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Downfield Proton Chemical Shifts Are Not Reliable Aromaticity Indicators

**Chaitanya S. Wannere, Clémence Corminboeuf, Wesley D. Allen,
Henry F. Schaefer, III, and Paul von Ragué Schleyer***

*Center for Computational Chemistry, Department of Chemistry, University of Georgia,
Athens, Georgia 30602-2525*

schleyer@chem.uga.edu

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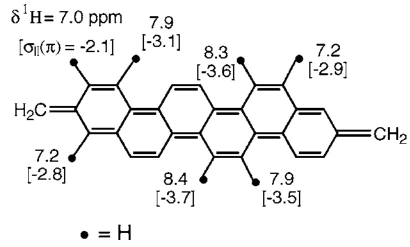
ABSTRACT



The downfield chemical shifts of arene hydrogens (δ ^{1}H) are due only in part to the π ring current contribution [$\sigma_{||}(\pi)$]; local framework effects are equally important. Neither proton chemical shifts nor even $\sigma_{||}(\pi)$ tensor elements, per se, are reliable aromaticity indicators. Unsaturated polycyclic hydrocarbons with nonaromatic quinoid structures have δ ^{1}H and $\sigma_{||}(\pi)$ values in the "aromatic range". Conversely, numerous aromatic protons, including those in five-membered ring heterocycles, resonate in the "nonaromatic range".

The chemical shifts of arene hydrogens generally resonate further downfield than those of olefins.[1] This characteristic, noted soon after the development of NMR spectroscopy, rapidly became a widely employed aromaticity criterion. And so it remains today, despite long known anomalies (cf. Figure 1). While such problems have been attributed to heteroatom influences,[2,3] Chesnut showed that there is no correlation between the measured δ ^{1}H values of five-membered ring heterocycles and other aromaticity indexes.[2]

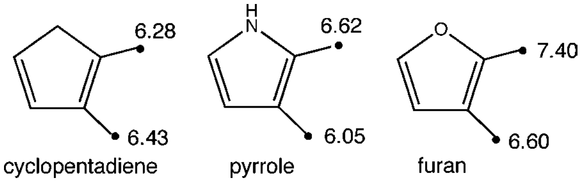


Figure 1. ^{1}H NMR chemical shifts (δ ^{1}H, in ppm) do not differentiate between aromatic and nonaromatic five-membered rings unambiguously.

The traditional arene proton chemical shift range beginning at about 7.0 ppm (benzene δ $^1\text{H} = 7.27$) is still regarded as being reliable to distinguish aromatic from nonaromatic polyunsaturated hydrocarbons.[4] Pople's induced ring current model[1a,5] continues to be invoked as the explanation.[6] As stated by Vogler, "In case of benzenoid hydrocarbons, it is a sufficient approach to take only $\delta^{\text{ring current}}$ into account."[4e] Pople's model is presented in most introductory organic

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(1) (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959. (b) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1998; p 85. (c) Silverstein, R. M.; Bassler, G. C.; Morill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley and Sons: New York, 1991.

(2) Chesnut, D. B. *Chem. Phys.* **1998**, *231*, 1. However, satisfactory agreement is achieved if the δ ^{1}H differences between the aromatic and its partially hydrogenated counterpart are employed instead.

(3) Corradi, E.; Lazzeretti, P.; Taddei, F. *Mol. Phys.* **1973**, *26*, 41.

(4) (a) Vogler, H. *J. Am. Chem. Soc.* **1978**, *100*, 7464. (b) Vogler, H. *J. Mol. Struct.* **1979**, *51*, 289. (c) Vogler, H. *Org. Magn. Reson.* **1979**, *12*, 306. (d) Vogler, H. *Mol. Phys.* **1980**, *39*, 1291. (e) Vogler, H.; Mitchell, R. H. *Tetrahedron* **1985**, *41*, 3771. (f) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301. Pitfalls are pointed out in this review.

(5) (a) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111. (b) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175.

