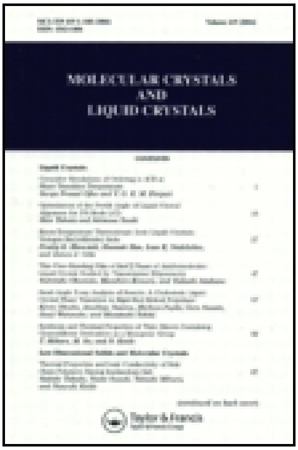
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 21 February 2013, At: 11:33
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystal Structure of the 2:1 Charge-Transfer Salt Derived from Hexamethylenetetraselenafulvalen (HMTSF) and 7,7,8,8-Tetracyano-p-Quinodimethane (TCNQ), $(HMTSF)_2(TCNQ)$

Thomas J. Emge [a] , Wayne A. Bryden [a] , Dwaine O. Cowan [a] & Thomas J. Kistenmacher [a]

[a] Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218

Version of record first published: 20 Apr 2011.

To cite this article: Thomas J. Emge , Wayne A. Bryden , Dwaine O. Cowan & Thomas J. Kistenmacher (1982): Crystal Structure of the 2:1 Charge-Transfer Salt Derived from Hexamethylenetetraselenafulvalene (HMTSF) and 7,7,8,8-Tetracyano-p-Quinodimethane (TCNQ), $(HMTSF)_2(TCNQ)$, Molecular Crystals and Liquid Crystals, 90:1-2, 173-184

To link to this article: http://dx.doi.org/10.1080/00268948208076180

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1982, Vol. 90, pp. 173–184
0026-8941/82/9002-0173$06.50/0
© 1982 Gordon and Breach, Science Publishers, Inc.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

Crystal Structure of the 2:1 Charge-Transfer Salt Derived from Hexamethylenetetraselenafulvalene (HMTSF) and 7,7,8,8-Tetracyano-*p*-Quinodimethane (TCNQ), $(HMTSF)_2(TCNQ)$

THOMAS J. EMGE, WAYNE A. BRYDEN, DWAINE O. COWAN
and THOMAS J. KISTENMACHER

Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland 21218

(*Received April 5, 1982*)

The 2:1 charge-transfer salt $(HMTSF)_2(TCNQ)$ crystallizes (from mesitylene) in the monoclinic system, space group $P2_1/c$, with the following cell constants: $a = 13.993(4)$ Å, $b = 10.723(3)$ Å, $c = 13.032(3)$ Å, $\beta = 112.71(2)°$, $V = 1803.8$ Å^3, $D_{\mathrm{measd}} = 2.10(1)$ g cm^{-3}, $D_{\mathrm{calcd}} = 2.114$ g cm^{-3} (for two formula units per cell). The crystal structure of $(HMTSF)_2(TCNQ)$ consists of linear chains of alternating donor diads and acceptor monads propagating along the crystallographic *b* axis. Within these mixed stacks, the donor/donor overlap is of the ring-over-double bond type (mean separation 3.72 Å), while the donor/acceptor overlap (mean separation 3.46 Å) is such that the HMTSF molecule is very nearly parallel to and directly centered above the adjacent TCNQ molecule. Strong interstack interactions of the types Se(HMTSF)···Se(HMTSF), 3.64 Å, and Se(HMTSF)···N(TCNQ), 3.29 Å, serve to couple adjacent mixed stacks. The crystal structure of this 2:1 salt is compared to that of its 1:1 stoichiometric congener, HMTSF-TCNQ, whose crystal structure exhibits uniform segregated stacks of donor and acceptor molecules.

INTRODUCTION

7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)[1] and its analogs have become frequently used electron acceptors in the synthesis of organic

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

charge-transfer salts which exhibit diverse physical and structural characteristics. Much of the interest in these salts has centered around the quasi one-dimensional nature of their physical properties.[2]

