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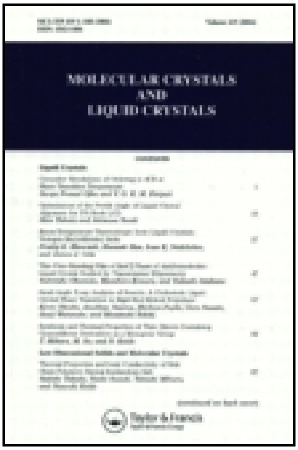

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Cohesive Energy Calculations and the Stabilization of Partially Ionic Lattices

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COHESIVE ENERGY CALCULATIONS AND THE STABILIZATION OF PARTIALLY IONIC LATTICES*

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The cohesion of organic ionic and partially ionic lattices is dominated by Madelung, polarization, and dispersion energies. Good atom-in-molecule charges and polarizabilities are important, and the cost of partial ionization needs a quantitative description. Several current inroads into these questions are discussed.

1. INTRODUCTION

The status of cohesive energy calculations for organic ionic and partially ionic crystals has been reviewed at biennial intervals in the recent past[1,2,3]. The present account speculates on future directions that might be profitable in studies of organic ionic cohesion.

Given the impracticality of elaborate _ab initio_ quantum chemical algorithms for crystalline cohesion for compounds like TTF TCNQ[4-8], viability is retained by the semiclassical atom-in-molecule approach pioneered by Kitaigorodskii[9]; this approach has been used with great success for neutral organic hydrocarbons by Williams[10] and for conformational energy calculations by Scheraga and coworkers[11], Allinger[12], Warshel[13], and many others.

The experimental Born-Haber cycle for TTF TCNQ is known[14] and is reproduced in Fig. 1. The goals of a theoretical study of cohesion in TTF TCNQ are (a) to reproduce the experimental enthalpy of stabilization:

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$$\Delta H_{exp} \equiv -\Delta H_f^\circ(TTF,g) - \Delta H_f^\circ(TCNQ,g) + \Delta H_f^\circ(TTF,TCNQ,c) = -235\pm6 \text{ kJ/mol} \quad (1)$$

(b) to reproduce the experimental cohesive energy U^ρ_{exp}:

$$U^\rho_{exp} \equiv \rho\Delta H_f^\circ(TTF^+,g) + \rho\Delta H_f^\circ(TCNQ^-,g) + (1-\rho)\Delta H_f^\circ(TTF,g) + (1-\rho)\Delta H_f^\circ(TCNQ,g) - \Delta H_f^\circ(TTF\ TCNQ,c) - P\Delta V = 471 \text{ kJ/mol} \quad (2)$$

where $\rho = 0.59$ is the amount of charge transfer in the TTF TCNQ crystal, and (c) to explain why the experimental charge transfer is $\rho = 0.59$[15]. It should also be noted that TTF TCNQ(c) is more stable than TTF(c) and TCNQ(c) by 37.5± 1.5 kJ/mol, thus invalidating an earlier speculation about the possible thermodynamic instability of TTF TCNQ[16].

