The Different Aromatic Characters of Some Localized Benzene Derivatives[†]

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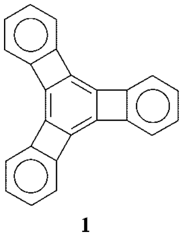
Localized benzene derivatives can be separated into two classes, one that retains large diamagnetic ring currents and a second that loses the diamagnetic ring current. Energetic criteria and NICS scan are used to evaluate the nature of the two classes. Hückel-type treatment, MO analysis, and comparison to model compounds suggest that there is no connection between geometric localization and the loss of aromaticity.

Introduction

In the last two decades, aromaticity has become a controversial topic. Shaik claimed that the π system in benzene is more stable when localized, counter to the notion that dates to the Hückel treatment of benzene, which claimed that delocalization stabilizes the π system (by 2β for benzene).[1] Vollhardt prepared the first cyclohexatriene (**1**),[2] the motif of which is found also in other triangular phenylenes.[3] Siegel prepared a triply annulated bicyclohexanobenzene (**2**), which showed localization of the central benzene ring.[4] Evidences for the localization properties of the bicyclohexenoic moiety were also found in other systems.[5] The question of whether strain or the aromaticity−antiaromaticity interplay is responsible for the bond localization is still debated.[6]

There is, however, a fundamental difference between localized systems like **1** and **2**. In systems like **1** (which can be viewed as substituted derivatives of **3**), the induced diamagnetic ring current in the six-membered ring almost disappears, and the four membered rings show small paramagnetic ring currents.[7] However, in **2**, the ring current is almost as strong as that in benzene.[8]

The questions that are dealt with here are, (a) Why do geometrically localized benzene derivative such as **2** and **4** show strong diamagnetic ring current, whereas systems that have additional six-conjugated π electrons (such as **1** and **3**) stop showing it? and (b) What is the aromatic character of systems like **1**-**4**?



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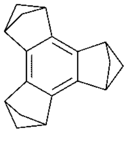

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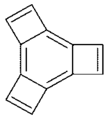

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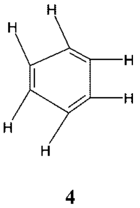

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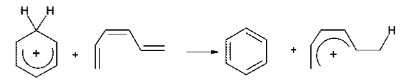
Computational Details

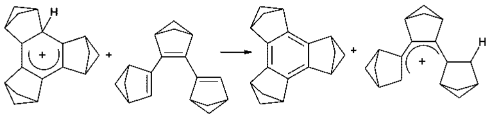
All calculations were performed with the Gaussian 03 suit of programs.[9] All of the molecules and ions underwent full geometry optimization (unless otherwise noted, e.g., when symmetry was imposed) and analytical frequency calculations to ensure real minima or the number of imaginary frequencies. NMR chemical shift calculations were preformed at the GIAO-HF/6-311+G*//B3LYP/6-311G* computational level. Energies reported for eqs 1–9 and in Table 1 are the ZPE-corrected energies, and in parentheses are $\Delta H_r°$ values in kcal mol^{-1}.

Energy Considerations

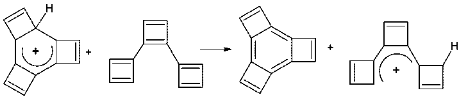
The use of ASE (aromatic stabilization energy)[10] is attempted to assess the aromaticity of the compounds under study. The idea behind the ASE method is that the proton affinity (PA) of a molecule is decreased relative to its open-chain analogue as the molecule is more aromatic since more aromatic stabilization energy is lost by protonation. Thus, eqs 1–3 should be more exothermic as the aromaticity of the benzene derivatives is increased.



