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# Why Downfield Proton Chemical Shifts Are Not Reliable Aromaticity Indicators

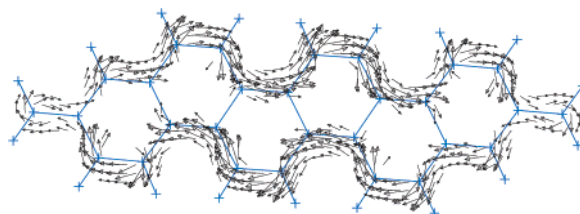
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## ABSTRACT



Traces of magnetizability, traces of magnetic shielding at the hydrogen nuclei, and nucleus-independent chemical shift are not reliable aromaticity quantifiers for planar conjugated hydrocarbons. A measure of aromaticity is provided by the out-of-plane tensor components, whose magnitude is influenced by the  $\pi$ -ring currents. The failure of nucleus-independent chemical shift in this regard was proved for the molecule shown in the abstract graphic, sustaining a diatropic  $\pi$ -current. The validity of the ring-current model is reaffirmed.

In a recent paper,<sup>1</sup> Wannere et al. claim that downfield proton chemical shifts are not reliable aromaticity indicators. This statement is acceptable, and we subscribe to this view, with some reservation. Nonetheless, we think that the motivations adduced in ref 1 are incorrect. The present note aims at elucidating the matter.

Proton magnetic shielding of arenes is usually rationalized via the ring-current model (RCM).<sup>2–4</sup> The related literature has recently been reviewed.<sup>5–8</sup> According to the RCM, the

delocalized currents induced in the mobile  $\pi$  electrons by an external magnetic field perpendicular to the molecular plane diminish (increase) the out-of-plane component  $\sigma_{||}^H$  of ring protons in diatropic (paratropic) unsaturated polycyclic hydrocarbons.<sup>9</sup> In benzene, for instance, the negative (also referred to as downfield, or paramagnetic) shift of  $\sigma_{||}^H$  caused by  $\pi$  currents is estimated to be as large as  $\sim -2.86$  ppm.<sup>10</sup> Approximately 10%, i.e.,  $\sim 19$  ppm of the out-of-plane component of carbon magnetic shielding,  $\sigma_{||}^C \approx 190$  ppm, arises from the positive (upfield, or diamagnetic) contribution from the  $\pi$ -ring currents flowing in the region

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(1) Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F., III; von Ragué Schleyer, P. *Org. Lett.* **2005**, *7*, 1457.

(2) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 673.

(3) Lonsdale, K. *Proc. R. Soc. (London)* **1937**, *A159*, 149.

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(5) Lazzeretti, P. Ring Currents. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Elsevier: New York, 2000; Vol. 36, p. 1.

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(7) von Ragué Schleyer, P. *Chem. Rev.* **2001**, *101*, 1115 and refs cited therein.

(8) Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217.

(9) An external magnetic field  $B_{||} \equiv B_z$ , at right angles to the xy molecular plane of benzene induces the magnetic field  $B_{||}^H = -\sigma_{||}^H B_{||}$ , perpendicular to the ring, at the protons. The total, positive, out-of-plane component  $\sigma_{||}^H$  of the proton shielding is biased by  $\pi$ -ring currents, which yield a negative contribution  $\sigma_{||}^H(\pi)$ , thus providing a positive contribution to  $B_{||}^H$  (i.e., in the same direction as  $B_{||}$ ), as shown in NMR textbooks. Therefore,  $\sigma_{||}^H$  is smaller than the average in-plane component  $\sigma_{\perp}^H = (\sigma_{xx}^H + \sigma_{yy}^H)/2$  and gives a measure of the effect of ring currents.

