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Alkyl Substituent Effects. Part 1. An Analysis of Alkyl Inductive Properties in Terms of Group Connectivity

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Formulae are derived which express the scales of the inductive substituent constants σ_I and σ^*, the group electronegativities χ_R, and the polarisability constants P of alkyl groups in terms of base-constants and 'connectivity characteristics,' pure numbers the values of which depend only on the number of carbon atoms a group contains and the pattern of their bonding. The formulae are of predictive value in calculating σ_I, σ^*, χ_R, or P for any alkyl group and in discerning what these scales of measurement have in common and where they differ. It is shown that alkyl σ^* is not an artefact as has been claimed, that σ_I and σ^* are linear functions of alkyl group electronegativity, and that P probably has a hyperconjugative element.

The first scale of measurement for inductive effects in general was the scale of σ^* defined by the Taft–Ingold equation [1] [equation (1)]. Here the polar effect of the substituent R is evaluated relative to Me by comparison of the specific rates of base- and acid-catalysed hydrolysis of esters, RCO_2R'. The factor 1/2.48 was intended to put the measure of inductive effects obtained in this way on a scale comparable with Hammett σ values.

$$\sigma^* = [\log(k_R/k_{Me})_B - \log(k_R/k_{Me})_A]/2.48 \qquad (1)$$

The application of equation (1) to alkyl groups met early criticism: Ritchie [2,3] maintained that since σ^* values for alkyl groups are small they are properly zero, experimental values being merely artefacts of shortcomings in Taft's analysis. This and similar views have been reviewed by Shorter.[4] Persistent criticism of the reality of the σ^* scale for alkyl groups has been maintained to recent times by Charton [5-7] and by DeTar.[8] Similarly, the scale of σ_I, derived initially from σ^* but defined relative to H rather than to Me, has met the same objections.[9] Nevertheless, a substantial body of opinion has been reluctant to relinquish the notion that alkyl groups are inductively electron-donating and differentially so. Much of the evidence for this and for significant values of σ^* and σ_I for alkyl groups comes from spectroscopic observations rather than reactivities.

Thus the fact that alkylation of benzene lowers the first ionisation potential implies electron donation by the alkyl group. Dewar and co-workers [10] have analysed the photoelectron spectra of various alkylbenzenes and have concluded, from the relative effects of alkylation on their first and higher ionisation potentials, that inductive rather than hyperconjugative effects are mainly responsible for the lowering of the first potentials. This same electron donation removes the degeneracy in the frontier orbitals of benzene on monoalkylation and governs the symmetry of the distribution of unpaired electron density in derived anion radicals which can be observed by e.s.r. spectroscopy.[11]

Danby and his co-workers [12] found that first ionisation potentials of several series of aliphatic compounds are correlated by alkyl σ^* values, and Levitt and Widing [13] made similar correlations using σ_I. Indeed, the latter have used their results in a statistical analysis to define optimal σ_I values and find that equation (2) relates σ_I and σ^* for groups traditionally regarded as being electron-donating relative to hydrogen.[13]

$$\sigma_I = -0.046(1 - 2\sigma^*) \qquad (2)$$

These interpretations of correlations of ionisation potentials in terms of alkyl inductive effects have been questioned by Houk and his co-workers,[14] who prefer explanations in terms of dominant hyperconjugative effects. They found that the differences between vertical ionisation potentials of compounds HX and MeX are apparently functions of the ionisation potential of HX and of the type of orbital involved in ionisation. Thus $n(\pi)$ ionisations show the largest effect on methyl substitution, π ionisations show an intermediate magnitude of effect and $n(\sigma)$ ionisations show the least effect. A hyperconjugative interaction between these various types of orbital and a methyl group π orbital will depend in degree both on an overlap of appropriate symmetry and on the energy difference between the interacting orbitals. A hyperconjugative explanation of the observed phenomena was thus apparently nicely apposite. However, it is difficult to reconcile Widing and Levitt's [15] finding that the first ionisation potentials of n-alkanes should also be correlated by the sum of σ_I values of the component alkyl groups with an explanation in terms of hyperconjugation.

The work of Fliszar and his co-workers [16-22] also relates σ^* values to the calculation of the charge distribution in alkanes and thence to physical manifestations of this: ionisation potentials, ^{13}C chemical shifts, and thermochemical parameters. It thus seems, on this kind of evidence, that alkyl groups do have real effects which are measured by the σ_I and σ^* scales. One should ask why reactivity data apparently do not manifest them rather than assert that they do not exist.

The concept of electronegativity is fundamental to the view of chemistry from the valence-bond stand-point. The inductive and field effects of polar groups are interpreted in terms of the polarisation of heteroatomic bonds caused by differences in electronegativity. Various factors determine the electronegativity of an atom in a molecule; [23] not only is the element important *per se* but also its valence state and charge. A hybrid orbital with a high proportion of low energy *s* character is more electronegative than one with a lower proportion and, obviously, an atom in a given hybridisation state with a positive charge will have a greater attraction for electrons than one in the same state but without the charge. On formation of a covalent bond between dissimilar atoms the simplest assumption is that orbital electronegativities are equalised: charge is transferred between the atoms until this is achieved, giving the phenomenon termed the inductive effect.

The dependence of the energy E of an atom in a particular state of hybridisation upon ionic charge q is of approximately quadratic form: [23]

$$E = \alpha q + \beta q^2 + \gamma$$

Electronegativity χ is defined as the derivative of E with respect to q

i.e. $$\chi = dE/dq = \alpha + 2\beta q$$

By replacing ionic charge q by partial charge δ and coefficients for convenience, equation (3) follows for application to atoms in a molecular context:

$$\chi = a + b\delta \qquad (3)$$

In equation (3) a represents the intrinsic electronegativity of the neutral atom and is identical with the Mulliken electronegativity; the coefficient b governs the linear response of the electronegativity to the partial charge carried by the atom.

