

57 peak in the conventional EI spectrum, and consecutive processes could occur.) In general, the quantitative basis for correlation of ion intensities with product stabilities appears to lie in the accessibility of the asymptotic portion of the  $k(E)$  curve for the competitive processes studied by collisional activation. This would generally be the case for small ions; we have seen it here for ions with up to 42 degrees of freedom, and our previous studies<sup>4,7</sup> have shown a poorer correlation for 142-154 degrees of freedom.

Correlations of high quality between CAD product ion intensities and product enthalpies are more general than previously supposed. Their usefulness for establishing the thermochemistry of novel small ions, radicals, and molecules, produced by the fragmentation of ions generated by EI, should be exploited.

Registry No. CH<sub>3</sub>COCH<sub>3</sub>, 67-64-1; CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>, 78-93-3; CH<sub>3</sub>COCH(CH<sub>3</sub>)<sub>2</sub>, 563-80-4; CH<sub>3</sub>CH<sub>2</sub>COCH(CH<sub>3</sub>)<sub>2</sub>, 565-69-5.

## Role of the Madelung Energy in the Neutral-Ionic Phase Transition of Tetrathiafulvalene Chloranil

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Received December 14, 1983

**Abstract:** In order to elucidate what determines the degree of charge transfer from donor to acceptor in charge-transfer solids, we have calculated the crystalline electrostatic Madelung energy,  $E_M$ , for tetrathiafulvalene (TTF) chloranil as a function of pressure and temperature. At 300 K between 1 bar and 11 kbar, where there is a transition between Neutral and Ionic ground states,  $E_M$  becomes more negative by  $\sim 0.10$  eV. This increase in binding energy suggests that the pressure dependence of the Madelung energy may be sufficiently large to drive the Neutral-Ionic phase transition at high pressures. The magnitude of  $E_M = -3.8$  eV at 11 kbar is used to show that the calculated energies of the Neutral and Ionic states become approximately equal at this pressure. On the other hand, at 1 bar between 300 and 50 K, where another transition between Neutral and Ionic ground states has been found,  $E_M$  becomes more negative by only  $\sim 0.05$  eV, or half as much as for the transition at high pressure. This suggests that there is an additional driving force for the Neutral-Ionic transition at low temperature (which we believe is the dimerization of the stacks). Better quantitative agreement for the transition and for the charge-transfer band energy is obtained by formally including partial charge transfer in the ground state.

Mulliken charge-transfer (CT) crystals of organic  $\pi$ -electron donors (D) and  $\pi$ -electron acceptors (A) usually form compounds with mixed stacks, in which planar donor molecules alternate with acceptors along the stack.<sup>1-3</sup> For this reason, these materials do not exhibit the high electrical conductivity often found in compounds which have segregated (or separate) donor stacks and acceptor stacks. For the case of mixed-stack materials, the amount of charge transferred from D to A has been calculated in the Hartree approximation by McConnell et al.<sup>4</sup> This simple model predicts that these compounds will be either completely neutral or completely ionic, with a sharp neutral-ionic boundary defined by

$$(I_D - A_A) + E_M = 0 \quad (1)$$

Here  $I_D$  is the ionization potential, or energy cost of ionizing the donor,  $A_A$  is the electron affinity of the acceptor, and  $E_M$  is the electrostatic Madelung energy<sup>5</sup> of the ionic lattice. Thus, a poor donor/acceptor combination (with large  $I_D - A_A$ ) is predicted to form a neutral solid, whereas an excellent D/A pair should form a solid with cations and anions. This simple model has been extended by Soos et al.<sup>6-10</sup> to include the effects of the Mulliken transfer integral  $\gamma$  between D and A along the stack.  $\gamma$  is usually taken to be proportional to the intermolecular overlap  $S$ . The overlap  $S$  hybridizes D and A, such that compounds previously expected to be completely neutral are only *nominally* neutral (henceforth called "Neutral"). Similarly, the ionic compounds are not fully ionic, but contain *nominally* ionic (or "Ionic") molecules. Nevertheless, there is still a sharp and well-defined boundary between Neutral and Ionic compounds. A tantalizing question has been to probe the interface or boundary between

Neutral and Ionic crystals, i.e., the region where eq 1 is almost satisfied.

In a recent experimental investigation, a large number of these compounds were systematically studied.<sup>11</sup> The Neutral-Ionic (N-I) boundary was identified in optical measurements of the charge-transfer band energy  $h\nu_{CT}$ : it was shown how compounds range from being near this boundary to being far from it. For 10 of the Neutral compounds near this boundary, it was discovered<sup>12</sup> that applying pressure above a certain threshold causes a distinct change in the color of the crystals. This reversible change was interpreted as a phase transition from a Neutral to an Ionic solid. In one of these materials that lies particularly close to the boundary, tetrathiafulvalene (TTF) chloranil, a similar transition could also be induced at low temperatures.<sup>12</sup> Most of the subsequent experimental work has focused on TTF chloranil.

