

Understanding proton magnetic shielding in the benzene molecule

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Abstract

According to the ring current model quoted in textbooks of nuclear magnetic resonance spectroscopy, the downfield chemical shifts of hydrogen nuclei in aromatic molecules is due to intense delocalized currents induced in the π -electron cloud by a magnetic field at right angles to the molecular plane. By using the Biot-Savart law, it was found that the delocalized ring currents deshield the out-of-plane component of proton shielding tensor via an essentially local mechanism taking place in the close vicinity of protons. The π ring currents over distant carbons shield the protons. π and σ electrons deshield benzene protons via different mechanisms clearly observed in plots of the shielding density function defined in the text. These results provide a novel interpretation of the phenomenology and suggest that the familiar model for interpreting chemical shifts of aromatics should be revised.

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The ab initio model for the current densities induced in the benzene molecule by a magnetic field perpendicular to the ring plane started being developed in the early 1980s [1,2]. Accurate representations of the streamlines and modulus of the current density field are now available [3].

However, current density maps are not sufficient to understand some aspects of magnetic response of the benzene molecule. In particular, nuclear magnetic shielding of both hydrogen and carbon nuclei are not fully understood. The present note is aimed at investigating the source of deshielding of benzenic hydrogen nuclei via magnetic shielding density maps [4,5]. It was found that these maps provide powerful analytical tools for interpreting nuclear magnetic shielding [6].

Let us consider a molecule interacting with a static magnetic field with flux \mathbf{B} , generating an electronic current density $\mathbf{J}^{\mathbf{B}}(\mathbf{r})$. The magnetic field induced at point \mathbf{r}_0 by a feedback effect is given by the Biot-Savart law [7,8],

$$\mathbf{B}_{\text{IND}}(\mathbf{r}_0) = \frac{1}{c} \int \frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|^3} \times \mathbf{J}^{\mathbf{B}}(\mathbf{r}) d^3r \equiv -\boldsymbol{\sigma}(\mathbf{r}_0) \cdot \mathbf{B}, \quad (1)$$

where \mathbf{r} is the distance of the volume element d^3r from the origin. The effective field acting on the point \mathbf{r}_0 is $\mathbf{B} + \mathbf{B}_{\text{IND}}(\mathbf{r}_0)$.

The second-rank dimensionless tensor $\boldsymbol{\sigma}(\mathbf{r}_0)$ describes the local magnetic shielding. If \mathbf{r}_0 coincides with \mathbf{R}_I , the position of nucleus I , the nuclear magnetic shielding can be defined via

$$\sigma_{\alpha\delta}(\mathbf{R}_I) \equiv \sigma_{\alpha\delta}^I = -\frac{1}{c} \epsilon_{\alpha\beta\gamma} \int d^3r \frac{r_\beta - R_{I\beta}}{|\mathbf{r} - \mathbf{R}_I|^3} \mathcal{J}_\gamma^{B_\delta}(\mathbf{r}), \quad (2)$$

where

$$\mathcal{J}_\gamma^{B_\delta} = \frac{\partial J_\gamma^{\mathbf{B}}}{\partial B_\delta} \quad (3)$$

is the second-rank current density tensor [9] and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor.

The integrand in Eq. (2) defines the magnetic shielding density introduced by Jameson and Buckingham [4,5], that is, a tensor function of position in three-dimensional space, which can be plotted over a plane specified by fixing one coordinate, e.g., z_0 . The shielding density function is useful to determine the regions of

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molecular domain where shielding and deshielding effects take place, and to weigh the contribution provided by local electron current density in quantitative terms [4,5], as shown in earlier work [6,10].

The shielding density

$$\Sigma_{zz}^H(\mathbf{r}) = -\frac{1}{c} \epsilon_{z\beta\gamma} \frac{r_\beta - R_{H\beta}}{|\mathbf{r} - \mathbf{R}_H|^3} \mathcal{J}_\gamma^{B_z}(\mathbf{r}) \quad (4)$$

has been used in the present study to rationalize proton magnetic shielding of the benzene molecule in the presence of a magnetic field at right angles to the molecular plane. The mobile π electrons sustain intense ring currents reinforcing the external field in the region of the hydrogen atoms. Thus, according to the ring-current model (RCM) [3,11,12], the out-of-plane σ_{zz}^H shielding component is smaller than the average in-plane component. This deshielding is observed as a down-field (paramagnetic) chemical shift of benzenic protons in nuclear magnetic resonance spectra [13].

