Bull. Chem. Soc. Jpn., 77, 101–102 (2004)

Incorrect NICS-Based Prediction on the Aromaticity of the Pentalene Dication

Jun-ichi Aihara

Department of Chemistry, Faculty of Science,
Shizuoka University, Oya, Shizuoka 422-8529

Received August 21, 2003; E-mail: scjaiha@ipc.shizuoka.ac.jp

Nucleus-independent chemical shift (NICS) values do not always reflect aromaticity. The pentalene dication exhibits large negative NICS values at the two ring centers although it is antiaromatic with a large negative topological resonance energy (TRE).

In 1996, Schleyer et al. proposed a new magnetic criterion for aromaticity: a nucleus-independent chemical shift (NICS),[1] which is defined as the negative of the magnetic shielding at some selected point in space, e.g., at a ring center. Positive and negative NICS values indicate paratropicity and diatropicity, respectively, and hence have been referred to as indicators of local aromatic character.[1,2] However, we recently noticed that NICS values do not always represent the local aromaticities of polycyclic π-systems.[3,4] In this short article, we show that the NICS concept makes an incorrect prediction on the aromaticity of the pentalene dication.

Our graph-theoretical variant[4–7] of Hückel–London theory[8] was employed to evaluate the π-electron currents induced in neutral and charged pentalene π-systems. The two rings in pentalene were assumed to be regular pentagons in shape. Current density maps thus obtained for pentalene and its molecular ions are graphically summarized in Fig. 1, where counterclockwise and clockwise arrows denote diamagnetic and paramagnetic currents, respectively. At the limit of zero magnetic field, the overall π-electron current is given as a superposition of circuit currents, i.e., currents induced independently in the individual circuits of the π-system.[6,7] There are one eight-membered and two five-membered circuits in the pentalene π-system.[6] All circuit currents induced in neutral and charged pentalene π-systems are presented in Fig. 2.

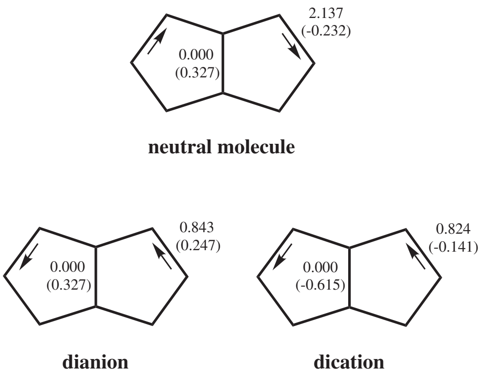

Fig. 1. π-Electron currents induced in pentalene and its divalent molecular ions, all in units of that for benzene. Values in parentheses are bond resonance energies (BREs) in units of $|\beta|$.

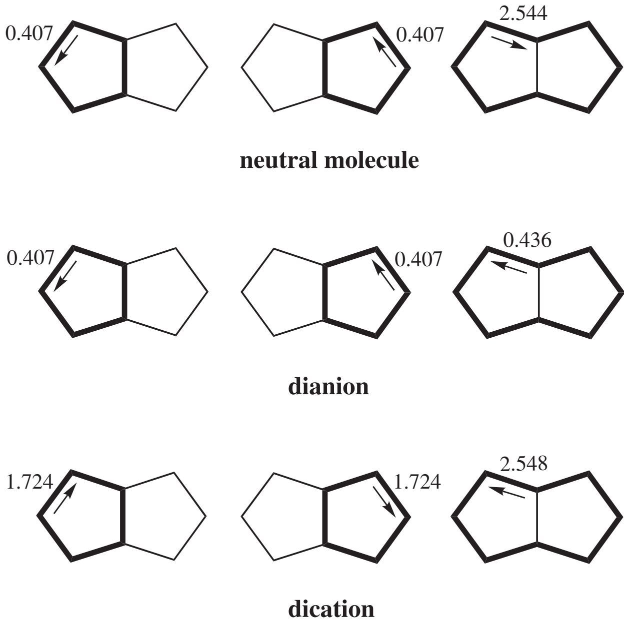

Fig. 2. Circuit currents induced in pentalene and its divalent molecular ions, all in units of that for benzene.

Neutral pentalene is highly antiaromatic, with a negative TRE of -0.215 $|\beta|$.[5,9] Here, β is a standard resonance integral for C–C π bonds. The two five-membered rings in this molecule are paratropic with a positive NICS value of 18.2,[2] which is apparently consistent with the negative TRE. In fact, this hydrocarbon is extremely reactive although it has been prepared.[10] As seen from Fig. 2, the two five-membered circuits of neutral pentalene are weakly diatropic. It is the peripheral eight-membered circuit that is highly paratropic. This circuit is primarily responsible for the large positive NICS value at the center of each five-membered ring.

