The Importance of Local Anisotropic Effects and Ring Currents on Proton Shieldings in Aromatic Hydrocarbons

Michael Barfield,*[1a] David M. Grant,*[1b] and Dennis Ikenberry[1b]

Contribution from the Departments of Chemistry, University of Arizona, Tucson, Arizona 85721, and University of Utah, Salt Lake City, Utah 84112.

Received January 16, 1975

Abstract: A significant part of the deshielding of protons in condensed aromatic hydrocarbons is shown to be due to anisotropic shielding effects at each of the carbon atoms. The remaining contribution of 50% or less is attributed to delocalized contributions, often referred to as ring current (RC) effects. In this study the classical model of a field due to a circular loop is used to calculate both the local anisotropic (LA) contributions and the delocalized ring current (RC) contributions. Calculated values for the LA effects are based on the experimentally determined shielding tensor for benzene. However, it is necessary to use an empirical criterion to determine the RC effects. The results of these procedures provide a correlation of the experimental data, which are in comparable agreement with recent theoretical results based on uncoupled Hartree-Fock theory and semiempirical wave functions. The theoretical formulation presented here is also completely consistent with the rather unusual situation which occurs for the [4*n*]- and [4*n* + 2]annulenes. For the [4*n*]annulenes the inner protons are more deshielded than the outer protons because of the LA effects and the absence of any significant RC effects. However, in the [4*n* + 2]annulenes the very large shielding of the inner protons and the deshielding of the outer protons is due to the very large RC effects in these systems. An incidental, but interesting, observation is the excellent correlation of the experimental data, which is obtained on multiplying the calculated LA contributions by a factor of 2. Since the dipole approximation is adequate for all except the bonded carbons, a very simple, but useful, formula can be used to calculate proton shieldings even in those cases in which the protons are presumed to be sterically crowded.

Both semiclassical[2] and quantum mechanical[3] ring current concepts have been used to interpret anisotropic magnetic susceptibilities.[4] These currents are presumed to flow in the cyclic π-electronic systems on application of a magnetic field perpendicular to the ring. With the development of the techniques of high resolution nuclear magnetic resonance (NMR) spectroscopy, it was found[5-8] that the ring current concept elegantly accounted for the deshielding of the protons in benzene and the polycyclic hydrocarbons. The ring current hypothesis was bolstered by the observation of very large upfield shifts in the series of annulenes.[9-15] Indeed, the ring current concept has been used extensively[12-16] as a criterion for aromaticity, although considerable caution has been advised[17,18] in the inference of aromaticity from NMR data.

The Pople[7] and McWeeny[8] modifications of the London[3] theory used simple LCAO-MO considerations. These have been extended to a variety of SCF methods[19-21] including density matrix perturbation methods,[22] and coupled[23] and uncoupled[24,25] versions of Hartree-Fock theory. Another formulation[26,27] of ring currents uses a classical model in which magnetic fields are produced by n electrons circulating in loops above and below the plane of the ring. This model has been applied[28] to condensed ring aromatics with ring current intensities based on the London theory.[2] A more recent treatment[29] uses the one-dimensional gas model.

It should be noted that the entire question of the existence of ring currents has been questioned[30,31] but this proposal has been strongly criticized[13,32] on the basis that the ring currents are essential in explaining the chemical shift data for the annulenes. Using a crude estimate for the local paramagnetic susceptibility in benzene and the simple dipolar formula for neighbor anistropy effects in chemical shift theory,[33,34] Pople[35] estimated a contribution of almost 50% of the deshielding of the protons in benzene as due to local anisotropic (LA) effects.

In this study use is made of the recent experimental[36] values of the carbon-13 tensor shielding components for solid benzene to show that LA effects make substantial contributions to proton chemical shifts for condensed ring systems as well as for benzene. It was the intention of this investigation to establish the importance of such contributions, so that *no parameters were varied in the calculations of the anisotropic shielding (LA) contributions.* The remainder, which must necessarily be determined empirically, is attributed to the delocalized (RC) effects. The introduction of only one parameter permits an excellent correlation of a large amount of experimental data. A consideration of the combined LA and RC effects provides a useful explanation of the reversal of the chemical shifts of the inner and outer protons in the series of [4*n*]- and [4*n* + 2]annulenes.

Results and Discussion

A. Local Anisotropic (LA) Contributions to Proton Shielding. Anisotropic shielding at carbon will occur in those cases in which the electronic environments deviate from spherical symmetry. The LA effects at carbon are large (in comparison with protons, for example) because the one-center integrals involve the 2p atomic orbitals on carbon, and these have a $1/r^3$ dependence. Contributions from the delocalized terms would involve the multicentered integrals and when combined with the $1/r^3$ dependence drop off rapidly with distance. There would also be an effect on the ^{13}C anisotropic shielding because of the decreased excitation energies (in aromatic and unsaturated systems), which enter the denominators of certain terms in the second-order perturbation sum.[31]

