Unusually Low ^{13}C Chemical Shift Sensitivity to Charge in Cyclic $4n\pi$ Anions. Potential Relation to Anisotropic Ring Current Effects

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For various pairs of neutral π-systems and their corresponding di- or tetra-anions, a relationship between the ^{13}C n.m.r. chemical shift/charge ratio (K_C) and the altered ^1H ring current anisotropy is observed. Thus for a $4n\pi$ anion system, the ^{13}C shift sensitivity to charge is significantly lower than the K_C value obtained for a diatropic anion. This is explained in terms of the average electronic excitation energy, which influences both the ^{13}C chemical shifts and the ring current intensities. An empirical model which describes the ^{13}C shifts on the basis of a charge term and an anisotropy term is postulated. The anisotropy term is shown to be linearly related to the ^1H ring current anisotropy.

Since ion-pairing and aggregation effects could have a profound influence on charge distribution in delocalized anions, organic chemists commonly prefer experimental estimates of charge density pattern in these species. In particular, relationships between n.m.r. chemical shifts and electron densities have been widely studied, both experimentally and theoretically.[1] In general, linear models have been applied, relating the observed chemical shift and the charge measure (q) as in equation (1),

$$\delta_C = \delta_N - K(q - 1) \qquad (1)$$

where δ_C is the chemical shift of the charged species and δ_N the corresponding value for the neutral precursor.[1–3] However, the proportionality factors depend strongly on the molecular structure (types of atoms, hybridization, *etc.*). They also vary with the types of orbitals involved (1*s*, 2*s*, σ, π, *etc.*), and with the MO calculation method. The two most commonly used correlations show a linear relationship between ^1H and ^{13}C shifts and π-charge, with proportionality constants of approximately 10.7 (K_H) and 160 p.p.m. per electron (K_C), respectively.[2,3] These values originate from studies of a few neutral and charged aromatic monocyclic hydrocarbons.

In our recent n.m.r. studies of conjugated polycyclic carbanions, ^{13}C shift data gave rise to sensitivity factors that were significantly lower than 160 p.p.m. per electron.[4] For instance, the two-electron reduction of pyrene and acepleiadylene yields K_C values in the range 28 to −1 p.p.m. per electron.[4c–e,h] These reductions are accompanied by unusually large high-field shifts of the ^1H resonances. In general, such behaviour is accounted for by a change from a diamagnetic ring current to a paramagnetic one.[5] Local shielding anisotropy at carbon may also affect the ^1H shielding,[6] but for true annulenes this is expected to be a minor contribution.[7]

Results and Discussion

In order to examine the relationship between variations in K_C and changes in ring current magnetic anisotropy, we returned to our recent work in which we succeeded in transforming various unsaturated hydrocarbons into dianions and tetra-anions.[4] The corresponding ^1H and ^{13}C n.m.r. data are compiled in the Table. From the peripheral protons, the difference in dia- or para-tropicity (X_H) between the neutral precursor and the anion can be approximated by the average change of the ^1H chemical shifts ($\Delta\delta_H$), corrected for the charge effect using K_H = 10.7 p.p.m. per electron (Table). Thus, equation (2) is obtained,

$$X_H = \Delta\bar{\delta}_H - 10.7\,\Delta\bar{\rho}_\pi \qquad (2)$$

where $\Delta\bar{\rho}_\pi$ is the average change in π-charge at the proton-bearing carbon atoms. The value of $\Delta\bar{\rho}_\pi$ was obtained by the HMO method, except for systems (**13**) and (**15**), for which SCF-PPP calculations were performed. Inspection of the K_C and the corresponding X_H values in the Table shows a clear relationship between these quantities. With an increased ^1H ring current shielding, a reduced K_C value is observed, *i.e.* a decreased ^{13}C shielding in comparison with that expected on the basis of charge. Some reductions which result in decreased ^1H ring current shielding and unusually high K_C values are also found, *e.g.* systems (**1**) $(2- \longrightarrow 4-)$ and (**2**). It is reasonable to assume that ring current contributions to K_C are small or absent, since theory predicts a zero ring current effect at the carbon nuclei which constitute the ring of the current, *i.e.* in the nodal plane of the π-system.[5] For carbon atoms not participating in sustaining the ring current, *e.g.* the two 'inner' (ethylene) carbon atoms in pyrene, such ring current effects may be significant.[8] Such contributions are not sufficient though to explain the observed ^1H ring current shielding/^{13}C deshielding correlation.

