Effects of Alkyl and Fluoroalkyl Substitution on the Heterolytic and Homolytic Bond Dissociation Energies of Protonated Amines

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Abstract: Thermochemical properties related to molecular basicity are examined for a series of alkyl and fluoroalkyl substituted amines using ion cyclotron resonance techniques and photoelectron spectroscopy. Proton affinities, PA(B), defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, and adiabatic first ionization potentials, IP(B), are determined. Homolytic bond dissociation energies $D(B^+\text{-}H)$ are obtained using the relation $PA(B) - D(B^+\text{-}H) = IP(H) - IP(B)$. Effects of alkyl and fluoroalkyl substitution on PA(B) and $D(B^+\text{-}H)$ are identified. While alkyl groups are known to increase PA and decrease $D(B^+\text{-}H)$, it is found that fluoroalkyl groups do just the reverse. However, the substituent effects on PA are unrelated to corresponding effects on $D(B^+\text{-}H)$; i.e., there is no correlation between structural effects on these two kinds of bond dissociation energies. The result is interpreted in terms of varying contributions from polarization, inductive (polar) and hyperconjugative interactions.

Systematic quantitative evaluation of substituent effects on properties related to molecular basicity has become possible through the recent development of techniques for the study of ion-molecule reactions and for the determination of molecular ionization potentials.[2-12] Ion cyclotron resonance (ICR) techniques[2-11] or high-pressure mass spectrometry[12] may be used to measure equilibrium constants for proton transfer between two bases, reaction 1, yielding accurate (±0.2 kcal/mol) relative free energies of protonation. Temperature dependence for simple bases is observed to be slight, confirming the expectation that ΔS for reaction 1 is small and can be accounted for by symmetry number changes.[12]

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+, \qquad \Delta H = PA(B_1) - PA(B_2) \tag{1}$$

$$BH^+ \rightarrow B + H^+, \qquad \Delta H = D(B\text{-}H^+) \equiv PA(B) \tag{2}$$

$$BH^+ \rightarrow B\cdot^+ + H\cdot, \qquad \Delta H = D(B^+\text{-}H) \tag{3}$$

$$PA(B) - D(B^+\text{-}H) = IP(H) - IP(B) \tag{4}$$

$$\begin{tikzcd}
BH^+ \arrow[r, "PA(B)"] \arrow[d, "D(B^+\text{-}H)"'] & B + H^+ \\
B^{\cdot+} + H\cdot & B + H\cdot \arrow[l, "IP(B)"'] \arrow[u, "IP(H)"']
\end{tikzcd} \tag{5}$$

Proton affinity, PA(B), is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, eq 2. The homolytic bond dissociation energy $D(B^+\text{-}H)$ defined by eq 3 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), eq 4, by the thermochemical cycle 5. A relative scale of PA(B) has been established by examining reaction 1 for a large number of organic and inorganic bases and calibrated by reference to a variety of species for which absolute values of PA(B) may be derived from appearance potential measurements.[11]

Variation of molecular properties related to basicity in a series of primary, secondary, and tertiary amines,[2-4,9,12] substituted pyridines,[5,9,13] nitriles,[10] and the methyl phosphines[6] has been examined. In particular, it has been demonstrated that for a homologous series, for example, the primary amines, molecular ionization potentials IP(B) and homolytic bond dissociation energies $D(B^+\text{-}H)$ are linear functions of PA(B).[3,4,10] Stabilization of the conjugate acid BH^+ or radical cation $B\cdot^+$ by resonance interactions or hyperconjugation may lead to important exceptions.[4,7,9,10]

The effects of direct fluoro substitution on nitrogen have been examined in studies of the ion chemistry of NF_3.[14] Fluorine substituent effects on the stabilities of carbenium ions[15] and carbanions[16] and on the acidities of carboxylic acids[17] and alcohols[18] have also been investigated. Theoretical approaches to the understanding of these effects have appeared.[19]

The present work uses ICR techniques and photoelectron spectroscopy (PES) to examine the effects of alkyl and fluoroalkyl substitution in a series of primary and tertiary amines.

