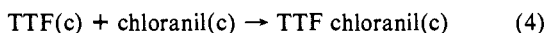


values for bromanil and chloranil is in the expected direction, and should be magnified in ionic crystals containing chloranil<sup>-</sup> and bromanil<sup>-</sup> ions. Thus,  $E_M + E_{pol}^1$  should be more negative by at least 0.5 eV for TTF bromanil than for TTF chloranil.

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  $E_M + E_{pol}^1 + E_d^1 + E_{cd}^1 + E_r^1$  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



aromatic systems, the amine group is commonly regarded as being a strong donor of  $\pi$ -type electronic charge (interpreted as a resonance effect) and a weak  $\sigma$  acceptor (through induction).<sup>1,2</sup> We found earlier, in agreement with the  $\pi$ -donor concept, that the substitution of an  $\text{NH}_2$  group into benzene (to form aniline) causes the electrostatic potentials above and below the ring to become more negative, thereby activating the ring toward electrophilic attack, especially in the ortho and para positions.<sup>2</sup> These findings are fully in accord with well-known experimental observations.<sup>1</sup> In the present work, we have sought to determine what are the effects of  $\text{NH}_2$  when it is a substituent in strained systems. Our approach has been to compute and analyze two key molecular properties: the bond-deviation index and the electrostatic potential.

### Bond Deviation Index

The bond deviation index provides a quantitative basis for characterizing chemical bonds in terms of their bond paths. The bond path concept was introduced by Bader and his colleagues<sup>3,4</sup> and refers to the path between two bonded nuclei that passes through the saddle point of the electronic density in the internuclear region and follows the density gradient from the saddle point to each nucleus. The bond path may be viewed as the ridge of maximum electronic density between the two nuclei; this is not necessarily the same as the internuclear axis (the straight line connecting the nuclei). For example, the bond paths of the C-C bonds in cyclopropane have been shown to have an outward curvature,<sup>5</sup> fully consistent with the "bent bond" model of the bonding in this molecule.<sup>6,7</sup>

In order to put the information conveyed by the bond path on a more quantitative basis, we have introduced the "bond deviation index",  $\lambda$ , as a measure of the difference between an actual bond path and a standard reference path.<sup>8</sup> We define the latter in terms of the superposed electronic densities of the corresponding free atoms, placed at the same positions as they occupy in the molecule. Thus, our reference path is given by the gradients of the superposed free atom electronic density between its saddle point in the internuclear region and the nuclei. This is not invariably the same as the internuclear axis, due to the contributions of the other atoms in the molecule. For example, the C-C reference paths in cubane show a slight curvature inward, toward the center of the cube.<sup>9</sup>

We define the bond deviation index by eq 1.<sup>8</sup>

$$\lambda = \frac{\left( \frac{1}{N} \sum_{i=1}^N r_i^2 \right)^{1/2}}{R} \quad (1)$$

The  $r_i$  values are the lengths of  $N$  equally spaced lines drawn between the two paths.  $N$  is taken to be 320, which is well beyond the point at which further increases in  $N$  produce no significant change in  $\lambda$ . Dividing by  $R$ , the internuclear distance, makes  $\lambda$

a scaled (and dimensionless) quantity that can be used to compare bonds of different lengths.

The bond deviation index makes it possible to characterize the individual bonds in a molecule and to gain insight into their natures and properties. It is a particular advantage to be able to focus specifically upon each individual bond, rather than being obliged to deal with the molecule as a whole.

We have now computed  $\lambda$  for the bonds in a number of molecules.<sup>8,9</sup> Its usefulness is not limited to those systems that are traditionally regarded as being strained; even the bonds in the water and the ammonia molecules have nonzero values for  $\lambda$ , apparently due to the effects of the lone pairs.<sup>8</sup>

### Electrostatic Potential

The electrostatic potential  $V(\vec{r})$  that is created at any point  $\vec{r}$  by the nuclei and electrons of a molecule is given rigorously by eq 2.

