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Crystal Structures for the Electron Donor Dibenzotetrathiafulavalene, DBTTF, and Its Mixed-stack Charge-transfer Salts with the Electron Acceptors 7,7,8,8-tetracyano-p-quinodimethane, TCNQ, and 2,5-difluoro-7,7,8,8-tetracyano-p-quinodimethane, 2,5-TCNQF2

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Crystal structures for the electron donor DBTTF and its charge-transfer salts with the acceptors TCNQ and 2,5-TCNQF2 are reported. Crystal data for the three systems are as follows: (a) neutral DBTTF; monoclinic, space group $P2_1/c$, a = 12.082(2) Å, b = 3.955(1) Å, c = 14.553(2) Å, β = 114.36(1)°, V = 633.6 Å^3; (b) DBTTF-TCNQ; triclinic, space group $P\bar{1}$, a = 9.215(3) Å, b = 10.644(4) Å, c = 7.734(2) Å, α = 113.32(3)°, β = 122.28(2)°, γ = 67.66(3)°, V = 574.6 Å^3; (c) DBTTF-2,5-TCNQF2; triclinic, space group $P\bar{1}$, a = 8.838(2) Å, b = 9.276(2) Å, c = 7.794(1) Å, α = 101.29(2)°, β = 100.89(1)°, γ = 107.42(2)°, V = 576.6 Å^3. The crystal structure of the neutral DBTTF donor is dominated by columns of DBTTF molecules as found in the similar structure of the donor TTF. The crystalline motifs adopted by the TCNQ and 2,5-TCNQF2 salts of DBTTF are composed of columns in which the donor and acceptor molecules alternate. These . . . DADADA . . . stacked columns are tied into sheets through weaker donor–donor overlapping. While the structures of the TCNQ and 2,5-TCNQF2 salts are very similar, they differ in the way sheets of donor-coupled . . . DADADA . . . stacks are

arranged relative to each other. Madelung energies for both salts have been computed from charge distributions obtained from LCAO-MO calculations. Degrees of charge transfer are evaluated from the molecular geometries of both the donor and acceptor molecules and from the cyano stretching frequencies of the acceptors.

INTRODUCTION

With the appearance of a large number of derivatives of the electron donor TTF[2] (Figure 1) and the electron acceptor TCNQ[3] (Figure 1), a wide assortment of organic charge-transfer compounds have followed.[4] The initially studied TTF-TCNQ, consisting of segregated stacks of donors and acceptors,[5] is a good electrical conductor down to ca. 60 K[6] and possesses many other interesting physical properties[7] and phase transition phenomena.[8] One particularly important aspect of TTF-TCNQ is that under ambient conditions the degree of charge transfer (z) is fractional, $z \cong 0.59$ e.[9]

In fact, the degree of charge transfer is of central importance to electron mobility and crystal cohesion in organic charge-transfer salts. Among other effects, z depends upon molecular polarizabilities, intramolecular Coulomb interactions, the Madelung constant and the

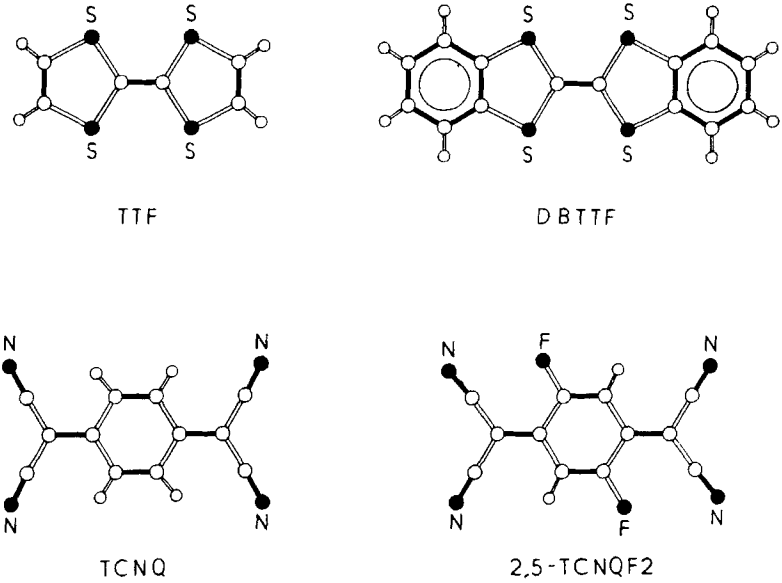


FIGURE 1 Molecular structures for the donors TTF and DBTTF and the acceptors TCNQ and 2,5-TCNQF2.

difference between the first ionization potential IP of the donor and the first electron affinity EA of the acceptor. In this regard, salts of the newer electron donor DBTTF[10] (Figure 1) with halogenated derivatives of TCNQ are of current interest. DBTTF is more difficult to oxidize in solution than TTF,[11] probably because its larger size makes it less effectively screened by polarizable solvents. Consistent with this reasoning the metallic segregated-stack salt DBTTF-2,5-TCNQCl2[12] apparently has $z \cong 0.5$ e despite a redox potential of the acceptor ca. 0.24 V higher than that of TCNQ.[13] However, in conjunction with the powerful electron acceptor TCNQF4 (EA about 0.4 eV higher than TCNQ),[14] DBTTF forms a dimerized, segregated-stack salt which has full charge transfer ($z = 1.0$ e) and is a Mott–Hubbard insulator.[15]

Following the same vein, one might expect that a fluorinated derivative of TCNQ with oxidizing power intermediate between TCNQ and TCNQF4 could (as for the case of DBTTF-2,5-TCNQCl2 noted above) yield a salt with z near 0.5 e. A suitable candidate is the symmetric acceptor 2,5-TCNQF2,[16] (Figure 1). As we will show here, the salt DBTTF-2,5-TCNQF2 has $z \cong 0.65$ e, near that of TTF-TCNQ.[8] However, this salt is not composed of segregated stacks of donors and acceptors but adopts a mixed-stack crystalline motif very similar, but not identical to, that found for DBTTF-TCNQ ($z \cong 0.47$ e).[17]

In this report, we detail the structural properties of the salts DBTTF-2,5-TCNQF2 and DBTTF-TCNQ and the neutral donor DBTTF. Analysis of the bond length trends in the donor molecules in all three systems gives evidence for the fractional charge on the DBTTF donors in the TCNQ and the 2,5-TCNQF2 salts. Similarly, degrees of charge transfer are derived from the molecular geometries of the TCNQ and 2,5-TCNQF2 acceptors, but our assignment of the z values for DBTTF-TCNQ and DBTTF-2,5-TCNQF2 rest largely on the previously established[18] linear relationship between the cyano stretching frequencies and the charge on the acceptor molecules. Finally, we examine the Madelung energy (evaluated from charges obtained from CNDO/INDO[19] molecular orbital computations) for both charge-transfer salts.

EXPERIMENTAL

The preparation of the neutral donor DBTTF[10] and the acceptor 2,5-TCNQF2[16] were carried out in our laboratories according to published synthetic routes. Co-diffusion of DBTTF with either acceptor, TCNQ

or 2,5-TCNQF2, at room temperature resulted in the respective 1:1 charge-transfer salts, DBTTF-TCNQ and DBTTF-2,5-TCNQF2. A least-squares fit to the setting angles of 15 carefully-centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer gave the unit-cell data listed in Table I. The characteristics of the single crystals used in our analyses are given in Table II, as well as details of the data collection and refinement for each of the three title compounds.

