

coupling into E_u and A_{1u} components, which are dipole allowed (x, y) and forbidden, respectively. We therefore assign the shorter-lived higher-energy emitting level to the E_u allowed state in agreement with the FCA analysis, and the lower-energy emitting level to A_{1u} .

The free-ion spin-orbit coupling constant ξ_{5d} for Pt(II) is $\sim 4000 \text{ cm}^{-1}$.²² The $\sim 50 \text{ cm}^{-1}$ spin-orbit splitting of the $^3A_{2u}$ term obtained from the lifetime vs. temperature data seems quite small for a metal-centered term. We propose that the small splitting is due to exceptionally small orbital angular momentum in this $^3A_{2u}$ term. The weak spin-orbit coupling also manifests itself in the nonexponential lifetimes observed at temperatures below 9 K, reminiscent of organic molecules.²³ In this view the relaxation rate between the levels in the $^3A_{2u}$ manifold below 9 K becomes comparable to or less than the radiative rates from the levels producing nonexponential decays and the observed spectral changes.

Application of the Strickler-Berg formula²⁴ to the strong ab-

sorption band leads to a predicted fluorescence radiative lifetime of 5.7 ns, well below our detection limit. Although the intensity formula was derived for strong singlet-singlet transitions, predictions for much weaker transitions will probably be correct within an order of magnitude.²⁴ If we assume that most of the intensity of the weak absorption band is carried by the $E_u(^3A_{2u})$ level, we calculate a phosphorescence radiative lifetime of 4.1 μs . If we make the reasonable assumption that the phosphorescence quantum yield is near unity at low temperature, then this calculated value is in good agreement with the measured lifetime from the $E_u(^3A_{2u})$ level of 1.58 μs .

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(22) Griffith, J. S. "The Theory of Transition Metal Ions"; Cambridge University Press: London, 1964; p 113.

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Three-Dimensional Structure of the Superconductor $(\text{TMTSF})_2\text{AsF}_6$ and the Spin-Charge Separation Hypothesis

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Abstract: The structure of the organic superconductor $(\text{TMTSF})_2\text{AsF}_6$ is described in detail. It is shown that the salts $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{PF}_6$ and AsF_6) are *pseudo-two-dimensional*. A structure-related hypothesis is presented in which spin-charge separation and charge localization can be used to explain why there are no charge density waves in $(\text{TMTSF})_2\text{X}$.

In the decade between our discovery of the electrical conductivity of the first chalcogenafulvalene salt [tetrathiafulvalenium chloride (TTFCl)]^{1,2} and the discovery of high-pressure superconductivity of another chalcogenafulvalenium salt [bis(tetramethyltetraselenafulvalene) hexafluorophosphate^{3,4} $((\text{TMTSF})_2\text{PF}_6)$], several important concepts have evolved.⁵ These concepts were initially biased by the historical importance of tetracyanoquinodimethane (TCNQ). For example, in the first organic metal (TTF-TCNQ), it was maintained for years that TTF was just a polarizable counterion to TCNQ.^{5f} In fact, we know now that all *highly* conductive organic metals are formed from radical ions based on chalcogenafulvalenoids⁶ and *not* on TCNQ

Table I. Intensity Measurements

instrument:	Enraf-Nonius CAD4 diffractometer
monochromator:	graphite crystal, incident beam
attenuator:	Zr foil, factor 20.7
take-off angle:	2.8°
detector aperture:	2.0-2.6 mm horizontal; 2.0 mm vertical
crystal-to-detector dist:	21 cm
scan type:	ω -2 θ
scan rate:	2-20°/min (in ω)
scan width:	(0.7 + 0.350 tan θ)°
max 2 θ :	58.0°
no. of reflctns measd:	3832 total, 3815 unique
correctns:	Lorentz-polarization; empirical absorption (from 0.85 to 1.00 on I); extinction (coefficient = 0.000 000 6)

and are single stack lattices in which the metallic conductivity is due only to long-range delocalization among donors.⁵

Prior to the advent of $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{BF}_4, \text{ClO}_4, \text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{NO}_3$),³ the principal requirements to achieve metallic be-

(1) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc. D* 1970, 1453.

(2) Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* 1972, 94, 670.

(3) Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* 1980, 33, 1119.

(4) (a) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* 1980, 41, L95. (b) Andres, K.; Wudl, F.; McWhan, D. B.; Thomas, G. A.; Nalewajek, D.; Stevens, A. L. *Phys. Rev. Lett.* 1980, 45, 1449.

(5) (a) Alcaicer, L., Ed. "The Physics and Chemistry of Low Dimensional Solids"; D. Reidel Publishing Co.: Dordrecht, Holland 1980. (b) Hatfield, W. E., Ed. "Molecular Metals"; Plenum Press: New York, 1979. (c) Miller, J. S.; Epstein, A. J., Eds. *Ann. N.Y. Acad. Sci.*, 1978, 313, "Synthesis and Properties of Low Dimensional Materials". (d) Keller, H. J., Ed. "Chemistry and Physics of One Dimensional Metals"; Plenum Press: New York, 1977. (e) Torrance, J. B. *Acc. Chem. Res.* 1979, 12, 79. (f) Garito, A. F.; Heeger, A. J. *Ibid.* 1974, 7, 232. (g) Soos, S. G. *Annu. Rev. Phys. Chem.* 1974, 25, 121.

