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Are Ring Currents Still Useful to Rationalize the Benzene Proton Magnetic Shielding?

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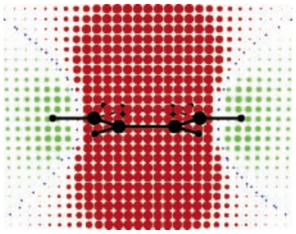
ABSTRACT



The conventional interpretation of proton NMR chemical shifts is supported by large basis set ab initio quantum mechanical calculations. The benzene protons are predicted to lie within the deshielding zone defined in terms of the out-of-plane magnetic shielding domain. However, ring currents by themselves are not sufficient to account quantitatively for the observed benzene proton downfield chemical shift. σ-Electron contributions must also be taken into account. The conventional explanation for the ethyne proton chemical shift is valid.

The ring current model (RCM) provides the conventional explanation for the peculiar magnetic properties of aromatic compounds. Its essential features were outlined by Pauling,[1] Lonsdale,[2] and London[3] as much as nearly seventy years ago, but it is still very popular thanks to further developments, especially due to Pople[4] for the interpretation of the observed ^{1}H NMR chemical shifts of outer protons in the benzene ring (downfield) and of protons inside and above aromatic rings (upfield). This phenomenology is a consequence of the ring currents induced within the π-electron cloud by a magnetic field perpendicular to the molecular plane; see, for example, any modern textbook of organic chemistry and NMR spectroscopy.[5]

The RCM has been both supported and criticized mainly for its interpretative ability, on one side, and for the fact that other possible contributions from σ-electrons are neglected, on the other side; see, for instance, ref 6 and references therein for full details.

Recently, in this journal, the RCM has been strongly disputed on the basis of results from IGLO calculations of the isotropic component of the magnetic shielding tensor.[7] In particular, the benzene protons were found to lie in the shielding rather than the deshielding zone. Indeed, the IGLO

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[4] Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.
[5] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley and Sons: New York, 1991.
[6] Lazzeretti, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1.
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dissection has shown that the C−C(π) bonds shield the benzene protons by +1.9 ppm on average. This was interpreted as a failure of the RCM.[7]

In the following we discuss the choice of the proper magnetic shielding tensor component to be used for analyzing the ring current effects. We report very large basis set ab initio calculations of shielding domains and proton magnetic shielding for benzene, ethene, and ethyne that confirm the relevant role of σ-electrons but, conversely, give firm support to the RCM.

Choice of the Magnetic Shielding Tensor Component. As is well-known, in the presence of an external, space-uniform, time-independent magnetic field of flux $\mathbf{B}$, assuming a linear response of the perturbed molecule, the magnetic field induced at point $\mathbf{r}_0$ by the currents generated within the electronic cloud is given by $\mathbf{B}_{\mathrm{IND}}(\mathbf{r}_0) = -\boldsymbol{\sigma}(\mathbf{r}_0)\mathbf{B}$, where the second-rank dimensionless tensor $\boldsymbol{\sigma}(\mathbf{r}_0)$ describes the local magnetic shielding. The effective field acting on the point $\mathbf{r}_0$ is $\mathbf{B}_{\mathrm{IND}}(\mathbf{r}_0) + \mathbf{B}$. When $\mathbf{r}_0$ coincides with $\mathbf{R}_\mathrm{I}$, the position of nucleus I, the nuclear magnetic shielding can be defined as $\boldsymbol{\sigma}(\mathbf{R}_\mathrm{I})$.

According to the RCM, π-electron ring currents are induced when $\mathbf{B}$ is at right angles to the benzene molecular plane. Then, from the above definitions, the out-of-plane component of the magnetic shielding tensor $\sigma_{||}$, *not the isotropic component*, must be considered in order to provide a proper analysis of the ring current effects.