Each structure was solved by means of a Patterson synthesis, yielding the positions of the two independent S atoms as well as the relative orientation of each DBTTF molecular plane. Subsequent Fourier and difference-Fourier techniques revealed the existence of a mixed-stack motif for the two salts and indicated the location of all non-hydrogen atoms. At an intermediate stage, the unique H atoms for each structure were positioned on the basis of a difference-Fourier synthesis, and both positional and isotropic thermal parameters of all H atoms were refined in subsequent stages. After the final cycle of least-squares refinement, difference-Fourier maps were essentially featureless, with maximum residual density peaks less than ± 0.3 e/Å^3 for DBTTF and DBTTF-2,5-TCNQF2 and ± 0.6 e/A^3 for DBTTF-TCNQ—all peaks lying in the vicinity of the anistropic S atoms.

Final derived atomic positional parameters for the three title compounds are given in Table III. Tables of thermal parameters and lists of observed and calculated structure factor amplitudes have been deposited. The crystallographic computations were carried out with a stand-

TABLE I

Crystal data for DBTTF and the salts DBTTF-TCNQ and DBTTF-2,5-TCNQF2

	DBTTF	DBTTF-TCNQ	DBTTF-2,5-TCNQF2
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	12.082(2)	9.215(3)	8.838(2)
b, Å	3.955(1)	10.644(4)	9.276(2)
c, Å	14.553(2)	7.734(2)	7.794(1)
α, deg	90.00	113.32(3)	101.29(2)
β, deg	114.36(1)	122.28(2)	100.89(1)
γ, deg	90.00	67.66(3)	107.42(2)
V, Å^3	633.6(2)	574.9(3)	576.6(3)
Z	2	1	1
mol wt	304.5	508.7	544.7
ρ(meas'd),[a] g cm^{-3}	1.60(1)	1.45(2)	1.59(2)
ρ(calc'd), g cm^{-3}	1.596	1.469	1.568

[a] The crystal densities were measured by means of a neutral buoyancy method using cyclohexane/bromoform solutions.

TABLE II

Summary of data collection and refinement results

	DBTTF	DBTTF-TCNQ	DBTTF-2,5-TCNQF2
color of crystals[a]	yellow	red	black
crystal habit	needle	thin needle	rhombohedron
crystal dimensions (mm) along a^*, b^*, c^*, respectively	$0.20 \times 0.22 \times 0.08$	$0.38 \times 0.08 \times 0.08$	$0.12 \times 0.22 \times 0.21$
approximate axis of diffractometer alignment	b	a	c
absorption coefficient, cm^{-1} [b]	6.99	4.26	4.44
max. and min. transmission factors	0.949,0.870	0.973,0.956	0.956,0.906
$(\sin\theta)/\lambda$ limit, $Å^{-1}$ [c]	0.7035	0.6497	0.7352
total no. of reflections measured	6746	5638	7728
no. of unique reflections	1876	2654	3875
no. of reflections with net counts above background (NO)[d]	1852	2402	3687
no. of variable parameters (NV)	98	178	183
$R(F) = \Sigma\|F_o\| - \|F_c\| / \Sigma\|F_o\|$[e]	0.045	0.121	0.054
$R[F > 3\sigma(F)]$	0.036	0.070	0.040
$R(wF) = \{\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2\}^{1/2}$	0.036	0.047	0.037
$GOF = \{\Sigma w(\|F_o\| - \|F_c\|)^2/(NO\text{-}NV)\}^{1/2}$	2.106	1.232	1.537
R_{ave}[f]	0.024	0.073	0.023

[a] Crystals of DBTTF were grown by evaporation of solvent (chlorobenzene), while the crystals of each of the two complexes were grown via diffusion through a solvent barrier (chlorobenzene for the donor, acetonitrile for the acceptor) in a straight tube.

[b] Data were also corrected for Lorentz and polarization effects and an approximate scale factor was derived by the method of Wilson.[20]

[c] A constant scan rate of 1.5°/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 each 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 1/4 of the total scan time.

[d] Also, NO = no. used in refinement. 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 $[\Sigma w(|F_o| - |F_c|)^2]$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$. Neutral non-hydrogen atomic scattering factors were taken from a compilation of Hanson, Herman, Lea and Skillman,[21] while those for the hydrogen atoms were from Stewart, Davidson and Simpson.[22] The real components of anomalous dispersion for the non-hydrogen atoms were accounted for using the values of Cromer and Liberman.[23]

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

ard set of computer programs, including ORTEP, with which all illustrations were prepared.[24]

We should note that the unit cell used for DBTTF-TCNQ is not the conventional Delauney reduced cell as chosen for DBTTF-2,5-TCNQF2, since the donor/acceptor stacking direction of the former salt is not along a unit-cell translation of the reduced cell. Reduced cell parameters for DBTTF-TCNQ are: a = 8.283(3) Å; b = 10.389(4) Å; c = 7.734(2) Å; $\alpha = 109.81(3)^0$; $\beta = 109.85(3)^0$; $\gamma = 72.10(3)^0$. The matrix for the transformation from the cell used here to the reduced cell is:

$$\begin{pmatrix} -1 & 0 & -1 \\ 0 & -1 & -1 \\ 0 & 0 & 1 \end{pmatrix}.$$

The inequivalence of the reduced cells for these two salts indicates that they are not isomorphous.

RESULTS AND DISCUSSION

I. Crystal structures

A) DBTTF. The crystal structures of a variety of heterofulvalene electron donors have been investigated. Reported analyses include those for the tetrathiafulvalene donors TTF[25] and tetracarbomethoxytetrathiafulvalene,[26] the tetraselenafulvalenes TSF[27] and TMTSF,[28] and the mixed-chalcogen donor diselenadithiafulvalene.[29] One of the principal motivations for these studies concerns the relationship between the mode of intermolecular interaction (e.g., molecular stacking[7a,30] and chalcogen· · ·chalcogen interactions[31-32]) observed in the structure of the neutral donor to that found in the structures of its charge-transfer salts. For example, the molecular stacking in the structure of TTF is very similar to that found in its charge-transfer salt with TCNQ,[33] but the short S· · ·S interatomic contacts in neutral TTF[25] are not observed in TTF-TCNQ, where interchain S· · ·N(TCNQ) interactions saturate the chalcogen sites.[33] As will be indicated below, the crystal structure of DBTTF is similar to that of TTF, with the notable exception that only weak intermolecular S· · ·S interactions are present.

