

The Structure of Di(2,3,6,7-tetramethyl-1,4,5,8-tetraselenafulvalenium) Hexafluorophosphate,* (TMTSF)₂PF₆, the First Superconducting Organic Solid

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Abstract

The structure of $2C_{10}H_{12}Se_4^{1/2+} \cdot PF_6^-$, $M_r = 1041.06$, a solid which exhibits superconductivity at 1.2 GPa below 0.9 K, has been determined at ambient pressure and temperature (295 K). (TMTSF)₂PF₆ crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.297$ (1), $b = 7.711$ (1), $c = 13.522$ (2) Å, $\alpha = 83.39$ (1), $\beta = 86.27$ (1), $\gamma = 71.01$ (1)°, $Z = 1$, $V = 714.3$ Å³, $D_c = 2.420$, D_m (floatation in CH₂Cl₂CH₂Cl₂/CH₂Br₂CH₂Br₂) = 2.43 Mg m⁻³, $\mu(\text{Mo } K\alpha) = 10.267$ mm⁻¹. Least-squares refinement of the structure gave $R = 0.038$ and $R_w = 0.043$ for 1466 reflections. The nearly planar TMTSF units are almost perpendicular to *a* (deviation 1.1°) and form stacks along *a*. Within a stack the units repeat by an inversion leading to overlap displacements alternating in the direction of the long molecular axis and two independent interplanar distances of 3.63 and 3.66 Å. The slight dimerization is clearly reflected in the intermolecular Se–Se distances. PF₆⁻ is centrosymmetric and shows considerable thermal motion.

Introduction

Recently, transport measurements at a hydrostatic pressure of 1.2 GPa have shown that (TMTSF)₂PF₆ (Fig. 1) exhibits the characteristics of a type II superconductor below 0.9 K (Jérôme, Mazaud, Ribault & Bechgaard, 1980). The superconducting state was characterized by resistance measurements, which show a drop in the electrical resistivity of the samples to zero at 0.9 K (at 1.2 GPa). The existence of diamagnetic currents in the bulk superconductor has also been reported (Ribault, Benedek, Jérôme & Bechgaard, 1980).

* Recommended IUPAC name: di(4,4',5,5'-tetramethyl-1,4,5,8-tetraselenafulvalenium) hexafluorophosphate.

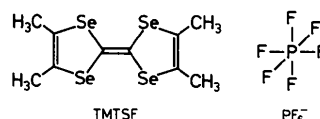


Fig. 1. Constituents of (TMTSF)₂PF₆.

(TMTSF)₂PF₆ belongs to a series of organic mixed-valence cation-radical salts (TMTSF)₂X, $X = PF_6^-$, AsF_6^- , SbF_6^- , BF_4^- , NO_3^- etc. (Bechgaard, Jacobsen, Mortensen, Pedersen & Thorup, 1980). These salts were found to conduct appreciably even at ambient pressure below 20 K.

Earlier, analogous S compounds, (TMTTF)₂X, have been investigated with respect to physical properties (Delhaes *et al.*, 1979) as well as crystal structures (Galigné *et al.*, 1978, 1979a, b; Galigné, Peytavin, Liautard & Brun, 1980). Molecular stacks of slightly dimerized TMTTF molecules are found in these structures. As mentioned by Delhaes *et al.* (1979), this dimerization in a triclinic crystal structure necessarily leads to a gap in the electronic band structure. The gap does not, however, open at the Fermi level, and it is thus uncertain how this influences the transport properties. In the S compounds fairly low conductivities are observed.

The present Se compounds are isostructural with the S analogues, but, unlike these, they remain metallic to very low temperatures ($T_c < 20$ K). Apparently, they are also slightly dimerized. The absence of any precursor effects, such as diffuse X-ray scattering (Pouget, 1980), makes it unlikely that the metal-to-insulator transition at 12–17 K in (TMTSF)₂PF₆ is of the same Peierls nature as the transition observed in most other quasi one-dimensional conductors. Alternatively, it has been suggested that this transition originates in a distortion of spin-density waves (Walsh *et al.*, 1980).

Since information about the structural details is essential for the understanding of the phenomena © 1981 International Union of Crystallography

observed in these compounds, we report the crystal structure of $(\text{TMTSF})_2\text{PF}_6$ at ambient pressure and temperature (295 K).

