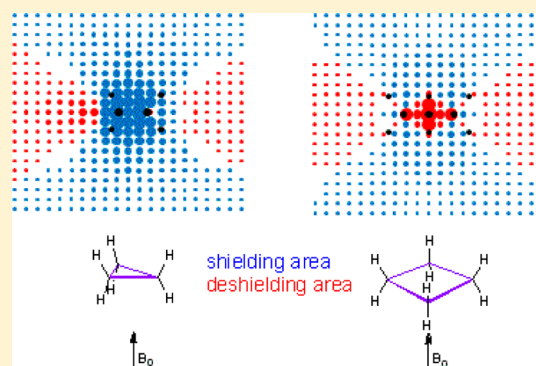


# $^1\text{H}$ NMR Chemical Shifts of Cyclopropane and Cyclobutane: A Theoretical Study

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## S Supporting Information

**ABSTRACT:** This study was undertaken in order to rationalize the peculiar  $^1\text{H}$  NMR chemical shifts of cyclopropane ( $\delta$  0.22) and cyclobutane ( $\delta$  1.98) which are shifted upfield and downfield with respect to larger cycloalkanes ( $\delta$  1.44–1.54). This is conventionally accounted for by shielding contributions arising from an aromatic-like ring current in cyclopropane, involving six electrons in the three C–C bonds, and deshielding coming from the  $\sigma$  antiaromatic CC framework of cyclobutane. The shielding pattern arising from the cyclopropane and cyclobutane CC framework response to a perpendicular magnetic field was visualized as two-dimensional grid distribution of NICS values. Further insight into the origin of chemical shift values was obtained by the NCS–NBO analysis of proton shielding tensor. In the case of cyclopropane, the CC framework shielding pattern implies the existence of both delocalized and localized currents that have a dominant shielding effect on protons. The magnitude of C–H bonds shielding effect is significant, too. Unlike the conventional interpretation, the CC framework shields cyclobutane hydrogens, and its response to a perpendicular magnetic field is quite similar to responses of other planar  $\sigma$  CC frameworks.



## INTRODUCTION

While  $^1\text{H}$  NMR chemical shifts of cycloalkanes, from cyclopentane and up to the larger rings, are quite similar ( $\delta$  1.44–1.54), protons in cyclopropane are highly shielded ( $\delta$  0.22) but those in cyclobutane deshielded ( $\delta$  1.98). The highly shielded position of cyclopropane resonance is conventionally accounted for in two ways.<sup>1,2</sup> According to the first explanation, it is the anisotropy of the C–C bond, just opposite to  $\text{CH}_2$  group in a three-membered ring, that shields the cyclopropane hydrogens. In the second explanation, an aromatic-like ring current involving the six electrons in the three C–C bonds ( $\sigma$  aromaticity) shields cyclopropane protons. In recent literature, the unusually high  $^1\text{H}$  NMR chemical shift of cyclobutane is attributed to a deshielding coming from the  $\sigma$  antiaromatic CC framework, including eight electrons in its C–C bonds.<sup>3,4</sup> Herein, we discuss the source of the observed upfield/downfield shift of cyclopropane/cyclobutane  $\delta$  values on the basis of theoretical calculations.

## COMPUTATIONAL DETAILS

All calculations were performed using the Gaussian 03 program package.<sup>5</sup> Geometries were optimized at the B3LYP/6-311+G\*\* level of theory, followed by frequency calculations to verify the nature of stationary points. Magnetic shieldings were computed at the same level using the GIAO method<sup>6,7</sup> and partitioned into contributions from all bonds by the natural chemical shielding–natural bond orbital (NCS–NBO) analysis.<sup>8</sup> The shielding pattern arising from molecular response to an applied external magnetic field has been quantitatively calculated

as nucleus independent chemical shieldings (NICS)<sup>9,10</sup> in a two-dimensional grid of points placed 0.5 Å from each other.

The difference in the strain energies between cyclopropane and cyclobutane, evaluated at the same level and with the same basis set, was in good agreement with the experimental value (see the Supporting Information).

