The Alkyl Inductive Effect, II
Theoretical Calculation of Inductive Parameters

Harry F. Widing and Leonard S. Levitt

Department of Chemistry, College of Science, The University of Texas at El Paso, El Paso, Texas 79968

Z. Naturforsch. **34b**, 321–326 (1979); received August 29, 1978

Alkyl Inductive Effect, Inductive Substituent Constants of Alkyl Groups

Three models of alkyl groups, "delocalization", "through-the-bond", and "electric field" models, are presented, all of which enable the calculation of $\sigma_I(R)$ from first principles, and excellent agreement is demonstrated for the calculated and experimental values of $\sigma_I(R)$. For the "delocalization" model it is found that $-\sigma_I(R) = 0.0455 + 0.0232(1-1/n)$, where n is the number of C atoms in an n-alkyl group, and for an infinite C-chain R group, $\sigma_I(R_\infty)$ is -0.0687, identical to the value found by a different method in Part I of this series. The "through-the-bond" model gives $-\sigma_I(R) = -0.0559 + 0.1015 \sum_1^n C_i/(2i-1)^2$, where C_i is the number of C-atoms in the i^{th} position from X in RX; and for the "electric field" model, we obtain $-\sigma_I(R) = 0.0463 + 0.0102 \sum_2^n C_i d_i^{-2}$, where d_i is the calculated distance from C_1 to C_n in the most probable conformation of the R-group. It is concluded that Taft's $\sigma_I(R)$ values have a real significance whether or not the physical and chemical effects of alkyl substitution reside ultimately in an internal induction mechanism, or in alkyl group polarization by charged centers in the molecule, or a combination of the two.

Introduction

This paper deals with the theoretical, rather than the experimental, basis of Taft's alkyl inductive substituent constants [1, 2] $\sigma_I(R)$. In the previous paper [3] we have found that the widely used equation [2]

$$\sigma_I(X) = 0.45\,\sigma^*(XCH_2) \qquad (1)$$

which directly relates σ_I to Taft's polar substituent constants, σ^*, to be completely invalid for alkyl groups, as is also the relation [4] $\sigma_I = 0.161\,\sigma^*$. A very simple and accurate relation between these two substituent constants was found to be [3]

$$\sigma_I(R) = \sigma_I(Me)[1-2.04\,\sigma^*(R)] \simeq -0.046\,(1-2\,\sigma^*) \qquad (2)$$

which was derived using Taft's best defined σ values: $\sigma_I(H) = 0.000$, $\sigma^*(H) = +0.490$, $\sigma_I(Me) = -0.046$, and $\sigma^*(Me) = 0.000$. Values of $\sigma_I(R)$ calculated from Taft's $\sigma^*(R)$ using Eq. (2) were found to be in excellent agreement [3, 5] with Taft's original $\sigma_I(R)$ values, and $\sigma_I(R)$ values were calculated for 23 groups for which no previous estimates were available [3]. Some of the new $\sigma_I(R)$ values have recently been used very successfully in the correlation of vapor-phase proton affinities of primary amines [6].

Since the σ parameters arising from LFER analyses are ultimately a function of the interactions within molecules, it is reasonable to predict that they will be related to spectroscopic data [7], dipole moments [2], bond energies [2], ionization potentials [8–10], and many other physical properties [2, 11, 12].

Molecular Ionization Potentials

It has been found that the first gas-phase ionization energies [8–10] of molecules RX, where R is an alkyl substituent and X a more electronegative group, correlate linearly with $\sigma^*(R)$ and $\sigma_I(R)$ for "ionization series" characterized by constant X and varying R. Some relationship is to be expected since the $\sigma(R)$ values are taken as measures of the polarizability and electron-releasing ability of the alkyl group R when attached to an electron-withdrawing group X. Hence, an R group which more effectively releases electrons to the ionization site of a molecule will correspondingly cause an increase in electron density there, and this will consequently reduce the minimum energy needed to remove an electron from it, *i.e.*, decrease the ionization potential of the molecule. Using the LFER method, the difference between the ionization

Requests for reprints should be sent to Prof. Dr. L. S. Levitt, Department of Chemistry, College of Science, The University of Texas at El Paso, *El Paso*, Texas 79968, USA.