As shown in the unit-cell stereoviews of Figure 2, the crystal structure of neutral DBTTF has a herringbone motif composed of interacting columns of DBTTF molecules. The average molecular planes

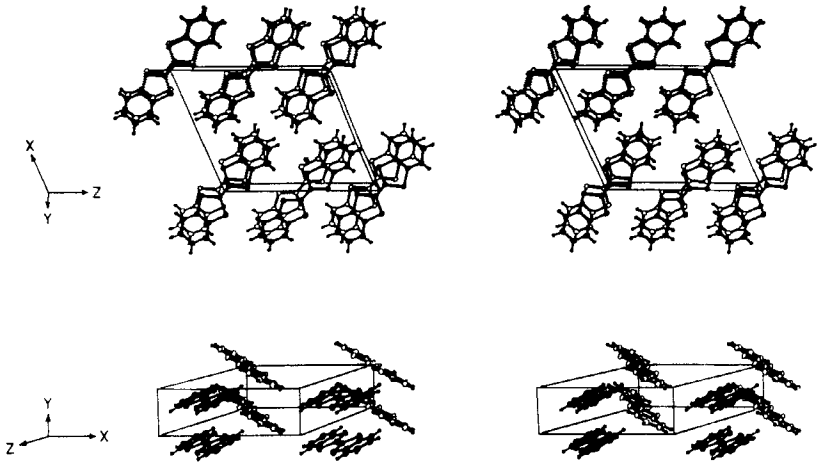


FIGURE 2 Illustrations of the crystal structure of neutral DBTTF. *Top:* A stereoview along the b^* axis. *Bottom:* A stereoview approximately along the [101] direction.

within these columns are separated by 3.60 Å, indicating an intracolumn interaction on the order of that for the similarly spaced (3.62 Å) molecules in the structure of neutral TTF.[25] The degree of intermolecular overlap in the DBTTF columns is depicted in Figure 3A. In contrast to the ring-over-bond overlap pattern in TTF which involves a shift from one molecule to the next along the long in-plane molecular axis, the molecular overlap pattern in the columns of DBTTF molecules exhibits a shift along the short in-plane molecular axis. Both of these types of overlap patterns avoid potentially unfavorable "hard atom-hard atom" intracolumn S· · ·S contacts,[30] while allowing a maximization of the intermolecular polarization forces through the minimization of the interplanar spacing.

The choice of different intracolumn overlap patterns in DBTTF and TTF may in part be a result of differing intercolumnar interactions. In particular, we note that the relatively short intercolumn S· · ·S interactions at 3.41 Å and 3.58 Å (expected van der Waals separation of 3.7 Å[34]) in the structure of neutral TTF are absent in the structure of DBTTF (with the shortest S· · ·S contacts exceeding 3.75 Å). Thus, intercolumnar cohesion in the structure of DBTTF depends on more general dispersive forces. In this context, Sandman and coworkers[35] have evaluated the lattice energy of neutral TTF to be ca. −1 eV. Calculations by these same authors[35] suggest that the lattice energy of TTF is primarily determined by non-bonded interactions, consistent with

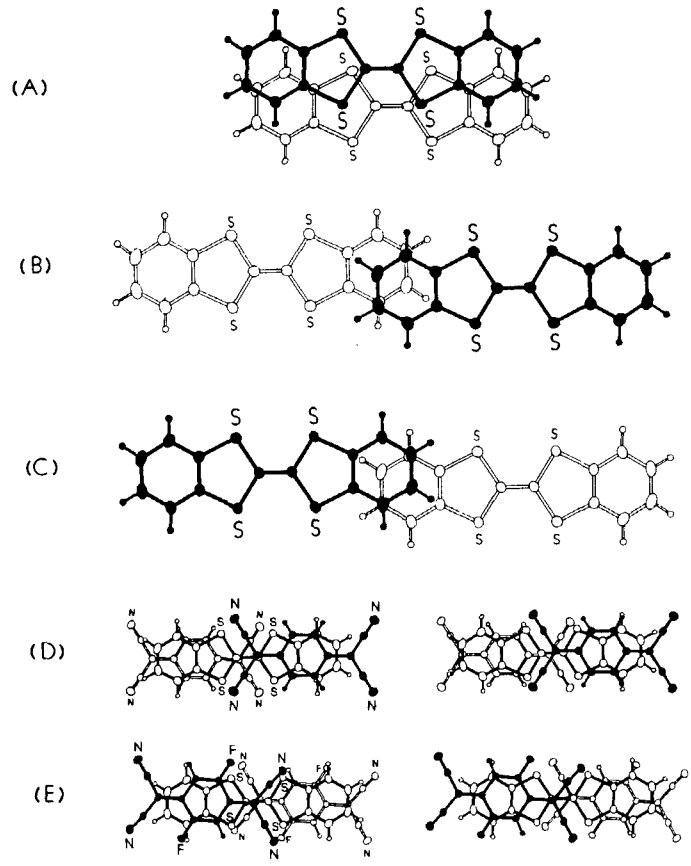


FIGURE 3 *Molecular overlap patterns for:* (A) neutral DBTTF; (B) the donor/donor overlap in DBTTF-TCNQ; (C) the donor/donor overlap in DBTTF-2,5-TCNQF2; (D) the intermolecular stacking in the . . . DADADA . . . columns in DBTTF-TCNQ; (E) the stacking in the . . . DADADA . . . columns in DBTTF-2,5-TCNQF2.

the absence of significant "atom-in-molecule" fractional charges (thus a negligible Madelung contribution) and the absence of a molecular dipole moment. From the structural comparisons given above for TTF and DBTTF, it might be expected that the lattice energy of DBTTF is very close to that of TTF, with perhaps a somewhat larger "intracolumn" contribution owing to the expected increase in polarizability of DBTTF relative to TTF, but possibly a smaller "intercolumn" contribution due to the absence of specific S· · ·S interactions.

B) DBTTF-TCNQ and DBTTF-2,5-TCNQF2. Simplistically, organic charge-transfer salts and complexes usually form crystal structures fall-

ing into one of two broad categories:[36] (1) those exhibiting homogeneous, segregated stacks of donors (D) and acceptors (A); and (2) those with alternating sequences of donors and acceptors in the same stack. Electrically, materials of the first type embrace a full range from insulators to metals whose conductivity often exceed $10^3\ \Omega^{-1}\ cm^{-1}$ at low temperatures, while those of the second type are limited to semiconducting behavior by simple band theory.

Most frequently, 1:1 heterofulvalene salts of TCNQ (and its analogs) adopt the segregated stack motif,[31] with the notable exception of TMTSF-TCNQ which crystallizes in *both* a segregated-stack form (a black conductor)[37] and a mixed-stack form (a red semiconductor).[38] At least two heterofulvalene complexes with TCNQ of other than 1:1 stoichiometry also crystallize in mixed-stack arrays, $(HMTSF)_2TCNQ$ with the repeat sequence (. . . ADDA . . .)[39] and tetraethyl-TTF$(TCNQ)_2$ with the repeat sequence (. . . DAAD . . .).[40]

In this section, we describe the crystal structures of two 1:1 mixed-stack heterofulvalene-TCNQ acceptor salts, namely DBTTF-TCNQ[41] and DBTTF-2,5-TCNQF2. These salts are, as expected, electrical semiconductors,[42-43] but somewhat unexpectedly possess significant charge transfer. It has recently been shown[44] that the charge transfer in the TCNQ salt can be increased by the application of hydrostatic pressure.