## RESULTS AND DISCUSSION

Our results on magnetic anisotropy of C–C single bond in ethane<sup>11</sup> showed that a proton located at its side would be either deshielded or, taking into account eclipsed conformation and distance of cyclopropane H from the opposite C–C bond, shielded by at most 0.02 ppm, apparently not enough to explain the observed upfield shift of cyclopropane. Thus, the first explanation seems inappropriate. As for the second explanation, the concept of  $\sigma$  aromaticity in cyclopropane, first proposed by Dewar,<sup>12</sup> is a still debated issue. While some authors find it to be  $\sigma$  aromatic,<sup>3</sup> others characterize it as nonaromatic.<sup>13</sup> Even conclusions based on the studies of the magnetically induced current density do not agree with each other: cyclopropane is either strongly  $\sigma$  aromatic<sup>14,15</sup> or nonaromatic.<sup>16–18</sup> Although it has been shown that a diatropic ring current is induced in the  $\sigma$  electrons by a perpendicular magnetic field,<sup>18</sup> the strength of which compares to the  $\pi$  ring current of benzene.<sup>19</sup> Why are cyclopropane hydrogens so highly shielded that their chemical

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shift is almost equal to that of methane (0.23 ppm)? Pelloni et al.<sup>17</sup> showed that the protons are immersed in a strong localized diatropic current about the C–H bonds when the ring is oriented at right angle to an external magnetic field and recognized it as a significant source of their shielding. Later, in a revised current density model of cyclopropane,<sup>18</sup> the same group added a delocalized current flowing on planes close to H nuclei as an additional source of shielding, but found  $\sigma$  CC ring current to have a minor role. Indeed, in a perpendicular orientation of the ring relative to a magnetic field the C–H bond shields hydrogen involved in that bond by 27.1 ppm, as estimated by the NCS analysis (Table 1). However, a rapid

**Table 1. Orbital Contributions (ppm) to  $\sigma$ (H) in Cyclopropane and Cyclobutane Obtained by the NCS Analysis of Proton Shielding Tensor<sup>a</sup>**

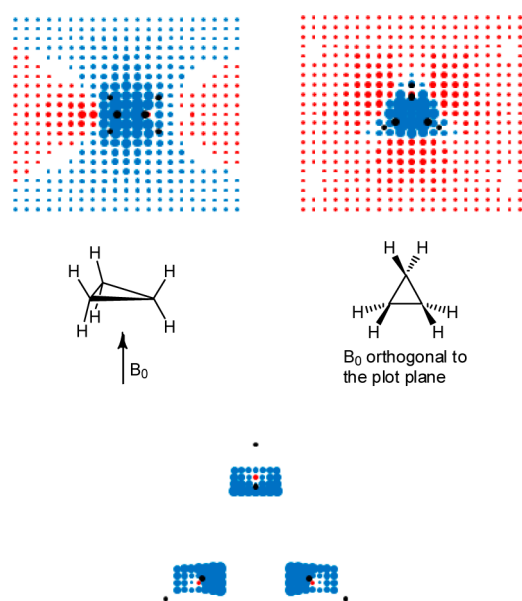
contribution	C <sub>3</sub> H <sub>6</sub> ( <i>D</i> <sub>3h</sub> )		C <sub>4</sub> H <sub>8</sub> ( <i>D</i> <sub>2d</sub> ) av <sup>b</sup>	
	$\sigma_{zz}$	$\sigma_{iso}$	$\sigma_{zz}$	$\sigma_{iso}$
CH <sub>main</sub>	27.10	25.62	27.98	26.28
CH <sub>other/same side</sub>	0.28	0.16	−0.82	−0.08
CH <sub>other/opposite side</sub>	2.62	1.93	1.53	1.78
CH <sub>other all</sub>	2.90	2.09	0.71	1.70
CC <sub>all</sub>	5.84	3.96	0.40	1.84

<sup>a</sup> $\sigma_{zz}$  and  $\sigma_{iso}$  denote contributions from a perpendicular orientation of a molecule with respect to a magnetic field and the average of all space orientations, respectively (see also ref 20). <sup>b</sup>Average for H<sub>axial</sub> and H<sub>equatorial</sub>.

tumbling of dissolved molecules averages this value to 25.62,<sup>20</sup> which is lower than the corresponding values for some (a)cyclic hydrocarbons (Table S1 in the Supporting Information). Even in perpendicular orientation, cyclobutane hydrogen is more shielded by the intrinsic C–H bond (Table 1). There must be an additional shielding effect. The most important shielding comes from the C–C bonds, 3.96 ppm (Table 1). Is it an aromatic-like ring current?

