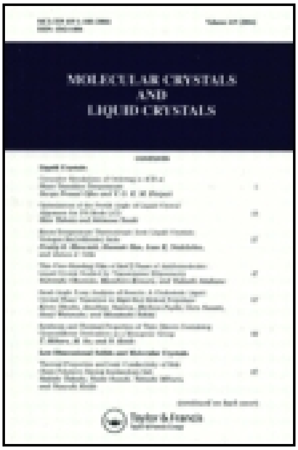

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On the Crystal Structure of the Organic Charge-Transfer Salt Derived from Hexamethylenetetraselenafulvalene (HMTSF) and Tetrafluoro-7,7,8,8-Tetracyano-*p*-Quinodimethane (TCNQF4), HMTSF-TCNQF4

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The charge-transfer salt HMTSF-TCNQF4 crystallizes in the monoclinic system, space group $C2/m$, with the following crystal data: a = 21.906(5) Å, b = 12.918(3) Å, c = 4.018(1) Å, β = 91.66(1)°, V = 1136.5 Å^3, Z = 2, D_{calc} = 2.186 g cm^{-3}, D_{obs} = 2.17(2) g cm^{-3}. A structural model was readily deduced from standard Patterson-Fourier methods and has been refined (based on 1175 counter-collected X-ray data) to an R value of 0.048. The crystalline motif is dominated by uniform, segregated stacks of donors and acceptors. Within each stack, the molecular overlap pattern is of the ring-over-bond type and the mean interplanar separations are 3.68 Å (donor column) and 3.24 Å (acceptor column). Principal intercolumn contacts are of two types: Se(donor)···F(acceptor) at 3.19 Å and Se(donor)···N(acceptor) at 3.36 Å. Comparisons are made between the crystal structure and physical properties of HMTSF-TCNQF4 and HMTSF-TCNQ (to which it is isostructural) and to those of HMTTF-TCNQ and HMTTF-TCNQF4 (to which it is closely related).

INTRODUCTION

Much attention has been focused on the organic charge-transfer salts derived from the electron donors hexamethylenetetraselenafulvalene

(HMTSF) and its sulfur analogue (HMTTF) and the electron acceptors 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and its perfluoro derivative (TCNQF4), Figure 1. It has been considered particularly noteworthy that the TCNQ salts of these donors are electrical conductors,[1,2] while their TCNQF4 salts are electrical insulators.[3,4]

The antecedents of the rather dramatic difference in the electrical properties of the TCNQ salts and their TCNQF4 congeners surely arises from a combination of molecular and solid-state effects. Substitution of Se for S in the heterofulvalene donor is expected to induce moderate modifications in such molecular properties as overall size,[5] ionization potential (*ca.* 0.2 eV)[6] and charge-density distribution for the molecular ions.[7] More marked alterations are expected for molecular polarizabilities[8] and spin density distributions for the radical cations.[9] In contrast, the substitution of F for H on going from TCNQ to TCNQF4 yields a notable increase (*ca.* 0.4 eV) in the electron affinity of the neutral acceptor[10] and leads to significant charge density on the fluoro substituents in the TCNQF$_4^-$ radical anion.[11] Less dramatic differences are suggested for molecular size,[10,11] polarizability,[12] spin densities[11] and on-site Coulomb energies.[4]

In the solid salts, many of the differences in the physical properties in these two classes of materials can be traced to the degree of charge-transfer from donor to acceptor. The electrical conductors HMTSF-TCNQ and HMTTF-TCNQ are known to have fractional charge transfer (*ca.* 0.7 e).[13]

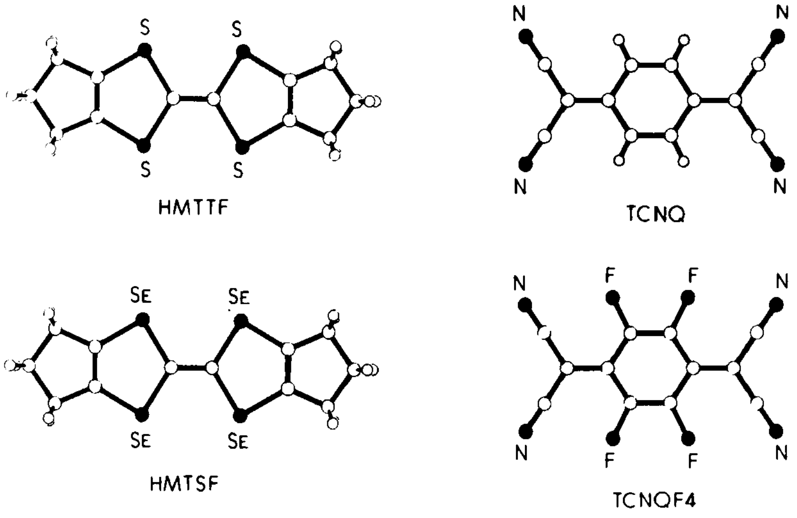


FIGURE 1 Molecular structures for the electron donors HMTTF and HMTSF and the electron acceptors TCNQ and TCNQF4.

