Theoretical Studies of Basicity. Proton Affinities, Li^+ Affinities, and H-Bond Affinities of Some Simple Bases

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Abstract: Quantum mechanical studies of different types of basicity are analyzed in light of the general question: what is the intrinsic basicity of a molecule and what molecular properties can one use to predict this basicity? We have found that for comparing very different bases, the electrostatic potential is a useful first guess to predict the basicity. However, even for comparing gas phase basicities of simple molecules, there are deviations from the basicities predicted by the electrostatic potential depending on the nature of the acid (the different weighting of electrostatic and charge redistribution effects) and on the substituent on the basic site. Specifically, methyl substituent effects are quite different for fluoro and amine bases. In the case of fluoro bases, electrostatic and charge redistribution effects reinforce each other; in amine bases, they oppose each other. By comparing H^+, HF, and Li^+ affinities of amines and amides, we conclude that the uniqueness of the H bond lies in the smallness of the exchange repulsion.

Two of the most useful concepts in modern chemistry are acidity and basicity. Since their elucidation by Lewis,[2a] these two concepts have been very important in the development of an understanding of the nature of molecules as well as an elucidation of the mechanisms of many chemical reactions. An important recent advance has been a series of articles by Pearson,[2b] who proposed the concepts of "soft" and "hard" acids and bases as useful empirical guides to understanding relative rates of reactions. Fundamental to this study was an analysis of what molecular property(ies) makes a base "hard" or "soft". Pearson[2b] used a high basicity toward a proton as a measure of "hardness" and a high polarizability as indicating "softness". In this study, we hope to further refine some of the concepts of basicity toward "hard" acids by comparing the proton affinity, Li^+ affinity, and H-bond affinity of some simple bases.

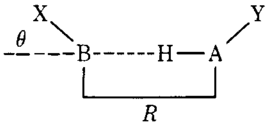
In recent years, the ability to measure gas phase proton affinities[3] and Li^+ affinities[4] has greatly increased our understanding of these acid–base interactions and the role of solvent in influencing their properties. Theory has also played a role in the studies of gas phase H bonding, hydrated protons, and hydrated Li^+.[5]

The experimental studies of Arnett et al.[6] were used to compare different types of basicity. They compared proton and H-bond affinities and concluded that intrinsic basicity is dependent on the acid used. They proposed that the proton is the best reference acid to compare bases. By comparing protons and other types of Lewis acids (Li^+, HF, HNH_2), we hope to examine, whether, for simple molecules in the gas phase, this (H^+ affinity) is an appropriate reference interaction. As bases we will study variously substituted N:, O:, F:, and Cl compounds, imines, nitriles, aldehydes, substituted ethylenes, CH_4, and H_2.

Other experimental and theoretical studies relevant to this study include papers by Martin and Shirley,[7] who related ESCA shifts to proton affinities and Lewis basicity, and by Davis and Rabelais, who related proton affinities to ESCA binding energies using a theoretical approach similar to the one employed here.[8]

Computational Details

As in our previous study of hydrogen bonding,[9] we used a 431G basis set[10] in our ab initio potential surfaces. We used the MOLE properties package[11] to evaluate the electrostatic potential surrounding some of the molecules studied. In potential surface studies of base B–X interacting with acid HAY, we considered, as we had previously,[9] variations of R and θ:



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When the acid was a proton, R was taken to be the B- - -H distance. When the acid was Li^+, R was taken to be the B- - -Li distance. For base-proton interactions, the *electrostatic* energy is equal to the electrostatic potential. The polarization energy is the difference between the interaction energy between the base and a point charge (+1.0) without basis functions and the electrostatic energy. It represents the charge redistribution within the base, not allowing charge transfer. The charge transfer energy is the difference between the calculated interaction energy between the base and proton (with basis functions) and the electrostatic and polarization energies. This decomposition is exactly analogous to that used by Morokuma for H bonds.[12] Proton–base interactions are simpler in that there is no exchange repulsion to consider.

As previously, we retained intramolecular geometries (Table I) during the intermolecular interaction. The properties of molecules considered in this study are reported in Table II. Retention of intramolecular geometries is a poorer approximation for proton affinities and Li^+ affinities than H-bond surfaces, but the purpose of this study is not reproduction of the experimental proton affinities but rather an analysis of the major factors determining basicity. A comparison with the experimental trends, where these are available, shows good agreement (Table III), supporting our justification for the incomplete optimization for neutral and anionic lone pair bases. However, we expect the retention of intramolecular geometry to be a poor approximation when the complex has a significantly different geometry than the isolated fragments, e.g., in CH_4 where the H^+ is attacking a σ bonded electron pair (CH_5^+ has a considerably different geometry than CH_4)[13] or when the H^+ attacks a π base.

Proton Affinities

We first examined proton affinities for some simple amines, ethers, and fluorides (with X = H, CH_3, F, and Cl). For amines, we used $R(N\text{–}H^+) = 1.01$ Å, $\theta = 0°$. For ethers, we used $R(O\text{–}H^+) = 0.957$ Å and optimized θ (for water, meth-

Table I. Total Energies of Molecules Studied[a]

Molecule	E_T, au	Molecule	E_T, au
Li^+	−7.233 21	HCl	−459.563 10
HF	−99.887 26	CH_3Cl	−498.522 60
CH_3F	−138.856 13	Guanidine[h]	−203.803 59
F–F	−198.458 40	H_2CO	−113.691 05
Cl–F	−558.209 38	HCH_3CO[i]	−152.685 21
H_2O	−75.907 39	$(CH_3)_2CO$[i]	−191.676 99
CH_3OH[b]	−114.869 28	NH_2HCO[i]	−168.677 22
$(CH_3)_2O$	−153.836 04	C_2H_4	−77.919 00
NH_3	−56.102 59[c]	C_2H_3–F[j]	−176.646 02
	(−56.104 79)[d]	C_2H_3–CN[j]	−169.152 31
NH_2F[e]	−154.752 63	C_2H_3–CH_3[j]	−116.546 05
NH_2Cl[f]	−514.462 10	H_2	−1.126 76
$NH_2(CH_3)$[g]	−95.068 19	CH_4	−40.139 33
$NH(CH_3)_2$[g]	−134.035 54	F^-	−99.247 82
$N(CH_3)_3$[g]	−173.005 90		

[a] Unless otherwise specified, experimental geometries were used.[14] [b] The C–O bond was assumed to lie along the C_3 axis of the CH_3 group. [c] R(N–H) = 1.0 Å; θ(HNH) = 106.7°. [d] R(N–H) = 1.0 Å; θ(HNH) = 109.47°. [e] R(N–H) = 1.0 Å, R(N–F) = 1.371 Å; θ(HNH) = θ(FNH) = 106.7°. [f] R(N–H) = 1.0 Å; R(N–Cl) = 1.76 Å; θ(HNH) = θ(ClNH) = 106.7°. [g] All R(N–H) = 1.0 Å; R(N–C) = 1.47°; R(C–H) = 1.09 Å; all angles tetrahedral. [h] Geometry from ref 15. [i] Used formaldehyde experimental geometry; added CH_3 group with R(C–C) as in acetaldehyde and acetone and R(C–N) as in formamide. [j] Used ethylene geometry, but added CN, CH_3, F groups with R(C–X) as in cyanoethylene, fluoroethylene, and propylene.

anol, and dimethyl ether, the minimum energy occurred for $\theta = 0$). For fluorides $R(F–H^+) = 0.917$ Å and the minimum energy θ turned out to be ~45°.