(6) Other sulfur and selenium, nonfulvenoid donors also give rise to single-chain organic metals; i.e., P. Delhaes in ref. 5a, above. Perylene forms highly conducting PF_6 and AsF_6 salts (Keller, H. J.; Nothe, D.; Pritzkow, H.; Wehe, D.; Werner, M.; Koch, P.; Schweizer, D. *Mol. Cryst. Liquid Cryst.* 1981, 62, 181).

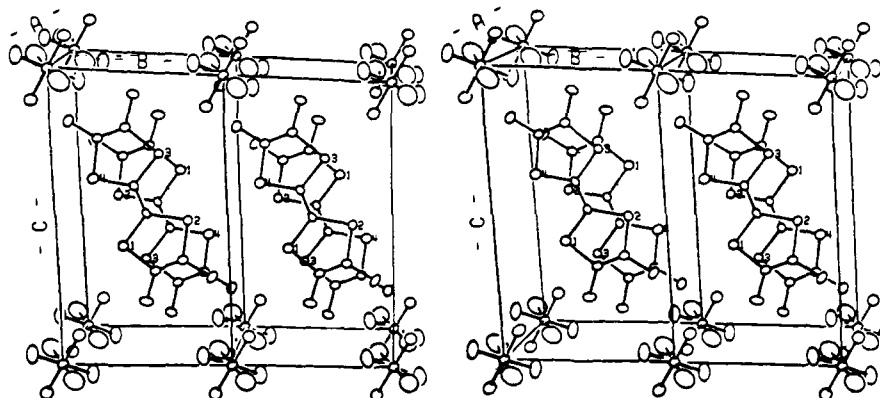


Figure 1. Stereoscopic view of two unit cells of $(\text{TMTSF})_2\text{AsF}_6$ along b . The numbering of the selenium atoms corresponds to Table I. The a axis direction is into the plane of the paper.

Table II. Structure Solution and Refinement

soln:	direct methods
hydrogen atoms:	not included
refinement:	full-matrix least squares
minimization function:	$\sum w(F_o - F_c)^2$
least-squares wts:	$4F_o^2/\sigma^2(F_o^2)$
"ignorance" factor:	0.050
anomalous dispersion:	all nonhydrogen atoms
reflctns included:	2400 with $F_o^2 > 3.0\sigma(F_o^2)$
parameters refined:	161
unweighted agreement factor:	0.031
weighted agreement factor:	0.044
factor including unobsd reflctns:	0.082
esd of observn of unit wt:	1.26
convergence, largest shift:	0.03σ
highest peak in final difference Fourier:	$0.39 (13) e/\text{\AA}^3$
computer hardware:	linked PDP-11/45-11/60
computer software:	Enraf-Nonius SDP and private programs of Molecular Structure Corp.

havior were believed to be (a) segregated chains of donor and acceptor molecules with *uniform intermolecular intrachain distances*, (b) incommensurability between the charge density waves (CDW's) due to the ions and donor lattice, (c) partial charge transfer between donors and acceptors, i.e., $p < 1$ (p = charge per molecule),^{5g} and (d) higher than one dimensionality^{5a} (strong interchain interactions).

Preliminary reports on the structure and properties of $(\text{TMTSF})_2\text{PF}_6$ indicated an apparent violation^{3,4a} of points a and b, above. In this paper we show via a study of the crystal structure of $(\text{TMTSF})_2\text{AsF}_6$ that this discrepancy and the unusual electric and magnetic properties can be explained in terms of unique interstack and intrastack interactions among the selenium atoms and the location and quality of the closed-shell anion lattice.

Crystal Structure⁷ of $(\text{TMTSF})_2\text{AsF}_6$. Black needles of $(\text{TMTSF})_2\text{AsF}_6$ were grown electrochemically from chlorobenzene by using twice crystallized Bu_4NAsF_6 as electrolyte.^{3,4b} Table I and II contain the pertinent experimental details,⁸ and Table III contains the unit-cell parameters. Inspection of Table II shows this to be a good structure solution; furthermore, the width at half-height of 0.20° with a take-off angle of 2.8° (Table I) indicates good crystal quality. The intramolecular bond distances and bond angles of the TMTSF molecules⁸ (Tables VII and VIII) were in agreement with those previously reported^{9,14} for charged

