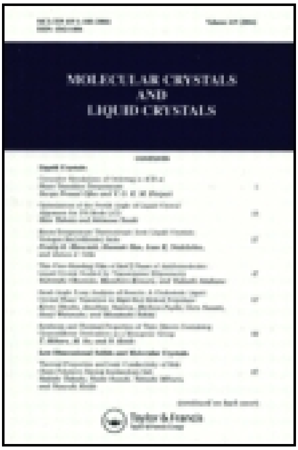

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Crystal Structure and Madelung Energy for the Charge-Transfer Complex Tetrathiafulvalene-2,5-Difluoro-7,7,8,8-Tetracyano-p-Quinodimethane, TTF-2,5-TCNQF2. Observations on a Dimerized Segregated Stack Motif.

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Crystal Structure and Madelung Energy for the Charge-Transfer Complex Tetrathiafulvalene-2,5-Difluoro-7,7,8,8-Tetracyano-*p*-Quinodimethane, TTF-2,5-TCNQF2. Observations on a Dimerized Segregated Stack Motif.

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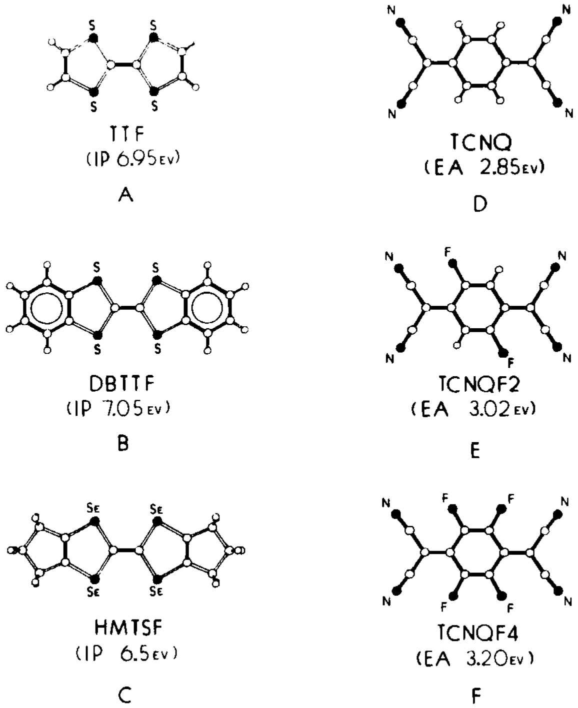
The twinned crystal structure of the charge-transfer complex TTF-2,5-TCNQF2 has been determined by single-crystal X-ray diffraction techniques. From intensity measurements on one twin component, a full structural model has been developed. The model encompasses segregated stacks of TTF donors and 2,5-TCNQF2 acceptors, with each chain exhibiting significant dimerization. The alternate interplanar spacings in the TTF stack are 3.34A and 3.60A, while those in the 2,5-TCNQF2 stack are 3.23A and 3.55A. Nearly eclipsed molecular overlap patterns are found within each of the dimerized pairs. The Madelung energy of TTF-2,5-TCNQF2 has been calculated at −2.65 eV per donor/acceptor pair for full charge transfer, utilizing partial atomic charges obtained from CNDO/INDO molecular orbital calculations. Full charge transfer is considered appropriate for this complex based primarily on the observed component molecular geometries. The dimerized structural motif observed at room temperature for the TTF-2,5-TCNQF2 system may reflect a phase transition at a higher temperature, owing to either an electronic- or a spin-Peierls instability. Diffraction data to temperatures on the order of 390 K do not indicate a solid-state phase transformation before crystal decomposition.

INTRODUCTION

A large number of derivatives of the electron donor tetrathiafulvalene,[2] TTF, and the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane,[3] TCNQ, have been synthesized in the past few years and some of these are illustrated in

Figure 1. These efforts have produced new organic charge-transfer complexes with enhanced metallic conductivities, new ranges for phase transformations, and a variety of crystalline motifs. Examples of new electron donors based on TTF are: DBTTF,[4] the dibenzo derivative; TMTSF,[5] the tetramethyltetraselena analog; and HMTSF,[6] the hexamethylenetetraselena derivative (see Figure 1). Concurrently, new acceptors which are fluoro-derivatives of TCNQ have been prepared: monofluoro-TCNQ,[3a,7] TCNQF; 2,5-difluoro-TCNQ,[3b,8] 2,5-TCNQF2; and perfluoro-TCNQ,[3c,9] TCNQF4 (Figure 1). Some of the well-characterized complexes derived from these donors and acceptors are: TTF-TCNQ;[10] DBTTF-TCNQ;[11] DBTTF-TCNQF4;[12] HMTSF-TCNQ;[13] HMTSF-TCNQF4;[14] and two forms of TMTSF-TCNQ.[15-16]

