

Bond-Length Equalization and Aromaticity in Charged π-Systems

Jun-ichi Aihara

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

Received March 8, 2004; E-mail: scjaiha@ipc.shizuoka.ac.jp

The conventional interpretation of bond-length equalization gives a misleading picture of the aromaticity on charged π-systems. A charged π-system in general is reluctant to undergo marked bond-length alternation, even if it is antiaromatic with a negative topological resonance energy. The pentalene dication and the C_{60} decacation are antiaromatic with a modest distortion of the molecular skeleton. Small maximum eigenvalues of the bond–bond polarizability matrices support the absence of second-order double-bond fixation in many charged antiaromatic π-systems.

Aromatic and antiaromatic molecules have quite dissimilar molecular geometries. Both kinds of molecules differ in the distribution of bond lengths from acyclic polyenes.[1,2] The highly aromatic benzene molecule has a structure of D_{6h} symmetry with the equal CC bond lengths. In contrast to benzene, bond-length alternation is characteristic of acyclic polyenes, such as 1,3-butadiene and 1,3,5-hexatriene. For antiaromatic molecules, the alternation is even more pronounced. A high-symmetry structure of an antiaromatic molecule does not correspond to the energy minimum. For example, the highly antiaromatic cyclobutadiene molecule has a rectangular structure of D_{2h} symmetry. The tub-shaped cyclooctatetraene molecule is also antiaromatic with marked bond-length alternation.

Bond-length equalization has then been equated with aromaticity. It has been widely accepted that the more nearly equal the bond lengths around the π-system are, the more aromatic the molecule is.[1,2] This approach to aromaticity is rather naive but is very useful for the characterization of neutral aromatic and antiaromatic molecules.[1,2] Recently some attempts were made to apply the same approach to charged π-systems, such as divalent pentalene ions and fullerene molecular ions.[3–7] However, these attempts were not successful in identifying aromatic species.[8,9] Many charged species have negative topological resonance energies (TREs), although the molecular skeleton is not heavily distorted. In this paper, we explicitly show that, for charged π-systems, the decreased distortion of the molecular skeleton is never a good feature characterizing an increase in aromaticity.

Theory

We employ some molecular theories in this study. TRE is a kind of energetic criterion of aromaticity that can be defined for not only neutral but also charged π-systems.[10–13] No other energetic criteria can reasonably be applied to charged species.[1] Positive and negative TREs indicate aromaticity and antiaromaticity, respectively. 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.[12–14] This quantity is useful for comparing the degrees of aromaticity of different π-systems. Bond resonance energy (BRE) represents the contribution of a given π bond to the TRE.[13,14]

Schleyer et al. proposed a new magnetic criterion for aromaticity: a nucleus-independent chemical shift (NICS),[3,15,16] which is defined as the negative of the magnetic shielding at some selected point in space, e.g., at a ring or cage center. Negative and positive NICS values have since been associated with aromatic and antiaromatic rings, respectively. It is indeed very useful for estimating the degree of magnetic shielding anywhere in a π-system.[3,15,16] However, when it comes to polycyclic π-systems, NICS is not always a reliable indicator of global or local aromaticity.[8,9,17–19] The NICS values relevant to the present study are available from the literature.[3,5,6]

Binsch et al. developed the theory of second-order double-bond fixation,[20–23] which enables us to predict the degree of bond-length alternation in a π-system. First-order double-bond fixation is such that the symmetry of the π-system is not lowered by the fixation of the double bonds or by the distortion of the molecular skeleton. It is second-order effects that lower the symmetry of the π-system. Binsch et al. calculated the bond–bond polarizabilities $\pi_{\mu\nu,\kappa\lambda}$ for the fully symmetric model of the π-system and then diagonalized the matrix $\pi = (\pi_{\mu\nu,\kappa\lambda})$ of order $M \times M$:

$$\det|\pi - \lambda I| = 0 \tag{1}$$

where M is the number of π-bonds. This equation will yield M eigenvalues. The largest or maximum eigenvalue $\lambda_{\max}$ is compared with the critical value λ_{crit}. λ_{crit} is usually taken to be $1.80\ \beta^{-1}$,[20–23] where β is the standard resonance integral in Hückel theory. If $\lambda_{\max}$ is larger than λ_{crit}, then it is highly probable that the π-system suffers from distortion as a consequence of second-order effects.

