is completely substituted with fluorine, the CC force constant returns to the value in the $C_3H_3^+$ ion.

Fluorine substitution also appears to affect the force constant for in-plane bending of the CH bond. Substituting one fluorine atom lowers the value of this constant to a value closer to the one in benzene. The substitution of the second fluorine atom brings the value to essentially that of benzene.

Acknowledgment. This research was supported by a Cottrell grant from Research Corp. and by National Science Foundation College Research Instrumentation grants (PRM-7911202 and PRM-8115415). We are grateful to Kevin L. Sloan for preliminary work on the synthesis of chlorocyclopropenes and to Janet L. Langon for some of the Raman spectra of complex anion systems.

Registry No. $C_3H_3^+$, 26810-74-2; $C_3D_3^+$, 59192-32-4; $C_3D_2H^+$, 102682-80-4; $C_3H_2D^+$, 93255-76-6.

Ionic Charge-Transfer Complexes. 1. Cationic Complexes with Delocalized and Partially Localized π Systems

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Abstract: The partially charge localized radical ion $C_6H_5NH_2^+$ and its *N*-methyl derivatives form stable complexes with the π-donor neutral $C_6H_5NH_2$ and its derivatives. The dissociation energies ($\Delta H°_D$, kcal/mol) of the complexes are determined by pulsed high pressure mass spectrometric equilibrium measurements as follows: $(An)_2^+$, 17.5; $(MA)_2^+$, 16.4; $(DMA)_2^+$, 15.9; $(DMA^+\cdot An)$, 14.2 kcal/mol (An = aniline; MA = *N*-methylaniline; DMA = *N*,*N*-dimethylaniline). In $(An)_2^+$, charge-transfer resonance $A^+\cdot A \leftrightarrow A\cdot A^+$ should be favorable, while in $(An^+\cdot Bz)$ [Bz = benzene] the large difference between the ionization energies of the components (ΔIP) rules out charge transfer. The differences between $\Delta H°_D$ of $(An)_2^+$ and $(An^+\cdot Bz)$ suggest that the contribution of the resonance energy $\Delta H°_{res}$ to the stability of $(An)_2^+$ is ≈5 kcal/mol. In another series of complexes, where the electron donors are delocalized aromatic hydrocarbons, $\Delta H°_D$ again decreases with increasing differences between the ionization potentials of the components (ΔIP), from 18.3 kcal/mol for $An^+\cdot AN$ (AN = acenaphthene) (ΔIP = 1.4 kcal/mol) to 13.2 kcal/mol for $An^+\cdot Bz$ (ΔIP = 35.1 kcal/mol). This trend is attributed to a decrease in intermolecular charge-transfer resonance as ΔIP increases. Again, the maximum contribution of $\Delta H°_{res}$ is about 5–6 kcal/mol. In contrast with the sandwich-type structures of the above complexes, complexes with highly polar cyano and nitro ligands seem to reorient to a linear structure which optimizes ion–dipole interactions. These complexes yield bonding energies of 16–20 kcal/mol, despite the large ΔIP of the components.

Charge-transfer complexes between molecular electron acceptors and donors have been investigated extensively.[1-5] In these systems the donor is often a π system with a partial deficiency of electrons. An extreme case of electron deficiency can be produced if an electron is removed from the π system, i.e., if the acceptor is an ionized unsaturated molecule. These complexes, which contain an extremely electron deficient acceptor and a net unit positive charge, are ionic charge-transfer complexes. Since they involve an extremely efficient cationic acceptor, the study of such complexes should help the understanding of charge-transfer complexes in general. The interactions between donor and acceptor π systems in ionic complexes are also relevant to the energy of charge holes in organic conductors[6] and to the behavior of ionized states of porphyrins in photosynthesis.[7] For a basic understanding of these interactions, it is especially important to investigate the energetics of the complexes in the gas phase, in the absence of complicating solvent effects.

While there are extensive data on gas-phase ion–molecule complexes, the large majority of such data pertain to closed-shell, hydrogen-bonded systems.[8] On radical ion–molecule complexes, the data pertain mostly to rare gases and diatomic and triatomic species of atmospheric interest, such as $N_2^+\cdot N_2$, $O_2^+\cdot O_2$, $O_2^+\cdot N_2$, etc. Some of these, such as $N_2^+\cdot N_2$, were subject to theoretical study, which showed that charge-transfer, i.e., covalent bonding makes an important contribution to the total dissociation energy ($\Delta H°_D$) of 23 kcal/mol.

