

Table 2. Distances (Å) and angles (°) in the hydrogen-bonding system

$D-H \cdots A$	Acceptor position	$D \cdots A$	$H \cdots A$	$\angle DHA$
N(2)—H(5)···O(5)	x, y, z	2.835 (4)	1.99 (3)	157 (3)
N(4)—H(6)···O(8)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.756 (6)	2.01 (4)	163 (5)
[N(4)—H(6)···O(7)]	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.072 (6)	2.34 (4)	158 (4)]
N(5)—H(7)···O(4)	$-1 + x, -1 + y, z$	3.096 (5)	2.39 (3)	164 (4)
N(5)—H(8)···O(3)	$x, -1 + y, z$	3.037 (4)	2.20 (3)	146 (3)
N(6)—H(9)···O(6)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	2.836 (5)	2.04 (4)	162 (3)
[N(6)—H(9)···O(7)]	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	3.079 (5)	2.39 (4)	141 (4)]
N(7)—H(10)···O(1)	$2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.770 (4)	1.93 (3)	158 (3)
N(7)—H(11)···O(2)	x, y, z	2.627 (4)	1.62 (3)	179 (2)
N(7)—H(12)···O(5)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	2.846 (4)	1.95 (3)	154 (3)
O(5)—H(13)···O(4)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.749 (4)	1.87 (3)	177 (3)
O(5)—H(14)···O(1)	$x, -1 + y, z$	2.800 (3)	2.07 (3)	172 (4)
O(6)—H(15)···O(3)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	2.704 (6)	2.07 (5)	142 (4)
O(6)—H(16)···O(3)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.733 (6)	1.78 (6)	164 (5)
O(8)—H(17)···O(4)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.585 (6)	1.99 (6)	150 (5)
O(8)—H(18)···O(6)	x, y, z	2.714 (7)	1.75 (6)	155 (5)
[O(7)—H(17)···O(4)]	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.891 (7)	1.99 (4)	147 (4)]

the plane of the rings and there is a double bond with the phthalazine system, as in the structures mentioned above. The $-\text{NH}-\text{NH}_3^+$ substituent at C(4) has an additional H atom at N(7); the bonds at N(6) are not planar and a much weaker conjugation with the phthalazine system can be inferred. The hydrogen-bond geometry of the structure is described in Table 2 and illustrated in Fig. 2. The dihydralazine cation is the donor in the hydrogen bonds to the O atoms of four different sulfate anions and to the water molecules. All available H atoms are involved in the hydrogen-bonding system, which forms a three-dimensional net. Additional cohesive forces in the crystals are from the stacking of the molecules along **a**. The distance between molecules related by two different inversion centers is the same and has the expected value of 3.34 Å.

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4,4',5,5'-Tetramethyl- $\Delta^{2,2'}$ -bis-1,3-diselenole, TMTSF*

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Abstract. TMTSF, $\text{C}_{10}\text{H}_{12}\text{Se}_4$, crystallizes from methylene chloride in the triclinic system, space group $P\bar{1}$, with the following crystal data: $a = 6.935$ (1), $b =$

A powder specimen of the title compound was obtained through the courtesy of POLFA, Pabianice.

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8.092 (2), $c = 6.314$ (1) Å, $\alpha = 105.51$ (2), $\beta = 95.39$ (1), $\gamma = 108.90$ (2)°, $V = 316.6$ Å³, $Z = 1$, $D_m = 2.34$ (1), $D_c = 2.35$ Mg m⁻³. Full-matrix, least-squares refinement (non-hydrogen atoms anisotropic, H atoms included but not refined) based on 1327 counter-collected F_o 's led to final R and weighted R

values of 0.052. The two halves of the heteronuclear fulvalene ring of TMTSF are slightly distorted in an anti-envelope conformation giving rise to an overall chair conformation. The parameters in the neutral TMTSF molecule are compared with those found in some of its conducting salts. The crystal packing is dominated by Se...Se, Se...CH₃, and CH₃...CH₃ contacts, all of which are close to their expected van der Waals separations.

Introduction. TMTSF is the tetramethyl, tetraselenium analog of tetrathiafulvalene (TTF). Like TTF (Kistenmacher, 1978, and references therein), TMTSF forms charge-transfer salts with good acceptors, yielding in some cases highly conducting, quasi one-dimensional organic conductors. For example, electrical and structural studies on the 1:1 conducting salts of TMTSF and TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), TMTSF-TCNQ (Bechgaard, Kistenmacher, Bloch & Cowan, 1977) and its dimethyl derivative, TMTSF-DMTCNQ (Andersen, Bechgaard, Jacobsen, Rindorf, Soling & Thorup, 1978) have been reported. Our recent interest in the structural properties of the 1:1 and 2:1 semi-conducting salts of TMTSF and TCNQ prompted us to investigate the molecular geometry and crystal packing in the neutral TMTSF molecule.

