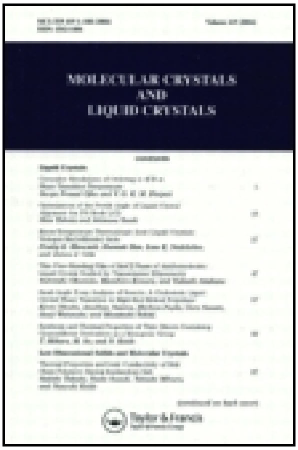

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# Elements of the Crystal Structure of a Solvated 1 : 1 Charge-Transfer Salt Derived from Tetrathiafulvalene (TTF) and Tetrafluorotetracyano-*p*-Quinodimethane (TCNQF4), TTF-TCNQF4

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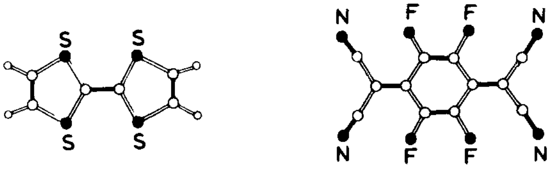
The 1 : 1 charge-transfer salt TTF-TCNQF4 crystallizes (from cyclohexane/acetonitrile) in the monoclinic system, space group $P2/m$, with $a = 16.562(4)$ Å, $b = 10.728(4)$ Å, $c = 7.013(1)$ Å, $\beta = 97.39(2)°$, $V = 1235.6$ Å$^3$. A structural solution has been obtained by Patterson–Fourier methods and refined (based on 2107 non-zero $F_0$'s) to an $R$ value of 0.18. The crystal structure of solvated TTF-TCNQF4 consists of segregated stacks of donors and acceptors propagating along the $c$ axis. Parallel to these columnar arrays are solvent channels of unresolved composition. Disorder within these solvent channels prevents a detailed description of their contents; the basic elements of the donor and acceptor stacks are, however, well-defined. The TCNQF4 acceptor column is both distance and overlap modulated (eclipsed, dimeric interaction at a mean separation of 3.25 Å, and ring-over-bond, monomeric interaction at 3.43 Å). The TTF donor column shows analogous eclipsed and ring-over-bond overlap patterns; however, the distance alternation (3.49 Å and 3.51 Å, respectively) is within experimental error (±0.02 Å in each case).

## INTRODUCTION

The strong electron acceptor TCNQF4[1] has become one of the principal components of low-dimensional organic charge-transfer salts. Because of the high electron affinity of TCNQF4 (3.20 eV),[2-5] most of these salts are thought to have unit charge transfer from the donor to the TCNQF4 acceptor. Examples of such systems with heterofulvalene donors are HMTSF (hexamethylenetetraselenafulvalene)-TCNQF4[6] and HMTTF (hexamethylenetetrathiafulvalene)-TCNQF4,[7] which are segregated-stack Mott insulators exhibiting a spin-Peierls instability at low temperature. More recently, the donor DTTTF (dithienotetrathiafulvalene) has been shown to crystallize as a 1 : 1 salt with TCNQF4 from solution[8] in two forms; both are Mott insulators, but one exhibits a uniform segregated-stack motif while the other consists of dimerized segregated stacks.[9] This latter form is similar in structure to the salt DBTTF (dibenzotetrathiafulvalene)-TCNQF4,[10] which shows evidence for a high-temperature phase transition (ca. 390 K) that is likely driven by the electron spin system.

In addition, Keller and coworkers[11-12] have shown that TMPD-(*N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine)-TCNQF4 contains regular mixed-stacks of alternating TMPD donors and TCNQF4 acceptors,[11] while NBP[5-(1-butyl)phenazine]-TCNQF4 exhibits an unusual mixed-stack structure consisting of repeating donor and acceptor diads.[12] In this context, Sandman and coworkers[13] have recently synthesized several salts of TCNQF4, with 1,1,4,4-tetrathiabutadiene donors, which also likely contain mixed stacks of donors and acceptors.

The parent low-dimensional organic salt with TCNQF4 as the acceptor can be considered to be TTF(tetrathiafulvalene)-TCNQF4 (Figure 1). This salt was originally synthesized and electrically characterized (compaction resistivity at room temperature of ca. $4 \times 10^3$ Ω cm) several years ago by Wheland and Gillson.[14] In the course of our systematic studies on TCNQF4 and its salts, it was decided that a knowledge of the structural properties of TTF-TCNQF4 was important to any comprehensive understanding of the crystal chemistry of its progeny. Thus, we have examined the crystal structure of solution-grown TTF-TCNQF4 and report our results briefly here. Our analysis is hampered by the presence in the structure of disordered solvent channels.