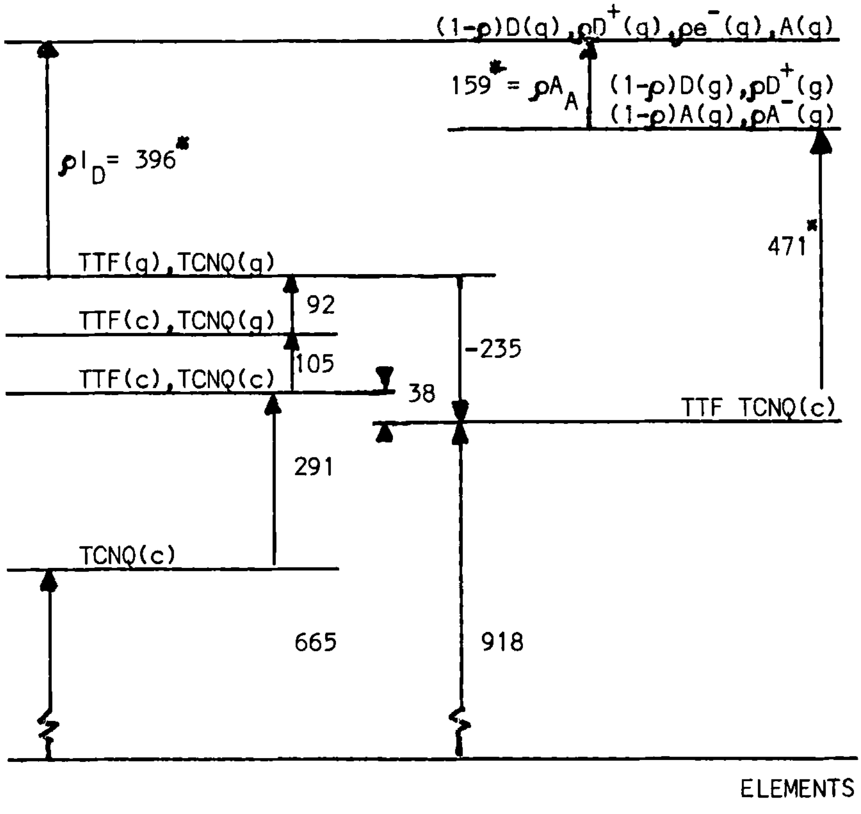

FIGURE 1 Schematic Born-Haber cycle for TTF TCNQ. Experimental data (in kJ/mol, rounded), from Ref. 14. (D = TTF, and A = TCNQ; ρ = 0.59 was assumed for quantities marked with asterisk)

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2. THEORETICAL COHESIVE ENERGY

The semiclassical treatment of the cohesive energy U, inspired by the early work of Born[17,18] and and others[18,19] and by the atom-atom potentials of Kitaigorodskii[9] and Williams[10] allows us to write:

$$U = E_M + (E_{cd} + E_\mu) + E_{pol} + E_t + (E_d - E_r) \tag{3}$$

The Madelung energy E_M is given by:

$$E_M = \sum_{i>j}\sum q_i q_j r_{ij}^{-1} \tag{4}$$

where $\sum_i$ and $\sum_j$ are lattice sums, r_{ij} are interatomic distances in the known crystal structure, and q_i are those theoretically ill-defined quantities known as atom-in-molecule charges. The use of an effective dielectric constant is used by some workers[11] but not by most others[3,10]. The "best" partial charges are difficult to determine a priori. Traditionally, the gross Mulliken populations from a quantum chemical calculation (ab initio, Hückel, Pariser-Parr-Pople or semi-empirical) have been used. Recently it was found that the off-diagonal one-center elements of the density matrix, which contribute the hybridization part (μ_{hyb}) of the molecular dipole moment[20] must also contribute to a "charge-dipole" energy E_{cd}[3,21]:

$$E_{cd} = -\sum_i \underset{\sim}{\mu}_i^{hyb} \cdot \underset{\sim}{F}_i^M \tag{5}$$

where $\underset{\sim}{\mu}_i^{hyb}$ are the atom-in-molecule hybrid moments, and the $\underset{\sim}{F}_i^M$ are the Madelung electric fields:

$$\underset{\sim}{F}_i^M = (1/2) \sum_j q_j \underset{\sim}{r}_{ij} r_{ij}^{-3} \tag{6}$$

where $\underset{\sim}{r}_{ij} = \underset{\sim}{r}_i - \underset{\sim}{r}_j$. It turns out that for TTF TCNQ E_{cd} (at $\rho = 1.0$) is nearly equal in magnitude, and opposite in sign, to E_M, so that $E_M + E_{cd} \sim 0$. For the mixed-stack salt TMPD TCNQ $E_M = -317$ kJ/mol[3,21], $E_{cd} = 77$ kJ/mol at $\rho = 1$[3]. The dipolar energy E_μ is small[21]:

$$E_\mu = \sum_i \sum_j (\underset{\sim}{\mu}_i^{hyb} \cdot \underset{\sim}{\mu}_j^{hyb}\, r_{ij}^{-3} - 3\underset{\sim}{\mu}_i^{hyb} \cdot \underset{\sim}{r}_{ij}\, \underset{\sim}{\mu}_j^{hyb} \cdot \underset{\sim}{r}_{ij}\, r_{ij}^{-5}) \tag{7}$$

An altogether different approach to the q_i is that of

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Scrocco and Tomasi[24]. They start from the theoretically well-defined molecular electrostatic potential obtainable from an ab initio calculation, and obtain effective charges q_i^e from it: these q_i^e should be better (if quite different) than the q_i of Eqs. (4,6) and eliminate the need for E_{cd} and E_μ; the use of the q_i^e is increasing for lattice energy calculations[25].