0340-5087/79/0200-0321/$ 01.0[illegible]/0

free-energy change of a molecule RX and some standard R_OX should be expressible as the difference between the ionization energy of RX, $E_I(RX)$, and that of R_OX, $E_I(R_OX)$, so that one has

$$E_I(RX) - E_I(R_OX) = a(X)\,\sigma(R), \qquad (3)$$

where a(X) and $\sigma(R)$ are $a_I(X)$ and $\sigma_I(R)$ when R_O is H, and a*(X) and $\sigma^*(R)$ when R_O is CH_3. Here the inductive or polar effect under consideration (Π^* or Π_I) is the difference in ionization potentials, *i.e.*, the change in E_I upon substitution of R for H in HX.

Recently, the most extensive work along these lines has been done by Levitt, Levitt, Widing, and Párkányi who have linearly correlated the first gas-phase ionization potentials of seventeen series of aliphatic organic molecules with alkyl $\sigma^*(R)$ and $\sigma_I(R)$ values [9]. We have also found good results for aldehydes [5], Cu and Cr acetylacetonates [10, 13], and benzene Cr tricarbonyls [13], as well as for benzene [14], pyridine and thiophene derivatives [15]. It is interesting to note that quantum mechanical calculations using simple Hückel molecular orbital theory for obtaining values of highest occupied molecular orbitals (HOMO) have resulted, for alkenes [16], disulfides [17], alkylbenzenes [14] and for pyridine and thiophene derivatives [15] in very accurate estimations of the ionization potentials, comparing very favorably with both the experimental values and those computed from the σ_I correlations. Therefore it is possible, in general, to use the relation

$$E_I(RX) = E_I(HX) + a_I(X)\,\sigma_I(R). \qquad (4)$$

Ionization energies are values which are relatively free of molecular interaction effects, unlike measurements of rate and equilibrium constants, which involve solvent-solvent and solvent-solute dipolar and polarization interactions. Thus the $E_I(M)$ values are essentially an *intrinsic* measure of the intramolecular properties of M. Of prime importance to this paper is the information about the intramolecular processes of alkyl induction and electron-withdrawal which analysis of the E_I data affords, and it has been shown that detailed statistical analysis of such data can lead to the calculation of very accurate and reliable values for the $\sigma_I(R)$ constants [5].

Equation (3) quantitatively states that the variable group R exerts some variable polar or inductive influence over group X, which is measured by the dimensionless parameter $\sigma_I(R)$. This influence is due to electron release from R to X, a more electronegative group. Thus, as R's ability to release electrons to X increases relative to R_O, *i.e.*, as $\sigma_I(R)$ becomes a more negative quantity, RX becomes more polarized as the electron charge density at X increases while decreasing in R. Consequently, the minimum energy needed to remove an electron from RX is reduced and therefore $E_I(RX)$ is decreased relative to $E_I(R_OX)$. Thus, from the forms of the $E_I(RX)$ *vs.* $\sigma_I(R)$ plots, it can be argued that R is the electron-releaser, and X the electron-withdrawer and the ionization site of molecule RX. It can also be argued [18–23] that it is only the electronegative X group which exerts a polarizing effect on the alkyl group, which is thereby forced to yield electron density to X; and the larger and bulkier (more branched) is the R group, the greater will be its polarizability. This view is, of course, also correct, but which is cause and which is effect is merely a matter of semantics. Analogous is an H^+ transfer reaction, and the question "does the acid donate H^+ or does the base take it?"

It is interesting to note further that the greater the polarization of electron charge toward X (whether X pulls electrons or R pushes them), the greater will be the basicity and gas-phase proton [19] and nitronium ion [23] affinity of X [24]. It has been found that the gas-phase acidities of the alcohols follow a trend opposite to that observed for the solution acidities, but the same trend as the solution basicities [19, 24]. Recent quantum mechanical calculations [20] have been used to estimate total energies of the neutral, protonated, and deprotonated molecules, with the result that they have been able to reproduce the known orderings of gas-phase proton affinities. It appears that alkyl substitution makes possible the stabilization of both negative and positive ions relative to a neutral molecule ($MeOH > H_2O$ in both gas-phase acidity and basicity) by providing an extended structure which can be more effectively polarized by both cationic and anionic centers [21, 22].

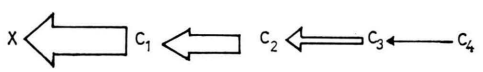
The General Nature of Polar Effects

For a molecule RX, the polar inductive effect of the group R comprises all those processes whereby it can modify the electrostatic forces operating at the reaction center X relative to the reference group

R_O acting in the molecule R_OX. Polarization resulting from differences in group electronegativities, consequent dipole formation, and electron delocalization may all contribute to these forces. In principle, polar effects can be separated into field, inductive, and resonance effects [1, 2, 11]. Field effects [25] are transmitted through space and solvent molecules (if present) in contrast to inductive effects which are transmitted directly along the bonds of the molecular chain.

