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$(\pi+\sigma)$-Double Aromatic and π,σ-Mixed Aromatic Boron Compounds with Two Electrons Delocalized over Three Centers

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ABSTRACT: *Using Schleyer's measure for aromaticity, computed nuclear independent chemical shifts (NICS), we review molecules with two electrons delocalized cyclically over three centers: one class with two π- as well as two σ-electrons, i.e. $(\pi+\sigma)$-double aromatics and a second class with two electrons intermediate between π and σ, i.e. π,σ-mixed aromatics. These classes show distinctly different patterns of NICS values. On this basis, sila-, germa-, and stannaboriranes, recently presented by Jemmis et al., are shown to be the first π,σ-mixed aromatics which are not homoaromatics. "Improvement of overlap by pyramidalization," a building principle introduced by Haddon in 1988, is the key to understanding the structure of π,σ-mixed aromatics. New representatives with large aromatic stabilization energies (up to 60 kcal mol^{-1}) and very strong pyramidalizations at tricoordinate B, C, and Si centers (up to 63°) are designed by computations.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:224–237, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20225

SCOPE AND LIMITATIONS

The following reviews experimental and computed results on $(\pi+\sigma)$-double aromatic and π,σ-mixed aromatic *compounds* containing two electrons cyclically delocalized over three centers. The majority involves boron atoms in the three-center bonding. Doubly aromatic *clusters as well as their anions and dianions,* which are reviewed by Boldyrev and Wang [1], will be mentioned here only to demonstrate their close electronic relationship to doubly aromatic compounds.

$(\pi+\sigma)$-DOUBLE AROMATICITY, π- AND σ- AS WELL AS π,σ-MIXED AROMATICITY

The concept of "double aromaticity" was introduced in 1979 by Paul von Ragué Schleyer [2] by means of the 3,5-didehydrophenyl cation **1** (Scheme 1), which was characterized by FT-ICR-MS investigations in 2001 [3]. This cation is stabilized by cyclic delocalization of six π-electrons over six centers, just like benzene, the prototype of π-aromatics. In addition, however, it is also stabilized by cyclic delocalization of two σ-electrons over three centers just like cyclopropane, the archetypal σ-aromatic [4]. The stabilization of benzene by π-aromaticity and that of cation **1** by σ-aromaticity can be quantified by the use of Eqs. (1) and (2) to be 35.7 (B3LYP/6-311+G**) [5] and 35.2 (MP4/6-31G*) [2b] kcal mol^{-1}, respectively.

Since double aromatics of type **1** and of the majority of those presented here are π-aromatics as well as σ-aromatics, we refer to them as $(\pi+\sigma)$-double aromatics [6–9]. These may not be confused with aromatics which have only one set of cyclically

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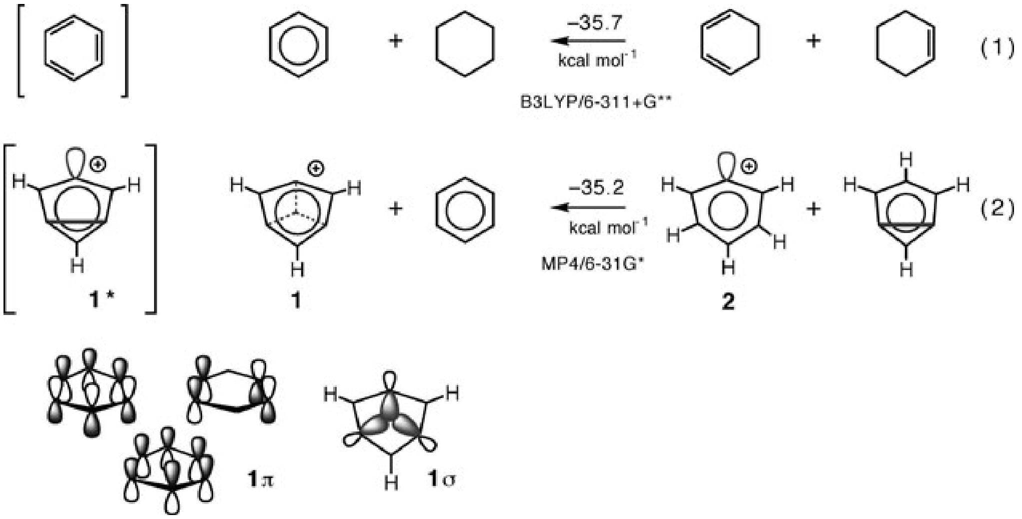
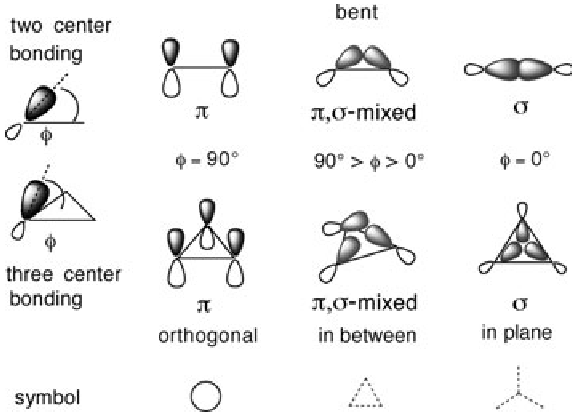


