CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700154

Double Aromaticity in Monocyclic Carbon, Boron, and Borocarbon Rings Based on Magnetic Criteria

Matthew D. Wodrich, Clémence Corminboeuf, Sung Soo Park, and Paul von Ragué Schleyer*[a]

Abstract: The double-aromatic character of selected monocyclic carbon, boron, and borocarbon rings is demonstrated by refined nucleus-independent chemical shift (NICS) analyses involving the contributions of individual canonical MOs and their out-of-plane NICS tensor component (CMO-NICS$_{zz}$). The double aromaticity considered results from two mutually orthogonal Hückel p AO frameworks in a single molecule. The familiar π orbitals are augmented by the in-plane delocalization of electrons occupying sets of radial (rad) p orbitals. Such double aromaticity is present in B_3^-, $C_6H_3^+$, C_6^{4+}, $C_4B_4^{4+}$, C_6, C_5B_2, C_4B_4, C_2B_8, B_{10}^{2-}, B_{12}, C_{10}, C_9B_2, C_8B_4, C_7B_6, C_6B_8, and C_{14}. Monocyclic C_8 and C_{12} are doubly antiaromatic, as both the orthogonal π and radial Hückel sets are paratropic. Planar C_7 and C_9 monocycles have mixed aromatic (π) and antiaromatic (radial) systems.

Keywords: aromaticity · borocarbon · carbon clusters · density functional calculations · magnetic properties

Introduction

Double aromaticity, as originally conceived by Chandrasekhar, Jemmis, and Schleyer in 1979,[1] is defined as the existence of two mutually orthogonal cyclically delocalized electronic systems in a single molecule, both of which provide significant stabilization. Thus, the usual Hückel $4n+2$ π electron system, comprised of p AOs perpendicular to a ring, may be augmented by an in-plane $4n+2$ electron system comprised of radial (rad; inward-pointing) p AOs. The $C_6H_3^+$ ion (Figure 1) provided the first theoretical prediction of double aromaticity. This cation benefits from six-π-electron aromaticity, as well as from its in-plane two-electron three-center (2e-3c) delocalization involving the three radial p AOs on the bare one, three, and five carbon atoms, similar to the topology found in Dewar's σ-aromaticity model.[2] Nelson and Kentäamaa's later mass spectral experiments identified this species.[3] The $C_6H_3^+$ ion, along with other early suggestions, opened the fields of double as well as radial in-plane aromaticity.[4,5] These concepts continue to receive considerable theoretical and experimental attention.[4,6–33]

Further early conceptual examples of double aromaticity included the illustrative $C_{10}H_5^-$ (10 π + six rad) and C_8H_4 (10 π + two rad) proposals (Figure 2); numerous in-plane candidates were also suggested.[4] The trannulenes (cyclically conjugated *trans* polyenes; an example is shown in Figure 2) were predicted as a class of in-plane aromatics[4,11,32–34] and an increasing number of experimental verifications now exist.[33,35–37]

More recently, Schleyer et al.[38] re-examined and analyzed the structures and magnetic properties of the 3,5-dehydrophenyl cation ($C_6H_3^+$) and the closely related cyclo[6]carbon (C_6) in greater detail. The six-membered rings of both species had equal C−C bond lengths,[5,39,40] and enhanced magnetic susceptibility anisotropy.

Carbon clusters have been studied extensively experimentally;[41–55] in particular, larger clusters may serve as precursors to fullerenes and nanotubes.[56–58] Mass spectrometry reveals the presence of "magic peaks", stoichiometries with above average abundances. Photoelectron spectra of monocyclic C_n^- anions also have shown clear differences between clusters with $n=4N$ and $n=4N+2$ carbon atoms.[59–61] Such distinctive patterns suggests that certain stoichiometric structures have an enhanced stability.

Complimentary theoretical computations of carbon clusters have probed their geometries, electronic structures, and properties. The first notable investigation, by Pitzer and

---

[a] Dr. M. D. Wodrich, Dr. C. Corminboeuf, Dr. S. S. Park,
Prof. P. v. R. Schleyer
Department of Chemistry and Center for Computational Chemistry
University of Georgia, Athens, Georgia, 30602 (USA)
Fax: (+1) 706-542-7514
E-mail: schleyer@chem.uga.edu

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

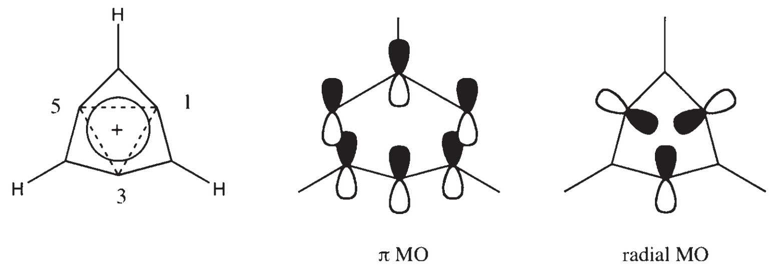


Figure 1. The planar $C_6H_3^+$ doubly aromatic 3,5-dehydrophenyl cation comprised of six π electrons in three benzene-like MOs (one is depicted above) and two electrons in the radial in-plane MO shown.

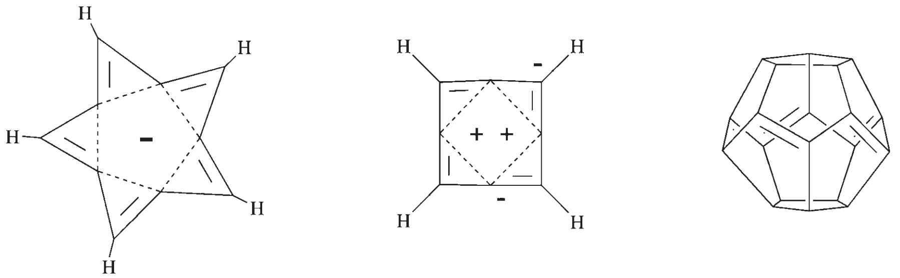
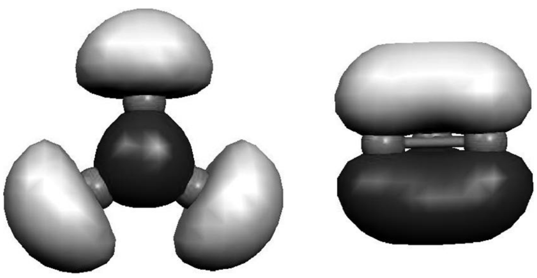


Figure 2. Illustrative double aromatic structures and an in-plane [10]trannulene as proposed by McEwen and Schleyer in 1986.[4] In the configurations shown, $C_{10}H_5^-$ has 10 π + six radial electrons, C_8H_4 has 10 π + two radial electrons, and [10]trannulene has 10 radial electrons occupying MOs comprised of inward pointing p AOs.

Clementi,[62] employed a refined Hückel p-electron model and predicted that smaller neutral C_n clusters would have linear geometries; rings might be favored around $n=10$. Hoffmann's extended Hückel theory[63] corroborated these predictions in 1966. In 1977, Slanina and Zahradnik considered C_n ($n=4$–7) clusters comprehensively for the first time by using Dewar's MINDO/2 method.[64] Three dimensional and monocyclic structures nearly always were preferred over linear species. In the middle 1970's, the Schleyer–Pople group undertook ab initio investigations of carbon clusters and were particularly interested in the possibility that rings with $4N+2$ carbon atoms might be doubly aromatic, due to stabilization by both perpendicular and in-plane Hückel systems. This work was hampered by the limited computational resources of the day. E. M. Engler did succeed at IBM in computing C_{10} at STO-3G,[65] but exploration of this idea at reliable, far more sophisticated ab initio levels lay many years in the future.

Extensive ab initio studies confirmed that linear (triplet) and cyclic (singlet) isomers of medium-size C_n clusters compete energetically.[66] The most recent theoretical analyses have shown that the monocyclic C_6 and C_{10} singlet states are lower in energy than their linear counterparts.[14,41,66–78] Interestingly, the lowest energy C_6 and C_{10} rings favor bond angle alternating D_{3h} and D_{5h} symmetries with equal C–C lengths, rather than polyacetylenes with equal angles but unequal lengths or polyallene structures with the highest possible D_{6h} and D_{10h} point groups. The most symmetrical forms are transition states. Despite showing sizable HOMO–LUMO gaps, the symmetry of the frontier molecular orbitals of these highest symmetry rings allows second-order Jahn–Teller distortion.[15,79,80] Alternatively, rings with $4N$ carbons are expected to be doubly antiaromatic according to the Hückel rule and to undergo first-order Jahn–Teller distortion to C_{2nh} polyinic geometries.[74,78,81] However, a formally doubly antiaromatic ($4n+4m$) ring might be doubly aromatic with an alternative $4n+2$ and $4m-2$ electron configuration involving the two orthogonal systems.[1]

Boron rings also can exhibit double aromaticity. Boldyrev and co-workers[26] have identified B_3^-, the simplest possible example, B_4 and B_5^+ as 2+2 doubly aromatic systems, containing a totally symmetric π (HOMO−1) and radial (HOMO), see Scheme 1, (the other occupied MOs are involved in conventional ring bonding).



Scheme 1. $B_3^{(1-)}$ radial HOMO and π HOMO−1.

A comprehensive recent review of boron clusters[26] did not identify any other monocyclic boron rings as being doubly aromatic, as polycyclic geometries typically featuring deltahedral bonding were more stable. However, the double aromaticity in these alternative species bonding arrangements was emphasized.[26] The larger rings can be stabilized, in effect, by the inclusion of one or more atoms inside.[26] However, this does not change the basic double aromatic character of the bonding. In another approach, Hofmann and Berndt[27] used the B_3 framework in $B_3H_3^{2-}$ and its isoelectronic analogue as a scaffold on which to build other doubly aromatic compounds. Moreover, double aromaticity need not be confined to small systems or simple rings; several double-aromatic structures, including boron wheels[28,29] and trannulene-type double boron rings,[30] have also been investigated.

