Nucleus-Independent Chemical Shifts (NICS): Distance Dependence and Revised Criteria for Aromaticity and Antiaromaticity

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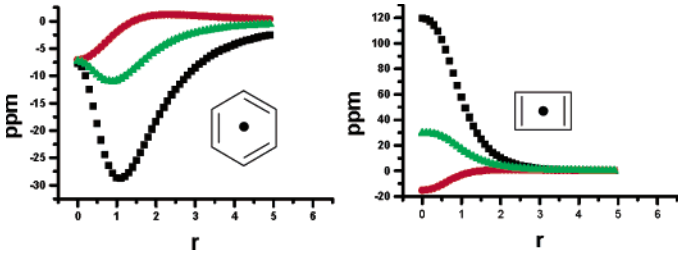

Nucleus-independent chemical shifts (NICS) have been used extensively for the identification of aromaticity properties of molecules, ions, intermediates, and transition states since their introduction in 1996 by Schleyer et al. Initially, probes (bq's) were placed at the centers of systems (NICS(0)) and later, 1Å above the molecular planes (NICS(1)). However, contradicting assignments of aromaticity by NICS and other methods were found for some systems. In this article, an alternative NICS-based method is introduced. The method is based on scanning NICS values over a distance and separating them into in-plane and out-of plane contributions. The shapes of the plots of the chemical shifts and their components as a function of the distance of the NICS probe (bq) from the molecular plane give a clear indication of diamagnetic and paramagnetic ring currents. This method is applied to several $(4n + 2)$- and $4n$ π-electron systems (molecules and ions) in the singlet and triplet electronic states, including some of the problematic systems mentioned above. It is also shown that relative aromaticities of rings in polycyclic systems (local aromaticities) cannot be estimated by comparing NICS or NICS-scan values.

Introduction

The concept of nucleus-independent chemical shifts (NICS) as a measure of the aromaticity of a system was introduced by Schleyer et al. in 1996.[1] The NICS method allows the evaluation of aromaticity, antiaromaticity, and nonaromaticity of single-ring systems and individual rings in polycyclic systems (local aromaticities). This method has been used extensively to asses the aromaticity and antiaromaticity of many organic and inorganic compounds, intermediates, and transition states.[2] Although it has received some criticism,[3] this method is generally accepted and widely used. Recently, total NICS values were used to asses the aromaticity of different families of polycyclic aromatic hydrocarbons with excellent agreement with other indices of aromaticity.[4] Quantitative values of NICS were also used by others.[5] Initially, NICS values were calculated at the geometric centers of the rings, but after it was realized that the σ frame influences these values (at least in some systems, e.g., in cyclopropane) it was suggested that to assess the aromaticity and antiaromaticity the NICS values should be

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* Fax: (+972)-4-829-3944.

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

(2) For some reviews, see (a) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349. (b) Lazzeretti, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1 and references therein. (c) Krygowski, T. M.; Cyrañski, M. K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 249. (d) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R. Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842−3888. (e) A CAS survey indicates a steady increase in the number of papers that contain the NICS keyword, from 10 in 1997 to 91 in 2004. Thus, the use of NICS is becoming a standard tool in aromatic chemistry.

(3) See, for example, ref 2b. See also (a) Poater, J.; Solá, M.; Viglione, R. G.; Zanasi, R. *J. Org. Chem.* **2004**, *69*, 7537. (b) Faglioni, F.; Ligabue, A.; Pelloni, S.; Soncini, A.; Viglione, R. G.; Ferraro, M. B.; Zanasi, R.; Lazzeretti, P. *Org. Lett.* **2005**, *7*, 3457. (c) Ahira, J.-I.; Sumio, O. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1363. (d) Ahira, J.-I. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 101.

(4) Moran, D.; Stahl, F.; Bettinger, H. F.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 6746.

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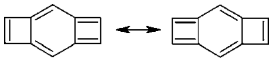
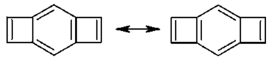
calculated at a distance from the plane of the ring; thus, the value at 1.0 Å above the plane of the molecule (denoted as NICS(1)) has become standard.[6]

In some cases, however, using NICS (or NICS(1)) values may mislead or contradict other indices of aromaticity. For example, the NICS value of the central ring in anthracene is more negative than that of the terminal rings. This was used to claim (applying the idea that the more negative the NICS value, the more aromatic the ring) that the central ring in anthracene was more aromatic than the terminal ring.[7] Anthracene undergoes an electrophilic attack at the 9 position, and the 9 and 10 positions also undergo Diels−Alder reactions, which are indicative of conjugated nonaromatic systems. Thus, the central ring in anthracene is more reactive than the terminal rings, counter to the notion that aromatic compounds are characterized (among others) by kinetic stability. Relative NICS(1) values were used to assess high local aromaticities to inner rings of olygoacenes,[8] which are systems that are clearly (experimentally) unstable, tend to dimerize, and perhaps are not closed-shell singlets.[9] Another case is the assignment of 5,5-disubstituted cyclopentadienes as aromatic when substituted with electropositive substituents, such as SiH_3, GeH_3, and SnH_3, and as antiaromatic when substituted with electronegative substituents, such as Cl and F, on the basis of NICS values and other criteria.[10] These assignments have no experimental support. Additionally, two more examples, in a somewhat more detailed manner, are given below.


1a **1a'**


1b **1b'**

At B3LYP/6-31G* and MP2/6-31G*, [1,2][4,5]-bicyclobutadienobenzene (**1**) shows two bond-stretching isomers that are very close in energy, and each is a minimum on the potential surface (i.e., $N_{\mathrm{imag}} = 0$).[11] According to geometric criteria, NRT analysis,[12] and VB calculations,[13] one isomer (**1a**) is a doubly bridged 10-annulene, that is, an aromatic system, whereas the second isomer (**1b**) is best described as two cyclobutadieno moieties annulated to benzene, that is, a central aromatic ring and two antiaromatic four-membered rings. The NICS(1) values for different basis sets are given in Table 1 and show that the six-membered ring is aromatic in **1a** but the four-membered rings have much more negative values, indicating higher aromaticity.[7] For **1b**, the emerging picture is different from the one obtained from the above-mentioned indices. The NICS(1) values suggest that the central ring is nonaromatic whereas the four-membered rings are highly antiaromatic.

TABLE 1. NICS(1) of 1a and 1b at the GIAO-HF/Specified Basis Set

basis set	**1a**, six[a]	**1a**, four[b]	**1b**, six[a]	**1b**, four[b]
3-21G	−11.3	−17.6	−4.6	11.8
6-31G*	−11.6	−17.6	−3.9	14.2
6-311G*	−11.5	−17.1	−3.2	14.3
6-311+G*	−10.5	−15.7	−2.3	15.0

[a] Above the six-membered ring. [b] Above the four-membered ring.

The second example is that of calicene (**2**). This system is a classic example of the driving force to form ($4n + 2$) π-electron systems (i.e., aromatic) that overcomes even the energy associated with charge separation: the cyclopentadienyl anion with 6 π electrons and the cyclopropenyl cation with 2 π electrons. Indeed, NRT[12] analysis, charges, and structural criteria (see below) suggest that the dipolar aromatic form (**2b**) contributes considerably to the character of the molecule. However, NICS(1) values are −6.5 and −9.5 for the five- and three-membered rings, respectively (at GIAO-HF/6-311G*//B3LYP/6-311G*), indicating nonaromaticity for the five-membered ring and slight aromaticity for the three-membered ring.


