PHYSICAL REVIEW B VOLUME 22, NUMBER 10 15 NOVEMBER 1980

Comparison of two isostructural organic compounds, one metallic and the other insulating

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(Received 17 June 1980)

The organic donor hexamethylenetetrathiafulvalene (HMTTF) forms charge-transfer salts with both tetracyano-*p*-quinodimethane (TCNQ) and its tetrafluoro derivative ($TCNQF_4$). We report here the preparation, structure, and conductivity of HMTTF-$TCNQF_4$. This salt is found to be isostructural with the corresponding TCNQ salt, but with a conductivity at 300 K approximately seven orders of magnitude lower, similar to the behavior previously found for the analogous salts of the selenium derivative, hexamethylenetetraselenafulvalene (HMTSF). In order to determine the cause of this large difference in conductivity, we have thoroughly examined the molecular and solid-state differences between HMTTF-$TCNQF_4$ and HMTTF-TCNQ. The hyperfine coupling constants, molecular-orbital energy levels, solution optical spectra, and electrochemical properties of $TCNQF_4^-$ and $TCNQ^-$ are compared. For the HMTTF salts, we compare the structures, conductivities, Madelung energies, magnetic susceptibilities, and optical spectra. It is concluded that the large difference in conductivity is caused by a difference in the degree of charge transfer, and not by a difference in the value of the intramolecular Coulomb repulsion U (as had been suggested). Thus, HMTTF-TCNQ is a mixed-valence metal with a degree of charge transfer of $\rho = 0.72$; the stronger electron affinity of $TCNQF_4$ causes the charge transfer in HMTTF-$TCNQF_4$ to be complete ($\rho = 1$), making it a Mott insulator. In addition, clear evidence is given that U on the $TCNQF_4$ stack is not screened by the excitonic polarizability of the HMTTF molecules.

INTRODUCTION

The 1:1 charge-transfer salt[1] of HMTSF with $TCNQF_4$ was recently prepared at Johns Hopkins University.[2,3] This material is remarkable because it is isostructural with one of the most highly conducting organic salts known,[4] HMTSF-TCNQ, yet has a room-temperature conductivity almost seven orders of magnitude lower. We report here the preparation of analogous compounds of the sulfur analog of HMTSF, namely HMTTF, and find similar results to those discovered by Hawley *et al.*[2,3] In Fig. 1, we compare the single-crystal dc electrical conductivity along the stacking axis of HMTTF-TCNQ and HMTTF-$TCNQF_4$. At high temperatures, the TCNQ salt has metallic conductivity,[5] with a metal-semiconductor transition near 48 K, while the $TCNQF_4$ salt is a semiconductor at all temperatures with a large activation energy of 0.21 eV. Near room temperature, the conductivities of these two materials differ by almost seven orders of magnitude, even though they are isostructural, as with HMTSF.

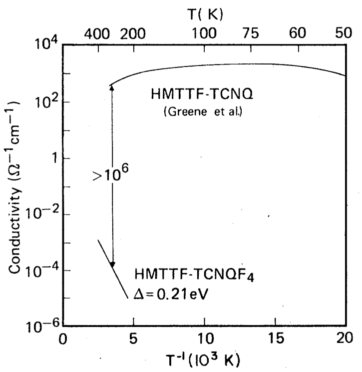
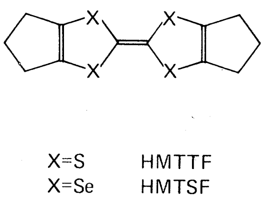
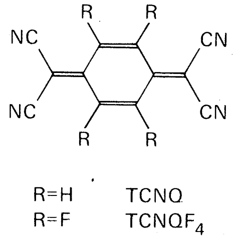


FIG. 1. Comparison of the conductivities of the isostructural HMTTF salts of TCNQ (after Greene *et al.*, Ref. 5) and $TCNQF_4$.





