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Strain-Induced Bond Localization. The Heteroatom Case

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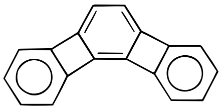
Abstract: Strain-induced bond localization (SIBL) has been a debated issue for almost 70 years. In the past decade there have been some developments that showed that strain can indeed localize aromatic bonds. However, some compounds that should have exhibited positive ΔR (Mills−Nixon distortion) showed instead negative ΔR (anti-Mills−Nixon distortion), apparently more coherent with π effects (aromaticity−antiaromaticity arguments). Using ab initio methods, the structure of cyclopropabenzenes, cyclobutabenzenes, and benzocyclobutadienes, where the three- and four-membered rings consist of carbon, nitrogen, or boron, were calculated at the B3LYP/6-31G* level of theory. Analyses of these structures show that SIBL and not aromatic factors are responsible for the localization observed in the aromatic moieties, both with positive and negative ΔR.

Introduction

Strain-induced bond localization (SIBL) has been a debated issue since its introduction in 1930 by Mills and Nixon.[1] It has become increasingly important since Shaik et al. published their views regarding the phenomenon of aromaticity.[2] Being a σ effect, SIBL is orthogonal to the π system of the aromatic moiety and as such can serve as a "handle" for the study of the π and σ effects in these systems. Another milestone in this area was the synthesis and structural characterization of the first cyclohexatrienes (e.g., bond-localized benzene), the angular-[3]-phenylene (**1**)[3] and the "star-phenylene" (**2**)[4] by Vollhardt.



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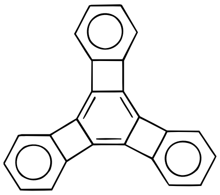

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These fascinating molecules and the new view of aromaticity revived the field of bond-localized aromatic systems. Recently, the topic of the Mills−Nixon effect has been reviewed,[5] and it was suggested that the phenomenon of bond localization in aromatic systems due to strain should not be called "Mills−Nixon effect".[5a] As we agree with this, the term SIBL is used throughout the paper.[6]

The problems in the experimental study of bond-localized aromatic systems is that in σ-strained systems that showed it (e.g., **2** and other systems; see below) the phenomenon could also be explained by other arguments. There are three approaches to explain bond localization in strained aromatic systems. One is the classic π approach, which relays on aromaticity−antiaromaticity arguments to explain the phenomenon.[3,5b,6b,7] This approach relies on π electron count in the small annelated ring. For example, if the electrons in the central ring of **2** would be delocalized, then each of the four-membered rings would have 4 π electrons. Thus, the bonds in the central ring localize in such a way that the antiaromatic destabilization is avoided. This approach predicts that if the small ring would contain $4n + 2$ π electrons, the systems should show negative ΔR.[6] A second approach explains the bond localization by SIBL. This approach is based on the strain effect that causes rehybridization in the strained atoms. Thus, the aromatic atoms are not sp^2 hybridized, but have a different hybridization at each of the bond directions, and consequently, the two "aromatic bonds" that each carbon atom forms are of different bond length. As this is a rehybridization effect, the bonds with the wider bond angles would have lower p character and therefore form shorter bonds to the adjacent carbon atom, namely, positive ΔR. A similar effect was found experimentally.[8] This model suggests that the π frame is a spectator in the process of localizing the aromatic bonds and follows the geometry that is dictated by the σ frame. One other important feature of this approach is the curvature of the bonds involved. Thus, if the bonds are curved, the effective bond angle (that is formed by the two maximum electron density paths) is different from the bond angles that are obtained by connecting the respective atoms by straight lines. Consequently, the rehybridization and therefore the bond localization at the strained atoms is different than

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[1] Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.

[2] (a) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (b) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (c) Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908. (d) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (e) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Chem. Phys* **1988**, *92*, 5086.

[3] Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

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[5] (a) Siegel, J. S. *Angew. Chem.* **1994**, *106*, 1808; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721. (b) Frank, N. L.; Siegel, J. S. In *Advances in Theoretically Interesting Molecules*; JAI Press Inc.: Greenwich, CT, 1995; Vol. 3, pp 209−260.

[6] (a) "Positive ΔR" means that the bonds exocyclic to the annulated small ring(s) are shorter than the endoyclic bonds (i.e., classically called "Mills−Nixon distortion"). "Negative ΔR" means the reverse. (b) Note that this definition is analogous to "delta" as previously defined by Baldridge and Siegel. See: Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

[7] See, for example: Faust, R.; Glendening, E. D.; Streitwieser, A. Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263.

[8] (a) Ermer, O.; Lex, J. *Angew. Chem.* **1987**, *99*, 455; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 447. (b) Ermer, O.; Bell, P.; Schäfer, J.; Szeimies, G. *Angew. Chem.* **1989**, *101*, 503; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 473.

