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# How Do Ring Currents Affect $^{1}$H NMR Chemical Shifts?

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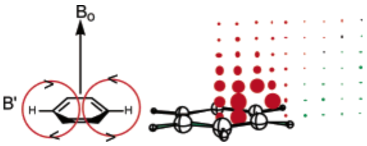
## ABSTRACT



**Conventional explanations of proton NMR chemical shifts need fundamental revisions. Ab initio (IGLO) analyses reveal that the downfield $\delta$ $^{1}$H of benzene is not due to *deshielding* ring current effects; the *shielding* is less than the $\pi$ contribution to vinyl $\delta$ $^{1}$Hs. Enhanced deshielding $\sigma$ CC influences are responsible for the more downfield $\delta$ $^{1}$Hs of the inner protons of naphthalene and anthracene. Double $\pi$ effects shield ethynyl Hs; there is no evidence for a special "ring current influence."**

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. The conventional explanation is based on Pople's ring current model[1] typically illustrated as in Figure 1a in almost all NMR monographs and organic textbooks, where the Hs are located in the deshielding region around benzene.[2] This scheme was based on the "Pauling−Lonsdale−London $\pi$ model"[3] and ignores other possible local contributions from the $\sigma$ C−H and C−C bonds. Musher's[4] suggestion that local contributions, rather than ring currents, were responsible for the downfield $^{1}$H shifts in aromatic hydrocarbons has been criticized[1c−e,5] and supported[6,7]

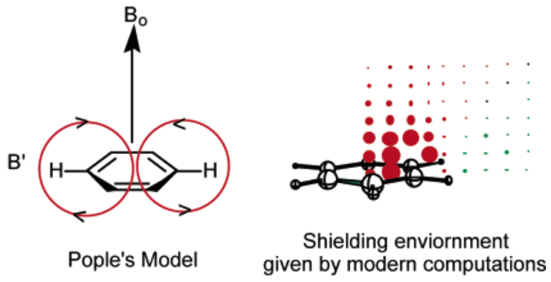


**Figure 1.** Comparison of the conventional ring current model[2] (B$_0$ and B′ are the applied and induced magnetic fields, respectively) with the shielding environment computed by the IGLO method.[10a] Red and green color dots represent magnetically shielded and deshielded points, respectively.

McConnell's[8] equation predicts the directional dependence of the NMR shielding tensors experienced by a nucleus in proximity to an anisotropic group. Evaluation of the sign of the shielding effect calculated by this equation gives rise to the familiar "shielding cone" depictions not only for benzene

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(1) (a) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111. (b) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175. (c) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303. (d) Lazzeretti, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1. (e) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349.

(2) (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.

(3) (a) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 673. (b) Lonsdale, K. *Proc. R. Soc. London*, **1937**, *159*, 149. (c) London, F. *J. Phys. Radium* **1937**, *8*, 397. (d) London, F. *J. Chem. Phys.* **1937**, *5*, 837.

(4) (a) Musher, J. I. *J. Chem. Phys.* **1967**, *47*, 1219. (b) Musher, J. I. *Adv. Magn. Reson.* **1966**, *2*, 177. (c) Musher, J. I. *J. Chem. Phys.* **1965**, *43*, 4041.

(5) Gaidis, J. M.; West, R. J. *J. Chem. Phys.* **1967**, *46*, 1218.

(6) (a) Blustin, P. H. *Chem. Phys. Lett.* **1979**, *64*, 507. (b) Blustin, P. H. *Mol. Phys.* **1978**, *36*, 1441. (c) Blustin, P. H. *Mol. Phys.* **1980**, *39*, 565.

(7) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(8) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 1.

10.1021/ol027327k CCC: $25.00

(Figure 1a) but also for other molecules modeling functional groups (Figure 2a).[9] Unfortunately, these depictions also result in incorrect predictions at variance with the shielding surfaces computed by ab initio and density functional methods.[10]