In organic systems involving π acceptors and donors, photoionization data are available on the ethylene dimer ion $C_2H_4^+\cdot C_2H_4$, where $\Delta H°_D = 17 \pm 1$ kcal/mol.[10] For larger π systems, spectroscopic observations were made on $(NP)_2^+$ (NP = naphthalene) and related systems.[11] In the case of these aromatic hydrocarbons spectral studies[12] revealed that the dimer cations have symmetric sandwich structures. The complex-for-

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mation constants K of ionic charge-transfer complexes in solution are usually low and vary in the range 1–10 L/mol, depending on the properties of the components and the solvent.[13] In most cases the formation constants K for neutral donor–cationic acceptor complexes are similar to those for π–π complexes of neutral molecules.

As for ionic π complexes in the gas phase, Field et al.[14] measured the dissociation energy of $(Bz)_2^+$,[15] as 17 kcal/mol.[15] Extending these studies, Meot-Ner et al.[16] investigated complexes of Bz^+ with a series of fluorobenzenes. These measurements were of interest because in symmetric dimers such as $(Bz)_2^+$ charge-transfer resonance should be efficient, since the two forms $B^+{\cdot}B \leftrightarrow B{\cdot}B^+$ are of equal energy. Furthermore, as the ionization potential difference between the components, ΔIP, increases, the charge should become more localized on the component with the lower IP, and the contribution of the charge-transfer resonance energy, ΔH°_{res},[15] to the bonding should decrease. Indeed, the results showed the ΔH°_D decreased with increasing ΔIP, approaching a lower limit of $\approx$11 kcal/mol. The same interaction energy was observed also in protonated complexes where resonance energy is not likely such as $C_6H_6H^+{\cdot}C_6H_6$ and $C_6H_6^+{\cdot}c\text{-}C_6H_{12}$. From these results, it was concluded that ΔH°_{res} contributes 6 kcal/mol to the bonding in $(Bz)_2^+$ and 11 kcal/mol arises from electrostatic, dispersion, and induction terms.

In dimer ions of polycyclic aromatics, e.g., $(NP)_2^+$, $(AT)_2^+$ (AT = anthracene), $(PR)_2^+$ (PR = pyrene),[17] etc., ΔH°_D remained about constant at 17–20 kcal/mol, regardless of molecular size. However, ΔE_{res}, as evaluated both from experimental data and calculations, was found to decrease with increasing molecular size, but this was compensated for by increasing dispersion forces. These studies yielded insights into ionic charge-transfer complexes where the charge on the ionic electron acceptor is delocalized evenly over the π system of the ion and the donor is also a delocalized π system.

In the present work we extend similar studies to systems where the charge of the acceptor is at least partially localized on the amine function of $C_6H_5NH_2^+$ and its N-methyl derivatives. The electron density on the donors may be partially localized, i.e., $C_6H_5NH_2$ and its derivatives, or delocalized as in aromatic hydrocarbons. Our interest is to evaluate ΔH°_{res} in these systems and to observe whether the trends with molecular size and ΔIP that were observed in the delocalized system also hold in these partially localized systems.

This paper will deal with the experimental results and the following paper will examine the structures and energies of the present complexes by ab initio and semiempirical calculations.

Experimental Section

The measurements were done on the NBS pulsed high-pressure mass spectrometer, utilizing standard techniques.[18] Mixtures of 0.01–1% of anilines in benzene were injected to a heated bulb, and the vapor was allowed to flow into the mass spectrometer ion source. An electron gun was used as the electron source. Pulsing was obtained by deflecting the electron beam away from the entrance hole, except when a pulse was applied to the focusing plates. Usually 500–1000-V electrons were used. The pulse width was 0.5–1.0 ms, and ions were observed to reaction times of 2–10 ms, in channels of 10- or 20-μs width. The ion signal was fed from the ion multiplier through an amplifier to a signal averager. Collected data were fed to a microcomputer, which was used to normalize ion intensities at each reaction time.