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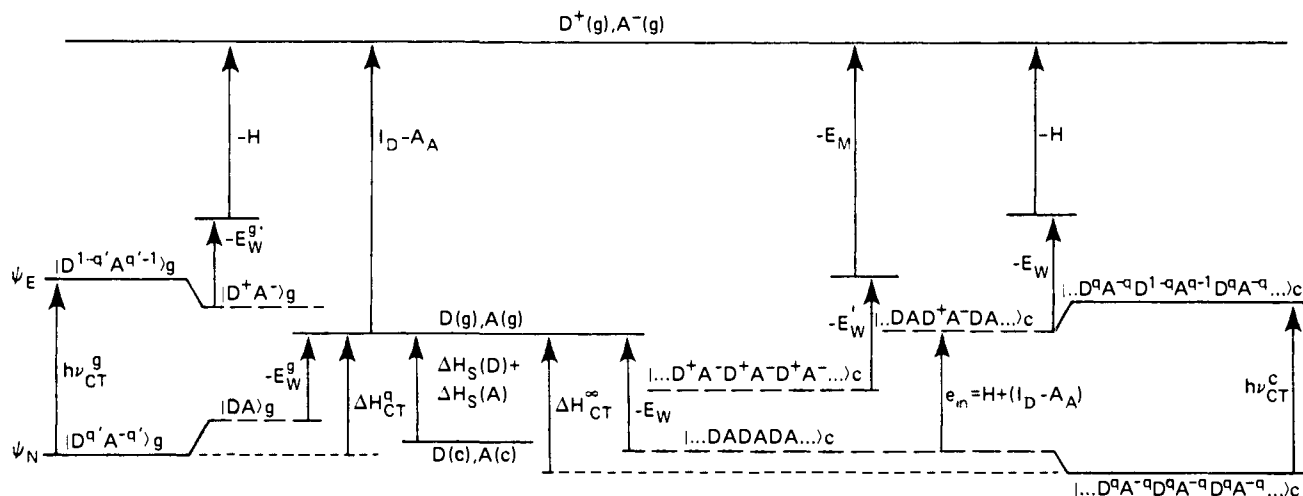
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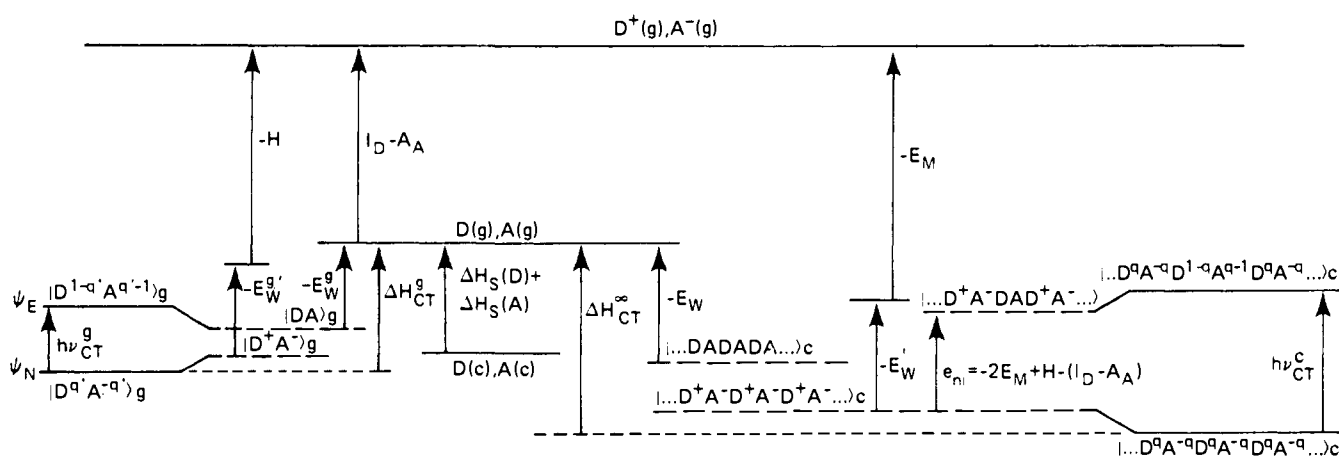
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**Figure 1.** Born-Haber cycle and optical charge-transfer bands for gaseous and crystal DA complexes, when energy levels  $|DA\rangle_g$  and  $|\dots DADA\dots\rangle_c$  are lower than the levels  $|D^+A^->_g$  and  $|\dots D^+A^-D^+A^-D^+A^- \dots\rangle_c$ , respectively.



**Figure 2.** Born-Haber cycles and optical-transfer bands for gaseous and crystal DA complexes for the case that the energy levels  $|D^+A^->_g$  and  $|\dots D^+A^-D^+A^-D^+A^- \dots\rangle_c$  are lower than the levels  $|DA\rangle_g$  and  $|\dots DADA\dots\rangle_c$ , respectively.