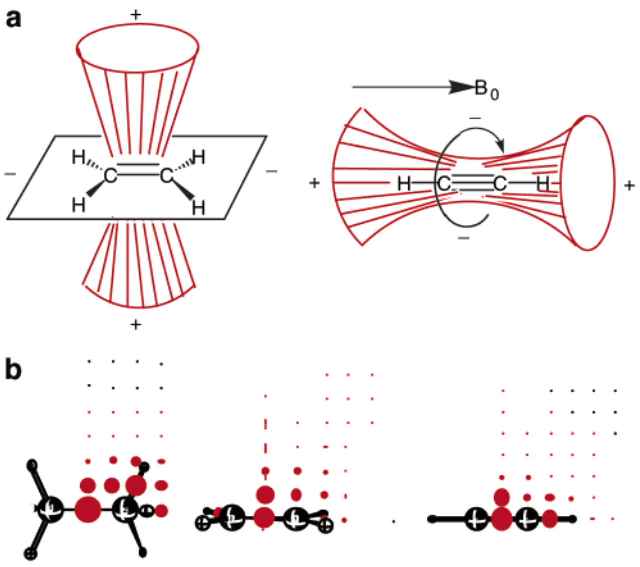

**Figure 2.** (Top) Classical anisotropy (shielding (+) and deshielding (−)) cones for ethene and ethyne. (Bottom) Computed shielding environments of ethane, ethene, and ethyne.

These modern computations[10] show (see Figure 1b) that the deshielding zone of benzene is weak in magnitude and begins farther away from the ring center than in Figure 1a. Schleyer et al.'s grid[10a] and Klod and Kleinpeter's informative graphical representations of the shielding environments of various molecules[10b,d] showed that the deshielding zone in benzene starts ca. 3.5 Å away from the center of the ring. Hence, the Hs fall into the *shielding* rather than into the *deshielding* cone. This paper analyzes, in detail, the reasons for the difference in the chemical shifts between arene and vinyl Hs. (Note that magnetic "shieldings" are absolute values and have the opposite sign convention than chemical "shifts", which are measured experimentally relative to a chosen standard.)

A similar study was first reported by Fleischer, Kutzelnigg, Lazzeretti, and Mühlenkamp in 1994.[7] They employed individual gauge for the localized orbitals (IGLO) method[11] to study the ring current and local effects on the $^{1}$H NMR chemical shieldings of benzene and related olefins. The IGLO method dissects total shieldings into individual CC($\pi$), CC($\sigma$), CH, lone-pair, and core electron-localized molecular orbital (LMO) contributions. After a complicated analysis, Kutzelnigg et al. concluded that ring currents are present in benzene but have "only a small effect on the $^{1}$H shift. So Musher is somehow right that a description of the magnetic properties of benzene is possible in terms of localized quantities." These conclusions have been ignored until very recently.[10] Textbooks continue to repeat the conventional explanation.

The data in Table 1 document the good agreement of the IGLO-computed[12] proton chemical shifts with the experimental[2,13] values and provide the details of the LMO dissection. The contribution of the intrinsic C−H bond itself to the H shielding is by far the largest. However, these contributions are almost the same in different hydrocarbon environments. The exceptions are acetylene and the three-membered rings, evidently due to the influence of the essentially sp C−H bond hybridization. The very small core (carbon 1s) electron contributions can be ignored. Likewise, nonvicinal CHs have negligible shielding effects. Hence, variations in hydrogen chemical shifts are mainly due to differences in the CC($\pi$) and the CC($\sigma$) contributions.

**Ethene and Ethyne.** Contrary to the usual depiction of completely different shielding environments of ethene and ethyne (Figure 2a), attributed to an alleged "ring current effect" in ethyne, the computed shielding environments (Figure 2b) show no qualitative differences among ethane, ethene, and ethyne.[10b] There is no discernible "ring current" effect in ethyne nor any indication of the "shielding-deshielding" cones depicted in Figure 2a. The upfield hydrogen chemical shift in $C_2H_2$ is not due to the alleged special "diatropic ring current effects," but primarily to normal $\pi$ shielding influences. The IGLO dissection, Table 1, reveals that the CC($\pi$) shielding of the Hs per $\pi$ bond is the same in ethene (2.6 ppm) and in ethyne (2.5 ppm for

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(9) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012

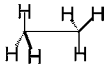
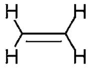
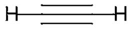
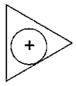
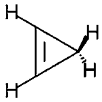
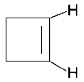
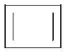
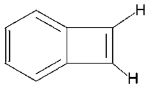
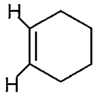
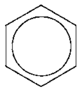
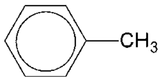
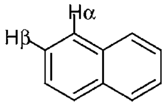
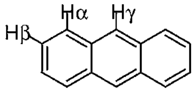
(10) (a) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465. (b) Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1893. (c) Martin, N.; Brown, J. D.; Nance, K. H.; Schaefer, H. F., III; Schleyer, P. v. R.; Wang, Z.-X.; Woodcock, H. L. *Org. Lett.* **2001**, *3*, 3823. (d) Klod, S.; Andreas, K.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1506. (e) Martin, N. H.; Allen, N. W., III; Minga, E. K.; Ingrassia, S. T.; Brown, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 11510.