Two models have been proposed to account for this large difference in conductivity behavior. In order to distinguish between these models, we shall make a brief but thorough comparison of the molecular properties of TCNQ and $TCNQF_4$, as well as the solid-state properties of their HMTTF salts. The molecular comparison includes hyperfine measurements, calculations of molecular orbitals, solution optical spectra, and solution electrochemical potentials for $TCNQ^-$ and $TCNQF_4^-$.

For the solid HMTTF salts, we compare their conductivities, structures, magnetic susceptibilities, Madelung energies, and optical spectra.

MODELS

Such large differences in conductivity at 300 K as that ($>10^6$) for these HMTTF salts (Fig. 1) are also found by comparing TCNQ salts with different donors.[6,7] Since these latter materials are not isostructural, comparison between materials have not been wholly convincing. Nevertheless, two general explanations for this behavior have been proposed:

(1) Different compounds have different values of the effective U. (U is the intramolecular Coulomb repulsion energy.) Insulators have a large U, which limits their conductivity. However, materials with polarizable molecules can screen U and are therefore metallic.[8,9]

(2) Different compounds have different degrees of charge transfer. Insulators have either complete charge transfer (and U limits the conductivity) or no charge transfer. Materials with incomplete charge transfer have unfilled bands and are mixed valence. Their conductivity is metallic since U is ineffective in limiting the conductivity in this case.[7,10-13]

Corresponding to these two general proposals, two specific explanations emerge for the large difference in conductivity of the HMTTF salts. The $TCNQF_4$ salt is insulating because:

(1) The effect of the fluorine substituents is to pull the π-electron density from the ends toward the center of the molecule. Since the electrons are more confined, the Coulomb repulsion between two electrons would be stronger. Thus, U for $TCNQF_4^-$ would be larger than for $TCNQ^-$ and, in fact, would be too large to be screened.[9,14]

(2) The effect of the fluorine substituents is to greatly increase the electron affinity of $TCNQF_4$ and hence favor complete charge transfer for the $TCNQF_4$ salt.[3,7,11,13]

In order to test these two hypotheses, we shall examine the molecular properties of TCNQ and $TCNQF_4$. We want to find the major effect of the fluorine substituents on the π-electron density, on U, and on the electron affinity. For the solids, we will also compare the structures and overlaps, and perform a calculation of the electrostatic Madelung energy, which could strongly influence the degree of charge transfer. Finally, we will examine optical evidence for the degree of charge transfer in both compounds.

COMPARISON OF MOLECULAR PROPERTIES

Since the conductivity of these salts involves the unpaired electrons of the constituent molecules, a comparison of TCNQ and $TCNQF_4$ should focus on the LUMO (lowest-lying unoccupied molecular orbital) of the neutral molecules or, equivalently, on the unpaired electron in $TCNQ^-$ and $TCNQF_4^-$. We find that the distribution of electron density in this orbital is nearly identical for $TCNQ^-$ and $TCNQF_4$, as indicated from experimental measurements[15] of hyperfine coupling and calculations[16] of the molecular orbitals. In addition, the solution optical spectra of the anions (Fig. 2) are very similar, also indicating virtually no difference in the relative spacings of the molecular orbitals of $TCNQ^-$ and $TCNQF_4^-$. The latter measurement also indicates that there are no large differences in the molecular polarizability of these two molecules.

One approximate measure of U for $TCNQ^-$ has been obtained[10,17,18] by measuring the energy of the charge-transfer band of an alkali-metal salt of TCNQ. The optical absorption spectra of K-TCNQ and K-$TCNQF_4$ powder dispersed in KBr are shown in Fig. 3. It is well established[10,17-19] that the low-frequency peak near 1 eV in these spectra is the charge-transfer band for exciting electrons along the stack of $TCNQ^-$ molecules. Thus, for $TCNQ^-$ one obtains $U \sim 1.1$ eV and a somewhat smaller value $U \sim 0.8$ eV for $TCNQF_4^-$. A similar measure of U can be obtained from the spectra of $(TCNQ^-)_2$ and $(TCNQF_4^-)_2$ dimers in solution, which also yields similar values of U for the two molecules.[20] An unrelated measure of U is from the difference between the first and second reduction potentials, measured electrochemically.[9] While we do not trust this measurement of U, that difference[21] is 0.55 V for TCNQ and 0.53 V for $TCNQF_4$. From all of the above estimates, we conclude that there is not a large difference in U between TCNQ and $TCNQF_4$.