Instead, the average energy for mixing (especially $\sigma \longrightarrow \pi^*$) of electrons from ground state to various low lying excited states (ΔE) forms a sound basis for rationalizing the various K_C values.[9] The ΔE factor enters the denominator in the Karplus–Pople equation for nuclear paramagnetic shielding, which is thought to dominate ^{13}C screening.[9a] ΔE also enters the denominator of some terms in the theoretical models of paramagnetic ring currents.[10] Hence, a reduced ΔE results in a low-field ^{13}C shift. Simultaneously, the ^1H resonances are shifted to higher field owing to the increased paramagnetic ring current. ΔE describes a weighted average of different mixings, with the low-energy excitations as the most important. Thus, while 'local' effects upon the different carbon atoms cannot be excluded, it seems likely that a change in ΔE can be considered to influence the individual sp^2 carbon atoms to a similar extent.

On an empirical level, we propose that the ^{13}C shifts can be expressed as the sum of a charge term and a variable anisotropy term (X_C) [equation (3), where $\Sigma\Delta\delta_C$ is the total ^{13}C shift

$$\Sigma\Delta\delta_C = \rho_\pi F_C + n_C X_C \qquad (3)$$

change, ρ_π is the total π-charge change (−2.0 for dianions or −4.0 for tetra-anions), F_C is the 'pure' chemical shift/charge factor, and n_C is the total number of carbon atoms in the

Table. ^{13}C N.m.r. chemical shift change per electron (K_C in p.p.m.) and ^{1}H n.m.r. shift anisotropy (X_H in p.p.m.) for reductions† of conjugated hydrocarbons

System	K_C	$\Delta\bar{\delta}_H$‡	$\Delta\bar{\rho}_\pi$§	X_H	$-n_C X_H/\rho_\pi$	Ref.
Acepleiadylene (**1**), 2– ⟶ 4–	238	4.96	−0.160	6.67	53.4	*a*
Heptalene (**2**)	195	0.97	−0.146	2.53	15.2	*b*
Biphenylene (**3**)	178	−0.38	−0.114	0.84	5.0	*c*
Aceheptylene (**4**)	173	0.3	−0.136	1.76	12.3	*d*
1,7-Methano[12]annulene (**5**)	169	1.34	−0.2¶	3.5	20.9	*e*
Octalene (**6**), 2– ⟶ 4–	168	0.07	−0.167	1.86	13.0	*f*
Dibenzo[*b*, *f*]pentalene (**7**)	159	−0.14	−0.149	1.45	11.6	*g*
Octalene (**6**), 0 ⟶ 4–	156	−0.44	−0.296	2.73	9.6	*f*
Pyraceheptylene (**8**)	156	−1.2	−0.116	0.04	0.3	*h*
Pleiadylene (**9**)	146	−1.21	−0.168	0.59	4.1	*h*
Octalene (**6**), 0 ⟶ 2–	145	−0.51	−0.129	0.87	6.1	*f*
Acepleiadylene (**1**), 0 ⟶ 4–	133	−3.12	−0.295	0.04	0.2	*a*
Fluoranthene (**10**)	124	−2.34	−0.145	−0.79	−6.3	*h*
Acenaphthylene (**11**)	123	−3.09	−0.223	−0.70	−4.2	*i*
Decacyclene (**12**) 0 ⟶ 6–	112	−3.29	−0.211	−1.03	−6.2	*c*
Tetradehydro[14]annulene (**13**)	112	−6.43	−0.060	−5.79	−40.5	*j*
Azulene (**14**)	107	−4.24	−0.204	−2.06	−10.3	*k*
Tetradehydro[18]annulene (**15**)	94	−8.14	−0.033	−7.79	−70.1	*j*
Anthracene (**16**)	89	−4.43	−0.193	−2.36	−16.5	*l,m*
1,6;8,13-Dimethano[14]annulene (**17**)	84	−3.07	−0.2¶	−0.93	−6.5	*n*
Phenanthrene (**18**)	52	−6.84	−0.177	−4.95	−34.7	*o*
Acepleiadylene (**1**), 0 ⟶ 2–	28	−8.07	−0.135	−6.63	−53.0	*a*
Pyrene (**19**)	20	−7.18	−0.179	−5.26	−42.1	*p,q*
Pyrene (**19**), Na$^+$	5	−7.84	−0.179	−5.92	−47.4	*r*
Acepleiadylene (**1**), K$^+$, 0 ⟶ 2–	−1	−8.40	−0.135	−6.96	−55.7	*h*

