

## Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe

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The ability to sustain a diatropic ring current is the defining characteristic of aromatic species.<sup>1-7</sup> Cyclic electron delocalization results in enhanced stability, bond length equalization, and special magnetic as well as chemical and physical properties.<sup>1</sup> In contrast, antiaromatic compounds sustain paratropic ring currents<sup>3</sup> despite their localized, destabilized structures.<sup>1-7</sup> We have demonstrated the direct, quantitative relationships among energetic, geometrical, and magnetic criteria of aromaticity in a wide-ranging set of aromatic/antiaromatic five-membered rings.<sup>5a</sup> While the diamagnetic susceptibility exaltation ( $\Lambda$ ) is uniquely associated with aromaticity, it is highly dependent on the ring size (area<sup>2</sup>) and requires suitable calibration standards.<sup>6</sup> Aromatic stabilization energies (ASEs) of strained and more complicated systems are difficult to evaluate. CC bond length variations in polybenzenoid hydrocarbons can be just as large as those in linear conjugated polyenes.<sup>2</sup>

The abnormal proton chemical shifts of aromatic molecules are the most commonly employed indicators of ring current effects.<sup>1</sup> However, the ca. 2–4 ppm displacements of external protons to lower magnetic fields are relatively modest (e.g.,  $\delta\text{H} = 7.3$  for benzene vs 5.6 for  $=\text{C}-\text{H}$  in cyclohexene). In contrast, the upfield chemical shifts of protons located *inside* aromatic rings are more unusual. The six inner hydrogens of [18]-annulene, for example, resonate at  $-3.0$  ppm vs  $\delta = 9.28$  for the outer protons. This relationship is inverted dramatically in the antiaromatic [18]annulene dianion,  $\text{C}_{18}\text{H}_{18}^{2-}$ , where  $\delta = 20.8$  and 29.5 (in) vs.  $-1.1$  (out).<sup>8</sup> Similar demonstrations of paratropic ring currents in antiaromatic compounds are well documented.<sup>3,8,9</sup> Chemical shifts of encapsulated  $^3\text{He}$  atoms are now employed as experimental and computed measures of aromaticity in fullerenes and fullerene derivatives.<sup>10</sup>

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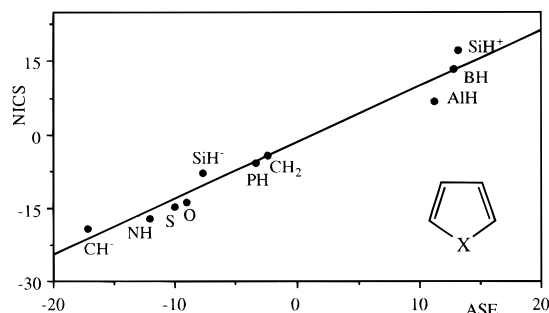
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**Figure 1.** Plot of NICSs (ppm) vs the aromatic stabilization energies (ASEs, kcal/mol)<sup>5a</sup> for a set of five-membered ring heterocycles,  $\text{C}_4\text{H}_4\text{X}$  (X = as shown) (cc = 0.966).

While the rings of most aromatic systems are too small to accommodate atoms internally, the chemical shifts of hydrogens in bridging positions have long been used as aromaticity and antiaromaticity probes.<sup>9</sup>  $\delta\text{Li}^+$  can be employed similarly, with the advantage that  $\text{Li}^+$  complexes with individual rings in polycyclic systems can be computed.<sup>4,11</sup>

We now propose the use of absolute magnetic shieldings, computed at *ring centers* (nonweighted mean of the heavy atom coordinates) with available quantum mechanics programs,<sup>12</sup> as a new aromaticity/antiaromaticity criterion. To correspond to the familiar NMR chemical shift convention, the signs of the computed values are reversed: Negative “nucleus-independent chemical shifts” (NICSs) denote aromaticity; positive NICSs, antiaromaticity (see Table 1 for selected results). Figure 1, a plot of NICSs vs the ASEs for our set of five-membered ring heterocycles,<sup>5a</sup> provides calibration. The equally good correlations with magnetic susceptibility exaltations and with structural variations establish NICS as an effective aromaticity criterion.

Unlike  $\Lambda$ ,<sup>6</sup> NICS values for [*n*]annulenes (Table 1) show only a modest dependence on ring size. The 10  $\pi$  electron systems give significantly higher values than those with 6  $\pi$  electrons. The antiaromatic  $4n$   $\pi$  electron compounds, cyclobutadiene (27.6), pentalene (18.1), heptalene (22.7), and planar  $D_{4h}$  cyclooctatetraene (30.1), all show highly positive NICSs.

