







Aromaticity and Relative Stabilities of  
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## ABSTRACT

						...	
NICS(0) <sub>πzzz</sub> (ppm)	-36.1	-35.9	-35.2	-34.8	-36.1	...	-37.4
ECREs (kcal/mol)	29.3	29.7	29.5	29.9	32.5/26.0	...	32.3
REs (kcal/mol)	61.4	61.3	60.9	59.7	63.8/53.4	...	40.1

The most refined nucleus-independent chemical shift index (NICS(0)<sub>πzzz</sub>) and the extra cyclic resonance energies (ECREs), based on the block localized wave function (BLW) method, show that the aromaticity of all azines is like that of benzene. The same is true for aza-naphthalenes relative to naphthalene. The lower relative energies of isomers with vicinal N's are due to the weakness of NN bonds rather than to reduced aromaticity.

Does the aromaticity of benzene change when N atoms substitute their CH groups sequentially? The answers in the literature diverge widely. We argue that nitrogen embedding should not decrease the strong diatropicity (aromaticity) of benzene appreciably since this does not arise primarily from having equal CC bond lengths and uniform  $\pi$  charge distribution. Indeed, pyridine (**1**, Abstract, see TOC Figure) showed about the same degree of aromaticity as benzene, according to the resonance energies (REs) calculated by Wiberg (benzene vs **1**: 36 vs 34 kcal/mol),<sup>1</sup> by Bird (benzene vs **1**: 45.8 vs 43.3 kcal/mol),<sup>2</sup> and by aromatic stabilization energies based on homodesmotic equations (benzene vs **1**: 28.8 vs 31.0 kcal/mol).<sup>3</sup> In contrast, Mosquera et al.<sup>4a</sup> concluded that “the insertion of N atoms decreases the aromaticity” of **1** substantially compared to benzene and of





























azines generally (“unless they form N–N bonds”). This analysis was based on the *n*-center delocalization index (*n*-DI), a measure of the degree of electron delocalization to all atoms in an aromatic ring.<sup>4</sup>

Quantitative analyses of the aromaticity of the whole azine series have led to inconsistent conclusions.<sup>1,2c,4</sup> Major discrepancies were found between contiguous (1,2-) and noncontiguous (1,3-, 1,4-, etc.) derivatives (e.g., diazines **2a–2c**, Abstract, see TOC Figure): contiguous isomers appear to be less aromatic according to their REs derived from isodesmic reactions (Wiberg)<sup>1</sup> and from the bond orders of their  $\pi$ -systems (Bird)<sup>2</sup> but are *more aromatic* according to their *n*-DI's (Mosquera).<sup>4</sup>

The results for the extreme case, hexazine, N<sub>6</sub> (*D*<sub>6h</sub> **6**, Abstract, see TOC Figure), vary and depend on the geometry employed; the minimum is nonplanar (*D*<sub>2</sub>). Despite its thermodynamic instability<sup>5</sup> (N<sub>6</sub> → 3N<sub>2</sub>,  $\Delta H = -223.7$  kcal/mol at B3LYP/6-311+G\*\*), an early nucleus-independent chemical shift study of *D*<sub>6h</sub> N<sub>6</sub> gave only a slightly less

<sup>†</sup> Beijing Institute of Technology.<sup>‡</sup> University of Georgia.(1) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.(2) See Bird's series of papers on “heteroaromaticity”, e.g.: (a) Bird, C. W. *Tetrahedron* **1992**, *48*, 335. (b) Bird, C. W. *Tetrahedron* **1996**, *52*, 9945. (c) Bird, C. W. *Tetrahedron* **1997**, *53*, 13111.(3) Schleyer, P. v. R.; Pühlhofer, F. *Org. Lett.* **2002**, *4*, 2873.(4) (a) Mandado, M.; Otero, N.; Mosquera, R. A. *Tetrahedron* **2006**, *62*, 12204. (b) Mandado, M.; Gonzalez, M. J.; Mosquera, R. A. *J. Comput. Chem.* **2007**, *28*, 127. Also see refs 9 and 25.