The diversity of physical properties exhibited by these complexes is more fully understood by critical analysis of their crystalline structures. For example, TTF-TCNQ, a conductor, crystallizes in a uniform segregated stack motif that accommodates extensive π-orbital overlap along donor and acceptor chains.[10] However, the complex DBTTF-TCNQF4 is an insulator and crystallizes in a non-uniform segregated stack array that contains strong dimer inter-



TTF (IP 6.95EV) A

TCNQ (EA 2.85EV) D

DBTTF (IP 7.05EV) B

TCNQF2 (EA 3.02EV) E

HMTSF (IP 6.5EV) C

TCNQF4 (EA 3.20EV) F

FIGURE 1 Molecular topology and nomenclature for various heterofulvalene donors (with IP's) and tetracyano-*p*-quinodimethane acceptors (with EA's).

actions in both donor and acceptor stacks.[12] The structural and physical contrasts evident in these two complexes are based, to a large measure, on the degree of charge transfer realized. The charge transfer of TTF-TCNQ has been experimentally determined to be 0.59 e,[17] while that of DBTTF-TCNQF4 from a variety of data seems to be near unity.[12,18] A theory by Bloch[19] maintains that the degree of charge transfer of such organic donor/acceptor complexes is indeed governed by chemical potentials similar to the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor. An example of the changes in donor IP and acceptor EA which come about upon chemical modification is given by the range for derivatives presented in Figure 1.[9,12,20–21]

An interesting example of the role that the (IP-EA) difference plays in determining the degree of charge transfer and the resulting physical properties is to be found in the complexes HMTSF-TCNQ and HMTSF-TCNQF4. The former complex shows partial charge transfer,[17] 0.74 e, has a uniform segregated stack motif,[13b] and is electrically conducting to very low temperatures.[13a] In comparison, HMTSF-TCNQF4 is isostructural with HMTSF-TCNQ, but fully charge transferred, and is electrically insulating.[14,18]

Alternatively, crystalline motifs other than the segregated stacks array are known for these complexes. Notable amongst these motifs is the alternating donor/acceptor chain (or "mixed" stack) exhibited by DBTTF-TCNQ[11] and the insulating form of TMTSF-TCNQ.[15] A second polymorph of TMTSF-TCNQ is conducting[16b] and has a structure[16a] similar to that of TTF-TCNQ.

In this general context, the title compound, TTF-2,5-TCNQF2, is an insulator[3b,22] and is shown here to crystallize in a dimerized segregated stack arrangement much in the same manner as DBTTF-TCNQF4.[12] In addition, the constituent molecular geometries for the TTF donor and the 2,5-TCNQF2 acceptor are suggestive of unit charge transfer. As such, the structure is largely ionic and we have calculated the electrostatic contribution to the crystal cohesion energy. Finally, it is suggested that the room-temperature structure is likely the low temperature phase of a system susceptible to a Peierls instability,[23] although high-temperature diffraction data presented here have not indicated a phase transition before crystal decomposition.

EXPERIMENTAL

Equimolar amounts of TTF and 2,5-TCNQF2 were combined in hot acetonitrile, giving a dilute solution that, upon cooling, yielded dark-green, acicular crystals of TTF-2,5-TCNQF2. Because of the small cross-sectional area and the extensive twinning of most crystals, selection of specimens for X-ray examination was quite difficult. Preliminary X-ray photographic data (oscillation/

Weissenberg method) showed that most cyrstals were of good quality, and that all were twinned and contained nearly equal volumes of each of the twin components. In addition, the scattered beams along the hk0 reciprocal lattice vectors were coincident, and scattering from planes with odd *l* index was quite weak. This latter observation indicated a possible subcell structure ($c' = c/2$) identical in projection to the supercell structure of twice the volume. The crystal density was measured by the neutral buoyancy method in a mixture of carbon tetrachloride and bromoform. The measured density allowed the presence of two formula units per triclinic supercell; therefore, no special symmetry conditions were required for either the TTF or the 2,5-TCNQF2 molecules. In the subcell (also triclinic), each of the molecular components is crystallographically-required to possess $\bar{1}(C_i)$ molecular symmetry.

The crystal employed for the room temperature data collection has the following crystal faces (indexed in the prominent twin lattice system) and mean interfacial distances: (100)–($\bar{1}$00), 0.09 mm; (010)–(0$\bar{1}$0), 0.04 mm; (001)–(00$\bar{1}$), 0.26 mm. The c^* axis was aligned approximately along the ϕ axis of a Syntex P$\bar{1}$ automated diffractometer. For this specimen, the ratio[24] of the scattered beams from the twin components was 1.41(4); intensities from the superimposed hk0 vectors were consequently reduced accordingly. The transformation matrix relating the orientation of the minor twin component (M) to the dominant one (D) was found to be:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_D = \begin{pmatrix} -1 & 0 & -0.24 \\ 0 & -1 & -0.59 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_M .$$

Precise cell dimensions were obtained from a least-squares fit to the setting angles of 15 carefully-centered reflections and are given along with other primary crystal data in Table I.

TABLE I

Crystal data for TTF-2,5-TCNQF2.

