

### THEORETICAL STUDIES OF THE INDUCTIVE EFFECT

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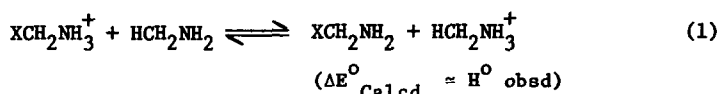
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**Abstract:** Ab-initio calculations (STO-3G) show no evidence for  $\sigma$ -inductive effects in the dissociation of certain alkylammonium ions. Substituents effects are suggested to arise from non-bonded interactions and polarisation of CH bonds as well as from direct field effects.

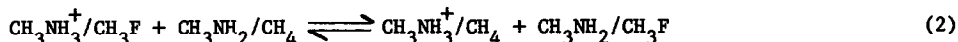
There is continued interest<sup>1-3</sup> in the mechanism of transmission of polar effects in  $\sigma$ -bonded systems. The two major mechanisms that have been considered<sup>2,4</sup> are the field effect, a direct through space electrostatic interaction, and the  $\sigma$ -inductive effect, a progressive but diminishing relay of polar effects along a chain of carbon atoms. Although field effects appear to predominate in many examples<sup>2-5</sup>, there is evidence<sup>1,3</sup> for an additional transmission mode particularly over short distances. We suggest below that there is indeed an additional mode but that it is not a  $\sigma$ -inductive effect; this has great significance for the understanding and investigation of the transmission of polar effects.

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. Theoretical calculations, by contrast, can be made for many different geometries, using fixed conformations. The relative proton affinities of substituted amines provide suitable examples. It has already been shown<sup>6</sup> that the experimental gas phase energies for isodesmic proton transfer equilibria (1) of substituted methylamines are well produced by ab-initio molecular orbital calculations at the minimal basis set STO-3G level.



A similar result is found for substituted ethylammonium<sup>6</sup>, quinuclidinium<sup>7</sup>, pyridinium<sup>8</sup> and anilinium<sup>8</sup> ions. This gives confidence that similar calculations on various conformations of  $\omega$ -substituted alkylammonium ions give realistic results. Such systems provide a wide variety of geometries and initial calculations<sup>9</sup> have been made on propyl-, butyl and hexyl-ammonium ions using fluorine as the substituent. Calculations were made using various conformations having the heavy atoms (C,N,F) coplanar.

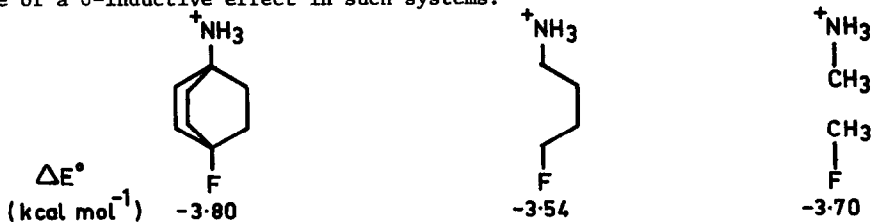
These results, for the butyl and hexyl ammonium systems, can be compared with isolated molecule calculations<sup>3</sup> using the methylammonium ion at corresponding distances and angles from methyl fluoride. Here the relevant isodesmic process is:



Comparison of such calculations shows whether the intervening carbon atom chains provide significant transmission pathways.

