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Spherical Aromaticity in Fullerenes and the Nucleus-Independent Chemical Shifts at the Cage Centers

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Nucleus-independent chemical shifts (NICSs) at the cage centers for closed-shell isolated-pentagon isomers of C_{82} fullerene lie in the wide range from -11 to $+48$ although all of the isomers are sufficiently aromatic. This decisively shows that NICS cannot be used as an indicator of spherical aromaticity for fullerenes. NICS is nothing other than the measure of local magnetotropicity. Diatropicity is compatible with aromaticity only for monocyclic π-systems.

In 1996, Schleyer et al. proposed a simple probe for local aromaticity: a nucleus-independent chemical shift (NICS),[1] which is defined as the negative of the magnetic shielding at some selected point in space. In general, negative and positive NICS values are associated with aromatic and antiaromatic rings, respectively. NICS often correlates with other criteria for aromaticity, such as energetic and geometric ones.[1,2] NICS has also been used as an indicator of spherical aromaticity in cage molecules.[3–6] 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, suggesting that they must be highly aromatic.[4,5] Here, N is the arbitrarily chosen positive integer.

Aromaticity is attributable to the extra stabilization energy due to cyclic conjugation.[7] Hess–Schaad resonance energy (HSRE)[8,9] and topological resonance energy (TRE)[10–15] were defined on this basis and have been utilized as energetic criteria for aromaticity. Positive and negative values of these resonance energies indicate aromaticity and antiaromaticity, respectively. TRE can be evaluated not only for neutral but also for charged fullerenes.[12–15] We 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.[16] It seems that spherical aromaticity in a fullerene π-system cannot always be predicted from the NICS value at the cage center.

However, there still is some possibility that the absence of relationship between NICS and spherical aromaticity might be limited to relatively small fullerene molecules and molecular ions since we have so far focused on their aromatic character.[16] In 2001, Chen et al. reported NICS values at the cage centers of many large fullerene molecules with up to 86 carbon atoms.[17] We were then taught that even NICS values for large fullerene molecules vary widely. We show below that these NICS values cannot be used as indicators of aromaticity and antiaromaticity.

Theory

TRE and HSRE are defined using Hückel molecular orbital (HMO) theory and were found to be highly correlative with chemical reactivity for a variety of π-electronic systems.[8–11] This implies not only that many aromatic and antiaromatic molecules are kinetically stable and unstable, respectively, but also that both TRE and HSRE are reasonable measures of aromaticity. The fact that the $2(N+1)^2$ rule of diatropicity hold for all possible fullerenes[4,5] indicates that NICS is primarily determined by the number of π-electrons and that there indeed are what can be called π-electrons in these molecules. The Hückel-London formulation of ring-current susceptibility[18] reasonably describes magnetic properties of fullerenes.[18,19] Thus, there is little doubt that HMO theory can be used to estimate π-electronic structure of fullerenes in general. The NICS values relevant to the present study are available from the literature.[17]

Results and Discussion

C_{82} fullerene has nine isolated-pentagon isomers.[21] The NICS values at their cage centers and some related quantities are summarized in Table 1. Isomer numbers are those proposed by Fowler and Manolopoulos.[21] Relative energy and the NICS value for isomer **7** are missing in this table because it is an open-shell species.[17] Only the lowest-energy isomer **3** has been extracted from the fullerene soot.[22] It is noteworthy that the NICS values for the eight isomers lie in the range of from -11 to $+48$.[17] According to the original interpretation of NICS,[1] some isomers must be antiaromatic with positive NICS values while others must be aromatic with negative NICS values.

HSRE is a simple but practical measure of aromaticity.[8] C_{60} (I_h) has a HSRE of 1.87 $|\beta|$.[9] In general, a larger fullerene molecule has a larger HSRE. As seen from Table 1, HSREs for C_{82} isomers studied are all positive in sign. TRE is not easy to evaluate for large fullerene molecules.[15] We found that the π-binding energy per carbon atom is almost constant for the polyene references of many fullerenes. This energy may be called a unit reference energy. For example, the unit reference energy is 1.5252 $|\beta|$ for C_{60} (I_h) and 1.5254 $|\beta|$ for C_{70} (D_{5h}).[12–15] These values are slightly larger than that obtained using Hess and Schaad's additive π-bond energy scheme (1.5216 $|\beta|$).[9] The quasi-TREs calculated using the unit refer-

Table 1. NICS Values and Resonance Energies for Isolated-Pentagon Isomers of C_{82} Fullerene