Unlike carbon[41–55] and boron clusters,[25,82–84] borocarbons are practically unknown as a class, despite several examples of remarkable structures.[85–89] Thus, three C_3B_4 isomers have planar hexacoordinate carbons.[89] In contrast, binary combinations of carbon with hydrogen, lithium, nitrogen, oxygen, fluorine, silicon, and other main-group elements have been studied in detail. Boron carbide[90–102] is one of the hardest materials known and has a number of important uses. Diatomic and larger BC clusters have been studied by using mass spectrometry[103,104] and EPR.[105–107] Other studies have probed the structure of B_nC_m ($n+m=2$–5) clusters.[108–118] Park[119] described structural and bonding trends in a series of isoelectronic borocarbon compounds. Potential energy-surface investigations reveal that the global isomers of $B_7C_1^{1-}$, B_6C_2, and $B_5C_3^{1+}$ all prefer monocyclic rings surrounding a heptacoordinate boron atom. Many other borocarbons have been found computationally to have planar terta-, penta-, and hexacoordinate carbon structures.[28,85,86,89,120–124]

Electronic structure analyses reveal that many of these molecules benefit from electron delocalization in orthogonal planes and are doubly aromatic. Recently, Martín-Santamaría and Rzepa[16] employed nucleus-independent chemical shifts (NICS) to study the double aromaticity (C_{10} and C_{14}) and double antiaromaticity (C_{12}) of small carbon rings. Introduced in 1996 by Schleyer et al.,[125] NICS provides a simple and effective magnetic aromaticity index; negative (diatropic) NICS values indicate magnetic aromaticity, while positive (paratropic) values indicate magnetic antiaromaticity. Typically, the magnetic environments of molecules are probed by computing a number of NICS points; those designated NICS(0) are computed at the geometric centers of rings, while NICS(1) are computed at 1 Å above the geometric center. Based on isotropic NICS(0) results, Martín-Santamaría and Rzepa suggested that D_{5h}-C_{10}, D_{7h}-C_{14}, 1,6-C_8N_2, 1,7-$C_{10}B_2$, C_s-quintet C_{12}, $C_{11}H_2$, and bicyclic C_{19} were doubly aromatic. However, $\mathrm{NICS(0)_{iso}}$ values do not reveal the contributions of the π and radial systems individually, and the data for some of these systems are ambiguous. The interpretations depend on the reference system chosen. For example, the bond angle alternating polyallene D_{5h} form of C_{10} is clearly aromatic, but its $\mathrm{NICS(0)_{iso}}$ value, −28.9, is not significantly larger that that of the singly aromatic C_{2v} [10]annulene (−28.6).[126] However, the D_{10h} symmetrical $C_{10}H_{10}$ Hückel reference molecule has a much smaller $\mathrm{NICS(0)_{iso}}$ value (−13.2), only half as large as that of the doubly aromatic D_{5h}-C_{10}. The difference can be attributed to the $\mathrm{NICS(0)_{iso}}$ contribution of the in-plane radial 10-electron system present in D_{5h}-C_{10}, but not in $C_{10}H_{10}$. Likewise, the $\mathrm{NICS(0)_{iso}}$ value (−35.6) of the 14-membered doubly aromatic polyallene ring (D_{7h}-C_{14}) is much larger than that of both the D_{2h} (−13.4) and the D_{14h} $C_{14}H_{14}$ (−15.8) forms of the singly (π) aromatic [14]annulene, evidently due to the contribution of the radial in-plane aromatic system of D_{7h}-C_{14}. Hofmann and Berndt[27] examined the double aromaticity of small boron-containing systems, by using enhanced isotropic NICS values as a criterion, and concluded that two-electron in-plane delocalization was a key feature in their unusual structures. They designed double aromatic molecules containing anionic B_3, neutral B_3, and CB_2 frameworks with two in-plane delocalized electrons (Figure 3).

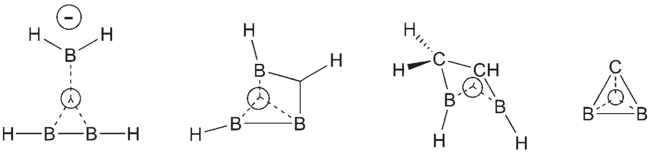


Figure 3. Double aromatic structures proposed by Hofmann and Berndt.[27]

Much more refined NICS methods are now available,[127–130] which allow the clear-cut analysis of double aromaticity by determining the contributions of individual molecular orbitals as well as those associated with the "ring current" (the out-of-plane tensor component of NICS). We have now applied these refined methods to investigate the nature of a number of carbon, boron, and borocarbon ring systems.

Methods

Carbon rings are difficult to compute reliably because of the diversity of structures and the possibility of having pronounced multireference character. Rings with an even number of carbon atoms may have polyacetylene geometries with alternating single and triple bonds or they may be polyallenes with equal bond lengths. However, cyclic polyallenes may either be "regular" with equal bond angles or "kinked" with unequal angles. The structure of the global minimum and the relative energy of linear and cyclic C_n isomers are generally extremely sensitive to the computational level. Nevertheless, DFT geometries and relative energies are in reasonable agreements with results using high-order correlation methods (for example, coupled-cluster expansion).[68,74,76] MP2 results were found to be qualitatively incorrect.[76] We optimized structures with the B3LYP[131,132] hybrid density functional and 6-311+G(d) basis set (6-311+G(d,p) for C_6H_6, $C_{10}H_{10}$, $C_{14}H_{14}$, and $C_6H_3^+$) by using Gaussian 98.[133] Comparisons with available CCSD(T) data are provided. The computed vibrational frequencies at the same DFT level characterized the nature of the stationary points. NICS(0), NICS(1), and the dissection of NICS into contributions of individual canonical molecular orbitals (CMO–NICS)[134] were performed at the GIAO-PW91[135]/IGLO-III level by using the NBO 5.0 program.[136,137] Because isotropic $\mathrm{NICS(0)_{iso}}$ values at ring centers do not reflect the "ring current" exclusively, we employed NICS_{zz} (the out-of-plane component of the NICS tensor) as a superior aromaticity measure due to its more accurate response to magnetic properties arising only from a magnetic field applied perpendicular to the molecular plane.[127,128,130,138,139]

The monocyclic and generally higher-symmetry carbon, boron, and borocarbon rings selected for this study had two potential double aromatic 4*n*+2 or double antiaromatic 4*n* electron systems (π and in-plane radial) based on simple electron counting expectations. Two valence electrons of both boron and carbon are assigned to the σ framework, leaving boron with one and carbon with two available electrons for π and in-plane radial bonding.

Results and Discussion

The $C_6H_3^+$ ion: The distorted[79] $C_6H_3^+$ ion (Figures 1 and 4), the doubly aromatic prototype, was predicted by Chandrasekhar, Jemmis, and Schleyer in 1979[1] and computed at higher levels in 1994.[38] We have now re-examined D_{3h} $C_6H_3^+$ by using a combination of NICS, NICS_{zz}, and CMO-NICS_{zz} to quantify the extent of its aromatic and doubly aromatic character. A large negative isotropic NICS(0) of −42.3 and −19.1 for NICS(1) (isotropic NICS taken at 1 Å above the ring center, Table 1) indicates the presence of a diatropic ring current. The large difference between isotropic NICS(0) and NICS(1) values indicates that the system contains a diatropic Hückel system in the molecular plane. If no diatropic in-plane radial system were present, one would expect the isotropic NICS(1) to be slightly larger than NICS(0) (as is the case for benzene NICS(0) = −7.5, NICS(1) = −9.6). The individual canonical molecular orbital contributions to NICS (CMO-NICS) as well as each out-of-plane NICS tensor component (CMO-NICS_{zz}), summarized in Table 1 and Figure 5, do indeed show the presence of a strongly aromatic six-electron π system perpendicular to the molecular plane, $\mathrm{NICS}_{\pi} = -32.8$ and a weakly diatropic two-electron in-plane radial system, $\mathrm{NICS}_{\mathrm{rad}} = -3.6$ (Figure 5). The out-of-plane component of the NICS tensor for the π system in $C_6H_3^+$ ($\mathrm{NICS}_{\pi zz} = -34.3$) is slightly weaker than that of benzene ($\mathrm{NICS}_{\pi zz} = -36.1$), while the $\mathrm{NICS}_{\mathrm{rad}zz}$ of $C_6H_3^+$ contributes an additional −5.3. The remaining negative contributions to the out-of-plane component ($\mathrm{NICS}_{zz} = -72.4$) arise from the balance of positive and negative contributions from low-lying orbitals. The NICS_{zz} value of benzene is reduced owing to an additional set of filled σ orbitals with a higher number of nodes which give large positive CMO-NICS values.[127] As shown by both grids of NICS_{zz} values and current density maps, low-lying orbitals have little or no effect on ring currents and mostly affect local magnetic shieldings.[140] (see the Supporting Information Figure 1). One expects $C_6H_3^+$ to be slightly more aromatic than benzene based on $\mathrm{NICS}_{\mathrm{rad}zz}$ and $\mathrm{NICS}_{\pi zz}$, but there is no straightforward way to compare the aromatic stabilization energies directly.

Are the C_6^{4+} and $C_4B_4^{4+}$ monocycles further examples of 6+2 doubly aromatic systems (see Figure 13) akin to $C_6H_3^+$? All three possess a single diatropic in-plane radial orbital, which is more diatropic in the tetracations ($\mathrm{NICS}_{\mathrm{rad}zz} \approx -15$) than in $C_6H_3^+$ ($\mathrm{NICS}_{\mathrm{rad}zz} = -5.3$). However, the overall aromatic character is dominated by the diatropic 6π electron systems, which are similar in all three ions ($\mathrm{NICS}_{\pi zz} \approx -34$). As a result, the three species have relatively similar NICS_{zz} (> -56) values and are doubly aromatic.

