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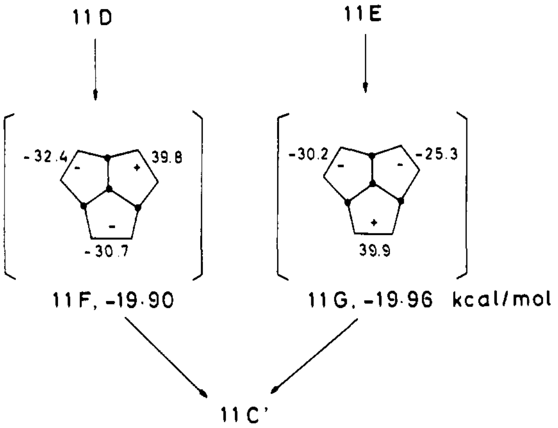
(45) In actual calculations, the 35.5° bridge of **11D**, for example, was first forced to take a dihedral angle of 39.8° and kept at this angle while the molecule was relaxed. The relaxation stopped when the other two bridges took dihedral angles of −32.4 and −30.7° (**11F**). **11F** is already close to **11C′** and its relaxation without constraint readily led to **11C′**. Essentially the same calculations were performed on **11E**, which gave **11G** as an artificial intermediate.



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The Inductive Effect in Molecules and Ions

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Abstract: The description of charge distribution in a molecule in terms of the electron density within defined spheres derived from molecular wave functions is used in the quantitative investigation of the inductive effect.

I. Introduction

One of the simplest concepts in the electronic theory of organic chemistry is the inductive effect. We present for the first time a rigorous method for examining the empirical concepts proposed by Ingold and others. This is achieved using the precise computation of the charge surrounding an atom in a molecule or ion defined by Dean and Richards.[1]

Following Ingold[2] "a group X may be said to be electropositive, or electron repelling, in a compound X-CR_3 if the electron content in the residue CR_3 is greater than in the compound H-CR_3. It is not a serious difficulty that there is no physically indicated point along the bond X-C or H-C at which X or H ends and C begins: it is known that the single bond radius of the carbon atom is a nearly constant quantity (0.77 Å) which it would be fair to accept as providing a conventional atomic boundary for the purposes of comparison". Ingold distinguishes two different cases when the inductive effect of the methyl group is considered. From a study of absorption spectra and dipole moments, methyl groups are seen to be very weakly electronegative in saturated alkanes. In most other systems, however, where electronegative groups are encountered, methyl groups are electropositive, i.e., electron donating. In this connection, the important property of a methyl group is that it is more polarizable than hydrogen.

II. Methods

There have been many ways suggested for partitioning the charge in molecules.[3] The simplest method is that due to Mulliken and is described as a population analysis.[4] In this method all the electronic charge in a molecule is assigned to the constituent atoms. The charge "belonging" to an atom A is that arising entirely from the atomic orbitals of A, and half of that arising from the overlap of atomic orbitals centered on A with those of all the other atoms in the molecule. In assigning all the one-center charge to the central atom and in partitioning overlap equally, this method is particularly unsuitable for an investigation into the inductive effect where slight electronegativity changes are critical.[5]

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Table I. A Comparison of Calculated and Experimental Dipole Moments

method	value, D
exptl	0.085
sphere charge	0.104
G.70 STO-3G basis set	0.023

Table II. A Comparison of Sphere Charges with the Mulliken Population Analysis

species	sphere charge around central atom	MPA charge around central atom	sphere charge around Me carbon
CH_4	4.470	6.252	
$C(CH_3)_4$	4.418	5.942	4.470
NH_4^+	5.140	7.423	
$N(CH_3)_4^+$	5.201	7.161	4.437

Table III. Sphere Charges for Two Fixed Radii for a Nitrogen Atom

species	sphere charge for radius[a]	
	r_N = 0.705 Å	r_N = 0.74 Å
NH_4^+	5.182	5.476
$N(CH_3)_4^+$	5.159	5.452
difference Δ	0.023	0.024

[a] 0.705 Å is the average value for the N^+ radius; 0.74 Å is the Schomaker covalent radius for nitrogen.

Table IV. Effect of a β-Substituted Methyl Group on an N^+ Atom

species	sphere charge[a]			Mulliken population analysis
	r_N = 0.68	r_N = 0.71	r_N = 0.74	
$CH_3NH_3^+$	4.970	5.222	5.470	7.351
$CH_3CH_2NH_3^+$	4.977	5.230	5.478	7.349

[a] r_N = 0.68 corresponds to r_C = 0.80; r_N = 0.71, r_C = 0.77; r_N = 0.74, r_C = 0.74.

