^{13}C Chemical Shift Sensitivity to Charge in Delocalized Carbocations and its Relation to Ring Current Anisotropy

Bertil Eliasson, Dan Johnels, Ingmar Sethson, and Ulf Edlund *
NMR Research Group, Department of Organic Chemistry, University of Umeå, S-901 87 Umeå, Sweden
Klaus Müllen
Department of Organic Chemistry, University of Mainz, Postfach 3980, D-6500 Mainz, Federal Republic of Germany

The total carbon shift changes that occur upon oxidation of a variety of delocalized hydrocarbons have been empirically separated into a charge term and a term related to ring current anisotropy. The largest low-field total shift is observed for the most paratropic di-cations, where the second term is the most significant one. The shielding contribution due to charge is considerably larger for di-cations than for the negatively charged species. Field and ion-pair effects are discussed in this context.

The relationship between NMR chemical shifts and electronic structure of organic ions is of fundamental interest to modern organic chemistry. For instance, knowledge of the ground-state properties of delocalized ions is a prerequisite for the understanding of the remarkable regioselectivity in many organic reactions.[1] Here, kinetically controlled attack is expected to occur at the position of highest net charge. 'Experimental' local charges based on NMR chemical shifts are often preferred to theoretical estimates since the chemical shift data will also reflect ion-pair effects or changes in external ion-pair solvation.

The idea that the chemical shift is a simple measure of charge, is one of the most used or misused relationships in NMR spectroscopy. Numerous examples exist where, for a limited series of compounds, a direct correlation between observed NMR shifts and calculated charges seems to support this proposal.[1] Although it has been pointed out that the empirical relationships are only proven for compounds with closely related structures, few attempts have been made to clarify their limitations. Hence, the abuse of these relationships could have been foreseen. The suggested equations for protons (1a) and for carbons (1b) seem to have gathered most support,[2] where the $\Delta\delta$ values are the chemical shift changes and ρ_π is the change in π-charge.

$$\Delta\delta_H = 10.7 \cdot \rho_\pi \qquad (1a)$$

$$\Delta\delta_C = 160 \cdot \rho_\pi \qquad (1b)$$

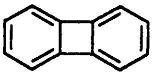
It is revealing to make a closer inspection of the NMR data sets which constitute the basis for these empirical correlations. Both the ^{1}H and ^{13}C linear chemical shift/charge models have been derived from monocyclic ions,[3,4] but the models are frequently used in a variety of bridged annulene type or polycyclic ions. A common feature of all these planar systems is their ability to sustain a diamagnetic ring current.

A major limitation of these models can be found from theory. If we limit our discussion to carbon shifts, it has been shown that the electron-orbital angular momentum (R) is the major contribution to shielding through the paramagnetic term in the Ramsey equation.[5] Consequently, bonding variation must be considered before any correlation is attempted.[6] When the angular momentum (R) terms or the bond structure are roughly constant throughout a series, as for cyclic sp^2 ions, the $\langle r^{-3}\rangle_{pA}$ term, *i.e.* the radius of the p-orbitals, becomes important and the shift will now reflect charge, provided that the average one-electron excitation term (ΔE), the magnetic field induced mixing of ground and excited states, is constant. This latter criterion puts another limitation to the set of compounds, as recently suggested by us.[7] Strong deviations from the expected 160 ppm per electron (ppm e^{-1}) have been found for multiply-charged anions that sustained a $4n\pi$ ring current, *i.e.* where a small HOMO–LUMO gap is inferred from HMO theory.[8] In such cases the estimated shift/charge correlation factors were significantly smaller than 160 ppm e^{-1}. A general empirical additivity model was suggested, where the total chemical shift change per electron (K_C) was expressed as the sum of a charge term (F_C) and a variable paramagnetic contribution (X_C) [equation (2)] where n_C is the number of conjugated carbons