SCHEME 1 Stabilization of benzene by π-aromaticity and of the double aromatic cation **1** by σ-aromaticity as estimated by isodesmic equations (1) and (2). **1**π and **1**σ visualize the π-aromatic and the σ-aromatic part of **1**, respectively. A slashed star instead of the slashed triangle is used here to depict the 3c-2e-σ bond because it mimics the directions of the axes of the atomic orbitals that form the molecular orbital that holds the delocalized σ electrons as shown in **1**σ.

delocalized electrons but which are neither pure π nor pure σ in character, but “intermediate between π and σ” as recognized by Winstein for homoaromatics nearly half a century ago [10,11]. We refer to these here as π,σ-mixed aromatics [12]. According to our analysis of the electronic structure of molecules described recently to be the first with pyramidal tricoordinate boron atoms [13], the class of “π,σ-mixed aromatics” involves now the first members which are not homoaromatics. These will be described in the second part of this review. The homo ($\pi + \sigma$)-double aromatics reviewed in this paper as well as a recently characterized in-plane σ-bishomoaromatic [14] do not belong to Winstein type homoaromatics. The aromatics presented may be classified according to the orientation of the axes [15] of the atomic orbitals forming the molecular orbital of the cyclically delocalized electrons, with respect to the plane of the centers of this delocalization (Scheme 2).

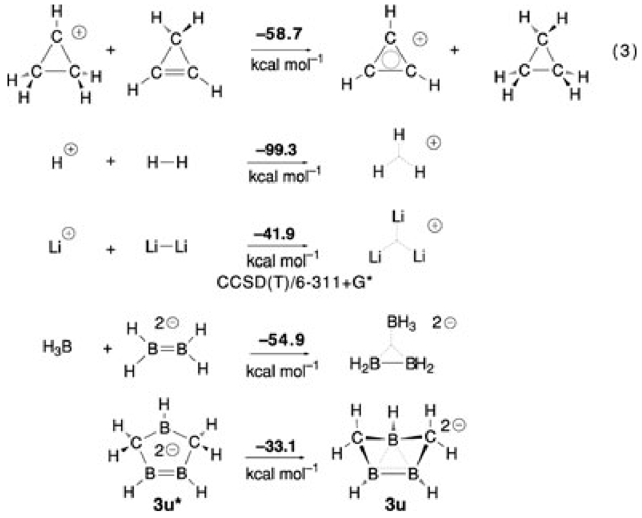


SCHEME 2 Molecular orbitals for 2c and 3c bonding classified according to the orientation of the atomic orbitals involved: Pure π-bonding results from side-on overlap of AO’s oriented perpendicular to the line (2c bonding) or plane (3c bonding) spanned by the atoms involved. Pure σ-bonding results from end-on overlap of AO’s pointing toward the center of the atoms involved. The in-between situations, e.g., bent 2c bonds and out of plane overlap in 3c bonds are termed “π,σ-mixed” bonds, here. The symbols used for the different types in the formulas of this review are shown at the bottom of Scheme 2.

According to the orientations of the axes the following types of two-electron (2e)-aromatics are possible: conventional π-aromatics like the cyclopropenylium cation where the axes of the atomic orbitals that build the molecular orbital which is responsible for cyclic delocalization are oriented *orthogonal* to the plane of the centers, σ-aromatics where they are located *in* this plane, and π,σ-mixed aromatics like homoaromatics of the Winstein-type where they can take any direction *in between* orthogonal and in-plane. ($\pi + \sigma$)-Double aromatics involve both a conventional π-aromatic and an in-plane σ-aromatic component (compare **1**π and **1**σ in Scheme 1 or **7**π and **7**σ in Scheme 6). Examples for the less familiar σ- as well as for π- and π,σ-mixed 2e-aromatics are shown in Scheme 3.

The Power of Two-Electron Aromaticity

Cyclic delocalization of two electrons over three centers is one of the most exergonic effects in chemistry. For π-systems, Schleyer pointed out repeatedly that the aromatic stabilization energy of 2e-aromatics



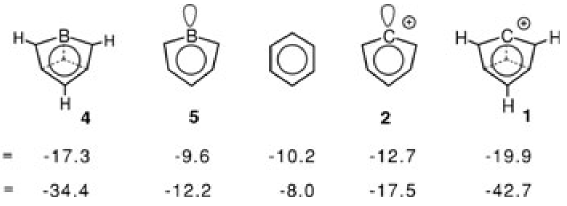
SCHEME 3 Energy gain upon cyclic delocalization of two electrons over three centers for a 2e-π-aromatic, for three 2e-σ-aromatics, and for the 2e-π,σ-mixed aromatic **3u**. Note that, due to two small BCB angles in **3u**, there is a considerable increase in strain going from classical **3u*** to **3u**. Therefore, the energy gain due to cyclic delocalization in **3u** is considerably larger than 33 kcal mol^{-1}.

like the cyclopropenylium cation is considerably larger (see isodesmic equation (3) in Scheme 3) than that of 6e-aromatics like benzene [16].

2e-σ-Aromatics like the prototype H_3^+ [17], and the less exotic Li_3^+ [18] and $B_3H_7^{2-}$ [19] also show large aromatic stabilization energies as does **3u** [20] (see discussion in caption of Scheme 3). Thus, cyclic delocalization of two electrons over three centers is powerful - independent of the orientations of the orbitals involved: *orthogonal* (π) to the plane of the three centers, *in-plane* (σ) or *in between* (π,σ-mixed).

