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Aromatic Stabilization Energy and Magnetic Properties in Fulvalenes: Is There a Connection Between These Two Aromaticity Indices?

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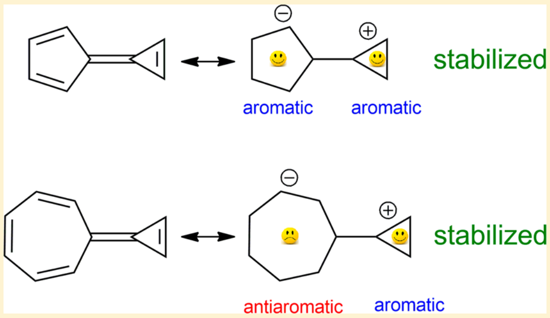
S Supporting Information

ABSTRACT: The nucleus-independent chemical shift (NICS) and Coulombic energy of 15 *j*,*k*-fulvalenes (*j*, *k* = 3, 5, 7, 9, 11) were investigated. It was found that in all of the hetero derivatives ($j \neq k$) charge transfer between the rings occurs. It occurs when the one ring contains $4n + 1$ and the other $4n + 3$ π electrons, forming two rings containing numbers of π electrons closer to $4n + 2$, and also when both rings contain either $4n + 3$ or $4n + 1$ π electrons, forming a partially aromatized ring and a partially antiaromatized ring. Both types of charge transfer are associated with aromatic stabilization energy. The NICS values are consistent with the above-described partial aromatization and antiaromatization. A semiquantitative relationship between the aromatic stabilization energy and NICS is given.



INTRODUCTION

Aromaticity is a term frequently used in chemistry to describe molecular properties such as structure, reactivity, stability, NMR chemical shifts, etc., as well as reactions (aromatic transition states) and intermolecular interactions. However, aromaticity and its counterpart, antiaromaticity, are not quantitatively or even qualitatively defined.[1] Hückel's definition, which is based on the number of cyclically conjugated π electrons ($4n + 2$ for aromatic, $4n$ for antiaromatic) has two major drawbacks. One is that it is a binary definition rather than a quantitative one. Thus, frequent chemical questions such as "Is X more or less aromatic than Y?" cannot be answered using Hückel's definition. The second drawback is that the Hückel definition for antiaromatic compounds can be applied only for model (unrealistic) systems. Specifically, Hückel's definitions of aromaticity and antiaromaticity assume that the system being studied is of D_{nh} symmetry (where n in the subscript is equal to the number of atoms forming the ring). For many (though not all) systems with $4n + 2$ π electrons, this geometry is indeed a stable geometry (i.e., a minimum of energy with respect to $3N - 6$ degrees of freedom), but for all systems with $4n$ π electrons, this geometry is a first- or higher-order saddle point.

Most of the efforts to study and define aromaticity (and antiaromaticity) are thus indirect, based on the properties resulting from aromaticity, among which the most popular are geometry, energy, and magnetic properties.[2] Although many (but not all) systems show geometric correlation to other aromaticity indices, the validity of the structural index[3] has been questioned[1] and therefore was not used in this work. The energy index suffers from a serious drawback, namely, the requirement of an appropriate nonaromatic reference system.[4] This problem may be circumvented if a family of isomers that differ only in their respective aromaticities (and/or antiaromaticities) is used[5] or if an unrelated type of energy (e.g., Coulombic energy; see below) is used. Magnetic properties result from diatropic or paratropic ring currents, which are induced under an external magnetic field. There are several computational methods that are used to estimate the induced ring currents or the resulting induced magnetic field, among which the most popular are current density analysis (CDA)[6] for direct calculation of the ring current densities and nucleus-independent chemical shift (NICS)[7] for measurement of the induced magnetic field. Each of these methods has its own disadvantages. CDA methods show the induced currents as arrows with different sizes and different directions to denote the strength and type (diatropic or paratropic) of current, respectively, and they are difficult to quantify. NICS is easy to quantify, but being integrative in its nature, it cannot distinguish between local effects and global effects (i.e., a magnetic field that results from a ring current that is spread over more than one ring), nor can it differentiate between the field that arises from currents in neighboring conjugated rings and the local ring current. To resolve some of these problems, many versions of NICS have been developed, among which the methods that consider only the π contribution to the *ZZ* component of the shielding tensor are considered to be best.[8] It is our belief that the single value provided by NICS may lead to erroneous conclusions, since local and σ effects may play different roles in different systems.[9] Therefore, we have developed our own version of NICS, the NICS-scan. In this method, a one-dimensional scan above the center of the ring is