(6) (a) Viglione, R. G.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 2265. (b) Pelloni, S.; Ligabue, A.; Lazzeretti P. *Org. Lett.* **2004**, *6*, 4451.

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textbooks and NMR monographs, but its assumptions and limitations usually are not emphasized. It is well recognized that π ring currents are only one of the reasons for the arene-vinyl hydrogen δ ^{1}H differences.[4−7]

Although the recent restatement that "The benzene protons are predicted *to lie within the deshielding zone defined in terms of the out-of-plane magnetic shielding domain*"[6a] [our emphasis] is accurate, it has been demonstrated computationally several times recently that these H atoms actually *lie in the isotropic shielding zone* of benzene.[7] Although seemingly in contradiction, both statements are correct. To reconcile these two viewpoints, it must be appreciated that the NMR chemical shift is fundamentally a tensor quantity ($\boldsymbol{\sigma}$) with three principal axes,[8] along which each component has contributions from both σ and π electrons. [Using boldfaced type, we differentiate the chemical shielding tensor ($\boldsymbol{\sigma}$), from the sigma (σ) electrons.] In the customary textbook visualization, the applied magnetic field is parallel ($||$) to the out-of-plane axis and perpendicular ($\perp$) to the two in-plane axes.

The traditional *ring current model* considers planar molecules and treats only the delocalized π electron contribution to the *out-of-plane* shielding component [$\boldsymbol{\sigma}_{||}(\pi)$]. It tacitly assumes that the contributions from the σ electrons and/or the in-plane tensor components [$\boldsymbol{\sigma}_{||}(\sigma)$, $\boldsymbol{\sigma}_{\perp}(\pi)$, $\boldsymbol{\sigma}_{\perp}(\sigma)$] do not affect the *differences* in the downfield chemical shifts of arene vs vinylic protons. Unfortunately, $\boldsymbol{\sigma}_{||}(\sigma)$ has a substantial effect on such chemical shift differences. A further drawback of the traditional model is that the $\boldsymbol{\sigma}_{||}(\pi)$ component cannot be measured directly experimentally.[8,9] The physically observable isotropic chemical shift is an orientationally averaged quantity, whose separate $\boldsymbol{\sigma}_{||}(\pi)$, $\boldsymbol{\sigma}_{||}(\sigma)$, $\boldsymbol{\sigma}_{\perp}(\pi)$, and $\boldsymbol{\sigma}_{\perp}(\sigma)$ contributions are inextricable.[10]

Although the ring current model rationalizes the proton chemical shifts of the larger antiaromatic or aromatic [*n*]annulenes well,[1b,11] Schneider, Bernstein, and Pople emphasized the inadequacy of the model to account for the proton chemical shifts of nonalternant and charged aromatics.[12] Also, this model has difficulties in interpreting proton chemical shifts of heteroaromatic five-membered rings (Figure 1),[2] extended conjugated nonaromatic compounds, bicyclic antiaromatic systems, and even the behavior of polybenzenoid hydrocarbons (PBHs).

The inner ring of phenanthrene (**7**) exemplifies the PBH set. This ring is firmly established to be less aromatic (more olefinic) than the outer rings by its chemical behavior, nucleus independent chemical shift (NICS),[13] current density properties, and CC bond lengths.[14] In contrast, the inner ring δ ^{1}H (7.8) and especially the large ($\boldsymbol{\sigma}_{||}(\pi) = -8.0$) shielding component (vs -4.0 to -6.2 for the outer ring) do not conform to all the other aromaticity criteria.

The four-membered ring (4MR) of benzocyclobutadiene (**13**) is *antiaromatic*, but δ $^1\text{H} = 6.5$ is just below the >7 ppm *aromatic* range.[15] The antiaromaticity of this 4MR is clearly established by its NICS[13] (+21.8 ppm), its current density map,[16] and the positive π contribution [$\boldsymbol{\sigma}_{||}(\pi) = +3.5$] to the out-of-plane shielding component (see Figure 2; compare the cyclobutadiene data in ref 7a). Similarly, the δ ^{1}H chemical shifts of the antiaromatic heptalene (**10**) are in the olefinic 4 to 6 ppm[17] range, in contrast to the NICS value (+10.9 ppm), which indicates, as expected, the presence of a paratropic ring current.

