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SOME OBSERVATIONS ON THE RELATIONSHIP BETWEEN CHARGE AND ^{13}C CHEMICAL SHIFT IN CYCLOHEXADIENYLIC ANIONS AND CATIONS

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Abstract—Carbon-13 chemical shifts $\delta^{\pm}$ in a variety of cyclohexadienylic cations and anions have been separated semi-empirically into contributions from (a) the hypothetical neutral framework, (b) charge effects and (c) interactions between ions and between ions and solvent molecules. Carbon-13 shifts for sites in neutral model compounds, δ^{0}, approximate contribution (a) the shift differences for the model carbons $\delta^{\mp}_{3,5}-\delta^{0}_{3,5}$ are assumed to reflect electric field effects (b). Thus what remains, $\delta^{\mp}_{s}-\delta^{0}_{s}-(\delta^{\mp}_{3,5}-\delta^{0}_{3,5})$ comes from the charge. The summation of these terms for each of the ions comes to *ca.* 165 ppm. This shows that a changein charge of ±1 of the neutral model, with correction for the electric field, brings about a change in shift of 165 ppm, thus supporting the linearity of charge with shift.

The concept of a linear relationship between ^{13}C chemical shift and electron density in π-electron systems has attracted a great deal of attention from the initial correlation from shift data for symmetric cyclic species[1,2] to different attempts to rationalize the results.[3–6] The treatment of Pope and Karplus[3] which utilizes the average energy approximation accounts for only half the shift/charge index. However, including explicitly the lower electronic excitation energies ($\sigma\rightarrow\pi^{*}$) of the azines nicely reproduced the observed shifts and confirmed their linearity with electron density.[4] Olah has reported a similar charge/shift relationship from ^{13}C NMR data for carbonium ions.[7–9]

Recently O'Brien pointed out that the average ^{13}C shifts, δ_{av}, in a large collection of typical π conjugated cations and anions are linearly related to the average electron densities at carbon, ρ_{av}.[10]

$$\delta_{\mathrm{av}} = -156.8\rho_{\mathrm{av}} + 289.9 \qquad (1a)$$

or

$$\delta_{\mathrm{av}} - 133.1 = 156.8z_{\mathrm{av}}. \qquad (1b)$$

Equation (1) would hold if the ^{13}C shifts, with respect to neutral model shifts, were individually proportional to tha electron densities. Alternatively, cancellation of deviations from a charge-shift linearity could still give eqn (1).

The above relationships of charge to shift come from NMR studies of carbenium and carbanion salts in solution.[1,2,7–10] These species undoubtedly form different kinds of ion pairs. No account has been taken of interactions between ions and solvent, nor have effects due to substituents been properly assessed. In fact ^{13}C NMR shifts of cyclohexadienyl anions and cations vary markedly with solvent, counterion and substituent. In this paper we present an empirical treatment which reduces the NMR data for a variety of these species to a single constant which is similar to the charge/^{13}C shift index.

RESULTS AND DISCUSSION

In principle the relationship of charge to shift can be tested by comparing the ion ^{13}C shifts with shifts for carbons in neutral molecular environments structurally similar to the site in the ion in question. Then the sum of the increments going from the neutral models to the ions should be *ca.* 160 ppm.[1,2] This procedure has now been tried out for a series of cyclohexadienylic anions and cations. Table 1 lists the salts used, together with their neutral compounds. All evidence so far indicates these ions to be planar from X-ray crystallography for **3b**[11] and NMR studies **1–6** carried out at low temperature.[12–14] The results, ^{13}C shifts for ions, $\delta^{\pm}$, the neutral models, δ^{0}, and the differences between them are listed in Table 2.

These shift increments qualitatively follow the alternating order expected for conjugated ions. However, their sums vary markedly with medium and counterion and depend on whether or not the saturated carbon shift increments are included in the summations.

