Some Notes on the Electron Repelling Property of Alkyl Groups

Sadhan Basu

Some Notes on the Electron Repelling Property of Alkyl Groups

SADHAN BASU

Mathematical Institute, Oxford University, England, and Department of Chemistry, University College of Science, 92 Upper Circular Road, Calcutta 9, India

(Received August 15, 1958)

Electron donation by alkyl groups and bond angle change due to steric requirement have been found to affect the physicochemical properties of simple saturated molecules in exactly similar manner.

IN the electronic interpretation of the reactivity of organic compounds assumption has been made about the electron-donating property of alkyl groups, which has helped us to a considerable extent in understand a large number of chemical reactions, although in a more-or-less qualitative manner.[1] Difficulties are encountered when an attempt is made to analyze the effect in a semiquantitative manner. Thus it may be assumed that the ionization potential of methylamine is lower than that of ammonia because the methyl group tends to donate electrons to the nitrogen thereby increasing the electron density at the latter. Consequently the lone pair electrons are less tightly bound to nitrogen in methylamine than in ammonia and are therefore more easily removed. But the ionization potential of methyl radical is 9.85 ev while that of ammonia is 10.15 ev.[2] So it is not clear why the methyl group should strongly donate electrons to the nitrogen in methylamine so as to lower the ionization potential to the extent of about 1.18 ev. This suggests the question: Is there any other effect which may be operative in these systems along with electron donation by the methyl group which may be responsible for such a large lowering of ionization potentials? (It is as high as 2.33 ev in trimethylamine.[3])

The recent electron diffraction[4(a)] and microwave[4(b)] studies on ammonia and methyl ammines show that (i) in ammonia the angle HNH is 106°, (ii) in monomethylamine the angle HNH is 106° but the angle CNH is 112°, and (iii) in trimethylamine all the angles CNC are 110°. In ammonia the hybridization is therefore close to sp^3, consequently the lone pair electrons in ammonia are also in the sp^3 hybridized state. In monomethylamine as one of the bond angles, i.e., the angle CNH, is 112°, the bonding orbital takes up more s character, hence the lone pair electrons are left with more p character in methylamine than in ammonia. In trimethylamine all the angles are 110°, so

the p character of the lone pair electrons is still further increased. (Although the statement is correct for trimethylamine, it is not necessarily so for mono- and di-substituted compounds without some additional assumption.) Thus from the experimental data on the bond angles we see that as we pass on from ammonia to trimethylamine the lone pair electrons of the nitrogen may take up more p character, the negative center of gravity of the lone pair orbital may move away from the nitrogen nucleus and consequently the ease with which they can be removed from the molecule may increase. This means that a change in bond angle alone may bring about a lowering of the ionization potential in going from ammonia to trimethylamine. And so the question is, is there any way by which we can make an estimate of the relative contribution of the two effects, bond deflection and electron donation, in lowering the ionization potentials of methylamines compared to ammonia?

Recently Higuchi[5] has made a detailed MO calculation on ammonia. He has shown that when the angle HNH is 90°, the lone pair electrons are more tightly bound to the nitrogen nucleus than are the bonded ones. But as the angle is increased the energy of the lone pair electrons goes down and that of the bonded ones goes up. In the table below are given the energy values of lone pair and bonded electrons in ammonia at various HNH bond angles.

	90.0°	97.5°	105.0°	112.5°	116.25°
Lone pair (ev)	27.16	24.78	22.12	18.51	16.63
Bonded (ev)	21.49	23.04	24.58	26.75	28.80

For a change in bond angle from 106° to 110° the energy of the lone pair electrons decreases by about 1.78 ev. As estimated experimentally, the bond angle changes by this amount when we pass on from ammonia to trimethylamine. Thus it is evident that out of about 2.33 ev change in ionization potential[3] in going from ammonia to trimethylamine, about 1.78 ev may be accounted for by the change in bond angle alone. The rest may therefore be due to electron donation by the methyl groups.

In view of the uncertainty in the experimental value of the bond angles and the approximate nature of

[1] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, New York, 1957), p. 71.

[2] Higasi, Omura, and Tsuchiyas, "Tables of ionisation potentials of molecules and radicals," Monograph Series of the Research Institute of Applied Electricity, Hokkaido University, No. 4 (1954–1957).