We also studied an sp^2 N base, guanidine (assuming $\theta = 60$, $R(N–H^+) = 1.01$ Å), and sp bases, HCN and CH_3CN (assuming $\theta = 0$ and $R(N–H^+) = 1.01$ Å). H_2CO, CH_3HCO, and $(CH_3)_2CO$ were studied, using R(O–H) = 0.957 Å and $\theta = 60°$. For chlorine protonation, we used $R(Cl–H^+) = 1.27$ Å and found a minimum energy θ of 60°. To broaden our horizons, we examined the proton affinity of H_2,[16] CH_4,[17] and substituted ethylenes.[18] The calculated proton affinities are listed in Table III and are in respectable qualitative agreement with the experimental values.

In addition to calculating proton affinities at the standard B–H distances, we evaluated the electrostatic potential surrounding some of the bases studied; we have earlier[9] found this to be a useful technique in understanding H-bond basicities. In this way, the minimum in the electrostatic potential surrounding these bases was determined (Table IV). Interestingly, all these minima occur near 1.16 Å (2.2 au) for the first row (N, O, F) bases and 1.69 Å (3.2 au) for Cl. So for the first row (N, O, F) bases we used this distance (1.16 Å) (and the optimum θ) to carry out the component analysis. For Cl bases we used 1.69 Å and the optimum θ.

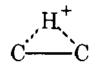
Since our actual $CH_4\cdots H^+$ [17] and $C_2H_4\cdots H^+$ [18] surfaces showed minima near 1.16 Å (2.2 au) ($C\cdots H^+$ in the case of methane, with the proton approaching along a twofold axis and center of C–C bond$\cdots H^+$ distance in the case of C_2H_4), we used this distance in carrying out the component analysis for CH_4 and C_2H_4 as well as substituted ethylenes. For H_2, we used the components at the minimum in the $H_2\cdots H^+$ surface.[16]

As one can see from Table III most of the calculated proton affinities are in respectable agreement with experiment. The larger deviation of the calculated proton affinity of propylene than that of ethylene from its experimental value is most probably due to the much larger error in our fixed geometry approximation; Hariharan et al.[19] have concluded that $C_3H_7^+$ has a "2-propyl cation" structure.

(a) Role of Electrostatics in Determining Proton Affinities. On a qualitative level, we can see the trends in proton affinities (Table III) are mirrored by the *electrostatic energies* for comparing differently hybridized nitrogen bases (guanidine vs. NH_3 vs. HCN); for comparing nitrogen, oxygen, and fluorine bases of similar structure (NH_3, vs. H_2O vs. HF); for comparing anions and neutral bases (F^- vs. the neutral N, O, F bases); and for comparing bases with substituents of very different electronegativity (NH_3 vs. NH_2F). The electrostatic energy follows the order classically expected, anion (F^-) > lone pair (N, O, F) > π electron pairs (C_2H_4) > bond pair; the calculated proton affinities follow the same order, with the exception of the π bases.

(b) Charge Redistribution Effects in Determining Proton Affinities. (1) π Bases. It is interesting that the charge transfer energy is significantly greater for the π electron molecule (C_2H_4) than the lone pair bases (N, O, and F). Comparing ammonia and ethylene, the highest occupied orbital energies are similar, but the charge transfer energy is significantly greater for C_2H_4. However, NH_3 has the higher proton affinity because of the electrostatic term.

One way to rationalize this greater "charge transfer" energy for the π bases is that one is actually forming a three center



electron "bond" in this orientation, which should lower the energy more than the normal lone pair$\cdots H^+$ interaction.

(2) Second-Row Bases. Comparing first- (N, O, F) and second-row (Cl) bases, we find that charge redistribution (polarization + charge transfer) is greater for the Cl bases than the F bases. We have not done explicit calculations on P and S bases, but it is likely that the charge distribution effects will be greater than those for the corresponding N and O bases.

(c) The Me Substituent Effect. For CH_3 substituent effects we see some extremely interesting differences. Methyl substitution decreases the dipole moment and the electrostatic energy in the amines (relative to NH_3); it decreases the dipole moment and the electrostatic energy in the ethers (relative to H_2O); but it actually increases the dipole moment and electrostatic energy in CH_3F relative to HF. The contribution to the polarization energy of a CH_3 substituent is somewhere between 7 and 11 kcal/mol greater than that of H in all these simple bases and the charge transfer energy also *tends* to increase in the Me substituted compounds, in line with ϵ(HOMO) (see Table II) (note that this is not true for the amines). This allows one to explain the difference in the Me substituent effect in fluorides ($\Delta PA(CH_3F–HF) = 26.5$ kcal/mol), ethers ($\Delta PA(CH_3OH–H_2O) = 15.1$ kcal/mol) and amines ($\Delta PA(CH_3NH_2–NH_3) = 9.6$ kcal/mol). In the fluorine bases, all three energy components increase on Me substitution, whereas in the amines, the longer range (electrostatic effect) decreases but the short range energy components increase on methyl substitution. The fact that all these terms reinforce each other for the fluorine bases leads to the much larger $\Delta PA(CH_3B–HB)$ than in the ethers or amines. Another interesting implication is that the CH_3B interacting with an acid should be greater at all distances than HB for B=F, but for B=N, there should be a "crossing" point for weak interactions, where the basicity of HB is greater than CH_3B.

(d) The Directionality of Proton Affinities. We examined the "directionality" of this component analysis in a number of the bases at $R(B–H^+) = 1.16$ Å and found (Table V) that the electrostatic energy, as expected, favors $\theta = 0$ for B=N and O, but $\theta \neq 0$ for B=F and Cl (this follows directly from the electrostatic potential maps).[20] The polarization energy in each case is largest for $\theta = 0$, as one would expect from the relative components of the polarizability tensors of the groups (for σ bonded systems $\alpha_{\parallel} > \alpha_{\perp}$). The charge transfer energies, as one

Table II. Properties of Molecules Considered in This Study

Molecule	μ(calcd)[a]	μ(exptl)[b]	q(B)[c]	ϵ(1s)[d]	ϵ(HOMO)[e]
HF	2.28	1.82	−0.48	−26.224	−0.628 (π) −0.735 (σ)
CH_3F	2.50	1.85	−0.45	−26.216	−0.522 (π) −0.653 (σ)
F-F	0	0	0.00	−26.386	−0.667 (π) −0.732 (σ)
Cl-F	1.58	0.88	−0.40	−26.301	−0.667 (σ) −0.710 (π)
H_2O	2.61	1.85	−0.78	−20.519	−0.500
CH_3HO	2.40	1.70	−0.73	−20.514	−0.447
$(CH_3)_2O$	2.05	1.30	−0.70	−20.516	−0.418
H_2CO	3.01	2.33	−0.48	−20.555	−0.532 (π) −0.438 (n)
CH_3HCO	3.32	2.69	−0.52	−20.535	−0.500 (π) −0.423 (n)
$(CH_3)_2CO$	3.50	2.88	−0.56	−20.519	−0.482 (π) −0.409 (n)
HNH_2CO	4.22	3.71	−0.60	−20.501	−0.430 (n) −0.409 (π)
H_3N	2.30	1.47	−0.90	−15.500	−0.414
CH_3H_2N	1.86	1.31	−0.80	−15.503	−0.375
$(CH_3)_2HN$	1.56	1.03	−0.71	−15.510	−0.358
$(CH_3)_3N$	1.24	0.61	−0.64	−15.520	−0.347
FH_2N	2.91 (1.29)[f]		−0.34	−15.611	−0.436
ClH_2N	2.53 (1.60)[f]		−0.78	−15.591	−0.399
HCN	3.24	2.98	−0.34	−15.591	−0.497 (π) −0.573 (σ)
CH_3CN	4.11	3.92	−0.42	−15.562	−0.461 (π) −0.547 (σ)
Guanidine	4.59		−0.73	−15.440	−0.377 (n) −0.319 (π)
C_2H_4	0	0	0.00	−11.215	−0.371
$F\text{-}C_2H_3$	2.07	1.43	−0.03	−11.272	−0.381
$CN\text{-}C_2H_3$	4.31	3.87	+0.02	−11.272	−0.391
$CH_3\text{-}C_2H_3$	0.54	0.37	−0.01	−11.224	−0.365
HCl	1.87	1.08	−0.23	−104.654	−0.469 (π) −0.606 (σ)
CH_3Cl	2.08	1.87	−0.06	−104.630	−0.425 (π) −0.552 (σ)