Table 1. Point groups, NICS, and dissected NICS for relevant compounds. NICS_{π} and $\mathrm{NICS}_{\mathrm{rad}}$ represent total contributions from the π and the radial orbitals. $\mathrm{NICS}_{\pi zz}$ and $\mathrm{NICS}_{\mathrm{rad}zz}$ represent the out-of-plane component of the NICS tensor from π and radial orbitals.

Compound	Point group	Electrons		NICS(0)	NICS(1)	NICS_{zz}	NICS_{π}	$\mathrm{NICS}_{\mathrm{rad}}$	$\mathrm{NICS}_{\pi zz}$	$\mathrm{NICS}_{\mathrm{rad}zz}$
		π	rad							
$C_6H_3^+$	D_{3h}	6	2	−42.27	−19.09	−72.44	−32.76	−3.59	−34.32	−5.30
C_6^{4+}	D_{6h}	6	2	−63.28	−17.72	−67.53	−49.79	−9.82	−38.51	−15.99
$C_4B_4^{4+}$	D_{4h}	6	2	−41.41	−20.56	−56.11	−34.85	−7.17	−29.64	−13.45
C_6H_6	D_{6h}	6	–	−7.52	−9.61	−14.92	−25.03	–	−36.12	–
C_6	D_{6h}	6	6	−36.93	−17.58	−68.36	−33.66	+1.29	−39.52	−15.17
C_6	D_{3h}	6	6	−23.97	−11.44	−31.57	−32.69	+11.98	−38.48	+19.36
C_5B_2	C_{2v}	6	6	−22.11	−13.41	−42.23	−25.15	+6.01	−29.52	+5.91
C_4B_4	D_{4h}	6	6	−29.94	−19.67	−66.14	−23.43	−7.63	−29.99	−23.78
C_2B_8	D_{2h}	6	6	−24.43	−18.74	−57.60	−16.86	−9.01	−24.40	−23.82
B_{10}^{2-}	D_{10h}	6	6	−25.03	−19.89	−62.33	−17.89	−6.07	−26.29	−19.27
B_{12}	D_{12h}	6	6	−21.76	−18.25	−55.15	−13.91	−9.63	−23.89	−25.32
C_7	C_{2v}	6	8	−12.51	−11.99	−27.55	−25.59	+14.30	−36.68	+27.36
C_8	D_{4h}	8	8	+48.84	+40.14	+169.34	+38.16	+11.87	+151.53	+28.86
C_9	C_{2v}	10	8	+5.65	+0.51	+49.23	−30.09	+36.60	−53.37	+108.47
$C_{10}H_{10}$	D_{10h}	10	–	−13.23	−12.27	−39.42	−29.21	–	−46.19	–
C_{10}[a]	D_{5h}	10	10	−28.2	−21.1	−69.5	−25.09	−3.86	−39.04	−13.89
C_9B_2	C_{2v}	10	10	−24.81	−19.45	−62.85	−19.90	−6.77	−40.29	−21.11
C_8B_4	D_{4h}	10	10	−30.40	−24.62	−79.25	−18.22	−14.81	−37.20	−42.92
C_7B_6	C_{2v}	10	10	−22.04	−18.50	−56.53	−14.75	−9.15	−29.33	−26.16
C_6B_8	C_{2v}	10	10	−22.46	−19.36	−59.36	−13.84	−10.16	−28.61	−28.39
C_{12}	C_{6h}	12	12	+56.92	+47.05	+180.56	+38.52	+16.79	+131.10	+49.43
$C_{14}H_{14}$	D_{14h}	14	–	−20.11	−20.27	−45.98	−19.56	–	−45.24	–
C_{14}	D_{14h}	14	14	−40.84	−34.34	−114.11	−22.93	−21.28	−56.71	−63.95
C_{14}[a]	D_{7h}	14	14	−35.44	−29.93	−97.98	−22.78	−15.03	−56.26	−44.46

[a] Polyallene structure.

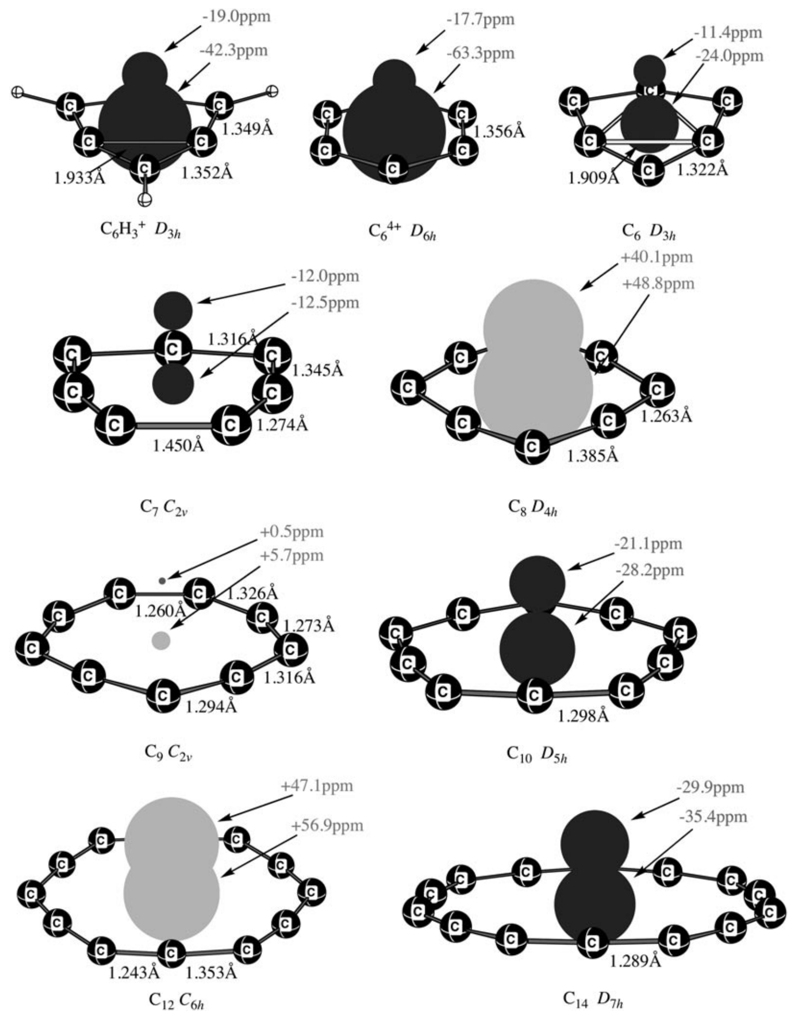


Figure 4. Geometries, point groups, and isotropic NICS values (black indicates diatropicity while grey indicated paratropicity) of carbon clusters.

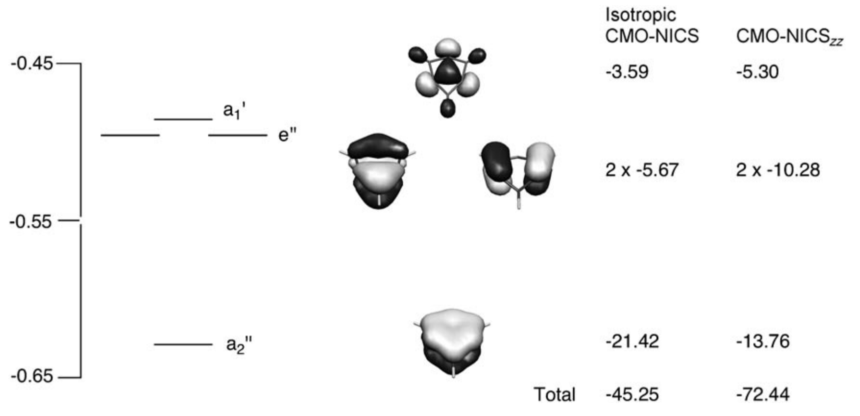
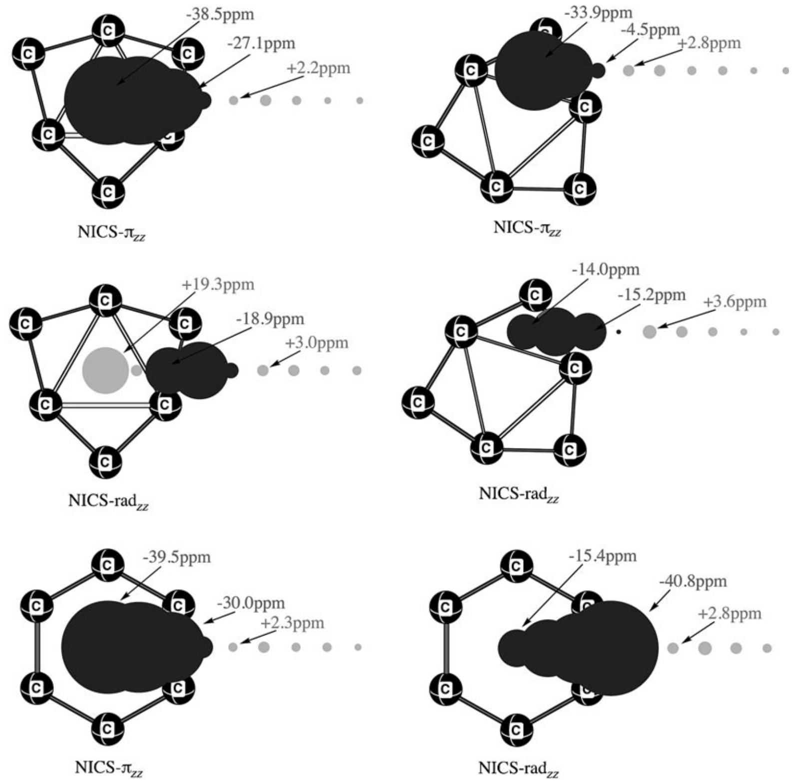


Figure 5. CMO-NICS plot of $C_6H_3^+$. CMO-NICS and CMO-NICS$_{zz}$ contributions are listed on the right side in ppm; the total listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

Even-numbered monocyclic carbon clusters: The most recent theoretical investigations conclude that cyclic C_6 prefers D_{3h} symmetry over both the D_{6h} and the linear chain forms (Figure 4).[68,77] This geometrical preference can be attributed to a second-order Jahn–Teller effect.[79] At the CCSD(T) level, Hutter and Lüthi[68] predicted the D_{3h} global minimum to lie 8.3 kcal mol^{-1} below the regular hexagon D_{6h} transition-state structure and obtained good agreement at the BP86/TZVP level for both geometries and energies. At the B3LYP/6-311+G(d) level, the interconversion barrier between the D_{3h} and D_{6h} structures is 13.6 kcal mol^{-1}.