Quasi one-dimensionality arises, at the most fundamental level, from the nature of the crystalline motif. A well-known occurrence[3] is the presence in the solid-state structure of linear, segregated stacks of donors (*D*) and acceptors (*A*), which can give rise through π–π molecular orbital overlap to narrow one-dimensional electronic bands. Partial transfer of electron density from the donor band to the acceptor band can lead to materials with nearly one-dimensional conductivities on the order of 10^3 Ω^{-1} cm^{-1}.[2] Examples of segregated stack conductors for heterofulvalene-TCNQ salts are TTF-TCNQ,[4] TMTTF-TCNQ,[5] TMTSF-TCNQ,[6] HMTTF-TCNQ[7] and HMTSF-TCNQ.[8,9] Alternatively, transfer of one electron from the donor to the acceptor yields half-filled donor and acceptor bands and leads to materials which are Mott insulators (typified by HMTTF-TCNQF4[10] and HMTSF-TCNQF4[11]). Such systems with antiferromagnetic coupling between adjacent spins are prone to the spin-Peierls' instability,[12] whereby the spin energy may be lowered by a structural dimerization. Two materials have been reported (TTF-2,5-TCNQF2[13] and DBTTF-TCNQF4[14]) where the pair-wise coupling of neighboring spins is apparently strong enough to produce dimerized segregated stacks of donors and acceptors at room temperature. In addition, it has recently been reported[15] that the salt DTTTF-TCNQF4 co-crystallizes from solution in two forms. It is now known[16] that both forms of DTTTF-TCNQF4 are Mott insulators, with one form consisting of uniform segregated stacks and the other exhibiting dimerized segregated stacks at room temperature.

Quasi one-dimensionality can also be imparted to the physical properties of an organic charge-transfer salt through the formation of stacks of alternating donor and acceptor molecules (i.e., mixed stacks).[17–18] Pertinent examples here are DBTTF-TCNQ,[19] DBTTF-2,5-TCNQF2,[20] and a second, insulating form of TMTSF-TCNQ.[21]

Such mixed stack arrays are not confined, however, to a simple (···*DADA*···) repeat sequence. An alternative pattern (given the presence of mixed stacks) is expected for a salt of other than 1 : 1 stoichiometry. Such a situation pertains to (TETTF) $(TCNQ)_2$,[22] which exhibits a (···*DAADAA*···) repeat. It has also been reported, however, that a 1 : 1 salt can show an "anomalous" sequence; for the salt NBP-TCNQF4, Keller and coworkers[23] found mixed stacks which contain alternating diads of donors and acceptors (···*DDAADDAA*···).

In this study, the crystal structure of the semiconducting salt

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

$(HMTSF)_2(TCNQ)$ is examined and found to contain mixed stacks of donor diads and acceptor monads ($\cdots$*DDADDA*$\cdots$), consistent with its 2 : 1 stoichiometry. Of particular interest is the fact that the HMTSF donor and the TCNQ acceptor also form a 1 : 1 salt (HMTSF-TCNQ), which is highly conductive to very low temperatures and exists as segregated stacks of donors and acceptors.[8]

EXPERIMENTAL

The 2 : 1 charge-transfer salt $(HMTSF)_2(TCNQ)$ appeared to be the only product after slow cooling of a hot mesitylene solution containing the neutral components[1,24] in a sealed ampule. This result is, however, not highly reproducible as under identical experimental conditions the 1 : 1 salt can predominate. The obtained crystals of $(HMTSF)_2(TCNQ)$ were small, dark-green platelets, while those of HMTSF-TCNQ were black, acicular needles.

The crystal of the 2 : 1 salt employed in our X-ray diffraction analysis was free of any observable imperfections and measured $0.08 \times 0.20 \times 0.07$ mm^3. X-Ray photographic data indicated that the crystal system was monoclinic and the space group $P2_1/c$. A neutral buoyancy measurement ($CCl_4/CHBr_3$) gave an experimental crystal density of 2.10(1) g cm^{-3}.

The following unit-cell dimensions and associated standard deviations were derived from a least-squares fit to the setting angles of 15 carefully-centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer: $a = 13.993(4)$ Å, $b = 10.723(3)$ Å, $c = 13.032(3)$ Å, $\beta = 112.71(2)°$ and $V = 1803.8$ Å^3. The calculated crystal density, assuming two formula units per cell, was 2.114 g cm^{-3}, requiring that only acceptor molecules lie on sites of special symmetry ($\bar{1}$, C_i). In the $+h$ hemisphere to $2\theta = 60°$, 10,742 reflections were surveyed on the diffractometer, employing graphite-monochromatized MoKα radiation ($\bar{\lambda} = 0.71069$ Å) and the $\theta/2\theta$ scan mode. A constant scan rate of 1.5°/min (in 2θ) was maintained for each diffraction profile. After every 100 reflections, three standard reflections were monitored and their intensities showed no unusual variation throughout data collection. The measured intensities and their estimated standard deviations were corrected for Lorentz and polarization effects. An absorption correction was also applied based on the crystal dimensions given above and the associated linear absorption coefficient ($\mu = 87.5$ cm^{-1}) [maximum and minimum transmission factors were 0.60 and 0.38, respectively]. Averaging of the two independent quadrants of data re-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

sulted in an R_{ave} value of 0.060

$$\left(R_{\text{ave}} = \sum_{i=1}^{N}\sum_{j=1}^{2}|F^2_{ij} - \bar{F}^2_i| \Big/ \sum_{i=1}^{N} \bar{F}^2_i \quad \text{for } N \text{ observations}\right).$$