In contrast, the electrical insulators HMTSF-TCNQF4 and HMTTF-TCNQF4 have unit charge transfer;[4,14] with one electron per site, electrical conduction is highly activated,[3,4] owing to large on-site Coulomb energies on the order of 1 eV. Furthermore, for the unit-charged TCNQF4 salts, spin-wave correlations are expected to be the dominant driving force for the observed phase transformations,[3,4,15] while charge-density wave correlations are the principal driving force for the phase transformations in the fractionally charged TCNQ salts.[1,2,16]

Of particular importance for the interpretation of the solid-state properties of these four charge-transfer salts is that their high-temperature crystal phases exhibit nearly identical structural motifs. More precisely, the TCNQ and the TCNQF4 salts of HMTSF are isomorphous, as are the TCNQ and TCNQF4 salts of HMTTF. However, these isomorphic pairs have fundamental differences between them. The subject matter of this paper encompasses two formal parts: (a) a description of the crystal structure of HMTSF-TCNQF4, and (b) a comparison of the similarities and differences in the basic structural patterns and physical properties found in the HMTSF salts to those found in the HMTTF salts.

EXPERIMENTAL

Crystals of HMTSF-TCNQF4, produced by solvent diffusion of solutions of the neutral donor in chlorobenzene and the neutral acceptor in acetonitrile, were plate-like with (100) as the principal face. Unit-cell data for HMTSF-TCNQF4 were obtained from a least-squares fit to the setting angles of 15 carefully centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer. Cell data are collected in Table I, along with analogous parameters for the salts HMTSF-TCNQ,[1] HMTTF-TCNQ[2] and HMTTF-TCNQF4.[4]

Details of the data collection, reduction and refinement procedures are given in Table II. A Patterson synthesis was employed for the structural solution; from this synthesis, positions for the Se atoms were determined as well as the molecular orientations of donor and acceptor molecules. Subsequent Fourier and difference-Fourier syntheses gave locations for all nonhydrogen atoms, and at an intermediate stage of the analysis, for those of the hydrogen atoms. Maximum residual density peaks in a final difference-Fourier map reached ±1 e/Å^3 near the Se atoms. Final nonhydrogen atomic positional parameters are given in Table III. Tables of thermal parameters for the nonhydrogen atoms, positional parameters for the H atoms (unrefined), least-squares planes for the donor and acceptor

TABLE I

Cell data for some heterofulvalene-acceptor charge-transfer salts

	HMTSF-TCNQ[1]	HMTSF-TCNQF4[2]
Space group	*C*2/*m*	*C*2/*m*
a(Å)	21.999(14)	21.906(5)
b(Å)	12.573(8)	12.918(3)
c(Å)	3.890(1)	4.018(1)
β(deg)	90.29(4)	91.66(1)
V(Å^3)	1076	1137
Z	2	2
D_{calc}(g cm^{-3})	2.087	2.186
MW	676.3	748.2

	HMTTF-TCNQ[3]	HMTTF-TCNQF4[4]
Space group	*Pmna*	*Pmna*
a(Å)	12.462(4)	12.614(4)
b(Å)	3.901(2)	4.070(2)
c(Å)	21.597(6)	21.396(7)
β(deg)	90.00	90.00
V(Å^3)	1050	1098
Z	2	2
D_{calc}(g cm^{-3})	1.546	1.695
MW	488.7	560.6

[1] From Ref. 1.
[2] This work.
[3] From Ref. 2.
[4] From Ref. 4.

molecules, and final observed and calculated structure-factor amplitudes have been deposited. The crystallographic computations were carried out with a standard set of computer programs.[21]

RESULTS

A) *Crystal structure of HMTSF-TCNQF4.* In the adopted crystalline motif of HMTSF-TCNQF4, each of the molecular components is required to possess at least C_{2h} symmetry, with the HMTSF donor centered about symmetry sites of the type (0, 0, 0) and the TCNQF4 acceptor centered about symmetry sites of the type (0,½,½). As is evident from the two unit-cell projections of Figure 2, uniform, segregated stacks of donors and acceptors propagate along the crystallographic *c* axis and dominate the crystal packing of HMTSF-TCNQF4.

TABLE II

Crystal structure solution and refinement results for HMTSF-TCNQF4

Color of crystals[a]	Dark-green
Crystal habit	Acicular plates
Crystal dimensions (mm) along a^*, b, c^*	0.02 × 0.06 × 0.20
Approx. axis of diffractometer alignment	c
Absorption coefficient (cm^{-1})[b]	70.0
Max and min transmission factors	0.87, 0.63
$(\sin\theta)/\lambda$ limit, Å^{-1}[c]	0.65
Total no. reflections measured ($\lvert F_0\rvert > 0$)	2401
No. of unique reflections	1338
No. of reflections with net counts above Background (NO)[d]	1175
No. of variable parameters (NV)	88
$R(F) = \sum \lvert\, \lvert F_0\rvert - \lvert F_c\rvert \,\rvert / \sum \lvert F_0\rvert$[e]	0.048
$R[F > 3\sigma(F)]$	0.039
$R_w(F) = \{\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2 / \sum wF_0^2\}^{1/2}$	0.034
$\mathrm{GOF} = \{\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2 / (NO - NV)\}^{1/2}$	1.30
R_{ave}[f]	0.055

[a] Crystals of HMTSF-TCNQF4 were grown in a straight tube via diffusion through solvent barrier (chlorobenzene for HMTSF, acetonitrile for TCNQF4).