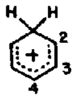
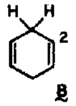
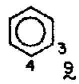
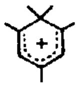
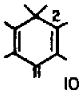
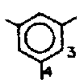
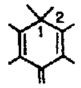
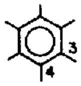
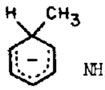
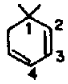
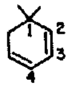
At first glance it would appear that these results negate the possible linearity of charge with shift. However, further inspection of Table 2 reveals that the deviation of the $\delta^{\pm}-\delta^{0}$ summations from charge/shift linearity comes from the $\delta^{\pm}_{3,5}-\delta^{0}_{3,5}$ terms. If the latter are subtracted from the former,

$$\sum_{s}(\delta^{\pm}_{s}-\delta^{0}_{s})-6(\delta^{\pm}_{3}-\delta^{0}_{3}) \qquad (2)$$

(where s goes over all ring carbons) the shifts which remain come to *ca.* 165 ppm each time for the conjugated salts **1–6**, see Table 3, which is close to the charge/shift index already reported by several groups. Thus it would appear that six times $\delta^{\pm}_{3,5}-\delta^{0}_{3,5}$ for each species represents the effect of the ion's environment on the total ^{13}C shift increment $\sum_{s}\delta^{\pm}_{s}-\delta^{0}_{s}$.

The foregoing result may be rationalized via the following considerations. It is well known that ^{13}C shifts in many molecules can be made up from a set of linearly additive substituent parameters.[15] Suppose contributions to the ring shifts come from (a) increments from the molecular skeleton, (b) effects due to electron density and (c) interactions within ion pairs and between ions and solvent molecules. Subtracting out the model shifts takes care of the skeleton (with substituents). Next we

Table 1. Salts and neutral model compounds[a]

Ref.		$R^{\pm}$ [a]	Solv.	Counter ion	Models[a]
12	**1**		SbF$_5$ FSO$_3$H	SbF$_6^-$ FSO$_3^-$	 **8**  **9**
	2		CH$_2$Cl$_2$	Al$_2$Cl$_7^-$	 **10**  **11**
b	**3a**		CF$_3$CO$_2$H	CF$_3$CO$_2^-$	  **12**
b	**3b**		CH$_2$Cl$_2$	AlCl$_4^-$	as for **3a**
12	**4**		NH$_3$	K$^+$	 **13**
12	**5**		NH$_3$	K$^+$	 **14**
13e	**6a**		THF	Li$^+$	 **15**
12	**6b**		NH$_3$	K$^+$	 **16**

[a] Numbers indicate correspondence of sites; [b] This work.

can assume that since C_3 and C_5 bear the smallest charges, their shift increments are most likely to come mainly from the ion's environment—interactions between ions and between ions and solvent, acting via the effects of electric fields.[16-19] The values of $\delta^{\pm}_{3,5} - \delta^0_{3,5}$ have the same sign for anions and cations, see Table 3, as would be expected.[16-18] If this electric field contribution is the same at all ring carbons then subtracting its value from all six $\delta^{\pm}_s - \delta^0_s$ terms should leave just shifts due to charge. The constancy of tha results, see last column in Table 3, supports this proposal.

The foregoing treatment requires a suitable choice of neutral model compounds and must include all ring shifts. This may imply significant mixing of the π-MO with σ^* orbitals associated with the C_1–C_2 and C_1–C_6 bonds. The method also assumes neutrality at $C_{3,5}$. Since these sums from eqn (2) seem to be constant, 165.3 ppm/e$^-$, it is attractive to speculate that the individual shifts corrected for skeletal and electric field effects are proportional to the charges at carbons,

$$z = \frac{\delta^{\pm}_s - (\delta^{\pm}_3 - \delta^0_3) - \delta^0_s}{165.3} \qquad (3)$$

where $\delta^{\pm}_3 - \delta^0_3$ is the electric field correction and δ^0_s the neutral model shift. Equation (3) resembles O'Brien's relationship with the *proviso* that the latter only handles the π-carbons and is derived via an averaging procedure. In contrast, the treatment reported here involves an analysis of the shifts individually.

It might be argued that the electric field correction could be different around the ring and that the shifts, as treated above, are not proportional to the individual charges. However, the consistency of the results supports the linearity of shift with charge.

In conclusion we find that ^{13}C shifts for cyclohexadienylic anions and cations can be empirically partitioned into contributions from different effects. The origin of the ion-environment correction is under continued study.