(1) -24.5 (-24.6)

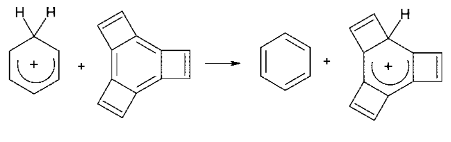


(2) -37.7 (-37.8)

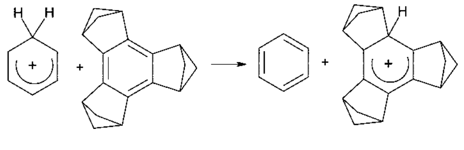


(3) -26.8 (-26.8)

This method suggests that **3** is more aromatic than benzene by 2.3 kcal mol^{-1} and **2** is more aromatic than benzene by 13.2 kcal mol^{-1}, namely, that the order of aromaticity is **2** > **3** > benzene. These results do not make any sense. In an attempt to understand these results, a direct comparison of the PAs of benzene, **3** and **2** (eqs 4 and 5), was undertaken.



(4) -16.9 (-17.0)



(5) -28.3 (-28.5)

[†] Part of the "Sason S. Shaik Festschrift".

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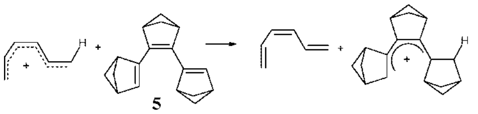
The PA of benzene is smaller than those of **3** and **2** by 16.9 and 28.3 kcal mol^{-1}, respectively. The comparison between the PAs of the open-chain analogues suggests that the PAs of **5** and **6** are larger by 19.2 and 41.5 kcal mol^{-1}, respectively (eqs 6 and 7), than the PA of hexatriene. A comparison of **2** and **3** through hexatriene (eqs 8 and 9) suggests that **3** and **2** are less aromatic than benzene by 16.9 and 28.3 kcal mol^{-1}, producing an aromaticity order of benzene > **3** > **2**.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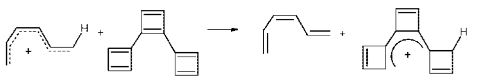
(6) -19.2 (-19.2)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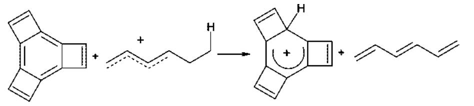
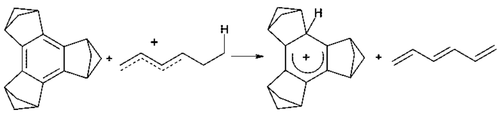
(7) -41.5 (-41.7)

The only possible conclusion from this discussion suggests that ASE is not a general method for assessing aromaticity and cannot be applied for the systems that are discussed here.[11]


(8) -7.6 (-7.7)


(9) +3.8 (+3.9)

Another energetic criterion is the heat of hydrogenation. Table 1 shows the heat of the first, second, and third hydrogenation of benzene, **2** and **3**. The first heat of hydrogenation of **3** is more exothermic than that of benzene by 18.8 kcal mol^{-1}, whereas that of **2** is more endothermic by ~2 kcal mol^{-1}, indicating similar aromaticities for benzene and **2**, whereas **3** is much less aromatic. The second hydrogenations of **2** and **3** are more exothermic than that of benzene by ~7 and 17.8 kcal mol^{-1}. These numbers indicate that in the hydrogenations of dihydro-**2** and dihydro-**3**, there are considerable amounts of strain released relative to the hydrogenation of 1,3-cyclohexadiene. If strain is released also on the first hydrogenation of **2**, then it may be somewhat less aromatic than benzene. The third hydrogenation energy of benzene (i.e., cyclohexene to cyclohexane) is, as expected, by ~1.5−2 kcal mol^{-1} more exothermic than the second hydrogenation, but the third hydrogenations of **2** and **3** are much less exothermic, ~−4 and −19 kcal mol^{-1}, respectively. This reflects the fact that, in agreement with experimental results for a similar system,[12] all-*cis*-hexahydro **2** and **3** are planar and, therefore, inherently contain much more strain than chair-cyclohexane. The hydrogenatoion energies therefore suggest that **2** is more-or-less aromatic as benzene and **3** are much less aromatic or nonaromatic. This conclusion is in accordance with the ring currents for these systems.[7,8] Please note that the total heat of hydrogenation cannot be a good measure for relative aromaticities and that, although the difference between the experimental heat of hydrogenation of benzene (49.3 kcal mol^{-1})[13] and the B3LYP/6-311G* heat of hydrogenation (43.9 kcal mol^{-1}) is significant, the differences between the systems should be rather accurate.