† Unless stated otherwise the reductions were performed with lithium. ‡ Average ^{1}H shifts for the reduction; a positive sign denotes a downfield shift. § Average change of π-charge at proton-bearing carbon atoms. ¶ π-Charge at proton-bearing carbon atoms assumed to be 2.0. [a] Refs. 4*c*,*d*. [b] J. F. M. Oth, K. Mullen, H. Konigshofen, J. Wassen, and E. Vogel, *Helv. Chim. Acta*, 1974, **57**, 2387. [c] (i) R. Benken, K. Finneiser, H. von Puttkamer. H. Gunther, B. Eliasson, and U. Edlund, submitted for publication in *Helv. Chim. Acta*; (ii) B. Eliasson and U. Edlund, unpublished results. [d] (i) G. Neumann and K. Mullen, to be published; (ii) G. Neumann, H. Schmickler and K. Mullen, *Angew. Chem.*, 1983, **95**, 238; *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 241. [e] J. F. M. Oth, K. Mullen, H. Konigshofen, M. Mann, Y. Sakata, and E. Vogel, *Angew. Chem.*, 1974, **86**, 232; *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 284. [f] K. Mullen, J. F. M. Oth, H.-W. Engels, and E. Vogel, *Angew. Chem.*, 1979, **91**, 251; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 229. [g] B. Eliasson and U. Edlund, *Org. Magn. Reson.*, 1983, **21**, 322. [h] Ref. 4*c*. [i] Refs. 4*c*,*g*. [j] (i) K. Mullen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *J. Am. Chem. Soc.*, 1982, **104**, 5403; (ii) K. Müllen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *Tetrahedron*, 1983, **39**, 1575. [k] Ref. 4*f*. [l] Ref. 4*a*. [m] M. L. Caspar, J. B. Stothers, and N. K. Wilson, *Can. J. Chem.*, 1975, **53**, 1958. [n] K. Mullen, T. Meul, E. Vogel, U. Kursdurer, H. Schmickler, and O. Wennerström, *Tetrahedron Lett.*, submitted for publication. [o] Ref. 4*b*. [p] Ref. 4*c*. [q] K. Mullen, *Helv. Chim. Acta*, 1978, **61**, 2307. [r] Refs. 4*e*,*h*.

system]. If the proton ring current contribution and the anisotropy on carbon are inter-related through ΔE, we can simply express this as $X_C = aX_H$, where a is a negative constant. The sign accounts for the fact that proton shielding due to ring current effects corresponds to carbon deshielding, owing to anisotropy on carbon.

If equation (3) is divided by the π-charge change, ρ_π, we obtain equation (4).

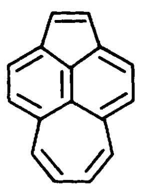
$$K_C = F_C + (n_C/\rho_\pi)aX_H \qquad (4)$$

A plot of K_C *vs.* $(n_C/\rho_\pi)aX_H$ is shown in the Figure, giving values of a = −2.4 and F_C = 134 p.p.m. per electron [systems (**13**) and (**15**) excluded, r = 0.971]. It should be noted that polycyclic systems which possess carbon atoms that experience significant ring current effects, *e.g.* the two inner carbon atoms in pyrene,[8] do not show any marked deviation. However, systems (**13**) and (**15**) deviate considerably. An obvious explanation is that these species have carbon atoms with acetylenic character, which may not fit the foregoing sp^2 carbon model. If 'in-plane–out-of-plane' ($\sigma \longrightarrow \pi^*$) mixing is important, one would expect the 'in-plane' components to be different for sp^2 and sp carbons.[11] Furthermore, the assessment of X_H from only one (**13**) or two (**15**) ^{1}H shifts may be too approximate.

Recently it was noted in a graph theoretical study of benzenoid dications that the average ^{13}C chemical shift, *i.e.* a quantity derived from local molecular properties, correlates with a global molecular property, the molecular resonance energy.[12] Increased molecular resonance energy, commonly interpreted as increased aromatic character, was expected to induce greater shielding on the average of carbon atoms of more aromatic molecules. This parallels nicely our findings in the present study.

Deviations from planarity or charge transfer from the anionic species to the alkali cation must also be considered as possible origins of the lower K_C values noted for the paratropic species. However, most of the neutral precursors and their anions have extremely rigid molecular frameworks and are not expected to suffer from charge-induced conformational changes, not even as $4n\pi$-systems. If anion–cation charge transfer occurs, one would expect such a transfer to be more pronounced for lithium compounds, since lithium has a stronger tendency to orbital overlap than sodium or potassium. Hence, if charge transfer or aggregation is causing the unusually low K_C values, this should be most obvious for the lithium compounds. However, according to our observations (Table), cation influence is noted for systems with enhanced paratropicity, such as (**1**) (Li$^+$, 0 ⟶ 2– and K$^+$, 0 ⟶ 2–) and (**19**) [see ref. *j* (ii) in Table] but the K_C values are lower for the sodium or potassium than for the lithium salts. This rules out a charge transfer explanation. Instead, this cation effect can be explained on the basis of a variable ΔE term, since a change to a smaller cation, *e.g.* $K^+ \longrightarrow Li^+$, causes a stabilization of the highest MO in a tight ion-pair structure.[13]

The absence of a charge-transfer mechanism is also supported



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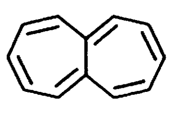