2a **2b**

The fundamental idea behind the NICS concept, that is, a measure of the magnetic properties of molecules, in particular those that contain π systems, by a nonchemical probe seems to be founded and useful;[14] perhaps, however, the use of a single value, that is, NICS(1), is too crude an approximation for the estimation of aromaticity, especially in more special systems, such as **1** and **2**. In this article, I suggest the use of the NICS idea in a more general way that leads to a better description of diatropic and paratropic effects. It is suggested that the NICS values be scanned over distances ranging from 0 (i.e., the probe is in the molecular plane) to larger distances (4.9 Å in this work) and the obtained NICS values be divided into in-plane and out-of plane contributions.[15,16] This procedure is denoted as NICS-scan. The shapes of the curves obtained by plotting the respective NICS values as functions of distance are shown to be much more indicative of the nature of the systems than a single NICS isotropic value. Moving the bq from a fixed position has precedence in the literature. For example, Schleyer et al.[17] have formed a 2D grid (with 0.5 Å intervals) of bq atoms above

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(5) For example, the comparison with HOMA. See (a) Krygowski, T. M.; Zachara, J. E.; Szatylowicz, H. *J. Org. Chem.* **2004**, *69*, 7038. (b) Krygowski, T. M.; Ejsmont, K.; Stêpieñ, B. T.; Cyrañski, M. K.; Poater, J.; Solá, M. *J. Org. Chem.* **2004**, *69*, 6634. (c) Stêpieñ, B. T.; Krygowski, T. M.; Cyrañski, M. K. *J. Org. Chem.* **2002**, *67*, 5987 and references therein. See also (d) Bühl, M. *Chem.−Eur. J.* **1998**, *4*, 734. See also (e) Krygowski, T. M.; Stêpiñ, B. T. *Chem. Rev.* **2005**, *105*, 3482−3512.

(6) NICS values have been rarely used at different distances. See, for example, (a) Frash, M. V.; Hopkinson, A. C.; Bohme, D. K. *J. Am. Chem. Soc.* **2001**, *123*, 6687. (b)

(7) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643.

(8) Portella, G.; Poater, J.; Bofill, J. M.; Alemany, P.; Sola, M. *J. Org. Chem.* **2005**, *70*, 2509, 4560.

(9) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416, 10493.

(10) Nyulásszi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872.

(11) Boese, R.; Benet-Buchholz, J.; Stanger, A.; Tanaka, K.; Toda, F. *J. Chem. Soc., Chem. Commun.* **1999**, 319.

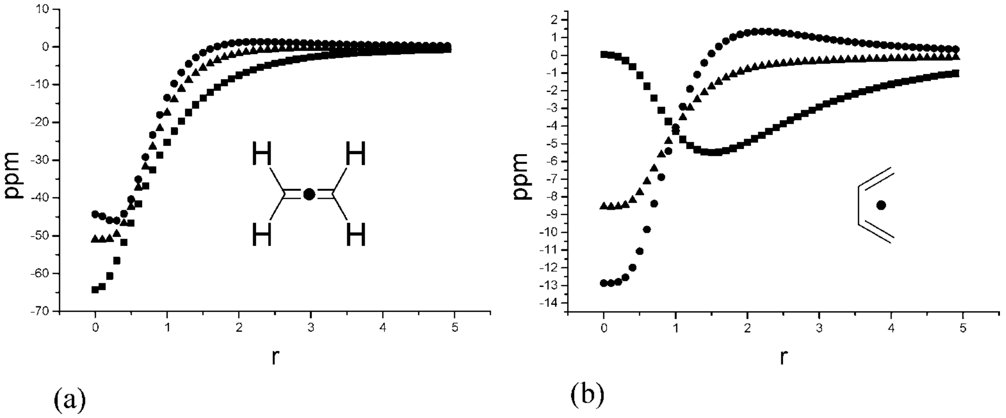
(12) NRT (natural resonance theory) is included in NBO 5.0. See Glendening, E. D.; Badenhoop, J. K.; Reed, A. J.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. 2001, http://www.chem.wisc.edu/~nbo5. This method uses the density matrix to produce canonic structures with assignments of their appropriate weight in the molecular structure.

(13) VB calculations: Shaik, S.; Shurki, A. Unpublished results.

(14) For an alternative use of the NICS concept, see Corminboeuf, C.; Heine, T, Weber, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 246.

(15) Both in-plain and out-of-plane components of the isotropic chemical shift contain σ and π contributions. However, the out-of-plane components consists of ca. two-thirds or more of the π contribution. Thus, it is safe to conclude that the out-of-plane component is mainly governed by the π system of the molecule.

(16) While this article was in the refereeing process, a letter that uses a similar idea but without NICS was published. See ref 3b.



(a) (b)

FIGURE 1. NICS values as a function of distance (angström) of (a) ethylene and (b) *s-cis*-1,3-butadiene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

benzene and cyclobutadiene and concluded that (a) NICS(1) is the best measure of aromaticity and (b) the ring current model (RCM) that explains the downfield and upfield shifts of the protons in aromatic and antiaromatic compounds, respectively, is not correct. These two conclusions are challenged by the inability of NICS(1) to assign the aromaticity type in some systems (a few examples are given above) coherently with other indices and by a later letter[18] that shows that the RCM is valid. Here, the bq's are moved, and the results are analyzed in a very different way, which lead to somewhat different conclusions.

Method

Gaussian 98 and Gaussian 03 codes were used.[19] The molecules and ions were structurally optimized at the B3LYP/6-311G* level of theory and underwent analytical frequency calculations to ensure real minima (i.e., $N_{\mathrm{imag}} = 0$). The NICS probes (bq's)[20] were placed above the geometric centers of the systems at distances ranging from 0.0 Å (i.e., at the center of the molecular plane) to 4.9 Å at a step size of 0.1 Å along the line perpendicular to the molecular plane. It turns out that some of the NICS values are basis-set-sensitive and thus all of the values used were obtained with the 6-311+G* basis set at the HF level using the standard GIAO procedure.[21] The NICS values are the isotropic chemical shifts of the respective bq's, and the eigenvalues of the chemical shift tensors were used to separate the isotropic NICS values into their in-plane and out-of-plane components. Because NICS values are distance-dependent, the abbreviation N@r will be used throughout this article to denote the NICS value (ppm) at distance *r* (Å) from the molecular plane.

Results and Discussion

Uncharged Nonaromatic Systems. Figure 1 shows the NICS-scan plots for ethylene and *s-cis*-1,3-butadiene.[22]

The structures of the isotropic-chemical-shift curves are typical for nonaromatic systems: negative values when the probe (bq) is close to the molecules, which decrease in absolute values (i.e., becoming more positive) when the distances increase, asymptotically going to zero. The magnitude of the chemical shift, however, is very different; the minimal values are ca. −51.0@0 and −12.9@0 for the isotropic chemical shifts in ethylene and butadiene, respectively. This is a result of the distance between the probe and the bonds. Whereas the geometric center is between the bonds in butadiene, it is in the bonds in ethylene. The separation of the isotropic value into in-plane and out-of plane contributions suggests that in ethylene, when the probe is above the bond, the out-of-plane component of the chemical shift becomes gradually less diatropic with distance whereas in the conjugated system the plot shows a minimum of −5.5@1.5 and the shifts are negative throughout the distance range studied. The in-plane components in both molecules behave similarly, that is, showing diatropic shifts at short distances and slightly paratropic shifts at long distances. The shapes of the curves are typical for in-plane components of noncharged molecules (see below). Another important feature is that the magnitudes of the contributions of the in-plane and out-of plane components to the chemical shifts are similar for both ethylene and butadiene. This is entirely different in aromatic and antiaromatic systems (see below).

Uncharged Aromatic and Antiaromatic Systems. Figures 2 and 3 show the behavior of the NICS-scans in benzene and cyclobutadiene that were chosen as the prototypes for aromatic and antiaromatic systems, respectively.

A few conclusions can be drawn by comparing the behavior between the nonaromatic systems, benzene, and cyclobutadiene: (1) Whereas the shapes of the NICS-scan curves in the

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(17) 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) Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 605.