The magnetic behavior of the global D_{3h} minimum is peculiar. The out-of-plane component of the NICS tensor for the π system (NICS$_{\pi zz}$) is slightly larger than that of benzene, yet the in-plane system is paratropic at the ring center. This suggests that D_{3h}-C_6 is π aromatic and radial antiaromatic. However, a grid of NICS$_{zz}$ points, dissected into π and radial contributions, shows a clear change from paratropic within the central triangle to diatropic within the outer triangles and, as expected for aromatic systems, a deshielding zone outside the molecular framework (Figure 6, an isotropic grid is given in Figure 2 in the Supporting Information). A possible explanation for this peculiar behavior is the presence of local diatropic ring currents within the three outer triangles, which necessarily causes the central triangle to be paratropic (Figure 7). Alternatively, similar paratropic NICS$_{radzz}$ patterns are observed at the center of cyclopropane and, more generally, at the center of six σ-electron D_{3h} aromatic rings.[141] Akin to this set of σ-aromatic D_{3h} three-membered rings, the paratropic shielding at the center of D_{3h}-C_6 arises essentially from the degenerate set of HOMOs with Möbius topology, as shown in Figure 8. While further analysis on this seemingly pathological NICS behavior are pending,



NICS-π_{zz} NICS-π_{zz}

NICS-rad$_{zz}$ NICS-rad$_{zz}$

NICS-π_{zz} NICS-rad$_{zz}$

Figure 6. NICS$_{\pi zz}$ and NICS$_{\mathrm{rad}zz}$ grids of C_6 (D_{3h} and D_{6h}). The NICS$_{\pi zz}$ grids indicate the π systems to be diatropic inside rings. The NICS$_{\mathrm{rad}zz}$ grids of D_{3h} C_6 indicate the radial system to be paratropic in the central triangle and diatropic in the outer triangles. In contrast, the NICS$_{\mathrm{rad}zz}$ grids for the D_{6h} form are diatropic overall.

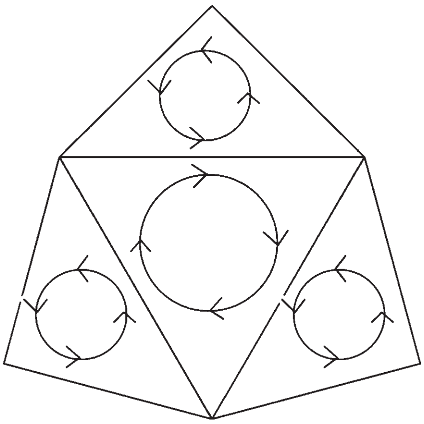


Figure 7. Proposed local ring current model for the radial system of D_{3h} C_6.

the computation of isotropic NICS(0) (or even better, dissected NICS) grids at several points is strongly recommended in order to characterize overall magnetic character of atypical molecules. The NICS$_{zz}$ grid reveals the doubly aromatic nature of D_{3h} C_6.

We also investigated the magnetic properties of the regular D_{6h}-C_6 structure, which is a transition state for the inner–outer interchange of carbon atoms. Surprisingly, the isotropic NICS(0) value of the less stable D_{6h} C_6 (−36.9) is appreciably larger than the −24.0 NICS(0)$_{\mathrm{iso}}$ of the D_{3h} minimum (Table 1). The NICS(0)$_{\mathrm{iso}}$ values do not predict the relative stability of the two forms. Several studies indicate that different aromaticity measures may provide divergent information.[129,142] For instance, the lowest-energy fused heterobicycles are not the most aromatic isomers.[143]

Akin to C_6, the C_{10} molecule has long been recognized to considerably favor a ring structure (with D_{5h} symmetry, see above) over the lowest-energy linear isomer (Figure 9).[66,71] The equivalent D_{5h} minima interconvert through the D_{10h} transition structure with an energy barrier of only 1.0 kcal mol^{-1} at the CCSD(T)/cc-pVTZ level.[74] B3LYP/6-311+G(d) optimization also results in a polyallene D_{5h}-C_{10} stationary point with a 2.5 kcal mol^{-1} interconversion barrier. While C_{4n+2} clusters larger than C_{10} have been studied at less accurate theoretical levels, experimental electronic spectra[144] suggest their structures to be monocyclic rings exhibiting double aromaticity. At B3LYP/6-311+G(d), the D_{14h} transition state of C_{14} is essentially isoenergetic with the D_{7h} cumulenic energy minimum.

NICS$_{\pi zz}$ of both C_{10} and C_{14} are similar to those of their parent annulenes[145] (for example, $C_{10}H_{10}$ and $C_{14}H_{14}$), but their enhanced total NICS$_{zz}$ indicates the presence of an additional diatropic subsystem. CMO-NICS and CMO-NICS$_{zz}$ analysis indeed confirms that both carbon monocyclics are doubly aromatic.[15,16] Note the π MOs of both C_n and C_nH_n ($n=10,14$) systems contribute nearly equally; thus, the NICS$_{\pi zz}$ values for both C_n and C_nH_n are nearly identical. However, C_{10} and C_{14} also contain a diatropic in-plane radial system, thus their total NICS$_{zz}$ is much greater (>30 ppm) than that of their annulene analogues (Table 1).

C_8 is an interesting example of a double antiaromatic polyinic ring,[66,67,70,74,81] possessing orthogonal eight radial + eight-π-electron systems (Figure 4). CCSD(T)/cc-pVDZ calculations predict the C_{4h} cyclic form to lie only 4 kcal mol^{-1} below the linear structure.[74] Alternatively, Slanina et al. identified a boatlike nonplanar D_{4d} structure as a minimum.[146,147] The energy difference between these two structures, less than 1 kcal mol^{-1} at the B3LYP/aug-cc-PVTZ level,[67] again reflects the fluxional character of these systems. Both the C_{4h} and D_{4d} minima have small HOMO–LUMO gaps (only 1.21 eV at PW91/IGLO-III//B3LYP/6-

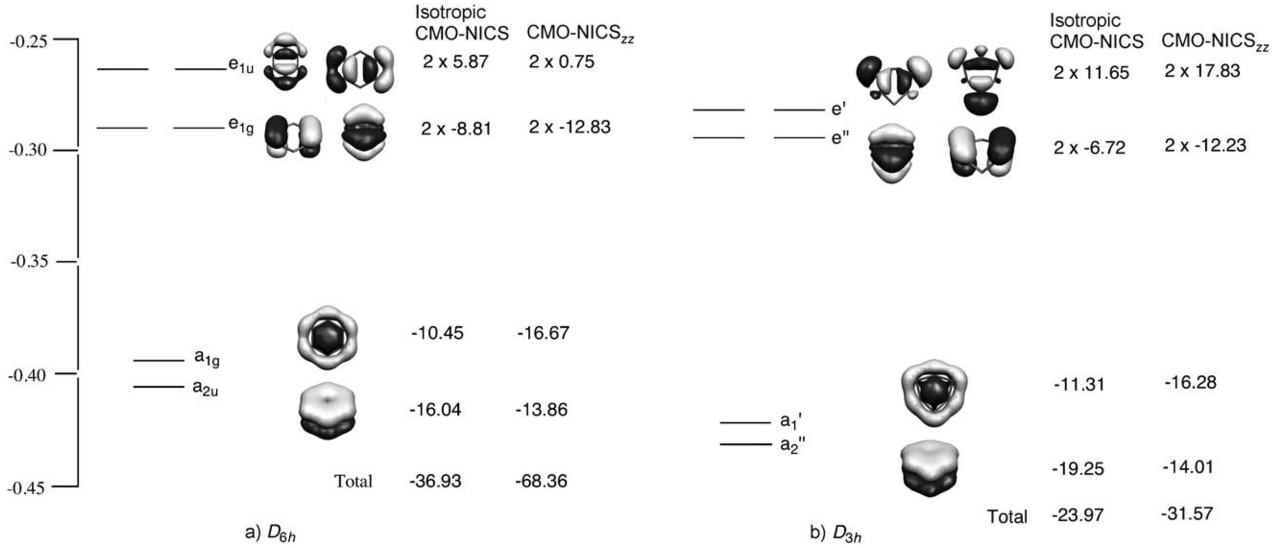


Figure 8. D_{6h} (A) and D_{3h} (B) CMO-NICS plots of C_6. CMO-NICS and CMO-NICS$_{zz}$ contributions are listed on the right side in ppm; the total listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

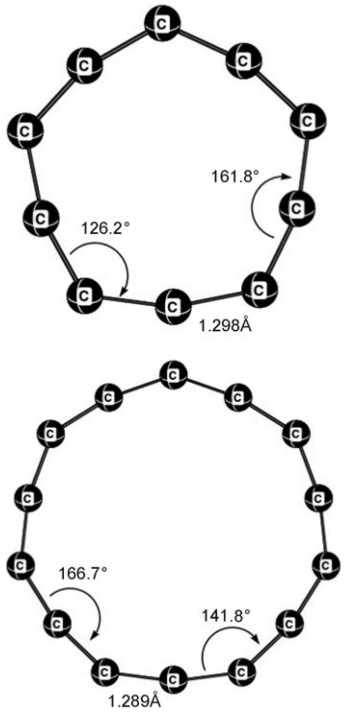


Figure 9. B3LYP/6-311+G(d)-optimized bond angles of cyclopolyallenes, D_{5h} C_{10} and D_{7h} C_{14}.