(10) Viglione, R. G.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 2265.

of distant carbons.<sup>11,12</sup> The  $\pi$  ring currents also enhance the out-of-plane component,  $\chi_{||}$ , of the molecular magnetizability tensor  $\chi_{\alpha\beta}$ .<sup>5</sup> The experimental value quoted by Flygare<sup>13</sup> is  $\chi_{||} = -94.6 \pm 2.5 \text{ erg G}^{-2} \text{ mol}^{-1}$ , compared to the in-plane component  $\chi_{\perp} = -34.9 \pm 2.0 \text{ erg G}^{-2} \text{ mol}^{-1}$ .

As recognized early on by Pauling,<sup>2</sup> and repeatedly stressed more recently,<sup>5,8–16</sup>  $\pi$ -ring currents bias only the out-of-plane components  $\chi_{||}$ ,  $\sigma_{||}^H$ , and  $\sigma_{||}^C$ . A number of different causes concur to determine the magnitude of the average in-plane components,  $\chi_{\perp}$ ,  $\sigma_{\perp}^H$ , and  $\sigma_{\perp}^C$ , which, however, is not influenced by the peculiar mobility of  $\pi$  electrons to any major extent. Therefore, criteria for diatropicity and aromaticity should only be established in terms of the out-of-plane component of magnetic tensors. Analyses based on average values, e.g., on  $\sigma_{av}^H = (\sigma_{xx}^H + \sigma_{yy}^H + \sigma_{zz}^H)/3$ , (i) imply a loss of information (two-thirds of the effects from  $\pi$  ring currents, e.g.,  $-2.86 \times (2/3) \approx -1.91$  ppm in benzene proton shielding) and (ii) bring in contributions from the in-plane components, that is, effects of  $\sigma$  and  $\pi$  electron mixing caused by a magnetic field parallel to the molecular plane. These contributions are to be regarded as spurious for evaluating aromaticity. Serious interpretation errors can be committed by confusing the averaged trace and the out-of-plane component of proton shielding in benzene.<sup>17</sup>

Therefore, neither downfield proton chemical shift  $\delta^H = \sigma_{av}^H(\text{tetramethylsilane}) - \sigma_{av}^H \equiv \delta^1\text{H}$  nor nucleus-independent chemical shift (NICS),<sup>18</sup> being average quantities, are reliable quantitative indicators of diatropicity.<sup>8</sup> Exalted  $\chi_{av}$  and downfield  $\delta^H$  may yield a qualitative indication of the presence of ring currents, but measures of magnetic aromaticity can only be proposed in terms of  $\chi_{||}$ ,  $\sigma_{||}^H$ , and, possibly,  $\sigma_{||}^C$ .

In Figure 2 of ref 1, whose numbering is retained in the present note, Wannere et al. “presented several provocative examples of polyunsaturated hydrocarbons that sustain no  $\pi$  ring currents but have protons shifted downfield more than those of benzene.” These systems should provide *experimenta crucis* invalidating the RCM, as “these nonaromatic hydrocarbons have  $\pi$  out-of-plane shielding components,  $\sigma_{||}(\pi)$ , as large as in benzene”.<sup>1</sup> We carried out a systematic analysis of these hydrocarbons. Molecular geometries have been optimized using Gaussian98<sup>19</sup> at the B3LYP/6-31G\*\* level, imposing planarity to all the systems. With no

exception, each geometry has been confirmed to correspond to an energy minimum by means of Hessian calculations.

Proton magnetic shielding tensors have been obtained by the damped variant of a method allowing for continuous transformation of the origin of the current density-diamagnetic zero (CTOCD-DZ2),<sup>20</sup> using the SYSMO program<sup>21</sup> and a (9s5p2d/5s2p) Gaussian basis set, contracted to [5s4p1d/3s1p].<sup>10</sup> The out-of-plane component of the proton magnetic shielding tensors,  $\sigma_{||}^H$ , has been dissected into core-electron plus  $\sigma$ - and  $\pi$ -electron contributions, indicated as  $\sigma_{||}^H(c + \sigma)$  and  $\sigma_{||}^H(\pi)$ . Within our approach, this partition is fully protected by symmetry.