By means of the technique of proton-enhanced nuclear induction spectroscopy,[37] the ^{13}C principal components of the shielding tensor of a number of organic solids have been determined.[36] For solid benzene at −50°C the three components are as follows: $\delta_{11}^{C} = 117 \pm 1$ ppm, $\delta_{22}^{C} = \delta_{33}^{C} = -63 \pm 1$ ppm relative to liquid benzene.[36] To estimate the importance of this large ^{13}C anisotropy on the proton shielding constants, consider a free electron model[26] in which the components of magnetic induction due to a loop of radius a are given in cylindrical coordinates, ρ, z, by the expressions[38]

$$B_\rho = \frac{\mu I}{2\pi}\frac{z}{\rho[(a+\rho)^2+z^2]^{1/2}}\left[-K+\frac{a^2+\rho^2+z^2}{(a-\rho)^2+z^2}E\right] \quad (1)$$

$$B_z = \frac{\mu I}{2\pi}\frac{1}{[(a+\rho)^2+z^2]^{1/2}}\left[K+\frac{a^2-\rho^2-z^2}{(a-\rho)^2+z^2}E\right] \quad (2)$$

where μ is the permeability, I is the current, and K and E are the complete elliptic integrals of the first and second kind with argument

$$k^2 = 4a[(a+\rho)^2+z^2]^{-1} \quad (3)$$

For points situated along the $\rho = 0$ axis,[38] $B_\rho = 0$ and

$$B_z = \frac{\mu a^2 I}{2(a^2+z^2)^{3/2}} \quad (4)$$

Now consider currents I_i flowing in atomic loops with radii a_i arising from magnetic fields perpendicular and in the plane of the aromatic ring as depicted in Figures 1a–c. For $z = 0$ it follows from eq 4 that

$$I_i = 2a_iB_{iz}{}^{C}/\mu \quad (5)$$

For a magnetic field perpendicular to the plane of the aromatic ring, local atomic currents of radius a_1 will be set-up in the plane of the ring as depicted in Figure 1a. In this case $z = 0$, $\rho = r_{CH}$, and it follows from eq 1–5 that $B_{1\rho}{}^{C} = 0$ and

$$B_{1z}{}^{H} = \frac{a_1}{\pi(a_1+r_{CH})}\left[K+\frac{a_1+r_{CH}}{a_1-r_{CH}}E\right]B_{1z}{}^{C} \quad (6)$$

Consider a current loop of radius a_2 arising from a magnetic field parallel to the C–H bond as depicted in Figure 1b. In this case $\rho = 0$, $z = r_{CH}$, and the magnetic induction follows from eq 4 and 5,

$$B_{2z}{}^{H} = \frac{a_2{}^3}{(a_2{}^2+r_{CH}{}^2)^{3/2}}B_{2z}{}^{C} \quad (7)$$

In the case where the external magnetic field lies in the aromatic ring but perpendicular to the C–H bond, a local atomic current of radius a_3 will be set up as depicted in Figure 1c. From eq 1–5 it follows that the components of magnetic induction at the hydrogen atom will be $B_{3\rho}{}^{H} = 0$ and

$$B_{3z}{}^{H} = \frac{a_3}{\pi(a_3+r_{CH})}\left[K+\frac{a_3+r_{CH}}{a_3-r_{CH}}E\right]B_{3z}{}^{C} \quad (8)$$

Division of eq 6–8 by the applied field $B_z{}^0$ gives expressions for the proton shielding components $\sigma_{11}{}^{H}$, $\sigma_{22}{}^{H}$, and $\sigma_{33}{}^{H}$ in terms of the carbon shielding components $\sigma_{11}{}^{C}$, $\sigma_{22}{}^{C}$, and $\sigma_{33}{}^{C}$. The isotropic proton shielding is given by averaging the components over the three equally probable orientations.

$$\langle\sigma^{H}\rangle = (1/3)[\sigma_{11}{}^{H}+\sigma_{22}{}^{H}+\sigma_{33}{}^{H}] \quad (9)$$

The expression for the averaged proton shielding can be simplified by noting that $\sigma_{22}{}^{C} = \sigma_{33}{}^{C}$ from the work of Pines, Gibby, and Waugh.[36] Furthermore, it may be assumed that atomic loops all have the same radii $a_i = a$. Because the effective nuclear charges differ for the σ- and π-electronic systems[39] the various a_i might also be expected to differ. However, in view of the crudeness of the model adopted here, this refinement was not thought to be justified. From eq 6–9 it follows that

$$\langle\sigma^{H}\rangle = \frac{1}{3}\left\{\frac{a^3\sigma_{22}{}^{C}}{(a^2+r_{CH}{}^2)^{3/2}} + \frac{a(\sigma_{11}{}^{C}+\sigma_{22}{}^{C})}{\pi(a+r_{CH})}\left[K+\frac{a+r_{CH}}{a-r_{CH}}E\right]\right\} \quad (10)$$

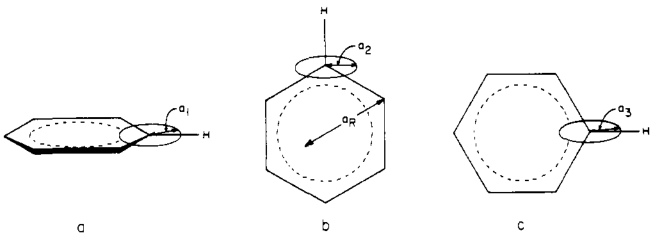


Figure 1. Schematic representations of the local anisotropic currents at one of the benzene carbons. In diagrams (a) and (c) the external field is perpendicular to the C–H bond, but perpendicular to and parallel to the plane of the ring, respectively. In (b) the field is directed along the C–H bond.

