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Summation of Nucleus Independent Chemical Shifts as a Measure of Aromaticity

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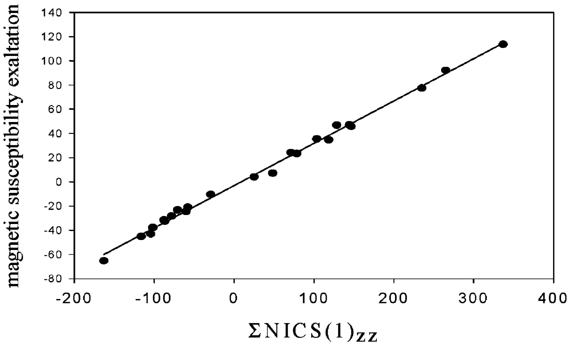

When the nucleus independent chemical shifts, NICS(1)$_{zz}$, for a set of aromatic and antiaromatic hydrocarbons are summed, they show an excellent linear relationship with the magnetic susceptibility exaltation, Λ, for neutral, cationic, and monoanionic species. Aromatic and antiaromatic dianions show a similar relationship but with a different slope. However, when both Λ and the summation of NICS(1)$_{zz}$ are divided by the area of the ring squared, the vast majority of the aromatic and antiaromatic species fall on the same line, indicating that both NICS and Λ are affected by the size of the ring. The species that deviate slightly from the line are a few of the anionic compounds, which may be a result of the difficulties of calculating magnetic properties of anions. This is the first report of the relationship of NICS to ring area. In addition, the excellent correlation between Λ and the summation of NICS(1)$_{zz}$ demonstrates that summation of NICS(1)$_{zz}$ values for individual ring systems of polycyclic ring systems to give a measure of the aromaticity of the entire system is justified. By extension, the excellent correlation also serves to demonstrate that the NICS(1)$_{zz}$ values for individual ring systems are reliable measures of local aromaticity/antiaromaticity. Finally, the excellent correlation between experimental shifts and the ^{13}C NMR shifts calculated with density functional theory, B3LYP/6-311+g(d,p), serves as an indirect validation of the accuracy of the NICS(1)$_{zz}$ calculated by the same method and basis set.

Introduction

There is currently a controversy about the nature of aromaticity and, by extension, antiaromaticity, based on the manner in which aromaticity is manifested. That is, when the properties described below are used to quantify aromaticity/antiaromaticity, the magnitude of the aromaticity/antiaromaticity may vary according to the method used. There are three general categories of properties associated with aromaticity, *energetic*, *structural*, and *magnetic*. Energetic properties examine the stability of the species, often in comparison to a localized reference system, as in aromatic stabilization energy calculations.[1] Structural properties reflect the fact that benzene is planar with a lack of bond length alternation. One approach toward the evaluation of such structural properties is the harmonic oscillator measure of aromaticity (HOMA) which examines the deviation of individual bond lengths from the average bond length of the aromatic/antiaromatic species.[2−4] Magnetic properties result from the presence of a ring current when the species