[b] The data were also corrected for Lorentz and polarization effects and an approximate scale factor was derived by the method of Wilson.[17]

[c] A variable scan rate of 2–24°/min(2θ) was employed in the θ–2θ scan mode. The MoKα radiation used ($\bar{\lambda} = 0.71069$ Å) was graphite monochromatized. Three standard reflections (monitored after every 100 reflections in the data collection) indicated no variations in intensities other than those expected from counting statistics. The background time measured at each side of the scan was ¼ of the total scan time.

[d] The standard deviation was taken to be $\sigma = [\sigma_c^2 + (0.03I)^2]^{1/2}$, where σ_c is from counting statistics.

[e] The quantity minimized was $[\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2]$, with weights $w = 4F_0^2/\sigma^2(F_0^2)$. Neutral nonhydrogen atomic scattering factors were taken from a compilation of Hanson, Herman, Lea and Skillman,[18] while those for the hydrogen atoms were from Stewart, Davidson and Simpson.[19] The real components of anomalous dispersion for the nonhydrogen atoms were accounted for, using the values of Cromer and Liberman.[20]

[f] R_{ave} upon averaging over m regions is $\sum_{i=1}^{n} \sum_{j=1}^{m} \lvert F_{ij}^2 - \bar{F}_i^2\rvert / \sum_{i=1}^{n} \bar{F}_i^2$, for n unique observations. In this case, a hemisphere of data was collected.

Within donor stacks, adjacent molecules exhibit the commonly observed "ring-over-bond" overlap arrangement[22] (Figure 3). The mean interplanar separation between HMTSF donors at 3.68(1) Å[23] is *ca.* 0.08 Å larger than between similar stacks of donors in HMTSF-TCNQ,[1] 3.60(2) Å and HMTSF-TNAP,[5,24] 3.58(1) Å. In this vein, intrastack Se· · ·Se contacts (eight per donor at 4.018 Å = c) are about 0.1 Å longer than in HMTSF-TCNQ and HMTSF-TNAP, but closely approximate twice the van der Waals radii of Se at 4.0 Å (as given by Pauling[25]). Similarly, the molecular overlap pattern within the TCNQF4 stack is of the "ring-over-bond" type,[22]

TABLE III

Final nonhydrogen atom positional parameters (x 10^4) of HMTSF-TCNQF4

Atom	*x*	*y*	*z*
Se	705.5(2)[a]	1229.0(3)	−1603(1)
C(1)	1390(2)	515(3)	−3050(10)
C(2)	1974(2)	968(3)	−4283(12)
C(3)	288(3)	0[b]	−661(14)
C(4)	2330(3)	0[b]	−5392(16)
N	1585(2)	3354(3)	−1147(11)
C(5)	1346(2)	4074(3)	−175(12)
C(6)	1060(3)	1/2[b]	949(15)
C(7)	539(3)	1/2[b]	2908(14)
C(8)	249(2)	4093(3)	4029(10)
F	475(1)	3165(2)	3139(6)

[a] Estimated standard deviations in the least-significant figure are enclosed in parentheses.
[b] Fixed by symmetry.

with a mean interplanar spacing, 3.24(1) Å, which is virtually identical to the acceptor spacings in HMTSF-TCNQ, HMTTF-TCNQ and HMTTF-TCNQF4 (see Table IV).

As is particularly visible in the (001) crystallographic projection of Figure 2, the mode of interchain packing in HMTSF-TCNQF4 is such that each donor column is surrounded by four acceptor columns, and *vice versa*. Upon examination of the (010) crystallographic projection of Figure 2, it is also clear that the tilts of the donor and acceptor molecules relative to the propagation axis (c) are similar ($\varepsilon_{\text{donor}}$ and $\varepsilon_{\text{acceptor}}$ of Table IV), leading to an interplanar dihedral angle (ϕ of Table IV) of 12.9(3)°. Resemblant interplanar donor-acceptor dihedral angles are found in HMTSF-TCNQ[1] and the TCNQ[2] and TCNQF4[4] salts of HMTTF (Table IV). This is to be contrasted, for example, with the rather large (and more typical[22]) interplanar dihedral angle, 58.5(2)°, found in the crystal packing pattern of TTF-TCNQ.[26] One of the consequences of the near coplanarity of donor and acceptors in the crystal packing arrangement of HMTSF-TCNQF4 is the presence of quite short interchain contacts along b (see Figure 2) involving the Se atoms of the donor and the F or N atoms of the acceptor. Pertinent contact distances are Se· · ·F at 3.19(1) Å (four per molecule) and Se· · ·N at 3.36(1) Å (four per molecule), which are, respectively, 0.16 Å and 0.14 Å shorter than the appropriate van der Waals radii sums.[25] In this context, it is noted that the Se· · ·N interchain contacts in HMTSF-TCNQ[1] are markedly shorter at 3.16(2) Å. Thus, the presence of the fluoro substituents of the TCNQF4 acceptor cause an increase in the intercolumnar separation (6.46 vs 6.29 Å) along b and the Se· · ·N contact distances; both