Experimental Section

ICR instrumentation and techniques used in these studies have been previously described in detail.[6,10,20,21] Photoelectron spectra were obtained using an instrument built in the Caltech shops employing a 127° electrostatic analyzer. Spectra were calibrated using the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ lines of an internal argon standard. Both the ICR and PES experiments were conducted at room temperature. We are indebted to Mr. F. F. Piszkiewiez for the preparation of samples of $F(CH_2)_2NH_2$, $F_2CHCH_2NH_2$, and $CF_3CH_2NMe_2$. The former two were prepared by borohydride reduction of the corresponding amides.[22] The latter, bp (748 mm) = 51°, was prepared by Eschwieler-Clarke methylation of $CF_3CH_2NH_2$ using H_2CO and HCO_2H. CF_3NMe_2, $CF_3(CH_2)_2NH_2$, and $CF_3(CH_2)_2NH_2$ were kindly supplied by Dr. W. A. Sheppard of DuPont Central Research Labs. All other compounds studied were commercially available and were used in recent investigations of the proton affinities of a large number of organic and inorganic bases.[11] All samples were purified by gas chromatography.

Results

Photoelectron spectra of various alkyl and fluoro substituted primary and tertiary amines were obtained and found to have a characteristic first band corresponding to removal of an electron from the nitrogen lone pair orbital, Figure 1. An adiabatic ionization potential was chosen near the beginning of this band for ethylamine, Figure 2, and in a similar location in each of the other spectra. Adiabatic and vertical ionization potentials for all of the molecules are given in Table I. Relative ionization potentials are estimated to be accurate to ±0.03 eV. Absolute values of adiabatic ionization potentials are estimated to be somewhat less accurate (±0.15 eV).[23]

