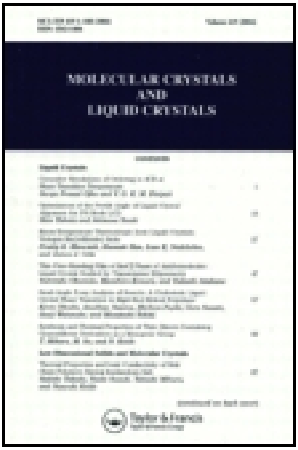


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Studies of the Solid State Properties of Molecular and Supramolecular Selenium and Tellurium Materials

Daniel J. Sandman [a], James C. Stark [a], Michael Rubner [a], Lewis A. Acampora [a], Lynne A. Samuelson [a] & Bruce M. Foxman [b]

[a] GTE Laboratories, Inc., 40 Sylvan Road, Waltham, MA, 02254, U.S.A.

[b] Department of Chemistry, Brandeis University, Waltham, MA, 02254, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: Daniel J. Sandman, James C. Stark, Michael Rubner, Lewis A. Acampora, Lynne A. Samuelson & Bruce M. Foxman (1983): Studies of the Solid State Properties of Molecular and Supramolecular Selenium and Tellurium Materials, Molecular Crystals and Liquid Crystals, 93:1, 293-305

To link to this article: http://dx.doi.org/10.1080/00268948308073535

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 293–305
0026-8941/83/9304–0293/\$18.50/0

Printed in the United States of America

STUDIES OF THE SOLID STATE PROPERTIES OF MOLECULAR AND SUPRAMOLECULAR SELENIUM AND TELLURIUM MATERIALS

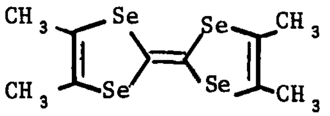
DANIEL J. SANDMAN, JAMES C. STARK,[1] MICHAEL RUBNER,
LEWIS A. ACAMPORA, and LYNNE A. SAMUELSON
GTE Laboratories, Inc., 40 Sylvan Road, Waltham, MA
02254, U.S.A.

BRUCE M. FOXMAN[2]
Department of Chemistry, Brandeis University, Waltham,
MA 02254, U.S.A.

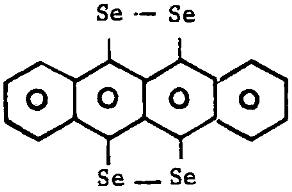
Abstract A three dimensional volume packing analysis of the crystal structures of quasi-one-dimensional ion-radical solids of the type $(D)_2^{+\cdot}X^-$ is presented. It is found that the $(TMTSF)_2^{+\cdot}X^-$ ($X \neq NO_3$) solids are loosely packed when compared with solids where D is an aromatic hydrocarbon. It is suggested that $(TMTSF)_2^{+\cdot}X^-$ ($X \neq NO_3$) are formed under conditions of kinetic control. A direct, broadly applicable approach to the synthesis of aromatic molecular (e.g. tetratellurotetracene (TTeT) and bis-(2-naphthyl)ditelluride) and supramolecular (e.g. poly-p-phenylene selenide (PPSe) and -telluride) materials is outlined. Our initial studies (powder data) of the structural and room temperature electrical properties of solids derived from TTeT and PPSe by electron transfer are summarized. The crystal and molecular structures of two forms of bis-(2-naphthyl) ditelluride have been determined using single crystal methods, and conformational polymorphism was observed.

INTRODUCTION

Since the Fifth International Conference on the Chemistry of the Organic Solid State (ICCOSS) in 1978, interest in low temperature organic metals has largely focused on ion-radical solids $(D)_2^{+\cdot}X^-$, where D represents the donors tetramethyltetraselenofulvalene (TMTSF, 1) and tetraselenotetracene (TSeT, 2) and X is a closed-shell anion. While the



1



2

observation[3] of ambient pressure pressure superconductivity at 1° K in (TMTSF)$_2^{+\cdot}$ ClO$_4^-$ has attracted the major share of attention, the other features of the salts (TMTSF)$_2^{+\cdot}$ X$^-$ including the spin density wave effects, perpendicular plasma edge, and reduced charge transfer in a commensurate phase provide a significant contrast to the now classical TTF-TCNQ family of two chain organic metals.[4] Since it is recognized that the intrinsic properties of (TSeT)$_2^{+\cdot}$X$^-$ (X = Cl, Br) have not been observed due to the presence of impurities,[5] our discussion will initially focus on the TMTSF materials.