On expanding K and E in terms of k^2 and assuming that $a \ll r_{CH}$, eq 10 reduces to the usual dipole-dipole type of expression

$$\langle\sigma^{H}\rangle = a^3(\sigma_{11}{}^{C}-\sigma_{22}{}^{C})/6r_{CH}{}^3 \quad (11)$$

The approximation of eq 11 is reasonable in all cases except for the contribution to the proton shielding from the bonded carbon as the assumption $a \ll r_{CH}$ is not valid. For $\sigma_{11}{}^{C} - \sigma_{22}{}^{C} = 180$ ppm[36] and $a = [\langle 2p_C|r^{-3}|2p_C\rangle]^{-1/3} = 0.047$ nm (this is the theoretical value for this integral using a Slater radial function with $\xi = 1.625$), and the usual aromatic C–H distance $r_{CH} = 0.108$ nm, a value of -2.47 ppm is obtained for eq 11 for the effect on proton shielding due to LA effects of the local carbon atom. With the same experimental and theoretical quantities (and one further assumption discussed below), eq 10 gives a value of -3.29 ppm. The difference in the results obtained via eq 10 and 11 is indicative of the error of the dipole approximation for shielding at the proton due to the directly bonded carbon.

In order to use eq 10 it is necessary to estimate the *absolute* value of the anisotropic ^{13}C shielding components whereas the experimental data[36] refer to shifts relative to benzene liquid. It is important to note that *only* the above calculated result for the directly bonded proton is sensitive to this derived number, and it becomes increasingly unimportant as the separation between the carbon atom and the hydrogen atom increases. Since methane has spherical symmetry, each of the principal components must equal the isotropic value of 131 ppm relative to benzene.[40] A recent theoretical value[41] of 205 ppm for the ^{13}C shielding for methane was based on an ab initio coupled Hartree-Fock scheme with gauge-invariant atomic orbitals. Since the calculated values were typically within 10 ppm of the experimental ones, this constitutes a reasonable value for estimating the absolute magnitudes of the components of the shielding tensor. Therefore, the addition of about 74 ppm (205 minus 131 ppm) to the experimentally determined anisotropic components[36] gives the following ^{13}C shielding components for benzene: $\sigma_{11}{}^{C} = 191$ ppm and $\sigma_{22}{}^{C} = \sigma_{33}{}^{C} = 11$ ppm. With these values in addition to $a = 0.047$ nm, $r_{CH} = 0.108$ nm, $r_{CC} = 0.140$ nm, and the assumption that all rings are hexagonal, local anisotropic proton shieldings in parts per million for benzene **1** and a series of condensed ring aromatics **2–15** were based on the equation

$$\langle\sigma^{H_j}\rangle = \frac{1}{3}\sum_i\left\{\frac{a^3\sigma_{22}{}^{C}}{(a^2+r_{C_iH_j}{}^2)^{3/2}} + \frac{a(\sigma_{11}{}^{C}+\sigma_{22}{}^{C})}{\pi(a+r_{C_iH_j})}\left[K+\frac{a+r_{C_iH_j}}{a-r_{C_iH_j}}E\right]\right\} \quad (12)$$

where $r_{C_iH_j}$ denotes the distance from the ith carbon atom to the jth hydrogen atom and the summation is over all of the carbon atoms in the ring system. Calculated results are entered in Table I.

The calculated LA results for benzene (**1** in Table I) include the summation over all six of the carbon atoms in the

Table I. Calculated Values of Local Anisotropic and Delocalized Contributions and Their Sum Compared with Experimental Values of Chemical Shifts of a Series of Condensed Ring Aromatics 2–15 Relative to Benzene