Another important molecular parameter is the electron affinity of the acceptor, which is unfortunately difficult to measure directly. However, a readily obtainable, semiquantitative estimate of this quantity can be obtained from electrochemical

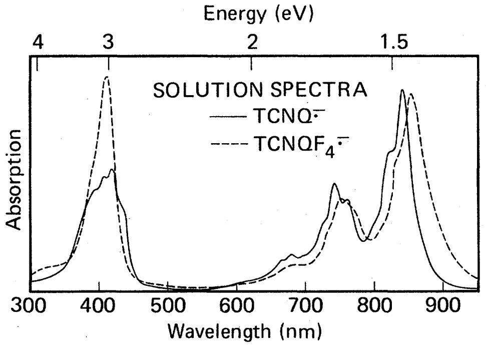


FIG. 2. Spectra of K-TCNQ and K-$TCNQF_4$ in acetonitrile solution.

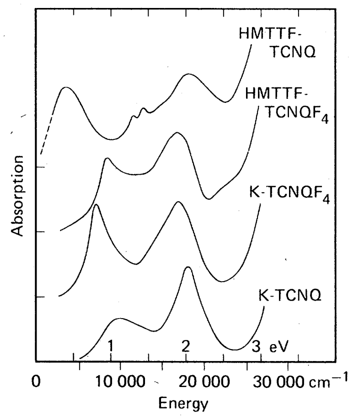


FIG. 3. Absorption spectra of HMTTF-TCNQ, HMTTF-TCNQF$_4$, K-TCNQF$_4$, and K-TCNQ as powders dispersed in KBr, illustrating the strong similarity in the latter three salts.

cyclic voltammetry. Thus, the reduction potentials of the acceptor molecule in solution can be used as a comparative measure of their electron affinities.[22] The fact that the observed[21] value for TCNQF$_4$ is 0.36 eV more positive than TCNQ indicates[22] that TCNQF$_4$ has a considerably higher (0.36 eV) electron affinity.

These results are consistent with what is known about the effects of fluorine substitutents on aromatic molecules.[23] The fluorines shift both σ and π orbitals, but the σ molecular orbitals are most strongly affected, since the latter more strongly overlap with the fluorines. For this reason, the largest changes in charge density are in the σ orbitals. Changes in the π-electron density are much smaller for a second reason: the π-orbital energies tend to be shifted equally. Since the lowest unoccupied molecular orbital (LUMO) of TCNQ is a π level, the changes in charge density would be expected to be small [although the changes indicated from the hyperfine[15] and optical measurements (Fig. 2) are surprisingly small]. A small lowering of the LUMO energy by ~0.36 eV is a reasonable shift due to fluorine substituents, and would account for the increase in electron affinity of TCNQF$_4$ compared with TCNQ.

COMPARISON OF SOLID-STATE PROPERTIES

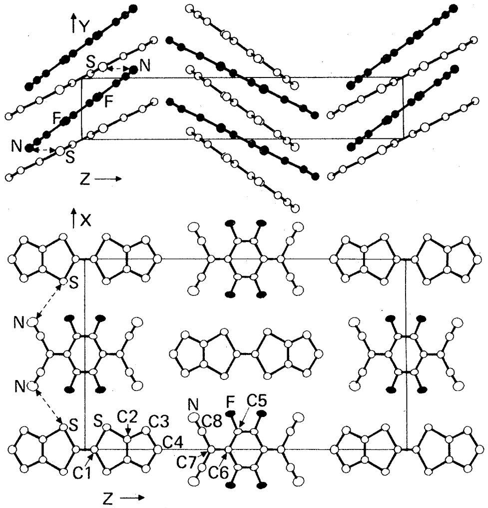


FIG. 4. Orthorhombic structure of HMTTF-TCNQF$_4$, which is isostructural with that of HMTTF-TCNQ.

