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

Madelung Energy Systematics in the Kekulerofulvalene-TCNQ Charge-Transfer Salts

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Version of record first published: 20 Apr 2011.

To cite this article: F. M. Wiygul, Robert M. Metzger & T. J. Kistenmacher (1984): Madelung Energy Systematics in the Kekulerofulvalene-TCNQ Charge-Transfer Salts, Molecular Crystals and Liquid Crystals, 107:1-2, 115-131

To link to this article: http://dx.doi.org/10.1080/00268948408072078

Mol. Cryst. Liq. Cryst. 1984, Vol. 107, pp. 115-131
0026-8941/84/1072-0115/$18.50/0

Printed in the United States of America

MADELUNG ENERGY SYSTEMATICS IN THE HETEROFULVALENE-TCNQ CHARGE-TRANSFER SALTS

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Abstract: The Madelung energies E_M of 15 charge-transfer salts analogous to TTF TCNQ have been calculated. In uniform as well as slightly dimerized segregated-stack crystals three (HMTSF TNAP, TMTSF TCNQ(black), TMTTF TCNQ) have an unusual titled structure with very poor counterion coordination and anomalously low E_M values; two (TTF TCNQ, TSF TCNQ) belong to a 'normal-I' structure type, with sheets of stacks of donors next to sheets of stacks of acceptors; seven (HMTTF TCNQ, HMTSF TCNQ, HMTTF $TCNQF_4$, HMTSF $TCNQF_4$, DBTSF $TCNQF_4$, DBTTF $TCNQF_4$, TTF $TCNQF_2$) have a 'normal-II' motif, with a checkerboard alternation of donor and acceptor stacks; the E_M values for normal-I structures are slightly lower than those for normal-II structures. Finally, three (DBTTF $TCNQF_2$, DBTTF TCNQ, TMTSF TCNQ(red)) have mixed-stack structures, with the highest Madelung energies.

INTRODUCTION

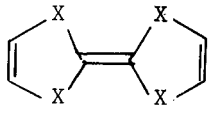
The strong organic one-electron π-acceptor 7,7,8,8-tetracyanoquinodimethan (TCNQ) was synthesized by du Pont chemists in 1960;[1,2] the very interesting chemistry of organic donor-acceptor salts attracted considerable early attention;[3-6] the quasi-metallic anisotropic electrical

conductivity of N-methylphenazinium TCNQ has been known since 1965.[7] However, it was the synthesis of the good organic one-electron π-donor tetrathiafulvalene (TTF) in 1970[8] and the quasi-one-dimensional metal TTF TCNQ[9-13] which ushered in a lively era of interactions between physicists (interested in low-dimensional electrical conductivity and superconductivity) and chemists (interested in synthesis and in correlations of structure with physical properties). An intensive synthetic program at Johns Hopkins University has prepared a great number of chemical variations of TTF and TCNQ and their complexes[14-16] (see Fig. 1) with a consequent wide spectrum of structural and conductivity properties.

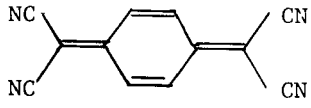
REVIEW OF THE COHESIVE ENERGY PROBLEM

Despite considerable effort,[17-27] the theoretical understanding of the cohesion of these ionic, neutral, and partially ionic donor-acceptor crystals has lagged behind their synthesis. Slowly, experimental cohesive energy data are becoming available.[28-30] Given a chemically narrow range of electron donors (D) and acceptors (A) (see Table I) one does obtain several crystal lattice stacking modes and degrees of ionization (Mulliken charge transfer ρ). In fact, to update Soos' nomenclature[6] of these possible lattices, we present a modest extension of his nomenclature in Table II.