(11) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360. (d) Kutzelnigg, W. *THEOCHEM* **1989**, *202*, 11. (e) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR: Basic Principles of Progress*; Springer: Berlin, 1990; Vol. 23, p 165.

(12) Absolute proton shieldings were computed using the IGLO method and the Pipek−Mezey localization procedure as implemented in the deMon NMR program (Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898) at the PW91/IGLO-III//B3LYP/6-311+G** level. The chemical shifts, in ppm, are evaluated relative to TMS (the proton chemical shieldings were converted to chemical shifts as the difference from the proton shieldings of TMS, 31.3 ppm). Geometry optimizations, in most stable conformations, were done at the B3LYP/6-311+G** level using Gaussian 98 (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998).

(13) (a) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; Wiley and Sons: New York, 1982. (b) Cram, D. J.; Tanner, M. E.; Thomas, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1024. (c) Trahanovsky, W. S.; Fischer, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 4971.

**Table 1.** LMO Contributions, Evaluated at the PW91/IGLO-III//B3LYP/6-311+G** IGLO Level, of Various LMOs (CH(main), CC($\pi$), CC($\sigma$), CH$_{\text{other}}$, and Core) to the Total Proton Shieldings ($\delta_{\text{calcd}}$ ($\delta_{\text{obs}}$), in Parts Per Million, Are the Computed (Experimental) Chemical Shifts Relative[12] to TMS)

| ring | | | total shielding | $\delta_{\text{calc}}$ ($\delta_{\text{obs}}$) | CH(main) | CC($\pi$) | CC($\sigma$) | CH$_{\text{other}}$ | core |
|---|---|---|---|---|---|---|---|---|---|
|  | $D_{3d}$ | | 30.5 | 0.8 (0.88) | 25.5 | - | 1.3 | 3.7[a] | 0.0 |
|  | $D_{2h}$ | | 25.8 | 5.5 (5.84) | 26.0 | 2.6 | -1.9 | -0.8 | -0.1 |
|  | $D_{\infty h}$ | | 29.8 | 1.5 (2.88) | 23.8 | 5.0 | 0.8 | 0.4 | 0.3 |
|  | $D_{3h}$ | | 20.9 | 10.4 (10.3) | 23.1 | 1.6 | -3.6 | -0.2 | -0.2 |
|  | $C_{2v}$ | =CH | 24.1 | 7.2 (7.06) | 24.5 | 2.5 | -2.7 | 0.0 | -0.2 |
| | | >CH$_2$ | 30.4 | 0.9 (0.93) | 26.0 | -1.7 | 4.2 | 1.9[a] | 0.0 |
|  | $C_{2v}$ | =CH | 25.0 | 6.3 (6.03) | 26.1 | 2.4 | -3.4 | 0.1 | -0.1 |
| | | >CH$_2$ | 28.7 | 2.6 (2.57) | 25.4 | -0.6 | 2.3 | 1.4[a] | 0.1 |
|  | $D_{2h}$ | | 25.4 | 5.9 (5.76)[b] | 25.5 | 2.8 | -2.9 | 0.0 | -0.1 |
|  | $C_{2v}$ | H$_{4MR}$ | 24.6 | 6.7 (6.36) | 25.3 | 2.8 | -3.5 | 0.0 | -0.1 |
|  | $C_2$ | =CH | 25.3 | 6.0 (5.59) | 26.2 | 2.9 | -3.9 | 0.1 | 0.0 |
|  | $D_{6h}$ | | 23.8 | 7.5 (7.27) | 25.8 | 1.9 | -3.6 | -0.1 | 0.0 |
|  | $C_s$ | CH$_3$ | 29.0 | 2.3 (2.32) | 25.1 | -0.5 | 0.6 | 4.0[a] | 0.1 |
|  | $D_{2h}$ | H$_\alpha$ | 23.2 | 8.1 (7.73) | 25.7 | 1.9 | -4.3 | 0.0 | -0.2 |
| | | H$_\beta$ | 23.5 | 7.8 (7.38) | 25.7 | 2.1 | -3.6 | -0.4 | -0.2 |
|  | $D_{2h}$ | H$_\alpha$ | 22.9 | 8.4 (7.93) | 25.7 | 1.7 | -4.1 | -0.1 | -0.2 |
| | | H$_\beta$ | 23.5 | 7.8 (7.39) | 25.7 | 2.0 | -3.7 | -0.4 | -0.1 |
| | | H$_\gamma$ | 22.5 | 8.8 (8.36) | 25.7 | 1.5 | -4.8 | 0.2 | -0.2 |
| | | H$_1$ | 22.1 | 9.2 (8.14) | 25.7 | 1.4 | -4.2 | -0.5 | -0.3 |

