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Charge Distributions and Chemical Effects. 30. Relationships between Nuclear Magnetic Resonance Shifts and Atomic Charges

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Abstract: In a series of closely related compounds, it may occur that the change in total (dia- plus para-) magnetic shielding of atomic nuclei is nearly that of the *local* paramagnetic term, because of cancellation effects involving nonlocal dia- and paramagnetic contributions. This offers a justification for relationships between nuclear magnetic resonance shifts and local atomic populations, which are occasionally observed. It is important, however, to consider the type (2s, 2p, σ, or π) of electrons which are responsible for the variations in atomic charges. Correlations between ^{13}C NMR shifts and atomic populations of aromatic compounds, for example, should not be interpreted in terms of π electrons only, because the slope of shift vs. π charge (i.e., the ~160-ppm/electron value which is usually invoked) does not describe an intrinsic effect of π charges on magnetic shielding but accounts for the fact that σ and π charges vary in opposite directions in this class of compounds. The explicit consideration of the inverse variations of σ and π charges, where appropriate, offers an explanation for the observation that charge-shift correlations can have positive or negative slopes. It appears, indeed, that an increase in total electronic population is accompanied (i) by a high-field shift when the electron enrichment results from a gain in π charge prevailing over the concurrent loss in σ electrons (aromatic and vinyl C, carbonyl O atoms) or (ii) by a downfield shift when the increase in charge is dictated by that of the σ population (sp^3 C, carbonyl C, and dialkyl ether O atoms).

Introduction

Carefully established correlations between nuclear magnetic resonance (NMR) shifts and atomic electron populations in well-defined series of closely related compounds can prove valuable for the evaluation of atomic charges in similar systems which are at, or beyond, the limits of practical computational feasibility. Unfortunately, charge-NMR shift relationships are not free from conceptual difficulties and have drawbacks of their own.[1-3] It is, therefore, important to be fully aware both of the possibilities offered by such correlations and of the limitations restricting their utilization.

In writing a linear relationship

$$\delta = aq + b \qquad (1)$$

between chemical shifts δ and net (i.e., nuclear minus electronic) charges q we keep in mind (i) that positive δ values correspond here to downfield shifts and (ii) that q becomes more negative as the corresponding electron population increases. Hence, a positive slope a indicates that an increase of electronic charge at an atom results in a high-field shift, reflected by a lowering of δ. Conversely, a negative slope a indicates that an increase in local electron population (more negative q) results in a downfield shift. The puzzling point is that both positive and negative slopes are met in applications of eq 1, e.g., $a > 0$ for vinyl carbon[4] and carbonyl oxygen atoms[5] and $a < 0$ for paraffinic carbon[6] and ether oxygen atoms.[5] This is a problem well worth looking into. Before doing so, however, let us examine a few general aspects regarding the postulated validity of charge-shift relationships.

Merits of Charge-Shift Relationships

The main conceptual difficulty stems from the fact that the attempts at correlating NMR shifts with atomic electron populations are rooted in one's intuition rather than being based on a formalism explicitly featuring the role of local charges in governing shielding constants. This situation paves the way to criticisms which are countered, in essence, by a significant number of "good" charge-shift relationships,[1-3] although the reason(s) for, or the validity of, this type of results always remains difficult to assess. Fortunately, we can take advantage of an indirect way of assessing the merits of charge-shift correlations by examining the average diamagnetic and paramagnetic contributions, σ^d and σ^p, respectively, to the total average magnetic shielding:

$$\sigma = \sigma^d + \sigma^p$$

The σ^d and σ^p results used in the following discussion were derived by means of the formalism given by Vauthier, Tonnard, and Odiot.[7] This approach is based on Pople's finite perturbation theory.[8] It involves the INDO approximations[9] on a GIAO basis[10] and London's approximation. Moreover, it satisfies the Hermitian requirement for the first-order perturbation matrix reflecting the effect of an applied external magnetic field. The latter condition results in a significant improvement of calculated ^{13}C magnetic shieldings, the average precision being of the order of ~5 ppm.[7] The point is that this formalism for σ permits a separation into mono-, di-, and triatomic contributions, thus revealing the relative importance of "local" and "distant" electron densities on the magnetic shielding of a given nucleus. In this manner, it becomes possible to gain a reasonable estimate about the chances that chemical shifts do, indeed, depend primarily on local electronic populations, at least in series of closely related compounds. The most detailed results are those derived for ethylenic and acetylenic sp^2 and sp carbon atoms, respectively.