TMTSF was prepared according to the procedure of Bechgaard, Cowan & Bloch (1974) and red-purple crystals were harvested from a methylene chloride solution at room temperature. The crystal density was measured by neutral buoyancy methods in a mixture of bromoform and carbon tetrachloride and indicated one formula unit per cell in a triclinic lattice. It was assumed that the space group was *P* $\bar{1}$ which requires that the TMTSF molecule display at least $\bar{1}$ symmetry.

The crystal used in data collection was a parallelepiped with the following faces and mean dimensions: (100)-(100) 0.18 mm, (010)-(010) 0.07 mm, (001)-(001) 0.30 mm. Unit-cell dimensions and their associated standard deviations were obtained from a least-squares fit to the setting angles of 15 carefully centered reflections measured on a Syntex *P* $\bar{1}$ automated diffractometer. The 2926 reflections in the full sphere to $2\theta = 55^\circ$ were surveyed on the diffractometer employing Mo *K* α graphite-monochromatized radiation and the θ - 2θ scan mode. Individual scan speeds (2θ) were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning ranged from 2-24° min⁻¹. Three standards were monitored after every 100 reflections, and their intensities showed no unusual variation over the course of the experiment. The 2926 measured intensities were symmetry-averaged to yield a set of 1327 non-zero reflections which were used as the basis of the structural solution and refinement. Observational variances were based on counting statistics plus a term (pI)², where p was taken to be 0.03. The intensities and their derived standard

deviations were corrected for Lorentz, polarization and absorption effects [$\mu(\text{Mo } K\alpha) = 12.42 \text{ mm}^{-1}$, with maximum and minimum transmission factors of 0.46 and 0.11, respectively]. An approximate absolute scale was derived by the method of Wilson (1942).

Positional parameters for the non-hydrogen atoms were obtained by Patterson and Fourier methods. The hydrogen atoms were located from a difference-Fourier synthesis at an intermediate stage in the analysis, and their isotropic thermal parameters set at 5.0 Å². Full-matrix, least-squares refinement (non-hydrogen atoms anisotropic with the inclusion but no refinement of the hydrogen atoms) led to a final *R* value [$\sum |F_o| - |F_c| / \sum |F_o|$] of 0.052. The final weighted *R* value [$(\sum w |F_o| - |F_c|)^2 / \sum w |F_o|^2$]^{1/2} and goodness of fit [$(\sum w |F_o| - |F_c|)^2 / (\text{NO} - \text{NV})$]^{1/2}, where NO = 1327 observations and NV = 64 variables} were 0.052 and 2.7, respectively. The quantity minimized in the least-squares refinement was $\sum w (|F_o| - |F_c|)^2$, where $w = 4F_o^2 / \sigma^2(F_o^2)$. A final difference-Fourier map was essentially featureless.

Neutral scattering factors for the non-hydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964), while those for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). The scattering curves for all non-hydrogen atoms were corrected for anomalous-dispersion effects (Cromer & Liberman, 1970). Final atomic positional parameters are collected in Table 1.*

The structure-factor and least-squares calculations were carried out with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); Fourier

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34076 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms)

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Se(1)	2402 (1)	3258 (1)	1819 (1)
Se(2)	7182 (1)	3873 (1)	2936 (1)
C(1)	3654 (9)	2254 (8)	-501 (9)
C(2)	5637 (9)	2505 (9)	-41 (9)
C(3)	4909 (9)	4421 (9)	3969 (9)
C(4)	6866 (11)	1798 (11)	-1642 (11)
C(5)	2179 (10)	1180 (10)	-2706 (10)
H(41)	650	170	-330
H(42)	740	80	-135
H(43)	840	270	-140
H(51)	190	200	-330
H(52)	85	46	-230
H(53)	310	70	-330

syntheses were computed with *FORDAP* (Zalkin, 1965); the absorption correction was applied using *ORABS* (Wehe, Busing & Levy, 1962); best planes were computed with *MEAN PLANE* (Pippy & Ahmed, 1968); illustrations were prepared with the aid of *ORTEP* (Johnson, 1965). Calculations not cited were performed with locally written programs.

Discussion. The molecular structure and dimensions in the neutral TMTSF molecule are presented in Fig. 1. The e.s.d.'s are about 0.007 Å for the Se—C and 0.009–0.01 Å for the C—C bond lengths; e.s.d.'s for the bond angles range from 0.3–0.6°. While the TMTSF molecule is only required to be centrosymmetric, it in fact has nearly $2/m$ (C_{2h}) symmetry, Fig. 1. The Se—C bond lengths are in excellent agreement with those found in the charge-transfer salts TMTSF—TCNQ (Bechgaard, Kistenmacher, Bloch & Cowan, 1977) and TMTSF—DMTCNQ (Andersen *et al.*, 1978) and close to the value of 1.92 Å established by Hope, Knobler & McCullough (1970) to be indicative of an aromatic Se-containing system. Thus, TMTSF, like its cation in the TCNQ and DMTCNQ salts, exhibits evidence of electron delocalization. The two formal C—C double bonds in the system, C(3)—C(3'); $1-x, 1-y, 1-z$ and C(1)—C(2), are significantly different with values of 1.352 (9) and 1.315 (9) Å respectively; in TMTSF—TCNQ these two bonds are virtually identical, but the DMTCNQ salt shows the same trend as observed here.