$a = 8.761(2)$A	$C_6H_4S_4 \cdot C_{12}N_4H_2F_2$
$b = 14.447(4)$A	MW = 444.53
$c = 7.082(1)$A	$Z = 2$
$\alpha = 98.26(2)°$	$D_{meas'd} = 1.68(1)$ g cm^{-3}
$\beta = 95.46(2)°$	$D_{calcd} = 1.672$ g cm^{-3}
$\gamma = 87.94(2)°$	$\mu(\lambda_{MoK\alpha} = 0.71069A) = 5.56$ cm^{-1}
V = 882.8(4)A^3	Space group: P$\bar{1}$

Intensity measurements were made employing graphite-monochromatized Mo Kα radiation and, except for the hk0 zone, all reciprocal lattice vectors surveyed were those of the dominant twin component. The 6144 reflections in the full sphere to $2\theta = 50°$ were measured on the diffractometer, utilizing the θ-2θ scan mode. A constant scan rate (2θ) of 1.5° min^{-1} was maintained for each of the diffraction profiles. After every 100 reflections, three standard reflections were monitored, whose intensities showed no unusual variation throughout the course of the experiment. The measured intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects (maximum and minimum transmission factors of 0.98 and 0.94, respectively). A symmetry-averaged set[25] of 2723 reflections of non-zero intensity formed the basis of the structural solution and refinement. An approximate scale factor was derived by the method of Wilson.[26]

Because of the very weak intensities of odd l index reflections, a reduced set of data (1423 reflections) with $l' = l/2 = n$ was collated from the larger set and used as a basis for the derivation of a subcell model. A Patterson synthesis indicated the positions of the S atoms of the TTF molecule and the orientation of donor and acceptor planes (both located about centers of inversion in the subcell). The positional parameters of the remaining nonhydrogen atoms were derived from Fourier and difference-Fourier methods. At an intermediate stage, the positions of the H atoms were obtained and later refined along with their isotropic thermal parameters. Full-matrix least squares refinement (all nonhydrogen atoms treated anisotropically) resulted in a final R value[27] of 0.086 for the subcell data.

The complete supercell model was derived by first transforming the subcell positional parameters by means of the following relationship: $(x, y, z) = (x', y', 1/4 + z'/2)$. Small perturbations were placed on these "idealized" positions according to difference-Fourier syntheses until a minimum in the R factor was obtained (0.18). Subsequent refinement using fixed, isotropic H atoms and anisotropic nonhydrogen atoms yielded final R values of 0.13 for the full supercell data set and 0.072 for the data with $F_0 > 3\sigma(F_0)$. The final weighted R value[28] and goodness-of-fit indicator[29] were 0.051 and 1.20, respectively. A final difference-Fourier synthesis gave maximum residual peaks of ± 0.8 e/A^3.

Neutral scattering factors for the nonhydrogen atoms[30a] and the H atoms[30b] were taken from common sources. The scattering curves for the nonhydrogen atoms were corrected for anomalous dispersion effects.[31] Final atomic positional parameters for the nonhydrogen atoms of the supercell model are given in Table II. Tables of anisotropic thermal parameters, the hydrogen atom parameters, and a list of observed and calculated factor structure amplitudes have been deposited for referral.[32] The crystallographic calculations were carried out with a standard set of computer programs.[33]

TABLE II

Fractional coordinates for the nonhydrogen atoms of TTF-2,5-TCNQF2 ($\times 10^4$). Estimated standard deviations in the least-significant figure are given in parentheses.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S(1)	9978(2)	1575(1)	3420(3)	C(4)	5647(7)	4096(4)	1621(9)
S(11)	9793(2)	8561(1)	1864(3)	C(14)	4469(8)	5767(4)	3017(10)
S(2)	7414(2)	315(1)	2904(3)	C(5)	3516(7)	5042(4)	2629(9)
S(12)	2300(2)	9848(1)	2361(3)	C(15)	6608(8)	4804(5)	2042(11)
C(1)	8187(9)	2067(5)	3700(11)	C(6)	4058(7)	4136(4)	1870(9)
C(11)	1584(8)	8101(5)	1468(10)	C(16)	6060(7)	5721(4)	2785(9)
C(2)	7028(9)	1497(5)	3453(11)	C(7)	3059(7)	3373(4)	1413(10)
C(12)	2728(8)	8698(5)	1672(10)	C(17)	7042(7)	6492(4)	3158(9)
C(3)	9339(7)	445(4)	2861(9)	C(8)	3555(8)	2420(5)	921(11)
C(13)	365(7)	9698(5)	2390(10)	C(18)	6551(7)	7420(5)	3808(10)
N(1)	3909(7)	1654(4)	495(10)	C(9)	1477(8)	3495(4)	1656(11)
N(11)	6246(7)	8183(4)	4303(10)	C(19)	8668(9)	6365(4)	3086(11)
N(2)	190(7)	3588(4)	1816(10)	F(1)	6225(4)	3253(2)	880(6)
N(12)	9957(7)	6280(5)	3005(11)	F(11)	3883(4)	6620(3)	3739(7)

Lastly, as it was suspected (*vide supra*) that a phase transformation might be attainable at elevated temperatures, several crystals of good quality were slowly heated in a stream of hot helium. The temperature was measured from a thermocouple wire placed in the He stream just behind the crystal specimen. The thermal expansion tensors of TTF-2,5-TCNQF2 were calculated[34] at 20° intervals using the measured unit-cell dimensions obtained from the setting angles of 8 supercell reflections. The thermal expansion was reversible to about 390 K, where crystal decomposition commenced.