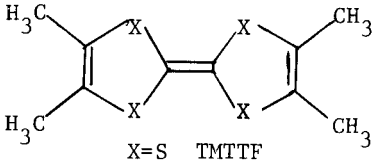
The experimental cohesive energies indicate that MSRN, MSRI, and SSRP lattices, such as anthracene TCNQ, TMPD TCNQ, and TTF TCNQ, respectively, are thermodynamically stable to the same extent, relative to their solid or gaseous neutral constituents D, A.[28,29] Therefore the



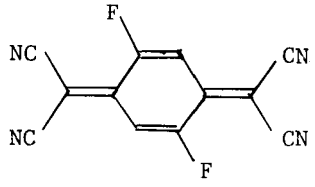
X=S TTF
X=Se TSF



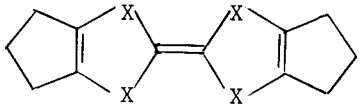
TCNQ



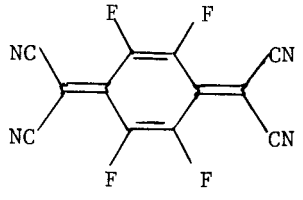
X=S TMTTF
X=Se TMTSF



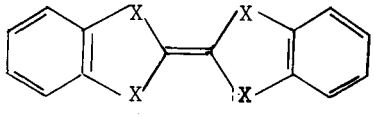
2,5-TCNQF$_2$



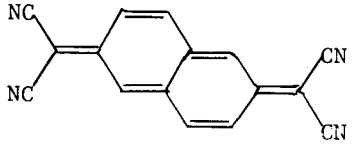
X=S HMTTF
X=Se HMTSF



TCNQF$_4$



X=S DBTTF
X=Se DBTSF



TNAP

FIGURE 1. Homologs of TTF and TCNQ.

TABLE I

Molecular Properties of Electron Donors and Acceptors

Molecule	Molecular Volume in Crystal V_m(Å^3)	Gas-Phase Ionization Potential I_D(eV)	Second Ionization Potential I_2(eV)	Gas-Phase Electron Affinity A_A(eV)	Second Electron Affinity A_2(eV)	First Electrochemical Half-Wave Potential[s] $E_{1/2}^1$	Second Electrochemical Potential[s] $E_{1/2}^2$
TTF	202.1[a]	6.83[k]	(11.2)[p]	-	-	0.27[n]	0.64[n]
TMTTF	296.6[b]	6.42[l]	-	-	-	0.24[n]	0.61[n]
HMTTF	305.5[c]	6.40[m]	-	-	-	0.27[n]	0.60[n]
TSF	222.1[d]	(7.21)[n]	-	-	-	0.42[n]	0.70[n]
TMTSF	316.6[e]	6.58[l]	-	-	-	0.35[n]	0.59[n]
HMTSF	335[d]	-	-	-	-	(0.35)[n]	0.59[n]
DBTSF	348.4[f]	-	-	-	-	-	-
DBTTF	328.4[g]	(7.0)[o]	-	-	-	-	-
TCNQ	256.3[h]	-	-	2.8[q]	(-1.04)[r]	0.17[n]	-
TCNQF4	280.0[i]	-	-	(3.20)[i]	-	0.53[n]	-
2,5-TCNQF2	267.6[j]	-	-	-	-	-	-
TNAP	-	-	-	-	-	-	-

[a]Ref. 31 [b]Ref. 32 [c]V_m(TMTTF)+18 [d]V_m(TMTSF)+V_m(TTF)-V_m(TMTTF) [e]Ref. 33 [f]Ref. 43
[g]V_m(DBTSF)+V_m(TMTSF)-V_m(TMTTF) [h]Ref. 35 [i]Ref. 36 [j]V_m(TCNQ)+11.32 [k]Ref. 37 [l]Ref. 38
[m]Ref. 39 [n]Ref. 40 [o]Ref. 41 [p]Ref. 42 [q]Ref. 43 [r]Ref. 44 [s]Volts versus SCE in CH_3CN

Table II
Extension of Soos' Classification Scheme (Ref. 6)