$$K_C = F_C + (n_C/\rho_\pi)\, X_C \qquad (2)$$

and ρ_π is the total π-charge change.[7] The term X_C, called earfbl the variable 'anisotropy' term, was assumed to be interrelated to the proton anisotropy X_H by the formula: $X_C = a \cdot X_H$. The term X_H is defined by the formula: $X_H = \Delta\bar{\delta}_H - 10.7\,\bar{\rho}_\pi$, where $\Delta\bar{\delta}_H$ is the average change of the proton shift δ_H between the reduced species and its precursor, and $\bar{\rho}_\pi$ is the average change of the HMO π-charge at the proton-bearing carbons. A reason for assuming a relationship between X_H and X_C is that magnetically induced mixing of the π^* orbital into ground state orbitals is of importance for both ring current effects at protons and the paramagnetic shielding (ΔE, R) at carbon.[7] Using induced shifts caused by reduction to di-anions or tetra-anions, the F_C term was estimated to 134 ppm e^{-1} and $a = -2.4$. Thus from the observed anisotropy X_H, one could estimate the average anisotropy on carbon (X_C). Hence, if the induced carbon shieldings are corrected by the X_C contributions, one will obtain more realistic π-charge values at the individual positions. The inherent assumption is that the 10.7 ppm charge factor for proton systems is also valid for the paratropic $4n\pi$ systems as well.

Since it could be argued that cation induced field effects and charge transfer effects between the alkali metal ion and the carbanion system could in part explain the deviating K_C values, there was a need to extend the previous study by including structures where such effects could be minimized, *e.g.* carbocation systems. If charge transfer or ring deformation were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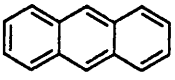
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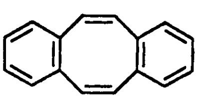
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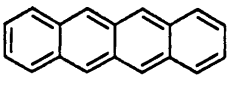
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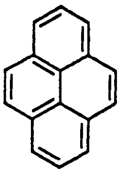
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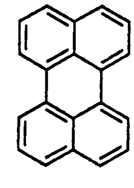
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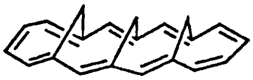
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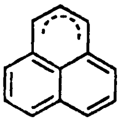
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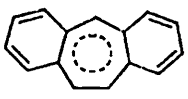
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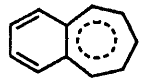
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Table 1. ^{1}H and ^{13}C NMR chemical shifts of the charged hydrocarbons and their precursors (1)–(11).