Our results provide reproducible evidence that a number of items are to be expunged from the paradigm of Wannere et al., as they do not fulfill the two hypotheses<sup>1</sup> quoted above. This is in particular the case of the “most dramatic challenge”<sup>9</sup> highlighted in the abstract of ref 1. The  $\pi$  contribution to  $\sigma_{||}^H$  of the vinyl protons H1 and H3, calculated by CTOCD-DZ2,<sup>20</sup> reported in Table 1, is fairly negligible. The deshielding

**Table 1.** Proton Magnetic Shielding in ppm<sup>a</sup>

molecule	<sup>1</sup> H	$\sigma_{\perp}$	$\sigma_{  }(c + \sigma)$	$\sigma_{  }(\pi)$	$\sigma_{  }$	$\sigma_{Av}$	$\delta^1\text{H}^b$	$\sigma_{  }(\pi)^c$
<b>7</b>	1	26.07	22.79	−4.99	17.81	23.32	7.83	−8.0
	3	25.89	22.89	−5.03	17.86	23.21	7.93	−5.0
	5	25.73	23.15	−3.78	19.37	23.61	7.54	−4.1
	7	25.82	22.93	−3.91	19.03	23.55	7.59	−4.0
	9	25.89	21.23	−6.20	15.03	22.27	8.87	−6.2
<b>8</b>	1	25.98	22.95	−0.84	22.11	24.69	6.46	−1.7
	3	26.18	22.96	−1.13	21.84	24.73	6.41	−1.7
	5	25.82	22.99	−0.77	22.22	24.62	6.52	−1.3
	7	26.05	21.22	−0.97	20.25	24.12	7.03	−1.4
	9	26.69	24.61	−0.16	24.45	25.94	5.20	
<b>9</b>	11	26.67	24.66	−0.10	24.55	25.96	5.18	
	1	26.57	24.54	−0.40	24.15	25.76	5.38	
	3	26.58	24.49	−0.46	24.02	25.72	5.42	
	5	25.85	22.79	−1.34	21.45	24.38	6.76	−2.1
	7	26.10	22.73	−1.91	20.82	24.34	6.81	−2.8
<b>11</b>	9	26.07	20.86	−1.97	18.89	23.68	7.47	−3.1
	11	26.06	22.40	−1.91	20.49	24.21	6.94	−2.9
	13	26.29	20.45	−2.54	17.91	23.50	7.64	−3.5
	15	26.25	20.54	−2.41	18.13	23.54	7.60	−3.6
	17	26.28	20.30	−2.68	17.63	23.40	7.75	−3.7
<b>13</b>	1	24.84	23.90	−4.38	19.52	23.07	8.07	6.5
	3	25.89	23.87	−5.21	18.66	23.48	7.67	−5.6
	5	25.40	22.11	−5.70	16.41	22.40	8.74	−5.7
	7	26.68	22.66	−3.89	18.78	24.05	7.10	−4.0
	8	25.72	22.68	−4.09	18.59	23.34	7.80	8.0
<b>12</b>	1	23.06	23.81	−2.90	20.92	22.34	8.80	3.1
	3	26.52	24.03	−3.08	20.95	24.66	6.48	5.3
<b>13</b>	1	24.05	24.57	1.66	26.23	24.78	6.37	3.5
	3	26.33	23.99	0.04	24.03	25.56	5.58	0.1
	5	25.77	23.82	−0.29	23.53	25.02	6.12	−0.1

<sup>a</sup>  $\sigma_{\perp}$  is the average of the in-plane components;  $\sigma_{||}$  is the out-of-plane component;  $\sigma_{||}(c + \sigma)$  and  $\sigma_{||}(\pi)$  are contributions to the out-of-plane component from core-electrons plus  $\sigma$ - and  $\pi$ -electrons. <sup>b</sup> Chemical shifts are in reference to benzene values:  $\sigma_{av} = 23.87$ ,  $\delta^1\text{H} = 7.27$ . <sup>c</sup> From ref 1.

of H5 due to  $\pi$  electrons is  $\sigma_{||}^H(\pi) \approx -1.3$  ppm. The estimated paramagnetic shifts of H7, H9, and H11 are  $\sim 1$

(11) Soncini, A.; Fowler, P. W.; Lazzeretti, P.; Zanasi, R. *Chem. Phys. Lett.* **2005**, *401*, 164.