[a] Calculated dipole moment. [b] Experimental dipole moments from R. D. Nelson, D. R. Lide, and A. Maryott, *Natl. Bur. Stand.* (*U.S.*), *Circ.*, **No. 10** (1967). [c] Mulliken charges on the atom functioning as the base. For substituted ethylenes, this is the average of the two ethylenic carbons. [d] Orbital energy in atomic units of 1s energy level on the base. For substituted ethylenes, this is the average of the two C(1s) levels. [e] Orbital energy of highest occupied molecular orbital, with symmetry designation in parentheses. [f] Component of the dipole moment along the N lone pair direction.

would expect, favor $\theta = 45$ over $\theta = 0$ for B═O, F, and Cl since the highest occupied MO for these bases is of "π" symmetry (i.e., has a node at $\theta = 0$). In fact the much greater difference in charge transfer energy for $\theta \neq 0$ than $\theta = 0$ for B═Cl than B═O and B═F is consistent with the much greater σ–π orbital energy difference for B═Cl, as we have previously pointed out.[21]

Li^+ Affinities

The results of Li^+-base interaction studies are presented in Table VI. We searched the R, θ surface for the parent compound in each series (NH_3, H_2O, HF, HCl, and CH_2O) and then used this minimum energy geometry for the substituted molecules. We tested this approximation with H_2O and methanol by varying R and θ for both: the minima occurred at $\theta = 0°$, with $R = 1.80$ Å (MeOH) and 1.81 Å (H_2O). The difference in energy between the $Li^+\cdots$MeOH interaction at the bottom of the potential well ($R = 1.80$ Å, $\theta = 0$) and that which one finds assuming identical $Li^+\cdots H_2O$ and $Li^+\cdots$MeOH geometries is 0.02 kcal/mol.

(a) Methyl Substituent Effect on Li^+ Affinities of N, O, F, and Cl Bases. Comparing the Li^+ affinities with the proton affinities for N, O, F, and Cl bases, we find similar CH_3 effects, CH_3 substitution having the largest effect on increasing the Li^+ affinity (LiA) for F and Cl bases, and less for O and N bases, methyl sutstitution actually causing trimethylamine (TMA) to be the weakest amine base toward Li^+. The experimental results of Staley and Beauchamp[4] for NH_3 and $(CH_3)_3N$ indicate that this decrease from NH_3 to trimethylamine is incorrectly predicted by the theory. However, our theoretical results *and* a comparison between the experimental Me effect on the Li^+ affinity of MeOH (ΔLiA = 4 kcal/mol) and dimethyl ether (ΔLiA = 5 kcal/mol) vs. H_2O and between NH_3 and trimethylamine (ΔLiA = 1.5 kcal/mol) *suggest* that the Li^+ affinity peaks at methyl- (MA) or dimethylamine (DMA). (Staley and Beauchamp did not report[4] Li^+ affinities for methylamine or dimethylamine.)

The differences between the N:Li^+ affinities are so small that they are sensitive to monomer geometry choice. The tetrahedral NH_3 (in parentheses in Table VI) is probably the more appropriate choice for comparison since we have used a tetrahedral geometry around N for methyl-, dimethyl-, and

Table III. Proton Affinity Calculations on Various Bases ($-\Delta E$ in kcal/mol)

Base	(1) Electrostatic[a]	(2) Polarization[b]	(3) Charge transfer[c]	(1) + (2) + (3)	Proton affinity (calcd)[d]	Proton affinity (exptl)[e]
H_3N	110.1	23.4	79.4	212.9	224.0 (221.9)[f]	207
CH_3H_2N	106.4	34.0	82.2	222.6	233.6	216
$(CH_3)_2HN$	102.4	44.9	82.0	229.3	237.0	222
$(CH_3)_3N$	97.2	55.2	81.3	233.7	243.0	227
FH_2N	75.6	27.2	80.7	183.5	191.9	
ClH_2N	84.6	32.8	78.5	195.9	204.8	
Guanidine	117.6	60.8	72.7	251.1	263.4	
HCN	56.7	54.9	58.2	169.8	180.8	170
CH_3CN	67.0	59.4	59.2	185.6	197.5	186
H_2O	85.6	27.3	50.5	163.4	181.8	164
CH_3HO	84.0	34.9	56.1	175.0	196.9	180
$(CH_3)_2O$	83.1	41.8	59.7	184.6	203.0	186
CH_2O	61.1	42.8	58.6	162.5	177.9	166
CH_3CHO	67.8	46.2	59.9	173.9	190.4	183
$(CH_3)_2CO$	70.6	50.2	60.6	181.4	198.8	190
$H(NH_2)CO$	78.7	46.5	58.9	184.1	201.8	194
HF	45.5	16.0	44.1	105.4	118.2	116
CH_3F	47.0	26.2	49.7	122.9	146.7	151
ClF[g]	23.8	33.4	46.5	103.7	114.6	
F-F	−10.4	34.1	44.1	67.8	73.0	
F^-	269.6	7.0	100.0	376.6	400.9	361
HCl	17.7	9.9	64.9	92.5	119	140
CH_3Cl	20.2	17.3	73.0	110.5	135	160
FCl[h]	−14.4	13.2	68.0	66.8	97.6	
H_2	−38.3	7.3	120.5	89.5	92.4	97
CH_4	−36.0	36.9	103.3	104.2	(104.2)	126
C_2H_4	9.1	41.4	114.6	165.1	(165.1)	160
$(CN)C_2H_3$	−21.7	55.9	104.8	139.0	(139.0)	
$(CH_3)C_2H_3$	1.6	50.5	111.8	163.9	(163.9)	179
$(F)C_2H_3$	−9.5	44.2	113.9	148.6	(148.6)	

[a] Electrostatic energy of interaction of +1 charge. [b] Polarization energy of interaction of +1 charge. [c] Charge transfer energy of interaction of proton with base. [d] Calculated proton affinities at, e.g., R(N-H) = 1.01 Å; these are not equal to (1) + (2) + (3), because in the component calculations we used $R(B\text{-}H^+)$ = 1.164 Å (except for the second-row bases where we used $R(B\text{-}H^+)$ = 1.69 Å for the component calculations). [e] See ref 3 and references therein; the value for H_2NCHO was provided by J. Beauchamp, personal communication. [f] Calculated proton affinity for tetrahedral NH_3. [g] Proton approaching F. [h] Proton approaching Cl.

Table IV. Electrostatic Potential Analysis of Different Bases

Molecule	R_{min},[a] Å	θ_{min},[a] deg	$(ESPOT)_{min}$,[a] au	$\theta(Li^+)$,[b] deg	$ESPOT(Li^+)$,[b] au	θ(H bond),[c] deg	ESPOT(H bond),[c] au
HF	1.16	40	−0.0726	0	−0.044	0	−0.0358
CH_3F	1.16	40	−0.0749	0	−0.046	0	−0.0378
H_2O	1.13	0	−0.1365	0	−0.075	0	−0.0589
CH_3OH	1.13	0	−0.1339	0	−0.073	0	−0.0573
$(CH_3)_2O$	1.13	0	−0.1325	0	−0.071	0	−0.0553
NH_3	1.14	0	−0.1756	0	−0.099	0	−0.0751
CH_3NH_2	1.14	0	−0.1697	0	−0.094	0	−0.0708
$(CH_3)_2NH$	1.14	0	−0.1633	0	−0.090	0	−0.0673
$(CH_3)N$	1.14	0	−0.1550	0	−0.085	0	−0.0633
HCl	1.69	60	−0.0282	55	−0.020	55	−0.0159
CH_3Cl	1.69	60	−0.0322	55	−0.023	50	−0.0183
H_2CO	1.16	45	−0.0940	10	−0.060	0	−0.0488

[a] Electrostatic potential minimum near the molecule. R, θ give the location of the minimum. [b] Optimum θ for $Li^+\cdots$base interaction and electrostatic potential at that location. [c] Optimum θ for the H-F···base interaction and electrostatic potential at 2.11 Å (4.0 au) for first-row bases and 2.91 Å (5.5 au) for second-row bases.

trimethylamine. With this geometry choice, our calculations predict that the Li^+ affinity peaks at *methylamine.* What we do feel is significant is the different methyl substituent effects for the different bases; this is also reflected in the experimental data, where Δ(LiA) for H_2O vs. dimethyl ether is greater than that for NH_3 vs. trimethylamine.