Using the method of Dean and Richards,[1] recently extended by Richards and Wallis,[6,7] we can calculate the total electronic charge in a sphere of required radius centered at any point in space to the limits of the accuracy of the wave function. The only arbitrary parameter is the choice of radius for a given type of atom. We consider the extent of a carbon atom to be a sphere of radius 0.77 Å, and the charge "belonging" to the atom as that within this sphere. In Table IV, it is shown that the variation of such charges for a given atom is almost linearly dependent on the radius over regions of chemical interest. This indicates that the choice of a sphere is an acceptable approximation for the definition of the extent of atoms in molecules, although there will always be a certain arbitrariness in the concept of atomic charge.[8]

III. Results and Discussion

The calculations were performed using the GAUSSIAN 70 program with an STO-3G basis set.[9] Throughout, charges are quoted in electrons and standard geometries are taken.[10] Only the following covalent radii need be defined: C, 0.77 Å; H, 0.33 Å.

Ingold recognized that to some extent σ-bond electrons are delocalized in alkanes resulting in the increase of electron density at the end of a chain. Laurie et al.[11] have determined the dipole moment of propane to be 0.085 D with the electron drift in the direction shown in Figure 1. As a consequence calculations were performed to examine the sphere charges on the three carbon atoms.

Table V. Inductive Effect of the Methyl Group in the Allene System

species		sphere charge on C_2 q	calcd inductive effect I_{Me}
$R_1 = R_2 = R_3 = R_4 = H$	allene	4.537	
$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$	methylallene	4.554	0.0170
$R_1 = R_2 = CH_3$; $R_3 = R_4 = H$	dimethylallene	4.566	0.0145
$R_1 = R_2 = R_3 = CH_3$; $R_4 = H$	trimethylallene	4.580	0.0143
$R_1 = R_2 = R_3 = R_4 = CH_3$	tetramethylallene	4.593	0.0140

Table VI. Sphere Charge Changes on Internal Rotation in Ethyl Cations $CH_2XCH_2^+$ as a Measure of Hyperconjugation

substituent X	barrier, kcal mol^{-1}	ΔC^+	$\Delta C\text{-}C^+$
$-CH_3$	2.52	0.0038	0.0024
-CCH	0.45	0.0006	−0.0024
-H	0.0	0.0	0.0
-CN	−1.95	−0.0051	−0.0034
-OH	−7.67	−0.0065	−0.0058
-F	−9.31	−0.0060	−0.0082

Table VII. Change in the C^+ Sphere Charge with Methyl Substitution

species	C^+ sphere charge
$CH_3CH_2^+$	3.8805
$CH_3CH_2CH_2^+$	3.8879
difference = I_{Me} (through bond)	0.0074

Table VIII. Inductive Effect of a Methyl Group in Acetylene

species	sphere charge on C_1	calcd inductive effect I_{Me}
$C^1H{\equiv}C^2H$ ethyne	3.4162	
$C^1H{\equiv}C^2CH_3$ propyne	3.4275	0.0113

This result confirms the drift of electron density toward the carbon with the greater number of hydrogen atoms. A charge difference method was used to calculate a dipole moment from sphere charges and this compares favorably with the experimental result of Laurie et al. (Table I).

A comparison is presented in Table II of the electronic charges from the sphere method and from the Mulliken population analysis in two series of related compounds.

From the sphere charge results, the methyl group is seen to be electron attracting in the substituted alkane but electron donating in the substituted ammonium ion. The Mulliken population analysis predicts the methyl groups to be significantly electron attracting in both series. This is hardly surprising when it is remembered that N^+ and C have widely differing electronegativities and yet the overlap charge density is divided equally between them in Mulliken's scheme; this ensures that the N atom is electron deficient and the methyl group electron attracting.

There remains a serious problem in attempting to calculate the inductive effect by considering the charge along only the C–N bond. In the present scheme, we fixed the carbon radius at 0.77 Å and chose the nitrogen radius to be (d − 0.77) Å where d is the C–N bond length. This implies that spheres should touch. If, however, a standard radius for nitrogen is chosen, the spheres may include an arbitrary amount of overlap or exclude more charge. The following results are obtained for

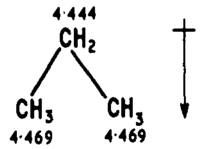

Figure 1. The direction of the dipole moment and the carbon sphere charges in propane.