(12) Ferraro, M. B.; Faglioni, F.; Ligabue, A.; Pelloni, S.; Lazzeretti, P. *Magn. Res. Chem.* **2005**, *43*, 316.

(13) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653.

(14) Ferraro, M. B.; Lazzeretti, P.; Viglione, R. G.; Zanasi, R. *Chem. Phys. Lett.* **2004**, *390*, 268.

(15) Pelloni, S.; Ligabue, A.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 4451.

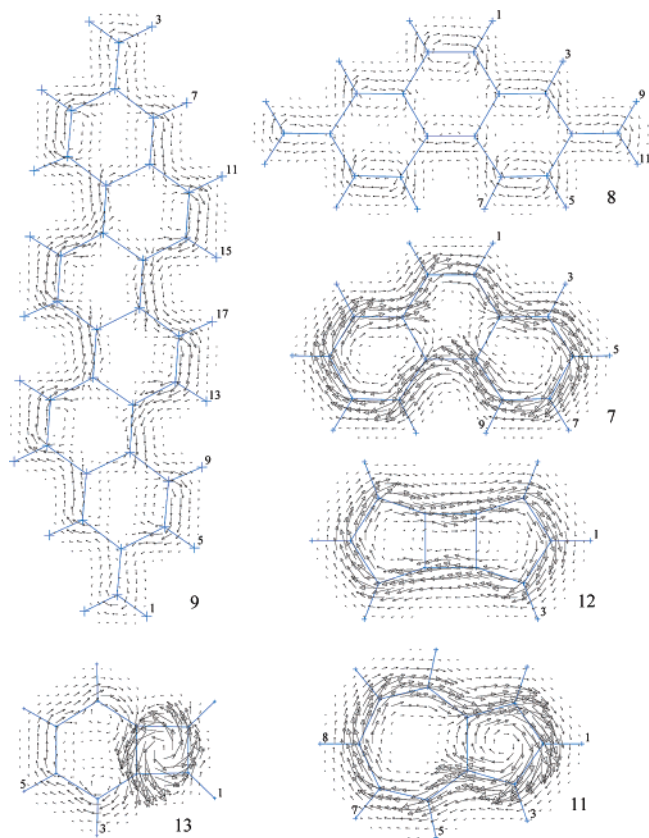
(16) Cuesta, I. G.; Ligabue, A.; Sánchez de Merás, A.; Lazzeretti, P. *Chem. Phys. Lett.* **2005**, *401*, 282.

(17) Wannere, C. S.; von Ragué Schleyer, P. *Org. Lett.* **2003**, *5*, 605. The statements made in this reference, namely, “The conventional explanation for the unusual downfield chemical shift of arene hydrogens needs a fundamental revision: arene hydrogens are NOT deshielded by ring current effects” and “... the protons [in benzene] are shielded and not “deshielded” by the  $\pi$  ring current” are untenable.<sup>8</sup>

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

ppm less negative than benzene's. On the other hand, the  $\pi$  contributions to  $\sigma_{\parallel}^H$  of protons H13, H15, and H17 are only  $\sim 0.2$ – $0.3$  ppm more positive than benzene's.