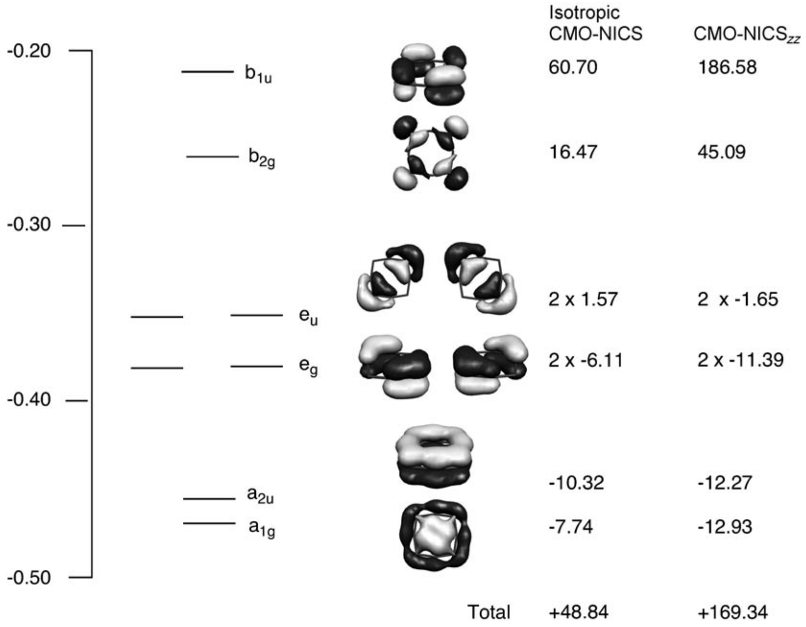


Figure 10. CMO-NICS and CMO-NICS$_{zz}$ of doubly antiaromatic C_8. CMO-NICS and CMO-NICS$_{zz}$ contributions are listed on the right side in ppm. The total values given represents the sum of *all* orbitals, not just those depicted. MO energies in a.u. are given on the left side.

311+G(d)) resulting in a large paratropic HOMO-NICS (see the Supporting Information Figure 3 for the D_{4d} structure).[148] As expected, the highest lying π MO (the HOMO), and the highest in-plane radial orbital (HOMO−1), dominate the overall molecular paratropicity (Figure 10). The +60.70 HOMO-NICS contribution (HOMO-NICS$_{zz}$: +186.58) is very large, while the highest lying occupied orbital of the in-plane radial system is also strongly paratropic (CMO-NICS: +16.47, CMO-NICS$_{zz}$: +45.09). Not surprisingly, C_8 has a smaller ionization potential than C_6 or C_{10}.[149] The polyynic C_{6h} ring was found to be lower in energy than the other C_{12} isomers at several DFT levels. However, uncertainties as to which structure is the minimum at higher theoretical levels remain.[75] Regardless of the relative energies, the C_{6h} ring structure exhibits the same double antiaromatic character as C_8 (see Figure 11 and

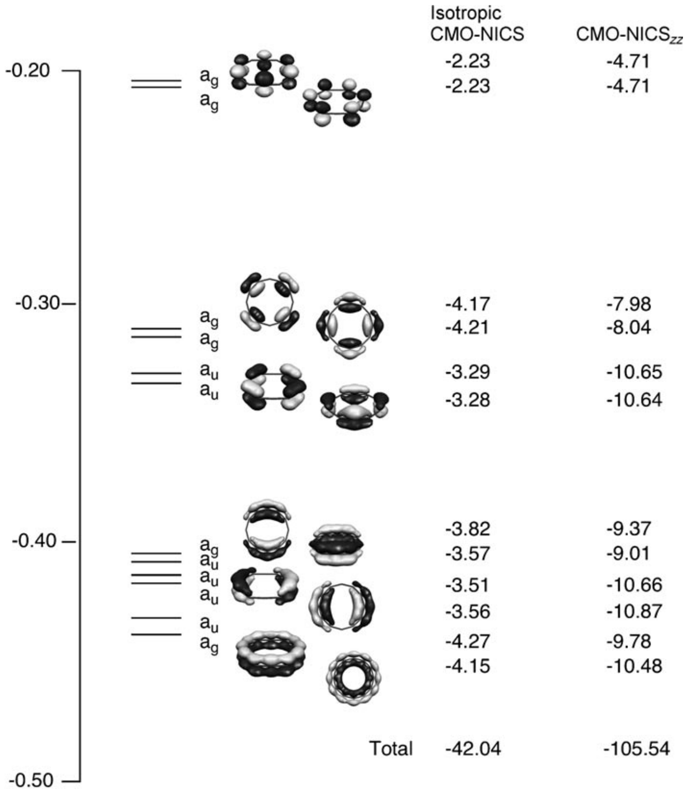


Figure 11. CMO-NICS and CMO-NICS$_{zz}$ of doubly antiaromatic C_{12}. CMO-NICS and CMO-NICS$_{zz}$ contributions on the right side are in ppm. The total values given represents the sum of *all* orbitals, not just those depicted. MO energies in a.u. are given on the left side.

Table 1), no electronic rearrangement to a double aromatic configuration ($4n+2$, $4m-2$) is seen.

Odd-numbered monocyclic carbon clusters: Martin et al.[76] showed by using DFT and CCSD(T) calculations that small monocyclic rings containing odd numbers of carbon atoms (C_n, $n=5$–9) are higher in energy than the corresponding linear structures. However, experimental evidence for cyclic C_7^+ exists[49] and small linear–cyclic isomerization energies (<15 kcal mol^{-1} at the CCSD(T) level) have been computed for C_7 and C_9.[76] The π and radial electron counts of such odd carbon monocycles are not easy to assign a priori. Mixed aromatic/antiaromatic electronic structures are possibilities. Cyclic C_7 and C_9 prefer C_{2v} over planar structures at both the CCSD(T) and B3LYP levels.[150] Triplet D_{nh} species are less stable than the singlets (CMO-NICS values for the C_7 and C_9 C_{2v} monocycles are given in Figure 4 and Table 1). The negative overall isotropic NICS values of C_7 indicate a diatropic ring current, but CMO-NICS/CMO-NICS$_{zz}$ reveals a mixed aromatic/antiaromatic 6π/8 in-plane system (Supporting Information, Figure 1). Similarly, C_9 has mixed π aromatic/in-plane antiaromatic character with a 10+8 system. These systems parallel the mixed aromatic/antiaromatic systems recently reported by Hofmann and Berndt (Figure 12).[27]

Boron and borocarbon clusters: The previously described NICS analyses also establishes double aromaticity in the two boron and eight borocarbon rings studied here (see Figure 13 and Table 1). C_4B_4 illustrates a 6+6 doubly aromatic borocarbon system (Figure 14). In contrast to C_6, another 6+6 system (Figure 8) with somewhat smaller isotropic NICS(0) and NICS(1) values, the NICS(0)$_{zz}$ of all three in-plane (radial) orbitals of C_4B_4 are diatropic. The enhanced diatropicity of the radial system compensates for the reduction in diatropic character of the C_4B_4 π system (see the CMO-NICS$_{\pi zz}$ data) as compared to both isomers of C_6 (Figure 8). Degenerate in-plane radial HOMOs offer the possibility of forming a 6+2 doubly aromatic system by removing four electrons from C_4B_4. Indeed, CMO-NICS$_{zz}$ shows $C_4B_4^{4+}$ to be doubly aromatic like C_6^{4+}. $C_4B_4^{4+}$ has slightly longer bond lengths than C_4B_4 (Figure 13), likely attributable to increased Coulomb repulsion and decreased in-plane bonding character. The in-plane radial system, which now has only two electrons, shows a significant decrease (10 ppm) in diatropic character of the out-of-plane component of the NICS tensor (NICS$_{zz}$). The two-electron in-plane radial system has enhanced diatropicity (CMO-NICS$_{\text{rad}zz}$: −13.45) relative to the prototype double aromatic $C_6H_3^+$ (−5.30) and is closer to the C_6^{4+} value (−15.99).

Like D_{3h}-C_6, C_5B_2 has two orthogonal six-electron systems, with both diatropic (the π system) and paratropic (in-plane radial system) character. Furthermore, NICS$_{zz}$ grids show behavior similar to C_6; the in-plane radial system is paratropic at the center but becomes strongly diatropic at distances as close as 0.5 Å away (Supporting Information, Figure 2). The perpendicular π system remains diatropic at all positions within the ring. The NICS$_{zz}$ grid shows that C_5B_2, like D_{3h} C_6, is doubly aromatic. C_6 and C_5B_2 are atypical cases requiring NICS grids to identify their double aromaticity; in general, dissection of NICS(0) values suffice for this purpose.