The Alkyl Inductive Effect

Treatment of induction and other transmitted interactions as electron displacement effects may help to elucidate the inductive mechanism. As the electronic theory of atoms and molecules requires, intramolecular electron displacements will preserve electron pairing, doublets, octets, and other stable electron groups as completely as possible. Assuming that all displaced doublets remain bound in their original octets, it can be shown that the unequal sharing of electrons between unlike atoms (due to electronegativity differences) and consequent electrical dissymmetry within a molecule can be propagated along a chain of bonded atoms by a mechanism of electrostatic polarization and dipole induction [1]. This so-called inductive mechanism of electron displacement can be symbolized, for a carbon chain, by



where the arrows indicate the direction and magnitude of electron shift. The attentuation of the inductive effect with distance from X is a property which will be of prime importance in the "model" derivations below.

The Attenuation of Alkyl Induction with Alkyl Size

A few general remarks about the relation of the magnitude of $\sigma_I(R)$ to the structure of R seems appropriate here. For the unbranched R groups the alkyl induction of R increases with increasing carbon chain length, *i.e.*, $\sigma_I(n\text{-}C_5H_{11}) > \sigma_I(n\text{-}C_4H_9) > \sigma_I(n\text{-}C_3H_7) > \sigma_I(C_2H_5) > \sigma_I(CH_3)$. However, the attentuation of the effect with distance results in a much greater difference between $\sigma_I(CH_3)$ and $\sigma_I(C_2H_5)$ than between $\sigma_I(n\text{-}C_3H_7)$ and $\sigma_I(n\text{-}C_4H_9)$, the differences between them being 0.009 for the former and 0.002 for the latter. It has been shown [3] that a plot of $\sigma_I(R)$ *vs.* the number of carbon atoms, n, of the corresponding normal alkyl group gives a rectangular hyperbola, and can be represented by an equation of the form [3, 26]

$$-\sigma_I(R_n) = -\sigma_I(R_\infty)\left(\frac{n}{b+n}\right) \tag{5a}$$

where $\sigma_I(R_\infty)$ is the theoretical limiting value for a straight chain alkyl group of infinite length; and b in an empirical constant. On evaluation of the constants in Eq. (10), it was found [3] that $\sigma_I(R_\infty) = -0.0686$ and $b = 1/2$, whence

$$\sigma_I(R) = -0.0686\,\frac{n}{\frac{1}{2}+n} = -0.137\,\frac{n}{2n+1} = -0.137\,\frac{n_c}{n_H} \tag{5b}$$

where n and n_c are the number of C atoms, and n_H the number of H atoms in the R-group.

The magnitude of $\sigma_I(R)$, for a given number of carbon atoms in a chain, also increases with the amount of branching and closeness of C atom packing in R, so that we may write: $\sigma_I(t\text{-}C_4H_9) > \sigma_I(s\text{-}C_4H_9) > \sigma_I(i\text{-}C_4H_9) > \sigma_I(n\text{-}C_4H_9)$. These relationships of $\sigma_I(R)$ to the structure of R can be rationalized by noting that the more carbon atoms in R and the closer they are to X in RX, the greater the effect X will have in pulling electrons from R, and the greater (more negative) will be $\sigma_I(R)$.

Delocalization Model of Alkyl Induction

Thus, $\sigma_I(R_n)$, where R_n is C_nH_{2n+1}, is indeed a good measure of the alkyl inductive effect and depends on the size and degree of branching in R. The size dependence can be thought of as a delocalization effect, larger alkyl chains being associated with less localized, and therefore more easily polarizable electron clouds. A crude quantitative measure of this delocalization is given by the ratio of the number of valence electrons in a certain R group to the size of the group and is approximated by $(2+6n)/n$. This expression, which we will call D_n, can then be taken as a rough measure of the amount of electron delocalization in a carbon chain with n atoms. Scaling this ratio so that D_1 is zero and D_∞ is one, corresponding to minimum and maximum delocalization respectively, we have

$$D_n = 1 - 1/n. \quad (6)$$

For normal (*i.e.*, unbranched) alkyl groups we find that the $\sigma_I(R_n)$ values are linearly related to D_n and given by the equation

$$-\sigma_I(R_n) = 0.0455 + 0.0232\, D_n \pm 0.002. \quad (7)$$

From equations (6) and (7) we see that in the limit of very long carbon chains, *i.e.*, as $n \to \infty$, $\sigma_I(R_\infty) = -0.0687$, and this leads to

$$\sigma_I(R_n) = \sigma_I(R_\infty) + 0.0232/n. \quad (8)$$

It is interesting to note that $\sigma_I(R_\infty)$ from Eq. (8) is the same as calculated from Eq. (5b) above.

