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Ionic Charge-Transfer Complexes. 2. Comparative ab Initio and Semiempirical Studies on Cationic Complexes of Aniline

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Abstract: The $(An)_2^+$ (An = aniline) dimer cation, in a planar sandwich geometry with head-to-head (HH) and to head-to-tail (HT) conformations, was studied by ab initio STO-3G, INDO, CNDO, and extended-Hückel theory (EHT) methods. For the HH conformation, all four methods show energy minima at the eclipsed conformation (slip = 0) and at a slip of 2.5 ± 0.1 Å and maxima at 1.3 and 3.7 Å. For the HT conformation, all the methods show minima at 0 and 1.9 ± 0.1 Å and maxima at 0.7, 3.3, and 4.3 Å. Both ab initio and EHT calculations show the eclipsed conformation most stable for the HH, and the slip = 1.9 Å conformation is most stable for the HT conformation. The agreement among EHT and the other methods suggests that the electronic interactions in the ionic complex are controlled by the overlap of the frontier orbitals. The EHT calculations also show that charge-transfer resonance electronic interaction contributes 4.7 kcal/mol to bonding in the complex, in good agreement with experiment-based estimates. The good agreement of EHT with ab initio results on geometries, and with experiment on the resonance energy, suggests that the method is useful for larger charge-transer complexes where ab initio calculations are prohibitive. An example is given on EHT results for a larger complex, $An^+{\cdot}HMB$ (HMB = hexamethylbenzene).

During the last decade, molecular orbital methods have been applied extensively to the study of intermolecular interactions.[1] An important type of such interactions occurs in charge-transfer complexes. An interesting subclass of charge-transfer complexes is ionic dimers, where the acceptor is a highly electron deficient species, i.e., a molecular cation. In the preceding paper we observed experimentally ionic charge transfer complexes, in which the electron acceptors are An^+ radical cations and the electron donors are aniline or aromatic hydrocarbons. The observed experimental trends suggested that in complexes where the components have equal or similar ionization energies, a substantial portion of the bonding is due to charge-transfer resonance. This also was observed previously in dimers of aromatic hydrocarbon radical cations.[2]

Unfortunately, the experimental results allow only indirect inference to the nature of the electronic interactions, and the geometry is also unknown. This information can be provided by theoretical calculations. Ideally, these calculations would be high-level ab initio methods such as were done on complexes of small molecular components by Schaefer,[3a] Pople,[3b] and Morokuma.[3c] However, for complexes with large components, semiempirical methods must be applied. It is necessary therefore to test the semiempirical methods on complexes of moderate size which exhibit the structural features of the larger complexes (e.g., delocalized π systems) yet are small enough to apply ab initio calculations.

In the present work, we apply STO-3G ab initio as well as CNDO, INDO, and extended-Hückel theory (EHT) calculations to the aniline dimer cation. Elsewhere, we shall apply comparative calculations to the $Bz^+{\cdot}Bz$ and $An^+{\cdot}Bz$ complexes. Our objectives are (1) to examine the experiment-based conclusions on resonance interactions in a more quantitative way, (2) to compare the four calculational methods by applying all to one common, fairly large system, and (3) to examine whether the EHT gives meaningful geometries for these complexes, as compared with the other methods.

Once establishing the applicability of EHT to calculate geometries of the complexes, we shall also demonstrate the application to a larger system where ab initio calculations would be prohibitive, i.e., the $An^+{\cdot}HMB$ complex. Comparing this with the $An^+{\cdot}An$ complex is of interest also since one involves a localized and the other a delocalized electron donor.

(1) Extended-Hückel Calculations. EHT has been applied with success to estimate the overlap interaction in usual, non-ionic charge-transfer complexes. Chesnut and Moseley[4] used an approximate version of the EHT to examine the effect of relative intermolecular geometry in a variety of planar charge-transfer and charge-resonance molecular complex pairs. The calculated structures showed good agreement with those observed for systems containing TCNQ-like fragments. They concluded that, using reasonable intermolecular separations, the qualitative features of the calculation are not affected significantly by truncating Hoffman's procedure to their π-only approximation.

Berlinsky[5a] and Lowe,[5b] independently, have reported EHT calculations on $(TCNQ)_2$, $(TTF)_2$, and their ionized forms. The total energy of the singly and doubly ionized TCNQ dimers exhibits minima for two different orientations, near a position for which the two molecules are directly over one another (eclipsed) and a position where there is significantly slip along the long axis of the molecule. It was shown[5] that the splitting energy of the HOMO of the dimer at various slip values agreed qualitatively with the change of the total EHT energy vs. slip values.

In this work, EHT has been applied by using standard parameters.[6] During the calculations, the geometry of each aniline, An, molecule was held fixed in the experimentally determined structure.[7] The barrier to inversion of the NH_2 group (~1 kcal mol) was neglected, and aniline was considered a planar molecule. In order to maximize the overlap, the parallel geometry for the dimer was adopted through two different configurations, namely head to head (HH) and head to tail (HT). These two structure types investigated here are illustrated in Figure 1 where we defined δ as the magnitude of slip relative to the fully eclipsed arrangement.

(a) Dependence of Orbital Overlap and E_{res} on Geometry. The geometry of the system is clearly reflected in the overlap matrix.