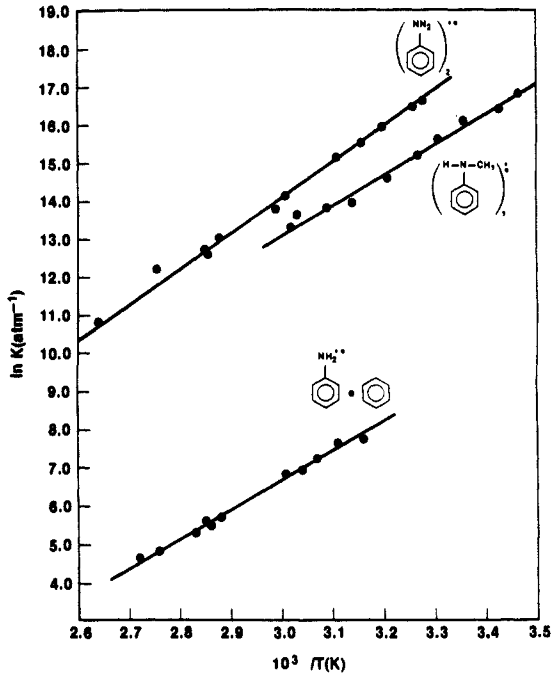

Figure 1. Van't Hoff plots for association equilibria $B^+ + B \rightleftarrows B_2^+$ and $B^+ + A \rightleftarrows B^+{\cdot}A$, forming the dimers as indicated.

The electron pulse and fast reactions generated $C_6H_6^+$ and $(C_6H_6)_2^+$ in the benzene carrier gas. The sample ions were generated by charge-transfer reactions from these ions. The aniline ions reacted with the neutral molecules present to form ionic complexes (reactions 1 and 2).

$$(An)^+ + An \rightleftarrows (An)_2^+ \tag{1}$$

$$(An)^+ + Bz \rightleftarrows (An^+{\cdot}Bz) \tag{2}$$

Equilibrium constants were calculated as in eq 3. Here $[An^+]$ and $[(An)_2^+]$ denote ion signal intensities at equilibrium.

$$K\ (\mathrm{atm^{-1}}) = \frac{[(An)_2^+]}{[An^+]}\frac{1}{P_{An}} \tag{3}$$

Measurements of K were carried out in the temperature range of 260–400 K and at total source pressures of 0.5–1.0 Torr. Checks were made to ensure that the equilibrium constants were independent of pressure and mixture composition. Conditions were selected to keep cluster ions to less than 50% of total ion intensity to minimize problems resulting from dissociation outside the ion source. Van't Hoff plots were constructed with use of the temperature dependence of the association constant (Figure 1). The average of the standard deviations of the slopes and the intercepts of the Van't Hoff plots gives and error estimate of ±1.1 kcal/mol for ΔH°_D and ±3 cal/(mol K) of ΔS°_D. For the association reactions involving DMA^+ (DMA = N,N-dimethylaniline) and DMT^+ (DMT = N,N-dimethyl-p-toluidine), we estimated ΔS°_D values from the corresponding reactions involving MA^+ (MA = N-methylaniline). For these cases ΔG°_D was measured only at one temperature, and we calculated ΔH°_D using the estimated ΔS°_D values. The error in ΔG° was estimated as ±0.5 kcal/mol at the median temperature of these measurements, 320 K. The uncertainty in ΔS°_D which is ±3 cal/(mol K) introduces at 320 K further uncertainty of 0.7 kcal/mol in the values of ΔH°_D calculated from $\Delta H^\circ_D = \Delta G^\circ_D + T\Delta S^\circ_D$. Added to the error in ΔG°_D, we estimate an uncertainty of ±1.2 kcal/mol for ΔH°_D obtained from single-temperature measurement. This is almost the same as the uncertainty of ΔH°_D values obtained from the temperature studies.

Since the measured entropies were all in the range 26 ± 2 cal/(mol K), we assign this to all of the systems where ΔS°_D is estimated, except for the electrostatic complexes with highly polar ligands (see below), where we use ΔS°_D = 22 cal/(mol K) since here, unlike in the sandwich dimers, a rotation is allowed about the ion–molecule bond.

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(15) We will use the abbreviations An, Bz, DMA, and DMT to denote aniline, benzene, N,N-dimethylaniline, and N,N-dimethyl-p-toluidine, respectively, throughout the text. We will denote theoretical resonance energies as ΔE_{res}^F and resonance energies derived from experimental (e.g., eq 4 and 5) as ΔH°_{res}.

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Table I. Thermodynamic Quantities[a] for the Dissociation of Cationic Complexes

	complex	ΔH°_D[b]	ΔS°_D[b]	ΔG°_D (T)[c]	ΔIP[d]
1.	$(An)_2^+$	17.5	24.6	9.5 (322)	0
2.	$(MA)_2^+$	16.4	23.3	9.5 (298)	0
3.	$(DMA)_2^+$	15.9	(26)	7.9 (304)	0
4.	$(DMT)_2^+$	16.9	(26)	8.2 (331)	0
5.	$(MA^+{\cdot}An)$	16.7	(26)	9.0 (298)	8.1
6.	$(DMA^+{\cdot}An)$	14.2	(26)	6.5 (298)	13.8
7.	$(DMT^+{\cdot}An)$	13.3	(26)	5.9 (283)	12.7
8.	$(An^+{\cdot}Bz)$	11.9	22.6	4.8 (322)	35.1
9.	$(MA^+{\cdot}Bz)$	12.3	(26)	4.6 (298)	43.1
10.	$(DMA^+{\cdot}Bz)$	10.0	(26)	2.2 (298)	48.9
11.	$(DMT^+{\cdot}Bz)$	11.2	(26)	2.6 (331)	47.7

