Charge Distributions and Chemical Effects. V. A Modified Population Analysis. Application to Carbon-13 Nuclear Magnetic Resonance Shifts

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Abstract: Atomic charges calculated from Taft's polar σ^* constants are in agreement with theoretical charges both for (i) the original set of theoretical results and (ii) a modified set which is deduced from the former under the assumption of a nonequal partitioning of the overlap populations between bonded C and H atoms. The charge distributions in alkanes corresponding to a "best electroneutrality" scheme are described. In terms of the inductive formulas, this condition is met with $n \simeq -4.4$. At this level, several different theoretical methods yield relatively similar results, quite unlike their original uncorrected counterparts. In alkanes, the C^+–H^- polarity appears to be representative of the inductive effects; the "retention" of negative charge by the H atoms is coherent with, and reflected by, the net electron transfer from the CH_N groups containing fewer H atoms toward the CH_N groups possessing more H atoms (*e.g.*, from CH_2 toward CH_3). This provides a simple rationale for the inductive effects exhibited by the alkyl groups. Finally, carbon-13 chemical shifts correlate with C net charges calculated for $n = -4.4122$, with a standard deviation of 0.3 ppm.

A comparison[2–4] of "inductive" charge distributions $f(n, \beta)$ with their quantum-mechanical counterparts has revealed that the latter are quite similar among themselves in that they reflect the customary inductive effects of the alkyl groups. The set of "inductive" charges $f(n, \beta)$ represents a summary of sets of theoretical results. Of course, the n and β values to be used differ from case to case:[4] $n = 0.525$, $\beta = -11$ melectrons (PCILO); $n = 25$, $\beta = -504$ melectrons (BO, *ab initio*); $n = 1.3325$, $\beta = -20.96$ melectrons (STO-3G, fully optimized). This raises the obvious question about the "true" value of n, and this shall be discussed keeping in mind possible comparisons with experimental data. The results,[2–5] presented in Table I, are used as examples.

To begin with, let us examine a property which we suppose to be linearly related to q_H. From the equation[4] $q_H = a\sigma^* + b = -(10\sigma^* + n + 1)\beta/3n$ it follows that the hydrogen net charges calculated using different n values are linearly related one to another. Consequently, such a property is linearly related to the H charges given by *any* theoretical method, irrespective of its corresponding n value, provided only that the theoretical results are in satisfactory agreement with the set of "inductive" charges.

The situation is different for the charges on carbon atoms;[4] a comparison between C net charges calculated from the "inductive" set of equations (Table I) using different n values indicates that the scaling, and even the relative ordering of the various C charges, depend upon the choice of n. Consequently, if a property is expected to correlate with C net charges, it is imperative that the latter correspond to the "proper" n value. In principle, the "proper" n value should be determined from an examination of the property–charge relation-

ship involving experimental results. Fortunately, this turns out to be relatively simple (as explained below) provided that an adequate set of theoretical results is available. There is, however, a particular value for n which merits attention: that which corresponds, in a certain way, to a condition of "best possible electroneutrality."

For the set of molecules, each of which contains two different C atoms q_i and q_j, a possible formulation can be derived from the condition that the sum $\Sigma(q_i - q_j)^2$ (over the set) be minimum, *i.e.*, that the various C atoms of the set be as similar as possible. Using the inductive equations of Table I, it is found[6] that the equation $\partial\Sigma(q_i - q_j)^2/\partial n = 0$ is satisfied by $n = -4.4$. This n value appears to correspond to a real physical situation which will be discussed further below.

Table I. Charge Distributions

Molecule	Atom	Net charge, rel units	Net charge, 10^{-3} eu		
			PCILO[a]	STO-3G[b]	Ab initio BO[c]
Methane	C	$4(n + 1)/3n$	−43.3	−48.92	−699
Ethane	C	1.000	−10.4	−20.96	−504
Propane	C_{prim}	$(3n + 0.55)/3n$	−14.6	−23.81	−508
	C_{sec}	$(2n - 3.8)/3n$	+20.2	+5.94	−303
	H_{prim}	$(0.15 - n)/3n$	+2.0	+6.23	+167
	H_{sec}	$(0.9 - n)/3n$	−3.9	+2.20	+160
Butane	C_{prim}	$(3n + 0.43)/3n$			−504
	C_{sec}	$(2n - 3.35)/3n$			−309
	H_{prim}	$(0.24 - n)/3n$			+165
	H_{sec}	$(1.1 - n)/3n$			+159
Isobutane	C_{prim}	$(3n + 1.03)/3n$	−19.6	−26.34	
	C_{tert}	$(n - 7.7)/3n$	+51.3	+33.39	
	H_{prim}	$(0.29 - n)/3n$	+1.1	+5.50	
	H_{tert}	$(2 - n)/3n$	−10.5	−3.51	
Neopentane	C_{prim}	$(n + 0.49)/n$	−19.9	−28.66	
	C_{quat}	$-4/n$	+82.0	+62.92	
	H	$(0.51 - n)/3n$	+0.2	+4.31	

