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Spherical Aromaticity in Charged Fullerenes and the $2(N + 1)^2$ Rule

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Spherical Aromaticity in Charged Fullerenes and the $2(N + 1)^2$ Rule[#]

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Abstract

Motivation. Fullerene has a large negative NICS value at the cage center when its π shells are filled with $2(N + 1)^2$ electrons. Here, N is an arbitrary positive integer. However, it still seemed uncertain whether or not such a NICS value indicates spherical aromaticity.

Method. The TREs calculated for neutral and charged fullerenes with $2(N + 1)^2$ π -electrons were compared with the NICS values at their cage centers.

Results. Many such fullerene cages were found to have large negative TREs, suggesting that diatropicity at the cage center does not always represent aromaticity.

Conclusions. Pronounced diatropicity at the cage center must arise mainly from large circuits in the cage, whereas relatively small circuits must be responsible for large part of aromatic stabilization.

Keywords. Fullerene; aromaticity; spherical aromaticity; $2(N + 1)^2$ rule; NICS; TRE.

Abbreviations and notations

NICS, nucleus-independent chemical shift	$\delta(\text{endo})$, nucleus-independent chemical shift at the cage center
TRE, topological resonance energy	%TRE, percentage topological resonance energy

1 INTRODUCTION

In 1996, Schleyer *et al.* proposed a new magnetic criterion for 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. It has been repeatedly demonstrated that NICS is a useful indicator of aromaticity that usually correlates well with other criteria for aromaticity, such as energetic, geometric, and magnetic ones [1–4].

In 2000 Hirsch *et al.* calculated the NICS values at the centers of cage molecules and proposed the $2(N + 1)^2$ rule for them [5,6]. The π -electronic system of fullerene, a kind of cage molecule, can

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be depicted approximately as a spherical electron gas that surrounds the surface of a sphere. π Shells in this model are fully filled with $2(N + 1)^2$ electrons, where N is an arbitrary positive integer. They found that neutral and charged fullerenes with $2(N + 1)^2$ π -electrons have large negative NICS values at the cage centers, suggesting that these carbon cages must be highly aromatic [5–8].

Topological resonance energy (TRE) is a graph-theoretical index of aromaticity that can be applied to cage molecules such as fullerenes and *closo*-borane dianions [9–13]. Positive and negative TREs indicate aromaticity and antiaromaticity, respectively. *closo*-Borane dianions with positive TREs [13] were found to have negative NICS values at their cage centers [3]. This apparently supports the view that the NICS value might be a good measure of spherical aromaticity [14,15]. However, it still seemed uncertain that this is always true. In this paper, we show explicitly that spherical aromaticity in neutral and charged fullerenes cannot be predicted from the NICS values evaluated at their cage centers.

2 THEORY

No new theories were developed. TREs were calculated for eleven fullerene molecules and their molecular ions with $2(N + 1)^2$ π -electrons. Some of them have been reported so far [9–12]. The percentage TRE (%TRE) for a given molecule is defined as 100 times the TRE, divided by the total π -binding energy of the polyene reference [9–11]. This quantity is useful for comparing the degrees of aromaticity in different molecules. A NICS value at the center of a fullerene cage is denoted by $\delta(\text{endo})$ [16]. The $\delta(\text{endo})$ values relevant to the present study are available from the literature [7,16]. We can then check whether there is a reasonable correlation between the TRE and the $\delta(\text{endo})$ value for neutral and charged fullerenes.

3 RESULTS AND DISCUSSION

The TREs and the %TREs calculated for typical fullerenes are listed in Table 1, together with their ring spiral indices [17,18]. Those for the fullerene molecular ions with $2(N + 1)^2$ π -electrons are given in Table 2. As far as neutral fullerenes are concerned, a larger one has a larger % TRE [11,12]. Note that the %TRE of C_{60} (I_h), a prototype of fullerene, is half as large as that of benzene (3.53) [9]. Fullerene molecular anions and cations have larger and smaller TREs than the corresponding neutral species, respectively.

Randić pointed out that, for a polycyclic π -electronic system, large part of aromatic stabilization arises from relatively small circuits in it [19,20]. Contributions of individual circuits to aromaticity obey the Hückel rule [19,20]. In the case of neutral fullerenes, each hexagon bears about six π -electrons and must hence be aromatic. However, each pentagon bears about five π -electrons and must be antiaromatic or at best nonaromatic. Thus, fullerenes are electron-deficient molecules with

twelve pentagons [21]. As a result, a larger neutral fullerene molecule with more hexagons has a larger %TRE. Fullerenes with more than 40 carbon atoms are aromatic with positive %TREs [11,12].