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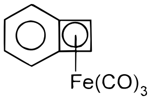
expected by the apparent bond angle. Some years ago we studied this approach, and it was predicted (a) that tricyclobutabenzene would show curved bonds and (b) what the requirements are for obtaining a bond-localized aromatic system.[9] These predictions were shown experimentally to be true by (for example) studying the structure and X−X electron density deformation of tricyclobutabenzene that showed that the bonds are indeed curved.[10] Aromatic systems annelated to bicyclic moieties were prepared, and their structures and other properties showed bond localization.[11] Transition metal complexes of cyclobutabenzene, benzocyclobutadiene, and tris(cyclobutadieno)benzene were shown to exhibit bond localization.[12] However, these results could have also be explained by the other two approaches. The third approach was developed by Shaik,[13] who suggested a combination of σ and π effects. SIBL is the reason for distorting the σ frame from equal bond lengths, but this distortion is not enough to account for the (relatively) large ΔR that are found. It is the distortive nature of the π system that is responsible for a large part of the localization. This approach successfully explains the alternating geometrical properties of the ground and excited states in localized and delocalized benzene moieties.[13a]

There were, however, some facts that were not explained by the above-mentioned studies, such as why some of the molecules (for example, **3**,[12a] **4**,[14] and **5**[15]) that should exhibit positive ΔR show, in fact, negative ΔR. Extreme examples of systems that show distortion which is apparently inconsistent with SIBL were studied by Maksic et al.[16] and by Siegel et al.,[6] who have calculated the structures of bora- and aza-substituted cyclopropabenzenes. The concept of these studies was to use heteroatoms in order to introduce different numbers of π electrons, leaving all the rest of the conditions almost unchanged. Thus, the comparison between **6**, **7**, and **8** should indicate whether aromatic factors or strain is dominating the geometry of the six-membered rings. Under the assumption that the three systems should have comparable amounts of strain, when the electrons in the six-membered rings are delocalized, the three-membered rings in **6** are nonaromatic, in **7** they are antiaromatic, and in **8** they are aromatic. The geometries of the central rings of these systems should therefore indicate how important these π (aromaticity−antiaromaticity) effects are. Calculations at the HF/6-31G(D) theoretical level suggested only a slight positive ΔR in **6**, a strong positive ΔR in **7**, and a strong negative ΔR in **8**. The straightforward conclusion was therefore that π effects (i.e., aromaticity−antiaromaticity) are much more important than strain in determining the geometry of the six-membered rings, in strong contradiction to our understanding of bond localization[9] and of Siegel's experimental results.[11] This dichotomy and the data presented above led to the present study.



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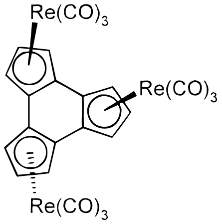

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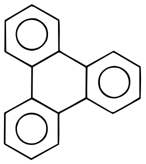

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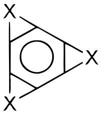

6 X=CH$_2$
7 X=NH
8 X=BH

In the mid 1980s Cremer et al. published a series of papers that reported study of the bond curvature in different systems. They found that, in cyclopropanes,[17] the electronegativity of a substituent or a heteroatom affects the bond curvatures, from very inflated "banana" bonds in electropositive substituted cases to "inverted banana" bonds in electronegative substituted systems. Another connection between atomic properties and molecular structure was suggested by Shaik et al. They have shown that the geometry of isoelectronic X_3 species (e.g., being more stable as a symmetric X_3 or as $X_2 + X$) is governed by the differences between their ionization potentials and electron affinities,[2e] properties that are related to electronegativity. These studies suggest that, even in molecules that bare conjugated π systems, the geometry is determined (at least to a large part) by the type of atoms involved and not by the number of π electrons. Thus, when replacing a carbon moiety (e.g., CH_2 in **6**) by nitrogen or boron moieties (i.e., NH in **7** and BH in **8**) it is not only the number of π electrons that is changed but also the electronegativity (and other atomic properties) that affects the bond curvature.

According to the Hückel concept, aromaticity and antiaromaticity are properties related to the number of π electrons in a cyclic conjugated π system. The centers that bear these π electrons are irrelevant to the question of whether the system is aromatic (or antiaromatic).[18] SIBL is an effect that depends on strain and on bond curvature. As such, it should be sensitive to the properties of the atoms building the system (i.e., electronegativity, ionization potential and electron affinity) but is not affected by the number of π electrons. Thus, SIBL and aromatic factors are orthogonal effects in small-ring-substituted aromatic moieties. As nitrogen is more electronegative than carbon, and boron more electropositive, systems **6**−**8** are not appropriate probes to distinguish between π and σ effects, *as*

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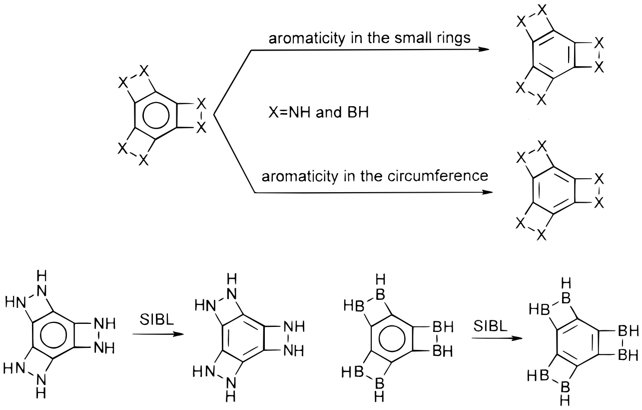
(15) (a) Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503. (b) Ferraris, G.; Jones, D. W.; Yerkess, J. *Z. Kristallog.* **1973**, *138*, 113.