	Example	Classification
1) STACKING:		
S = Segregated Stacks (DDDDD and AAAAA)	TTF TCNQ	SSRP
M = Mixed Stacks (DA)	TMPD TCNQ	MSRI
L = Lone Dimers	NBP TCNQ	LSRI
2) STOICHIOMETRY:		
S = Simple (1:1 D:A ratio)	TTF TCNQ	SSRP
C = Complex (n:1 or 1:n DA ratio)	TEA $TCNQ_2$	SCA_2I-->SCA_4I
B = Berthollitic (non-integer D:A ratio)	$TMTTF_{1.3}$ $TCNQ_2$	SB
3) INTERMOLECULAR DISTANCES:		
R = Regular	TTF TCNQ	SSRP
A_2 = Alternating, Diads	$TMTSF_2PF_6$	SCA_2P
A_3 = Alternating, Triads	Cs_2TCNQ_3	SCA_3D
A_4 = Alternating, Tetrads	TEA $TCNQ_2$	SCA_2I-->SCA_4I
4) IONICITY, or VALENCY:		
N = Neutral Molecular Solid (mostly)	Anthracene TCNQ	MSRN
P = Partial Ionicity, Mixed-Valent	TTF TCNQ	SSRP
D = Partial Ionicity, Discrete Valencies	Cs_2TCNQ_3	SCA_3D
I = Full Ionicity (mostly)	TMPD TCNQ	MSRI

choice of mixed stacks versus segregated stacks is probably made by a subtle interplay between the cost of ionizing some or all of the D,A, (ionization potential I_D, electron efficiency A_A) and the consequent increase in cohesive energy (Madelung, polarization, charge-transfer dependent dispersion energies).

The early studies[17,18] concentrated mainly on the Madelung energy E_M. However, the partially ionic lattice ($0 < \rho < 1$), which is the common feature of all the known good organic conductor and superconductors, cannot be stabilized if only $\rho(I_D-A_A)+\rho^2E_M$ is considered for lattices with uniform change transfer ρ. One can obtain shallow cohesive energy minima[20] at intermediate charge transfer, if one computes E_M for the several possible Wigner lattices that are close in E_M; these Wigner lattices can minimize short-range Coulomb repulsion along the segregated stacks, but then dynamic charge correlations must be invoked to *''detune''* these *''frozen''* Wigner lattices and regain the experimental average lattice.[20] Other studies[21-27] established the importance of the charge-transfer-independent London dispersion (E_d) and repulsion (E_r) energies in the calculation of absolute cohesive energies.[21-27] Some efforts to evaluate polarization and charge-transfer-dependent dispersion energies[45] were hampered by inadequate CNDO/2-FP atom-in molecule polarizabilities.[46] A satisfactory CNDO/2-FPP polarizability algorithm has been developed[47,48] but it is too slow for molecules of the size of TTF or TCNQ.

A. N. BLOCH'S THEORY

A comprehensive theory has been developed (but, alas not

yet published in full) by A. N. Bloch.[49-51] He showed that the cohesive energy of a metallic molecular crystal (= energy of the crystal relative to that of its neutral gaseous components) can be written as:

$$\Delta E = [\rho(I_D - A_A) + E_M(\rho)] + \{\rho(\rho-1)\bar{U}\} + (E_d - E_r) + \rho E_d' + \Theta(t) \quad (1)$$

Here $E_M(\rho)$ is written as the power series $-M_o - \rho M_1 - \frac{1}{2}\rho^2 M_2$, with coefficients determined by calculations of E_M at ρ = 0, 1, and 2 (no Wigner lattices!). $\rho E_d'$ is the charge-transfer dependent dispersion energy; $\Theta(t)$ is the difference between two small quantities: the zero-point energy of the plasmons and the one-electron tight-binding energy. The term in square brackets in Eq. (1) is what was considered previously;[17,18] the underlined terms are estimated by Bloch from optical data. The truly new and significant term is the term enclosed in braces: it can stabilize the partially ionic state. $\bar{U}$ is the average value of the unscreened Hubbard on-site repulsion U; $\bar{U}$ can be estimated from

$$\bar{U} = [(I_2 - I_D) + (A_A - A_2)]/2 \quad (2)$$

where I_2, A_2 are the second ionization potential and electron affinity, respectively. Brief discussions of Eq. (1) can be found in Refs. 45 and 51. The experimental ingredients for calculations of ΔE are values of I_D, A_A, I_2, A_2, and optical data necessary for the calculation of E_d, E_r, and E_d'; the computational data are E_M values at ρ = 0, 1, and 2. In unpublished results[51,52] Bloch has shown that Eq. (1) predicts a charge transfer ρ = 0.63 for TTF TCNQ (0.59 is observed) and ΔE = -2.2 eV (-2.3 eV is observed).[28] The present report is a summary of Madelung energy calculations started by two of us (FMW and RMM) in 1979 on the Johns Hopkins TTF TCNQ homologs. Ideally such

calculations would follow, or be combined with, the full presentation of the derivation of Eq. (1). In eager anticipation of the publication of A. N. Bloch's theory in its full form, we report here our E_M findings sofar, and discuss the structural reasons for the trends in the calculated Madelung energies.