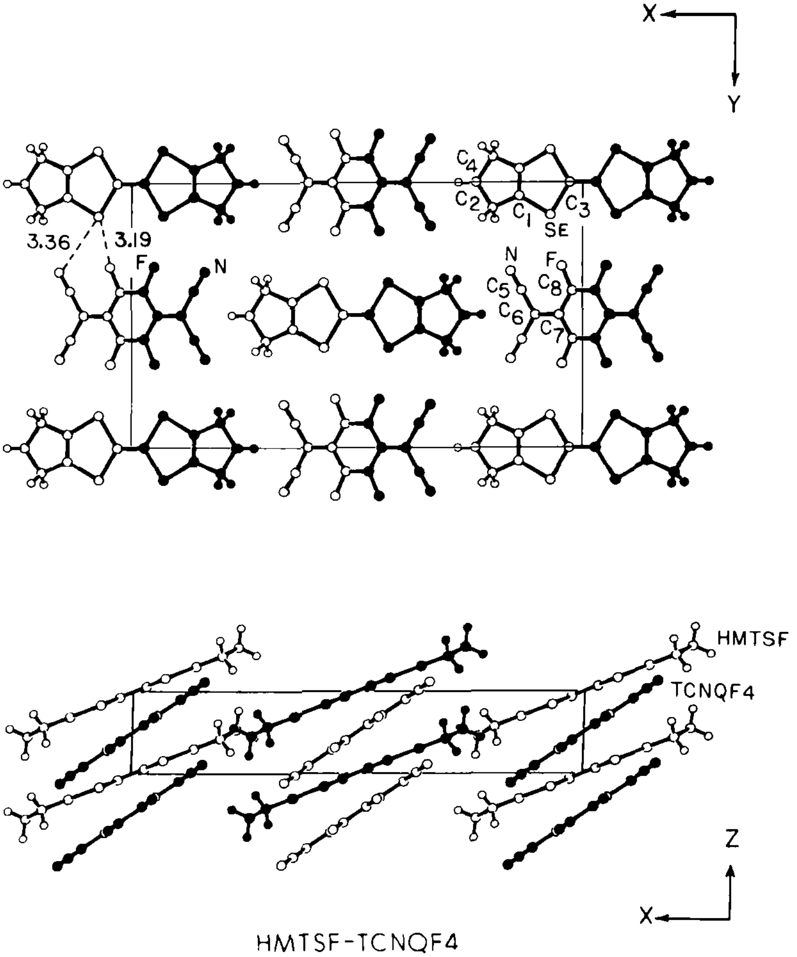


FIGURE 2 The (001) and (010) crystallographic projections for the crystal structure of HMTSF-TCNQF4.

of which are presumably compensated for by the addition of the electrostatically favorable Se· · ·F interactions. A similar (but smaller) effect can be, and has been,[4] noted in a comparison of the intercolumnar interactions in HMTTF-TCNQ and HMTTF-TCNQF4 (Table IV).

B) *Molecular structure of the constituent molecules.* In this section, some comments are offered on the molecular geometry of the donor and acceptor molecules. To this end, average (D_{2h} symmetry) bond lengths and

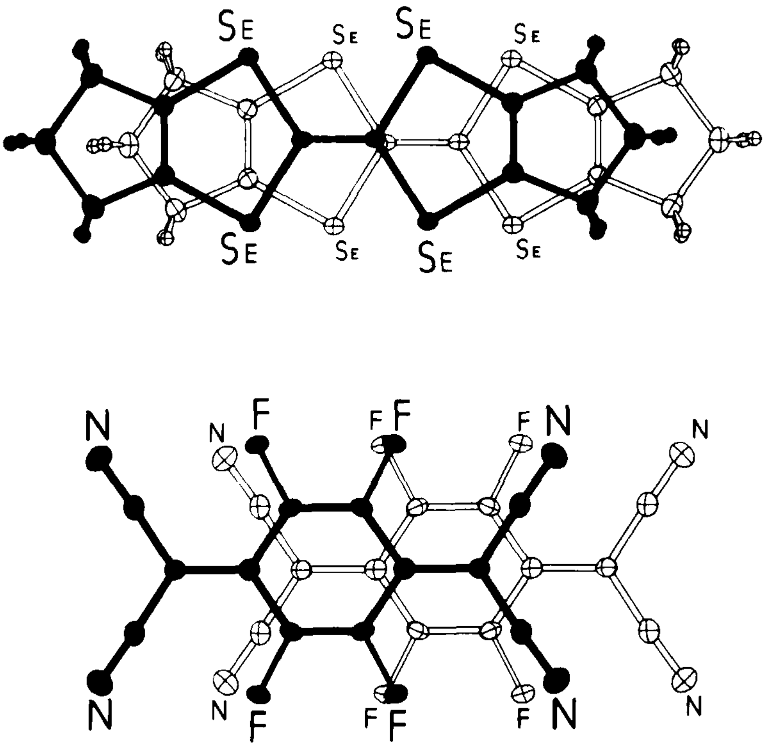
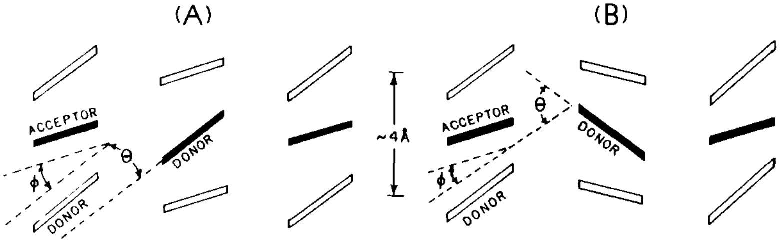