The averaged, non-zero F_0's (4868) formed the basis for the structural solution and refinement and were scaled according to the method of Wilson.[25]

Standard Patterson methods were used to locate the Se atom positions and the relative orientations of the HMTSF and TCNQ molecules. This vector synthesis confirmed that the acceptors occupy $\bar{1}$ symmetry sites and that the donors lie in general positions. All other non-hydrogen atom positions were obtained by Fourier and difference-Fourier techniques. At an intermediate stage of the refinement, the 14 unique hydrogen atoms were located on the basis of a difference-Fourier synthesis, but positioned *via* calculated coordinates (fixed isotropic temperature factors were used for the H atoms).

TABLE I

Final non-hydrogen atom positional parameters (× 10^4) for $(\text{HMTSF})_2(\text{TCNQ})$

Atom	*x*	*y*	*z*
Se(1)	−1135(1)[a]	1650(1)	−1574(1)
Se(2)	−555(1)	1585(1)	1068(1)
Se(3)	1375(1)	2089(1)	−1150(1)
Se(4)	2005(1)	1968(1)	1503(1)
C(1)	−2182(5)	1500(7)	−1025(6)
C(2)	−3311(5)	1301(8)	−1660(6)
C(3)	−3777(6)	1408(9)	−769(7)
C(4)	−2884(6)	1231(8)	358(7)
C(5)	−1955(5)	1448(7)	62(6)
C(6)	−68(5)	1758(7)	−99(5)
C(7)	914(5)	1915(6)	34(5)
C(8)	2784(5)	2287(7)	−164(6)
C(9)	3964(6)	2456(9)	−481(7)
C(10)	4577(6)	2602(13)	644(8)
C(11)	4157(6)	2384(9)	1541(6)
C(12)	3018(5)	2226(7)	936(6)
N(1)	−3519(5)	4661(8)	−2455(6)
N(2)	−2837(6)	4397(8)	1054(6)
C(13)	−693(5)	4966(7)	−1104(6)
C(14)	−314(6)	4884(7)	892(6)
C(15)	−1072(5)	4839(7)	−240(6)
C(16)	−2114(6)	4674(7)	−461(6)
C(17)	−2880(6)	4691(8)	−1581(7)
C(18)	−2505(6)	4522(8)	391(7)

[a] Estimated deviations in the least significant figures are enclosed in parentheses.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

Full-matrix least-squares refinement of all non-hydrogen positional and anisotropic thermal parameters resulted in a final R value $[R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ of 0.066 for the 3315 data with $F_0 > 3\sigma(F_0)$, and 0.098 for the full 4868 data set. The final weighted R value (full data) $[R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2}]$ and goodness-of-fit $[\mathrm{GOF} = \{\Sigma w(|F_0| - |F_c|)^2/(NO\text{-}NV)\}^{1/2}$ where $NO = 4868$ observations and $NV = 217$ variables] were 0.060 and 1.86, respectively. The quantity minimized in the least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 4F_0^2/\sigma^2(F_0^2)$ with $\sigma^2(F_0^2)$ derived from counting statistics plus an applied correction term of $[(0.03)F_0^2]$. A final difference-Fourier map contained residual density peaks of ± 1.65 $e/\text{Å}^3$ in the vicinity of the Se atoms.

Neutral scattering factors for the nonhydrogen[26a] and hydrogen[26b] atoms were taken from common sources. The scattering curves for the nonhydrogen atoms were corrected for the effects of anomalous dispersion.[26c] Final derived position parameters for the nonhydrogen atoms are given in Table I. Tables of nonhydrogen atom anisotropic thermal parameters, hydrogen atom positional and isotropic thermal parameters, intramolecular bond angles, and final observed and calculated structure-factor amplitudes have been deposited. The crystallographic computations were carried out with a standard set of computer programs,[27a] including Johnson's algorithm[27b] from which all illustrations were prepared.