The concept of group electronegativity seeks to express the electronegativity of functional groups in similar form. Some years ago Huheey [24-26] calculated coefficients a and b for a large number of functional groups, including alkyl groups, and sought to relate the charges they induce in the ethoxycarbonyl group to the σ^* scale of inductive effects. We shall re-examine these results for alkyl groups in the course of this paper.

The final parameter relating to the electronic properties of alkyl groups which will be considered is the polarisability parameter P.[27] It has been found that gas-phase acid and base equilibria often show structural dependences very different from the corresponding equilibria in solution. One striking contrast has been the observation that alkyl groups *stabilize* anionic charge in the gas phase.[28,29] This is contrary to expectation if alkyl groups have electron-donating effects, but not so if the effects of alkyl groups are truly inductive, *i.e.* are *induced* by the function to which they are attached. Taft and his co-workers [27] (in a treatment reminiscent of Taft's classical separation [1] of inductive and steric effects leading to the scale of σ^*) attempted to separate electron-donating effects, *i.e.* the $+I$ effects ' inductive ' by common current usage, from polarisability effects P which stabilise charge of either sign, by comparison of the gas-phase protolytic equilibria (4) and (5). It was assumed that the importance of P and I is similar for the two equilibria.

$$\mathrm{ROH} + \mathrm{CH_3OH_2}^+ \rightleftharpoons \mathrm{ROH_2}^+ + \mathrm{CH_3OH} \quad -\Delta G^\circ_1 \qquad (4)$$

$$\mathrm{ROH} + \mathrm{CH_3O}^- \rightleftharpoons \mathrm{RO}^- + \mathrm{CH_3OH} \quad -\Delta G^\circ_2 \qquad (5)$$

Electron-donating I and P effects in R co-operate to drive equilibrium (4) to the right, but an electron-donating I effect opposes an electron accepting P effect in displacement of equilibrium (5) to the right.

Thus
$$-\Delta G^\circ_1 = I + P$$
$$-\Delta G^\circ_2 = -I + P$$

whence $I = 0.5(\Delta G^\circ_2 - \Delta G^\circ_1)$ and $P = -0.5(\Delta G^\circ_1 + \Delta G^\circ_2)$. The free energy differences, I, were found for different alkyl groups R to be accurately linearly correlated by Levitt and Widing's [13] σ_I, indicating that a separation of inductive effects had been achieved. The free energy sums P for different alkyl groups R thus represent their ability to stabilise adjacent charge, either positive or negative, in gas-phase ions.

Results and Discussion

(*a*) *The Scale of* σ_I.—Levitt and Widing [13] showed that σ_I values of linear alkyl groups, when plotted against n, the number of carbon atoms in the group, lie along a branch of a rectangular hyperbola given by equation (6). Although they quoted other expressions of limited applicability for reproducing σ_I for branched alkyl groups, no expression of general applicability was given.

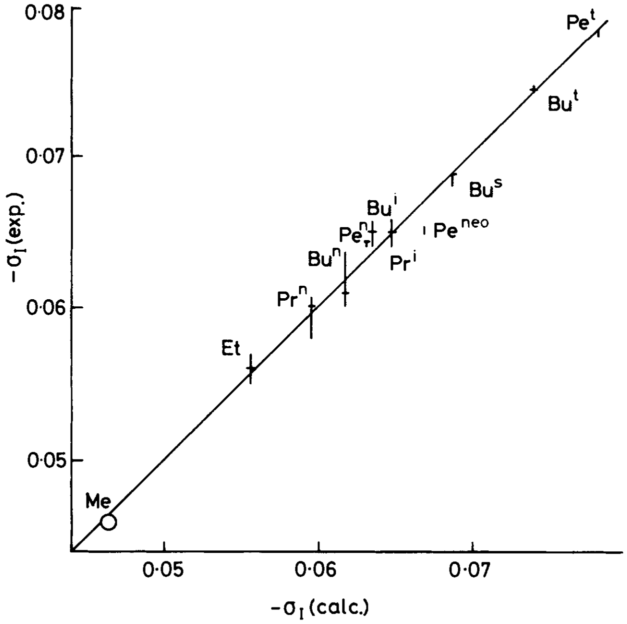

Figure 1. Plot of experimental *versus* calculated σ_I values. Vertical bars denote ranges of experimental σ_I quoted in ref. 13; horizontal bars correspond to optimal σ_I values found from ionisation potential data relative to $\sigma_\mathrm{I}(\mathrm{Me}) = -0.046$, ref. 13. The line has unit slope

This may be achieved as follows:

$$\sigma_\mathrm{I} = -0.137\,\frac{n}{(2n+1)} \qquad (6)$$

therefore

$$\sigma_\mathrm{I} = -0.137\left[\frac{(3n+1)}{(2n+1)} - 1\right]$$

whence we notice that when $n = 1$

$$\sigma_\mathrm{I} = -0.137\left\{\frac{(3n+1)}{(2n+1)} - \frac{[3(n-1)+1]}{[2(n-1)+1]}\right\}$$