FIGURE 3 Molecular overlap pattern for the donor and acceptor columns in the structure of HMTSF-TCNQF4. Within the donor column, the interplanar spacing is 3.68(1) Å, while the interplanar spacing for the acceptor column is 3.24(1) Å.

bond angles for the donor and acceptor in HMTSF-TCNQF4 are collected in Table V. Analogous data for HMTSF-TCNQ (which are to be viewed with special care as major crystallographic problems, *vide infra*, limit the reliability of the molecular geometry in this case[1]), HMTTF-TCNQ (also less reliable than normal owing to crystallographic problems[2]), and HMTTF-TCNQF4[4] complete Table V. In general, the molecular geometries of the four heterofulvalene donors are in quite close agreement, especially when one excludes parameters (bonds *b* and *c* and angles γ and ε of Table V) directly affected by the substitution of Se for S. In particular, the central C $=$ C bond, denoted *a* in Table V, which has been indicated to be sensitive to the degree of charge transfer,[2,27,28] is expectedly smaller in HMTTF-TCNQ (charge transfer, z, *ca.* 0.72 e)[13b] than in HMTTF-TCNQF4 ($z = 1$);[4] a similar trend is noted on going from HMTSF-TCNQ (z *ca.* 0.74 e)[13a] to HMTSF-TCNQF4 ($z = 1$).[3]

TABLE IV

Intercolumnar orientations and interactions for some heterofulvalene-acceptor salts



Compound (motif)	ε_{donor} (deg)[a]	$\varepsilon_{acceptor}$ (deg)[a]	ϕ(deg)[b]	T[c]	θ_{donor} (deg)[d]	$\theta_{acceptor}$ (deg)[d]
HMTTF-TCNQ(B)	24.2	33.6	9.4	(1/2, 0, 1/2)[e]	48.4	67.2
HMTTF-TCNQF4(B)	27.0	36.3	9.3	(1/2, 0, 1/2)[e]	54.0	72.6
HMTSF-TCNQ(A)	22	33	11	(1/2, 1/2, 0)[e]	0	0
HMTSF-TCNQF4(A)	23.5	36.4	12.9	(1/2, 1/2, 0)[e]	0	0

	D^{f}_{donor}	$D^{f}_{acceptor}$	S···N[g]	Se···N[g]	S···F[g]	Se···F[g]
HMTTF-TCNQ(B)	3.55	3.26	3.25			
HMTTF-TCNQF4(B)	3.62	3.27	3.42		3.20, 3.23	
HMTSF-TCNQ(A)	3.60	3.26		3.16		
HMTSF-TCNQF4(A)	3.68	3.24		3.36		3.19

[a] ε is the angle between plane normals and the stacking direction.

[b] $\phi = [\varepsilon_{acceptor} - \varepsilon_{donor}]$.

[c] T is the translational operation between nearest neighbor chains (donor-to-donor or acceptor-to-acceptor).

[d] θ is the angle between planes related by T.

[e] Related by C-face centering (monoclinic) or by a glide plane.

[f] D is the mean interplanar separation (Å).

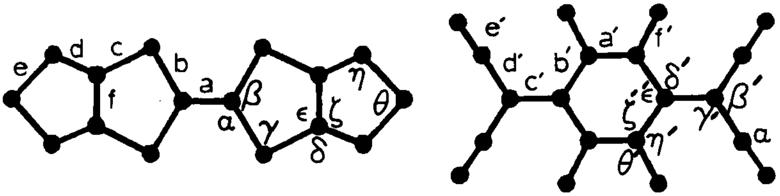
[g] Closest interchain contacts (Å). Van der Waals radii are as follows: Se, 2.0 Å; N, 1.50 Å; F, 1.35 Å.