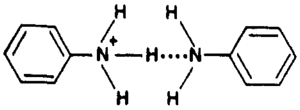
[a] All energies in kcal/mol, entropies in cal/(mol K). MA = *N*-methylaniline; DMA = *N*,*N*-dimethylaniline; DMT = *N*,*N*-dimethyl-*p*-toluidine. [b] ΔS°_D values in parentheses are estimated from the average of all measured ΔS°_D values including those in Table II. ΔH°_D values in these cases calculated from $\Delta G^\circ_D - T\Delta S^\circ_D$. Error estimate: ±1.2 kcal/mol. [c] ΔG values given here. Temperature in K. [d] ΔIP is the difference between the ionization potentials of the two molecules in the complex. IP values from ref 20.

The chemicals were purchased from commercial sources at stated purities of 98% or higher and used after vacuum distillation.

Results and Discussion

(1) Partially Localized Acceptors and Donors: Complexes of Anilines. van't Holt plots for some dimer containing An^+ and MA^+ are shown in Figure 1, and the thermochemical data are given in Table I.

As in the previous studies,[16,17] we intend to estimate ΔH°_{res} in $(An)_2^+$. In the hydrocarbon dimer ions, we used the difference $\Delta H^\circ_D(M_2^+) - \Delta H^\circ_D(M_2H^+)$ for this purpose, since the electrostatic and dispersion forces should be similar in the open-shell and closed-shell dimers, while resonance is absent in the latter. However, this method cannot be applied to anilines, since the protonated ion $C_6H_5NH_3^+$ may form the strong hydrogen bonded complex **1**. In relation to hydrogen bonding, we must comment that the hydrogen-bonded structure **2** may be possible for the observed $(An)_2^+$ dimers. The stability of **2** will depend on the charge density on the hydrogen atoms of $C_6H_5NH_2^+$. This is not known, but the charge density sould be small due to delocalization. Another possibility is hydrogen bonding between the NH_2^+ function and the π-electron ring (**3**). For example, we recently observed the $NH_4^+{\cdots}$benzene complex with a ΔH°_D of 19.3 kcal/mol.[19] Again, however, the charge density on the NH_2^+ hydrogens in An^+ should be smaller than that in NH_4^+, where the ab initio calculated value is ≈0.45 e.



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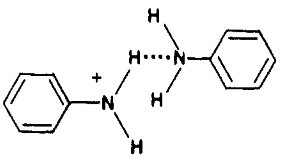

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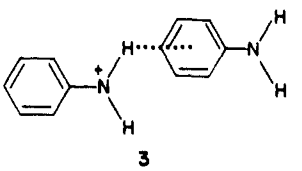


3

Experiment-based evidence against the hydrogen-bonded structure **2** or **3** is that the ΔH°_D of $(DMA)_2^+$ and $(DMT)_2^+$ are only slightly lower than that of $(An)_2^+$ (Table I), although hydrogen bonding is blocked in the former two. We shall therefore consider the present complex to be of the charge-transfer-sandwich type, similar to $(Bz)_2^+$.

Since we cannot use $\Delta H^\circ_D((An)_2H^+)$ to estimate electrostatic interactions, we use, in analogy with the results from the $C_6H_6^+{\cdot}C_6H_nF_{6-n}$ series,[16] a complex with large ΔIP and therefore negligible ΔH°_{res}. For the present purpose we use $(An^+{\cdot}Bz)$, where $\Delta IP = 34.6$ kcal/mol as a model, and estimate ΔH°_{res} in $(An)_2^+$ from eq 4. Similarly, we obtain ΔH°_{res} for $(MA)_2^+$ and $(DMT)_2^+$ as 4.1 and 5.7 kcal/mol, respectively.

$$\Delta H^\circ_{res}((An)_2^+) \approx \Delta H^\circ_D((An)_2^+) - \Delta H^\circ_D((An^+{\cdot}Bz)) = 5.6\ \text{kcal/mol} \quad (4)$$

$$\Delta H^\circ_{res}((DMA)_2^+) = \Delta H^\circ_D((DMA)_2^+) - \Delta H^\circ_D((DMA^+{\cdot}Bz)) = 5.9\ \text{kcal/mol} \quad (5)$$

We justify eq 4 on the basis that the polarization, dispersion, and repulsive forces should be similar in $(An)_2^+$ and $(An^+{\cdot}Bz)$ and the only significant difference would be an ion-permanent dipole contribution in $(An)_2^+$. However, the dipole moment of the neutral aniline molecule in a sandwich dimer is oriented in an unfavorable angle for such an interaction (see section 2 and ion **4** below).