The power of these methods is evident from preliminary calculations. The centre of charge of the methylammonium ion was found from calculated Mulliken atomic charges to be  $0.2\text{\AA}$  from the nitrogen on the NC axis towards the carbon atom. Using the isolated molecule approach it was found that  $\Delta E^0$  values calculated for the process (2) where the heavy atoms were coaxial in the order NC,CF were accurately linear versus  $1/r^2$  for  $r > 5.5\text{\AA}$  where  $r$  is the distance between the centre of charge on the methylammonium ion and the centre of the CF bond. (The interatomic distances being kept constant in any one set of calculations for equilibrium (2)). For smaller values of  $r$ ,  $\Delta E^0$  values deviate increasingly in the sense of being more negative than anticipated, as shown in Figure 1. The linearity with  $1/r^2$  is expected for a field effect but an additional transmission mechanism occurs where  $r$  is less than  $5.5\text{\AA}$ . This distance represents a nearest non-bonded hydrogen to hydrogen distance of  $2.66\text{\AA}$  between the molecules. It is found that where  $r$  is less than  $5.5\text{\AA}$ , the energies of the corresponding  $\text{CH}_3\text{NH}_3^+/\text{CH}_4$  pairs also vary increasingly from the constant value found at greater separations. The Mulliken charges show repulsion from the methyl to the ammonium end of the ion and, in addition, quite significant amounts of charge are transferred intermolecularly. (Thus for  $r = 7.44\text{\AA}$ ,  $E^0 = 134.18074$  au,  $\Sigma q(\text{methane}) = 10.0000$  while at  $r = 4.20\text{\AA}$ ,  $E^0 = -134.10270$  au,  $\Sigma q(\text{methane}) = 9.9793$ ). The replacement of the hydrogen atom by fluorine lessens this charge transfer while still polarising the ammonium ion in the same sense as at greater distances. This effect thus causes acid strengthening in the fluoro substituted case additional to that caused by the field effect.

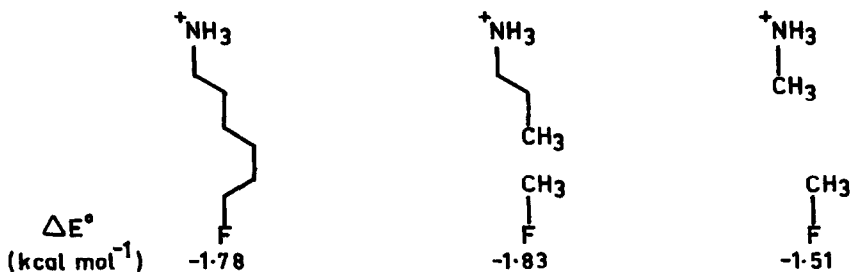
Isolated molecule calculations give energies similar to those for the corresponding butyl or hexyl ammonium systems. Thus in the case below, the isolated molecules give a  $\Delta E^0$  value, more negative than found for the corresponding butyl-ammonium ion and approximately the same for the bicyclooctyl ammonium ion<sup>10</sup> ( $r = 4.50\text{\AA}$  in each case). This is strong evidence against the presence of a  $\sigma$ -inductive effect in such systems.



That the substituent effect is basically a dipole-point charge interaction is also supported in that the formula  $E = q\mu \cos \theta / r^2$  yields  $E = 3.82$  kcal mol<sup>-1</sup> for  $r = 4.5\text{\AA}$  using  $\mu(\text{CH}_3\text{F}) = 1.12\text{D}$ <sup>3,9</sup>.

In some systems the  $\Delta E^0$  values are greater for the joined than isolated molecules. This appears to arise from the polarisation of CH bonds adjacent to the  $\text{NH}_3^+$  centre. That this is

likely, and that the effect is not a  $\sigma$ -inductive one, is shown by calculations such as the series below where  $r$  is constant. Clearly removal of an isolated part of the connecting carbon skeleton does not alter the magnitude of the substituent effect.



Thus we conclude that the  $\sigma$ -inductive effect is not an important mode of transmission in these systems, at least in the gas phase. Polar substituent effects can, however, be transmitted via orbital interactions and indirect polarisation effects in addition to direct electrostatic interaction. We are extending this investigation to gain a greater understanding of these effects, including the previously reported<sup>11</sup> relationship between energy and charge, the effects of charged substituents<sup>1</sup>, and the existence of reversed substituent effects.