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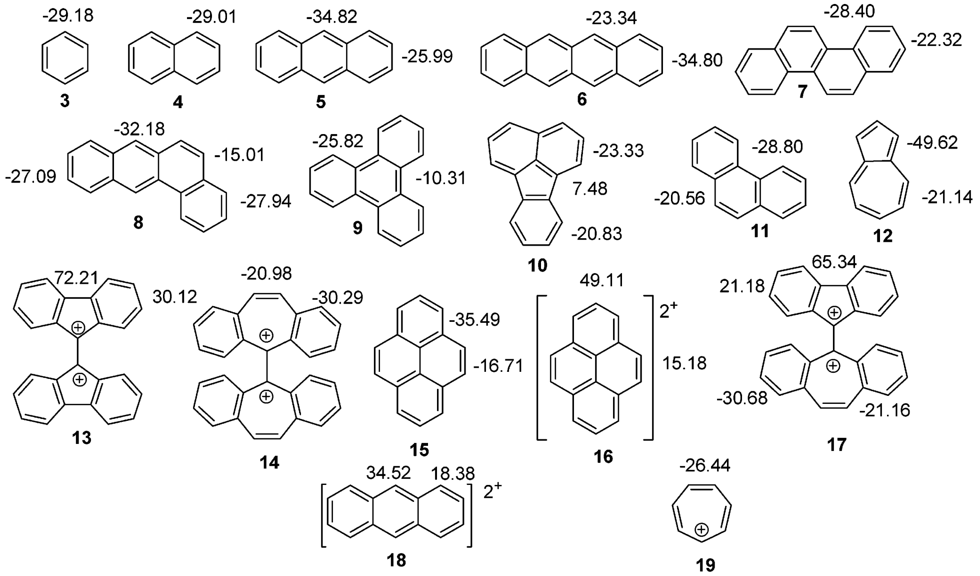
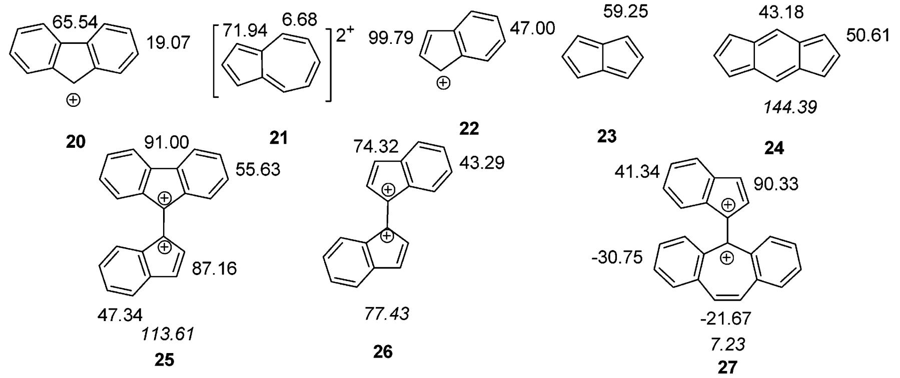
SCHEME 1. NICS(1)$_{zz}$ for Each Ring System of a Set of Aromatic and Antiaromatic Neutral Molecules and Cations

Group 1. Species for which experimental NMR shifts have been obtained



Group 2. Species as yet uncharacterized by ^{13}C NMR spectroscopy



is placed in a magnetic field. The ring current causes a shift of the proton resonances on the aromatic ring in the NMR spectrum,[5] a change in the magnetic susceptibility of the species, magnetic susceptibility exaltation, Λ,[6–9] and a difference in the chemical shift for a dummy atom in the center of the ring system, called the nucleus independent chemical shift, NICS,[10] which is opposite in direction to the change in the shift seen in the ^{1}H NMR spectrum. In general, all three categories very often assign a species as aromatic, nonaromatic, or antiaromatic, but they may disagree in the degree of this aromaticity/antiaromaticity.[11] The disagreement suggests that the properties may not be measuring the same phenomenon. Because the concept of aromaticity is "a cornerstone of organic chemistry",[12] it is crucial to resolve these discrepancies.

The magnetic criterion is the most commonly used measure of aromaticity/antiaromaticity[13]and has been suggested as the most appropriate measure of aromaticity.[14] ^{1}H chemical shifts are the traditional magnetic measure of aromaticity, but because the ^{1}H shift is affected by factors other than ring current, its use has been recently questioned.[15,16] Magnetic susceptibility exaltation, Λ, reflects the additional magnetic susceptibility, Χ, of an aromatic/antiaromatic species because of the presence of a ring current and is determined by the difference between Χ of the species of interest and the summation of Χ from increments for the species in which the bonds are localized. Because the exaltation is determined in comparison to an artificial nonaromatic reference system, the choice of reference system can be controversial.

For many of these reasons, NICS has emerged recently as the most frequently used property in the magnetic criterion. It is inexpensive and easy to compute, is implemented in many quantum mechanical programs, is not limited to planar molecules, and does not require a reference compound.[13] However, it has important limitations. The magnitude of NICS is affected

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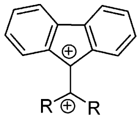
by the electrons of the σ-system, requiring that the dummy atom used for the calculation of chemical shift be positioned above the ring under examination, usually 1 Å.[17,18] The original suggestion for the calculation of NICS[10] used the average of the three components of the tensors of the chemical shift, the isotropic value. Because the component of the tensor most closely related to the π-system is the one perpendicular to the plane of the ring, the isotropic value understates its effect. NICS have recently been refined as NICS$(1)_{zz}$ in which only the magnitude of the tensor perpendicular to the plane of the ring is used.[19,20]