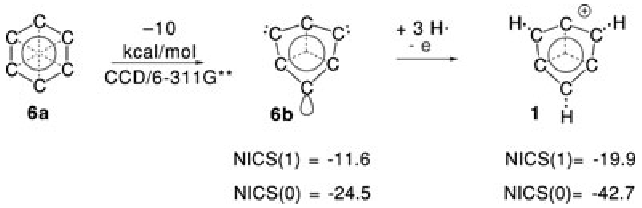
NICS OF DOUBLY AROMATIC COMPOUNDS

Nuclear independent chemical shifts (NICS) [21a] are widely accepted now as a quantitative measure for aromaticity. To eliminate the disturbing effects of localized σ bonds, NICS values at a distance of 1 Å above the center of the aromatic, the so-called NICS(1) values are used [21b,22]. For double aromatic **4**, which in turn is isoelectronic with **1**, Sander et al. [23] have calculated a NICS(1) value of −17.3 (see Scheme 4). This is considerably bigger than that of the π-aromatic borabenzene **5** (−9.6) [23], which is close to that of the π-aromatic benzene (−10.2). The difference (−7.7) of the NICS(1) values of **4** and **5** indicates enhanced aromaticity which is due to an additional aromatic system in **4**, namely the σ-aromatic component. For the double aromatic **1** and the phenyl cation **2** which is isoelectronic with **5**, we computed NICS(1) values of −19.9 and −12.7, the difference of which points to the additional σ-aromatic part in **1**. Both differences assigned to σ-aromatic parts of double aromatics are close to the NICS(1) value −8.9 (−8.6 at the level used here) computed for the archetypal σ-aromatic cyclopropane [4]. Also characteristic for σ-aromaticity are especially large [24,25] NICS(0) values: −42.8 and −43.3 for cyclopropane [4], −33.5 for H_3^+, −42.7 for **1**, and −34.4 for **4** (see Scheme 4).

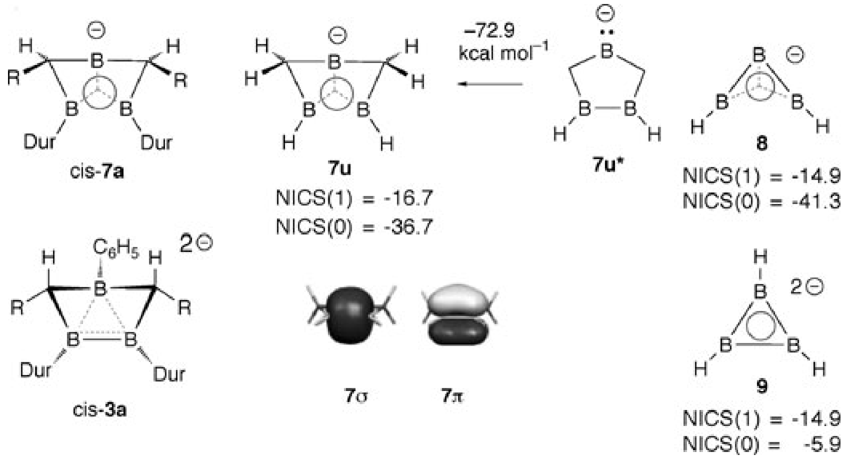


SCHEME 4 NICS values of the double aromatics **4** and **1** are significantly larger than those of the π-aromatics **2** and **5**, the NICS values of which are similar to that of benzene, the prototype of π-aromatics.

The double aromaticity of the cyclic C_6-clusters **6a** and **6b** was discussed by Schleyer in 1994 [2b]. Recent computations by Minkin [26] at the CCD/6-311G**-level revealed that **6a** is about 10 kcal mol^{-1} higher in energy than **6b**, which was characterized by FT-IR-spectroscopy at 10 K in 1997 [27]. The NICS(1) value calculated for **6b**, −11.6, is surprisingly small, close to that of benzene (−10.2), in spite of its 3c,2e-σ-aromatic part as in **1**, which can be deduced from its distorted geometry and from an NBO analysis. The small NICS(1) value of **6b** can be explained, however, if one takes into account the cyclic delocalization of four lone-pair-type electrons which generates an additional σ-*anti*aromatic part (see Scheme 5). The positive NICS(1) value to be expected for this reduces the total NICS(1) value of **6b**. Antiaromaticity is known for carbon clusters [7] as well as for boron clusters [1,28].



SCHEME 5 The double aromatic two-dimensional C_6-cluster **6b** is also σ-antiaromatic due to cyclic delocalization of its four lone-pair-type electrons. This is indicated by its NICS(1) and NICS(0) values which are surprisingly small for a double aromatic. Upon the formal transformation of **6b** to **1**, the antiaromaticity is lost.



SCHEME 6 The anion *cis*-**7a** (R = $SiMe_3$, Dur = 2,3,5,6- tetramethylphenyl) is the first double aromatic which was characterized by an X-ray structural analysis. Its prototype **7u** is the bishomo form of the double aromatic **8**.

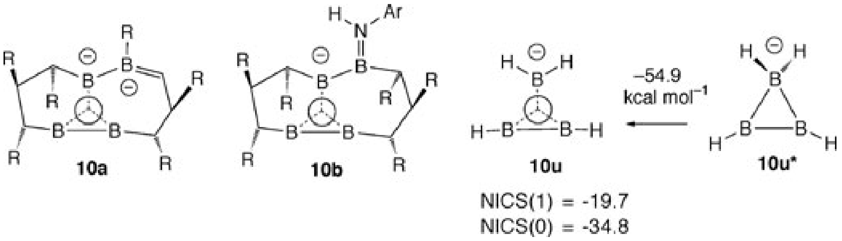
Double Aromatics with an Anionic B_3-Skeleton

The bishomotriboriranid *cis*-**7a** (Scheme 6) is the first double aromatic compound which was characterized by an X-ray structural analysis [29a]. The twofold transannular bonding in the bishomo-double aromatic *cis*-**7a** as compared to a single one in the bishomoaromatic *cis*-**3a** [12,30] is evident from a transannular B-B distance shortened by not less than 20 pm. The transformation of a B-B-σ bond and a 3c,2e-π,σ-mixed bond in *cis*-**3a** into two 3c,2e-BBB bonds (one σ and one π) in *cis*-**7a** leads to an elongation of the B-B edge by 5 pm.