Experimental

A 0.01 *M* solution of TMTSF in CH_2Cl_2 containing *n*- Bu_4NPF_6 (0.1 *M*) was oxidized on a platinum anode (25 mm^2) at constant current (5–10 μA) to approximately 70% conversion. The resulting black needles, mostly with dimensions of about $5.0 \times 1.0 \times 0.2$ mm, were collected, washed with dry CH_2Cl_2 and dried. The TMTSF used was doubly gradient sublimed, CH_2Cl_2 redistilled and of spectrograde quality. The supporting electrolyte was recrystallized six times from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, and the electrolytic cell was loaded in an inert atmosphere.

A single crystal with dimensions $0.23 \times 0.05 \times 0.03$ mm (needle axis *a*) was selected for intensity data collection. This small crystal size was necessary to obtain data of satisfactory quality. (More recently it has been possible to prepare larger high-grade crystals.) Unit-cell dimensions were determined from 25 carefully centered reflections on an Enraf–Nonius CAD-4 diffractometer, which was also used for intensity measurements. Graphite-monochromatized Mo *K* α radiation ($\lambda = 0.71073$ Å) was applied. Space group $P\bar{1}$ rather than *P1* was indicated by intensity statistics and confirmed by the subsequent structure refinement.

A complete set of reflections in the range $2^\circ < \theta < 28^\circ$ was measured using the ω -scan technique ($\Delta\omega = 1.00^\circ + 0.35^\circ \tan \theta$). The intensities were corrected for Lorentz and polarization effects as well as absorption (transmission: 0.50–0.77). During data collection a minor decrease (7%) of control intensities was observed. This was taken into account by fitting an exponential-type function to the intensity *vs* time observations. Symmetry-equivalent reflections were merged to produce a set of 3442 unique reflections. The internal consistency index $R_{ic}(F^2) = \sum |F^2| - \langle |F^2| \rangle / \sum |F^2|$ was 0.036. Among the unique reflections, 1466 with $|F^2| > 3\sigma(|F^2|)$ were considered observed and were used in the structure refinement.

The structure was solved by direct methods and refined by full-matrix minimization of $\sum w(|F_o| - |F_c|)^2$ using the program system *SHELX* (Sheldrick, 1976). The weighting function applied was: $w = 1.0/[\sigma^2(|F_o|) + 0.0004|F_o|^2]$, where $\sigma(|F_o|)$ is derived from counting statistics. Neutral-atom scattering factors and anomalous-dispersion corrections for Se were taken from *International Tables for X-ray Crystallography* (1974); for other atoms the values contained in *SHELX* (Sheldrick, 1976) were used. Difference electron-density maps did not reveal satisfactory positions for the methyl H atoms, which is

Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters (\AA^2)

B_{eq} is equivalent to the anisotropic parameters actually refined (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Se(1)	2925 (2)	3391 (1)	6147 (1)	3.00 (4)
Se(2)	1681 (2)	7458 (1)	5116 (1)	2.85 (4)
Se(11)	3672 (2)	1746 (1)	3880 (1)	2.81 (4)
Se(12)	2343 (2)	5819 (1)	2839 (1)	2.71 (4)
P	0	0	0	3.68 (14)
F(1)	362 (15)	−1074 (10)	1066 (5)	8.75 (37)
F(2)	2119 (13)	−984 (14)	−266 (8)	11.12 (44)
F(3)	442 (15)	1644 (11)	380 (7)	9.36 (42)
C(1)	2212 (14)	5377 (16)	6959 (7)	2.88 (35)
C(2)	1670 (14)	7093 (15)	6516 (7)	2.74 (34)
C(3)	2524 (13)	4927 (12)	4943 (7)	2.31 (28)
C(4)	1030 (16)	8839 (14)	7034 (8)	3.27 (38)
C(5)	2282 (19)	4744 (18)	8085 (8)	4.57 (48)
C(11)	3653 (14)	2138 (15)	2463 (6)	2.71 (32)
C(12)	3127 (15)	3856 (14)	2033 (7)	2.93 (33)
C(13)	2796 (14)	4278 (13)	4026 (7)	2.56 (31)
C(14)	3052 (17)	4353 (16)	932 (7)	3.94 (41)
C(15)	4351 (18)	411 (15)	1960 (8)	4.05 (41)

probably due to the high Se content. Therefore, H atoms have been omitted in the present study. At the end of refinement (maximum shift 0.02 σ) using anisotropic temperature factors the residuals were: $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.038$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.043$. Final positional and thermal parameters are given in Table 1.* Subsequent structure analysis calculations were performed with the program system *XRAY* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and the program *THMI* (Trueblood, 1978). *ORTEP* (Johnson, 1965) was used to produce crystal-structure illustrations.