Structural,<sup>13,14</sup> vibrational,<sup>12,15-17</sup> optical,<sup>11,12,18-20</sup> and magnetic measurements<sup>21</sup> all support the assignment of this transition as one between the Neutral and the Ionic phase (although there is some controversy as to the detailed mechanism and Ehrenfest order of the phase transition).<sup>10,12,14,18,19,22-24</sup>

We discuss here the energetics of the N-I phase transitions in this mixed-stack material.<sup>25</sup> It has been assumed<sup>11-16,20-22</sup> that the N-I transitions are driven by the expected increase in electrostatic Madelung energy,  $E_M$ , at either high pressure or low temperature. That assumption is quantitatively tested here by calculating  $E_M$  as a function of pressure and temperature. The

observed crystal lattice compression to 11 kbar and its thermal contraction down to 50 K are shown to increase the Madelung energy *enough* to account for both transitions. In addition, the Neutral-Ionic transition offers us a unique opportunity to test and compare some of the most general factors involved in charge transfer. Thus, the N-I boundary and  $h\nu_{CT}$  will be linked to molecular properties (such as  $I_D$  and  $A_A$ ) known for TTF<sup>26</sup> and chloranil<sup>27</sup> and to the calculated energies  $E_M$  and  $(e^2/a)$ . Finally, a Madelung calculation for the Ionic mixed-stack compound<sup>28</sup> TTF bromanil is also reported.

### Calculation

The relevant energetics (Born-Haber cycles) for a Neutral and for an Ionic crystal are shown in Figures 1 and 2, respectively. The thermodynamically stable states are indicated by thick horizontal lines; dashed horizontal lines identify theoretically convenient (if fictitious) states. On the left of Figures 1 and 2 are the gas-phase complexes  $|D^{q'}A^{-q'-1}g\rangle$  with nominal charge transfer  $q'$ ,  $0 \leq q' \leq 1$ ; on the right are the crystalline complexes  $|\dots D^qA^{-q}D^qA^{-q}D^qA^{-q} \dots\rangle_c$  with Avogadro's number  $N$  of D and A species, and with charge-transfer  $q$ ,  $0 \leq q \leq 1$ .

Also shown on Figures 1 and 2 are the Madelung energy  $E_M$ , the Coulomb energy  $H = (e^2/a)$  that binds the  $D^+$  and  $A^-$  ions in the gas-phase complex  $|D^+A^->_g$  or in the crystalline case of  $|\dots DADA^+A^-DA \dots\rangle_c$  (where there are  $N-1$   $D^0$  and  $A^0$  molecules and *one* nearest-neighbor  $D^+A^-$  pair); the energy  $e_{in} = H + I_D - A_A$  required<sup>4</sup> to form a nearest-neighbor ion pair in an otherwise neutral lattice, the energy  $e_{ni} = -2E_M$

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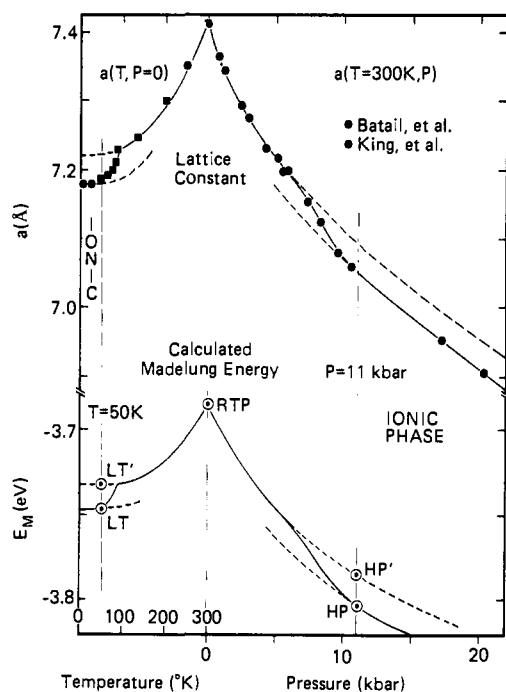
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Table I

point <sup>a</sup>	TTF chloranil				TTF bromanil			
	a/Å	b/Å	c/Å	β/°	E <sub>M</sub> /eV (MNDO charges)	E <sub>M</sub> /eV CNDO/2 charges)	H/eV (MNDO charges)	E <sub>M</sub> /eV (CNDO/2 charges)
RTP	7.411	7.621	14.571	99.20	-3.686	-3.534	-2.771	-3.478
HP	7.055	7.455	14.114	99.20 <sup>b</sup>	-3.803	-3.630	-2.848	
HP' <sup>c</sup>	7.093	7.523	14.169	99.20 <sup>b</sup>	-3.785	-3.617	-2.840	
LT	7.187	7.534	14.425	99.20 <sup>b</sup>	-3.747	-3.586	-2.819	
LT' <sup>d</sup>	7.215	7.590	14.488	99.20 <sup>b</sup>	-3.733	-3.575	-2.813	
(I <sub>D</sub> - A <sub>A</sub> )						4.08 <sup>e</sup>		4.39 <sup>e</sup>

