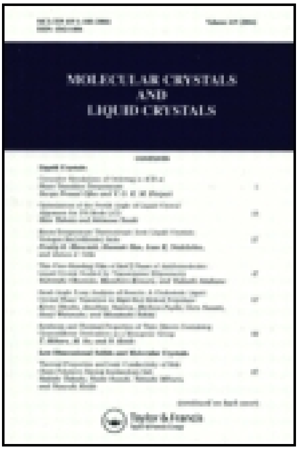

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Crystal Structure of Monofluoro-7,7,8,8-Tetracyano-p-Quinodimethane, TCNQF. Evidence for Strong One-Dimensional Coupling of Molecular Dipole Moments

F. Mitchell Wiygul [a b], Thomas J. Emge [a b], John P. Ferraris [a b] & Thomas J. Kistenmacher [a b]

[a] Contribution from the Departments of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218

[b] The University of Texas at Dallas, P.O. Box 668, Richardson, Texas, 75080

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Crystal Structure of Monofluoro-7,7,8,8-Tetracyano-*p*-Quinodimethane, TCNQF. Evidence for Strong One-Dimensional Coupling of Molecular Dipole Moments

F. MITCHELL WIYGUL,[1a] THOMAS J. EMGE,[1a] JOHN P. FERRARIS[1b] and THOMAS J. KISTENMACHER[1a]

Contribution from the Departments of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218 and The University of Texas at Dallas, P.O. Box 668, Richardson, Texas 75080

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The crystal structure of the asymmetric electron acceptor TCNQF has been determined by X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/n$, with the following primary crystallographic data: $a = 7.596(3)$A, $b = 8.204(4)$A, $c = 8.428(2)$A, $\beta = 90.90(3)°$, $V = 525.3(3)A^3$, $Z = 2$, $D_{meas} = 1.42(2)$ g cm^{-3}, $D_{calcd} = 1.405$ g cm^{-3}. The presence of two molecules per cell requires $\bar{1}(C_i)$ molecular symmetry, inconsistent with the molecular structure of TCNQF. A centrosymmetrical twin model has been developed and refined by the full-matrix least-squares method based on counter-collected intensities. The dominant intermolecular interaction in the crystal is the one-dimension coupling of TCNQF molecules through their electric dipole moments. An estimation from an LCAO-MO calculation yields a molecular dipole moment of 2.0 D for TCNQF.

INTRODUCTION

The solid-state chemistry of organic charge-transfer complexes took on a new dimension in the early 1970's with the introduction of the highly-conducting, quasi one-dimensional complex tetrathiafulvalene-tetracyanoquinodimethane, TTF-TCNQ.[2] A prerequisite for the systematic advancement of this, or any other, branch of organic charge-transfer chemistry rests largely on the synthesis and characterization of new donor and acceptor molecules.

In this regard, synthetic routes to progressively fluorinated TCNQ acceptors have recently been developed to the degree that the monofluoro,[3] TCNQF, one of the difluoro,[4] 2,5-TCNQF2, and the tetrafluoro,[5-6] TCNQF4, derivatives of TCNQ are known. Important to the charge-transfer chemistry of this family of TCNQ derivatives has been the recognition[3-4,6] that there is a monotonic increase in the electron affinity (EA) as the number of fluoro substituents is increased: EA(TCNQ) = 2.85 eV,[6-9] EA(TCNQF) = 2.95 eV,[3,6] EA(2,5-TCNQF2) = 3.02 eV, and EA(TCNQF4) = 3.20 eV.[6-7] Moreover, this systematic variation in acceptor affinity is achieved without a similar degree of variation in molecular size,[3-4] the latter point being essential to the maintenance of favorable intra- and inter-stack interactions in charge-transfer complexes. A critical display of the role of acceptor affinity in structurally homologous charge-transfer systems has come with the segregated-stack complexes HMTSF(hexamethylenetetraselenafulvalene)-TCNQF4[10-11] and HMTTF(hexamethylenetetrathiafulvalene)-TCNQF4,[12] fully-charged Mott-Hubbard insulators, which are isostructural with HMTSF-TCNQ[13] and HMTTF-TCNQ,[14] partially-charged one-dimensional conductors. Similarly, the physical property-acceptor affinity relationship is strikingly different for the complexes TTF-TCNQ and TTF-2,5-TCNQF2. Like TTF-TCNQ,[15] the structural motif for TTF-2,5-TCNQF2[16] is that of segregated stacks of donors and acceptors. However, while the stacks in partially-charged TTF-TCNQ are uniform at room temperature,[15] there is a significant dimerization observed in both the donor and acceptor stacks in fully-charged TTF-2,5-TCNQF2.[16] As a consequence, the conductivity for TTF-2,5-TCNQF2[4] is nearly seven orders of magnitude smaller than for TTF-TCNQ.