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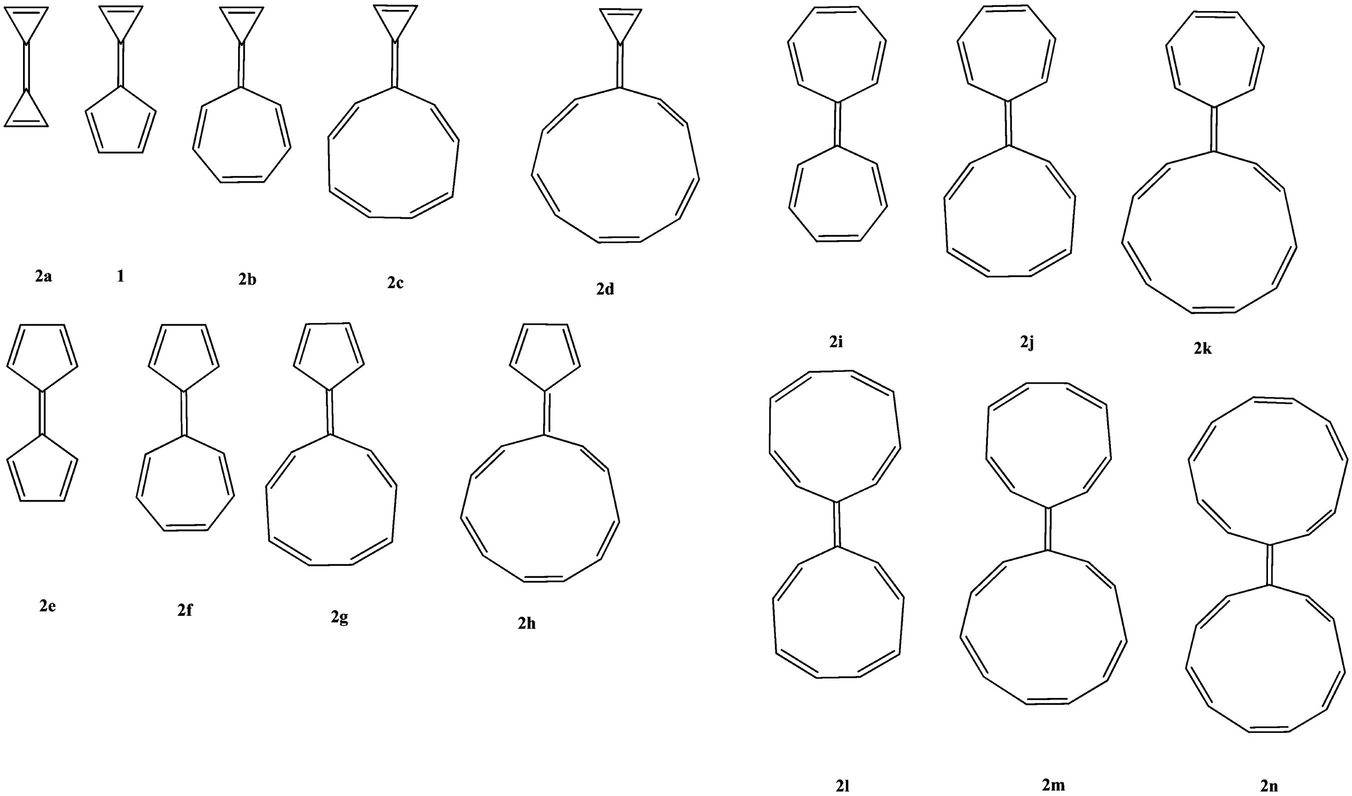
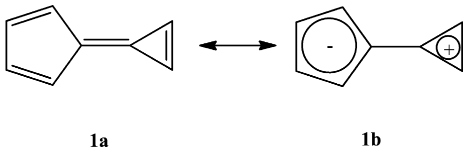
Chart 1. Fulvalenes Studied in This Work



implemented, and examining the out-of-plane tensor as a function of distance yields typical curves for diatropic and paratropic ring currents.[10] This approach has been developed by others,[11] but attempts to use some of these developments have not yielded any greater information than the original procedure did in our hands. Later, a chemical model for the σ system was developed, and subtraction of the NICS-scan of the model from the NICS-scan of the aromatic/antiaromatic compound yields the clean π contribution, which can be easily quantified so that comparison of aromaticity (and antiaromaticity) among different compounds is possible.[12] In the present work, we used this method and the canonical molecular orbital NICS (CMO-NICS) method[7] applied in the NICS-scan procedure and quantified in a manner that is explained in Computational Methods. It is noted that Kleinpeter and coworkers developed a method that is based on a three-dimensional grid of ghost atoms (BQs) around the studied molecules, reporting maps of isochemical-shielding surfaces (ICCS) as lobes of different colors.[13] This method proved to be efficient in predicting experimentally measured substitution effects on chemical shielding, but as far as aromaticity and antiaromaticity are concerned, this method, which is based on isotropic NICS values, is contaminated by the σ effects on the NICS. Moreover, since the induced magnetic field that is produced by the induced ring current has a defined shape, a one-dimensional scan at (and above) the center yields all of the necessary information in a quantitative fashion. Thus, we believe that for the purpose of an aromaticity study a three-dimensional scan is superfluous.