[a] Enhanced by geminal CH effects. [b] Based on $\delta$ 7.27 for benzene and the experimentally[13b] observed difference of 1.51 ppm between CBD and benzene in a clathrate.

each of the two $\pi$ bonds). The total 5.0 ppm $\pi$ effect in ethyne is additive rather than enhanced as one would expect if special "ring currents" were operative.

**Benzene.** Statements such as "the downfield chemical shift of the arene protons ($\delta$ ~7.3) relative to those of vinylic protons (cyclohexene $\delta$ ~5.6) is because arene protons lie in the deshielding zone (Figure 1a)"[2b,2c,14] are incorrect. Figure 1b shows the arene protons to lie in the *shielding* zone rather than the deshielding zone! The C−C($\pi$) bonds *shield* the benzene Hs by +1.9 ppm (Table 1).

Why then are the benzene protons downfield (by 1.7 ppm, experimental) relative to the vinyl protons in cyclohexene? Comparison of the data for both hydrocarbons in Table 1 reveals that small variations in all the C−C($\sigma$) and the C−H contributions together account for only about half of the total difference. The other half is due to the 1.0 ppm *decrease* in the $\pi$ bond *shielding* of benzene (1.9 ppm) relative to cyclohexene (2.9 ppm).

**Toluene.** Note that the methyl Hs in toluene do lie in the *deshielding* ring current zone of benzene. However, the paratropic C−C($\pi$) contribution, −0.5 ppm (Table 1), to the total methyl hydrogen shielding is small.

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(14) For a comparison of CC($\pi$) shielding grids of benzene, acetylene, cyclobutadiene, and *trans*-dihydropyrene, see Supporting Information.

**Naphthalene and Anthracene.** The proton chemical shifts of polycyclic arenes often vary in systematic ways. Thus, the benzene ($\delta$ $^1$H 7.3) and outer $\beta$-protons of naphthalene and anthracene (both $\delta$ $^1$H 7.3) resonate at ca. 0.5 ppm higher fields than the inner α-protons (Table 1). The $\gamma$-Hs on the central ring of anthracene ($\delta$ $^1$H 8.3) are deshielded even more. Although Blustin[6] rationalized these trends by employing Musher's localized model,[4] Haigh and Mallion[15] showed that the chemical shifts predicted by the traditional ring current model also agree with experimental values. According to the currently accepted explanation, paratropic ring current contributions from adjacent rings help deshield the α-protons in naphthalene and anthracene and the $H_\gamma$s to a greater extent in the latter.[1d]

As in benzene, the CC($\pi$) contributions in Table 1 *shield* all the naphthalene and anthracene Hs. While the shielding is 0.2−0.3 ppm less for $H_\alpha$ and 0.5 ppm less for $H_\gamma$ than for $H_\beta$, larger differences, 0.7 and 1.2 ppm, respectively, are found in the deshielding CC($\sigma$) contributions. The more detailed analysis given in the SI material shows that the larger CC($\sigma$) differences depend on the number of nonadjacent C−C bonds; there are two for $H_\beta$s, three for $H_\alpha$s, and four for $H_\gamma$s. Hence, $\sigma$ rather than $\pi$ effects are primarily responsible for the $\delta$ $^1$H variations in these acene systems.

**Cyclopropene and the Cyclopropenium Ion.** The three-membered rings in Table 1 exhibit unusually deshielded proton chemical shifts, $\delta$ 10.3 for the cyclopropenium cation and $\delta$ 7.06 for the =C−Hs of cyclopropene (i.e., in the "aromatic region"). However, the $\pi$ contributions are *shielding* in both cases. The observed deshielding arises from the paratropic CC($\sigma$) contributions and the lower inherent main C−H bond shieldings. The latter effect evidently is due, as in ethyne, to the essentially sp hybridization of the CH bonding.