In addition to the charge-transfer chemistry of fluorinated TCNQ derivatives, we have been investigating other properties of these compounds; in particular, we have been studying the intermolecular interactions in the crystalline structures of the neutral acceptors and the relationship of these interactions to those observed in their charge-transfer complexes. We have recently shown[6] that the structure of TCNQF4 is dominated by long-range amphoteric interactions, unlike those displayed by TCNQ[17] or TCNQF4 charge-transfer complexes. In this report, we address the question of the principal intermolecular interactions in the crystalline structure of the asymmetric acceptor TCNQF, Figure 1. Of the presently known fluorinated TCNQ derivatives, TCNQF is the sole example with a permanent molecular dipole moment. The role of such a permanent moment on self association and the creation of periodic (ordered) or aperiodic (disordered) potentials arising from the dipolar field of extended systems is central to the chemistry of TCNQF. Our present study suggests that dipolar fields in the crystal structure of TCNQF are critical to the determination of its primary structural motif.

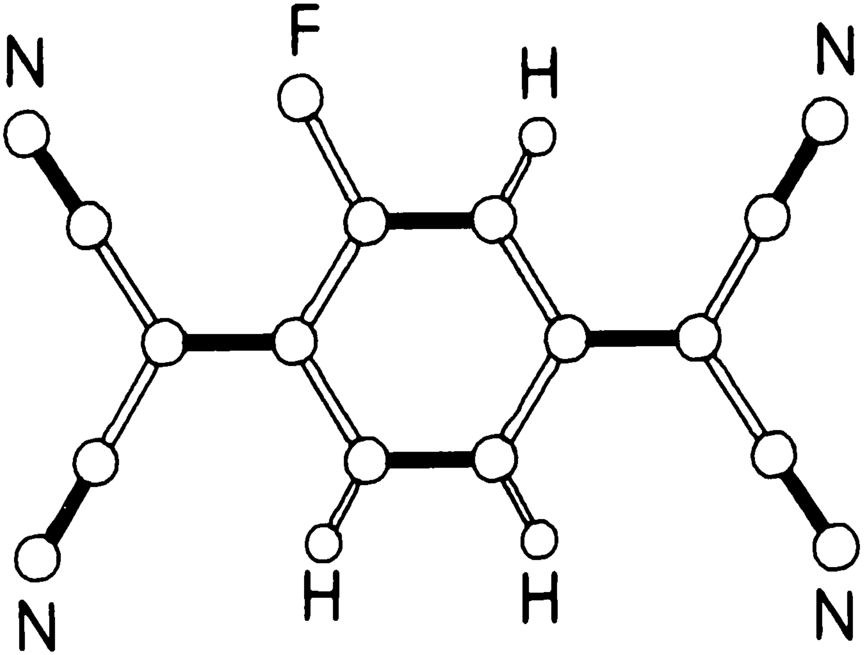

FIGURE 1 The idealized molecular structure of the TCNQF molecule. Shaded bonds indicate bond orders greater than unity in the quinone resonance form.