RESULTS AND DISCUSSION

The crystal structure of (HMTSF)$_2$(TCNQ), as illustrated in Figure 1, consists of stacks of alternating donor diads and acceptor monads, extending along the crystallographic b axis. Within these columns, the interplanar separations between two donors and between donor and acceptor are 3.72 Å and 3.46 Å, respectively. The donor–donor spacing is somewhat long compared to a HMTSF uniform-stack separation as found in the crystal structures of HMTSF-TCNQ[8] (3.60 Å) and HMTSF-TNAP[28] (3.58 Å), but near to that observed in HMTSF-TCNQF4[11] (3.68 Å). The donor–acceptor interplanar distance within a stack is on the same order as that observed (ca. 3.5 Å) in the structures of the insulating form of TMTSF-TCNQ[21] and (TETTF) (TCNQ)$_2$,[22] the only other heterofulvalene-TCNQ mixed-stack systems reported to data. Crystallographic symmetry requires that the components of the donor diads be parallel; the interplanar dihedral angle between the

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

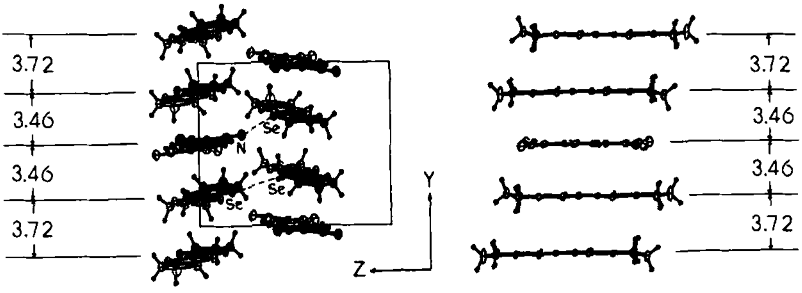


FIGURE 1 Two views of the molecular packing in the crystal structure of $(HMTSF)_2(TCNQ)$. (LEFT) A projection onto the (100) crystallographic plane; (RIGHT) The ($\cdots DDADDA \cdots$) columnar stack viewed along the short in-plane molecular axis of the HMTSF donor. Intermolecular interactions of the types Se(1)$\cdots$N(2; x, $1/2 - y$, $-1/2 + z$) at 3.29 Å and Se(3)$\cdots$Se(4; x, $1/2 - y$, $-1/2 + z$) at 3.64 Å are indicated.

tetraselenaethylene moiety of the HMTSF donor and the quinone ring of the TCNQ acceptor at 0.01° indicates nearly parallel donor diads and acceptor monads as well. In Table II, selected mean planes are given, which demonstrate the general planarity of the TCNQ molecule and the slight boat-shaped conformation of the HMTSF molecule.

The donor–donor interactions within a mixed stack are weak, with all Se$\cdots$Se contacts greater than or equal to 4.08 Å (which is some 0.08 Å larger than twice the van der Waals radius (*vdW*) of Se, 2.0 Å).[29] The observed molecular overlap pattern within donor diads (see Figure 2A) is the common ring-over-bond motif[2] found in uniform HMTSF stacks. The uniform stack systems exhibit, however, somewhat shorter intrastack Se$\cdots$Se contacts: HMTSF-TCNQ[8] (3.89 Å); HMTSF-TNAP[28] (3.92 Å); and, HMTSF-TCNQF4[11] (4.02 Å).

The donor–acceptor interactions for $(HMTSF)_2(TCNQ)$ are stronger than those within the donor diad (Figure 1 and Table III). The direct overlap of HMTSF and TCNQ molecules (Figure 2B) permits Se atoms of the donor to interact with C atoms of the quinone framework of the acceptor, Table III. The result is the presence of Se$\cdots$C contacts as close as 3.57 Å or ca. 0.2 Å less than the expected *vdW* sum.[29] Similar Se$\cdots$C contacts (3.5–3.6 Å) are found between alternating TMTSF donors and TCNQ acceptors in the insulating form of TMTSF-TCNQ.[21]

Strong interactions also serve to couple together the mixed ($\cdots DDADDA \cdots$) stacks in the crystal structure of $(HMTSF)_2(TCNQ)$, Table III. Contacts of particular note in this regard (see Figure 1) include Se(3)$\cdots$Se(4) at 3.64 Å (*vdW* = 4.0 Å) and Se(1)$\cdots$N(2) at 3.29 Å (*vdW* = 3.50 Å). These close contacts couple molecules of different stacks which are near to coplanarity, with a dihedral angle be-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

TABLE II

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

In each of the equations of the planes, X, Y and Z are coordinates (Å) referred to the orthogonal axis X along a, Y parallel to b, and Z along c^*. Atoms indicated by an asterisk (*) were given zero weight in calculating the plane; all others were equally weighted.