Compd	H_j	Local anisotropic contribution,[a] ppm	Delocalized contribution,[b] ppm	Total, ppm	Exptl,[c] ppm
(1) Benzene	1	(−4.177)	(−0.219)	(−4.396)	
(2) Naphthalene	1	−0.286	−0.151	−0.44	−0.46
	2	−0.084	−0.097	−0.18	−0.11
(3) Anthracene	1	−0.345	−0.172	−0.52	−0.66
	2	−0.112	−0.131	−0.24	−0.12
	3	−0.567	−0.321	−0.89	−1.09
(4) Phenanthrene	1	−0.330	−0.178	−0.51	−0.53
	2	−0.119	−0.119	−0.24	−0.24
	3	−0.143	−0.129	−0.27	−0.30
	4^d	−0.622	−0.264	−0.89	−1.35
	9	−0.368	−0.210	−0.58	−0.38
(5) Chrysene	1^d	−0.706			−1.39
	2	−0.429			−0.66
	3	−0.355			−0.63
	4	−0.158			−0.25
	5	−0.161			−0.35
	6^d	−0.664			−1.45
(6) Triphenylene	1^d	−0.669	−0.285	−0.95	−1.34
	2	−0.154	−0.129	−0.28	−0.31
(7) Pyrene	1	−0.398	−0.312	−0.71	−0.73
	3	−0.429	−0.292	−0.72	−0.83
	4	−0.167	−0.233	−0.40	−0.66
(8) 1,2-Benzanthracene	$1'^d$	−0.692	−0.312	−1.00	−1.50
	2′	−0.168	−0.138	−0.31	−0.32
	3′	−0.134	−0.122	−0.26	−0.26
	4′	−0.348	−0.181	−0.53	−0.49
	3	−0.395	−0.292	−0.69	−0.28
	4	−0.429	−0.246	−0.67	−0.45
	5	−0.368	−0.224	−0.59	−0.68
	6	−0.128	−0.143	−0.27	−0.20
	7	−0.133	−0.145	−0.28	−0.20
	8	−0.402	−0.237	−0.64	−0.76
	9^d	−0.905	−0.418	−1.32	−1.81
	10	−0.615	−0.332	−0.95	−1.01
(9) 1,2-Benzpyrene	$1'^d$	−0.691	−0.319	−1.01	−1.49
	2′	−0.188	−0.154	−0.34	−0.38
	3^d	−0.704	−0.370	−1.07	−1.54
	4	−0.227	−0.238	−0.46	−0.66
	5	−0.418	−0.288	−0.71	−0.80
	6	−0.425	−0.316	−0.74	−0.67
(10) Perylene	1^d	−0.709	−0.230	−0.94	−0.84
	2	−0.224	−0.129	−0.35	−0.11
	3	−0.389	−0.169	−0.56	−0.30
(11) 1,2:3,4-Dibenzanthracene	$1'^d$	−0.739	−0.298	−1.04	−1.41
	2′	−0.202	−0.131	−0.33	−0.27
	3′	−0.193	−0.125	−0.31	−0.26
	$4'^d$	−0.687	−0.254	−0.94	−1.21
	7	−0.148	−0.144	−0.29	−0.19
	8	−0.425	−0.235	−0.66	−0.70
	9^d	−0.952	−0.400	−1.35	−1.70
(12) 1,2:5,6-Dibenzanthracene	$1'^d$	−0.716	−0.333	−1.05	−1.54
	2′	−0.179	−0.151	−0.33	−0.36
	3′	−0.143	−0.134	−0.28	−0.28
	4′	−0.360	−0.196	−0.56	−0.55
	3	−0.416	−0.245	−0.66	−0.40
	4	−0.486	−0.283	−0.77	−0.61
	9^d	−0.952	−0.441	−1.39	−1.81
(13) Pentaphene	1	−0.425	−0.181	−0.61	−0.80
	2	−0.144	−0.083	−0.23	−0.23
	3	−0.136	−0.078	−0.21	−0.21
	4	−0.380	−0.158	−0.54	−0.68
	5	−0.632	−0.323	−0.96	−0.91
	6	−0.475	−0.248	−0.72	−0.31
	13^d	−0.975	−0.481	−1.46	−1.91
(14) 1,2:7,8-Dibenzanthracene	$1'^d$	−0.790	−0.360	−1.15	−1.69
	2′	−0.197	−0.158	−0.36	−0.39
	3′	−0.148	−0.138	−0.29	−0.29
	4′	−0.362	−0.199	−0.56	−0.56
	3	−0.411	−0.243	−0.65	−0.39
	4	−0.452	−0.269	−0.72	−0.53
	9^d	−1.244	−0.528	−1.77	−2.71
	10	−0.456	−0.354	−0.81	−1.02
(15) Coronene	1	−0.460	−0.550	−1.01	−1.55

[a] Local anisotropic contributions were based on eq 12. The entry for benzene (**1**), enclosed in parentheses, is the absolute value from the equation. Subsequent entries exclude the contributions from the six carbons in the immediate ring associated with the hydrogen atom H_j. [b] Delocalized contributions were based on eq 14 with ring currents relative to an empirical one for benzene. Ring currents for compounds **2–4, 6,** and **7** were from ref 28, and for compounds **8–15** from ref 42. Values for chrysene, item **5**, appear not to have veen reported. [c] C. W. Haigh and R. B. Mallion, *Mol. Phys.*, 18, 737 (1970). [d] Sterically crowded protons.

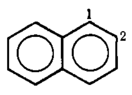
ring. Most of the calculated value of −4.18 ppm arises from the contribution due to the attached carbon atom (−3.29 ppm). Therefore, it must be concluded that a significant part of the deshielding of the protons in aromatic systems is due to LA effects at the carbon atoms. The remaining entries in Table I (items **2–15**) *excluded* the contributions from the six carbon atoms in the ring to which the hydrogen atom was attached. This was done so that the calculated results could be compared with the experimental values (last column of Table I) relative to benzene.

An interesting and useful result (without theoretical justification) can be obtained if it is noted that the LA results in the third column of Table I are very nearly one-half of the experimental results in the last column. Indeed, multiplication of the results in the third column by a factor of 2 provides an excellent empirical correlation of the experimental data. If this is done for the 72 proton shielding points in Table I, linear regression gives a slope of 1.010, intercept −0.10, and correlation coefficient 0.93. It is important to note that this correlation includes the *sterically crowded protons*, which are ordinarily omitted from comparisons of experimental and theoretical results for chemical shielding with the statement that the theory is not adequate for such situations. Clearly exclusion of LA effects in favor of RC effects would lead to greater disparities in just these situations. The contributions from the carbons in the ring to which the proton is attached are subtracted out of the sum for the purposes of comparison with experimental results relative to the benzene value. These include the three closest carbons and so it would not be unreasonable simply to use the dipole–dipole approximation. Empirical multiplication of eq 11 by a factor of 2 gives

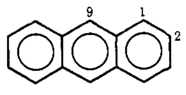
$$\langle \sigma^{H_j} \rangle = -6.22 \times 10^{-3} \sum_i r_{C_iH_j}{}^{-3} \text{ ppm} \qquad (13)$$

where the summation is over all of the carbons C_i other than those associated with the ring to which H_j is attached. Values calculated in this way are entered in the third column of Table II for compounds **2–10.** These values are plotted as a function of the experimental values in Figure 2.