The crystal structure[24] of HMTTF-TCNQF$_4$ is shown in Fig. 4 and atomic positions listed in Table I. The material is isomorphous with HMTTF-TCNQ, as can be seen by comparing Fig. 4 to Fig. 1 and 2 of Ref. 5. It crystallizes in the orthorhombic space group Pmna with unit-cell parameters $a = 12.614(4)$, $b = 4.070(2)$, and $c = 21.396(7)$ Å. The corresponding parameters[5,25,26] for HMTTF-TCNQ are $a = 12.470$, $b = 3.906$, and $c = 21.602$ Å. The structure consists of separate stacks of uniformly spaced HMTTF and TCNQF$_4$ molecules arrayed parallel to the c axis. The interplanar spacing is 3.62 Å within the donor stacks and 3.27 Å within the acceptor stacks. The corresponding spacings in HMTTF-TCNQ are 3.57 and 3.25 Å, respectively. The donor and acceptor molecules make angles of 27.0 and 36.3°, respectively, to the (010) plane. The similar values in HMTTF-TCNQ are 23.8 and 34.2°.

The most significant difference between the structures of HMTTF-TCNQ and HMTTF-TCNQF$_4$ is the increase in the interstack S–N distance (shown in Fig. 4) from 3.25 Å in the former com-

TABLE I. Final atomic positional parameters (×10^4) for HMTTF-TCNQF$_4$, including atomic charges, q, used in Madelung calculation of ionic solid. Standard deviations are in parentheses; space group Pmna (orthorhombic), $a = 12.614(4)$, $b = 4.070(2)$, $c = 21.396(7)$, and $Z = 2$.

	x	y	z	q
S	1162(1)	1842(2)	669(1)	0.0666
C1	0	774(11)	287(2)	0.0426
C2	533(2)	3552(7)	1309(1)	0.0501
C3	999(2)	4970(10)	1891(1)	0.0119
C4	0	6126(12)	2254(2)	0.0040
H4*A*	0	8531(126)	2234(24)	0.0257
H4*B*	0	5410(139)	2725(25)	0.0269
H3*A*	1483(30)	6971(89)	1808(18)	0.0382
H3*B*	1379(29)	2938(92)	2135(17)	0.0336
F	1878(1)	6908(5)	4451(1)	−0.2082
N	1673(3)	1329(9)	3374(2)	−0.2400
C5	936(2)	5967(8)	4748(1)	0.1370
C6	0	7117(11)	4447(2)	−0.0083
C7	0	9164(11)	3914(2)	−0.0915
C8	947(2)	274(9)	3624(1)	0.1111

pound to 3.42 Å in the latter. This is caused by the bulk of the fluorine atoms, the van der Waals radius[27] of which is 1.35 Å compound to that of 1.20 Å for hydrogen. Another interchain contact of note is that of 3.25 Å between sulfur and fluorine atoms which, of course, is absent in HMTTF-TCNQ. While these slight structural differences may be of some significance, it is hard to imagine that they are responsible for the seven-orders-of-magnitude difference in the conductivities shown in Fig. 1.

The molecular overlaps between neighboring HMTTF molecules and between neighboring $TCNQF_4$ molecules are shown in Fig. 5. They are almost identical with those in the corresponding TCNQ salt, as are the interplanar spacings (above). A measure of the electronic overlap along the stacks is provided by the magnitude[28] of the magnetic spin susceptibility. The total spin susceptibilities at high temperatures for both compounds are shown[29] in Fig. 6. [In order to more properly compare the magnitudes,[28] we also show χ of the TCNQ salt[30,31] scaled up to compensate for its low density[32] ($\rho = 0.72$) of electrons.] The fact that the magnitudes of χ are approximately the same for both salts indicates that the overlaps are not appreciably different.