(18) Viglione, R. G.; Zanasi, R. *Org. Lett.* **2004**, *6*, 2265.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(20) The probes are ghost atoms that are called bq's in the Gaussian program. This term will be used throughout this article.

(21) The NICS-scan for benzene was calculated at the following levels, using a GIAO procedure: HF: 6-31G, 6-31G*, 6-311G*, 6-311G**, 6-311+G*; B3LYP: 6-311G*, 6-311G**; MP2−6-311G*, 6-311G**. The level used throughout the article was found to be the minimal satisfactory level.

(22) Calculated is the planar *s-cis*-1,3-butadiene with one negative frequency.

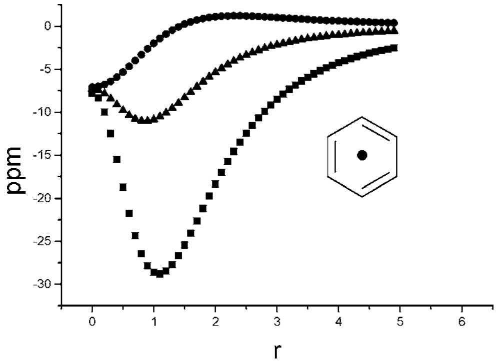


FIGURE 2. NICS values as a function of distance (angström) of benzene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

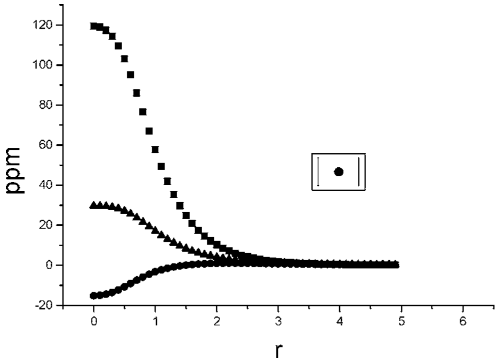


FIGURE 3. NICS values as a function of distance (angström) of cyclobutadiene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

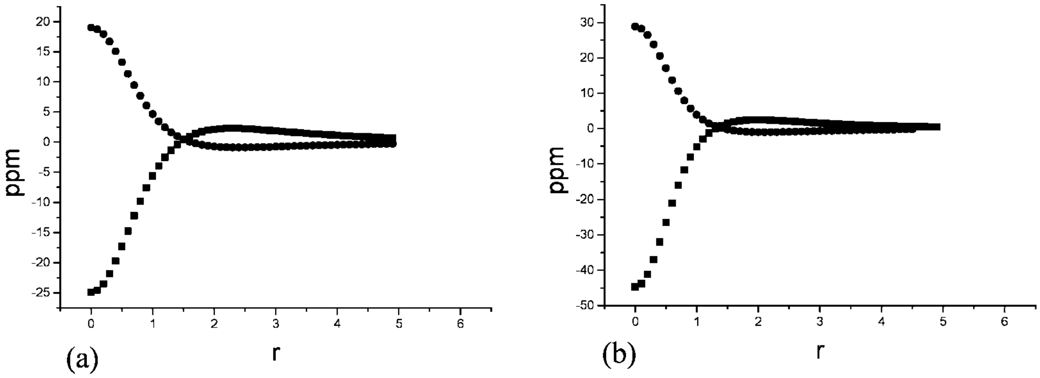
nonaromatic molecules are equally controlled by the in-plane and out-of-plane components, the shapes of the curves of the aromatic and the antiaromatic systems are controlled by the out-of-plane components. (2) The shapes of the curves describing the in-plane contributions are similar for all four systems, with minimum values that depend on the proximity of the probe to the bonds. Thus, the minimum values of the in-plane contributions to the isotropic NICS are −44.3, −8.6, −15.2, and −7.1 ppm for ethylene, *s-cis-* 1,3-butadiene, cyclobutadiene, and benzene, respectively. (3) The major difference can clearly be attributed to the out-of-plane contributions. The nonaromatic systems show diatropic chemical shifts with small magnitudes, either decreasing through the range (ethylene) or showing a shallow minimum (−5.5@1.5 in butadiene). The aromatic system (benzene) shows a minimum of −28.8@1.1, and the antiaromatic cyclobutadiene is highly paratropic with a maximum value of 119.4@0.

To gain further insight into the NICS-scan values, the diamagnetic and paramagnetic contributions to the bq's chemical shifts were studied. Figures 4 and 5 show the diamagnetic and paramagnetic contributions to the in-plane and the out-of-plane components of the chemical shifts, respectively, for benzene and cyclobutadiene. (Note the differences in the ppm ranges in Figure 5a and b.)

As expected from the average contribution values, the in-plane diamagnetic and paramagnetic components are similar in benzene and cyclobutadiene. The diamagnetic contributions to the out-of-plane components in benzene and cyclobutadiene are also similar, both in shape and value, whereas a major difference is observed in the paramagnetic contributions. In benzene, the paramagnetic contribution at short distances is smaller than the diamagnetic contribution and decreases steeply with distance (24.8@0.0, about $^1/_2$ at 0.65 Å). In cyclobutadiene, the paramagnetic contribution is much larger and decreases at a slower rate with distance (162.1@0.0, about $^1/_2$ at 1.1 Å). Thus, the out-of-plane contribution to the NICS values (and the isotropic NICS value that is dominated by the out-of-plane contribution) in benzene shows a minimum, whereas in cyclobutadiene, it is governed by the large paramagnetic contribution, leading to a steady decrease in chemical shift with no minimum.

In summary, the prototypes of aromatic, antiaromatic, and nonaromatic molecules suggest that the NICS-scan values should be negative and show a relatively deep minimum in aromatic systems, highly positive and decrease with the probe's distance in antiaromatic systems, and small in nonaromatic systems. The in-plane components of all types of systems are similar. The differences in the out-of-plane components originate from the paramagnetic contribution to the chemical shift, whereas the diamagnetic contributions are similar for the different systems. This results in a minimum for the aromatic system and a decreasing curve in the antiaromatic systems. It is also observed that the general shapes of the curves describing the isotropic NICS values as functions of the probe's distance are governed by the out-of-plane component in the aromatic and antiaromatic systems and about equally by the in-plane and out-of-plane components in the nonaromatic molecules.

The NICS-scans of anthracene, phenanthrene, and naphthalene are shown in Figures 6, 7, and 8, respectively. Both NICS-scans of anthracene (above the central ring, Figure 6a, and above the terminal ring, Figure 6b) show that the rings are aromatic. The most negative NICS values for the out-of-plane components are −27.1@1.1 and −38.0@0.9 for the terminal and central rings, respectively, and the respective isotropic NICS values are −10.4@0.8 and −15.1@0.7. In comparison, the respective



(a) (b)

FIGURE 4. Diamagnetic (■) and paramagnetic (●) contributions to the in-plane component of the NICS-scan in (a) benzene and (b) cyclobutadiene.

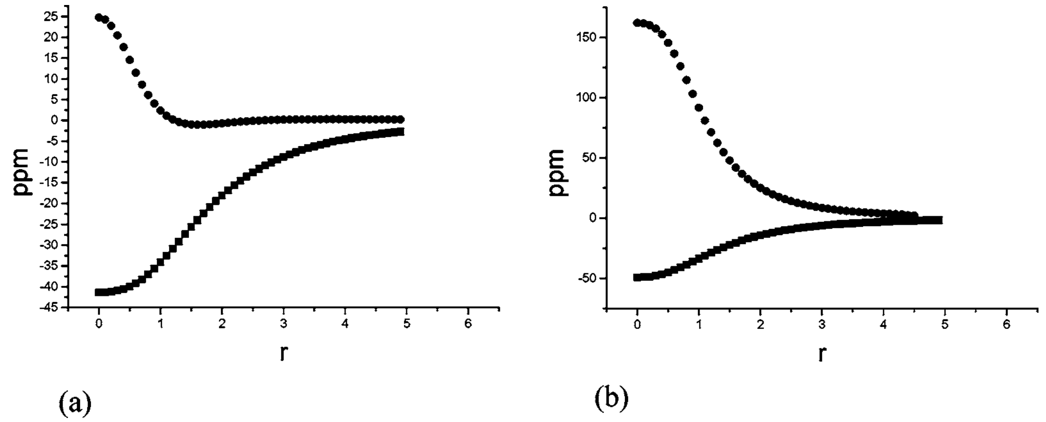


FIGURE 5. Diamagnetic (■) and paramagnetic (●) contributions to the out-of-plane component of the NICS-scan in (a) benzene and (b) cyclobutadiene.

