Graph-Theoretical Re-interpretation of NICS Values for Polycyclic Aromatic Hydrocarbons: Naphthalene and Azulene

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Even for the simplest polycyclic aromatic hydrocarbons, such as naphthalene and azulene, the nucleus-independent chemical shift (NICS) calculated at a ring center does not always represent local aromaticity. NICS reflects currents induced in many cyclic paths in a π-system.

Ring currents and ring-current susceptibility have been widely used as conventional measures of aromaticity.[1] There indeed is a rather complicated relationship between these quantities and aromaticity.[2] In 1996, Schleyer et al. proposed a new magnetic criterion for local aromaticity: a nucleus-independent chemical shift (NICS),[3] 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 at ring centers were then associated with paramagnetic and diamagnetic ring currents, respectively.

According to our graph theory,[4,5] a ring current induced in a polycyclic π-system can be partitioned exactly among all the possible cyclic paths in it. In other words, a ring current is a superposition of currents induced in two or more circuits. This implies that the NICS value at a given ring center must be related to currents induced in all nearby circuits. Therefore, there is a possibility that NICS does not reflect the aromatic character of the ring concerned.[6] In this note, we point out that even the NICS values for the simplest polycyclic aromatic hydrocarbons, such as naphthalene and azulene, should be interpreted with great care.

We apply our graph-theoretical variant[4,5] of Hückel-London theory[7] to polycyclic species. Let a π-system from which n circuits are chosen be denoted by G; then a current intensity, I_i, induced in the ith circuit, r_i, can be expressed in the form:

$$\frac{I_i}{I_0} = 18\frac{S_i}{S_0}\sum_{j}^{\text{occ}}\frac{P_{\mathrm{G}-\mathrm{r}_i}(X_j)}{P'_{\mathrm{G}}(X_j)} \tag{1}$$

Here I_0 is the intensity of a current induced in the benzene ring; S_i and S_0 are the areas of r_i and the benzene ring, respectively; $\mathrm{G}-\mathrm{r}_i$ is the subsystem of G, obtained by deleting r_i from G; $P_{\mathrm{G}}(X)$ and $P_{\mathrm{G}-\mathrm{r}_i}(X)$ are the characteristic polynomials for G and $\mathrm{G}-\mathrm{r}_i$, respectively; X_j is the jth largest zero of $P_{\mathrm{G}}(X)$; and j runs over all occupied π orbitals. If there are degenerate π orbitals or heteroatoms, this formula must be replaced by others.[8] Positive and negative values for I_i signify diatropicity and paratropicity, respectively. Equation 1 indicates that at the limit of zero magnetic field currents flow independently in the individual circuits.[4,5] We assumed that all rings are regular pentagons.

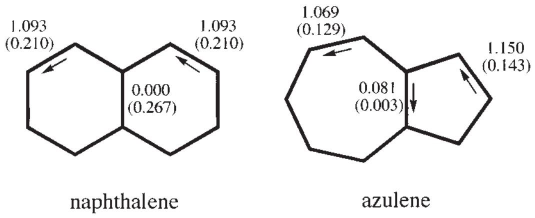

Fig. 1. Ring currents induced in naphthalene and azulene, all in units of that for benzene (I_0). Values in parentheses are the bond resonance energies (BREs) in units of $|\beta|$.

Intensities of a ring current induced at peripheral and central or bridging CC bonds of naphthalene and azulene are presented in Fig. 1, together with the bond resonance energies (BREs) for them.[9,10] Counterclockwise and clockwise arrows indicate diamagnetic and paramagnetic currents, respectively. BRE represents the contribution of a given π bond to the topological resonance energy (TRE).[9–12] Three circuits can be chosen from bicyclic naphthalene and azulene.[4] Circuit currents assigned to them are given in Fig. 2. Overall ring currents in Fig. 1 are obtained by superposing these circuit currents.