<sup>a</sup>See Figure 3b. <sup>b</sup>Assumed. <sup>c</sup>Obtained from data at HP by adding Δa = 0.038 Å, Δb = 0.068 Å, Δc = 0.055 Å. <sup>d</sup>Obtained from data at LT by adding Δa = 0.028 Å, Δb = 0.056 Å, Δc = 0.063 Å. <sup>e</sup>Using I<sub>D</sub> = 6.83 eV for TTF (ref 26), A<sub>A</sub> = 2.75 ± 0.2 eV for chloranil (ref 27), and A<sub>A</sub> = 2.44 ± 0.2 eV for bromanil (ref 27).



**Figure 3.** (Top): Dependence of stacking axis lattice constant (*a*) on the temperature (at *P* = 0) and on pressure (at *T* = 300 K). The Neutral-Ionic phase transitions are evident at both low temperatures and high pressures, with the ionic phase stable below 50 K and (*P* = 0) and above 11 kbar (*T* = 300 K). (Bottom): Calculated Madelung energy using MNDO charges at different temperatures and pressures. (The lines are schematic.)

+  $H - (I_D - A_A)$  required<sup>4</sup> to form a nearest-neighbor neutral pair in an otherwise ionic crystal; the energy  $E_W$  that represents dispersion and repulsion energies, and the relevant Mulliken charge-transfer band energies  $h\nu_{CT}^g$  and  $h\nu_{CT}^c$  for the gas-phase and the crystal complexes.

If Mulliken CT indeed stabilizes the ground state by mixing  $|DA\rangle_g$  and  $|D^+A^-\rangle_g$ :

$$\psi_N = |D^q A^{-q}\rangle_g = (q)^{1/2} |D^+ A^-\rangle_g + ((1 - q + q^2 S^2)^{1/2} - S(q)^{1/2}) |DA\rangle_g \quad (2)$$

Then  $\Delta H_{CT}^{\pm}$  is the relevant (excess) enthalpy of stabilization of the gaseous CT complex.<sup>2</sup> Similar excess enthalpies  $\Delta H_{CT}^{\pm}$  can be defined, and have recently been measured<sup>29</sup> for some crystalline DA complexes. If the state  $|\dots DADADA \dots\rangle_c$  is lower than the state  $|\dots D^+ A^- D^+ A^- D^+ A^- \dots\rangle_c$  (Figure 1) the crystal is Neutral; if it is higher (Figure 2) the crystal is Ionic.

The N-I phase transitions in TTF chloranil have been followed by the pressure and temperature dependence of the measured lattice constants of the X-ray unit cell, as shown at the top of Figure 3. On the left, the *a*-axis is plotted vs. temperature at atmospheric pressure (*p* ~ 0 kbar) using the powder data of Batail et al.<sup>13</sup> and, on the right, that measured at 300 K vs. pressure from the excellent work of King, LaPlaca, et al.<sup>14</sup> on single crystals in a diamond anvil cell. The *a*-axis is the stacking axis,

Table II. Charge Distributions

atom label (ref 25)	TTF <sup>+</sup> in TTF chloranil CNDO/2	TTF(A) <sup>+</sup> in TTF bromanil CNDO/2	TTF(B) <sup>+</sup> in TTF bromanil CNDO/2	TTF <sup>+</sup> <i>D</i> <sub>2h</sub> optimized MNDO
S1	0.1147	0.1027	0.1044	0.29
S2	0.1077	0.1046	0.1088	0.29
C1	0.0201	0.0280	0.0227	-0.12
C2	0.0453	0.0436	0.0425	-0.12
C3	0.0309	0.0287	0.0234	-0.14
H1	0.0929	0.0965	0.0993	0.15
H2	0.0884	0.0959	0.0989	0.15
	chloranil <sup>-</sup> in TTF chloranil CNDO/2	bromanil(A) <sup>-</sup> in TTF bromanil CNDO/2	bromanil(B) <sup>-</sup> in TTF bromanil CNDO/2	chloranil <sup>-</sup> <i>D</i> <sub>2h</sub> optimized MNDO
O	-0.3249	-0.3230	-0.3226	-0.3726
C11	-0.2067	-0.2040	-0.2033	-0.1172
C12	-0.2101	-0.2030	-0.2029	-0.1172
CA	0.1923	0.1833	0.1855	0.2560
CB	0.0233	-0.0245	0.0243	-0.0745
CC	-0.0261	-0.0222	0.0189	-0.0745

along which one expects (and indeed finds) the largest compression and thermal contraction. At low temperatures, there is an extra contraction starting below 84 K, and extending to ~50 K, marking an intermediate region of the Neutral-Ionic phase transition. There is a similar extra contraction starting near 6.5 kbar and continuing until 11 kbar (which is seen more clearly in the changes in *b* and β). The details of this intermediate transition region are controversial and will not be discussed here. One theory of this transition<sup>22</sup> indicates that the N-I transition, if it were simple, would have occurred at ~50 K and ~11 kbar. For the present calculations, we shall therefore assume that the transition occurs at 50 K and at 11 kbar.