In addition, the ring current model does not account for the proton chemical shifts of nonaromatic unsaturated compounds. Figure 2 gives a number of examples, including cyclopentadiene-annulated polycyclic unsaturated hydrocarbons and dibenzotropone derivatives. Isoindenes **1** and **4**, as well as the five-membered ring in indene **2**, have δ ^{1}H values very close to the aromatic range ($\approx$ 7 ppm). Some of the hydrogens in nonaromatic **8** and *all of the H atoms* in **9** clearly resonate in the aromatic range (up to 8.4 ppm!).

Nonaromatic **9** (highlighted in the Abstract) is our most dramatic challenge to "arene proton shifts as a criterion of aromaticity."[6] All the ring δ ^{1}H values of **9** are clearly in the aromatic range (>7.0), but **9** unquestionably is a conjugated, nonaromatic polyene with considerable CC bond alternation (0.08 Å). The small NICS(0) values displayed in Figure 2 [-0.7 (terminal ring), -1.4 (central ring), and -2.6 (middle ring)] confirm that **9** does not sustain diatropic ring currents. Likewise, the π out-of-plane components of the NICS(π) shieldings[18] for the three rings are much smaller (-14.3 ± 0.1) than for benzene (-36.3). Although **9** is nonaromatic, the downfield proton chemical shifts (7.0 to 8.4 ppm) are due to the π electron contribution to the out-of-plane component ($\boldsymbol{\sigma}_{||}(\pi)$). [Fascinatingly, the range is from -2.1 to -3.7 vs -3.1 ppm for benzene.] Thus, like the δ

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(7) (a) Schleyer, P. V. R.; Manoharan, M.; Wang. Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465. (b) Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1893. (c) Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1506. (d) Martin, N. H.; Allen, N. W., III; Minga, E. K.; Ingrassia, S. T.; Brown, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 11510. (e) Wannere, C. S., Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 605. (f) Merino, G.; Heine, T.; Seifert, G. *Chem. Eur. J.* **2004**, *10*, 4367.

(8) NMR chemical shielding tensor ($\boldsymbol{\sigma}$) relates the induced magnetic field ($\mathbf{B}_{\text{ind}}$) to the applied external field ($\mathbf{B}_{\text{ext}}$) as $\mathbf{B}_{\text{ind}} = -\boldsymbol{\sigma}\mathbf{B}_{\text{ext}}$. The $\boldsymbol{\sigma}$ tensor is fully specified by its diagonal elements (δ_{11},δ_{22},δ_{33}) (eigenvalues) along its principal axes (eigenvectors) in the molecule-fixed frame. In principle, individual tensor components can be measured by solid-state NMR, employing magic angle spinning. Powder samples give broad signals arising from the chemical shifts of all possible orientations. In solution (the usual measurement condition), molecules tumble freely and the tensor information is lost. The measured (isotropic) chemical shift is the average of the tensor components $1/3[\delta_{11} + \delta_{22} + \delta_{33}]$.

(9) Technical limitations preclude the direct experimental determination of absolute magnetic shieldings. It is not possible to measure field strengths to the parts per billion accuracy required for the determination of $\mathbf{B}_{\text{ind}}$. Consequently, experimental chemical shifts are commonly defined relative to an arbitrary standard. Explicit separation of π and σ effects on $\mathbf{B}_{\text{ind}}$ is not possible experimentally.

(10) Our IGLO values of these components for benzene protons are -3.1 [$\sigma_{||}(\pi)$], 4.7 [$\sigma_{\perp}(\pi)$], 23.8 [$\sigma_{||}(\sigma)$], and 20.7 [$\sigma_{\perp}(\sigma)$] and those for H(2) of cyclohexadiene are 0.4, 4.2, 23.2, and 21.6, respectively.