The properties observed in the ion-radical solids derived from TMTSF and TSeT have stimulated interest in the synthesis of tetratellurofulvalenes[6] and tetratellurotetracene (TeT).[7] While molecular properties of Te compounds such as polarizability are enhanced vs. their Se counterparts, it is the reduction of quasi-one-dimensionality following from the chalcogen-chalcogen contacts in the anticipated crystal structures that continues to fuel speculation about superconductivity at truly elevated temperatures in this class of materials. Since it is the need to control crystal structure that is central to progress along these lines, it may be fruitful to reflect further on phase formation and the details of crystal packing in order to refine ideas on the design of low temperature organic metals and superconductors.

A VOLUME PACKING ANALYSIS OF (D)$_2^{+\cdot}$ X$^-$

At the Fifth ICCOSS, a volume packing analysis of ion-radical solids noted that, from room temperature structural data, compared to its neutral precursors, TTF-TCNQ underwent a ten percent volume contraction on charge transfer.[8] In solids of the TTF-TCNQ type where the volume contraction was ca. one percent, the electrical properties were markedly less metallic than TTF-TCNQ. In contrast, the metallic TTT

$(TCNQ)_2$ shows volume expansion on charge-transfer. This type of analysis is now presented for representative solids $(D)_2^{+\cdot} X^-$, where D is TMTSF,[9] TMTTF,[10] TSeT,[11] fluoranthene,[12] and naphthalene.[13] The assumptions implicit in this approach have been detailed.[14] The ratio V_{D°/V_{CT} for these solids is given in Table 1; V_{CT} is obtained by subtraction of the volume of X^-, obtained from the structures of alkali metal salts estimating the volume of the metal ion from Pauling or Goldschmidt radii, from the unit cell volume of $(D)_2^{+\cdot} X^-$.

With reference to Table 1, we note that for $(TMTSF)_2^{+\cdot} X^-$ $(X \neq NO_3)$, the volume contraction is of the order of 3%; analogous results are noted for the TMTTF solids. For the recently reported $(TMTSF)_2^{+\cdot} H_2F_3^-$,[9g] the V_{D°/V_{CT} value is 1.053. To facilitate further discussion of these numbers, we compare them with other solids of the $(D)_2^{+\cdot} X^-$ type where D is derived from the hydrocarbons fluoranthene or naphthalene. For these solids, note that the volume contraction is 8-10%, comparable to TTF-TCNQ. Compared to the hydrocarbon ion-radical solids, the TMTTF and TMTSF $(X \neq NO_3)$ solids are relatively loosely packed, and it is suggested that their formation occurs under conditions of kinetic control. For $(TMTSF)_2^{+\cdot} NO_3^-$, where the volume contraction is comparable to the hydrocarbons, superconductivity has not been observed upon application of pressure, while X-ray diffuse scattering reveals a low temperature superstructure which might involve anion ordering.[15]

For the TMTSF ion-radical solids, the trends noted above in the ratio V_{D°/V_{CT} are also found in the c/a ratio of the lattice constants. For the NO_3 and H_2F_3 salts, c/a = 1.78, while for the other salts discussed above, as well as the FSO_3 and BrO_4 salts,[16] c/a falls between 1.82 and 1.87. In contrast to the trend in the c/a ratio, the b/a ratio varies only from 1.048 for the NO_3 to 1.067 for H_2F_3 with all other salts falling in between.

Several independent observations support the contention that $(TMTSF)_2^{+\cdot} X^-$ $(X \neq NO_3)$ are formed under conditions of kinetic control. An attempt to grow salts of HMTSF by anodic oxidation in chlorobenzene led to a salt of 3:2 stoichiometry which included solvent in the unit cell.[17] Electrocrystallization of the parent TSF with ClO_4^- gave single crystals of a semiconducting salt.[18]

Analogous to TTT $(TCNQ)_2$, the metallic $(TSeT)_2^{+\cdot} Cl^-$ reveals a slight volume expansion upon charge transfer, and the