Our values of ΔH°_{res} obtained for $(DMA)_2^+$ and $(DMT)_2^+$ are overestimated since the ion-dipole, ion-induced dipole, and dispersion interactions are higher in these systems relative to the reference systems, $(DMA^+{\cdot}Bz)$ and $(DMT^+{\cdot}Bz)$, respectively. Thus, the increasing ΔH°_{res} values do not reflect only the increase in ΔE_{res} but also the contributions by the classical forces.

The results in Table I show that the dissociation energies vary in the following order:

(a) $(An)_2^+ > (DMT)_2^+ > (MA)_2^+ > (DMA)_2^+$

(b) $(An)_2^+ > (MA{\cdot}An)^+ > (DMA{\cdot}An)^+ > (DMT{\cdot}An)^+$

(c) $(An^+{\cdot}Bz) > (MA^+{\cdot}Bz) > (DMT^+{\cdot}Bz) > (DMA^+{\cdot}Bz)$

Group c represents complexes stabilized mainly by electrostatic and dispersion ion-molecule forces, where the contribution of the resonance energy is negligible due to the large values of ΔIP (35-53 kcal/mol).

The order of varying ΔH°_D in group b shows that ΔH°_D decreases as ΔIP increases, which indicates the significance of the resonance energy in stabilizing these systems, particularly at the limit of $\Delta IP = 0$. These results also suggest that there is a considerable degree of localization of the positive charge on the NH_2 group in the aniline radical cation. This degree of localization is reduced by methyl substitution on the nitrogen atom, due to the inductive effect of the methyl group. This should make resonance delocalization to an extramolecular electron donor less significant than in complexes of An^+. This conclusion is similar to the observed effect of molecular size on ΔH°_D in complexes of polycyclic aromatic ions.[17] The trend in group b as well as in group a also suggests the importance of nitrogen-nitrogen interaction in providing resonance stabilization in $(An)_2^+$. The presence of the methyl groups in $(DMA)_2^+$ or in $(DMA^+{\cdot}An)$ may hinder the nitrogen-nitrogen interaction and hence the interaction through the phenyl rings may become the predominant one.

(2) Partially Localized Acceptor, Delocalized Donors: Complexes of An⁺ with Aromatic Hydrocarbons. Van't Hoff plots are presented in Figure 2, and measured thermochemical values are presented in Table II.

For reasons that will be elaborated below, we divide the complexes into two groups. Complexes 12-26 involve nonpolar or moderately polar ligands (μ = 0-1.7 D). In analogy with the complexes in preceding studies, we consider these to be sandwich-type complexes with some charge-transfer contributions. In contrast, complexes 27-30 contain highly polar ligands. These will be considered in the second section.

The ligands in complexes 12-26 in Table II have a wide range of IPs, and we can examine the relation between ΔH°_D and ΔIP over a ΔIP range of 3.0-50.7 kcal/mol. Figure 3 shows that in these series again ΔH°_D decreases asymptotically with increasing ΔIP, to a low limit of 11-13 kcal/mol. We shall assume at first that, in analogy with the previous systems, ΔH°_{res} is negligible at the limit of large ΔIPs, and the stronger bonding in the complexes with smaller ΔIPs results from charge resonance. We shall therefore use eq 6 to calculate ΔH°_{res}.

$$\Delta H^\circ_{res}(An^+{\cdot}M) = \Delta H^\circ_D(An^+{\cdot}M) - \Delta H^\circ_D(An^+{\cdot}Bz) \quad (6)$$