System	^{1}H	^{13}C
(1)$^{2+}$	9.00; 9.36[a.(b)]	135.8; 169.9; 177.9[a.(b)]
(1)	6.60; 6.70[b]	117.1; 128.4; 151.7[b]
(2)$^{2+}$	7.68; 7.92; 8.38[a.(c)]	138.4; 152.5; 164.1; 186.1[a.(d)]
(2)	7.39; 7.93; 8.36[e]	125.4; 126.3; 128.2; 131.8[f]
(3)$^{2+}$	10.89; 10.89; 11.94[a.(g)]	146.3; 149.5; 151.8; 160.8[a.(g)]
(3)	6.72; 7.06; 7.06[g]	128.1; 130.4; 134.5; 138.4[g]
(4)$^{2+}$	8.24; 8.37; 8.96[a.(c)]	136.9; 140.7; 150.0; 152.3; 175.6[a.(d)]
(4)	7.33; 7.94; 8.60[a.(h)]	125.1; 126.3; 128.3; 130.3; 131.6[a.(i)]
(5)$^{2+}$	6.31; 7.02; 7.27[a.(j)]	133.9; 143.3; 145.2; 156.3; 184.1[a.(d)]
(5)	8.11; 8.31; 8.20[k]	124.4; 124.5; 125.4; 126.4; 130.9[k]
(6)$^{2+}$	9.01; 9.89; 10.35[a.(c)]	124.3; 135.3; 138.6; 139.4; 152.1; 168.2[a.(d)]
(6)	7.59; 7.82; 8.40[a.(k)]	121.0; 127.3; 128.5; 129.6; 132.1; 135.9[a.(k)]
(7)$^{2+}$	6.13; 7.15; 7.72; (6.83; 9.27)[l]	139.9; 147.3; 161.2; 167.9; (33.0)[l]
(7)	7.28; 7.72; 7.89; (−1.13; 0.95)[l]	104.7; 126.4; 133.3; 136.8; (25.2)[l]
(8)$^{2+}$	6.07; 7.07; 7.27; (4.53; 7.58; 8.25)[l]	127.4; 133.9; 144.6; 151.6; 164.8; (24.7; 32.8)[l]
(8)	6.95; 7.55; 7.62; (−0.45; 0.53; 1.32)[l]	96.6; 107.0; 126.5; 137.0; 138.4; (14.1; 26.7)[l]
(9)$^{+}$	8.55; 9.38[m]	123.7; 132.9; 133.7; 155.5[m]
(9)$^{-}$	5.36; 6.10[m]	103.4; 128.0, 139.6; 145.0[m]
(10)$^{+}$	8.53; 8.76; 8.76; 9.02; 9.15; 10.43[a.(n)]	135.1; 136.3; 138.6; 142.5; 143.7; 144.9; 147.5; 173.3[a.(n)]
(10)$^{-}$	0.33; 2.42; 3.28; 3.53; 3.95; 4.65[a.(o)]	82.9; 112.5; 120.6; 131.9; 132.4; 137.9; 138.8; 163.3[a.(p)]
(11)$^{+}$	8.04; 8.23; 8.26; 8.61; 9.07[q]	138.2; 139.6; 141.2; 145.2; 158.3; 161.1[q]
(11)$^{-}$	0.03; 0.69; 2.45; 2.92; 4.32[q]	84.2; 108.8; 123.9; 127.0; 150.2; 159.3[q]

References in parentheses contain earlier reported shift values, for assignments refer to the earlier reports. [a] This paper. [b] G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, 1977, **99**, 6045. [c] D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1110. [d] D. A. Forsyth and G. A. Olah, *J. Am. Chem. Soc.*, 1976, **98**, 4086. [e] J. D. Memory and N. K. Wilson, in 'NMR of Aromatic Compounds,' Wiley Interscience, New York, 1982. [f] P. E. Hansen, *Org. Magn. Reson.*, 1979, **12**, 109. [g] G. A. Olah, J. S. Staral, G. Liang, L. A. Pacquette, W. P. Melega, and M. J. Carmody, *J. Am. Chem. Soc.*, 1977, **99**, 3349. [h] R. H. Martin, N. Defay, F. Geerts-Evrard, and S. Delavarenne, *Tetrahedron*, 1964, **20**, 1073. [i] W. Storek, J. Sauer, and R. Stösser, *Z. Naturforsch., Teil A*, 1979, **34**, 1334. [j] K. Müllen, *Helv. Chim. Acta*, 1978, **61**, 2307. [k] A. Minsky, A. Y. Meyer, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1982, **104**, 2475. [l] K. Müllen, T. Meul, P. Schade, H. Schmickler, and E. Vogel, *J. Am. Chem. Soc.*, 1987, **109**, 4992. [m] I. Sethson, U. Edlund, D. Johnels, and A. Sygula, *J. Chem. Soc., Perkin Trans. 2*, in press. [n] G. A. Olah and G. Liang, *J. Org. Chem.*, 1975, **40**, 2108. [o] The ^{1}H chemical shifts of the sodium salt have been reported by H. W. Vos, Y. W. Bakker, C. MacLean, and N. H. Velthorst, *Chem. Phys. Lett.*, 1974, **25**, 80. [p] The ^{13}C chemical shifts of the potassium salt have been reported by A. Ceccon, A. Gambaro, and A. Venzo, *J. Organomet. Chem.*, 1984, **275**, 209. [q] I. Sethson, D. Johnels and U. Edlund, *Acta Chem. Scand.*, in press.