EXPERIMENTAL

The TCNQF utilized in the study was synthesized according to the published procedure.[3] Crystals were obtained by slow evaporation of saturated solutions with dry, distilled acetonitrile as the solvent. The harvested crystals were golden-orange in color and plate-like (001) in habit; many of the crystals were ill-formed or had obvious imperfections. Preliminary X-ray photographic data indicated monoclinic symmetry and systematic absences [$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$] consistent with the space group $P2_1/n[C^5_{2h}]$. The crystal density, 1.42(2) g cm^{-3}, was measured by the neutral buoyancy method in a mixture of cyclohexane and carbon tetrachloride. Cell parameters and intensity data were obtained from a well-formed, optically clear platelet possessing the following crystal faces and mean dimensions: (001)-$(00\bar{1})$ 0.090 mm, (101)-$(\bar{1}0\bar{1})$ 0.312 mm, (011)-$(0\bar{1}\bar{1})$ 0.40 mm, $(01\bar{1})$-$(0\bar{1}1)$ 0.40 mm. Standard crystallographic data are as follows: $a = 7.596(3)$A, $b = 8.204(4)$A, $c = 8.428(2)$A, $\beta = 90.90(3)°$, $V = 525.2(3)\text{A}^3$. The calculated crystal density for $Z = 2$ [based on a mol wt of 222.2 for $C_{12}N_4H_3F$] is 1.405 g cm^{-3};

in space group $P2_1/n$, the presence of two formula units per cell demands $\bar{1}(C_i)$ molecular symmetry for the TCNQF molecule. As such a requirement is clearly inconsistent with the noncentrosymmetrical molecular structure of TCNQF, Figure 1, we expected disorder or twinning in the specimens under examination.

Intensity data were collected on a Syntex automated diffractometer, employing graphite-monochromatized MoKα ($\bar{\lambda} = 0.71069$A) radiation and the $\theta/2\theta$ scan mode [scan rate of 1.5° min^{-1} in 2θ]. The intensities of the 2508 reflections in the + h hemisphere to $2\theta = 55°$ were surveyed. The intensities of three standards were monitored after every 100 reflections and showed no unusual or systematic variation over the course of the data collection. From the presence of broad and ofttimes split diffraction profiles, we interpret the crystal under study as an intimate, centrosymmetric intergrowth twin. The overall consequences of the twin nature of the crystalline specimen will become apparent.

The measured intensities were assigned observational variances based on counting statistics plus a term $(pI)^2$, where p was taken to be 0.03 and represents the expected error proportional to the diffracted beam intensity.[18] The intensities and their estimated standard deviations were corrected for Lorentz and polarization effects. An absorption correction was also applied based on the crystal dimensions and face assignments given above and a calculated linear absorption factor of 1.13 cm^{-1}. The maximum and minimum transmission factors were 0.99 and 0.96, respectively. A symmetry-averaged set of 1130 (out of a possible 1216) non-zero reflections formed the basis of the structure solution and refinement. The R value on averaging[19] over the two independent quadrants of data was 0.043. An approximate scale factor was derived by the method of Wilson.[20]

A centrosymmetric model for the nonhydrogen atom structure of TCNQF was readily obtained by direct methods employing the MULTAN series of programs.[21] Subsequent isotropic refinement of this model by full-matrix least squares, minimizing the quantity $\Sigma w(|F_o|-|F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, gave an R value $(= \Sigma||F_o|-|F_c||/\Sigma|F_o|)$ of 0.13 for the reflection data with $\sin\theta/\lambda \leq 0.5$. Two further cycles of refinement were then computed employing anisotropic thermal parameters and the complete set of data. A difference-Fourier synthesis at this stage allowed the positioning of the unique quininoid hydrogen atom labeled H(2). In addition, we introduced another hydrogen atom, called H(1), along the C—F bond of the centrosymmetrical TCNQF model. The contribution from the hydrogen atoms was included in subsequent cycles but no attempt was made to refine any of their parameters. Two further cycles of refinement produced convergence (maximum shift/error of 0.3) and a final R value of 0.103. The final weighted R $\{= [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ and goodness-of-fit values $\{[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$,

TABLE I

Final atomic parameters[a]

