

independent of whether they are formed by molecular ionization or isomerization from **a**. Thus such data would result if the metastable **a** and **c** ions are formed with substantially different distributions of internal energy values (which will not necessarily affect appreciably the kinetic energy released in metastable decomposition).²² The low proportion of **a** ions formed with the low energy required for complete scrambling could be due to a low-energy dissociation of the molecular ion which competes with formation of such **a** ions. In support of this, Wesdemiotis¹⁵ has recently shown that metastable **a** ions prepared from different precursors show substantial variations in their extent of scrambling. At ion lifetimes giving 95% scrambling of **c** from CD₃COOCH₃, **a** ions from (CH₃)₂CHCH₂CH₂COOCD₃ show 81% scrambling, while **a** ions from DOCH₂CH₂COOCH₃ show 72% scrambling.

Conclusion

The potential energy surface involving ions **a**, **b**, and **c** is unique in that the energy barriers for the [1,4]-H isomerizations **a** \rightleftharpoons **b** and **b** \rightleftharpoons **c** are nearly the same as the barrier for the major dissociation pathway **c** \rightarrow CH₃CO⁺. However, the reasons for this behavior appear to be generally applicable to other tautomeric systems. Enolic ions are generally more stable than their ketonic isomers, both in terms of the lower heat-of-formation values of enols⁶ and the more facile α -cleavage dissociation of keto isomers.^{2-5,8} The latter will thus also provide a favored dissociation channel for an enol if isomerization to its keto isomer is facile. The [1,4]-H shift provides such a path here, while the symmetry-forbidden [1,3]-H shift has a much higher activation energy.^{5,8,21,23} For these C₃H₆O₂⁺ ions the [1,2]-H shift¹⁴ is also much

less facile than the [1,4]-H shift, although it is favored over the [1,3]-H isomerization in specific cases²³ such as eq 4.⁸ There is no evidence for concerted hydrogen exchange such as isomerization through the bicyclic transition state **d**.¹¹

Experimental Section

Mass spectra were recorded on AEI-MS-902 and reversed-geometry Hitachi RMU-7²⁴ mass spectrometers, both operated at 8-kV ion acceleration, 70-eV electron energy, and source temperatures of 120-150 °C unless indicated otherwise. Samples were admitted through all-glass heated inlet systems. For the MS-902, fragmentation reactions occurring in the first drift region (between the source and electrostatic sector) were observed by scanning the accelerating voltage at constant electrostatic sector voltage using a β (energy-defining) slit width of 0.008 in. The kinetic energy releases reported were obtained from the width at half-height after correction for the main beam width. Fragmentation reactions occurring in the second drift region were evaluated from the metastable peaks in the normal mass spectra. CA spectra, obtained as described previously,^{24,25} were the averages of several multiscan runs on the RMU-7.

Methyl hexanoate-2,2-*d*₂ and methyl-*d*₃ acetate were obtained from Merck, Sharp, and Dohme, Montreal, while methyl-*d*₃ pentanoate was prepared by esterification of pentanoic acid with methyl-*d*₃ alcohol.

Acknowledgment. The authors are indebted to the National Research Council of Canada and the National Institutes of Health (Grant GM16609) for financial support, to Dr. C. Wesdemiotis for key recent experiments, to Professor J. L. Holmes for communication of results prior to publication, and to Professor H. Schwarz for helpful correspondence.

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The Isolated Molecule Approach. Theoretical Studies of the Inductive Effect

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Abstract: The proton affinities of a variety of ω -substituted alkylamines, determined by ab initio molecular calculations, have been shown to be in rough accord with the operation of an electrostatic field effect. Calculations using isolated molecules, one having the probe attached and one the substituent, are in excellent agreement with such a field effect and indicate that any through-bond inductive transmission is insignificant in the systems investigated. The isolated molecule approach is used to estimate the magnitude of the direct field effect in the proton affinities of substituted amines.

There is continued interest¹⁻⁵ in the mechanism of transmission of polar effects in σ -bonded systems. The two major mechanisms that have been considered^{2,6} are the field effect, a direct through space electrostatic interaction, and the σ -inductive effect, a progressive but diminishing relay of polar effects along a chain of

carbon atoms. Although field effects appear to predominate in many examples,^{2,3,6,7} there is evidence^{1,3} for an additional transmission mode, particularly over short distances.

One of the major problems in experimental investigations of the transmission of polar effects is to obtain a sufficient variety of systems of fixed geometry. Great ingenuity and effort have been put into the synthesis of model compounds,^{6,7} but the flexibility of many molecules and the difficulty of obtaining a reasonable range of substituents in others have provided severe limitations.