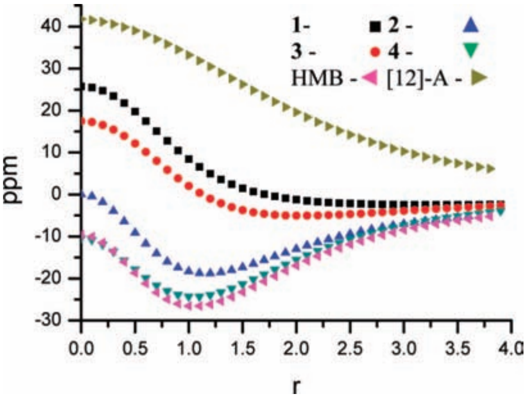


Figure 1. The out-of-plane components of the NICS-scans of **1**−**4**, HMB (hexamethylbenzene) and [12]-A D$_{3}$h-[12]-annulene).

Magnetic Criteria

The NICS scans[14] of **2** and **4** (see Supporting Information) show large induced diamagnetic ring currents. The out-of-plane components show minima of −18.8@1.3 and −24.3@1.1 for **2** and **4**, respectively, which indicate diamagnetic ring currents almost as strong as that in benzene (−28.8@1.1) and hexamethylbenzene (−26.6@1.1). The reason for this is found in the π-MOs. The D_{3h} systems **2** and **4** retain the same π-MO structures as that of D_{6h} benzene (although at different eigenvalues) and, therefore, although geometrically localized, maintain the electronic properties that result from delocalization, as in benzene. This looks like a strong contradiction to the Hückel treatment, which assigned different structures of energy levels to benzene and cyclohexatriene. This point will be discussed below. The NICS scans of **1** and **3** show completely different pictures (see Supporting Information). In **3**, both rings show minima of the out-of-plane component (which indicate diamagnetic ring current)[14] but a very shallow and remote one (−5.1@2.1 and −6.1@1.7 for the six- and four-membered rings, respectively) that is similar to what was found for nonaromatic conjugated systems (e.g., 1,3-butadiene).[14] The situation in **1** is principally similar, with minimum values of −2.5@3.3 and −4.0@2.5 for the central six- and four-membered rings, respectively. The terminal rings show large diamagnetic ring currents with minima of −25.1@1.1.[15] However, in contrast to other nonaromatic systems, the values at short distances from the systems are highly positive, indicating paramagnetic ring currents. Figure 1 shows the out-of-plane components of **1**−**4** with hexamethylbenzene and the hypothetical all-*cis*-planar [12]annulene[16] as the references for the behavior of the out-of-plane component of aromatic and antiaromatic systems, respectively. It can be clearly observed that **2** and **4** have a diamagnetic ring current similar to that of hexamethylbenzene, whereas **1** and **3** show a NICS scan behavior which is in between the aromatic and antiaromatic models.

TABLE 1: First, Second, Third and Total Hydrogenation Energies (kcal mol^{-1}) of Benzene, 2 and 3

	benzene	2	3
1st hydrogenation	+10.9 (+9.3)	+13.0 (+11.2)	−7.6 (−9.5)
2nd hydrogenation	−23.9 (−25.8)	−30.7 (−32.9)	−41.6 (−43.6)
3rd hydrogenation	−25.5 (−27.4)	−1.7 (−3.6)	−17.5 (−19.3)
total	−38.5 (−43.9)	−19.3 (−25.3)	−66.7 (−72.4)