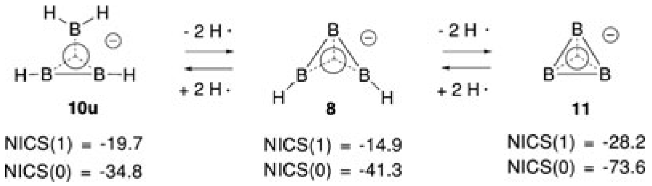
The double aromatic *cis*-**7a** is a derivative of the prototype **7u**, the bishomo form of **8**. An ion of this mass was identified in the gas phase, its geometry was computed [31]. NBO analyses for **7u** and **8** revealed a 3c-2e-π bond (**7**π) as well as a 3c-2e-σ bond (**7**σ) between three boron atoms for both of them [29b]. The strong stabilization of **7u** by double aromaticity is indicated by the energy difference relative to classical **7u*** without cyclically delocalized π- and σ-electrons. Since the transformation of **7u*** into **7u** requires the two B-C-B bond angles to become smaller which leads to additional ring strain, the energy gain by double aromaticity in **7u** must be bigger than 73 kcal mol^{-1}. The NICS(1) values of **7u** and **8**, −16.7 and −14.9, are of the order of magnitude of the double aromatics **1** and **4**. However, they are not significantly bigger than those of the π-aromatic **9**. The unusual big NICS(1) value of **9** is reminiscent of the corresponding one of the isoelectronic cyclopropenylium cation, which has been shown to be due to the strong shielding effect of the σ bonds of the three-membered ring [32]. The big NICS(0) values of the double aromatics **7u** (−36.7) and **8** (−41.3) as compared to −5.9 of the aromatic **9** indicate the existence of a σ-aromatic part in **7u** and **8**.

Double aromatics like **10a** and **10b** (Scheme 7), which are derivatives of the prototype **10u** [31,33], became accessible recently [34a,b]. The strong double aromatic stabilization of **10u** is indicated by the big energy difference relative to **10u*** [33].

The NICS(1) and NICS(0) values of the doubly aromatic **10u**, −19.7 and −34.8, respectively, are of the same order of magnitude as those of the double aromatics **1** and **4**. Upon the formal dehydrogenation of **10u** leading to **8**, the double aromaticity is conserved. This is also true for



SCHEME 7 **10a** and **10b** (R = $SiMe_3$, Ar = 3,5-di-*t*-butylphenyl) are derivatives of the double aromatic prototype **10u**. The additional boron centers in **10a,b** do not take part in the cyclic delocalizations because of their double bonds. The lithium gegenions of **10a** and **10b** have been ommitted for clarity.



SCHEME 8 **8** and **10u** are doubly aromatic di- and tetrahydroforms, respectively, of the doubly aromatic cluster **11**.

the formal dehydrogenation of **8** leading to the two-dimensional cluster **11**, which was characterized by photoelectron-spectroscopy [35] and UV-spectroscopy [36], recently. The NICS values of **11**, −28.2 and −73.6, are remarkably big (see Scheme 8).

Closed Shell Double Aromatics with Uncharged B_3-skeletons

As compared to the classical triboracyclopropane **12u***, the double aromatic **12uc** is lower in energy by not less than 64.5 kcal mol^{-1} (68.5 at the MP2/6-31G* level) [33]. A considerable part of this stabilization is due to the transformation of a B-B-σ bond of **12u*** into a 3c,2e-π bond in **12ua**. The π aromatic **12ua** is stabilized by twofold hyperconjugation of the B-B bonds with the formally empty in-plane p-orbitals at the dicoordinate boron atoms: an NBO analysis reveals an occupation of 0.2 electrons for each for these orbitals and an occupation of the B-B bonds of only 1.82 electrons.

The NICS(1) value of **12ua** is in agreement with a π-aromatic, the moderate NICS(0) value rules out a σ-aromatic part. **12ub** with NICS values characteristic for double aromatics is only by 2.1 kcal mol^{-1} lower in energy than the π-aromatic **12ua**, which is stabilized by B-B hyperconjugation. Two-fold B-H-hyperconjugation with the formally empty p-orbital at the symmetry unique boron explains the bending of the B-H bonds with respect to the classical B-B bond in **12ub**. **12uc** with a 3c,2e-BHB bond instead of twofold B-H-hyperconjugation in **12ub** is only slightly lower in energy than **12ub** (see Scheme 9).