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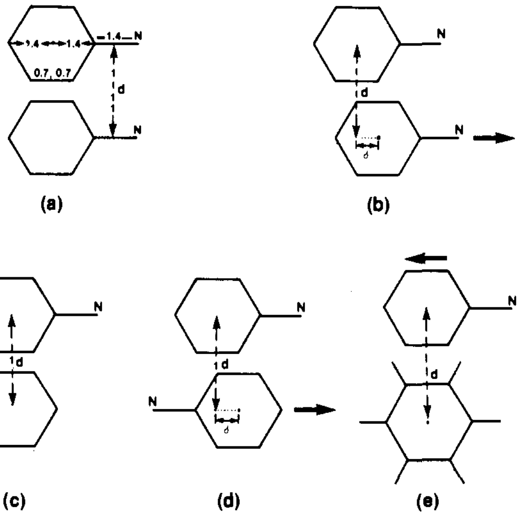

Figure 1. Schematic diagrams showing the configurations considered in $(An)_2^+$. The parallel molecules are separated by the interplanar distance *d*. Bond lengths are indicated in Å. δ is the distance of slip from the completely eclipsed configuration. (a) Eclipsed head to head, (b) slipped head to head, δ = 0.7 Å, (c) eclipsed head to tail, (d) slipped head to tail, δ = 0.7 Å, (e) eclipsed An·HMB. In the slipped arrangements, δ increases in the direction of the solid arrows as indicated.

In a heteroatom-containing molecule such as $C_6H_5NH_2$ or its complexes, an individual MO will usually have much larger magnitudes on some atoms than on others, thus overlap between a pair of such MOs will vary significantly with slip, according to whether the "favored" atoms are close together or far apart. The shift of the HOMO energy of An due to complexation is directly related to a net increase or decrease of overlap among constituent AOs upon the nuclear displacement in question (slip or interplanar distance). We will use this energy shift as a measure of the resonance energy in $(An)_2^+$ We defined the frontier resonance energy, ΔE_{res}^F, for $(An)_2^+$ as

$$\Delta E_{res}^F = [\epsilon_{HOMO}((An)_2) + 2\epsilon_{MO}((An)_2)] - 3\epsilon_{HOMO}(An) \qquad (1)$$

Here $\epsilon_{MO}((An)_2)$ is the energy of the MO of $(An)_2$ that results from the interaction between the HOMO on one An molecule and its twin on the other molecule. Examples of such interactions are given in Figure 2. One finds that the energy rise due to the formation of $\epsilon_{HOMO}((An)_2)$ is greater than the lowering due to $\epsilon_{MO}((An)_2)$. This is caused by the difference in normalizing factors.[5b,8] Therefore a fully occupied orbital pair will contribute to a net energy rise, hence repulsion in an EHT calculation. This is referred to as repulsion between closed shells. The larger the overlap, the greater we expect this energy splitting and net repulsion to be.[5] In contrast to the neutral dimer, the attractive nature of the interaction in the ionic dimer results from the fact that one electron is removed from the HOMO. The frontier resonance energy calculated by eq 1 is a direct measure of the overlap interaction between the HOMOs of the two An molecules. This result is demonstrated in Figure 2 for the eclipsed and slipped (HH) configurations of $(An)_2^+$. As will be shown in the next section, these configurations correspond to a minimum and maximum, respectively, in the ΔE_{res}^F vs. slip curves for $(An)_2^+$ (Figure 3).

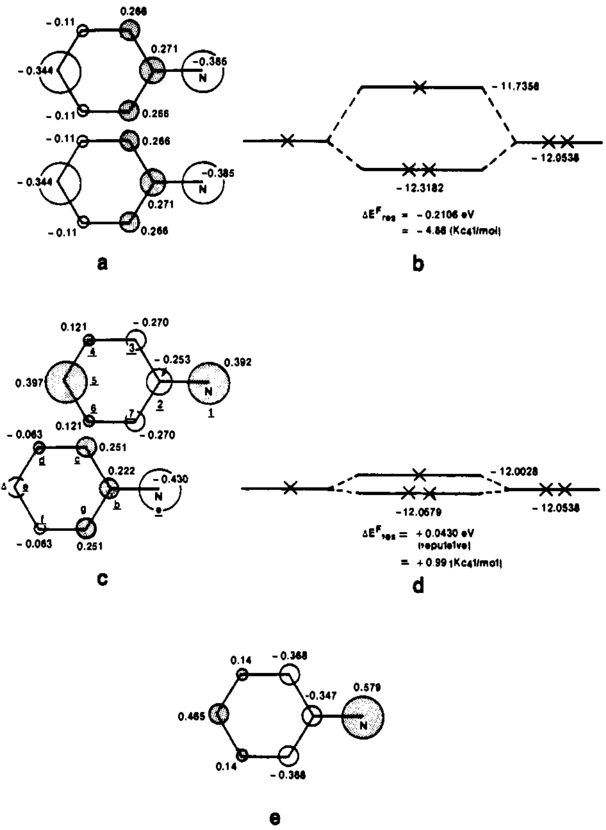

Figure 2. (a) The HOMO of $(An)_2$ in the eclipsed HH arrangement at *d* = 3.1 Å and δ = 0. Numbers on the atoms are the coefficients of the constituent $2p_z$ AO's in the HOMO. (b) Splitting of the HOMO of An in $(An)_2$ at the eclipsed HH, *d* = 3.1 Å and δ = 0. Numbers indicate orbital energies in eV. (c) The HOMO of $(An)_2$ in the slipped HH at *d* = 3.1 Å and δ = 1.4 Å. (d) Splitting of the HOMO of An in $(An)_2$ at the slipped HH, *d* = 3.1 Å and δ = 1.4 Å. (e) The HOMO of An monomer. The $2p_z$ AO on the nitrogen contributes 34% to the formation of the HOMO.

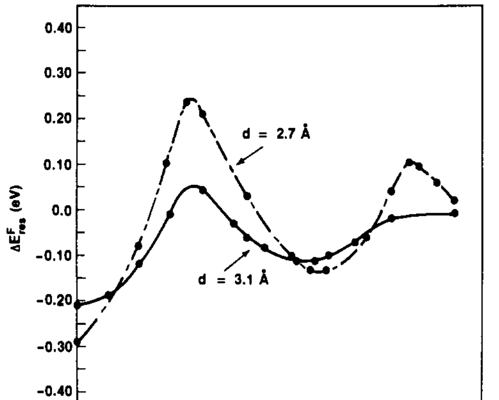

Figure 3. Frontier resonance energy vs. slip, δ, for the HH arrangement of $(An)_2^+$ at interplanar distances of 2.7 and 3.1 Å from EHT calculations. In all figures, points show calculated energies at the respective geometries, and the curves are drawn through these points.