As can be observed in Figure 1, a magnetic field **B** at right angles to the molecular plane of **9** gives rise to



**Figure 1.** Ring-current model for molecules **7–9** and **11–13** of ref 1. The ordering is the same as in Table 1. Each plot displays a view of the  $\pi$  electron contribution to the current density in a plane parallel to that of the molecule, displaced from it by 0.75 bohr, close to the maximum of  $\pi$  electron density. Diamagnetic circulation is clockwise. The length of the arrows is normalized to the maximum modulus in benzene,  $|J_{\max}| = 0.080c$  cgs-emu au ( $c$  is the speed of light,  $\sim 137.036$  au). The maximum modulus for molecules **7**, **8**, **9**, **11**, **12**, and **13** is 0.088, 0.034, 0.047, 0.114, 0.077, and 0.117  $c$  cgs-emu au, respectively. To emphasize the perimeter  $\pi$  ring current, intensities lower than 0.015  $c$  cgs-emu au were omitted in the map highlighted in the abstract graphic.

diamagnetic  $\pi$  vortices localized in the region of the formal C–C double bonds. However, it can be noticed that the outward current is much more intense than the return current inside the rings. Therefore, **B** induces a  $\pi$  ring current flowing all over the carbon skeleton. Accordingly, one can easily understand why “... all the ring  $\delta^1H$  values... are clearly in the aromatic range”<sup>1</sup>. This system, which “unquestionably is a conjugated, nonaromatic polyene” for Wannere et al.,<sup>1</sup> is in fact diatropic according to our findings. The plot in Figure 1 proves that the statement “The small NICS(0) values... confirm that **9** does not sustain diatropic ring currents”<sup>1</sup> is not correct. Thus, a molecule that should

give evidence for the failure of Pople’s theory<sup>22</sup> in favor of the “antitheory” of ref 1 constitutes a crucial test showing inadequacies of NICS as a diatropicity/paratropicity detector of polycyclic hydrocarbons.<sup>8</sup>

The polycyclic system **9** is interesting and deserves further studies. A possible explanation of  $\delta^1H$  values of protons H13, H15, and H17, typical of aromatics, may be sought via methods proposed by Havenith et al.<sup>23</sup> Investigations on the  $\alpha,\omega$ -bicyclopentadiene-polyacene series showed that larger molecules in this series become gradually more aromatic, despite the fact that all have  $4n$   $\pi$  electrons. The induced current density reverses from paratropic, in pentalene and *s*-indacene, to diatropic with increasing chain length. In fact, the diamagnetic perimeter circulation grows in from **8** (in which vortices about the double bonds are clearly discernible) to **9**. Whereas the former retains the features of a conjugated cyclic polyene, the latter is actually diatropic, as documented in Figure 1.

To explain the peculiar properties of **9** in a simple way, let us consider a long chain of fused benzene rings, characterized by the same structure as **9** and carrying a pair of vinyl moieties at the ends. Irrespective of the chain length, there is only one Kekulé structure, describing the molecule as a nonaromatic, conjugated polyene. This description, however, is only topological. It is not supported by any physical argument. Just the other way around, there exist valid physical arguments suggesting that **9** possesses some aromatic character. This is proven by the ring currents sustained by the delocalized  $\pi$  cloud, weaker on the terminal hexagonal rings and stronger in the middle and all over the perimeter of the molecule. Whereas local diamagnetic vortices, typical of ethylenic C=C bonds, are observed in **8**, no closed current loops are found in the region of formal double bonds within the bays of **9**. The map shows a quasi-naphthalenic kernel sustaining a peripheral delocalized current. There is no current nearby the central C–C bond of this kernel. The maximum intensity is as large as  $\sim 0.05c$  au, smaller than the strong value  $\sim 0.08c$  au determined in benzene but bigger than the maximum intensity,  $\sim 0.03c$  au, for the nonaromatic system **8**; see the caption of Figure 1. Such a pattern is in complete agreement with the negative  $\sigma_{\parallel}(\pi)$  contributions to proton shielding shown in Table 1. In fact, it is reasonable to assume that the perturbation produced on the central benzenoid rings by the methylene groups at both ends goes to zero with increasing the chain length. In other words, for a certain chain length, removing the head and tail  $CH_2$  groups would not cause any significant alteration of the benzenoid structure of the central rings. Each hexagon of carbon atoms should exhibit a variable degree of aromaticity, smoothly decreasing from the central aromatic kernel to the ends of the chain. The estimated anisotropy of the magnetic susceptibility, as large as  $\sim -200$  erg  $G^{-2}$   $mol^{-1}$ ,

(19) Frisch, M. J. et al. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(20) Zanasi, R. *J. Chem. Phys.* **1996**, *105*, 1460.