Results and Discussion

In 1998, Zywietz et al. studied the aromaticity of bicyclic pentalene and its molecular ions in terms of NICS and bond-length alternation.[3] The % TREs and NICS values for these π-systems are reproduced in Table 1, together with the maximum eigenvalues of the bond–bond polarizability matrices ($\lambda_{\max}$). We employ the NICS values calculated at points 0.5 Å over the individual ring centers to avoid the local paramagnetic contributions of the σ bonds.[3]

Pentalene is highly antiaromatic with a large negative %

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Table 1. % TREs and NICS and λ_{max} Values for Pentalene and Its Divalent Molecular Ions

Species	% TRE	NICS[a)]	λ_{max}/β^{-1}
Pentalene	−2.02	18.2	2.357
Pentalene dianion	4.64	−11.7	0.552
Pentalene dication	−4.78	−11.6	1.312

a) Values at points 0.5 Å over the ring centers calculated at the GIAO-SCF/6-31+G*//B3LYP/6-31G* level.[3]

TRE.[13,14] Positive NICS values at the ring centers[3] are apparently consistent with the negative % TRE. The pentalene dianion is iso-π-electronic with naphthalene and is predicted to be highly aromatic with a large positive TRE. Negative NICS values at the ring centers of the dianion[3] are also consistent with the positive % TRE. In contrast, the pentalene dication is iso-π-electronic with extremely reactive butalene.[24,25] This dication is predicted to be highly antiaromatic with a large negative % TRE. However, it has large negative NICS values at the two ring centers,[3] which are apparently incompatible with the negative % TRE. Thus, NICS cannot always be used as an indicator of aromaticity. The pentalene dication has not been synthesized yet.

Distributions of CC bond lengths in pentalene and its molecular ions are presented graphically in Fig. 1, which are those calculated at the B3LYP/6-31G* level.[3] Antiaromatic pentalene has a bond-altered structure of C_{2h} symmetry, whereas the aromatic pentalene dianion has a symmetric D_{2h} structure.[3] However, the dication also has a D_{2h} structure.[3] This structural

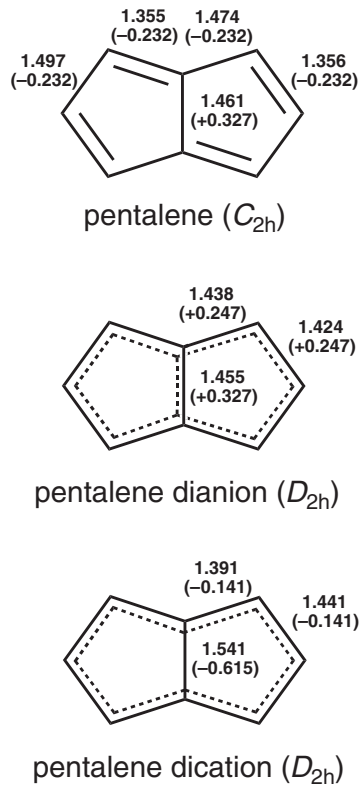

Fig. 1. Distributions of CC bond lengths (in Å) in pentalene and the divalent molecular ions.[3] Values in parentheses are the BREs.

aspect of the π-system constitutes part of the evidence with which Zywietz et al. interpreted the pentalene dication as an aromatic species.[3] Peripheral bond-length variation in the dication (0.049 Å) is much smaller than that of the neutral species (0.118 Å).[3] Such different distributions of CC bond lengths are fully consistent with the λ_{max} values. As shown in Table 1, the λ_{max} value for the neutral species are larger than 1.80 β^{-1}, but those for the dianion and dication are much smaller.

To what extent does bond-length alternation reflect the degree of aromaticity? It is very true that the degree of bond-length alternation can be used to predict the aromatic character of neutral species.[1,2] As has just been seen, however, the absence of bond-length alternation in charged π-systems cannot be viewed as structural evidence for the aromaticity of such species. In general, it must be much less easy for π-electrons to localize in pairs in charged π-systems, because the number of π-electrons is not equal to the number of conjugated carbon atoms. Negatively and positively charged π-systems have too many and too few π-electrons, respectively, to form the maximum number of localized double bonds. This is the most important aspect of π-systems in charged hydrocarbons. Therefore, it is obvious that charged species are reluctant to undergo second-order double-bond fixation. We cannot imagine the pentalene dication with bond-length alternation or double-bond fixation. Binsch and Heilbronner clearly showed that a charged annulene has a smaller λ_{max} value than that for the neutral one of the same size.[22]

The absence of bond-length alternation in the pentalene dication can be further rationalized in the following manner. A peripheral eight-membered circuit with six π-electrons but without marked bond length alternation is favorable to the stabilization of the entire π-system. Here a circuit stands for any cyclic path in a π-system. However, the central CC bond is predicted to be very long, with a length of 1.541 Å.[3] Elongation of this bond is necessary to decrease the degree of antiaromaticity arising from two five-membered circuits. As shown in Fig. 1, a large negative BRE for the central CC bond of the dication supports the view that two five-membered circuits must be highly antiaromatic. Smaller negative BREs for the peripheral CC π bonds suggest that the eight-membered circuit is more or less aromatic, although the entire π-system is antiaromatic.[9]