Generalising for the ith carbon in the chain and summing over i we obtain for any linear alkyl group:

$$\sigma_\mathrm{I} = -0.137\sum_i\left[\frac{(3i+1)}{(2i+1)} - \frac{(3i-2)}{(2i-1)}\right]$$

$$\sigma_\mathrm{I} = -0.137\sum_i\frac{1}{(4i^2-1)} \qquad (7)$$

Equation (7) presents the σ_I value of the group as the sum of contributions from each carbon atom of the chain. Chain branching is now accommodated by introducing integral weighting coefficients n_i for carbon atoms of ith type.

i.e.
$$\sigma_\mathrm{I} = -0.137\sum_i\frac{n_i}{(4i^2-1)} \qquad (8)$$

This expression is marginally improved as a predictor of σ_I for alkyl groups of all types, not just linear, by modifying the initial constant to -0.139. In Figure 1 are plotted ranges of experimental values of σ_I, determined in both gas-phase

Table 1. Connectivity characteristics and inductive substituent constants for principal alkyl groups

R [a]	$\sum \frac{n_i}{(4i^2-1)}$	$-\sigma_I$ (calc.) [b]	$-\sigma_I$ (exp.) [c]	$-\sigma^*$ (calc.) [d]	$-\sigma^*$ (exp.) [e]
Me	0.333	0.0463	0.0460	0.000	0.000
Et	0.400	0.0556	0.0560	0.100	0.100
Pr^n	0.429	0.0596	0.0607	0.143	0.130
Pr^i	0.467	0.0649	0.0649	0.200	0.190
Bu^n	0.444	0.0617	0.0637	0.166	0.130
Bu^i	0.457	0.0635	0.0657	0.185	0.125
Bu^s	0.495	0.0688	0.0687	0.242	0.210
Bu^t	0.533	0.0741	0.0743	0.300	0.300
Pe^n	0.454	0.0631	0.0643	0.181	
Pe^i	0.460	0.0639		0.190	
Pe^{neo}	0.486	0.0675	0.0691 [e]	0.229	0.165
Et_2CH	0.524	0.0728		0.286	0.225
Pe^t	0.562	0.0781	0.0785 [e]	0.343	
Hx^n	0.461	0.0641		0.191	
$Bu^t(Me)CH$	0.552	0.0767		0.328	0.25

[a] Pe = pentyl; Hx = hexyl. [b] By equation (9). [c] Optimal values from ionisation potentials; ref. 13. [d] By equation (10). [e] Ref. 1. [f] Interpolated value, ref. 13.

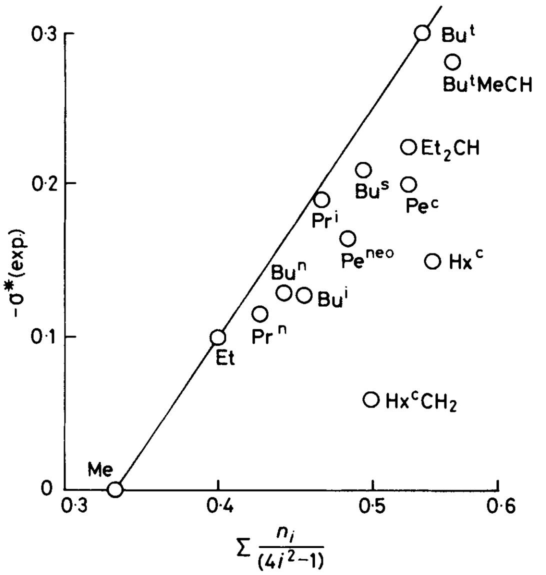

Figure 2. Plot of Taft's σ^* *versus* the connectivity characteristic for the scale of σ_I (Pe = pentyl, Pe^c = cyclopentyl, Hx^c = cyclohexyl)

and liquid-phase work and quoted by Levitt and Widing in their review,[13] against values calculated using equation (9); the line has unit slope.

$$\sigma_I = -0.139 \sum_i \frac{n_i}{(4i^2-1)} \qquad (9)$$

Equation (9) encapsulates the whole of the σ_I scale for alkyl groups; in it σ_I is equated to the product of a constant, which we call the *base constant* of the σ_I scale, and a sum of terms which we call the *connectivity characteristic* of the alkyl group for the σ_I scale. The usage ' connectivity ' is preferred to ' structure ' since the latter word usually implies information about bond lengths and angles, conformation, *etc.* Connectivity characteristics are determined solely by the number of atoms in the group and the pattern of their bonding. Values are tabulated in Table 1.

(b) *The Scale of* σ^*.—If the σ^* scale has any validity in measuring the same property of alkyl groups as does the σ_I scale it should be a function of a similar connectivity characteristic, due account being taken of the fact that the one scale is referred to Me whilst the other is referred to H. In Figure 2 Taft's original σ^* values [1] are plotted against the characteristics of the appropriate alkyl groups, given in Table 1. The α-branched sequence Me, Et, Pr^i, and Bu^t are correlated by equation (10), whilst the remaining points are scattered, apparently unsystematically, to one side of this such that their σ^* values are less than expected from the values of their connectivity characteristics.

$$\sigma^* = 0.50 - 1.50 \sum \frac{n_i}{(4i^2-1)} \qquad (10)$$

The intercept of equation (10) corresponds to the σ^* value for H (0.490) with reasonable accuracy. Other common alkyl groups such as Pr^n, Bu^n, Bu^s lie close to the line at distances comparable with the deviations in their σ^* values originally quoted by Taft.[1] A least-squares regression of σ^* upon the connectivity characteristic for all the acyclic alkyl groups gives equation (11).

$$\sigma^* = 0.44 - 1.31 \sum \frac{n_i}{(4i^2-1)}, r = 0.9679 \qquad (11)$$
$$= 0.87\left[0.50 - 1.50 \sum \frac{n_i}{(4i^2-1)}\right]$$

Thus it is evident that whether one takes the limited sequence of substituents H, Me, Et, Pr^i, Bu^t, which, however, encompasses the whole range of negative literature σ^* values, or whether one selects all the common alkyl groups, σ^* is found to be a function of the same connectivity characteristic as σ_I. Substitution of σ_I in equation (10) and rearrangement leads to Levitt and Widing's relationship [13] [equation (2)].