(16) (a) Maksić, Z. B.; Eckert-Maksić, M.; Pfeifer, K., −H. *J. Mol. Struct.* **1993**, *300*, 445. (b) Yánes, O. M. O.; Eckert-Maksić, M.; Maksić, Z. B. *J. Org. Chem.* **1995**, *60*, 1638. (c) Eckert-Maksić, M.; Glasovac, Z.; Maksić, Z. B.; Zrinski, I. *J. Mol. Struct. (THEOCHEM)* **1996**, *366*, 173.

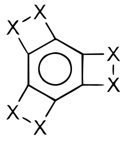
(17) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(18) Of course, the magnitude of "aromaticity" is different for heteroatoms in aromatic systems (e.g., pyridine and furan are "less aromatic" than benzene), and in some cases, where the interacting orbitals are energetically too different the magnitude of aromaticity is negligible.

Scheme 1. Geometrical Effects of SIBL and Aromaticity in **8** and **9**



both aromaticity−antiaromaticity and SIBL (i.e., bond curvature) result in the same geometrical distortions of the central six-membered ring. A system where the two factors would impose opposite geometrical effects is therefore needed, to distinguish between the two. Such systems are **9**−**11**. In **9**, as predicted theoretically[9] and later verified experimentally,[10] the bonds are curved and therefore the central ring shows only a small positive Δ*R*. In each of the four-membered rings of **10** and **11** there are $4n + 2$ π electrons if the central ring is delocalized. An alternative way of counting electrons in these systems is by regarding them as triply bridged 12-annulenes. In this case, the electrons have to be counted in the circumference, where both **10** and **11** have $4n + 2$ π electrons.[19] Thus, counting the electrons in each four-membered ring separately, aromaticity factors and SIBL predict that **10** should show negative, Δ*R*, aromaticity arguments because of the 2 π electrons in each four-membered ring, and SIBL because the bond curvature is large (as boron is electropositive)[20] and therefore the effective bond angle is much larger than the observed bond angle. In **11**, aromaticity factors suggest negative Δ*R* (because of the 6 π electrons in each four-membered ring), but SIBL predicts positive Δ*R* as nitrogen is electronegative,[20] and the bonds should be much less curved. Counting the electrons on the circumference predicts that **10** and **11** should show positive Δ*R*. Therefore, aromaticity arguments predict negative Δ*R* (if the electrons are counted in each four-membered ring separately) or positive Δ*R* (if the electrons are counted in the circumference) for both systems, whereas SIBL arguments predict opposite localization for each (Scheme 1). The comparison between **9**, **10**, and **11** is therefore expected to determine the relative importance of SIBL and aromaticity factors in localizing aromatic moieties annulated to small rings.



9 X=CH_2
10 X=BH
11 X=NH

Method. Gaussian 94W[21] was used for the calculations. The geometries of the systems were optimized under the B3LYP/6-31G* theoretical level. This,[12b] and similar,[11a] levels of theory were shown to reproduce well the geometries of systems of the type discussed here. To further test this, we have optimized the structures of cyclopropabenzene, cyclobutabenzene, [1,2]-[3,4]-bicyclobutabenzene, tricyclobutabenzene, and triphenylene under the B3LYP/6-31G* theoretical level and compared the calculated geometries to X-ray and neutron diffraction data.[22] All the experimental structures were reproduced by B3LYP/6-31G* within experimental errors, except from cyclopropabenzene, where the calculated bonds were longer than those determined experimentally by 0.01−0.02 Å. Thus, although the aim of this work is not to reproduce (or predict) exact geometries, we are quite confident that at least for comparative purposes the B3LYP/6-31G* calculated structures are good enough.[23]

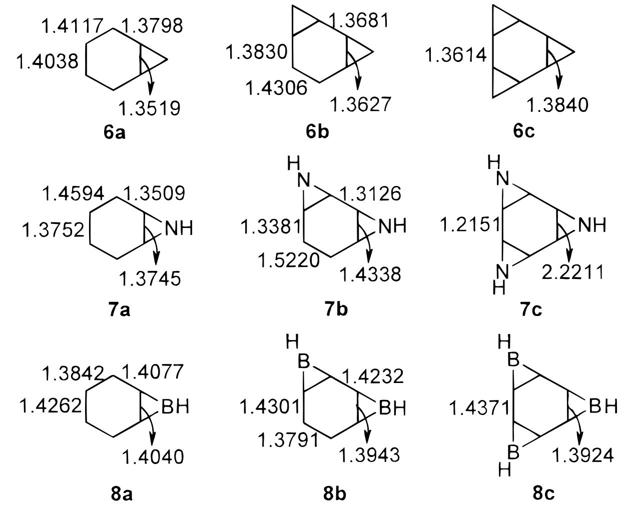


Figure 1. B3LYP/6-31G*-optimized geometries of **6**−**8**.

