3)–C(4)–Cl(2)	119·3 (0·2)	C(10)–N(4)–N(3)	112·2 (0·2)
Cl(2)–C(4)–C(5)	118·6 (0·2)	N(4)–C(10)–O	129·2 (0·2)
C(5)–C(4)–C(3)	122·1 (0·2)	O–C(10)–C(7)	127·1 (0·2)
C(4)–C(5)–C(6)	118·7 (0·2)	C(7)–C(10)–N(4)	103·7 (0·2)
C(5)–C(6)–N(1)	121·8 (0·2)	N(4)–C(11)–C(12)	118·9 (0·2)
N(1)–C(6)–C(1)	119·0 (0·2)	C(12)–C(11)–C(16)	120·1 (0·2)
C(1)–C(6)–C(5)	119·2 (0·2)	C(16)–C(11)–N(4)	121·0 (0·2)
C(6)–N(1)–N(2)	119·8 (0·2)	C(11)–C(12)–C(13)	119·1 (0·2)
N(1)–N(2)–C(7)	116·5 (0·2)	C(12)–C(13)–C(14)	120·9 (0·2)
N(2)–C(7)–C(8)	126·1 (0·1)	C(13)–C(14)–C(15)	119·7 (0·2)
C(8)–C(7)–C(10)	105·5 (0·2)	C(14)–C(15)–C(16)	120·7 (0·2)
C(10)–C(7)–N(2)	128·4 (0·2)	C(15)–C(16)–C(11)	119·5 (0·2)
C(7)–C(8)–C(9)	126·5 (0·2)		

projected on to the plane containing the atoms Cl(2), N(2) and C(11).

The interatomic distances N(1)–Cl(1) and N(1)–O suggest that there is a bifurcated hydrogen bond from N(1) to Cl(1) and O. According to Pimental & McClellan (1960) the average distance for a hydrogen bond from N to Cl is 3·21 Å. N–H···Cl bonds with similar lengths to the present one have been found in other pigment structures (Whitaker, 1977, 1983, 1988). There would appear to be another hydrogen bond from C(16) to O; although this is weak, it is nevertheless significantly shorter than the sum of the van der Waals radii given by Bondi (1964). These hydrogen bonds inhibit rotation about neighbouring bonds and tend to hold parts of the molecule in the same plane.

Although the molecule is almost planar, most atoms show significant deviation from this plane (Fig. 1). Both phenyl groupings are planar, the substituted one within 3·6σ and the unsubstituted one [C(11)–C(16)] within 3·1σ; the pyrazolone grouping is planar within 2·1σ. However, the unsubstituted phenyl group [C(11)–C(16)] is inclined at an angle of 11·02 (7)° with respect to the weighted least-squares plane through the molecule whereas the inclinations of both the other groups are each less than 1°.

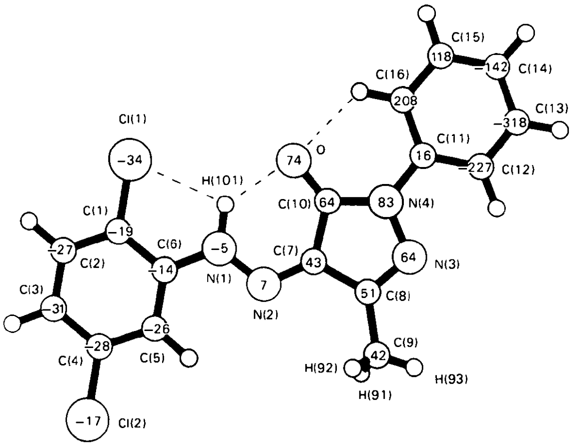


Fig. 1. Structure of the molecule projected on to the plane containing Cl(2), N(2) and C(11). The deviations of the atoms (in 10^{-3} Å) from the weighted least-squares plane of the molecule are also given. The errors in the atomic coordinates correspond to a mean of 0·001 Å for the Cl and a mean of 0·002 Å for the other atoms. The intramolecular hydrogen bonds are indicated by broken lines and involve the following hydrogen-atom contacts: Cl(1)···H(101) 2·45, O···H(101) 1·94 and O···H(16) 2·31 Å.

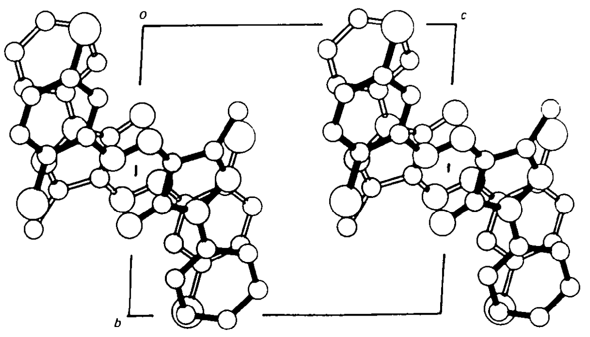


Fig. 2. The packing of CI Pigment Yellow 10 molecules in the unit cell, *a*-axis projection. The molecules at a higher level in the cell (*i.e.* those with larger x coordinates) are indicated by solid bonds.