(b) Head-to-Head Configuration. Figure 3 shows the variations of ΔE_{res}^F as a function of slip values from 0 to 4.2 Å at an interplanar distance of 2.7 Å which is the optimized distance for the frontier resonance energy calculated according to eq 1. In order to interpret this unreasonably small equilibrium interplanar

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Table I. Maximum Calculated Resonance Energies in $(An)_2^+$ Obtained at Optimized Interplanar Distances

configuration	first minimum			second minimum			third minimum		
	δ, Å	d, Å	$-\Delta E_{res}^F$, eV	δ, Å	d, Å	$-\Delta E_{res}^F$, eV	δ, Å	d, Å	$-\Delta E_{res}^F$, eV
heat to head	0.0	2.7	0.294	2.6	2.7	0.134			
head to tail	0.0	3.2	0.07	1.9	2.6	0.317	4.4	2.4	0.211

distance, it must be remembered that this quantity was obtained considering only the charge resonance due to the overlap between the HOMOs, with complete neglect of the overlap due to other orbitals. The inclusion of all the doubly occupied orbitals ($\sigma + \pi$) resulted in an optimized interplanar distance of 4.0 Å. The lower curve in Figure 3 corresponds to an interplanar separation of 3.1 Å which is a reasonable, experimentally accepted value.[5] It is clear that both curves in Figure 3 exhibit the same features. There is a minimum at $\delta = 0$ and a second one around 2.6 Å and a maximum at $\delta = 1.3$ Å and a second one around 3.7 Å. These calculations indicate that the energy at the eclipsed minimum is lower than the energy at the slipped minimum ($\delta = 2.6$ Å). The eclipsed minimum reflects an optimum phasing of AOs (between monomers) that compose the π-MO of the highest occupied level of the dimer. The form of the HOMO of the monomer and the weight of each AO can yield information on the favorably interacting configurations. When we examine the HOMO of An, Figure 2e, we see that it is concentrated heavily on the nitrogen 2p orbital (34%). Consequently, the charge resonance interaction should be largest when the nitrogen atoms are eclipsed. As the two moieties slip away from $\delta = 0$ at constant interplanar distance, the degree of overlap between each AO on the HOMO of An with its counterpart on the An cation decreases. Therefore, the orbital energy's splitting decreases and so does the net attraction produced (Figure 3). The overlap changes in a non-uniform way. At $\delta = 0$, a total of 7 atoms (excluding hydrogens) in the An molecule eclipse those in the cation. At $\delta = 1.4$, 2.8, and 4.2 there are respectively 3, 2, and 3 eclipsing pairs. According to the weight of each AO in the HOMO we should expect some maxima and minima in our curve of ΔE_{res}^F vs. δ as we pass through regions with a large number of close approaches. The maxima around $\delta = 1.3$ Å corresponds to dimer configuration with minimum overlap between the HOMOs. Figure 2c shows a sketch of this configuration at $\delta = 1.4$ Å as it appears on the HOMO of the dimer. The interaction starts to become less repulsive when full overlap between the nitrogen (a) and carbon (2) occurs as well as when carbons (c and g) on one fragment and (4 and 6) on the other fragment slip away from each other. Therefore, ΔE_{res}^F increases and reaches a minimum at about $\delta = 2.6$ Å (Figure 3), which reflects the favorable interaction between carbons b and 5. The second minimum ($\delta = 2.6$ Å) is about 50% the depth of the first one (eclipsed). This behavior does not change with a change in the interplanar distance.

Figure 4 shows the variation of ΔE, the total interaction energy of $(An)_2^+$, vs. slip values. ΔE is the total EHT energy of $(An)_2^+$ minus the sum of the energies of $(An)_2^+$ and An^+. ΔE was calculated by substracting the corresponding energies of the HOMOs from the total EHT energies of $(An)_2$ and An, respectively. The inclusion of all the doubly occupied orbitals ($\sigma + \pi$) increases the repulsive terms and hence decreases the interaction energy which in this case does not represent the resonance energy, but it should be considered as the total interaction in the frame of the EHT. The important observation is that both the frontier orbitals (Figure 3) and the total energy curves (Figure 4) are governed mainly by the same features. This is even more so at the expected and reasonable interplanar distance (3.1 Å), where the full and frontier orbital approaches show the same positions for the maxima and minima in the energy vs. slip curves. Table I summarizes the results of the HH configuration.

(c) Head-to-Tail Configuration. Figure 5 shows the variations of ΔE_{res}^F with the interplanar separations at fixed slip values. When $\delta = 0$ the minimum in energy occurs at $d = 3.24$ Å. In this configuration the effective overlap comes mainly from the benzene rings and the system is very much like $(Bz)_2^+$. In fact we carried out the EHT calculation on $(Bz)_2^+$ and obtained 3.2 Å as an equilibrium separation for the best frontier resonance energy. Unlike the eclipsed HH configuration, the HT structure for $\delta = 0$ results in a reasonable interplanar distance, since the interaction becomes more repulsive due to the absence of the nitrogen–nitrogen overlap, and also each carbon atom now interacts with the corresponding para atom from the other fragment (Figure 1c). Starting from the HT configuration with $\delta = 0$ as