In order to answer the question, the CC framework response to a perpendicular magnetic field should be examined since a ring current can be induced only in that orientation. (De)shielding zones are shown in Figure 1, in two planes: the  $\sigma_v$  plane (top left) and the plane of the carbon nuclei (top right). The nonequivalence in the shielding pattern near the carbon nuclei arises from the mismatch between the triangular molecule and square plotting grid and disappears on use of a finer grid, with a step width of 0.1 Å (bottom). Note that these plots are equivalent to spatial NICS <sub>$\sigma$ (CC)zz</sub> or induced magnetic field.<sup>21,22</sup>

A seemingly typical response of an aromatic system (shielding above/below the ring plane and inside the ring, deshielding around it) is disrupted by a decrease in shielding and even appearance of slight deshielding near the carbon atoms. This picture is not consistent with a strong diatropic ring current, as found by Fowler et al.<sup>14</sup> and Fliegl et al.<sup>15</sup> Rather, it may result from a combined effect of localized electron circulations within the cyclopropane bent bonds surrounded by a delocalized flow. According to these findings, a certain degree of aromaticity may exist, based on a magnetic criterion,<sup>23</sup> not found in the previous studies.<sup>16–18</sup> In this perpendicular orientation, the three C–C bonds shield a hydrogen nucleus by as much as 5.84 ppm,<sup>24</sup> followed by all other C–H bonds, 2.9 ppm (Table 1), contributing 5.84/3  $\approx$  1.9 and 2.9/3  $\approx$  1 ppm to the average shielding.<sup>20</sup>

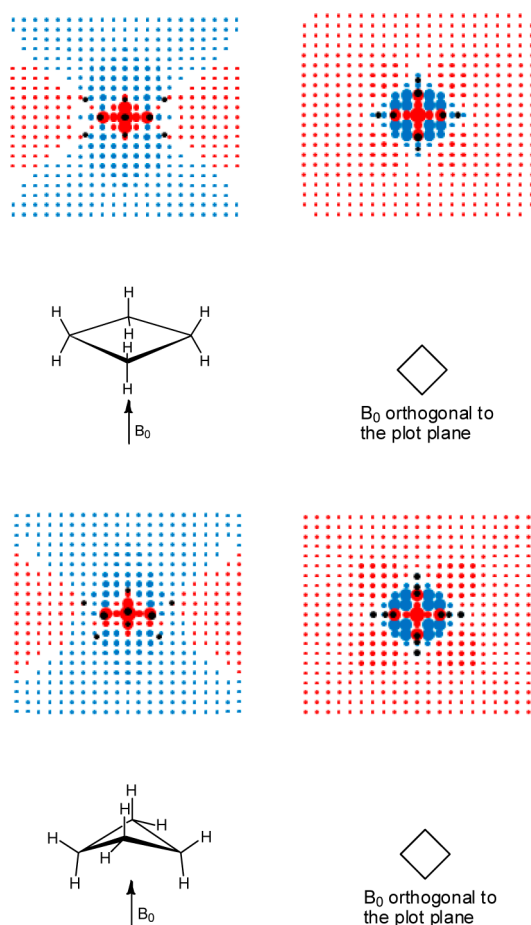


**Figure 1.** Visualization of (de)shielding contributions of cyclopropane CC framework for a magnetic field applied perpendicularly to the ring plane: view in the  $\sigma_v$  plane (top left) and in the plane of the carbon nuclei (top right). Shielding pattern around carbon nuclei on use of a finer grid, with a step width of 0.1 Å, is shown at the bottom. Blue and red points denote shielding and deshielding effects, respectively. The radius of points is proportional to the absolute value of the contribution (the points merge into one another inside the ring). Positions of carbon and hydrogen nuclei are marked by black points.

Contributions from the two parallel orientations are shielding as well, about two times less (Tables S2 and S5 in the Supporting Information). It is worth noting that when a field direction is parallel to the C<sub>2</sub> symmetry axis a very strong shielding, exerted by the CC framework, of the two protons attached at the carbon lying on the axis is observed. It is almost equal in magnitude to shielding coming from the C–C bonds in the perpendicular orientation and amounts to 5.88 ppm ( $\sigma_{yy}$  for H-4 in Table S2 in the Supporting Information). It is mainly caused by the two adjacent bonds, 5.12 ppm, and contributes 5.88/3  $\times$  3  $\approx$  0.7 ppm to the  $\delta$  value obtained from an NMR experiment.<sup>20,25</sup> Total anisotropic effects of cyclopropane are given in Figure S1 in the Supporting Information.