Proton affinities were available from studies of a large

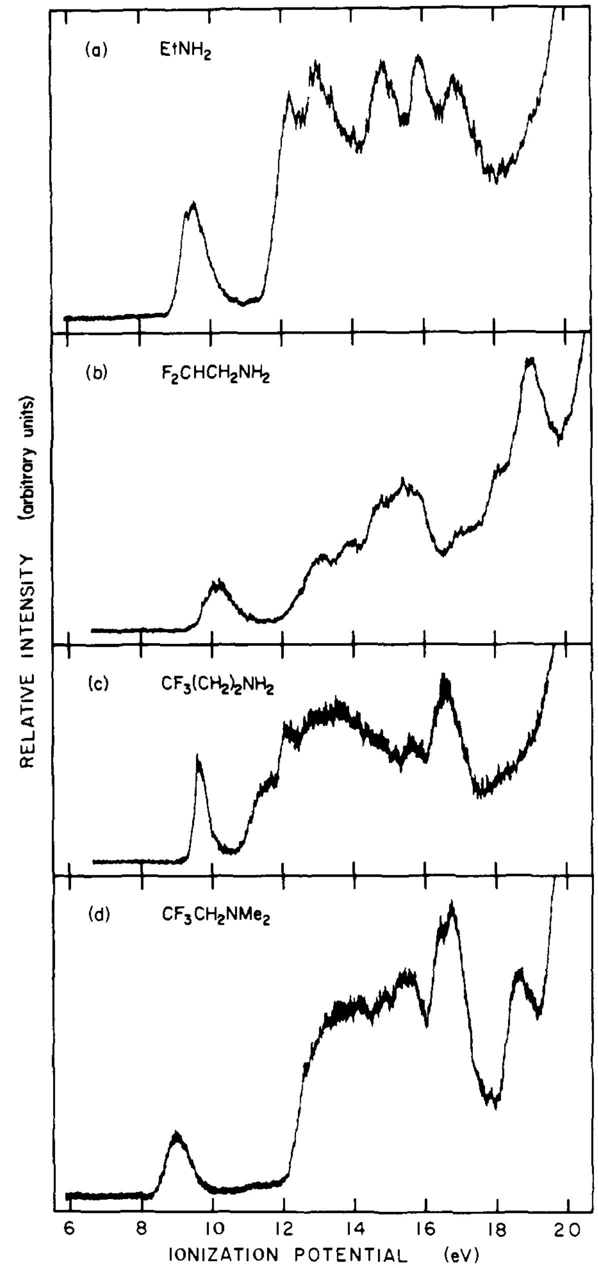


Figure 1. He(I) photoelectron spectra of (a) $EtNH_2$, (b) $F_2CHCH_2NH_2$, (c) $CF_3(CH_2)_2NH_2$, and (d) $CF_3CH_2NMe_2$.

number of organic and inorganic bases, details of which will be published separately.[11] Relative values for closely spaced proton affinities ($\Delta PA < 3$ kcal/mol) could be measured directly and are estimated to be accurate to ±0.2 kcal/mol. The cumulative error for relative values of widely spaced proton affinities is estimated to be less than ±1.0 kcal/mol. All proton affinity values are relative to $PA(NH_3) = 202.3 \pm 2.0$ kcal/mol.[11] Proton affinities, adiabatic ionization potentials, and homolytic bond dissociation energies calculated using eq 4 are given in Table II for all of the molecules studied.

Discussion

Structural effects on heterolytic (proton affinity) and on homolytic (hydrogen atom affinity) bond dissociation energies of BH^+ are in general markedly different.[2-14,20] Reference to the contrasting processes which are involved anticipates such a result. Equation 6 gives the process involving the proton affinity of a general base, B, relative to a reference base, B_0, in the gas phase. Since "saturated" cations are formed from "saturated" neutral bases in eq 6, the effects of alkyl and fluoroalkyl substituents on ammonia will be determined predominantly by polarization and inductive (or polar) effects associated with the change in charge.

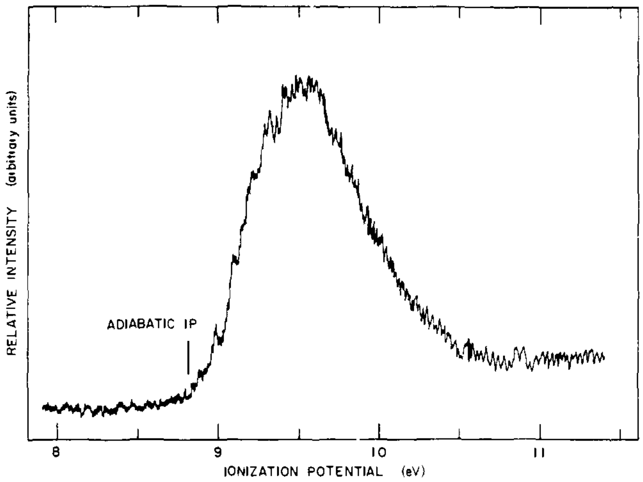


Figure 2. He(I) photoelectron spectrum of the first band in $EtNH_2$. The adiabatic first ionization potential is indicated.

Table I. Adiabatic and Vertical Ionization Potentials for Some Alkyl and Fluoroalkyl Substituted Amines[a]

Molecule	aIP[b]	vIP[c]	vIP − aIP
$EtNH_2$	8.80[d]	9.53	0.73
Me_3N	7.87[d]	8.55	0.68
Me_2EtN	7.79	8.47	0.68
$MeEt_2N$	7.63	8.35	0.72
Et_3N	7.42	8.13	0.71
Quinuclidine	7.69[e]	8.02[e]	0.32
$FCH_2CH_2NH_2$	9.11	9.86	0.75
$F_2CHCH_2NH_2$	9.38	10.15	0.77
$F_3CCH_2NH_2$	9.73	10.46	0.73
$CF_3(CH_2)_2NH_2$	9.31	9.70	0.39
$CF_3(CH_2)_3NH_2$	9.05	9.80	0.75
CF_3NMe_2	9.22	9.99	0.77
$CF_3CH_2NMe_2$	8.26	8.98	0.72