Table II. Thermochemistry[a] of Dissociation of $An^+{\cdot}M$ Complexes

	M	$\Delta H^\circ{}_D{}^b$	$\Delta S^\circ{}_D{}^b$	$\Delta G^\circ{}_D$ $(T)^c$	ΔIP^d	μ (M)
12.	aniline	17.5	24.6	9.5 (322)	0	1.53
13.	acenaphthene	17.5	27.6	8.8 (321)	1.4	0.8
14.	hexamethylbenzene	17.1	24.3	9.3 (325)	2.3	0
15.	azulene	14.0	(26)	5.8 (315)	−6.2	1.0
16.	acenaphthylene	17.2	(26)	8.7 (325)	11.9	
17.	*p*-xylene	14.2	(26)	5.8 (322)	15.5	0
18.	mesitylene	15.3	25.6	7.1 (321)	17.3	0
19.	*n*-butylbenzene	13.9	(26)	5.3 (330)	22.6	0.83
20.	iodobenzene	13.3	(26)	4.8 (324)	22.4	1.70
21.	toluene	13.7	26.0	5.5 (320)	25.8	0.36
22.	bromobenzene	13.6	(26)	5.1 (325)	29.5	1.70
23.	chlorobenzene	11.7	(26)	4.0 (297)	32.3	1.69
24.	fluorobenzene	11.7	26.5	3.8 (300)	34.6	1.60
25.	1,1,1-trifluorotoluene	11.8	(26)	4.0 (300)	45.7	2.86
26	hexafluorobenzene	11.3	(26)	3.5 (298)	50.7	0
27	benzonitrile	19.4	(21)	12.3 (338)	44.3	4.18
28	nitrobenzene	17.7	21.2	10.7 (324)	51.4	4.2
29	CH_3CN	17.3	17.8	11.6 (323)	71.0	3.9
30.	CH_3NO_2	14.4	(18)	8.2 (343)	77.7	3.4
31	CH_3I	9.7	(18)	4.3 (299)	42.4	1.6

[a–d] See footnotes to Table I.

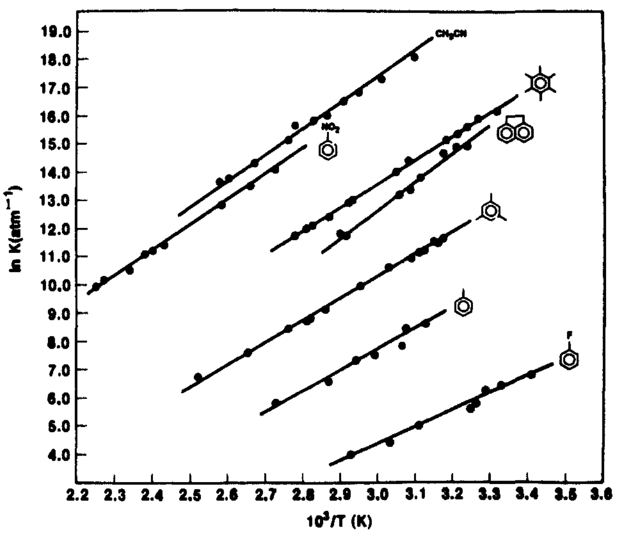


Figure 2. Van't Hoff plots for association equilibria $An^+ + M \rightleftarrows An^+{\cdot}M$, with molecules (M) as indicated.

We observe that in this series $\Delta H^\circ{}_{res}$ again contributes up to 5.6 kcal/mol. This contribution is similar to that observed in $(Bz)_2{}^+$ and $(An)_2{}^+$. However, unlike in the symmetric dimers, in the present case this large resonance contribution occurs when the components are quite dissimilar. For example, in aniline$^{+\cdot}$acenaphthene where the acceptor is charge localized and the donor is a delocalized hydrocarbon, $\Delta IP = 0$ and $\Delta H^\circ{}_{res} = 5.6$ kcal/mol. It therefore appears that at $\Delta IP = 0$, $\Delta H^\circ{}_{res}$ is insensitive to the nature of the aromatic components.

With respect to this point, it is also interesting that we observed the $AZ^+{\cdot}An$ (AZ = azulene) dimer. Unlike the other dimers of localized acceptor and delocalized donor, here the IP of azulene is lower than that of aniline. Therefore, this is a complex of a charge delocalized acceptor with a partially electron localized donor. The $\Delta H^\circ{}_D$ value obtained for this dimer is less than what one expects based on the $\Delta H^\circ{}_D$ vs. ΔIP relationship for complexes with localized acceptors. This can be attributed to the intramolecular charge delocalization on AZ^+ which should make resonance delocalization to an extramolecular electron donor less significant. From this it appears that, unlike when $\Delta IP = 0$, when $\Delta IP \neq 0$ the structures of the components are also important in determining the stability of the complex.

The use of eq 6 to estimate $\Delta H^\circ{}_{res}$ must be considered with caution. Throughout the ligand series in Figure 3 the molecular size increases roughly with decreasing ionization potentials. Therefore, the ion–induced dipole and the dispersion interactions will also increase in general with decreasing ΔIP. The increasing bonding energies do not reflect only the variation in $\Delta H^\circ{}_{res}$ but also the contribution by these other forces.