In his endeavour to disprove the validity of the σ^* scale for alkyl groups, Charton [6,7] applied the Taft–Ingold equation to acid- and base-catalysed amide hydrolyses and used it to define new σ^*_{amide} values which were then claimed to bear no relation to the original σ^* values, so supporting his contention. Charton's σ^*_{amide} values determined from hydrolysis at 75 °C are plotted in Figure 3 against the connectivity characteristics used above. Four of the points define a line given by equation (12); the remaining points are not correlated.

$$\sigma^*_{\text{amide}} = 0.178 - 0.538 \sum \frac{n_i}{(4i^2 - 1)},\ r = 0.9997 \quad (12)$$

$$= 0.358 \left[0.5 - 1.5 \sum \frac{n_i}{(4i^2 - 1)} \right]$$

Although only a minority of the points plotted are linearly correlated it surely is significant that their correlation takes precisely the same form as was observed in equations (10) and (11). The most deviant points are those for cycloalkyl groups. Their σ^* values are less secure than those of acyclic alkyl groups[1] and also we do not currently know whether the acyclic connectivity characteristic is strictly appropriate for them. We conclude, therefore, that although the Taft–Ingold equation gives results which are liable to large errors when applied to alkyl groups, to be expected since the right-hand side is a difference between comparable quantities, it *is* capable of discerning, in data obtained from reactivities in solution, the differences between groups that become accurately distinguishable by spectroscopic means. Thus both sides in the controversy that has arisen over the alkyl σ^* scale have a measure of right: the doubt which arose over the scale did so because the data set is flawed by error; however, once one has a criterion for making a judicious selection of data (connectivity) one may recognise in the chosen data an order which vindicates the σ^* scale and the ideas which led to it. Certainly, no major reappraisal [6,7,30] of results which have used it to describe the inductive properties of the principal α- and β-branched alkyl groups appears necessary.

(c) *The Scale of* χ_R.—Huheey [24] showed that for a general group $^-$W(X)(Y)(Z) the group electronegativity χ_{WXYZ} is given by equation (13) when orbital electronegativities are

$$\chi_{WXYZ} = \frac{a_W b_X b_Y b_Z + a_X b_W b_Y b_Z + a_Y b_W b_X b_Z + a_Z b_W b_X b_Y}{b_X b_Y b_W + b_X b_Z b_W + b_X b_Y b_Z + b_Y b_Z b_W} + \frac{b_W b_X b_Y b_Z}{b_X b_Y b_W + b_X b_Z b_W + b_X b_Y b_Z + b_Y b_Z b_W} \delta_{WXYZ} \quad (13)$$

$$= a_{WXYZ} + b_{WXYZ} \,.\, \delta_{WXYZ}$$

equalised, where a_X, a_Y *etc.* represent the intrinsic electronegativities (Mulliken electronegativities) of the atoms W, X, Y, and Z, b_X, b_Y *etc.* represent the corresponding charge coefficients, and δ_{WXYZ} is the charge carried by the group. Adapting this equation for the methyl group we obtain, after simplification, equation (14).

$$\chi_{Me} = \frac{a_C b_H + 3a_H b_C}{3b_C + b_H} + \frac{b_C b_H}{3b_C + b_H} \,.\, \delta_{Me} \quad (14)$$

$$= a_{Me} + b_{Me} \,.\, \delta_{Me}$$

If a_{Me} and b_{Me} are substituted in their explicit forms from equation (14), in equation (13), it is readily shown that for the α-branched family of alkyl groups χ_R is given by equation (15) where n is the number of carbon atoms. Similarly, by substitution of the derived expressions for a_{Et} and b_{Et} *etc.*, it is readily shown that equation (15) applies equally for linear alkyl groups and for β-branched groups and is thus of general applicability.

$$\chi_R = \frac{na_C b_H + (2n + 1)a_H b_C}{(2n + 1)b_C + nb_H} + \frac{b_C b_H}{(2n + 1)b_C + nb_H} \,.\, \delta_R \quad (15)$$

$$= a_R + b_R \,.\, \delta_R$$

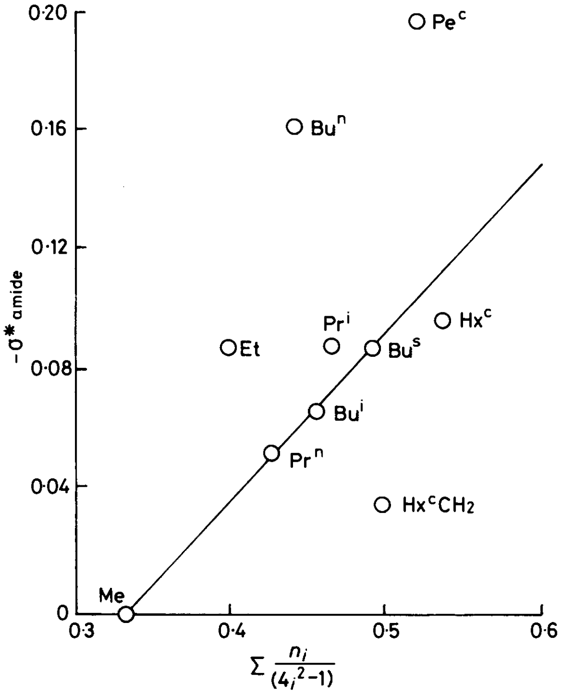

Figure 3. Plot of Charton's σ^*_{amide} *versus* the connectivity characteristic for the scale of σ_I