RESULTS AND DISCUSSION

The general features of the crystal structure of TTF-2,5-TCNQF2 are presented in Figure 2. Emphasis is given to the most striking aspect of the structure, namely the presence of a strong dimerization component in both the donor and acceptor columns, in Figure 3. The dimeric design of both segregated stacks in TTF-2,5-TCNQF2 is uncommon to most organic charge-transfer complexes, but also appears in the room-temperature structure of the DBTTF-TCNQF4 complex.[12]

In the donor stack, a strong degree of dimerization is indicated by the large difference (0.26A) in alternate mean stacking distances of molecular planes. The short intradimer distance of 3.34A between nearly-eclipsed TTF molecules, Figure 4A, is comparable to the 3.35A distance of eclipsed DBTTF dimers in DBTTF-TCNQF4 and equal to the 3.34A distance of the eclipsed and somewhat isolated dimers in the structure of TTF-Br.[35] As a result, two short

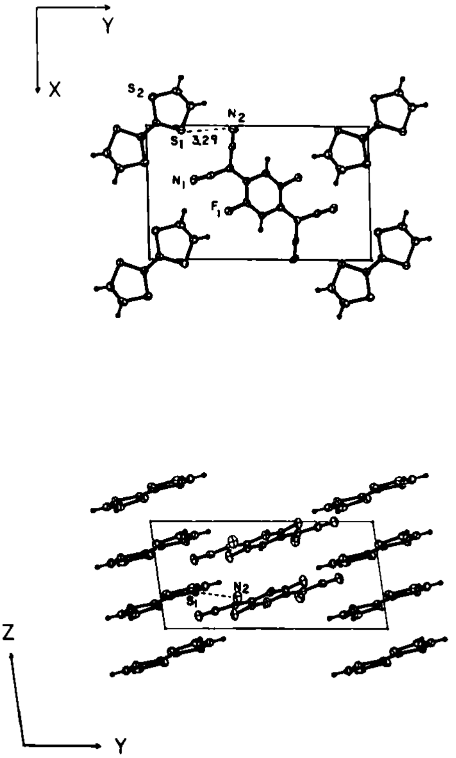


FIGURE 2 Two projection views of the crystal structure of TTF-2,5-TCNQF2. Top: The (001) projection. Bottom: The (100) projection. The labeled atoms have their coordinates as given in Table II.

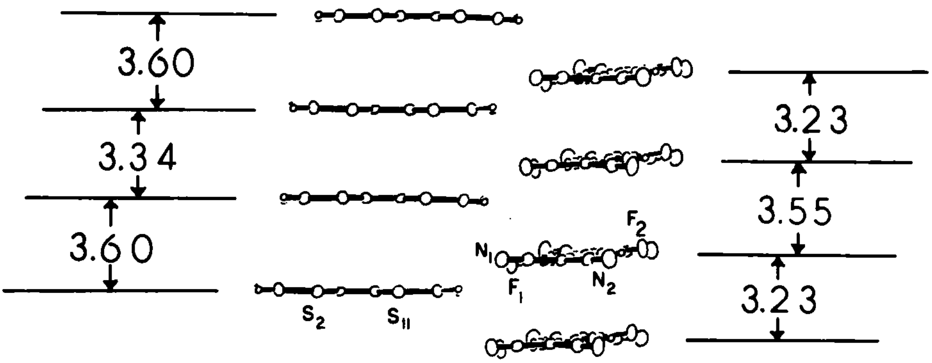


FIGURE 3 The dimerized donor and acceptor stacks as viewed along the TTF plane. Distances indicated are mean separations between molecular planes.