(11) Müllen, K.; Meul, T.; Schade, P.; Schmickler, H.; Vogel, E. *J. Am. Chem. Soc.* **1987**, *109*, 4992.

(12) Schneider, W. G.; Bernstein, H. J.; Pople, J. A. *J. Am. Chem. Soc.* **1958**, *80*, 3497.

(13) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(14) Ligabue, A.; Pincelli, U.; Lazzaretti, P.; Zanasi, R. *J. Am. Chem. Soc.* **1999**, *121*, 5513.

(15) Trahanovsky, W. S.; Fisher, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 4971.

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(17) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 4659.

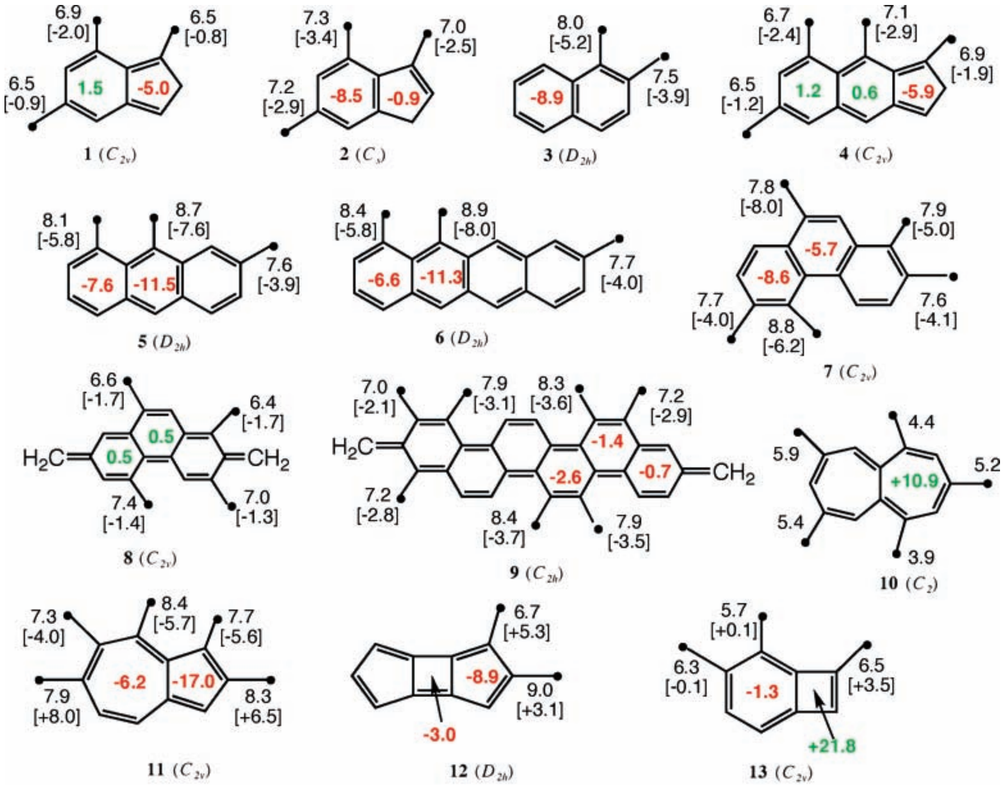

Figure 2. Computed isotropic NMR δ ^{1}H values referenced to the benzene proton chemical shift (taken to be $\delta = 7.3$). The magnitude of the π out-of-plane component of the shielding tensor, $\boldsymbol{\sigma}_{||}(\pi)$, is given in brackets. NICS(0) values in ring centers are bold (red = diatropic; green = paratropic). Note the downfield δ ^{1}H values (in the aromatic region) of various polycyclic unsaturated *nonaromatic* hydrocarbons (**1**, **4**, **8**, and **9**), whose small NICS values indicate the absence of significant ring currents. Remarkably, protons in the 10 π electron species **12**, as well as those along the C_2 axis of azulene (**11**), lie in the π *shielding zone* [positive $\boldsymbol{\sigma}_{||}(\pi)$ values]. The proton chemical shifts and the $\boldsymbol{\sigma}_{||}(\pi)$ values were computed at the PW91/IGLO-III//B3LYP/6-311+G** level using the deMon NMR program.[25]

^{1}H chemical shifts, $\boldsymbol{\sigma}_{||}(\pi)$ should not be taken as a reliable measure of delocalized π ring current effects.