Table 1. TREs and $\delta(\text{endo})$ Values for Neutral Fullerenes

species	ring spiral ^a	TRE / $ \beta $	%TRE	$\delta(\text{endo})$
C ₁₆ (<i>D</i> _{4d})	[1] 2 3 4 5 6 7 8 9 [10]	-1.318	-5.40	-1.1 ^b
C ₂₀ (<i>I</i> _h)	1 2 3 4 5 6 7 8 9 10 11 12	-1.096	-3.59	-36.7 ^b
C ₂₈ (<i>T</i> _d)	1 2 3 5 7 9 10 11 12 13 14 15	-1.219	-2.86	-13.0 ^b
C ₃₂ (<i>D</i> _{3d})	1 2 3 4 5 9 12 13 14 16 17 18	-0.621	-1.27	-39.3 ^b
C ₃₂ (<i>D</i> ₃)	1 2 3 5 7 9 10 12 14 16 17 18	-0.133	-0.27	-53.2 ^b
C ₃₆ (<i>C</i> _{2v})	1 2 3 4 11 12 13 14 15 16 17 18	-0.226	-0.41	-17.6 ^b
C ₃₆ (<i>D</i> _{2d})	1 2 4 7 9 10 12 13 14 16 18 20	-0.097	-0.18	-15.4 ^b
C ₄₀ (<i>D</i> ₂)	1 2 4 7 9 11 13 15 17 19 20 22	0.034	0.06	4.0 ^b
C ₄₀ (<i>D</i> _{5d})	1 2 4 7 9 11 13 15 18 19 21 22	0.136	0.22	2.8 ^b
C ₅₀ (<i>D</i> _{5h})	1 2 9 10 12 14 15 17 20 22 24 26	0.708	0.93	-37.1 ^b
C ₆₀ (<i>I</i> _h)	1 7 9 11 13 15 18 20 22 24 26 32	1.643	1.79	-11.2 ^c

^a Numbers in square brackets indicate the locations of square rings

^b Values at the GIAO-SCF/6-31G**/B3LYP/6-31G* level [7]

^c Value at the GIAO-SCF/DZP//BP86/3-21G level [16]

Table 2. %TREs and $\delta(\text{endo})$ Values for Neutral and Charged Fullerenes with $2(N + 1)^2$ π -Electrons

species	N_π	N_π / N_C	TRE / $ \beta $	%TRE	$\delta(\text{endo})$
C ₁₆ ⁸⁺ (<i>D</i> _{4d})	8	0.500	0.315	1.74	-58.6 ^a
C ₁₆ ²⁻ (<i>D</i> _{4d})	18	1.125	-0.105	-0.44	-32.7 ^a
C ₂₀ ²⁺ (<i>I</i> _h)	18	0.900	-0.733	-2.43	-73.1 ^a
C ₂₈ ⁴⁺ (<i>T</i> _d)	32	1.143	1.327	3.18	-35.5 ^a
C ₃₂ (<i>D</i> _{3d})	32	1.000	-0.621	-1.27	-39.3 ^a
C ₃₂ (<i>D</i> ₃)	32	1.000	-0.133	-0.27	-53.2 ^a
C ₃₆ ⁴⁺ (<i>C</i> _{2v})	32	0.889	-1.052	-1.94	-57.9 ^a
C ₃₆ ⁴⁺ (<i>D</i> _{2d})	32	0.889	-1.051	-1.94	-64.0 ^a
C ₄₀ ⁸⁺ (<i>D</i> ₂)	32	0.800	-1.533	-2.63	-62.1 ^a
C ₄₀ ⁸⁺ (<i>D</i> _{5d})	32	0.800	-1.682	-2.88	-82.2 ^a
C ₅₀ (<i>D</i> _{5h})	50	1.000	0.708	0.93	-37.1 ^a
C ₆₀ ¹⁰⁺ (<i>I</i> _h)	50	0.833	-1.800	-2.03	-81.4 ^b

^a Values at the GIAO-SCF/6-31G**/B3LYP/6-31G* level [7]

^b Value at the GIAO-SCF/3-21G//B3LYP/6-31G* level [7]

If a fullerene molecule bears a negative charge, constituent pentagons are more or less aromatized. Therefore, smaller fullerene molecules with fewer hexagons, such as C₁₆ (*D*_{4d}) and C₂₈ (*T*_d), increase the %TRE markedly by acquiring one or more π -electrons [11]. Conversely, fullerene decreases the %TRE by losing one or more π -electrons. If the ratio of the number of π -electrons to that of carbon atoms is close to 0.4 or 1.2, each constituent pentagon will bear about two or six π -electrons, respectively, and must be highly aromatic. Squares in C₁₆⁸⁺ (*D*_{4d}) must be aromatic with about two π -electrons. For C₆₀ (*I*_h), the %TRE remains fairly large on going up to the dodecaanion [22]. This is a result of compensation between the dearomatization of twenty hexagons and the

aromatization of twelve pentagons. Thus, the sign and the magnitude of the %TRE can roughly be explained in terms of the charges which reside on individual rings.