(a) HMTSF central, fulvalene plane ($0.1304X - 0.9914Y - 0.0130Z = -1.8788$ Å)

Se(1)	0.046(1)	C(8)	−0.031(8)
Se(2)	0.006(1)	C(12)	−0.013(8)
Se(3)	0.003(1)	C(2)	0.027(9)*
Se(4)	0.030(1)	C(3)	−0.245(10)*
C(1)	−0.031(8)	C(4)	0.015(9)*
C(5)	−0.022(8)	C(9)	−0.019(10)*
C(6)	0.006(8)	C(10)	−0.014(14)*
C(7)	0.007(6)	C(11)	−0.022(10)*

(b) HMTSF interior plane ($0.1325X - 0.9911Y - 0.0108Z = -1.8610$ Å)

Se(1)	0.023(1)	C(3)	−0.274(10)*
Se(2)	−0.012(1)	C(4)	−0.010(9)*
Se(3)	−0.013(1)	C(5)	−0.045(8)*
Se(4)	0.021(1)	C(8)	−0.041(8)*
C(6)	−0.012(8)	C(9)	−0.026(10)*
C(7)	−0.008(6)	C(10)	−0.107(14)*
C(1)	−0.056(8)*	C(11)	−0.025(10)*
C(2)	−0.003(9)*	C(12)	−0.020(8)*

(c) TCNQ molecular plane ($0.1298X - 0.9908Y - 0.0371Z = -5.3124$ Å)

N(1)	∓0.009(9)	C(15)	±0.003(8)
N(2)	∓0.009(9)	C(16)	±0.013(8)
C(13)	±0.032(8)	C(17)	∓0.021(9)
C(14)	∓0.032(8)	C(18)	±0.010(9)

(d) TCNQ central, quinone plane ($0.1284X - 0.9917Y - 0.0110Z = -5.3168$ Å)

C(13)	∓0.003(8)	C(17)	∓0.066(9)*
C(14)	∓0.003(8)	C(18)	±0.028(9)*
C(15)	∓0.003(8)	N(1)	∓0.081(9)*
C(16)	±0.003(8)	N(2)	±0.049(9)*

tween molecular planes (either $D \cdots D$ or $D \cdots A$) of 15.3°. Significantly weaker interchain contacts couple together the alternating donor–acceptor stacks in the insulating form of TMTSF-TCNQ (Se···Se at 3.76 Å and Se···N at 3.56 Å).[21]

In fact, Se···Se interchain interactions as short as those exhibited by $(HMTSF)_2(TCNQ)$ are rarely found in selenafulvalene-acceptor salts. The closest example known to us is that found in the uniform-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

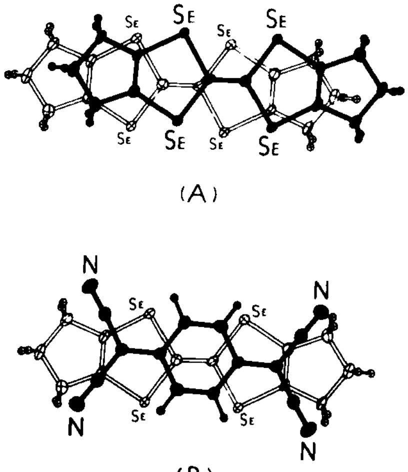


FIGURE 2 (A) Intradiad molecular overlap pattern for two HMTSF donors; the view direction is along the normal to the molecular plane and the mean separation is 3.72 Å. (B) Donor diad/acceptor monad overlap pattern; the view direction is again along the normal to the molecular planes and the mean separation is 3.46 Å.

TABLE III

Some intermolecular interactions for the crystal structure of $(HMTSF)_2(TCNQ)$

Contact	Distance (Å)	*vdW* (Å)
(A) Interstack Interactions		
(1) Donor···Donor:		
Se(3)···Se(4; *x*, 1/2 − *y*, −1/2 + *z*)	3.64	4.00
Se(2)···Se(3; *x*, 1/2 − *y*, 1/2 + *z*)	3.86	4.00
Se(1)···Se(2; *x*, 1/2 − *y*, −1/2 + *z*)	3.95	4.00
(2) Donor···Acceptor:		
Se(1)···N(2; *x*, 1/2 − *y*, −1/2 + *z*)	3.29	3.50
(B) Intrastack Interactions, [Donor···Acceptor, only]		
Se(2)···C(14; *x*, *y*, *z*)	3.57	3.75
Se(1)···C(13; *x*, *y*, *z*)	3.62	3.75
Se(3)···C(14; −*x*, 1 − *y*, −*z*)	3.64	3.75
Se(4)···C(13; −*x*, 1 − *y*, −*z*)	3.70	3.75