Pople[12] noted problems with the ring current model for nonalternant systems such as azulene (**11**). While the δ ^{1}H values of **11** are all in the aromatic range, the downfield shifts of the two protons lying on the C_2 axis are due to the counterbalancing of the **positive** π electron contributions and the **negative** $\boldsymbol{\sigma}_{||}(\sigma)$ values [$\boldsymbol{\sigma}_{||}(\pi) = 6.5$ vs $\boldsymbol{\sigma}_{||}(\sigma) = -4.9$ for the five-membered ring H; $\boldsymbol{\sigma}_{||}(\pi) = 8.0$ vs $\boldsymbol{\sigma}_{||}(\sigma) = -4.5$ for the seven-membered ring H]. Likewise, the *σ-electron contributions* shift the analogous protons in bicyclopentadienylene (**12**) far downfield (to $\delta = 9.0$). Despite its 10 π perimeter and negative NICS, the π-out-of-plane components of **12** are strongly *shielding*, as evident from the positive $\boldsymbol{\sigma}_{||}(\pi)$ values in Figure 1.

These results demonstrate that the contribution of the σ system cannot be neglected in rationalizing δ ^{1}H NMR downfield shifts. Accordingly, the current density and the π-out-of-plane component of the proton shielding tensor are condemned to be virtual quantities, at least as unmeasurable experimentally as NICS![13]

Finally, compounds can be aromatic (or antiaromatic) due to the *induced circulation of their σ electrons*. This is shown for cyclopropane by Herges' ACID plot,[19] by Dauben's enhanced magnetic susceptibility,[20] and by NICS.[21] However, cyclopropane[22] and cyclopropene (Table 1) cannot be characterized as aromatic, either by the δ ^{1}H chemical shifts of the sp^3 hybridized CH groups (δ = ca. 0-0.7 ppm) or by the π-electron contributions to the out-of-plane component of the shielding tensor [$\boldsymbol{\sigma}_{||}(\pi)$]. Note that the chemical shift (δ ^{1}H = 7.0 ppm) of the in-plane cyclopropene vinyl H is deshielded and is in the aromatic range, despite the shielding of its out-of-plane component. Cyclobutane is σ-antiaromatic,[21,23] but its δ ^{1}H values are *downfield* from those of cyclopropane.

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(18) This is the π out-of-plane component of the NICS(π) value (also denoted δ_{zz}; see: Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R.; Weber, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273). It was argued recently that NICS(0) is not the best aromaticity criterion; the "π out-of-plane component of the central shielding values" (δ_{zz}) was proposed instead (see: Lazaretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217). We find that NICS(0) and the π out-of-plane NICS(0) component correspond reasonably well; e.g., the NICS(0) and δ_{zz} values for **9** (ca. −1.5 and −14.3, respectively), are close to those for cyclohexadiene (4.6 and −12.4) but are far away from the benzene values (−8.8 and −36.6).