TTF TCNQF4

FIGURE 1 Molecular topology for the TTF donor and the TCNQF4 acceptor.

## EXPERIMENTAL

Crystals of TTF-TCNQF4 were grown in an H-tube. Solutions of the components in acetonitrile were placed in each arm, and the H-tube was then filled with cyclohexane. Needle-like crystals were harvested after several days. Crystal quality was such that a specimen suitable for diffraction study was obtained only with considerable difficulty.

Preliminary Weissenberg photographs indicated a monoclinic lattice. Lack of any systematic absences implied one of the space groups *P*2, *Pm* or *P*2/*m*; *P*2/*m* has been used throughout our analysis.

Unit-cell dimensions and estimated standard deviations, obtained from a least-squares fit to the setting angles (Syntex P$\bar{1}$ automated diffractometer) of 15 carefully-selected reflections, were: $a = 16.562(4)$ Å, $b = 10.728(4)$ Å, $c = 7.013(1)$ Å, $\beta = 97.39(2)°$, $V = 1235.6$ Å$^3$. The crystal density, measured by the neutral buoyancy technique in $CCl_4/CHBr_3$, was 1.57(2) g/cm$^3$. The calculated crystal density for a 1 : 1 salt with 2 molecules per unit cell is 1.29 g/cm$^3$; clearly some constituents of the crystal structure are not described by a simple 1 : 1 stoichiometry of donor to acceptor.

Intensity data were collected on the diffractometer using graphite-monochromatized MoK$\alpha$ radiation ($\bar{\lambda} = 0.71069$ Å) and the $\theta$–$2\theta$ scan mode to a maximum $2\theta$ of 50°. The scan rate (in $2\theta$) varied from 1.5°/min to 3.0°/min. The intensities of three standards were monitored after every 97 reflections and indicated no large variation in crystal stability over the course of the experiment.

Estimated standard deviations in the collected intensities were assigned as $\sigma_I = [\sigma_c^2 + (0.03I)^2]^{1/2}$, where $\sigma_c$ was derived from counting statistics.[15] The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was attempted.

A total of 2107 unique non-zero data (for each of which at least two symmetry-equivalent intensities were averaged) were used in the structural solution and refinement. The *R* value on averaging[16] was 0.064. An approximate scale factor was determined by the method of Wilson.[17]

A structural solution was initiated from a Patterson synthesis, which revealed molecular stacking along the *c* axis and allowed the position and orientation of the TTF donor to be deduced. Subsequent difference-Fourier maps yielded atomic positions for the TCNQF4 acceptor. In this model, both the donor and acceptor molecules are required to possess at least $m(C_s)$ symmetry, with the normal to the mirror plane parallel to the *b* axis of the cell and the short in-plane molecular axis of both components. Least-squares refinement, minimizing the quantity

$\Sigma w(|F_O| - |F_c|)^2$ [where $w = 4F_O^2/\sigma^2 (F_O^2)$] and including anisotropic thermal factors, led to an $R$ value $(\Sigma||F_O| - |F_c||/\Sigma|F_O|)$ of 0.24. A difference-Fourier map showed rather structureless areas of electron density forming channels along $c$—one intersecting the $ab$ plane at $x = 1/2$, $y = 0$ and one at $x = 0, y = 1/2$. We assume that disordered molecules are present in these channels, either acetonitrile or cyclohexane or, less likely owing to packing constraints, excess donor or acceptor molecules. An attempt was made to model these channels using carbon atoms with low population parameters and fixed positions. In addition, reflection data with (sin $\theta/\lambda$) less than 0.15 Å$^{-1}$ were excluded from the data set as these reflections would be most affected by the inadequacies of the solvent channel model. Further refinement reduced the $R$ value to 0.18; additional refinement was not judged worthwhile as a final difference—Fourier synthesis allowed no improvement in the model for the solvent regions.