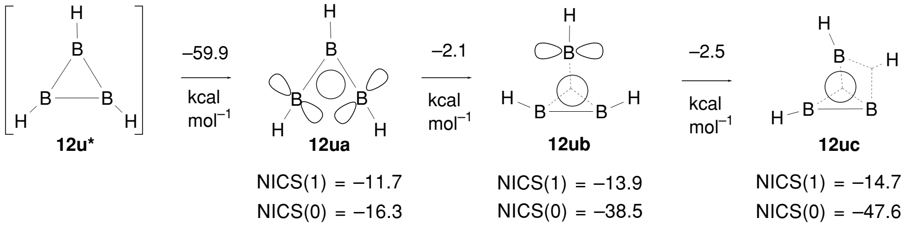
Strong hyperconjugation thus can lead to a stabilization comparable to 3c,2e-σ-delocalization, which may be regarded as extreme version of hyperconjugation following the argumentation of Olah concerning the continuum of hyperconjugation, unsymmetric bridging, and symmetric bridging [37]. The latter clearly corresponds to a σ-aromatic from the point of view taken here. The formation of the BHB bridge upon going from **12ub** to **12uc** is accompanied by a small change of the NICS(1) value.

According to our computations, the double aromatic **13u**, the homoform of **12uc**, also is considerably lower (by 41 kcal mol^{-1}) in energy than the classical triboracyclobutane **13u***, which is not an energy minimum (see Scheme 10). The NICS values clearly support the double aromaticity of **13u**; two different values for NICS(1) correspond to different sides of the BBB plane and are the consequence of the hydrogen of the BHB bridge to be located out of the B_3 plane. The dianion **14u** [38] of **13u*** is the homoform of the π-aromatic **9**.

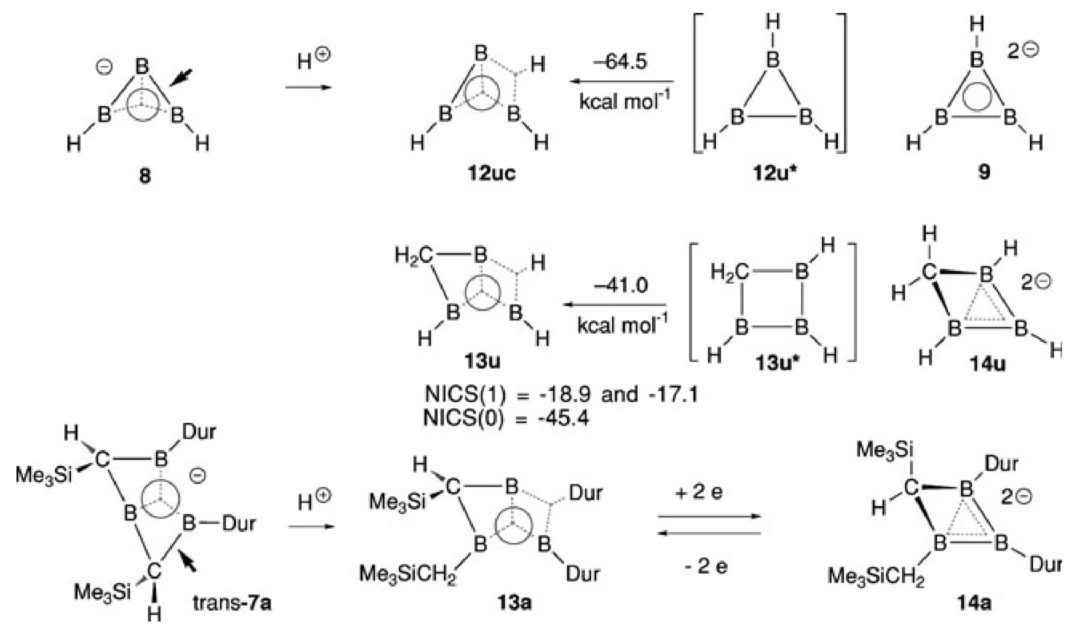
The double aromatic **13a**, a derivative of the homoform **13u** of **12uc**, is obtained upon protonation of the bishomo double aromatic *trans*-**7a** [30] at −100°C [39]. The short-lived **13a** can be stabilized by reaction at −100°C with two equivalents of lithium naphthalenide to yield the dianion **14a**. Its dilithium salt was characterized by an X-ray structural analysis [39]. Two-electron oxidation of **14a** by 1,2-dibromoethane at −90°C leads back to **13a** (see Scheme 10), which was fully characterized by ^{13}C- and ^{11}B-NMR-spectroscopy at this temperature [39]. ^{11}B-NMR chemical shifts of 14, 25, and 29 ppm exclude classical structures containing tricoordinate boron atoms, for which ^{11}B-NMR chemical shifts in the vicinity of 100 ppm are to be expected.

Double Aromatics with a CB_2-Skeleton

Isoelectronic with the double aromatics **11, 8**, and **10u** (Scheme 8) is the series **15, 16**, and **17** (Scheme 11). The double aromatic electronic structure of the cluster **15** was recognized on the basis of