Atom	x	y	z	B_{AVE}[c]
F[b]	1662(5)	2650(5)	1537(5)	7.5
N(1)	−740(4)	5340(3)	2019(4)	7.0
N(2)	−5210(5)	3024(4)	−277(5)	8.5
C(1)	813(4)	1301(3)	739(4)	4.6
C(2)	−1768(4)	33(3)	−459(4)	4.9
C(3)	−1008(4)	1431(3)	307(3)	4.2
C(4)	−1979(4)	2801(3)	609(3)	4.3
C(5)	−1278(4)	4204(4)	1403(4)	4.9
C(6)	−3764(5)	2910(4)	129(4)	5.7
H(1)[b]	137	220	125	6.0
H(2)	−298	6	−78	6.0

[a] Nonhydrogen atom coordinates × 10^4; hydrogen atom coordinates × 10^3. Values in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure.

[b] Atomic population factors of 0.5.

[c] Equivalent isotopic thermal parameters derived from the anisotropic thermal coefficients for the nonhydrogen atoms. See the deposited material.

where NO = 1130 non-zero observations and NV = 82 parameters} were 0.090 and 3.7, respectively. A final difference-density synthesis showed a maximum peak of 0.65 e/A^3 near H(2) and may be indicative of a very small percentage of two-fold or mirror twin domains.

Neutral scattering factors for the nonhydrogen[22] and the hydrogen[23] atoms were taken from common sources. The scattering curves for the nonhydrogen atoms were corrected for anomalous dispersion effects.[24] Final atomic positional parameters are collected in Table 1. Tables of thermal parameters and a list of final calculated and observed structure factor amplitudes are available.[25] The crystallographic computations were carried out with a standard set of computer programs.[26]

RESULTS

The average molecular dimensions for the TCNQF molecule as found in its crystal structure are presented in Figure 2 (bond lengths) and Table 2 (bond angles). Perhaps surprisingly, the centrosymmetric averaging imposed by the twinned nature of the crystal may not have had a dramatic effect on the molecular distances. We note, in particular, that the observed bond lengths, C(1)—C(2)′ = 1.336(4)A and C(3)—C(4) = 1.370(4)A, for the formal double bonds in the quinone resonance structure for TCNQF, Figures 1 and 2, are virtually equivalent to those found in TCNQ,[17] 1.334(3)A and 1.373(3)A, and

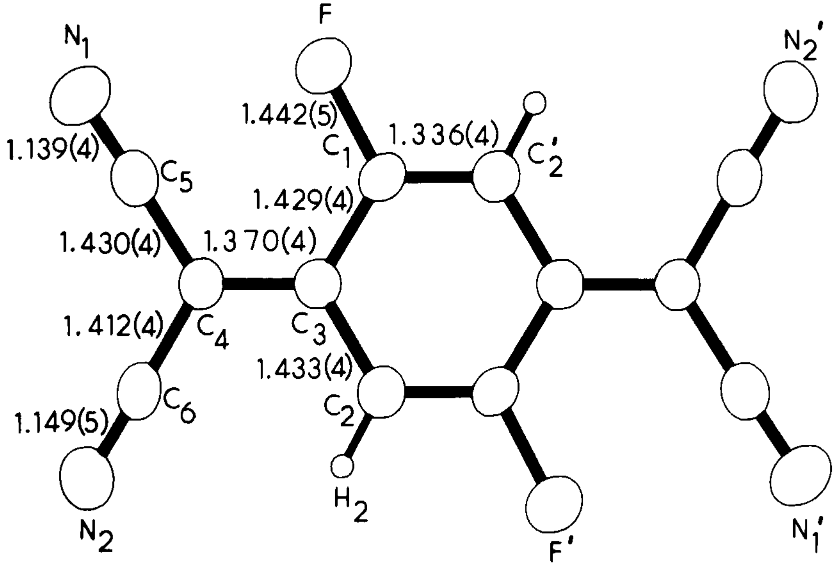

FIGURE 2 The molecular geometry for the TCNQF molecule as observed in its crystal structure.