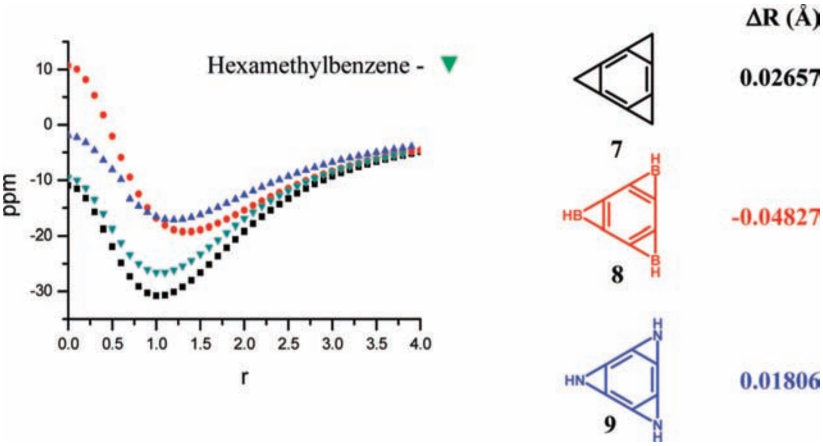


Figure 2. ΔR and the out-of-plane components of the NICS-scans of **7**−**9** hexamethylbenzene.

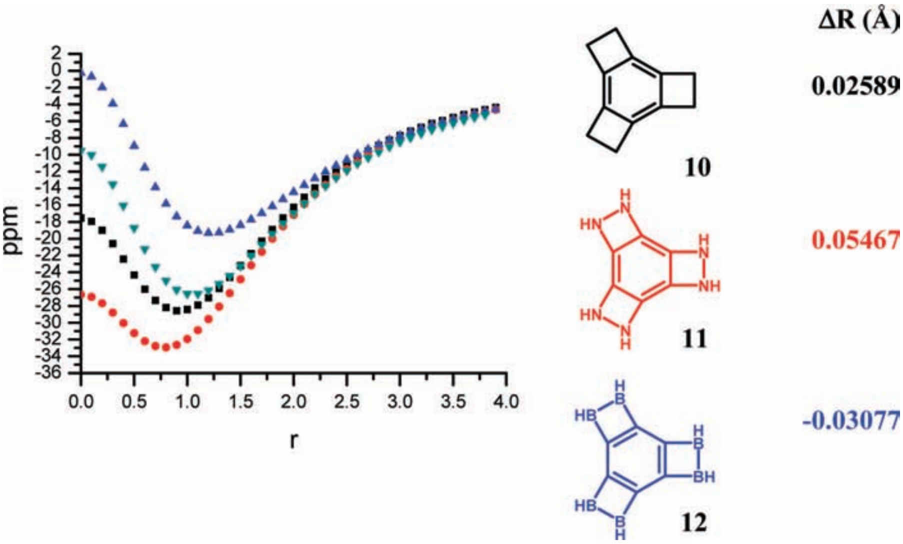


Figure 3. ΔR and the out-of-plane components of the NICS-scans of planar **10**−**12** and hexamethylbenzene.

In order to further understand the effect of bond localization on the ring current, other systems (which were studied in the past for probing the importance of aromaticity−antiaromaticity interactions and strain on the localization of aromatic bonds) were studied here. Figure 2 shows the out-of-plane components of **7**−**9**[17] together with the amount and direction of the bond localization. Figure 3 shows the respective data for planar **10**−**12**[18] and Figure 4 the respective data for fully optimized **10**−**12**. In all cases, the localized systems maintain their diamagnetic ring current regardless of the amount and direction of the bond localization. Even for the fully optimized **12** in which the B−B−C−C dihedral angle is 30.2° (namely, the molecule is far from planarity), a large portion of the diamagnetic ring current is maintained. It looks like all of these systems (and **2** and **4**) retain their diamagnetic ring current regardless of the size and the direction of the bond localization. The strength of the diamagnetic ring current is governed by the electron densities in the six-membered rings. Substituents which donate electron density to the ring (e.g., nitrogen) increase the diamagnetic current. On the other hand, substituents which withdraw electron density from the ring (e.g., boron) decrease the ring current. There is no apparent correlation between the size and direction of the bond localization and the intensity of the ring current. It must therefore be concluded that **1** and **3** are exceptions among bond-localized benzene derivatives. The following paragraph explains why **1** and **3** loose their diamagnetic ring currents.