In 2000, Hirsch et al. calculated the NICS values at the centers of neutral and charged fullerenes and proposed the so-called $2(N+1)^2$ rule of spherical aromaticity,[4–7] where N is zero or an arbitrary positive integer. A fullerene π-system can be viewed naively as a spherical electron gas that surrounds the surface of a sphere.[26–30] The shell of angular momentum quantum number k in such a free-electron model consists of $2k-1$ levels. Therefore, the shells with angular momentum quantum numbers of up to $N+1$ are fully filled with $2(N+1)^2$ electrons. Hirsch et al. found that fullerenes with $2(N+1)^2$ π-electrons have large negative NICS values at the cage centers.[4–7] The NICS values at the cage centers of fullerene molecular ions with $2(N+1)^2$ π-electrons are presented in Table 2, together with their ring spiral indices and % TREs.[31]

The π-electron distribution of a closed-shell fullerene ion is uniform or near-uniform, with the angular momenta being dis-

Table 2. Ring Spiral Indices, % TREs, and NICS and λ_{max} Values for Charged Fullerenes with $2(N+1)^2$ π-Electrons

Species	Ring spiral[a)]	% TRE	NICS	λ_{max}/β^{-1}
C_{20}^{2+} (I_h)	1 2 3 4 5 6 7 8 9 10 11 12	−2.43	−73.1[b)]	1.124
C_{28}^{4-} (T_d)	1 2 3 5 7 9 10 11 12 13 14 15	3.18	−35.5[b)]	0.770
C_{36}^{4+} (C_{2v})	1 2 3 4 11 12 13 14 15 16 17 18	−1.94	−57.9[b)]	1.228
C_{36}^{4+} (D_{2d})	1 2 4 7 9 10 12 13 14 16 18 20	−1.94	−64.0[b)]	1.181
C_{40}^{8+} (D_2)	1 2 3 4 11 12 13 14 15 16 17 18	−2.63	−62.1[b)]	1.222
C_{40}^{8+} (D_{5d})	1 2 4 7 9 11 13 15 18 19 21 22	−2.88	−82.2[b)]	1.291
C_{60}^{10+} (I_h)	1 7 9 11 13 15 18 20 22 24 26 32	−2.03	−81.4[c)]	1.258

a) Ref. 31. b) Values at the cage centers calculated at the GIAO-SCF/6-31G*//B3LYP/6-31G* level.[5] c) Value at the cage center calculated at the GIAO-SCF/3-21G//B3LYP/6-31G* level.[4,5]

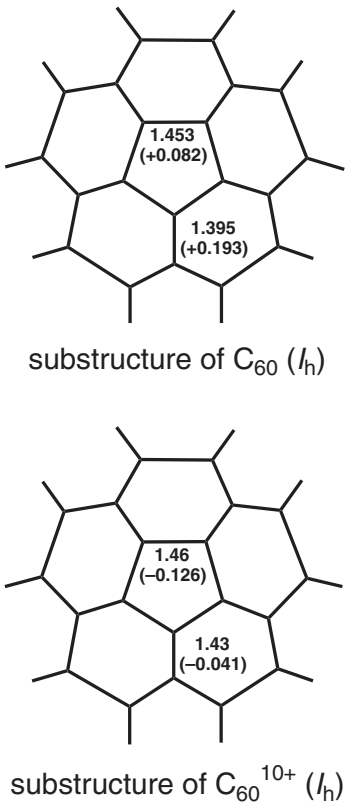

Fig. 2. Distributions of CC bond lengths (in Å) in C_{60} (I_h) and the molecular decacation.[4,32] Values in parentheses are the BREs.

tributed symmetrically.[4,7] Hirsch et al. then anticipated that the molecular skeletons of neutral and charged fullerenes with $2(N+1)^2$ π-electrons might exhibit little distortion induced by the π-electrons.[4,7] On this basis, they presumed that the maximum aromatic character is reached when fullerenes have $2(N+1)^2$ π-electrons. For example, the B3LYP/6-31G* computed lengths of the 6/6 and 5/6 bonds of C_{60}^{10+} (I_h) are 1.43 and 1.46 Å, respectively.[4] As shown in Fig. 2, their alternation (0.03 Å) is slightly smaller than that of C_{60} (I_h) (0.06 Å).[32] Here an m/n bond indicates a CC bond shared by m- and n-membered rings. However, C_{60}^{10+} (I_h) turned out to have a negative % TRE of −2.03, although the negative NICS value is as large as −81.4 at the cage center. BREs for all CC bonds in the decacation are negative in sign, indicating that all bonds make a negative contribution to the TRE. C_{60} (I_h) is moderately aromatic with a % TRE of 1.795.