Calicene (**1**) has a dipole moment of 5.6 D.[14] This large dipole moment is explained by charge transfer from the three-membered ring to the five-membered ring, affording partial aromatic character to both rings (**1b**). The stability that is gained by the (partial) aromatization of the two rings compensates for the energetic cost of the charge separation. Indeed, many studies have found that the diatropicity in **1** is larger than in model compounds.[10,14] If so, these types of systems, which comprise a conjugated ring connected by a double bond to another conjugated ring and are commonly called fulvalenes, present a unique opportunity to study aromatic stabilization energies (ASEs) in relation to magnetic properties. The aromatization energy compensates for the charge separation energy, which can be calculated from the charge separation by Coulomb's law (as a lower limit of the ASE), and NICS can be used to assess the change in the ring current. Thus, we performed calculations on 15 systems of this type, namely, all of the *j*,*k*-fulvalenes with *j*, *k* = 3, 5, 7, 9, and 11 (Chart 1).



The questions that we attempted to answer here are the following: (a) Is there a relationship between the magnetic properties and the energies associated with aromaticity (and antiaromaticity)?[15] (b) What happens when both rings of the fulvalene compete for the same charge in order to become aromatic [i.e., both need to lose or gain an electron, such as in triheptafulvalene (**2b**) and pentanonafulvalene (**2g**)]: is there no charge separation, or does charge separation occur to partially aromatize one ring and partially antiaromatize the second ring, creating overall stabilization? It should be noted here that Kleinpeter and co-workers recently published a paper[16] that analyzes most of the systems studied here (except those containing 11-membered rings) using their own developed NICS-density maps.[13] However, they studied different aspects of the systems, focusing on the double bond between the two rings (as a measure of the contribution of the charged resonance structures) and the magnetic properties through their ICCS maps, and they allowed full geometrical relaxation of the studied systems while not addressing energy issues at all. In this study, we focused on aromatic stabilization energies and used different NICS methods that are more appropriate for the study of aromaticity (see above) while keeping the molecules planar (see Computational Methods). Indeed, the molecules whose optimized geometries are not planar are less realistic but fit much better to the principal study of aromaticity and antiaromaticity as phenomena. As a result, some of Kleinpeter's conclusions are different than ours.

■ COMPUTATIONAL METHODS

Gaussian 09[17] was used for all of the calculations. All of the molecules underwent geometry optimization within C_{2v} symmetry at the B3LYP/6-311G* computational level. For the smaller ring systems (j, k = 3, 5, and in most cases 7), these are true minima (as verified by analytical frequencies calculations with $N_{\text{imag}} = 0$). For the larger ring systems, 1−7 imaginary frequencies were found in this symmetry. There were two reasons for keeping the symmetry (i.e., the planarity, since all of the imaginary frequencies are out-of-plane vibrations) and not allowing full geometry optimization of the systems. One is that this maximizes the aromatic and antiaromatic interactions, which are the issue of this work. The second is that while the σ-only model does not depend on the geometry of the molecule, CMO-NICS can be studied only in planar systems. The comparison between these two methods for the calculation of $\text{NICS}_{\pi ZZ}$ is also of interest in this paper. Therefore, we preferred to use planar molecules despite the fact that in some cases they are not minima on the potential surface.

NICS-scan calculations were performed at the GIAO-B3LYP/6-311+G* level[18] at the B3LYP/6-311G* C_{2v} optimized geometries (as explained above). The ghost atoms (BQs) were placed above the geometrical centers of the rings at distances of 0 Å (i.e., in the molecular plane) to 3.9 Å above the molecular plane with a step interval of 0.1 Å. The σ-only models were built as explained before[12] and underwent NICS-scan calculations as explained above. CMO-NICS values were obtained from the NCS procedure implemented in NBO 5.G.[19] For some of the systems the Aroma software was used.[20] The data were analyzed with Microsoft Excel and OriginPro 8.6.0.[21] The results of the σ-only model (Δoopc and 3Δiso) and the CMO-NICS for each BQ were plotted against the distance from the ring plane (starting at a distance of 1 Å).[12] There are two ways to analyze the data. One way is that used in the original work: a plot of the natural logarithm of the chemical shift against distance yields a straight line. The second way is to fit the curve with a third-order polynomial function. For either fitting approach, the reported chemical shifts used as the basis for comparison of the ring currents among different systems were recalculated from the fits at a distance of 1 Å from the molecular plane. The results of the two fitting approaches are practically identical, and the third-order polynomial fit is somewhat advantageous for systems in which the chemical shift changes sign with the distance. NBO charges were used to determine the charges in each ring. Figure 1 shows a plot of the total charges in all of the rings against the respective π charges. The good linear correlation, the slope, and the intercept ensure that all of the charges reside in the π framework and are thus relevant for this study. The charge separation energy was calculated from Coulomb's law assuming point charges at the geometrical centers of the rings.