Description of the structure and discussion

Geometry of constituents

Bond lengths and angles are given in Fig. 2. The values for TMTSF are in good agreement with those found in the charge-transfer salts (1:1 compounds) with TCNQ, 7,7,8,8-tetracyanoquinodimethane (Bechgaard, Kistenmacher, Bloch & Cowan, 1977), and DMTCNQ, 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane (Andersen, Bechgaard, Jacobsen, Rindorf, Soling & Thorup, 1978). In neutral TMTSF (Kistenmacher, Emge, Shu & Cowan, 1979) the formal double

* Lists of structure factors, anisotropic thermal parameters and rigid-body-motion parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35955 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds corresponding to C(3)—C(13) and C(1)—C(2) [C(11)—C(12)] are slightly shorter than in the present compound (namely 1.352 and 1.315 Å respectively). This is also to be expected because of the larger extent of electron delocalization in a charge-transfer salt with a formal charge of +0.5 on the donor molecule.

No crystallographic site symmetry is imposed on TMTSF in this structure, and the molecule is somewhat distorted from the idealized *mmm* symmetry. This is barely reflected in the bond distances and angles, but is clearly observed when considering the deviations from planarity (Table 2). The TMTSF molecule as a whole deviates significantly from planarity. The two halves of the molecule, however, exhibit a considerable degree of planarity with a mutual angle of 1.2°. This feature has also been observed in the S compounds, *e.g.* in (TMTTF)₂Br (Galigné *et al.*, 1978) where the angle is 1.6°.

The PF₆⁻ anion is necessarily centrosymmetric in this structure since the P atom is located at an inversion center. The shape of the anion is a somewhat distorted octahedron (see Fig. 2). The F atoms have rather large thermal parameters (see Table 1) and ¹⁹F-NMR measurements (Nevald & Bechgaard, 1979) suggest free rotation of the ions. However, distinct maxima corresponding to the F positions were observed in a difference electron-density map calculated after a refinement without F atoms. This discrepancy between indications from NMR data and X-ray diffraction data may be explained by the difference in time scale.

Packing

The TMTSF units are stacked along the short axis *a* with two molecules per unit cell. Within a stack the

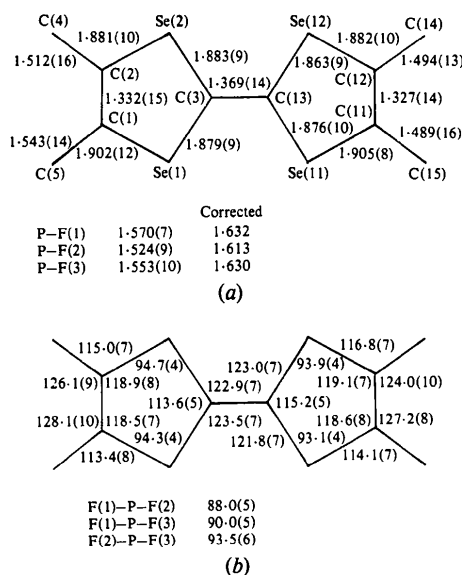


Fig. 2. (a) Bond lengths (Å) and (b) bond angles (°). P—F distances corrected for thermal motion are also given.

units repeat by an inversion leading to overlap displacements alternating in the direction of the long molecular axis [C(3)—C(13)], which is depicted in Fig. 3, where three adjacent, necessarily parallel, units are shown. The two molecules on each side of a given molecule are related by a unit translation along *a*, but because this axis makes an angle (1.1°) with the normal to the molecular plane, these molecules do not coincide in the figure, *i.e.* two slightly different overlaps exist. This repetition by inversion leads to two crystallographically independent distances between neighboring planes in the stack. The observed values are 3.63 and 3.66 Å, the difference being on the edge of significance.

The question naturally arises whether this 'zig-zag' stacking mode could be regular in the sense of producing equal contacts between a given molecule and those above and below. Accidental regularity (within experimental error) would be observed if TMTSF were planar, the molecular plane were perpendicular to *a* and the interplanar distances were identical (equal to *a*/2).