Accurate ab initio calculations indicate that the average deshielding (that is the negative contribution to one third of the trace of the shielding tensor) is ≈ -1 ppm [14–16]. A non contracted (13s10p5d2f/8s4p1d) basis set [17,18], containing 714 primitive Gaussian functions, has been used in this study to evaluate proton magnetic shielding and function (4) within the procedure of continuous transformation of the origin of the current density-diamagnetic zero (CTOCD-DZ) [9], allowing for the coupled Hartree–Fock (CHF) approximation [19]. The experimental geometry [15], $r_{CC} = 1.395$ Å, $r_{CH} = 1.085$ Å, has been used. The results for in-plane, σ_\perp , and out-of-plane, σ_\parallel , proton magnetic shielding, partitioned in contributions from σ + core electrons and from π -electrons, are shown in Table 1. The present near Hartree–Fock calculation predicts a deshielding as large as -2.86 ppm for the σ_\parallel component.

A preliminary study has been done to obtain the stagnation graph [20,21] of benzene, Fig. 1. This graph provides a fundamental piece of information to complete the topology of RCM [3], and provides a three-dimensional perception of the essentials of the current density vector field.

Fig. 1 shows that, at the height of ≈ 2.1 – 2.5 Å, the primary diamagnetic vortex flowing in the tail regions of the molecule branches out into six diamagnetic vortices, ending up in the region of C–C bonds, and one para-

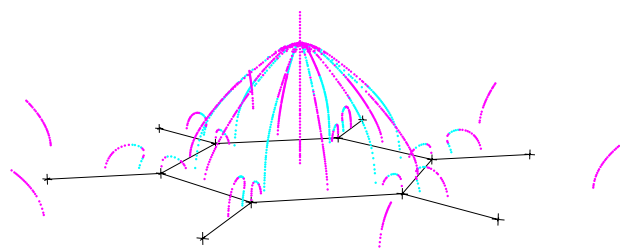


Fig. 1. Perspective view of the stagnation graph of the CTOCD-DZ current density vector field of benzene. The inducing magnetic field is perpendicular to the molecular plane. The graph is contained within a cube with side 6 bohr. The centre of the cube coincides with that of the molecule. Vortical (saddle) lines are represented in magenta (blue). The (0,0) branching point lies in the region 2.1–2.4 bohr. A corresponding pattern is observable in the region beneath the molecular plane.

magnetic vortex about the sixfold symmetry axis. The branching point coincides with the origin of six saddle stagnation lines, so that the Gomes conservation theorem [20,21] is satisfied [22].

The stagnation graph, Fig. 1, shows that electronic currents above the branching point of the primary vortex are purely diamagnetic, i.e. atom-like. These currents are less intense, and the regime in planes lying beyond 2.6–3.0 Å is comparatively less important for the phenomenology of proton deshielding. Thus proton shielding density was investigated over four planes, i.e., the molecular plane at $z = 0$, the planes at $z = 0.75$, 1.5 and 3.0 bohr. The results are of near Hartree–Fock quality. They are reported in Figs. 2–5 as contour maps and corresponding three-dimensional perspective views.

The plane of the plot in Fig. 2 is that of the molecule. It shows a very sharp spike-up accounting for σ_{zz}^H shielding. A sharp spike-down in the region between the proton and the adjacent carbon atom, much closer to the proton, evidences the intense deshielding effect of core and σ electron currents (the plane of the plot is a nodal plane for the π electrons). Shielding and deshielding effects attributable to σ electron circulation close to

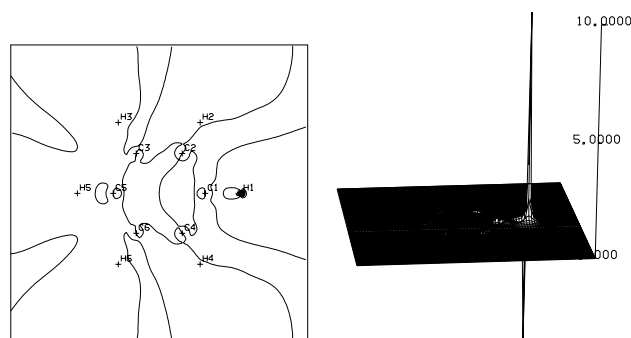


Fig. 2. Proton magnetic shielding density Σ_{zz}^H on the molecular plane of benzene. In the contour map on the left, solid lines mean positive values. The values of the solid lines decrease in steps of 0.9 a.u. $\times c^2$ (c is the velocity of light, ≈ 137.036 a.u.) from the innermost contour at ≈ 9.2 a.u. $\times c^2$. Minimum at ≈ -5.5 .