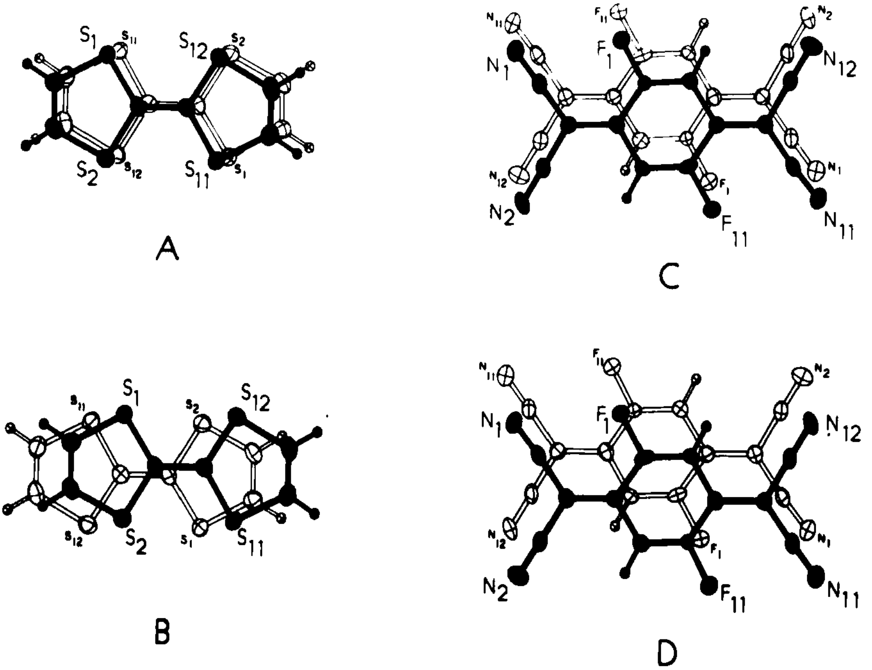


FIGURE 4 Molecular overlap patterns within the donor and acceptor stacks for: (A) the dimer interaction in the TTF stack; (B) the monomer interaction in the TTF stack; (C) the dimer interaction in the 2,5-TCNQF2 stack; (D) the monomer interaction in the 2,5-TCNQF2 stack.

intradimer S···S contacts [S(1)···S(11; $-x$, $-y$, $1 - z$) at 3.36A and S(2)···S(12; $-x$, $-y$, $1 - z$) at 3.38A] are found at distances substantially shorter (0.32A–0.34A) than the sum of van der Waals radii.[36] In a further comparison to the donor stacks in the crystal structure of DBTTF-TCNQF4, the molecular plane of the TTF donor is bowed away from the other dimer component, Figure 3. The close proximity of these dimerized TTF donors suggests extensive π-orbital overlap and perhaps a large degree of charge transfer. The monomer interaction (mean interplanar separation = 3.60A) between dimeric pairs contains only weak contacts between S atoms at 3.73A [S(1)···S(11; $-x$, $-y$, $-z$) and S(2)···S(12; $-x$, $-y$, $-z$)] or greater. This arrangement parallels that in the structure of DBTTF-TCNQF4, where S···S contacts are found at 3.68A and greater and the interdimer overlap is a ring-over-bond pattern as found here in the TTF columns, Figure 4B.

Dimerization is also observed in the 2,5-TCNQF2 acceptor stacks, whose center is related to that of the donor stack by the translation $a/2 + b/2 + c/2$. Qualitatively, as in the structure of DBTTF-TCNQF4, dimer pairs in the acceptor column abut monomer pairs in the donor column and *vice versa,* Figure 3. The stacking distance of the 2,5-TCNQF2 acceptors in the dimer mode at 3.23A is comparable to the separation between acceptor planes in HMTSF-TCNQF4 (3.24A, in a ring-over-bond uniform stack),[14] but farther apart than the TCNQ acceptors in TTF-TCNQ (3.17A, in a ring-over-bond pattern)[37] or the TCNQF4 molecules in DBTTF-TCNQF4 (3.18A, in an eclipsed dimeric pairing).[12] The 2,5-TCNQF2 dimers do not contain the nearly direct molecular overlap that is observed in the TTF dimers, but the degree of π-orbital overlap, Figure 4C, is much more intense than that observed in neutral 2,5-TCNQF2[8] and perhaps, as for the TTF stack, indicative of high charge transfer. Several contacts in the 2,5-TCNQF2 dimer interaction occur in the range 3.26A [as for C(7)···C(17; $1 - x$, $1 - y$, $-z$)] and 3.38A [as for C(9)···C(19; $1 - x$, $1 - y$, $-z$)]. No close contacts between atoms in the 2,5-TCNQF2 monomer interaction are observed, Figure 4D. Despite a similar overlap to that in the 2,5-TCNQF2 dimer interaction, the monomer interaction is weaker (3.55A separation), and one may assume that the interdimer cohesive forces are primarily dispersive in character.

Two types of prominent interchain interactions are observed in the TTF-2,5-TCNQF2 structure and all appear at or near the sum of their respective van der Waals radii. The first type involves the commonly found interaction[38] between a S atom of TTF and the N atom of one of the cyano groups of 2,5-TCNQF2: S(1)···N(2; $1\,x$, y, z) = 3.29A. The second type of interaction occurs between the hydrogen atoms of the TTF donor and the electronegative N or F atoms of the 2,5-TCNQF2 acceptor; the shortest amongst these are: H(1)···F(11; $-x$, $1 - y$, $1 - z$) = 2.47A and H(2)···N(11; $-x$, $-y$, $-z$) = 2.60A; H(11)···F(1; $1 - x$, $-y$, $-z$) = 2.48A and H(12)···N(1; $-x$, $1 - y$, $1 - z$) = 2.56A.