The bond lengths for the TCNQF4 acceptor (D_{2h} symmetry imposed) in HMTSF-TCNQF4 are in close agreement with those in HMTTF-TCNQF4 (except for the inexplicably elongated C—F bond, f', in the HMTTF salt[4]) and other unit charge-transferred TCNQF4 salts, such as DBTTF-TCNQF4,[27c] DTTTF-TCNQF4,[29] NBP-TCNQF4[30] and TMPD-TCNQF4.[31] Similar agreement for the bond angles are evident in Table V, with the effect of the fluoro substituents on the molecular geometry of the TCNQF4 acceptor, relative to the TCNQ acceptor, most noticeable in the angles δ' and ε', as ascertained previously.[10]

In fact the close agreement of the TCNQF4 geometry in the aforementioned salts as well as a comparison with the molecular geometry of the

TABLE V

Average geometries for the component molecules of HMTTF-TCNQ(I), HMTTF-TCNQF4(II), HMTSF-TCNQ(III) and HMTSF-TCNQF4(IV)*



	Distance Å					Distance Å			
	I	II	III	IV		I	II	III	IV
a	1.374	1.380	1.36	1.383	a'	1.356	1.335	1.36	1.360
b	1.742	1.734	1.89	1.876	b'	1.434	1.424	1.43	1.413
c	1.731	1.729	1.90	1.868	c'	1.397	1.412	1.42	1.405
d	1.512	1.493	1.36	1.504	d'	1.421	1.420	1.48	1.430
e	1.537	1.553	1.56	1.546	e'	1.138	1.144	1.06	1.142
f	1.343	1.345	1.30	1.331	f'		1.401		1.360
	Angle(deg)					Angle(deg)			
	I	II	III	IV		I	II	III	IV
α	122.2	122.3	122.2	122.2	α'	178.5	175.6	179.4	177.7
β	115.7	115.4	115.5	115.6	β'	117.3	114.6	115.0	113.6
γ	94.5	95.0	92.2	92.6	γ'	121.4	122.7	122.1	123.2
δ	129.4	129.5	128.1	127.5	δ'	121.3	124.0	120.8	124.0
ε	117.7	117.3	120.1	119.6	ε'	117.4	112.0	118.6	112.1
ζ	112.9	113.2	111.8	112.9	ζ'	121.3	124.0	120.7	124.0
η	101.8	102.4	109.9	102.8	η'		114.1		118.7
θ	110.2	108.4	95.6	108.0	θ'		121.8		117.3

*Individual esd's for bond distances range from 0.006–0.007 Å for HMTTF-TCNQ; 0.003–0.004 Å for HMTTF-TCNQF4; 0.01–0.02 Å for HMTSF-TCNQ; and 0.005–0.006 Å for HMTSF-TCNQF4. Corresponding esd's for bond angles lie in the ranges 0.3–0.4°, 0.2–0.3°, 0.6–1.0° and 0.3–0.4°.

TCNQF4 neutral molecule[10] offer a corroborative indication of the degree of charge transfer in HMTSF-TCNQF4 and HMTTF-TCNQF4. In particular, the charge-sensitive exocyclic quinone double bond, *c'* in Table V, averages at 1.411(3) Å for eight unit charge-transferred TCNQF4 salts (including the two examples under discussion here), while this bond length is 1.372(2) Å in neutral TCNQF4.[10] This trend directly parallels that predicted[32] and observed[28b,33] for bond elongation on going from $TCNQ^0$ to $TCNQ^-$.

DISCUSSION

The main element of discussion in this section will be a quantitative elucidation of the similarities and differences in the crystal structures of HMTSF-TCNQ, HMTSF-TCNQF4, HMTTF-TCNQ and HMTTF-TCNQF4 and how these comparisons correlate with certain physical properties of these charge-transfer salts. To facilitate this discussion, primary crystal data (Table I) and a summary of intracolumn and intercolumn interaction parameters (Table IV) have been documented for each of the four systems. In addition, projection views for the crystal structure of HMTTF-TCNQF4[4] are displayed in Figure 4. That these pictorial representations are necessary will become obvious; that they are sufficient is underscored by the recollection that HMTSF-TCNQ and HMTTF-TCNQ are isostructural with their TCNQF4 congeners (Table I).

Fundamental similarities in the four structures under consideration are, at least, two-fold. Firstly, each salt contains (in its high-temperature crystal phase) uniform stacks of donors and acceptors (*c* for the HMTSF salts and *b* for the HMTTF salts). Interestingly, while the mean interplanar separation within each of the four acceptor columns is virtually constant ($D^{\text{minimum}}_{\text{acceptor}}$ = 3.24(1) Å for HMTSF-TCNQF4, $D^{\text{maximum}}_{\text{acceptor}}$ = 3.27(1) Å for HMTTF-TCNQF4), there is a considerable variability in the mean interplanar spacing in the donor columns, D_{donor} of Table IV. This variability of donor-donor spacing is apparently stimulated either by a change in the molecular donor (as expected, D_{donor} is *ca.* 0.05–0.06 Å larger in the HMTSF salts than in their respective HMTTF salts) or by a change in the molecular acceptor (D_{donor} is *ca.* 0.07–0.08 Å larger in the TCNQF4 salts than in their respective TCNQ salts). This trend culminates in an interdonor spacing which is 0.13 Å larger in HMTSF-TCNQF4 than in HMTTF-TCNQ (Table IV). The sensitivity of D_{donor} to either a change in donor (HMTSF for HMTTF) or acceptor (TCNQF4 for TCNQ) signifies that intercolumnar as well as intracolumnar forces are operative in determining the intermolecular separation within the donor column.