In most studies, **3** is treated as a benzene derivative. However, it can be viewed as a triply bridged [12]-annulene. Figure 1 shows the out-of-plane component of the NICS scan of D_{6h}-[12]-annulene (see Supporting Information for the full scan).[16] It is different from the picture obtained for **3** and clearly shows a paramagnetic ring current, as expected from a singlet 4nπ electrons system.[14] The comparison between the π-MOs of [12]-annulene and **3** (see Supporting Information) suggests that the lowest π-MOs in both systems are similar. Also, topologically similar are the HOMO of [12]-annulene and HOMO-1 of **3**. However, the other π-MOs are different. In **3**, the pair of HOMO orbitals is composed of a pair of the benzene's HOMO orbitals. The next pair of degenerate orbitals contain combinations of the benzene's HOMO and benzene's π^* orbitals. Both the HOMO and HOMO-2 four orbitals contain some bonding contribution from the four-membered rings' p orbitals. The respective orbitals in [12]-annulene are completely different. Thus, the π-MOs of **3** show a partial character of [12]-annulene and a partial character of benzene. The energies of the lowest MO and HOMO-1 are 123.9 and 2.2 kcal mol^{-1} below the HOMO. Thus, the character arising from these orbitals should be manifested at close proximity to the ring, whereas the diamagnetic (aromatic) character is farther away. This is exactly what is observed by the NICS scan (Figure 1) and leads to a system that is overall nonaromatic. The similarity between the NICS scans of **1** and **3** suggests that the same argumentation is valid also for triangular phenylenes.

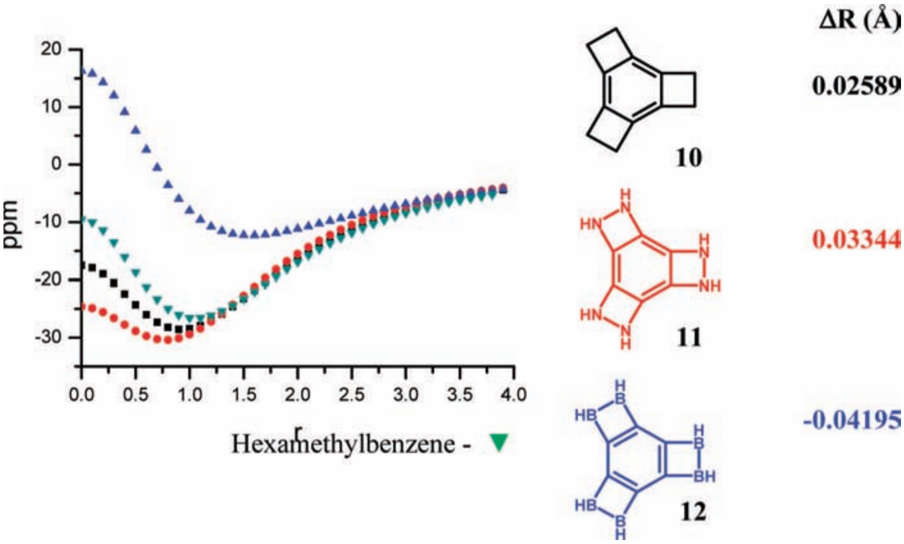


Figure 4. ΔR and the out-of-plane components of the NICS-scans of fully optimized **10**−**12** and hexamethylbenzene.