TCNQF4,[6] 1.334(2)A and 1.372(2)A. Similarly, the formal single bond lengths [C(1)—C(3), C(2)—C(3), C(4)—C(5) and C(4)—C(6), Figure 2] average to 1.426(9)A, a value only slightly smaller than those found in TCNQ,[17] 1.439(5)A, and in TCNQF4,[6] 1.437(2)A. A basis for this rather striking agreement may be found in our previous detailed comparison[6] of the molecular geometries of TCNQ and TCNQF4. There, we showed that the effects of the fluoro substituents were in the main confined to the intramolecular bond angles, with only minor differences noted for the intramolecular bond lengths. Thus, the average bond lengths presented in Figure 2 for TCNQF may, in fact, be only slightly different from their respective individual contributors.

For the intramolecular bond angles, the situation is surely more complicated, and we hesitate to make any detailed comparison between the average values determined here and those for the uncomplicated TCNQ[17] and

TABLE II

Intramolecular bond angles for the nonhydrogen atoms[a]

F—C(1)—C(2)'	118.1(3)°	C(2)—C(3)—C(4)	121.7(3)°
F—C(1)—C(3)	119.0(3)	C(3)—C(4)—C(5)	123.3(3)
C(2)'—C(1)—C(3)	122.8(3)	C(3)—C(4)—C(6)	121.1(3)
C(1)'—C(2)—C(3)	121.3(3)	C(5)—C(4)—C(6)	115.6(3)
C(1)—C(3)—C(2)	115.9(3)	C(4)—C(5)—N(1)	178.7(4)
C(1)—C(3)—C(4)	122.4(3)	C(4)—C(6)—N(2)	178.8(5)

[a] Primed atoms are related to unprimed atoms by the symmetry transform $-x$, $-y$, $-z$.

TABLE III

Planarity of the fluoroquininoid ring in TCNQF and deviations (A) of individual atoms from this plane

In the equation of the plane below, *X*, *Y*, and *Z* are coordinates(A) referred 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 equally weighted.

$$(0.2671X + 0.3739Y - 0.8882Z = 0.0A)$$

F	∓.006A	C(4)	∓0.000A
C(1)	±0.008	C(5)	∓0.025*
C(2)	∓0.003	C(6)	±0.032*
C(3)	±0.004	N(1)	∓0.030*
		N(2)	±0.079*

TCNQF4[6] analyses. We do wish to note, however, that for all but one bond angle [C(3)—C(4)—C(6)] we find values for the intramolecular bond angles for TCNQF lying between those found in TCNQ and TCNQF4. That the C(3)—C(4)—C(6) bond angle in TCNQF at 121.1(3)° is essentially identical to that found in TCNQ,[17] 121.9(2)°, and ~2° smaller than found in TCNQF4,[6] 123.5(1)°, is consistent with the realization that even in the presence of the centrosymmetric averaging process this bond angle is not subjected to the steric influence of the fluoro substituent.

The average TCNQF molecule is nominally planar, Table 3. The relatively small deviations of the atoms of the malonitrile moiety from the plane of the fluoroquininoid nucleus are probably related to the imposed symmetry averaging.

The twin-averaged crystal structure of TCNQF is presented in Figure 3. Consistent with the macroscopic crystal morphology, the structure of TCNQF can be qualitatively separated into layers parallel to the (001) plane.

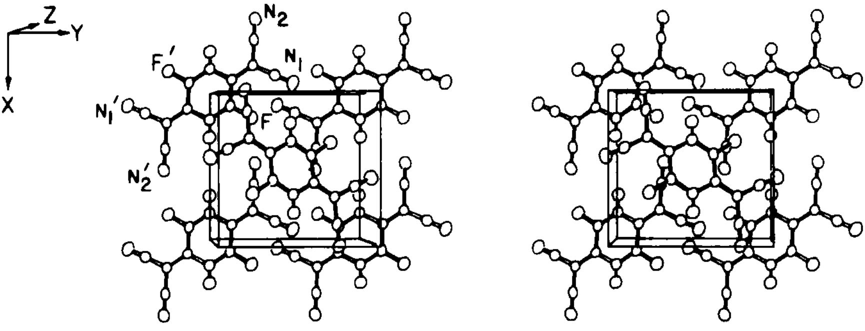

FIGURE 3 A stereoview of the crystal structure of TCNQF, viewed approximately normal to the (001) crystallographic plane.