Outside the transition region, the X-ray data for *a*, *b*, *c*, and β in the Neutral (N) phase can be fitted by a quadratic function of *T* and *P*, and those in the Ionic (I) phase can be fitted by the same quadratic function, but with a constant shift Δ at the transition. The quadratic fits to the unit-cell data were used to obtain the dashed lines in Figure 3 and the lattice parameters listed in Table I. RTP refers to the room temperature and pressure crystal structure.<sup>25</sup> These shifts, Δ*a*, Δ*b*, Δ*c*, Δβ are shown in a footnote to Table I and are seen to be remarkably similar for the pressure and temperature-induced transitions. This is consistent with the interpretation and evidence that this extra contraction is caused by the decreasing length of the C-H...O hydrogenic contacts upon going into the Ionic phase,<sup>13</sup> which should be the same at low temperature (LT) and at high pressure (HP). Since the extra contraction is related to a different phenomenon, we will neglect its contribution to the transition and focus on the calculated Madelung energy at the extrapolated N-phase points HP' and LT' (rather than HP and LT) as indicated on the bottom of Figure 3. (In any case, the extra contractions HP' → HP and LT' → LT cause only a small (~0.015 eV) shift in  $E_M$ .)

Since separate, complete crystal structure determinations are not available at all the relevant temperatures and pressures, we approximate the structure by displacing the molecules in the 300 K structure<sup>25</sup> according to the changes in lattice parameters. The intramolecular geometries and orientations of the molecules were kept constant and the small shifts in the monoclinic angle were ignored. Several charge distributions for TTF<sup>+</sup> and chloranil<sup>-</sup> were tested; the two that gave the lowest and highest energy are given in Table II. The CNDO/2 distributions were

obtained for the fixed geometry of the TTF chloranil 300 K crystal structure,<sup>25</sup> while the MNDO charges were obtained from geometry-optimized calculations for the  $D_{2h}$  idealized radical ions.<sup>30,31</sup> Since the calculation of the Madelung energy<sup>32</sup> should be made in the Ionic phase, the MNDO results should be more reliable because they were calculated for the geometry of the ion radicals.

An "internal consistency check" on calculations and predictions for TTF chloranil can be made by studying TTF bromanil. This compound crystallizes as a mixed-stack material,<sup>28</sup> and its optical spectrum shows it to be Ionic<sup>28</sup> even at ambient temperature and pressure. However, the  $D^+A^-$  stacks occur in an unusual arrangement: a plane, or sheet of stacks growing along the  $a$ -axis alternates with a second sheet of stacks growing along the  $b$ -axis almost perpendicular to the first sheet. The higher ionicity of TTF bromanil compared to TTF chloranil at 300 K and 1 bar must somehow occur even though  $I_D - A_A$  is larger by 0.31 eV for TTF bromanil. Since MNDO calculations are not possible for bromine-containing molecules, we were restricted to using an extended form<sup>33</sup> of CNDO/2: the relevant charge distributions are listed in Table II.

The Madelung energies  $E_M$  and the nearest-neighbor Coulomb energies  $H$  were obtained by using the programs CELMAP and EWALD described elsewhere.<sup>5,33</sup> The results are listed in Table I. The ratio  $\alpha = E_M/H$  for TTF chloranil yields the Madelung "constants"  $\alpha = 1.330, 1.335, \text{ and } 1.329$  for points RTP, HP, and LT, respectively.