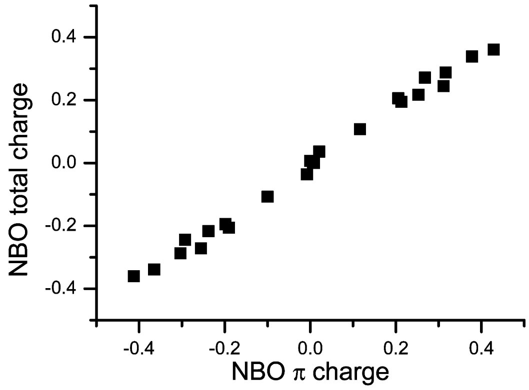


Figure 1. Plot of the NBO total charges against the NBO π charges in **1** and **2**. Linear regression results: intercept = −0.0062 ± 0.0037, slope = 0.9070 ± 0.0155, R^2 = 0.9931.

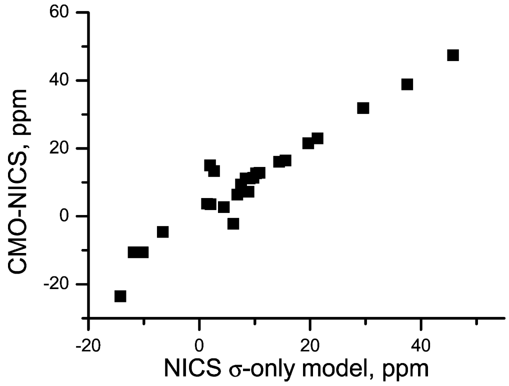


Figure 2. Plot of NICS values from the σ-only model against CMO-NICS values. Linear regression data: intercept = 0.888, slope = 1.044, R^2 = 0.916.

■ RESULTS AND DISCUSSION

(a). Magnetic Aspects. Figure 2 shows the $\text{NICS}_{\pi ZZ}$ values calculated using CMO-NICS and the σ-only model. The agreement between the two methods is excellent. Both methods show relatively large errors for small ring currents—this is the reason for the somewhat scattered points at small values. The only point with large values that deviates considerably from the straight line is that for the nine-membered ring of trinonafulvalene (**2c**). The σ-only model suggests a chemical shift of −14.2 ± 2.9 ppm, whereas CMO-NICS suggests −23.5 ppm. The source of the disagreement in this particular system is unclear. However, on the basis of the facts that (a) the chemical shifts of cyclononatetraenyl anion are −40.9 ± 1.2 ppm (σ-only model) and −41.3 ppm (CMO-NICS) and (b) the charge in this ring is −0.36, the chemical shift suggested by the σ-only model is more reasonable.[22] The discussion is therefore based on the σ-only model, but as suggested by Figure 2, it should be similar for CMO-NICS.

When there is no charge separation, each ring has $4n + 1$ or $4n + 3$ π electrons and is therefore neither aromatic nor antiaromatic. This is reflected by the relatively small NICS values shown by the "homo" ($j = k$) systems (**2a**, **2e**, **2i**, **2l**, and **2n**) (Table 1). All of the rings show relatively small paratropic

Table 1. NICS Values and p_π Orbital Charges of the Carbon Atoms Connecting the Rings of the "Homo" Systems

	2a	**2e**	**2i**	**2l**	**2n**
NICS (σ-only)	8.9	2.0	21.3	10.9	19.7
CMO-NICS	7.3	3.5	22.9	12.8	21.5
$p_{C=C}$ charge	−0.1458	+0.0744	−0.0426	+0.09146	−0.01988

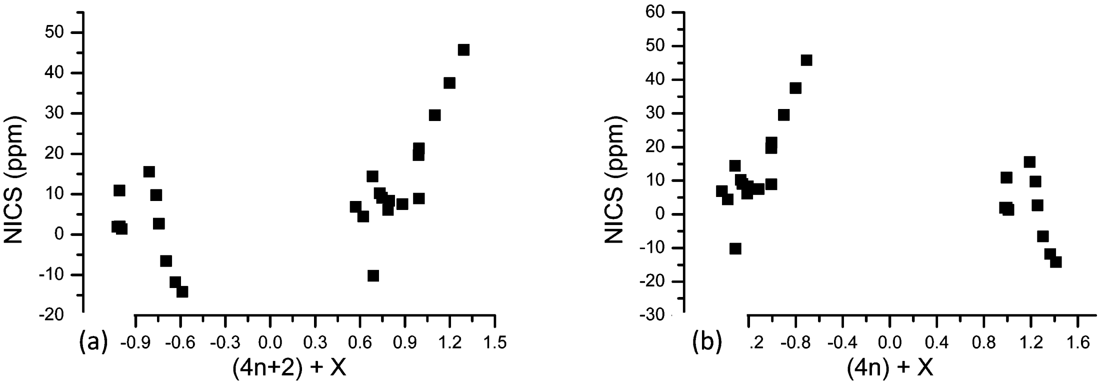


Figure 3. Plots of NICS as functions of (a, left) the number of electrons relative to 4*n* + 2 and (b, right) the number of electrons relative to 4*n*.