As can be seen from Fig. 1, two six-membered rings in naphthalene are diatropic, in the sense that the NICS values are −9.9 at the ring centers.[3] Therefore, this hydrocarbon may possibly be aromatic. This naive reasoning is apparently consistent with the positive TRE of $0.389|\beta|$.[10–12] Here, β is a standard resonance integral for CC bonds. In fact, naphthalene is a typical aromatic hydrocarbon. Not only six- but also ten-membered circuits in naphthalene are moderately diatropic.[4] It then follows that the currents induced in all these circuits are equally responsible for the large negative NICS value at the center of each six-membered ring.

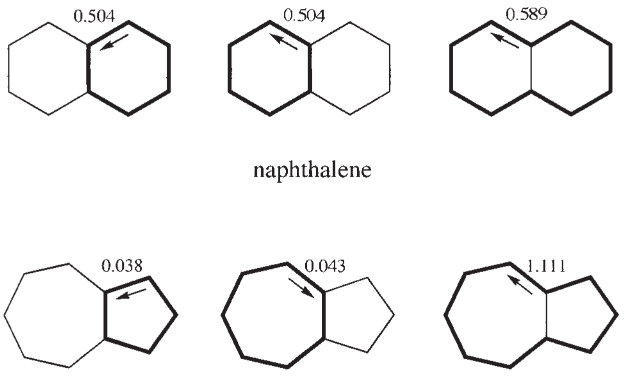

Fig. 2. Circuit currents for naphthalene and azulene, all in units of that for benzene (I_0).

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Azulene is also predicted to be aromatic with a positive TRE of $0.151|\beta|$.[10–12] The NICS values are −19.7 and −7.0 at the centers of the five- and seven-membered rings, respectively.[3] These large negative NICS values are again consistent with the positive TRE. However, it is noteworthy that the five- and seven-membered circuits are marginally diatropic and paratropic, respectively. There is no doubt that the current induced in the ten-membered circuit dominates the ring currents. Therefore, the large negative NICS values at two ring center must necessarily be associated with the highly diatropic peripheral ten-membered circuit.

Calculated BREs for CC bonds support the above interpretation of NICS values. As for naphthalene, large positive BREs for all CC bonds indicate that this molecule is highly aromatic. In addition, the largest positive BRE for the central CC bond strongly suggests that two six-membered circuits might be highly aromatic. BREs for all CC bonds in azulene are likewise positive in sign. However, the BRE for the central CC bond is negligibly small. All these BREs justify our view that only the peripheral circuit contributes much to aromaticity and diatropicity. A very small BRE for the central CC bond in azulene is fully consistent with its fairly long bond length (1.482 Å).[13]

It is now evident that the NICS values for a polycyclic π-system cannot be interpreted naively as indications of local aromaticity. The negative NICS values at the two ring centers in naphthalene reflect the aromaticity of both six- and ten-membered circuits that share the same benzene ring. On the other hand, the large negative NICS values at the two ring centers in azulene are associated with the aromaticity of the peripheral ten-membered circuit. In this context, what can be said most safely about individual NICS values of azulene is that the two ring centers in this hydrocarbon are in diatropic environments.

It is still interesting to note that the ring-current distributions in naphthalene and azulene are very similar in appearance to each other. Figure 1 shows that net currents circulate mainly along the perimeter of each π-system. As has been seen, this phenomenon has quite different meanings for the two hydrocarbons. In naphthalene, currents induced in the two six-membered circuits cancel out at the central bond. In azulene, little current flows through the bridging CC bonds because very small currents are induced in the two circuits that share the bond. The NICS values calculated at the ring centers cannot distinguish these two situations.

In summary, the NICS values calculated for a polycyclic π-system cannot be related straightforwardly to its local aromatic character. This is very true even for the simplest bicyclic hydrocarbons, naphthalene and azulene. A negative NICS value at a given ring center does not always indicate that the ring is aromatic. Our graph theory proved to be very useful for relating the NICS values to the geometry of the π-system. Note that all of the TREs, BREs, ring currents, and circuit currents are defined exactly within a single theoretical framework and can be dealt with consistently.

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