The pentalene dianion is iso-π-electronic with naphthalene, and is highly aromatic with a positive TRE of 0.478 $|\beta|$.[5,9] Since all three circuits are diatropic and presumably aromatic, the negative NICS value for each ring (-11.7)[2] can naturally be attributed to all these circuits. Indeed, the dianion was synthesized in 1962.[11] In contrast, the pentalene dication is iso-π-electronic with extremely reactive butalene.[12] This dication is highly antiaromatic, with a large negative TRE of -0.464 $|\beta|$, which explains the fact that it has not been synthesized yet. Nevertheless, it has large negative NICS values at the two ring centers (-11.6).[2] As shown in Fig. 2, the five-membered circuits in the dication are paratropic, but the peripheral eight-membered one is highly diatropic. It is obvious that the negative NICS values arise from a partial cancellation of the diamagnetic current induced in the eight-membered circuit by paramagnetic ones induced in the five-membered circuits.

This magnetotropic aspect of the pentalene dication can be justified in the following manner. Since six π-electrons reside

Published on the web January 13, 2004; DOI 10.1246/bcsj.77.101

along the eight-membered circuit, it must be aromatic and diatropic in nature. Two five-membered circuits must be antiaromatic and paratropic because ca. four π-electrons reside along each of them. As pointed out repeatedly,[5–7] the intensity of a circuit current is proportional to the area of the circuit. Therefore, an intense current induced in the eight-membered circuit is due partly to its large area. It then follows that the current induced in the eight-membered circuit dominates the peripheral π-electron current. This is why an antiaromatic pentalene dication exhibits negative NICS values.

Interestingly, the peripheral bond length variation in the dication (0.049 Å) is much smaller than that of the neutral species (0.118 Å).[2] However, this cannot be viewed as structural evidence for aromaticity since charged species tend to suppress bond localization.[13] A peripheral eight-membered circuit with six π-electrons but without marked bond localization is favorable to the stabilization of the entire π system. A central C–C π bond in the dication is predicted to be extraordinarily long, with a length of 1.541 Å.[2] Elongation of this bond is necessary to decrease antiaromaticity due to two five-membered circuits. Even if so, the $2p_z$–$2p_z$ overlap integral for a C–C π bond with a length of 1.541 Å is still 0.78 time as large as those for the benzene C–C π bonds,[14] so the pentalene dication remains antiaromatic.

Calculated bond resonance energies (BREs) added in Fig. 1 support the above interpretation of aromaticity and magnetotropicity. BRE represents the contribution of a given π bond to the topological resonance energy (TRE).[9,15] As for neutral pentalene, large negative BREs for the peripheral C–C π bonds indicate that this molecule is antiaromatic, whereas a large positive BRE for the central C–C π bond suggests that this bond or two five-membered circuits tend to decrease antiaromaticity due to the eight-membered circuit. BREs for all C–C π bonds in the dianion are positive in sign and consistent with our view that all the circuits contribute to aromaticity. The pentalene dication is in an opposite situation to the neutral species. A large negative BRE for the central C–C π bond indicates that two five-membered circuits must be highly antiaromatic. Therefore, smaller negative BREs for the peripheral C–C π bonds suggest that the eight-membered circuit is aromatic. Thus, the signs of BREs are fully consistent with the magnetotropicity of individual circuits in neutral and charged pentalene π-systems.

In summary, the conventional interpretation of NICS values may sometimes give a misleading picture of a polycyclic π-system.[3,4] As in the case of the pentalene dication, negative NICS values at all ring centers do not always mean that the entire π-system is aromatic.

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 T. K. Zywietz, H. Jiao, P. v. R. Schleyer, and A. Meijere, *J. Org. Chem.*, **63**, 3417 (1998).

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

4 J. Aihara and S. Oe, *Bull. Chem. Soc. Jpn.*, **76**, 1363 (2003).

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

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

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

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

9 J. Aihara, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 2185.

10 K. Hafner, *Nachr. Chem. Technol. Lab.*, **28**, 222 (1980).

11 T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

12 R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975).

13 G. Binsch and E. Heilbronner, "Structural Chemistry and Molecular Biology," ed by A. Rich and N. Davidson, W. H. Freeman, San Francisco (1968), pp. 815–836.

14 A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York (1961), Chap. 4.

15 J. Aihara, *J. Am. Chem. Soc.*, **117**, 4130 (1995).