TABLE I

Final positional and equivalent isotropic thermal parameters[a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| (a) TTF donor | | | | |
| S(1) | 748(2) | 1354(3) | 2464(4) | 4.5 |
| S(2) | −1187(2) | 1361(3) | 2718(4) | 4.4 |
| C(1) | 1693(9) | 590(10) | 2262(15) | 5.4 |
| C(2) | −2074(8) | 593(9) | 2775(13) | 4.7 |
| C(3) | 260(14) | $0^b$ | 2496(20) | 3.6 |
| C(4) | −659(16) | $0^b$ | 2547(20) | 5.0 |
| (b) TCNQF4 acceptor | | | | |
| C(5) | 7419(9) | 3930(15) | 5056(16) | 5.3 |
| C(6) | 6920(12) | $5000^b$ | 4612(23) | 3.7 |
| C(7) | 6128(10) | $5000^b$ | 3770(20) | 2.7 |
| C(8) | 5645(9) | 3921(11) | 3268(16) | 4.5 |
| C(9) | 4885(8) | 3881(10) | 2436(16) | 3.7 |
| C(10) | 4407(11) | $5000^b$ | 1948(19) | 2.8 |
| C(11) | 3626(11) | $5000^b$ | 1173(23) | 3.8 |
| C(12) | 3156(9) | 3801(16) | 543(15) | 5.5 |
| F(1) | 6053(5) | 2805(6) | 3650(12) | 8.3 |
| F(2) | 4516(5) | 2839(6) | 2029(12) | 7.4 |
| N(1) | 7823(8) | 2971(13) | 5451(17) | 7.3 |
| N(2) | 2770(9) | 2986(11) | 98(19) | 7.6 |
| (c) Solvent atoms | | | | |
| C(A)[c] | 5000 | $0^b$ | 2700 | 8.0 |
| C(B)[c] | 3920 | $0^b$ | 3700 | 5.0 |
| C(C)[c] | 4200 | $0^b$ | 5800 | 5.0 |
| C(D)[d] | 1050 | $5000^b$ | 7400 | 5.0 |

[a] Positional parameters × $10^4$ (with esd's in parentheses);
[b] Fixed by symmetry;
[c] Population of 0.15;
[d] Population of 0.30.

We note that in an earlier report of TTF-TCNQF4[14] elemental analysis seemed to indicate a simple 1 : 1 stoichiometry. However, differences in sample preparation and handling may well be responsible for differing degrees of solvation.

Neutral scattering factors for the nonhydrogen atoms were taken from a common source.[18] Final derived positional parameters are collected in Table I. Tables of thermal parameters, molecular geometry, least-squares planes and final observed and calculated structure-factor amplitudes have been deposited. The crystallographic computations were carried out with a standard set of computer programs.[19]

## RESULTS AND DISCUSSION

The crystal structure of solvated TTF-TCNQF4 is presented in the unit-cell projections of Figure 2. The dominant elements of the crystal structure are the presence of segregated, columnar arrays of molecular donors and acceptors. The relative openness of the crystal structure is evident from the (001) projection, with solvent containing channels propagating along the crystallographic *c* axis, Figure 2. The constitution of these solvent channels is unanswered in this study, although likely candidates are cyclohexane and acetonitrile—the solvents from which the crystals were obtained. Such a conjecture is consistent, for example, with the crystal chemistry of the mixed-stack benzidine-TCNQ system,[20] which exhibits several solvated complexes (acetone, acetonitrile, dichloromethane, 1,2-dichloroethane and benzene solvates) as well as a solvent-free form. It cannot be completely ruled out, however, that these channels could accommodate to a degree excess donor or acceptor molecules (see, for example, Ref. 21). What our analysis does suggest is that for TTF-TCNQF4 the structure within these channels is disordered; and, in the likely case of occupation by cyclohexane or acetonitrile, the channel composition may be variable in both content and time.

Of particular interest for the crystal structure of TTF-TCNQF4 is the nature of the intermolecular interactions within the donor and acceptor columns. For the acceptor stacks, significant distance modulation is observed, with alternate interplanar spacings of 3.25(2) Å and 3.43(2) Å. Pairs of acceptors separated by 3.25 Å will be referred to as "dimers". The intradimer overlap pattern is displayed in Figure 3C and is clearly indicative of a nearly eclipsed motif. The intradimer separation in the TCNQF4 column in TTF-TCNQF4 is slightly larger than that found in the eclipsed dimers in DBTTF-TCNQF4 (3.18(1) Å),[10] but essentially equal to those found in the nearly eclipsed dimers