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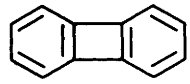

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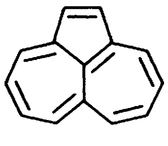

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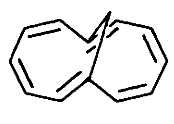

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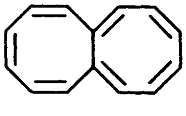

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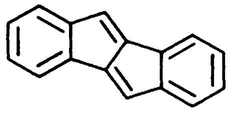

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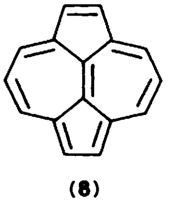

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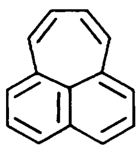

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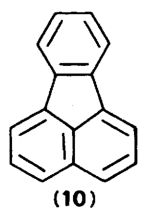

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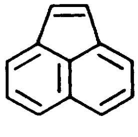

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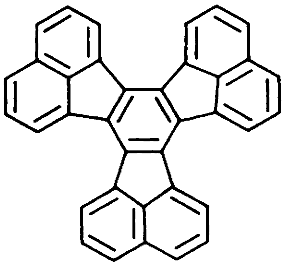

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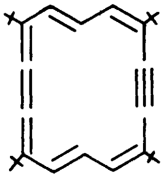

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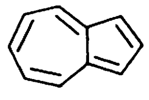

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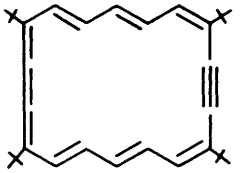

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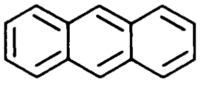

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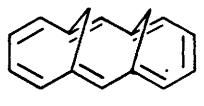

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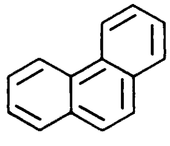

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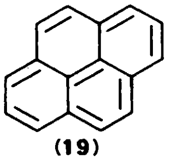

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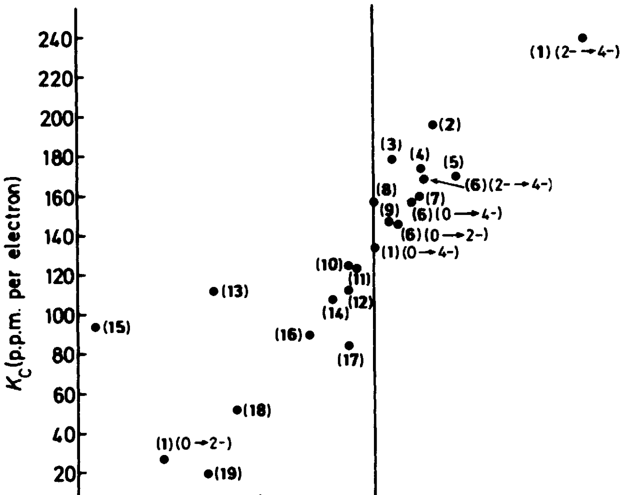

Figure ^{13}C N.m.r. chemical shift change *versus* change in ^1H ring current shielding for reductions of various conjugated hydrocarbons

by the results from n.m.r. experiments on various polycyclic dications, where charge transfer can be safely excluded. In these systems, a deshielding contribution due to anisotropy on carbon should be added to the induced deshielding due to charge and one expects therefore a K_C value larger than a value due to charge only. For the $4n\pi$ anthracene dication, a 'system-specific' K_C of 208 p.p.m. per electron is thus obtained, to be compared with the K_C value for the paratropic dianion of 89 p.p.m. per electron.[4a] The mean K_C value (148.5) is then closer to the true shift/charge term, F_C. To conclude, in addition to charge, there is a deshielding contribution to the dication carbon atoms, which is similar in magnitude to the ^{13}C anisotropy term found for anionic systems.

In summary, to obtain experimental charge maps for ions of cyclic or polycyclic conjugated systems, it is recommended that the individual ^{13}C chemical shifts should be corrected for the anisotropy contribution X_C. The charge density at each carbon atom can then be determined by dividing the corrected ^{13}C chemical shift change by the true charge term F_C.

Experimental

The ^1H and ^{13}C n.m.r. chemical shift data were taken from references listed in the Table. Unless stated otherwise, the data correspond to two-electron reductions with Li metal and the spectra were recorded for solutions in tetrahydrofuran or [$^{2}H_{8}$]tetrahydrofuran.

Acknowledgements

Financial aid by the Deutsche Forschungsgemeinschaft (to K. M.) and the Swedish Natural Science Research Council (to U. E.) is gratefully acknowledged.

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Received 26*th April* 1985; *Paper* 5/687