[3] K. Watanabe and J. R. Mottl, J. Chem. Phys. 26, 1773 (1957).

[4] (a) L. E. Sutton (private communication to Professor C. A. Coulson); (b) Nishikawa, Itoh, and Shimade, J. Chem. Phys. 23, 1735 (1955).

[5] J. Higuchi, J. Chem. Phys. 24, 535 (1956).

314

Higuchi's calculation, not much significance could be attached to the absolute value of these quantities; but it emerges from the present analysis that a substantial part of the change of ionization potential is due to change in bond angles, which must be in some way related to the steric conditions prevailing in the molecule when a hydrogen is replaced by bulky substituents. But the steric factor alone can not explain all the experimental observations as shown by the unusually large variation in ionisation potentials in going from mono methyl (8.97 ev) through monoethyl- (8.86 ev) to monopropylamine (8.78 ev).[3] So the conventional electron-repelling effect is a reality, but it is not the only factor responsible for the observed variation in ionization potential of alkyl amines.

Recently Ellison and Shull[6] have made a detailed MO calculation on the electronic structure of water molecule and their result has been used by Burnelle and Coulson[7] in calculating the lone pair dipole moment of water. It has been shown that as the angle HOH is increased the long pair dipole moment also increases, i.e., the center of negative charge moves away from oxygen and consequently the energy of the lone pair electrons goes down with an increase in the angle in HOH, as in ammonia, at least for small deformation. In water, methyl alcohol, and dimethyl ether the XOX are 105°, 108° and 110°, respectively.[8] Consequently the ionization potentials of these compounds should be in the order water>methyl alcohol>dimethyl ether, as is actually the case. The experimental value of the ionization potentials being 12.59 ev for water, 10.52 ev for methyl alcohol and 10.00 ev for dimethyl ether.[2] So we see that in this case also a variation in bond angle brings about a change in energy in the same direction as the electron repelling effect.

In the case of carbon compounds like R_4C, the state of hybridization of the carbon orbitals may be expressed as $(s+\lambda p)$, such that $\lambda^2 = -\cos$ angle RCR. If the angle be tetrahedral, i.e., 109°28′, then $\lambda = 0.577$. If now the bond angles are increased to, say, 112°, λ increases to 0.617, i.e., bond takes up more p character. It was pointed out by Coulson[9] that whereas the

familiar atomic orbital, s or p, possesses a center of symmetry, this is no longer the case with hybrids. Thus with an orbital $(s+\lambda p_x)$ in which the hybrid may be said to point in the x direction, the mean value of the coordinate is given by

$$x = (2\lambda/1+\lambda^2) \int s x p_x dx.$$

This is zero only for s or p orbitals. For hybrid bonds it increases up to $\lambda = 1$, and then drops. It is evident therefore that an increase in bond angle from 109°28′ to 112° will increase the dipolemoment of the bond or in other words the bond will become more polar.

It is well established that in the solvolytic $(S_N 1)$ reactions alkyl iodides react faster than bromides, which in turn react faster than chlorides. It may be suggested that this is due to increased polar character of the bonds in the order $I^- > Br^- > Cl^-$ or to steric factor or to both.[10] From the analysis set forth it is clear that the steric and polar effect go together, i.e., an increase in bond angle which is necessary for steric effect also increases the polar character of the bond. Further it has been shown as the alkyl group gets more and more branched the solvoletic reaction rate increases markedly and in some cases to an enormously high value, which again is, in all probability, the result of the increase in bond angle causing the bond to take up more polar character.

The object of the present investigation has been to analyze the role of bond angle in determining the reactivity of chemical compounds. It has been established at least qualitatively that the experimental determination of bond angles combined with Higuchi-Ellison-Shull type of calculation, will be extremely fruitful in understanding the reactivity of simple saturated compounds.

[6] F. O. Ellison and H. Shull, J. Chem. Phys. **21**, 1420 (1953).
[7] L. Burnelle and C. A. Coulson, Trans. Faraday Soc. **53**, 403 (1957).
[8] Venkateswarlu, Edwards, and Gordy, J. Chem. Phys. **23**, 1195, 1200 (1955).
[9] C. A. Coulson, Proc. Roy. Soc. (London) **A207**, 67 (1951).

[10] *Steric Effect in Organic Chemistry*, edited by Newman (John Wiley and Sons, Inc., New York, 1956), p. 71.