ORGANIC
LETTERS

2006
Vol. 8, No. 5
863−866

Which NICS Aromaticity Index for Planar π Rings Is Best?

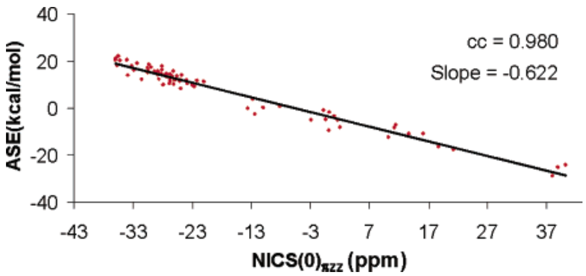
**Hossein Fallah-Bagher-Shaidaei,*,[†],[‡] Chaitanya S. Wannere,[‡]
Clémence Corminboeuf,[‡] Ralph Puchta,[§] and Paul v. R. Schleyer*,[‡]**

*Department of Chemistry, Islamic Azad University-Rasht Branch, P.O. Box
41335-3516, Rasht, Iran, Department of Chemistry, Center for Computational
Chemistry, University of Georgia, Athens, Georgia 30602-2556, and Computer
Chemistry Center, University of Erlangen-Nuremberg, Nägelsbachstr. 25,
D-91052 Erlangen, Germany*

schleyer@chem.uga.edu; h_fallah@iaurasht.ac.ir

Received December 6, 2005

ABSTRACT



Five increasingly sophisticated aromaticity indexes, based on nucleus-independent chemical shifts (NICS), were evaluated against a uniform set of aromatic stabilization energies (ASE) for 75 mono- and polyheterocyclic five-membered rings. While acceptable statistical correlations were given by all of the NICS methods, the most fundamentally grounded index, NICS(0)$_{\pi zz}$ (based on the π contribution to the out-of-plane *zz* tensor component), performed best statistically (cc = 0.980) and in practice. The easily computable NICS(1)$_{zz}$ index is a useful alternative (cc = 0.968).

Aromaticity is of fundamental importance to chemistry.[1] Even after two centuries, the concept that electron delocalization in closed circuits endows molecules with special properties continues to increase in its scope of applicability and in its importance.[1,2] Since aromaticity is not a directly measurable quantity, its magnitude is now generally evaluated in terms of structural, energetic, and magnetic criteria. However, magnetic properties are the most closely related to aromaticity, as they depend directly on the induced ring currents associated with cyclic electron delocalization. Several methods for the evaluation of magnetic aromaticity,[2] including proton chemical shifts,[3,4] exaltation of magnetic susceptibilities,[4−6] nucleus-independent chemical shifts

---

[†] Islamic Azad University-Rasht Branch.

[‡] University of Georgia.

[§] University of Erlangen-Nuremberg.

(1) (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; John Wiley & Sons: New York, 1994. (b) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. (c) Lloyd, D. J. *Chem. Inf. Comput. Sci.* **1996**, *36*, 442. (d) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z. et al. *Tetrahedron* **2000**, *56*, 1783. (e) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385. (f) Schleyer, P. v. R., Guest Editor. Thematic issue on Aromaticity, *Chem. Rev.* May issue, **2001**, *101*. (g) Special issue on Aromaticity, *Phys. Chem. Chem. Phys.* **2004**, 2. (h) Lazzeretti, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1. (i) Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217. (j) Schleyer, P. v. R., Guest Editor. Thematic issue on Delocalization-Pi and Sigma, *Chem. Rev.* **2005**, *105*.

(2) (a) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349 and references therein. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(3) Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F., III; Schleyer, P. v. R. *Org. Lett.* **2005**, *7*, 1457. (b) Faglioni, F.; Ligabue, A.; Pelloni, S.; Soncini, A.; Viglione, R. G.; Ferraro, M. B.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2005**, *7*, 3457-3460.

(4) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.

(5) London, F. *J. Phys. Radium.* **1941**, *8*, 397.

(6) (a) Davies, D. W. *The theory of the electric and magnetic properties of molecules*; Wiley: London, 1967. (b) Benson, R. C.; Flygare, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 7523. (c) Schmalz, T. G.; Norris, C. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1973,** *95*, 7961.