Another relevant energy is the electrostatic Coulomb or Madelung energy contribution to the binding of these ionic materials. For HMTTF-$TCNQF_4$, we calculate[33] a Madelung energy of 2.60 eV, compared to the value of 2.62 eV previously calculated[25] for the TCNQ salt. This small difference of 0.02 eV undoubtedly plays a much smaller role than the 0.36-eV difference in electron affinities in causing the difference in the degree of charge transfer between the two salts.

In order to understand the large differences in the conductivities of these two materials (Fig. 1), we will examine their optical absorption spectra, shown in Fig. 3 for powdered samples dispersed in KBr. The spectrum of HMTTF-TCNQ is very similar to that[10,18] of TTF-TCNQ, which is asserted[10,18,34] to be characteristic of a mixed-valence compound. Indeed, the charge transfer in HMTTF-TCNQ is known[32] to be incomplete: $\rho = 0.72$. The spectrum of HMTTF-$TCNQF_4$, on the other hand, is very different and does not have the very-low-frequency, mixed-valence band near 0.3 eV. The absence of this absorption indicates that there is complete charge transfer in HMTTF-$TCNQF_4$. This fact is also evident in the dramatic similarity of the spectra of HMTTF-$TCNQF_4$, K-$TCNQF_4$, and K-TCNQ. The spectrum of K-TCNQ is characteristic[10,17-19] of that of a stack of $TCNQ^-$ molecules: the absorption near 2 eV is intramolecular, while the absorption peak near 1 eV is the charge-transfer absorption along the stack and is a measure of the effective U. The fact that this peak has approximately the same energy in these three compounds (Fig. 3) indicates that TCNQ and $TCNQF_4$ have roughly the same U and that the HMTTF stack does not appreciably affect this value; that is, these data provide clear evidence that the excitonic polarizability does not appreciably screen U in these compounds. The mechanism of excitonic screening of U is the basis[8,9] of model (1) above and the basis for Little's mechanism[35] for super-conductivity in organic solids.

Thus, the spectra in Fig. 3 show that HMTTF-$TCNQF_4$ is an insulator because it has complete charge transfer and U limits the conductivity, i.e., HMTTF-$TCNQF_4$ is a Mott insulator. Further evidence for this conclusion is contained in the behavior[29] of $\chi(T)$ which for the $TCNQF_4$ salt is moderately large and only weakly temperature dependent (Fig. 6), while over the same temperature range the conductivity is exponentially decreasing (Fig. 1). Thus, there is an energy gap affecting σ, but not χ. This behavior is expected of, and hence strong evidence for, a Mott insulator.

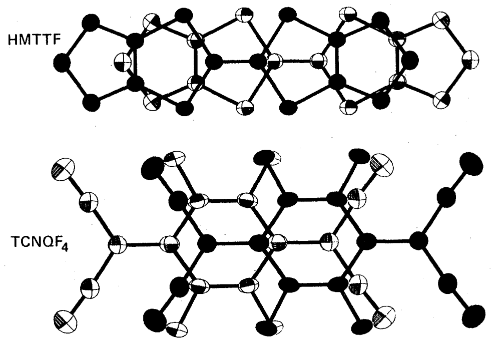


FIG. 5. Molecular overlap between neighboring molecules in the HMTTF and the $TCNQF_4$ stacks in HMTTF-$TCNQF_4$.