Table 1
CTOCD-DZ orbital contributions to proton magnetic shielding of benzene in ppm

| | σ_\perp | σ_\parallel | σ_{Av} |
|-----------------|----------------|--------------------|---------------|
| π | 3.596 | -2.862 | 1.443 |
| core + σ | 22.177 | 23.335 | 22.563 |
| Total | 25.771 | 20.473 | 24.005 |

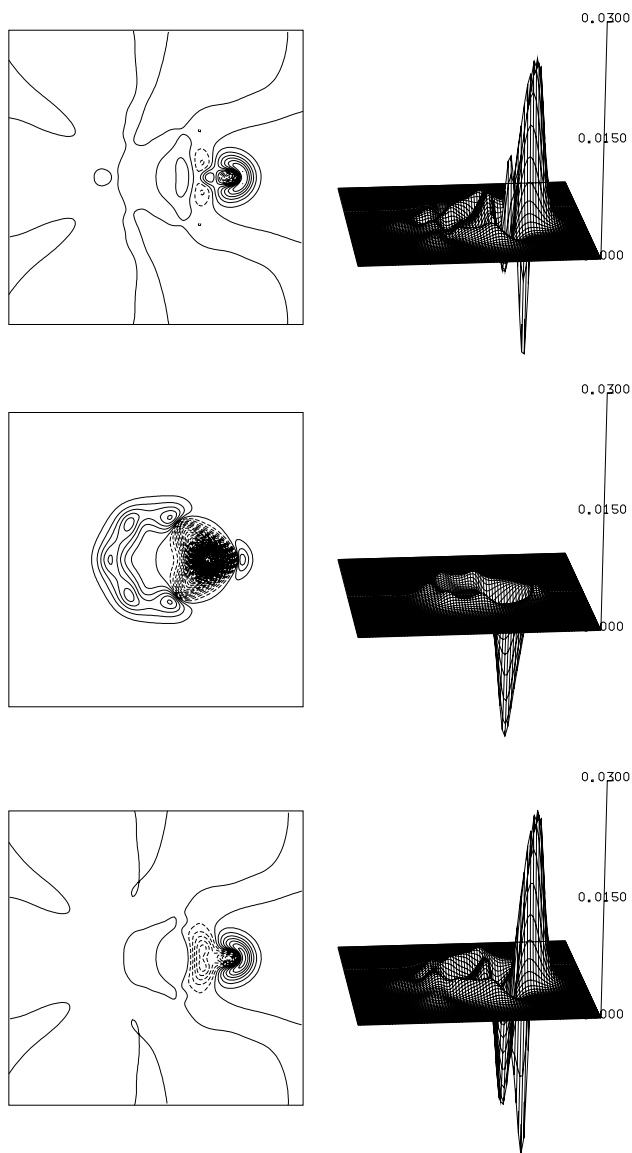


Fig. 3. The conventions are the same as in Fig. 2. From top to bottom: contributions from core and σ orbitals, from π orbitals, and total values of Σ_{zz}^H . The plot plane is parallel to that of the molecule and displaced from it by 0.75 bohr. In the contour map on the top left, the values of the solid (dashed) lines decrease (increase) in steps of 3.0×10^{-3} a.u. from the innermost contour at $\approx 2.1 \times 10^{-2}$ a.u. $\times c^2$ (minimum at $\approx -1.9 \times 10^{-2}$). The same step is used in the other contour maps.

the molecular plane of benzene are several orders of magnitude larger than that found for other plot planes, see Figs. 3–5, but involve very small domains within the C–H bond. The position of the six carbon nuclei in the ring is visible in the figure. Their contribution is comparatively negligible.

The plot plane in Fig. 3 corresponds approximately to the highest π electron density. The contributions provided by core and σ electrons in different regions of the molecule can be observed on top of the figure.