The crystal structures of DBTTF-TCNQ and DBTTF-2,5-TCNQF2 are compared in the stereoviews of Figure 4 and the projections of Fig-

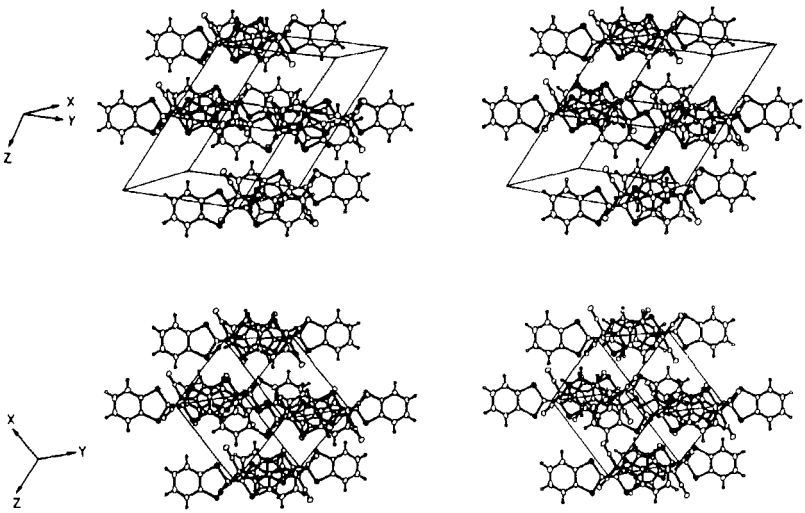


FIGURE 4 Stereoview of the crystal packing in DBTTF-TCNQ (top) and DBTTF-2, 5-TCNQF2 (bottom). In each case the view direction is approximately parallel to the layers of stacked donors and acceptors.

TABLE III

Atomic positional parameters for DBTTF and the two complexes DBTTF-TCNQ and DBTTF-2,5-TCNQF2[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
A) Fractional Coordinates of DBTTF.							
S(1)	18655(4)	81110(12)	5890(3)	C(6)	3692(2)	7060(5)	2482(2)
S(2)	3920(4)	111496(11)	15789(3)	C(7)	466(1)	9832(4)	450(1)
C(1)	2537(1)	8297(4)	1905(1)	H(3)	189(2)	1101(4)	372(1)
C(2)	1848(1)	9749(4)	2374(1)	H(4)	382(2)	886(5)	470(2)
C(3)	2329(2)	10010(5)	3412(1)	H(5)	495(2)	642(4)	388(1)
C(4)	3484(2)	8787(5)	3977(1)	H(6)	413(2)	593(5)	215(2)
C(5)	4160(2)	7320(5)	3515(2)				
B) Fractional Coordinates of DBTTF-TCNQ.							
S(1)	14162(15)	16818(12)	21753(16)	C(8)	4644(5)	76(4)	−1959(6)
S(2)	−1091(14)	6126(12)	−24561(15)	C(9)	5794(5)	961(4)	1876(6)
C(1)	1522(5)	2591(4)	800(6)	C(10)	5443(5)	1104(4)	−96(6)
C(2)	787(5)	2086(4)	−1395(6)	C(11)	5912(5)	2167(4)	−162(5)
C(3)	817(6)	2742(5)	−2606(7)	C(12)	5620(5)	2300(4)	−2101(6)
C(4)	1569(6)	3877(5)	−1638(8)	C(13)	6718(5)	3191(4)	1703(6)
C(5)	2280(6)	4375(5)	509(9)	N(1)	7362(5)	4016(4)	3163(5)
C(6)	2274(6)	3744(4)	1770(7)	N(2)	5395(5)	2432(4)	−3616(5)

C(7)	262(5)	492(4)	−58(6)	H(8)	437(4)	18(3)	−322(4)
H(3)	36(4)	241(3)	−405(5)	H(9)	624(4)	163(3)	300(4)
H(4)	156(5)	438(4)	−249(6)				
H(5)	278(5)	517(4)	131(6)				
H(6)	281(4)	401(3)	327(5)				
C) Fractional Coordinates of DBTTF-2,5-TCNQF2.							
S(1)	22118(5)	−6111(5)	556(5)	C(8)	−339(2)	4658(1)	1547(2)
S(2)	−332(5)	−8304(5)	24404(5)	C(9)	1391(2)	4849(2)	−546(2)
C(1)	2768(2)	−1219(2)	1996(2)	C(10)	1105(1)	4470(1)	1090(2)
C(2)	1716(2)	−1314(2)	3129(2)	C(11)	2174(2)	3954(2)	2133(2)
C(3)	2051(2)	−1807(2)	4684(2)	C(12)	2014(2)	3553(2)	3795(2)
C(4)	3446(2)	−2194(2)	5088(2)	C(13)	3588(2)	3776(2)	1606(2)
C(5)	4488(2)	−2100(2)	3974(3)	N(1)	4714(2)	3609(2)	1211(2)
C(6)	4162(2)	−1617(2)	2416(2)	N(2)	1981(2)	3191(2)	5109(2)
C(7)	468(2)	−290(2)	537(2)	F	−627(1)	4311(1)	3073(1)
H(3)	132(2)	−191(2)	544(2)	H(9)	232(2)	476(2)	−96(2)
H(4)	368(2)	−251(2)	614(3)				
H(5)	544(2)	−235(2)	419(2)				
H(6)	489(2)	−154(2)	167(2)				

[a] Estimated standard deviations of the least-significant figure are enclosed in parentheses. Parameters for S atoms are $\times 10^5$; for C, N, and F atoms $\times 10^4$; and for H atoms are $\times 10^3$.

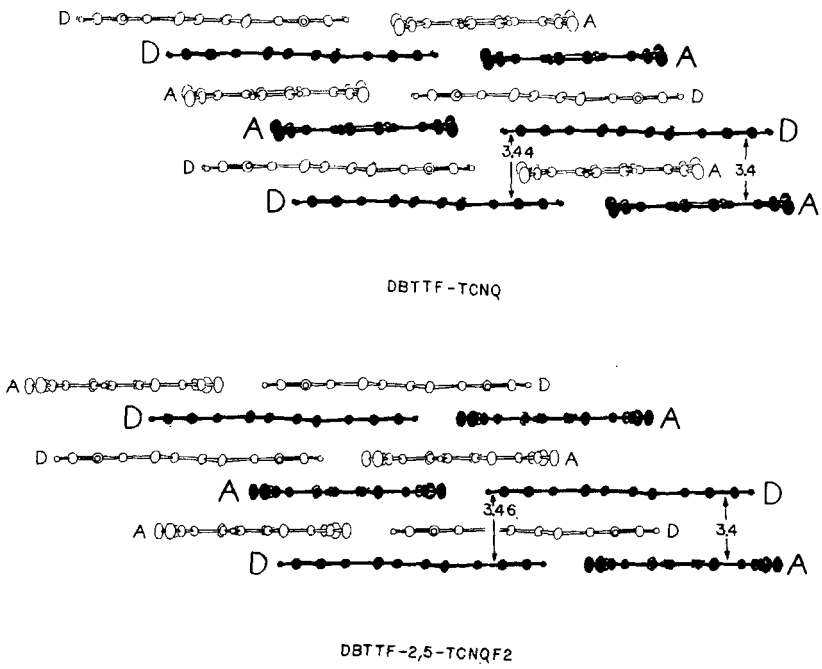


FIGURE 5 Illustrations of the interlayer packing in DBTTF-TCNQ and DBTTF-2,5-TCNQF2. Note the interlayer shift by one . . . DADADA . . . column on going from the TCNQ salt to the 2,5-TCNQF2 salt.