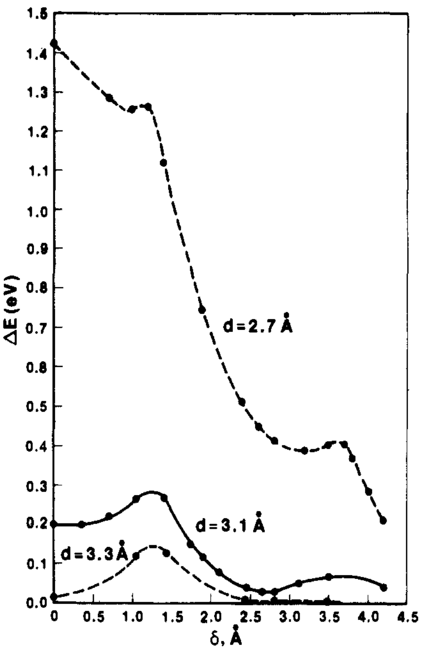

Figure 4. Total EHT interaction energy vs. slip, δ, for the HH arrangement of $(An)_2^+$ at the interplanar distances of 2.7, 3.1, and 3.3 Å.

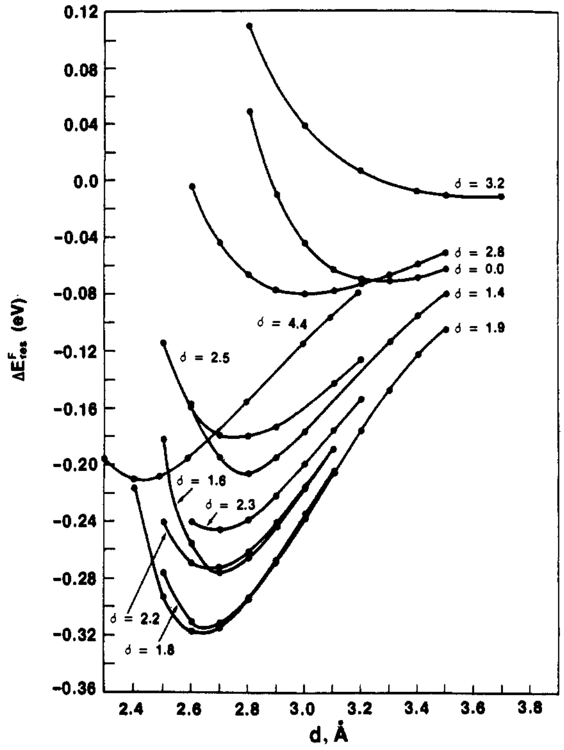

Figure 5. Frontier resonance energy vs. interplanar distance, d, for the HT arrangement of $(An)_2^+$ at fixed slip values as indicated.

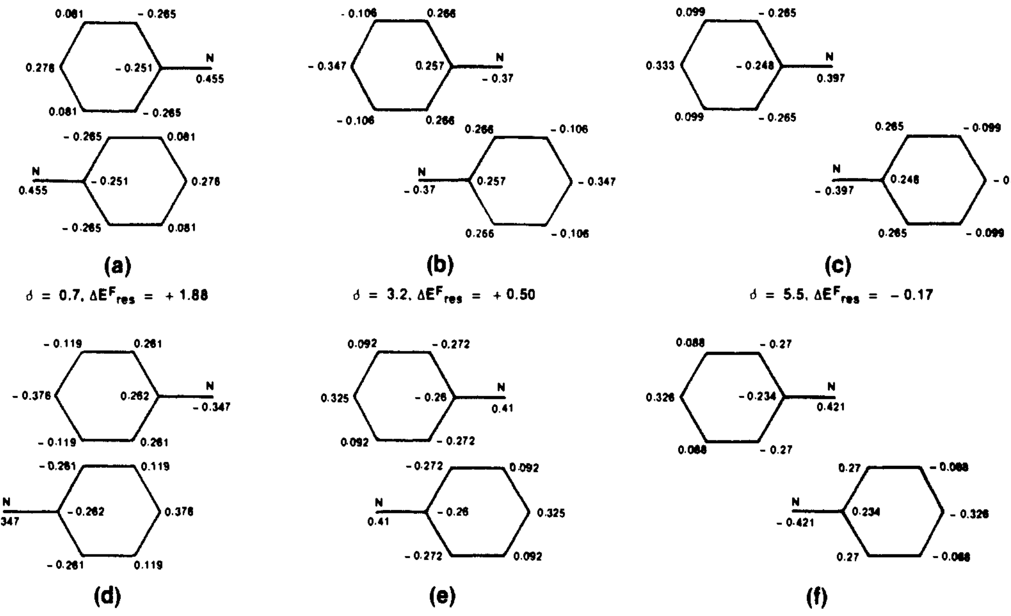

Figure 6. The HOMO of $(An)_2$ in the HT arrangement at fixed interplanar distance of 3.1 Å and δ values of (a) 0.7 Å, (b) 3.2 Å, (c) 5.5 Å, (d) 0, (e) 1.9 Å, and (f) 4.4 Å. Configurations a, b, and c correspond to maxima (repulsive contributions) while configurations d, e, and f correspond to minima (attractive contributions) in the $\Delta E_{res}{}^{F}$ vs. δ plots. Numbers on the atoms are the coefficients of the constituent $2p_z$ AO's in the HOMO.

Table II. Maximum Calculated Resonance Energies in $(An)_2{}^+$ and $(Bz)_2{}^+$ Obtained at a Fixed Interplanar Distance of 3.1 Å

dimer	δ, Å	d, Å	$-\Delta E_{res}{}^{F}$, eV	$-\Delta E_{res}{}^{F}$, kcal/mol	$-\Delta H°_{res}$ (expt based), kcal/mol
$(An)_2{}^+$					
head to head	0.0	3.1	0.211	4.85	
head to tail	1.9	3.1	0.207	4.76	4.3
$(Bz)_2{}^+$	0	3.1	0.262	6.03	6.0

a primary structure (Figure 1c), we varied the slip value in a way that allowed each nitrogen atom to overlap with the ring of the other fragment as shown in Figure 6 for some values of δ. The deepest minimum occurs at δ = 1.9 Å with optimum separation of 2.6 Å. Figure 7 shows the variation of $\Delta E_{res}{}^{F}$ with δ at different fixed values of interplanar separation over the range $0 < \delta < 5.75$ Å. We found minima at δ = 0, 1.9, and 4.4 Å and maxima at 0.7, 3.2, and 5.5 Å. The configurations corresponding to these values are illustrated in Figure 6 as they appear on the HOMO of the dimer. The calculated results are summarized in Table II.