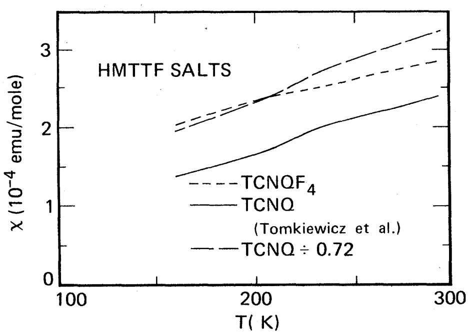


FIG. 6. Comparison of the magnitudes of the high-temperature spin susceptibilities of the TCNQ and $TCNQF_4$ salts of HMTTF. The data (Ref. 30) for HMTTF-TCNQ have also been plotted scaled up to compensate for its lower electron-spin density, $\rho = 0.72$.

CONCLUSION

The mechanism is now clear how substitution of fluorine for hydrogen can cause the 300-K conductivity of HMTTF-TCNQ to plunge more than six orders of magnitude: the fluorine substituents increase the electron affinity of TCNQ, which causes an increase in the degree of charge transfer of HMTTF-TCNQ from $\rho = 0.72$ to $\rho = 1$ in the TCNQF$_4$ salt, making the latter a Mott insulator. The explanation readily accounts for the change in conductivity and the disappearance of the mixed-valence absorption band. Moreover, it emphasizes that the degree of charge transfer is the most significant variable in these materials.[7,10] There are other examples of Mott insulatiors,[7,10] such as K-TCNQ, morpholinium-TCNQ, and tetramethyl-*p*-phenylenediamine iodide. What is significant about HMTTF-TCNQF$_4$ and its selenium analog HMTSF-TCNQF$_4$ is that they are the first Mott insulators with two types of potentially conducting stacks and that they are isostructural with mixed-valence metals.

ACKNOWLEDGMENTS

We wish to acknowledge C.F. Pike for making the electrical measurements. We also wish to thank the Johns Hopkins group for keeping us informed of their work.

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[1] HMTSF = hexamethylenetetraselenafulvalene, HMTTF = hexamethylenetetrathiafulvalene, TCNQ = tetracyano-*p*-quinodimethane, and TCNQF$_4$ = tetrafluoro-tetracyano-*p*-quinodimethane.

[2] M. E. Hawley, T. O. Poehler, T. F. Carruthers, A. N. Bloch, D. O. Cowan, and T. J. Kistenmacher, Bull. Am. Phys. Soc. 23, 424 (1978); and (unpublished).

[3] J. P. Stokes, A. N. Bloch, W. A. Bryden, D. O. Cowan, M. E. Hawley, and T. O. Poehler, Bull. Am. Phys. Soc. 24, 232 (1979); M. E. Hawley, W. A. Bryden, A. N. Bloch, D. O. Cowan, T. O. Poehler, and J. P. Stokes, *ibid.* 24, 232 (1979).

[4] A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, Phys. Rev. Lett. 34, 1561 (1975).

[5] R. L. Greene, J. J. Mayerle, R. R. Schumaker, G. Castro, P. M. Chaikin, S. Etemad, and S. J. La Placa Solid State Commun. 20, 943 (1976).

[6] See, for example, Z. G. Soos, Ann. Rev. Phys. Chem. 25, 121 (1974).

[7] J. B. Torrance, Acc. Chem. Res. 12, 79 (1979).

[8] O. H. LeBlanc, J. Chem. Phys. 42, 4307 (1965).

[9] A. F. Garito and A. J. Heeger, Acc. Chem. Res. 7, 232 (1974).

[10] J. B. Torrance, B. A. Scott, and F. B. Kaufman, Solid State Commun. 17, 1369 (1975).

[11] R. C. Wheland, J. Am. Chem. Soc. 98, 3926 (1976).

[12] J. B. Torrance and B. D. Silverman, Phys. Rev. B 15, 788 (1977).

[13] J. B. Torrance, in *Molecular Metals*, NATO Conference Series VI: Material Science, edited by W. E. Hatfield (Plenum, New York, 1979), p. 7.

[14] See discussion on p. 233 at end of J. B. Torrance, Ann. N. Y. Acad. Sci. 313, 210 (1978).