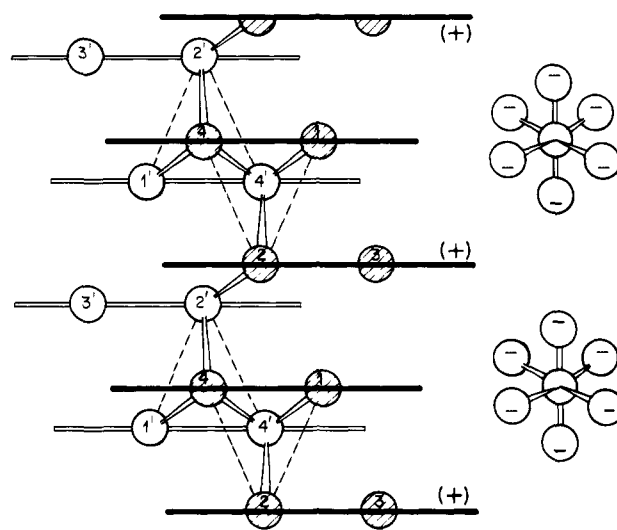


Figure 2. Schematic view of two stacks of $(\text{TMTSF})_2\text{AsF}_6$. The heavy horizontal lines represent edge-on TMTSF molecules nearest the observer. The lighter horizontal lines represent TMTSF molecules behind the front stack. The numbering arrangement corresponds to a mirror image relative to the b - c plane (cf. a direction) of the view shown in Figure 1. The shaded circles are seleniums on the back of the front TMTSF's (only two seleniums per donor are shown in this figure). The open circles are front seleniums on the back stack. The primed numbers refer to the back stack. The anion octahedra on the left side were omitted for clarity. The negative charges imply that the whole anion bears a full negative charge which is distributed among six fluorine atoms. The plus signs imply some positive charge density in that region of the donors (near Se3). The a axis direction is from bottom to top, the c axis from right to left, and the b axis into the page.

TMTSF but substantially different from neutral TMTSF^{9b} (see Table VI).

Figure 1 shows two unit cells along the b axis. As can be seen, this structure is isomorphous with that of $(\text{TMTSF})_2\text{PF}_6$.^{3,4a,14} Upon examination of a three-dimensional model of the structure containing two stacks with five donors per stack, it became apparent that there existed some unusual, previously unobserved, homoatomic interactions. Figure 2 is an attempt to illustrate these unique selenium-selenium interactions. It is a view approximately down the b axis (into the page) with the donor molecules edge-on (dark lines represent donors nearest to the observer and shaded circles are the seleniums within these donors which are farthest from the observer). The c axis runs from right to left and the a axis from bottom to top. For the sake of clarity the selenium atoms are not drawn to scale but the anions, which are excluded from the left side of the figure, are shown in detail with each fluorine bearing a partial negative charge. This figure, in conjunction with Table IV, shows quite dramatically a chain of selenium atoms (*involving two stacks*) reminiscent of selenium metal.¹⁰ Another feature of the structure demonstrated by the

(7) Structure determined by M. W. Extine, B. A. Frenz, R. A. Meisner, and J. M. Troup at the Molecular Structure Corp.

(8) Additional experimental details will be published in the future.

(9) (a) Andersen, J. R.; Bechgaard, K.; Jacobsen, C. S.; Rindorf, G.; Soling, H.; Thorup, N.; *Acta Crystallogr., Sect. B* **1978**, *B34*, 1901. (b) Kistenmacher, T. J.; Emge, T. J.; Shu, P.; Cowan, D. O. *Acta Crystallogr., Sect. B* **1979**, *B35*, 772.

Table III. Comparison of Parameters of (TMTSF)₂X

X	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	closest interstack selenium-selenium distances, Å	"interplanar distances", ¹⁶ Å	unit-cell vol, Å ³
PF ₆ ¹⁴	7.297 (1)	7.711 (1)	13.522 (2)	83.39 (1)	86.27 (1)	71.01 (1)	3.879	3.63, 3.66	714.3
AsF ₆	7.277 (2)	7.711 (1)	13.651 (2)	83.16 (1)	86.00 (2)	71.27 (2)	3.905	3.65, 3.62	719.9

Table IV. Intermolecular Selenium-Selenium Contacts to 5.0 Å

atom 1	atom 2	dist, Å	symmetry code ^a
Se1	Se2	4.053	(-1,1,1,1)
Se1	Se2	4.128	(-1,2,1,1)
Se1	Se3	4.026	(-1,1,1,1)
Se1	Se3	3.874	(-1,2,1,1)
Se1	Se4	3.945	(-1,1,2,1)
Se2	Se2	3.905	(-1,2,0,1)
Se2	Se3	4.977	(-1,2,1,1)
Se2	Se4	4.151	(1,0,-1,0)
Se2	Se4	3.970	(-1,1,1,1)
Se2	Se4	3.919	(-1,2,1,1)
Se4	Se4	3.963	(-1,1,2,1)

^a The symmetry code "ijkl" denotes the symmetry operation $n^*(x, y, z) + (i, j, k)$. For example, the code "-1,1,1,1" corresponds to $(-x, -y, -z) + (1, 1, 1)$ or $(1-x, 1-y, 1-z)$. Intrastack close contacts will have codes of "-1,1,1,1" or "-1,2,1,1". The remaining codes are for various interstack contacts.