Each layer consists of parallel, but not coplanar (interplanar distance = 3.07A), TCNQF molecules. Interlayer extension is primarily achieved through two contacts, each with a distance near that expected for a dispersive, van der Waals (vdW) interaction:[27] F . . . C(6)[1/2 + x, 1/2 − y, 1/2 + z] = 3.084(5)A, vdW sum = 3.10A; N(1) . . . C(6)[−1/2 − x, 1/2 + y, 1/2 − z] = 3.224(6)A, vdW sum = 3.25A. The intralayer coupling along the *a* axis consists of the favorable dispersive interaction through the F . . . N(2)[1 + x, y, z] contact at 2.862(6)A (vdW sum = 2.85A) and the through space interaction of TCNQF molecular dipoles.

It is, however, the rather intimate nature of the intermolecular interactions along the crystallographic *b* axis that we find most intriguing, Figure 3. About crystallographic inversion centers of the type (0, 1/2, 0), one finds the C(5)—N(1) cyano groups of symmetry-related TCNQF molecules in anti-parallel orientations at very close quarters: C(5) . . . C(5)[−x, 1 − y, −z] = 3.348(6)A, vdW sum = 3.50A; N(1) . . . C(5)[−x, 1 − y, −z] = 3.309(5)A, vdW sum = 3.25A, and similarly for the inverse contact C(5) . . . N(1)[−x, 1 − y, −z]. We believe that the anti-parallel coupling of the local C≡N bond moments provides a means through which strong one-dimensional interaction of the permanent molecular dipole moments of the TCNQF molecules can be achieved.

Obviously, even a qualitative description of the relative degree of dipolar interaction along the *b* axis must rely on an estimate of the electric dipole moment for the TCNQF molecule. In an attempt to provide such an estimate, we have computed the net atomic charges for TCNQF, utilizing the INDO approximation[28] and the observed crystalline molecular structure with the simple positioning of a hydrogen atom off the carbon atom directly opposite the C—F bond. The net atomic charges given by the LCAO-MO calculation are presented in Figure 4 and are similar to those obtained for TCNQF4 by the same methodology.[29] From the net charges, with a nominal contribution from atomic rehybridization,[28] we obtain a calculated dipole moment ($|\bar{\mu}_{calc}|$) of 2.0 D.

Two aspects of the calculated dipole moment are of interest: (1) $|\bar{\mu}_{calc}|$ as obtained by the INDO method is reasonable since it is similar to, although larger than, that experimentally determined for fluorobenzene (1.60 D);[30] (2) the major contribution to the magnitude of μ_{calc} is the local C—F bond dipole, estimated from the calculated charges to be ~1.9 D. However, there is sufficient polarization of the malonitrile moiety near the fluoro substitution, Figure 4, so that $\bar{\mu}_{calc}$ is canted by ~34° to the C—F bond and lies within 5° of being parallel to the short in-plane molecular axis. While the magnitude and orientation of $\bar{\mu}_{calc}$ for TCNQF are subject to the usual errors associated with the INDO procedure and the utilization here of the uncorrected crystalline geometry, they are a basis upon which some aspects of the observed crystalline motif can be rationalized.