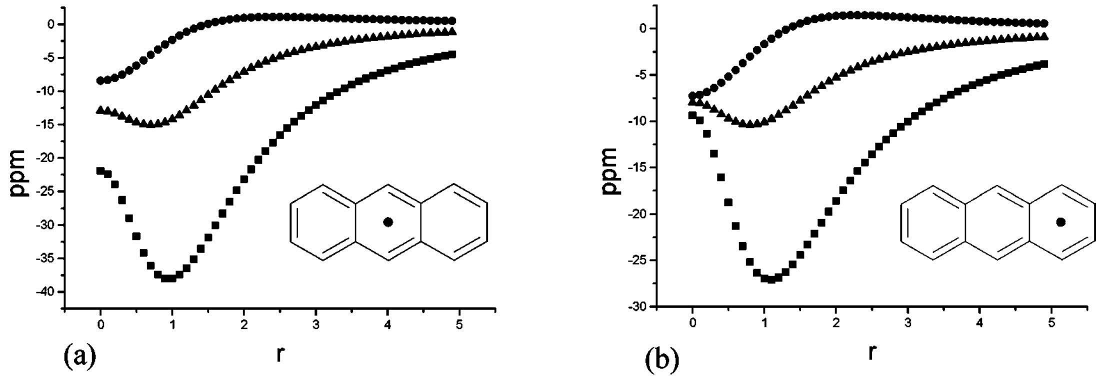


FIGURE 6. NICS values as a function of distance (angström) of anthracene. (a) Central ring. (b) Terminal ring. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

NICS(1) values are −10.1 and −14.2 ppm. Thus, all of the NICS-type values are more negative for the central ring, relative to those of the terminal rings. Does this really indicate that the central ring in anthracene is more aromatic than the terminal ring? The answer becomes clear when one looks at the NICS-scan curves of phenanthrene (Figure 7) and naphthalene (Figure 8). The six-membered rings in both systems (Figures 7a and b and 8a) show aromatic behavior, but the NICS-scans above the geometric centers of the systems do not. Both the out-of-plane component of the NICS and the isotropic values above the center of phenanthrene (Figure 7c) show unconvincing shallow minima, which completely disappear in naphthalene (Figure 8b). Interestingly, NICS(1) values for the centers of naphthalene and phenanthrene are −19.4 and −11.5, respectively, thus qualifying as aromatic according to the single-NICS-value criterion. However, the NICS-scan shows that these are only arbitrary values that may be different in other systems (see below) and that there are no appreciable diamagnetic ring currents above the centers of naphthalene and phenanthrene. Note also that the middle ring in phenanthrene shows less negative isotropic and out-of-plane NICS values than the terminal ring (−8.2@0.9 vs −11.2@0.9 and −20.7@1.3 vs −28.2@1.1, respectively). Thus, in anthracene, the ring that shows more negative NICS values is more reactive whereas in phenanthrene the ring with less negative NICS values is more reactive. All of this suggests that relative (or absolute) local aromaticities for polycyclic aromatic systems cannot be assigned by NICS(1) or NICS-scans simply because the diamagnetic (and paramagnetic) ring current of each ring is influenced by the neighboring rings. This is even better demonstrated in the case of **1** (below).

Calicene (2). Figure 9 shows the bond lengths in calicene relative to those in cyclopropene, cyclopentadiene, and ethylene. Figure 10 shows the NRT[12] analysis of calicene, which assigns 43.8% to localized structure **2a** and 53.3% to delocalized charged structures **2b**.

These two methods support the notion that calicene has aromatic character along with the charge analyses that assign a negative charge to the five-membered ring and a positive charge to the three-membered ring (0.31 and 0.52 using Mulliken and APT charges,[23] respectively). However, NICS(1) values are −6.5 and −9.5 for the five- and three-membered rings, respectively. Figure 11 describes the NICS-scan of **2** above the three-membered ring and the NICS-scan of cyclopropene. The shapes of the curves are not the usual shapes for aromatic and nonaromatic systems. This is a result of the σ system of the three-membered ring that causes a large in-plane diatropic contribution. However, the comparison between the out-of-plane components of cyclopropene and the three-membered ring in calicene clearly indicates a stronger diamagnetic ring current in the latter. Figure 12 describes the NICS-scans above the five-membered rings of calicene and cyclopentadiene.[24] The two scans are very similar; however, both the out-of-plane component and the isotropic chemical shifts show more negative

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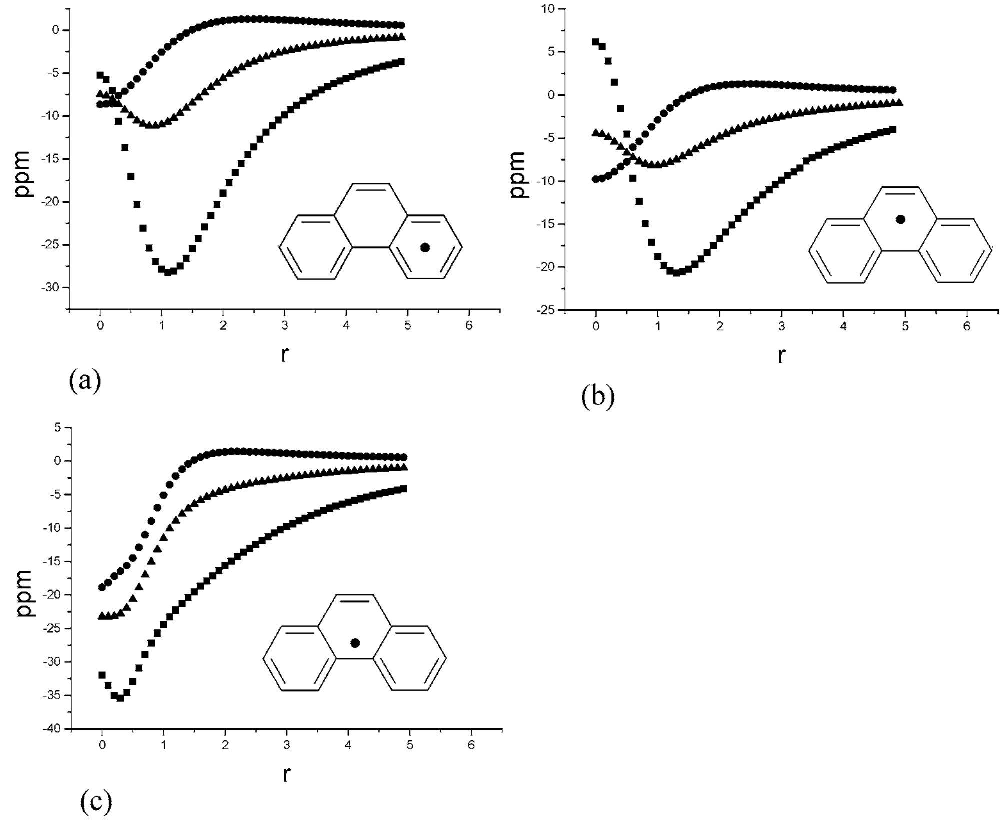
(23) Atomic polar tensor charge. See Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

(24) Stanger, A. *Chem.−Eur. J.*, in press.