There would appear to be no abnormal bond lengths. The molecules lie in columns parallel to the *a* axis, and adjacent molecules within each column are antiparallel (Fig. 2). The normal to the weighted least-squares molecular plane is 41·20 (1)° offset with respect to the column axis; this plane makes an angle of 3·18 (3)° with the (212) plane. The interplanar spacing for (212) planes is 3·306 Å and because there are substantial deviations from the molecular plane, all molecular distances (excluding those involving hydrogen) below 3·50 Å were calculated; there are 16 of these. The intermolecular linkages are due to van der Waals forces and there are no abnormal intermolecular distances.

The author thanks Dr M. Hursthouse and the Science and Engineering Research Council National X-ray Crystallographic Service for collecting the data and Hoechst (UK) Limited for providing the pigment.

References

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Colour Index (1971). Vol. 4, p. 4040. Bradford: The Society of Dyers and Colourists.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753.

DOHERTY, R. M., STEWART, J. M. & HALL, S. R. (1983). *BONDLA. Calculation of Bond Lengths and Angles. A Subroutine of the XTAL System of Crystallographic Programs*, edited by J. M. STEWART & S. R. HALL. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

GOLINSKI, B., RECK, G. & KUTSCHABSKY, L. (1982). *Z. Kristallogr.* **158**, 271–278.

HIRSCHFELD, F. L. & RABINOVICH, D. (1973). *Acta Cryst.* B**29**, 510–513.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 270–276. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JONES, R., RYAN, A. J., STERNHELL, S. & WRIGHT, S. E. (1963). *Tetrahedron*, **19**, 1497–1507.

LEWIS, P. A. (1985). *Pigments in Paint*, p. 34. Cincinnati, Ohio: Sun Chemical Corporation, Pigments Division.

MASON, R. (1964). *Acta Cryst.* **17**, 547–555.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. Univ. of Parma, Italy.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

PARENT, R. A. (1976). *J. Soc. Dyers Colour.* **92**, 371–377.

PELZ, W., PÜSCHEL, W., SCHELLENBERGER, H. & LÖFFLER, K. (1960). *Angew Chem.* **72**, 967–973.

PIMENTAL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 290. San Francisco: Freeman.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SNAVELY, F. A., TRAHANOVSKY, W. S. & SUYDAM, F. H. (1962). *J. Org. Chem.* **27**, 994–997.

WHITAKER, A. (1977). *Z. Kristallogr.* **146**, 173–184.

WHITAKER, A. (1983). *Z. Kristallogr.* **163**, 19–30.

WHITAKER, A. (1988). *Acta Cryst.* C**44**, 1587–1590.

WILSON, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.

WILSON, A. J. C. (1978). *Acta Cryst.* A**34**, 474–475.

Acta Cryst. (1988). C**44**, 1770–1772

The Structure of 3,3′,4,4′-Tetrakis(ethyltelluro)-2,2′,5,5′-tetrathiafulvalene (TTeC$_2$-TTF)

BY J. Y. BECKER, J. BERNSTEIN,* S. BITTNER, J. A. R. P. SARMA, L. SHAHAL AND S. S. SHAIK

The Organic Metals Group, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, *Israel*

(*Received* 11 *January* 1988; *accepted* 23 *March* 1988)

Abstract. $C_{14}H_{20}S_4Te_4$, tetra(telluroethyl)-TTF (TTeC$_2$-TTF), $M_r = 826\cdot4$, monoclinic, $P2_1/n$, $a = 9\cdot242$ (2), $b = 9\cdot039$ (3), $c = 14\cdot787$ (6) Å, $\beta = 112\cdot92$ (2)°, $V = 1137\cdot8$ (6) Å^3, $Z = 2$, $D_x = 2\cdot41$ g cm^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 50\cdot7$ cm^{-1}, $F(000) = 752$, $T = 293$ K, final $R = 0\cdot062$ for 2026 independent observed reflections, $wR = 0\cdot065$. The ethyl groups which are directed out of the TTF-moiety plane prevent close approach of the molecules. The shortest Te···Te distance is 3·99 Å which is 0·35 Å longer than that reported for TTeC$_1$-TTF.

Introduction. Te-TTF derivatives are promising molecular π donors for a number of reasons. On the one hand they are expected to stabilize further (compared to the S and Se analogs) the metallic state of radical cation salts derived from them owing to increased intrachain coupling; on the other hand they may increase interchain interactions owing to short intermolecular Te···Te distances analogous to the Se···Se distances found in Se-TTF derivatives (Williams *et al.*, 1985) and the interchain Te···Te distances in elemental tellurium (Cherin & Unger, 1967).

The chemistry of organic tellurium donors has been developing in recent years since the synthesis of

---

* To whom all correspondence should be addressed.