### Discussion of Results

The calculated<sup>34</sup> Madelung energies are listed in Table I and those obtained using the MNDO charge distribution (Table II) are plotted on the bottom of Figure 3. It is clear that the lattice contraction at low temperatures and high pressures gives rise to an increase in the electrostatic binding energy of the crystal. Focusing on the Madelung energy of TTF chloranil calculated at 300 K (RTP in Figure 3), we find that  $E_M$  for the MNDO charge distribution is  $\sim -3.7$  eV, while CNDO/2 charges give  $\sim -3.5$  eV. These are the high and low values, as a variety of other choices of charges gives intermediate values (not listed in Table II). Thus, the charge distribution has a relatively small effect on the calculated Madelung energy. Since the actual charge distribution is unknown, there is an uncertainty in the absolute value of  $E_M$  for TTF chloranil. These results illustrate the uncertainties inherent in Madelung calculations on such a compound and remind us of their limited accuracy. At 300 K and atmospheric pressure (RTP), we estimate  $E_M \sim -3.7 \pm 0.2$ . This behavior is consistent with the experience in other Madelung calculations. The all-valence ( $\sigma\pi$ ) charge distributions (CNDO/2, INDO, MINDO/3, MNDO) seem to yield somewhat smaller Madelung energies than the older,  $\pi$ -only charge distributions (Hückel, Pariser-Parr-Pople): for the ionic salts TMPD-TCNQ [ $E_M = 3.94$  eV ( $\pi$ ),<sup>35</sup>  $-3.29$  eV ( $\sigma\pi$ )<sup>29</sup>] and TMPD chloranil [ $-4.43$  ( $\pi$ )<sup>35</sup>], for the neutral salts (in fictitious  $\rho = 1$  states) the calculated values are for hexamethylbenzene chloranil [ $-4.41$  ( $\pi$ )<sup>35</sup>], naphthalene TCNE [ $-4.31$  ( $\pi$ )<sup>35</sup>], naphthalene TCNQ [ $-3.38$  ( $\sigma\pi$ )<sup>11</sup>], anthracene TCNQ [ $-3.19$  ( $\sigma\pi$ )<sup>29</sup>]. Note that the value ( $-3.7 \pm 0.2$  eV) of  $E_M$  established here for TTF chloranil is similar to the values of other mixed-stack compounds, which average  $-3.3$  eV (for  $\sigma\pi$  charge densities). Hence, the variations in  $E_M$  from compound to compound are of order  $\sim 0.4$  eV, whereas variations in ( $I_D - A_A$ ) are generally many times larger.<sup>11</sup> Also, for a given charge distribution the changes in  $E_M$  calculated due to high pressure, for example, are quite small: for large variations in the charge distribution, we find that between RTP and HP',  $E_M$  varies only by 0.02 eV.

It was estimated<sup>11</sup> that at 300 K and atmospheric pressure, TTF chloranil is energetically  $\sim 0.1$  eV away from the Ionic phase. The Madelung calculations presented here (Table I) indeed indicate that  $E_M$  increases (becomes more negative) by  $0.10 \pm 0.01$  eV going from  $p = 0$  to  $p = 11$  kbar at HP' (not including the 0.01 eV contribution from the extra contraction caused by the hydrogen

contacts). In contrast, the increase at  $p = 0$  is only  $0.050 \pm 0.005$  eV caused by the thermal contraction between 300 and 50 K. We suggest that the increase in Madelung energy resulting from the thermal contraction and from the compressibility at high pressure can be sufficiently large to provide much of the driving force for the Neutral-Ionic transitions in TTF chloranil and presumably other materials,<sup>11</sup> as well.

Since a considerably smaller increase in  $E_M$  is required to induce the transition at low temperature than at high pressure, there may be an additional driving force for the former transition. Optical<sup>11,12</sup> and structural<sup>13,14</sup> measurements suggest that both transitions are N-I. A potentially important difference between them is the possible occurrence of a structural dimerization of the stacks: X-ray measurements<sup>14</sup> at the high-pressure Ionic phase indicate that the molecules are uniformly spaced within the stack, whereas magnetic susceptibility,<sup>21</sup> IR,<sup>15,21</sup> and EPR measurements<sup>21</sup> all indicate that there is a dimerization of the stacks in the low-temperature Ionic phase. Thus, we propose that a gain in energy associated with the dimerization may be the additional driving energy of the low-temperature Ionic phase: this makes it possible for the transition to occur despite the smaller increase in Madelung energy. There are two models for the driving energy for this dimerization: the gain in magnetic energy of the Ionic phase (Spin-Peierls)<sup>21</sup> and a gain in electronic energy by forming a soliton lattice.<sup>24</sup> It also follows that the transition at HP is simpler than that at LT, since the HP transition does not involve a dimerization. Thus, in the following comparisons, we shall focus on the transition at high pressure.

The comparison of  $E_M$  (Table I) based on CNDO/2 charges for TTF chloranil and TTF bromanil yields ( $I_D - A_A$ ) +  $E_M = 0.55$  and 0.91 eV, respectively. Yet, the latter is Ionic and the former is Neutral. Two possible origins of this discrepancy come to mind: (i) the charge distributions used are far from adequate,<sup>34,36</sup> and the Mulliken population analysis must be abandoned in favor of molecular electrostatic potential-derived charges, and (ii) other contributors to the total lattice energy<sup>5,37</sup> (polarization energy, charge-transfer-dependent part of the London dispersion energy) stabilize TTF bromanil more than TTF chloranil.