[a] All data in eV measured from photoelectron spectra. [b] Adiabatic ionization potential. [c] Vertical ionization potential. [d] K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962), report $IP(EtNH_2) = 8.86$ eV, $IP(Me_3N) = 7.82$ eV, and $IP(Et_3N) = 7.50$ eV; A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **49**, 1135 (1971), report $IP[(CH_3)_3N] = 7.80$ eV. [e] Data from ref 7.

$$B_0H^+ + B \rightleftharpoons BH^+ + B_0$$

$$-\Delta H^\circ = PA(B) - PA(B_0) = \delta_R PA \qquad (6)$$

Equation 7 gives the process involving the homolytic bond dissociation energy of the conjugate acid of a general base, B, relative to that for a reference base, B_0, in the gas phase. In this process, all species are monovalent cations and there is no change in charge.

$$B_0\cdot^+ + BH^+ \rightleftharpoons B\cdot^+ + B_0H^+$$

$$\Delta H^\circ = D(B^+\text{-}H) - D(B_0{}^+\text{-}H) = \delta_R D(B^+\text{-}H) \qquad (7)$$

The change of importance in eq 7 is the interconversion of "saturated" or even electron conjugate acids to "unsaturated" or odd electron cation radicals. As a consequence of these two conditions, hyperconjugative interactions in the cation radicals will determine predominantly the substituent effects on $\delta_R D(B^+\text{-}H)$. Included are the inductive effects of fluorine upon the hyperconjugative interactions.

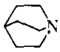
Equation 6 involves little or no steric effects since both bases and their conjugate acids have very similar geometries, i.e.,

Table II. Proton Affinities, Adiabatic Ionization Potentials, and Homolytic Bond Dissociation Energies for Some Alkyl and Fluoroalkyl Substituted Amines[a]

Molecule	PA[b]	IP	$D(B^+-H)$[c]
NH_3	202.3	234.5[d]	123.1
Me_2NH	217.9	190.3[e]	94.5
Me_3N	222.1	181.5	89.9
Me_2EtN	224.5	179.6	90.4
$MeEt_2N$	226.7	175.9	88.9
Et_3N	229.0	171.1	86.4
Quinuclidine	228.6	177.3	92.2
$CH_3CH_2NH_2$	214.0	202.9	103.2
$FCH_2CH_2NH_2$	210.2	210.1	106.6
$F_2CHCH_2NH_2$	205.9	216.3	108.5
$F_3CCH_2NH_2$	200.3	224.4	111.0
$CF_3(CH_2)_2NH_2$	209.0	214.7	110.0
$CF_3(CH_2)_3NH_2$	212.3	208.7	107.3
CF_3NMe_2	192[f]	212.6	90.9
$CF_3CH_2NMe_2$	212.5	190.5	89.3

[a] All data in kcal/mol. [b] Proton affinities relative to $PA(NH_3)$ = 202.3 ± 2.0 kcal/mol, ref 11. Relative values of PA have been obtained from ICR equilibrium constant determination (ref 2) as described in ref 9. Reference 9, p 38, gives stepwise overlapping sequences in standard free energy changes involving all of the bases in this table except (a) CF_3NMe_2, (b) $CF_3CH_2NH_2$, (c) NH_3, (d) quinuclidine, and (e) Et_3N. Direct determinations for these are: (a) essentially the same gas phase base strength as 1,4-dioxane; (b) 1.0 kcal/mol less basic than *i*-PrOEt and 1.6 kcal/mol more basic than EtOAc; (c) 0.8 kcal/mol more basic than *i*-PrOEt; (d) 0.5 kcal/mol less basic than (e); (e) 2.2 kcal/mol more basic than $MeEt_2N$. [c] Calculated using eq 4. [d] K. Watanabe and S. P. Sood, *Sci. Light (Tokyo)*, **14**, 36 (1965). [e] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **49**, 1135 (1971). [f] ±1 kcal/mol. Loss of HF from the conjugate acid was observed to be a facile process which complicated determination of an accurate value.