ure 5. In each case, there are two principal intermolecular interactions which aid in the description of their structures. First, there are columns of alternating donors and acceptors, within which the planar TCNQ or 2,5-TCNQF2 acceptor lies nearly parallel to and strongly overlaps the dithiabenzene moieties of adjacent DBTTF donors and *vice versa* (Figure 3D and 3E). For the TCNQ salt, the angle between the dithiabenzene plane of the DBTTF donor and the quinone ring of the TCNQ acceptor is $2.1(3)^0$; the analogous angle involving the difluoroquinone ring in the 2,5-TCNQF2 salt is $1.1(3)^0$ (Table IV). For both salts, the mean distance between donor dithiabenzene plane and the quinone plane of the acceptor is ca. 3.4 Å. Secondly, each structure contains significant intercolumn donor/donor overlap (Figure 3B and 3C), using the extremities of the dithiabenzene moieties. The extent of donor/donor overlap in these intercolumn interactions is considerably smaller than in the columnar arrays of neutral DBTTF (compare Figures 3A, 3B and 3C); however, the mean separation between parallel donors is significantly less in the salts (3.44 Å for DBTTF-TCNQ and

TABLE IV

Least-squares planes and deviations (Å) of individual atoms from these planes

A) Least-squares planes for DBTTF.[a]

1) The tetrathiaethylene plane ($0.4017X + 0.9096Y - 0.1060Z = 0.0000$ Å)

S(1) ± 0.001(1)	C(1)* ∓ 0.109(2)	C(4)* ∓ 0.264(2)
S(2) ± 0.001(1)	C(2)* ∓ 0.100(2)	C(5)* ∓ 0.287(2)
C(7) ∓ 0.006(2)	C(3)* ∓ 0.168(2)	C(6)* ∓ 0.213(2)

2) The dithiabenzene plane ($0.4386X + 0.8975Y - 0.0470Z = 0.1158$ Å)

S(1) + 0.011(1)	C(1) + 0.004(2)	C(4) + 0.005(2)
S(2) − 0.014(1)	C(2) + 0.001(2)	C(5) − 0.007(2)
C(7)* − 0.075(2)	C(3) + 0.011(2)	C(6) − 0.011(2)

B) Least-squares planes for DBTTF-TCNQ.[b]

1) The tetrathiaethylene plane of DBTTF ($-0.7173X + 0.6909Y - 0.0903Z = 0.000$ Å)

S(1) ∓ 0.002(1)	C(1)* ± 0.106(4)	C(4)* ± 0.266(5)
S(2) ∓ 0.002(1)	C(2)* ± 0.115(4)	C(5)* ± 0.264(6)
C(7) ± 0.011(4)	C(3)* ± 0.197(5)	C(6)* ± 0.183(5)

2) The dithiabenzene plane of DBTTF ($-0.7628X + 0.6412Y - 0.0836Z = -0.1085$ Å)

S(1) + 0.001(1)	C(1) + 0.001(4)	C(4) − 0.004(5)
S(2) − 0.007(1)	C(2) + 0.007(4)	C(5) − 0.002(6)
C(7)* + 0.074(4)	C(3) + 0.005(5)	C(6) − 0.001(5)

3) The quininoid plane of TCNQ ($-0.7694X + 0.6278Y - 0.1179Z = -3.5448$ Å)

C(8) ∓ 0.002(4)	C(9) ∓ 0.002(4)	C(10) ± 0.011(4)
C(11) ∓ 0.005(4)	C(12)* ∓ 0.032(4)	C(13)* ± 0.003(4)
N(1)* ± 0.006(4)	N(2)* ∓ 0.047(4)	

C) Least-squares planes for DBTTF-2,5-TCNQF2.[b]

1) The tetrathiaethylene plane of DBTTF ($-0.1967X - 0.8002Y - 0.5666Z = 0.0000$ Å)

S(1) ± 0.002(1)	C(1)* ∓ 0.131(2)	C(4)* ∓ 0.303(2)
S(2) ± 0.002(1)	C(2)* ∓ 0.140(2)	C(5)* ∓ 0.297(2)
C(7) ∓ 0.012(2)	C(3)* ∓ 0.223(2)	C(6)* ∓ 0.207(2)

2) The dithiabenzene plane of DBTTF ($-0.1525X - 0.8406Y - 0.5197Z = 0.1180$ Å)

S(1) + 0.002(1)	C(1) − 0.010(2)	C(4) + 0.004(2)
S(2) + 0.002(1)	C(2) − 0.014(2)	C(5) + 0.006(2)
C(7)* − 0.078(2)	C(3) − 0.004(2)	C(6) + 0.003(2)

3) The difluoroquininoid plane of 2,5-TCNQF2 ($-0.1697X - 0.8367Y - 0.5207Z = -3.4670$ Å)

C(8) ∓ 0.000(2)	C(9) ∓ 0.002(2)	C(10) ∓ 0.001(2)
C(11) ± 0.001(2)	C(12)* ∓ 0.006(2)	C(13)* ± 0.011(2)
N(1)* ± 0.005(2)	N(2)* ± 0.032(2)	F ∓ 0.001(1)

[a] In each of the equations of the planes, X, Y and Z are coordinates (Å) which refer to the orthogonal axes X along a, Y along b, and Z along c^*. Atoms indicated by an asterisk were given zero weight in calculating the plane—all other atoms were weighted equally. Estimated deviations are enclosed in parentheses.

[b] For the triclinic cases, X, Y and Z refer to the orthogonal axes X along a, Y in the ab plane, and Z along c^*.

3.46 Å for DBTTF-2,5-TCNQF2) than in the structure of the neutral donor (3.60 Å).

Thus, it is convenient to consider the crystal structures of both DBTTF-TCNQ and DBTTF-2,5-TCNQF2 as consisting of columns of alternating donors and acceptors linked into sheets *via* donor/donor interactions. In fact, it is in the arrangement of these sheets of donor-coupled . . . DADA . . . stacks relative to each other that the two crystal structures differ; the crystallographic projections of Figure 5 clearly illustrate this point. For DBTTF-TCNQ, adjacent layers of mixed stacks are "in register", in that columns of sequence . . . ADA . . . abut with columns of the same sequence. In contrast, adjacent layers of coupled mixed stacks in the structure of DBTTF-2,5-TCNQF2 are one step "out of register", so that columns of sequence . . . ADA . . . are in proximity to columns of the sequence . . . DAD . . . .