Intramolecular bond lengths for the TTF donor and the 2,5-TCNQF2 acceptor are given in Figure 5. Intramolecular bond angles are collected in Table III. The interior C—S bond lengths of the TTF donor range from 1.707(7)A to 1.727(7)A and the exterior C—S distances vary from 1.702(7)A to 1.725(8)A. The average interior and exterior C—S bond lengths of 1.716A and 1.714A, respectively, compare closely to those found in TTF^{+}ClO$_4^{-}$ (1.713A and 1.725A).[39] Similarly, the central C═C double bond length (considered[40] to be sensitive to the degree of charge transfer) as found here at 1.403(9)A compares well with the bond lengths observed in high charge-transfer complexes and salts containing heterofulvalene donors: TTF^{+}ClO$_4^{-}$, 1.40(1)A;[39] TTF^{+}HgCl$_3^{-}$, 1.40(1)A;[41] DBTTF-TCNQF4, 1.393(6)A.[12] The relative planarity of the TTF donor is shown by the deviations of individual atoms from their mean planes, given in Table IV. The interior fulvalene plane is markedly more planar than the entire molecular plane and reflects the boat-shape of the donor alluded to above.

The molecular geometry of the 2,5-TCNQF2 acceptor is shown in Figure 5 and its planarity is assessed in Table IV. The 2,5-difluoroquininoid plane is

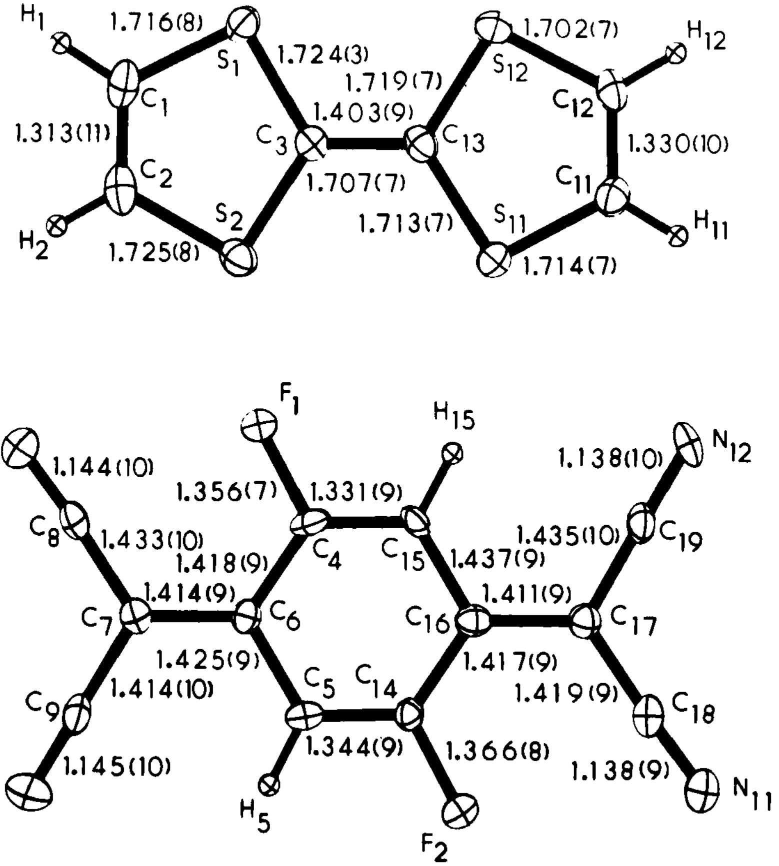


FIGURE 5 Intramolecular bond lengths for the TTF donor (top) and the 2,5-TCNQF2 acceptor (bottom).

appreciably more planar than the complete molecular frame, but systematic bowing as in the TTF donor is not observed. The C—F bond lengths, 1.356(7)A and 1.366(8)A are similar to those in neutral 2,5-TCNQF2 (1.339(2)A),[8] neutral TCNQF4 (C—F$_{AVE}$ = 1.337A)[9] and the TCNQF4 acceptors in DBTTF-TCNQF4[12] and HMTSF-TCNQF4 (1.347A and 1.349A, respectively). Like the TTF donor, the 2,5-TCNQF2 acceptor geometry is suggestive of unit charge transfer. For example, a significant shift from a quininoid structure to a benzenoid structure for the acceptor TCNQ with increasing charge transfer has been considered in theory[42] and observed in experiment.[11d,43] A similar shift could be expected for derivatives of TCNQ. In fact, the C—C single and C=C double bonds of the 2,5-difluoroquininoid nucleus follow the observed trend for TCNQ. Comparing the 2,5-TCNQF2 acceptor

TABLE III

Final nonhydrogen atom bond angles (deg)