For branched alkyl groups (*i*-Pr, *i*-Bu, *s*-Bu, and *t*-Bu), equation (7) is modified by assuming that delocalization contributions made by the various parts of such groups are almost additive. For example, in order to calculate σ_I(*i*-Pr), we note that the effect on σ_I(Me) of substituting one Me group for H, thus forming the Et group, from Table I is $\sigma_I(Et) - \sigma_I(Me) = -0.009$. Therefore, assuming perfect additivity, σ_I(*i*-Pr) $- \sigma_I$(Me) should be about 2(—0.009), which it is. Any discrepancies between the perfect additivity model and the results for the branched groups in Eq. (7) have been minimized in the following equation:

$$-\sigma_I(R_n) = 0.0455 + 0.0232 \sum_{i=2}^{n} C_i (D_i - D_{i-1}). \quad (9)$$

Here C_i is the number of carbon atoms which are i bonds removed from X in RX, unless there are two or more (as in the case of branched groups), in which case C_i is multiplied by 0.845. The need for this "branching factor" can be rationalized on the following grounds: the electron releasing ability of R is thought to be affected by branching in the group because of interference effects resulting from the bonding of more than one carbon atom to another carbon atom in the group, a structural feature not found in the unbranched groups. A crude analogy to this phenomenon is seen in the case of two vector forces of equal magnitude and unequal direction acting on the same point. The resultant magnitude is not twice that of either component force, but rather a reduced value which is a function of the angle between the two forces.

Table I. $-\sigma_I(R)$ values of the model calculations compared with Taft's values.

R	(Taft)[a]	Eq. (16)	Eq. (17)	Eq. (18)	Ave. Eqs. (10, 11, 12)
Me	0.046	0.0455	0.0456	–[d]	0.046
Et	0.055	0.0571	0.0569	0.0565	0.057
n-Pr	0.058	0.0610	0.0609	0.0603	0.061
i-Pr	0.064	0.0651	0.0649	0.0649	0.065
n-Bu	0.060[b]	0.0630	0.0630	0.0629	0.063
i-Bu	0.064[c]	0.0694	0.0638	0.0604	0.064
s-Bu	0.068[c]	0.0683	0.0688	0.0687	0.068
t-Bu	0.074	0.0748	0.0744	0.0741	0.074
n-Am	0.064[c]	0.0641	0.0643	0.0651	0.064
n-R_∞	–	0.0687	–	–	0.069

[a] Ref. [1, 2]; [b] ref. [27]; [c] ref. [28]; [d] not calculated; value of 0.0460 assumed.

Written in a simpler computational form, equation (9) becomes

$$-\sigma_I(R_n) = 0.0455 + 0.0232 \sum_{i=2}^{n} C_i/i\,(i-1) \quad (10)$$

which applies to all alkyl groups, branched and unbranched, with about 1% error, except in the case of *i*-Bu whose σ_I value deviates by about 7%.

Through-the-Bond Model of Alkyl Induction

An alternative approach to the alkyl inductive effect is to consider the electrical through-the-bond interaction between R and X in RX. In deriving the final expression, the following assumptions are made: (1) the interaction between R and X is transmitted through the C–C bonds of the R group and manifested at the covalent radius of that carbon in the group which is bonded directly to X, *i.e.*, C_1, and in the direction of X; (2) the contributions of the carbon atoms of the group depend on their respective through-the-bond separation from X and are attenuated as d^{-2}; (3) the contributions are almost additive, as in the first model.

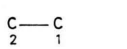
In this model a carbon atom in an R group will be notated C_i if it is i bonds removed from X. Such an atom has, from assumptions (1) and (2) an action distance of $(2i-1)r_c$ (where $r_c = 0.77$ Å) and therefore an inductive contribution to $\sigma_I(R)$ of $k(2i-1)^{-2}$, where k includes the r_c term. This through-the-bond expression is found to be linearly related to $\sigma_I(R_n)$ with less than 1% error by the equation

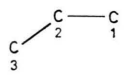
$$-\sigma_I(R_n) = -0.0559 + 0.1015 \sum_{i=1}^{n} C_i/(2i-1)^2 \quad (11)$$

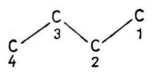
where again C_i is the number of carbon atoms in the i^{th} position from X and 0.845 times that number in the case of branching.