**Table 1.** NICS (ppm) (at PW91/IGLOIII//B3LYP/6-311+G\*\*); BLW ECREs and REs (kcal/mol) (at B3LYP/6-31G\*) Based on Planar Rings and the Most Stable Resonance Contributor (MSRC) as Shown (the Number of MSRC NN Single Bonds Is Given in Parentheses); and the B3LYP/6-311+G\*\* Relative Energies ( $E_{rel}$ ) of Azines\*

	NICS(0) (NICS(1)) <sup>a</sup>	NICS(0) <sub>zz</sub>	ECRE	Reference Molecules <sup>b</sup>	BLW RE	MSRC	Wiberg, Bird RE's	$E_{rel}$ (exptl)
<b>1</b>	 -6.27 (-12.38)	-35.94	29.68	CCCC+CCCN+CCNC	61.30		34, 43.3	
<b>2a</b>	 -5.00	-35.15	29.46	CCCN+CNCN+CCNC	60.87		33, 40.6	0.00
<b>2b</b>	 -4.76	-34.75	29.93	CCNC+NCCN+CCNC	59.69		32, 40.9	3.86(0.1)
<b>2c</b>	 -4.56 (-12.50)	-36.11	32.50	CCCC+2CCNN	63.82		26, 33.5	21.88(19.7)
<b>3a</b>	 -3.55	-33.77	28.02	3CNCN	59.49		-, 44.9	0.00
<b>3b</b>	 -2.93	-35.88	31.63	CCNC+NCNN+CCNN	60.85		-, 32.9	25.84
			28.44	CNCN+CNCC+NCCN	54.25(1)			
<b>3c</b>	 -3.24 (-12.48)	-36.34	27.21	CCCN+CNCC+CCNN	53.74(1)		25, 43.1	41.43
<b>4a</b>	 -1.34	-35.50	31.34	CNNN+CNCN+NCNN	56.04(1)		-, 35.1	0.00
<b>4b</b>	 -0.79	-36.66	32.44	CNNC+2NCNN	55.82(1)		16, 21.6	6.97
<b>4c</b>	 -1.39 (-12.47)	-36.36	29.80	NNNN+2CCNN	53.02(1)		-, 29.7	19.38
			26.80	CNNN+NCCN+CNCC	47.16(2)			
<b>5</b>	 0.75 (-12.14)	-36.70	31.50	NCNN+CNCC+NNNN	48.31(2)		-, 16.5	
<b>6</b>	 3.18 <sup>c</sup> (-12.24)	-37.36 <sup>d</sup>	32.32	3NNNN	40.12(3) <sup>e</sup>		-, -8.2	
<b>A</b>	 -7.52 (-12.81)	-36.12	29.29	3CCCC	61.39		36, 45.8	

\* Wiberg's<sup>1</sup> and Bird's<sup>2</sup> REs are given for comparison. <sup>a</sup> NICS(1) data at HF/6-31G\*\*//MP2/6-31G\* in parentheses from ref 25. Cf. Supporting Information (SI) Table S1. <sup>b</sup> The H's are shown in the following key: B3LYP/6-31G\* BLW REs (kcal/mol) for the acyclic conjugated reference molecules (imposed planar symmetries) are (*syn*, *inner*  $H(N)$ ): CH<sub>2</sub>=CH-CH=CH<sub>2</sub> (CCCC), 10.70; CH<sub>2</sub>=CH-CH=NH (CCCN), 9.91; CH<sub>2</sub>=CH-N=CH<sub>2</sub> (CCNC), 11.01; CH<sub>2</sub>=CH-N=NH (CCNN), 10.31; CH<sub>2</sub>=N-N=CH<sub>2</sub> (CNCC), 7.58; CH<sub>2</sub>=N-CH=NH (CNCN), 10.49; NH=CH-CH=NH (NCCN), 7.74; CH<sub>2</sub>=N-N=NH (CNNN), 6.31; NH=CH-N=NH (NCNN), 7.90; NH=N-N=NH (NNNN), 2.60. <sup>c</sup> NICS(0)  $D_{6h}$  2.80;  $D_2$  -8.92 ppm; NICS(0)<sub>zz</sub>  $D_{6h}$  +1.03;  $D_2$  -27.68 ppm at BP86/def2-TZVP. <sup>d</sup> NICS(0)<sub>zz</sub>  $D_{6h}$  -38.01;  $D_2$  -32.29 ppm at BP86/def2-TZVP. <sup>e</sup> See ref 8.

