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REGRESSION ANALYSIS OF RING-CURRENT EFFECTS ON PROTON CHEMICAL SHIFTS IN POLYCYCLIC AROMATIC HYDROCARBONS

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Earlier quantum-mechanical calculations (1) based on the assumption of "ring-currents" involving delocalized π-electrons in polycyclic aromatic hydrocarbons, provided values of chemical shifts in poor agreement with experience. The calculated deshielding was always much too large. An explanation of this discrepancy was given by DAILEY (2) and POPLE (3) who suggested that local anisotropic contributions may play an important part in the observed difference in chemical shifts between ethylenic and aromatic protons. On the other hand, MUSHER (4) pointed out that the anisotropic magnetic susceptibility of aromatic hydrocarbons can be correctly represented as the sum of contributions from localised electrons of both π and σ character, "ring-currents" being only an artifact of LONDON's approximate calculations (5). In order to determine if the "ring-current" representation can really be an aid for organic chemists, a regression analysis of "ring-current" effects on proton chemical shifts in polycyclic aromatic hydrocarbons has been carried out.

Ring-currents were calculated by Mc WEENY's second order perturbation theory (6); by the use of a unitary transformation, the results are obtained in the form

$$\delta \times 10^{-6} = \frac{H'}{H} = 2\,\beta(2\pi e/hc)^2\ (S^2/a^3).\ \sum_{\mu} J_{\mu}.K_{\mu} \qquad (1),$$

where δ is the proton chemical shift, H and H' respectively the applied and induced magnetic fields, β the Hückel resonance integral, S the

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area of the benzene ring and a the lenght of the benzene C–C bond.

As pointed out by Mc WEENY (6)(7) and MEMORY (8), J_μ can be identified as the "ring-current" in the μ^{th} ring, K_μ being a distribution function of the effect of the diamagnetic anisotropy of ring μ in space. Table I gives our calculated values for the ring-current intensities of some polycyclic aromatic hydrocarbons as compared with benzene. These values were obtained by a self-consistent iterative Hückel method for the variation of β_{CC} with bond lenght (9) and taking into account the variation of coulomb integrals with substitution; following RASCH's suggestion (10), we have adopted the following parameters :

$$\alpha_{C(CCH)} = \alpha_0 \qquad \text{and} \qquad \alpha_{C(CCC)} = \alpha_0 + 0{,}04\,\beta \qquad ,$$

the atoms in brackets being the first neighbours of the carbon atom considered.

Our results are in fair agreement with those obtained by JONATHAN, GORDON and DAILEY (1) using POPLE's theory (11), some ring-currents being however substantially lower (e.g. for the central ring of triphenylene).

As suggested by MEMORY (8), WAUGH and FESSENDER's distribution function (12)(13) was used to evaluate the ring-current effects on non-hindered proton chemical shifts in benzene, naphthalene, anthracene, pyrene and phenanthrene. Regression analysis of a relation of the form

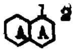
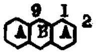
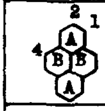
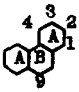
$$\delta_{obs} = \delta_0 + \alpha . \sum_{\mu} J_{\mu} . K_{\mu} \qquad (2)$$

was applied in order to obtain the optimum value of the current loop separation. The results are shown in Figure I; the residual sum of squares of deviation obviously passes through a minimum for a separation of 2 Z = 0,72 benzene radii or 1,00 A°. It is interesting to note that the separation of points of maximum electron density in the $2p_z$ orbital of carbon, according to a single screening constant calculation (14), is about 0,7 A°. The "best" linear relation can then be written :

$$\delta_{calc.} = -6{,}129 + 32{,}285 . \sum_{\mu} J_{\mu} . K_{\mu} \qquad (3)$$

As shown in Table I, calculated values fit very well with the experimental values, the concordance being in most cases better than 0,08 ppm. According to this equation, the ring-current effect in the benzene molecule is about 1,15 ppm, which is much less than the conventional 1,50 ppm derived from comparison with ethylenic protons, and is in fair agreement with some crude calculations of DAILEY (2) and POPLE (3)

TABLE I.

Molecule	Ring	Ring-current intensity	Proton	Chemical Shift observed[*]	calculated
	A	1,000	1	7,342[$]	7,276
	A	1,079	1 2	7,81 7,46	7,747 7,489
	A B	1,059 1,274	1 2 9	7,91 7,39 8,31	7,896 7,539 8,360
	A B	1,315 0,927	1 2 4	8,16 7,99 8,06	7,982 7,928 8,181
	A B	1,125 0,937	1 2 3 4 9	7,855[#] 7,570 7,612 8,648 7,702	7,828 7,577 7,604 8,104 7,764
	A B	1,098 0,699	1 2	8,56 7,61	8.056 7,593

[*] In ppm. with respect to T.M.S.; experimental values obtained from ref.1 unless otherwise stated.

[$] Obtained in this laboratory in 5% $CDCl_3$ solution.

[#] R.C.FAHEY and G.C.GRAHAM, J.Phys.Chem., 69, 4417 (1965).