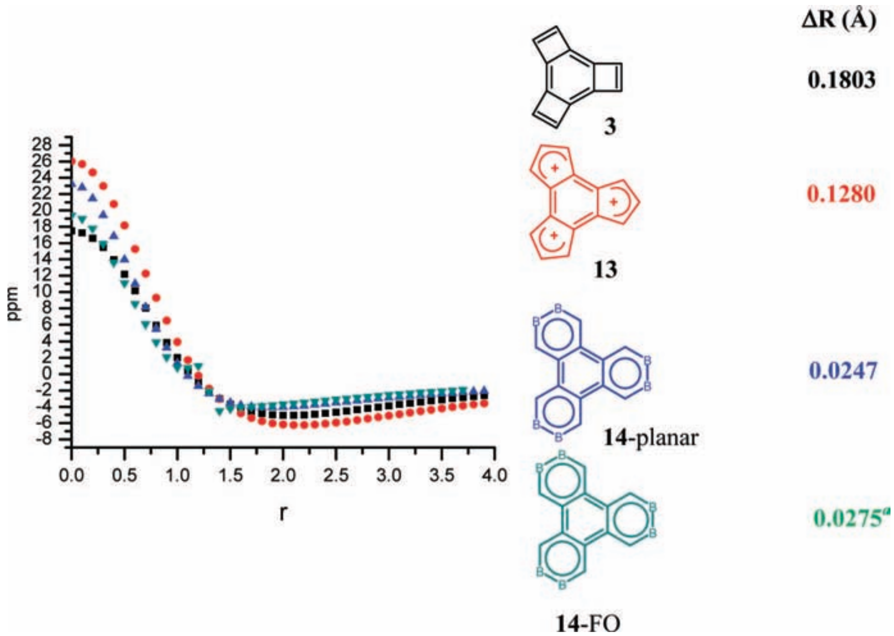
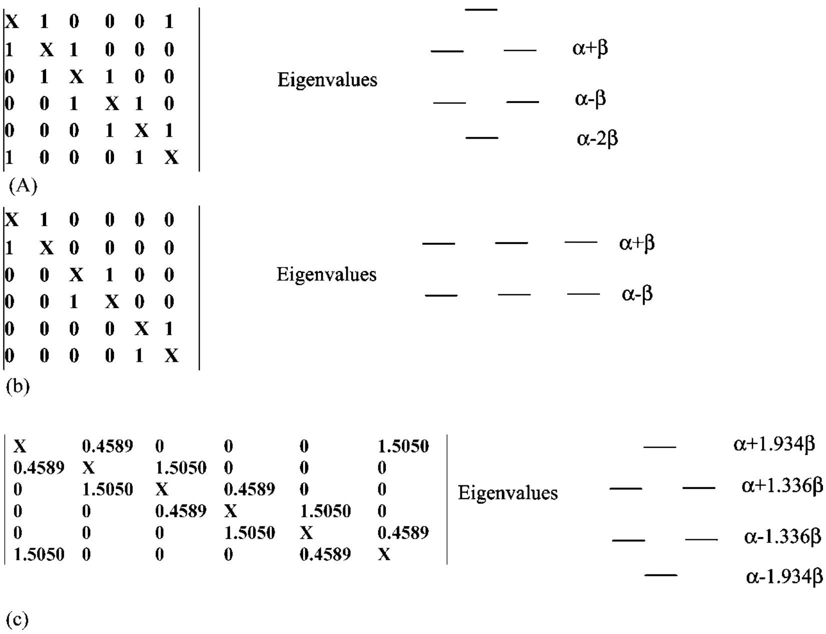


Figure 5. ΔR and the out-of-plane components of the NICS-scans of **3**, **13**, planar-**14** and fully optimized-**14**. (a) Average.

The analysis presented above, namely, heat of hydrogenation and ring currents analyses, suggests that there is no apparent connection between the loss of aromaticity and bond localization. All bond-localized benzene derivatives are strained and therefore exhibit strain-induced bond localization (SIBL).[19] To shut down the diamagnetic ring current, the presence of additional π electrons in the annulated rings seems to be necessary. If this is indeed the case, then the same loss of diamagnetic ring current should be observed in isoelectronic derivatives which are less or not geometrically localized. For this purpose, the structures of **13** and **14** were optimized (**14** at D_{3h} symmetry[20] and fully optimized), and the NICS scan was studied (see Supporting Information). Figure 5 shows the out-of-plane components of the NICS scans of **3**, **13**, and **14** together with the localization of the systems.[21] Although the amount of bond localization varies considerably (between 0.18 Å in **3** and less than 0.03 Å in **14**), the three systems show almost identical ring current properties. These finding reinforce the conclusion that there is no connection between bond localization and the loss of diamagnetic ring current, in general and specifically for **1** and **3**.