Table III. Substituent Effects on Proton Affinity and Homolytic N–H Bond Dissociation Energy[a]

RNH_2^+	$\delta_R(PA)$[b]	$\delta_R D(B^+-H)$[c]
Series I.	Primary Amines	
NH_4^+	(0.0)[d]	(0.0)[d]
$CH_3CH_2NH_3^+$	11.7	−19.9
$FCH_2CH_2NH_3^+$	7.9	−16.5
$F_2CHCH_2NH_3^+$	3.6	−14.6
$F_3CCH_2NH_3^+$	−2.0	−12.1
$F_3C(CH_2)_2NH_3^+$	6.7	−13.1
$F_3C(CH_2)_3NH_3^+$	10.0	−12.1
Series II.	Tertiary Amines	
$Me_2NH_2^+$	(0.0)[e]	(0.0)[e]
$Me_2MHCH_3^+$	4.2	−4.6
$Me_2NHCF_3^+$	−26	−4
$Me_2NHCH_2CH_3^+$	6.6	−4.1
$Me_2NHCH_2CF_3^+$	−5.4	−5.2
$MeNH(CH_2CH_3)_2^+$	8.8	−5.6
$NH(CH_2CH_3)_3^+$	11.1	−8.1
 NH$^+$	10.7	−2.30

[a] All data in kcal/mol. [b] Substituent effect on proton affinity, defined by eq 6 in text. [c] Substituent effect on homolytic N–H bond dissociation energy, defined by eq 7 in text. [d] $PA(NH_3)$ = 202.3 and $D(NH_3^+-H)$ = 123.1. [e] $PA(Me_2NH)$ = 217.9 and $D(Me_2NH^+-H)$ = 94.5.

both are pyramidal. Equation 7 may involve steric effects, however, since the cation radicals apparently favor planar over pyramidal structures of BH^+.[24] Further, both eq 6 and 7 can involve effects associated with internal H-bonding chelation[3,12,22,25] in the fluoroalkyl substitution. Such chelation interactions, however, probably tend to be more important in the conjugate acid form, BH^+, than in the corresponding cation radical form, $B\cdot^+$. This conclusion follows from two considerations. The pyramidal form of BH^+ is more favorably disposed for internal H-bond chelation than is the planar form for $B\cdot^+$. Delocalization of positive charge into alkyl groups is more extensive in $B\cdot^+$ than BH^+, a consideration which reduces the proton donating ability of hydrogen atoms bonded to nitrogen cation radicals compared to corresponding ammonium ions.

Table II lists proton affinities, adiabatic ionization potentials, and homolytic bond dissociation energies for the alkyl and fluoroalkyl substituted amines of this study. Substituent effects on proton affinities and homolytic bond dissociation energies, i.e., standard enthalpies for eq 6 and 7, are shown in terms of two series, the primary amine series I, and the tertiary amine series II. For both series we examine the influences of replacing a hydrogen on nitrogen by alkyl and fluoroalkyl substituents, i.e., for series I, B_0 of eq 6 and 7 is NH_3, and for series II, B_0 is Me_2NH. Enthalpies corresponding to eq 6 and 7 are given for series I and II in Table III as $\delta_R PA$ and $\delta_R D(B^+-H)$, respectively.