Table 2. Deviations (Å) from planarity in TMTSF

The atoms were given equal weights in the derivation of the least-squares planes. Distances marked with an asterisk correspond to atoms not defining the plane. R.m.s. deviation and r.m.s. σ (atomic position) refer to defining atoms only. ψ is the angle between *a* and the normal to the plane.

	1st half	2nd half	Se only	All atoms
Se(1)	-0.001	0.030*	-0.015	-0.007
Se(2)	0.002	0.091*	0.015	0.024
Se(11)	-0.012*	-0.006	0.015	-0.008
Se(12)	-0.070*	-0.006	-0.015	-0.038
C(1)	0.015	0.076*	-0.011*	0.013
C(2)	0.003	0.089*	-0.011*	0.013
C(3)	-0.007	0.046*	0.005*	0.005
C(4)	-0.006	0.105*	-0.027*	0.008
C(5)	-0.008	0.044*	-0.058*	-0.023
C(11)	-0.030*	-0.020	0.026*	-0.013
C(12)	-0.029*	0.006	0.038*	0.000
C(13)	-0.029*	0.013	0.000*	-0.014
C(14)	-0.040*	0.001	0.049*	0.000
C(15)	0.027*	0.012	0.089*	0.040
R.m.s. dev.	0.007	0.011	0.015	0.019
R.m.s. σ (a.p.)	0.009	0.009	0.001	0.009
ψ	1.0°	0.9°	1.7°	1.1°

Distances (Å) to inversion-related planes in stack

	3.63	3.63
	3.66	3.66

Angle between the two halves of TMTSF: 1.2°

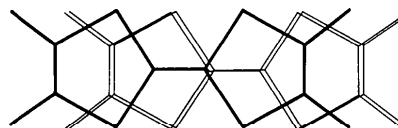


Fig. 3. TMTSF overlaps, viewed along the normal to the molecular plane. Thin lines denote the adjacent molecules above and below the molecule drawn with heavy lines.

Strict crystallographic regularity is not possible, of course, in the present structure type, as opposed to the TCNQ salts mentioned above and also (TMTSF)(Br)_{0.8}, which crystallizes (with solvent) in the orthorhombic space group *Cmcm* (Somoano, 1979).

The slightly irregular stacking in the present case is clearly reflected in the intermolecular Se—Se distances. As seen in Fig. 4, there are two distances shorter than 4.0 Å (3.874 and 3.927 Å) downwards and only one (3.983 Å) upwards, *i.e.* a slight dimerization is present. 4.0 Å is the contact distance derived from Pauling's (1960) van der Waals radius for Se (2.0 Å), whereas 3.80 Å is obtained from Bondi's (1964) value (1.9 Å). In TMTSF, TMTSF—TCNQ and TMTSF—DMTCNQ (references above) the shortest intermolecular Se—Se distances are 3.91, 3.88 and 3.94 Å respectively. In the latter two compounds the TMTSF interplanar spacings are 3.59 (TCNQ) and 3.64 Å (DMTCNQ).

The interchain distances, which are given in Fig. 5, show irregular contacts between TMTSF stacks. Two

different couplings are observed; a short contact (3.879 Å) to one neighbor and three somewhat longer contacts (two equivalent of 3.934 and one of 3.959 Å) to the other neighbor. The stacks are arranged in sheets parallel to the *ab* plane.

The hexafluorophosphate anion is located in a cavity produced by the TMTSF molecules. In this manner, the 2:1 stoichiometry of the compound is fixed, as opposed to nonstoichiometric salts such as (TTF)(Br)_{0.71–0.76} (La Placa, Corfield, Thomas & Scott, 1975), where the anions are located in channels in the structure. The PF₆⁻ ions are repeated by the *a* translations and also form sheets parallel to the *ab* plane, but with no intrasheet contacts. The Se(12)—F(1) contact of 3.233 Å, which is also shown in Fig. 5, is significantly shorter than the expected van der Waals contact [Pauling (1960): 3.35; Bondi (1964): 3.37 Å]. An electrostatic attraction is not unreasonable in view of the probable excess positive charge on Se.