Table V

	no. of interstack selenium in homoatomic TMTSF (cf. Figure 2) nearest neighbors	no. of interstack selenium in homoatomic TMTSF nearest neighbors
Se4	3	Se1 1
Se2	2	Se3 0

three-dimensional model and depicted in Figure 2 by dotted lines is selenium clustering. These clusters are "bonded" via the shortest interstack selenium distance (Se2-Se2') of 3.905 Å in this solid. These clusters reflect the fact that each one of the four selenium atoms in the TMTSF stacks has a different "connectivity" as shown in Table V. The Se3's have an "interstack" methyl and an AsF₆ as nearest neighbor (cf. Figure 1).

All selenium-selenium distances, with the exception of Se2-Se4' (4.151 Å), are shorter than the van der Waals radius of selenium as given by Pauling¹¹ (4.0 Å) or just beyond the Bondi¹² (3.8-Å) value.

Comparisons with Other Highly Conductive Triclinic Salts. Kistenmacher has determined and compared the structures of the organic metals TMTSF·TCNQ, HMTSF·TNAP, and their sulfur analogues.¹³ The full structure of (TMTSF)₂PF₆ has recently been completed.¹⁴ These three solids have two aspects in common: (a) they are all triclinic and (b) they all have relatively short interstack Se-Se contacts (TMTSF·TCNQ, 3.98, 4.04 Å; HMTSF·TNAP, 3.77 Å; (TMTSF)₂PF₆, 3.879, 3.959, 3.934 Å). They differ in that the first two have uniform stacks of donors and acceptors where the donors are stacked in roughly "double-bond-over-ring" fashion.¹³ On the other hand, in the PF₆ salt and the AsF₆ salt the donors repeat with a displacement alternating in the long molecular axis direction while forming stacks along

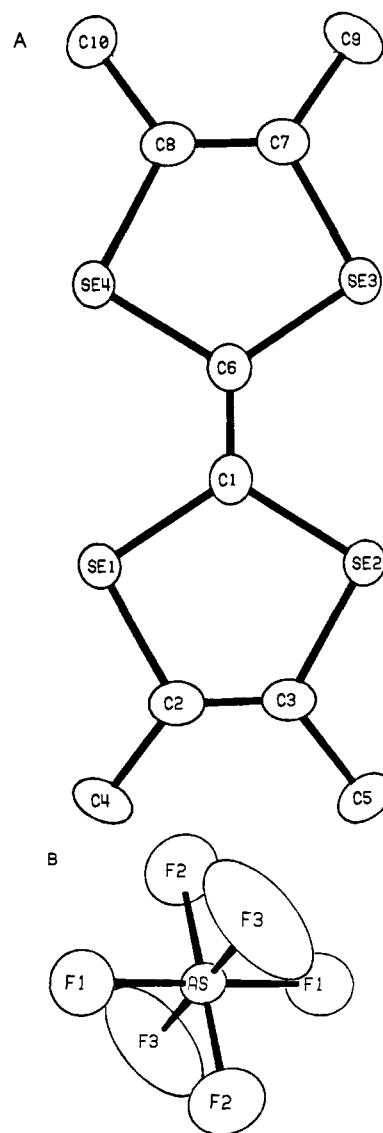


Figure 3. (A) TMTSF. (B) AsF₆. See Tables VII and VIII for bond distances and angles.

a, similar to (TMTTF)₂X (X = BF₄, ClO₄, Br)¹⁵ but without alternation¹⁶ in "interdimer" distance. Of all these salts, HMTSF·TNAP is the most "three-dimensional" from a structural point of view¹³ because of close approach of interstack selenium-nitrogen atoms.

Table III contains a comparison of unit-cell parameters and other important distances of the PF₆⁻ and AsF₆⁻ salts. The most interesting aspect of this comparison is that while AsF₆⁻ is larger than PF₆⁻, the a dimension of the former salt's unit cell is shorter

(10) Cherin, P.; Ungar, P. *Inorg. Chem.* **1967**, *6*, 1589. Of course in selenium metal the intrachain distances are much shorter (2.32 Å), but there is still a resemblance to the chain shown in Figure 2.

(11) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, N.Y., 1960.

(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(13) Kistenmacher, T. J. in ref. 5c.

(14) Thorup, N.; Rindorf, G.; Solig, H.; Bechgaard, K. *Acta Crystallogr., Sect. B*, in press. A preprint from N. Thorup is greatly appreciated.

(15) Galigne, J. L.; Liutard, B.; Peytavin, S.; Brun, G.; Maurin, M.; Fabre, J. M.; Torreilles, E.; Giral, L. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1129.

(16) In (TMTSF)₂AsF₆, the differences between three consecutive least-squares planes are 3.648 and 3.626 Å; i.e., an "alternation" of 0.022 Å. But the selenium atoms themselves are at roughly ±0.014 from these planes, and we, therefore, believe that it is practically meaningless to attach any significance to 0.02-Å alternation in the planes.⁸

than the same parameter of the latter salt. The difference in size of the anions is reflected correctly in the *c* dimension and the volume of the respective unit cells. Examination of the closest interstack selenium distances¹⁴ (Table III) and interplanar distances reveals that, from a structure point of view, the AsF₆⁻ salt is slightly more "one-dimensional" than the PF₆⁻ salt; i.e., the difference between the shortest intrastack and interstack selenium contacts in the latter salt is only¹⁴ 0.005 Å (negligible) whereas that same difference is 0.031 Å in the former salt (cf. Table IV).