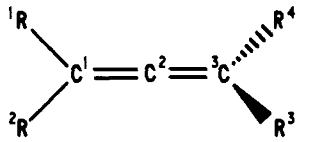

Figure 2. The allene system. $I_{\mathrm{Me}} = [q(\text{substituted allene}) - q(\text{allene})]/n$ where n = number of $-CH_3$ groups.

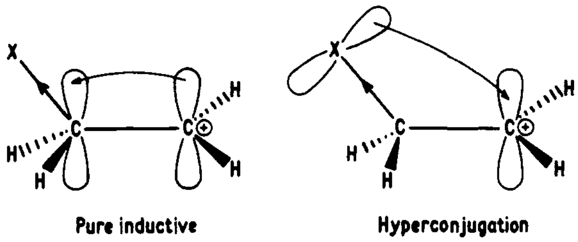

Figure 3. The electronic interactions in substituted ethyl cations.

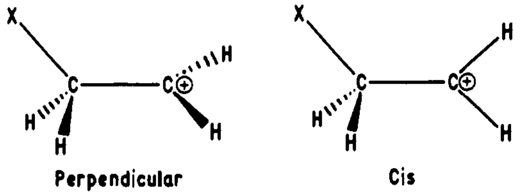

Figure 4. The relevant conformations of the substituted ethyl cations.

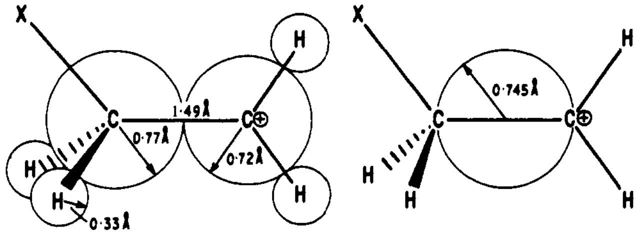

Figure 5. The positioning of sphere charges in the alkyl cations.

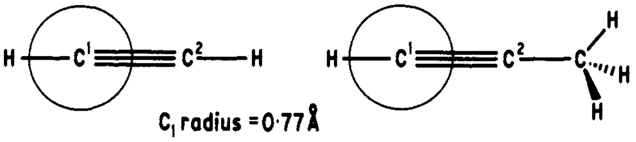

Figure 6. The C_1 atom charge sphere in ethyne and propyne.

the sphere charge around the central carbon atom for two standard radii.

Methyl groups could be seen to be electron attracting even in the presence of the highly electronegative N^+. The artifact of geometry changes in any series of compounds, contrary to Ingold's statement, does present conceptual difficulties when a quantitative investigation of the inductive effect is attempted. We, therefore, have used an approach which enables the qualitative concept of an atom in a molecule to be retained and which avoids the debate as to whether the spheres we choose should overlap.

The difficulties attendant when only the C-X bond is considered can be avoided by examining the effect of methyl substitution in the β position, for example, in the difference in sphere charges around the nitrogen in methyl- and ethylammonium cations (Table IV).

These results are in complete agreement with the initial calculations set out in Table II both in showing that the methyl group is electron donating toward the N^+ and in giving a contradiction between the trends of the sphere charge and Mulliken population analysis.

We next performed calculations on a series of substituted allenes which may be regarded as analogues of substituted methanes. Again, the inductive effect of methyl groups in a β position on the central carbon atom can be examined without the problem of bond length variations and steric effects. The results are presented in Table V with reference to Figure 2.

We conclude that a methyl group is electron repelling when attached to an unsaturated system. The gradual decrease of I_{Me} with the increase of the electron charge on C_2 is as expected. (I_{Me} is defined in Figure 2.)

Hyperconjugation in Alkyl Cations. Radom et al.[12] demonstrated using the Mulliken population analysis that for a series of β-substituted alkyl cations a distinction exists between a pure inductive effect acting along bonds and a hyperconjugative effect acting through space (Figure 3). The two relevant conformations of a substituted alkyl cation are shown in Figure 4, and are denoted perpendicular and cis.

This hyperconjugative effect, which acts only in the perpendicular case, is defined as the ability of the C-X bond to release electrons into the $2p(C^+)$ orbital, with the subsequent stability of the perpendicular conformation over the cis. With a series of common substituents Radom et al. concluded that this effect was greatest for the methyl group and least for fluorine, although in the former case "the mechanism of the electron donation into the $2p(C^+)$ orbital is not clear since the Mulliken populations indicate the methyl group to be slightly electron withdrawing (relative to hydrogen)".