Ratio of ring-current intensities compared with benzene and proton chemical shifts according to equation 3.

taking into account local anisotropic contributions of both π and σ character.[**]

[**] Theoretically, comparison of equations (1) and (3) must provide the value of the Hückel resonance integral β; this gives $\beta = -10{,}62$ kcal/mole, a value much lower than the adopted value of about −56 kcal/mole. This descrepancy is not disturbing, keeping in mind that the Hückel method furnishes only semi-quantitative information about molecular structure.

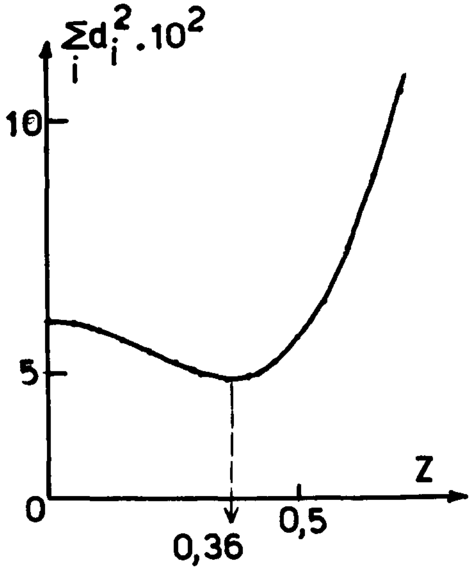


FIGURE I.

Determination of the optimum value of the current loop separation in the distrubition function.

Introduction of an additional independent variable N in the regression analysis with

N = 0 for H-φ or H-β protons (15),

N = 1 for H-α or H-αβ protons (15),

and N = 2 for H-γ protons (15),

seems to have no influence on the regression analysis (+ 0,1 cps in the case of H-γ protons). For each of these classes of protons, N may be regarded as the number of *peri* carbon-hydrogen bonds or as the number of *ortho* carbon atoms common to two rings (which, according to MUSHER (4), may have an appreciable diamagnetic anisotropy), or roughly as the net π-charge at the carbon atom to which the hydrogen is bonded (Figure II and Table II).

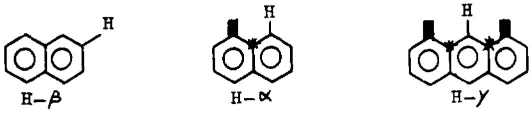


FIGURE II.

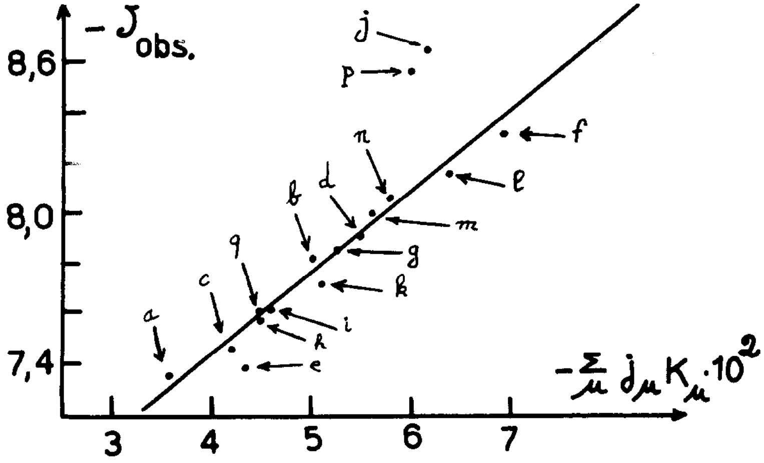
This means that none of these properties makes an important extre contribution to the observed chemical shifts, or that nearly perfect compensation occurs.

TABLE II.

Proton	$1-q_C$	Proton	$1-q_C$
a) H-φ or H-β		b) H-α or H-$\alpha\beta$	
benzene	0	1-naphthalene	+ 0,034
2-naphthalene	+ 0,017	1-anthracene	+ 0,035
2-anthracene	+ 0,018	1-phenanthrene	+ 0,042
2-phenanthrene	+ 0,026	9-phenanthrene	+ 0,038
3-phenanthrene	+ 0,027	1-pyrene	+ 0,035
2-pyrene	+ 0,020	4-pyrene	+ 0,076
b) H-γ			
9-anthracene	+ 0,096		

Net π-charge on the carbon atoms bearing the aromatic protons.

Equation 3 was then used to predict the chemical shift of H_1 and H_2 in triphenylene and of H_4 in phenanthrene. Clearly, the position of δH_2 is correctly computed (calculated: -7,59 ppm;observed: -7,61 ppm).



Benzene proton = a; naphthalene : H_1=b, H_2=c; anthracene : H_1=d, H_2=e, H_9=f; phenanthrene : H_1=g, H_2=h, H_3=i, H_4=j, H_9=k; pyrene : H_1=l, H_2=m; H_4=r; triphenylene H_1=p; H_2=q.

FIGURE III.

Relation between observed chemical shift and ring-current effect.

As shown in Figure III, the hindered protons (H-χ3) however are to much lower fields than predicted;the discrepancy is relatively constant and may be attributed to a mutual VAN DER WAALS effect of the angular hydrogen atoms. The magnitude of the effect (0,50 ppm) is in qualitative agreement with the recent work of NAGATA, TERESAWA and TORI (16) on substituted octahydro-phenanthrenes, in which a deshielding of H_4 of approximately 0,20 ppm was observed.

We plan to apply these results to the case of substituted benzene and polycyclic aromatic derivatives.

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