To begin with, it appears that the local diamagnetic contribution to the magnetic shielding is practically the same for all sp^3, sp^2, and sp carbon nuclei (57.85 ± 0.6 ppm). Moreover, the results for sp^2 carbons indicate that the *total* diamagnetic part (including all contributions from distant atoms) *plus* the paramagnetic part due to the distant atoms is nearly constant (82.7 ppm), within ~0.4 ppm. The gap between this sum and the total magnetic

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Table I. Paramagnetic Shielding Contributed by Neighboring Atoms (ppm)[a]

molecule (atom*)	shielding	molecule (atom*)	shielding
C^*H_4	0.17	$(CH_3)_2C{=}C^*HCH_3$	0.38
$CH_3C^*H_3$	−0.11	$(CH_3)_2C^*{=}CH_2$	−1.15
$CH_2{=}C^*H_2$	−1.21	$(CH_3)_2C^*{=}CHCH_3$	1.22
$CH_3CH{=}C^*H_2$	0.70	$(CH_3)_2C^*{=}C(CH_3)_2$	1.52
$(CH_3)_2C{=}C^*H_2$	1.52	$CH{\equiv}C^*H$	1.65
$CH_3C^*H{=}CH_2$	−2.15	$CH_3C{\equiv}C^*H$	3.79
$CH_3C^*H{=}CHCH_3$ cis	0.62	$CH_3C^*{\equiv}CH$	1.15
$CH_3C^*H{=}CHCH_3$ trans	0.67	$CH_3C^*{\equiv}CCH_3$	3.09

[a] These results were calculated from those indicated in ref 7 and represent $\sigma^P(KK) + \sigma^P{}_0(MK)$, as defined in this reference. The local paramagnetic shielding discussed in the text is $\sigma^P(M)$ (eq 9 of ref 7).

shielding represents the paramagnetic contribution excluding that of distant atoms, i.e., the local paramagnetic shielding plus the paramagnetic part contributed by the neighbors of the nucleus under study. It is this gap which reflects the total variation in magnetic shielding (or, at least, its major part by far) for a given nucleus in a series of closely related compounds; it is now at the center of our attention. The effects of the neighboring atoms which are included in this paramagnetic shielding are reported in Table I. The results reflect the smallness of these effects.

For ethylenic and acetylenic carbon atoms, one can consider the neighbors' contributions as being constant, or nearly so (within ~1.5 ppm), and the corresponding uncertainty introduced by assuming constant neighbors' contributions for sp^3 carbon atoms probably does not exceed ~0.3 ppm. As a consequence, in a series of closely related compounds, the variations of the local paramagnetic shielding appear to represent the largest part, by far, of the total changes in shielding experienced by a given nucleus due to structural changes, e.g., by sp^2 carbons in a series of ethylenes. Therefore, within the precision of the present type of analysis, it seems quite reasonable to anticipate correlations between nuclear magnetic resonance shifts and atomic charges which, of course, are strictly local properties. Following this analysis of the individual nonlocal effects revealing, namely, the small participation of tricentric integrals involving distant atoms, the practical validity of charge–shift relationships rests largely with cancellation effects of a number of terms which, to begin with, are small or relatively constant. The importance of the nonlocal contributions is further reduced with the selection of a scale tailored for comparisons between atoms of the same type, with reference to an appropriately chosen member of that series. With hydrogen atoms, however, the situation is different because of the large weight of the three-center integrals in the calculation of their magnetic shielding.[7]

So far we have learned that, in certain series of closely related compounds, it is the local paramagnetic shielding which governs the changes in total shielding, i.e.,

$$\Delta\sigma_{\text{total}} \simeq \Delta\sigma^{P}{}_{\text{local}} \tag{2}$$

and, hence, that under these circumstances it may well be justified to expect correlations between NMR shifts and local electron populations. It remains, however, that charge–shift correlations are essentially empirical in nature; while the definition of "closely related compounds" may be linked to the approximate validity of eq 2, the practical answer stems ultimately from the actual examination of shift vs. charge results.

Relationships Involving sp^2 Carbon Atoms

To begin with, let us examine the probably most quoted plot, that of the familiar Spiesecke and Schneider work[11] relating the ^{13}C NMR shifts of tropylium ion, benzene, cyclopentadienyl anion, and cyclooctatetraene dianon to the corresponding carbon atomic charges. The latter were deduced by assuming the local π electron density to be known from the number of π electrons and the number of carbon atoms over which the π cloud was distributed. The estimated shift, ~160 ppm per electron, has become an almost unerasable part of our grammar. The linear correlation between ^{13}C chemical shifts and π charge density was later extended to 2π electron systems,[12-14] as well as to the 10π cyclononatetraene anion.[15] A plot of this correlation for the whole series was presented by Olah and Mateescu[12] who used, where appropriate, simple Hückel molecular orbital theory for deducing charge distributions. At a quite different level of approximation, this class of compounds is now investigated by means of STO-3G calculations involving a detailed optimization of all the geometrical and ζ exponent parameters (Appendix I). The Mulliken net atomic charges and chemical shifts (Table II) yield the correlation presented in Figure 1. In spite of some scatter about the correlation line, a point which is discussed further below, it appears that eq 1 is reasonably well satisfied with the use of total ($\sigma + \pi$) net atomic charges, with $a \simeq 300$ ppm/electron.