Discussion

(A) Correlation of Structure and Properties. Bechgaard et al.³ reported a (TMTSF)₂PF₆ room-temperature σ_{parallel} value (conductivity parallel to the needle axis, *a* crystal axis) of 540 Ω⁻¹ cm⁻¹ and anisotropies of 350 and 36 000.³ These anisotropies, presumably along the *b* and *c* axes, respectively, should be very difficult to measure and are therefore not expected to reflect the intrinsic property of the solid (particularly σ_b). Low-temperature optical measurements indicate that the conductivity along *b* may be higher than that measured by DC techniques since a bandwidth in the *b* direction of ~0.2 eV was found.¹⁷

From an examination of our three-dimensional model of (TMTSF)₂AsF₆ (Figure 2) and intermolecular distances (Tables VI and IX), it is clear that the conductivity cannot arise from carbon-carbon π orbital overlap since the distances are much too large to produce a bandwidth of ~1 eV. Therefore, this bandwidth, which is ca. 2^{1/2} times that of TTF-TCNQ must be derived entirely from homoatomic selenium overlap.¹⁸ The same model and tables reveal that the difference between interstack and intrastack selenium distances is practically zero for the PF₆⁻ salt and almost negligible for the AsF₆⁻ salt, indicating that *these compounds are pseudo-two-dimensional* consisting of sheets of donors and sheets of anions. Thus all theories based on premises of one dimensionality¹⁹ developed to explain the properties of these salts may not be applicable.

The theoretically most interesting features of these salts are (a) nonlinear field dependence of the conductivity,^{20a,b} (b) absence of charge density waves as established by diffuse X-ray scattering measurements,^{21,22} and (c) superconductivity.²² As part of an explanation of a and b, above, and other magnetic properties, the metal-to-semiconductor transition²⁰ in these solids has been ascribed to weak pinning of spin density waves (SDW). It still remains to be explained,^{20b} however, how a magnetic interaction which is weaker than an electron-hole or electron-phonon interaction can be responsible for a metal-to-semiconductor transition.

(17) C. S. Jacobsen, H. J. Pedersen, K. Mortensen, and K. Bechgaard (*Chem. Scr.*, in press) found that the (TMTSF)₂X salts are more two-dimensional than implied by earlier measurements.³ Jacobsen, C. S.; Tanner, D. B.; Bechgaard, K., *Phys. Rev. Lett.* **1981**, *46*, 1142.

(18) Whereas in TTF⁺ the highest spin density is on the central carbon atoms; in TSeF⁺ the highest spin density is on the seleniums: cf. Bramwell, F. B.; Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100* 4612 and ref 17 therein. However, the fact that a very short distance between two atoms is observed does not necessarily imply orbital overlap because the directionality of the orbitals involved must also be considered. Thus, if the Se atoms in TMTSF were sp² hybridized, the overlap in the crystallographic *a* direction (stacking direction) will be larger than in the crystallographic *b* direction even though the two distances are equal in (TMTSF)₂PF₆. In the absence of detailed electron density measurements, one cannot know the hybridization of selenium in (TMTSF)₂PF₆. Experiments with highly refined X-ray crystallography data are currently in progress to find an answer to this fundamental question.

(19) Proceedings of the International Conference on Low Dimensional Synthetic Metals, Helsingor, Denmark, 1980; *Chem. Scr.* **1981**, *17*, 1-230.

(20) (a) Walsh, W. M., Jr.; Wudl, F.; Thomas, G. A.; Nalewajek, D.; Hauser, J. J.; Lee, P. A.; Poehler, T. O. *Phys. Rev. Lett.* **1980**, *45*, 829; (b) P. M. Chaikin, G. Gruner, E. M. Engler, Greene, T. O. *Ibid.* **1980**, *45*, 1874.

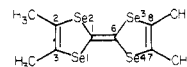
(21) Thomas, G. A.; Moncton, D., unpublished. Pouget, J. P., ref 19, above.

(22) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440 found (while this manuscript was in progress) that (TMTSF)₂ClO₄ is isomorphous with the AsF₆⁻ and PF₆⁻ salts and is superconducting at atmospheric pressure and 1.4 K. This salt has oxygen positional disorder in the perchlorate sheets. See: Ribault, M.; Pouget, J.-P.; Jerome, D.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L607 for superconductivity of (TMTSF)₂AsF₆.