Strictly speaking, the cohesive energy of a neutral (ionic) crystal can be expanded<sup>5,37</sup> as  $E_{\text{coh}}^{\text{N}} = E_{\text{pol}}^{\text{N}} + E_{\text{d}}^{\text{N}} + E_{\text{cd}}^{\text{N}} + E_{\text{r}}^{\text{N}} + \dots$  ( $E_{\text{coh}}^{\text{I}} = E_{\text{pol}}^{\text{I}} + E_{\text{d}}^{\text{I}} + E_{\text{cd}}^{\text{I}} + E_{\text{r}}^{\text{I}} + \dots$ ), where  $E_{\text{pol}}^{\text{N}}$ ,  $E_{\text{d}}^{\text{N}}$ ,  $E_{\text{cd}}^{\text{N}}$ , and  $E_{\text{r}}^{\text{N}}$  ( $E_{\text{pol}}^{\text{I}}$ ,  $E_{\text{d}}^{\text{I}}$ ,  $E_{\text{cd}}^{\text{I}}$ ,  $E_{\text{r}}^{\text{I}}$ ) are the polarization, London dispersion, charge-dipole, and repulsion energies for the neutral (ionic) lattices, respectively. Thus the N-I interface is given by

$$E_M + (E_{\text{pol}}^{\text{I}} - E_{\text{pol}}^{\text{N}}) + (E_{\text{d}}^{\text{I}} - E_{\text{d}}^{\text{N}}) + (E_{\text{cd}}^{\text{I}} - E_{\text{cd}}^{\text{N}}) + (E_{\text{r}}^{\text{I}} - E_{\text{r}}^{\text{N}}) + \dots + I_D - A_A = 0 \quad (3)$$

rather than by eq 1.

Both the polarization and the dispersion energies depend on the molecular polarizability which is charge transfer dependent:<sup>38</sup> open-shell radical ions are more polarizable than closed-shell neutral molecules. This effect had been calculated for TTF-TCNQ, using minimum-basis MINDO/3-FP atom-in-molecule polarizabilities.<sup>38</sup>  $E_{\text{pol}}^{\text{N}} = -0.73$  eV and  $E_{\text{pol}}^{\text{I}} = -2.96$  eV for  $q = 0, 1$ , respectively.<sup>37</sup> Unfortunately, MINDO/3-FP polarizabilities are not satisfactory in the  $\pi$  or molecular stacking direction.<sup>38</sup> Better CNDO/2-FPP polarizabilities are available for molecules up to the size of benzene,<sup>39</sup> but CNDO/2-FPP requires too much computer time for TTF, chloranil, or bromanil. However, for neutral TTF, chloranil, and bromanil crystals  $E_{\text{pol}}^{\text{N}}$  has been estimated experimentally from shifts of the ultraviolet photoelectron spectrum of solid samples, relative to the gas-phase spectrum:  $E_{\text{pol}}^{\text{N}} = -1.4, -1.6, -2.2$  eV, respectively, for TTF, chloranil, and bromanil.<sup>40</sup> This difference of 0.6 eV between  $E_{\text{pol}}^{\text{N}}$

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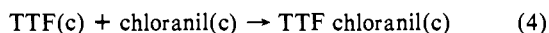
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values for bromanil and chloranil is in the expected direction, and should be magnified in ionic crystals containing chloranil<sup>-</sup> and bromanil<sup>-</sup> ions. Thus,  $E_M + E_{pol}^1$  should be more negative by at least 0.5 eV for TTF bromanil than for TTF chloranil.

The arguments given in this paper are based on  $E_M$  values, which already show relative trends in agreement with experiment. More elaborate calculations of  $E_M + E_{pol}^1 + E_d^1 + E_{ed}^1 + E_r^1$  are likely to confirm the points made here.

The next point to be considered is whether TTF chloranil is thermodynamically stable in the sense of Figures 1 and 2, i.e., whether  $\Delta H \approx \Delta G$  is negative for the chemical reaction



The answer is not known experimentally. There are at least three different adducts<sup>16,17,25</sup> of TTF and chloranil. Given this polymorphism, it is difficult to speculate which crystal is the most stable form, or whether  $\Delta H_{CT}^\infty < 0$  should be expected for it, as has been observed recently for the Neutral mixed-stack complexes naphthalene TCNQ<sup>11</sup> and anthracene TCNQ.<sup>11</sup>

In the case of TTF chloranil, we have a unique chance to compare the magnitudes of many of the factors influencing the charge transfer. For TTF,  $I_D = 6.83$  eV,<sup>26</sup> while for chloranil,  $A_A = 2.75 \pm 0.2$  eV,<sup>27</sup> so that  $(I_D - A_A) = 4.08 \pm 0.2$  eV. As discussed earlier, we calculate that  $E_M = -3.8$  eV for the Ionic phase (HP'). Thus, we can readily examine the simplest criterion<sup>4</sup> for the Neutral-Ionic phase transition, namely  $(I_D - A_A) + E_M = 0$  (eq 1). In this case, the numbers would predict that at the transition the Neutral phase is more stable by  $\sim 0.3 \pm 0.2$  eV. Using these numbers we can also calculate the energy of the charge transfer band as

$$h\nu_{CT} = (I_D - A_A) - H \quad (5)$$

and obtain  $h\nu_{CT}(\text{RTP}) = 1.3$  eV (compared to the observed<sup>20</sup> value of 0.65 eV). The predicted temperature dependence of  $h\nu_{CT}$  is due to the dependence of  $H$ , which increases by  $\sim 0.04$  eV between RTP and LT' (while a shift of  $\sim 0.10$  eV is measured<sup>20</sup>).