[a] From ref 2. [b] From ref 3 and 4. [c] From ref 5.

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(2) S. Fliszár and J. Sygusch, *Can. J. Chem.*, **51**, 991 (1973).

(3) G. Kean and S. Fliszár, to be submitted for publication.

(4) S. Fliszár, G. Kean, and R. Macaulay, *J. Amer. Chem. Soc.*, **96**, 4353 (1974).

(5) J. R. Hoyland, *J. Chem. Phys.*, **50**, 473 (1969).

(6) The propane, butane, isobutane, and neopentane results were used for this calculation. The results for 2,2,3,3-tetramethylbutane, the only other molecule possessing two different carbon atoms, are not available.

It is noted that $n = -4.4$ is equivalent to saying that in the alkanes the carbon atoms carry net positive charges,[7] a result which is also indicated by Bader's calculations on methane.[8] The chemical aspects associated with this C^+-H^- polarity are discussed further below. First, we shall examine how this result can be tied in with the "usual" theoretical results indicating (INDO is an exception[4,9]) a C^--H^+ polarity.

A Modified Population Analysis

In the Mulliken "population analysis" method[10] for calculating the gross electronic charge, Q_μ, associated with atom μ, the overlap population $\Sigma P_{\mu\nu}S_{\mu\nu}$ is divided equally between atom μ and its overlap partner. Several modifications of the Mulliken scheme have been proposed[11] in an attempt to find a more realistic basis for partitioning the overlap charge. In any such attempt, the basic difficulty rests in the proper choice of the criterion guiding the allocation of the overlap population.

Here we suggest a modification concerning only the distribution of the overlap population $\Sigma P_{\mu\lambda}S_{\mu\lambda}$ between bonded, dissimilar atoms (i.e., bonded C-H atoms in the present case), all other overlap terms $\Sigma P_{\mu\nu}S_{\mu\nu}$ being treated in the usual way (eq 1).

$$Q_\mu = \Sigma P_{\mu\mu} + {}^1\!/_2 \Sigma P_{\mu\nu}S_{\mu\nu} + {}^1\!/_2(1 \pm k)\Sigma P_{\mu\lambda}S_{\mu\lambda} \quad (1)$$
$$\text{(bonded C-H)}$$

The weighting factor k causes the departure from the half-and-half assignment to C and H of the C-H overlap population. The $+$ sign is chosen for the calculation of Q_H and $-$ for Q_C. The difference between this expression for the gross electron population and the corresponding Mulliken gross charge $Q_\mu{}^0$ is thus $\pm {}^1\!/_2 k \Sigma P_{\mu\lambda}S_{\mu\lambda}$.

$$Q_\mu = Q_\mu{}^0 \pm (k/2)\Sigma P_{\mu\lambda}S_{\mu\lambda} \quad (2)$$

With this modification, the "net" charges $q_H = 1 - Q_H$ and $q_C = 6 - Q_C$ are therefore

$$q_H = q_H{}^0 - (k/2)\Sigma P_{\mu\lambda}S_{\mu\lambda} \quad (3)$$

$$q_C = q_C{}^0 + (k/2)\Sigma P_{\mu\lambda}S_{\mu\lambda} \quad (4)$$

where $q_H{}^0$ and $q_C{}^0$ are the net charges corresponding to

(7) The Taft order of electron-releasing ability $tert$-$C_4H_9 > \ldots >$ CH_3 is satisfied only when the ethane polarities are C^+-H^- with $n < 0$ or C^--H^+ if $n > 0$.[2,4] It should also be noted that the term "C^+-H^- polarity" is not interpreted in a restrictive way as a bond polarity since the bond itself has not been defined. Moreover, when saying that a C atom is positive in a hydrocarbon molecule, one simply means that this atom has lost some of its electronic charge in the molecule with respect to its atomic state. It is not implied that the charge released by the carbon atoms in the molecule should necessarily "belong" to the H atoms. At this stage, it is only a question of practical formalism, conforming with a simple charge normalization scheme, that all the charges released by the carbon atoms are attributed to the H atoms as if they belonged to them.