By contrast, theoretical calculations can be made for many different geometries by using fixed conformations of aliphatic

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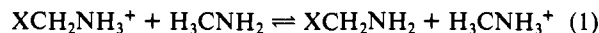
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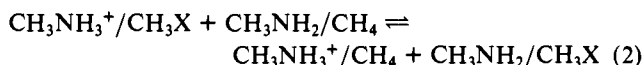
molecules. Recent results have shown that ab initio molecular orbital calculations at the STO-3G level give relative energies in good agreement⁸ with experimental gas-phase results for a variety of proton-transfer equilibria. Thus, for example, the experimental gas-phase energies of isodesmic proton-transfer equilibria 1 of



substituted methylamines are well reproduced⁹ by STO-3G ab initio calculations. Other examples include substituted quinuclidinium,¹⁰ pyridinium,¹¹ and anilinium¹¹ ions and substituted phenols.¹² Such ab initio calculations have also been extended^{8c,11,12,13} to the measurement of substituent interaction energies in the neutral and in the charged forms in these equilibria; within a series, the proton affinity is usually found to result mainly from substituent effects in the charged form in accord with concepts of substituent effects. Theoretical calculations have also been used^{13,14} to investigate the relationship between substituent effects on energy and on charge in proton transfer equilibria. It has been shown,¹⁴ for example, that a linear relationship exists between the relative proton affinities for reaction 1 and the charge on the acidic hydrogens of the methylammonium ions.

Overall the ab initio results above give confidence that similar calculations on various conformations of ω -substituted alkyl derivatives should give meaningful results even though experimental comparison may not be possible. We chose to study the proton affinities of alkylamines because of the close agreement found between experiment and calculation for many such examples. We have used fluorine as a substituent in most of the work because of its significant polar effect and its geometric simplicity. The ω -substituted alkylamines such as structures 2–10 below provide a variety of geometries for the substituent relative to the probe.

Unfortunately, a systematic study of the dependence of inductive effects on geometry is still not possible as the number of structures is limited, and it is not possible to readily separate direct field effects from transmissions either through the carbon framework (the σ -inductive effect) or via polarization of intervening carbon-hydrogen bonds. The use of isolated molecule calculations should provide both a direct measure of the transmission through space and also allow a thorough study of the geometry dependence of such field effects. In these calculations the probe, an amino group, is located on one methyl group and the substituent on a second isolated methyl group. The relevant isodesmic process that describes the relative proton affinity is (2), where the relative



geometry of each pair is constant for each separate calculation of proton affinity. Only limited use has been made of isolated molecule calculations to date. They have been used to examine the through-space electronic effects in para-substituted styrenes³ by examining methyl derivatives and ethylene molecule pairs taken at the same geometry, and similar calculations have been made for benzoic acids.¹⁵ Other examples are in investigations of proximity and electric field effects on carbon-13 chemical shifts¹⁶ and of effects in 1,2-diaminoethanes.¹⁷ A preliminary report of

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Table I. Ab Initio Molecular Orbital (STO-3G) Calculated Proton Affinities for ω -Fluoroalkylamines^a

structure	ΔE°	r	θ	$\cos \theta / r^2$	$\Delta E^\circ r^2 / \cos \theta$
2	-6.13	2.85	329.3	0.106	57.8
6	-4.37	3.83	355.3	0.068	64.3
4	-3.76	4.11	40.1	0.045	83.6
9	-3.54	4.50	0	0.049	72.2
3	-3.02	2.26	85.2		
7	-2.60	5.37	328.3	0.030	86.7
10	-1.78	6.71	347.5	0.022	80.9
5	-1.59	3.64	276.4		
8	-0.73	4.49	93.9		

^a See text for structures and description of r and θ . ΔE° is in kcal mol⁻¹ relative to parent alkylamine, r in Å, and θ in deg.

Table II. Ab Initio Molecular Orbital (STO-3G) Calculations on the Proton Affinities of Methylamine in the Presence of a Methyl Fluoride Moleculeⁱ

r	β	θ	$-\Delta E^\circ$	cations	
				$\Delta q(\text{H})^a$	$\Delta q(\text{H})^b$
10.44 ^c	0	0	0.65	1.3	1.3
7.44 ^c	0	0	1.27	3.1	3.1
6.44 ^c	0	0	1.70	5.0	5.0
5.44 ^c	0	0	2.39	8.7	8.7
4.74 ^d	0	0	3.31	14.2	14.2
4.50 ^{c,e}	0	0	3.70	17.3	17.3
4.20 ^c	0	0	4.44	23.6	23.6
3.94 ^c	0	0	5.39	32.9	32.9
3.94 ^d	0	0	5.83	36.8	36.8
3.74 ^d	0	0	7.36	51.0	51.0
5.44	0	45	1.76	2.8	7.3
5.44	0	60	1.34	0.7	6.3
5.44	0	75	0.79	-1.6	4.7
5.44	0	90	0.19	-3.9	3.0
5.44	0	180	2.38	-4.2	-4.3
5.44	0	270	0.00	5.5	-1.7
5.44	90	0	2.11	9.9	-5.4
5.44	180	0	2.38	-4.2	-4.3
5.44	270	0	2.66	-18.6	7.0
5.44	340.6	0	2.42	5.4	9.2
4.99 ^f	47.8	266.1	0.22	-1.0	8.8
5.37 ^g	31.7	31.7	1.97	9.8	1.9
6.71 ^h	12.5	12.5	1.50	5.2	3.3