It is not immediately obvious that there is a useful physical reality for NICS. NICS are a measure of local aromaticity, because magnetic shielding is proportional to the inverse third power of the distance of the electrons from the probe. Thus, it is unable to reflect the behavior of electrons in distant regions of the system. For NICS to accurately describe a ring current, some local circulation associated with the ring probed by each NICS value is required. This appears to be the case for a number of polycyclic aromatic hydrocarbons because current density maps[21,22] show localized electron circuits as well as circulation around the perimeter of the molecule. An additional concern is that NICS for a specific ring system may include contributions from adjacent ring systems.[23,24] If NICS is to be used as a measure of aromaticity for polycyclic systems through summation of NICS for the individual ring systems,[25] there is the potential for "double-counting" the magnetic character of separate ring systems. This could limit the ability of NICS to be compared to measures of aromaticity such as Λ or ASE which are necessary measures of an entire system. Finally, NICS has been considered as a *virtual* property because it is nonmeasurable.[26] ^{3}He NMR chemical shifts of endohedral helium−fullerene complexes[13,27] demonstrate the same sort of relationship as NICS, but the small number of compounds for which this relationship can be tested limits this test of the quality of NICS. The validity of NICS has also been supported by the experimental measures of aromaticity in dimethyldihydropyrene derivatives,[28] but again, the number of appropriate species is limited.

We have come to this issue from our experience in preparing a series of antiaromatic dications such as **1** and **2**.[29−40] Their antiaromaticity has been established using various energetic and magnetic measures, but NICS are of particular value because they allow us to understand subtle differences in the individual ring systems caused by changes in R. However, these conclusions require that the magnitude of each NICS be meaningful. That is, are NICS affected by adjacent ring systems to a significant extent? If there is a good correlation between the summation of NICS and a measure of aromaticity/antiaromaticity for the entire system, this would suggest that double-counting of the magnetic character is not occurring. Because it is not clear that magnetic, energetic, and structural measures of aromaticity/antiaromaticity are related for all species, it seemed prudent to consider a magnetic measure of aromaticity/antiaromaticity, Λ. This study reports on the relationship between the summation of NICS perpendicular to the plane of the ring system ($\sum$NICS$(1)_{zz}$) and Λ. In addition, we examine the relationship of calculated and experimental ^{13}C shifts as support for the validity of calculated chemical shifts, including NICS.



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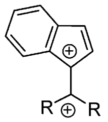

2

Results and Discussion

Choice of the Species for Study. While our primary interest was in understanding the behavior of NICS in **1** and **2** and their ability to reliably predict antiaromaticity, we included in our study neutral molecules whose aromaticity is not in dispute as well as neutral antiaromatic molecules. Scheme 1 gives the NICS$(1)_{zz}$ values calculated at the B3LYP/6-311+g(d,p) level for each ring system of a variety of linear (**3**−**6**) and nonlinear (**7**−**9**, **11**, **15**) neutral PAHs, aromatic and antiaromatic neutral hydrocarbons with seven- and/or five-membered rings (**10**, **12**, **23**, **27**), and aromatic and antiaromatic mono- and dicationic hydrocarbons (**13**, **14**, **16**−**22**, **24**−**26**), including those related to **1** and **2**. The compounds were chosen to represent a group of aromatic and antiaromatic hydrocarbons that were very diverse in terms of molecular geometry, charge type, and aromaticity/antiaromaticity. The summation of NICS$(1)_{zz}$ for each system, its magnetic susceptibility, Χ, and magnetic susceptibility exaltation, Λ, are given in Table 1.