We should also note recent studies on Li^+ affinities of amines by Pullman and Brochen[22] using an STO-3G basis set. These authors found the order of Li^+ affinities to be $H_3N >$ MA > DMA > TMA. Our results using the experimental geometry for NH_3 and the tetrahedral geometry for the remaining amines are in the same order, but if we use the tetrahedral geometry for all (parentheses, Table VI), the order is MA > DMA > NH_3 > TMA. The differences between the Li^+ affinities of the different amines is only ~1 kcal/mol in these studies compared with a 6.6 kcal/mol difference found between NH_3 and trimethylamine using the minimal basis set. It appears that the relative Li^+ affinities calculated here are

Table V. Directionality of Component Analysis Energies (kcal/mol) for Protonation of a Number of Bases

Molecule	θ^a	Electrostatic[b]	Polarization[b]	Charge transfer[b]
H_3N	0	110.1	23.4	79.4
CH_3H_2N	0	106.4	34.0	82.2
$(CH_3)_2HN$	0	102.4	44.9	82.0
$(CH_3)_3N$	0	79.2	55.2	81.3
H_2O	0	85.6	27.3	50.5
H_2O	45	80.4	20.2	61.7
CH_3OH	0	84.0	34.9	56.1
CH_3OH	45	8.7	30.3	65.2
$(CH_3)_2O$	0	83.1	41.8	59.7
$(CH_3)_2O$	45	76.3	38.2	68.4
HF	0	41.9	23.1	33.7
HF	45	45.5	16.0	44.1
CH_3F	0	45.0	33.1	38.9
CH_3F	45	47.0	26.2	49.7
F-F	0	−27.8	49.3	32.2
F-F	45	−10.4	34.1	44.1
Cl-F	0	18.4	44.9	36.5
Cl-F	45	23.8	33.4	46.5
HCl	0	0.2	23.2	35.3
HCl	60	17.7	9.9	64.9
CH_3Cl	0	0.3	35.4	41.3
CH_3Cl	60	20.2	17.3	73.0
FCl	0	−50.6	27.8	29.0
FCl	60	−14.4	13.2	68.0

[a] See Figure 1 for definition of angle. [b] See Table III for definition of these quantities.

in somewhat better agreement with experiment,[4] but neither basis set does perfectly. In any case, both show a significant difference between H^+ and Li^+ affinities.

(b) Li^+ Affinities of Other Bases. The CH_3 effect on the C=O base is well reproduced by the theory, as is the fact that $N(Me)_2$ formamide has the highest Li^+ affinity of all the molecules studied by Staley and Beauchamp.[4,23] Since guanidine has such a high proton affinity, we calculated its Li^+ affinity and found it to be even greater than that of formamide.

(c) Li^+ Affinities. First- vs. Second-Row Bases. For the first-row bases, the ten comparisons between theory and experiment yield an average overestimate of the Li^+ affinity of 10.63 (mean square deviation = 0.54) kcal/mol. Much of the reason for the overestimate is clearly the overestimated dipole moments of the first row bases, which lead to too great an electrostatic energy. The one comparison for a second row base, CH_3Cl, predicts a too small (~4 kcal/mol) Li^+ affinity, despite the overestimated dipole moment (Table I) for this molecule. Thus, the error must be in either the polarization or charge transfer attractions (or both), which appear to be underestimated by this limited basis set.

(d) Directionality of Li^+ Affinity. Another intriguing difference between the first- and second-row bases is that the minimum energy for the $Li^+\cdots$ base complex occurs at $\theta = 58$ for B=Cl, whereas for $Li^+\cdots O$, N, or F interactions, $\theta = 0$ at the minimum energy geometry. This is clearly explicable from the electrostatic potential maps we have calculated as a function of R and θ for the N, O, F, and Cl bases. At $R(B-H^+)$ the minimum electrostatic potential occurs at $\theta \neq 0$ for B=F and B=Cl and this is consistent with the geometries of HF_2^+ and HCl_2^+. At $R = 1.74$ Å, the minimum electrostatic potential for HF and CH_3F occurs at $\theta = 0$ and this is where ($R = 1.74$, $\theta = 0$) the minimum in the $Li^+\cdots F$ potential surface occurs. At $R = 2.35$ Å, where the $Li^+\cdots Cl$ minimum occurs, the minimum in the electrostatic potential for HCl and CH_3Cl occurs at $\theta = 60$, near the θ minimum for the actual $Li^+\cdots Cl$ potential surface.

Table VI. Li^+ Affinities of Bases

Molecule	$R_{min}{}^a$	$\theta_{min}{}^b$	Calcd affinity, $-\Delta E$, kcal/mol	Exptl Li^+ affinity,[c] kcal/mol
NH_3	1.93	0	50.67 (49.40)[d]	39
CH_3H_2N	(1.93)	(0)	50.17	
$(CH_3)_2HN$	(1.93)	(0)	49.96	
$(CH_3)_3N$	(1.93)	(0)	49.16	41
H_2O	1.81	0	47.90	34
CH_3HO	(1.81)	(0)	49.61	38
$(CH_3)_2O$	(1.81)	(0)	49.99	39
HF	1.75	0	34.48	
CH_3F	(1.75)	(0)	39.31	31
HCl	2.41	58	17.68	
CH_3Cl	(2.41)	(58)	22.63	25
CH_2O	1.76	0	47.33	36
$CH(CH_3)O$	(1.76)	(0)	52.30	42
$C(CH_3)_2O$	(1.76)	(0)	56.22	45
$CH(NH_2)O$	(1.76)	(0)	59.78	51
Guanidine	(1.93)	(60)	66.72	

[a] Minimum energy $B\cdots Li^+$ distance. The values in parentheses were not energy optimized but taken from the corresponding unsubstituted compound. [b] Minimum energy angle (see **1**). Values in parentheses taken from corresponding unsubstituted compound. [c] Reference 4. [d] In parentheses is the Li^+ affinity of NH_3 with $\theta = 109.47°$.

HF and HNH_2 Affinities

We now consider basicities relative to H-bonding proton donors and use HF and HNH_2 as examples of H-bond proton donors. For the interactions of these two proton donors with the sp^3 F, N, O, and Cl bases, we searched the R, θ potential surface and the calculated energies of interaction are presented in Table VII.

(a) HF as Proton Donor. With HF, a "strong" H-bond proton donor, the order of the ΔE calculated is as expected, with Me substitution causing a larger increase in H-bond strength in those cases where all the interaction energy components (electrostatic *and* charge distribution) increase on Me substitution. Again in the case of the amines, the optimum base strength occurs at methylamine, since electrostatics are weighted correspondingly more for this "long range" interaction than for protonation. For HF and HCl, Me substitution causes the largest increase in H-bond energy.

We also examined H bonding to HF where R(F-B) was kept at 4 Å, and at this separation the interaction energies followed the order expected from the electrostatic energy term, with ammonia the best N: base, H_2O the better O: base, CH_3F the better F: base, and CH_3Cl the better Cl: base.