^a H in plane of NC, CF skeleton. ^b Two H's out of plane of NC, CF skeleton. ^c Eclipsed form. ^d Staggered form. ^e Model for structure 9. ^f Model for structure 8. ^g Model for structure 7. ^h Model for structure 10. ⁱ ΔE° is in kcal mol⁻¹, Δq in 10⁻⁴ electrons, β and θ in deg, and r in Å. For a description of β , θ , and r see text.

some of the present work has also appeared.¹⁸

Calculations

All calculations were made at the ab initio molecular orbital STO-3G level¹⁹ by using the Gaussian 70 series of programs.²⁰ Standard geometries²¹ were used with nitrogen, all carbon atoms and the first atom of the substituted being held coplanar. The center of charge in the methylammonium ion was determined from a Mulliken²² population analysis. It is located 0.20 Å from the nitrogen atom on the line connecting it to the carbon atom. This center of charge was used as the origin in determining the distances (r) to the substituent; in the case of fluorine the distance was taken

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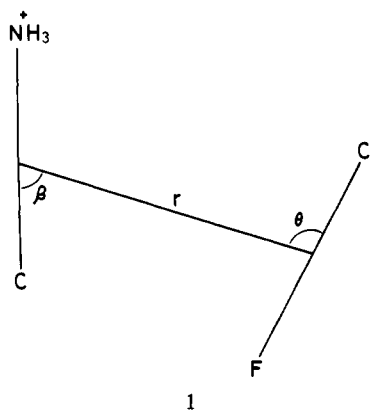
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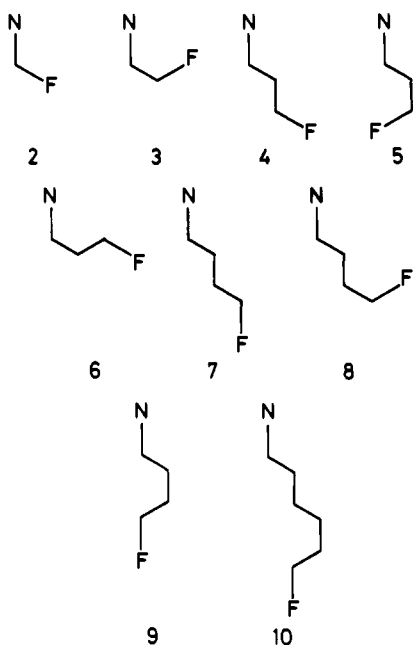
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to the midpoint of the CF bond as shown in 1 below.



Results and Discussion

The calculated relative proton affinities for a variety of planar structures (2-9) of β -fluoroethylamine, γ -fluoropropylamine, δ -fluorobutylamine, and one fluoroethylamine (10) are given in Table I.

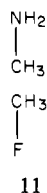


It can be seen that the relative proton affinities are in approximate agreement with the simple electrostatic theory which gives eq 3. Values of $\Delta E^\circ r^2 / \cos \theta$ are also listed in Table I, except

$$\Delta E^\circ \propto \mu \cos \theta / r^2 \quad (3)$$

for structures 3, 5, and 8, where the CF bond is close to perpendicular to the line to the center of charge and hence $\cos \theta$ is small and very sensitive to changes in θ . The values are almost constant for the smaller values of $\cos \theta / r^2$ and apparently decrease somewhat for larger values. There is no evidence for any σ -inductive effect which would be expected to lead to the opposite effect since in the structures with two or three carbon atoms $\cos \theta / r^2$ is generally greater than for the butylamines.