10.1021/ol0529546 CCC: $33.50

(NICS),[2b,7−12] ring current density plots,[13] and aromatic ring current shieldings (ARCS).[14] Since its introduction in 1996,[7] NICS continues to gain popularity[2b] as an easily computed, generally applicable criterion to characterize aromaticity and antiaromaticity of rings,[15] clusters,[16] transition states,[17] and transition-metal complexes.[18] NICS is based on the magnetic shielding (with the sign reversed) computed at chosen points in the vicinity of molecules. Significantly negative (shielded) NICS values inside rings or cages are due to induced diatropic ring currents and denote aromaticity, whereas positive (deshielded) values denote paratropic ring currents and anti-aromatic behavior. Isotropic NICS values (Glossary in the Supporting Information) can be computed readily using commonly available programs and do not require model compounds for evaluation.

However, due to its conceptual imperfections, NICS has been refined considerably[2b] since its introduction in 1996.[7] The present paper compares the performance of various NICS-based indexes by means of statistical evaluations against the published aromatic stabilization energies (ASE) of a set of 75 aromatic, nonaromatic, antiaromatic neutral, positively, and negatively charged five-membered ring mono-C_4H_4X (Tables S1 and S3, Supporting Information) and polyheterocycles with planar minima (Tables S2-S4, Supporting Information).[10] Magnetic properties are directional physical quantities and depend on the orientation of the molecules relative to the applied magnetic field. Pople's famous depiction of the induced magnetic field surrounding benzene[4] is based on the assumption that the external magnetic field is applied in the direction perpendicular to the ring plane (the "*z*" direction, by the usual convention; Glossary, Supporting Information). In contrast, experimental NMR measurements in solution are isotropic (unoriented). Spinning tumbles molecules about rapidly and averages the magnetic shielding tensor components. Hence, the original NICS index[7] (now termed NICS(0)$_{\text{iso}}$) was based on the total isotropic shielding (average shielding) computed at ring centers. But this index is *not* a "pure" measure of π aromaticity, as the local contributions of the σ framework (as well as by the in-plane contributions of the *p*-system are quite appreciable. It is well-known that CH and CC single bonds also influence their magnetic environments.[19] Hence, it is not surprising that these local effects result in non-zero NICS(0)$_{\text{iso}}$ for nonaromatic rings.[20] For planar or nearly planar molecules, these local contributions fall off rapidly at points above the ring centers where the π contributions dominate.[9] Consequently, isotropic NICS(1) values (i.e., at points 1 Å above ring centers; see the Glossary, Supporting Information) were recommended in 1997 as being better measures of π effects than NICS(0).[8,9] However, NICS(1) is still based on the total isotropic shielding value, rather than on just the contributions arising from the *zz* component of the shielding tensor as envisioned by Pople.[4]

Refined ("dissected") NICS methods, assessing individual contributions of individual orbitals to isotropic NICS, were first based on the localized MO (LMO), dissection inherent in the IGLO (individual gauge for local orbitals) method.[21,22] GIAO-based methods provide individual canonical molecular orbital (CMO) contributions to NICS.[11] Both LMO and CMO give the total isotropic π contributions to NICS for planar molecules. While earlier statistical analyses indicated that isotropic NICS(1)$_{\pi}$ values of related series of molecules may be even better measures of aromaticity than isotropic NICS(1) or NICS(0),[8,9,12] we do not corroborate this finding here.

However, all of these *isotropic* NICS values (including NICS$_{\pi}$) are the average of the three diagonal elements of the shielding tensor (*xx*, *yy*, and *zz*), which differ in magnitude and can be positive or negative. In particular, the most commonly computed isotropic NICS(0)$_{\text{iso}}$ and NICS(1)$_{\text{iso}}$ indexes do not model Pople's ring currents conceptually.[4] Since ring currents due to the cyclic π electron delocalization are induced primarily by the external magnetic field applied perpendicular to the ring (the *z* direction), the out-of-plane component of the NICS tensor should contain the information most relevant for aromaticity evaluations.

---

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

(8) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(9) Schleyer, P. v. R.; Manoharan, Z. Wang.; Kiran, X. B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465. Also see Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1893−1898.

(10) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. L.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333. Also see ref 2b.