Considering the simplicity of including only  $(I_D - A_A)$  and the electrostatic energies, the above agreement is remarkably good. One can improve on these simple notions by including the effect of the overlap between molecules, and hence the fact that the molecules in the ground state have a net charge  $\pm q$ , where  $q \neq 0, 1$ , but  $0 < q < 1$ . The condition for the neutral-ionic transition (that the two energies are equal) then becomes

$$(I_D - A_A)q_N + E_M q_N^2 = (I_D - A_A)q_I + E_M q_I^2 \quad (6)$$

This new criterion is satisfied at the transition within 0.1 eV (since we know  $q_N = 0.3$  and  $q_I = 0.73$ , appropriate for the LT

phase<sup>15,20</sup>). Similarly, the energy of the charge-transfer band becomes

$$h\nu_{CT} = (1 - 2q)[(I_D - A_A) + (1 - 2q)H + 2qE_M] \quad (7)$$

(Note that this equation reduces to the correct formula in the neutral ( $q = 0$ ) and ionic ( $q = 1$ ) limits). Using eq 7 we calculate  $h\nu_{CT}(\text{RTP}) = 0.57$  eV, in improved agreement with the observed<sup>20</sup> energy of 0.65 eV. The calculated shift at low temperature is very sensitive to the degree of charge transfer:  $\Delta h\nu_{CT} = 0.28$  eV (for  $q = 0.3$ ) and 0.17 eV (for  $q = 0.25$ ), compared with the observed 0.1 eV shift. We conclude that the agreement with experiment is improved by including finite charge transfer in the ground state. The remaining discrepancy is presumably due to other effects not included here, such as the polarization energy, the charge-transfer dependent dispersion forces, the repulsive interactions, etc.

## Conclusions

In order to probe what factors control the degree of charge transfer from donor to acceptor in charge-transfer solids, we have calculated the crystalline electrostatic Madelung energy,  $E_M$  for tetrathiafulvalene (TTF) chloranil as a function of pressure and temperature. At 300 K between 1 bar and 11 kbar (where there is a transition between Neutral and Ionic ground states)  $E_M$  is calculated to increase by  $\sim 0.1$  eV. This increase indicates that the pressure dependence of the Madelung energy may be sufficiently large to drive the Neutral-Ionic phase transition at high pressures. The magnitude of  $E_M = -3.8$  eV at 11 kbar is used to show that the calculated energies of the Neutral and Ionic states become approximately equal at this pressure. On the other hand, at 1 bar between 300 and 50 K (where another transition between Neutral and Ionic ground states has been found)  $E_M$  increases by only  $\sim 0.05$  eV, or half as much as for the transition at high pressure. This suggests that there is an additional driving force for the Neutral-Ionic transition at low temperature (which we believe is the dimerization of the stacks).

It is concluded that the simplest notions of  $(I_D - A_A)$  and the Madelung energy are remarkably successful in describing both the observed variations in the charge transfer from donor to acceptor in TTF chloranil and the energy of the optical charge-transfer band. Further improvement in quantitative agreement has been obtained by including the effects of the charge transfer in the ground state.

**Acknowledgment.** We thank Hubert King, Sam La Placa, et al. for allowing us to present their high-pressure data. We are also grateful for the computing assistance of Stuart Parkin.

**Registry No.** TTF chloranil, 70608-85-4; TTF bromanil, 71703-67-8.

## Some Effects of Amine Substituents in Strained Hydrocarbons

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**Abstract:** The bond-deviation index and the electrostatic potential have been used to study the effects of the amine group as a substituent in several strained systems: cyclopropane, triprismane, and cubane. For the parent hydrocarbons, the bond-deviation index shows triprismane to have both cyclopropane-like and cubane-like C-C bonds, a conclusion that is confirmed by these molecules' electrostatic potentials. In all three hydrocarbons, there are negative electrostatic potentials associated with the C-C bonds, showing these to be reactive sites toward electrophilic attack. The introduction of amine substituents, which we normally find to have pyramidal geometries in these systems, weakens these negative regions. When the  $\text{NH}_2$  is forced to be coplanar with the carbon to which it is attached, however, it has the effect of strengthening the negative C-C bond potentials. This can be interpreted as involving a  $\pi$ -type charge donation by the amine group to the carbon framework.

As part of a continuing study of the reactive behavior of strained molecules, we have examined some amine derivatives of cyclo-

propane (I), triprismane (II) (tetracyclo[2.2.0.0<sup>2,6</sup>.0<sup>3,5</sup>]hexane), and cubane (III) (pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane). In