The deepest minimum at δ = 1.9 Å corresponds to a configuration in which the end-to-end interaction between the two components of the dimer allows the overlap of the nitrogen atom of an An molecule with the para carbon of the other molecule. By examining the HOMO of An (Figure 2e), one can predict that this kind of overlap has to be effective since the para carbon $2p_z$ orbital contributes the second heaviest weight (22%) to the HOMO after the nitrogen $2p_z$ orbital (34%). The second deepest minimum, δ = 4.4 Å, reflects the interaction between the nitrogen atom of one moiety and the carbon bonded to the nitrogen of the other moiety. It is interesting that this minimum has almost the same depth as the one occurring at δ = 0 for interplanar separation of 3.2 Å. At shorter distances (<3.2 Å) the minimum at δ = 0 becomes more repulsive while the one at δ = 4.4 Å becomes more attractive and reaches its deepest point at d = 2.4 Å. This indicates that the minimum at δ = 0 reflects unfavorable interaction between the two rings when they approach each other head to tail at short distances. On the other hand, the minimum at δ = 4.4 Å is associated with nitrogen–carbon overlap (Figure 6) in the absence of ring-to-ring interaction and hence the two moieties can be closer to each other as it is shown by the equilibrium distance of 2.4 Å. A related terminology used by Lowe[5b] would refer to the interactions of δ = 0 and 4.4 Å as "hard" and "soft", respectively.

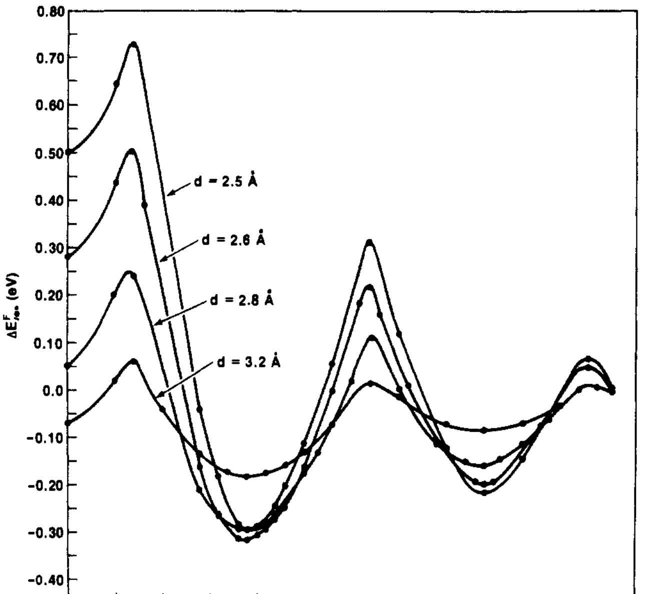

Figure 7. Frontier resonance energy vs. slip, δ, for the HT arrangement of $(An)_2{}^+$ at fixed interplanar distances from EHT calculations.

Figure 8 shows the variation of ΔE vs. δ at fixed interplanar distances. As it was illustrated for the HH configuration, these curves have the same features as the corresponding ones for $\Delta E_{res}{}^{F}$ vs. δ (Figure 7).

A comparison between the EHT calculations for $(An)_2{}^+$ and $(Bz)_2{}^+$ at fixed interplanar distance of 3.1 Å is given in Table II.

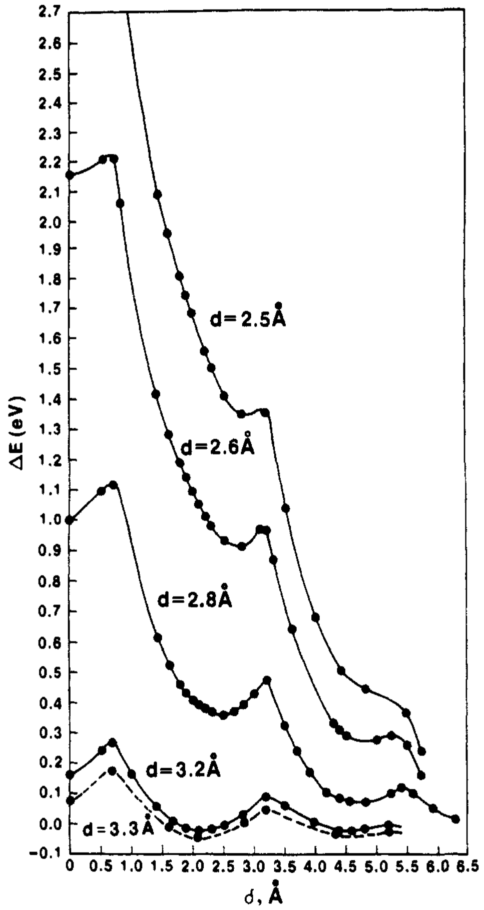

Figure 8. Total EHT interaction energy vs. slip, δ, for the HT arrangement of $(An)_2$ at various interplanar distances.