significant, these effects should probably be most pronounced in the strongly charged alternating 4nπ systems.[1] If the anion–alkali metal orbital interaction is important, one would also expect the paratropicity of the lithium carbanions to be reduced compared with the potassium species. Field effects due to the counter ion would also be most severe under contact ion-pair conditions. These latter predictions gained some support from the proportionality constants observed for the acepleiadylene dilithium ($K_C = 20$) and dipotassium salts ($K_C = -1$).[8a] According to our model, a low K_C for the anions indicates increased paratropicity.

In the present study, we have considered the two-electron oxidation to various singly or doubly charged carbocations. To minimize the problems with changes in ring conformation, we have restricted this study to polycyclics or bridged annulene-type ions.

Results and Discussion

The ^{1}H and ^{13}C NMR chemical shifts of a variety of delocalized hydrocarbons and their corresponding di-cations are reported in Table 1. For a comparison, we have also included three systems where the oxidation process from a mono-anion to a mono-cation is monitored. Under superacid conditions, it is generally argued that ion-pairing effects are rather insignificant. We have recently been able to prove this claim by measuring the

Table 2. Total induced ^{13}C chemical shifts (K_C) and observed proton anisotropy (X_H) by two-electron oxidation.

System No.		K_C	$n_C X_H/\rho_\pi$
(1)	$0 \longrightarrow 2^+$	173	7.8
(2)	$0 \longrightarrow 2^+$	199	−13.6
(3)	$0 \longrightarrow 2^+$	154	23.7
(4)	$0 \longrightarrow 2^+$	221	−10.2
(5)	$0 \longrightarrow 2^+$	235	−25.3
(6)	$0 \longrightarrow 2^+$	173	3.5
(7)	$0 \longrightarrow 2^+$	202	−12.4
(8)	$0 \longrightarrow 2^+$	203	−16.4
(9)	$(1)^- \longrightarrow 1^+$	139	7.8
(10)	$(1)^- \longrightarrow 1^+$	96	30.5
(11)	$(1)^- \longrightarrow 1^+$	94	20.9

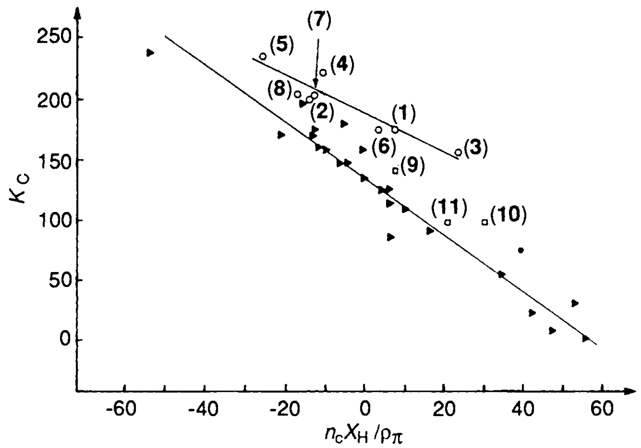

Figure. Plot of the total ^{13}C chemical shifts *vs.* the paramagnetic term derived from the magnetic anisotropy effects on ^1H chemical shifts. The open symbols correspond to the systems **(1)**–**(11)** in this work while the filled symbols refer to the reduction to sp^2 anions in ref. 7.

^{13}C chemical shifts of the benzotropylium cation as a function of solvent, counter ion and temperature.[9] No significant chemical shift changes could be observed, in sharp contrast with the corresponding isoelectronic indenyl anion system.

