ORGANIC LETTERS

2001
Vol. 3, No. 16
2465−2468

Dissected Nucleus-Independent Chemical Shift Analysis of π-Aromaticity and Antiaromaticity

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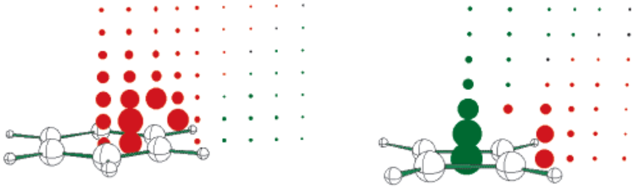
Received June 1, 2001

ABSTRACT



Analysis of the basic π-aromatic (benzene) and antiaromatic (cyclobutadiene) systems by dissected nucleus-independent chemical shifts (NICS) shows the contrasting diatropic and paratropic effects, but also reveals subtleties and unexpected details.

The magnetic behavior of cyclic conjugated π-electron systems is increasingly employed to access aromaticity and antiaromaticity.[1] The diamagnetic and paramagnetic effects of the ring currents associated with aromatic and antiaromatic compounds (i.e., shielding and deshielding of nuclei) are measured by a simple and efficient criterion viz. nucleus-independent chemical shift (NICS).[2] Since its introduction in 1996,[2] the "NICS" index is widely used to characterize aromaticity and antiaromaticity of rings,[3] clusters,[4] transition states,[5] transition metal complexes,[6] etc. with cyclically delocalized or localized electrons. NICS can now be computed with MNDO[3e] as well as ab initio and DFT methods. Based on computed magnetic shieldings, the NICS data are reported[2−6] with reversed signs in order to conform to the NMR chemical shift sign conventions (negative upfield and positive downfield). NICS are computed at selected points

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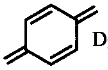
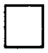
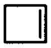
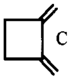
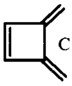
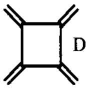
10.1021/ol016217v CCC: $20.00

Table 1. Dissected NICS (in ppm) at Ring Centers and 1 Å above at the PW91/IGLO−III//B3LYP/6-311+G** Level. Planar Geometries Were Employed for Uniformity and To Enforce σ,π-Separation

structure	ring	NICS(x) x	NICS (total)	CC(σ)	CC(π)	CH	core
1	 D_{6h}	0	-1.8	+6.6	-	-8.4	0.0
		1	-1.1	+1.8	-	-3.0	+0.1
2	 C_{2v}	0	-1.4	+8.1	-2.9	-6.6	0.0
		1	-1.0	+2.5	-0.8	-2.6	-0.1
3	 D_{2v}	0	+4.6	+11.9	-5.0	-2.0	-0.3
		1	+1.9	+2.8	+0.4	-1.2	-0.1
4	 D_{2h}	0	+2.5	+11.8	-7.6	-1.6	-0.1
		1	+0.3	+3.0	-1.6	-1.4	+0.3
5	 D_{2h}	0	+1.7	+13.0	-10.4	-0.4	-0.5
		1	-2.1	+1.8	-1.8	-2.0	-0.1
6	 D_{6h}	0	-8.8	+13.8	-20.7	-1.3	-0.6
		1	-10.6	+2.3	-9.6	-3.0	-0.3
7	 D_{4h}	0	+2.6	+15.2	-	-12.8	0.0
		1	+1.1	+2.4	-	-1.2	0.0
8	 C_{2v}	0	+0.9	+17.2	-10.0	-6.0	-0.4
		1	-2.1	+0.9	-1.5	-1.4	-0.2
9	 C_{2v}	0	+4.8	+17.9	-5.6	-7.6	+0.2
		1	-1.0	+0.9	+0.2	-1.6	0.0
10	 C_s	0	+2.6	+19.3	-13.1	-3.0	-0.3
		1	-2.6	-0.1	-1.0	-1.5	-0.2
11	 C_{2v}	0	+5.3	+20.6	-15.4	-0.8	-0.2
		1	-2.5	-0.5	+0.4	-2.2	-0.2
12	 D_{4h}	0	+7.8	+21.2	-14.0	+0.8	+0.4
		1	-2.2	-1.4	0.0	-0.8	0.0
13	 D_{2h}	0	+20.8	+23.2	-0.2	-1.6	-0.4
		1	+12.7	+1.5	+14.1	-2.8	0.0