CALCULATIONS

For the 15 crystals listed in Table III the atom-in-molecule (partial point) charge distributions (= core charge minus Mulliken gross atomic populations) were determined by INDO[76] (by CNDO/2[76] for S and Se[77] - containing molecules) using program CNINDO[78] and the molecular geometry obtained in each crystal structure; this was done separately for the neutral molecules ($\rho = 0$), the radical anions and cations ($\rho = 1$), and the dianions and dications ($\rho = 2$). The energies which are quoted to ± 0.001 eV in Table III were obtained with programs CELMAP[79] and EWALD[79] (using the two-series Ewald[80] method; convergence to 10^{-6} eV). For HMTTF TCNQ and for HMTTF $TCNQF_4$ ($\rho = 1$) the E_M values were calculated by the IBM group by the Ewald method.[59,61] For the rest, the single-series Bertaut[81] method was used; the Bertaut series energies were found to agree with the Ewald series energies to within ± 0.01 eV.

The 15 TTF TCNQ homologs listed in Table III range from segregated-stack to mixed-stack salts, and from metals to poor semiconductors. If one looks carefully at their crystal structures, four distinct types of stacking can be identified (Fig. 2). The MSRP lattice type shows how organic Mulliken charge-transfer salts mimic the NaCl lattice: a sheet of D and A molecules (with partial charge

TABLE III

Solid-State Data and Madelung Energies for 15 TTF-TCNQ Homologs

Crystal	Lattice Type	Space Group	Packing Ratio, PR	Ionicity ρ_{exp}	Organic Metal?	Madelung Energies E_M (ev/DA pair) ρ=0	ρ=1	ρ=2
HMTSF TNAP	SSRP(A)[a]	$P\bar{1}$	-	-	yes	0.168	-0.207	1.692
TMTSF TCNQ black	SSRP(A)[b]	$P\bar{1}$	1.053	0.57[p]	yes	0.110	-0.304	0.866
TMTTF TCNQ	SSRP(A)[c]	P2/c	1.042	0.48[p]	yes	0.121	-0.407	0.693
TTF TCNQ	SSRP(N1)[d]	$P2_1/c$	1.092	0.59[q]	yes	-0.023[w]	-2.337[w]	-8.417[w]
TSF TCNQ	SSRP(N1)[e]	$P2_1/c$	1.101	0.63[r]	yes	0.012	-2.205	-8.155
HMTTF TCNQ	SSRP(N2)[f]	Pmna	1.070	0.72[s]	yes	-	-2.62[f]	-10.181
HMTSF TCNQ	SSRP(N2)[g]	C2/m	1.100	0.74[t]	yes	0.036	-2.579[g]	-9.946
HMTTF TCNQF4	SSRI(N2)[h]	Pmna	1.064	1.00[u]	no	-	-2.60[h]	-10.930
HMTSF TCNQF4	SSRI(N2)[i]	C2/m	1.081	1.00[u]	no	0.435	-2.834	-10.751
DBTSF TCNQF4	SSRI(N2)[j]	C2/m	1.042	1.00[u]	no	-	-2.65	-10.187
DBTTF TCNQF4	SSA_2I(N2)[k]	$P\bar{1}$	1.047	1.00[u]	no	-	-2.79	-10.39
TTF TCNQF2	SSA_2I(N2)[l]	$P\bar{1}$	1.065	1.00[u]	no	-	-2.65	-9.36
DBTTF TCNQF2	MSRP[m]	$P\bar{1}$	1.037	0.65[m]	no	-	-2.69[m]	-11.47
DBTTF TCNQ	MSRP[n]	$P\bar{1}$	1.007	0.2[w]	no	-	-2.97[n]	-12.48
TMTSF TCNQ red	MSRP[o]	$P\bar{1}$	1.014	0.21[o]	no	-0.084	-3.079	-12.812