Correlation between $\sum$NICS and Λ. The relationships between the $\sum$NICS$(1)_{zz}$ and Λ for **3**−**27** are shown in Figure 1 and demonstrate an excellent agreement between $\sum$NICS and Λ, with $r^2 = 0.995$. The correlation is slightly poorer when

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TABLE 1. Summation of NICS(1)$_{zz}$,[a] X,[b] and Λ[b] for 3−27

	ΣNICS(1)$_{zz}$	X, in ppm cgs	Λ, in ppm ccgs
3	−29.18 (−29.08)	−52.90 (−46.07)	−10.47 (−10.22)
4	−58.02 (−57.90)	−88.99 (−79.96)	−20.98 (−21.97)
5	−86.80 (−86.46)	−125.46 (−114.66)	−32.49 (−34.87)
6	−116.28 (−115.59)	−163.09 (−150.55)	−45.16 (−48.96)
7	−101.45 (−102.50)	−156.88 (−143.38)	−37.72 (−41.11)
8	−102.23 (−102.30)	−156.38 (−143.19)	−37.84 (−41.26)
9	−87.76 (−89.13)	−150.52 (−136.94)	−31.37 (−34.67)
10	−60.00 (−58.62)	−128.87 (−115.67)	−24.47 (−25.69)
11	−78.14 (−78.47)	−121.82 (−110.56)	−28.24 (−30.43)
12	−70.76 (−71.01)	−90.58 (−80.74)	−23.19 (−23.09)
13	264.90 (274.24)	−62.05 (−36.25)	92.19 (93.59)
14	−163.11 (−163.28)	−247.75 (−218.69)	−65.23 (−64.94)
15	−104.41 (−104.07)	−148.22 (−150.55)	−44.09 (−60.57)
16	128.57 (132.14)	−40.94 (-23.53)	46.79 (49.41)
17	25.18 (27.26)	−164.32 (−137.36)	4.06 (4.44)
18	71.27 (74.46)	−50.61 (−34.58)	24.20 (27.09)
19	−26.44 (−26.22)	−54.92 (−45.53)	−13.81 (−11.83)
20	103.69 (87.80)	−42.69 (−29.25)	35.42 (36.78)
21	78.62 (81.08)	−25.19 (−13.53)	23.43 (25.65)
22	146.78 (154.12)	−6.70 (3.52)	45.83 (47.41)
23	118.50 (126.10)	−18.66 (−11.43)	34.59 (34.27)
24	144.39 (154.60)	−31.17 (−19.01)	47.04 (48.49)
25	336.76 (356.64)	−15.06 (11.46)	113.61 (119.16)
26	235.22 (243.38)	−25.67 (−7.06)	77.43 (78.50)
27	48.50 (53.42)	−135.58 (−110.37)	7.23 (9.29)

[a] Calculated with the GIAO method at B3LYP/6-311+g(d,p). Values calculated at B3LYP/6-31g(d) are shown in parentheses; all geometries were optimized at B3LYP/6-31g(d). [b] Calculated with the CSGT method at B3LYP/6-311+g(d,p). Values calculated at B3LYP/6-31g(d) are shown in parentheses; all geometries were optimized at B3LYP/6-31g(d).

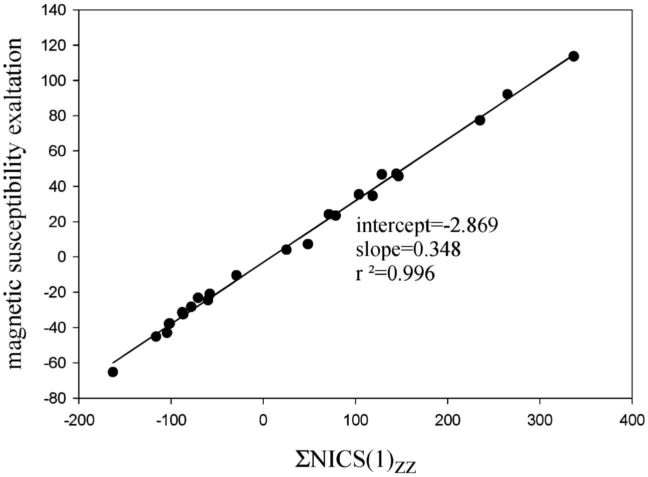

FIGURE 1. Relationship between of ΣNICS(1)$_{zz}$ and Λ. NICS(1)$_{zz}$ for **3**−**27**, calculated with the GIAO method, B3LYP/6-311+g(d,p) on geometries optimized at B3LYP/6-31g(d); magnetic susceptibility exaltation, Λ, determined from magnetic susceptibilities calculated with the CSGT method, B3LYP/6-311+g(d,p) on geometries optimized at B3LYP/6-31g(d); see Supporting Information for details.

calculated without diffuse functions (B3LYP/6-31g(d)), $r^2 = 0.990$ (see Supporting Information). Magnetic susceptibility exaltation is known to be dependent upon ring area, specifically, the square of the ring area,[7] so the good correlation supports the suggestion that NICS is related to ring area (vide infra).