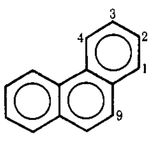
In a quantum mechanical description the major contribution to the shielding due to LA effects would be associated with the large local paramagnetic term arising from magnetic field mixing of $2p_\sigma$ and $2p_\pi$ orbitals in orientations b and c in Figure 1. Both the excitation energies and p-electron density are, of course, very favorable for this σ–π shielding mechanism, and such circulations of electronic charge lead to large downfield shifts which cancel to a large extent the upfield, isotropic diamagnetic terms associated principally with the 1s electrons. Thus, both σ_{22} and σ_{33} are



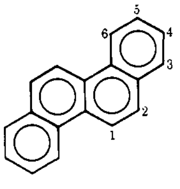
2



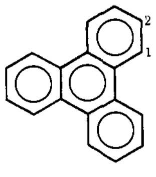
3



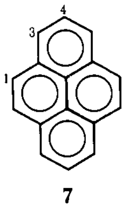
4



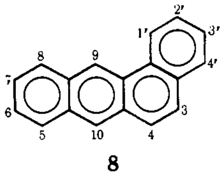
5



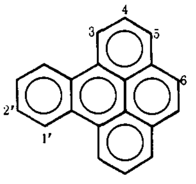
6



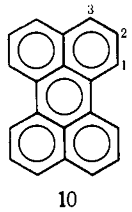
7



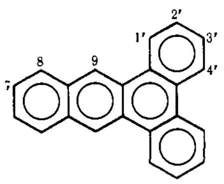
8



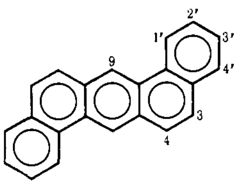
9



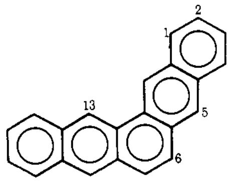
10



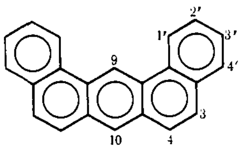
11



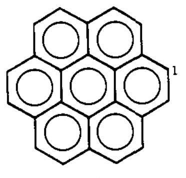
12



13



14



15

Table II. Representative Calculated Values of Chemical Shifts (ppm) Relative to Benzene Compared with the Experimental Values

Compd	H_j	I[a]	II[b]	III[c]	Exptl[d]
(1) Benzene	1				0
(2) Naphthalene	1	−0.54	−0.48	−0.44	−0.46
	2	−0.16	−0.21	−0.18	−0.11
(3) Anthracene	1	−0.66	−0.70	−0.52	−0.66
	2	−0.22	−0.28	−0.24	−0.12
	9	−1.09	−0.93	−0.89	−1.09
(4) Phenanthrene	1	−0.63	−0.63	−0.51	−0.53
	2	−0.23	−0.30	−0.24	−0.24
	3	−0.28	−0.23	−0.27	−0.30
	4[e]	−1.19	−0.67	−0.89	−1.35
	9	−0.71	−0.67	−0.58	−0.38
(5) Chrysene	1[e]	−1.36	−0.90		−1.39
	2	−0.82	−0.69		−0.66
	3	−0.68	−0.75		−0.63
	4	−0.31	−0.41		−0.25
	5	−0.31	−0.33		−0.35
	6[e]	−1.27	−0.85		−1.45
(6) Triphenylene	1[e]	−1.28	−0.73	−0.95	−1.34
	2	−0.33	−0.36	−0.28	−0.31
(7) Pyrene	1	−0.77	−0.88	−0.71	−0.73
	3	−0.70	−0.79	−0.72	−0.83
	4	−0.33	−0.56	−0.40	−0.66
(8) 1,2-Benzanthracene	1'[e]	−1.33	−0.68	−1.00	−1.50
	2'	−0.33	−0.21	−0.31	−0.32
	3'	−0.26	−0.31	−0.26	−0.26
	4'	−0.67	−0.68	−0.53	−0.49
	3	−0.76	−0.74	−0.69	−0.28
	4	−0.83	−0.88	−0.67	−0.45
	5	−0.59	−0.86	−0.59	−0.68
	6	−0.20	−0.33	−0.27	−0.20
	7	−0.21	−0.25	−0.28	−0.20
	8	−0.65	−0.71	−0.64	−0.76
	9[e]	−1.73	−0.96	−1.32	−1.81
	10	−1.20	−1.09	−0.95	−1.01
(9) 1,2-Benzpyrene	1'[e]	−1.33	−0.81	−1.01	−1.49
	2'	−0.35	−0.38	−0.34	−0.38
	3[e]	−1.35	−0.86	−1.07	−1.54
	4	−0.42	−0.54	−0.46	−0.66
	5	−0.78	−0.91	−0.71	−0.80
	6	−0.82	−1.08	−0.74	−0.67
(10) Perylene	1[e]	−1.48	−0.55	−0.94	−0.84
	2	−0.50	−0.32	−0.35	−0.11
	3	−0.83	−0.65	−0.56	−0.30

[a] Calculated results from eq 13. [b] Uncoupled Hartree-Fock results from ref 25. [c] Sum of the local anisotropic and delocalized contributions from Table I. [d] See footnote *c* of Table I. [e] Sterically crowded protons.

relatively small on an absolute chemical shift scale due to this mutual cancellation of two otherwise large terms. The localized paramagnetic circulation of electrons about each carbon in the plane of the ring, however, involves only σ electrons and as such is considerably reduced. This leaves the 1s diamagnetic term as the dominant term, and $\sigma_{\parallel}$ appears at high fields actually above the methane value. The concentration of shielding currents into effective current loops instead of three-dimensional pathways involving electron distribution along the magnetic field axis would involve placing small loops above and below the planes shown in Figure 1. There could be some value in this approach which might account in part for the factor of 2 which was used to obtain the excellent empirical correlation embodied in eq 13.