[a]Refs. 53,54 [b]Ref. 55 [c]Ref. 56 [d]Ref. 57 [e]Ref. 58 [f]Ref. 59 [g]Ref. 60 [h]Ref. 61 [i]Ref. 62 [j]Ref. 63
[k]Ref. 64 [l]Ref. 65 [m]Ref. 66 [n]Ref. 41 [o]Ref. 67 [p]Ref. 68 [q]Refs. 69,70 [r]Ref. 71 [s]Ref. 72 [t]Ref. 73
[u]Assumed from the lack of metallic conductivity and other physical properties [v]Ref. 74 [w]Ref. 75

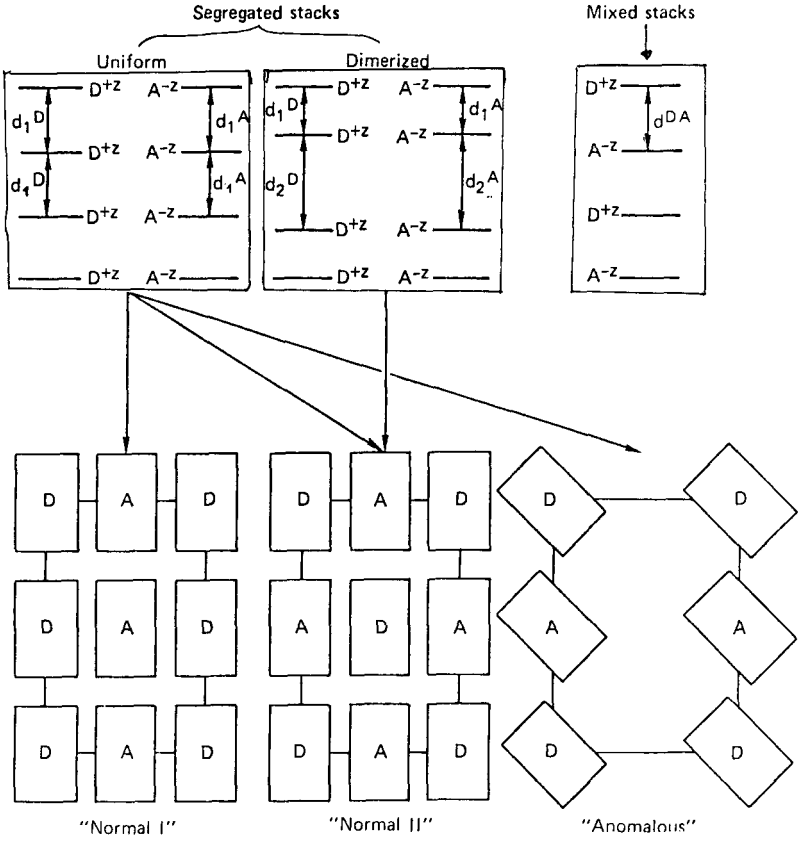


FIGURE 2. Stacking possibilities among the heterofulvalene TCNQ salts

transfer ρ) is superposed by a sheet of A and D molecules, respectively, to provide a very distorted octahedron of counterions around each ion. This arrangement yields, relatively, the largest Madelung energies. The segregated simple lattices exhibit three different packing geometries, as observed in the plane normal to the stacking axis: (i) they attain a rough four-fold in-plane coordination of attractive counterions, around each ion (the Normal-II (N2) structure, e.g. HMTSF TCNQ) or (ii) they show two repulsive (D-D) and two attractive (D-A) ions around each D (the Normal-I (N1) structure, e.g. TTF-TCNQ) or (iii) the N2 structure is modified by twisting the molecules around their centers of symmetry (the Anomalous (A) structure, e.g. TMTTF TCNQ). The Madelung energies reported in Table III are plotted as a function of ρ in Fig. 3.