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

stack salt HMTSF-TNAP (Se···Se at 3.76 Å and Se···N at 3.05 Å).[28] For $(HMTSF)_2(TCNQ)$ and HMTSF-TNAP, these interchain interactions increase the dimensionality of the system. The influence of Se···Se interactions on the dimensionality of stacked organic systems is particularly evident for the superconducting salts of TMTSF: $(TMTSF)_2X$ ($X = PF_6^-$, AsF_6^- and ClO_4^-).[30] In these systems, Se···Se interchain interactions, which are considerably weaker (ca. 3.9 Å) than those found here, are likely contributors[30] to the three-dimensional nature of their superconductivity.[31]

Less noteworthy are the Se···N interchain interactions in $(HMTSF)_2(TCNQ)$. As in the case of HMTSF-TNAP alluded to above, the Se···N contacts here are also longer than in HMTSF-TCNQ[8] (3.16 Å); however, this latter segregated stack structure shows no intercolumn Se···Se contacts of any consequence.

Finally, the direct mode of overlap between donor diads and acceptor monads (Figure 2B) ought to yield a near zero charge-transfer integral given the nature of the frontier molecular orbitals on the HMTSF donor (b_{1u} in point group D_{2h}) and the TCNQ acceptor (b_{2g} in point group D_{2h}). If the overlap integral between donor diads and acceptor monads is really zero, then the transfer of charge from the donor to the acceptor cannot be fractional—indeed, it must be identically zero or unity.[32]

In an attempt to estimate the actual degree of charge transfer in $(HMTSF)_2(TCNQ)$, the molecular geometries of the constituents have been analyzed, particularly those features which are expected to be sensitive to charge transfer.[21] The bond lengths within the HMTSF donor and the TCNQ acceptor are depicted in Figure 3. Bond angles have been deposited. Corrections to the derived molecular geometries for rigid-body librational effects[33] were on the order of the *esd*'s, but are not applied to the parameters given here. The interior and exterior Se—C bond lengths for the HMTSF donor (which average 1.92 and 1.88 Å, respectively) are more divergent than those for the HMTSF donor in HMTSF-TCNQ (1.89 and 1.90 Å)[8] and HMTSF-TCNQF4 (1.88 and 1.87 Å),[11] both of which are known to have high degrees of charge transfer. In addition, the central C=C bond of the donor (1.33 Å) is shorter in $(HMTSF)_2(TCNQ)$ than in HMTSF-TCNQ (1.36 Å) and HMTSF-TCNQF4 (1.38 Å). Both of these observations suggest a low degree of charge transfer for the 2:1 salt.

Similarly, variations in molecular geometry with charge transfer for the TCNQ acceptor have been thoroughly studied.[34-36] From the observed molecular geometry of the TCNQ acceptor in $(HMTSF)_2(TCNQ)$ displayed in Figure 3B and applying a recent empirical method,[21] a

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

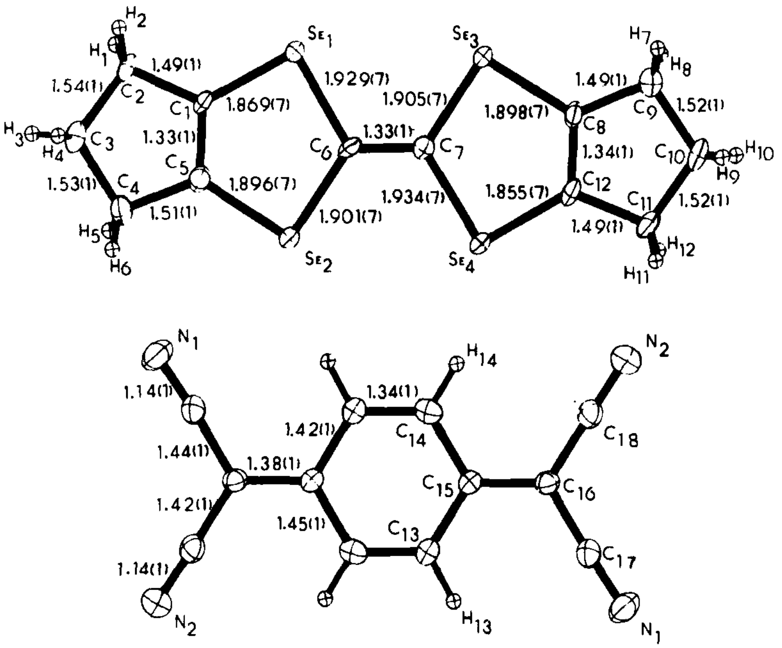


FIGURE 3 Molecular topology and intramolecular bond lengths for the HMTSF donor (TOP) and the TCNQ acceptor (BOTTOM).

charge transfer of *ca.* 0.3*e* to the TCNQ acceptor is estimated. The charge on each donor molecule would in this case be 0.15*e*. If the charge transfer in (HMTSF)$_2$(TCNQ) is indeed other than zero, then it is likely[21] that excited states of *g* symmetry of the HMTSF donor contribute significantly to the realization of a non-zero charge-transfer integral.