diatropic NICS(0.5)<sub>π</sub> value than benzene.<sup>6</sup> Although Sakai<sup>7</sup> found planar N<sub>6</sub> to be less aromatic than benzene, most aromatic indexes (e.g., n-DI)<sup>4a</sup> only indicate a slightly lower aromatic character of N<sub>6</sub>, even for the  $D_2$  geometry.<sup>8,9</sup>

Solà et al.'s recent assessment of the performance of several structural (HOMA), magnetic (NICS), and electronic (PDI, FLU, MCI, I<sub>ring</sub>) indexes of benzene, the diazines, and

triazine revealed divergent aromaticity orders.<sup>9</sup> Furthermore, none of these indexes followed Bird's RE's aromaticity order, benzene > **1** > **2c** > **2b** > **2a** > **3a** (see Table 1).<sup>10</sup> Unlike HOMA, the newly revised HOMED (harmonic oscillator model of electron delocalization) geometric index found all the azines to have essentially the same aromaticity as benzene.<sup>11</sup>

Such aromaticity studies also have been extended to N-substituted polycyclic heteroaromatic arenes. An analysis of isotropic NICS values and conformational flexibility<sup>12</sup> concluded that mono- and diazanaphthalenes are less aromatic than naphthalene. However, Lazzarotti et al.'s<sup>13</sup> theoretical magnetic shielding plots of tetraazaphthalenes

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(8)  $D_2$  symmetry N<sub>6</sub> is only 2.6 kcal/mol more stable at B3LYP/6-311+G\*\*+ZPE than the  $D_{6h}$  form. See Table 1 and SI Figure S2 for detailed CMO NICS dissections and related data on both forms.

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closely resemble those of naphthalene. Bunz et al. found that diazapentacenes<sup>14</sup> and diazatetracenes<sup>15</sup> were as aromatic as pentacene and tetracene.

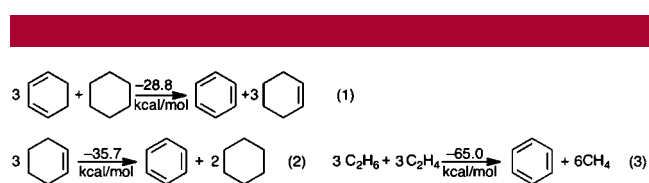
We now present refined evidence based on magnetic (NICS(0)<sub>πzz</sub>)<sup>16</sup> and energetic (extra cyclic resonance energy, ECRE)<sup>17</sup> criteria documenting the essential *invariance of aromaticity* along the whole azine series including benzene.

The GIAO<sup>18</sup> approach in conjunction with the NBO 5.0<sup>19</sup> and Gaussian 03<sup>20</sup> programs was used to compute NICS(0)<sub>πzz</sub><sup>16b</sup> values (at ring centers). These include only the contributions of the out-of-plane (zz) tensor components of the π MOs directly relevant to aromaticity.

ECREs are based on the block localized wavefunction (BLW)<sup>21</sup> method (using GAMESS R5)<sup>22</sup> and are defined as the difference in REs between a cyclic conjugated compound and that of appropriate acyclic polyenes having the same number and type of diene conjugations. BLW separates all the electrons and basis functions into sets of localized MOs. Orbitals of the same subspaces are mutually orthogonal, but those of different subspaces overlap freely. This “disables” the intramolecular interactions among the selected subgroups. BLW computes REs as the difference in the total energy between the completely delocalized, fully optimized planar molecule (planarity was imposed to ensure the uniform treatment of the π systems) and its most stable resonance contributor (MSRC). The geometries of the latter employed here were optimized with the BLW constraint. This gives the adiabatic BLW REs and ECREs<sup>21e</sup> for azines shown in Table 1. Note that negative-NICS (positive-ECRE) values measure the magnitude of aromaticity, while positive-NICS (negative-ECRE) values correspond to antiaromatic systems. Nonaromatic rings have NICS and ECRE values close to zero.

We employed three appropriate conjugated dienes (coded in Table 1) as reference molecules to evaluate the ECRE of each azine. On the basis of the same approach, the ECRE estimate of benzene (29.3 kcal/mol), derived from the RE difference

between benzene (61.4 kcal/mol) and three *syn*-butadienes (10.7 kcal/mol each), matches the 28.8 kcal/mol aromatic stabilization energy (ASE) evaluated from eq 1 (Figure 1).