Like the  $\text{Li}^+$ -complex probe,<sup>4</sup> the NICS evaluates the aromaticity and antiaromaticity contributions of individual rings in polycyclic systems. Scheme 1 (HF/6-31+G\*, data from Table 1) shows NICSs for selected examples. The benzenoid aromatic NICSs provide evidence both for localized and “perimeter” models. The naphthalene (**1**) NICS ( $-9.9$ ) resembles that of benzene ( $-9.7$ ), as do the NICSs for the outer rings of phenanthrene (**2**) ( $-10.2$ ) and triphenylene (**3**); the aromaticity of the central rings of the latter two are reduced. The NICS of the central ring of anthracene (**4**) ( $-13.3$ ) exceeds the benzene value in contrast to the outer ring NICS ( $-8.2$ ). Remarkably, the NICS ( $-7.0$ ) for the seven-membered ring of azulene (**5**) is very close to that of the tropylium ion ( $-7.6$  ppm), whereas the azulene five-membered ring NICS ( $-19.7$ ) is even larger in magnitude than that of the cyclopentadienyl anion ( $-14.3$ ).

The four-membered rings in benzocyclobutadiene (**6**) (NICS = 22.5) and in biphenylene (**7**) (19.0) are antiaromatic, but less so than cyclobutadiene itself (27.6). The six-membered rings in these polycycles are still aromatic, but their NICSs ( $-2.5$

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**Table 1.** GIAO-SCF Calculated NICSs (ppm) for the Set of Five-Membered C<sub>4</sub>H<sub>4</sub>X Ring Systems (Figure 1),<sup>a</sup> [n]Annulenes (n = 5–10), and Polycyclic Ring Systems as Well as Cage Molecules<sup>b</sup>

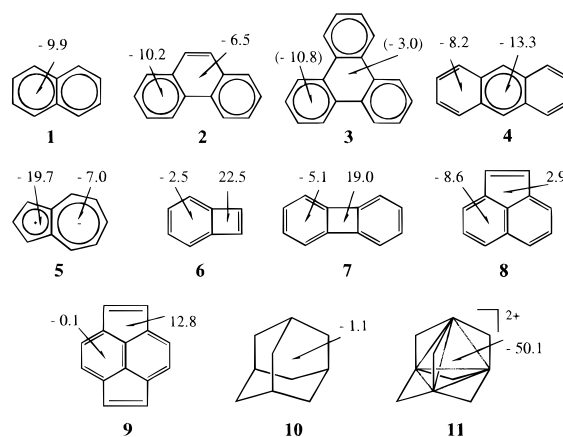
compounds	point group	NICS (6-31+G*) <sup>c</sup>	NICS (6-31G*) <sup>c</sup>	Λ <sup>d</sup>
pyrrole	C <sub>2v</sub>	-15.1	-17.3	-12.1
thiophene	C <sub>2v</sub>	-13.6	-14.7	-10.0
furan	C <sub>2v</sub>	-12.3	-13.9	-9.1
silolyl anion (C <sub>4</sub> H <sub>4</sub> SiH <sup>-</sup> )	C <sub>s</sub>	-6.7	-8.0	-7.7
C <sub>4</sub> H <sub>4</sub> PH (phosphole)	C <sub>s</sub>	-5.3	-5.9	-3.3
cyclopentadiene	C <sub>2v</sub>	-3.2	-4.2	-2.4
alumol (C <sub>4</sub> H <sub>4</sub> AlH)	C <sub>2v</sub>	6.5	6.9	11.2
borol (C <sub>4</sub> H <sub>4</sub> BH)	C <sub>2v</sub>	17.5	17.2	12.8
silolyl cation (C <sub>4</sub> H <sub>4</sub> SiH <sup>+</sup> )	C <sub>2v</sub>	12.8	13.4	13.2
cyclopentadienyl anion	D <sub>5h</sub>	-14.3	-19.4	-17.2
benzene	D <sub>6h</sub>	-9.7	-11.5	-13.4
tropylium ion	D <sub>7h</sub>	-7.6	-8.2	-20.5
cyclooctatetraenyl dication	D <sub>8h</sub>	-6.4	-7.6	-31.3
cyclooctatetraenyl dianion	D <sub>8h</sub>	-13.9	-19.9	-55.6
cyclononatetraenyl anion	D <sub>9h</sub>	-15.1	-17.6	-60.4
<i>all-cis</i> -[10]annulene	D <sub>10h</sub>	-14.9	-16.0	-80.1
naphthalene (1)	D <sub>2h</sub>	-9.9	-11.4	-28.2
phenanthrene (2), central ring	C <sub>2v</sub>	-6.5	-7.4	-47.9
outer ring		-10.2	-11.7	
triphenylene (3), central ring	D <sub>3h</sub>		-3.0	-57.6
outer ring			-10.8	
anthracene (4), central ring	D <sub>2h</sub>	-13.3	-14.3	-49.8
outer ring		-8.2	-9.6	
azulene (5), 5-ring	C <sub>2v</sub>	-19.7	-21.5	-42.9
7-ring		-7.0	-8.3	
cyclobutadiene	D <sub>2h</sub>	27.6	28.8	18.0
pentalene	C <sub>2h</sub>	18.1	16.9	30.9
heptalene	C <sub>2h</sub>	22.7	21.7	76.6
cyclooctatetraene, planar	D <sub>4h</sub>	30.1	29.2	60.4
benzocyclobutadiene (6), 6-ring	C <sub>2v</sub>	-2.5	-4.2	9.0
4-ring		22.5	21.5	
biphenylene (7), 6-ring	D <sub>2h</sub>	-5.1	-6.5	-7.9
4-ring		19.0	18.2	
acenaphthylene (8), 6-ring	C <sub>2v</sub>	-8.6	-9.8	-32.5
5-ring		2.9	2.1	
pyracyclene (9), 6-ring	D <sub>2h</sub>	-0.1		-8.4
5-ring		12.8		
cyclohexane	D <sub>3d</sub>	-2.2	-2.1	-0.7
adamantane (10)	T <sub>d</sub>	-1.1	-1.1	-6.5
1,3-dehydro-5,7-adamantanediyl dication (11) <sup>a</sup>	T <sub>d</sub>	-50.1	-49.6	-51.1
<i>closo</i> -B <sub>12</sub> H <sub>12</sub> <sup>2-</sup>	I <sub>h</sub>		-34.4	

