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Local Aromaticities in Fullerenes as Estimated by the Bond Resonance Energy Model

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Local Aromaticities in Fullerenes as Estimated by the Bond Resonance Energy Model[#]

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Abstract

Small fullerenes exhibit large negative nucleus–independent chemical shift (NICS) values at the centers of many rings even if they are antiaromatic with negative topological resonance energies (TREs). This apparent contradiction was examined using the bond resonance energy (BRE) model. It was found that these diatropic rings consist of π–bonds with large negative BREs, which suggests that the negative NICS value does not always represent local aromaticity. π–Electron currents induced in circuits that surround more than one ring must contribute significantly to the NICS value at each ring center.

Keywords. Bond resonance energy (BRE); fullerene; local aromaticity; nucleus–independent chemical shift (NICS); ring current; topological resonance energy (TRE).

1 INTRODUCTION

In 1996, Schleyer *et al.* proposed a simple probe for local aromaticity: a nucleus–independent chemical shift (NICS) [1,2], which is defined as the negative of the magnetic shielding at some selected point in space, *e.g.*, at a ring center. In general, negative and positive NICS values are associated with aromatic and antiaromatic rings, respectively. NICS usually correlates with other criteria for aromaticity, such as energetic and geometric ones [1,2]. Hirsch *et al.* calculated the NICS values at the centers of fullerene cages and found that neutral and charged fullerenes with $2(N+1)^2$ π–electrons have large negative NICS values at the cage centers, suggesting that they must be highly aromatic [3,4]. Here, N is an arbitrarily chosen positive integer.

Topological resonance energy (TRE) has been utilized as one of the energetic criteria for aromaticity, which can be applied rather easily to cage molecules including fullerenes [5–8].

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.
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Positive and negative TREs indicate aromaticity and antiaromaticity, respectively. We recently noticed that neutral and charged fullerenes with $2(N + 1)^2$ π–electrons do not always have positive TREs even if they are highly diatropic at the cage centers [8]. It seems that spherical aromaticity in the π–system of a fullerene cannot be predicted from the NICS value calculated at the cage center.

We then are not sure that the NICS value calculated at the center of each ring in fullerene can be interpreted as a reasonable measure of local aromaticity in that place. In order to solve this problem, we examined whether or not the bond resonance energies (BREs) and π–bond orders for bonds around every ring are consistent with the NICS value at the ring center. The BRE represents the contribution of a given bond to the TRE [9–16]. We show below that NICS is not always suited for estimating the degree of local aromaticity.

2 THEORY

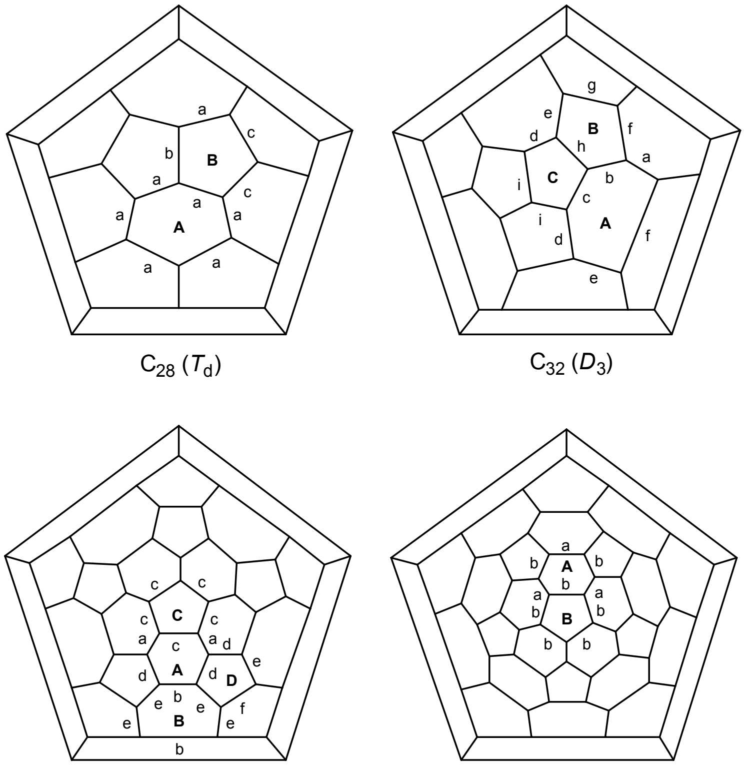
Both TRE and BRE are exactly defined within the framework of Hückel molecular orbital (HMO) theory. Reasonable values of TREs and BREs have so far been obtained for many fullerenes [5–16]. The fact that the $2(N + 1)^2$ rule holds true for all possible fullerenes [3,4] indicates that NICS is primarily determined by π–electronic structure. Haddon *et al.* showed that the Hückel–London model is suited for describing magnetic properties of fullerenes [17–19]. Thus, there is little doubt that HMO theory can be used to estimate energetic and magnetic properties of fullerenes in general.