The values of a_R and b_R given in Table 2 were obtained using equation (15) with $a_C = 7.98$, $a_H = 7.17$, $b_C = 13.27$, and $b_H = 12.85$; these values [24] are in eV and those taken for carbon are appropriate to *sp* [3] hybridisation. As expected from Huheey's work, equation (15) does not distinguish isomeric groups. Huheey [25] maintained, however, that the group electronegativities of isomeric polar groups could be discriminated by allowing incomplete equalisation of orbital electronegativity on the formation of bonds. Values of a' and b', used as a and b above, but corrected for partial equalisation (80%) of orbital electronegativity were found; [25] the electronegativities χ of isomeric groups such as 1-, 2-, 3-, and 4-fluorobutyl groups differed principally *via* their values of a'. It was shown that for a general group $^-$W(X)(Y)(Z), a'_{WXYZ} is given by equation (16), W being the atom of attachment and p the fraction of orbital electronegativity equalised. Clearly,

$$a'_{WXYZ} = pa_{WXYZ} + (1 - p)a_W \quad (16)$$

the application of this expression to alkyl groups, equation (17), cannot distinguish isomers.

$$a'_R = p\left[\frac{na_C b_H + (2n + 1)a_H b_C}{(2n + 1)b_C + nb_H}\right] + (1 - p)a_C \quad (17)$$

Similarly we find, contrary to Huheey [25], that b'_R values derivable for alkyl groups are given by equation (18), which

$$b'_R = pb_R + (1 - p)b_C$$

$$= \frac{pb_C b_H}{(2n + 1)b_C + nb_H} + (1 - p)b_C \quad (18)$$

again does not distinguish isomeric groups. Consequently, allowance for incomplete equalisation of orbital electronegativity does not permit different group electronegativities to be distinguished for isomeric alkyl groups. However, this may be done by rearranging equation (15) as equation (19) and expressing the dependence on connectivity as was done for equation (6) in equation (8).

The coefficient B_R governs the response of the group electronegativity to the charge carried. Inverting this to obtain a parameter which increases with the size of the alkyl group, equation (24) is obtained, *i.e.* $1/B_R$ is seen to be the product of a base constant and a connectivity characteristic but also of a term which depends only on the number of carbon atoms in the group.

$$\chi_R = \frac{\dfrac{n}{(2n+1)}\dfrac{a_C b_H}{b_C} + a_H}{1 + \dfrac{n}{(2n+1)}\dfrac{b_H}{b_C}} + \frac{\dfrac{b_H}{(2n+1)}}{1 + \dfrac{n}{(2n+1)}\dfrac{b_H}{b_C}} . \delta_R \tag{19}$$

Thus,

$$\chi_R = \frac{\dfrac{a_C b_H}{b_C}\sum \dfrac{n_i}{(4i^2-1)} + a_H}{\dfrac{b_H}{b_C}\sum \dfrac{n_i}{(4i^2-1)} + 1} + \frac{\dfrac{b_H}{(2n+1)}}{\dfrac{b_H}{b_C}\sum \dfrac{n_i}{(4i^2-1)} + 1} . \delta_R \tag{20}$$

$$= A_R + B_R . \delta_R$$

Values of A_R and B_R, obtained using equation (20), are given in Table 2; there is a small but significant variation in A_R and a considerably greater one in B_R. In Figure 4 is plotted the variation of A_R with the connectivity characteristic for the scale of σ_I: the linear correlation is given by equation (21).

$$A_R = 7.244 + 0.378 \sum \frac{n_i}{(4i^2-1)}, \; r = 0.9987 \tag{21}$$

$$= 7.244\left[1 + 0.052 \sum \frac{n_i}{(4i-1)}\right] \tag{22}$$

Rearranged as equation (22) we have A_R, the group electronegativity for *uncharged* alkyl groups, expressed in terms of a base constant (7.244) and a connectivity characteristic. The base constant is the intrinsic electronegativity of the substituent with no carbons, *i.e.* it is the Mulliken electronegativity for H (actual value 7.17).

Further rearrangement gives equation (23), comparison

$$\frac{1}{0.378}\left(\frac{A_R}{7.244} - 1\right) = \frac{1}{7.244}\sum \frac{n_i}{(4i^2-1)}$$

i.e.

$$2.645\left(1 - \frac{A_R}{7.244}\right) = -0.138 \sum \frac{n_i}{(4i^2-1)} \tag{23}$$

of which with equation (9) shows that σ_I is a simple linear function of the electronegativity of *neutral* alkyl groups. Two points ensue: first, the base constant of the σ_I scale is recognised to be equal in magnitude to the reciprocal of the Mulliken electronegativity of hydrogen, the substituent to which the scale is referred; secondly, and paradoxically, the property measured by σ_I is not truly *inductive*. It is a property of alkyl groups which depends only on structure and is independent of the charge induced by any attached heteroatom. This finding relates to the results obtained by Fliszar,[16-22] who found that as the alkane structure is elaborated by formal substitution of the hydrogens of methane by methyl groups, redistribution of fractional charges occurs between C and H so that negative charge accumulates on residual unsubstituted hydrogen. By extension, ramification of the hydrocarbon structure of alkyl groups results in fractional negative charge effectively increasing at the first attached atom independently of the nature of that atom.