(8) R. F. W. Bader and H. J. T. Preston, Theor. Chim. Acta, 17, 384 (1970).

(9) D. R. Salahub and C. Sándorfy, Theor. Chim. Acta, 20, 227 (1971).

(10) R. S. Mulliken, J. Chem. Phys., 23, 1833, 1841, 2338, 2343 (1955).

(11) P. O. Löwdin, J. Chem. Phys., 21, 374 (1953); D. Peters, J. Chem. Soc., London, 2015 (1963); P. Ros and G. C. A. Schuit, Theor. Chim. Acta, 4, 1 (1966); M. Pollak and R. Rein, J. Chem. Phys., 47, 2045 (1967); E. R. Davidson, ibid., 46, 3320 (1967); C. A. Coulson and G. Doggett, Int. J. Quantum Chem., 2, 825 (1968); E. W. Stout and P. Politzer, Theor. Chim. Acta, 12, 379 (1968); G. Doggett, J. Chem. Soc. A, 229 (1969); P. Politzer and R. R. Harris, J. Amer. Chem. Soc., 92, 6451 (1970); K. Jug, Theor. Chim. Acta, 31, 63 (1973).

the original mode of partitioning of the overlap populations.

It is further assumed that the C-H overlap populations are practically the same in all cases considered here and, hence, that the term $p = k\Sigma P_{\mu\lambda}S_{\mu\lambda}/2$ can be safely treated as a constant. This is supported by the STO-3G calculations[3] which indicate that no C-H overlap charge deviates by more than 1% from the average $\Sigma P_{\mu\lambda}S_{\mu\lambda}$ value of 0.759 for one C-H bond. Therefore, noting that the C atoms can have N hydrogen atoms bonded to them, in this approximation one obtains the result that

$$q_H = q_H{}^0 - p \quad (5)$$

$$q_C = q_C{}^0 + Np \quad (6)$$

We can now examine how the modified charges q_H and q_C compare with their original counterparts within the scheme of inductive effects. Applying the "inductive" equations to the compounds R-H it is found that

$$q_H = -(10\sigma^*{}_R + 1 + n)\beta/3n \quad (7)$$

and

$$q_H{}^0 = -(10\sigma^*{}_R + 1 + n^0)\beta^0/3n^0 \quad (8)$$

where n^0 and β^0 are the parameters corresponding to the original densities $q_H{}^0$. It is clear that the transformation (eq 5) does not change the slope of the hydrogen net charges vs. $\sigma^*{}_R$, thus indicating that

$$\beta/n = \beta^0/n^0 \quad (9)$$

From the comparison of eq 5, 7, 8, and 9, it also follows that

$$n = n^0(1 + (3p/\beta^0)) \quad (10)$$

as well as

$$p = (\beta - \beta^0)/3 \quad (11)$$

Finally, from the charge of the quaternary C atom in neopentane (Table I), $q_{C_{quat}} = -4\beta^0/n^0 = -4\beta/n$, it follows that

$$\beta = -nq_{C_{quat}}/4 \quad (12)$$

The discussion of the above equations and of some interesting implications contained therein shall be presented further below. First we wish to look at the results.

Results

The modification which was suggested for the partitioning of the overlap populations does not concern the C-C overlap terms. Consequently, the charges of the groups listed in Table II, all of which are attached only to carbon atoms, are not affected by this modification. Severe errors in the estimate of these group charges are therefore unlikely since the usual halving of the overlap charge between the group C atom and the C atom(s) of the remainder of the molecule is reasonable.

These results indicate that the group charges predicted by the different methods are not nearly as dissimilar as one might expect from a superficial inspection of the results given in Table I. The comparison made in Table II appears to be more significant than a mere comparison of charges on C atoms attached to H atoms

Table II. Net Charges of Isolated Groups[a]