Results and Discussion

(a) Cyclopropa Annulated Systems. To bring Siegel's[6b] and Maksić's results to the same theoretical level used here, and in order to study the effect of successive annelation, the systems **6**−**8** have been recalculated at the B3LYP/6-31G* level of theory. Figure 1 presents the geometrical parameters of the six-membered rings obtained for each of the systems, Table 1 shows the average bond lengths in each of the systems, and Figure 2 graphically describes the localization as a function of the number of annelated rings. Qualitatively, the results obtained here are similar to those obtained by Siegel[6b] and Maksić.[16] Systems **6** show a small positive Δ*R*, and **7** and **8** show positive and negative Δ*R*, respectively. However, there

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(19) If the electron count is carried out on the circumference, the aromaticity−antiaromaticity argument would predict localization in **7** and **8** that is opposite to the observed. However, as in **10** and **11** the small annelated rings are larger, this possibility is considered.

(20) Relative to carbon (i.e., **9**) that shows a small positive Δ*R*.

(21) Gaussian 94, Revision E.1. Frischm, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A. Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W. Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J. Baker,V.; Stewart, J. P. Head-Gordon, M.; Gonzalez, V; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(22) Experimental structures. (a) Cyclopropabenzene: Neidlein, R.; Christen, D.; Poignèe, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Angew. Chem.* **1988**, *100*, 292; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294. (b) Cyclobutabenzene: Boese, R.; Bläser, D. *Angew. Chem.* **1988**, *100*, 293; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304. (c) [1,2][3,4]-bicyclobutabenzene and tricyclobutabenzene: See ref 10. (d) Triphenylene: X-ray structure: See ref 15a. Neutron diffraction structure: See ref 15b.

(23) To test the π effects, all the bora and aza derivatives were kept planar, thus enforcing each to have zero and two electrons in a p orbital, respectively, that are conjugated to the π system of the six-membered ring.

Table 1. Average Endo and Exo Bond Lengths (Å) in **6**−**8**

	av endo	av exo	Δ
6a	1.3918	1.3878	0.0040
6b	1.3583	1.3780	0.0073
6c	1.3840	1.3614	0.0226
7a	1.4311	1.3590	0.0721
7b	1.4632	1.3296	0.1336
7c	2.2211	1.2151	1.006
8a	1.3908	1.4134	−0.0226
8b	1.3892	1.4278	−0.0386
8c	1.3924	1.4371	−0.0447

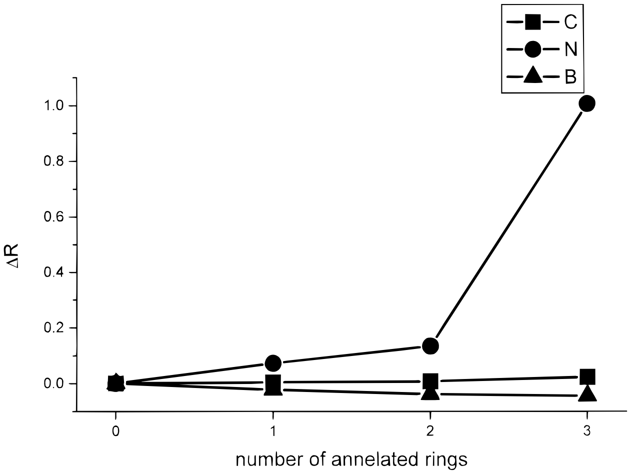

Figure 2. ΔR as a function of the number of annelated rings in **6**−**8**.

are some more conclusions that can be drawn: One is that annelation is an additive effect (with the exception of **7c**[24]).[25] Thus, adding an annelated three-membered ring causes the localization effect to increase (i.e., the value of |ΔR| is larger). Another effect is that the six-membered rings shrink with the annelation of cyclopropanes **6** and inflate with the annelation of boracyclopropanes **8**. A part of this effect was discussed by Maksic,[16] and will be further discussed elsewhere.[26] Overall, it can be concluded that the phenomena reported by Siegel[6b] and Maksić[16] are reproduced at the B3LYP/6-31G* theoretical level.

(b) Cyclobuta Annelated Systems. Figures 3 and 4 and Table 2 describe the results for the cyclobutabenzene derivatives **9**−**11**. The all-carbon systems **9** show small positive ΔR values (for example, the endocyclic and exocyclic bond lengths in **9c** are 1.4098 and 1.3857 Å, respectively, ΔR = 0.0241 Å). The bora systems **10** show negative ΔR of −0.0302 Å in **10c**, and **11** show a relatively (to **9** and **10**) large positive ΔR, 0.0527 Å in **11c**. Thus, the calculations show that the systems behave exactly as expected from SIBL (i.e., positive ΔR in **11** and negative ΔR in **10**) and not as aromatic considerations predict (i.e., positive or negative ΔR for both **10** and **11**). The behavior of the systems is regular; i.e., the distortion from equal bond lengths in the six-membered rings increases with the degree of annelation (Figure 4). Furthermore, the magnitude of the localization in **10** and **11** is similar to that in **9** and not to the localization in unsaturated systems such as benzotricyclobutadiene (see below) for which π factors should be similar to those in **10** and **11**. Thus, it is concluded that SIBL is responsible for the distortion of the six-membered rings in **6**−**11** and not aromatic factors.