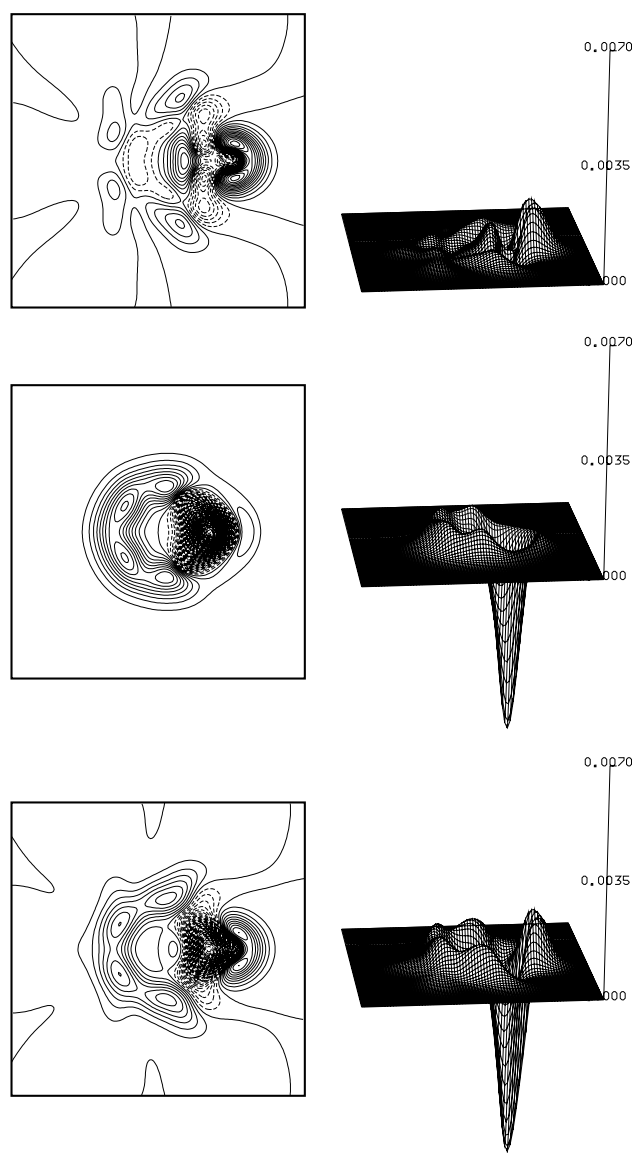


Fig. 4. The conventions are the same as in Figs. 2 and 3. The plot plane is parallel to that of the molecule and displaced from it by 1.5 bohr. In the contour map on the top left, values decrease in steps of 1.0×10^{-4} a.u. from the innermost contour at $\approx 1.4 \times 10^{-3}$ a.u. $\times c^2$. Minimum at $\approx -8.7 \times 10^{-4}$.

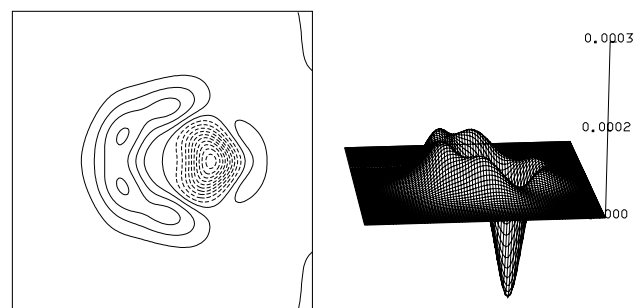


Fig. 5. Total (core + σ + π -electron contributions) magnetic shielding density Σ_{zz}^H in the plane at 3.0 bohr. In the contour map on the left, values decrease in steps of 2.0×10^{-5} a.u. from the innermost contour at $\approx 8.3 \times 10^{-5}$ a.u. $\times c^2$. Minimum at $\approx -2.1 \times 10^{-4}$.

A deshielding zone is found in the vicinity of the hydrogen nucleus. Small shielding effects from the ring carbon atoms are visible.

The deshielding caused by π electrons is observed within a small area nearby the proton. Then the *delocalized* ring currents documented by the ab initio RCM of benzene [3] deshield the hydrogen nuclei via an essentially local mechanism taking place in a small region in the vicinity of each proton. In fact, the π electron flow over the ring is *weakly shielding*.

The plot for the total shielding map in Fig. 3 clearly shows that the deshielding spikes-down for σ and π electrons do not merge. The same pattern has been observed in all the maps obtained by a series of basis sets of increasing extension and flexibility. One can conclude that, at least at the CTOCD-DZ CHF level of accuracy, a sort of σ - π electron separability [23] can be ascertained by magnetic criteria. Different electrons would seem to play different roles. However, this result should be confirmed by future calculations including electron correlation.

The situation observable for the plot plane $z = 1.5$ bohr, see Fig. 4, is qualitatively the same as that of Fig. 3. Again it is found that the proton deshielding due to π electrons is confined to a relatively small zone in the proximity of the proton. Ring currents over the carbon skeleton have a *weakly shielding* effect, approximately four-five times smaller than that on the plane for $z = 0.75$ bohr.

The shielding density (4) goes smoothly to zero over higher planes, see, for instance, Fig. 5, where the function (4) on the plane at $z = 3.0$ bohr is shown. This finding is consistent with the topology of the stagnation graph in Fig. 1. However, the strongly local character of proton deshielding is still observable.

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