A. TTF cation			
S(1)—C(3)—S(2)	115.7(4)[a]	S(11)—C(13)—S(12)	114.8(4)
S(1)—C(3)—C(13)	120.7(5)	S(11)—C(13)—C(3)	122.5(5)
S(2)—C(3)—C(13)	123.6(5)	S(12)—C(13)—C(3)	122.6(5)
C(1)—S(1)—C(3)	94.7(3)	C(11)—S(11)—C(13)	95.3(3)
C(2)—S(2)—C(3)	94.4(3)	C(12)—S(12)—C(13)	95.4(3)
S(1)—C(1)—C(2)	117.1(6)	S(11)—C(11)—C(12)	117.1(6)
S(2)—C(2)—C(1)	118.0(6)	S(12)—C(12)—C(11)	117.3(6)
B. 2,5-TCNQF2 anion			
F(1)—C(4)—C(6)	116.2(5)	F(11)—C(14)—C(16)	116.4(5)
F(1)—C(4)—C(15)	117.6(6)	F(11)—C(14)—C(5)	118.2(6)
C(6)—C(4)—C(15)	126.1(6)	C(16)—C(14)—C(5)	125.4(6)
C(6)—C(5)—C(14)	120.8(6)	C(16)—C(15)—C(4)	120.4(6)
C(4)—C(6)—C(5)	113.5(6)	C(14)—C(16)—C(15)	113.7(6)
C(4)—C(6)—C(7)	125.1(6)	C(14)—C(16)—C(17)	124.8(6)
C(5)—C(6)—C(7)	121.3(6)	C(15)—C(16)—C(17)	121.4(6)
C(6)—C(7)—C(8)	124.3(6)	C(16)—C(17)—C(18)	123.9(6)
C(6)—C(7)—C(9)	120.6(6)	C(16)—C(17)—C(19)	121.0(6)
C(8)—C(7)—C(9)	114.6(6)	C(18)—C(17)—C(19)	114.8(6)
C(7)—C(8)—N(1)	177.9(8)	C(17)—C(18)—N(11)	175.6(7)
C(7)—C(9)—N(2)	178.7(8)	C(17)—C(19)—N(12)	178.5(8)

[a] Estimated standard deviations are enclosed in parentheses.

to the neutral molecule, one finds the C—C single bonds, on the average, contracted (1.425A vs 1.441A) and the C=C double bonds expanded (1.413A vs 1.376A, for the exterior C=C double bond; 1.338A vs 1.328A, for the interior C=C double bond). The bond lengths of the sensitive exterior quininoid C=C double bonds (C(6)-C(7) and C(16)-C(17) in Figure 5) are similar to related bond lengths in the TCNQF4 acceptors for the unit charge-transfer complexes of HMTSF-TCNQF4 and DBTTF-TCNQF4 (1.405A and 1.412A, respectively). Thus, both the donor TTF and the acceptor 2,5-TCNQF2 geometries are suggestive of unit charge transfer for the TTF-2,5-TCNQF2 complex.

As such, the structure of TTF-2,5-TCNQF2 can be considered to be highly ionic in character and an assessment of the electrostatic contribution to the crystal cohesion (the Madelung energy) is of interest. For the purposes of this calculation, partial atomic charges[44] for the TTF$^+$ cation and the 2,5-TCNQF2$^-$ anion were computed employing the CNDO approximation for the TTF$^+$ cation and the INDO approximation for the 2,5-TCNQF2$^-$ anion and are presented in Figure 6. Utilizing these partial atomic charges, we obtain a value for the Madelung energy[45] of TTF-2,5-TCNQF2 which is −2.65 eV/donor-acceptor pair. This value is comparable to that calculated for the dimerized stack motif of DBTTF-TCNQF4 (−2.79 eV)[12] and somewhat larger than

TABLE IV

Least-squares planes and deviations (A) of individual atoms from these planes.[a]