The most stable structures of HH and HT configurations are the eclipsed and 1.9 Å slipped ones, respectively. It is interesting that both structures give the same resonance stabilization of 4.7 kcal/mol which is in good agreement with the experimental value of 4.3 kcal/mol. The calculation also predicts that the resonance stabilization in $(Bz)_2^+$ is larger than in $(An)_2^+$ which agrees with the experimental results.[18,20]

(2) CNDO and INDO Calculations. The EHT calculations neglect the very large core–core and electron–electron electrostatic repulsions. Therefore, the success of any EHT dimer calculation will depend on how much these two interactions cancel one another.

The simplest levels of theory that take into account these interactions are the CNDO and INDO methods developed by Pople et al.[9] Silverman and co-workers[10a] have reported CNDO/2 calculation on TTF and TCNQ dimers and their ionized forms using molecular geometries taken from the TTF–TCNQ crystal structure.[11] He observed that the core–core repulsion energy decreased and the electronic energy increased over the range of slip investigated. The sum of these two energies, that is, the total energy, gave features similar to the results obtained from EHT calculation. The optical properties of dimer cations of styrene, 1-methylstyrene, 1,1-diphenylethylene, and naphthalene have been investigated theoretically, using the Parriser–Pople–Parr method, by several groups.[10b,c] They considered only the eclipsed configurations. The interplanar distance was not optimized for any of the dimers. Although their calculated electronic transition energies were in reasonable agreement with the experimental ones, we believe that it would be worthwhile to repeat those calculations at the optimal interplanar and slip values.

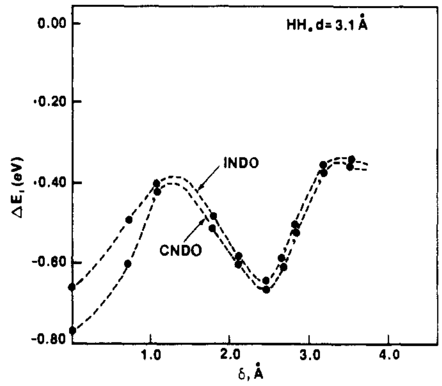

Figure 9. CNDO and INDO total interaction energies, ΔE, vs. slip for the HH arrangement of $(An)_2^+$ at d = 3.1 Å.

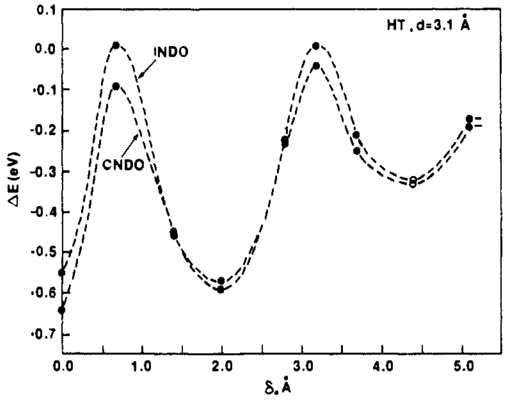

Figure 10. CNDO and INDO total interaction energies, ΔE, vs. slip for the HT arrangement of $(An)_2^+$ at d = 3.1 Å.

In this section, the CNDO and INDO methods were applied to calculate ΔE vs. slip for $(An)_2^+$ at the HH and HT configurations. All the calculations were performed for the neutral dimers of $(An)_2$ with use of the same geometries used in the EHT calculations. The total energy of the singly ionized dimer, $(An)_2^+$, was approximated as the total energy of the neutral dimer minus the energy of the HOMO of the dimer (Koopmans' theorem).[12] The total interaction energy, ΔE, was calculated according to the equation

$$\Delta E((An)_2^+) = E_{tot}((An)_2^+) - (E_{tot}((An)^+) + E_{tot}(An)) \qquad (2)$$

The total energy of the monomer cation, $(An)^+$, was also estimated according to Koopmans' theorem.

Figures 9 and 10 show the variation of ΔE vs. slip at a fixed interplanar distance of 3.1 Å for the HH and HT configuration of $(An)_2^+$, respectively. If we compare Figures 9 and 10 with the EHT calculations, done at comparable intermolecular distance (Figures 4 and 8), we note the following:

(1) The methods predict the same positions of minima and maxima along the displacement of the two monomers in the dimer at fixed interplanar distance. There are minima at the eclipsed geometries as well as at the slipped ones. For $(an)_2^+$, the slipped minima occurs near δ = 2.45 and 1.9 Å for the HH and HT configurations, respectively.

(2) Both methods, CNDO and INDO, predict that the HH configuration of $(An)_2^+$ is more stable than HT. At the assumed interplanar distance of 3.1 Å, the CNDO calculations result in stabilization energies of 17.8 and 15.1 kcal/mol for the eclipsed and slipped (δ = 2.45 Å) HH configuations of $(An)_2^+$, respectively. These stabilization energies are in excellent agreement with the experimental value of 17.5 kcal/mol, but this should not be taken as evidence for the adequacy of these methods in calculating the binding energies of charged dimers.

(3) Both INDO and CNDO calculations predict comparable stabilities for the eclipsed and slipped configurations. For HH configurations, the minima at δ = 0 and 2.0 Å result in binding

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(20) See paper 1: *J. Am. Chem. Soc.*, preceding paper in this issue.

energies of 14.8 and 13.6 kcal/mol, respectively, as obtained from CNDO calculations and 12.7 and 13.1 kcal/mol, respectively, as obtained from INDO calculations. The EHT calculations predicted more stabilization for the slipped HT minima (δ = 1.9 Å) than for the eclipsed one (δ = 0). One would expect that the inclusion of the coulomb interactions in CNDO and INDO methods would favor the slipped over the eclipsed structure (this point will be dealt with later in the ab initio section).

(4) In contrast to the EHT results, for both HH and HT, the minima at the eclipsed geometry has the lowest total energy. This seems to reflect a general tendency of the zero differential overlap methods to yield lower energies for the more closely connected structures.[9,13]

(5) The total energy change vs. slip for EHT, CNDO, and INDO compares well with the frontier resonance energy change vs. slip shown in Figures 3 and 7.