(11) (a) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifer, G.; Reviakine, R.; Weber. *J. Phys. Chem. A* **2003**, *107*, 6470. (b) Corminboeuf, C.; Heine, T.; Weber, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 246.

(12) Corminboeuf, C.; Heine, T.; Seifert, G., Schleyer, P. v. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.

(13) (a) Fowler, P. W.; Steiner, E.; Zanasi, R.; Cadioli, B. *Mol. Phys.* **1999**, *96*, 1099. (b) Fowler, P. W.; Steiner, E. *Mol. Phys.* **2000**, *98*, 945. (c) Steiner, E.; Fowler, P. W.; Jennesskens, L. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 362. (d) Steiner, E.; Fowler, P. W. *Chem. Commun.* **2001**, 2220. (e) Krygowski, T. M.; Ejsmont, K.; Stepien, B. T.; Cryanski, M. K.; Poater, J.; Sola, M. *J. Org. Chem.* **2004**, *69*, 6634. (f) Krygowski, T. M.; Stepien, B. T.; Cryanski, M. K. Ejsmont, K. *J. Phys. Org. Chem.* **2005**, *18*, 886.

(14) Juselius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3429.

(15) (a) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2638. (b) Jiao, H.; Schleyer, P. v. R.; Beno, R. B.; Houk, K. N.; Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2761. (c) Folkin, A. A.; Jiao, H.; Schleyer. P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 9634. (d) Zywietz, T. Jiao, H.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1998**, *63*, 3417. (e) Patchkovskii, S.; Thiel, W. J. *Mol. Mod.* **2000**, *6*, 67 and references cited.

(16) (a) Bühl, M. *Chem. Eur. J.* **1998**, *4*, 734. (b) Ferrer, S. M.; Molina, J. M. *J. Comput. Chem.* **1999**, *20*, 1412. (c) McKee, M. L.; Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2000**, *122*, 4781. (d) Hirsch, A.; Chen, Z.; Jiao, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3915. (e) Bühl, M.; Hirsch, A. *Chem. Rev.* **2001**, *101*, 1153. (f) Hirsch, A.; Chen, Z.; Jiao, H. *Angew. Chem., Int. Ed.* **2001**, *40*,.

(17) (a) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655. (b) Cossio, F. P.; Marao, I.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6737. (c) Sawicka, D.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 864. (d) Manoharan, M.; De Proft, F.; Geerlings, P. *J. Org. Chem.* **2000**, *65*, 7971. (e) Lera, A. R.; Alvarez, R.; Lecea, B.; Torrado, A.; Cossio, F. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 557. (f) Verevkin, S. P.; Beckhaus, H. D.; Rückhardt, C.; Haag, R.; Kozhushkov, S. I.; Zywietz, T.; de Meijere, A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 11130.

(18) Schleyer, P. v. R.; Kiran, B.; Simon, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **2000**, *122*, 510.

(19) (a) Günther, H. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed.; Wiley: Chichester, 1995**.** (b) Martin, N. H.; Brown, D. *Int. J. Mol. Sci.* **2000**, *1*, 84 and references cited. (c) Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 605. (d) Pelloni, S.; Ligabue, A.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 4451−4454. (e) Soriano Jartin, R.; Ligabue, A.; Soncini, A.; Lazzeretti, P. *J. Phys. Chem. A.* **2002**, *106*, 11806.

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

(21) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.

(22) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

Fowler and Steiner suggested a NICS index in 2000 (designated NICS$_{zz}$ in the Glossary, Supporting Information) based on the total contribution to the out-of-plane component of the NICS tensor.[13b.c] Although suffering contamination from non$-\pi$ contributions, NICS$_{zz}$ is computed directly by the commonly available programs and some advantages have been demonstrated. [13e,f]

The most refined index,[12,13c] designated NICS$_{\pi zz}$ (Glossary, Supporting Information), eliminates this contamination by using LMO or CMO dissection to select only the π contribution to the zz component of the tensor. The final index evaluated in Figure 1, NICS$_{4e\pi zz}$, is based on the contributions from only the two highest energy π MO's. NICS$_{4e\pi zz}$ is expected to correlate most closely with the induced ring current densities.[13d] All of the π-based methods share the disadvantage of requiring LMO or CMO dissection.