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r}' - \vec{r}|} \quad (2)$$

$Z_A$  is the charge on nucleus A, located at  $\vec{R}_A$ , and  $\rho(\vec{r})$  is the electronic density function of the molecule. The electrostatic potential is known to be an effective guide to the reactive behavior of molecules;<sup>10-13</sup> for example, an approaching electrophile will initially be attracted to those regions in which  $V(\vec{r})$  is negative, and particularly to those points at which  $V(\vec{r})$  is a minimum. An important feature of the electrostatic potential is that it is a real physical property, which can be determined not only computationally but also experimentally.<sup>12,14</sup>

We have shown that the strained C-C bonds in cyclopropane and cubane possess the interesting property of having significant negative electrostatic potentials associated with them.<sup>5,9</sup> These are located to the outside of the molecular framework, with their most negative points (the potential minima) being near the midpoints of the bonds. Such negative potentials have not been detected for more typical C-C single bonds, as in ethane and propane.<sup>10,15</sup> Their existence is consistent with the bond paths in cyclopropane and cubane,<sup>5,9</sup> which indicate that the internuclear electronic distributions are not concentrated along the internuclear axes (as in many C-C single bonds<sup>4</sup>) but rather along curved paths to the outside. (It should be noted, however, that an electronic distribution of this sort does not invariably give rise to a negative potential.<sup>5</sup>)

The presence of these negative electrostatic potentials means that these C-C bonds can be regarded as reactive sites, attractive to electrophiles, and helps to explain why the C-C bonds in some three-membered ring molecules, such as cyclopropane, show certain olefin-like chemical properties, including the ability to undergo some addition reactions.<sup>16-20</sup> There is also experimental evidence that the C-C bonds in cubane act as sites for electrophilic attack, in rearrangement reactions that are catalyzed by metal ions.<sup>21,22</sup> The initial step appears to be an interaction between

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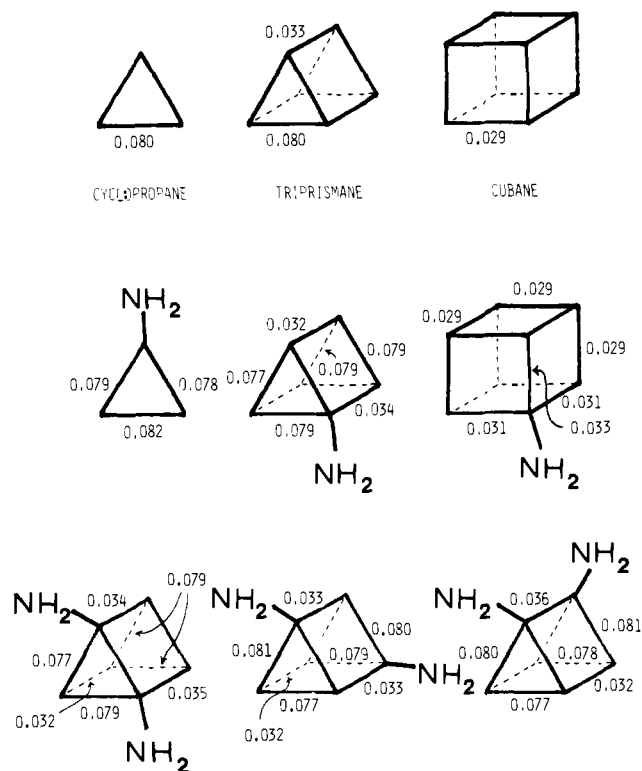


Figure 1. Bond deviation indices for the C-C bonds in cyclopropane, triprismane, cubane, and some of their amine derivatives.

the positive ion and a C-C bond.

#### Methods

All of the bond deviation indices and electrostatic potentials to be discussed in this paper were computed from *ab initio* self-consistent-field molecular orbital wave functions, using STO-5G or STO-6G basis sets.<sup>23</sup> (These give essentially identical results for the properties of present interest.) The molecular geometries used in these computations were determined by extensive optimization at the STO-3G level, which has been shown to be effective for this purpose.<sup>24</sup>

#### Results and Discussion

**Bond Deviation Indices.** Figure 1 shows our calculated bond-deviation indices for three strained hydrocarbons—cyclopropane (I),<sup>8</sup> triprismane (II), and cubane (III)<sup>8,9</sup>—and for some of their amine derivatives.

The case of triprismane illustrates the kind of insight that can be obtained through the use of the bond deviation index. The  $\lambda$  values for triprismane indicate that the C-C bonds in the three-sided faces are very much like those in cyclopropane, while the C-C bonds in the four-sided faces are quite similar to those in cubane. Thus, triprismane can be regarded, in this context, as two cyclopropane rings linked by three cubane-like bonds. The validity of this description shall be seen later.

The introduction of the amine group does not greatly affect the bond deviation indices (Figure 1). There is a tendency for a small decrease in the  $\lambda$  values for the cyclopropane-like bonds, and a slight increase in  $\lambda$  for the cubane-like bonds that lead to the site of substitution. The same trends are observed in the diamine derivatives of triprismane (Figure 1).