Molecule	Group	"Inductive"	EHMO	CNDO/2	INDO	PCILO	STO-3G	BO
		n	9.5	0.35	−2	0.525	1.3325	25
Propane	CH_3	$\beta/3n$	−12.5	−6.5	−8	−6.2	−5.12	−7
Butane	CH_3	$1.15\beta/3n$	−15	(−8.3)	−13	(−8.0)	(−6.03)	−9
Isobutane	CH_3	$1.9\beta/3n$	−24.3	−11.7	−19	−13.6	−9.96	(−13)
Neopentane	CH_3	$3\beta/3n$	−34.3	−15.4	−23	−20.5	−15.73	(−20)
Propane	CH_2	$-2\beta/3n$	+25	+13	+20	+12.4	+10.34	+17
Butane	CH_2	$-1.15\beta/3n$	+14	(+8.3)	+13	(+8.0)	(+6.03)	+9
Isobutane	CH	$-5.7\beta/3n$	+73	+35.1	+55	+40.8	+29.89	(+38)
Neopentane	C_{quat}	$-4\beta/n$	+137	+61.5	+97	+82.0	+62.92	(+81)

[a] The results indicated in parentheses are calculated from the inductive formulas. All other values are deduced from the original literature: EHMO (R. Hoffmann, *J. Chem Phys.*, **39**, 1397 (1963)); CNDO/2, ref 2; INDO, ref 9; PCILO, ref 2; STO-3G, ref 3 and 4; BO, ref 5.

Table III. Modified Population Analyses ($n = -4.4$)

Molecule	Atom	Relative charge	Modified PCILO	"Inductive" from PCILO	STO-3G modified	BO modified
Methane	C	1.0303	93.8	94.6	71.31	91.8
Ethane	C	1.0000	92.4	91.8	69.21	89.1
Propane	C_{prim}	0.9583	88.2	88.0	66.36	85.1
	C_{sec}	0.9545	88.7	87.7	66.05	92.4
	H_{prim}	−0.3447	−32.3	−31.7	−23.83	−30.7
	H_{sec}	−0.4015	−38.2	−36.9	−27.86	−37.7
Butane	C_{prim}	0.9674		88.8		89.1
	C_{sec}	0.9205		84.5		86.4
	H_{prim}	−0.3515		−32.3		−32.7
	H_{sec}	−0.4167		−38.3		−38.7
Isobutane	C_{prim}	0.9220	83.2	84.6	63.81	
	C_{tert}	0.9167	85.6	84.2	63.44	
	H_{prim}	−0.3553	−33.2	−32.6	−24.59	
	H_{tert}	−0.4848	−44.8	−44.5	−33.56	
Neopentane	C_{prim}	0.8886	82.8	81.6	61.51	
	C_{quat}	0.9091	82.0	83.5	62.92	
	H	−0.3720	−34.1	−34.1	−25.75	

(*e.g.*, the C charges in ethane), since the latter are strongly dependent upon the choice made for partitioning the C–H overlap populations.

We can now transform the charge densities derived from theoretical methods into equivalent sets of results corresponding to any n value of our choice. In the following example, n is taken as −4.4. First, the relative charges (in terms of n) of Table I are calculated for $n = -4.4$. The results are given in Table III. Next, we must calculate the value of β for $n = -4.4$. This calculation is illustrated taking the STO-3G results as an example.

For this set of results, it is deduced from eq 9 that $\beta = -4.4\beta^0/n^0 = 69.21$ melectrons. From eq 11, it follows that $p = 30.0567$ melectrons. With this p value, the modified charges derived using *only* the original STO-3G data are calculated by means of eq 5 and 6 (Table III). The corresponding "inductive" charges are simply obtained from a multiplication of the charges indicated in relative units by $\beta = 69.21$ melectrons. Of course, the sets of "inductive" and modified theoretical results are virtually identical.

Similar recalculations from PCILO and BO results (given in Table I) are also reported in Table III, for $n = -4.4$. These modified charges turn out to be similar in magnitude to the corresponding STO-3G charges, quite unlike the original results of Table I.

Another example indicating that very dissimilar original sets of charge distributions generate sets of similar magnitude after correction to a common n value is presented in Table IV. Here, the STO-3G results of

Table IV. A Comparison of STO-3G Results Modified for $n = 42.3$ with *Ab Initio* 7s3p/3s Results

Molecule	Atom	Net charges, eu Modified STO-3G	7s3p/3s
Methane	C	−0.84	−0.79
Ethane	C	−0.61	−0.57
Propane	C_{prim}	−0.62	−0.58
	C_{sec}	−0.39	−0.38
Butane	C_{prim}	−0.61[a]	−0.56
	C_{sec}	−0.39[a]	−0.37
Isobutane	C_{prim}	−0.62	−0.55
	C_{tert}	−0.16	−0.18

[a] Calculated using the "inductive" formulas for the original STO-3G charges.