Table I. **CRYSTAL PACKING IN ION-RADICAL SALTS $(D)_2^{\dot{+}}X^-$**

DONOR	X^-	$V_{cell} - V_x$ (Å)^3	V_{D°/V_{CT}
TMTSF	PF_6	609.6	1.039
TMTSF	AsF_6	614.4	1.031
TMTSF	ClO_4	613.2	1.033
TMTSF	BF_4	614.0	1.031
TMTSF	ReO_4	618.0	1.024
TMTSF	NO_3	589.3	1.074
TMTTF	BF_4	574.4	1.033
TMTTF	Br	584.9	1.014
TSeT	Cl	753.7	0.977
TSeT	PF_6	1609.56	0.915
TSeT	AsF_6	1615	0.912
Fluoranthene	PF_6	981.4	1.087
Fluoranthene	AsF_6	989.7	1.078
Fluoranthene	SbF_6	985.4	1.105
Naphthalene	PF_6	645.6	1.101
Naphthalene	AsF_6	654.0	1.086

relatively loosely packed PF_6 and AsF_6 salts of TSeT are semiconductors.[11c]

Given that $(TMTSF)_2^{\dot{+}}X^-$ ($X \neq NO_3$) are formed under conditions of kinetic control and are relatively loosely packed, it is possible to speculate that more tightly packed phases of TMTSF with anions $X \neq NO_3$ may exist at values of charge transfer different from 0.5. It is also of interest to inquire into reasons for the relatively loose packing of $(TMTSF)_2^{\dot{+}}X^-$ ($X \neq NO_3$), and several *ad hoc* possibilities are now discussed. It should be borne in mind that the packing analysis uses structural data at elevated temperature and will not be useful for detailed interpretation of physical properties.

Assuming that crystallographic Se-Se contacts are a structural manifestation of the transverse band widths in these solids, it is conceivable that the relatively loose packing may allow the Se atoms to optimize their relative orientation. Theoretical discussions of the transverse bandwidth have been given,[19] and an experimental electron density study of $(TMTSF)_2^{+\cdot}\ AsF_6^-$ has been performed.[20]

Since the linear chain crystal structures have positively charged cation-radicals packed on one another, the relatively loose packing may allow some relief of local coulomb repulsion. This suggestion may be tested by a systematic study of Madelung energies of these solids. The Madelung energy of $(TMTSF)_2^{+\cdot}\ PF_6^-$ has been calculated.[21]

It may be relevant to recall that the inorganic superconductors with relatively high transition temperatures have kinetically controlled crystal structures. It is conceivable that this may also be a feature of the crystal structures of organic superconductors.

Given the novel structural and electrical properties of the TMTSF salts, it is important to recognize that numerous other organochalcogen donors with molecular properties comparable or superior to those of TMTSF either have been or can be synthesized. The crystal structures of ion-radical solids derivable from these additional donors will exhibit nonbonded interactions different from those of the TMTSF solids, and their preparation and characterization will lead to a fuller understanding of this class of materials.

The size of AsF_6^- used in the packing analysis[22] is in accord with current views of structural models for conducting polymers.[23]

A DIRECT SYNTHETIC APPROACH TO AROMATIC SELENIUM AND TELLURIUM MATERIALS

The topics discussed below are related by the method used to synthesize the materials. We have developed a direct broadly applicable approach to the synthesis of aromatic molecular and supramolecular selenium and tellurium materials.[24] The first step in our procedure involves reaction of an alkali metal directly with selenium or tellurium in either 1:1 or 2:1 ratios in dipolar aprotic solvents, thus avoiding liquid ammonia which is widely used to prepare these reagents. These alkali chalcogenide reagents undergo facile reaction with aromatic halides which are not activated for a nucleophilic substitution.

Using this approach, we have been able not only to synthesize new molecular and polymeric materials, but we have also developed one step syntheses of known materials which had previously been prepared by multistep routes.

TETRATELLUROTETRACENE (TTeT)

The synthesis of TTeT and the expected shift of its solution and solid state spectrum to lower energies compared to TSeT have been reported.[7b] A comparative study of the solution properties of the cation-radicals of the three tetrachalcogenotetracenes has been carried out using cyclic voltammetry and electron spin resonance.[25] In benzonitrile solution, analogous to its lighter chalcogen analogs, TTeT exhibits two reversible one electron oxidations, but is oxidized at slightly lower potentials. The dichloromethane solution esr spectrum of $TTeT^{\ddagger}$ reveals no hyperfine splitting, a linewidth of 20 Gauss, and an isotropic g value of 2.0588. These observations are attributed to increasing spin-orbit interaction as one moves from lighter to heavier chalcogens.