The two halves of the heteronuclear fulvalene ring system are slightly distorted in an anti-envelope conformation giving rise to an overall chair conformation for the molecule, Table 2. This type of molecular distortion is also found in TMTSF—TCNQ and TMTSF—DMTCNQ, although the distortion is largest in the neutral molecule. We note, for example, that the dihedral angle between the central plane defined by Se(1), Se(2), C(3) and their inversion-related mates and the exterior plane defined by one half of the

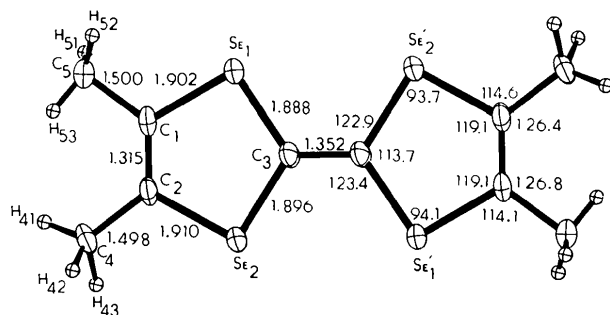


Fig. 1. The TMTSF molecule viewed normal to the mean interior plane. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level. The isotropic thermal parameters for the H atoms have been artificially set to 1.0 Å².

Table 2. Two least-squares planes and deviations (Å) of individual atoms from these planes

In each of the equations of the planes, X , Y , and Z are coordinates (Å) referred to the orthogonal axes X along a , Y in the ab plane and Z along c^* . Atoms indicated by an asterisk were given zero weight in calculating the plane; all other atoms were equally weighted.

(1) TMTSF interior plane ($-0.0006X + 0.9378Y - 0.3472Z = 1.6207$ Å)

Se(1)	± 0.0020	C(1)	$\pm 0.1934^*$
Se(2)	± 0.0020	C(2)	$\pm 0.1918^*$
C(3)	∓ 0.0100	C(4)	$\pm 0.3136^*$
		C(5)	$\pm 0.2906^*$

(2) TMTSF exterior plane ($-0.0272X + 0.9679Y - 0.2497Z = 1.7738$ Å)

Se(1)	0.0003
Se(2)	-0.0094
C(1)	0.0139
C(2)	0.0079
C(4)	-0.0002
C(5)	-0.0125

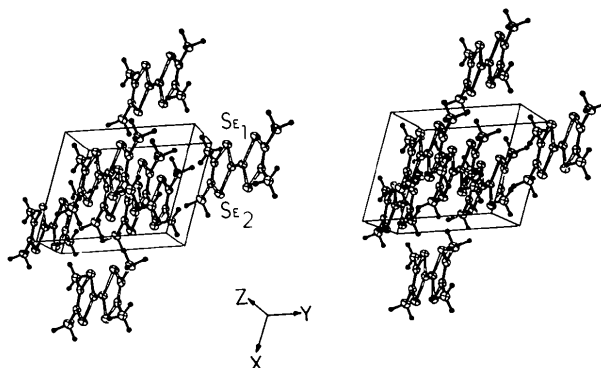


Fig. 2. A stereoview of the crystal packing in TMTSF viewed along the c^* axis.

molecule excluding C(3) are 1.7 and 2.3° in TMTSF—TCNQ and TMTSF—DMTCNQ, respectively. This angle rises markedly in the neutral molecule to 6.1°.

The crystal packing in the structure of TMTSF is essentially that of an anisotropic van der Waals solid, Fig. 2. The shortest intermolecular contact occurs between Se(1) and Se(2); $-1+x, y, z$ at 3.91 Å and is similar to the Se...Se contacts in the charge-transfer salts (3.88 Å in TMTSF—TCNQ and 3.94 Å in TMTSF—DMTCNQ); all of these contacts are close to the expected van der Waals separation of 4 Å (Pauling, 1960). Similarly, there are two $\text{CH}_3 \cdots \text{CH}_3$ contacts [C(4)...C(5); $1+x, y, z$, 3.97 Å and C(5)...C(4); $1-x, -y, -z$, 3.98 Å] and two Se...CH₃ interactions [Se(1)...C(4); $-1+x, y, z$, 3.88 Å, and Se(1)...C(4); $1-x, 1-y, -z$, 3.90 Å] which are instrumental in determining the crystal packing.