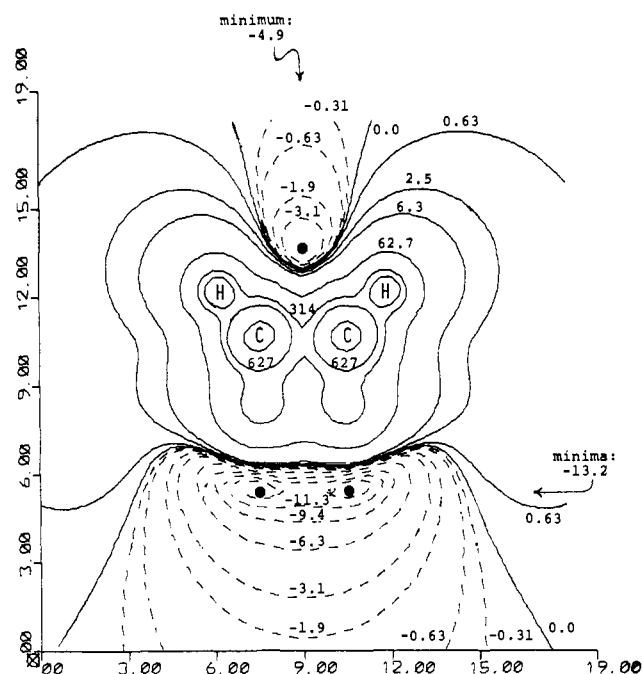


Figure 2. Electrostatic potential of triprismane in the mirror plane perpendicular to the three-sided faces, passing through one carbon in each of these faces and the midpoints of the opposite C-C bonds. The values of the potential are given in kcal/mol; the positions of the minima are indicated by solid circles. Axes show distances, in bohrs.

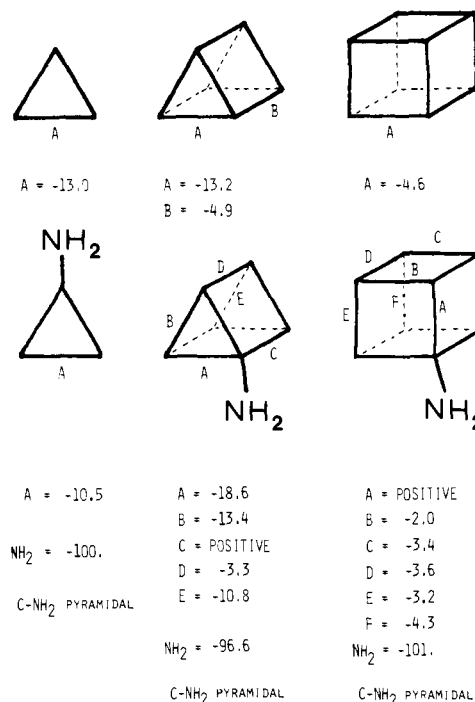


Figure 3. Electrostatic potential minima, in kcal/mol, associated with the C-C bonds and with the NH<sub>2</sub> groups in cyclopropane, triprismane, cubane, and their monosubstituted amine derivatives. The C-NH<sub>2</sub> portions of the latter have their optimized (pyramidal) configurations.

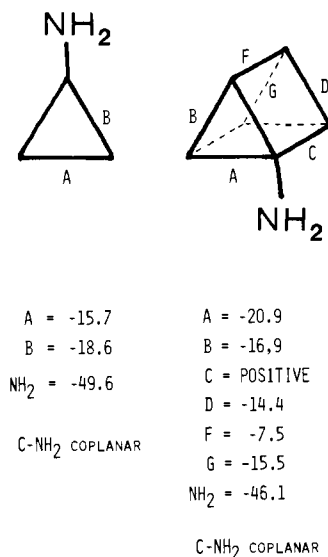
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**Electrostatic Potentials.** To illustrate some of the negative regions associated with the C-C bonds in these strained hydrocarbons, Figure 2 shows our calculated electrostatic potential for triprismane. Figure 3 summarizes some key features of the electrostatic potentials of the hydrocarbons and their monoamine derivatives. The figure indicates the values and approximate locations of the local minima (i.e., most negative points) of these potentials.