By now it should be clear that the LA contributions as distinguished from RC contributions are sufficient to account for the major fraction of the downfield shift of aromatic protons. Note that the −4.18 ppm downfield shift in benzene constitutes 72% of the approximately 5.8 ppm shift separating benzene and rapidly interconverting cyclohexane, and invalidates in a large measure the traditional explanation used in almost all textbooks to account for the downfield shift in aromatic protons. Furthermore, the LA model is based only on simple laws of electrodynamics in conjunction with the very fine experimental results of Waugh and coworkers on anisotropic shielding tensors.

The overall aromatic proton shielding range could be explained as entirely due to the anisotropic localized paramagnetic currents on carbon if some empirical parameter were to be introduced into the equations. However, it is just as plausible to discuss these relatively small discrepancies in terms of delocalized shielding currents (RC) involving flow of electrons from one atom to another. Providing these loops can be closed in some way such as a molecular ring, the RC model does find theoretical verification as indicated by a very extensive literature. Attention is, therefore, now directed to a discussion of RC contributions to proton shielding.

B. Delocalized (RC) Contributions to Proton Shielding. Previous estimates of the RC contributions based on the free electron model tended to overestimate the deshielding. The difficulty in using the model is the absence of any way to obtain the ring current *I* in benzene, and in the absence of an estimate of the localized anisotropic contribution,

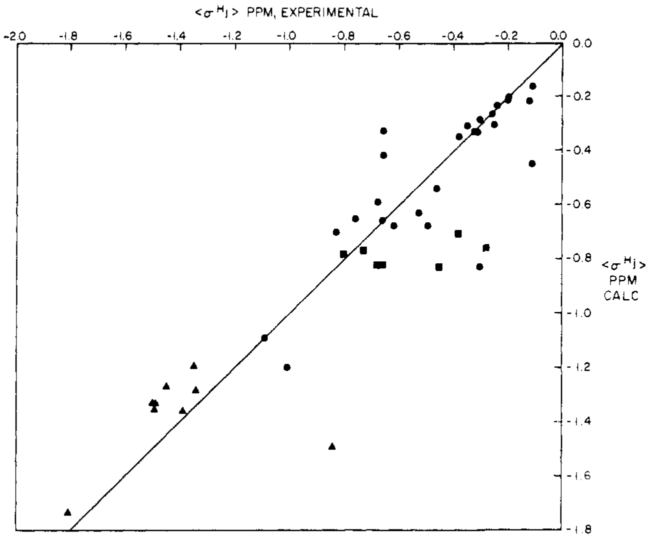


Figure 2. A plot of $\langle\sigma^{H}\rangle$ in ppm calculated from eq 13 as a function of the experimental values for the protons in the condensed ring aromatics **2-10.** The solid line is that corresponding to perfect agreement. "Normal" protons are indicated by circles, "crowded" protons by triangles, and those typified by the 9 proton of phenanthrene are represented by squares.

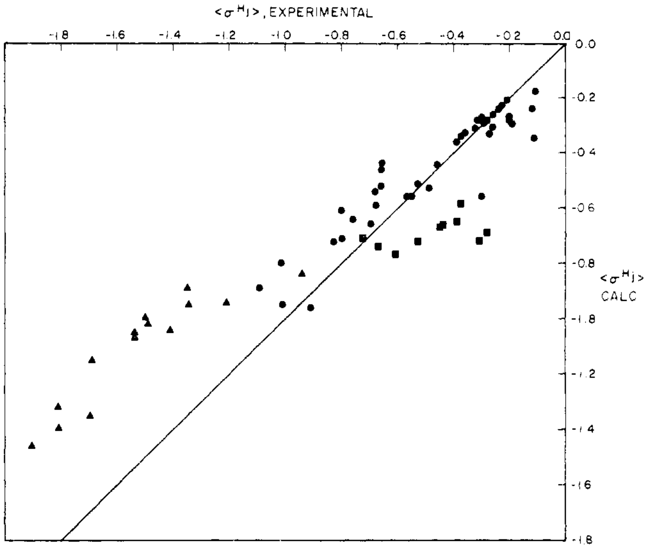


Figure 3. A plot of the sum of the local anisotropic and delocalized contributions to $\langle\sigma^{H}\rangle$ as a function of the experimental values for the condensed ring aromatics **2-15.** Data points are represented by circles, triangles, and squares for the "normal," "crowded," and phenanthrene H-9 type protons, respectively.

some workers have been tempted to attribute the whole anisotropic shielding effect in aromatic protons to the delocalized ring currents. For this reason, the current I for benzene was scaled in this study to give satisfactory agreement of the chemical shifts for representative hydrocarbons in Table I after taking proper account of the LA terms. The formula which was used to take account of the geometrical dependence of the RC contributions follows from eq 2,