In summary, the crystal structure of the weakly ionized salt (HMTSF)$_2$(TCNQ) is composed of mixed stacks of alternating donor diads and acceptor monads. Strong interactions of the types Se···Se and Se···N serve to couple weakly-interacting mixed stacks into a two-dimensional network. Quite opposite conditions prevail in its 1 : 1 congener HMTSF-TCNQ, where intrachain interactions within segregated stacks are fairly strong, interstack interactions are weaker and charge transfer is high.

Acknowledgments

This investigation was supported by the National Science Foundation under grants DMR 78-23957 and 80-15318.

Supplementary Material

Tables of nonhydrogen atom thermal parameters, hydrogen atom parameters, intramolecular bond angles, 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.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

References

1. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
2. (a) I. F. Schegolev, *Phys. Stat. Solidi*, **12**, 9 (1972); (b) F. H. Herbstein, in *Perspectives in Structural Chemistry*, Vol IV, J. D. Dunitz and J. A. Ibers, Eds., John Wiley and Sons, New York (1971); (c) A. F. Garito and A. J. Heeger, *Acct. Chem. Res.*, **7**, 232 (1974); (d) J. B. Torrance, *Acct. Chem. Res.*, **12**, 79 (1979); (e) A. N. Bloch, *Acct. Chem. Res.*, in press.
3. T. J. Kistenmacher, *Ann. N. Y. Acad. Sci.*, **313**, 333 (1978).
4. (a) J. P. Ferraris, D. O. Cowan, V. Walatka and J. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973); (c) T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, *Acta Crystallogr.*, **B30**, 763 (1974).
5. (a) J. P. Ferraris, T. O. Poehler, A. N. Bloch and D. O. Cowan, *Tett. Lett.*, 2553 (1973); (b) T. E. Phillips, T. J. Kistenmacher, A. N. Bloch, J. P. Ferraris and D. O. Cowan, *Acta Crystallogr.*, **B33**, 422 (1977).
6. (a) A. N. Bloch, T. F. Carruthers, T. O. Poehler and D. O. Cowan, in *Chemistry and Physics of One-Dimensional Metals*, H. J. Keller, Ed., Plenum Press, New York (1977), pp. 47–58; (b) K. Bechgaard, T. J. Kistenmacher, A. N. Bloch and D. O. Cowan, *Acta Crystallogr.*, **B33**, 417 (1977).
7. (a) R. L. Greene, J. J. Mayerle, R. R. Schumaker, G. Castro, P. M. Chaikin, S. Etemad and S. J. La Placa, *Solid State Commun.*, **20**, 943 (1976); (b) D. Chasseau, G. Comberton, J. Gaultier and C. Hauw, *Acta Crystallogr.*, **B34**, 689 (1978); (c) B. D. Silverman and S. J. La Placa, *J. Chem. Phys.*, **69**, 2585 (1978).
8. (a) A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle and R. H. Banks, *Phys. Rev. Lett.*, **34**, 1561 (1975); (b) T. E. Phillips, T. J. Kistenmacher, A. N. Bloch and D. O. Cowan, *J. Chem. Soc. Chem. Commun.*, 344 (1976).
9. Abbreviations mentioned in the text are: TCNQ (tetracyano-*p*-quinodimethane); TCNQF4 and 2,5-TCNQF2 (perfluoro-TCNQ and 2,5-difluoro-TCNQ); TNAP (tetracyano-3,7-naphthoquinodimethane); TTF (tetrathiafulvalene); TMTTF, HMTTF, DBTTF, DTTTF, and TETTF (tetramethyl-TTF; hexamethylene-TTF; dibenzo-TTF; dithieno-TTF; and, tetraethyl-TTF); HMTSF and TMTSF (hexamethylene- and tetramethyl-tetraselenafulvalene); NBP (5-(1-butyl)-phenazine).
10. J. B. Torrance, J. J. Mayerle, K. Bechgaard, B. D. Silverman and Y. Tomkiewicz, *Phys. Rev. B*, **22**, 4960 (1980).
11. 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).
12. (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).
13. T. J. Emge, F. M. Wiygul, J. P. Ferraris and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, **78**, 295 (1981).
14. T. J. Emge, W. A. Bryden, F. M. Wiygul, A. N. Bloch, D. O. Cowan and T. J. Kistenmacher, *J. Chem. Phys.*, in press.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:33 21 February 2013