Table VI. Comparative Bond Lengths (Å)^a

	TMTSF	(TMTSF) ₂ AsF ₆
C1-C6	1.352	1.345
C2-C3	1.315	1.338
C7-C8	1.315	1.355

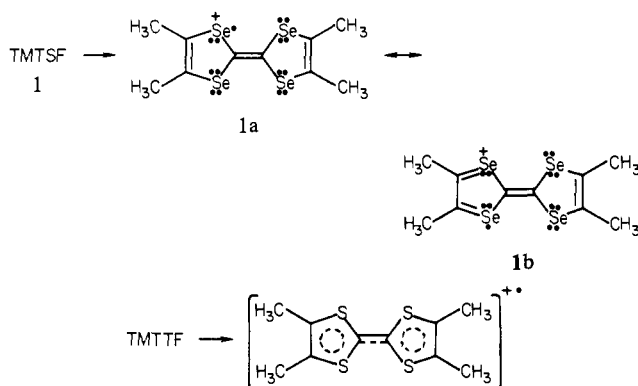
^a Numbering corresponds to the diagram



On the basis of the foregoing structural analysis, a model can be constructed which can explain why spin density waves (antiferromagnetic ordering) and not charge density waves exist in these solids.

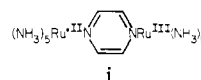
(B) The Spin-Charge Separation and Charge-Localization Hypothesis. This SCSCS hypothesis is based on two relatively unorthodox premises: (a) separation of spin and charge in a radical ion and (b) localization²⁵ of charge due to electrostatic ion-pairing in the solid state.

(a) Separation of Spin and Charge (SSC). Simple molecular orbital theory assumes that under normal circumstances (solution, gas phase), both the charge (positive or negative) and the spin (unpaired electron) of a radical ion such as TMTSF⁺ are always delocalized and indistinguishable. There are, however, situations when this may not apply.^{23a,c} Since selenium is a relatively high atomic number element, organic radical ions containing this element will exhibit a substantial decrease in conjugation due to mismatch in C-Se orbital size.^{18,23d} As a result of this poor overlap, there will be a more inhomogeneous charge and spin distribution in TMTSF¹⁸ than in TMTTF as depicted.



In the solid state, resonance structures (1a and 1b)⁺ become important contributors to the valence-bond wave function of 1⁺. In structures (1a and 1b)⁺, the valence shell of selenium is expanded making use of d functions; thus, in 1b⁺, the unpaired spin would be in a selenium spd orbital.^{18,24} Corroboration for the importance of resonance contributing structure 1b⁺ stems from comparisons of intramolecular bond distances in neutral TMTSF^{9b} and TMTSF in the (TMTSF)₂AsF₆ salt. Table VI contains the

(23) (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472 has found that



i (analogous in symmetry to TMTSF⁺) has two distinguishable rutheniums via X-ray photoelectron spectroscopy. (b) For a further discussion of the ongoing debate on compound i see: Citrin, P. H.; Ginsberg, A. P. *J. Am. Chem. Soc.*, in press. (c) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (d) Engler, E. M.; Kaufman, F. B.; Green, D. C.; Klotz, C. E.; Compton, R. N. *J. Am. Chem. Soc.* **1975**, *77*, 2921.

(24) There exists a continuing controversy over the effect of d orbitals on the chemistry of organosulfur compounds and less of a dispute in the case of organoselenium compounds. Selenium is more apt to expand its valence shell as corroborated by the increased stability of its tetravalent compounds (Klayman, D.; Gunther, W. H. H. "Organic Selenium Compounds"; Wiley-Interscience: New York 1973).

Table VII. Bond Distances (Å)^a

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Se1	C1	1.881 (4)	Se4	C8	1.894 (5)	C8	C10	1.506 (6)
Se1	C2	1.905 (4)	C1	C6	1.345 (6)	As	F1	1.679 (4)
Se2	C1	1.886 (4)	C2	C3	1.338 (7)	As	F1	1.679 (4)
Se2	C3	1.893 (4)	C2	C4	1.489 (6)	As	F2	1.664 (4)
Se3	C6	1.872 (4)	C3	C5	1.503 (6)	As	F2	1.664 (4)
Se3	C7	1.897 (5)	C7	C8	1.355 (6)	As	F3	1.648 (4)
Se4	C6	1.884 (4)	C7	C9	1.489 (6)	As	F3	1.648 (4)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Bond Angles (Deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C1	Se1	C2	95.0 (2)	Se3	C6	Se4	114.2 (2)	F1	As	F3	91.7 (3)
C1	Se2	C3	94.5 (2)	Se3	C6	C1	123.4 (3)	F1	As	F2	89.6 (2)
C6	Se3	C7	94.8 (2)	Se4	C6	C1	122.4 (3)	F1	As	F2	90.4 (2)
C6	Se4	C8	94.3 (2)	Se3	C7	C8	118.0 (3)	F1	As	F3	91.7 (3)
Se1	C1	Se2	113.5 (2)	Se3	C7	C9	116.6 (4)	F1	As	F3	88.3 (3)
Se1	C1	C6	123.4 (3)	C8	C7	C9	125.4 (4)	F2	As	F2	180.0 (3)
Se2	C1	C6	123.1 (3)	Se4	C8	C7	118.6 (3)	F2	As	F3	86.1 (3)
Se1	C2	C3	117.6 (4)	Se4	C8	C10	116.0 (3)	F2	As	F3	93.9 (3)
Se1	C2	C4	114.5 (3)	C7	C8	C10	125.3 (4)	F2	As	F3	93.9 (3)
C3	C2	C4	127.8 (4)	F1	As	F1	180.0 (5)	F2	As	F3	86.1 (3)
Se2	C3	C2	119.4 (3)	F1	As	F2	90.4 (2)	F3	As	F3	180.0 (7)
Se2	C3	C5	114.5 (3)	F1	As	F2	89.6 (2)				
C2	C3	C5	126.1 (4)	F1	As	F3	88.3 (3)				