Table 2. ^{13}C NMR ring $C_{\#}$ shifts for ions, $\delta^{\pm a}$ and models δ^{a}

Cpd	$C_{\#}$	$\delta^{\pm}$	δ°	$\delta^{\pm} - \delta^{\circ}$	$(\delta^{\pm} - \delta^{\circ})$ $-(\delta^{\pm}_{3} - \delta^{\circ}_{3})$
1	1	52.2	26.0	26.2	17.9
	2	186.6	124.5	62.1	53.8
	3	136.9	128.6	8.3	0
	4	178.1	128.6	49.5	41.2
2	1	53.5	26.0	27.5	19.2
	2	193.2	136.3	57.1	48.6
	3	134.9	126.6	8.3	0
	4	193.4	136.3	57.1	48.8
3a	1	57.78	41.3	16.48	8.39
	2	198.87	137.26	61.61	53.52
	3	140.39	132.30	8.09	0.0
	4	192.40	132.30	60.10	52.09
3b	1	56.70	41.3	15.40	8.31
	2	197.17	137.26	59.91	52.82
	3	139.39	132.30	7.09	0.0
	4	190.9	132.30	58.60	51.51
4	1	30.0	22.6	7.4	0.4
	2	75.8	126.1	-50.3	-57.3
	3	131.8	124.8	7.0	0.0
	4	78.0	124.8	-46.8	-53.8
5	1	34.0	31.3	2.7	-2.5
	2	86.2	133.0	-46.8	-52.0
	3	129.1	123.9	5.2	0.0
	4	77.5	124.5	-47.0	-52.2
6a	1	30.8	38.9	-8.1	-13.6
	2	91.7	137.7	-46.0	-51.5
	3	127.9	122.4	5.5	0.0
	4	78.1	123.4	-45.3	-50.8
6b	1	33.5	38.9	-5.4	-10.0
	2	90.9	137.7	-46.8	-51.4
	3	127.0	122.4	4.6	0.0
	4	78.0	123.7	-45.7	-50.3

[a] ppm/TMS

Table 3. Total ^{13}C chemical shift increments for carbenium ions and carbonions

System	$\Sigma_{s} \delta^{\pm}_{s} - \delta^{\circ}_{s}$	$\Sigma[(\delta^{\pm}_{s} - \delta^{\circ}_{s})$ $-6(\delta^{\pm}_{3} - \delta^{\circ}_{3})]$
1	216.5	166.7
2	214.8	165.2
3a	216.0	167.5
3b	208.0	166.0
4	126.0	168.0
5	127.5	158.7
6a	134.4	167.4
6b	135.5	163.1

EXPERIMENTAL

Cation **3a**. A sample of 1,1,2,3,5,6 - hexamethyl - 4 - methylene - 2,5 - cyclohexadiene **7** (1.17 g, 6.7 mmole) dissolved in 7.6 ml of purified CS_2 was added under argon via syringe to a well stirred suspension of 0.978 g (7.337 mmole) anhydrous $AlCl_3$ in 2.0 ml CS_2 contained in a 25 ml round bottom flask equipped with a stopcock/serum cap assembly and a magnetic stirbar. HCl gas was added slowly to the solution via syringe needle and the resulting complex was found to be largely insoluble in CS_2. The solvent was next removed slowly *in vacuo* with rapid stirring of the solution by adjusting the stopcock opening which was attached to the vacuum takeoff. After returning the residue to an argon atmosphere (a trace of CS_2 was left for ^{13}C NMR referencing purposes) the solution was cooled to 0°, and 5.5 ml CH_2Cl_2 was added (total volume = 7.45 ml, 0.90 M). A 3.40 ml sample of this solution was combined with 0.15 ml TMS (4.2%) and the solution (0.86 M in cation **3a**) was examined by ^{13}C NMR revealing only cationic complex **3a** (>98%) and no detectable impurities.

Synthesis of **3b**. To a sample of **7** (1 g, 5.7 mmole) was added 1.2 ml CF_3COOH (16.15 mmole), 0.05 ml cyclopentane and 0.05 ml TMS. The ^{13}C NMR spectrum of this sample indicated only species **3b** (2.48 M).

NMR equipment. All ^{13}C NMR spectra were obtained using a Bruker HX-90 pulse NMR spectrometer in the ft mode at a frequency of 22.63 MHz and a home-built multinuclear pulse NMR instrument at a frequency of 15.09 MHz. Spectra are referenced to tetramethylsilane or cyclopentane.

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