15. 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).
16. W. A. Bryden, T. J. Emge, J. P. Stokes, A. N. Bloch, D. O. Cowan and T. J. Kistenmacher, to be published.
17. Z. G. Soos, *Ann. Rev. Phys. Chem.*, **25**, 121 (1974).
18. P. J. Strebel and Z. G. Soos, *J. Chem. Phys.*, **53**, 4077 (1970).
19. (a) R. N. Lyubovska, *Izv. Akad. Nauk SSSR Ser. Khim.*, 177 (1975); (b) M. T. Jones, R. Kellerman, A. Troup and D. J. Sandman, *Proc. Intl. Conf. on Low Dimensional Synthetic Metals*, Helsingor, Denmark (1980); (c) T. J. Kistenmacher, T. J. Emge, F. M. Wiygul, W. A. Bryden, J. S. Chappell, J. P. Stokes, L. Y. Chiang, D. O. Cowan and A. N. Bloch, *Solid State Commun.*, **39**, 415 (1981).
20. T. J. Emge, F. M. Wiygul, J. S. Chappell, A. N. Bloch, J. P. Ferraris, D. O. Cowan and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, **87**, 137 (1982).
21. T. J. Kistenmacher, T. J. Emge, A. N. Bloch and D. O. Cowan, *Acta Crystallogr.*, **B38**, 1193 (1982).
22. J. L. Galinge, J. M. Fabre and L. Giral, *Acta Crystallogr.*, **B33**, 3827 (1977).
23. 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).
24. K. Bechgaard, D. O. Cowan, A. N. Bloch and L. Henriksen, *J. Org. Chem.*, **40**, 746 (1975) and references therein.
25. A. J. C. Wilson, *Nature* (*London*), **150**, 151 (1942).
26. (a) H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); (b) R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); (c) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
27. (a) Crystallographic programs used include Wehe, Busing and Levy's ORABS, Busing, Martin and Levy's ORFLS (modified), Zalkin's FORDAP, and Pippy and Ahmed's MEAN PLANE; (b) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).
28. T. J. Kistenmacher, M. Rossi, D. O. Cowan and A. N. Bloch, to be published.
29. Van der Waals radii employed include the following: Se (2.0 Å); C (1.75 Å); N (1.5 Å). Values taken from L. Pauling, *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca (1960).
30. (a) N. Thorup, G. Rindorf, H. Soling and K. Bechgaard, *Acta Crystallogr.*, **B37**, 1236 (1981); (b) F. Wudl, *J. Am. Chem. Soc.*, **103**, 7064 (1981); (c) K. Bechgaard, K. Caneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pederson and J. C. Scott, *J. Am. Chem. Soc.*, **103**, 2442 (1981).
31. K. Murata, H. Anzai, G. Saito, K. Kajimura and T. Ishiguro, *J. Phys. Soc.* (*Japan*), **50**, 3529 (1981).
32. (a) H. M. McConnell, B. M. Hoffman and R. M. Metzger, *Proc. Natl. Acad. Sci.*, **53**, 46 (1965); (b) P. L. Nordio, Z. G. Soos and H. M. McConnell, *Ann. Rev. Phys. Chem.*, **17**, 237 (1966).
33. A rigid-body analysis of the thermal motion for the TCNQ molecule and the tetraselenaethylene moiety of the HMTSF molecule was performed employing the methodology of V. Schomaker and K. N. Trueblood, *Acta Crystallogr.*, **B24**, 63 (1968). The largest librational amplitudes are 4.9° and 4.6° about the longitudinal inplane molecular axes of the donor and acceptor, respectively. Bond length and bond angle corrections were on the order of their *esd*'s. The RMS difference between the calculated and observed anisotropic thermal parameters for the HMTSF donor and the TCNQ acceptor were acceptably low at 0.0031(35) and 0.0045(48) Å^2, respectively.
34. A. Hoekstra, T. Spoelder and A. Vos, *Acta Crystallogr.*, **B28**, 14 (1972).
35. P. Coppens and T. N. G. Row, *Ann. N. Y. Acad. Sci.*, **313**, 244 (1978).
36. W. Flandrois and D. Chasseau, *Acta Crystallogr.*, **B33**, 2744 (1977).