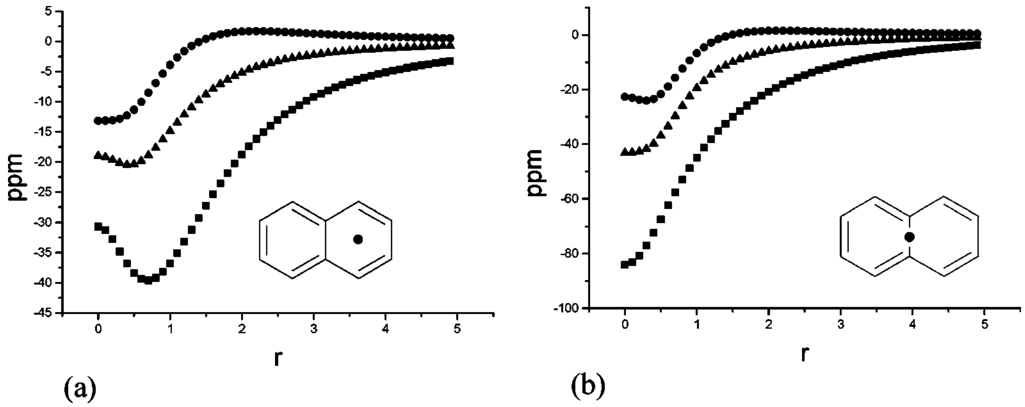


(a)

(b)

(c)

FIGURE 7. NICS values as a function of distance (angström) of phenanthrene. (a) Terminal ring. (b) Central ring. (c) Center of the system. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.



(a)

(b)

FIGURE 8. NICS values as a function of distance (angström) of naphthalene. (a) Terminal ring. (b) Center of the system. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

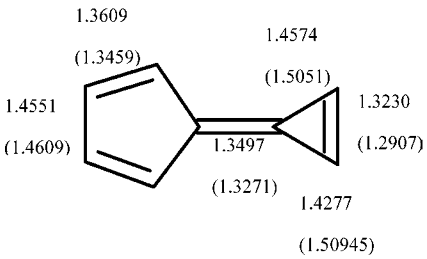


FIGURE 9. Bond lengths (angström) of calicene (B3LYP/6-311G*). Within parentheses are the respective bond lengths of cyclopentadiene, ethylene, and cyclopropene, where applicable, at the same theoretical level.

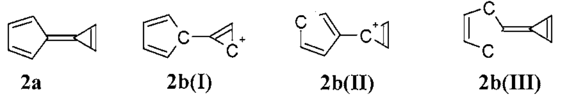
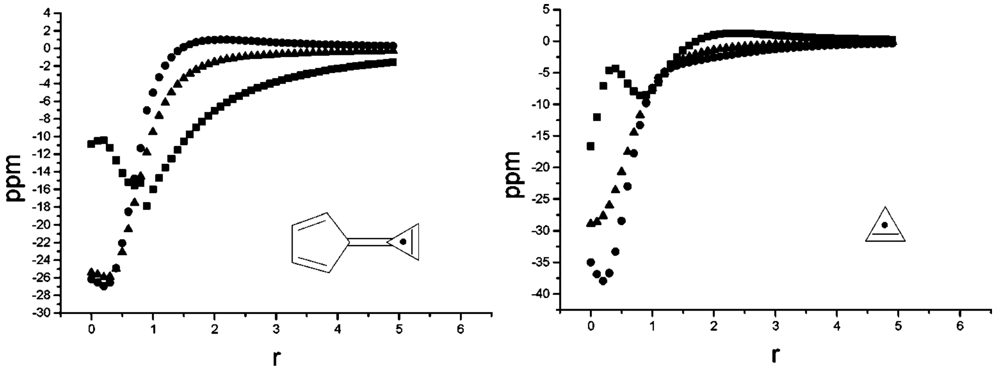


FIGURE 10. Main canonic structures of calicene as obtained from the NRT analysis. **2a**, 43.8%; **2b(I)**, 30.0%; **2b(II)**, 12.2%; and **2b-(III)**, 11.1%.

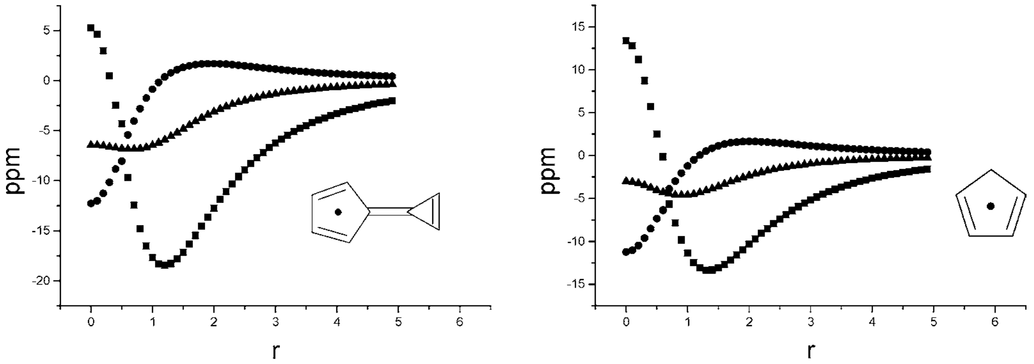
minima for calicene's five-membered ring: −18.5@1.2 versus −13.4@1.3 for the out-of-plane components and −6.9@0.65 versus −4.7@0.9 for the isotropic chemical shifts. Thus, the NICS-scan gives a picture that is similar to the one obtained from geometry, charges, and NRT analysis—a picture that a single NICS value fails to represent.

Bicyclobutadienobenzene (1). It was shown above that the NICS(1) values for **1** are not coherent with the picture obtained from the structure, VB calculations,[13] and NRT[12] analysis.



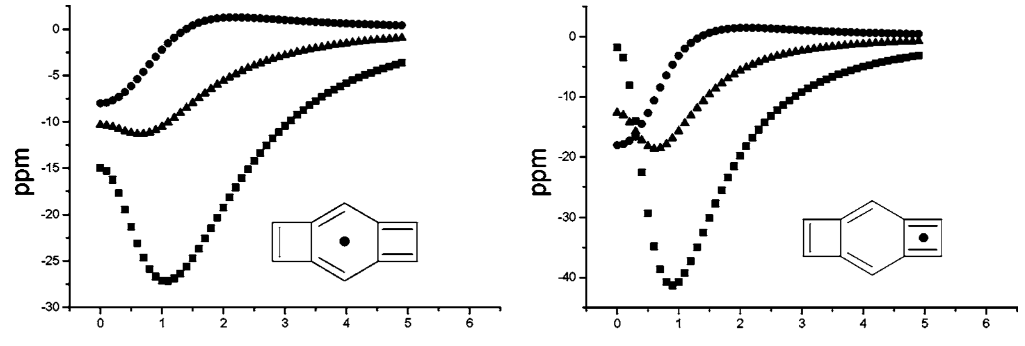
(a) (b)

FIGURE 11. NICS values as a function of distance (angström) of (a) calicene, above the three-membered ring, and (b) cyclopropene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.



(a) (b)

FIGURE 12. NICS values as a function of distance (angström) of (a) calicene, above the five-membered ring, and (b) cyclopentadiene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.



(a) (b)

FIGURE 13. NICS values as a function of distance (angström) of **1a** (one canonic structure is drawn) (a) above the six-membered ring and (b) above the four-membered ring. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

Figures 13 and 14 show the NICS-scan results for **1a** and **1b**, respectively.