(d) *The Scale of P.*—Alkyl σ_I values [13] and P values [27] bear no very obvious relation to each other (Tables 1 and 3). However, a correlation becomes apparent if each value of σ_I and P is multiplied by the square root of the number of carbon atoms in the corresponding alkyl group. Figure 5 shows the variation of $P\sqrt{n}$ with $\sigma_I\sqrt{n}$; the σ_I values used in this correlation are Levitt and Widing's experimental values, determined from first ionisation potential data and given in

$$1/B_R = \frac{(2n+1)}{b_H}\left[1 + \frac{b_H}{b_C}\sum \frac{n_i}{(4i^2-1)}\right]$$

$$= 0.078(2n+1)\left[1 + 0.966 \sum \frac{n_i}{(4i^2-1)}\right] \tag{24}$$

$$P\sqrt{n} = -7.80 - 167.62\sigma_I\sqrt{n}, \; r = 0.9996 \tag{25}$$

therefore $$P = -7.80\left(\frac{1}{\sqrt{n}} + 21.48\sigma_I\right)$$

$$= -7.80\left[\frac{1}{\sqrt{n}} - 3\sum \frac{n_i}{(4i^2-1)}\right] \tag{26}$$

Table 2. Group electronegativity coefficients for alkyl groups

R	a_R	b_R	A_R	B_R
Me	7.368	3.238	7.368	3.238
Et	7.396	1.852	7.396	1.852
Pr^n	7.406	1.297	7.406	1.297
Pr^i	7.406	1.297	7.422	1.264
Bu^n	7.414	0.998	7.414	0.998
Bu^i	7.414	0.998	7.418	0.990
Bu^s	7.414	0.998	7.432	0.965
Bu^t	7.414	0.998	7.446	0.942
Pe^n	7.417	0.811	7.417	0.811
Pe^i	7.417	0.811	7.419	0.808
Pe^{neo}	7.417	0.811	7.429	0.794
Et_2CH	7.417	0.811	7.443	0.775
Pe^t	7.417	0.811	7.455	0.756
Hx^n	7.420	0.683	7.420	0.683
$Bu^t(Me)CH$	7.420	0.683	7.452	0.644

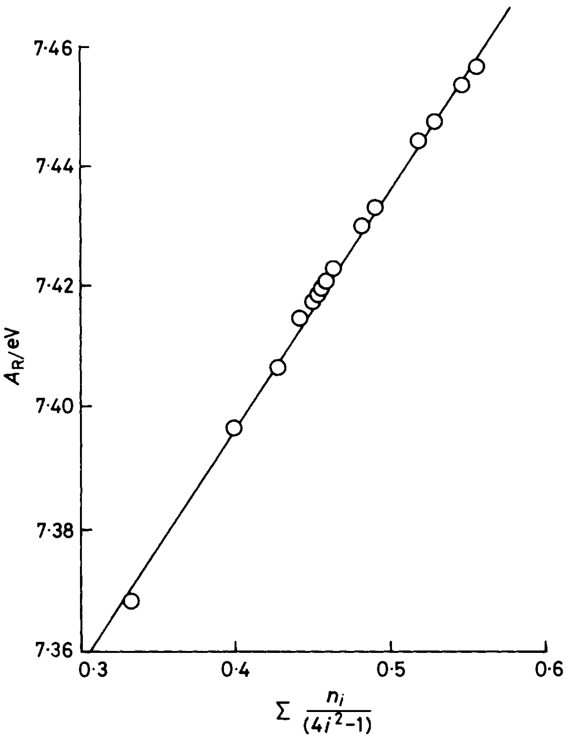

Figure 4. Variation of the intrinsic group electronegativities of neutral alkyl groups with the connectivity characteristic for the scale of σ_I

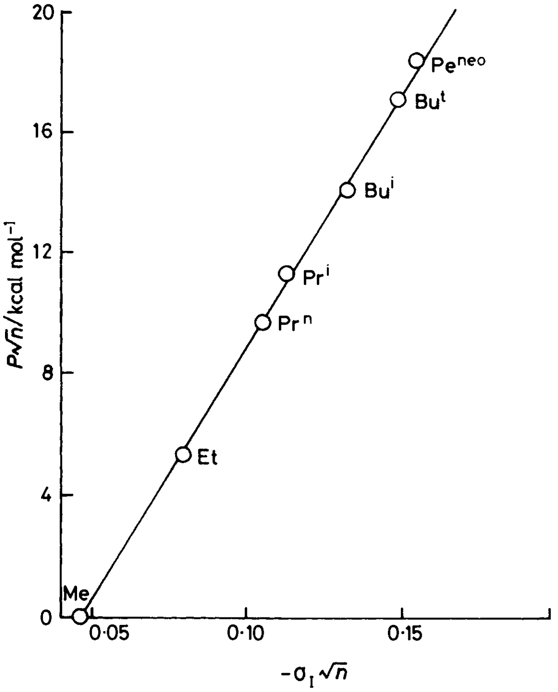

Figure 5. Variation of $P\sqrt{n}$ with $\sigma_I\sqrt{n}$ for alkyl groups

Table 3. Experimental and calculated alkyl group polarisabilities (P)

R	P (exp.) [a]	$P\sqrt{n}$	$-\sigma_I\sqrt{n}$	P (calc.) [b]	P (calc.) [c]
Me	0.0	0.00	0.0460	0.00	0.00
Et	3.8	5.37	0.0792	3.84	3.96
Pr^n	5.6	9.70	0.1051	5.53	5.60
Pr^i	6.5	11.26	0.1124	6.42	6.50
Bu^i	7.0	14.00	0.1314	6.79	6.90
Pe^{neo}	8.2	18.33	0.1545	7.88	8.01
Bu^t	8.5	17.00	0.1486	8.57	8.40

[a] In kcal mol^{-1} (±0.2); ref. 27. [b] By equation (26). [c] By equation (31).