The difference in the two crystalline motifs can be characterized as an interlayer shift, involving a translation of one sheet relative to the next (approximately along the long in-plane axes of the molecules) of ca. 9.6 Å. Qualitatively, this seems to yield a slightly looser motif for DBTTF-2,5-TCNQF2 relative to DBTTF-TCNQ. This difference can be expressed in terms of the most significant atom· · ·atom interlayer contacts in each system. For DBTTF-TCNQ, the shortest interlayer heteroatom contacts are: (1) S(2)· · ·S(2; $-x$, $-y$, $-1-z$) at 3.72 Å [van der Waals sum[34] (ΣvdW) = 3.70 Å]; (2) S(1)· · ·N(2; x, y, $1+z$) at 3.48 Å (ΣvdW = 3.35 Å); and (3) C(4)-H(4)· · ·N(1; $1-x$, $1-y$, $-z$) at 2.59 Å (ΣvdW = 2.70 Å). In comparison, the structure of DBTTF-2,5-TCNQF2 yields: (1) no S· · ·S interlayer contacts below 3.8 Å, (2) a comparable S(2)· · ·N(2; $-x$, $-y$, $-1-z$) contact at 3.47 Å, and (3) a similar C(3)-H(3)· · ·N(2; $1-x$, $-y$, $-1-z$) interaction at 2.62 Å. The shortest S· · ·F interlayer contact distance in the structure of DBTTF-2,5-TCNQF2 is S(1)· · ·F(8; $-x$, $-y$, $-z$) = 3.50 Å, some 0.3 Å larger than the appropriate van der Waals sum.[34]

It is not expected, however, that these alterations lead to a major difference in interlayer dispersive forces for the two structural motifs. In view of this, it is somewhat surprising that the two salts are not formally isomorphous. To investigate this, we simplemindedly placed F atom substituents in appropriate places on the acceptor molecules in the DBTTF-TCNQ structure to simulate an isomorphous DBTTF-2,5-TCNQF2 motif. In doing so, we found, in either possible difluoro substitution pattern, unfavorable interlayer N· · ·F or F· · ·F contacts (some closer than 0.2 Å less than the van der Waals sums).[34] Thus, it may be that DBTTF-2,5-TCNQF2 chooses its alternative mode of in-

terlayer packing to minimize unfavorable repulsions, with a loss of the potentially favorable S· · ·S contacts.

II. Molecular geometries and charge transfer

A variety of experimental procedures are available which give a measure of the degree of charge transfer (z) from the donor to the acceptor in heterofulvalene-TCNQ acceptor salts. Included amongst these techniques are: Raman measurements of symmetric donor stretching frequencies,[45] correlation with the nonsymmetric IR-active nitrile stretching frequencies of the acceptor,[18,46] diffuse X-ray or neutron scattering measurements for systems which exhibit electron–phonon anomalies,[8–9] and correlation of metric changes for the donors and acceptors as charge is transferred from the HOMO of the donor to the LUMO of the acceptor.[47–48] In this section, we employ two of these methods to ascertain the degree of charge transfer in DBTTF-TCNQ[17] and DBTTF-2,5-TCNQF2. First, we compare the molecular geometries of the donors in DBTTF-TCNQ and DBTTF-2,5-TCNQF2 to that of the neutral donor and the donor in the unit-charge transfer salt DBTTF-TCNQF4.[15] Next, we examine the molecular geometries of the TCNQ and 2,5-TCNQF2 acceptors relative to their neutral[49–50] and their ionized geometries.[47,51] Lastly, we present infrared stretching frequency data for a variety of donor-TCNQ[18] and donor-2,5-TCNQF2 salts.

A) Donor geometries. In Figure 6, thermally uncorrected bond lengths and angles for the DBTTF donor as observed in the structure of the neutral molecule and its salts with TCNQ and 2,5-TCNQF2 are presented. In Table V, we compare averaged, librationally-corrected geometries[52] for the donors in these systems; similar data for the donor molecule in the unit charge-transfer salt DBTTF-TCNQF4 complete Table V.

In attempting to deduce a value for the degree of charge transfer, we concentrate on the length of the central C=C bond (denoted a in Table V) and the lengths of the C—S bonds (denoted as b and c in Table V). Focusing on these bonds is indicated by large π-spin densities among the S atoms and the C atoms of the central bond[53] and theoretical arguments[54] based on the change in molecular geometry with the transfer of electron density from the HOMO of the donor. First, we note that there is a marked expansion (0.058 Å) in the central C=C bond on going from neutral DBTTF to the unit-charged cation in DBTTF-TCNQF4. Secondly, in neutral DBTTF, the exterior C—S bond length

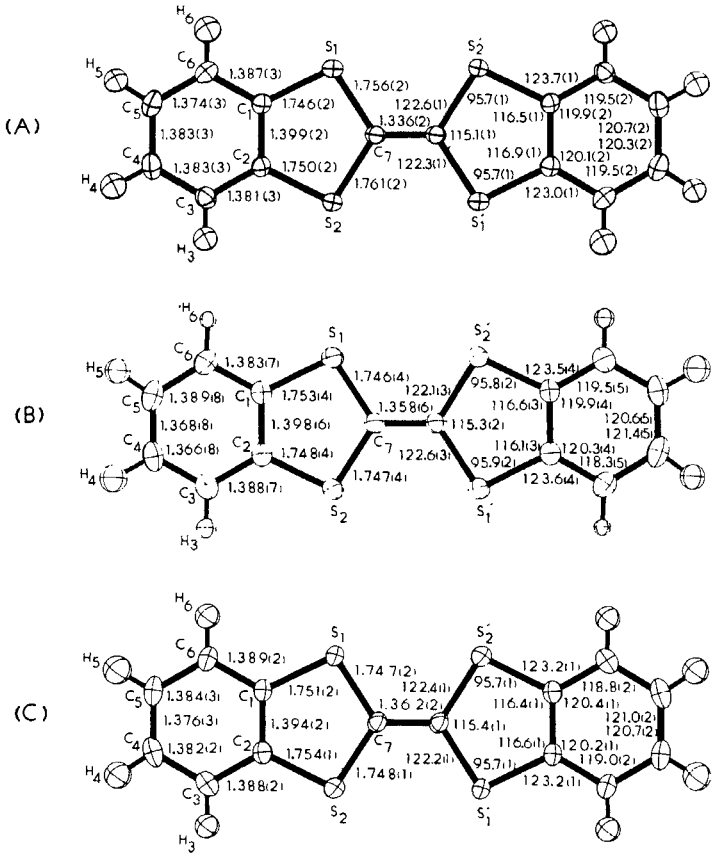
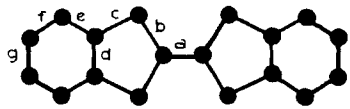


FIGURE 6 Molecular dimensions for the DBTTF donors in (A) neutral DBTTF, (B) DBTTF-TCNQ and (C) DBTTF-2,5-TCNQF2.

(bond c of Table V) is slightly shorter than the interior C—S bond length (bond b of Table V), while the opposite is true for the $DBTTF^+$ cation. Very similar results are observed in TTF-containing systems.[48] For example, the difference in the central C=C bond length on going from neutral TTF[25] to the TTF^+ cation[45b,55] is ~0.06 Å. Assuming that the degree of charge transfer scales with the increase in the length of the central C=C bond, we ascribe z values to DBTTF-TCNQ and DBTTF-2,5-TCNQF2 of 0.38 and 0.45 e, respectively. In the same vein, the equivalence of the b and c bonds of the donors in DBTTF-TCNQ and DBTTF-2,5-TCNQF2 again suggest a significant charge transfer. Finally, we note that the geometry of the DBTTF donor in either the TCNQ or the 2,5-TCNQF2 salt is very similar to that found

TABLE V

Averaged, librationally-corrected bond distances for the donor DBTTF[a]



	DBTTF (D_{2h} symmetry imposed) from neutral molecule	from TCNQ complex	from 2,5-TCNQF2 complex	from TCNQF4 complex
a	1.337_1 Å	1.359_1 Å	1.363_1 Å	1.395_1 Å
b	1.763_2	1.753_2	1.753_2	1.724_4
c	1.750_2	1.753_2	1.754_2	1.744_4
d	1.404_1	1.406_1	1.400_1	1.402_2
e	1.386_2	1.387_2	1.390_2	1.389_4
f	1.380_2	1.380_2	1.385_2	1.380_4
g	1.388_1	1.375_1	1.381_1	1.376_2