As for calicene, the picture obtained from the NICS-scan is much more consistent with other indices of aromaticity than the one obtained from a single NICS value. Thus, **1a** shows minima for the out-of-plane contributions in the six- and four-membered rings (−27.2@1.1 and −41.4@0.9) and the isotropic values (−11.3@0.6 and −18.7@0.6). These values suggest that the system is indeed one delocalized π system, that is, a doubly bridged [10]-annulene[25] that cannot be treated as a separate unit. For example, for planar [10]-annulene[26] the NICS(1) value above the center is −13.5, and at 1.65 Å off center (which is 72.3% of the distance to the edge—the same proportion that the bq is above the four-membered ring in **1a**) NICS(1) is −20.8. Isomer **1b** shows aromatic behavior for the six-membered ring (−5.8@1.3 and −2.5@0.9 for the out-of-plane component and the isotropic chemical shifts, respectively) and a clear antiaromatic picture for the four-membered ring. Note that despite the paramagnetic effect of the conjugated four-membered rings the

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[25] This case is similar to that of anthracene. Thus, it is a single π system; therefore, the chemical shifts at different locations above the system cannot be quantitatively compared. The fact that the NICS above the four-membered ring is more negative than that above the six-membered ring actually supports the [10]-annulene structure for **1a**.

[26] Planar all *cis*-[10]-annulene has two negative frequencies associated with out-of-plane vibrations.

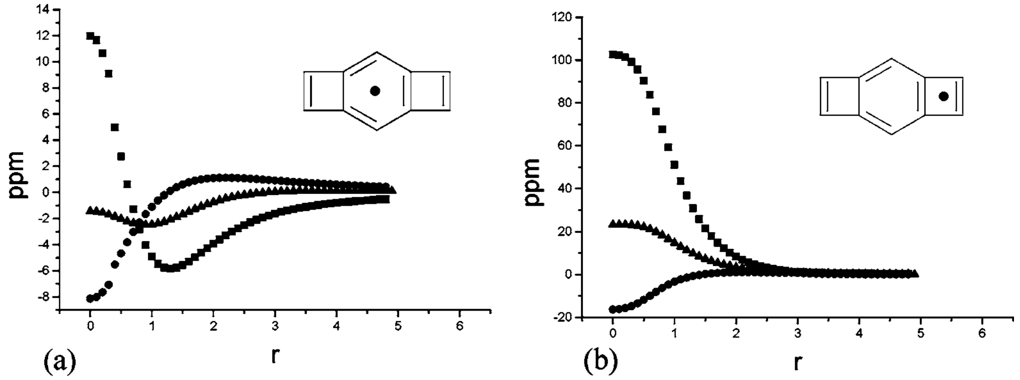

FIGURE 14. NICS values as a function of distance (angström) of **1b** (one canonic structure is drawn) (a) above the six-membered ring and (b) above the four-membered ring. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

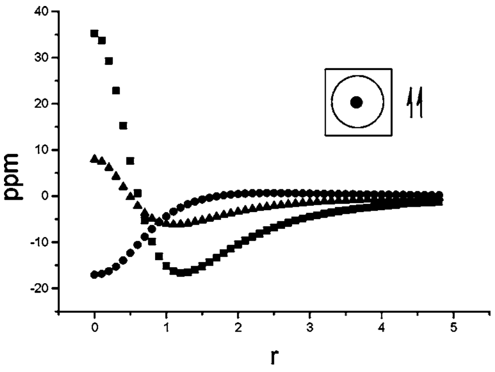

FIGURE 15. NICS values as a function of distance (angström) of triplet cyclobutadiene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

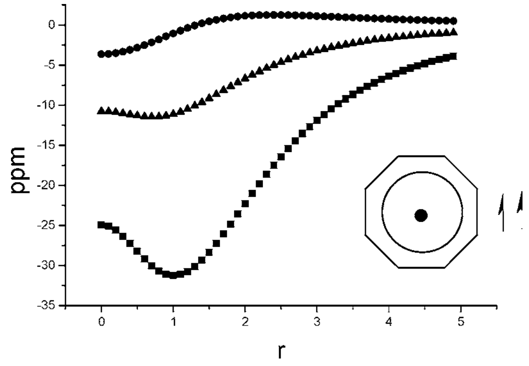

FIGURE 16. NICS values as a function of distance (angström) of triplet cyclooctatetraene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

six-membered ring retains its diamagnetic character although with relatively small negative values. The NICS-scan results for **1**, therefore, reaffirm that relative local aromaticities in a polycyclic system cannot be assigned by comparing NICS(1) or NICS-scan values.

Triplet 4*n* π Systems. Gogonea, Schleyer, and Schreiner showed that triplet 4*n* π systems are aromatic according to a few indices.[27] Can the NICS-scan show the same property? Figures 15 and 16 show the NICS-scans of triplet cyclobutadiene and triplet cyclooctatetraene.

Evidently, the two systems show typical aromatic behavior. The in-plane components show behavior that is identical to that of the singlet systems. The out-of-plane contribution in triplet cyclobutadiene has positive values at short distances, and the minimum is relatively shallow and at a somewhat larger distance (−6.2@1.1). This is probably due to the proximity of the probe to the atoms and the bonds that enhances the paramagnetic contribution relative to the diamagnetic contribution. Triplet cyclooctatetraene shows a rather usual aromatic NICS-scan picture, with minimum values of −31.3@1.0 and −11.5@0.7 for the out-of-plane contribution and isotropic value, respectively. It is worth noting that at GIAO-HF/6-311+G*//B3LYP/6-311G* the NICS(1) value of triplet cyclobutadiene is −5.6 and that of triplet cyclooctatetraene is −11.1. Thus, according to a single NICS criterion, triplet cyclobutadiene is nonaromatic, but triplet cyclooctatetraene is aromatic.

Charged Systems. A Hückel type rationalization suggests that a charged system is as aromatic for a (4*n* + 2) π-electron system (e.g., cyclopentadienyl anion) and as antiaromatic for a 4*n* π-electron system (e.g., cyclopentadienyl cation) as their π-isoelectronic uncharged systems (e.g., benzene and cyclobutadiene, respectively). In the following paragraph, the NICS-scan method is tested for these systems.

Figure 17 shows the NICS-scans of the cyclopentadienyl anion and cation. The isotropic NICS-scan of a cyclopentadienyl anion (Figure 17a) behaves like that of an uncharged nonaromatic system, with NICS(1) = −10.2. Separating the isotropic shift into in-plane and out-of-plane contributions explains the somewhat unexpected behavior of the isotropic curve. Thus, although the general shape of the NICS-scan plot of the in-plane contribution is similar to that of noncharged systems, it has a maximum that is rather paratropic in the same region that the out-of-plane component has a minimum. The out-of-plane component behaves like a typical aromatic NICS-scan with a minimum of −36.3@0.9. Thus, it seems that the negative charge affects the in-plane component of the NICS, making it more paratropic and consequently changing the shape of the isotropic NICS-scan curve. However, the antiaromatic cyclopentadienyl cation shows a normal antiaromatic NICS-scan plot (Figure 17b). Note, however, that the in-plane contribution shows a minimum, which is the effect of the positive charge. This is even more pronounced in the dication of cyclooctatetraene (Figure 18a, normal aromatic NICS-scan behavior) and is the same in the triplet cyclopentadienyl cation (Figure 18b) and tropylium cation (Figure 18c). Note that in the three 6 π-electron systems (i.e., cyclopentadienyl anion, Figure 17a, tropylium

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(27) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew Chem., Int. Ed.* **1988**, *37*, 1945.