Table II. Carbon Net Charges and NMR Shifts of Selected Aromatic Hydrocarbons[a] (me, viz. ppm from Me_4Si)

compound	q_σ	q_π	q_{tot}	δ
1, cyclopropenium cation, $C_3H_3{}^+$	−223.5	333.3	109.8	176.8
2, cycloheptatriene cation, $C_7H_7{}^+$	−120.5	142.9	22.4	155.4
3, benzene, C_6H_6	−47.4	0	−47.4	128.7
4, cyclononatetraenide anion, $C_9H_9{}^-$	5.1	−111.1	−106.0	108.8
5, cyclopentadienide anion, $C_5H_5{}^-$	26.5	−200.0	−173.5	102.1
6, cyclooctatetraenide dianion, $C_8H_8{}^{2-}$	75.0	−250.0	−175.0	85.3

[a] Results calculated from Table VIII, relative to 1, 5, and 6 electrons, respectively, for the π, σ, and total net charges. A negative sign indicates an increase in electron population.

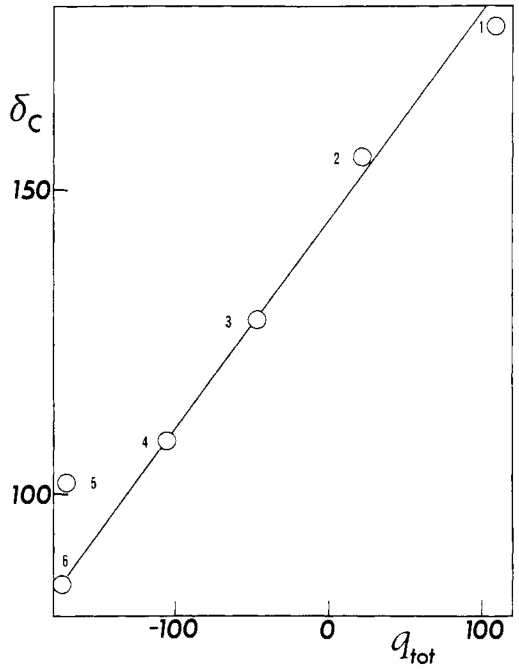

Figure 1. ^{13}C chemical shifts of the aromatic compounds indicated in Table II vs. total ($\sigma + \pi$) net charges (ppm from Me_4Si viz. 10^{-3} eu).

A closely related example concerns the para carbon atoms of substituted benzenes. The Mulliken net charges, at the STO-3G

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Table III. Charge Analysis and NMR Shifts of Para Carbon Atoms in Monosubstituted Benzenes[a]

	substituent	q_π (me)	q_σ (me)	q_{tot} (me)	δ (ppm)
1	NH_2	−46	−35	−81	119.2
2	OH	−39	−39	−78	120.8
3	F	−21	−50	−71	124.3
4	CH_3	−12	−56	−68	125.6
5	H	0	−63	−63	128.7
6	CN	28	−78	−50	130.1
7	NO_2	43	−87	−44	134.7

[a] The Mulliken net charges, from "standard" STO-3G calculations, are those given in ref 3. The shift results (from Me_4Si) are taken from Stothers.[16]

Table IV. Carbon Net Charges and NMR Shifts of Azulene (me, viz. ppm from Me_4Si)

atom	q_π	q_σ	q_{tot}	δ^a
1, 3	−102.2	−4.3	−106.5	119.2
2	25.2	−77.2	−52.0	137.7
4, 8	88.7	−117.6	−28.9	136.9
5, 7	−40.7	−35.4	−76.2	123.2
6	69.6	−101.5	−31.9	137.4
9, 10	2.9	−3.5	−0.6	140.8

[a] Converted data extracted from Stothers.[16]

level, were calculated by Hehre, Taft, and Topsom[3] who presented a most instructive study of these compounds. Selected charge results are indicated in Table III, together with the corresponding NMR shifts. The correlation between the total ($\sigma + \pi$) net charges and the NMR shifts resembles closely that shown for the compounds listed in Table II, with $a \simeq 384$ ppm/electron. A similar study on meta carbons, while giving results of the same type,[3] is perhaps somewhat less conclusive because of the very limited range of variation of the meta carbon NMR shifts (~1.5 ppm). It remains, however, that the major conclusions drawn here and further below for the para carbons apply to the meta carbons as well.

As one would anticipate from the similarity in the chemical nature of the compounds indicated in Table II and III the gross features are quite similar, namely, as regards the increase in electron population at carbon resulting in a high-field shift. Not too much importance should be given to the difference between the slopes a calculated for the two series of compounds. Part of this difference is possibly due to the fact that the substituted benzenes were calculated using the "standard" STO-3G method, which is certainly a reasonable approach for this class of molecules, whereas the STO-3G remake of the Spiesecke–Schneider correlation has involved extensive geometry and scale factor optimizations, dictated by the diversity of the members of this series. In addition, one should consider that the Spiesecke–Schneider correlation involves cycles of different size, a circumstance which introduces an uncertainty regarding the validity (or lack of it) of interpreting chemical shift differences as a function of Mulliken charge density only, disregarding possible effects linked to its shape. An indication about the overall influence or ring size on the quality of simple charge–shift correlations in this class of compounds is offered by the study of azulene. From the results (Table IV) it appears that two distinct, parallel correlation lines describe the charge–shift dependence, one for the seven-membered, the other for the five-membered ring carbon atoms, indicating some sort of ring-size effect. When transposed on the scale of the correlation given in Figure 1, however, this effect is relatively modest. On these grounds we may regard that the shift–charge correlation presented in Figure 1 is, on the whole, reasonably good, mainly because it covers an important range of shift and charge results, but also that one should not attempt to extract more from it than it is capable of giving in terms of general trends. The results for monosubstituted benzenes are more significant because they do not suffer from possible drawbacks linked to ring size, and, indeed, their correlation is superior in quality to that given in Figure 1. Finally, an excellent correlation with chemical shifts is also obtained for the vinyl carbon atoms of a series of methyl-substituted ethylenes, using fully optimized STO-3G ($\sigma + \pi$) net charges, with $a = 291$ ppm/electron.[4]