values.[23] However, an alternation of the magnitude is observed, where the three-, seven-, and 11-membered rings show larger currents than the five- and nine-membered rings. The charges of the p_π orbitals of the carbon atoms connecting the rings offer a qualitative explanation. In the rings that need to lose an electron in order to become aromatic (**2a**, **2i**, and **2n**), these p_π orbitals are negatively charged, while in the rings that need an extra electron to become aromatic (**2e** and **2l**) they are positively charged. Thus, in **2a**, **2i**, and **2n**, the rings push electron density into the C═C π* bond, while in **2e** and **2l**, electron density is pulled from the C═C π bond into the rings. It seems that the second interaction is more efficient than the first, bringing the number of π electrons in the rings in **2e** and **2l** closer to 4*n* + 2, reducing more efficiently the paratropic ring currents. Thus, even in the homo systems there is a tendency for the rings to become aromatic, which is manifested by pushing or pulling electrons from or into the double bond connecting the rings. Hence, although the π charge of each ring is zero, the electrons are not equally distributed within the ring, a fact that is reflected in the different NICS values of the homo systems.

Different-sized rings have different numbers of π electrons. Thus, perhaps the best approach is to show how the NICS changes with respect to the number of electrons that are missing or in excess relative to 4*n* + 2 or 4*n*.[24] This is shown in Figure 3.[25] The trends that are shown are clear. The closer the number of electrons is to 4*n* + 2, the more negative the NICS value becomes (Figure 3a). This is true for both less and more than 4*n* + 2 electrons. The opposite trend is shown in Figure 3b, where the NICS values are plotted as a function of the number of electrons missing or in excess relative to 4*n*. Because of the large scattering at small NICS values, a quantitative analysis is not possible. However, some conclusions may be drawn. First, for each of the graphs in Figure 3, the slope (absolute value) and the intercept of the left part are equal to those of the right part (within statistical error). This suggests that the ring current decreases equally if there are more or less than 4*n* + 2 (or 4*n*) π electrons. Second, the values of the intercepts are of interest. The values of the intercepts are −34.4 ± 8.4 ppm for Figure 3a and +78.1 ± 10.8 ppm for Figure 3b, which are in fact the NICS values expected for a 4*n* + 2 π electron system (e.g., benzene) and a 4*n* π electron system (e.g., cyclobutadiene and D_{4h}-cyclooctatetraene), respectively. The NICS values of benzene, cyclobutadiene, and D_{4h}-cyclooctatetraene are −34.0 ± 4.2, +42.0 ± 3.7, and +101.0 ± 2.5 ppm, respectively.[12,26] Thus, it can be concluded that the NICS corresponds to the number of π electrons missing or in excess relative to 4*n* + 2.

(b). Energy Aspects. As mentioned above, the aromatic stabilization energy (ASE) is usually defined relative to a similar nonaromatic reference system. Since such systems are not generally defined, this poses an inherent problem. In order to circumvent this problem, we have used a different approach in this work. Charge separation costs energy. Thus, when charge separation occurs in fundamentally nonpolar molecules, such as the fulvalenes, there must a stabilizing effect that is achieved by the charge separation. It is assumed that this effect is aromaticity that and the energy required for charge separation is (at least) the ASE that is gained by this charge separation. The charge separation energy (E_{sp}) was calculated using Coulomb's law. The π charge in each ring was calculated by summing the populations of all of the p_π orbitals and subtracting this sum from the number of π electrons in the uncharged ring. For the Coulombic energy calculations, it was assumed that the charges are point charges at the geometrical centers of the rings, and the distance between the centers was taken from the optimized geometry. The amount of energy required to transfer a full electron (E_{full}) over the same distance was also calculated. E_{full} represents the energy for full aromatization of one ring and either full aromatization (e.g., in **1**) or full antiaromatization (e.g., in **2b**) of the other ring. Therefore, the quantity $\%E_{FS} = 100\% \times (E_{sp}/E_{full})$ represents the percentage of aromaticity (or antiaromaticity) of each system. Figure 4 shows a plot of $\%E_{FS}$ for each ring of **1**−**2n** as a function of the number of electrons missing or in excess relative to 4*n* + 2 π electrons. It can be divided into three parts.