Because we have begun to prepare antiaromatic dianions, we were interested in extending this examination to include the anionic species shown in Scheme 2 and Table 2. However, as Figure 2 demonstrates, there is indeed a linear relationship in anionic species between ΣNICS(1)$_{zz}$ and Λ, but it is a different relationship than that shown for neutral and cationic species.

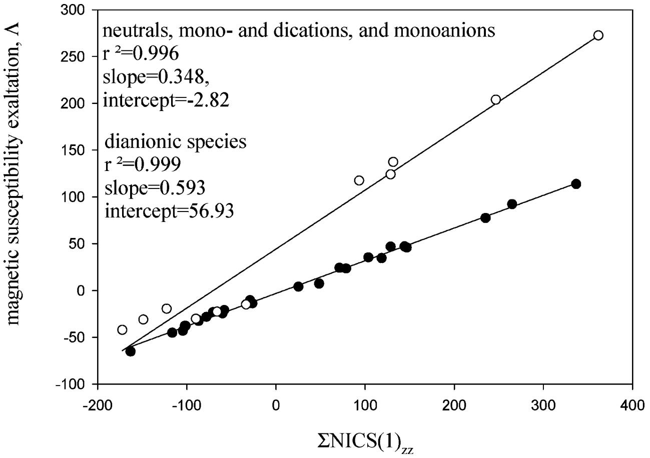

FIGURE 2. Relationship between ΣNICS(1)$_{zz}$ and Λ. NICS(1)$_{zz}$ for **3**−**39**, anionic species are shown by open circles, neutral and cationic species by closed circles.

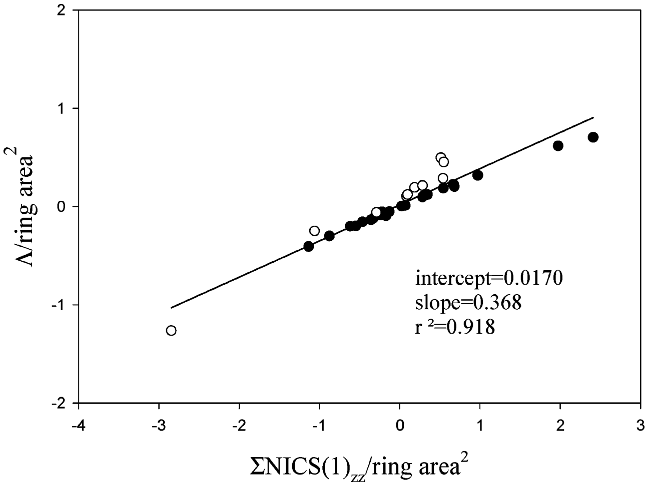

FIGURE 3. Relationship between the summation of NICS(1)$_{zz}$/ring area^2 and Λ/ring area^2 for **3**−**39**, calculated as in Figure 1. Anionic species are shown by open circles, neutrals and cations by closed circles.

Anions are known to be larger than the corresponding cations (see Supporting Information for the areas of **3**−**39**). While cations are also larger than the neutral species, for the compounds included in this study, the dications are approximately 0.4% larger than the neutral species while the dianions are approximately 2% larger (Supporting Information). Monoanions **28**, **29**, and **39** fall on the same line as the neutrals and dications. Monoanions **29** and **39** are only 0.7% larger than the corresponding cations (Supporting Information). Aromatic monoanion **28** is actually smaller than the corresponding, and antiaromatic, cation **41** (vide infra). While anions are normally larger than cations, in this case, the bond alternation shown for antiaromatic **41** results in it being larger than the symmetrical **28**. The effect of bond length alternation is much smaller in **29** and **39** because benzannulation restricts it. It is not surprising that the neutrals, cationic, and monoanionic species show the same relationship, which is different for dianionic species.