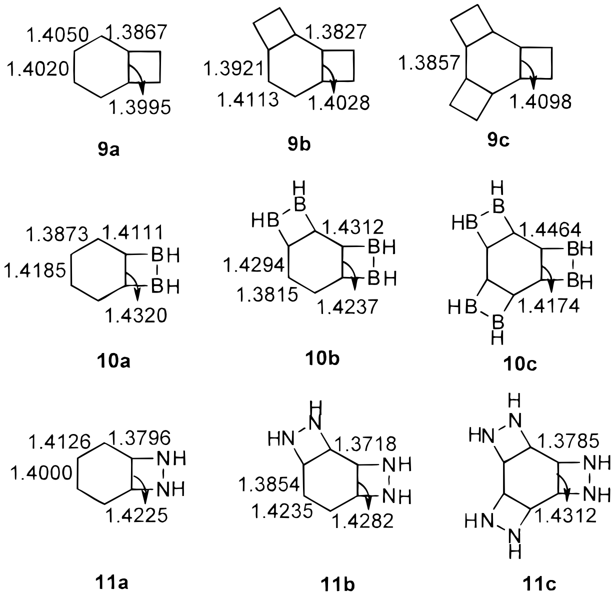

Figure 3. B3LYP/6-31G*-optimized geometries of **9**−**11**.

Table 2. Average Endo and Exo Bond Lengths (Å) in **9**−**11**

	av endo	av exo	Δ
9a	1.4032	1.3918	0.0114
9b	1.4056	1.3890	0.0166
9c	1.4098	1.3857	0.0241
10a	1.4022	1.4136	−0.0114
10b	1.4096	1.4300	−0.0204
10c	1.4174	1.4476	−0.0302
11a	1.4159	1.3864	0.0263
11b	1.4266	1.3809	0.0457
11c	1.4312	1.3785	0.0527

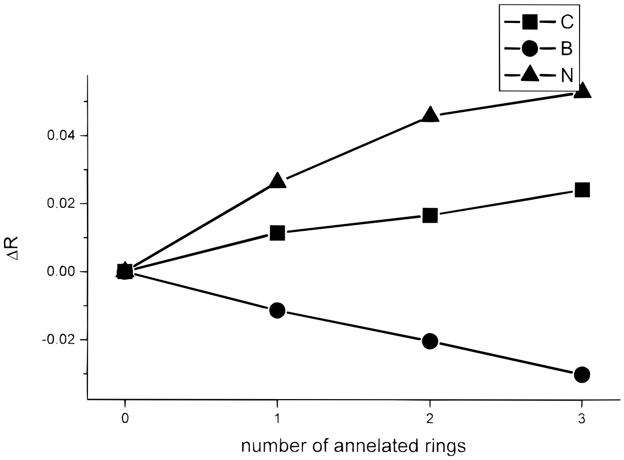

Figure 4. ΔR as a function of the number of annelated rings in **9**−**11**.

(c) Benzocyclobutadiene Derivatives. Previously, we showed that introducing unsaturation at the small ring(s) causes pronounced bond localization in the "aromatic" ring, due to the reduced ability of the unsaturated atoms (as compared to their saturated analogues) to form curved bonds.[9] To investigate the

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[24] Due to the large localization effect, **5c** (as a triazatricyclopropabenzene) is not a minimum at B3LYP/6-31G*, and within D_{3h} symmetry, it is actually 1,4,7-triazacyclodeca-2,5,8-triyne. This causes a break in the line (Figure 1) that describes the effect of successive annelation.

[25] This was shown before for similar systems. See: Jemmis, E. D.; Kiran, B. *J. Org. Chem.* **1996**, *61*, 9006. Note, however, that the additivity is not a general rule for small-ring annelated benzene systems. See ref 12b.

[26] The inflation and deflation of the six-membered rings in the different substituted system is important but is irrelevant to the issue discussed in this paper, namely, localization of the aromatic bonds. As SIBL is a σ effect, it is localizing also pure σ bonds. Thus, the hexahydro-star-phenylene (tris(benzocyclobutacyclohexane)) shows a larger bond localization than tricyclobutabenzene (0.088 and 0.030 Å, respectively). See: Mohler, D. L.; Vollhardt, K. P. C.; Wolf, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 115, and ref 10).