Systematic evaluations of aromaticity and antiaromaticity are best carried out on sets of closely related molecules with similar structural features, such as five-membered ring heterocycles. Schleyer et al.[23] showed that excellent correlations exist among the energetic, geometric, and magnetic criteria of a set of 11 C_4H_4X rings. This approach was extended subsequently to more compounds and to evaluate relations among other aromaticity criteria, e.g., between stabilization energies and NICS[24] as well as proton chemical shifts.[25]

The most extensive statistical analyses of geometrical, ASE, magnetic susceptibility exaltation, and NICS indexes to date involved a set of 105 aromatic and antiaromatic five-membered heterocycles. Statistically significant correlations among these various criteria were found when the whole set of molecules were considered.[10] However, these criteria did not differentiate among "closely bunched" sets of points for the most aromatic compounds satisfactorily. Geometries, energies, and isotropic magnetic criteria are influenced, or even dominated, by effects other than "aromaticity", and "may be measuring different things". Besides the possibility that these criteria may be inherently unable to differentiate "aromaticity" from other influences, they may be insufficiently refined. The conceptual deficiencies of isotropic NICS measures illustrate the latter possibility.

Consequently, we have now evaluated NICS$_{\pi zz}$ and the other NICS indexes against ASE values for 75 molecules with planar minima; these should be less prone to methodological evaluation errors. The NICS data (computed at the IGLO-PW91/IGLO-III level), listed in Tables S1$-$S4, Supporting Information) are plotted against ASE in Figure 1 (and Figure S2, Supporting Information). The statistical correlation coefficient (cc) shows that all the NICS indexes correlate significantly with ASE. The performance of NICS(0)$_{\pi zz}$ (Figure 1e) is best (cc $=$ 0.980) followed closely by NICS(0)$_{4e\pi zz}$ (cc $=$ 0.971, Figure 1d). (The corresponding data at 1 Å, Figure S2d,e in the Supporting Information, are nearly as good.) These results confirm impressively expectations based on the theory of magnetic properties.

