Proton Nuclear Magnetic Resonance Spectroscopic Studies of Aromatic Hydrocarbons: Induced Paramagnetic Ring-current in the Four-membered Ring of Biphenylene and Related Hydrocarbons[1]

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THE observation that the aromatic protons of biphenylene resonate at a higher field than the benzene resonance[2,3] led us to calculate the ring-current effect in this molecule using McWeeny's LCAO-pertubation theory.[4] The required exchange integrals were calculated by a modified Wolfsberg–Helmholz approximation[5,6] from the bond-length values derived from the *X*-ray analysis of Mak and Trotter.[7]

The results show that the six-membered rings have comparatively small diamagnetic ring-currents, while the central four-membered ring has a large paramagnetic ring-current (+0·563 and −1·028, respectively; benzene = +1). The contributions $\delta_{\text{R.C.}}$ of the different rings to the calculated chemical shifts are given in the Table.

TABLE

Contributions of the different rings to the calculated chemical shifts of protons 1 *and* 2 *in biphenylene* (*Figure A*)

Proton	Ring I	$\delta_{\text{R.C.}}$ in p.p.m.[a] Ring II	Ring III	Calc. chemical shift (p.p.m.)
1	+0·648	−0·165	+0·050	6·662
2	+0·648	−0·040	+0·019	6·756

[a] Obtained by assuming $\delta_{\text{R.C.}}$ = 1·15 p.p.m. for the benzene molecule (ref. 1).

The calculated chemical shifts are in good agreement with experimental values: 6·598 and 6·702 p.p.m. in $CDCl_3$,[8] 6·47 and 6·60 p.p.m. in CCl_4 solution.[2] The theory, however, suggests that proton 2 is more deshielded than proton 1, as opposed to the attribution based on the presumption that deuteration goes faster in the 2- than the 1-position.[2]

In order to settle this problem experimentally, biphenylenes deuterated in known positions are being synthesized.†

The spectrum of benzo[*b*]biphenylene provides experimental evidence of an induced paramagnetic ring-current in the four-membered ring; indeed, the spectrum contains one broad singlet at 6·907 p.p.m. which has been attributed[2] to protons 1, 2, 3, 4, 5, and 10 (Figure B); protons 6 to 9 give an A_2B_2 multiplet with $\delta_{\text{H-6}} = \delta_{\text{H-9}} = 7{\cdot}427$ and $\delta_{\text{H-7}} = \delta_{\text{H-8}} = 7{\cdot}226$ p.p.m.[9] However, in the hypothesis of "deshielding" ring-currents, $\delta_{\text{H-1}}$ should appear at a lower field than $\delta_{\text{H-2}}$, whatever the relative values of the individual ring-currents, owing to the closer proximity of rings II, III, and IV. The only way to explain the experimental observations is to postulate an induced paramagnetic ring-current in the four-membered ring, whose difference of shielding effect on protons 1 and 2 is almost exactly compensated for by the difference in deshielding effects of rings III and IV.

In the absence of *X*-ray data, LCAO-calculations of the ring-currents in benzo[*b*]biphenylene have been carried out by a self-consistent iterative method taking into account the variation of β_{CC} with bond length[1,6] except for the C(4a)–C(4b)and C(10a)–C(10b) bonds, whose lengths were assumed to be 1·52 Å.[7] The following values were obtained: I, 0·578; II, −0·949; III; 0·577; IV, 0·926 (with reference to benzene as 1·0). The calculated chemical shifts are: $\delta_{\text{H-1}} = \delta_{\text{H-4}} = 6{\cdot}716$, $\delta_{\text{H-2}} = \delta_{\text{H-3}} = 6{\cdot}78$, $\delta_{\text{H-5}} = \delta_{\text{H-10}} = 6{\cdot}899$, $\delta_{\text{H-6}} = \delta_{\text{H-9}} = 7{\cdot}314$ and $\delta_{\text{H-7}} = \delta_{\text{H-8}} = 7{\cdot}241$ p.p.m., in fair to good agreement with experimental values and supporting the previous attribution.

Similar calculations on other benzo- and dibenzobiphenylenes show that the occurence of an induced paramagnetic ring-current in the four-membered ring is a general feature in the whole series.

This is an interesting new example of a "reversed" ring-current, other cases being known in the monocyclic $4n$ π-electron annulene and dehydroannulene series.[10]

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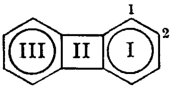

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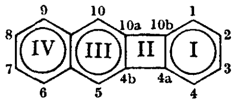

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