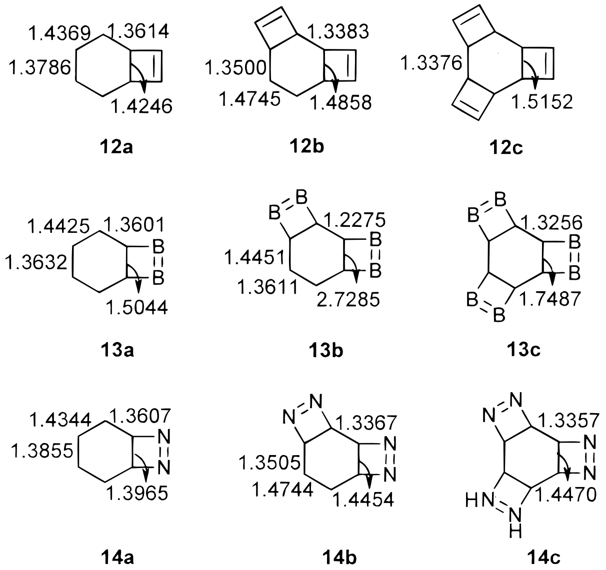
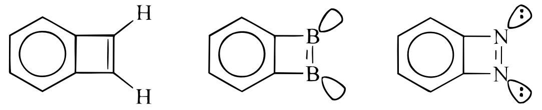
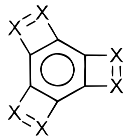


Figure 5. B3LYP/6-31G*-optimized geometries of **12**−**14**.

Chart 1. Electronic Structure of the Double Bonds in (from Left to Right) **12**, **13**, and **14**



effect of unsaturation in the aza- and bora-substituted systems, we have calculated the structures of **12**−**14**.



12 X=CH
13 X=B
14 X=N

Introduction of unsaturation renders the molecules isoelectronic with regard to their π system. All have π bonds in the four-membered rings within the same plane of the benzene's π frame. The systems differ electronically in the σ frame: Whereas the benzocyclobutadienes have C−H bonds, the aza-substituted systems have lone pairs, and the bora-substituted systems have empty orbitals (Chart 1).[27] Thus, all the unsaturated systems have 4 π electrons in the four-membered rings (when the six-membered ring is delocalized).

The results of the calculation are presented in Figure 5, Table 3, and Figure 6. Obviously, the localization observed in all the systems is larger than in the analogous saturated systems (**9**−**11**). The largest difference is observed in the bora systems: Whereas **10c** shows a negative ΔR of −0.0302 Å, **13c** exhibits a large positive ΔR of 0.4231 Å. How can this be accounted for?

Table 3. Average Endo and Exo Bond Lengths (Å) in **12**−**14**

	av endo	av exo	Δ
12a	1.4328	1.3671	0.0657
12b	1.4820	1.3461	0.1359
12c	1.5152	1.3376	0.1776
13a	1.4631	1.3611	0.1020
13b	2.2727	1.3726	0.9001
13c	1.7487	1.3256	0.4231
14a	1.4218	1.3690	0.0528
14b	1.4551	1.3459	0.1092
14c	1.4770	1.3357	0.1413

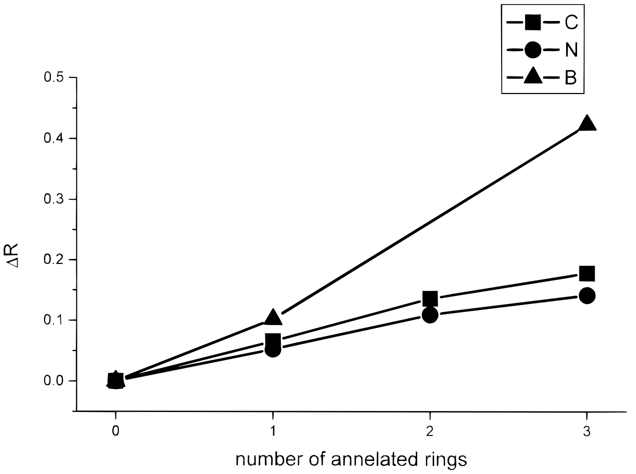


Figure 6. ΔR as a function of the number of annelated rings in **12**−**14**. The parameters of **13b** were omitted for clarity.

Table 4. Energy of the HOMO in Benzene and Various Cyclobutenesa

	E_{HOMO}[b]	ΔE_{HOMO}[b]	bond length[c]
benzene[a]	−0.25490	0.01145	1.4728
cyclobutene	−0.24345		
benzene[a]	−0.25282	0.09064	1.4674
1,2-diboracyclobutene	−0.16218		
benzene[a]	−0.25724	0.08616	1.4523
1,2-diazacyclobutene	−0.3430[d]		

[a] With HCC angles equal to XCC angles in **12**−**14**, respectively. [b] Hartrees. [c] C−X bond lengths in **12**−**14**, respectively. [d] Energy of the π bond (HOMO-2). The HOMO and HOMO-1 are the lone pairs of the nitrogen atoms.

The antiaromatic interaction between the X═X fragment (X = CH, B, N) and the central ring π system in **12**−**14** is an inverse function of the distance between the interacting orbitals and the energy gap between them. To assess the energy gap, we have calculated (at B3LYP/6-31G*) benzene molecules with HCC angles identical to those found in **12**−**14** and cyclobutene, 1,2-diazacyclobutene, and 1,2-diboracyclobutene. The results are given in Table 4. Clearly, the smallest energy gap is in **12**, whereas the shortest bond is in **14**. Thus, if π factors are the localization driving forces, the localization order should be **12** > **14** ≥ **13**. The data show that **13** is by far the most localized system, a fact that is not coherent with aromaticity−antiaromaticity arguments. The reason for this is that the fragment B═B is the least prone for curved bond formation (see below) and due to SIBL **13** is the most localized system.