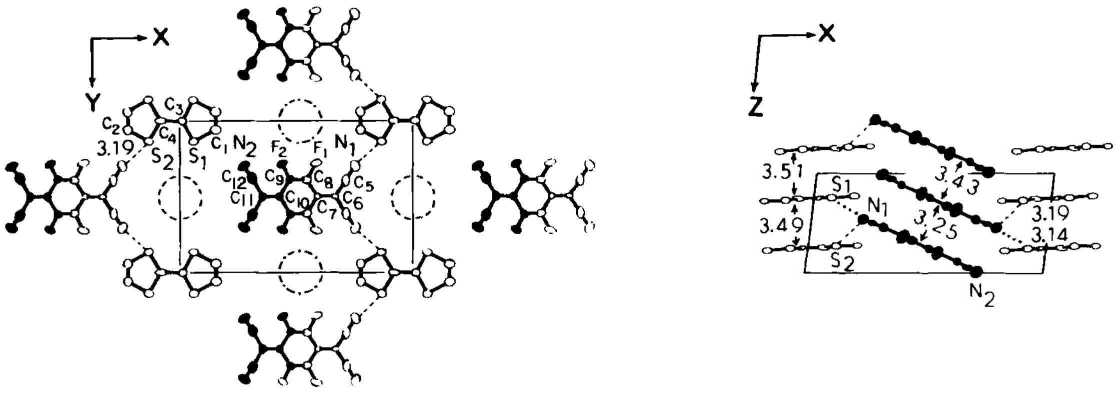


FIGURE 2 The (001) and (010) projections for the crystal structure of TTF-TCNQF4. In the (001) projection, the (– – – –) and (–•–•) circles denote solvent channels along the *c* axis. The principal interchain *S* • • • *N* contacts are also indicated where appropriate in each view.

in TTF-2,5-TCNQF2 (3.23(1) Å)[22] and the uniform, ring-over-bond acceptor stack in HMTSF-TCNQF4 (3.24(1) Å).[6]

The interdimer interaction in the TCNQF4 column displays a ring-over-bond overlap pattern (Figure 3D) and a mean separation (3.43 Å) which is suggestive of a weaker interaction. Similarly, the weaker interdimer interactions in the acceptor columns of DBTTF-TCNQF4 (3.54(1) Å)[10] and TTF-2,5-TCNQF2 (3.55(1) Å)[22] exhibit a ring-over-bond overlap pattern.

Within the TTF donor column, a quite different situation obtains. While alternate pairs of donors display an eclipsed or a ring-over-bond overlap pattern (Figures 3A and 3B), the distance modulation is weak (3.49(2) Å *vs.* 3.51(2) Å) and, in fact, is within our error limits. This is in contrast to DBTTF-TCNQF4[10] and TTF-2,5-TCNQF2[22] where significant distance variation along the donor stack (3.35(1) Å/3.65(1) Å for DBTTF-TCNQF4 and 3.34(1) Å/3.60(1) Å for TTF-2,5-TCNQF2) accompanies the alternate overlap patterns.

Finally, the high room-temperature resistivity[14] and the presence of "dimerized" donor and acceptor columns in the crystal structure of TTF-TCNQF4 (as in similar systems[9,10,22]) suggest that this likely unit-charge transferred salt is susceptible to a high-temperature, spin-driven phase transition[23] (such a transition has been observed at ca. 390 K in the closely-related compound DBTTF-TCNQF4[10]). Unfortunately, the

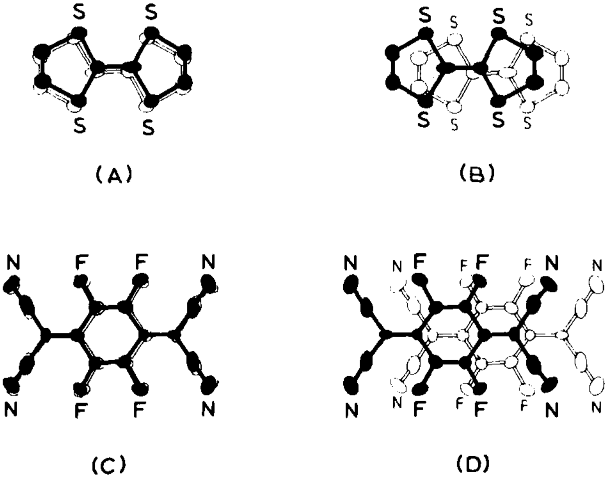


FIGURE 3 Molecular overlap patterns for: (A) the "dimer" interaction in the TTF column (mean separation (D) = 3.49 Å); (B) the "monomer" interaction in the TTF column (D = 3.51 Å); (C) the "dimer" interaction in the TCNQF4 column (D = 3.25 Å); and, (D) the "monomer" interaction in the TCNQF4 column (D = 3.43 Å).

quality and stability of crystals presently available do not allow for experimentation designed to further probe the crystal physics of TTF-TCNQF4.