Calculations have been carried out by means of the procedure of continuous transformation of the origin of the current density-diamagnetic zero (CTOCD-DZ),[8] allowing for the coupled Hartree−Fock (CHF) approximation,[9] as implemented within the SYSMO package of computer programs,[10] using a noncontracted (13s10p5d2f/8s4p1d) basis set[11] for benzene, ethene, and ethyne and a (9s5p2d/5s2p) primitive Gaussian basis set contracted to [5s4p1d/3s1p] for naphthalene and anthracene.[12] Experimental geometries were used.

Considering the out-of-plane shielding domain of benzene displayed in Figure 1, determined by computing $\sigma_{||}$ at several spatial points, it can be observed that benzene protons lie well inside the deshielding zone, quite close to the minimum value of $\sigma_{||}$. The so-called “anisotropy cone” (see small blue spots) is found to intersect the C−H bond nearly in the middle.

The shielding zone extends quite far above (and below) the molecular plane, showing that ring current effects are more pronounced for nuclei inside the benzene ring than outside. At a point 5 b above the molecular plane, on the main symmetry axis, $\sigma_{||} = 7.62$ ppm, which corresponds to a contribution of 2.5 ppm upfield to the chemical shift of a nucleus. This is in agreement with the RCM.

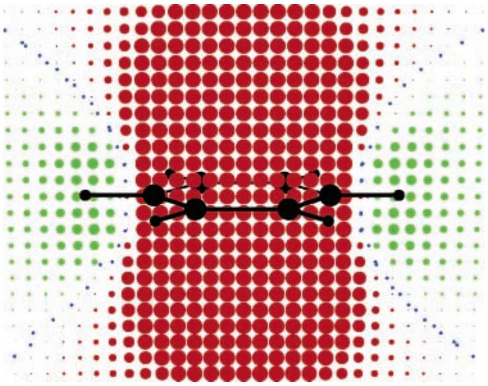

Figure 1. Benzene: π-electron contribution to $\sigma_{||}$ at points uniformly distributed in space (0.5 b apart in each direction) on a symmetry plane containing the C_6 axis of symmetry and a pair of C−H bonds. Red and green circular spots represent shielding (positive) and deshielding (negative) zones, respectively. The radius of each spot is proportional to the absolute value of the contribution. Small blue spots indicate points in space where the contribution is vanishing.

Historically, the anisotropy cone concept has been applied also to ethene and ethyne to explain, especially for the latter, their ^{1}H NMR chemical shift. The IGLO calculation of the isotropic shielding domain has not discerned any ring current effect in ethyne nor any indication of the shielding/deshielding cones.[7] On the other hand, our numerical determination of the out-of-plane shielding domain clearly evidences the presence of the anisotropy cone in both molecules, see Figures 2 and 3 for ethene and ethyne, respectively.

In particular it can be observed that ethene protons lie nearly on the anisotropy cone, i.e., they are neither shielded

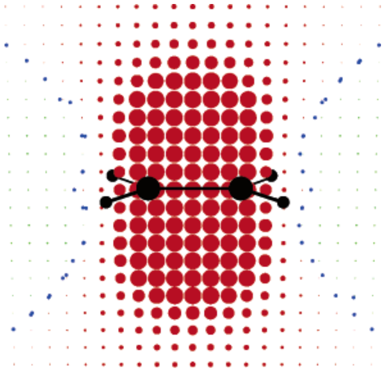

Figure 2. Ethene: the same as in Figure 1 for the out-of-plane component of the local magnetic shielding tensor. Points are on a symmetry plane containing a C_2 axis and the C−C bond.

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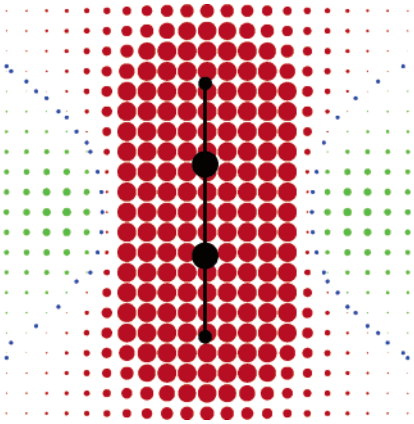

Figure 3. Ethyne: the same as in Figure 1 for a symmetry plane containing the main axis of symmetry.