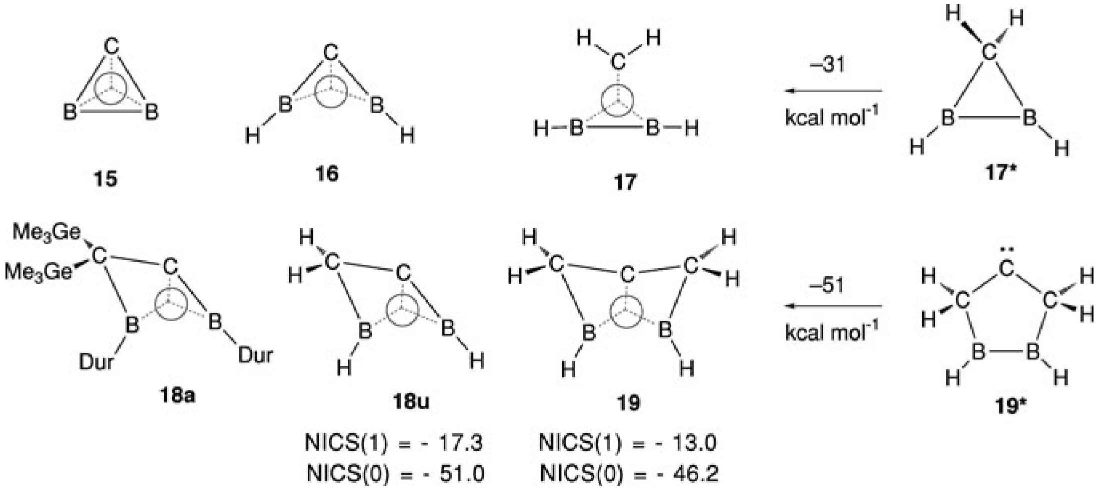
SCHEME 9 The double aromatics **12ub** and **12uc** are only a few kcal mol^{-1} lower in energy than the π-aromatic **12au**, which is stabilized by twofold hyperconjugation of the B-B bonds with the in-plane p-orbitals shown. Strong hyperconjugation in **12ua** can compete with σ-aromaticity in **12ub**.



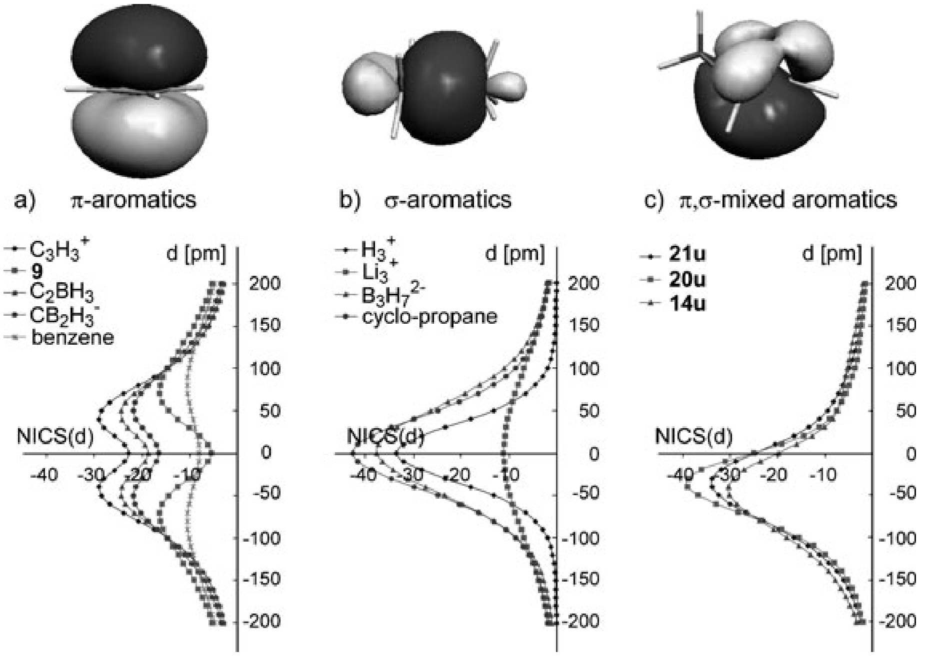
SCHEME 10 The double aromatic **13u** is the homoform of **12uc**. The derivative **13a** is obtained upon protonation of *trans*-**7a**, and fully characterized by NMR-spectroscopy at −100°C. *trans*-**7a** is a derivative of the bishomoform of **8**. The arrows point to σ bonds which are protonated with conservation of double aromaticity.

computations by Martin and Taylor as early as 1994 (“involves two aromatic systems with two electrons each, a ‘conventional’ one … and an ‘in-plane’ aromatic system (as is well known in carbon clusters”) [40]. Experimental characterization of **15** by FT-IR spectroscopy in an argon matrix at 10 K was achieved in 1999 [41]. Compound **18a** [42a], a derivative of the homoform **18u** of the dihydroform **16** [42a] of the cluster **15**, was characterized by an X-ray structural analysis as early as 1990 [42b]. Its double aromaticity, however, was recognized only in 1997 [29a], 14 years after the synthesis [42c] of the first derivative of **18u** (see Scheme 11). The NICS values of **18u** are in full agreement with its double aromatic electronic structure.

The double aromatic stabilization energy of **18u** was estimated by means of an isodesmic equation to be 94 kcal mol^{-1} [29a]. The double aromatic **17** is a transition state according to more recent computations [43], 31 kcal mol^{-1} lower in energy than the classical diboracyclopropane **17*** [44]. The bishomo double aromatic **19** is stabilized by



SCHEME 11 Double aromatics with CB$_2$-skeletons: experimentally characterized are **15** and **18a**, a derivative of the homoform **18u** of **16**. The bishomoform **19** is considerably stabilized by double aromaticity as seen from the computed energy difference with respect to **19***.