Isomer number	Relative energy/ kcal mol^{-1} a)	NICS b)	HSRE/$\|\beta\|$	quasi-TRE/$\|\beta\|$	HOMO–LUMO gap/eV a)
1	7.8	−7.1	3.13	2.83	1.25
2	6.7	−11.2	2.85	2.55	1.64
3	0.0	−10.6	2.76	2.46	1.56
4	3.9	−10.3	2.67	2.37	1.56
5	8.3	−7.5	2.51	2.22	1.29
6	12.2	−3.6	2.37	2.07	1.11
7	—	—	2.48	2.18	—
8	30.8	48.3	2.20	1.90	0.75
9	18.3	6.2	2.23	1.94	0.75

a) Relative total energies at the B3LYP/6-31G* level of theory.[17]
b) NICS values at the GIAO-SCF/3-21G//B3LYP/6-31G* level of theory.[17]

ence energy for C_{60} (I_h) are added in Table 1. These quasi-TREs again indicate that all isomers of C_{82} have large aromatic stabilization energies. C_{60} (I_h) has a TRE of 1.64 $|\beta|$.[12–14] TRE is positive in general for fullerenes with more than 40 carbon atoms.[13,14]

It is noteworthy that isomer **8** of C_{82} is higher in energy than any other closed-shell isomers[17] but has a fairly large positive HSRE and a fairly large positive quasi-TRE. The Schlegel diagram for this isomer is shown in Fig. 1. Even open-shell isomer **7** has a large positive HSRE and a large positive quasi-TRE. In fact, incompletely occupied molecular orbitals in this isomer are low in energy. Besides this C_{82} isomer, isomer **2** of C_{76} and isomers **6** and **7** of C_{80} have open-shell electronic configurations; these isomers likewise have fairly large positive HSREs of 2.02, 2.06, and 1.78 $|\beta|$, respectively. Their quasi-TREs can be obtained simply by subtracting 0.0036 $|\beta|$ times the number of carbon atoms from their respective HSREs.

The conjugated circuit theory[23–27] also supports the above view that large fullerene molecules are aromatic without exceptions. As the size of a fullerene cage increases, the number of hexagons increases monotonously, with the number of pentagons always being twelve. Considering that small $(4n + 2)$-membered conjugated circuits are the main origin of aromaticity,[23,24,28] one may quite reasonably suppose that larger fullerene molecules have aromatic character. As illustrated in Fig. 1, isolated-pentagon isomers of large fullerenes have many benzene rings but no highly antiaromatic substructures, such as cyclobutadiene- and pentalene-like ones. Therefore, the conjugated-circuit resonance energies (CCREs) calculated by Liu et al.[27] are positive in sign and large in magnitude. Even the open-shell isomer **7** has a large CCRE. Thus, there are no reasons to deny that all isolated-pentagon isomers of C_{82} fullerene are aromatic.

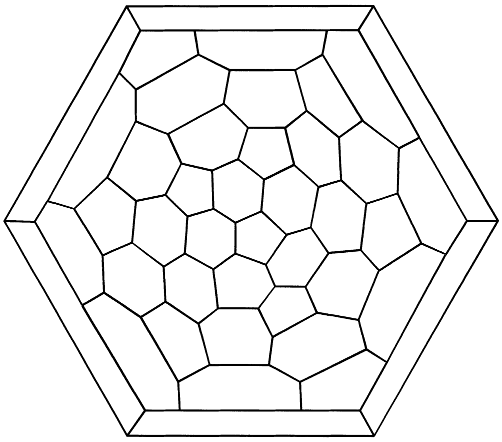

Fig. 1. Schlegel diagram for isomer **8** of C_{82} fullerene.

We can now safely say that isomers **8** and **9** of C_{82} are really aromatic although they have positive NICS values.[17] This convinced us that the NICS value at the cage center is not related directly to aromaticity and therefore cannot be used as an indicator of spherical aromaticity for fullerenes. Like chemical shifts of protons attached to aromatic nuclei, the NICS value should be regarded as an indicator of local magnetotropicity. The negative NICS value simply indicates that the species concerned is diatropic at the cage center.[16] As stated above, aromaticity is determined primarily by small conjugated circuits,[23,24,28] whereas magnetotropicity is determined not only by small circuits but also by larger circuits that enclose larger areas.[29–33] Bühl presumed that some fraction of the NICS value at the cage center might arise from currents induced in large circuits and those around the perimeter of the cage in particular.[3]

According to Pasquarello et al.,[19,20] 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 small ring-current susceptibility for C_{60} (I_h) results because of a compensating effect of strong paramagnetic currents induced in the five-membered rings and diamagnetic ones flowing around the molecule.[19,20] Therefore, it is quite likely that, for many 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 to the values at the individual ring centers. At least, large negative NICS values at the cage centers of $C_{60}{}^{6-}$ (I_h) and C_{70} (D_{5h}) are attributable to large diatropic currents induced along the equatorial belts.[20] However, circuits that can be chosen along the equator must contribute little to aromatic stabilization since they are large in size.[23,24,28]

In general, the ring-current susceptibility is very sensitive to the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap. π-Systems with very small HOMO–LUMO gaps, such as $[4n]$annulenes, are paratropic in nature.[34] As can be seen from Table 1, the NICS value is likewise correlative with the HOMO–LUMO energy gap. Two C_{82} isomers with positive NICS values have very small HOMO–LUMO gaps, which are supposed to be closely associated with paramagnetic ring currents induced in some or many circuits. Isolated-pentagon isomers **8** and **9** of C_{86} fullerene likewise have positive NICS values of 6.1 and 24.8, respectively, at the cage centers.[17] They are of course aromatic but have fairly small HOMO–LUMO energy gaps.