[15] The electron paramagnetic resonance (EPR) hyperfine splitting parameters measured at 25 C in acetonitrile are: $a_{\mathrm{H}} = 1.02g$, $a_{\mathrm{N}} = 1.44g$ (for TCNQ$^-$); $a_{\mathrm{F}} = 1.0g$, $a_{\mathrm{N}} = 1.4g$ (for TCNQF$_4^-$).

[16] The electron density of the unpaired electron is calculated using CNDO/2 for TCNQ$^-$ and TCNQF$_4^-$, using the molecular geometry of the HMTTF salts. We find the density for TCNQ$^-$ is 0.0582 on C5, 0.0794 on C6, 0.2067 on C7, 0.0011 on C8, 0.0476 on N, and 0.0001 on H5; while the corresponding density for TCNQF$_4^-$ is 0.0470 on C5, 0.0714 on C6, 0.2069 on C7, 0.0008 on C8, 0.0580 on N, and 0.0051 on F. The electron (spin) density distribution *in this orbital* is, of course, very different from the *total* charge density (Table I and Ref. 25).

[17] S. K. Khanna, A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2139 (1974).

[18] J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, Bull. Chem. Soc. Jpn. 49, 2358 (1976).

[19] Y. Iida, Bull. Chem. Soc. Jpn. 42, 71 (1969); S. Hiroma, H. Kuroda, and H. Akamatu, *ibid.* 44, 9 (1971).

[20] F. B. Kaufman (unpublished results).

[21] The electrochemical half-wave reduction potentials [V versus saturated calumel electrode (SCE)] are: +0.20 and −0.35 for TCNQ; +0.56 and +0.03 for TCNQF$_4$. The cyclic voltammograms were measured at 100 mV/sec in acetonitrile with 0.1*M* Bu$_4$NBF$_4$ electrolyte and a Pt electrode.

[22] See, for example, E. C. M. Chen and W. E. Wentworth, J. Chem. Phys. 63, 3183 (1975).

[23] See, for example, C. R. Brundle, M. B. Robin, and N. A. Kuebler, J. Am. Chem. Soc. 94, 1466 (1972).

[24] Tables of anisotropic thermal parameters, bond distances and angles, as well as observed and calculated structure factors, are available from J. J. Mayerle.

[25] B. D. Silverman and S. J. La Placa, J. Chem. Phys. 69, 2585 (1978).

[26] D. Chasseau, G. Comberton, J. Gaultier, and C. Hauw, Acta Crystallogr. Sect. B 34, 689 (1978).

[27] L. Pauling, *The Nature of the Chemical Bond* (Cornell University, Ithaca, N. Y., 1960), p. 257.

[28] J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, Phys. Rev. B 15, 4738 (1977).

[29] The magnetic susceptibility of HMTTF-TCNQF$_4$ is discussed further in Y. Tomkiewicz, K. Bechgaard, J. B. Torrance, R. Bozio, and C. Pecile (unpublished).

[30] Y. Tomkiewicz, B. Welber, P. E. Seiden, and R. Schumaker, Solid State Commun. 23, 471 (1977).

[31] P. Delhaes, S. Flandrois, J. Amiell, G. Keryer, E. Toreilles, J. M. Fabre, L. Giral, C. S. Jacobsen, and K. Bechgaard, J. Phys. (Paris), Lett. 38, L233

(1977).

[32] S. Megtert, J. P. Pouget, and R. Comès, in *Molecular Metals*, NATO Conference Series VI: Material Science, edited by W. E. Hatfield (Plenum, New York, 1979), p. 87.

[33] Madelung calculations were performed as in Ref. 25, using the atomic positions and charges in Table I, calculated using CNDO/2 for TCNQF_4^- and HMTTF$^+$.

[34] J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, Phys. Rev. B 19, 730 (1979).

[35] D. Davis, H. Gutfreund, and W. A. Little, Phys. Rev. B 13, 4766 (1976); W. A. Little, Phys. Rev. A 134, 1416 (1964).