(b) HNH_2 as Proton Donor. We expected these same "long range" trends to be reflected when we used HNH_2 as the acid, since this molecule is a much weaker proton donor than HF. At $\theta = 0$, we found that the trends were actually very similar to those for HF and the charge redistribution effect at these distances ($R(B\cdots N) = 3.2$ Å for B=N, O, F) was still important enough to make Me amine a better base than NH_3. However, at the optimum θ, we found, much to our surprise, that the $CH_3F\cdots HNH_2$ H bond appeared to be weaker than that for $HF\cdots HNH_2$, despite the fact that all of the attractive energy components should favor CH_3F as a base. An even larger ΔE was found for H_2O vs. CH_3OH vs. $(CH_3)_2O$ as bases, with water now the strongest base, whereas the amines followed a similar order for H bonding to HNH_2 and HF.

What is the reason for this result? Remember that the energy components we considered (Table III) were based on a single point charge acid. If our acid now has a much more complicated charge distribution and structure, the simple

Table VII. H-Bond Potential Surfaces for sp^3 N, O, F, and Cl Bases

		B···HF				B···HNH_2			
Molecule	ES-H bond[a]	R^b	θ^c	ΔE^d	ΔE (R = 4 Å, θ = 0)[e]	R^b	θ^c	ΔE^d	ΔE (R, θ = 0)[f]
H_3N	−0.075	2.67	0	16.31	5.66	3.28	0	4.05	4.05
$(H_3N)^g$	−0.073	2.68	0	16.07	5.57	3.30	0	4.00	4.00
CH_3H_2N	−0.077	2.66	0	16.36	5.47	3.32	0	4.08	4.08
$(CH_3)_2HN$	−0.067	2.64	0	16.32	5.28	3.32	0	4.02	4.02
$(CH_3)_3N$	−0.063	2.65	0	15.99	5.04	3.32	0	3.77	3.77
H_2FN	−0.049	2.80	0	10.23					
H_2ClN	−0.056	2.73	0	12.63					
H_2O	−0.059	2.64	0	13.40	4.24	3.24	53	4.21	3.42
CH_3HO	−0.057	2.63	0	13.75	4.19	3.23	50	4.00	3.47
$(CH_3)_2O$	−0.055	2.63	0	14.06	4.11	3.23	44	3.81	3.47
HF	−0.036	2.69	42	7.88	2.57	3.22	78	3.56	2.36
CH_3F	−0.038	2.71	30	8.31	2.74	3.24	67	3.46	2.44
FF	−0.002	3.15	70	1.22					
ClF	−0.021	2.80	50	4.80					
HCl	−0.016	3.42	71	3.40	0.93	3.90	85	1.62	0.36
CH_3Cl	−0.018	3.40	70	4.20	1.17	3.80	82	1.92	0.68

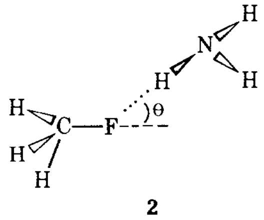
[a] Electrostatic potential at 2.12 Å (4.0 au) from first-row bases; 2.69 Å (5.5 au) for second-row bases. [b] Minimum energy R for H bond (**1**) (Å). [c] Minimum energy θ for H bond (**1**). [d] H-bond energy (kcal/mol) at optimum R, θ. [e] Interaction energy for base···HF interaction at R = 4 Å, θ = 0°. [f] Interaction energy for base···HNH_2 at optimum R, θ = 0. [g] NH_3 with θ = 109.47°.

Table VIII. Morokuma Component Analysis Energies for HF···HNH_2 and CH_3F···HNH_2[a] (kcal/mol)

	θ = 0	θ = 60	θ = 75	θ = 90
		HF···HNH_2		
ΔE(total)[b]	−2.34	−3.39	−3.53	−3.44
ΔE(electrostatic)[c]	−2.20	−2.89	−2.88	−2.65
ΔE(polarization)[d]	−0.14	−0.11	−0.08	−0.05
ΔE(charge transfer)[e]	−1.18	−1.81	−2.05	−2.28
ΔE(exchange)[f]	1.18	1.42	1.48	1.54
		CH_3F···HNH_2[g]		
ΔE(total)[b]	−2.44 (−2.44)	−3.42 (−3.49)	−3.42 (−3.62)	−2.94 (−3.12)
ΔE(electrostatic)[c]	−2.31 (−2.31)	−2.93 (−2.97)	−2.93 (−3.04)	−2.88 (−3.31)
ΔE(polarization)[d]	−0.18 (−0.18)	−0.15 (−0.15)	−0.12 (−0.13)	−0.11 (−0.14)
ΔE(charge transfer)[e]	−1.17 (−1.18)	−1.78 (−1.79)	−1.91 (−2.01)	−1.95 (−2.40)
ΔE(exchange)[f]	1.22 (1.23)	1.44 (1.42)	1.54 (1.56)	2.01 (2.73)

[a] See ref 12; R(N···F) = 3.22 Å in all cases. [b] Total SCF calculated interaction energy, which is the sum of the four contributions below. [c] Electrostatic interaction energy between fixed charge distributions of the two monomers. [d] Polarization energy — energy due to charge redistribution within the monomers, not allowing charge transfer from one monomer to another. [e] Charge transfer energy — energy due to allowing electron transfer between monomers; this energy also contains contributions from second-order exchange; see ref 24. [f] Pauli exchange repulsion between fragments. [g] Values in parentheses refer to conformation in which hydrogens are rotated 60° from their location in **2**; thus a C–H bond is in the same plane and cis to the approaching N–H bond.

considerations we have proposed might not hold true. If one compares the H-bonded structure of CH_3F···HNH_2 and



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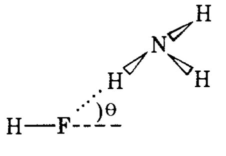

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HF···HNH_2 as θ increases, we see that there may be "repulsive" interactions between the N–H bond and the C–H bonds not present when H–F is the base. To attempt to determine the origin of these effects, we carried out a Morokuma component analysis[12] of the interaction energy for HF···HNH_2 and CH_3F···HNH_2 as a function of θ. These results are presented in Table VIII and indicate the following: (1) The electrostatic attraction for CH_3F···HNH_2 is greater than that for HF···HNH_2 at all angles, just as we would have expected on the basis of the electrostatic potential of HF and CH_3F monomers. (2) However, the exchange repulsion is larger for CH_3F···HNH_2 than HF···HNH_2 and at θ = 90° this difference is very large. (3) Part of the reason for the stronger HF···HNH_2 interaction than CH_3F···HNH_2 is the greater charge transfer" energy with HF as a base. In view of the relative orbital energies of HF and CH_3F (Table II) and the relative charge transfer contribution to proton affinities (Table III), this is surprising. However, one must realize that the "charge transfer" term we have used here really contains both charge transfer and second order exchange energies[24] and it may be the latter which are determining the smaller "attraction" of the charge transfer + second order exchange energy for CH_3F···HNH_2 than HF···HNH_2. (4) The minimum energy θ for these two examples is reasonably well predicted by the minimum in the electrostatic energy; in the case of the HF···HNH_2, charge transfer effects do increase the minimum energy θ from the 67° predicted by the electrostatic energy to 76°.