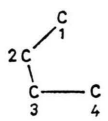
The Electric Field Model of Alkyl Induction

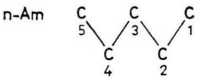
Another approach to the problem is to consider electric field effects [25]. Here the group X is considered to have a net electron-shielded charge and to interact through space with the various shielded carbon atoms of its associated alkyl substituent group. In this model, the increase in electron release from R to X, as R increases in size or becomes more branched, is again measured by $\sigma_I(R_n)$, and the following simplifications have been devised to facilitate the calculations. As with the two previous approaches, the effects of the carbon atoms in R are assumed to be almost additive. These effects are treated as coulombic interactions between point charges located at the vicinity of X and at each carbon atom of R so that the electric field effect of the i^{th} carbon's electric cloud on X is approximately $k d_i^{-2}$, where d_i is the spatial separation of the carbon atom or atoms which are i number of bonds removed from X. However, in order to render the calculation of $\sigma_I(R)$ independent of the size of X, d_i is taken as the spatial separation of C_i and C_1, where C_1 is the carbon bonded directly to X. This simplification should not seriously affect the final results since relative interactions are being considered. The interaction of C_1 and X is arbitrarily assigned the value -0.046 ($=\sigma_I(Me)$) and the action distances between C_i and C_1 were then calculated from the geometries of the unbranched R groups shown schematically below:

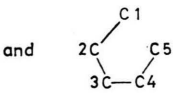
Et  $d_{12} = d_2 = 1{,}54$ Å

n-Pr  $d_{13} = d_3 = 1{,}62\, d_2$

n-Bu  $d_{14} = 1{,}5\; d_3 = 2{,}43\, d_2$

and  $d'_{14} = d_3 = 1{,}62\, d_2$

n-Am  $d_{15} = 2\, d_3 = 3{,}24\, d_2$

and  $d'_{15} = d_2$

The appropriate spatial separations given to the right of these diagrams were calculated using the C–C bond length ($d_2 = 1.54$ Å) as a reference, by assuming all C–C–C bond angles to be tetrahedral (109.5°), and by application of the law of cosines. For *n*-Bu and *n*-Am, two such distances are shown, corresponding to the smallest and largest separations of C_4 and C_5 from C_1. Since the R groups are free to rotate internally around their C–C bonds into any conformation conserving the tetrahedral angles and C–C bond lengths, the action distances of *n*-Bu and *n*-Am are approximated by the arithmetic mean of their extreme conformational separation distances. Therefore, we have $d(R_2) = d_2$, $d(R_3) = 1.62\, d_2$, $d(R_4) = (2.43 + 1.62)d_2/2 = 2.03\, d_2$, and $d(R_5) = (3.24 + 1)d_2/2 = 2.12\, d_2$. Assuming additivity to calculate branched $\sigma_I(R_n)$ values, the resulting equation is

$$-\sigma_I(R_n) = 0.0463 + 0.0102 \sum_{i=2}^{n} C_i d_i^{-2}. \quad (12)$$

The results for the 3 model calculations of $\sigma_I(R)$ (Eqs. (10, 11, 12)) are summarized in Table I and compared with the generally accepted values.

The results obtained in this paper, as well as Taft's original determination of the alkyl inductive substituent constants and the results in refs. [3] and [5] should put to rest the ideas held in some quarters, that the alkyl inductive effect is nonexistent and that $\sigma_I(R) = 0$ for all alkyl groups [18]; or that the effect does, indeed, exist but is a minor one, and the σ_I values can be known only to one significant figure [4].

[1] R. W. Taft, in M. S. Newman (ed.): Steric Effects in Organic Chemistry, Ch. 13, John Wiley & Sons, New York 1956; R. W. Taft, J. Am. Chem. Soc. **75,** 4231 (1953); R. W. Taft, J. Chem. Phys. **26,** 93 (1957).

[2] R. W. Taft and I. C. Lewis, J. Am. Chem. Soc. **80,** 2436 (1958); Tetrahedron **5,** 210 (1959).

[3] Part I: L. S. Levitt, Z. Naturforsch. **34b,** 81 (1979).