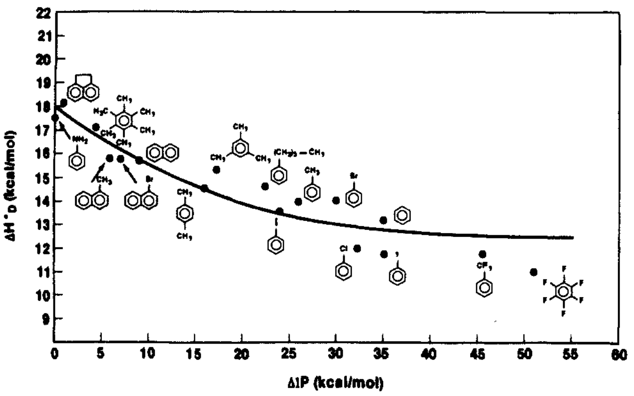
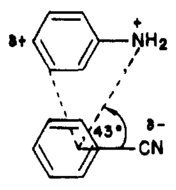


Figure 3. Relation between enthalpy of dissociation ($\Delta H^\circ{}_D$) and the difference between the ionization potentials of the reactants, ΔIP = IP(M) − IP(aniline). Molecules (M) as indicated. Data for naphthalene, 1-methylnaphthalene and 1-bromonaphthalene complexes are from ref 21.

Another component that may affect the bonding energies is the ion–permanent dipole interaction. A sample model is represented by ion **4**. We consider a $C_6H_5NH_2{}^+{\cdot}C_6H_5CN$ complex where the charge center on the ion is represented by a +0.5 charge on the NH_2 function. The C_6H_5CN ligand is represented by a dipole of 4.2 D and a polarizable center of 9.5 cm^{-3} at the center of mass of the molecule; the interplanar distance is 3.2 A. Electrostatic calculations yield an interaction energy of 14 kcal/mol. In contrast, the linear geometry **5** (below) gives an interaction energy of 44 kcal/mol. While the absolute numbers are too large, the model shows that the sandwich geometry is inefficient for ion–dipole interactions. Further, in the actual An^+ ion, part of the positive charge is localized on the CH group in the 4 position. These charges give a repulsive ion–dipole interaction with the ligand in geometry **4**, and this further weakens the attractive contribution of the overall ion–permanent dipole interaction. As an experimental support for these arguments, we note that complexes with the most polar ligands (but with large ΔIPs) in Figure 3 are the most weakly bonded. In fact, the complexes of An^+ with the polar C_6H_5F, C_6H_5Cl, and C_6H_5Br ligands yield dissociation energies similar to complexes with nonpolar ligands.

(3) Complexes with Highly Polar Ligands. In contrast to the weak bonding of moderately polar ligands ($\mu < 2$ D), the highly polar cyano and nitro compounds give strongly bonded complexes, wtih $An^+{\cdot}CB$ (CB = cyanobenzene) being the most strongly bonded complex. This complex clearly deviates from the $\Delta H^\circ{}_D$ vs. ΔIP correlation, which would suggest that $\Delta H^\circ{}_D$ for this



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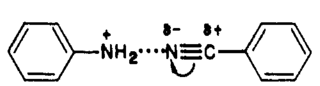
complex should be about 12 kcal/mol, in contrast with the observed value of 20.3 kcal/mol. Similar considerations apply to the An$^+$·NB (NB = nitrobenzene) complex. Thus, in the cyano and nitro complexes the bonding results from strong electrostatic interactions due to the very large dipoles. Since the behavior of these polar ligands does not fit the trend in sandwich complexes, we assign to these complexes the structures **5** and **6**. This assignment is supported by the fact that CH_3CN and CH_3NO_2 also give strongly bonded complexes. In these latter cases a sandwich structure is of course impossible, and the only reasonable structure is that similar to **5** and **6**. The somewhat stronger bonding to cyanobenzene and nitrobenzene vs. the respective methyl compounds can be assigned to the larger polarizabilities and dipole moments of the aromatic compounds.



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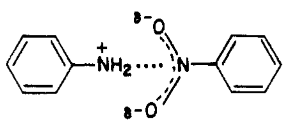

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Comparing the cyanobenzene vs. nitrobenzene ligands shows stronger bonding to the former despite the fact that the dipole moments are equal. The difference may be due to the fact that in **5** the partial negative charge on the cyano group is highly localized on the nitrogen atom which is accessible to the positive charge on the radical cation, while in **6** the partial negative charge on the nitro group is delocalized on the two oxygen atoms.