To summarize the CNDO and INDO findings, both methods give results similar to the EHT results. This is due to the near cancellation between the core–core and electron–electron contributions to the total energy as the dimers are slipped. The deeper minima at the eclipsed geometries observed for the CNDO and INDO methods reflect the fact that the zero differential overlap methods are incapable of predicting relative positions of minima.[10] This inadequacy of the CNDO and INDO methods prompted us to pursue this point further with ab initio calculations.

(3) Ab Initio Calculations. Ab initio studies of intermolecular interactions have mostly used the "super molecule" approach.[3,14–16] This should be the method of choice for small complexes where quantitative predictions are required. This approach would be rather difficult to carry out for the $(An)_2^+$ system. Milosevich et al.[17] have reported open shell ab initio calculations on benzene dimer cation using five different contracted Gaussian basis sets. They adopted the parallel structure and examined the variation of the total energy with slip. Their calculations predicted the occurrence of energy minima at δ = 0, 1.4, and 2.8 Å along the long axis with binding energies of 9.9 and 12 kcal/mol, respectively, and a minimum at 2.4 Å along the short axis with a binding energy of 9 kcal/mol. Ab initio STO-3G[19] calculations on the $(Bz)_2^+$ ion were done by El-Shall[18] and gave geometries for energy minima in good agreement with those of Milosevich et al. Furthermore, El-Shall[18] also used EHT calculations for $(Bz)_2^+$ and found a minimum at the eclipsed conformation and two minima along the long axis at 1.4 and 3.2 Å. The EHT geometries were in reasonably good agreement with Milosevich's and STO-3G geometries, which is encouraging for using EHT on the $(An)_2^+$ and larger complexes.

In this section, the reliability of EHT, CNDO, and INDO dimer calculations was tested by ab initio calculation on $(An)_2^+$ at the STO-3G level.[19] The calculations were carried out considering the parallel geometry as before. The total energy of $(An)_2^+$ was obtained from eq 2 and Koopmans' theorem. The interplanar distance, d, was optimized for both the HH and HT $(An)_2^+$ at the eclipsed configurations. An optimum interplanar distance of 3.3 Å was obtained for the HH configuration and 3.4 Å for the HT. Similar to the EHT, CNDO, and INDO, the ab initio method predicts the HH and $(An)_2^+$ to be more stable than the HT.

Figures 11 and 12 show the variation of the total energy as a function of slip, δ, at a fixed interplanar distance of 3.3 Å for the HH and HT $(An)_2^+$, respectively. Included also in Figures 11 and 12 are the CNDO and INDO results calculated at 3.3 Å.

The most important finding from the ab initio calculations is that the positions of minima and maxima along the slip of $(An)_2^+$ at fixed interplanar distance are mainly the same as those predicted by CNDO and INDO calculations, as well as EHT which considers only orbital overlap. *This result suggests that predicted structural features may be essentially intrinsic to the aniline dimer cation in the parallel geometry and basically governed by the overlap of the frontier molecular orbitals, since EHT considers only these orbitals.*

Inspection of Figure 11 shows that the ab initio method puts the eclipsed minimum of the HH $(An)_2^+$ at a slightly lower energy than the slipped one. This difference is even more pronounced in the CNDO and INDO methods which reflects the extra, artificial, stability of closely connected structures in CNDO and INDO. On the other hand, Figure 12 shows that the slipped minimum at 1.9 Å for the HT is lower in energy than the eclipsed one. This is in agreement with the EHT calculations. (See Figures 4 and 8.) The good agreement between the EHT and ab initio calculations reinforced our hope that similar EHT calculations for series of large ionic dimers including π acceptor and donor can explain trends in bonding energies.

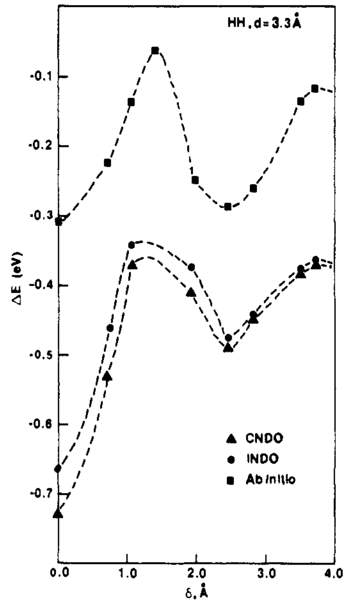

Figure 11. Ab initio, CNDO, and INDO total interaction energies, ΔE, vs. slip for the HH arrangement at d = 3.3 Å. (The EHT results are plotted in Figure 4.)

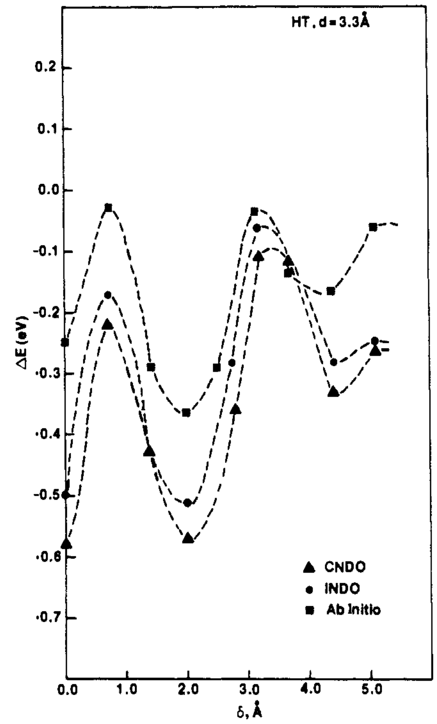

Figure 12. Ab initio, CNDO and INDO total interaction energies, ΔE, vs. slip for the HT arrangement at d = 3.3 Å. (The EHT results are plotted in Figure 8).