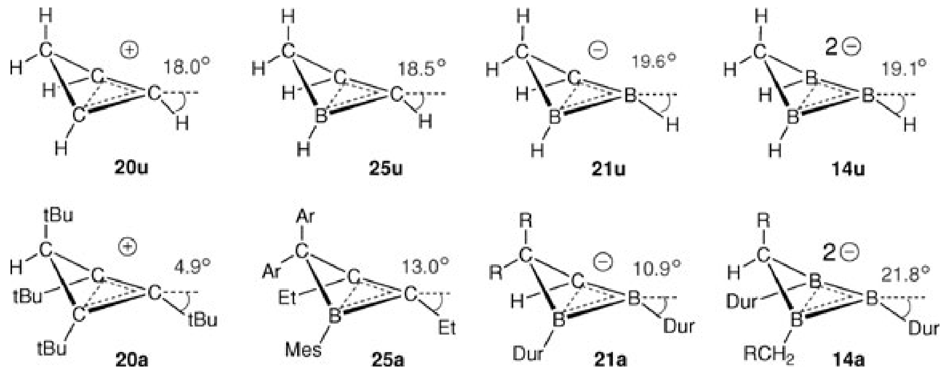
SCHEME 12 Isodensity plots of the 3c bonding MO for the two-electron π-aromatic **9**, σ-aromatic $B_3H_7^{2-}$, and π,σ-mixed aromatic **14u** as well as NICS value pattern for them and additional representatives. Note that NICS values at comparable distances above and below the plane of the centers of cyclic delocalization are *different* from another only for π,σ-mixed aromatics.

51 kcal mol^{-1} (B3LYP/6-311+G**) with respect to the classical carbene **19*** without delocalized π- and σ-electrons. Derivatives of **19** with appropriate substituents can be expected to show comparable stability as the isoelectronic double aromatics *cis*- and *trans*-**7a**. Therefore, they are candidates for the first X-ray structural analysis of a compound containing a planar-tetracoordinate carbon atom *not* connected to metals. Up to now, compounds of this type are known only in solution [44]. In all structurally established compounds with a planar-tetracoordinate carbon atom, it is coordinated to metals [45].

π,σ-*MIXED AROMATICS*

Unsymmetry in the Pattern of NICS Values of Winstein-Type Homoaromatics

Homoaromatics of the Winstein type are characterized by an *unsymmetrical* overlap with respect to the plane of the centers of the cyclic delocalization (Scheme 2) and termed here π,σ-mixed aromatics. This unsymmetry is evident from an MO isodensity surface plot of the homoaromatic **14u** (Scheme 12, top right) and shows up informatively in the NICS values of **14u** and the isoelectronic π,σ-mixed aromatics **20u** [46] (Scheme 13) and **21u** [38]. The



SCHEME 13 Pyramidalizations at tricoordinate carbon and boron centers in π,σ-mixed aromatics as computed and experimentally determined (Ar_2C = fluorenylidene, R = $SiMe_3$).

corresponding plots and NICS data of the π-aromatic **9** and the σ-aromatic $B_3H_7^{2-}$ are presented for comparison in Scheme 12.

While all the NICS values of π-, σ-, and (π + σ)-double aromatics are symmetric with respect to the plane of the centers of cyclic delocalization, the NICS values at comparable distances above and below this plane are *different* from another in π,σ-mixed homoaromatics. They are bigger on the side of stronger overlap, where the orbitals are bent toward another, than on the side of smaller overlap, i.e. they mirror the overlap. NICS(0) of **20u** is not the maximum NICS value which is found 40 pm out of the plane of the centers and opposite to the homobridge.

Scheme 13 summarizes experimental and computed results on pyramidalization of known π,σ-mixed monohomoaromatics: **20u** [38,46], **25u** [38,47], **21u** [38], **14u** [38], **20a** [48–50], **25a** [51], **21a** [38], and **14a** [39,52]. The tricoordinate centers of all of them are pyramidally surrounded by their three neighbors.

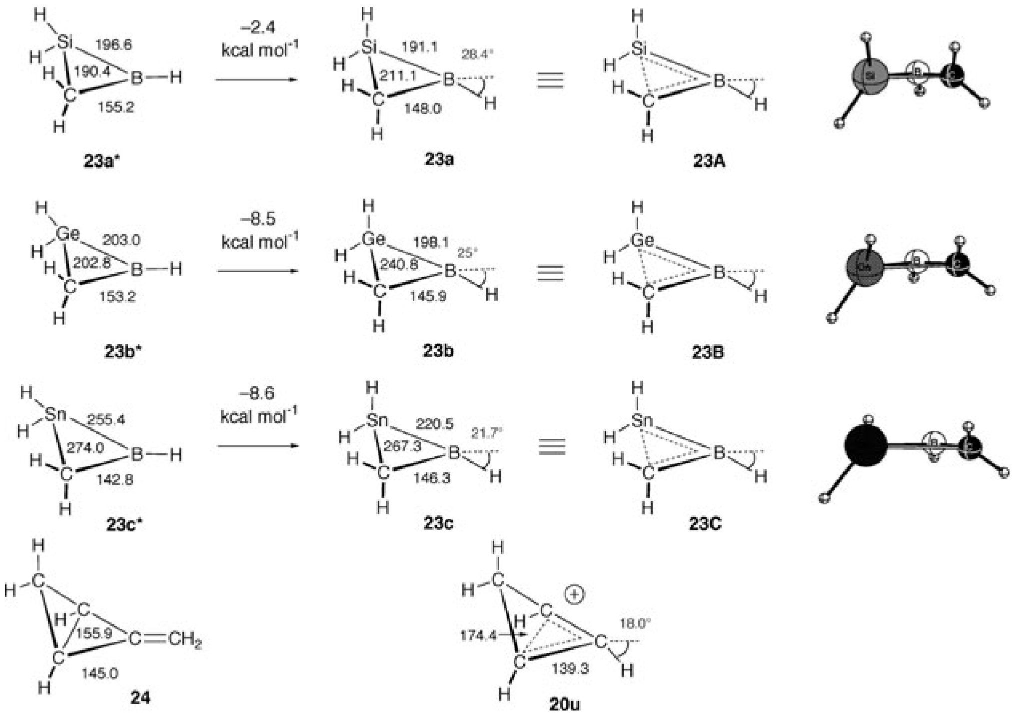
π,σ-*Mixed Aromatics Which Are Not Homoaromatics*

The silaborirane **23a** (Scheme 14) was recently presented by Jemmis et al. with the following comments: "We report here, for the first time, the computational discovery of a neutral-ground-state molecule, silaborirane .., which contains a tricoordinate pyramidal boron center," and "pyramidalization, therefore, is an attempt to involve the vacant p orbital on the boron atom in bonding to the Si atom" [13].