TTeT is a monoclinic crystal whose structure exhibits a uniform linear chain array manifested by a b lattice constant of 4.364Å and rather short interstack Te-Te contacts of 3.701Å.[7] After it was noted that both TTT and TTeT had a lattice constant which was twice the van der Waals radius of the relevant chalcogen, while the known vapor grown TSeT phase lacked such a lattice constant, a polymorph of TSeT which is isomorphous to TTeT was isolated and characterized.[5]

Ion-radical solids of TTeT prepared by interaction with iodine, TCNQ, $CuCl_2$, and $CuBr_2$ have polycrystalline conductivities in the range 10^{-1} to $1(\text{ohm-cm})^{-1}$. The solids from TCNQ, $CuCl_2$,[26] and $CuBr_2$[26] appear to be isomorphous to TSeT $(TCNQ)_2$, $(TSeT)_2^{\ddagger}Cl^-$, and $(TSeT)_2^{\ddagger}Br^-$, as judged by X-ray powder diffraction. Occasionally, elemental Te is detectable in the powder patterns of the solids derived from TTeT. Additionally, samples of "$(TTeT)_2^{\ddagger}Cl^-$" typically contain ca. 0.1% Cu, easily detected by emission spectra. For example, a sample found free of elemental Te by X-ray powder analysis was found to have the composition $C_{17.7}H_{9.8}Te_4Cl_{0.7}Cu_{0.08}$ by elemental analysis. It is concluded that the samples of ion-radical solids of TTeT prepared to date are unlikely to be crystallographic single phases. In view of the preceding observation, it is of interest to inquire into the homogeneity of analogous TSeT phases. A sample of $(TSeT)_2^{+\cdot}$ Cl^-, prepared from TSeT and $CuCl_2$ as described by Eremenko, et al.,[27] and identified by X-ray diffraction, was found by emission spectrographic analysis to contain amounts of Cu comparable to the TTeT samples noted above. This observation reinforces the perspective[5] that the intrinsic properties of $(TSeT)_2^{+\cdot}$ X ($X = Cl$, Br) have not yet been observed, and improved synthetic routes are required. We have been able to prepare $(TSeT)_2^{+\cdot}$ Br^- by anodic oxidation.

POLY-P-PHENYLENE SELENIDE (PPSe)[28] AND-TELLURIDE (PPTe)[24]

The selenium and tellurium analogs of the thermoplastic poly-p-phenylene sulfide (PPS), a thermoplastic of additional interest as an example of a polymer without a continuous conjugated carbon π-system which is rendered conductive when exposed to strong oxidants, have been synthesized. The electronic spectra of PPSe and PPTe exhibit maxima near 300 nm and tail into the visible. While X-ray diffraction of PPSe indicates a crystal structure isomorphous to PPS, PPTe appears to have a different structure. Analogous to PPS, PPSe undergoes a weight increase of 40-45% on exposure to AsF_5, becomes crosslinked, and reaches a room temperature conductivity of 10^{-2} $(ohm\text{-}cm)^{-1}$, a slightly lower value than attained by PPS. Compared to PPS, our samples of PPSe have shorter chain lengths and more intrachain disorder due to the presence of diselenide bonds.

CONFORMATIONAL POLYMORPHISM[29] OF BIS(2-NAPHTHYL)DITELLURIDE

Two polymorphs of bis(2-naphthyl)ditelluride were initially identified by their melting behavior and powder diffraction. The solid of m.p. 116-118° is designated "Polymorph A", while the higher melting (122-124°) form is termed "Polymorph B". Solution grown single crystals of each polymorph were obtained.

The crystallographic and X-ray data collection parameters are given in Table II. Polymorph A exhibits a "transoid" molecular conformation (Figure 1); further, the intermolecular Te-Te contacts are not unusually short. A "transoid" conformation has not been perviously observed in the structural chemistry of aromatic ditellurides.

TABLE II[a] Crystal data for bis-(2-naphthyl)ditelluride.

	Polymorph A	Polymorph B
Space Group	Monoclinic $P2_1/n$	Monoclinic $C2/c$
a	8.406(3) Å	36.654(11) Å
b	6.304(2) Å	7.840(2) Å
c	31.960(9) Å	12.084(4) Å
β	95.08(3)°	104.56(3) Å
V	1687 $Å^3$	3361 $Å^3$
Z	4	8
No. of Reflections $F > 3.92\sigma$ (F)	1582	1830
$2\Theta_{max}$ (MoK_α)	42°	45°
R	0.055	0.036

[a] At the present stage of refinement, Te atoms have been assigned anisotropic thermal parameters, C atoms isotropic thermal parameters, and H atom contributions have not been included.