Other evidence for SIBL can be obtained by correlating the bond angle to the localization. We have previously shown[9] that ΔR is proportional to $\mathrm{Sin}^2(120 - \alpha)$, where α is the "effective bond angle", i.e., the angle formed by the maximum electron density paths.[28] Figure 7 shows the relationship between $(\Delta R_{\mathbf{9-11}} - \Delta R_{\mathbf{12-14}})$ and $\mathrm{Sin}^2\,\phi$, where ϕ is the $\varphi_{\mathbf{9-11}} - \varphi_{\mathbf{12-14}}$

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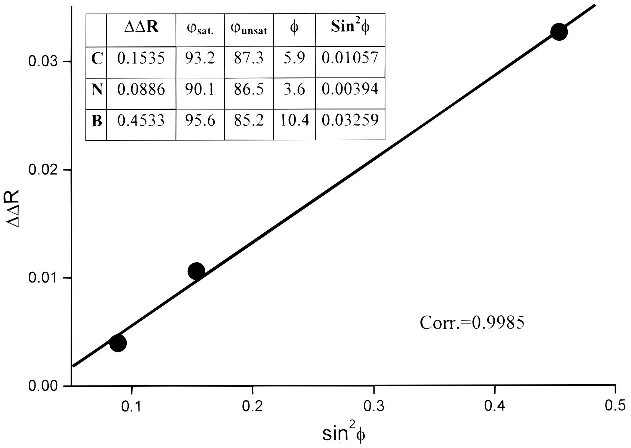
(27) Neither of these (i.e., C−H bond, N lone pair and empty B orbital) are real sp^2 or sp hybrids, as these require bond angles of 120 or 180°, respectively.

(28) See ref 9. This was quantitatively verified by X−X electron density deformation study (see ref 10) and by the fact that the measured bond angle in Siegel's system (ref 11b) is almost identical to that obtained from using ΔR in the above-mentioned relationship.



	ΔΔR	$\varphi_{sat.}$	φ_{unsat}	ϕ	$Sin^2\phi$
C	0.1535	93.2	87.3	5.9	0.01057
N	0.0886	90.1	86.5	3.6	0.00394
B	0.4533	95.6	85.2	10.4	0.03259

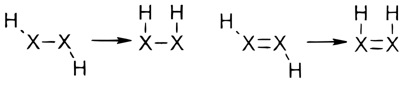
Figure 7. $Sin^2\ \phi$ as a function of $\Delta(\Delta R_{sat} - \Delta R_{unsat})$. See text for details.

(φ is the bond angle in the four-membered rings), respectively. The correlation is clearly linear, indicating a SIBL phenomenon.

(d) Effect of Unsaturation on the Properties of the Benzylic Atoms. Decreasing the p orbital contribution in the hybridization causes the atom to be less prone to the rehybridization that is needed for curved bond formation.[9] However, the very large differences in behavior of the carbon, nitrogen, and boron systems on increasing unsaturation needs explanation.

The localization of an aromatic moiety that is caused by SIBL depends on the effective bond angle $C_{arom}-C_{arom}-X_{benzyl}$ (i.e., the angle formed by the maximum electron density paths). This angle is a result of two opposing factors. Strain, which is imposed by the small bond angles (resulting in positive ΔR) and rehybridization of the benzylic atoms, to form bent bonds that enlarge the effective bond angle and minimize ΔR. The ability of the benzylic atoms to rehybridize depends on its degree of saturation (see above) and on its atomic properties (e.g., electronegativity). Thus, the localization in the unsaturated systems **12**−**14** is expected to be much more strain-dependent relative to the saturated analogues **9**−**11**, due to the extended ability of the last to form curved bonds.

Table 5. Bending Energies (See Text) at MP4/6-311+G**//MP2/6-311+G**[a]



entry	X	HXX angle[a]	ΔH (kcal mol^{-1})
i	CH_2	86.8	27.2
ii	NH[b]	89.9	31.4
iii	BH	84.4	33.7
iv	CH	92.3	32.4
v	N	93.5	17.4
vi	B	85.2	67.0

[a] HX=X angles for iv−vi (degrees). Identical to the C_{arom}−X−X angles in **9**−**14**, respectively. [b] Planar.