As mentioned previously, magnetic susceptibility exaltation is known to be related to the square of the ring area. Dividing Λ and ΣNICS(1)$_{zz}$ for each species by the square of its area would serve to correct each species for the larger size of the anions. Figure 3 shows the relationship that resulted, with the

SCHEME 2. NICS(1)$_{zz}$ for Each Ring System of a Set of Aromatic and Antiaromatic Anions

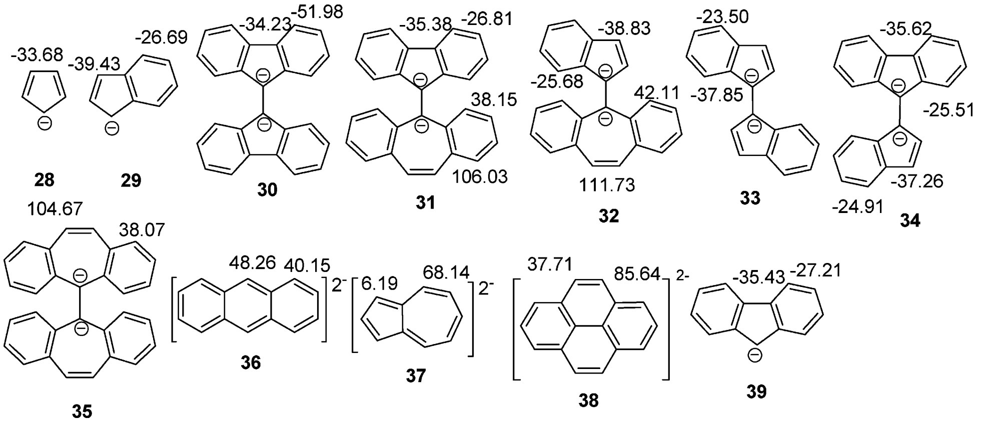

TABLE 2. Summation of NICS(1)$_{zz}$,[a] X,[b] and Λ[b] for 28−39

	NICS(1)$_{zz}$	X, in ppm cgs	Λ, in ppm ccgs
28	−33.67	−52.03	−14.95
29	−66.12	−85.31	−22.65
30	−172.42	−233.95	−42.14
31	93.32	−88.48	117.47
32	131.44	−43.10	137.28
33	−122.69	−160.16	−19.50
34	−148.81	−197.23	−31.00
35	361.60	52.41	258.36
36	128.56	9.62	87.73
37	64.31	−21.59	58.59
38	246.70	78.53	167.47
39	−89.84	−118.42	−30.19

[a] Calculated with the GIAO method at B3LYP/6-311+g(d,p). All geometries were optimized at B3LYP/6-31g(d). [b] Calculated with the CSGT method at B3LYP/6-311+g(d,p). All geometries were optimized at B3LYP/6-31g(d).

anions showing basically the same relationship as the neutral and cationic species. While the relationship is not quite as good for Λ/area^2 and ∑NICS(1)$_{zz}$/area^2, the value of r^2 is respectable. Close inspection of Figure 3 reveals that there are two distinct relationships. The neutral and cationic species have a linear relationship, $r^2 = 0.994$, which is slightly different from that of the anionic species, $r^2 = 0.976$. We believe that the anionic species are more sensitive to the level of the calculation than cations and neutrals (vide infra). The good correlation for a diverse group of species also demonstrates that NICS are related to the square of the ring area. While the dependence of NICS on ring area has been suggested,[41] to the best of our knowledge, this is the first result that shows the empirical relationship to the square of the ring area.

While the agreement is satisfying, the relationship needs to be documented for monocyclic aromatic and antiaromatic hydrocarbons in which the local aromaticity/antiaromaticity evaluated through NICS values for the individual ring system is of necessity the same as the aromaticity/antiaromaticity of the entire system. That relationship is shown in Figure 4a for the species in Scheme 3, with the values for X, Λ, and NICS(1)$_{zz}$ in Table 3. When species **3**−**39** are included with the monocyclic compounds, the relationship is basically the same, as shown in Figure 4b.

The relationship between NICS(1)$_{zz}$/area^2 and Λ/area^2 for monocyclic species deserves comment. The points that show the poorest agreement with the linear relationship in Figure 4b are for the cyclopentadienyl anion and cyclooctatetraene dianion, suggesting that anions with greater charge density may be more sensitive to calculational level. These species would have the greatest charge/ring area. As noted by others[42] and previously noted in this study, calculation of magnetic properties of anions is particularly susceptible to the basis set. Partial support of this premise comes from the improvement of the correlation coefficient, r^2, to 0.990 for the species in Figure 4a when the calculations are done at the B3LYP/6-311+g(3df,2p) level (see Supporting Information).