A. TTF cation			
(1) TTF molecular plane $(-0.0480X + 0.2500Y - 0.9671Z = -1.7833\text{A})$			
S(1)	−0.033(2)	S(11)	−0.022(2)
S(2)	−0.018(2)	S(12)	−0.012(2)
C(1)	0.023(10)	C(11)	0.013(9)
C(2)	0.040(10)	C(12)	0.037(9)
C(3)	−0.022(7)	C(13)	−0.005(8)
(2) Central tetrathiaethylene plane $(-0.0493X + 0.2531Y - 0.9662Z = -1.8007\text{A})$			
S(1)	−0.008(2)	S(11)	−0.010(2)
S(2)	0.005(2)	S(12)	0.002(2)
C(3)	−0.001(7)	C(13)	0.011(8)
C(1)*	0.053(10)	C(11)*	0.021(9)
C(2)*	0.068(10)	C(12)*	0.046(9)
B. 2,5-TCNQF2 anion			
(1) 2,5-TCNQF2 molecular plane $(-0.0647X + 0.3171Y - 0.9462Z = 0.3394\text{A})$			
C(4)	0.088(8)	C(14)	−0.046(9)
C(5)	−0.055(8)	C(15)	0.066(10)
C(6)	0.025(8)	C(16)	0.002(8)
C(7)	0.049(9)	C(17)	0.041(8)
C(8)	−0.074(10)	C(18)	0.043(9)
C(9)	0.027(9)	C(19)	−0.059(10)
N(1)	−0.149(9)	N(11)	0.067(9)
N(2)	0.032(9)	N(12)	−0.115(9)
F(1)	0.181(5)	F(11)	−0.121(6)
(2) 2,5-difluoroquininoid plane $(-0.1085X + 0.3531Y - 0.9293Z = 0.4385\text{A})$			
C(4)	−0.007(8)	C(14)	0.003(9)
C(5)	−0.009(8)	C(15)	−0.026(10)
C(6)	−0.004(8)	C(16)	−0.014(8)
C(7)	0.015(9)	C(17)	0.028(8)
F(1)	0.014(5)	F(11)	0.000(6)
C(8)*	−0.179(10)	C(18)*	0.103(9)
C(9)*	0.063(9)	C(19)*	−0.141(10)
N(1)*	−0.311(9)	N(11)*	0.182(9)
N(2)*	0.124(9)	N(12)*	−0.252(9)

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

that computed for the uniform segregated stack structure of TTF-TCNQ at unit charge transfer (−2.34 eV).[46] We do note, however, that the Madelung energy contribution for the uniform segregated structure of HMTTF-TCNQ is −2.62 eV,[47] only slightly smaller than we obtain here. Thus, the lack of a substantial difference in the Madelung energy between uniform and dimerized structures indicates that there is no apparent electrostatic driving force on going from a uniform to a dimerized motif.[48]

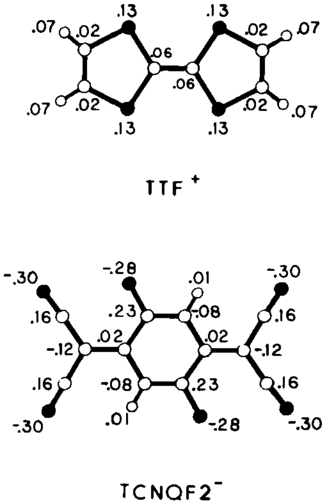


FIGURE 6 Partial atomic charges for the TTF$^+$ cation (top) and the 2,5-TCNQF2$^-$ anion (bottom) derived from MO calculations based on the observed crystalline geometry.

Finally, the question naturally arises as to the physical state of the TTF-2,5-TCNQF2 complex, i.e. whether the room-temperature structure that is presented here is susceptible to a Peierls-driven solid-state phase transformation.[23] In this regard, the dimerized-stack structure of TTF-2,5-TCNQF2 may switch to a uniform stack motif at some higher temperature, much in the same way as observed for the spin-Peierls systems (methylethylmorphilinium) $(TCNQ)_2$[49] and K-TCNQ.[50] We have examined the unit volume expansion[34] for TTF-2,5-TCNQF2 up to about 390 K, which seems to be unchanging or slightly decreasing, Figure 7. There is, however, no direct indication of a phase transition as we have observed by diffraction methods for DBTTF-TCNQF4 (~390 K)[12] and as has been found from an examination of the magnetic susceptibility for (methylethylmorpholinium) $(TCNQ)_2$,[49] K- and other alkali metal-TCNQ

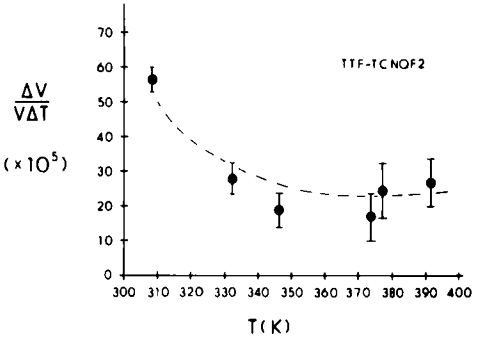


FIGURE 7 Unit volume expansion with temperature for TTF-2,5-TCNQF2 over the range 310 K to 390 K.

salts,[50–51] and HMTSF-TCNQF4.[14] Whether our diffraction studies are inadequate to delineate the phase transition, or the twinning of the present specimens mechanically mitigates against the development of the phase transformation, is a subject we are presently investigating. A study of the magnetism of TTF-2,5-TCNQF2 at elevated temperatures may provide additional information in this regard.

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SUPPLEMENTARY MATERIAL

Tables of nonhydrogen atom thermal parameters, hydrogen atom parameters and calculated and observed structure factor amplitudes have been deposited. This material may be obtained by contacting Gordon & Breach, 1 Park Avenue, New York, NY, Attn: P. Bardi, Ref. No.

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$$R_{ave} = \sum_{i=1}^{N} \sum_{j=1}^{2} |F_{ij}^2 - \bar{F}_i^2| / \sum_{i=1}^{N} \bar{F}_i^2,$$

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