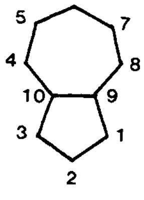

Table V. Mulliken Net Charges (me) and NMR Shifts (ppm from Me_4Si) of Carbonyl Carbon Atoms[a]

molecule	q_σ	q_π	q_{tot}	δ
CH_3CHO	100.3	111.3	211.6	199.6
C_2H_5CHO	93.1	111.1	204.2	202.4
$i\text{-}C_3H_7CHO$	86.8	111.1	197.9	204.3
$(CH_3)_2CO$	123.0	136.7	259.7	204.9
$CH_3COC_2H_5$	113.6	140.0	253.6	207.0
$CH_3CO\text{-}i\text{-}C_3H_7$	109.0	130.0	245.0	210.0
$(C_2H_5)_2CO$	104.2	143.2	247.4	209.4
$C_2H_5CO\text{-}i\text{-}C_3H_7$	99.6	139.2	238.8	212.3
$(i\text{-}C_3H_7)_2CO$	92.0	141.8	233.8	215.5

[a] The NMR shifts are taken from Delseth and Kintzinger.[17] The charges were obtained from "standard" STO-3G calculations.[5] The linear correlation of δ with q_{tot} is very good.[5]

All the charge–shift relationships presented so far have one important point in common. They do, indeed, indicate a shift toward higher fields when the total ($\sigma + \pi$) electron population at a carbon atom increases. Qualitatively, this is the trend which is usually invoked in shift vs. charge-related discussions although in many cases reference is made only to changes in π-electron densities.[11-14,18] This type of trend is, however, no longer observed for the carbonyl carbon atoms,[5] as indicated by the results given in Table V. For these atoms, any increase in total electron population is clearly reflected in a downfield shift; i.e., $a < 0$. This change in the sign of a is certainly intriguing, a point which shall be discussed further below. A brief examination of other systems reveals that $a < 0$ is by no means an uncommon situation.

Relationships Involving sp³ Carbon and Oxygen Atoms

The validity of eq 1 has been carefully established for linear and branched paraffins, cyclohexane and methylated cyclohexanes, and molecules consisting of several cyclohexane rings in the chair conformation (namely, *trans*-decalin, *cis*-decalin, bicyclo[3.3.1]nonane, adamantane, and methylated adamantanes) as well as in boat conformation (i.e., iceane and bicyclo[2.2.2]octane).[6] No special effect seems to contribute to the chemical shift, specifically because of the cyclic structure of cyclohexane. For this class of molecules, the slope $a = -3420$ ppm/electron (deduced from fully optimized STO-3G charges) indicates that any increase in electron population at carbon is accompanied by an important downfield shift.[6] This is a result we shall keep in mind when discussing carbon atoms in typical σ systems. Note that the carbon net charges of these compounds are given by the approximation[6]

$$q_C = q_C^{\text{Mulliken}} + N_{CH}p \qquad (3)$$

which allows for an uneven partitioning of overlap populations in heteronuclear situations, p being the departure (for one CH bond) from the usual half-and-half assignment of CH overlap terms implied in Mulliken's scheme,[19] and N_{CH} the number of CH bonds formed by the carbon under study. It is important to stress that this type of analysis does not introduce any artifact which could be held responsible for the conclusion reached above.

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Table VI. Mulliken Orbital Populations of Selected Carbon Atoms from Optimized STO-3G Calculations (electron units)[a]

type of carbon	molecule	orbital population 1s	2s	2p
primary	ethane	1.9903	1.1459	2.8848
	propane	1.9903	1.1491	2.8844
	isobutane	1.9892	1.1513	2.8859
	neopentane	1.9907	1.1540	2.8840
secondary	propane	1.9906	1.1522	2.8512
	cyclohexane	1.9913	1.1550	2.8509
	adamantane	1.9914	1.1559	2.8531
tertiary	isobutane	1.9916	1.1551	2.8199
	adamantane	1.9917	1.1569	2.8193
secondary	cyclopentane	1.9918	1.1584	2.8618
	cyclobutane	1.9907	1.1611	2.8726
	cyclopropane	1.9910	1.1364	2.9603

[a] Results extracted in part from ref 22.