**Figure 1.** Evaluations (exptl) of the aromatic stabilization (eq 1) and resonance energies (eq 2, badly flawed, due to neglect of cyclohexene hyperconjugation,<sup>21e,23,24</sup> and eq 3) of benzene.

As has been stressed,<sup>21e,23,24</sup> the 36 kcal/mol historical evaluation from eq 2 (Figure 1) grossly underestimates the RE of benzene, particularly since it neglects the large, partially counterbalancing hyperconjugative stabilization of the three cyclohexenes. The adiabatic BLW RE of benzene (61.4 kcal/mol,<sup>21e,23,24</sup> using localized cyclohexatriene as the MSRC, SI Figure S1) agrees with the isodesmic bond separation energy of eq 3 (Figure 1). The BLW RE of naphthalene, ca. 111 kcal/mol based on the MSRCs (SI Figure S1), compares well with the azanaphthalene REs (SI Table S2). Table S2 (SI) gives the relative experimental energies and NICS values for these bicyclic species.

A very thorough previous study of all the azines<sup>25</sup> included an isotropic NICS analysis of the contiguous-N species. The NICS(1) index performed well<sup>6,16</sup> and, even for *D*<sub>6h</sub> N<sub>6</sub>, gave remarkably constant values much like benzene<sup>25</sup> (see Table 1 and SI Table S1). In contrast, the NICS(0) data (cf. the PW91/IGLOIII/B3LYP/6-311+G\*\* data in Table 1 and SI Table S1) are badly distorted by in-plane *xx*, *yy* tensor component and σ contaminations.<sup>6,16b,c,26</sup> The refined NICS(0)<sub>πzz</sub> index<sup>16b</sup> is definitive as it eliminates these contaminations and shows almost no change of aromaticity from benzene (−36.1 ppm) through all the azines (−35.6 ± 1.8 ppm), even including *D*<sub>6h</sub> hexazine (−37.36) (6)! NICS(0)<sub>πzz</sub> of *D*<sub>2</sub> N<sub>6</sub> (see Table 1 and the CMO dissection in SI Figure S2) agrees with the small decrease in aromaticity relative to *D*<sub>6h</sub> N<sub>6</sub> found earlier.<sup>9</sup> In contrast, the NICS(0) and NICS(0)<sub>zz</sub> results for *D*<sub>6h</sub> N<sub>6</sub> are so badly contaminated that they have positive values.

The roughly constant ECRE azine data (30 ± 2.8 kcal/mol in Table 1) for the whole benzene to hexazine (6) set confirm the general NICS(0)<sub>πzz</sub> conclusions impressively. Both these results refine “the expected order” of azines used to test aromaticity criteria employed by Solà et al.<sup>9</sup> and refute Mosquera’s<sup>4a</sup> n-DI findings discussed above.

The REs of azines depend on the presence or absence of N=N single bonds in the MSRCs employed. Thus, the two REs given for **2c**, **3b**, and **4c** (Table 1) differ by about 7 kcal/

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mol. In agreement with Bird's finding,<sup>2</sup> our BLW computations reveal a relatively small RE for  $D_{6h}$  N<sub>6</sub> (**6**), compared to the other azines (Table 1; Abstract, see TOC Figure). We attribute this to the three formal N–N single bonds in the MSRC of **6**. The CC, CN, and NN “ $\pi$  bond component energies” can be evaluated simply by subtracting the single (sigma) bond energy from the total double bond energies. The available experimental<sup>27</sup> and G3<sup>28</sup>-based single and double bond energy data for CC, CN, and NN agree well (Table 2). (Sanderson's widely

**Table 2.** Bond Energies Deduced from Atomization Energies [e.g., a Constant C–H Bond Energy, Derived from 1/4 (CH<sub>4</sub> → C + 4H), Is Assumed]<sup>a</sup>

	exptl	G3	Sanderson
C=C	140.9	140.7	146
C–C	79.0	78.8	83
C=N	–	127.0	147
C–N	65.2	64.6	73
N=N	92.7	94.6	109
N–N	37.9	36.9	38
C–H	99.4	99.4	99
N–H	93.4	93.2	93

<sup>a</sup> The same method was used for C=C (C<sub>2</sub>H<sub>4</sub>), C–C (C<sub>2</sub>H<sub>6</sub>), C=N (CH<sub>2</sub>NH), C–N (CH<sub>3</sub>NH<sub>2</sub>), N=N (N<sub>2</sub>H<sub>2</sub>), and N–N (N<sub>2</sub>H<sub>4</sub>).