[a] Subscripts refer to the number of contributors for the average value.

for the TTF donor [a = 1.372(4) Å, b = 1.745(3) Å, c = 1.739(3) Å] in TTF-TCNQ where the charge transfer is known to be 0.59 e.[18]

B) Acceptor geometries. In Figure 7, were present thermally uncorrected molecular geometries for the TCNQ and 2,5-TCNQF2 acceptors from the structures of their DBTTF salts. In Table VI, we contrast averaged, librationally-corrected[52] bond lengths for these acceptors with those for neutral TCNQ[49] and 2,5-TCNQF2.[50]

First, we note that the geometries of the acceptors in DBTTF-TCNQ and DBTTF-2,5-TCNQF2 are very close to those of their neutral precursors, and, thus indicative of a reasonably small charge transfer. Secondly, it is expected from theory,[56] and confirmed by experiment,[47-48] that on population of the LUMO of TCNQ the electronic structure becomes more benzenoid and less quininoid in character. Recently, we have proposed[38] a scheme to evaluate the degree of charge transfer from TCNQ acceptor geometry in terms of a ratio of bond distances, namely c/(b + d) (see Table VI). We expect this ratio to be a good index of charge transfer as there is a significant concentration of spin density[57] on the atoms in the vicinity of these bonds. In addition, previous estimates derived from the c/(b + d) ratio have matched well[38] with values based on other physical properties.

In the present case, we estimate from the bond lengths of Table VI a charge transfer of 0.25 e from the acceptor geometry in DBTTF-TCNQ. Under the assumption (reasonably quantified[50-51]) that the

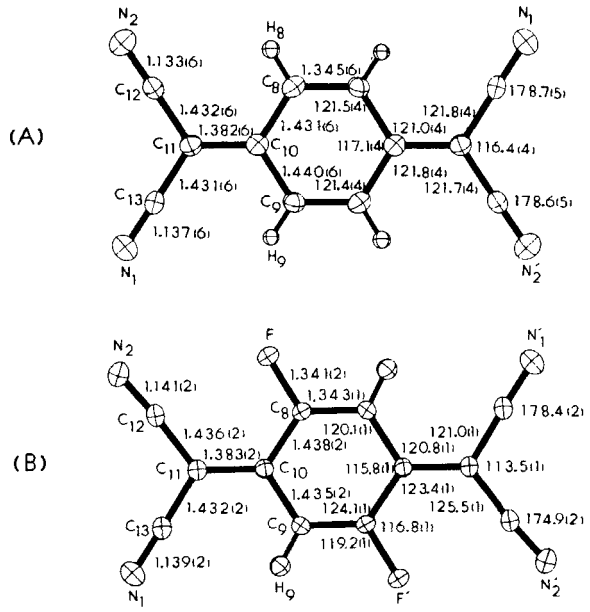


FIGURE 7 Molecular dimensions for the TCNQ acceptor in DBTTF-TCNQ and for the 2,5-TCNQF2 acceptor in DBTTF-2,5-TCNQF2.

fluoro substituents do little to alter the π-electronic structure, we apply the same ratio procedure to the 2,5-TCNQF2 acceptor in DBTTF-2,5-TCNQF2 and again estimate a charge transfer of 0.25 e.

Thus, both the donor and acceptor geometries are in accord with a moderate charge transfer in DBTTF-TCNQ and DBTTF-2,5-TCNQF2.

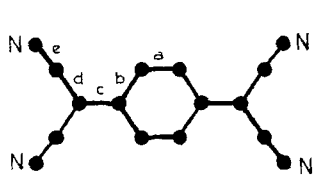
C) Infrared stretching frequency data. It has recently been established that a linear correlation exists between the stretching frequency (ω_0) of the nitrile groups and the charge (z) on the TCNQ acceptor in many of its charge-transfer salts.[18] Extension of this analytical procedure to salts of 2,5-TCNQF2 is presented in Table 7, where we also include data points from our previous analysis of TCNQ systems.[18]

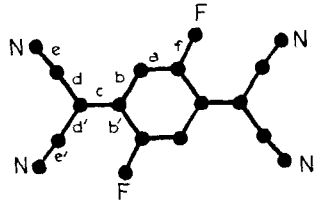
There are two potential problems in deriving the degree of charge transfer from the nitrile stretching frequency data of Table VII for the 2,5-TCNQF2 salts: (1) first, there are a limited range of 2,5-TCNQF2 salts for which comparisons with z values from other physical data can be made; (2) for DBTTF-2,5-TCNQF2, the infrared absorption band used is broader than usual and, thus, the derived z value is less precise.

Nonetheless, assuming a linear correlation for the 2,5-TCNQF2 salts, as determined elsewhere for TCNQ salts,[18] we arrive at a z value

TABLE VI

Average, librationally-corrected bond distances for the acceptors TCNQ and 2,5-TCNQF2





	TCNQ (D_{2h} symmetry imposed) from neutral molecule	TCNQ (D_{2h} symmetry imposed) from DBTTF-complex	2,5-TCNQF2 (C_{2h} symmetry imposed) from neutral molecule	2,5-TCNQF2 (C_{2h} symmetry imposed) from DBTTF-complex
a	1.346 Å	1.346 Å	1.329 Å	1.345 Å
b	1.448[a]	1.442	1.445	1.440
b′			1.448	1.443
c	1.374	1.384	1.377	1.386
d	1.441[a]	1.438[a]	1.442	1.436
d′			1.441	1.441
e	1.140[a]	1.138[a]	1.140	1.142
e′			1.138	1.143
f			1.342	1.344

[a] These averaged values have two contributors, all others have only one.

TABLE VII

Nitrile stretching frequency data for TCNQ, 2,5-TCNQF2 and some of their charge-transfer salts

Material	ω_0(cm^{-1})	z	Motif[a]
(a) TCNQ systems			
TCNQ	2227[b]	0	
TMTSF-TCNQ(Red)	2217[b]	0.23	MS
DBTTF-TCNQ	2206[c]	0.47	MS
TTF-TCNQ	2201[b]	0.59	USS
TMTSF-TCNQ(Black)	2199[b]	0.63	USS
HMTTF-TCNQ	2195[b]	0.72	USS
TBA-TCNQ	2182[c]	1	
(b) 2,5-TCNQF2 systems			
2,5-TCNQF2	2230	0	
DBTTF-2,5-TCNQF2	2200–2204	0.6–0.7	MS
TTF-2,5-TCNQF2	2188	1.0	DSS
HMTSF-2,5-TCNQF2	2188	1.00	?
TBA-2,5-TCNQF2	2188	1	

[a] MS = mixed-stack; USS = uniform segregated-stack; DSS = dimerized segregated-stack; ? = unknown.
[b] Taken from Ref. 18.
[c] Taken from Ref. 17.

for DBTTF-2,5-TCNQF2 of 0.6–0.7 e. This value is about 0.15–0.23 e larger than for DBTTF-TCNQ[17] (as also suggested by the donor geometries).