Isolated Molecule Calculations. Results are given in Table II. The first series ($\beta = 0^\circ$, $\theta = 0^\circ$) refers to systems where NC and CF bonds are collinear as in 11. Almost identical ΔE° values



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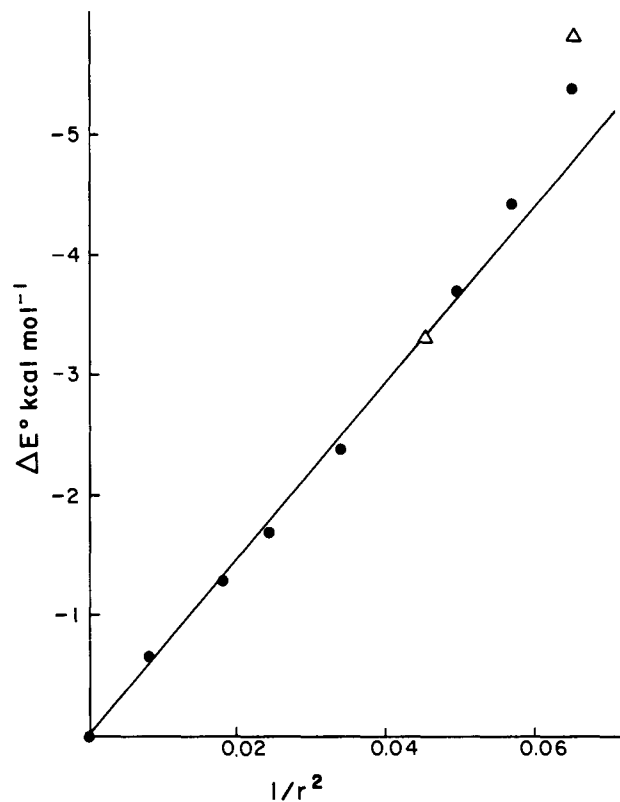


Figure 1. Plot of the calculated proton affinities, ΔE° , of $\text{NH}_2\text{CH}_3/\text{CH}_3\text{F}$ pairs vs. $1/r^2$ ($\theta = 0^\circ$). (Methyl groups: eclipsed, ●; staggered, Δ.)

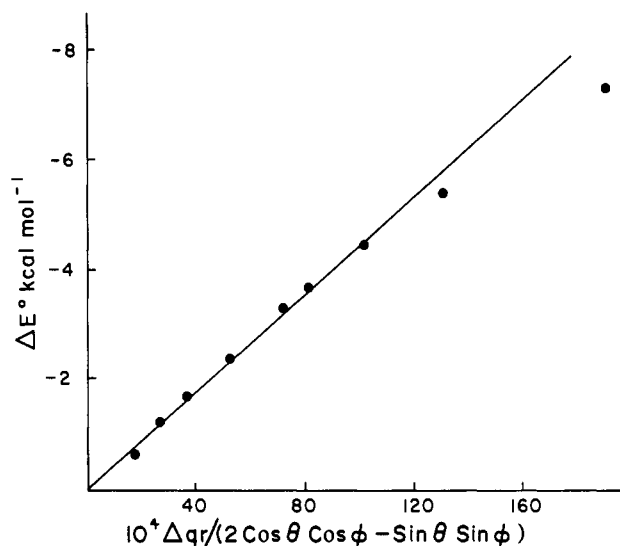


Figure 2. Plot of the calculated proton affinities, ΔE° , of $\text{NH}_2\text{CH}_3/\text{CH}_3\text{F}$ pairs vs. $\cos \theta$ ($r = 5.44 \text{ \AA}$).

are obtained for structures having either staggered or eclipsed arrangements of the two methyl groups relative to one another. The results follow eq 3 accurately down to r values of less than 5 \AA as shown in Figure 1.

That the substituent effect here is basically a dipole-point charge interaction can be seen by using eq 4 with $\mu = 1.12 \text{ D}$.

$$E = q\mu \cos \theta / r^2 \quad (4)$$

This yields $3.82 \text{ kcal mol}^{-1}$ for $r = 4.5 \text{ \AA}$ in good agreement with the value in Table I. An r value of 5 \AA corresponds to a closest hydrogen-hydrogen intermolecular distance of 2.16 \AA , less than the sum of two hydrogen van der Waals radii. For closer approach the values of ΔE° are of greater magnitude than anticipated, suggesting an additional transmission mechanism for the sub-