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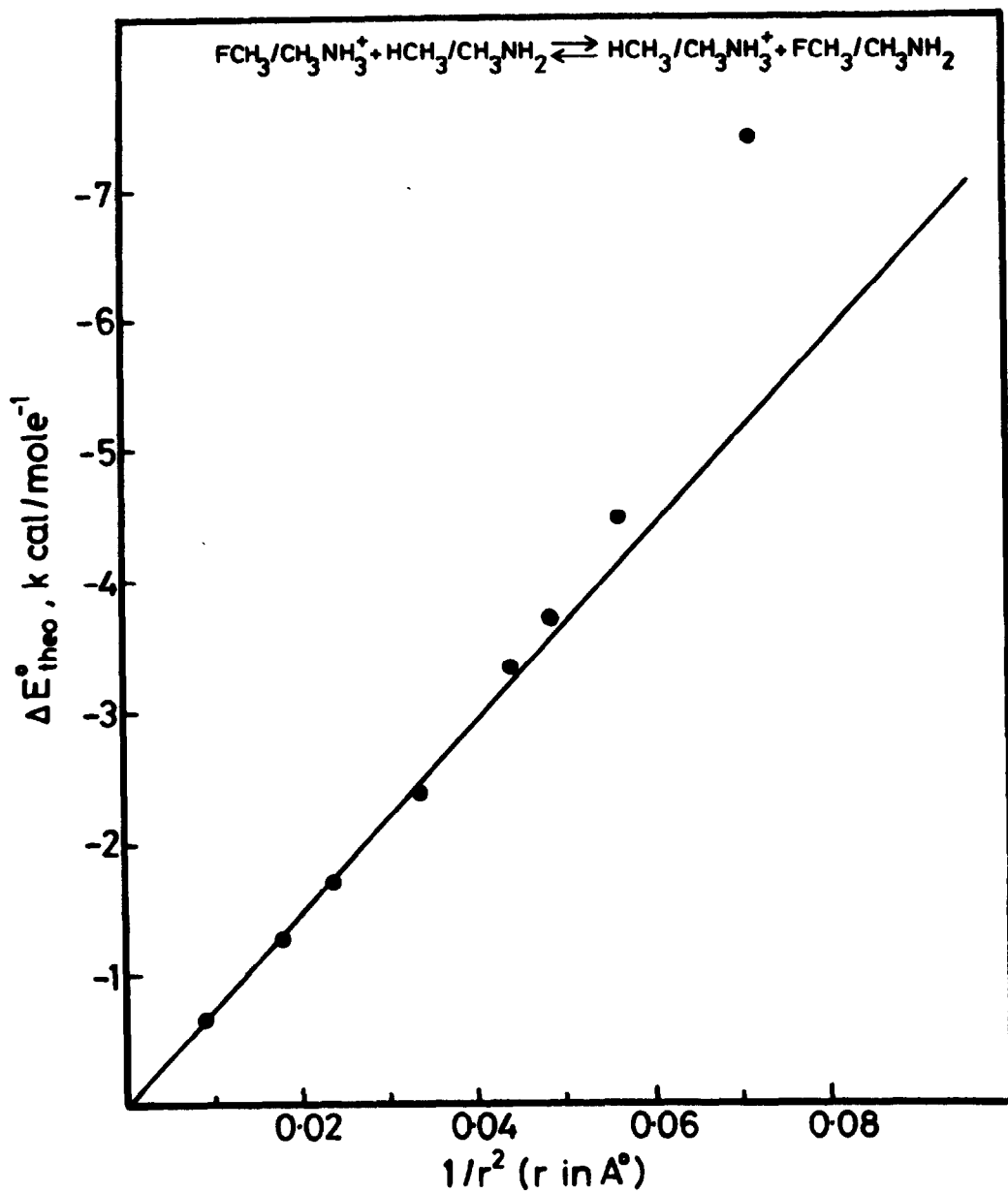


Figure 1.  $\Delta E_{\text{theo}}^{\circ}$  vs.  $1/r^2$  for the isodesmic process shown.

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