**Cyclobutadiene and Benzocyclobutadiene.** Contrary to the expectation that the paramagnetic ring currents of antiaromatic compounds[16] should shield the cyclobutadiene (CBD) protons, these $\delta$ Hs are *not found upfield*. Instead, they appear in the vinyl H regions because the paratropic contributions from the $\pi$ bonds at the ring center in CBD are close to zero.[10a,14] The experimentally measured[13b] upfield proton chemical shift of CBD relative to benzene in a clathrate, 1.51 ppm, is in agreement with the computed difference, 1.6 ppm (Table 1). Moreover, the computed proton chemical shift for CBD, $\delta$ 5.9, is close to $\delta$ 5.38, measured[17] for the tri-*tert*-butyl-cyclobutadiene ring H. The slight upfield shift of the CBD Hs is due to an increase in the $\pi$ bond shielding (2.8 ppm) relative to that in cyclobutene (2.4 ppm). Note that the total CC($\sigma$), $CH_{other}$, and intrinsic CH contribution in both these cases are almost the same.

The greater downfield chemical shift of benzocyclobutadiene protons ($H_{4MR}$) relative to those of CBD is attributed (Table 1) to the larger paratropic contributions from the $\sigma$ C−C bonds. Also note that the total CC($\pi$), $CH_{other}$, and core contributions are nearly the same for both of these hydrocarbons.

We conclude that the deshielding cone of benzene actually begins farther away (>3 Å) from the ring center[10a,b] than the Johnson−Bovey prediction.[9] Consequently, the protons are *shielded* and not "deshielded" by the $\pi$ ring current. However, this diatropic effect is 1.0 ppm less than the $\pi$ shielding of the vinyl protons of cyclohexene by the C=C double bond. Small differences in the CH and CC($\sigma$) shielding also contribute to the $\delta$ $^1$H of benzene. Likewise, the protons of cyclobutene and CBD are also in the shielding zone; the higher field chemical shift of the CBD Hs is due to the increase in $\pi$ bond shielding relative to cyclobutene. Although arene proton chemical shifts have long served as a major criterion of aromaticity, the findings in this paper and the related literature[10] undermine at least part of the theoretical basis for this connection.

No direct relationship between external arene H chemical shifts and other magnetic, geometric, and energetic aromaticity criteria is apparent from the data in Table 1. Neither the NICS(1)[18] of benzene (−10.6), naphthalene (−10.8) and anthracene (−9.9 outer rings, −13.1 inner ring) nor the HOMA values[18] parallel the proton shifts. The ASE/electron for naphthalene and anthracene are not larger than benzene,[18] but the Hs are farther downfield. The ASE/electron of the *trans*-dimethyldihydropyrene [14]annulene (see Supporting Information) perimeter is less than that of benzene, but the H shifts are farther downfield.[19] Likewise, the outer H chemical shifts of [18]annulene ($\delta = 9.2$)[13a] are among the most deshielded of any aromatic hydrocarbon, but the ASE/e is much less[19] than benzene's. We will show in a subsequent paper that the proton chemical shifts of conjugated olefin systems can fall in the "aromatic region".

**Acknowledgment.** This paper is dedicated to the memory of Jeremy Musher. We thank Ned H. Martin, Rainer Herges, and Thomas Heine for helpful discussions as well as S. Klod and E. Kleinpeter for information prior to publication. The University of Georgia and the National Science Foundation Grant CHE-0209857 provided financial support.

**Supporting Information Available:** Table A, containing IGLO analysis of *trans*-15,16-dihydropyrenes; Table B, containing detailed LMO contributions, of various bonds, from the IGLO output for cyclohexene, benzene, naphthalene, anthracene, and *trans*-15,16-dihydropyrene; Table C, containing Cartesian coordinates of all the structures (optimized at B3LYP/6-311+G**); and Figure A, showing the dissected CC($\pi$) shielding grids of acetylene, benzene, cyclobutadiene, and *trans*-dihydropyrene. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Haigh, C. W.; Mallion, R. B. *J. Chem. Phys.* **1982**, *76*, 4063.

[16] (a) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811. (b) We will analyze large antiaromatic systems in a separate paper.

[17] Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.

[18] Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643.

[19] (a) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383. (b) Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 745. (c) Choi, C. H.; Kertesz, M. *J. Chem. Phys.* **1998**, *108*, 6681. (d) Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* Submitted.