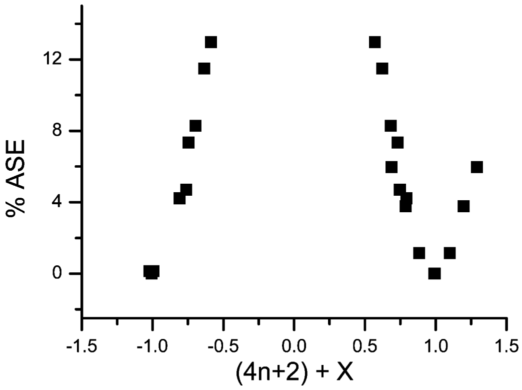


Figure 4. Plot of $\%E_{FS}$ as a function of the number of electrons missing or in excess relative to 4*n* + 2.

The left part, where there are fewer than $4n + 2$ π electrons ($X < 0$), the middle part where $0 < X < 1$, and the right part where $X \geq 1$. The left and middle parts are easy to understand, since the closer the number of π electrons is to $4n + 2$, the larger the ASE is. The two lines have slopes with the same absolute value (28.9 ± 2.1 and −28.9 ± 2.7 for the left and middle parts, respectively) and the same intercept (−28.8 ± 1.8 and −27.9 ± 2.7, respectively). The intercept suggests that the maximum ASE for a ring with $4n + 2$ π electrons in the molecules studied here is 28−30% of the ASE of fully aromatic rings, probably because of the high energetic cost of charge polarization.

The right part of the graph is unexpected. It suggests that the systems become more stable when their π systems contain more than $4n + 3$ electrons (i.e., approaching the antiaromatic value of $4n$ π electrons). The linear regression parameters (slope = 19.4 ± 1.5, intercept = 19.5 ± 1.5, $R^2 = 0.970$) are completely different from those of the other two parts. This suggests that these particular rings are destabilized by having $4n + 2$ π electrons and are stabilized by 19.5 kcal mol^{-1} by $4n$ π electrons.

The rings belonging to this group are those of **2a**, **2i**, **2n**, the 11-membered ring of **2k**, the seven-membered ring of **2b**, and the 11-membered ring of **2d**. Thus, all contain $4n + 3$ π electrons (and therefore need to lose an electron in order to become aromatic) and are connected to the same type of ring. In the homo systems **2a**, **2i**, and **2n**, there is no charge transfer between the rings, but in **2k**, **2b**, and **2d** there is a charge transfer, causing the other ring (the three-membered rings in **2b** and **2d** and the seven-membered ring in **2k**) to become more aromatic. Is there any additional evidence of this?

Table 2 gives values of ΔE for eqs 1−6, which measure the bond separation energies for systems in which one ring has $4n + 1$ and the other $4n + 3$ π electrons, that is, systems in which both rings gain ASE from charge transfer. The results suggest that the stabilization of the mixed systems ranges between 3.4 and 28.6 kcal mol^{-1} relative to their respective homo systems. It should be noted that this stabilization is divided (probably not equally) between the two rings in each system.

Table 2. Energies of Equations 1−6 and Stabilization Energies per System[a]

equation	ΔE	ΔE/system
1	−23.1	−11.6
2	−57.2	−28.6
3	−13.7	−6.9
4	−22.9	−11.5
5	−15.8	−7.9
6	−7.1	−3.4

[a] Energies are given in kcal mol^{-1}. Zero-point-corrected total energies were used to calculate the ΔE values.

$$\mathbf{2a} + \mathbf{2e} \rightarrow 2\,\mathbf{1} \quad (1)$$

$$\mathbf{2a} + \mathbf{2l} \rightarrow 2\,\mathbf{2c} \quad (2)$$

$$\mathbf{2e} + \mathbf{2i} \rightarrow 2\,\mathbf{2f} \quad (3)$$

$$\mathbf{2e} + \mathbf{2n} \rightarrow 2\,\mathbf{2h} \quad (4)$$

$$\mathbf{2i} + \mathbf{2l} \rightarrow 2\,\mathbf{2j} \quad (5)$$

$$\mathbf{2l} + \mathbf{2n} \rightarrow 2\,\mathbf{2m} \quad (6)$$

The values of ΔE for eqs 7−10 measure the bond separation energies for systems in which both rings have either $4n + 3$ π electrons (eqs 7−9) or $4n + 1$ π electrons (eq 10). The results (Table 3) suggest that these systems are stabilized as well. The straightforward interpretation is that one of the rings in each of these compounds gains an ASE that is larger than the antiaromatic destabilization energy of the other ring. Qualitative evidence for this interpretation is obtained from the difference between the NICS values for the homo systems (e.g., **2a** and **2i**) and the mixed systems (e.g., **2b**). These are given in Table 4.[27] The changes suggest that this interpretation is correct: eqs 7−10 describe systems in which one ring becomes more aromatic (shows a more diatropic ring current, more negative NICS value) while the second ring becomes more antiaromatic (shows a more paratropic ring current, more positive NICS value).