## Acknowledgments

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## Supplementary material

Tables of atomic thermal parameters, intramolecular geometry, and observed and calculated structure factor amplitudes have been deposited. This material may be obtained by contacting Gordon and Breach, One Park Avenue, New York, NY 10016.

## References

1. R. C. Wheland and E. L. Martin, *J. Org. Chem.*, **40,** 3101 (1975).
2. A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **63,** 2369 (1967).
3. C. E. Klots, R. N. Compton and V. F. Raaen, *J. Chem. Phys.*, **60,** 1177 (1974).
4. E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63,** 3183 (1975).
5. T. J. Emge, M. Maxfield, D. O. Cowan and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, **65,** 161 (1981).
6. M. E. Hawley, T. O. Poehler, T. F. Carruthers, A. N. Bloch, D. O. Cowan and T. J. Kistenmacher, *Bull. Am. Phys. Soc.*, **23,** 424 (1978).
7. J. B. Torrance, J. J. Mayerle, K. Bechgaard, B. D. Silverman and Y. Tomkiewicz, *Phys. Rev. B*, **22,** 4960 (1980).
8. P. Shu, L. Chiang, T. Emge, D. Holt, T. Kistenmacher, M. Lee, J. Stokes, T. Poehler, A. Bloch and D. Cowan, *J. Chem. Soc. Chem. Commun.*, **920** (1981).
9. W. A. Bryden, T. J. Emge, J. P. Stokes, A. N. Bloch, D. O. Cowan and T. J. Kistenmacher, to be published.
10. T. J. Emge, W. A. Bryden, F. M. Wiygul, D. O. Cowan, T. J. Kistenmacher and A. N. Bloch, *J. Chem. Phys.*, in press.
11. Z. G. Soos, H. J. Keller, K. Ludolf, J. Queckborner, D. Wehe and S. Flandrois, *J. Chem. Phys.*, **74,** 5287 (1981).
12. R. H. Harms, H. J. Keller, D. Nothe, D. Wehe, N. Heimer, R. M. Metzger, D. Gundel and H. Sixl, *Mol. Cryst. Liq. Cryst.*, **85,** 249 (1982).
13. D. J. Sandman, G. D. Zoski, W. A. Burke, G. P. Hamill, G. P. Ceasar and A. D. Baker, *J. Chem. Soc. Chem. Commun.*, **829** (1981).
14. R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98,** 3916 (1976).
15. W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26,** 563 (1957).
16. The $R$ value on averaging over the two quadrants of data is given by

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

where $N =$ the total number of unique observations.
17. A. J. C. Wilson, *Nature* (London), **150,** 151 (1942).

18. H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Crystallogr.*, **17,** 1040 (1964).
19. Crystallographic programs employed include: Busing, Martin and Levy's ORFLS (modified); Zalkin's FORDAP; Pippy and Ahmed's MEAN PLANE; Johnson's ORTEP.
20. (a) K. Yakushi, I. Ikemoto and H. Kuroda, *Acta Crystallogr.*, **B30,** 835 (1974); (b) I. Ikemoto, K. Chikaishi, K. Yakushi and H. Kuroda, *Acta Crystallogr.*, **B28,** 3502 (1972); (c) K. Yakushi, I. Ikemoto and H. Kuroda, *Acta Crystallogr.*, **B30,** 1738 (1974).
21. T. J. Kistenmacher, T. E. Phillips, D. O. Cowan, J. P. Ferraris, A. N. Bloch and T. O. Poehler, *Acta Crystallogr.*, **B32,** 539 (1976).
22. T. J. Emge, F. M. Wiygul, J. P. Ferraris and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, **79,** 327 (1982).
23. (a) E. Pyte, *Phys. Rev. B,* **10,** 4637 (1974); (b) I. S. Jacobs, J. W. Bray, H. R. Hart, L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober and J. C. Bonner, *Phys. Rev. B,* **14,** 3036 (1976).