Polymorph B, which has the "cisoid" conformation, exhibits rather short intermolecular Te-Te contacts (Figure 2). It is noteworthy that these contacts are among the shortest Te-Te contacts observed.[7,30,31] However, in the latter cases, the observed contacts occur in cyclic Te compounds, while in the present case, the short contacts occur between Te atoms in an acyclic environment.

Diffuse reflectance of Polymorphs A and B reveals broad maxima at 400-410 nm, a slight red shift compared to the solution spectrum, while Polymorph B exhibits a shoulder near 500 nm found neither in solution nor in Polymorph A. The short intermolecular Te-Te contacts found in Polymorph B suggest the structural origin for this additional spectral feature.

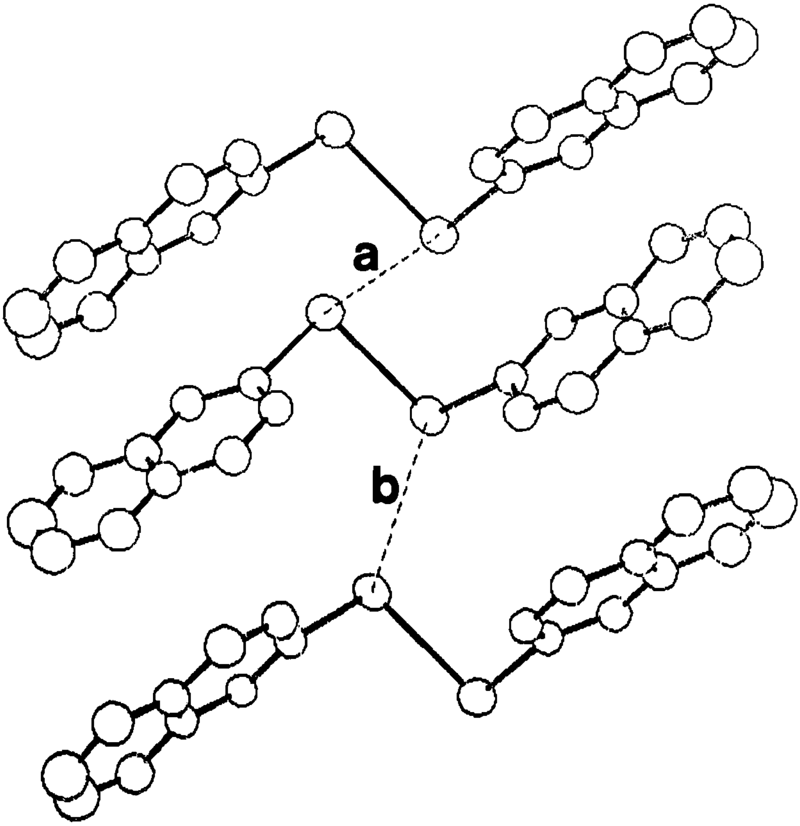


Figure 1. Polymorph A. The packing of transoid molecules in stacks along the crystallographic a direction is shown. The shortest Te-Te intermolecular Te-Te distances are: a = 4.128; b = 4.413 Å.