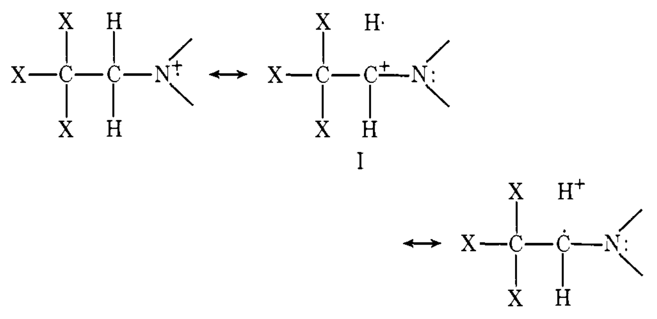
The polarizability and inductive effects of alkyl groups increase the proton affinity ($\delta_R PA$ values of Table III are positive). Successive substitution on NH_3 of the hydrocarbon substituents $HC{\equiv}CCH_2$, $H_2C{=}CHCH_2$, CH_3, C_2H_5, *n*-C_3H_7, and *i*-C_3H_7 have all been found to be remarkably regular.[9] The effect of the second substitution is 86% of the additive value and that for the third substitution is 74% of the additive value. The results in Table III for the series II amines Me_3N, Me_2NEt, $MeNEt_2$, and NEt_3 follow this behavior.[9]

Alkyl substituents on NH_3 decrease $D(B^+-H)$, i.e., stabilize $B\cdot^+$ relative to the corresponding BH^+. Consequently, $\delta_R D(B^+-H)$ values of Table III are negative for alkyl substituents. Hyperconjugative stabilization of the cation radical is the predominant contribution.[4] Presumably as a consequence of the different origins of the effects, successive substitution of the alkyl groups gives results which are somewhat less additive than for the proton affinities.[4] For example, the increase of PA(B) for Me_3N relative to NH_3 (19.8 kcal/mol) is 73% of three times the increase for $MeNH_2$ relative to NH_3 (9.0 kcal/mol),[26] i.e., 19.8/(3 × 9.0) = 0.73. From the results given in Table II it may be seen that the lowering of $D(B^+-H)$ for Me_3NH^+ relative to NH_4^+ (33.2 kcal/mol) is only 62% of three times the lowering for $MeNH_3^+$ relative to NH_4^+ (17.8),[23] i.e., 33.2/(3 × 17.8) = 0.62.

Fluoroalkyl groups, relative to the corresponding unsubstituted alkyl group, cause a significant decrease in proton affinities (eq 6) and somewhat smaller increases in homolytic bond dissociation energies (eq 7). The greater effects on proton affinity are explained by the direct inductive (polar) effects of fluorine substitution on the change in charge accompanying eq 6, since polarizability effects should apparently act in the opposite direction (the polarizability of F is slightly greater than H[27]).

The effect of the CF_3 substituent on PA, i.e., 30.1 kcal/mol comparing CF_3NMe_2 to CH_3NMe_2, is similar in size to the effect of comparable fluorine substitution in acetic acid. The gas phase acidity of CF_3CO_2H is 25.2 kcal/mol greater than that of CH_3CO_2H.[17] In its effects on acidities, fluoro substitution has the effect of stabilizing negative charge development in contrast to its effects on basicity, where it destabilizes positive charge development.

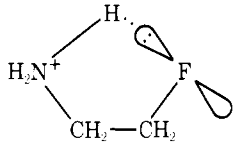
The effect of fluorine substitution in raising homolytic bond dissociation energies is interpreted as an inductive effect of the second kind, i.e., an inductive effect which decreases the alkyl group hyperconjugative stabilization of cation radicals. Since F relative to H inductively repels positive charge, structures I and II are destabilized for X = F and hyperconjugative stabilization of $B\cdot^+$ is less for fluoroalkyl than corresponding alkyl substituents.



I

II

In series I, each successive substitution of β-F in the ethyl substituent lowers $\delta_R D(B^+\text{-}H)$ by 3 kcal/mol, i.e., the effect is additive within the experimental error (cf. Figure 3). The nonadditive increments in PA for this series, i.e., 3.8, 4.1, and 5.5 kcal, respectively, have been interpreted as due to (weak) H-bonding chelation in the fluoroethyl- and difluoroethylammonium ions,[9] e.g., structure III. The more nearly additive $\delta_R D(B^+\text{-}H)$ values are suggestive of open (rather than chelate) cation radical structures, a matter on which we have already commented.