Table IX. Intermolecular Contacts to 3.75 Å [Bond Distances (Å)]^a

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Se3	C2'	3.709 (0)	C9	F3	3.631 (0)	C9'	F1	3.432 (0)
Se3	F1'	3.196 (0)	C9	F1'	3.432 (0)	C9'	F2	3.686 (0)
C1	C1'	3.627 (0)	C9	F2'	3.686 (0)	C9'	F3	3.583 (0)
C2	Se3'	3.709 (0)	C9	F3'	3.583 (0)	C9'	F3'	3.631 (0)
C4	F2'	3.616 (0)	C10	F2	3.478 (0)	C10'	F3'	3.364 (0)
C5	C8'	3.748 (0)	C10	F3	3.364 (0)	C1	C1'	3.662 (0)
C5	F1	3.188 (0)	Se3'	F1	3.196 (0)	C5	C8'	3.743 (0)
C5	F2'	3.622 (0)	C4'	F2	3.616 (0)	C8	C5'	3.743 (0)
C8	C5'	3.748 (0)	C5'	F2	3.622 (0)	C9'	F2	3.387 (0)
C9	F2	3.387 (0)	C5'	F1'	3.188 (0)	C10'	F2'	3.478 (0)

^a Estimated standard deviations were not calculated. Primed and unprimed atoms are related by an inversion center.

bonds in question. Note that C7–C8 is longer in the salt than in the neutral molecule whereas the reverse is true for C1–C6, implying more central double-bond character in the salt than in neutral TMTSF. Furthermore, in the salt, C8–C7 (adjacent to Se3) is longer than C2–C3.

(b) Charge Localization. The structures of (TMTSF)₂PF₆ and (TMTSF)₂AsF₆ are unique compared to other organic metals in that the anions form a well-defined lattice (sheets in the *a*–*b* plane), giving rise to uniformly spaced regions of localized negative charge. These negative centers provide a driving force for the above described SSC. The positive charges then become "localized"²⁵ next to the anions as shown schematically in Figure 2, more specifically near the Se3's since the Se3 to F1 (from PF₆⁻) distance is only 3.196 Å. Interestingly (see Table V), the Se3's have as their closest nearest neighbors the PF₆⁻ counterions and, as mentioned above, do not interact with other interstack Se atoms.

As is shown below, this SCSCSCL hypothesis applies only to the explanation of the physical properties of salts of the solid state structure of (TMTSF)₂X (X = AsF₆, PF₆, ClO₄) because the electrostatic field associated with the X⁻–Se³⁺ interaction gives this family of solids a more polarized character than is possible in other organic metals.

(C) Implications of the SCSCSCL Hypothesis. (a) Stiffening of the lattice, as a result of the ion pairing described above (see Figure 2), interferes effectively with the electron–phonon coupling responsible for charge density wave formation along the *a* direction

or the *a*–*b* plane. (b) Since sulfur is of lower atomic number than selenium, SCSCSCL is not expected to be dominant in (TMTTF)₂X salts, and hence, these tend to dimerize just below room temperature¹⁵ (CDW condensation?). (c) The two-stack systems, for example, TMTSF·DMTCNQ²⁶ and HMTSF·TNAP²⁷ which are analogous (particularly the latter) in the interstack arrangement of TMTSF in (TMTSF)₂X, show metal to semiconductor transitions typical of CDW-driven low-dimensional metals [even though HMTSF·TNAP should be considered "three-dimensional" (see above)]. The reason for this behavior, according to the SCSCSCL hypothesis, is that the charge of the TMTSF⁺ counterions (DMTCNQ, TNAP, TCNQ) is delocalized along the anion stack and is thus too diffuse to stabilize SSC via ion pairing. (d) The SCSCSCL hypothesis predicts that introduction of disorder in the anion²² stack can wash out the condensation of SDW's because it would destroy their periodicity. In other words, the more the negative charge is located near Se3, the more the SSC will be stabilized. If there is a nonperiodic variation in Coulomb field strength due to disorder in the negative charges near the Se3's, there will be a corresponding variation in SSC and consequently spin density in the stack. Perfectly periodic SSC would lead to an insulating state because the TMTSF⁺ molecules will behave more like typical organic neutral radicals ("TMTSF⁺") which have a strong driving force toward spin pairing (antiferromagnetic ordering). An external electric field will influence the periodic Se³⁺–X⁻ interaction, resulting in a weakening of

(25) "Localization" in this context means that the positively charged π molecular orbital of the TMTSF molecules is extensively polarized in the crystallographic *c* direction by the adjacent anions.