The larger borocarbons, with 10+10 double aromatic systems, show widely varying NICS$_{\pi zz}$ values, all of which are smaller than those of D_{10h} [10]annulene (−46.2). C_9B_2 has the most diatropic π system (NICS$_{\pi zz}$=

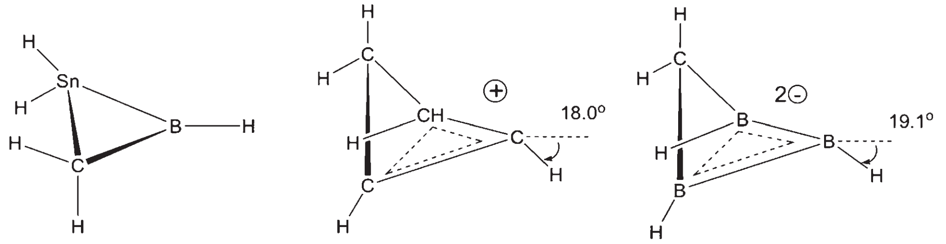
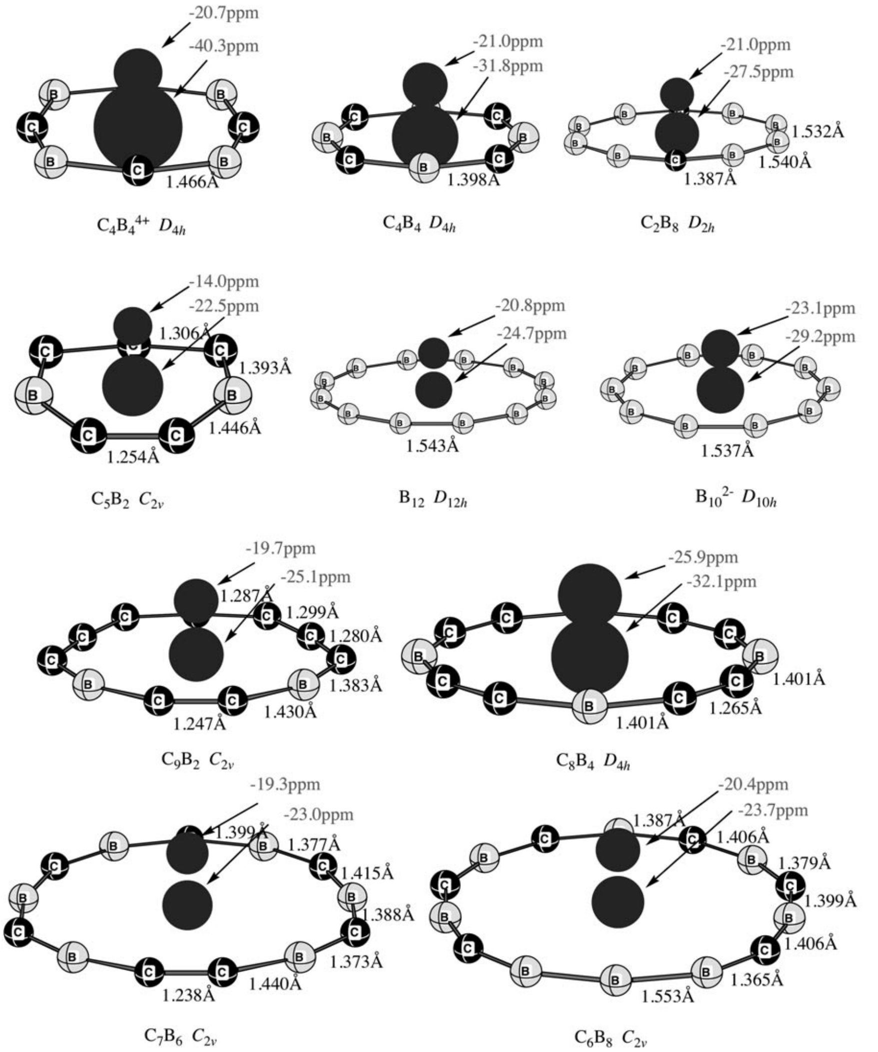


Figure 12. Mixed aromatic/antiaromatic systems reported by Hofmann and Berndt.[27]



$C_4B_4^{4+}$ D_{4h} — C_4B_4 D_{4h} — C_2B_8 D_{2h}

C_5B_2 C_{2v} — B_{12} D_{12h} — B_{10}^{2-} D_{10h}

C_9B_2 C_{2v} — C_8B_4 D_{4h}

C_7B_6 C_{2v} — C_6B_8 C_{2v}

Figure 13. Geometries, point groups, and isotropic NICS values (black signifies diatropic) of various rings.

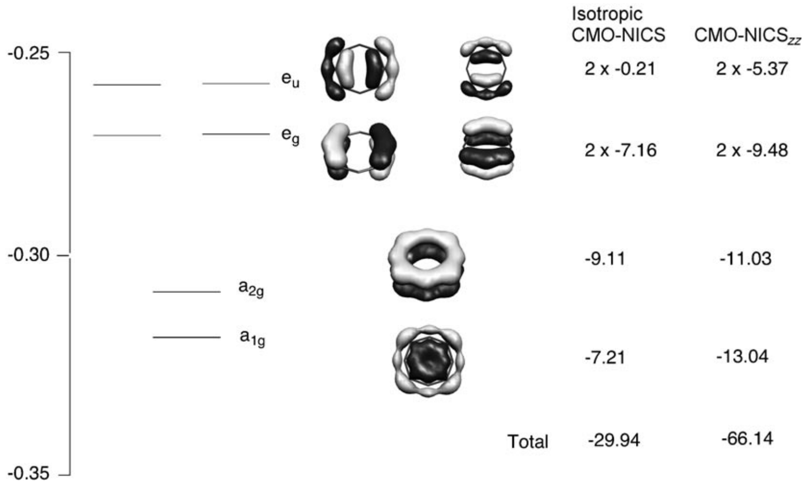


Figure 14. CMO-NICS and CMO-NICS$_{zz}$ from canonical molecular orbitals of C_4B_4. CMO-NICS and CMO-NICS$_{zz}$ contributions are listed on the right side in ppm. The total values given are the sums of *all* orbitals, not just those depicted. MO energies in a.u. are given on the left side.

−40.3), but these values decrease in magnitude as more boron atoms are inserted into the ring (C_8B_4 −37.2, C_7B_5 −29.3, and C_6B_8 −28.6). In contrast, the in-plane radial system (NICS$_{\mathrm{rad}zz}$) values for C_9B_2, C_7B_6, and C_6B_8 range from −21.1 to −28.4. The highly symmetric D_{4h} C_8B_4 possesses an exceptionally diatropic in-plane radial system (NICS$_{\mathrm{rad}zz}$ −42.9).

As expected from their 6+6 electron count, the B_{10}^{2-} and B_{12} monocyclic boron rings are doubly aromatic; their NICS$_{zz}$ values for both the perpendicular π and the in-plane radial systems are similar to those of 6+6 borocarbons. Unlike the C_{10} carbon monocycle, the frontier orbital symmetry of B_{10}^{2-} does not result in a second-order Jahn–Teller distortion; the highest possible D_{10h} ring symmetry is favored. However, polycyclic B_{10} (as well as B_{12}) structural alternatives are more stable than the monocyclic forms.[26] These polycyclic isomers also exhibit double aromaticity.

General trends: NICS$_{\mathrm{iso}}$, NICS$_{zz}$, and CMO-NICS$_{zz}$ values show the overall diatropic character of doubly aromatic compounds is greater than their singly aromatic counterparts. The second additional set of in-plane delocalized electrons increases the total diatropicity. Increasing ring size and the number of Hückel electrons of carbon clusters results in larger NICS$_{zz}$ values for each system (for example, $C_{14} > C_{10} > C_6$). For borocarbons the larger rings have smaller NICS$_{\pi zz}$ values ($C_6B_8 < C_7B_6 < C_8B_4 < C_9B_2$). The NICS$_{\mathrm{rad}zz}$ values correlate weakly with the number of radial electrons. The NICS$_{\mathrm{rad}zz}$ values of systems with two in-plane radial electrons overlap with those containing six in-plane radial electrons.

The 10 radial electron C_8B_4 shows remarkable in-plane diatropic character, nearly equal to that of the 14 in-plane electron C_{14}. Overlap of $\mathrm{NICS}_{\pi zz}$ values is also seen in systems containing six and 10 π electrons. The six π and 10 π electrons range from −23.9 to −39.5 and from −28.6 to −40.3, respectively. However, the 14 π and radial electron C_{14} has both the largest $\mathrm{NICS}_{\pi zz}$ (−56.7) and the most diatropic in-plane radial system ($\mathrm{NICS}_{\mathrm{rad}zz} = -44.5$). For antiaromatic systems, smaller ring systems possessing fewer radial electrons have smaller $\mathrm{NICS}_{\mathrm{rad}zz}$ values than larger ring systems with more radial electrons. In contrast, the $\mathrm{NICS}_{\pi zz}$ values decrease with an increasing electron number and increasing ring size (for example, the π system of C_{12} is less paratropic than that of C_8; Scheme 1).

Conclusion

The concept of double aromaticity, originally conceived by Chandrasekhar, Jemmis, and Schleyer,[1] has been subjected to detailed NICS analysis. While many of the monocyclic boron, carbon, and borocarbon rings examined in Table 1 have negative isotropic NICS(0) values, the individual π and σ (in-plane radial) MO contributions (CMO-NICS) reveal diverse behavior. In particular, their out-of-plane NICS_{zz} tensor components ($\mathrm{NICS}_{\pi zz}$ and $\mathrm{NICS}_{\mathrm{rad}zz}$) provide clear evidence not only for double aromaticity (C_6, C_6^{4+}, C_{10}, and C_{14}), but also for double antiaromaticity (C_8 and C_{12}, each containing two orthogonal eight electron systems) and for mixed aromaticity/antiaromaticity (C_7 and C_9; Table 1). B_{10}^{2-} and B_{12} monocyclic rings also exhibit double aromaticity, but are not the most stable isomers.[26] The doubly aromaticity of the $C_4B_4^{4+}$, C_4B_4, C_5B_2, C_2B_8, C_9B_2, C_8B_4, C_7B_6, and C_6B_8 borocarbon rings should result in considerable stability, at least as local minima, and encourage abundance mass spectrometric investigations and further studies of their potential energy surfaces.