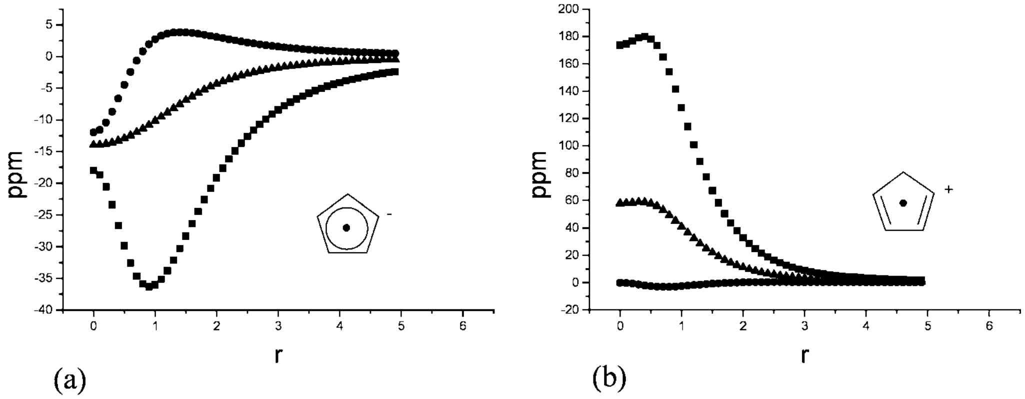

FIGURE 17. NICS values as a function of distance (angström) of (a) the cyclopentadienyl anion and (b) the cyclopentadienyl cation. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

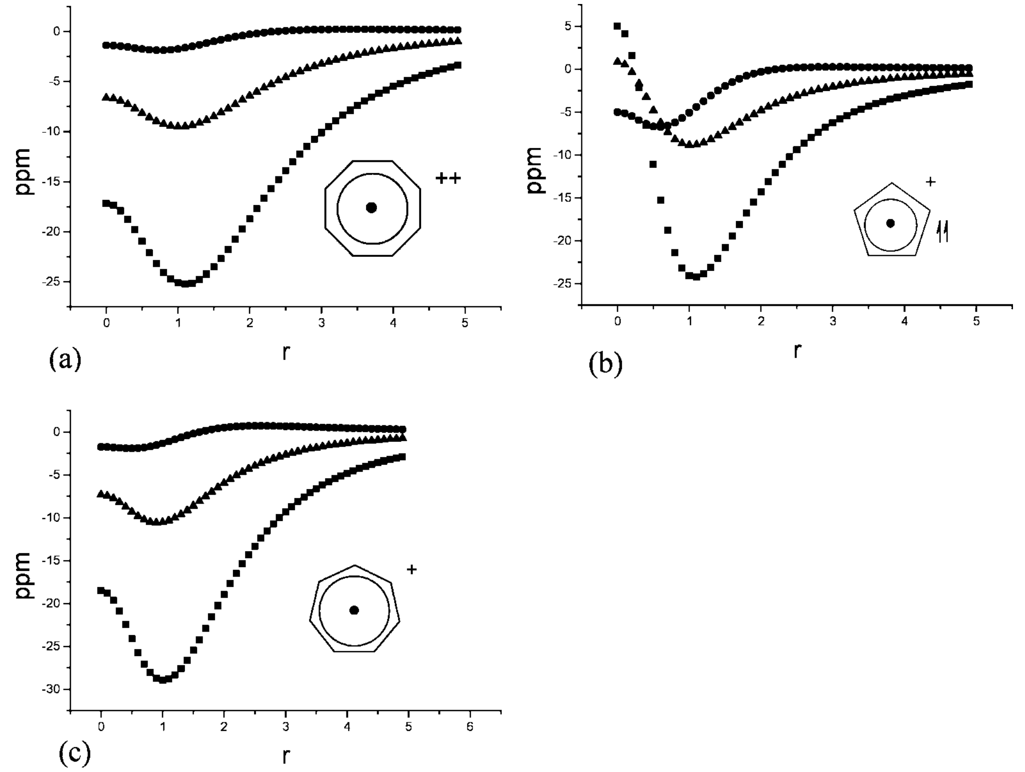

FIGURE 18. NICS values as a function of distance (angström) of (a) the cyclooctatetraene dication, (b) the triplet cyclopentadienyl cation, and (c) the tropylium ion. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

cation, Figure 18c, and cyclooctatetraene dication, Figure 18a) the out-of-plane components are almost identical. The small differences result from the distances between the probes and the bonds. The main differences between the three 6 π-electron systems are found in the in-plane components. Thus, the charge effect in the NICS-scan of cyclic conjugated systems is in the in-plane contribution: positive charge causes diatropic behavior, whereas negative charge causes paratropic behavior. This is well manifested in ^{13}C chemical shifts. Whereas aromatic carbons resonate at only a slightly lower field than olefinic carbons, positively charged carbons (even, for example, in carbonyl compounds) are much more deshielded. The out-of-plane components in charged systems show behavior similar to that in uncharged systems.

Heterocyclic Aromatic Systems. These systems perhaps best demonstrate the need to dissect the NICS-scan into in-plane and out-of-plane contributions. Thus, pyridine (Figure 19) shows an NICS-scan picture that is very similar to that of benzene, with isotropic and out-of-plane minima of −11.4@0.8 and −30.9@1.0, respectively, and an NICS(1) value of −11.1. However, pyrrole, furan, and thiophene show very different pictures (Figure 20), which are similar to that of a cyclopentadienyl anion. None of these compounds show a minimum in the isotropic curve, and their NICS(1) values are −10.5 (pyrrole), −9.2 (furan), and −10.3 (thiophene). However, the out-of-plane components clearly show the large diamagnetic ring current, with minima of −32.3@0.9 (pyrrole), −26.3@0.9 (furan), and −28.0@1.0 (thiophene). Thus, the out-of-plane component of the chemical shift indicates that the ring current of pyrrole is even larger than that of pyridine although no minimum is observed for the isotropic curve, and it has a less negative NICS(1) value.

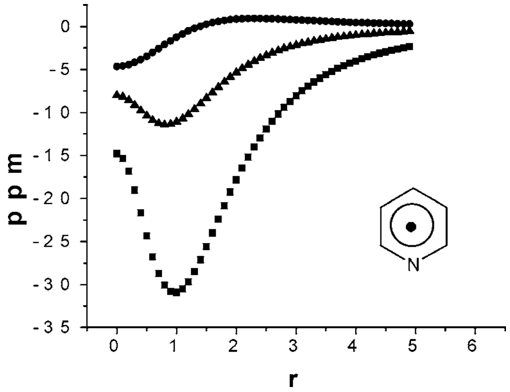

FIGURE 19. NICS values as a function of distance (angström) of pyridine. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

Other Systems. Most of the aromatic systems discussed so far show that the minimum NICS isotropic values and, more importantly, the most negative value of the out-of-plane contribution are about 1 Å above the molecular plane, which may therefore imply that there is no need for the NICS-scan procedure. This may be the case for carbon compounds, but it cannot be taken as a general conclusion. The paratropic and diatropic out-of-plane NICS effects originate mainly from the π system. Substituents and/or heteroatoms will cause different sizes of p orbitals that must be manifest in different sizes of π systems; therefore, the maximum diatropic effect should appear at different distances from the plane of the ring. Two examples are given below.