inside or around molecules, typically at ring centers and above. Significantly negative (i.e., magnetically shielded) NICS values in interior positions of rings or cages indicate the presence of induced diatropic ring currents or "aromaticity” whereas positive values (i.e., deshielded) at each position denote paratropic ring currents and “antiaromaticity”.

In several sets of related molecules, NICS has been shown to correlate well with other aromaticity indexes based on geometric, energetic, and other magnetic criteria.[1b,2,7] Since NICS at a point in space is zero, NICS, in principle, has the advantage over other aromaticity criteria, in not requiring reference molecules, increment schemes, or calibrating (homodesmotic) equations for evaluation.[2] Unfortunately, NICS approaches being an “absolute” measure of cyclic electron delocalization only when the radii of the systems are relatively large, and hence “local shielding effects” are negligible.

As has been known since the early days of NMR, functional groups, e.g., olefins and acetylenes, as well as CH and CC single bonds, influence their magnetic environments.[8] Hence, it is not surprising that the local effects of the sigma CC and CH influence not only the benzene NICS but also result in nonzero NICS for nonaromatic, saturated, and unsaturated hydrocarbon rings.[9] For this reason, we have recommended that NICS(1) values, i.e., 1 Å above the ring centers, where the local contributions are diminished relative to the ring current effects, be employed as an aromaticity index, rather than NICS(0) (computed in the ring centers).[10] This point is reinforced in the present paper. A more refined

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analysis, "dissected NICS,[10]" based on Kutzelnigg's individual gauge for localized orbitals (IGLO) method,[9] reveals the individual contributions of bonds, lone-pairs, and core electrons to the total shielding of a molecule.[6,9,11] IGLO with the Pipek−Mezey localization procedure[12] (which separates σ and π multiple bond contributions) is applied here to compare benzene with other six-membered ring hydrocarbons[9] and to reveal the remarkable and unexpected magnetic behavior of cyclobutadiene[13] and its relationship with other four-membered ring structures.

The six- and four-membered ring structures in Table 1 were optimized at the B3LYP/6-311+G** DFT level[14] using the Gaussian 98 program.[15] Planar ring symmetries were imposed for interpretative simplicity, e.g., to enforce $\sigma-\pi$ separation, but NICS for the fully relaxed systems show no fundamental differences. NICS points were computed at 0.5 Å successions of points from the ring center or as grids of points (see Figures 1 and 2) using the Perdew−Wang-91 functional with the IGLO-III TZ2P basis set available in the deMon NMR program.[16]

With total NICS(0) of −1.4 to +4.6 ppm (Table 1), six-membered reference rings (**1**−**5**) are "nonaromatic". The paratropic CC(σ) contributions are largely canceled by the diatropic CC(π) and CH effects. Moreover, rough additivity is discernible for each type of contribution. Thus, NICS(π) increases with the increasing number of π-electrons from **1** to **5**. But benzene (**6**) is quite different. Instead of a NICS(π) of about −10 ppm, expected on the basis of additivity and the other examples in Table 1, the diamagnetic CC(π) contribution to **6** (Table 1) is exceptionally large (−20.7) and dominates the CC(σ) (+13.8) and CH (−1.8) contributions (which are in line with those of **1**−**5**). The resulting uniquely large diatropic total NICS(0) −8.8 denotes the aromaticity of **6**. This picture is consistent with the current density circulations diatropic for CC(π) and CH, but paratropic for CC(σ), shown by Fowler and others.[17]

The dissected contributions to NICS(1), 1 Å above the **1**−**6** rings, generally are smaller in magnitude (Table 1). But the diamagnetic CC(π) contribution of benzene (**6**) at NICS(1) remains unusually large (−9.6). Owing to this even more dominating diatropic π-influence, the total NICS(1) value (−10.6) actually is larger than NICS(0) (−8.8) for the benzene π-ring current.