The greater repulsive effect for the methyl compound does not appear to be important in comparing HCl···HNH_2 and CH_3Cl···HNH_2, where the methyl protons are presumably too

Table IX. Interaction Energies for $CH_3F\cdots HNH_2$[a]

	N-H···H-C eclipsed	N-H···H-C staggered
Quantum mechanical[b] (qm)	−3.62	−3.44
CH_3F qm; HNH_2 point charge[c]	−3.90	−3.81
HNH_2 qm; CH_3F point charge[d]	−4.08	−3.98
Both point charge[e]	−5.78	−5.66

[a] $R = 3.19$, $\theta = 73°$; in kcal/mol. [b] Calculated as all the other potential surfaces in Table VII. [c] Calculated using the wave function for CH_3F in the presence of point charges representing HNH_2; $q_N = -1.6674$ and $q_H = 0.5558$ reproduces the 431G dipole moment. [d] Calculated using the wave function for HNH_2 in the presence of CH_3F point charges, taken from the Mulliken populations; $q_F = -0.456$, $q_C = -0.030$, $q_H = 0.162$. [e] Using point charges for both, chosen as in footnotes *c* and *d*.

Table X. H-Bond Potentials for Other Selected Bases with HF as the Proton Donor

Molecule	ES–H bond[a]	R, Å[b]	θ,[c] deg	$-\Delta E$,[d] kcal/mol
H_2CO	−0.049	2.73	40	10.00
CH_3HCO	−0.052	(2.73)	40	11.02
$(CH_3)_2CO$	−0.057	(2.73)	40	12.11
NH_2HCO	−0.060	(2.73)	40	12.96
C_2H_4	−0.026	3.3		4.90
$F\text{-}C_2H_3$	−0.012	(3.3)		2.70
$CN\text{-}C_2H_3$	+0.001	(3.3)		1.17
$CH_3C_2H_3$	−0.019	(3.3)		4.00
Guanidine	−0.082	(2.65)	(60)	21.86
HCN	−0.050	2.90	0	8.90
CH_3CN	−0.057	(2.90)	(0)	10.46
H_2	−0.001	3.4		0.28

[a] Electrostatic potential at 4 au from the base. [b] Minimum energy R (see **1**); values in parentheses not optimized. [c] Minimum energy θ (see **1**); values in parentheses not optimized. [d] H-bond energy for base in HF.

far away from the N–H proton. It also does not appear crucial when we consider HOH as acid, since we find that CH_3F is a better base than HF toward this acid. For $HF\cdots HOH$, the optimum interaction geometry is $R = 2.94$, $\theta = 60°$ with $\Delta E = 5.42$ kcal/mol; for $CH_3F\cdots HOH$, $R = 2.92$, $\theta = 55°$ with $\Delta E = 5.63$ kcal/mol. However, just as for $R\text{-}F\cdots HNH_2$, the difference in the ΔE (0.21 kcal/mol) at the optimum θ is less than this quantity at $\theta = 0$ (0.29 kcal/mol).

In **2** and in our search up to now of the $CH_3F\cdots HNH_2$ surface we show the methyl hydrogens staggered with respect to the approaching N–H bond; we thus rotated the hydrogens by 60° and optimized the R, θ surface for this methyl fluoride conformation. We found $R = 3.19$ Å, $\theta = 73$ at the minimum, with $-\Delta E$(H bond) = 3.63 kcal/mol, 0.17 kcal/mol stronger than the $HF\cdots HNH_2$ H-bond energy.

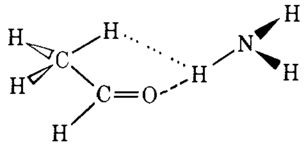
We used the Morokuma component analysis on this $CH_3F\cdots HNH_2$ interaction and the results are given in parentheses in Table VIII. As one can see, much of the reason for the lower energy for this $CH_3F\cdots HNH_2$ interaction ($\phi = 60°$) is due to electrostatic effects, although more charge transfer (or less second-order exchange) also contributes significantly.

To further examine the origin of this energy difference we compared the energies calculated quantum mechanically with those calculated using "partial" electrostatic and completely electrostatic models. These results are given in Table IX and show clearly that the lower energy of the N–H···H–C eclipsed structure is qualitatively explicable at the electrostatic level. In fact, with the completely classical simple point charge calculations, one can break down the interaction energy into atom–atom interactions and it is the weak C–H···N attraction in the "eclipsed" conformation which makes this conformation the more stable.[25]

In CH_3Cl, the 60° methyl rotation from the conformation in **2** increases the basicity of CH_3Cl toward HNH_2 by 0.08 kcal/mol.

(c) **HF as Proton Donor to Other Bases.** We also examined a few other bases, using HF as our reference acid, this time optimizing R and θ only for the parent compound and using this geometry for the substituted compound (Table X). As one might expect substituent effects on the H bonding of an sp hybridized N base (HCN), sp^2 hybridized O base (H_2CO) and a π base (ethylene) follow the order expected from the electrostatic potential. In addition, H bonding of HF to H_2 and guanidine follows the trends expected from the electrostatic potential, providing further confirmation of its usefulness in predicting H-bond energies.

(d) **HNH_2 H Bonding to H_2CO and CH_3HCO.** We studied H bonding of HNH_2 to H_2CO and CH_3HCO to see if the same strange reversal of H-bonding strength we observed in comparing $HF\cdots HNH_2$ and $CH_3P\cdots HNH_2$ would occur in this case. The minimum energy geometry for $H_2CO\cdots HNH_2$ was $R = 3.28$ Å and $\theta = 75°$, with $\Delta E = -3.62$ kcal/mol. For $CH_3CHO\cdots HNH_2$ at this geometry, $\Delta E = -3.80$ kcal/mol with the CH_3 trans to the HNH_2 and $\Delta E = -4.13$ kcal/mol with the CH_3 cis. Not only was H bonding stronger in acetaldehyde, but the most stable orientation of the methyl group was cis to the HNH_2. The geometry of this complex is such (with an extra atom separating the Me group from the base) that one might postulate a weak C–H···N attraction in this conformation, just as we have seen in $CH_3F\cdots HNH_2$.



Discussion

These studies indicate that even for simple, *gas phase* interactions, the order of basicity of various compounds varies significantly, depending on the nature of the acid. At very long distances (R(B–A) ~ 4 Å) the order of basicities follows the order of the electrostatic energy (potential). One must emphasize that this electrostatic energy is not just a dipole–dipole energy; for example, NH_3 has a greater H^+ and HF affinity than H_2O despite its smaller dipole moment. The reason for this is that a simple dipole–dipole model is too crude near the minimum energy acid–base distance (even at R(A···B) = 4 Å). As the acid approaches the base, polarization and charge transfer effects come into play and are weighted progressively more importantly in determining the overall interaction energy. Even for the weakest acid studied, HNH_2, charge redistribution effects are clearly important and make, for example, methylamine a stronger base than ammonia toward HNH_2.

(a) **The Methyl Substituent Effect. Possible Explanations.** The methyl substituent effect is found to be significantly different, depending on the base studied, due to its differing influence on the electrostatic and charge transfer energies on N, O, F, and Cl bases. These differences in energy components allow one to rationalize the difference ΔE(H–B vs. CH_3–B) of N, O, F, and Cl bases when the acid is H^+, Li^+, or H–F.

It is worth examining possible "explanations" for this interesting methyl substituent effect. The Mulliken populations for the monomers in Table II show that for B=N, O, F, Cl the base loses electrons upon methyl substitution, although B=F

Table XI. Number of Valence Electrons in Outer Valence Orbitals of Basic Atoms (F, O, N, or Cl)

Molecule	No. of electrons[a]	Molecule	No. of electrons[a]
HF	3.374	MA	2.798
CH_3F	3.404	DMA	2.733
H_2O	3.175	TMA	2.700
MeOH	3.130	HCl	3.981
DME	3.118	CH_3Cl	3.784
NH_3	2.874		

[a] Mulliken population in outer valence region of bases. With this 431G basis, this is the sum of the electrons in the outer 2s, 2px, 2py, and 2pz orbitals, each of which are represented by a single Gaussian function. For HCl and CH_3Cl, sum of electrons in 3s and 3p orbitals.

loses less than B=O and B=N. Thus, total Mulliken populations on the base appear not to be able to rationalize the better basicity of CH_3F than HF. However, when one examines the Mulliken populations in the *outer* valence orbital, as noted in Table XI, the basicity trend is correctly reproduced for B=F, O, and N, the former gaining electrons in the outermost orbitals, the latter two losing them. However, for B=Cl, charge is actually lost in these outer orbitals upon methyl substitution.