Table I are modified for $n = 42.3$, which is the n value corresponding to André's 7s3p/3s calculations.[12]

The similarity of the charges derived from a variety of methods after modification to a common n value is illustrated in Table V. This comparison is made as follows. First, we calculate the β values corresponding to each theoretical method, assuming in each case the same n value, chosen arbitrarily. Next, the average $\bar\beta$ is calculated from these data and is chosen as a common arbitrary reference. Finally, the ratios $\beta/\bar\beta$ are calculated. These ratios indicate that the charges given by each selected method are $\beta/\bar\beta$ times those of the corresponding charges of the standard of reference.

(12) J. M. André, P. Degand, and G. Leroy, *Bull. Soc. Chim. Belg.*, **80**, 585 (1971).

Table V. A Comparison of the Ratio $\beta/\bar{\beta}$ for Any Common n Value

Method	$\beta/\bar{\beta}^a$
INDO	1.5
CNDO/2	0.94
PCILO	0.90
RCNDO	1.0
PPP	0.73
EHMO	1.6
STO-3G standard	1.1
STO-3G optimized	0.68
BO	0.87
7s3p/3s	0.58

^{a} Calculated from the original charge distributions: CNDO/2,[2] PCILO,[2] STO-3G,[3] BO,[5] INDO,[9] RCNDO,[9] EHMO (R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963)), 7s3p/3s,[12] and PPP (S. Katagiri and C. Sándorfy, *Theor. Chim. Acta*, **4**, 203 (1966)).

Figure 1. Proton chemical shifts, relative to TMS, *vs.* Taft's polar σ^* constants. In the order of increasingly negative σ^* values, the empty circles[23] correspond to C_3H_8, C_4H_{10}, i-C_4H_{10}, *neo*-C_5H_{10} (H_{prim}, $\delta \sim 1$), C_3H_8, C_4H_{10}, C_5H_{10} (H_{sec}, $\delta \sim 1.4$), and H_{tert} of i-C_4H_{10}. The other points are, in the same order, those measured (A. G. Moritz and N. Sheppard, *Mol. Phys.*, **5**, 361 (1962)) for CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, *neo*-C_5H_{10} (H_{prim}), C_3H_8 (H_{sec}), and i-C_4H_{10} (H_{tert}).

The fact that for both semiempirical and *ab initio* calculations all the $\beta/\bar{\beta}$ values lie in a narrow range indicates that for any common n value the modified charges are not nearly as dissimilar as their original counterparts.

There is one final observation which is of practical use. Suppose we are studying a property P which we assume to be related linearly to the carbon charges by the equation $P = Aq_C + B$, where the q_C's are C charges corresponding to the "proper" but unknown n value.[13] By means of eq 6 it is found that $P = A(q_C^0 + Np) + B$, where the q_C^0's are the nonmodified theoretical charges. The modified set of charges can then be calculated without the knowledge of the inductive equations using a least-squares analysis of the results. From the sum of the squared errors $\Sigma e^2 = \Sigma[P - A(q_C^0 + Np) - B]^2$ the values of A, B, and p are calculated by solving the equations $\partial \Sigma e^2/\partial A = 0$, $\partial \Sigma e^2/\partial B = 0$, and $\partial \Sigma e^2/\partial p = 0$. With the p value thus determined, the modified charge distributions are obtained from eq 5 and 6. Of course, a similar treatment is applicable to other forms of relationships $P = P(q_C)$.

Example. Chemical Shifts

Considerable efforts have been devoted to the theoretical treatment of ^{13}C chemical shifts, including attempts to correlate them with substituent electronegativities[14,15] or with charge distributions.[16-18] Various

approaches using CNDO,[19] extended Hückel,[20] and INDO[21] calculations have not been entirely successful. To date, the most useful approaches are semiempirical ones,[22-24] based on the now considerable body of experimental evidence.

It is usually understood that one of the major factors governing the shielding of a specific nucleus is its local electron density. Along these lines, Sichel and Whitehead[20] used the extended Hückel theory to calculate charges on carbon atoms in alkanes and halogenated alkanes. These charge distributions were such, however, that a unique correlation with chemical shifts could not be obtained for primary carbons and di-, tri-, and tetra-substituted C atoms. Baird and Whitehead[25] suggested that part of the failure of these results may lie in an underestimation of the ionic characters, and charges therein, of the C–C and the C–H bonds. Here it is shown that the failure in obtaining a unique correlation between ^{13}C chemical shifts (for the alkanes) and carbon net charges can be attributed to an improper evaluation of the latter.