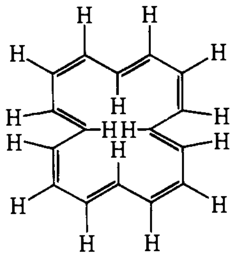
$$\langle\sigma^{H_j}\rangle = C\sum_i \left\{(I_i/I)[(a_R + R_i)^2 + z^2]^{-1/2} \times \left[K + \frac{a_R^2 - R_i^2 - z^2}{(a_R - R_i)^2 + z^2}E\right]\right\} \qquad (14)$$

where $C = 1.889 \times 10^{-3}$ is the empirical scaling value to give the best fit, (I_i/I) is the current relative to the benzene value, $a_R = 0.140$ nm is the radius of each ring, R_i is the distance from the center of the ith ring to the proton H_j, $2z = p$ is the separation between the upper and lower current loops. The benzene value of -0.219 ppm which was obtained from eq 14 with $(I_i/I) = 1$ was subtracted from the values for items **2-15** before entering them in the fourth column of Table I. For these multicyclic hydrocarbons the values of I_i/I were taken from the works of Jonathan et al.[28] and Memory.[42] The value for p is a theoretical value which was taken as twice the expectation value of r for the upper lobe of a Slater $2p_z$ atomic orbital again with $\xi = 1.625$. With this approximation the separation between the two ring currents is 0.163 nm which may be compared with the *empirically adjusted* one of 0.128 nm used by Johnson and Bovey.[27] However, this particular feature of the calculation was somewhat superfluous in that the empirical choice for C in eq 14 would compensate for a wide variation in p.

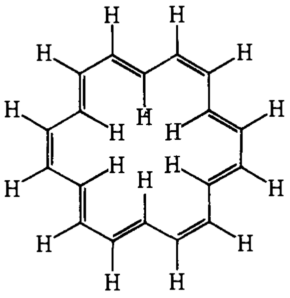
Calculated RC contributions are entered in the fourth column of Table I. In most cases the LA values are of smaller magnitude than the RC values in the third column. It should be noted that the differences from the benzene value of -0.219 ppm are much less than the differences of the LA contributions from the benzene value of -4.177 ppm. The sum of the LA and RC contributions is given in the fifth column of Table I. These summed values for items **2-15** in the table are plotted as a function of the corresponding experimental values in Figure 3. In view of the empirical nature of the RC calculations, it is essential to examine the areas of disagreement and to compare the calculated results with others based on quantum mechanical considerations. The most obvious disparity between calculated and experimental results is for the "crowded" protons. Data for these are usually omitted from plots such as that in Figure 3 on the basis that other factors are involved. Several schemes[43] to rationalize the increased deshielding of these crowded protons have been proposed, but it now seems clear that the inclusion of LA effects may be the most important factor.

The other group of protons in which the calculated values tend to be *greater* in magnitude than the experimental ones is typified by the proton at the 9 position of phenanthrene (**4**). However, it should be noted that this inadequacy is also present in recent quantum mechanical results,[25] which are included in the fourth column of Table II. Since these positions (K region) in many of the condensed-ring aromatics have been associated with special carcinogenic activity,[44] it seems likely that this inadequacy may be associated with substantial changes in charge densities, for example. The single determinant descriptions do not provide an adequate description of a number of properties of these systems.[45]

C. Localized and Delocalized Contributions in the Annulenes. It is of interest to put the experimental results for the annulenes[13,14] in the perspective of the theoretical discussion in sections A and B of this study. In the $[4n]$annulenes the inner protons tend to be substantially deshielded relative to the outer protons, whereas in the $[4n + 2]$annulenes the inner protons are substantially shielded relative to the outer protons. For example, in the [16]annulene (**16**) the inner and outer protons are at τ -0.32 and 4.8, respectively,[46] and in the [18]annulene (**17**) the inner and outer protons at τ 13.0 and 0.72, respectively.[13,47] For purposes of discussion, consider the [18]annulene. Since the inner protons are closer to more carbons, the LA contributions will be greater. From the methods of section A it is predicted that the LA contribution for the inner protons will be deshielded by 0.76 ppm more than the outer protons. Steric effects (especially in **16**) due to the other inner protons would make this difference much greater, and so the direction is consistent with the experimental observations for the $[4n]$annulenes in which bond alternation is expected to minimize RC contri-



16



17

butions. The ring current effect will, however, produce shifts in the opposite direction. If it is assumed that the Faraday induction law is appropriate for comparing the annulenes with benzene, then I' is proportional to the area of the ring around which the current flows and $I' = 7I$ in the [18]annulene. For $a_R = 0.3403$ nm (a weighted average of the distance of the carbons from the center of the ring), $R = 0.172$ and 0.474 nm for inner and outer protons, respectively, and $2z = 0.1618$ nm, eq 14 yields the following results:

$$\langle \sigma^{H_{in}} \rangle = 12.6 \text{ ppm}$$

$$\langle \sigma^{H_{out}} \rangle = -3.2 \text{ ppm}$$

This calculated difference, 15.8 ppm, between the shieldings of the inner and outer protons of the [18]annulene is slightly greater than the experimental value but it does not include the effects of local anisotropy or steric effects as discussed above. The important points to note are the consistency of both the LA and RC contributions with the experimental results for this series of compounds as well as for the condensed ring aromatics. A much larger discrepancy would have been noted if the greater values used previously for benzene currents had been employed with the simple Faraday induction dependence on ring size to estimate the current in the [18]annulene. Thus, in the [4*n* + 2]annulenes delocalized shielding (RC) terms are comparable to or greater than the corresponding localized (LA) contributions to proton shifts because of the unique structural features of these large rings.