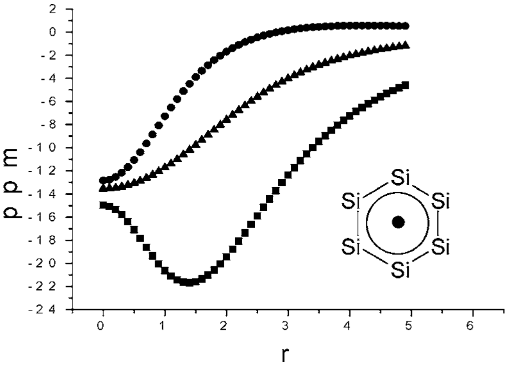

FIGURE 21. NICS values as a function of distance (angström) of D_{6h} hexasilabenzene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

Planar D_{6h} hexasilabenzene is a transition state between the two more stable chair structures ($N_{\mathrm{imag}} = 1$). Its π-orbital structure is identical to that of benzene, and its calculated proton chemical shifts (at GIAO-HF/6-311+G*//B3LYP/6-311G*) are about 1.25 ppm higher than those of benzene at the same theoretical level and are downfield shifted relative to saturated Si−H bonds.[28] Thus, this structure should be aromatic. Indeed, its NICS(1) is −11.7 ppm, which is the average between the in-plane contribution (−7.3 ppm) and the out-of-plane contribution (−20.6 ppm). The in-plane and out-of-plane contributions in benzene at 1.0 Å are −2.0 and −28.6 ppm, respectively, so that the similar average for benzene and hexasilabenzene results from completely different sources. The NICS-scan reveals a much more complicated picture (Figure 21). The isotropic

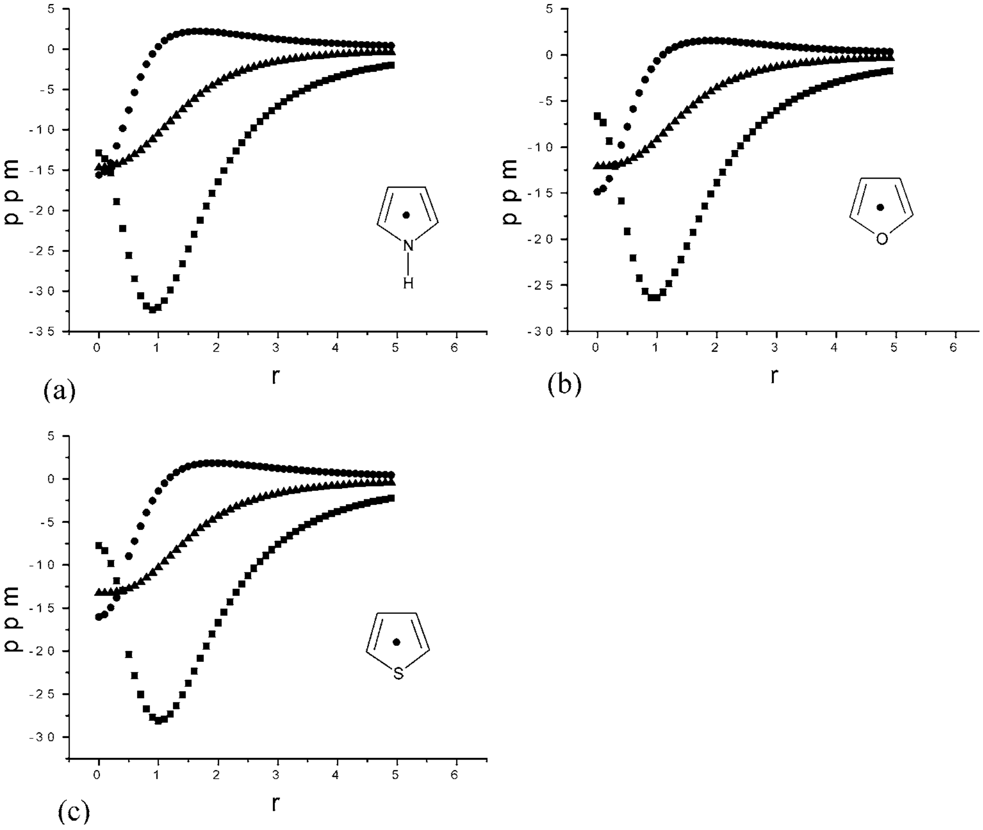

FIGURE 20. NICS values as a function of distance (angström) of (a) pyrrole, (b) furan, and (c) thiophene. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

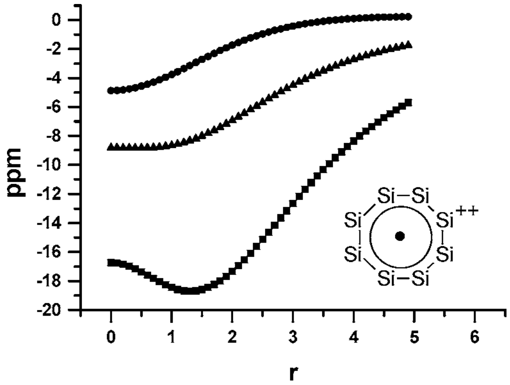

FIGURE 22. NICS values as a function of distance (angström) of the D_{6h} octasilacyclooctatetraene dication. ■ − Out-of-plane component. ● − In-plane component. ▲ − Isotropic chemical shift.

chemical shift has no minimum, and both the in-plane and out-of-plane contributions change much less steeply with distance than in carbon compounds. The minimum value for the out-of-plane contribution is −21.7@1.4. A comparison between NICS(1) of benzene (−10.9) and that of hexasilabenzene (−11.7) may suggest that hexasilabenzene is more aromatic than benzene. In fact, the isotropic NICS values of hexasilabenzene are more negative than those of benzene through the bq distance studied. However, the NICS-scan clearly shows that this is due to the in-plane component of the chemical shift. The minimum for the out-of-plane component of the chemical shift of benzene is more negative and less remote than that of hexasilabenzene (−28.8@1.1 vs −21.7@1.4), indicating a smaller diamagnetic ring current in the latter.

Another example is that of octasilacyclooctatetraene dication. The planar system is a transition state between two crown conformations ($N_{\mathrm{imag}} = 1$), and its occupied π-orbital structure is identical to that of benzene and the cyclooctatetraene dication. Its NICS(1) is −8.6, thus hardly qualifying as aromatic. Figure 22 shows its NICS-scan. A comparison to the NICS-scan of the cyclooctatetraene dication (Figure 18a) suggests that the general shapes are the same. The isotropic curve in the octasila derivative has a much shallower minimum. The in-plane component does not show a minimum but has more negative values than the carbon analogue (e.g., −4.9@0.0, −3.8@1.0 vs −1.4@0.0, and −1.7@1.0, respectively). The out-of plane component shows a minimum (−18.7@1.3) that is shallower and more remote than in the carbon analogue (−25.3@1.1), thus indicating a diamagnetic ring current, but a smaller one than in the carbon analogue. More important for this discussion is the minimum isotropic value. The values of the isotropic NICS are more negative for the carbon analogue at shorter distances. At ca. 1.75 Å, the two systems show an equal value, and at larger distances, the Si derivative shows more negative values.

Summary and Conclusions

The NICS-scan method in which the chemical shifts of a probe (bq) are scanned over a distance above the center of the molecular plane and dissected into their in-plane and out-of-plane components was introduced. Several neutral, charged, and triplet systems were examined. It was shown that the NICS-scan approach is more consistent with other data and indices of aromaticity than a single isotropic NICS value. The picture obtained from the NICS-scan procedure is indicative of diamagnetic and paramagnetic ring currents and thus can be rationalized in a much more coherent way than a single NICS value. Therefore, it is suited to systems that are more problematic in nature, of which a few examples were discussed in the article. It is further shown that the separation between the in-plane and out-of-plane components of the isotropic NICS is necessary for assessing the diamagnetic and paramagnetic properties of the systems under study and that local aromaticities cannot be obtained by comparing NICS or NICS-scan values of different rings within the same systems. It is certainly true that an NICS-scan shows diamagnetic and paramagnetic ring currents. However, the curves obtained for cyclopentadiene (Figure 12b) raise the question of its use in unambiguously determining aromaticity. This is discussed elsewhere.[24]

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Supporting Information Available: Optimized geometries (in Cartesian coordinates or ***Z***-matrix formats) and total energies of all of the molecules and ions discussed in the article. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) The ^{1}H chemical shifts of CH_4 and SiH_4 are 0.23 and 3.2 ppm, respectively (SDBS, http://www.aist.go.jp/RIODB/SDBS/menu-e.html). Thus, the magnitude of the downfield shift in benzene is much larger than that in D_{6h} hexasilabenzene, although NICS(1.0) for both are very similar. The NICS-scan explains this.