Table 1, with the exception of the value for Pe^{neo} (−0.069) which is an interpolated value given in Table 9 of their review.[13] The least squares line of Figure 5 is given by equation (25). Substitution for σ_I in terms of the connectivity characteristic previously deduced [equation (9)] enables P to be expressed as the product of a base constant and a connectivity characteristic, equation (26).

From equation (26) we see that this connectivity characteristic comprises a difference between two terms, both of which vary with the alkyl group, the one merely with the number of carbon atoms contained, the other with their connectivity. When the stability of a gaseous ion is influenced by both the polarisability and the inductive effects of an alkyl substituent, the relative weighting of the two terms within the characteristic varies: the inductive effect will diminish or augment the second term according to whether the ion is cationic or anionic and the two effects therefore co-operate or oppose each other.

Further light is shed on the nature of P by the following observations. First, for the α- and β-branched alkyl groups $P\sqrt{n}$ is a linear function of n. The lines of Figure 6 are given by equations (27) and (28). It is apparent also from Figure 6 that

$$\alpha\text{-branching}\quad P\sqrt{n} = -5.81 + 5.69n, \quad r = 0.9998 \qquad (27)$$

$$\beta\text{-branching}\quad P\sqrt{n} = -3.26 + 4.32n, \quad r = 1.0000 \qquad (28)$$

the values of $P\sqrt{n}$ for *linear* alkyl groups lie along a curve. If it is assumed that this curve is a branch of a rectangular hyperbola (hyperbolic character seems reasonable in view of the linear correlation for $P\sqrt{n}$ with $\sigma_I\sqrt{n}$, where σ_I is hyperbolic), equation (29) may be deduced for linear alkyl groups which reproduces the P values of Me, Et, and Pr^n within the experimental errors quoted by Taft *et al.*[27] Moreover, by evaluating the increments in $P\sqrt{n}$ for integral increase in n, it is readily shown that equation (30), which sums the contribution of individual carbon atoms, is equivalent to equation (29).

$$P\sqrt{n} = \frac{36.23(n-1)}{(4.47+n)} \qquad (29)$$

$$P\sqrt{n} = 36.23 \sum_{i=2} \frac{5.47}{(4.47+i)(3.47+i)} \qquad (30)$$

The introduction of weighting terms into this expression allows for branching in the alkyl group, *cf.* the treatment of equations (6), (7), and (8), and yields equation (31) which reproduces all the P values given by Taft *et al.*[27] within their experimental errors (Table 3). Equation (31) is the product of

$$P = \frac{198.18}{\sqrt{n}} \sum_{i=2} \frac{n_i}{(4.47+i)(3.47+i)} \qquad (31)$$

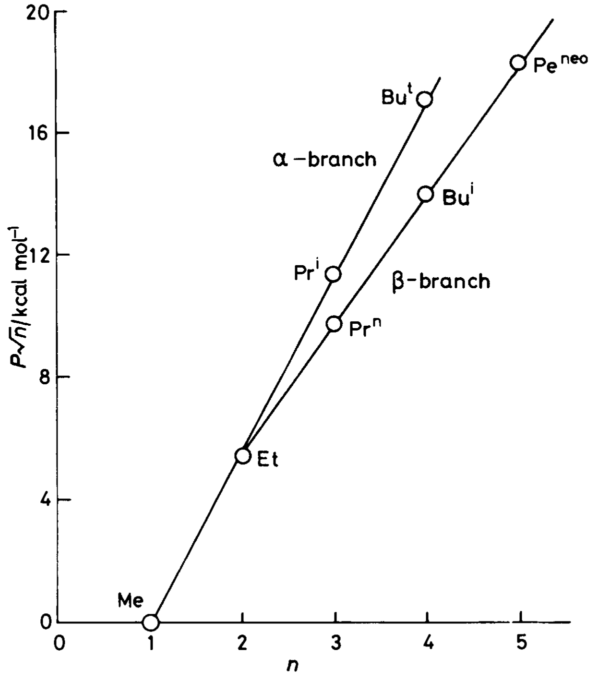

Figure 6. Variation of $P\sqrt{n}$ with n for simple α- and β-branched alkyl groups

a base constant for the scale of P and a connectivity characteristic obtained independently of the characteristic for σ_I. However, like its alternative, it shows a $1/\sqrt{n}$ dependence.

Recent treatments of the ambivalent behaviour of alkyl groups in stabilising both positive and negative charge have involved hyperconjugative mechanisms. Hudson and his co-workers[31] considered the effect of alkylation on the gas-phase and solution acidities of alcohols in terms of a perturbational treatment, and Hehre and his co-workers[32-35] used a similar method in interpretation of secondary isotope effects on gas-phase equilibria. Brauman *et al.*[36,37] have elaborated the method in accounting for trends in electron affinities, pointing out that the quantum mechanical treatment is the equivalent of the classical ion-induced dipole model of polarisability and predicting that alkyl group polarisabilities should correlate with the stabilities of gas-phase alkoxide anions. If this is so and the scale of P indeed measures alkyl polarisabilities, then P should relate to alkoxide ion stabilities.