We thus compared the electron density in HCl and methyl chloride in the lone pair region from $R = 1$-5 au, $\theta = -90$ to 90. Throughout *most* of this lone pair region, there is more charge density in MeCl than HCl. Thus, the Mulliken populations may reflect charge density differences elsewhere in the molecule (e.g., at the Cl nucleus, where the charge density is significantly greater in HCl than CH_3Cl). However, the electrostatic potential is more negative for CH_3Cl than HCl *throughout* the lone pair regions (including *at* the Cl nucleus).

It should be noted that Hehre et al.[26] found that a minimal basis set incorrectly predicts MeF to have a smaller dipole moment than HF; this is quite explicable in terms of our Mulliken population results. Methyl substitution *polarizes* the fluorine and the atom loses net charge, but more charge ends up in the outermost valence region, thus interacting more strongly with approaching acids. A minimal basis is not sufficiently flexible to allow this polarization. For B=Cl, one can only speculate that the polarity of the methyl group may contribute to make the electrostatic potential near CH_3Cl greater than that of HCl. In methyl chloride, the carbon has a net charge of −0.58 and the hydrogens +0.21; in methylamine, the carbon charge is −0.26 and the hydrogens +0.15; in methanol, the carbon charge is −0.14 and the hydrogens +0.16; and in methyl fluoride, the carbon charge is −0.03 and the hydrogens +0.16. Thus, there may be an important contribution of the methyl groups $C^{\delta-}$-$H^{\delta+}$ dipole to the electrostatic portion of the Cl basicity.

A second criterion for greater basicity could be the 1s orbital energy,[7,8,27] which should be less tightly bound the more "basic" the atom on which it resides. With the exception of $(CH_3)_2O$ vs. CH_3OH, the change in the 1s orbital energies does indeed parallel the electrostatic potential and thus is a reasonably good criterion for predicting the electrostatic portion of "basicity".

We also examined the methyl substituent effect in a qualitative manner following the approach of Libit and Hoffmann.[28] These authors concluded that one of the main effects of a methyl substituent replacing hydrogen when attached to a π system was a polarization of the π cloud and transfer of electrons from the $\pi \rightarrow \pi^*$ polyene orbitals. The highest occupied orbital energies of HF, H_2O, NH_3, and HCl are in Table II; the LEMO orbital energies are 0.215 (HF), 0.209 (H_2O), 0.223 (NH_3), and 0.169 (HCl) (all in atomic units).

If one uses the HOMO ($\epsilon = -0.542$ au) and LEMO ($\epsilon = 0.256$ au) of methane to represent the "methyl" orbitals and considers the orbital energy gaps Δ_1 = LEMO(HB) − HOMO(CH_4) and Δ_2 = LEMO(CH_4) − HOMO(HB), one finds for B=F, $\Delta_1 = 0.757$ and $\Delta_2 = 0.884$ au; for B=Cl, $\Delta_1 = 0.711$ and $\Delta_2 = 0.725$; for B=O, $\Delta_1 = 0.751$ and $\Delta_2 = 0.755$; and for B=N, $\Delta_1 = 0.765$ and $\Delta_2 = 0.670$. Δ_1 should qualitatively represent the energy required for charge transfer from the methyl group to the base and Δ_2 the energy required for the charge transfer from the base to the methyl group. Interestingly, this simple picture "predicts" more $CH_3 \rightarrow B$ charge transfer for B=F, about equal charge transfer $CH_3 \rightarrow B$ and $B \rightarrow CH_3$ for B=O and Cl, and $B \rightarrow CH_3$ charge transfer for B=N. When one actually compares the HOMO for the CH_3B substituted compounds and HB (Table II), it is clear that the F orbital is much more strongly perturbed by the methyl group than are the others and the N is perturbed least.

In any case, the simple picture that emerges is as follows: A methyl group causes net electron migration to the π^* diffuse orbitals of F, whereas charge flows the other way for O and N bases. Second-row (Cl) bases are made better electrostatic bases by CH_3 substitution, but this difference is not obvious from just examining the Mulliken populations and one is required to compare the charge densities and electrostatic potentials in the lone pair of HCl and CH_3Cl in order to observe this.

The methyl substitution effect on C=O and C≡N groups follows the order expected on the basis of charge distribution effects given by Pople et al.[29] where a methyl group polarizes the carbonyl group $C^{\delta+}$-$O^{\delta-}$ and the cyano group $C^{\delta+}$-$N^{\delta-}$ relative to a hydrogen substituent. The presence of the carbon atom between the CH_3 group and the heteroatom as well as the alternating inductive effect make a methyl group increase the short and long range basicity of C=O and C≡N groups but decrease the long range basicity of N and O groups.

These calculations predict that for amines the Li^+ and H-F affinities should peak at methyl- or dimethylamine. It will be of great interest to see if this prediction is correct. Differential solvent effects cause aqueous pK_a's to follow a different order than gas phase proton affinities, but the physical basis of the effect found here is the differential weighting of electrostatic vs. charge redistribution effects in proton affinities and Li^+ or HF affinities.

For most crude trends, the electrostatic potential (energy) gives good insight into the relative basicities and allows one to predict them correctly. For the simple molecules studied there, the change in (Table II) dipole moment upon methyl substitution parallels the change in the electrostatic potential; thus, we expect that variously methylated phosphines, sulfides, bromides, and iodides will be stronger bases than the corresponding H-B compound, *whatever* the acid, since the experimental dipole moments of the methylated compounds are larger. Experimental proton affinities[3] are consistent with the greater basicities of the methylated compounds toward H^+. We can use our results for the Cl bases and the experimental dipole moments to rationalize the fact that the increase in proton affinity is greatest upon single methyl substitution ($PH_3 \rightarrow CH_3PH_2$ ($\Delta\mu = 0.52$ D) and $H_2S \rightarrow CH_3SH$ ($\Delta\mu = 0.55$ D)) and becomes smaller upon further addition of methyl groups. ($\Delta\mu((CH_3)PH_2 \rightarrow (CH_3)_2PH) = 0.13$ D, $\Delta\mu((CH_3)_2PH \rightarrow (CH_3)_3P) = -0.04$ D, and $\Delta\mu((CH_3)SH \rightarrow (CH_3)_2S) = 0.02$ D.) Each addition of a methyl group increases the polarization and charge transfer energy, but as one can see from the dipole moments only the first methyl group causes a significant increase in the electrostatic energy.

For all bases, we expect the predicted order of basicity to more closely follow the electrostatic potential the weaker the acid. Guanidine has been found to be by far the strongest

Table XII. Morokuma Component Analysis Energies of $Li^+\cdots$Base Interactions (kcal/mol)

	NH_3, R = 1.76 Å	NH_3, R = 1.96 Å	TMA, R = 1.76 Å	Formamide, R = 1.76 Å
ΔE(total)[a]	−46.09	−50.67	−45.31	−59.78
ΔE(electrostatic)[a]	−72.01	−56.86	−62.72	−52.41
ΔE(polarization)[a]	−10.57	−7.04	−22.97	−17.46
ΔE(charge transfer)[a]	1.45	−1.88	5.36	−1.30
ΔE(exchange)[a]	35.05	15.11	35.02	11.39

[a] See Table VIII for definitions.

neutral base toward all the acids; this prediction will be of interest to test experimentally.