If we consider the oxidation processes to dications and if the suggested factor, n_C X_C, (or more strictly the ΔE and R terms in the Ramsey equation) is significant, one would expect K_C values larger than the shift/charge factor F_C for the systems where the di-cations are more paratropic than their precursors. In this case, both charge effects and the other paramagnetic shielding contributions (X_C) will cause downfield shifts. This means that the most paratropic di-cations are expected to give the highest K_C values. Oxidation to diatropic di-cations will be accompanied by values close to the charge factor (F_C) if the HOMO–LUMO gaps for the di-cation and its neutral precursor are both large.

The induced ^{13}C chemical shift changes upon two-electron oxidation are reported as K_C values in Table 2. It can be observed that the K_C values for the di-cations cover a range of *ca.* 80 ppm with the pyrene dication as the most paratropic ion (K_C = 235 ppm e^{-1}). This range is considerably narrower than the range of K_C measured for the reduced species (*ca.* 240 ppm).[7] As seen from a plot of K_C *vs.* $n_C X_H/\rho_\pi$ (see Figure), a similar correlation is obtained compared with the correlation using multiply charged anions only, with a slope of $a = -1.6 \pm 0.6$ (for the reduction processes $a = -2.4 \pm 0.3$). A more significant difference between the cation and anion systems is revealed by the intercept. A charge factor (F_C) of 133 ± 7 is obtained for the reduced species, while a considerably higher F_C is found for the oxidation to di-cations; $F_C = 186 \pm 10$. One can also note that cases representing transformation from mono-anion to mono-cation fall in between these two lines.

It has earlier been suggested that ion-pair effects in the negatively charged species are responsible for this difference in sensitivity to charge.[10] Both field effects and effects due to charge transfer will work in this direction for the carbanion ^{13}C shifts. Field effects in strongly alternating delocalized cations and anions have been roughly estimated to generate downfield shifts of the individual resonances of the order of 5–10 ppm e^{-1}.[10] The reduced K_C values observed by reduction to anions may also be explained by some charge transfer to the alkali cation as proposed by Vogler.[11,12] A partial electron transfer was suggested under contact ion-pair conditions which reduces the effective charge of the anion. However, it was argued that the charge transfer is not sufficient to significantly affect the ring current (RC) contribution. Based on the ion-pair studies of the indenyl system,[13] we claim that charge transfer effects only give a minor contribution to the observed difference of F_C between anions and cations. The total shift increment of the indenyl carbon shifts going from a proven contact-ion-pair condition (indenyl lithium in diethyl ether) to an ion pair where the tetramethylammonium ion is chosen as a counter-ion is close to experimental error.[13b]

Our results are in accordance with the value 200 ppm e^{-1} reported by Olah for $4n\pi$ di-cations.[4d] In another study, oxidation of dibenzo[*b,f*]pentalene showed a change of the mean carbon shift that corresponded to a K_C of 184 ppm e^{-1}.[14] This value is considerably higher than the value obtained by two-electron reduction of the same species; K_C = 159 ppm e^{-1}.[15] Both these doubly charged ions are $4n + 2$ π peripheral systems and show the same degree of diatropicity. A related situation can be seen from the phenalenyl system, where the two-electron oxidation from mono-anion to mono-cation yields a K_C of 139 ppm e^{-1}. This value is within the F_C range of 133–186 ppm e^{-1} and approximately equal 'tropicity' is therefore anticipated for the two non-Hückel ions.

For the strongly alternating cyclohexadienylic anions and cations, Fraenkel reported that the total ^{13}C shift increments for the anions were considerably lower than those for the corresponding cations; of the order of 70–80 ppm e^{-1}.[10] This value is obtained without correction for any field or charge-transfer effects. In that study, different neutral reference compounds were used for the calculation of the carbanion and carbocation shift changes. If we recalculate these data of the cyclohexadienylic ions using various neutral references in common for the anion and cation, we obtain shift/charge factors in the range of 130–150 ppm e^{-1} for the anions, while the transformation to cations yields values of *ca.* 180–200 ppm e^{-1}. Hence, for these atropic systems, the K_C values are very close to the shift/charge values (F_C) found in this report.