For an alkoxide anion regarded as resulting from the union of a tetrahedral alkyl radical with O—•, the stabilisation of a $p(\pi)$ lone pair orbital φ_O on O by interaction with an alkyl π^* anti-bonding orbital φ_R is given to second order by perturbation theory[38] to be approximately ΔE in equation (32), where E_R is the energy of φ_R and E_O is the energy of

$$\Delta E = \frac{|\int \varphi_R \varphi_O d\tau|^2}{|E_O - E_R|} \qquad (32)$$

φ_O. Such stabilisation will be large when E_R and E_O are similar, so their difference in the denominator of equation (32) is small. Thus the greatest stabilisation of the alkoxide ion will result from the interaction of φ_O with the lowest unoccupied molecular orbital (LUMO) of appropriate symmetry and will be the greater the lower is the energy of the LUMO of the alkyl group.

Figure 7 shows the variation of the first ionisation potentials of alkanes, I_p, with $1/\sqrt{n}$. The linear correlation is given

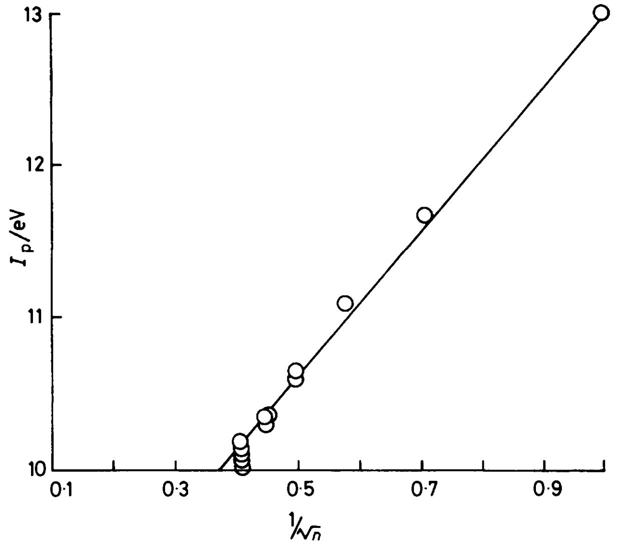

Figure 7. Plot of first vertical ionisation potentials for C_1—C_6 alkanes *versus* $1/\sqrt{n}$; data from ref. 20

by equation (33). (Previously, Widing and Levitt[15] reported

$$I_p = 8.26 + 4.69/\sqrt{n}, \ r = 0.9975 \qquad (33)$$

a hyperbolic correlation for linear alkanes but this had specifically excluded methane.) From equation (33) and Koopmans' theorem,[39] it follows that the energies of the alkane HOMOs are given by an expression of the form of equation (34). If such an expression is also valid for the energies E_R of

$$E = \frac{K\sqrt{n} + L}{\sqrt{n}} \qquad (34)$$

alkyl group LUMOs used in equation (30), the occurrence of a $\sqrt{n}$ dependence of P can be understood, but an explicit correlation of $\delta\Delta E$ and P in terms of n requires information on the n-dependence of both the numerator of equation (32) and the number of interactions of the type it represents.

(e) *Conclusion.*—The additivity of isotropic electronic properties of alkyl derivatives, such as molecular refractivity,[40] has long been known. The definition and use of connectivity characteristics permits their anisotropic properties to be quantified in terms of notional diminishing contributions from successive shells of carbon atoms which radiate from the carbon atom of attachment of the group. Such a treatment for the alkyl inductive effect reflects the traditional 'through-bond' view of the effect. The fact that the scale of σ_I, derived from ionisation potentials, can be accurately expressed in terms of a simple connectivity characteristic supports the contention that σ_I measures a through-bond effect.

The correlation of σ^* values of the principal alkyl groups by a connectivity characteristic similar to that for σ_I (the difference between the two characteristics arising from the different reference points of the two scales) proves that the σ^* scale is not spurious; it is flawed by error but the connectivity approach permits both the detection of the erroneous experimental values and the calculation of correct ones. Both the σ_I and σ^* scales measure a unidirectional electron-donating effect, the origin of which lies in the variation of alkyl group structure and not in the inductive properties of any attached heteroatom. This conclusion, which is generally consistent with Fliszar's [16-22] work on alkanes, is strongly supported by the relation of the σ scales to the intrinsic electronegativities of the neutral alkyl groups and hence to 'fundamental' quantities such as the valence-state electronegativities of carbon and hydrogen. Additionally, this correlation militates against any hyperconjugative dependence of the inductive σ scales.

When alkyl groups are attached to heteroatoms, charged in either sense, their response appears to be governed by a characteristic which depends in part on the connectivity of the group. It seems reasonable to identify this as the truly inductive part, and to assume that adjacent charge elicits from the alkyl group a redistribution of its internal partial charges, the nature of which is governed, like the I effect, by the bonding pattern. Both P and $1/B_R$ are measures of the response of alkyl groups to adjacent charge and both their connectivity characteristics contain the same connectivity-dependent term, *cf.* equations (24) and (26). Interestingly, both also show an additional dependence on n, although on different functions of n. As measures of alkyl response to adjacent charge of either sign, P and $1/B_R$ are quite independent; the former is of a more direct experimental origin; the latter being theoretical and based on an initial assumption that group electronegativity is a linear function of borne charge. On these grounds we prefer P, and believe it is the more likely to exhibit the truer n-dependence. As further evidence for this is the finding that an independently deduced connectivity characteristic for P [equation (31)] also shows $1/\sqrt{n}$ dependence. Current views on the polarisability of alkyl groups include a hyperconjugative element; since alkane ionisation potentials have a $1/\sqrt{n}$ dependence it seems plausible to generalise this to alkyl group frontier orbitals and ascribe to the $1/\sqrt{n}$ dependence of P a hyperconjugative origin.

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