[4] M. Charton, J. Org. Chem. **29,** 1222 (1964).

[5] L. S. Levitt and H. F. Widing, Progr. Phys. Org. Chem., in press.
[6] R. W. Taft and L. S. Levitt, J. Org. Chem. **42,** 916 (1977).
[7] D. G. O'Sullivan and P. W. Sadler, J. Chem. Soc. **1957,** 4144; T. L. Brown, J. Am. Chem. Soc. **80,** 6489 (1958); R. K. Gosavi and C. N. R. Rao, Can. J. Chem. **45,** 1897 (1967).
[8] A. Streitwieser, Prog. Phys. Org. Chem. **1,** 1 (1963); B. J. Cocksey, J. H. Eland, and C. J. Danby, J. Chem. Soc. B **1971,** 790.
[9] B. W. and L. S. Levitt, Experientia **26,** 1183 (1970); B. W. and L. S. Levitt, Israel J. Chem. **9,** 71 (1971) and 711 (1971); L. S. and B. W. Levitt, J. Org. Chem. **37,** 332 (1972); L. S. and B. W. Levitt, Chem. Ind. (London) **1972,** 724; **1973,** 132; **1973,** 185; L. S. Levitt, H. F. Widing and B. W. Levitt, Can. J. Chem. **51,** 3963 (1973); H. F. Widing and L. S. Levitt, Tetrahedron **30,** 611 (1974); L. S. Levitt, B. W. Levitt, and C. Párkányi, Tetrahedron **28,** 3369 (1972); L. S. Levitt, Chem. Ind. (London) **1973,** 637; B. W. Levitt, H. F. Widing, and L. S. Levitt, Chem. Ind. (London) **1973,** 793; L. S. Levitt and C. Párkányi, Int'l Sulfur Chem. **8,** 329 (1973); H. F. Widing, B. W. Levitt, and L. S. Levitt, Israel J. Chem. **13,** 69 (1975).
[10] B. W. Levitt and L. S. Levitt, J. Coord. Chem. **3,** 187 (1973); Chem. Ind. (London) **1974,** 302.
[11] L. P. Hammett, Chem. Revs. **17,** 125 (1935); L. P. Hammett, J. Am. Chem. Soc. **59,** 96 (1937); P. R. Wells, Linear Free Energy Relationships, Academic Press, New York 1968.
[12] R. W. Taft *et al.*, J. Am. Chem. Soc. **88,** 3146 (1963).
[13] L. S. Levitt and B. W. Levitt, Tetrahedron **31,** 2355 (1975); Inorg. Nucl. Chem. **38,** 1907 (1976).
[14] C. Párkányi, B. W. Levitt, and L. S. Levitt, Chem. Ind. (London) **1977,** 356.
[15] C. Párkányi and L. S. Levitt, Z. Naturforsch. **32b,** 1160 (1977).
[16] L. S. Levitt, B. W. Levitt, and C. Párkányi, Tetrahedron **28,** 3369 (1972).
[17] L. S. Levitt and C. Párkányi, Int'l. J. Sulfur Chem. **8,** 329 (1973).
[18] C. D. Ritchie and W. F. Sager, Prog. Phys. Org. Chem. **2,** 323 (1964).
[19] J. I. Brauman and L. K. Blair, J. Am. Chem. Soc. **90,** 6561 (1968); **92,** 5986 (1970).
[20] W. J. Hehre and J. A. Pople, Tetrahedron Lett. **34,** 2959 (1970).
[21] A. Streitwieser, P. H. Owens, and R. Wolf, Tetrahedron Lett. **38,** 3385 (1970).
[22] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51,** 2657 (1969).
[23] W. B. Nixon and M. M. Bursey, Tetrahedron Lett. **1970,** 4389.
[24] L. S. Levitt and B. W. Levitt, J. Phys. Chem. **74,** 1812 (1970); Tetrahedron **27,** 3777 (1971).
[25] J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys. **6,** 506 (1938); S. Ehrenson, Prog. Phys. Org. Chem. **2,** 195 (1964).
[26] L. S. Levitt, Can. J. Chem. **31,** 915 (1953); L. S. Levitt and E. R. Malinowski, J. Am. Chem. Soc. **77,** 4517 (1955) and **80,** 5334 (1958).
[27] B. W. Levitt and L. S. Levitt, Chem. Ind. (London) **1970,** 990.
[28] L. S. Levitt and B. W. Levitt, Tetrahedron **29,** 941 (1973).