III

Even though $\delta_R D(B^+\text{-}H)$ for $CF_3CH_2NH_3^+$ is 7.8 kcal/mol less than that for $CH_3CH_2NH_3^+$, it is clear from Table III that all of the alkyl and fluoroalkyl groups in series I provide very sizable stabilizations of $B\cdot^+$ relative to the corresponding BH^+. With removal of the CF_3 substituent to γ and δ positions, the fluorine substitutional destabilizing effect becomes particularly small. The relatively large magnitude of the substituent effects on $\delta_R D(B^+\text{-}H)$ values for series I (values range from 12 to 20 kcal/mol) is ascribed to the presence of the single substituent group. This group is called upon fully to stabilize $B\cdot^+$ relative to BH^+ by the hyperconjugative interaction in the former.

The results for Me_2NHR^+ ions (series II) provide particularly compelling evidence for these ideas. Values of $D(B^+\text{-}H)$ for this series now range only by 5 kcal/mol for R = H, CH_3, C_2H_5, CF_3, or CH_2CF_3. In the cation radicals for series II, delocalization of charge is largely accommodated by the two common CH_3 groups, therefore placing little or no demand upon the third (substituent) group.

Variation of $D(B^+\text{-}H)$ in the series II for $Me_{3-n}Et_nNH^+$, $n = 0\text{-}3$, is also shown in Figure 3. Especially for Et_3NH^+, a larger stabilizing effect of substitution on $B\cdot^+$ compared to BH^+ is evident for ethyl substitution. This result probably reflects principally steric crowding in pyramidal BH^+ (and B) as compared to planar $B\cdot^+$ with increased size of the alkyl substituents. This conclusion, which was reached earlier,[7] is supported by the fact that the cation radical of quinuclidine, which is constrained to pyramidal geometry (therefore no relief of strain), has even a larger value of $D(B^+\text{-}H)$ than does Me_3NH^+.

The photoelectron spectrum of $CF_3(CH_2)_2NH_2$, Figure 1c, shows a significantly narrowed first band compared to all of the other amines, resulting in an unusually small difference in vIP and aIP for this amine (Table I). This narrowing could result either from the neutral molecule adopting a planar configuration at nitrogen or from the radical cation having a preferred pyramidal configuration at nitrogen. The six-membered ring conformation IV for this amine and its cation radical might conceivably be responsible.[28] However, the value of $\delta_R D(B^+\text{-}H)$ of Table III does not indicate any major energetic effects.

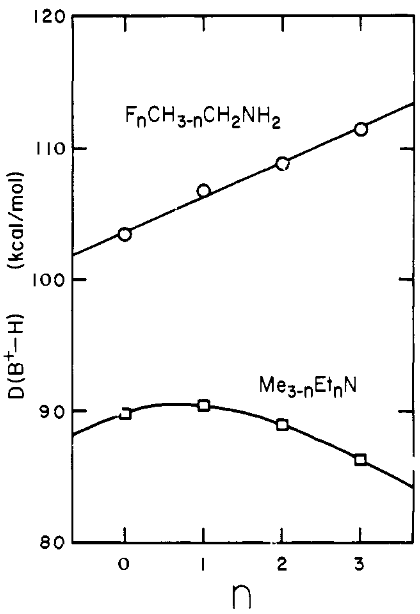
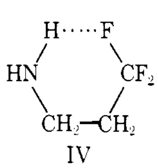


Figure 3. Variation of $D(B^+\text{-}H)$ with n for the series (○) $F_nCH_{3-n}CH_2NH_2$ and (□) $Me_{3-n}Et_nN$.