Experimental Validation of the Calculation of NICS. As discussed in the beginning of this paper, other than the ^{3}He NMR studies of endohedral helium−fullerene complexes[27] and the dimethyl dihydropyrene derivatives of Mitchell,[28] there are no experimental probes of aromaticity that provide a probe near the center of an aromatic/antiaromatic ring system. However, it is possible to document that the method, including basis set, for the calculation of NICS accurately calculates the chemical shifts for the species under examination. The comparison of calculated and experimental ^{13}C NMR shifts for the species in Scheme 1 shows a very good correlation, with $r^2 = 0.989$, when calculated using the GIAO method with B3LYP/6-311+g(d,p) (see Supporting Information). The relationship was poorer, $r^2 = 0.958$, with B3LYP/6-31g(d). We explored this correlation only for neutral and cationic species because it is known that anionic species show a much stronger dependence on counterion.[43,44]

Summary. A diverse set of aromatic and antiaromatic neutral and charged hydrocarbons shows a linear relationship between the summation of NICS(1)/area^2 and Λ/area^2. Because it is known that Λ is related to the square of the ring area, the good agreement suggests that NICS(1)$_{zz}$ also is related to the square of the ring area, the first time this empirical relationship has been reported. There are several additional consequences of this relationship that deserve comment. If the summation of NICS(1)$_{zz}$ correlates well with Λ for a wide variety of compounds, this would suggest that NICS(1)$_{zz}$ can be summed as a measure of aromaticity/antiaromaticity of a polycyclic species. In addition, the excellent correlation between ∑NICS(1)$_{zz}$ and Λ suggests that the magnitudes of the NICS values have meaning, that NICS(1)$_{zz}$ is an ac-

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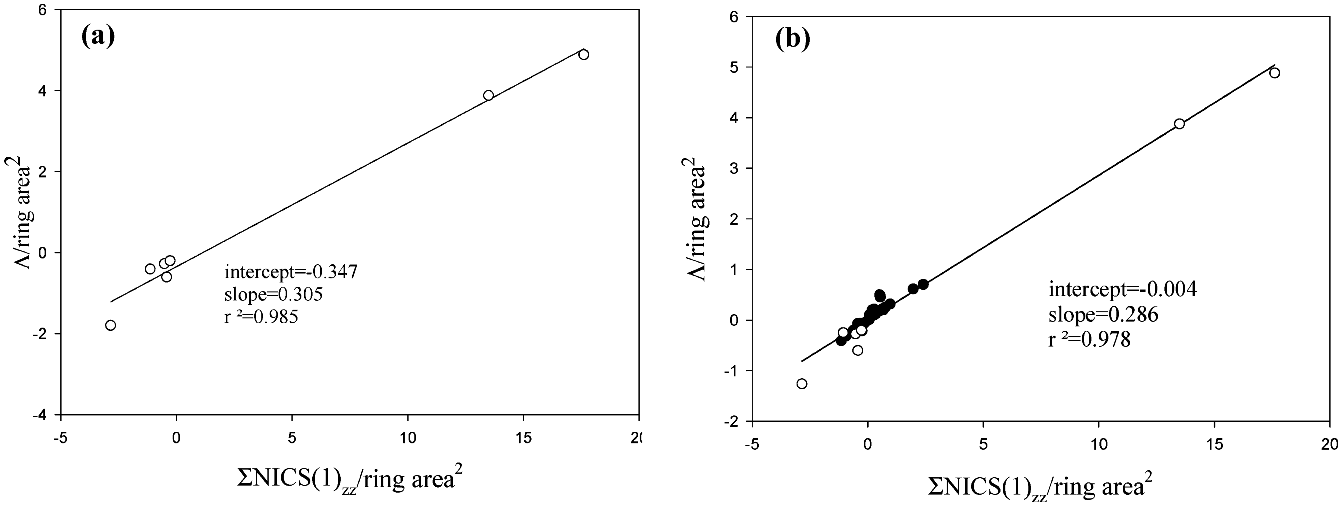

FIGURE 4. (a) Relationship between ∑NICS(1)$_{zz}$ and Λ as a function of ring area^2. Monocyclic species, **3**, **19**, **28**, **40**−**43**. (b) Monocyclic species and **3**−**39**, calculated as in Figure 1. Monocyclic species shown as open circles.