The three SSRP(A) salts (HMTSF TNAP, the black form of TMTSF TCNQ, and TMTTF TCNQ) are all organic metals, and the Madelung energies contribute the least binding. In fact, for $\rho = 2$ the SSRP(A) structure has a repulsive E_M. This result is reminiscent of the zero[81] or positive[83] E_M calculated for NMP TCNQ, a situation relieved only when Wigner lattices are considered, or charge distributions are seriously altered.[84]

As counterion coordination increases, i.e. as one goes from SSRP(A) to SSRP(N1) to SSRP(N2) to SSA_2I(N2) to MSRP lattices, the E_M values at $\rho = 1, 2$ increase gradually, as expected (Fig. 3). At $\rho = 0$ the E_M values are not all strictly zero: this effect was neglected in Fig. 3.

The E_M values at $\rho = 1,2$ show more ''one-dimensionality'' (lack of Coulomb attraction) for the N1 structures than for the N2 structures. No significant E_M

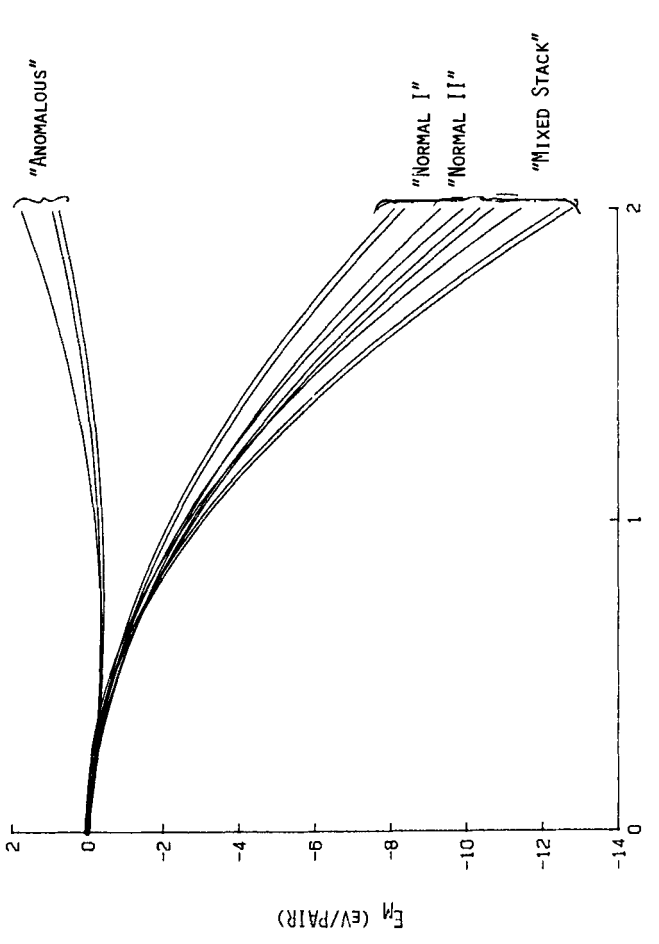


FIGURE 3. Plot of computed Madelung energies versus charge transfer

trends are seen when one passes from regular to alternating N2 structures, i.e. from SSRP(N2) to $SSA_2P(N2)$ salts. Finally, TMTSF TCNQ is dimorphic: the red crystals have a potentially high E_M, but are insulators with low charge transfer, whereas the black crystals have low E_M, higher ρ_{exp}, and are excellent organic metals.

The experimental ionicities ρ given in Table II were obtained by a variety of indirect techniques.

The experimental packing ratios reported here are defined as $PR = [V_m(D) + V_m(A)]/V_m(DA)$: their use was pioneered by Kitaogorodosky[85] and first applied extensively to organic metals by Sandman.[32,86] The trends of the PR values are not dramatic, but the approximate ordering is SSRP(N1) > SSRP(N2) > $SSRI(N_2)$ > SSA_2 > SSRP(A) > MSRP: this indicates that in organic metals ''denser'' lattices are possible, despite decreasing Madelung energies. Put in another way, the PR and E_M values indicate again that the TTF-TCNQ homologs, upon crystallization, maximize a lattice energy other than just E_M. Thus, the final full publication of Bloch's theory is eagerly awaited.

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