Table VII. Mulliken Charges and ^{17}O NMR Shifts of Carbonyl Oxygen Atoms (me, viz. ppm from water)

molecule	q_σ	q_π	q_{tot}	δ^a
$(CH_3)_2CO$	−104.5	−162.2	−266.7	569.0
$CH_3COC_2H_5$	−103.6	−165.9	−269.5	557.5
$CH_3CO\text{-}i\text{-}C_3H_7$	−106.3	−161.9	−268.1	557.0
$(C_2H_5)_2CO$	−102.7	−169.3	−272.1	547.0
$C_2H_5CO\text{-}i\text{-}C_3H_7$	−105.3	−165.4	−270.7	543.5
$(i\text{-}C_3H_7)_2CO$	−104.1	−169.6	−273.8	535

[a] From ref 17.

Indeed, the same conclusion follows from comparisons involving only carbon atoms bearing the same number of H atoms, in which case $\Delta q_C = \Delta q_C^{\text{Mulliken}}$. The value of p reflects, in fact, an experimental calibration for the assignment of overlap populations, in replacement of their arbitrary halving. Its value, 30.12 me from optimized STO-3G calculations, has been deduced independently from comparisons with the ^{13}C NMR shifts of linear and branched paraffins, six-membered cycloalkanes,[6] and vinyl carbon atoms,[4] as well as from ionization potentials[20] and energies of atomization.[21] Finally, the orbital populations shown in Table VI indicate a regular increase of ~32.7 me in 2p population at carbon for each hydrogen atom attached to it, suggesting that 2p electrons largely make up for the p correction term for one CH bond so that, indeed, the change in total net charge appears to be mainly one of 2s electrons for acyclic and six-membered cycloalkanes.

Similar conclusions are no longer true for smaller cycles (e.g., cyclopropane) which, not unexpectedly, fail grossly to follow the correlation established for cyclohexanic and noncyclic saturated hydrocarbons. It is also true that the electronic structure of cyclopropane, for example, differs significantly from the pattern exhibited by the compounds satisfying this correlation. Indeed, its 2p-electron population is ~110 me larger than that of other CH_2 carbon atoms (like those of propane or cyclohexane, for example), with an actual loss of 2s electrons. Under these circumstances it is clear that cyclopropane and, for the same reason, cyclopentane and cyclobutane, cannot be considered on the same footing as the sp^3-hybridized carbon atoms of simple alkanes and cyclohexane, not to speak about the anticipated effects linked to the change in shape of the electron clouds.

Contrasting with the typical σ hydrocarbons, whose ^{13}C shifts appear to be governed by the changes in 2s populations, the orbital populations calculated for the oxygen atoms in dialkyl ethers reveal that their net charges vary almost exclusively at the 2p level. The slope of the shift vs. charge correlation is less pronounced by a factor of ~1.8 than that deduced for the alkane–carbon atoms, giving $a = -1900$ ppm/electron.[5] This a value indicates that any increase in 2p population is accompanied by a downfield ^{17}O NMR shift. With the carbonyl oxygen atoms, however, the situation is different. As shown by the results given in Table VII, a gain in total electronic charge is accompanied by a shift toward higher fields.[5] This conclusion is clear, but not too much importance should be given to the value of the slope, $a \simeq 4300$ ppm/electron, because this correlation is not of the same quality as those presented for carbon and dialkyl ether oxygen atoms. With the carbonyl oxygens, calculated at the STO-3G level without geometry and exponent optimization, an uncertainty of ~1 me in charge is, indeed, sufficent to explain the average deviation (~3 ppm) of shift results derived from these charges.

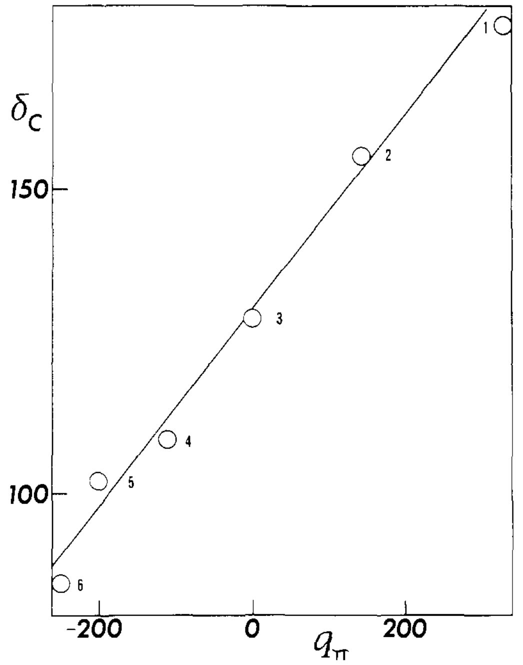

Figure 2. ^{13}C NMR shifts (from Me_4Si) vs. π net charge (relative to one electron) for the aromatic compounds indicated in Table II.

At this stage we have enumerated a number of correlations involving sp^2 and sp^3 carbon atoms, as well as dialkyl ether and carbonyl oxygen atoms. In σ systems it has appeared that a gain of 2s or 2p electron population is accompanied by important downfield shifts, while the opposite trend is observed in other systems, namely, with vinyl carbon but not with carbonyl carbon atoms. This is the point which shall now be examined.