Acknowledgements

We thank Chaitanya Wannere and Zhongfang Chen for helpful discussions, the Research Computing Center of the University of Georgia for providing computer time, and financial support by NSF Grant CHE-0209857 and the Petroleum Research Fund. C.C. acknowledges the support of the Swiss NSF Grant PA002–115322/1.

---

[1] J. Chandrasekhar, E. D. Jemmis, P. v. R. Schleyer, *Tetrahedron Lett.* **1979**, *20*, 3707.
[2] M. J. S. Dewar, *J. Chem. Soc.* **1954**, 1625.
[3] E. D. Nelson, H. I. Kenttämaa, *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 258.
[4] A. B. McEwen, P. v. R. Schleyer, *J. Org. Chem.* **1986**, *51*, 4357.
[5] See I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, *Aromaticity and Antiaromaticity, Electronic and Structural Aspects*, Wiley, New York, **1994**, Chapter 8 of V.
[6] A. A. Fokin, H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 9364.
[7] I. Morao, B. Lecea, F. P. Cossío, *J. Org. Chem.* **1997**, *62*, 7033.
[8] I. Morao, F. P. Cossío, *J. Org. Chem.* **1999**, *64*, 1868.
[9] F. P. Cossío, I. Morao, H. J. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1999**, *121*, 6737.
[10] C. Lepetit, B. Silvi, R. Chauvin, *J. Phys. Chem. A* **2003**, *107*, 464.
[11] G. A. Burley, *Angew. Chem.* **2005**, *117*, 3238; *Angew. Chem. Int. Ed.* **2005**, *44*, 3176.
[12] A. I. Boldyrev, L.-S. Wang, *Chem. Rev.* **2005**, *105*, 3716.
[13] W. Chen, Z.-R. Li, D. Wu, Y. Li, C.-C. Sung, *J. Chem. Phys.* **2005**, *123*, 164306.
[14] K. Raghavachari, R. A. Whiteside, J. A. Pople, *J. Chem. Phys.* **1986**, *85*, 6623.
[15] T. Torelli, L. Mitas, *Phys. Rev. Lett.* **2000**, *85*, 1702.
[16] S. M. Martin-Santamaria, H. S. Rzepa, *Chem. Commun.* **2000**, 1503.
[17] F. Stahl, P. v. R. Schleyer, H. Jiao, H. F. Schaefer III, K.-H. Chen, N. L. Allinger, *J. Org. Chem.* **2002**, *67*, 6599.
[18] P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209.
[19] H.-J. Zhai, A. E. Kuznetsov, A. I. Boldyrev, L.-S. Wang, *ChemPhysChem* **2004**, *5*, 1885.
[20] C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2002**, *114*, 1597; *Angew. Chem. Int. Ed.* **2002**, *41*, 1526.
[21] C. Präsang, A. Mlodzianowska, Y. Sahin, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2002**, *114*, 3529; *Angew. Chem. Int. Ed.* **2002**, *41*, 3380.
[22] C. Präsang, A. Mlodzianowska, Y. Sahin, G. Geiseler, W. Massa, M. Hofmann, A. Berndt, *Pure Appl. Chem.* **2003**, *75*, 1175.
[23] W. Mesbah, C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2003**, *115*, 1758; *Angew. Chem. Int. Ed.* **2003**, *42*, 1717.
[24] P. Amseis, W. Mesbah, C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Organometallics* **2003**, *22*, 1594.
[25] A. N. Alexandrova, E. Koyle, A. I. Boldyrev, *J. Mol. Model.* **2006**, *12*, 569.
[26] A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai, L.-S. Wang, *Coord. Chem. Rev.* **2006**, *250*, 2811.
[27] M. Hofmann, A. Berndt, *Heteroat. Chem.* **2006**, *17*, 224.
[28] H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, L.-S. Wang, *Angew. Chem.* **2003**, *115*, 6186; *Angew. Chem. Int. Ed.* **2003**, *42*, 6004.
[29] Q. Li, Y. Zhao, W. Xu, N. Li, *Int. J. Quantum Chem.* **2005**, *101*, 219.
[30] W. An, S. Bulusu, Y. Gao, X. C. Zeng, *J. Chem. Phys.* **2006**, *124*, 154310.
[31] K. Exner, O. Cullmann, M. Vögtle, H. Prinzbach, B. Grossmann, J. Heinze, L. Liesum, R. Bachmann, A. Schweiger, G. Gescheidt, *J. Am. Chem. Soc.* **2000**, *122*, 10650.
[32] R. W. A. Havenith, A. Rassat, P. W. Fowler, *J. Chem. Soc. Perkin Trans. 2* **2002**, 723.
[33] K. Tahara, Y. Tobe, *Chem. Rev.* **2006**, *106*, 5274.
[34] A. A. Fokin, H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 9364.
[35] X.-W. Wie, A. D. Darwish, O. V. Boltalina, P. B. Hitchcock, J. M. Street, R. Taylor, *Angew. Chem.* **2001**, *113*, 3077; *Angew. Chem. Int. Ed.* **2001**, *40*, 2989.
[36] T. Canteenwala, P. A. Padmawar, L. Y. Chiang, *J. Am. Chem. Soc.* **2005**, *127*, 26.
[37] P. A. Troshin, R. N. Lyubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem.* **2005**, *117*, 238; *Angew. Chem. Int. Ed.* **2005**, *44*, 235.
[38] P. v. R. Schleyer, H. J. Jiao, M. N. Glukhovtsev, J. Chandrasekhar, E. Kraka, *J. Am. Chem. Soc.* **1994**, *116*, 10129.
[39] P. J. Garratt, *Aromaticity*, Wiley, New York, **1986**.
[40] A. T. Balaban, M. Bancin, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo- Derivatives, and Their Valence Isomers*, CRC Press, Boca Raton, **1994**.
[41] W. Weltner, Jr., R. J. van Zee, *Chem. Rev.* **1989**, *89*, 1713.
[42] N. Fuerstenau, F. Hillencamp, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *35*, 135.