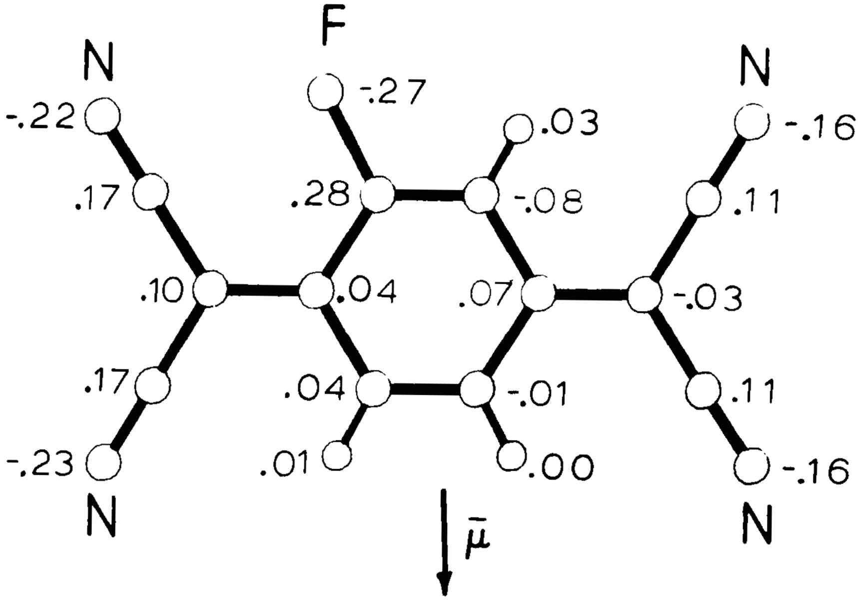

FIGURE 4 Calculated net atomic charges of TCNQF. The calculated molecular dipole moment has a magnitude of 2.0 D and an orientation nearly parallel to the short in-plane molecular axis.

DISCUSSION

In the previous section, we have presented a detailed description of the twinned crystal structure for the acceptor TCNQF. We have also given an estimate of its permanent electric dipole moment. The dominant intermolecular coupling is along the crystallographic *b* axis, Figure 3, with an intimate, anti-parallel orientation of the cyano groups of adjacent TCNQF molecules. A reasonable hypothesis is that this coupling of terminal cyano groups provides an efficient mechanism through which the permanent electric dipoles on individual TCNQF molecules electrostatically interact.

In Figure 5, we present two possible renditions for the untwinned molecular interaction motif along the *b* axis. The first case invokes anti-parallel coupling of dipole moments(ACDM), while the second offers the possibility of parallel coupling of dipole moments(PCDM). Each of these one-dimensional motifs yields the observed twinned structure upon the addition of the $\bar{1}$ twinning operation, Figure 5. Given the apparently large electric dipole moment for TCNQF, we prefer the ACDM motif based on its favorable electrostatic contribution to the crystal cohesion.

The observation that the one-dimensional coupling of molecular dipole moments is the dominant interaction in the structure of TCNQF is, as ex-