(4) Application of EHT to $(An^+{\cdot}HMB)$ Dimer Cation. To demonstrate the application of EHT to large ionic complexes, we carried out calculations on the $An^+{\cdot}HMB$ dimer cation. In this system, the difference in ionization potentials, ΔIP, between An

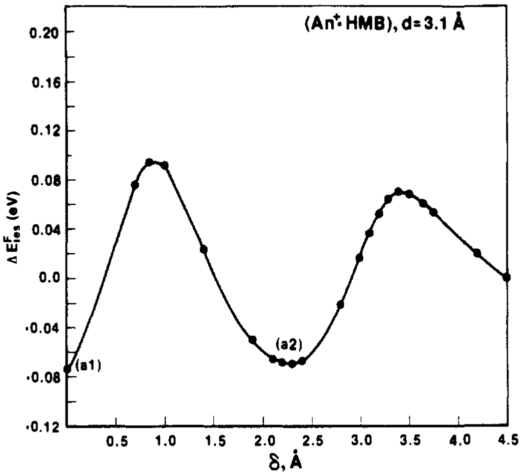

Figure 13. The frontier resonance energy, $\Delta E_{\mathrm{res}}{}^{\mathrm{F}}$, vs. slip, δ, for (An$^{+}\cdot$HMB) from EHT calculations.

and HMB is 2.3 kcal/mol. The frontier resonance energy, $\Delta E_{\mathrm{res}}{}^{\mathrm{F}}$, was calculated according to the equation

$$\Delta E_{\mathrm{res}}{}^{\mathrm{F}} = [\epsilon_{\mathrm{HOMO}}(\mathrm{An{\cdot}HMB}) + 2\epsilon_{\mathrm{MO}}(\mathrm{An{\cdot}HMB})] - [2\epsilon_{\mathrm{HOM}}\mathrm{O}(\mathrm{An}) + \epsilon_{\mathrm{HOMO}}(\mathrm{HMB})] \quad (3)$$

where ϵ_{MO}(An·HMB) is the energy of the MO of (An·HMB) that results from the interaction between the HOMO of An and the HOMO of HMB. The bond lengths and angles of the monomers were obtained from the work of Gerhard et al.[21] The interplanar distance was 3.1 Å. The direction of slip, δ, is shown in Figure 1e. In Figure 13, $\Delta E_{\mathrm{res}}{}^{\mathrm{F}}$ is plotted as a function of δ. There is a minimum at $\delta = 0$ and another one at $\delta = 2.3$ Å which reflects optimum overlap between the HOMOs of the two components of the complex. The optimum interplanar distances at $\delta = 0$ and 2.3 Å are 3.1 and 3.0 Å, respectively, which correspond to $\Delta E_{\mathrm{res}}{}^{\mathrm{F}}$ of −1.71 and −1.68 kcal/mol. The experimentally determined value is −5.2 kcal/mol.[18,20]

The EHT energy schemes of (An$^{+}\cdot$An) vs. (An$^{+}\cdot$HMB) are reasonable in terms of orbital overlaps. For the HH $(\mathrm{An})_2{}^{+}$ configuration at $d = 3.1$ Å (Figure 3), the minimum at $\delta = 0$ reflects overlap of atomic orbitals on the nitrogens as well as on the ring carbons. This is stable ($\Delta E_{\mathrm{res}} = -4.8$ kcal/mol), since the overlap is primarily between an electron-rich nitrogen of the An ring and the electron-dificient nitrogen of An^{+} (see Figure 2c). In contrast, in (An$^{+}\cdot$HMB) at $\delta = 0$ the localized nitrogen–nitrogen overlap of $(\mathrm{An}_2)^{+}$ is absent and the principal overlaps are between the rings giving only a $\Delta E_{\mathrm{res}} = -1.7$ kcal/mol. This is similar to ΔE_{res} at $\delta = 2.3$ Å for (An$^{+}\cdot$HMB), where the principal overlap is between a ring carbon of HMB and the nitrogen of An^{+}.

Conclusions

The main conclusions that can be drawn from MO calculations performed on ionic aniline complexes are the following:

(1) EHT calculations on charged dimers are useful models for understanding equilibrium geometries for these dimers. The energy changes as a function of slip appear to be qualitatively reasonable. The EHT calculations can display the relation between the energy separation of the HOMOs of the monomers and the extent of molecular overlap.

(2) There exists an overall similarity between the qualitative features of EHT, CNDO, INDO, and STO-3G ab initio calculations on aromatic dimer cations in the parallel geometry. It is of interest that the more sophisticated CNDO, INDO, and STO-3G calculations yield results concerning equilibrium geometries that are similar to the results of EHT calculations. This suggests that the only feature represented in EHT calculations, i.e., the overlap between orbitals, is crucial in characterizing the positions of minima and maxima along the slip of aromatic dimer cations in the parallel geometry. This reflects the close cancellation between variations in some very large quantities, namely between the repulsive core–core interactions and the electronic interactions.

(3) One can obtain meaningful potential energy curves for radical dimer cations by carrying out ab initio STO-3G minimal basis set calculations. The results from the ab initio calculations on $(\mathrm{An})_2{}^{+}$ indicate that the potential energy surfaces are generally shallow. There are minima at slipped as well as eclipsed geometries. Furthermore, for a given dimer, the energy differences between different minima are relatively small, and several conformations may exist in equilibrium for most aromatic dimer cations.

(4) The usefulness of EHT approach lies mainly in its simplicity. The simplicity of the method coupled with the fairly good qualitative agreement with ab initio calculations makes it a useful first approach to the very complicated problem of the geometry of large molecular dimers and solids.

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[21] Gerhards, J.; Ha, T. K.; Perhia, X. *Helv. Chim. Acta (Berlin)* **1970**, *42*, 13.