These results allow one to understand recent calculations by Lucchese and Schaeffer,[30] who found trimethylamine a weaker base than ammonia toward weak electrophiles; at the minimum energy distances between acid and base they predict one should expect the electrostatic energy to dominate. Johansson et al.[31] pointed out the difference between their calculated CH_3 and NH_2 substituent effects on proton affinities (these groups increased proton affinities relative to the hydride substituted compounds) and calculations by Del Bene,[32] who found that CH_3 and NH_2 decrease *H-bond* affinity of N: and O: bases. Again, we see this as a consequence of the greater role of charge redistribution effects (polarization and charge transfer) in determining relative proton affinities and the greater weighting of the electrostatic energies in H bonds; Del Bene's H-bond affinities did follow the order of the partial negative charge on the base. Radom[33] also found that alkyl substitution increased basicity (toward a proton) in ROH, RNH_2, and RCCH, with the larger alkyl groups having a larger substituent effect.

When this study had been completed, we learned of a similar component analysis study of proton affinities for amine and ether bases by Umeyama and Morokuma.[34] Although these authors carried out a more extensive search (R(B–H^+)) than employed here and evaluated the energy components at different geometries, the qualitative interpretation of the energy components was the same as here, lending further support to our choice of R(B–H^+) = 1.16 Å as a reasonable reference point for our component analysis. They make an additional very instructive comment when they point out the difference between H^+ and BH_3 as Lewis acids toward the amines,[35,36] with exchange repulsion playing an important role in the latter case.

(b) The Uniqueness of the Hydrogen Bond. The comparison of the proton affinity, Li^+ affinity, and H–F affinity of formamide and trimethylamine is relevant to the role that exchange repulsion may play in determining the order of some basicities. As Table III indicates, all three attractive energy components for proton affinity are greater for trimethylamine than for formamide, and TMA does, indeed, have a greater proton affinity than formamide. It also has a greater H–F affinity, as one can see from Tables VII and X. However, formamide has a greater Li^+ affinity. Since we have experimental data for the Li^+ and H^+ affinities, we have additional confidence that these calculated trends are "real". We thus compared formamide$\cdots H^+$ and trimethylamine$\cdots H^+$ at the optimum formamide–Li^+ distance and found that at this distance the *proton* affinity of the amine (154.3 kcal/mol) was greater than formamide (89.0). In fact, the proton affinity of TMA at 1.96 Å is greater (130 kcal/mol) than the proton affinity of formamide at 1.76 Å. We thus carried out Morokuma component analysis calculations on Li^+ interactions of NH_3, trimethylamine, and formamide and these results are presented in Table XII. It is clear from these results that the exchange terms are crucial in making the amine$\cdots Li^+$ interaction weaker than the amide (C=O$\cdots Li^+$) interaction, since the sum of the attractive terms (electrostatic, polarization, and charge transfer) is significantly greater for an amine. The greater magnitude of the exchange repulsion in the amine can also be indirectly inferred by comparing the minimum energy R(B$\cdots Li^+$) and R(B$\cdots$H–A) distances. The amine has the shorter R(B$\cdots$H–A) but the longer R(B$\cdots Li^+$). Coulson[37] originally pointed out that the uniqueness of a hydrogen bond may be the relatively small magnitude of the exchange repulsion and we have an interesting example here where this appears to be playing a crucial role in making Li^+ affinities very different from H^+ or H–F affinities of different bases. The origin of such an effect can be inferred from the nature of the atoms themselves. The charge cloud of the N atom is more diffuse than O; this leads to a greater electrostatic attraction for acids approaching N than O. However, this more diffuse electron cloud will have a greater exchange repulsion with the electrons on the acid for N than O bases. This exchange repulsion is nonexistent for H^+ as acid, small for H–F and other H-bond donors as acids, but probably of importance for other Lewis acids, for example, Li^+ and BH_3.

It is not a typographical error that the charge transfer energy for $NH_3\cdots Li^+$ and TMA$\cdots Li^+$ is *repulsive* at 1.76 Å; in this case it appears that second-order exchange terms[24] are larger than conventional charge transfer effects.

(c) Limitations of This Theoretical Study. We have used a rather limited basis set in this study; one needs to approach closer to the Hartree–Fock limit to reproduce the experimental interaction energies quantitatively. However, more accurate studies on the proton affinity of H_2O[38] and Li^+ affinity of H_2O and NH_3[39] indicate that correlation effects probably play a minor role in most polar acid–base interactions. Thus, we feel a single determinant model is adequate for such studies as reported here.

The major source of error in this study is that a double-ζ basis, such as that employed here, consistently overestimates polarity, as a comparison of the calculated and experimental dipole moments in Table II shows. This leads to a prediction that H_3O^+ is planar, rather than pyramidal,[20] and that θ for $H_2O\cdots HF$ is 0°, rather than 40°;[40] more extended basis sets are required to more quantitatively represent specific intermolecular geometries and interaction energies. We hope, however, that trends and comparisons of the interaction energies and geometries for closely related bases are correctly represented; the extensive comparison we have made with experimental proton affinities and Li^+ affinities show this to be a reasonable hope.

For both Li^+ affinities and proton affinities, this basis set overestimates these quantities for first-row bases N, O, F and underestimates them for the second row (Cl). Since polarities (and thus the electrostatic energies) are overestimated for both first- and second-row bases, this implies that charge redistribution effects (polarization and charge transfer) must play a much greater role in contributing to the proton and Li^+ affinities of Cl bases than for O, N, and F bases. It is clear that double-ζ basis sets do a poor job in reproducing the static polarizability (α) of small molecules[39] and that extended basis sets are required to represent this property; it is also probable that the 431-G basis set for Cl containing bases is relatively poorer in describing its polarizability than this basis set for O, N, and F bases. In any case, our purpose here has not been to reproduce the absolute values of these properties but to look at differences in substituent effects (e.g., HCl vs. CH_3Cl basicity); based on the comparisons with experimental proton and Li^+ affinities, this basis set appears to be sufficiently accurate for that purpose.

The use of nonoptimized geometries for monomers is expected to cause us to overestimate interaction energies.[40,41] We do feel our "fixed geometry" model is probably adequate to analyze trends; however, in cases where the energy differences are very small (e.g., Li^+ affinities of amines), or when the geometrical reorganization is large (e.g., protonation of propylene), one must view the results with caution.

Conclusions

The most interesting points that have emerged from this study, are: (1) The electrostatic potential is a very good first approximation to predicting the relative H^+, HF···, and Li^+ affinity of molecules for anions, lone pairs, and π and σ bonds functioning as the basic sites. Unsaturated species have much larger proton affinities than expected on the basis of electrostatic considerations. (2) The methyl substituent effect is very dependent on the atom to which it is attached; for example, we have made explicable why the difference in proton affinity of CH_3F and HF is so much greater than the difference in the proton affinity of CH_3NH_2 and NH_3. (3) Methyl-substituted amines are an interesting case where electrostatic energies decrease and charge distribution effects increase on methyl substitution. Thus, we predict that the optimum base in the series NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ toward the acids Li^+, HF, and HNH_2 will be CH_3NH_2 or $(CH_3)_2NH$. This is in contrast to proton affinities, where the charge redistribution energies are sufficiently large to overcome the decrease in the electrostatic energy upon successive methylation. (4) A comparison of $HF\cdots HNH_2$ and $CH_3F\cdots HNH_2$ H-bonded surfaces is instructive because it shows how interactions between atoms not directly involved in the B···H–A hydrogen bond can crucially affect the geometry and relative energies of intermolecular surfaces. This has been noted before.[42] (5) Finally, and probably most importantly, there is a crucial difference between the order of basicities for H^+ and HF and for Li^+. The fact that amines are stronger bases than amides toward H^+ and HF, but weaker bases toward Li^+, is interpreted as being due to the crucial role of the exchange repulsion in determining Li^+ affinities. This suggests that the uniqueness of the H bond compared to the Li bond is due to the smallness of the exchange repulsion in the H bond.

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