A Note about Hückel Treatment of Benzene and Cyclohexatriene

The Hückel matrices of benzene and cyclohexatriene are shown in Figure 6a and b, respectively. Hückel's assumption for cyclohexatriene was that the overlap interaction ($H_{i,j}$) remains β (i.e., the same as that in D_{6h} benzene between each couple of adjacent carbon atoms) over the short bonds and goes to zero over the long bonds. This may be a too crude approximation; the C−C bond length in benzene is ∼1.4 Å, and in cyclohexatriene, it should be ∼1.5 and 1.3 Å for the long and short bonds, respectively. Thus, the value of $H_{i,j}$ across the short bond must be larger than β, and across the long bond, it should be smaller than β but perhaps not zero. Estimation of these values was obtained by comparison of the respective elements of the density matrices in D_{6h} and D_{3h} benzenes (i.e., fully optimized benzene and **4**) and found to be 0.4589β across the long bond and 1.5050β across the short bond. The corrected matrix for cyclohexatriene is shown in Figure 6c with its eigenvalues. Even within this very crude level of theory, when only the approximation for the values of $H_{i,j}$ is refined, the results show



$$\begin{vmatrix} X & 1 & 0 & 0 & 0 & 1 \\ 1 & X & 1 & 0 & 0 & 0 \\ 0 & 1 & X & 1 & 0 & 0 \\ 0 & 0 & 1 & X & 1 & 0 \\ 0 & 0 & 0 & 1 & X & 1 \\ 1 & 0 & 0 & 0 & 1 & X \end{vmatrix}$$

$$\begin{vmatrix} X & 1 & 0 & 0 & 0 & 0 \\ 1 & X & 0 & 0 & 0 & 0 \\ 0 & 0 & X & 1 & 0 & 0 \\ 0 & 0 & 1 & X & 0 & 0 \\ 0 & 0 & 0 & 0 & X & 1 \\ 0 & 0 & 0 & 0 & 1 & X \end{vmatrix}$$

$$\begin{vmatrix} X & 0.4589 & 0 & 0 & 0 & 1.5050 \\ 0.4589 & X & 1.5050 & 0 & 0 & 0 \\ 0 & 1.5050 & X & 0.4589 & 0 & 0 \\ 0 & 0 & 0.4589 & X & 1.5050 & 0 \\ 0 & 0 & 0 & 1.5050 & X & 0.4589 \\ 1.5050 & 0 & 0 & 0 & 0.4589 & X \end{vmatrix}$$

Figure 6. Hückel matrices for (a, top) benzene, (b, middle) cyclohexatriene according to Hückel's approximation, and (c, bottom) cyclohexatriene with correction of $H_{i,j}$ (see text) and the respective eigenvalues for each. $X = (\alpha - E)/\beta$.

that the orbital structures of benzene and cyclohexatriene are identical. An added benefit of this treatment is the effect of delocalization on the energy of the π system. The energy of the occupied π system in delocalized benzene is $6\alpha-8\beta$, whereas in cyclohexatriene (Figure 6c) it is $6\alpha-9.212\beta$.[22] Thus, even within the Hückel framework, once one approximation is refined, the delocalization destabilizes the π system, in accordance to Shaik's conclusions.[1] Historically and philosophically, it seems that Hückel's "one approximation too much" led to more than six decades of a notion that there is a connection between bond localization in aromatic compounds and the loss of (some) aromatic properties, creating a debate that has still not been settled.[6]

Conclusions

The fact that the first cyclohexatriene which was experimentally prepared (**1**) is strained and represents aromatic–antiaromatic interactions is a coincidence. This paper shows that there is no connection between bond localization and the loss of aromatic properties. It is shown that some localized systems (in some cases, very localized systems) retain aromatic properties such as endothermic first hydrogenation and diamagnetic ring current. On the other hand, systems that have additional external six-conjugated π electrons loose these aromatic properties regardless of the size of the bond localization. It is therefore concluded that bond localization in aromatic compounds and the loss of aromatic properties such as diamagnetic ring current are two phenomena which are completely unrelated to each other.

Supporting Information Available: NICS scans and molecular orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) It is noted that the four- and six-membered rings are conjugated. Thus, the NICS values of each ring are influenced by the annulated ring(s). See ref 14.

(16) [12]-annulene is a nonplanar molecule. However, for the sake of comparison to the planar **3**, the D_{6h} planar [12]-annulene, which includes three imaginary frequencies, was used.

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(21) Note that the central six-membered ring in optimized **14** is nonplanar. Thus, the distance for the minimum value of the out-of-plane component of the NICS is from an averaged point, not from the ring plane as that in the D_{3h} species.

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