Discussion

Traditionally, much of the discussion reported in the literature about ^{13}C NMR shifts and electronic structure has related to aromatic systems, following Lauterbur's suggestion[18] that in these systems the shielding is governed primarily by the π electron density at the carbon nuclei. Although the analysis presented here has emphasized relationships with total ($\sigma + \pi$) atomic charges, there is not doubt that correlations with π electron populations have their merit. For example, the aromatics described in Table II yield the correlation with π charges presented in Figure 2, but it is also true that an equally good result is obtained if σ charges are used instead (Figure 3). This observation alone suffices to warn us that for aromatic (and, more generally, sp^2 carbon) systems the evaluation of the dependence of NMR shifts on electronic charge should not be restricted to π electrons only, disregarding σ charges. In fact, the study of σ systems would otherwise come to an abrupt end before it has even started.

The reason why σ, π, and total ($\sigma + \pi$) charges yield correlations of similar quality for the aromatics is due to the linear decrease in σ population accompanying any increase in π electronic charge. Figure 4 illustrates this behavior for the compounds described in Table II. Similarly, in the series of monosubstituted benzenes, the calculated changes in σ and π populations at the para carbon atom are accurately inversely related, as convincingly demonstrated in the Hehre–Taft–Topsom study.[3] The π population shows the greater change and the σ population seems to

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[20] H. Henry and S. Fliszâr, *Can. J. Chem.*, **52**, 3799 (1974).

[21] S. Fliszâr, *J. Am. Chem. Soc.*, **102**, 6946 (1980); S. Fliszâr and M.-T. Bêraldin, *Can. J. Chem.*, **60**, 792 (1982).

[22] G. Kean and S. Fliszâr, *Can. J. Chem.*, **52**, 2772 (1974).

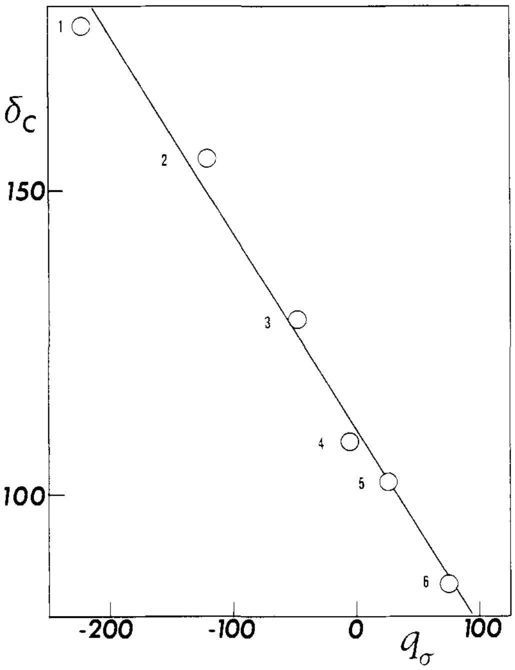

Figure 3. Correlation between the ^{13}C shifts (from Me_4Si) of aromatic compounds (Table II) and σ charges (expressed in 10^{-3} eu, relative to 5 electrons).

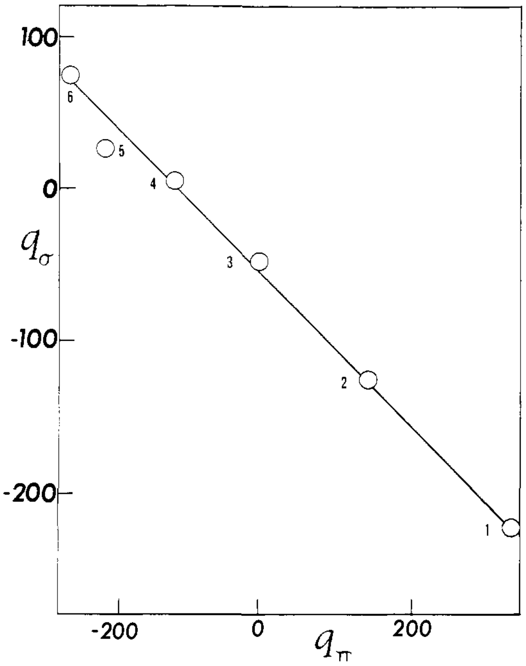

Figure 4. Comparison between σ and π net charges in aromatic compounds (Table II), expressed in 10^{-3} eu.

be consequently altered by ~55% in the opposite direction. Similar results are also obtained for the π and σ populations at the meta carbon atom, but these points show some scatter from linearity. However, most of the meta points fall close to the correlation line drawn for the para carbon atoms. Finally, a decrease in σ population accompanying a gain in π population is also observed for the vinyl carbon atoms.[4] This result is best extracted from comparisons involving carbon atoms carrying the same number of hydrogen atoms (e.g., the CH_2 carbons of ethylene, propene, and isobutene). In this manner we avoid the uncertainties associated with the p terms (eq 3) and can reasonably hope that Mulliken charge differences reflect the trends in a correct fashion, at least qualitatively. Moreover, it must be borne in mind that with alkyl substitution the correct evaluation of π charges is biased by overlap with out-of-plane atoms, an effect which is difficult to account for in a reliable manner. The same argument applies to carbonyl carbon atoms. However, while σ and π populations vary in opposite directions in the ketones, the π population of the aldehyde carbonyl C atoms seems to remain fairly constant (Table V). For the latter, the observed trend indicates that $a(\sigma \text{ electrons}) < 0$.