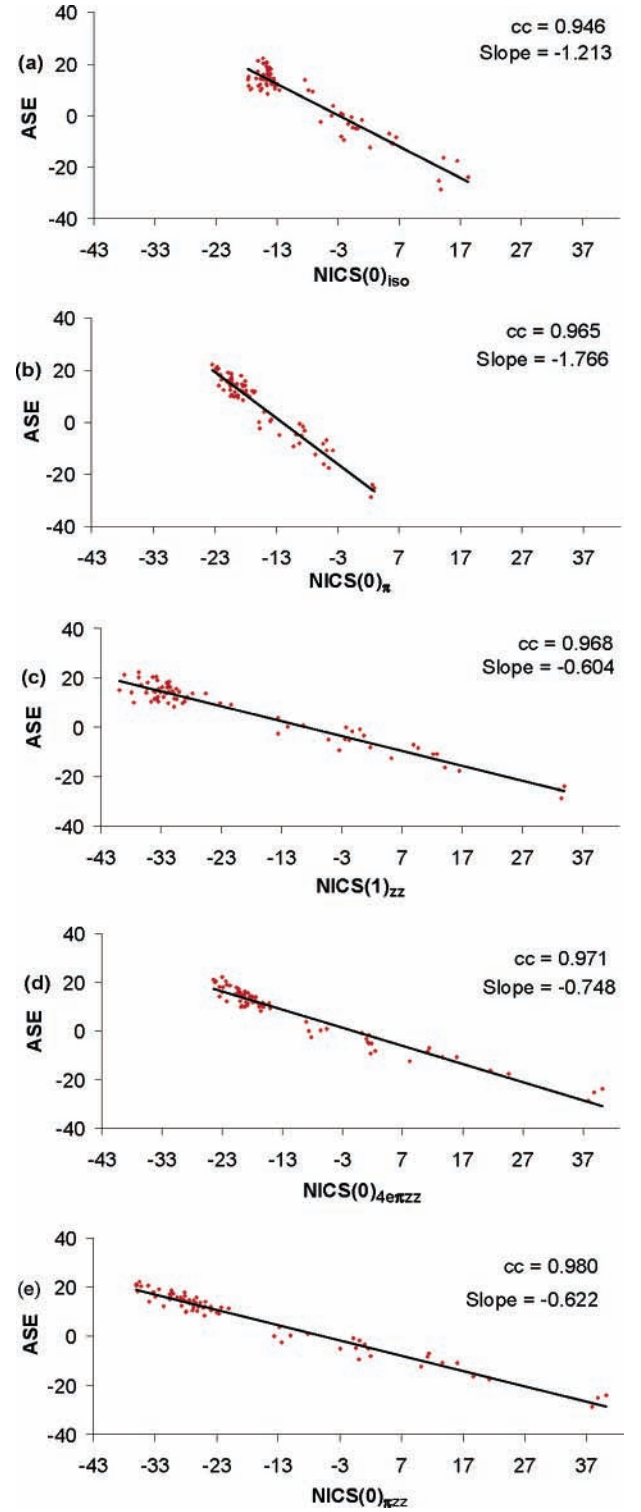


Figure 1. Comparison plots of ASE versus five NICS indexes, at the distance where each performs best statistically: the ring centers for NICS(0)$_{\text{iso}}$, NICS(0)$_{\pi}$, NICS(0)$_{4e\pi zz}$, and NICS(0)$_{\pi zz}$, but 1 Å above for NICS (1)$_{zz}$.

Note that the nonarbitrary ring-center location of NICS(0)$_{\pi zz}$ is much less prone to the interferences suffered by the isotropic NICS(0) indexes as well as NICS(0)$_{zz}$ (cc $=$ 0.948, Figure S2c, Supporting Information). In ring centers, the xx,

---

[23] Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

[24] Nyulaszi, L.; Schleyer. P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872.

[25] Chesnut, D. B. *Chem. Phys. Lett.* **1998**, *231*, 1.

yy, and *zz* components all contribute appreciably. The NICS(1)$_{zz}$ performance (cc = 0.968, Figure 1c) is substantially better since the *xx* and *yy* components are much smaller than *zz* away from the ring center. Consequently, NICS(1)$_{zz}$ is included in Figure 1 (as part c) rather than NICS(0)$_{zz}$.

The very significant advantage of the much larger NICS values resulting from the use of a single tensor component, rather than the average of all three, is apparent from Figure 1. The wide range of NICS(1)$_{zz}$ and NICS(0)$_{\pi zz}$ values facilitates aromatic, nonaromatic, and antiaromatic differentiation. In contrast, the very small NICS(0)$_{\pi}$ range suggests erroneously that none of the heterocycles are significantlty antiaromatic! Some of the obviously *antiaromatic* 4 π electron compounds have *negative* NICS(0)$_{\pi}$ (which should denote *aromaticity*). These drawbacks are not overcome by NICS(1)$_{\pi}$ (Figure S2b, Supporting Information), which gives the worst correlation (cc = 0.935) in the set. In view of its conceptual superiority, performance, and extended 70 ppm range, *NICS(0)$_{\pi zz}$ clearly is the method of choice for NICS evaluation of the π aromaticity of planar rings.* Furthermore, the "bunching" of the points for the most aromatic compounds (at the top left of each plot) is reduced by the NICS$_{\pi zz}$ indexes (compare Figures S3c and S4c in the Supporting Information with the other statistical evaluations in Figures S3−S6).

Since *xx* and *yy* tensor component contributions to NICS(0)$_{\pi}$ are non-negligible, both its cc value and especially its range diminution due to isotropic averaging are inferior to NICS(0)$_{\pi zz}$. Although we have supported the use of NICS(1)$_{\pi}$ earlier,[2b] its performance in the present statistical test is disappointing. However, NICS(1)$_{zz}$ is a worthy alternative.

The original and most "primitive" isotropic NICS(0)$_{\text{iso}}$ index, despite the contributions of the σ bonds, performs moderately well (cc = 0.946), and its range is 40 ppm (Figure 1a). Although being more soundly based, NICS(1)$_{\text{iso}}$ is somewhat inferior in both respects (Figure 1a). Still, NICS(0)$_{\text{iso}}$ (and NICS(1)$_{\text{iso}}$) data can be employed (with reservations) at least as a rough indication of aromaticity. While we do not agree that "NICS [referring to the original index] should be abandoned as a measure of aromaticity",[1i] the conceptual imperfections of all isotropic NICS indexes should be recognized. NICS(1)$_{zz}$ shows promise as a readily computable and superior-performing substitute for NICS$_{\text{iso}}$ and NICS$_{\pi}$.