SCHEME 3

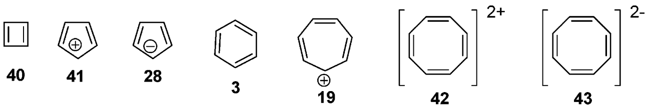

TABLE 3. NICS(1)$_{zz}$, X, and Λ for 3, 19, 28, and 40−43

	NICS(1)$_{zz}$[a]	X[b]	Λ[b]	ring area
3	−29.18	−52.90	−10.47	5.067
19	−26.49	−54.92	−13.81	7.111
28	−33.67	−52.03	−21.25	3.441
40	59.88	−11.09	17.20	2.106
41	204.93	33.88	60.84	3.530
42	−25.24	−58.34	−18.55	9.619
43	−39.84	−104.11	−56.70	9.701

[a] Calculated with the GIAO method at B3LYP/6-311+g(d,p). All geometries were optimized at B3LYP/6-31g(d). [b] Calculated with the CSGT method at B3LYP/6-311+g(d,p). All geometries were optimized at B3LYP/6-31g(d).

curate reflection of local aromaticity. Maps of induced current density show local as well as global patterns of delocalization for aromatic and antiaromatic species and have shown qualitative agreement with NICS values,[21,22,45,46] and the relationship discussed here shows that the agreement is quantitative.

Experimental Section

Calculation of NICS(1)$_{zz}$ and Λ. NICS(1)$_{zz}$ was calculated using the component of the magnetic shift tensor in the *z* direction, perpendicular to the plane of the ring, for a dummy atom 1 Å above the plane of the ring.[20] The recent work by Stanger[24] shows a minimum for NICS(1)$_{zz}$ at 1 Å above the plane of the ring for aromatic species, indicating the maximum amount of aromaticity and giving some support for this location. We have calculated NICS(1)$_{zz}$ using two basis sets, B3LYP/6-31g(d) and B3LYP/6-311+g(d,p) on geometries optimized at the B3LYP/6-31g(d) level. Geometries for hydrocarbons calculated with density functional theory at this level have been shown to agree well with experimental data.[47−49]

Magnetic susceptibility exaltation, Λ, is the difference between the calculated magnetic susceptibility, X, for the molecule of interest and that of a reference system. The reference system is formed by the summation of X for increments representing the bonds of the localized species. Details of the calculations can be found in the Supporting Information. In Table 1 are listed the values for the summation of NICS(1)$_{zz}$, X, and Λ for the species in Scheme 1. For some of the species, Λ had been calculated using other methods.[10,50,51] While the absolute values for Λ were not identical, presumably because of differences in the calculation method or basis set used, a plot of Λ from Table 1 versus Λ calculated by other methods showed good linearity, in general (see Supporting Information), thus giving some support to the quality of our calculations. In addition, Λ for pyrene, calculated with CSGT-B3LYP/6-31g(d)/B3LYP/6-31g(d) level but using a comparison of methyl-substituted isomers, gave good agreement with our results with the same basis set and method, −57.7 ppm cgs[52] compared to our value of −60.57 ppm cgs.

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Supporting Information Available: Details of the calculations; increment system for calculation of Λ; plot of Λ from Table 1 versus Λ calculated by other methods; plot of NICS(1)$_{zz}$ versus Λ

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for **3**−**27**, calculated at the B3LYP/6-31g(d) level; ring areas for **3**−**39**, ratio of ring areas by charge type; plot of NICS(1)$_{zz}$/ring area^2 versus Λ/ring area^2 for **3**, **19**, **28**, and **40**−**43**, calculated at B3LYP/6-311+g(3df,4p); table of able of NICS(1)$_{zz}$, Χ, and Λ for **3**, **18**, **28**, and **40**−**43**, calculated at the B3LYP/6-311+g-(3df,2p) level; calculated versus experimental ^{13}C NMR shifts, calculated at two levels; B3LYP/6-31g(d) and B3LYP/6-311+g(d,p); plot of calculated versus experimental ^{13}C NMR shifts at two levels; calculated total energies, and [*x*,*y*,*z*] coordinates for **3**−**43**. This material is available free of charge via the Internet at http://pubs.acs.org.

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