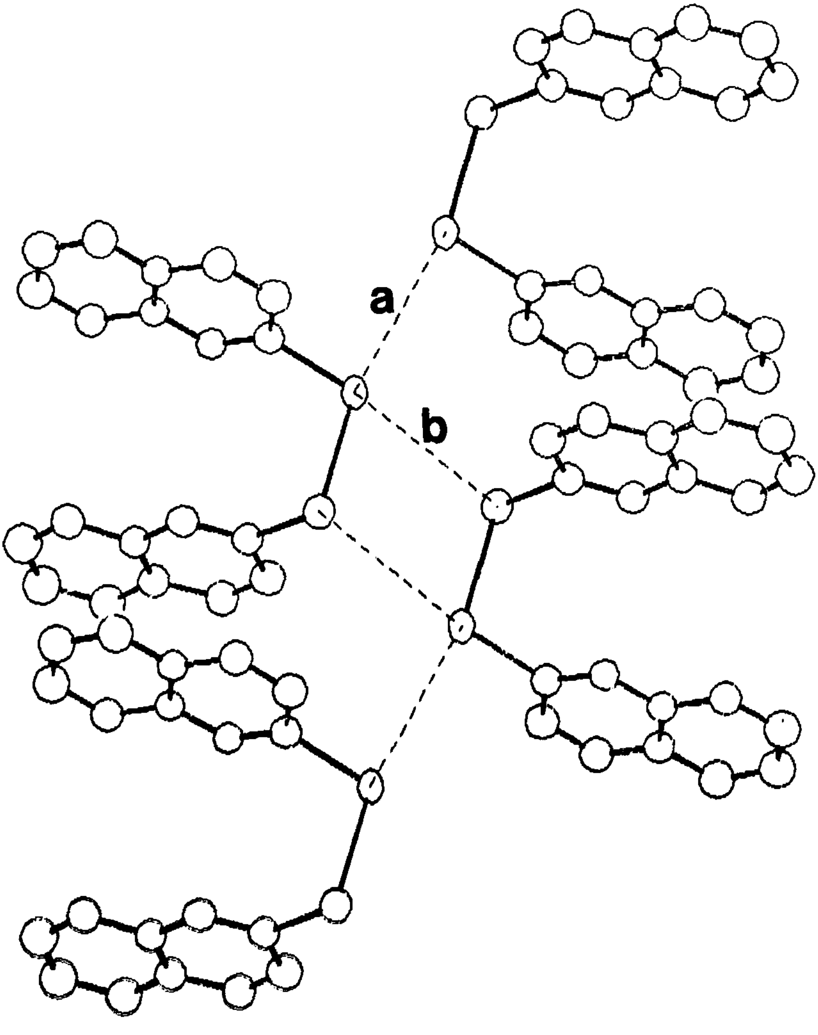


Figure 2. Polymorph B. The packing of cisoid molecules in stacks along the crystallographic b direction is shown. Intermolecular Te-Te distances are: a = 3.707, b = 4.002 Å.

ACKNOWLEDGMENTS

The authors thank M. Downey and J. Mullins for furnishing X-ray powder diffraction patterns, F. X. Pink for performing emission spectroscopic analysis, and K. Graham for typing the manuscript. D. J. S. thanks P. M. Grant, N. Thorup, and F. Wudl for sending preprints and E. M. Engler and J. Strähle for useful discussions.

REFERENCES

1. Permanent address: Department of Chemistry, Eastern Nazarene College, Quincy, MA 02170. This work was supported in part by National Science Foundation Grant SPI-8160202.

2. The work at Brandeis University was supported in part by the Office of Naval Research.

3. K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen, and J. C. Scott, J. Am. Chem. Soc., 103, 2440 (1981).

4. "$(TMTSF)_2X$ and Superconductivity," Proc. Internat. Conf. on Low-Dimensional Conductors, A. J. Epstein and E. M. Conwell, ed., Mol. Cryst. Liq. Cryst., 79, 1-362 (1982).

5. D. J. Sandman, G. P. Hamill, and W. A. Burke, Mol. Cryst. Liq. Cryst., 82, 69 (1982).

6. (a) F. Wudl and E. Aharon-Shalom, J. Am. Chem. Soc., 104, 1154 (1982); (b) K. Lerstrup, D. Talham, A. Bloch, T. Poehler, and D. Cowan, J. Chem. Soc., Chem. Comm. 336 (1982).

7. (a) D. J. Sandman, J. C. Stark, G. P. Hamill, W. A. Burke, and B. M. Foxman, Mol. Cryst. Liq. Cryst., 86, 79 (1982); (b) D. J. Sandman, J. C. Stark, and B. M. Foxman, Organometallics, 1, 739 (1982).

8. D. J. Sandman, Mol. Cryst. Liq. Cryst., 50, 235 (1979).

9. (a) TMTSF°: T. J. Kistenmacher, T. T. Emge, P. Shu, and D. O. Cowan, Acta Cryst., B35, 772 (1979); (b) PF_6^-: N. Thorup, G. Rindorf, H. Soling, and K. Bechgaard, Acta Cryst., B37, 1236 (1981);

(c) AsF_6^-: F. Wudl, J. Am. Chem. Soc., 103, 7064 (1981); (d) ClO_4^- and ReO_4^-: G. Rindorf, H. Soling, and N. Thorup, Acta Cryst. B., submitted; (e) BF_4^-: H. Kobayashi, A. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett., 245 (1982); (f) NO_3^-: H. Soling, G. Rindorf, and N. Thorup, Cryst. Struct. Commun., submitted; (g) $H_2F_3^-$: M. A. Beno, G. S. Blackman, J. M. Williams, and K. Bechgaard, Inorg. Chem., 21, 3860 (1982).