The negative potentials associated with the C-C bonds of cyclopropane and cubane have already been discussed. Triprismane



**Figure 4.** Electrostatic potential minima, in kcal/mol, associated with the C-C bonds and with the NH<sub>2</sub> groups in aminocyclopropane and aminotriprismane. The C-NH<sub>2</sub> portions have been forced into planar configurations.

faithfully reflects the bonding pattern revealed by its bond deviation indices (Figure 1); its cyclopropane-like C-C bonds have essentially the same minima as do those in cyclopropane, while its cubane-like bonds similarly match those in cubane. This is a striking demonstration of the power of the bond deviation index to characterize chemical bonds.

Figure 3 shows that the substitution of amine groups into these strained molecules has the general effect of causing the C-C bond potentials to become less negative. (Exceptions to this are some of the C-C bonds near the sites of substitution, which receive significant contributions from the strong negative potentials associated with the amine nitrogens.) In each of these derivatives, the optimized geometry of the NH<sub>2</sub> group is pyramidal (roughly similar to that of ammonia). (This is consistent with the observed photoelectron spectrum of aminocyclopropane.<sup>25</sup>)

Thus, instead of the  $\pi$ -type donation that is exhibited by NH<sub>2</sub> in aromatic systems,<sup>2</sup> some degree of inductive charge withdrawal may be occurring in these strained aliphatic amines. However, it is not nearly to the extent found for the NO<sub>2</sub> group; in nitrocyclopropane, for example, the negative C-C bond potentials have been completely eliminated.<sup>5</sup>

It is interesting to observe the marked change in the role of the amine group when it is forced into a configuration in which it is coplanar with the carbon to which it is attached, as is actually the case in some aromatic molecules (for example, the nitroanilines<sup>2</sup>). In aminocyclopropane and aminotriprismane, the effect of a planar NH<sub>2</sub> is to make the electrostatic potentials associated with the C-C bonds in the three-membered rings more negative

(compare Figures 3 and 4). This can be interpreted as reflecting  $\pi$  donation by the substituent, the planar configuration having put its lone pair into a p-type orbital that is favorably aligned for donating charge to the lowest unoccupied ( $\pi^*$ -type) molecular orbital, which encompasses the carbons in the three-membered ring.<sup>26,27</sup>

The contrast between the pyramidal and the planar NH<sub>2</sub> groups is reflected in the negative electrostatic potentials associated with the nitrogens. The highly localized lone pairs of the former produce potentials of roughly -100 kcal/mol, which is approximately twice the magnitude of the most negative potential on either side of the planar NH<sub>2</sub>. (The corresponding values in ground-state, pyramidal ammonia and aniline are -110 and -75 kcal/mol,<sup>2</sup> respectively, while in planar ammonia this potential is -57 kcal/mol.)

## Conclusions

The value of the bond deviation index as a means for characterizing chemical bonds and gaining insight into their natures is brought out very clearly by the example of triprismane. Comparisons of the respective bond deviation indices show the C-C bonds in the three-sided faces of triprismane to be very similar to those in cyclopropane, while the C-C bonds in the four-sided faces resemble those in cubane. This bonding pattern is fully confirmed by the negative electrostatic potentials associated with the C-C bonds in triprismane, which are very much like the corresponding potentials in cyclopropane and in cubane.

The electrostatic potentials of the amine derivatives of cyclopropane, triprismane, and cubane in their ground states (NH<sub>2</sub> pyramidal) show that the presence of the NH<sub>2</sub> group has weakened, perhaps through induction, the negative regions associated with the C-C bonds, which should make the latter less reactive toward electrophiles than in the unsubstituted hydrocarbons. When the NH<sub>2</sub> is forced into a planar configuration, it produces the opposite effect in aminocyclopropane and in the three-sided faces of aminotriprismane; the potentials of these C-C bonds become more negative than in the parent hydrocarbons. This appears to result from a  $\pi$ -type donation of charge to the carbon framework. The negative electrostatic potential characteristically associated with an amine nitrogen is much weaker in the planar configuration.<sup>28</sup>

**Acknowledgments.** We are grateful to Drs. Arthur Greenberg and Joel F. Liebman for pointing out an error in the original version of this paper. We greatly appreciate the support of this work, provided primarily by the U.S. Army Research Office, with some auxiliary support from the Large Caliber Weapon Systems Laboratory, U.S. Army Armament, Research and Development Center, Dover, NJ.

**Registry No.** Cyclopropane, 75-19-4; triprismane, 650-42-0; cubane, 277-10-1; aminocyclopropane, 765-30-0; aminotriprismane, 91443-17-3; aminocubane, 91424-46-3.

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