Concluding Remarks

NICS is indeed meaningful for determining the degree of aromaticity in monocyclic π-systems.[1,2] However, global aromaticity in a polycyclic π-system cannot be estimated from the NICS values. A negative NICS value at the cage center of fullerene represents neither global nor local aromaticity in the molecule. We recently found that even for planar polycyclic aromatic hydrocarbons NICS cannot always be used as an indicator of local aromaticity.[35] It always indicates diatropicity. Only for monocyclic π-systems is diatropicity compatible with aromaticity.[36] The HSRE and the quasi-TRE defined above can be used to estimate the degree of aromaticity for large fullerene molecules. Whatever the NICS values might be at the cage centers, all isolated-pentagon isomers of large fullerenes are aromatic with large positive HSREs and large positive quasi-TREs. However, most of them have not been isolated from the fullerene soot since they are kinetically very unstable.[37] As pointed out previously,[37,38] aromatic fullerene molecules are not always kinetically stable.

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References

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

2 S. Patchkovskii and W. Thiel, *J. Mol. Model.*, **6**, 67 (2000), and many references cited therein.

3 M. Bühl, *Chem. Eur. J.*, **37**, 734 (1998).

4 A. Hirsch, Z. Chen, and H. Jiao, *Angew. Chem. Int. Ed.*, **39**, 3915 (2000).

5 Z. Chen, H. Jiao, and A. Hirsch, *J. Mol. Model.*, **7**, 161 (2001).

6 Z. Chen, H. Jiao, M. Bühl, A. Hirsch, and W. Thiel, *Theor. Chem. Acc.*, **106**, 352 (2001).

7 V. I. Minkin, M. N. Glukhovtsev, and B. Ya. Simkin, "Aromaticity and Antiaromaticity: Electronic and Structural Aspects," Wiley-Interscience, New York (1994).

8 B. A. Hess Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971).

9 B. A. Hess Jr. and L. J. Schaad, *J. Org. Chem.*, **51**, 3902 (1986).

10 J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976).

11 I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977).

12 J. Aihara and H. Hosoya, *Bull. Chem. Soc. Jpn.*, **61**, 2657 (1988).

13 J. Aihara, *J. Mol. Struct. (Theochem)*, **311**, 1 (1994).

14 M. Manoharan, M. M. Balakrishnarajan, P. Venuvanalingam, and K. Balasubramanian, *Chem. Phys. Lett.*, **222**, 95 (1994).

15 D. Babić and O. Ori, *Chem. Phys. Lett.*, **234**, 240 (1995).

16 J. Aihara, *Internet Electron. J. Mol. Des.*, **1**, 236 (2002), [www.biochempress.com/av01_0236.html].

17 Z. Chen, J. Cioslowski, N. Rao, D. Moncrieff, M. Bühl, A. Hirsch, and W. Thiel, *Theor. Chem. Acc.*, **106**, 364 (2001).

18 F. London, *J. Phys. Rad.*, **8**, 397 (1937).

19 A. Pasquarello, M. Schlüter, and R. C. Haddon, *Science*, **257**, 1660 (1992).

20 A. Pasquarello, M. Schlüter, and R. C. Haddon, *Phys. Rev. A*, **47**, 1783 (1993).

21 P. W. Fowler and D. E. Manolopoulos, "An Atlas of Fullerenes," Clarendon Press, Oxford (1995).

22 K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, and Y. Achiba, *Nature*, **357**, 142 (1992).

23 W. C. Herndon and M. L. Ellzey Jr., *J. Am. Chem. Soc.*, **96**, 6631 (1974).

24 M. Randić, *J. Am. Chem. Soc.*, **99**, 444 (1977).

25 T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, *J. Am. Chem. Soc.*, **110**, 1113 (1988).

26 X. Liu, T. G. Schmalz, and D. J. Klein, *Chem. Phys. Lett.*, **188**, 550 (1992).

27 X. Liu, D. J. Klein, and T. G. Schmalz, *Fullerene Sci. Technol.*, **2**, 405 (1994).

28 H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37 (1975).

29 J. Aihara, *J. Am. Chem. Soc.*, **101**, 5913 (1979).

30 J. Aihara, *J. Am. Chem. Soc.*, **103**, 5704 (1981).

31 J. Aihara, *Pure Appl. Chem.*, **54**, 1115 (1982).

32 J. Aihara and T. Horikawa, *Bull. Chem. Soc. Jpn.*, **56**, 1853 (1983).

33 J. Aihara, *J. Am. Chem. Soc.*, **107**, 298 (1985).

34 J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966).

35 J. Aihara, *Chem. Phys. Lett.*, **365**, 34 (2002).

36 J. Aihara and H. Ichikawa, *Bull. Chem. Soc. Jpn.*, **61**, 223 (1988).

37 J. Aihara, *Bull. Chem. Soc. Jpn.*, **72**, 7 (1999).

38 J. Aihara, *Theor. Chem. Acc.*, **102**, 134 (1999).