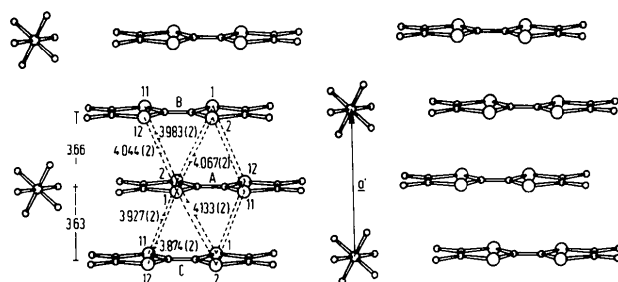


Fig. 4. Side-view of stacks (tilted 10°) showing shorter distances (Se—Se) (Å) within a stack. *a'* is the projection of *a*. Each contact between two TMTSF units occurs twice because of the inversion center mid-way between the units. The symmetry operations are: *A*(*x*, *y*, *z*), *B*(1 - *x*, 1 - *y*, 1 - *z*) and *C*(-*x*, 1 - *y*, 1 - *z*).

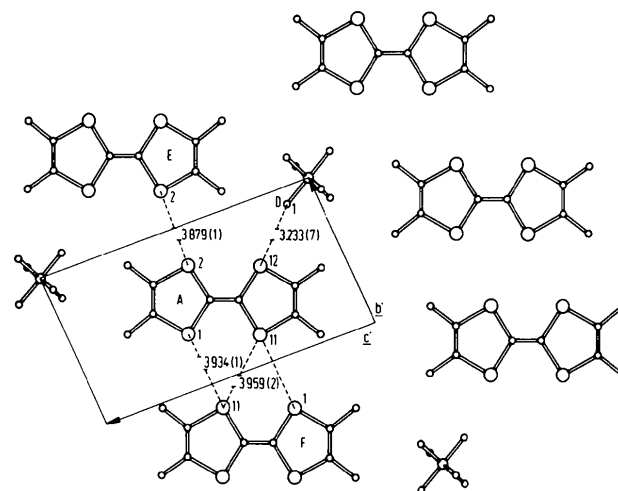


Fig. 5. View along *a* showing shorter interchain distances (Se—Se and Se—F) (Å). *b'* and *c'* are the projections of *b* and *c* respectively. The symmetry operations are: *A*(*x*, *y*, *z*), *D*(*x*, 1 + *y*, *z*), *E*(-*x*, 2 - *y*, 1 - *z*) and *F*(1 - *x*, -*y*, 1 - *z*).

Rigid-body motion

In recent years, there has been an increasing interest in rigid-body motion in TTF—TCNQ and related compounds (*e.g.* Weger & Gutfreund, 1978; Weger, 1980). Therefore, rigid-body motion parameters were derived from the individual anisotropic temperature factors using the TLS model (Schomaker & Trueblood, 1968; Trueblood, 1978). For TMTSF the translation tensor is almost isotropic, whereas the libration tensor is anisotropic with the largest libration amplitude around the axis of smallest moment of inertia [C(3)—C(13)]. For PF₆⁻ the translation and libration amplitudes are all very large, and the *L* tensor exhibits pronounced anisotropy with the axis of least libration almost parallel to the *a* axis. If the bond lengths are corrected for thermal motion they do not change significantly within the TMTSF molecule. The P—F bond lengths, however, change considerably (see Fig. 2) and become more equal. The thermal parameters derived in the present study are not very accurate and should be interpreted with proper caution.

References

- ANDERSEN, J. R., BECHGAARD, K., JACOBSEN, C. S., RINDORF, G., SOLING, H. & THORUP, N. (1978). *Acta Cryst.* **B34**, 1901–1905.
- BECHGAARD, K., JACOBSEN, C. S., MORTENSEN, K., PEDERSEN, H. J. & THORUP, N. (1980). *Solid State Commun.* **33**, 1119–1125.
- BECHGAARD, K., KISTENMACHER, T. J., BLOCH, A. N. & COWAN, D. O. (1977). *Acta Cryst.* **B33**, 417–422.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- DELHAES, P., COULON, C., AMIELL, J., FLANDROIS, S., TORREILLES, E., FABRE, J. M. & GIRAL, L. (1979). *Mol. Cryst. Liq. Cryst.* **50**, 43–58.