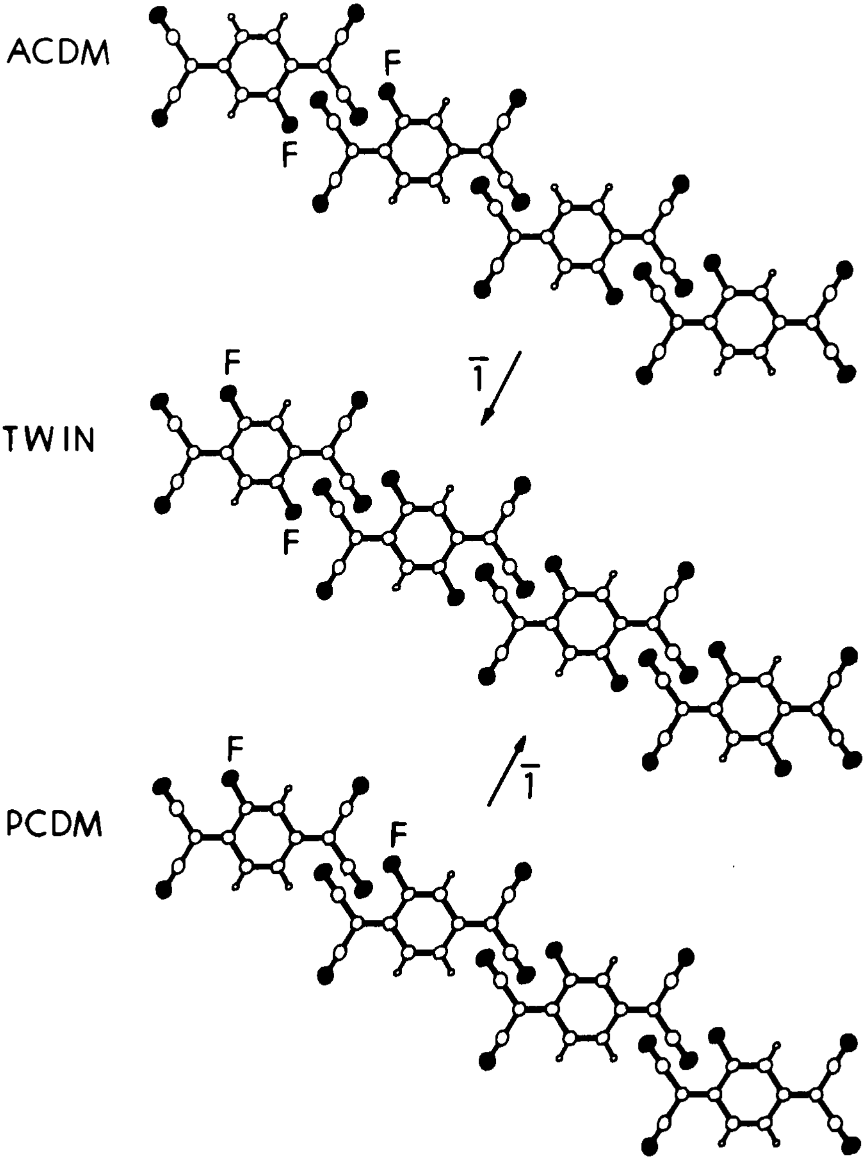

FIGURE 5 Comparison of two possible coupling schemes for the molecular dipole moments along the one-dimensional chains parallel to *b* and the inversion-generated twin structure. (A) ACDM - ordered anti-parallel coupling of dipole moments; (B) TWIN - the observed twin motif; (C) PCDM - ordered parallel coupling of dipole moments. Note that in each chain, the molecules are parallel but not coplanar (see Figure 3 and the text).

pected, in contrast to observations on the solid-state structures of non-dipolar TCNQ[17] and TCNQF4.[6] The structure of TCNQ is dominated by intermolecular stacking and local dipole-induced dipole coupling, while the structure of TCNQF4 exhibits subtle amphoteric donor/acceptor interactions. We are presently investigating the crystalline structure of 2,5-TCNQF2 to see where within this scheme its structure and intermolecular interactions can be placed.

The dilution of the intermolecular dipolar coupling shown by TCNQF on the formation of some of its charge-transfer complexes[3] allows disorder and may suppress the metal-insulator or insulator-insulator transition common to charge-transfer complexes of TCNQ, TCNQF2 and TCNQF4. On the other hand, charge-transfer complexes of TCNQF with asymmetric electron donors offer the possibility of donor-acceptor dipolar coupling, and systems of this type are presently under investigation.

Acknowledgments

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Supplementary Material

Tables of atomic thermal parameters and observed and calculated structure factor amplitudes have been deposited.

This material may be obtained by contacting Gordon & Breach, One Park Avenue, New York, NY 10016, attn: P. Bardi, Ref. No. MCLC81-1001.

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

    where N = the total number of unique reflections.
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26. Crystallographic programs employed include Germain, Main and Woolfson's MULTAN; Busing, Martin and Levy's ORFLS; Zalkin's FORDAP; Pippy and Ahmed's MEAN PLANE; and Johnson's ORTEP. Calculations other than those specifically noted were performed with locally written programs.
27. Van der Waals radii employed are as follows: H, 1.2A; F, 1.35A; N, 1.50A; C, 1.75A. Values are from L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 3rd. Ed., 1960.
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