The percentage TRE (%TRE) is useful for comparing the degrees of aromaticity in different molecules [5,6,8,12]. It is defined as 100 times the TRE, divided by the total π–binding energy of the polyene reference. C_{28} (T_d) alone is assumed to be in a quintet electronic state since it has quadruply degenerate highest occupied molecular orbitals [20]. The %TREs and NICS values relevant to the present study are available from the literature [5,6,20,21].

3 RESULTS AND DISCUSSION

Schlegel diagrams for four typical fullerenes studied are shown in Figure 1. The NICS values at the cage centers and the TREs for these molecules are listed in Table 1. The TRE for benzene is added for comparison's sake. In general, a larger fullerene molecule has a larger %TRE. As pointed out above, NICS values at the cage centers are not always related to the %TREs. Large negative NICS values at the cage centers of C_{32} (D_3) and C_{50} (D_{5h}) never indicate that they are highly aromatic [8]. They simply imply that these molecules have a closed–shell electronic configuration with $2(N+1)^2$ π–electrons [3,4].

NICS values at the ring centers for benzene and four fullerenes are presented in Table 2. The BREs and π–bond orders for all their non–identical π–bonds are given in Table 3. Here, a π–bond shared by *m*– and *n*–membered rings is denoted by *m*/*n*. Fullerenes that violate the isolated–pentagon rule have one or more 5/5 bonds. In general, the BREs for 5/5 bonds are less than –0.100 |β| [9–11]. It is noteworthy that bonds with large negative BREs have very small π–bond orders. We are now ready to examine the local aromaticities in individual rings of fullerenes.



C_{28} (T_d)

C_{32} (D_3)

C_{50} (D_{5h})

C_{60} (I_h)

Figure 1. Schlegel diagrams for four fullerenes.

Table 1. NICS Values at the Cage Centers and the %TREs for the Four Fullerenes in Figure 1. The %TRE for Benzene is Added for Comparison

Species	NICS	TRE / |β|	%TRE
benzene		0.273	3.53
C_{28} (T_d, quintet)	–13.0[a]	–1.219	–2.86
C_{32} (D_3, singlet)	–53.2,[a] –52.7[b]	–0.133	–0.27
C_{50} (D_{5h}, singlet)	–37.1,[a] –36.6[b]	0.708	0.93
C_{60} (I_h, singlet)	–11.2[b]	1.643	1.79

[a] Values at the GIAO–SCF/6–31*//B3LYP/6–31G* level [20]
[b] Values at the GIAO–SCF/DZP//BP86/3–21G level [21]