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Table 1. Magnetic Properties of Monocyclic Hydrocarbons.[a] The Protons of Neither the σ Aromatic Cyclopropane nor the σ Antiaromatic Cyclobutane Are Shifted Downfield

	NICS	δ ^{1}H	$\boldsymbol{\sigma}_{||}$ (π)
cyclopropane-H	−42.8	0.0	0.0
cyclopropene-H(3)	−29.1	0.7	0.1
cyclopropene-H(1)		7.0	0.6
cyclobutane-H	2.6	2.0	0.0
cyclohexene-H(1)	−0.6	5.9	0.3
1,3-cyclohexadiene-H(1)	4.6	5.5	0.2
1,3-cyclohexadiene-H(2)		6.1	0.4
cyclopentadiene-H(1)	−4.1	6.5	−0.7
cyclopentadiene-H(2)		6.8	−1.2
benzene	−8.8	7.3	−3.1

[a] δ ^{1}H values are based on the benzene proton chemical shift, taken to be 7.27. The $\boldsymbol{\sigma}_{||}$ (π) quantity is the π contribution to the out-of-plane component of the shielding. Data at the PW91/IGLO-III//B3LYP/6-311+G** level were computed with the deMon NMR program.[25] The sp^2-CH vinyl protons of cyclopentadiene are *deshielded* by the π out-of-plane component, $\boldsymbol{\sigma}_{||}$ (π).

The seemingly divergent statements, that benzene protons lie (1) in the *deshielding* region of the π out-of-plane component and (2) in the *shielding* region of the isotropic domain, are both correct as specified. Although the shielding region of the isotropic domain (statement 2) is not measurable absolutely, it corresponds more nearly to the usual conditions of NMR measurement, where the molecules are tumbled about in the magnetic field. Statement 1 is restricted to oriented molecules but represents the consequences of the ring current model more closely. However, statement 1 does not consider the $\boldsymbol{\sigma}_{||}(\sigma)$ component, which makes significant contributions for *all* the orientations. In addition, π out-of-plane effects cannot be measured in isolation even if molecules are somehow oriented in the NMR magnetic field.[9]

We have presented several provocative examples of polyunsaturated hydrocarbons that sustain no π ring current but have protons shifted downfield more than those of benzene. Nonetheless, these nonaromatic hydrocarbons have π out-of-plane shielding components, $\boldsymbol{\sigma}_{||}(\pi)$, as large as in benzene. Even though these nonaromatic systems lack cyclic electron delocalization, they exhibit the deshielded δ ^{1}H values typically associated with "aromatic ring currents".

The NMR chemical shifts of the protons of pyrrole (average = 6.3, Figure 1), a classical aromatic heterocycle, resemble the vinyl H atoms of cyclopentadiene (average 6.4 ppm) but not those of benzene (7.3 ppm). Hydrocarbons such as cyclopropane and cyclopropene are σ aromatic, but their protons neither are downfield shifted nor show any π ring-current influence (e.g., from the cyclopropane CH$_2$ group). Interpretations that discount the effect of σ electrons and considering π electron circulations to be the sole origin of ring current effects, are oversimplified. Given the comparable magnitudes of $\boldsymbol{\sigma}_{||}(\pi)$, $\boldsymbol{\sigma}_{||}(\sigma)$, $\boldsymbol{\sigma}_{\perp}(\pi)$, and $\boldsymbol{\sigma}_{\perp}(\sigma)$ and their individual variability due to molecular environment, statements such as "the chemical shifts of arene protons are downfield relative to those of vinylic protons because the arene protons lie in the deshielding zone [of $\boldsymbol{\sigma}_{||}(\pi)$ ring currents]"[6a] are naive. Moreover, the ring current model cannot be applied strictly to explain the proton chemical shifts of the many known nonplanar aromatic systems (e.g., Möbius[24] annulenes). Numerous aromatic structures are devoid of protons in critical positions (or, as in the fullerenes, lack H atoms completely), and hence the δ ^{1}H chemical shift aromaticity criterion cannot be applied. Finally, antiaromatic molecules such as heptalene and cyclobutadiene have protons that lie in the vinylic region and are not upfield shifted by the isotropic shielding influences. No apparent relationship between the arene H chemical shifts and other aromaticity criteria are found, unless comparisons are restricted to closely related models.[2,7e] Taken at face value, neither proton chemical shifts nor their out-of-plane tensor components are generally reliable aromaticity indicators.

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