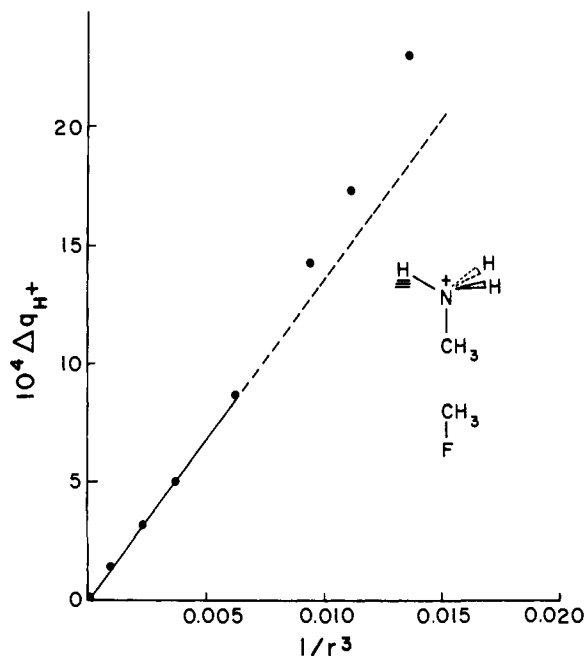


Figure 3. Plot of the change in calculated electron population on the acidic hydrogen, Δq_H , of ${}^+\text{NH}_3\text{CH}_3/\text{CH}_3\text{F}$ pairs vs. $1/r^3$ ($\theta = 0^\circ$).

stituent effect. The calculations show that for these small values of r , the total electronic energy of the $\text{CH}_3\text{NH}_3^+/\text{CH}_4$ pairs increasingly deviates from the near constant values found for $r > 5^\circ$. (For eclipsed conformations: $r = 10.44 \text{ \AA}$, $E = -134.18061 \text{ au}$; $r = 7.44 \text{ \AA}$, $E = -134.18074 \text{ au}$; $r = 6.44 \text{ \AA}$, $E = -134.18086 \text{ au}$; $r = 5.44 \text{ \AA}$, $E = -134.18047 \text{ au}$; $r = 4.50 \text{ \AA}$, $E = -134.15462 \text{ au}$; $r = 4.20 \text{ \AA}$, $E = -134.10270 \text{ au}$; $r = 3.94 \text{ \AA}$, $E = -133.98431 \text{ au}$.) At the same time charge transfer from the methane molecule to the methylammonium ion occurs for values of r less than 5 \AA (0.021 electron at $r = 4.20 \text{ \AA}$; 0.042 electron at $r = 3.94 \text{ \AA}$). In the $\text{CH}_3\text{NH}_3^+/\text{CH}_3\text{F}$ pairs the charge transfer is found to be less for corresponding distances. Thus the fluorine substituent causes an additional acid-strengthening effect (charge transfer, 0.019 electron at 4.20 \AA , 0.033 electron at 3.94 \AA).

The effect of alteration of θ has also been studied keeping $r = 5.44 \text{ \AA}$ and $\beta = 0^\circ$. The results (Table II) are presented in Figure 2, and it is seen that ΔE° values accurately follow $\cos \theta$ in accord with eq 3. A number of structures with $\beta \neq 0^\circ$ were also examined, and again the results (Table II) were in accord with eq 3.

Effects on Charge. Studies were also made of the substituent effect on the atomic electron population of the acidic hydrogen atoms on the methylammonium ion. These are of interest in understanding the charge-energy relationships observed in various proton-transfer equilibria. The appropriate relationship for the polarization energy of an isolated bond is eq 5, where φ is the angle

$$E_{\text{bond}} = \mu(2 \cos \theta \cos \varphi - \sin \theta \sin \varphi) / r^3 \quad (5)$$

subtended at the polarized bond by the line drawn to the midpoint of the CF bond.²³ The charge induced by the substituent (Δq) should thus follow $1/r^3$ rather than the $1/r^2$ for energy, and further, the relative geometry of the NH bond is now significant.

A plot of Δq vs. $1/r^3$ for a linear NC and CF arrangement ($\beta = 0^\circ$) is shown in Figure 3 which is seen to correspond generally with Figure 1. Figure 4 is a plot of ΔE° vs. $\Delta q r / (2 \cos \theta \cos \varphi - \sin \theta \sin \varphi)$ which is reasonably linear for values of r greater than 4 \AA .

It is thus clear that while substituent-induced effects on energy may be a linear function of those on charge, since both depend on the substituent dipole μ , the proportionately constant will

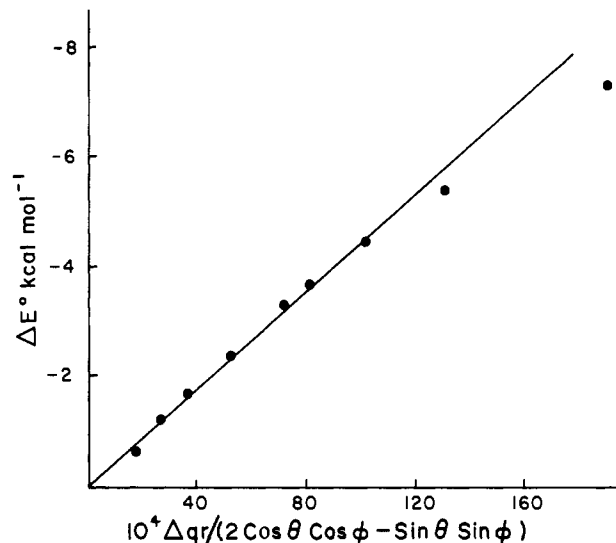
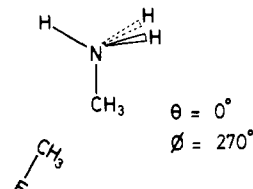