We are now ready to compare the %TRE with the $\delta(\text{endo})$ value for fullerene cages. The $\delta(\text{endo})$ values for typical fullerenes and their molecular ions are added in Tables 1 and 2, respectively. It is noteworthy that the sign of the %TRE is often the same as that of the $\delta(\text{endo})$ value. If $\delta(\text{endo})$ is really an indicator of spherical aromaticity, its value must be different in sign from the TRE or the %TRE. In fact, many small neutral fullerenes have negative TREs but have negative $\delta(\text{endo})$ values, which implies that many antiaromatic fullerenes are paratropic at the center of the cage. Many fullerene cations also have large negative $\delta(\text{endo})$ values although they have negative %TREs.

For example, two C_{32} isomers and C_{50} (D_{5h}) have $2(N + 1)^2$ π -electrons with $N = 4$ and 5 , respectively. The two C_{32} isomers have large negative $\delta(\text{endo})$ values but negative %TREs. C_{50} (D_{5h}) happens to have a large negative $\delta(\text{endo})$ value and a positive %TRE. Therefore, we can safely say that the $2(N + 1)^2$ rule is irrelevant to spherical aromaticity in neutral fullerenes. The same is true for charged fullerenes. All fullerene ions in Table 2 have large negative $\delta(\text{endo})$ values presumably because they have $2(N + 1)^2$ π -electrons. However, only two of them, C_{16}^{8+} (D_{4d}) and C_{28}^{4-} (T_d), have positive TREs. All other ionic species are antiaromatic with negative %TREs. Thus, it is obvious that $\delta(\text{endo})$ cannot be used as an indicator of aromatic stabilization.

Such a lack of correlation between the %TRE and $\delta(\text{endo})$ must be attributed to the fact that large circuits, which enclose large areas, contribute slightly to the TRE but much to magnetic properties [23,24]. This must be the primary reason why $\delta(\text{endo})$ does not represent the degree of aromaticity in fullerenes. Many large circuits can be chosen from a fullerene π -electronic system. Large negative $\delta(\text{endo})$ values for antiaromatic species must arise from many large diatropic circuits. Bühl pointed out that $\delta(\text{endo})$ can roughly be estimated by summing up the NICS value over all rings [16]. This aspect of the $\delta(\text{endo})$ value is not inconsistent with our interpretation based on the sizes of circuits. A current induced in each bond is given as a superposition of currents induced in many circuits [25,26].

The situation with kekulene is somewhat similar to that with fullerenes. This hydrocarbon is unambiguously aromatic with a large %TRE of 2.34 [27]. Jiao and Schleyer found that the NICS values in individual six-membered rings are all negative in sign, indicating that all these rings are aromatic [2]. However, the value at the center of the cavity is +5.3 at the GIAO-SCF/3-21G//B3LYP/6-31G* level of theory. There is no doubt that this positive NICS value does not represent the high aromaticity in kekulene itself. This value instead may reflect the degree of superaromaticity due to many macrocyclic circuits that enclose the central cavity [2,28]. Likewise, the large negative $\delta(\text{endo})$ values for fullerenes may arise from many large circuits in them.

4 CONCLUSIONS

$\delta(\text{endo})$ has been very useful for analyzing local aromaticities in polycyclic π -electronic systems [1–4]. However, we found that the sign and the magnitude of $\delta(\text{endo})$ are not suited for estimating the degree of spherical aromaticity in cage molecules. Fullerenes are electron-deficient in nature [21]. Therefore, realistic fullerene cations must be much less aromatic than the neutral species even if they have large negative $\delta(\text{endo})$ values. It is still true that the $2(N + 1)^2$ rule can be used to rationalize the high diatropicity at the center of a cage molecule with $2(N + 1)^2$ electrons. Fullerenes not satisfying this rule, such as $C_{20}(I_h)$, may likewise have large negative $\delta(\text{endo})$ values.

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