As already noted, in recent literature an unusually high <sup>1</sup>H NMR chemical shift of cyclobutane is attributed to a deshielding coming from the  $\sigma$  antiaromatic CC framework.<sup>3,4</sup> However, conclusions arrived at in ref 3 were based on the computation of a grid of total, isotropic<sup>20</sup> NICS points, bisecting the four-membered ring (*D*<sub>4h</sub>), which included contributions from C–C and C–H bonds and the average of all space orientations of the molecule with respect to a magnetic field. Since a ring current is induced when magnetic field acts at right angle to the ring plane, an evaluation of the cyclobutane “ $\sigma$  antiaromaticity” must refer only to this orientation and must exclude C–H bond contributions. The obtained shielding pattern is shown in Figure 2. Apparently, it does not look like a response of an antiaromatic system (deshielding above/below the ring plane, shielding around it)<sup>26</sup> and is almost the same for planar (*D*<sub>4h</sub>) and nonplanar (*D*<sub>2d</sub>) rings.

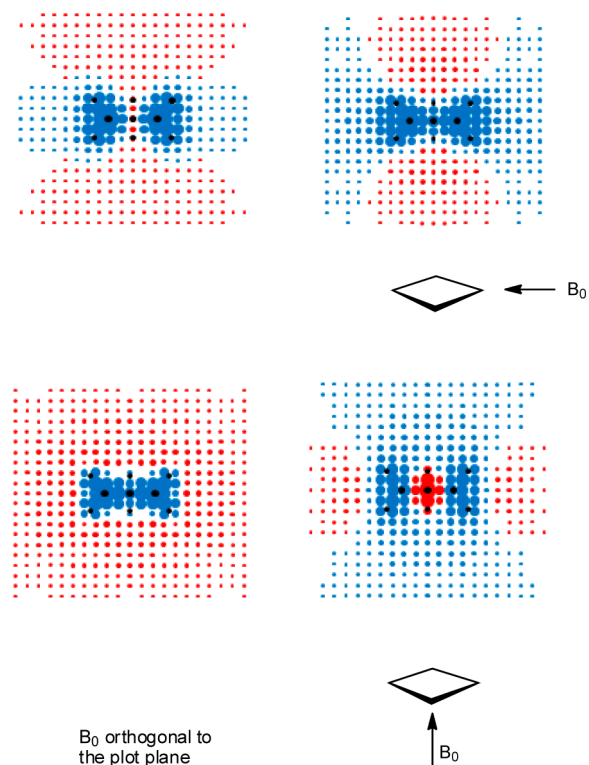
In addition, a quite similar response of the CC framework to a perpendicular magnetic field is obtained for planar cyclopentane (*D*<sub>5h</sub>) and cyclohexane (*D*<sub>6h</sub>) (Figure S2 in the



**Figure 2.** Visualization of (de)shielding contributions of cyclobutane  $D_{4h}$  (upper part) and  $D_{2d}$  (lower part) CC framework for a magnetic field applied perpendicularly to the ring plane: the first view is in the  $\sigma_v$  plane, passing through the  $\text{CH}_2$  groups and the second view is in the plane orthogonal to the first (plane of carbon nuclei for  $D_{4h}$ ). Other details are the same as for Figure 1.

Supporting Information). It is worth noting that there is a stronger deshielding region inside the  $\text{C}_4\text{H}_8$ . This central deshielding, which distinguishes nonaromatic and antiaromatic rings from the aromatic ones with no paratropic region inside the ring, originates from the central paratropic flow seen in current density maps for cyclobutane ( $D_{4h}$ ) and cyclopentane ( $D_{5h}$ )<sup>14</sup> as well as in maps of currents induced in the  $\sigma$  framework of  $\pi$ -aromatic hydrocarbons.<sup>27</sup> Its intensity is obviously higher in  $\text{C}_4\text{H}_8$  giving its CC framework slightly paratropic character. The total anisotropic effects of cyclobutane, typical for an antiaromatic system<sup>3</sup> (see also Figure 3, top left), actually arise from the two parallel orientations of the molecule relative to a magnetic field (Figure 3, top right and bottom left), not from the  $\sigma$  antiaromatic character of the CC framework.<sup>28</sup> Quite similar responses are found for cyclobutane  $D_{2d}$  (Figure S3 in the Supporting Information).

Electron currents induced in the CC framework of  $\text{C}_4\text{H}_8$  ( $D_{2d}$ ) by a magnetic field parallel to the  $\text{C}_2$  symmetry axis contained in the  $\sigma_v$  planes deshields only equatorial protons by  $-0.23$  ppm, while axial protons are shielded by  $1.04$  ppm, which results in average shielding by  $0.4$  ppm (Tables S3 and S4 in the Supporting Information) contributing negligibly to the cyclobutane chemical shift,  $0.4/3 \approx 0.1$  ppm.<sup>20</sup> Thus, there is no paramagnetic  $\sigma$  CC flow that deshields cyclobutane