Figure 4. Plot of the calculated proton affinities, ΔE° , of $\text{NH}_2\text{CH}_3/\text{CH}_3\text{F}$ vs. $\Delta q r / (2 \cos \theta \cos \varphi - \sin \theta \sin \varphi)$.

change with geometry as indeed observed.^{13,14} Further, for similar values of θ and φ one can expect the proportionality constant in kcal mol^{-1} per electron to increase as r increases, as found,¹⁴ for example, for aniline compared to pyridines and for ethylamines compared to methylamines.

The relationship of effects on ΔE and Δq is not quite so simple for examples where $\theta \neq 0^\circ$. The change in Δq now differs according to which H is considered, since r and φ vary but in neither case is a close relationship with eq 3 found. Thus for structure 12, eq 5 predicts zero polarization at the NH bond

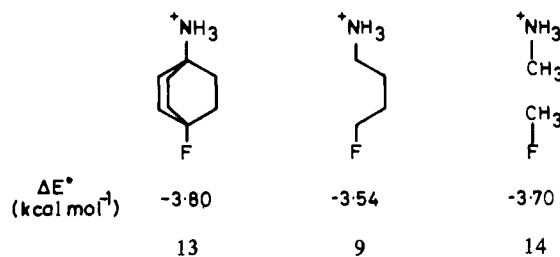


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indicated. In practice a value of 5×10^{-4} electron is found for Δq . This lack of agreement with eq 5 probably arises because the polarization of the NH bond is not isolated from other parts of the molecule. Further work is proceeding on this problem.

Thus $\Delta E/\Delta q$ relationship not only depends on r but also on the direction of the NH bond relative to that of the CX dipole and probably on the polarization of the molecule as a whole.

Comparison between Alkylamines and Isolated Molecules. Isolated molecule calculations have been made for the same geometries of the terminal atoms as the alkylamines 7, 8, 9, and 10. Nonbonded interactions precluded the use of isolated molecule models for the ethylamines and propylamines. One series is shown below, r being constant. The other results (Tables I and II) are alkylamine structure 7 ($\Delta E = -2.60 \text{ kcal mol}^{-2}$), isolated molecule ($\Delta E = -1.97 \text{ kcal mol}^{-1}$), 8 ($\Delta E = -0.73, -0.22 \text{ kcal mol}^{-1}$), and 10 ($\Delta E = -1.78, -1.50 \text{ kcal mol}^{-1}$). It is seen that the ΔE° values are fairly similar whether the probe is connected or isolated from the substituent. The values for the series 13,¹⁰ 9, 14 indicate that



(23) The angle θ in formula 5 should refer to the midpoint of the NH bond but is here taken as before to the center of charge; the error introduced is small.

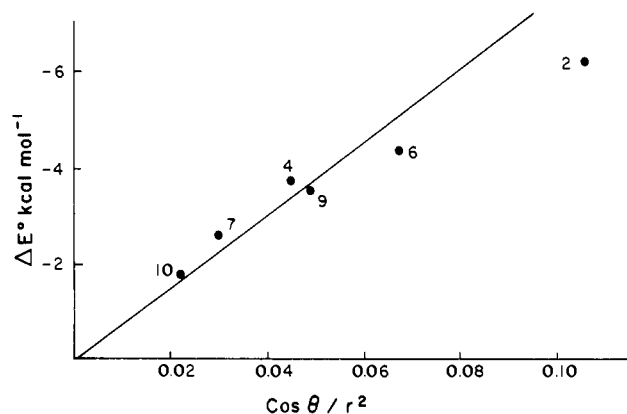
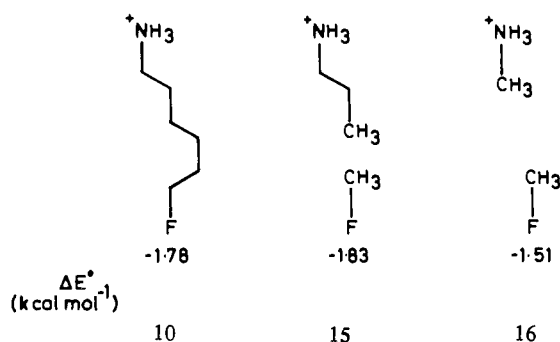


Figure 5. Plot of the calculated proton affinities, ΔE° , of ω -fluoroalkylamines (see Table I for identification) vs. $\cos \theta / r^2$. The line shown is that of Figure 1.

any through-bond (σ -inductive) transmission must be very small here. This is further shown in the series 10, 15, 16 where r and

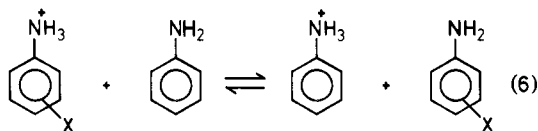


β are constant. Clearly removal of part of the connecting carbon skeleton does not alter the magnitude of the substituent effect.