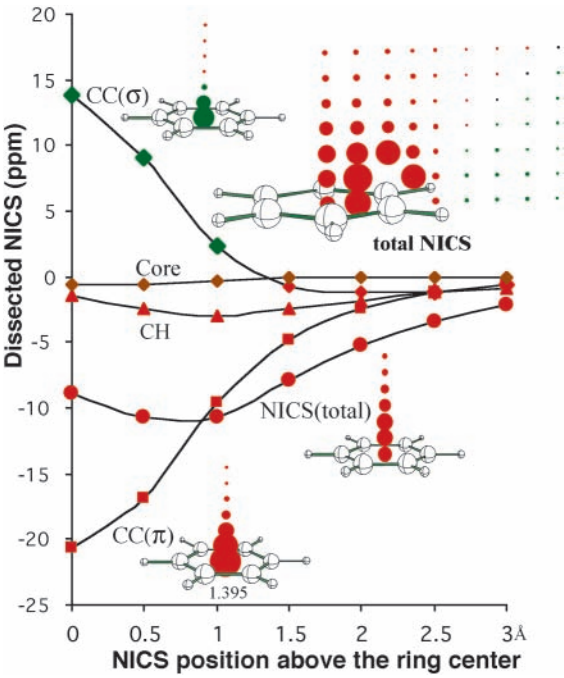
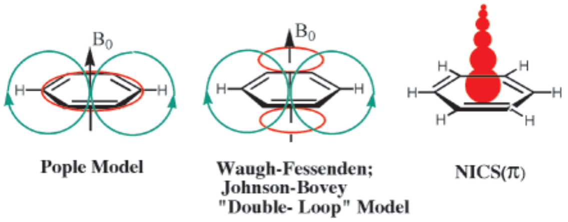


Figure 1. A plot of the various NICS contributions at the ring center of benzene and up to 3 Å above (also shown by the inserts). The red, green, and brown colors denote negative, positive, and near zero NICS values, respectively. A grid of total NICS points also is shown.

The dissection of NICS points above the ring center (Figure 1) further highlight the subtlety of the benzene ring current behavior. The paratropic CC(σ) curve drops off more rapidly than the diatropic CC(π) rises. Consequently, NICS(total) is diatropic. The nearly identical values of both NICS(1)$_{\pi}$ and NICS(1)$_{\mathrm{total}}$ document the effectiveness of NICS(1) to measure aromaticity.



The early "double dipole" or "double-loop" models,[18] based on the assumed maximum π-electron overlap effects above and below the ring, improved the quantitative predictions of Pople's point dipole model.[19] Such models have been revived recently[5b,e] on the basis of the greater NICS(total) values away from the ring center. Even though dissected NICS (see Figure 1) shows the π- contribution to be the greatest in the ring center, the "double loop model" also can fit this result (but only if the loops are not too far apart). However, the dissected NICS behavior of cyclobutadiene (see below) seems difficult to reconcile with double loop models. The shielding grid of NICS points in Figure 1 also reveals