From eq 7, it follows that a linear dependence of the proton chemical shifts on the charges q_H is tantamount to saying these shifts are linearly related to σ^*_R. This correlation, presented in Figure 1, indicates (i) that the linear dependence of the δ_H's on the charges q_H does not depend on any particular choice for n and (ii) that the chemical shifts for the electron-richer H atoms are farther downfield than those of the more positive H atoms, at variance with common views.

For ^{13}C chemical shifts, the situation is quite different

(13) It is regarded that although the "real" distributions of charges are unique in unperturbed molecules, individual properties are possibly associated with different n values. This, because properties which are originally thought of as being related to "*some electrons*" in appropriate amounts are described instead in terms of "*charges belonging to specific centers;*" the latter can thus be viewed as "effective charges" with respect to individual properties but should not be interpreted as "real" charge distributions. Charge alternation (S. Fliszár, *J. Amer. Chem. Soc.*, **94**, 1068, 7386 (1972)), for example, should be interpreted in this way. This approximate property is an aspect common to charge distributions with $n > 0$; its expression in terms of mutually repelling charges allocated to adjacent atoms approaches both the "inductive" and the theoretical charge distributions for sufficiently large n values.[2] This suggests (eq 10 with increasingly negative p values) that in the evaluation of repulsions between electrons, important contributions from the CH overlap terms should be included in the "effective charges," without implying that these charges actually "belong" to specified atoms.
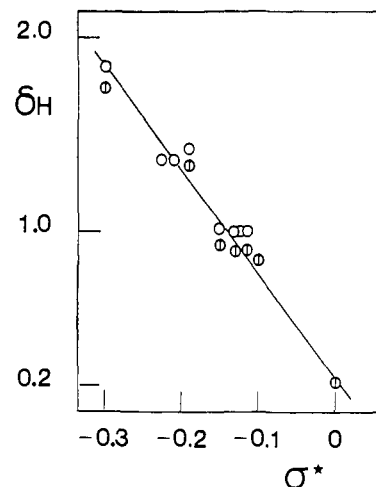
(14) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(15) B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955).
(16) G. Fraenkel, R. H. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).
(17) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
(18) M. A. Whitehead, N. C. Baird, and M. Kaplansky, *Theor. Chim. Acta*, **3**, 135 (1965).

(19) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
(20) J. M. Sichel and A. Whitehead, *Theor. Chim. Acta*, **5**, 35 (1966).
(21) P. D. Ellis, G. E. Maciel, and J. W. McIver, Jr., *J. Amer. Chem. Soc.*, **94**, 4069 (1972).
(22) E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1701 (1963).
(23) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).
(24) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(25) N. C. Baird and M. A. Whitehead, *Theor. Chim. Acta*, **6**, 167 (1966).
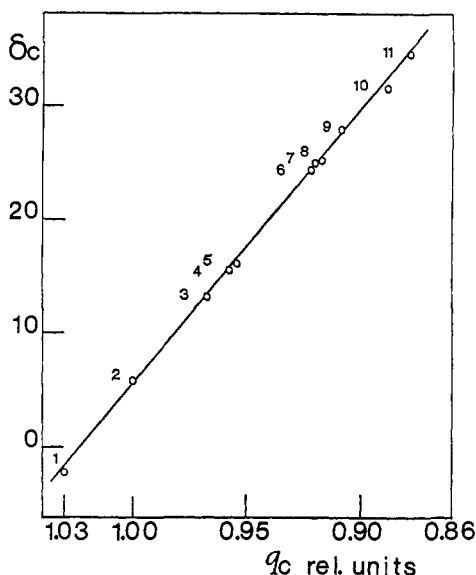
Figure 2. Carbon chemical shifts, relative to TMS, vs. carbon net charges, in relative units q_C(ethane) = 1.

because the "proper" value of n is critical if the chemical shifts are to be related to the carbon charges. While ultimately the "proper" n to be used in the "inductive" equations of Table I should be determined from an experimental study of the property-charge relationship, there appears to be an n value of particular interest ($n \simeq -4.4$), that corresponding to a situation of "best electroneutrality." The comparison of the observed chemical shifts (Table VI) with the relative net