Acknowledgment. The National Institutes of Health provided partial support of this work under Grants RR 00574 and GM 08521 and their assistance is gratefully acknowledged.

References and Notes

(1) (a) University of Arizona; (b) University of Utah.
(2) L. Pauling, *J. Chem. Phys.*, **4,** 673 (1936).
(3) F. London, *J. Phys. Radium*, **8,** 387 (1937).
(4) L. Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966, Chapter 4; D. W. Davies, "The Theory of the Electric and Magnetic Properties of Molecules", Wiley, New York, N.Y., 1967, Chapter 5.
(5) J. A. Pople, *J. Chem. Phys.*, **24,** 1111 (1956).
(6) H. J. Bernstein, W. G. Schneider, and J. A. Pople, *Proc. R. Soc. London, Ser. A*, **236,** 515 (1956).
(7) J. A. Pople, *Mol. Phys.*, **1,** 175 (1958).
(8) R. McWeeny, *Mol. Phys.*, **1,** 311 (1958).
(9) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84,** 4307 (1962).
(10) J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88,** 4811 (1966).
(11) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, **No. 21,** 109 (1967).
(12) H. C. Longuet-Higgins and L. Salem, *Proc. R. Soc. London, Ser. A*, **257,** 445 (1960).
(13) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, **No. 21,** (1967).
(14) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Top. Curr. Chem.*, **16,** 103 (1971).
(15) R. C. Haddon, *Tetrahedron*, **28,** 3613, 3635 (1972).
(16) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).
(17) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, 43 (1965).
(18) J. A. Elvidge, *Chem. Commun.*, 160 (1965).
(19) G. G. Hall and H. Hardisson, *Proc. R. Soc. London, Ser. A*, **268,** 328 (1962).
(20) D. W. Davies, *Trans. Faraday Soc.*, **57,** 2081 (1961).
(21) A. T. Amos and H. G. Ff. Roberts, *Theor. Chim. Acta*, **13,** 421 (1969).
(22) T. G. Edwards and R. McWeeny, *Chem. Phys. Lett.*, **10,** 283 (1971).
(23) P. Lazzeretti and F. Taddei, *J. Chem. Soc., Faraday Trans. 2*, **68,** 839, 1825 (1972).
(24) H. G. Ff. Roberts, *Theor. Chim. Acta*, **15,** 63 (1969); **17,** 151 (1970); **22,** 105 (1971).
(25) H. G. Ff. Roberts, *Mol. Phys.*, **27,** 843 (1974).
(26) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79,** 846 (1957).
(27) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29,** 1012 (1958).
(28) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36,** 2443 (1962).
(29) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch., A*, **22,** 103 (1967).
(30) J. I. Musher, *J. Chem. Phys.*, **43,** 4081 (1965); **46,** 1219 (1967).
(31) J. I. Musher, *Adv. Magn. Reson.*, **2,** 177 (1966).
(32) J. M. Gaidis and R. West, *J. Chem. Phys.*, **46,** 1218 (1967).
(33) J. A. Pople, *Proc. R. Soc. London, Ser. A*, **239,** 550 (1957). We would like to thank a referee for pointing out that local anisotropies were first considered by G. Berthier, M. Mayot, A. Pullman, and B. Pullman, *J. Phys. Radium*, **13,** 15 (1952).
(34) H. M. McConnell, *J. Chem. Phys.*, **27,** 226 (1957).
(35) J. A. Pople, *J. Chem. Phys.*, **41,** 2559 (1964).
(36) A Pines, M. G. Gibby, and J. S. Waugh, *Chem. Phys. Lett.*, **15,** 373 (1972).
(37) A Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **56,** 1776 (1972); S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128,** 2042 (1962).
(38) W. R. Smythe, "Static and Dynamic Electricity", 3rd ed., McGraw-Hill, New York, N.Y., 1968, pp 290 and 291.
(39) G. Vincow, S. Y. Chang, and E. R. Davidson, *J. Chem. Phys.*, **54,** 4121 (1971), found optimized orbital exponents for the methyl radical as follows: $\xi_{1sC} = 5.68$, $\xi_{2sC} = 1.75$, $\xi_{2p\sigma C} = 1.80$, and $\xi_{2p\pi C} = 1.46$.
(40) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35,** 722 (1961). A more recent value of 133.94 ppm has been obtained by R. J. Pugmire and D. K. Dalling, University of Utah, private communication.
(41) R. Ditchfield, *Mol. Phys.*, **27,** 789 (1974).
(42) J. D. Memory, *Biochem. Biophys. Acta*, **66,** 168 (1963); J. D. Memory, *J. Chem. Phys.*, **38,** 1341 (1963).
(43) C. Reid, *J. Mol. Spectrosc.*, **1,** 18 (1957); B. V. Cheney, *J. Am. Chem. Soc.*, **90,** 5385 (1968).
(44) C. A. Coulson, *Adv. Cancer Res.*, **1,** 1 (1953).
(45) H. Gutfreund and W. A. Little, *J. Chem. Phys.*, **50,** 4468 (1969).
(46) G. Schröder and J. F. M. Oth, personal communication in ref 13.
(47) Y. Gaoni, A. Melera, F. Sondheimer, and R. Wolovsky, *Proc. Chem. Soc., London*, 397 (1964).