Conclusions

To conclude we have shown that other paramagnetic contributions, in addition to charge, make a significant contribution to the carbon shifts in multiply charged annulene-type ions. By using the induced ^{13}C chemical shifts upon reduction/oxidation, it is possible to calculate the experimental charges with reasonable accuracy, provided that the anisotropy changes are accounted for. This can approximately be achieved by an estimation of the induced charge-corrected ^1H shieldings as previously described. The applicability of our empirical model to predict the charge pattern in other series of heterocyclic aromatic systems has recently been demonstrated.[16] It is also shown that the charge factor (F_C) is lower for negatively charged species than for di-cations. This can be explained by field effects that influence the sp^2 carbons of the cations and anions in a similar way, with regard to both sign and magnitude.[10] Finally, it should be emphasized that a large or nearly constant energy gap between filled and vacant orbitals is a prerequisite if experimental charges should be derived from usual one-parameter shift/charge relationships. It must also be assumed that the orbital angular momentum terms are roughly constant, as one would expect for a given series of rigid sp^2 cyclic ions.

Experimental

Dibenzo[*a,d*]cyclohepten-5-one, SbF_5, SO_2ClF, perylene and tetracene were purchased from Aldrich; D_2SO_4, THF, $NaBH_4$ and MeOH from Merck; TFA and pyrene from Fluka; biphenylene from ICN Pharmaceuticals; anthracene from AB Reagens (Gothenburg, Sweden); and $[^2H]_8$THF and $[^2H]_6$-acetone from Stohler Isotope Chemicals. Dibenzocyclo-octene was synthesized according to earlier methods.[17]

All NMR spectra were recorded on a Bruker WM 250 NMR spectrometer. The di-cations were recorded at −40 to −20 °C, using $[^2H]_6$acetone as an external reference (the shifts were converted into the ppm scale using $\delta = 2.04$ ppm (CHD_2) and $\delta = 206.0$ ppm (C=O). The shift values were then corrected for solvent bulk effects by adding 0.96 ppm to the ^1H shift values and 1.8 ppm to the ^{13}C shift values. This correction was determined by measuring the tropylium cation in SbF_5 and SO_2ClF (1:1) and $ClSO_3H$, using the same external reference. However, in the latter case cyclohexane was added, and the deviation from the expected shift values was used as a correction value. The foundation for this procedure lies in the small effects of the medium on the observed shift values of the benzotropylium cation in a variety of different solvents.[9] All other spectra were recorded at room temperature, using cyclohexane as an internal reference (in this case the shifts were converted into the ppm scale using $\delta = 1.43$ ppm and $\delta = 27.7$ ppm). The spectra of neutral tetracene was obtained using $CDCl_3$ and the neutral perylene was measured in THF.

The electron densities were calculated by the Hückel MO method.

The dications were typically generated by the addition of *ca.* 100–150 mg of the hydrocarbon to 3 cm^3 of a 1:1 mixture of SbF_5 and SO_2ClF at −78 °C.

5*H*-Dibenzo[*a,d*]cycloheptatriene was prepared by $NaBH_4$ reduction of the corresponding ketone, according to literature procedures.[18] The dibenzo[*a,d*]cycloheptatrienyl anion was prepared by dissolving 10 mg of the hydrocarbon in 0.5 cm^3 of dry $[^2H]_8$THF under an argon atmosphere, followed by the addition of 10 mm^3 of 6.5 mol dm^{-3} n-BuLi at room temperature.

The dibenzo[*a,d*]cycloheptatrienyl cation was prepared as follows. The methoxy ether of 5*H*-dibenzo[*a,d*]cycloheptene was prepared by $NaBH_4$ reduction of the corresponding ketone in MeOH, according to standard procedures. The ether obtained was used to generate the cation by adding 40 mg of the ether to 1 cm^3 of D_2SO_4 at room temperature.

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