(26) Jacobsen, C. S.; Mortensen, K.; Andersen, J. R.; Bechgaard, K. *Phys. Rev. B: Condens. Matter* 1978, 18, 905.

(27) Bloch, A. N., private communication.

SCSCL with concomitant restoration of conductivity. Furthermore, SCSCL should be particularly sensitive to electric fields in the crystallographic *c* direction. Thus, with the metal-to-semiconductor transition eliminated via nonperiodic SCSCL, the smooth transition from metal to superconductor becomes possible.²² So far, the superconducting properties of the available triclinic (TMTSF)₂X salts can still be explained by an electron-phonon coupling (rather than electron-exciton coupling)²⁸ BCS theory.

Conclusion

A detailed study of the three-dimensional structure of (TMTSF)₂AsF₆ (isomorphous to the PF₆⁻ and ClO₄⁻ salts²²) has led to the conclusion that these salts are pseudo-two dimensional, that there are strong interactions between certain selenium atoms in specific ways (clustering),²⁹ and that there is a periodic lattice

(28) Gutfreund, H.; Little, W. A., in reference 5d p 279. The problem with their detailed platinum chain model was to establish a realistic way to separate the conducting (platinum spine) electrons from the "polarizable" electrons (ligands around Pt).

of anions. These anion sheets could stabilize partial separation of positive charges and unpaired electron (spins). This separation can be used to formulate an hypothesis to explain the apparent absence of CDW's in these salts.

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Supplementary Material Available: A listing of structure factors, a table of positional and thermal parameters and their estimated standard deviations, a table of temperature factor expressions, and a table of torsional angles (21 pages). Ordering information is given on any current masthead page.

(29) A structural correlation with superconductivity ("clustering hypothesis") was recently proposed by: Vandenberg, J. M.; Matthias, B. T. *Science (Washington, D.C.)* 1977, 198, 194 for ternary superconductors where there are clusters of atoms separated by intercluster distances which are slightly larger (ca. 20%) than the intracenter distances.

Neophyl Rearrangements in Crystalline Bis(3,3,3-triphenylpropanoyl) Peroxide. 1. Dynamic Studies by EPR¹

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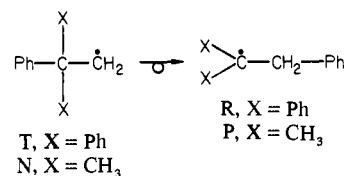
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. Received November 12, 1980

Abstract: The neophyl rearrangement of 2,2,2-triphenylethyl radical (T) to 1,1,2-triphenylethyl radical (R) was studied by EPR in photolyzed single crystals of the benzene solvate of bis(3,3,3-triphenylpropanoyl)peroxide (TPPP) and deuterated analogues. Six radical pairs were identified: TT*, TT, TR₁, TR₃, R₃R₃, and R₃R₁, where the asterisk denotes a strained structure and the subscript of R denotes which of the phenyl groups of T participated in rearrangement. No other species were observed by EPR. First-order rate constants and approximate activation parameters were determined for disappearance of each of these radical pairs. The temperatures at which they have a half-life of 1 min are 160, 166, 165, 169, 204, and 256 K, respectively. Three of these reactions involve neophyl rearrangement. They have activation energies of about 10 kcal/mol and are retarded by a factor of 10²-10⁴ as compared to rearrangement in solution. For each thermal rearrangement there is a corresponding photochemical rearrangement which yields the same product. The chromophore responsible for rearrangement has not been identified, but sensitization by neighboring peroxide molecules seems plausible.

It is hardly surprising that a rigid molecular environment can exert strong influence over reactions which require association or separation of independent molecules. Having studied matrix control of a number of reactions of this type,² we undertook the present study of the conceptually more subtle influence of matrix over an intramolecular process. This work on ground-state reactions complements the investigations of Scheffer and co-workers on lattice control over unimolecular photochemical rearrangements.³

We chose to study the free-radical neophyl rearrangement, because previous work suggested that rearrangement of 2,2,2-

triphenylethyl to 1,1,2-triphenylethyl (T → R) might be rapid enough to compete with radical-pair collapse in a crystalline solid.⁴



From studies at 283-307 K Maillard and Ingold estimated log *A* (s⁻¹) = 11.7 and *E*_a = 13.6 kcal/mol for rearrangement of neophyl itself (N → P) in fluid solution.⁵ At 163 K, a temperature at which pairs of T radicals in our crystal turn out to collapse only slowly, the half-life of N → P in solution would be about 1 month. Whether because steric hindrance is relieved or because the product radical is conjugated, T rearranges much faster than N. From Kaplan's work on triphenyltin hydride reduction of the

(1) Based on the Ph.D. Thesis of D. W. Walter, Yale University, 1980. Presented in part at the 15th Conference on Reaction Mechanisms, Colorado State University, Ft. Collins, CO, June 28, 1974, and at the Fifth International Symposium on Chemistry of the Organic Solid State, Brandeis University, Waltham, MA, June 13-16, 1978.

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(3) Scheffer, J. R. *Acc. Chem. Res.* 1980, 13, 283.

(4) Wilt, J. W. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.

(5) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, 98, 1224.