Table 3. Energies of Equations 7−10 and Stabilization Energies per System[a]

equation	ΔE	ΔE/system
7	−13.9	−7.0
8	−49.9	−25.0
9	−0.9	−0.5
10	−16.9	−8.5

[a] Energies are given in kcal mol^{-1}. Zero-point-corrected total energies were used to calculate the ΔE values.

Table 4. Changes in NICS Values for the Individual Rings in Equations 7−10

	ΔNICS (ppm)	
equation	small ring	large ring
7	−2.7	+16.2
8	−19.1	+26.1
9	−13.7	+8.3
10	−0.6	−8.9

$$\mathbf{2a} + \mathbf{2i} \rightarrow 2\,\mathbf{2b} \quad (7)$$

$$\mathbf{2a} + \mathbf{2n} \rightarrow 2\,\mathbf{2d} \quad (8)$$

$$\mathbf{2i} + \mathbf{2n} \rightarrow 2\,\mathbf{2k} \quad (9)$$

$$\mathbf{2e} + \mathbf{2l} \rightarrow 2\,\mathbf{2g} \quad (10)$$

The energetic consequences are interesting. The linear regression parameters of the lines in Figure 4 suggest that when a full electron is transferred between rings that initially contain $4n + 1$ and $4n + 3$ π electrons (to form two rings with $4n + 2$ π electrons) the $\%E_{FS}$ is ca. 30%, while a full electron transfer between two rings that both contain either $4n + 1$ or $4n + 3$ π electrons to form one ring with $4n + 2$ π electrons and one ring with $4n$ π electrons stabilizes the system by 19.5%. Hence, in fulvalenes, the loss of aromaticity and the addition of antiaromaticity in one ring destabilizes the system by ca. 10% overall. However, since the slopes of the lines are different, this difference depends on the charge that is transferred. For example, transfer of half an electron between two rings in systems of the first type results in a stabilization of 15.5%, while systems of the second type are stabilized by 9.8%, suggesting destabilization of 5.7%, more than half of that for transfer of a full electron.

Despite the lack of sensitivity of the NICS values and the energy to the value of n in $4n + 2$ π electrons (Figure 4), it is noted that in the three systems in which the charge transfer makes one ring more aromatic and the second more antiaromatic (Figure 4, right part) the small ring becomes positively charged (and aromatic) while the larger ring becomes negatively charged (and antiaromatic). This is probably due to charge repulsion within one ring, which is smaller in the observed case relative to the alternative (namely, a negatively charged small ring and a positively charged large ring).

■ SUMMARY AND CONCLUSIONS

The question of whether there is a relationship between energetic and magnetic consequences of aromaticity was investigated in the fulvalene family. The aromatic stabilization energy was estimated from the energy required for the charge separation, while a refined version of $\mathrm{NICS}_{\pi ZZ}$ was used to assess the ring currents. It has been shown that the energy and NICS are both correlated to the number of π electrons in the fulvalene and thus are correlated to each other. It has also been shown that when both rings need to lose or gain an electron in order to become aromatic (i.e., when they "compete" for the same charge), one ring becomes more aromatic while the second becomes more antiaromatic, resulting in the overall stabilization of the system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimized geometries, σ-only model geometries, total energies, and ZPE-corrected total energies of all the compounds discussed; NBO orbital populations and atomic populations; tables of NICS and $\%E_{FS}$ values; a plot of NICS with error bars; and a short discussion of $\mathrm{NICS}/(\mathrm{area})^2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) For example, see: (a) Foroutan-Nejad, C.; Shahbazian, S.; Rashidi-Ranjbar, P. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12630−12637. (b) Stanger, A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12652−12654. (c) Noorizadeh, S.; Dardab, M. *Chem. Phys. Lett.* **2010**, 376−380.

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(15) Ahira, using his own developed methods that are based on graph theory, found a linear relation between electronic resonance energy and ring current. See: (a) Ahira, J.-I. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 241−247. It should be noted that both the energy and magnetic property are different from what we studied in the present work. Also, Ahira's work disagrees with other investigations, which concluded that there is no connection between magnetic and energy properties. See: (b) Jug, K.; Köster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163−169. (c) Balaban, A. T.; Onicui, D. C.; Katritzky, A. R. *Chem. Rev.* **2004**, *104*, 2777−2812.