Table 3. % TREs and NICS and λ_{max} Values for C_{60} (I_h) and the Molecular Decacation

Species	% TRE	NICS[a)]	λ_{max}/β^{-1}
C_{60} (I_h)	1.79	−8.0	0.893
C_{60}^{10+} (I_h)	−2.03	−81.4	1.258

a) Values calculated at the GIAO-SCF/6-31+G*//B3LYP/6-31G* level.[4,5]

All charged fullerenes in Table 2 have large negative NICS values because they have closed-shell electronic configurations.[5] However, it is only one of them, C_{28}^{4-} (T_d), that is aromatic with a positive % TRE. All other ionic species are antiaromatic with negative % TREs. Considering that all uncharged fullerenes are electron deficient in nature,[33] not only C_{60}^{10+} (I_h) but also many other highly charged fullerene cations must be antiaromatic in nature. It is evident that the NICS value at a cage center cannot be used as an indicator of aromatic stabilization for fullerenes and fullerene ions.[17,18,29] C_{28}^{4-} (T_d) is aromatic with a positive % TRE since it has four extra π-electrons. Thus, TREs are fully consistent with the electron deficiency of fullerene molecules.

The λ_{max} values for charged fullerenes are added in Table 2. The absence of second-order distortion in the molecular skeletons of charged fullerenes is supported not only by B3LYP/6-31G* geometries[6] but also by the relatively small λ_{max} values, which lie in the range 0.68–1.26 β^{-1}. These values are obviously smaller than λ_{crit}. Therefore, there is no doubt that the second-order bond-length alternation cannot be associated with the degree of aromaticity in fullerene ions. Even if a fullerene molecular ion is not distorted appreciably, it may possibly be antiaromatic. A broad variety of smaller, less symmetric fullerenes behave in essentially the same manner as demonstrated with NICS calculations.[4–7]

One should note that first-order double-bond fixation occurs in neutral fullerenes even if they have $2(N+1)^2$ π-electrons; see, e.g., the geometries of C_{32} (D_3) and C_{50} (D_{5h}) calculated at the B3LYP/6-31G* and B3LYP/3-21G levels of theory, respectively.[34,35] These are the lowest-energy fullerene isomers with 32 and 50 carbon atoms. C_{32} (D_3) and C_{50} (D_{5h}) are slightly antiaromatic and aromatic, respectively. These carbon molecules suffer from first-order distortion. Bond-length variations in C_{32} (D_3) (0.129 Å)[33] and in C_{50} (D_{5h}) (0.098 Å)[34] are

Table 4. Ring Spiral Indices, % TREs, and NICS and λ_{max} Values for Neutral Fullerenes with $2(N+1)^2$ π-Electrons

Species	Ring spiral[a)]	% TRE	NICS	λ_{max}/β^{-1}
C_{32} (D_3)	1 2 3 5 7 9 10 12 14 16 17 18	−0.27	−53.2	1.046
C_{50} (D_{5h})	1 2 9 10 12 14 15 17 20 22 24 26	0.93	−37.2	1.080

a) Ref. 31. b) Values at the cage centers calculated at the GIAO-SCF/6-31G*//B3LYP/6-31G* level.[5]

comparable to that in pentalene (0.118 Å). As pointed out previously,[36] CC bonds shared by two pentagons have negative BREs, so they are elongated to reduce the degree of antiaromaticity. The $2(N+1)^2$ rule does not take into account the effect of such local structures on aromaticity. This is why the $2(N+1)^2$ rule failed to predict the aromaticity of a cage molecule.

The $2(N+1)^2$ rule for spherical aromaticity is not compatible with the existence of a leapfrog class of fullerene isomers.[33,37,38] As pointed out by Fowler and Ceulemans,[33] C_{60} and other leapfrog-class fullerenes have six low-lying empty orbitals. The leapfrog class of fullerenes and their dodecaanions are thermodynamically stable and then highly aromatic even if they do not obey the $2(N+1)^2$ rule. Note that most of these fullerenes and their dodecaanions do not correspond to the closed-shell configurations in the spherical free-electron model. As in the case of C_{60} (I_h), even the molecular skeletons of these fullerenes undergo first-order distortion.

Concluding Remarks

We pointed out that the conventional interpretation of bond-length equalization gives a misleading picture on the aromaticity of charged π-systems. The absence of bond-length alternation is not always indicative of aromaticity. Charged π-systems are very reluctant to undergo bond-length alternation even if they are antiaromatic with negative % TREs. The pentalene dication and many fullerene cations are the first explicit examples of antiaromatic species with reduced bond-length alternation. Relatively small maximum eigenvalues of the bond–bond polarizability matrices support the absence of bond-length alternation in such charged π-systems. Note that all of the TRE, BRE, and the bond–bond polarizability matrix are defined exactly within the same Hückel framework, so these quantities must be consistent with each other in all senses.

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