Describing now, where appropriate, the observed changes in σ and π populations by the equation

$$q_\sigma = mq_\pi + \text{constant} \tag{4}$$

it appears that eq 1 can be written as follows

$$\delta = a_\sigma q_\sigma + a_\pi q_\pi + \text{constant} \tag{5}$$

where

$$ma_\sigma + a_\pi = (m + 1)a$$

represents the apparent slope of δ vs. q_π (e.g., 160 ppm/electron), which is now seen to account also for the fact that σ and π charges vary in opposite directions (from eq 4 and 5). Note that when eq 4 applies, the individual a_σ and a_π parameters cannot be obtained from simple regression analyses using eq 5 because q_σ and q_π are not independent variables. In σ systems ($q_\pi = 0$) or if eq 4 does not apply because q_π = constant, eq 1 takes the form

$$\delta = a_\sigma q_\sigma + \text{constant} \tag{6}$$

Saturated hydrocarbons, dialkyl ether oxygen, and aldehyde carbonyl C atoms indicate that $a_\sigma < 0$.

Of course, there is no reason to assume that the values of a_σ and a_π are the same in all systems. The observed charge vs. shift trends can be explained on a qualitative basis provided that

$$a_\sigma < 0,\ a_\pi < 0,\ |a_\sigma| > |a_\pi| \tag{7}$$

or $a_\sigma < 0$ and $a_\pi > 0$. The latter alternative presents no difficulty considering the inverse variations in σ and π populations (Tables II–V) because both an increase in π population and the concurrent decrease in σ electronic charge would result in a shift toward higher fields. In this case, if the gain in π electrons is more important than the loss in σ population ($-1 < m < 0$ in eq 4), the high-field shift would be accompanied by a gain in total charge, i.e., $a > 0$ (ethylenic and aromatic hydrocarbons; carbonyl O atoms), but if $m < -1$, i.e., if the loss in σ electrons is more important than the gain in π population (carbonyl carbon atoms), it would appear that $a < 0$ because of the actual decrease in total charge. On the other hand, it seems reasonable to assume that a_σ and a_π have the same sign (as in eq 7), meaning that the same qualitative trend is expected from a variation in σ charge (at constant π population) or in π charge (at constant σ population). In that event, a downfield shift promoted by a gain in π electronic charge would be opposed by an inverse effect due to the concurrent loss in σ electrons. Provided that $|a_\sigma| > |a_\pi|$, the resulting effect can still consist in a high-field shift, even if the loss in σ population is less than the gain in π electrons (aromatic hydrocarbons, for example). The high-field shift would, of course, also be observed anytime the loss in σ electrons exceeds the gain in π charge, for a net decrease in electron population, in which case $a < 0$.

Whichever, $a_\pi < 0$ or $a_\pi > 0$, turns out to be ultimately the "good" answer, this rationale is rooted in an anticipated difference in behavior between σ and π electrons. So, while it would have appeared that aromatic systems offer a simple access to the study of shift–charge relationships, particularly in situations where one has not to worry about possible drawbacks arising from the use of Mulliken charges,[6] it turns out that the way σ and π populations vary in opposite directions is of outmost importance a circumstance which, if not properly recognized, is a source of difficulties concealed under a deceitful appearance of simplicity. The present interpretation should be understood at a qualitative level, and not too much weight should be given to the numerical values of the shift vs. charge slopes because they depend on calculated charges which, in turn, are basis set dependent.

It is important to be aware that both situations, i.e., high- or downfield shifts with increasing electron populations may be encountered, depending on the type of system under study. Hence,

Table VIII. Mulliken Orbital Populations of Selected Aromatic Hydrocarbons (electron units)

compound	orbital population			
	1s	2s	$2p_x + 2p_y$	$2p_z$
1 $C_3H_3^+$	1.99232	1.18153	2.04962	0.66667
2 $C_7H_7^+$	1.99178	1.15295	1.97580	0.85714
3 C_6H_6	1.99178	1.13282	1.92281	1.00000
4 $C_9H_9^-$	1.99199	1.11693	1.88599	1.11111
5 $C_5H_5^-$	1.99218	1.11388	1.86741	1.20000
6 $C_8H_8^{2-}$	1.99217	1.10775	1.82507	1.25000

Table IX. Optimized Geometries and Scale Factors of Selected Hydrocarbons

compound	r_{CC} (Å)	r_{CH} (Å)	C(1s)	C(2s2p)	H(1s)
1 $C_3H_3^+$	1.376	1.095	5.702	1.753	1.303
2 $C_7H_7^+$	1.398	1.089	5.704	1.738	1.247
3 C_6H_6	1.394	1.090	5.704	1.720	1.207
4 $C_9H_9^-$	1.390	1.085	5.704	1.700	1.174
5 $C_5H_5^-$	1.394	1.080	5.703	1.676	1.170
6 $C_8H_8^{2-}$	1.399	1.089	5.703	1.670	1.132

charge–shift correlations established for a given series of molecules should not be indiscriminately assumed to be valid in all systems. In series of closely related compounds, however, the judicious use of charge–shift correlations can give valuable information about atomic charges. It has been shown, indeed, that the definition of charge (eq 3) satisfying eq 1 is the same as that satisfying molecular energies expressed in terms of electron distributions.[21] In this manner, charge–shift relationships offer the possibility of studying large molecules of biological interest, which would otherwise lie outside the range of computational feasibility; whether honestly earned from lengthy (and expensive) theoretical calculations, or simply "stolen" from critically established empirical correlations, a charge is a charge and a useful quantity as long as its reliability can be assessed.