<sup>a</sup> MP2/6-31G\* geometries. <sup>b</sup> Becke3LYP/6-31G\* geometries. <sup>c</sup> NICS values are only somewhat sensitive to the basis set; use of 6-31+G\* (where possible) is recommended. <sup>d</sup> The magnetic susceptibility exaltations (Λ, ppm cgs)<sup>5</sup> are given for comparison. Exaltations computed via an increment scheme for the entire system.

and -5.1) are reduced considerably relative to that of benzene (-9.7). The five-membered rings of acenaphthylene (8) (NICS = 2.9) and especially of pyracyclene (9) (12.8) are antiaromatic, and the aromaticity of the six-ring of 8 is reduced (-8.6), whereas the six-ring of 9 is nonaromatic (NICS = -0.1)! Hence, antiaromaticity is distributed over the entire ring systems of these molecules.<sup>4</sup>

The aromaticity of fullerenes<sup>10</sup> is considered to be a balance between the diatropic six-ring and the paratropic five-ring contributions.<sup>13,14</sup> Hydrogens in fullerene derivatives located above five rings are shifted downfield, whereas hydrogens above six rings are found upfield.<sup>13</sup> The NICS values (GIAO/3-21G/

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**Scheme 1**

/HF/3-21G) for the five- (5.4) and six-membered (-6.8) rings of C<sub>60</sub> confirm the expected "antiaromatic-aromatic" nature of the parent fullerene,<sup>14</sup> but the magnitudes are not large.

The NICS for "Kekule benzene" (D<sub>3h</sub>, with rCC fixed at 1.350 and 1.449 Å, the central distances in 1,3,5-hexatriene is only 0.8 ppm less than the NICS for D<sub>6h</sub> benzene itself (-9.7). With 1.53 Å (ethane-like) and 1.33 Å (ethene-like) distances, the Kekule benzene NICS is reduced only by 2.6 ppm. This confirms the relative insensitivity of diatropicity to geometry variations in aromatic systems.<sup>7</sup>

The local shielding of nearby σ bonds complicates the analysis of three-membered ring NICSs, and these are not included in Table 1. However, such local shieldings are not a problem in larger, nonaromatic rings (note the very small adamantane (10) (-1.1) and cyclohexane (-2.2) NICS values in Table 1). In contrast, the very negative NICS confirms the considerable aromaticity of the 1,3-dehydro-5,7-adamantanediyl dication (11) (-50.1).<sup>15</sup> The magnetic susceptibility exaltation of this four-center two-electron-delocalized dication (Λ = -51.1) also is extremely large. Spherical aromaticity<sup>16</sup> also is demonstrated by the NICS for *closo*-B<sub>12</sub>H<sub>12</sub><sup>2-</sup> (-34.4), which is representative of the behavior of the entire *closo*-borane dianion family.

The maximum chemical shieldings are often found away from the ring centers (e.g., reflecting the π electron toroid densities).<sup>7,17</sup> More detailed assessments of diatropicity and paratropicity are facilitated since the same computation can give chemical shieldings at many points. Nevertheless, the ring centers are easiest to define, and the NICS evaluates the aromaticity/antiaromaticity of the examples listed in Table 1 well.<sup>18</sup>

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