used bond energies<sup>29</sup> are outmoded.) Both the G3  $\pi$ (CC) and  $\pi$ (CN) bond energies are essentially identical (62 kcal/mol). Hence, the BLW REs of **1**, **2a**, **2b**, and **3a** and the larger values of **2c**, **3b**, and **4c** are nearly constant ( $61.7 \pm 2.2$ ) and resemble that of benzene. However,  $\pi$ (NN) (ca. 56 kcal/mol) is much smaller. Thus, less energy is needed to “convert” the  $\pi$ (NN) bond in delocalized azines to the N–N single bond in the MSRCs, under the applied BLW constraint. Table 1 shows that each formal N–N single bond in the MSRCs decreases the azine BLW REs by roughly 7 kcal/mol, e.g., from  $54.5 \pm 1.5$  (one formal N–N bond) to  $47.7 \pm 0.6$  (two N–N's) to 40.1 kcal/mol (three N–N's). The same effect is found in the REs of the mono- (**7a–7b**), di- (**8a–8j**), and tetra-substituted (**9a–9m**) aza-naphthalenes (SI Table S2).

*Vicinal* NN lone pair repulsion is the conventional explanation for the ca. 20 kcal/mol higher total energies of contiguous azines (like **2a**) than their noncontiguous isomers (like **2b,c**, last column, Table 1).<sup>4,5</sup> However, mono- or diprotonation of the diazine lone pairs of **2a–2c** does not eliminate these energy differences (Table 3). Since the ca. 6

(27) NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 15a, April 2010, <http://cccbdb.nist.gov/>.







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**Table 3.** B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\*+ZPE Relative Energies (kcal/mol) of Protonated and Diprotonated Diazines

	<b>2a</b>	<b>2b</b>	<b>2c</b>
$E_{rel} (+H^+)$	0.0 	8.8 	15.7 
$E_{rel} (+2H^+)$	0.0 	4.1 	29.1 

kcal/mol smaller  $\pi$ (NN) than  $\pi$ (CC) or  $\pi$ (CN) energy is insufficient to account for the relative energies of the azine isomers,  $\sigma$  skeleton effects must dominate. *Geminal* N lone pair–NN  $\sigma$  bond pair repulsion, as stressed by Sanderson,<sup>29</sup> and the unfavorably shorter NN distances (“bond length strain”) may be responsible.<sup>30</sup>

**Conclusions.** Sequential hetero-N substitution has little effect on the aromaticity of benzene. The isotropic NICS(1) values,<sup>25</sup> the most refined (NICS(0) <sub>$\pi_{zz}$</sub> ) index (SI Table S1), and the BLW-based extra cyclic resonance energies (ECREs) (Table 1) agree that *the aromaticity of the entire set of azines is nearly the same and resembles that of benzene*. The aromaticity of benzene is altered very little by substitution, either on<sup>10,31</sup> or in the C<sub>6</sub> ring (Table 1). The NICS(0) <sub>$\pi_{zz}$</sub>  (magnetic) and ECRE (energetic) agreement also establishes a defining benchmark for quantifying azine aromaticity, better founded than “expected” aromaticity orders based on chemical intuition,<sup>9</sup> which have been used to support n-DI findings.<sup>4,9</sup>

The azine BLW REs, based on MSRCs without formal NN single bonds, are almost the same as benzene. The BLW REs are smaller (nearly 7 kcal/mol per NN bond) in azines when their MSRCs include formal N–N single bonds. This is consistent with the ca. 6 kcal/mol lower  $\pi$ (NN) energy compared to those of  $\pi$ (CC) and  $\pi$ (CN). Aza-naphthalenes behave similarly: like the azines, their relative isomer stabilities are strongly influenced by the NN bond weakness arising from *geminal* N lone pair–NN  $\sigma$  bond repulsion.<sup>29</sup> The widely invoked *vicinal* NN lone pair repulsion explanation<sup>4,5,25</sup> is refuted by the energetics of their protonated and diprotonated analogs (cf. Table 3).

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**Supporting Information Available:** BLW REs of benzene and naphthalene; CMO NICS data for  $D_2$  and  $D_{6h}$  N<sub>6</sub>; azine NICS data; BLW REs, and relative energies of azanaphthalenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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