III. Electronic structures, atomic charges and Madelung energies

In the previous section, we examined the degree of charge transfer (z) for DBTTF-TCNQ and DBTTF-2,5-TCNQF2 and found that the 2,5-TCNQF2 salt is probably significantly more ionized than the TCNQ salt. In general, z depends[58] on the polarizabilities of the donor and acceptor, their on-site Coulomb energies, the Madelung energy of the adopted structure, and the difference in the first ionization potential of

TABLE VIII

Donor IP's, acceptor EA's, E_M's and z's for several pairs of "isostructural" heterofulvalene salts

Compound	IP (eV)	EA (eV)	E_M (eV/pair)	z[a]
TTF-TCNQ	6.9[b]	2.8[c]	−2.34[d]	0.59
TSF-TCNQ	7.2[e]	2.8	−2.21[f]	0.63
HMTSF-TCNQ	~6.6[g]	2.8	−2.58[h]	0.74
HMTTF-TCNQ	~6.4[g]	2.8	−2.62[i]	0.72
HMTSF-TCNQ	~6.6	2.8	−2.58	0.74
HMTSF-TCNQF4	~6.6	3.2[c]	−2.55[h]	1.0
HMTTF-TCNQ	~6.4	2.8	−2.62	0.72
HMTTF-TCNQF4	~6.4	3.2	−2.60[j]	1.0
DBTTF-TCNQ	~7.1[k]	2.8	−2.97[l]	0.47[l]
DBTTF-2,5-TCNQF2	~7.1	3.0[c]	−2.69[l]	~0.65[l]

[a] See Ref. 18 of the text and references therein unless otherwise indicated.

[b] R. Gleiter, E. Schmidt, D. O. Cowan and J. P. Ferraris, *J. Electron Spectr.*, **2**, 207 (1973).

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[f] R. M. Metzger, private communication.

[g] IP(HMTSF) assumed to be the same as that for TMTSF and IP(HMTTF) assumed to be the same as that for TMTTF; see R. Gleiter, M. Kobayashi, J. Spranget-Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard and D. O. Cowan, *Ber der Brensen-Gesell.*, **79**, 1218 (1975).

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[k] See Ref. 15 of the text and references therein.

[l] This work.

the donor and the first electron affinity of the acceptor. For the present DBTTF salts, the polarizability, first ionization potential and on-site Coulomb energy of the donor are, of course, identical. If one assumes that the polarizability of the TCNQ and 2,5-TCNQF2 acceptors are not dramatically different and similarly assumes a small difference in the on-site Coulomb potentials for each acceptor (this has been shown to be the case for TCNQ and TCNQF4, see Ref. 10j of Table VIII), then the difference in the degree of charge transfer for DBTTF-TCNQ and DBTTF-2,5-TCNQF2 ought to depend directly on two variables—the difference in the electron affinities[14d] of the acceptors (~0.2 eV) and the Madelung energies of each structure.

To explore these two possibilities, we have made LCAO-MO computations of the INDO/CNDO type[19] for DBTTF, $DBTTF^+$, and 2,5-$TCNQF2^-$. Molecular orbital computations of this type have been previously reported for TCNQ, $TCNQ^-$, 2,5-TCNQF2.[50] From these computations, we find: (1) that the molecular-orbital coefficients (Figure 8) and binding energy (−0.35 eV) for the π-HOMO of DBTTF are identical to those for TTF; (2) similarly, the "atom-in-molecule" charges for DBTTF and $DBTTF^+$ (Figure 8) are virtually equivalent to those for TTF and TTF^+ (see Ref. 4d of Table VIII). From the calculated

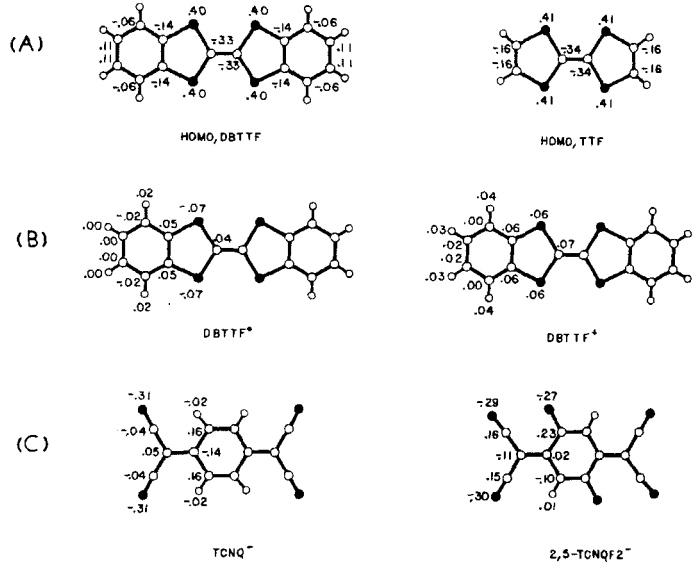

FIGURE 8 Comparison of: (A) the molecular orbital coefficients for the π-HOMO(b_{1u} in point group D_{2h}) for DBTTF and TTF; (B) the calculated atomic charges for neutral DBTTF and $DBTTF^+$; and (C) the calculated atomic charges on the $TCNQ^-$ and the 2,5-$TCNQF2^-$ anions.

charge distributions for $DBTTF^+$, $TCNQ^-$ and $2,5\text{-}TCNQF2^-$ given in Figure 8, we derive Madelung energies ($z = 1$) for DBTTF-TCNQ and DBTTF-2,5-TCNQF2 to be −2.97 and −2.69 eV/donor-acceptor pair, respectively. The former is very close to that calculated (−3.08 eV/pair) for the red, mixed-stack form of TMTSF-TCNQ.[38] The computed Madelung energy of DBTTF-2,5-TCNQF2 is, however, significantly lower and more typical of segregated stack 1:1 salts, Table VIII. Assuming that the principal electrostatic contribution to the crystal cohesion for these partially-charged salts goes as z^2E_M, there would be a larger electrostatic cohesive energy contribution for DBTTF-2,5-TCNQF2 for as small a charge transfer as 0.5 e than there would be for DBTTF-TCNQ ($z = 0.47$ e).

Thus, it appears that the greater electron affinity of 2,5-TCNQF2 and the electrostatic cohesive energy both favor a larger degree of charge transfer in DBTTF-2,5-TCNQF2 than in DBTTF-TCNQ.

SUMMARY

The crystal structures of the neutral donor DBTTF and its charge-transfer salts with the acceptors TCNQ and 2,5-TCNQF2 have been examined. For the neutral donor, there appears to be a significant contribution to crystal cohesion from the columnar formation of stacked molecules. The charge-transfer salts are qualitatively separable into layers which contain columns of alternating donor and acceptor molecules linked by donor/donor overlap. The two structures differ in their mode of interlayer coupling. The charge transfer in each system has been evaluated from donor and acceptor geometries and the nitrile stretching frequency of each acceptor. These results suggest significant degrees of charge transfer for each case, with a somewhat larger value being appropriate for the 2,5-TCNQF2 salt.

Acknowledgments

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SUPPLEMENTARY MATERIAL

Tables of nonhydrogen atom anisotropic thermal parameters and observed and calculated structure factor amplitudes for each structure have been deposited. This material may be obtained by contacting Gordon and Breach, One Park Avenue, New York, NY 10016.

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