(21) Lazzaretti, P.; Malagoli, M.; Zanasi, R. Technical report on project “sistemi informatici e calcolo parallelo”, Research Report 1/67, CNR, 1991.

(22) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175.

(23) Havenith, R. W. A.; Engelberts, J. J.; Fowler, P. W.; Steiner, E.; van Lenthe, J. H.; Lazzaretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 289.



provides another indication in favor of diatropicity of **9**. The out-of-plane component is  $\chi_{\parallel} \approx -332 \text{ erg G}^{-2} \text{ mol}^{-1}$ , compared to the average in-plane component  $\chi_{\perp} \approx -132 \text{ erg G}^{-2} \text{ mol}^{-1}$ . One-third of the former is due to  $\pi$  electrons,  $\chi_{\parallel}(\pi) \approx -97 \text{ erg G}^{-2} \text{ mol}^{-1}$ . We have also checked the assertion that **9** is characterized by a “considerable CC bond alternation ( $0.08 \text{ \AA}$ )”<sup>1</sup>. The sequence of the B3LYP/6-31G\*\*<sub>opt</sub>-optimized distances<sup>24</sup> confirms this value for the entire perimeter. However, within the bays, where the ring current is stronger, the bond lengths of formal single and double linkages are 1.43, 1.42, and 1.44  $\text{\AA}$ . Therefore, we cannot agree that **9** “unquestionably is a conjugated, nonaromatic polyene”<sup>1</sup>. On the other hand, an example of a fused ring chain, strongly biased by the presence of the two vinyl groups and whose length is insufficient to give rise to diatropicity, is offered by **8**. Actually, the current density map in Figure 1, the pattern of  $\sigma_{\parallel}^H(\pi)$  contributions displayed in Table 1, and the CC bond alternation (1.45, 1.39, and 1.45  $\text{\AA}$  for the formal single–double–single bond sequence within the bay, and 1.35  $\text{\AA}$  for the formal double bond outside the bay) indicate that **8** is nonaromatic.

A substantial agreement was found between our computed proton chemical shifts,  $\delta^1\text{H}$ , and those reported in ref 1, despite the different methods of calculation and basis sets employed. On the other hand, noticeable discrepancies can be observed in Table 1 for  $\sigma_{\parallel}^H(\pi)$ , in magnitude (for H1 of **7**<sup>25</sup> and **13**<sup>26–28</sup>) and sign (for H1 and H8 of **11** and for H1 and H3 of **12**<sup>29</sup>). Our results for  $\sigma_{\parallel}^H(\pi)$  in these systems are fully consistent with the plots of Figure 1 and prove the diatropicity of **11** and **12**. Our interpretation of azulene **11**<sup>30</sup> is also supported by the work of Havenith et al.<sup>31</sup> Likewise, bicyclopentadienylene **12** is a system with remarkable diatropicity.<sup>31,32</sup> The conclusions arrived at in ref 1 are

(24) In the counterclockwise direction, from the C–C bond adjacent to the upper hexocyclic bond in Figure 1, 1.45, 1.36, 1.44, 1.42, 1.43, 1.36, 1.43, 1.42, 1.44, 1.36, 1.44, 1.38, 1.44  $\text{\AA}$ .

(25) Chemical shift  $\delta^1\text{H1}$  calculated here is 7.83 ppm; that quoted in the ref 1 is 7.8 ppm. An excellent agreement is found for the other chemical shifts and for  $\sigma_{\parallel}^H(\pi)$ , with the exception of H1. Our estimate is  $-4.99 \text{ ppm}$ ; that in ref 1 is  $-8.0 \text{ ppm}$ . This value is anomalously high and hard to reconcile with the other estimates and with the current density maps.