The polarization energy E_{pol}:

$$E_{pol} = -(1/2)\sum_i \underset{\sim}{F}_i^M \cdot \underset{\sim}{\alpha}_i \cdot \underset{\sim}{F}_i^M \tag{8}$$

involves atom-in-molecule polarizability tensors $\underset{\sim}{\alpha}_i$[22,23] whose more reliable calculation is presented elsewhere in these proceedings[26].

The band structure contribution to the cohesive energy, E_t, is small for narrow-band metals like TTF TCNQ[27] but very significant for wide-band metals like C_6Li or C_8K[28].

The dispersion energy, or van der Waals energy E_d is given by:

$$E_d = -\sum_i \sum_j C_i\, C_j\, r_{ij}^{-6} \tag{9}$$

where the C_i are coefficients that for neutral crystals can be parametrized from experimental cohesive energies, along with the parameters for the ad hoc repulsion energy

$$E_r = \sum_i \sum_j D_i\, D_j \exp(-E_{ij}\, r_{ij}) \tag{10}$$

or

$$E_r = \sum_i \sum_j D_i\, D_j\, r_{ij}^{-n} \tag{11}$$

where n is between 9 and 12.

A more theoretical approach to E_d is to extend to atoms inside molecules the London expression[29] for the $C_i\, C_j$:

$$C_i\, C_j = \overline{\alpha}_i\, \overline{\alpha}_j\, (3/8\sqrt{I_i}\,\sqrt{I_j}) \tag{12}$$

where I_i is a typical electronic excitation energy (e.g. ionization energy) of the molecule to which atom i belongs, or else the Slater-Kirkwood expression[30]:

$$C_i\, C_j = \overline{\alpha}_i\, \overline{\alpha}_j\, (3/2\, e\hbar\, m_e^{-1/2})\,[(\overline{\alpha}_i/N_i)^{1/2} + (\overline{\alpha}_j/N_j)^{1/2}]^{-1} \tag{13}$$

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where e and m_e are the electronic charge and mass, respectively, $2\pi\hbar$ is Planck's constant, and N_i is the "effective number of electrons" for atom i, or even the Salem expression[31]

$$C_i\ C_j = \alpha_i\ \alpha_j\ e^2[\alpha_i/\langle(\sum_R \underset{\sim}{r}_R)^2\rangle + \alpha_j/\langle(\sum_R r'_R)^2\rangle]^{-1} \qquad (14)$$

where $\langle(\sum_R r_R)^2\rangle$ is a quantum-mechanical second moment integral. Eq. (14) seems promising for a development of a dispersion energy formalism that uses the $\underset{\sim}{\alpha}_i$ instead of the $\overline{\alpha}_i$.

In all, the ingredients of a good cohesive energy calculation must be good charges q_i or q_i^e (and, if required, good μ_i^{hyb}) and good polarizabilities $\underset{\sim}{\alpha}_i$. For dispersion energies, one must obtain the correct ρ-dependence of the C_i coefficients.

3. STABILIZATION OF PARTIALLY IONIC LATTICES

If one postulates with McConnell et al.[32] (a) that an organic ionic crystal is mainly held together by its Madelung energy E_M (which, for the partial charge transfer case, scales as ρ^2), (b) that it costs the ionization potential I_D of the electron donor D minus the electron affinity A_A of the electron acceptor A to ionize the lattice (and this cost of ionization scales as ρ), then the energy:

$$E(\rho) = \rho^2 E_M + \rho(I_D - A_A) \qquad (15)$$

will always have a maximum, and not a minimum at intermediate charge transfer[33]. Possible escapes from this theoretical dilemma are (a) the dielectric screening of $I_D - A_A$ in the solid state[34] (which may be a complicated and hitherto unknown function of ρ), or (b) the conceptual importance of the difference between ionizing a fraction of the molecules in the TTF TCNQ lattice and, in a solid state sense, ionizing <u>all</u> of them to the same fractional extent[35].