10. (a) Lattice constants of TMTTF°: ref. 8; (b) BF_4^-: J. L. Galigne, et al., Acta Cryst., B35, 1129 (1979); (c) Br^-: J. L. Galigne, et al., Acta Cryst., B34, 620 (1978).

11. (a) TSeT°: ref. 5; (b) Cl^-: R. P. Shibaeva and V. F. Kaminskii, Kristallografiya, 23, 1183 (1978); (c) PF_6^-, AsF_6^-: B. Hilti, C. W. Mayer, and G. Rihs, Solid State Commun., 41, 787 (1982).

12. (a) Fluoranthene°: A. C. Hazell, et al., Acta Cryst., B33, 1516 (1977); (b) PF_6^-, AsF_6^-, and SbF_6^-: V. Enkelmann, et al., Chem. Phys., 66, 303 (1982).

13. (a) Naphthalene°: C.P. Brock and J. D. Dunitz, Acta Cryst., B38, 2218 (1982); (b) PF_6^- and AsF_6^-: H. P. Fritz, et al., Z. Naturforsch., 33b, 498 (1978).

14. (a) F. H. Herbstein, "Perspectives in Structural Chemistry," eds J. D. Dunitz and J. A. Ibers, Wiley, 1971, Vol. 4, p. 166 ff.; (b) J. D. Dunitz, "X-Ray Analysis and the Structure of Organic Molecules," Cornell University Press, 1979, p. 412 ff.

15. J. P. Pouget, R. Moret, R. Comes, and K. Bechgaard, J. Physique-Lett., 42, L-543 (1981).

16. J. M. Williams, et al., Mol. Cryst. Liq. Cryst., 79, 319 (1982).

17. M. M. Lee, et al., Mol. Cryst. Liq. Cryst., 79, 145 (1982).

18. E. M. Engler, et al., Mol. Cryst. Liq. Cryst., 79, 15 (1982).

19. (a) M. H. Whangbo, W. M. Walsh, Jr., R. C. Haddon, and F. Wudl, *Solid State Commun.*, *43*, 637 (1982); P. M. Grant, *Phys. Rev. B*, in press.

20. F. Wudl, D. Nalewajek, J. M. Troup, and M. W. Extine, *Science*, to be published.

21. R. M. Metzger, *J. Chem. Phys.*, *75*, 482 (1981).

22. D. J. Sandman, *J. Electronic Materials*, *10*, 173 (1981).

23. G. Wegner and V. Enkelmann, private communication.

24. D. J. Sandman, J. C. Stark, L. A. Acampora, and P. Gagne, paper presented at the Twelfth Northeast Regional Meeting of the American Chemical Society, Burlington, Vermont, June 27-30, 1982, Abstract 158, and to be published.

25. M. T. Jones, L. A. Acampora, and D. J. Sandman, *J. Phys. Chem.*, to be published.

26. E. B. Yagubskii, *et al.*, *Izv. Akad. Nauk. SSSR*, *Ser. Khim.*, 1432 (1981), have also reported preparation of $(TTeT)_2^+ X^-$ $(X = Cl,Br)$.

27. O. N. Eremenko, *et al.*, *Izv. Akad. Nauk. SSSR*, *Ser. Khim.*, 1507 (1979).

28. D. J. Sandman, M. Rubner, and L. Samuelson, *J. Chem. Soc., Comm Commun.*, 1133 (1982).

29. J. Bernstein and A. T. Hagler, *J. Am. Chem. Soc.*, *100*, 673 (1978); B. M. Foxman, P. L. Goldberg, and H. Mazurek, *Inorg. Chem.*, *20*, 4368 (1981).

30. S. L. Bender, N. F. Haley, and H. R. Luss, *Tetrahedron Lett.*, *22*, 1495 (1981).

31. P. J. Carroll, *et al.*, *J. Chem. Soc.*, *Chem. Commun.*, in press.