Table 1. Orbital Contributions to the Proton Magnetic Shielding Tensor in ppm[a]

molecule		contribution	$\sigma_\perp$	$\sigma_\parallel$	σ_{Av}
benzene		π	3.596	−2.862	1.443
		core + σ	22.177	23.335	22.563
		total	25.771	20.473	24.005
ethene		π	3.378	0.172	2.309
		core + σ	22.670	25.324	23.555
		total	26.048	25.496	25.864
ethyne		π	2.452	13.565	6.156
		core + σ	22.477	27.133	24.029
		total	24.929	40.698	30.185
naphthalene	H_α	π	3.346	−4.835	0.619
		core + σ	22.678	23.315	22.890
		total	26.024	18.480	23.509
	H_β	π	3.122	−3.526	0.906
		core + σ	22.977	23.518	23.157
		total	26.099	19.992	24.063
anthracene	H_γ	π	3.728	−7.176	0.093
		core + σ	22.609	22.876	22.698
		total	26.337	15.700	22.791
	H_α	π	3.508	−5.314	0.567
		core + σ	22.658	23.124	22.813
		total	26.166	17.810	23.380
	H_β	π	3.177	−3.525	0.943
		core + σ	23.077	23.507	23.220
		total	26.254	19.982	24.163

[a] $\sigma_\parallel$ is the out-of-plane component. For benzene, ethene, naphthalene, and anthracene, $\sigma_\perp$ is the average of the in-plane components.

nor deshielded by in-plane π-electron currents, and that the ethyne protons are inside an intense shielding zone in agreement with earlier suggestions; see, for instance, ref 5.

Calculated proton magnetic shielding tensors partitioned into π, core + σ, and total contributions are given in Table 1. First of all, one can observe a substantial agreement between the average values of the various contributions estimated in this study and the results of the IGLO calculation in ref 7, despite the different methods of calculation and basis sets employed.

Nevertheless, whereas the benzene π-electrons actually shield the hydrogen nuclei by +1.4 ppm on average, the ring currents provide a significant proton deshielding as large as $-2.9/3 \approx -1$ ppm, which corresponds approximately to the difference between π contributions in benzene and ethene proton magnetic shielding. In fact, the $\sigma_\parallel(\pi)$ of ethene is vanishingly small (see also Figure 2), whereas $\sigma_\perp(\pi)$ is almost equal to that of benzene.

The large π contribution to the ethyne proton magnetic shielding is given by π-electron currents perpendicular to the molecular axis, as indicated by the value of $\sigma_| = 13.7$ ppm, see Figure 3.

However, the results of Table 1 also reveal important contributions from σ-electrons. In particular, only about one-half of the total difference between ethene and benzene proton shieldings, 1.9 ppm (1.4 ppm experimental), is due to ring currents. A contribution of 0.9 ppm comes from σ-electrons.

Ring current effects on naphthalene and anthracene protons are even more evident. As can be observed in Table 1, the ring currents *deshield* the outer β-protons by $-3.5/3 \approx -1.2$ ppm and deshield the inner protons to an even greater extent, reaching the value $-7/3 \approx -2.3$ ppm for the anthracene γ-protons. The present findings fully rationalize the observed proton downfield chemical shifts of these molecules. There is no need to invoke any other contributions. Therefore, these results, together with the ring current patterns reported in refs 12, 13, re-establish the theoretical basis for the arene proton chemical shifts as a criterion of aromaticity questioned in ref 7.

The answer to the question in the title of this note is, then, affirmative: yes, ring currents are still useful to rationalize the benzene proton magnetic shielding. Fundamental revisions of the RCM are not needed. Statements such as “the downfield chemical shift of arene protons relative to those of vinylic protons is because arene protons lie in the deshielding zone” are correct. There is evidence for a “special ring current” influence in ethyne. However, the RCM by itself is not sufficient to account quantitatively for the observed downfield of benzene protons. Contributions coming from σ-electrons must also be taken into account.

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Supporting Information Available: Molecular geometries and magnetic properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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