(26) Soncini, A.; Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. W.; Steiner, E. *J. Org. Chem.* **2002**, 67, 4753. The RCM for **13** in this reference nicely agrees with that of Figure 1.

(27) The value 3.5 ppm of Wannere et al.<sup>1</sup> is twice as large as ours and larger than the  $\sigma_{\parallel}^H(\pi) = 2.54 \text{ ppm}$  predicted<sup>15</sup> via extended calculations for cyclobutane.

incompatible with the  $\pi$  current density maps and with the results of our calculations. Therefore, RCM is not invalidated by the calculations of ref 1 for **7**, **9**, **11**, and **12**.

As discussed here, these calculations should be revised. We have shown why downfield proton chemical shifts are not reliable *quantitative* aromaticity indicators. This assertion is not proven via the findings of ref 1. A trustworthy measure is the  $\sigma_{\parallel}^H$  out-of-plane component.<sup>33,34</sup>

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(28) The maximum modulus of the  $\pi$  current density,  $|J_{\max}|$ , is almost the same in the paratropic four-membered ring of **13** ( $\sim 0.117c \text{ au}$ ) and in the diatropic system **11** ( $\sim 0.114c \text{ au}$ ). However,  $\sigma_{\parallel}^H(\pi)$  in the latter is, in absolute value, three times as large as that in the former ( $-4.38$  vs  $1.66 \text{ ppm}$ ). This difference is understood recalling the  $r^{-2}$  dependence in the Biot–Savart law expression for nuclear magnetic shielding<sup>15</sup> and observing in the maps of Figure 1 that the maximum modulus of the current lies in the vicinity of the carbon nuclei in **13** and closer to the proton in **11**.

(29) The discrepancies are striking. For **11**, compare  $-4.38$  with  $6.5 \text{ ppm}$  for H1 and  $-4.09$  with  $8.0 \text{ ppm}$  for H8 in Table 1. For **12**, compare  $-2.90$  with  $8.80 \text{ ppm}$  for H1 and  $-3.08$  with  $5.3 \text{ ppm}$  for H3. Positive  $\sigma_{\parallel}^H(\pi)$  values are incompatible with the RCMs of Figure 1.

(30) The statement “... the downfield shifts of the two protons lying on the  $C_2$  axis are due to the counterbalancing of the **positive**  $\pi$  electron contributions and the **negative**  $\sigma_{\parallel}(\sigma)$  values ...”<sup>1</sup> is unjustifiable on the basis of the RCM in Figure 1 and the computed  $\sigma_{\parallel}^H(\pi)$  in Table 1.

(31) Havenith, R. W. A.; Lugli, F.; Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **2002**, 106, 5703.

(32) The assertion “Despite its 10  $\pi$  perimeter and negative NICS, the  $\pi$ -out-of-plane components of **12** are strongly *shielding*, as evident from the positive  $\sigma_{\parallel}(\pi)$  values...”<sup>1</sup> is contradicted by our results in Table 1.

(33) Revised calculations would offer no evidence to substantiate the claim that “...  $\sigma_{\parallel}(\pi)$  should not be taken as a reliable measure of delocalized  $\pi$  current effects”<sup>1</sup>. The conviction of Wannere et al. is discounted by our investigations.

(34) The  $\pi$  contributions to the out-of-plane component of NICS(0), NICS<sub>||</sub>( $\pi$ ) are, for **8**,  $-2.4$  and  $-2.1 \text{ ppm}$ , respectively for the outer and inner rings. For **9**, starting from the outer and moving to the inner ring, the calculated values are:  $-5.7$ ,  $-8.2$ , and  $-11.5 \text{ ppm}$ . Interestingly, the value corresponding to the midpoint of the C–C bond in the quasi-naphthalenic core is  $-12 \text{ ppm}$ , very close to that of the inner rings. These pieces of information, fully consistent with the current plots and with other data discussed here, corroborate the conviction that, in the limit of long chains, hydrocarbons of type **9** have a quasi-naphthalenic kernel whose magnetic response is insensitive to removal of the methylene moieties at the ends.