Figure 5 shows a plot of the calculated ΔE° values for the fluoroalkylamines (Table I) against $\cos \theta / r^2$. The line shown is that calculated for isolated molecules (Figure 1). The values found for the alkylamines are in close agreement with those for the isolated molecules apart from larger values of $\cos \theta / r^2$ where they fall below the line indicating a lower than expected transmission.

Thus we conclude that the σ -inductive effect is not an important mode of transmission in these systems, at least in the gas phase. The small differences found in some cases between the alkylamine and the isolated molecule calculations suggest that some other mechanisms, helping or impeding the transmission, may exist. This may result from the polarization of the intermediate CH bonds and will be the subject of future studies as will be the importance of the nonbonded orbital interactions observed on close approach of the two molecules. This later phenomena may help us to understand²⁴ the electronic interactions observed in ortho-disubstituted benzenes.

Inductive Effects in the Relative Basicities of Anilines. One example of the use of the isolated molecule approach is to investigate substituent effects on the proton-transfer equilibria of anilines (eq 6). The ΔE° values¹¹ are listed in Table III. A



dual substituent parameter analysis²⁵ leads to eq 7 with a goodness

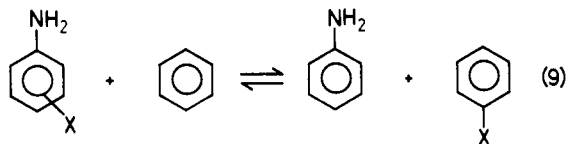
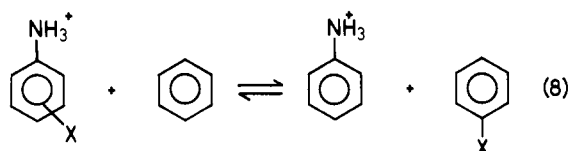
$$\Delta E^\circ = 10.3\sigma_I + 15.7\sigma_R^- \quad (7)$$

Table III. Ab Initio Molecular Orbital Calculations (STO-3G) of the Proton Affinities of Substituted Anilines and $\text{CH}_3\text{NH}_2/\text{CH}_3\text{Y}$ Pairs at the Same Geometry^b

subst	anilines ^a		$\text{CH}_3\text{NH}_2/\text{CH}_3\text{X}$		
	ΔE°	ΔE_{int}	ΔE°	ΔE_{int}	
		cation	neutral	cation	neutral
Me	2.4	2.0	-0.5	0.4	0.4
NH ₂	6.1	4.5	-1.6	-1.1	-0.7
OMe	4.2	2.8	-1.5	-2.4	-1.9
F	-1.1	-2.0	-0.8	-3.3	-2.7
CN	-10.4	-9.0	1.4	-6.4	-5.3
CF ₃	-5.9	-5.1	0.8	-3.5	-3.3
CHO	-4.2	-3.2	1.0	-2.2	-2.1
NO ₂	-14.8	-12.6	-2.2	-8.5	-7.8

^a Data from ref 11. ^b ΔE is in kcal mol⁻¹.

of fit (standard deviation of the estimates divided by the root-mean-square of the data), $f = 0.07$. The interaction energies¹¹ in the acidic (eq 8) and neutral forms (eq 9) are also given in Table



III. Most of the substituent effect in (7) can be ascribed to the effects in the charged ions (8). The dsp analysis gives eq 10 (process 8) and 11 (process 9) with fits of $f = 0.08$ in both cases.

$$\Delta E_{\text{int}} = 9.6\sigma_I + 12.2\sigma_R^- \quad (10)$$

$$\Delta E_{\text{int}} = 0.7\sigma_I + 3.6\sigma_R^- \quad (11)$$

These figures indicate that the inductive effect is important in the cations and hence in the overall process 6. This effect includes² in this case not only any direct electrostatic interaction between the substituent and the cationic center but also any effect of polarization of the intervening π system (the π -inductive effect) as well as any field-induced charge transfer between the NH_3^+ or NH_2 groups and the benzene ring (the field-induced resonance effect²⁶). A more detailed analysis^{11,27} has suggested that eq 7, 10, and 11 are to some extent artifacts since π -electron-withdrawing groups have very small resonance interactions when in the para position in anilinium ions. Equation 12²⁷ closely fits the data for the interaction energies of such ions where the resonance term is only applied in the case of π -electron donors (cf. eq 10).