Secondly, there is a clear tendency in all four structures for near coplanarity (a small interplanar dihedral angle, ϕ of Table IV) between donor and acceptor in columns along the short in-plane molecular axis of each component (*b* for the HMTSF salts, Figure 2, and *a* for the HMTTF salts, Figure 4). This inclination toward coplanarity surely arises from a maximization of various crystal packing forces; however, for these high charge-transfer salts, the specific Se···N, Se···F or S···N, S···F interactions

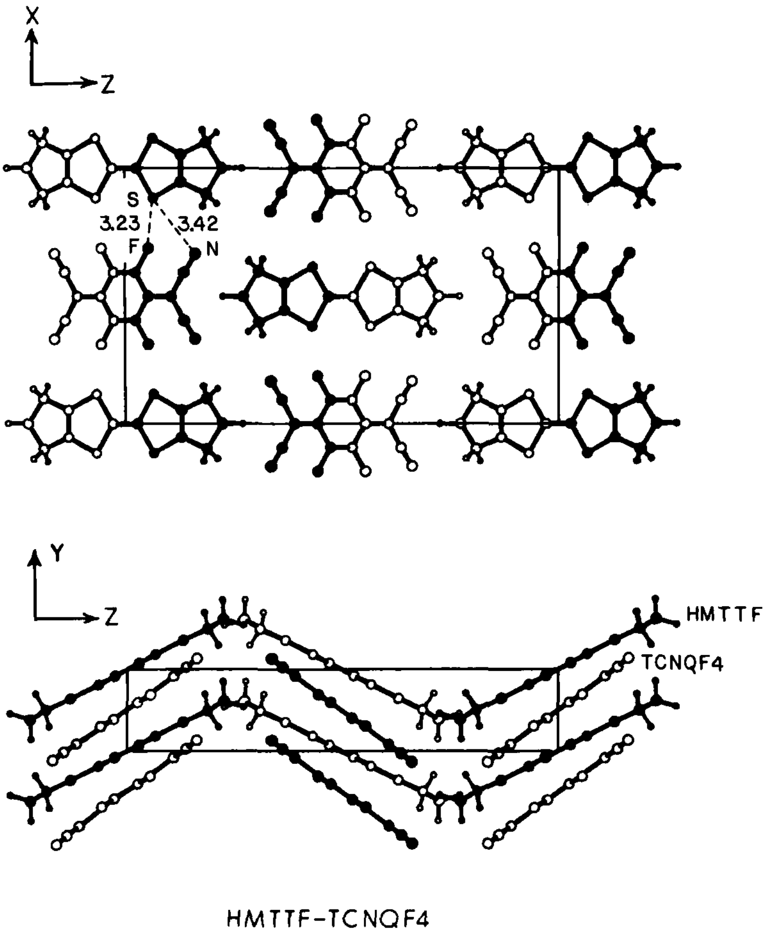


FIGURE 4 The (010) and (100) crystallographic projections for the crystal structure of HMTTF-TCNQF4 (after Ref. 4).

(see Table IV and Figures 2 and 4) with their expectedly large electrostatic components, and possibly some covalent contribution,[1] may play a significant role.

The major difference between the two structural types under discussion (denoted (A) and (B) in Table IV) lies in the relationship between donor and acceptor columns along the long in-plane molecular axes of the molecular constituents (*a* for the HMTSF salts and *c* for the HMTTF salts, see Figures 2 and 4). This difference can be quantified in terms of the three-dimensional space group which describes the symmetry of each crystal structure type. For the HMTSF salts (type (A)), the symmorphic,[34] monoclinic space group $C2/m$ is applicable; while for the HMTTF salts (type (B)), the nonsymmorphic,[34] orthorhombic space group $Pmna$ pertains. Comparison of the (010) projection of Figure 2 for HMTSF-TCNQF4 with the (100) projection of Figure 4 for HMTTF-TCNQF4 (or in schematic form at the top of Table IV) shows that non-unit-translation-related columns of donors (or acceptors) have constituent molecules oriented parallel to each other for HMTSF-TCNQF4 but nonparallel for HMTTF-TCNQF4 (yielding a herringbone motif for the latter[4]). This difference is most easily recounted in terms of the symmetry operation relating donor and acceptor columns for each structural type: (A) for HMTSF-TCNQF4 (and HMTSF-TCNQ), nearest-neighbor columns of the same kind are generated by the C centering operation of space group $C2/m$ and involves *only* a fractional translational component (½, ½, 0). Thus, planes of nearest-neighbor donors (or acceptors) are parallel (denoted by the interplanar dihedral angle θ_{donor} and θ_{acceptor} of Table IV) *by symmetry;* (B) in contrast, nearest-neighbor columns of the same kind for HMTTF-TCNQF4 (and HMTTF-TCNQ) are generated by the diagonal glide operation (n) normal to b of space group $Pmna$ (or equivalently in these cases by the axial glide (a) normal to c) and involve a mirror operation and a fractional lattice translation (½, 0, ½). For the HMTTF salts, then, plane normals of nearest neighbor donor or acceptor chains are oriented directly opposite (*by symmetry*) to the propagation axis (b), so that θ_{donor} (or θ_{acceptor}) is rather large.