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(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

(18) It was noted by a reviewer that NICS values calculated by the CASSCF method are very different than those calculated at the B3LYP level (especially for paratropic currents) and therefore that the analyses based on the current values may be wrong. See: (a) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 7303−7309. (b) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 12707−12713. (c) Karadakov, P. B.; Horner, K. E. *J. Phys. Chem. A* **2013**, *117*, 518−523. (1) As NICS values cannot be verified experimentally, it is difficult to judge which computational level produces a more "correct" value. However, NMR values (which are closely related to NICS values) can be compared. The absolute ^{13}C chemical shift of benzene is 57.2 ppm. See: (d) Jameson, A. K.; Jameson, C. J. *Chem. Phys. Lett.* **1987**, *134*, 461−466 (http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/cre_index.cgi). The chemical shift relative to TMS cannot be calculated coherently by CASSCF. (2) On the other hand, there is plenty of evidence suggesting good fits between GIAO-B3LYP and experimental ^{13}C chemical shifts for a broad spectrum of aromatic and antiaromatic compounds. For example, see: (e) Levy, A.; Rakowitz, A.; Mills, N. *J. Org. Chem.* **2003**, *68*, 3990−3998. (f) Mills, N. S.; Benish, M. *J. Org. Chem.* **2006**, *71*, 2207−2213. (g) Dahl, B.; Mills, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 10179−10186. (h) Piekarski, A. M.; Mills, N. S.; Yousef, A. *J. Am. Chem. Soc.* **2008**, *130*, 14883−14890. (i) Do, C.; Hatfield, J.; Patel, S.; Vasudevan, D.; Tirla, C.; Mills, N. S. *J. Org. Chem.* **2011**, *76*, 181−187. (j) Mills, N. S.; Cheng, F. E.; Baylan, J. M.; Tirla, B. C.; Hartmann, J. L.; Patel, K. C.; Dahl, B. J.; McClintock, S. P. *J. Org. Chem.* **2011**, *76*, 645−653. (k) Black, M.; Woodford, C.; Mills, N. S. *J. Org. Chem.* **2011**, *76*, 2286−2290. (3) No form of $\mathrm{NICS}_{\pi ZZ}$ can be calculated with CASSCF. Thus, quantitative calculations of the

effect of only the π electrons on NICS are impossible with CASSCF, and since even the NICS_{ZZ} may be contaminated with σ contributions, using CASSCF for quantitative assessment of aromaticity may result in errors. (4) The procedure for obtaining the $\text{NICS}_{\pi ZZ}$ from the σ-only model (ref 12) involves subtraction of the NICS of the model from the NICS of the system and thus is analogous to obtaining the chemical shift relative to TMS (above). As shown, this minimizes the errors. (5) In summary, it is quite clear that for the purpose of obtaining accurate and dependable NICS values, B3LYP yields results that are much superior relative to the much more expensive CASSCF method.

(19) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5*;http://www.chem.wisc.edu/~nbo5.

(20) Rahalkar, A.; Stanger, A. *Aroma*; http://schulich.technion.ac.il/Amnon_Stanger.htm.

(21) *OriginPro*, version 8.6.0; OriginLab Corporation: Northampton, MA.

(22) The charge in this ring (−0.36) suggests 36% aromaticity in relation to the fully aromatic cyclononatetraenyl anion (with a −1 charge). The NICS values for this ring are 35% and 57% of the NICS values for fully aromatic cyclononatetraenyl anion for the σ-only model and CMO-NICS, respectively. Thus, it appears that the NICS value from the σ-only model is more coherent with the charge than the one calculated by CMO-NICS.

(23) Paratropic ring currents in antiaromatic systems are much stronger than diatropic ring currents in aromatic systems. For example, the $\text{NICS}_{\pi,\text{oop}}$ values for benzene and D_{4h}-cyclooctatetraene are −34.0 and +101.0 ppm, respectively (see ref 10). Also, the $\text{NICS}_{\pi,\text{oop}}$ values of nonaromatic systems such as 1,3-cyclohexadiene are ca. +4 ppm (unpublished results). Thus, the values that the homo systems show can be considered as small, and the systems are nonaromatic.

(24) One of the referees suggested using $\text{NICS}/(\text{area})^2$ instead of NICS. See page S307 in the Supporting Information.

(25) A more rigorous definition of X in Figure 3a is the following: If A is the number of π electrons in a ring (obtained from summing up the NBO p_π populations), then $X = A - (4n + 2)$ for the value of n that yields $-1 < X < 1$. The rigorous definition of X in Figure 3b is similar: $X = A - 4n$ for the value of n that yields $-1 < X < 1$.

(26) It should be noted that while the NICS values for diatropic systems are not sensitive to the ring size, the paratropic values may be, as exemplified by the very different values for cyclobutadiene and D_{4h}-cyclooctatetraene. For another example, see: Mills, N. S.; Llagostera, K. B. *J. Org. Chem.* **2007**, *72*, 9163−9169.

(27) The only value that disagrees with this assessment is the value for the five-membered ring of **2g**, which should have shown a positive value. This can be explained by the very small NICS values in the homo system **2e** (+2.0 ppm) and the five-membered ring in **2g** (+1.4 ppm), considering the large scattering for small NICS values (Figure 2). Also, the negative charge in this ring is only 0.008 electrons. It should also be noted that the two rings of **2g** fit within the left and middle parts of Figure 4, probably because of the very small charge transfer in this system.