Table VI. Net C Charges and ^{13}C Chemical Shifts

Molecule	Atom[a]	Net charges,[b] rel units ($n = -4.4$)	Chemical shifts,[c] relative to TMS
Methane	C (1)	1.0303	−2.1
Ethane	C (2)	1.0000	5.9
Propane	C_{prim} (4)	0.9583	15.6
	C_{sec} (5)	0.9545	16.1
Butane	C_{prim} (3)	0.9674	13.2
	C_{sec} (7)	0.9205	25.0
Isobutane	C_{prim} (6)	0.9220	24.3
	C_{tert} (8)	0.9167	25.2
Neopentane	C_{prim} (10)	0.8886	31.5
	C_{quat} (9)	0.9091	27.9
Pentane	C_{centr} (11)	0.8788	34.5

[a] The numbers in parentheses refer to the points of Figure 2. [b] Calculated from the "inductive" formulas.[4] [c] Results extracted from ref 23.

charges calculated for $n = -4.4$ is presented in Figure 2.

This comparison speaks for itself. It must be noted that the line in Figure 2 represents the *only monotonic dependence* of the δ's on q_C since the use of any value other than $n \simeq -4.4$ would destroy the monotonicity. Consequently, we find here an experimental justification for using a *linear* relationship between the δ and q_C values. A least-squares analysis of the data presented in Table VI indicates $n = -4.4122$ and

$$\delta(^{13}C) = -237.1q_C(rel) + 242.64 \tag{13}$$

from TMS, with a standard error of ±0.3 ppm.

Recalling now that the fully optimized *ab initio* results perfectly agree with these "inductive" charges,[4] it can also be said that the correlation of Figure 2 corresponds to a comparison with *ab initio* charges, modified for $n = -4.4$. Hence, *ab initio* charges can be used for calculating C chemical shifts without having recourse to the "inductive" formulas. For example, the "fully optimized" STO-3G calculation of cyclohexane[26] indicates $q_C = 2.76$ melectrons. From eq 6, using $p = 30.1213$ melectrons (as calculated for the alkanes), it follows that $q_C = 63.00$ melectrons (for $n = -4.4122$), *i.e.*, with $\beta = 69.404$ melectrons, q_C(rel) = 0.9078. Finally (eq 13), it is found that δ 27.4 ppm (exptl: 27.7 ppm from TMS), which is satisfactory when considering that a 1% error in the evaluation of q_C(rel) corresponds to an error of $\sim$2.4 ppm in the chemical shift.

Discussion

In this study of the alkanes, use was made of the fact that charge distributions derived from both semiempirical and *ab initio* methods, although apparently unreconciliable among themselves, obey simple patterns reflecting the customary inductive effects.

Any original set of charges, corresponding to definite values for n and β, can be transformed into a set corresponding to another value for n. This has been linked to the fact that the partitioning of the C–H overlap populations largely determines the charge distributions. The choice of the "proper" n value is particularly important in any study of molecular properties involving carbon charges since their relative scaling depends strongly on n. For a property $P = P(q_C)$, the "proper" transformation can be made without the knowledge of the "inductive" formulas for the q_C's, provided that an adequate set of theoretical results is available. Clearly, the choice of the "proper" n and, in a way, the "proper" mode for partitioning C–H overlap populations are made by "chemical calibration."

It is noteworthy that the "calibrated" results, *i.e.*, the modified charges deduced from different theoretical methods for a common n value, are not nearly as dissimilar as their original counterparts. For example, all the charges derived from the optimized STO-3G, Hoyland's BO, 7s3p/3s, and 6-31G[27] *ab initio* calculations are in a ratio of 1 : 1.3 : 0.86 : 0.84 after readjustment to a common n value, whereas the original ethane C charges are in a ratio of 1 : 24 : 27 : 23. Such a behavior would be expected considering the similarities in the group charges of Table II.

There is one particular value of n which attracted attention, *i.e.*, that corresponding to a "best possible electroneutrality," a condition which is met for n equal (or close to) −4.4. This n value indicates a C^+–H^- polarity and corresponds in spirit to an intuitive picture suggested by the group charges of Table II. These charges, which are not affected by the "chemical calibration," indicate that the retention of electrons in a

(26) R. Roberge and S. Fliszár, to be submitted for publication.
(27) A STO 6-31G calculation performed according to Pople's recipe[28] gave the following net charges on C atoms (in melectrons): −630 (CH₄), −469 (C₂H₆), −460 (C₃H₈, primary), and −318 (C₃H₈ secondary), with $n = 36$.
(28) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

group drops as the number of H atoms in the group decreases. Compared to the CH_2 group, the CH group looses about twice as much charge to each adjacent CH_3 group. Of course, the charge transfer occurs in favor of the H-richer group. This suggests that, in a way, the H atoms "retain" electrons in the groups in qualitative accord with a scheme depicting the hydrogens as electron attractors. This qualitative picture of electron retention by H atoms in CH_N groups is then the common point from which the inductive effects for the alkyl groups can be rationalized. INDO calculations[9] are in qualitative accord with such a picture.