This fundamental difference in the crystalline motifs adopted by the HMTSF salts and the HMTTF salts has some clear ramifications in their physical behavior. For example, HMTSF-TCNQ is a highly disordered system with stacking faults arising from the weak a-axis coupling between highly-interacting bc crystal planes.[1] On the other hand, HMTTF-TCNQ has a less-disordered structure, with stronger c-axis coupling between highly interacting ab crystal planes. The stronger interplanar (c-axis) coupling in the HMTTF-TCNQ structure possibly arises from the more intimate association of the terminal methylene group of the HMTTF donor with the malonitrile moiety of the nonparallel TCNQ acceptor along c than is permitted by the more nearly parallel donor and acceptor molecules along a in the HMTSF-TCNQ structure. Following this vein, the HMTSF salt remains metallic to very low temperatures,[1] while the HMTTF salt[2] undergoes a metal-insulator transition at *ca.* 50 K (which is stimulated by condensation of charge-density waves which can be suppressed at high pressures[35]). Speculation[1] as to the absence of a strong metal-insulator transition in HMTSF-TCNQ has centered about the roles of structural disorder and dimensionality effects.

For the unit charge-transferred TCNQF4 salts of HMTSF[3] and HMTTF,[4] physical consequences of molecular and crystal structure differences are also evident. In neither case is structural disorder a problem, even though there is almost surely weaker interchain coupling along *a* than in the *bc* plane for HMTSF-TCNQF4 and similarly weaker coupling along *c* than in the *ab* plane for HMTTF-TCNQF4. It is permissible, however, to speculate that the higher charge transfer in these TCNQF4 salts allows sufficiently stronger electrostatic interactions along these directions to suppress the tendency for disorder.

More interesting is a perusal of the phase transformation phenomena in these TCNQF4 salts. For HMTTF-TCNQF4, the spin-driven phase transformation is biphasic, with spin-wave condensation occurring on the TCNQF4 acceptor stack at a significantly higher temperature (T_c^{acceptor} at *ca*. 145 K) than on the donor stack (T_c^{donor} at *ca*. 90 K).[4] For HMTSF-TCNQF4, the spin-driven transformation lies at a higher temperature (*ca*. 204 K) and is uniphasic in that the spin waves of both stacks condense at the same temperature.[3] The higher T_c for HMTSF-TCNQF4 seems to be directly related to the presence of the Se atoms of the donor and their intrastack Se···Se interactions; the observation that both stacks simultaneously undergo a spin-driven phase transformation is more likely related to the strength of the interchain donor-acceptor (again directly involving the Se atoms) coupling, both as regards the strong *bc* plane interactions and the weaker *a* axis component.

Finally, although it is improbable that the total crystal cohesive energies of HMTSF-TCNQF4 and HMTTF-TCNQF4 (or their TCNQ analogues) are significantly different from one another, the substantial molecular rearrangement necessary to "transform" one structural type into the other probably precludes interconversion at temperatures below that of material decomposition. In this context, we have recently reported[29] on the synthesis and some physical properties of the Mott insulator DTTTF-TCNQF4. This salt is now known to crystallize at room temperature in two phases—one containing uniform, segregated stacks of donors and acceptors in a motif very close, but not isomorphous, to that of HMTSF-TCNQF4, and one containing dimerized, segregated stacks of donors and acceptors in a packing arrangement like that of HMTTF-TCNQF4. At this juncture, although phase transformations are present within each form of DTTTF-TCNQF4, no evidence for structure-type interconversion has yet been obtained before crystal decomposition occurs.

SUMMARY

The crystal structure of the Mott insulator HMTSF-TCNQF4 has been described in detail. Interestingly, the structure of HMTSF-TCNQF4 is isomorphous with that of the semimetal HMTSF-TCNQ. The difference in the electrical properties of these two salts is most directly related to their degree of charge transfer, which is unit for the TCNQF4 insulator and fractional for the TCNQ semimetal. This situation directly parallels that for the Mott insulator HMTTF-TCNQF4 and its isostructural organic metal HMTTF-TCNQ as shown by other investigators.[2,4] All four salts are not isomorphous, however, and this lack of strict isomorphism over this set of materials has some interesting physical ramifications, a few of which have been discussed here.

SUPPLEMENTARY MATERIALS

Tables of anisotropic thermal parameters for the nonhydrogen atoms, positional parameters for the hydrogen atoms, least-squares planes for the donor and acceptor molecules, and final observed and calculated structure factor amplitudes are available. This material may be obtained by contacting Gordon and Breach, One Park Avenue, New York, NY 10016.

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