A polycyclic aromatic molecule has one or more diatropic rings [1,2]. Likewise, a polycyclic antiaromatic molecule is expected to have one or more paratropic rings. However, all rings in C_{28} (T_d) were found to be diatropic with negative NICS values although this molecule is highly antiaromatic with a %TRE of –2.86. All the bonds have negative BREs, indicating that all of them contribute significantly to antiaromaticity. Among them, 5/5 bonds, *i.e.*, bonds **b** and **c**, have very large negative BREs together with very small π–bond orders. 5/6 Bonds have smaller negative

BREs. Therefore, it seems that five–membered (5–MRs) and six–membered rings (6–MRs) in C_{28} (T_d) might be antiaromatic and aromatic, respectively. Small negative or positive BREs for 5/6 bonds possibly result from a cancellation of aromatic character of a 6–MR and antiaromatic one of an adjacent 5–MR. All rings in slightly antiaromatic C_{32} (D_3) exhibit diatropicity as well. However, bonds **g**, **h**, and **i** in this molecule, all of which are shared by two 5–MRs, have large negative BREs and very small π–bond orders. Therefore, at least rings **B** and **C** appear to be antiaromatic.

Table 2. NICS Values at the Ring Centers for Benzene and the Four Fullerenes in Figure 1. Values in Parentheses are the Number of Identical Rings. Five–Membered Rings are Denoted by Asterisks

species	A	B	C	D
benzene	–10.8 [a] (1)			
C_{28} (T_d, quintet)	–7.1 [a] (4)	–5.3 [a] (12*)		
C_{32} (D_3, singlet)	–26.36 [b] (6)	–21.51 [b] (6*)	–18.35 [b] (6*)	
C_{50} (D_{5h}, singlet)	–17.93 [b] (10)	–11.12 [b] (5)	–12.21 [b] (2*)	–6.71 [b] (10*)
C_{60} (I_h, singlet)	–6.61 [b] (20)	7.00 [b] (12*)		

[a] Values at the GIAO–SCF/6–31*//B3LYP/6–31G* level [20]
[b] Values at the GIAO–SCF/DZP//BP86/3–21G level [21]

Table 3. π–Bond Orders and BREs for Benzene and the Four Fullerenes in Figure 1

Species	bond	bond type	π–bond order	BRE / |β|
Benzene			0.667	0.273
C_{28} (T_d, quintet)	**a**	5/6	0.538	–0.080
	b	5/5	0.383	–0.162
	c	5/5	0.461	–0.175
C_{32} (D_3, singlet)	**a**	6/6	0.507	0.077
	b	5/6	0.572	0.004
	c	5/6	0.554	0.045
	d	5/6	0.502	0.020
	e	5/6	0.629	–0.033
	f	5/6	0.479	–0.002
	g	5/5	0.416	–0.131
	h	5/5	0.381	–0.217
	i	5/5	0.476	–0.133
C_{50} (D_{5h}, singlet)	**a**	6/6	0.625	0.100
	b	6/6	0.543	0.115
	c	5/6	0.460	0.026
	d	5/6	0.455	–0.035
	e	5/6	0.560	–0.070
	f	5/5	0.383	–0.308
C_{60} (I_h, singlet)	**a**	6/6	0.601	0.193
	b	5/6	0.476	0.082

It is evident that large negative NICS values at the ring centers of C_{28} (T_d) and C_{32} (D_3) cannot be viewed as indicators of local aromaticity. They are still indicative of diatropicity. A major fraction of such diatropicity in small fullerenes must be associated with diamagnetic currents induced in large circuits that enclose two or more rings [22–26]. Considering that odd–membered rings may contribute little to aromaticity [27,28], it must be reasonable to say that 5–MRs in C_{28} (T_d) and C_{32} (D_3) are antiaromatic or part of antiaromatic circuits. 6–MRs are presumably aromatic or more aromatic in general than 5–MRs. Fullerenes with less than 40 carbon atoms are antiaromatic with negative %TREs [5–7]. At least, C_{20} (I_h), C_{32} (D_{3d}), and C_{36} (D_{6h}) have negative NICS values at all ring centers [20]. All these NICS values do not reflect local aromaticity as in the case of C_{28} (T_d) and C_{32} (D_3).