However, the π contributions to the tensor components needed to obtain NICS$_{\pi zz}$ data are now readily available. Besides computer programs, like deMon-Master (IGLO implementation), which have been distributed privately for many years,[26] NBO 5.0[27] has now been released for use with the widely employed Gaussian 03 package.[28] NBO 5.0g gives both LMO and CMO tensor data, which result in identical NICS$_{\pi zz}$ (as well as other NICS) values.

The use of a virtual (experimentally nonmeasurable) index (NICS) to evaluate another intangible quantity (aromaticity) has raised philosophical concerns.[1h,29] Our more pragmatic viewpoint is encouraged by the statistically significant correlations of all the NICS values with ASE (Figures 1, S2 and S3 (Supporting Information)). This evidence supports earlier conclusions[10,24] that even the originally proposed NICS(0)$_{\text{iso}}$ method characterizes the aromaticity of five-membered rings reasonably well, provided the data set includes a wide range of aromatic and antiaromatic compounds. Plotted against NICS$_{\pi zz}$ (Figure S7, Supporting Information), NICS(0)$_{\text{iso}}$ performs creditably.

Nevertheless, the impressive performance of NICS$_{\pi zz}$ (Figures 1e, 2e, and S3c (Supporting Information)) encourages the use of NICS(0)$_{\pi zz}$ as the most soundly based and best performing NICS aromaticity index.[30] However, NICS(1)$_{zz}$ is a more readily available, easy to use, and very good alternative. This is documented by the direct comparison of NICS(1)$_{zz}$ with NICS(0)$_{\pi zz}$ (Figure S9b, Supporting Information): the slope is 0.999(!) and cc = 0.982. Further evaluations of NICS(1)$_{zz}$ as an aromaticity index are being carried out.

All isotropic magnetic indexes used to characterize π-aromaticity of two-dimensional systems have conceptual limitations. As the response to a magnetic field applied along each of the three principal directions may be quite different, important features inherent to each direction (tensor component) can be masked when considering the averaged isotropic values of NICS and other magnetic measures. Alternative magnetic indexes based on the out-of-plane tensor component have a physical origin closer to the current density. These indexes not only are sounder conceptually, but they also perform better in practice for planar rings. They may also be applied to cyclic planar moieties within clusters and cages. Isotropic NICS is highly useful for spherical (isotropic) systems.

Acknowledgment. Financial support by NSF Grant No. CHE-0209857 and the Research Counsel of the Islamic Azad University is gratefully acknowledged. H.F.B.S. thanks Professor T. Clark and Dr. N. J. R. v. E. Hommes, Computer Chemistry Center, Erlangen, for their assistance.

Supporting Information Available: Complete ref 28. Data for mono- and polyhetero five-membered heterocycles (Tables S1−S4). NICS vs ASE plots for the NICS indexes at other distances (Figure S2) and for only the most aromatic molecules (Figures S3−S6). Plots of the other NICS indexes vs NICS(0)$_{\pi zz}$ (Figures S7−S10). Glossary of terms. Manual for evaluating dissected NICS. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0529546

---

(26) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *Modern Density Functional Theory*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; p 273. (b) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.

(27) *NBO 5.0.* Glendening, E. D.; Badenhoop, J, K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin: Madison, 2001. *NBO 5.0g* update, 2005, for use with Gaussian 03.

(28) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004. See the Supporting Information for the full reference.

(29) (a) Aihara, J.; Kanno, H. J. *J. Phys. Chem. A* **2005**, *109*, 3717. (b) Aihara, *J. Bull. Chem. Soc. Jpn.* **2004**, *77*, 101. (c) Aihara, J.; Oe, S. *International Electronic Journal of Molecular Design* **2002**, *1*, 443.

(30) (a) Steiner, E.; Fowler P. W.; Jenneskens, L. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 362. (b) Cernusak, I.; Fowler, P. W.; Steiner, E. *Mol. Phys.* **2000**, *98*, 945.