IV

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(1) (a) California Institute of Technology, work supported in part by Energy Research and Development Administration; (b) University of California, Irvine, work supported in part by the National Science Foundation; (c) IREX Exchange Scholar, UCI, 1974–1975; (d) Camille and Henry Dreyfus Teacher-Scholar, 1971–1976.
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Molecular Orbital Studies of Electron Donor–Acceptor Complexes. 4. Energy Decomposition Analysis for Halogen Complexes: $H_3N–F_2$, $H_3N–Cl_2$, $H_3N–ClF$, $CH_3H_2N–ClF$, $H_2CO–F_2$, $HF–ClF$, and $F_2–F_2$

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Abstract: The energy and charge distribution decomposition analyses are carried out for a series of electron donor-acceptor complexes of halogens. Based on the energy components essential for binding, the complexes are qualitatively classified as follows: $H_3N–F_2$ $H_3N–Cl_2$, and $H_2CO–F_2$, weak electrostatic charge transfer complexes; $H_3N–ClF$, intermediate electrostatic complex; HF–ClF, weak electrostatic complex; and $F_2–F_2$, very weak dispersion-charge transfer complex. The energy components determining the equilibrium geometry as well as the *N*-methyl substituent effect are also identified, and comparisons between various complexes have been made. The predicted geometry of an anti-hydrogen bonded complex FCl–FH is in good agreement with experiment, but the hydrogen bonded counterpart ClF–HF appears to be comparable in energy. The SCF interaction energy for $(F_2)_2$ favors an open L shape.

I. Introduction

The origin of attractive intermolecular interactions and the factors determining the geometry of molecular complexes have been sought after for decades using numerous experimental and theoretical techniques.[1,2] For hydrogen bonding, which in earlier days had been considered to be a purely electrostatic interaction, the importance of the charge transfer interaction has long been emphasized.[1] The electron donor-acceptor (EDA) complex or the charge transfer complex was originally thought to be stabilized principally by the charge transfer interaction between the donor and acceptor molecules.[2,3] Later studies have suggested that many such complexes, especially weak complexes, are bound primarily due to the electrostatic and polarization interactions.[4,5] Since the interaction is quantum mechanical in nature, quantum chemical calculations should be able to provide substantial information regarding the nature of the binding.

The ab initio SCF molecular orbital (MO) method has been very successful in both predicting the equilibrium geometry and stabilization energy of many hydrogen bonded and EDA complexes and in interpreting the nature of such interactions.[6,1b] The energy and charge distribution decomposition (ECDD) analyses proposed by Morokuma[7] and Kitaura and Morokuma[8] have provided a means for direct examination of the origin of molecular interactions.[9-15] Using either the model wave function or model Hartree–Fock operator they unambiguously defined components of the total interaction, ΔE_{SCF}, which are in accord with traditional viewpoints.[16]

$$\Delta E_{SCF} = ES + PL + EX + CT + MIX \qquad (1)$$

The individual components have the following physical significance.[17]

ES is the electrostatic interaction, i.e., the interaction between the undistorted electron distribution of a monomer A and that of a monomer B. This contribution includes the interactions of all permanent charges and multipoles, such as dipole–dipole, dipole–quadrupole, etc. This interaction may be either attractive or repulsive.

PL is the polarization interaction, i.e., the effect of the distortion (polarization) of the electron distribution of A by B, the distortion of B by A, and the higher order coupling resulting from such distortions. This component includes the interactions between all permanent charges or multipoles and induced multipoles, such as dipole–induced dipole, quadrupole–induced dipole, etc. This is always an attractive interaction.

EX is the exchange repulsion, i.e., the interaction caused by exchange of electrons between A and B. More physically, this is the short-range repulsion due to overlap of electron distribution of A with that of B.

CT is the charge transfer or electron delocalization interaction, i.e., the interaction caused by charge transfer from occupied MO's of A to vacant MO's of B, and from occupied MO's of B to vacant MO's of A, and the higher order coupled interactions.

MIX is the coupling term which is the difference between the total SCF interaction energy ΔE_{SCF} and the sum of the above four components and accounts for higher order interaction between various components.

In addition to the above components calculated within the Hartree–Fock scheme, there is a contribution of the correlation