Up to this point we observed a division of the ligands into a moderately polar group which seem to give sandwich complexes and the highly polar ones that seem to reorient to give electrostatic complexes. This raises the question as to how large a dipole moment is necessary for such reorientation. The behavior of the trifluorotoluene ligand is particularly interesting in this respect. The dipole moment of this ligand, 2.86 D, is intermediate between the moderately polar group and the highly polar group. The experimental results show weak bonding, and the complex fits the position expected on the basis of the ΔIP on Figure 3. This suggests that the dipole moments of over 3 D may be required to effect reorientation. However, the electrostatic conformation also may be destabilized in this case because the partial negative charge on the trifluoro group is distributed over the three fluorine atoms.

The significance of the large dipole moments of the ligands in the electrostatic complexes is also shown by the fact that the complex An$^+$·IM (IM = iodomethane) where μ = 1.6 D, with ΔH°_D = 10.8 kcal/mol, is more weakly bonded than complexes with the more polar cyanomethane and nitromethane ligands.

Conclusions

In summary, it is possible to classify the complexes of aromatic ions and molecules into the following categories:

(a) Complexes Involving Nonpolar or Moderately Polar Ligands with ΔIP < 35 kcal/mol. At ΔIP ≈ 0, the total attractive energy is made up from the sum of the electrostatic, resonance, induction, and dispersion energies with comparable contributions and the net interaction is termed "strong", $\Delta H^\circ_D \approx$ 18 kcal/mol. The resonance energy decreases as ΔIP increases and vanishes at ΔIP ≈ 35 kcal/mol. Between ΔIP = 0, $\Delta H^\circ_D \approx$ 18 kcal/mol and ΔIP ≈ 35 kcal/mol, $\Delta H^\circ_D \approx$ 12 kcal/mol, the interaction may be called "intermediate".

(b) Complexes Containing Nonpolar or Weakly Polar Ligands with ΔIP > 35 kcal/mol. These complexes are termed "weak". Induction and dispersion energies contribute most of the stabilization energy. Examples are (An$^+$·HFB (HFB = hexafluorobenzene) and (An$^+$·TFB (TFB = 1,3,5-trifluorobenzene). The bonding energy for this class of complexes is in the order of 11 ± 2 kcal/mol.

(c) Complexes Containing Highly Polar Molecules with ΔIP > 35 kcal/mol. The interaction is "strong" and dominated by strong electrostatic forces even though induction and dispersion energies are not negligible. Examples are (An$^+$·CB) and (An$^+$·NB). For this class of complexes, the electrostatic energies dominate in determining the equilibrium geometries of the complexes.

A principal interest is the contribution of ΔH°_{res} to the interaction in these complexes. With respect to the relation between ΔH°_{res} and structure, we have now observed in this work and preceding papers[16,17] all possible combinations between charge-localized and delocalized electron acceptors and donors, as well as apolar to highly polar systems. The principal conclusions are the following:

(1) Mass spectrometric studies yield the bonding energies in dimer radical cations of aromatic molecules. Studies on series of dimers are useful in order to identify the contributions of the various energy factors, especially that of charge-transfer resonance. This can be derived from series of dimers of a common electron acceptor with a series of donors, or a common donor with series of acceptors. Within this context, it is useful to choose groups of molecules that have similar physical properties (dipole moment or polarizability) but differ sharply in one property (IP).

(2) Studies in such series of dimers yield an inverse relation between ΔH°_D and ΔIP. In complexes with ΔIP = 0, charge resonance contributes about 4–7 kcal/mol to the bonding, but it becomes negligible as ΔIP increases to 15–30 kcal/mol.

(3) With increasing molecular size of the electron acceptor cations, intramolecular charge delocalization becomes efficient, and the importance of intermolecular charge resonance decreases. Ion–dipole and ion–reduced dipole interactions also decrease, but a compensating increase in dispersion forces keeps ΔH°_D approximately constant.

(4) Classical forces which include electrostatic (all permanent dipole interactions), induction (dipole–induced dipole interaction), and dispersion forces contribute at least 70% to the total stabilization of the complex. At the limit of ΔIP = 0, charge transfer resonance contributes about 30% to the total stabilization with increasing ΔIP and the resonance interaction becomes negligible and the bonding can be fully described by the classical forces only.

(5) The above trends apply in all combinations of complexes involving delocalized or partially localized acceptors and donors. In particular, we note that the magnitude of resonance contributions depends mainly on ΔIP rather than on the structures of the components of the complex.

(6) When the neutral molecules are highly polar (μ > 3 D) the ion–dipole interaction becomes predominant, and the complex reorients from a sandwich structure to a linear charge···dipole geometry.

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