Another possible resolution of this dilemma is the use of the Wigner lattice[36]: for ρ = rational fraction (e.g. 1/2, 2/3) one constructs a highly artificial superlattice, for which E_M maximizes the interionic Coulomb attractions. This procedure yields dramatic improvements in the Madelung energy[1-3,35,37,38] and allows the use of $\rho(I_D - A_A)$ for the cost of ionization. Unfortunately such rational superlattices, or perfectly correlated charge density waves, have not been observed. Nevertheless, the Wigner lattice model does "improve" E_M considerably (but not E_{pol}[21]).[3]

An escape from Eq. (15) could be in the preserved ρ dependence of E_{pol}. However, this was not found to be helpful when inadequate MINDO/3-FP polarizabilities α_i[23] were used for TTF TCNQ[21].

A more fundamental departure from Eq. (15) has been suggested by Soos[39] (and echoed by Nethercot[40]). As is customary in the theory of inorganic mixed-valence complexes[41], a polynomial interpolation between various ionization states should replace the non-smooth linear interpolation suggested by Eq. (15). Thus, a simple quadratic fit to ρ = -1, 0, and 1 values for the cost of ionization $a_1\rho + a_2\rho^2$ yields for TTF TCNQ a minimum in:

$$E'(\rho) = \rho^2 E_M + (a_1\rho + a_2\rho^2) \tag{16}$$

at $\rho \cong 0.4$[39]. Adding E_{cd}, E_μ, and E_{pol} does not shift this minimum very much[21], but this could again be due to the bad α_i values which were available at that time. A limitation in Eq. (16) is that it is not valid for finite values of the interionic Mulliken charge transfer integral t. An extension to the theory to the finite t case requires excited valence bond configurations[42] but the theory is not yet fully elaborated.

A radically new and highly original cohesive energy theory has been elaborated, but not yet been published, by Bloch[43,44]. It uses the ρ = 0, 1, and 2 states as reference states and Madelung energy calculations $E_M^{(0)}$, $E_M^{(1)}$, and $E_M^{(2)}$ for these states. Bloch's theory fits a quadratic function in ρ, $E_M(\rho)$, to those three values. Thus Bloch's expression for U becomes, approximately:

$$U_{Bloch} = E_M(\rho) + \rho(I_D - A_A) + \rho(\rho - 1)\bar{U} + (E_d - E_r) + E_d^{(\rho)} \tag{17}$$

where $\bar{U}$ is the average on-site repulsion, that is, $\rho(1-\rho)\bar{U}$ provides a very considerable <u>binding</u> contribution due to the on-site repulsion of processes of double ionization $D^+ \rightarrow D^{++} + e^-$ or $A^- + e^- \rightarrow A^{--}$ and $E_d^{(\rho)}$ is the charge-transfer-dependent part of the dispersion energy.

4. NUMERICAL EXAMPLE: TTF TCNQ

In Table 1 are listed the numerical values of several lattice energies obtained recently[3,21] for TTF TCNQ, as a function of charge transfer.

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Table 1 Lattice Energies (kJ/mol) of TTF TCNQ as a Function of Charge Transfer, Using MINDO/3-FP Charges, q_i, Polarizabilities α_i and hybrid moments μ_i^{hyb} (1 eV = 96.487 kJ/mol)[3,21,23]

Energy	Eq.	ρ=0	ρ=0.5	Wigner ρ=1/2	ρ=1.0
E_M (Madelung)	4	-2	-52	-135	-194
E_{pol} (polarization)	8	-70	-126	-154	-286
E_{cd} (charge-dipole)	5	91	146	145	205
E_μ (dipolar)	7	-12	-10	13	-8
E_d (dispersion)	9,12	-265	---	---	-391
$\rho(I_D - A_A)$		0	194	194	389
$E_M + E_{pol} + E_{cd} + E_\mu + \rho(I_D - A_A)$		6	153	62	107

The values of E_d are to be considered preliminary; E_d for $\rho = 1$ agrees with an atom-atom potential value $E_d = -415$ kJ/mol obtained by Govers[45]; E_d is shown to be strongly charge-transfer dependent. The charge-dipole energy at $\rho = 1$ nullifies, roughly, the binding obtained by either E_M or E_{pol}. This justifies omitting E_{pol} from Eq. (17). However, using all lattice energies (except E_d) plus $\rho(I_D - A_A)$ (bottom line of Table 1) should yield an energy that, except for the omission of $E_d - E_r$ and of $P\Delta V$ effects should compare with $\Delta H_{exp} = -235\pm6$ kJ/mol (Eq. (1)). The agreement is terrible[3,21]. Much careful work with better α_i values and dispersion and repulsion energies remains to be done.