**Figure 3.** Visualization of total anisotropic effects of cyclobutane ( $D_{4h}$ ) in the  $\sigma_v$  plane, passing through the two  $\text{CH}_2$  groups: average of all space orientations (top left), when magnetic field is parallel to the  $\text{C}_2$  symmetry axis, passing through the two carbons (top right), when magnetic field is orthogonal to the plot plane (bottom left), when magnetic field is orthogonal to the ring plane (bottom right). Other details are the same as for Figure 1.

hydrogens. The only deshielding comes from the C–H bonds located at the same side as the examined proton,  $-0.08$  ppm (Table 1). Its magnitude is, however, small to explain the high frequency resonance position of cyclobutane. In fact, there is no any specific deshielding effect contributing to high  $\delta$  value. The total C–C and C–H bonds shielding contributions are just lower than in other hydrocarbons (for example,  $\text{CH}_{\text{main}} = 26.28$  for  $\text{C}_4\text{H}_8$ , but  $26.54$  for  $\text{C}_6\text{H}_{12}$  in the chair conformation,  $\text{CH}_{\text{other}} = 1.70$  for  $\text{C}_4\text{H}_8$ , but  $1.81$  for  $\text{C}_6\text{H}_{12}$ ,  $\text{CC}_{\text{total}} = 1.84$  for  $\text{C}_4\text{H}_8$ , but  $1.95$  for  $\text{C}_6\text{H}_{12}$ ; for more details, see the Supporting Information).

Of note is the observation that in a perpendicular orientation of a ring relative to a magnetic field the C–H bonds of cyclopropane shield a proton (both those at the same side as the examined proton and those at the other side), while C–H bonds in cyclobutane positioned at the same side as the proton in question deshield it (Table 1, Tables S3 and S4 in the Supporting Information). This cannot be a consequence of different geometries, since the difference in the C–C bond lengths between  $\text{C}_3\text{H}_6$  ( $1.51$  Å) and  $\text{C}_4\text{H}_8$  ( $1.55$  and  $1.56$  Å for  $D_{2d}$  and  $D_{4h}$ , respectively) is small but can be accounted for by the formation of a delocalized  $\sigma$  C–H diatropic current in cyclopropane (referred to only as a delocalized current in ref 18), but existence of localized circulations within the C–H bonds of cyclobutane.<sup>29</sup> The shielding pattern originating from the C–H bonds as a result of action of a perpendicular magnetic field is given in Figure S4, in the Supporting Information.

## CONCLUSIONS

The main cause of chemical shift differences between cyclopropane and cyclobutane is seen in the perpendicular orientation of a ring relative to magnetic field direction when C–C and C–H bonds contribute 5.84/0.4 and 2.9/0.71 ppm, respectively. The shielding pattern arising from the cyclopropane CC framework response to a perpendicular magnetic field implies the existence of both delocalized and localized currents. Nevertheless, the most important proton shielding comes from the C–C bonds in that orientation, 5.84 ppm, followed by the C–H bonds shielding, 2.9 ppm. Unlike the belief that the CC framework deshields cyclobutane protons, based on the idea of its antiaromaticity, it shields hydrogens by 1.84 ppm, on average, and its response to a perpendicular field is quite similar to responses of other planar  $\sigma$  CC frameworks. Actually, there is no any specific deshielding effect that could account for the experimentally observed high  $^1\text{H}$  NMR chemical shift.

## ASSOCIATED CONTENT

### Supporting Information

Orbital contributions to proton shielding tensor, visualization of (de)shielding contributions, absolute energies,  $x$ ,  $y$ ,  $z$  coordinates and vibrational frequencies of the optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (20) Magnetic shielding depends on the orientation of a molecule with respect to  $B_0$  and is described by a second-rank tensor  $\sigma$ , which is fully specified by its diagonal elements,  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$  along its principal axes. When an NMR experiment is carried out in solution, where molecules tumble rapidly, the measured isotropic shielding is the average of different orientations,  $\sigma_{\text{iso}} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ .
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- (25) It should be noted that the current density model developed in ref 18 showed that the C–C bond opposite to  $\text{CH}_2$  group takes part in a strong diatropic delocalized current in a field direction parallel to the  $C_2$  symmetry axis.
- (26) For a response of an antiaromatic system to a perpendicular magnetic field, see: Heine, T.; Islas, R.; Merino, G. *J. Comput. Chem.* **2007**, *28*, 302.
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- (28) A weak  $\sigma$  antiaromaticity, also found in refs 13 and 14, is not excluded by this study. Some authors consider it as nonaromatic, i.e., ref 21.
- (29) Formation of a weak delocalized current is not excluded.