$$\Delta E_{\text{int}} = 12.7\sigma_I + 5.50\sigma_R^+ \quad (12)$$

Table III also lists the relative energies of the proton-transfer reactions, using isolated molecules as in eq 2 with the substituent and probe groups in the same spatial arrangement as in aniline. The dsp analysis for ΔE° ($f = 0.21$) and ΔE_{int} of the cations ($f = 0.21$) are (13) and (14). The ΔE_{int} figures for the neutrals

$$\Delta E^\circ = 10.1\sigma_I + 2.0\sigma_R^- \quad (13)$$

$$\Delta E_{\text{int}} = 8.8\sigma_I + 2.2\sigma_R^- \quad (14)$$

are small and not well fitted. The small resonance terms are almost certainly not significant; the relationship to σ_I alone is almost as good. The most important result is that the inductive

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effect on the interaction energies in the anilinium cations (eq 12) is significantly greater than found in the isolated molecules. This result means that either (or both) the substituent-induced polarization of the ring π -electrons or the change in s hybridization of the ring carbon atoms is of importance here and accounts for almost one-third of the total inductive effect.

Further work is continuing on the use of the isolated molecule approach.

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3,3'-Bicyclopropenyl: Evidence for Novel Long-Range Conjugation of π Orbitals

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Abstract: Ab initio calculations employing the STO-3G and 4-31G basis sets indicate that 3,3'-bicyclopropenyl is the highest energy accessible (CH)₆. The calculations indicate the presence of long-range interactions between the two π systems of this molecule, and the predictions are supported by photoelectron spectroscopy data. Calculational studies of model compounds are included, and the origin of the electronic effect of 3,3'-bicyclopropenyl is discussed in light of the electronic distribution in cyclopropene.

The dipole moment of cyclopropene is unusual in its direction and magnitude. Its "reversed polarity" is the result of net electron donation from the π_{CC} to $\sigma^*_{CH_2}$ "component orbitals" imposed by the molecule's symmetry.² The magnitude of the dipole moment (0.455 debye³) originates in the extensive mixing between these "component orbitals". (A qualitative appreciation of this factor may be gained upon comparison of computer drawings of the π orbitals of cyclopropene and propene;⁴ furthermore, the presence of an appreciable diamagnetic ring current in cyclopropene has been suggested following magnetic susceptibility anisotropy studies.)^{5,6}

The appreciable π -electron density at C3 of cyclopropene raises the interesting question of the interaction between two such rings joined at these positions. The resulting molecule, 3,3'-bicyclopropenyl (**1**), is the only accessible benzene valence isomer, (CH)₆, to elude synthesis, although simple derivatives have been reported.⁷⁻⁹

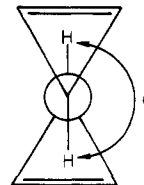


In the present study, ab initio molecular orbital calculations have been applied to a study of the structure and energy of 3,3'-bicyclopropenyl. This allows its comparison with the other four (CH)₆. The electronic interactions between cyclopropene rings have been studied as a function of conformation and com-

pared with those present in model cyclic and acyclic molecules.

Methods

Ab initio molecular orbital calculations used in this work employ the GAUSSIAN 70 program series¹⁰ at the STO-3G¹¹ and 4-31G¹² levels. The geometry of the rings in **1** (and simple derivatives) is assumed to be the same as calculated for cyclopropene.¹³ The C3-C3' bond is found to be 1.51 Å and the H3-C3-C3' angle equal to 114.7° (assumed to be bisected by the ring plane containing C3) following a limited geometry search (STO-3G) on the anti conformer. Bicyclopropyl was employed as a partial model for **1**. It is known to exist as a mixture containing almost equal fractions of an anti conformer (torsional angle $\theta = 180^\circ$) having rotational amplitude $\pm 80^\circ$ and a gauche conformer ($\theta = 49^\circ$) having rotational amplitude $\pm 18^\circ$.¹⁴⁻¹⁶ In the present study, analogous anti ($\theta = 180^\circ$, **1a**) and gauche ($\theta = 45^\circ$, **1b**) as well as syn ($\theta = 0^\circ$, **1c**) conformers of 3,3'-bicyclopropenyl have been investigated at the 4-31G level. These conformers, as well as others ($\theta = 30, 60, 90, 120, 135, 150^\circ$), have also been investigated by using the STO-3G basis set.



1a, $\theta = 180^\circ$
1b, $\theta = 45^\circ$
1c, $\theta = 0^\circ$

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