We present next some preliminary work[46,47] that applies Bloch's cohesive energy theory[48] to TTF TCNQ. The Madelung energy values at ρ = 0, 1, 2 being 0.023, -2.337, and -8.417 eV/(molecule: TTF TCNQ) (using CNDO/2 charges),

$$E_M(\rho) = 0.023 - 0.500\rho - 3.721\rho^2 \tag{18}$$

From averages of the first and second ionization potentials and electron affinities, $\bar{U} = 4.1$ eV. From optical data $E_d - E_r = -1.33$ eV[46,48] and $E_d(\rho) = -1.19$ eV[46,48]: this strong dependence of the net dispersion energy on charge transfer is also mirrored on the London formula estimates of $E_d = -265$ kJ/mol ($\rho = 0$) and -391 kJ/mol ($\rho = 1.0$) in Table 1. The resulting final values are $U_{Bloch} = -2.69$ eV, $\rho = 0.62$, which compare very well indeed with the experimental values $\Delta H = -2.40$ eV (Eq. (1)) and $\rho = 0.59$. These numerical values suggest that Bloch's theory is a

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major advance in the understanding of cohesion in the TTF TCNQ family of compounds, and its publication is eagerly awaited.

5. MORE RECENT MADELUNG ENERGIES

To update the most recent review of cohesive energies[3], an account is given here of several Madelung energy calculations performed since its compilation.

In order to study the neutral-to-ionic phase transition in TTF chloranil[49,50], E_M values were obtained as a function of both temperature and pressure, as well as a comparison value for the ionic salt TTF bromanil. Preliminary representative data are listed in Table 2.

Table 2 Madelung Energies for TTF Chloranil and TTF Bromanil

Salt	T(°K)	p(bar)	V_{cell} (Å^3)	E_M (kJ/mol)	$I_D - A_A$ (kJ/mol)
TTF-Chloranil	300	1	812.4	-340.933	~440
TTF-Chloranil	300	10,500	735.3	-350.034	~440
TTF-Chloranil	48.8	1	771.0	-345.967	~440
TTF-Bromanil	300	1	-----	-335.6	~440

At a rapid glance, $E_M + I_D - A_A \approx 100$ kJ/mol so that by the old criterion of McConnell et al[32] neither TTF chloranil nor TTF bromanil should ever be ionic. However, the CNDO/2 charges q_i may be quite questionable and a sizeable polarization energy should also be able to rescue the situation. Or, to turn the argument around, if TTF bromanil is ionic, then the similarities in both structure and Madelung energy would argue that TTF chloranil could be ionic with about equal likelihood. Thus, a small lattice compression at either low temperature or high pressure should be able to drive TTF chloranil across the neutral-to-ionic phase transition[47].

For the two triplet exciton salts N-butylphenazinium TCNQ and N-butylphenazinium $TCNQF_4$[49] the Madelung energies are -254.8 and -280.5 kJ/mol respectively. The salts are insulators with a highly unusual $D^+D^+A^-A^-$ stacking mode. The dissimilarities in space group ($P\bar{1}$ and $P2_1/c$ respectively) and simmilarities in stacking merge in relatively similar E_M values, which, however, are smaller than the E_M with a better counterion stacking, such as TMPD chloranil[3].

Finally, the Madelung energy of the organic superconductor, $(TMTSF)_2PF_6$[52] is -236.580 kJ/mol if the PF_6^- ions are fixed at their poorly defined lattice positions, and -237.315 kJ/mol if the PF_6^- ions become spherically symmetric rotors at the P site in the lattice.

6. CONCLUSIONS

Madelung energy calculations have spearheaded more elaborate cohesive energy calculations for organic ionic lattices.

Better choices of atom-in-molecule charges and polarizabilities, and a careful understanding of the energetics of partial ionization are required in order to assure a predictive role to cohesive energy calculations.

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