C_{50} (D_{5h}) is slightly aromatic with a %TRE being about one–fourth that for benzene. All rings in this fullerene have larger negative NICS values than that for benzene. However, we cannot imagine that pentagonal ring **D** in C_{50} (D_{5h}) would be more aromatic than benzene since bond **f** has not only a very large negative BRE but also a very small π–bond order. All such 5/5 bonds must be part of antiaromatic circuits. It is probable that ring **D** is highly antiaromatic. Otherwise, the bond **f** must be shared by one or more larger highly antiaromatic circuits. All 6–MRs must be more or less aromatic since all 6/6 bonds have large positive BREs.

According to Haddon *et al.* [18,19], the ring currents in C_{60} (I_h) can be thought of as the superposition of two types of currents: currents induced in the individual rings and those circulating all around the molecule. The vanishingly small ring–current susceptibility for C_{60} (I_h) then results because of a compensating effect of strong paramagnetic currents induced in the 5–MRs and diamagnetic ones flowing around the molecule [18,19]. Therefore, it is quite likely that, for small fullerene molecules, π–electron currents induced along the equatorial belt of the molecule contribute much to not only the NICS value at the cage center but also those at the individual ring centers. Bühl also presumed that some fraction of the NICS value at the center of the fullerene cage might arise from currents induced in large circuits, in particular those around the perimeter of the cage [21].

For C_{60} (I_h) and higher fullerenes, the 5–MRs show local non– or antiaromatic character with small negative or positive NICS values [21]. The 6–MRs usually display notable local aromaticity with large negative NICS values. There also are 6–MRs with small negative or positive NICS values [21]. Typical such examples are the ones surrounded by six other 6–MRs. If all the seven 6–MRs are aromatic in nature, the diatropic current induced in the central 6–MR is totally or partially cancelled by those induced in the surrounding 6–MRs. In this case, a small negative or positive NICS value at the center of the central 6–MR will not represent local non– or anti–aromaticity.

The BRE model is free from this kind of difficulty. Most 6/6 bonds in higher fullerenes, such as bond **a** in C_{60} (I_h), have a large positive BRE value and a large π–bond order, indicating that all or most 6–MRs have aromatic character [9,10,14]. It is very true even for bonds that constitute 6–MRs surrounded by six other 6–MRs in fullerene molecules [14]. Two isolated–pentagon isomers of C_{78} fullerene have one or two such substructures. In contrast, most 5/6 bonds in higher fullerenes, such as bond **b** in C_{60} (I_h), have small positive or negative BREs, together with small π–bond orders, suggesting that the 5–MRs are non– or anti–aromatic [9,10,14]. In this context, Bühl noted that the central 6–MR in coronene, which is surrounded by six other 6–MRs, is apparently nonaromatic with a very small positive NICS value [21]. We presume that the central 6–MR in coronene is highly aromatic since the BREs for the bonds shared by the central and peripheral 6–MRs are as large as 0.219 |β| [12].

4 CONCLUSIONS

As has been seen, negative NICS values at the ring centers of fullerenes do not always represent local aromaticity. The BREs and π–bond orders can instead be used to roughly estimate the degree of local aromaticity. If a π–bond is shared by two aromatic rings, it will have not only a large positive BRE but also a large π–bond order. Conversely, if all π–bonds located around a given ring have large π–bond orders and large positive BREs, the ring must be highly aromatic. However, it is still true that the BRE is associated with aromaticities in many circuits that share the π–bond in question. π–Bond order is determined not only by local aromaticity but also by many other factors. In fact, local aromaticity is not a quantity that can be defined exactly for polycyclic π–systems. We have shown that we can obtain some meaningful information on the local aromaticities in fullerenes by carefully examining the BREs and π–bond orders for all the bonds.

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