Acknowledgment. The financial aid given by the National Research Council of Canada and the cooperation of the "Centre de Calcul de l'Universitê de Montrêal" are gratefully acknowledged.

Appendix I

The geometries of the compounds indicated in Table VIII were deduced from standard STO-3G calculations, using standard scale factors, i.e., C(1s) = 5.67, C(2s2p) = 1.72, and H(1s) = 1.24. Using the optimized geometries, extensive scale factor optimizations have been carried out, giving the final charge results indicated in Table VIII. The optimized geometries and scale factors are reported in Table IX.

In the evaluation of atomic charges, we have considered that the usual halving of overlap populations implied in Mulliken's scheme[19] may not be appropriate in heteronuclear situations.[6] For this reason, one should not make comparisons between, say, primary, secondary, etc., carbon atoms using Mulliken charges. In order to avoid this sort of drawbacks, comparisons are made only between atoms engaged in the same type of bonding, e.g., the CH carbon atoms of the compounds indicated in Table VIII, in which case charge differences expressed in terms of Mulliken charges should represent valid estimates.

Registry No. CH_3CHO, 7507-0; C_2H_5CHO, 123-38-6; i-C_3H_7CHO, 78-84-2; $(CH_3)_2CO$, 67-64-1; $CH_3COC_2H_5$, 78-93-3; CH_3CO-i-C_3H_7, 563-80-4; $(C_2H_5)_2CO$, 96-22-0; C_2H_5CO-i-C_3H_7, 565-69-5; (i-$C_3H_7)_2CO$, 565-80-0; CH_4, 74-82-8; $CH_2{=}CH_2$, 74-85-1; $CH_3CH{=}CH_2$, 115-07-1; $(CH_3)_2C{=}CH_2$, 115-11-7; *trans*-$CH_3CH{=}CHCH_3$, 624-64-6; *cis*-$CH_3CH{=}CHCH_3$, 590-18-1; $(CH_3)_2C{=}CHCH_3$, 513-35-9; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $CH{\equiv}CH$, 74-86-2; $CH_3C{\equiv}CH$, 74-99-7; $CH_3C{\equiv}CCH_3$, 503-17-3; cyclopropenium cation, 19553-81-2; cycloheptatriene cation, 26811-28-9; benzene, 71-43-2; cyclononatetraenide anion, 45730-23-2; cyclopentadienide anion, 12127-83-2; cyclooctatetraenide dianion, 34510-09-3; azulene, 275-51-4; ethane, 74-84-0; propane, 74-98-6; isobutane, 75-28-5; neopentane, 463-82-1; cyclohexane, 110-82-7; adamantane, 281-23-2; cyclopentane, 287-92-3; cyclobutane, 287-23-0; cyclopropane, 75-19-4.

The 3,3-Dimethyl-2-azabicyclo[2.2.2]octyl System as a Bredt's Rule Kinetically Stabilized Dialkylamino Group in Electron-Transfer Studies

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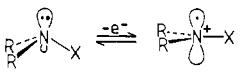
Abstract: PE and CV data are reported for electron removal from 2-substituted 3,3-dimethyl-2-azabicyclo[2.2.2]octyl (2-ADO) derivatives in which the substituent is chloro, dimethylamino, 2-ADO, and —N=N-2-ADO and compared with that for their 9-azabicyclo[3.3.1]nonyl (9-ABN) analogues. The differences observed in both IP_1 and $E^{\circ\prime}$ in the two series of compounds are dominated by their steric differences; 2-ADO has *tert,sec*-alkyl substitution at N while 9-ABN has *sec,sec*-alkyl substitution. The $E^{\circ\prime}$ values for chloramines and 2-tetrazenes are dominated by the ease of flattening at nitrogen, but RN–N′R interactions dominate the $E^{\circ\prime}$ observed for the hydrazines. The 2-ADO dimer (**3**) has ΔG^* of 18.8 kcal/mol (+63 °C) for methyl interconversion, which is >8.8 kcal/mol greater than twice that of its 2-dimethylamino analogue (**5**). **3** is argued to have significant flattening at both nitrogens at the transition state, in contrast to all previously studied tetraalkylhydrazines. $3^{+}\cdot PF_6^-$ proved isolable.

The principal problem in studying electron removal from dialkylamino-containing compounds[1] (the reaction shown in eq 1)



1 $1^{+\cdot}$ (1)

is that for most X groups, the radical cation is extremely short-lived because it rapidly loses a proton from a carbon α to the nitrogen atom. This undesired decomposition can be successfully inhibited by "Bredt's rule kinetic stabilization",[2] by which is meant forcing

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(1) For a review, see: Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45.

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