Table VI gives, for each substituent, the calculated barrier to internal rotation (energy(cis) − energy(perpendicular)) and the changes (in going from perpendicular to cis) in the charge within a sphere of radius 0.72 Å on the C^+ atom (ΔC^+), and within a sphere of radius half the $C-C^+$ bond length placed at the center of the bond ($\Delta C-C^+$). These spheres are shown in Figure 5. Identical geometries were taken as in the previous study, and changing the value of the radii taken for the sphere charges over a wide range did not alter the general conclusions.

These figures suggest that in determining the relative stabilities of the two conformers this hyperconjugative effect gives rise to changes in electron density not only in the close vicinity of the carbonium center but along the whole $C-C^+$ bond.

In the cis conformation the change in the sphere charge on C^+ in replacing a β hydrogen by a methyl group yields a measure of the "through-bond" inductive effect of a methyl group in the ethyl cation system.

This gives (Table VII) a value of I_{Me} (through bond) of $+0.0074$ as opposed to $+0.0038$ for I_{Me} (hyperconjugation) as taken from ΔC^+ in Table VI. The sum of these two is the right order predicted by the previous calculations and suggests that it is the ease of polarization of the methyl group which is responsible to a large extent for the stabilization of the perpendicular conformer of the propyl cation. The mechanism of release of electrons in methyl groups by polarization is not confined to changes in electron density along the narrow line we draw as the chemical bond.

A system in which there can be little "through-space" effect is that of the substituted acetylenes. Calculations were performed to examine the inductive effect of a methyl group on the C_1 carbon atom (Figure 6).

The results (Table VIII) show that the methyl group is electropositive in this system. The calculated inductive effect

I_{Me} of +0.011 is of the same order as that in the allenes and confirms that the electron donation through the bond is dominant.

IV. Conclusions

The following conclusions can be drawn about methyl groups.

1. They are electron attracting in alkanes but electron repelling in other systems.

2. Methyl groups in systems other than alkanes should be regarded as more polarizable than hydrogen though the major electron donation occurs through the bond.

This confirms Ingold's empirical ideas about methyl groups. However, partitioning of inductive residues by calculation does require a conventional boundary for not merely the carbon atom. In organic species it requires a boundary for carbon and hydrogen and we suggest spheres of radii 0.77 and 0.33 Å, respectively. This choice is arbitrary but does not affect the conclusions if the β position approach is followed. The exclusion of approximately 25% of the charge by using spheres is mediated by the increase in the calculated inductive effect with the radius of the sphere. A number of authors[13] have commented on the result that, in molecular orbital calculations, a methyl group can appear electron attracting relative to hydrogen. We suggest that this is an artifact of the Mulliken population analysis, in particular, the equal division of the overlap charge.

The use of sphere charges is at present being applied to an investigation of orientation in aromatic substitution.

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Role of Hyperconjugation in Secondary β-Deuterium Isotope Effects

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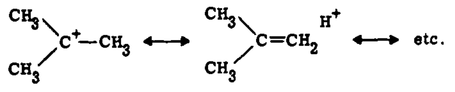
Abstract: The effect of hyperconjugation on the magnitudes of secondary β-deuterium isotope effects has been investigated by ion cyclotron resonance spectroscopy and ab initio molecular orbital theory. Isotope effects measured for ion-molecule equilibria involving formation either of a nonbonded pair of electrons or of a vacant orbital adjacent to a methyl probe have been compared to theoretical calculations which have been restricted to consideration of changes in CH stretching force constants alone. Although this simple theoretical model successfully mirrors the observed β effects in the former systems in which the methyl group acts to accept excess electron density, it fails to properly account for the observed effects in those systems where the methyl probe is adjacent to an electron-deficient center.

Introduction

The origin of β secondary deuterium isotope effects on the rates of solvolysis reactions proceeding through carbocation-like transition states has been ascribed to hyperconjugation.[2] Within the framework of transition-state theory, such isotope effects are interpreted similarly to those associated with purely equilibrium processes.[3] Thus, the observation that, in 60% ethanol, *tert*-butyl-d_9 chloride solvolyzes 2.4 times more slowly than the corresponding protio compound[4] demonstrates that the force constants involving the hydrogen positions in the transition state are smaller than those in the reactant.[5] This suggests that the structure of the *tert*-butyl cation, to which the solvolysis transition state is expected to be closely related, can be described in terms of hyperconjugative resonance structures of the form



$$(CH_3)_2C^+{-}CH_3 \longleftrightarrow H^+\ (CH_3)_2C{=}CH_2 \longleftrightarrow \text{etc.}$$

The molecular orbital analogue of hyperconjugation is the withdrawal of electrons from the filled π symmetry orbital of the methyl group into the vacant p function at the carbocation center.[6]

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