[43] H. Hintenberg, J. Franzen, K. D. Schuy, *Z. Naturforsch. Teil A* **1963**, *18*, 1236.
[44] R. E. Honig, *J. Chem. Phys.* **1954**, *22*, 126.
[45] M. Leleyter, P. Joyes, *Radiat. Eff.* **1973**, *18*, 105.
[46] E. A. Rohlfing, D. M. Cox, A. Kaldor, *J. Chem. Phys.* **1984**, *81*, 3322.
[47] N. Fürstenau, F. Hillencamp, R. Nitsche, *Int. J. Mass Spectrom. Ion Phys.* **1979**, *31*, 85.
[48] N. Fürstenau, F. Hillencamp, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 135.
[49] G. von Helden, N. G. Gotts, M. T. Bowers, *Chem. Phys. Lett.* **1993**, *212*, 241–246.
[50] L. A. Bloomfield, M. E. Geusic, R. R. Freeman, W. L. Brown, *Chem. Phys. Lett.* **1985**, *121*, 33.
[51] R. D. Beck, C. Warth, K. May, M. M. Kappes, *Chem. Phys. Lett.* **1996**, *257*, 557.
[52] S. Díaz-Tendero, G. Sánchez, M. Alcamí, F. Martín, P.-A. Hervieux, M. Chabot, G. Martinet, P. Désesquelles, F. Mezdari, K. Wohrer-Béroff, S. Della Negra, H. Hamrita, A. LePadellec, L. Montagnon, *Int. J. Mass Spectrom.* **2006**, *252*, 126.
[53] H. W. Kroto, H. W. Allaf, S. P. Balm, *Chem. Rev.* **1991**, *91*, 1213.
[54] S. L. Wang, C. M. L. Rittby, W. R. M. Graham, *J. Chem. Phys.* **1997**, *107*, 6032.
[55] J. D. Presilla-Marzuez, J. Harper, J. A. Sheehy, P. G. Carrie, C. W. Larson, *Chem. Phys. Lett.* **1999**, *300*, 719.
[56] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162.
[57] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 350.
[58] S. Iijima, *Nature* **1991**, *354*, 56.
[59] K. Kaizu, K. Kohno, S. Suzuki, H. Shiromaru, T. Moriwaki, Y. Achiba, *J. Chem. Phys.* **1997**, *106*, 9954.
[60] Y. Kato, T. Wakabayashi, T. Momose, *J. Chem. Phys.* **2003**, *118*, 5390.
[61] L. Belau, M. Ahmed, S. R. Leone, B. Ticknor, S. E. Wheeler, H. F. Schaefer III, M. A. Duncan, to be submitted.
[62] K. S. Pitzer, E. Clementi, *J. Am. Chem. Soc.* **1959**, *81*, 4477–4485.
[63] R. Hoffmann, *Tetrahedron* **1966**, *22*, 521.
[64] Z. Slanina, R. Zhradnik, *J. Phys. Chem.* **1977**, *81*, 2252.
[65] E. M. Engler, unpublished computations, **1975**. Included in the Carnegie-Mellon Archive of ab initio computations.
[66] K. Raghavachari, J. S. Binkley, *J. Chem. Phys.* **1987**, *87*, 2191.
[67] V. I. Baranovski, *Chem. Phys. Lett.* **2005**, *408*, 429.
[68] J. Hutter, H. P. Lüthi, *J. Chem. Phys.* **1994**, *101*, 2213.
[69] J. D. Watts, R. J. Bartlett, *Chem. Phys. Lett.* **1992**, *190*, 19.
[70] V. Parasuk, J. Almlöf, *Theor. Chim. Acta* **1992**, *83*, 227.
[71] C. Liang, H. F. Schaefer III, *J. Chem. Phys.* **1990**, *93*, 8844.
[72] W. Andreoni, D. Scharf, P. Gianozzi, *Chem. Phys. Lett.* **1990**, *173*, 449.
[73] J. Hutter, H. P. Lüthi, F. Diedrich, *J. Am. Chem. Soc.* **1994**, *116*, 750.
[74] J. M. L. Martin, P. R. Taylor, *J. Phys. Chem.* **1996**, *100*, 6047–6056.
[75] R. O. Jones, *J. Chem. Phys.* **1999**, *110*, 5189–5200.
[76] J. M. L. Martin, J. El-Yazal, J.-P. François, *Chem. Phys. Lett.* **1996**, *252*, 9.
[77] V. Pless, H. U. Suter, B. Engels, *J. Chem. Phys.* **1994**, *101*, 4042–4048.
[78] M. S. Deleuze, M. G. Giuffreda, J. P. Francois, L. S. Cederbaum, *J. Chem. Phys.* **2000**, *112*, 5325–5338.
[79] R. G. Pearson, *Proc. Natl. Acad. Sci. USA* **1975**, *72*, 2104–2106.
[80] M. Saito, Y. Okamoto, *Phys. Rev. B* **1999**, *60*, 8939–8942.
[81] J. M. L. Martin, J. El-Yazal, J.-P. François, *Chem. Phys. Lett.* **1995**, *242*, 570.
[82] M. Atis, C. Özdogan, Z. B. Güvenç, *Int. J. Quantum Chem.* **2006**, *107*, 729.
[83] H.-J. Zhai, B. Kiran, J. Li, L.-S. Wang, *Nat. Mater.* **2003**, *2*, 827.
[84] J. Aihara, H. Kanno, T. Ishida, *J. Am. Chem. Soc.* **2005**, *127*, 13324.
[85] Z.-X. Wang, P. v. R. Schleyer, *Science* **2001**, *292*, 2465.
[86] Z.-X. Wang, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2001**, *123*, 994.
[87] Z.-X. Wang, P. v. R. Schleyer, *Angew. Chem.* **2002**, *114*, 4256; *Angew. Chem. Int. Ed.* **2002**, *41*, 4082.
[88] S. Erhardt, G. Frenking, Z. Chen, P. v. R. Schleyer, *Angew. Chem.* **2005**, *117*, 1102; *Angew. Chem. Int. Ed.* **2005**, *44*, 1078.
[89] K. Exner, P. v. R. Schleyer, *Science* **2000**, *290*, 1937.
[90] B. K. Rao, P. Jena, *Phys. Rev. B* **1985**, *32*, 2058.
[91] S. Hira, A. K. Ray, *Surf. Sci.* **1991**, *249*, 199.
[92] T. L. Aselage, D. Emin, S. S. McCready, R. V. Duncan, *Phys. Rev. Lett.* **1998**, *81*, 2316.
[93] H. T. Hall, L. A. Compton, *Inorg. Chem.* **1965**, *4*, 1213.
[94] S. Han, J. Ihm, S. G. Louie, L. Cohen, *Phys. Rev. Lett.* **1998**, *80*, 995.
[95] S. Ulrich, H. Ehrhardt, J. Schwan, R. Samlenski, R. J. Brenn, *Diamond Relat. Mater.* **1998**, *7*, 835.
[96] I. J. McColm, *Ceramic Hardness*, Plenum, New York, **1990**.
[97] A. Joly, C. R. Hebd, *Seances Acad. Sci.* **1883**, *97*, 456.
[98] R. R. Rigdway, *Trans. Am. Electrochem. Soc.* **1934**, *66*, 117.
[99] F. Mauri, N. Vast, C. J. Pickard, *Phys. Rev. Lett.* **2001**, *87*, 085506.
[100] R. Lazzari, N. Vast, J. M. Besson, S. Baroni, A. D. Corso, *Phys. Rev. Lett.* **1999**, *83*, 3230.
[101] U. Jansson, J. Carlsson, *Thin Solid Films* **1985**, *124*, 101.
[102] A. O. Sezer, J. I. Brand, *Mater. Sci. Eng. B* **2001**, *79*, 191.
[103] G. Verhaegen, F. E. Stafford, J. Drowart, *J. Chem. Phys.* **1964**, *40*, 1622.
[104] S. Becker, H.-J. Dietze, *Int. J. Mass Spectrom. Ion Proc.* **1988**, *82*, 287.
[105] W. C. Easley, W. Weltner, *J. Chem. Phys.* **1970**, *52*, 1489.
[106] L. B. Knight, S. T. Cobranchi, J. T. Petty, E. Earl, D. Feller, E. R. Davidson, *J. Chem. Phys.* **1989**, *90*, 690.
[107] L. B. Knight, S. T. Cabranchi, E. Earl, *J. Chem. Phys.* **1996**, *104*, 4927.
[108] J. D. Presilla-Marzuez, P. G. Carrick, C. W. Larson, *J. Chem. Phys.* **1999**, *110*, 5702.
[109] M. Wyss, M. Grutter, J. P. Maier, *J. Phys. Chem. A* **1998**, *102*, 9106.
[110] J. D. Presilla-Marzuez, C. W. Larson, P. G. Carrick, C. M. L. Rittby, *J. Chem. Phys.* **1996**, *99*, 12.
[111] J. E. Kouba, Y. Öhrn, *J. Chem. Phys.* **1970**, *53*, 3923.
[112] G. Hirsch, R. J. Buenker, *J. Chem. Phys.* **1988**, *87*, 6004.
[113] N. Oliphant, L. Adamowicz, *Chem. Phys. Lett.* **1990**, *168*, 126.
[114] W. T. M. L. Fernando, L. C. O'Brien, P. F. Bernath, *J. Chem. Phys.* **1990**, *93*, 8482.
[115] J. M. L. Martin, P. R. Taylor, *J. Chem. Phys.* **1994**, *100*, 9002.
[116] C. G. Zhan, S. Iwata, *J. Phys. Chem.* **1997**, *101*, 591.
[117] C. Leonard, P. Rosmus, M. Wyss, J. P. Maier, *Phys. Chem. Chem. Phys.* **1999**, *1*, 1827.
[118] C. Liu, M. Tang, H. Wang, *J. Phys. Chem. A* **2007**, *111*, 704.
[119] S. S. Park, *Bull. Korean Chem. Soc.* **2005**, *26*, 63.
[120] T. N. Gribanova, R. M. Minyaev, V. I. Minkin, *Mendeleev Commun.* **2001**, *5*, 169.
[121] R. M. Minyaev, T. N. Gribanova, A. G. Starikov, V. I. Minkin, *Mendeleev Commun.* **2001**, *6*, 213.
[122] R. M. Minyaev, T. N. Gribanova, V. I. Minkin, A. G. Starikov, R. Hoffmann, *J. Org. Chem.* **2005**, *70*, 6693.
[123] A. N. Alexandrova, A. I. Boldyrev, H. H. Zhai, L.-S. Wang, *J. Phys. Chem. A* **2004**, *108*, 3509.
[124] K. Ito, Z. Chen, C. Corminboeuf, C. S. Wannere, X. H. Zhang, Q. S. Li, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2007**, *129*, 1510.
[125] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
[126] C. S. Wannere, P. v. R. Schleyer, *Org. Lett.* **2003**, *5*, 865.
[127] T. Heine, P. v. R. Schleyer, C. Corminboeuf, G. Seifert, R. Reviakine, J. Weber, *J. Phys. Chem. A* **2003**, *107*, 6470.
[128] C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer, *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.
[129] Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.
[130] H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863.
[131] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[132] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[133] Gaussian 98 (Revision A.9), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.
[134] J. A. Bohmann, F. Weinhold, T. C. Farrar, *J. Chem. Phys.* **1997**, *107*, 1173.
[135] J. P. Perdew in *Electronic Structure of Solids '91* (Eds.: P. Ziesche and H. Eschig), Akademie Verlag, Berlin, **1991**, p. 11.
[136] NBO 5.0. E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison **2001**.
[137] We have observed a strong basis set dependence for the use of CMO-NICS. Large Pople-type basis sets (for example, 6-311+G-(2d,2p) and 6-311+G(3df,2p)) result in large divergence from results obtained by using IGLO-III, Karlsruhe, and smaller Pople basis sets. This results from a poor balance of the larger Pople basis sets (low ratio of sp/d functions).
[138] P. W. Fowler, E. Steiner, *Mol. Phys.* **2000**, *98*, 945.
[139] E. Steiner, P. W. Fowler, L. W. Jennesskens, *Angew. Chem.* **2001**, *113*, 375; *Angew. Chem. Int. Ed.* **2001**, *40*, 362.
[140] E. Steiner, P. W. Fowler, *Chem. Commun.* **2001**, 2220.
[141] C. Corminboeuf, P. v. R. Schleyer, R. B. King, *Chem. Eur. J.* **2007**, *13*, 978 .
[142] M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333.
[143] G. Subramanian, P. v. R. Schleyer, H. Jiao, *Angew. Chem.* **1996**, *108*, 2024; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2638.
[144] A. E. Boguslavskiy, H. Ding, J. P. Maier, *J. Chem. Phys.* **2005**, *123*, 034305.
[145] We have calculated NICS on D_{10h} and D_{14h} $C_{10}H_{10}$ and $C_{14}H_{14}$ due to their structural similarities with monocyclic C_{10} and C_{14}.
[146] Z. Slanina, J. Kurtz, L. Adamowicz, *Mol. Phys.* **1992**, *79*, 387.
[147] Z. Slanina, S.-L. Lee, J.-P. Francois, J. Kurtz, L. Adamowicz, *Chem. Phys. Lett.* **1994**, *223*, 397.
[148] C. Corminboeuf, R. B. King, P. v. R. Schleyer, *ChemPhysChem* **2007**, *8*, 391.
[149] S. B. H. Bach, J. R. Eyler, *J. Chem. Phys.* **1990**, *92*, 358–363.
[150] The structures of C_7 and C_9 tested for aromaticity are not minima on the potential energy surface.

Received: January 29, 2007