- GALIGNÉ, J. L., LIAUTARD, B., PEYTAVIN, S., BRUN, G., FABRE, J. M., TORREILLES, E. & GIRAL, L. (1978). *Acta Cryst.* **B34**, 620–624.
- GALIGNÉ, J. L., LIAUTARD, B., PEYTAVIN, S., BRUN, G., MAURIN, M., FABRE, J. M., TORREILLES, E. & GIRAL, L. (1979a). *Acta Cryst.* **B35**, 1129–1135.
- GALIGNÉ, J. L., LIAUTARD, B., PEYTAVIN, S., BRUN, G., MAURIN, M., FABRE, J. M., TORREILLES, E. & GIRAL, L. (1979b). *Acta Cryst.* **B35**, 2609–2613.
- GALIGNÉ, J. L., PEYTAVIN, S., LIAUTARD, B. & BRUN, G. (1980). *Cryst. Struct. Commun.* **9**, 61–63.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- JÉRÔME, D., MAZAUD, A., RIBAUT, M. & BECHGAARD, K. (1980). *J. Phys. (Paris) Lett.* **41**, L95–L98.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KISTENMACHER, T. J., EMGE, T. J., SHU, P. & COWAN, D. O. (1979). *Acta Cryst.* **B35**, 772–775.
- LA PLACA, S. J., CORFIELD, P. W. R., THOMAS, R. & SCOTT, B. A. (1975). *Solid State Commun.* **17**, 635–638.
- NEVALD, R. & BECHGAARD, K. (1979). Private communication.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- POUGET, J. P. (1980). Private communication.
- RIBAUT, M., BENEDEK, G., JÉRÔME, D. & BECHGAARD, K. (1980). *J. Phys. (Paris) Lett.* **41**, L397–L399.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHELDRICK, G. M. (1976). *SHELX 76*. Univ. of Cambridge, England.
- SOMOANO, R. B. (1979). Private communication.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TRUEBLOOD, K. N. (1978). *Acta Cryst.* **A34**, 950–954.
- WALSH, W. M. JR, WUDL, F., THOMAS, G. A., NALEWAJEK, D., HAUSER, J. J., LEE, P. A. & POEHLER, T. (1980). *Phys. Rev. Lett.* **45**, 829–832.
- WEGER, M. (1980). *The Physics and Chemistry of Low Dimensional Solids*, edited by L. ALCÁ CER, pp. 77–100. Boston: Reidel.
- WEIGER, M. & GUTFREUND, H. (1978). *Comments Solid State Phys.* **8**, 135–146.

Acta Cryst. (1981). **B37**, 1240–1244

The α Form of Piperidinium 1-Piperidinecarbodithioate

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Abstract

[C₅H₁₂N]⁺[C₆H₁₀NS₂]⁻ is orthorhombic, space group *Pbc*2₁, with $a = 6.466$ (1), $b = 14.941$ (2), $c = 27.665$ (4) Å, $Z = 8$, $V = 2672.6$ Å³, $D_x = 1.225$ Mg m⁻³, phase transition $\alpha \rightarrow \beta$ at ca 354 K. The non-centrosymmetric structure has been refined to $R(F^2) = 0.108$ for 3167 reflections and 446 parameters. Two cations and two anions are linked by eight N–H...S hydrogen bonds to form a dimer with pseudosymmetry $2/m$. The dimers are packed at van der Waals distances, mainly as close-packed layers between which the distances are fairly long. The most notable interdimeric distances are six S...S contacts per dimer, two of each of 3.853 (3), 3.871 (3) and 3.922 (3) Å.

Introduction

The present investigation forms part of a series of polymerism studies on amphiphilic [R₂NH₂]⁺[R₂NCS₂]⁻

salts, where R is an alkyl substituent (Wahlberg, 1978a,b,c, 1979, 1980).

In preparing crystals of piperidinium 1-piperidinecarbodithioate, two phases, α and β , were obtained simultaneously (Wahlberg, 1980), and the structure of the β form was determined.

The crystals of the α form appeared as very thin pale-yellow flakes. The polar direction [001] was perpendicular to the flakes. On heating, the crystals lost their brightness at the phase-transition temperature of ca 354 K as a zone passed through them. Some crystals remained up to ca 5 K higher and then shattered. The phases in the transition $\alpha \rightarrow \beta$ were identified by powder diffraction. The reverse transition could not be established. Systematically absent reflections among $0kl$ for k odd and $h0l$ for l odd indicated the space groups *Pbcm* or *Pbc*2₁ [non-standard form of *Pca*2₁; the present symmetry relations are: x, y, z ; $\bar{x}, \bar{y}, \frac{1}{2} + z$; $\bar{x}, \frac{1}{2} + y, z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$]. The statistical distribution of normalized structure factors indicated non-centrosymmetry. *Pbcm* is inconsistent with the final structure. The cell parameters were based on 53 lines

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