While the mathematical isolation of the groups is relatively easy from a conceptual point of view (because it suffices to split the C–C overlap populations in halves), the attribution of the electrons within the CH_N groups reveals the artificial character of any man-made partitioning. In this sense, one conceptual advantage contained in the present scheme of charge distributions with positive carbon atoms resides in the fact that the "chemical calibration" is capable of indicating how much charge is lost by the individual C atoms in a molecule (with respect to their atomic state) without being specifically required to allocate these "lost" charges to any other specified atoms in that molecule. Fortunately, this uncertainty affecting the charge distribution in the interior of the CH_N fragments does not cause the loss of one of the most popular concepts, that of atomic charges, for discussions of chemical problems.

Intramolecular Nonbonded Attractions in Molecules?

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Abstract: Recently, Epiotis has published an analysis of bonding in the difluoroethylenes and has attempted to rationalize the bonding and energetics in these compounds by "lone-pair attractions." We have examined the source of the smaller XCX angle in 1,1-difluoroethylene (X = F) than in ethylene (X = H) by carrying out *ab initio* molecular orbital calculations on ethylene and mono- and difluoroethylenes. The orbital energies, Edmiston-Ruedenberg localized orbitals, and electron density distribution in these compounds have been examined, and model calculations simulating the fluoroethylene by changing the nuclear charges in the ethylene have been done. It is shown that the "attraction" in these compounds is not due to "lone pair" interactions but rather to changes in the nature of the C–X bonding orbital as X becomes more electronegative. Further implications of these results for rationalizing other molecular geometries are discussed.

The fact that the FCF angle in 1,1-difluoroethylene is smaller than the corresponding HCH angle in ethylene is interesting because it goes against most chemists' intuition that one would expect greater nonbonded repulsions between the more electronegative and electron-rich fluorines. A more precise analysis along the lines of electrostatics is difficult, because of the fact that the C–X bond distances are significantly different for X = H and F. Fluorine will attract its electrons more tightly than hydrogen and thus at a given XCX angle (*e.g.*, 120°), the larger F–F distance might well imply less X · · · X repulsion for X = F than for X = H.

Using valence bond ideas, Mellish and Linnett[1] found a simple hybridization explanation for the smaller FCF angle; the more electronegative fluorines cause the carbon to rehybridize and use its less tightly bound p orbitals in bonding to the fluorines while using more s character in the carbon–carbon σ bond. Rehybridization of the sp^2 carbon toward sp^n ($n > 2$) would shrink the angle between those hybrids which had acquired more p character. These hybridization arguments are useful for rationalizing molecular geometries,

but they need to be examined with actual wave functions.

From a molecular orbital viewpoint, Walsh's rules[2] have been used to rationalize molecular geometries. For AB_2 molecules of C_{2v} symmetry, one examines the orbital energy dependence on the BAB angle of the a_1 and b_1 orbitals (which have no node between the B atoms) and b_2 and a_2 orbitals (which are antibonding between the B atoms). Unfortunately, the sum of the orbital energies often does very poorly in predicting the actual BAB angle, so one has to resort to after the fact reasoning on the relative importance of the a_1 (bonding) and b_2 (antibonding) orbitals.

Epiotis[3] rationalized the fact that 1,1-difluoroethylene has a smaller XCX angle than ethylene in the following way: there is a preferential charge transfer out of a F($p\sigma$) antisymmetric MO, which leads to a slightly favorable "bonding" interaction between the fluorines. A similar interaction involving the F($p\pi$) orbitals is antibonding, but the bonding effect wins out, thus bringing the fluorines closer together. In support of his argument, he notes that the $p\pi$–$p\pi$ INDO bond order is negative and the $p\sigma$–$p\sigma$ bond order is larger than the

(1) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954); and for a review, H. L. Bent, *Chem. Rev.*, **61**, 275 (1961).

(2) A. D. Walsh, *J. Chem. Soc., London*, 2260 (1953).
(3) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 3087 (1973).