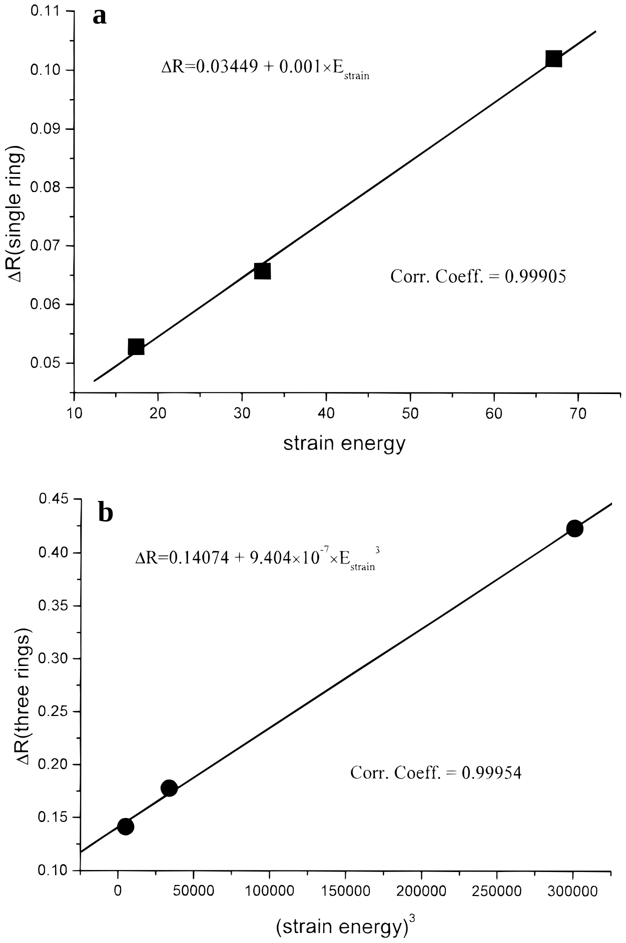


Figure 8. (a) Correlation between strain energy (Table 6) and ΔR in single-ring annelated systems (top) and (b) correlation between (strain energy)^3 and ΔR in tris-annelated systems (bottom).

The strain in the four-membered rings was mimicked by calculating the energy differences between the benzylic fragments connected to hydrogen atoms instead of to aromatic carbon atoms (for example, H_3C-CH_3 for **6**) at optimized geometries and to the same molecules where the H−X−X angles were frozen to the C_{arom}−X−X angles found in the actual tris-annelated systems **9**−**14**. The reasoning of this model is that hydrogen atoms are the least prone to curved bond formation, and therefore they are the best choice to mimic strain.[29] The results of these calculations are given in Table 5. Clearly, the localization in the saturated systems **9**−**11** does not reflect strain alone, as there is no correlation between the amount of strain (Table 5, entries i−iii) and the localization found in the respective tricyclobutabenzene systems (**9**−**11**). Rather, these results reflect the ability of strained saturated boron compound to form inflated banana bonds in order to relieve the excess strain (Table 5, entry iii), so that the C_{arom}−B−B effective bond angle becomes as large as possible (more than 120°), resulting in negative ΔR. The nitrogen derivative, although much less strained (Table 5 entry ii), shows a relatively large ΔR, due to its reduced ability to form curved bonds. When unsaturation is introduced, the situation changes. All the atoms have a much smaller ability to form curved bonds, and therefore, pure strain must be more important in the localization of the six-membered ring. A semiquantitative analysis of the effect of strain is presented below.

When strain is introduced into a system, the system will accommodate it by distributing it on all available sites. When additional strain is imposed, the system has to accommodate a larger amount of strain but on relatively fewer sites that are already strained. Thus, the result of the strain should depend on $(E_{strain})^n$, where n is the amount of strain quanta that are introduced.[30] Specifically for the systems studied here, if strain is the dominant factor in localizing the systems **12**−**14**, its result (ΔR) for the single rings systems (**12a**, **13a**, **14a**) should correlate to E_{strain} (Table 5, entries iv−vi), and ΔR for the tris-annelated systems (**12c**, **13c**, **14c**) should correlate to $(E_{strain})^3$.

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(29) This approach was successfully used before. See ref 9 for the theoretical work and refs 10 and 11 for the experimental verifications.

Figure 8 shows the above-mentioned relationships.[31] Both show good linear correlations (correlation coefficients larger than 0.999), suggesting that indeed strain is responsible for the localization in **12**−**14**. Note that there is no correlation between π destabilization energies and the amount of localization (Table 4 and discussion above). Thus, the relationship between strain and localization in **12**−**14** also supports SIBL as the dominant localizing factor, whereas aromatic factors are much less important (or even unimportant) in localizing the aromatic ring's bonds.

Conclusions

All the data obtained in this work are coherent with aromaticity−antiaromaticity considerations being unimportant in determining the geometries of small-ring annulated aromatic systems. Even in systems in which π (aromaticity) arguments apparently look like important factors, a more detailed investigation suggests that they are not, and all the observations can be more coherently explained by SIBL arguments. These results neither support nor contradict the role of the π system in localizing the aromatic bonds in the way presented by Shaik et al.,[13] as their approach would predict the same localization trends predicted by SIBL. However, due to the correlation between strain energy and the amount of localization in **12**−**14** (Figure 8), the strain effects and the distortive π forces must be linearly dependent in these systems. A better distinction between Shaik's approach and SIBL may be achieved by studying the excited states, which is beyond the scope of this work. However, these results strongly support the view of the σ frame being dominant in determining the structures of strained aromatic molecules.

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(30) Actually, the dependence should be in $(E_{\text{strain}})^{f\times n}$ as although the effect should be synergistic it may be factorized by f, where $f \leq 1$. The results show, however, that the f value is very close to 1.

(31) Unfortunately, the correlation between $(E_{\text{strain}})^2$ and ΔR in the bis-annulated systems (**10b**, **11b**, **12b**) could not have been tested as **11b** is a macrocycle and not a bis-annelated benzene system.