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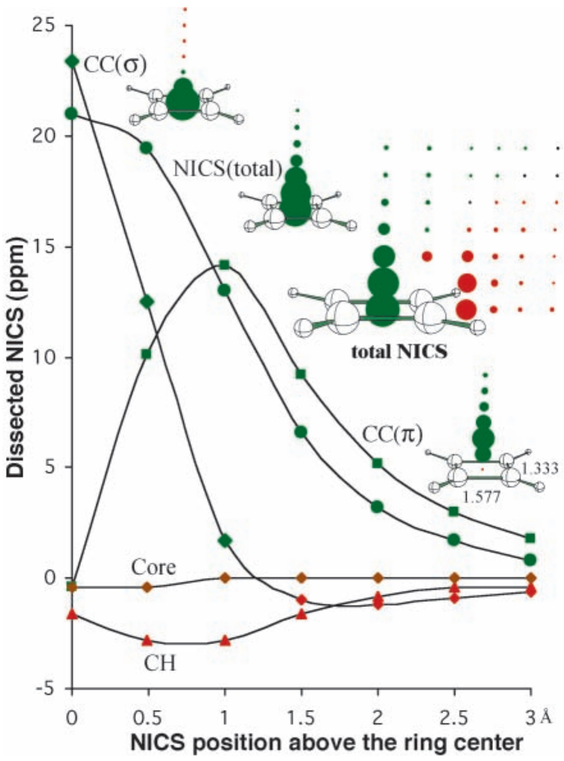

Figure 2. A plot of the various NICS contributions at the ring center of cyclobutadiene and up to 3 Å above (also shown by the inserts). The red, green, and brown colors denote negative, positive, and near zero NICS values, respectively. A grid of total NICS points also is shown.

the extent of the shielding zone, which extends farther from the ring center than predicted by the “Johnson−Bovey approximation.”[18b]

The magnetic behavior of cyclobutadiene (**13**) is quite different from benzene in some unexpected ways. Table 1 and Figure 2 show that the total NICS(0) is highly positive (paratropic), but that this is due to the CC(σ) rather than to the CC(π) contribution! The latter is almost exactly zero! The NICS(0) data for the four-membered reference rings (**7**−**12**) in Table 1 show that the large positive CC(σ) contributions are usual for four-membered rings, but tend to be balanced by the CH and CC(π) effects. The latter are roughly additive, −10 ppm for an endocyclic π-bond and −3 ppm for an exocyclic π-bond. On this basis, the cyclobutadiene π-effect is expected to be −20 ppm. Hence, the −0.2 NICS(0)$_\pi$ value (Table 1) really does indicate a strong but hidden paratropic influence. This is confirmed by the large paratropic NICS(0)$_\pi$ anisotropic component perpendicular to the ring which, fortuitously, is balanced by the diatropic components in the plane of the ring.

The NICS(1) behavior and that farther away from the ring center of cyclobutadiene (**13**) (Figure 2) follows expectations. The NICS(1)$_\pi$ and NICS(1)$_{\text{total}}$ are strongly paratropic and are almost the same (Figure 2). The CC(σ) and CH contributions become relatively small away from the ring center, but the π-contribution becomes quite positive (Table 1 and Figure 2).

In conclusion, the NICS(1)$_\pi$ and NICS(1)$_{\text{total}}$ values are nearly identical for both benzene and cyclobutadiene. On this basis and similar behavior generally, we recommended NICS(1) as being a better aromaticity diagnostic than NICS(0).[10] A detailed analysis shows that the unique near zero value of NICS(π) at the cyclobutadiene ring center is due to cancelation by large and opposite anistropic components. In fact, the paratropic π-effect in cyclobutadiene is much larger than that of any other four-membered ring. In a nutshell, the aromatic/antiaromatic ring currents reflect the extra π-effects that the molecules experience. These extra π-effects to NICS(0), evaluated by additivity comparisons from Table 1, are about −10 ppm (diatropic) for benzene and +20 ppm (paratropic) for cyclobutadiene.

Acknowledgment. We thank the University of Georgia for support, Dr. V. Malkin and Dr. O. L. Malkina for their version of the deMon IGLO program with the Pipek-Mezey localization implementation, and Dr. Michael Mauksch for discussions.

Note Added in Proof: Attention is called to a related paper: Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2*, in press.

OL016217V