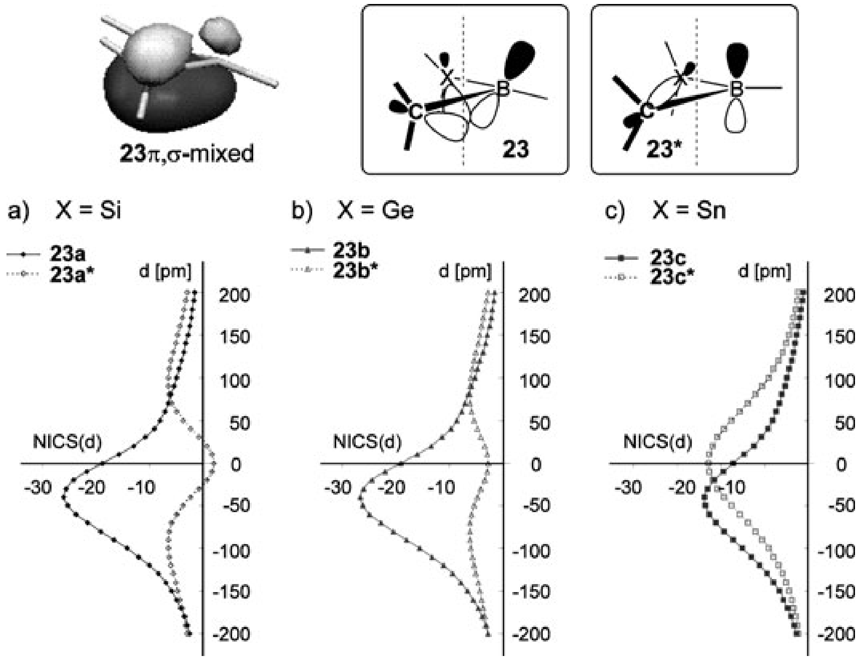
The C—Si bond of **23a** with a pyramidal-tricoordinate boron center is significantly elongated as compared to that in planar **23a*** while the B—C and B—Si bonds are shortened.

Similar changes in geometry upon pyramidalization as in **23a** versus **23a*** are computed for germaborirane **23b** as compared to **23b***. However, **23c** has a longer C—B bond as well as a shorter C—Sn bond than **23c***.

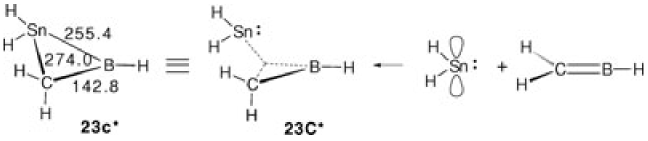
The elongated and shortened bond lengths in **23a,b** as compared to **23a,b*** are reminiscent



SCHEME 14 The sila-, germa-, and stannaboriranes **23a--c** [13] with pyramidal tricoordinate boron centers are lower in energy than their isomers **23a--c*** (all transition states) with planar tricoordinate boron centers. Geometrical changes upon pyramidalization at the boron center of **23a,b** are similar to those of the homoaromatic **20u** as compared to **24** where the HC—CH bond interacts with the very weak acceptor π^* of the double bond as compared to the strong acceptor "H—C$^+$" in **20u**. Data presented were obtained at the level used here [5]. Note the pyramidalized boron atom and the twisted EH_2 and CH_2 groups in the optimized molecular structures of **23a--c**.



SCHEME 15 Overlap in **23a--c** is very similar to that in **14u** (Scheme 12), the NICS values of **23a--c** are unsymmetric with respect to the plane of the centers of cyclic delocalization, and their most negative NICS values are located 40–50 pm below the plane of the centers of cyclic delocalization. These features are characteristic of the class of π,σ-mixed aromatics as demonstrated in Scheme 12. For comparison, the NICS values of classical **23a,b*** with a trigonal planar boron center are symmetrical with respect to the molecular plane and rather small.



SCHEME 16 Planar stannaborirane **23c*** is a σ-aromatic stannylene complex of methyleneborane as seen from its NICS pattern (Scheme 14).

of the geometries of long known two-electron-homoaromatics like the prototype homocyclopropenylium cation **20u** as compared to corresponding bicyclobutanes like **24** without a center of strong electron deficiency (Scheme 14) [53–55]. An NBO analysis for **23a** revealed a 3c-2e bond with the following composition: 17% B, 59% C, and 25% Si. The isodensity surface plot of the corresponding NLMO that holds the delocalized electrons of **23** is shown in Scheme 15: it is very similar to that of **14u** in Scheme 12.

23c*, however, is a σ-aromatic as described by **23C*** (Scheme 16). This is evident from its symmetric NICS pattern including NICS(0) = −22.7, which is easily explained assuming **23c*** to be a complex of methyleneborane and stannylene SnH_2 [56].

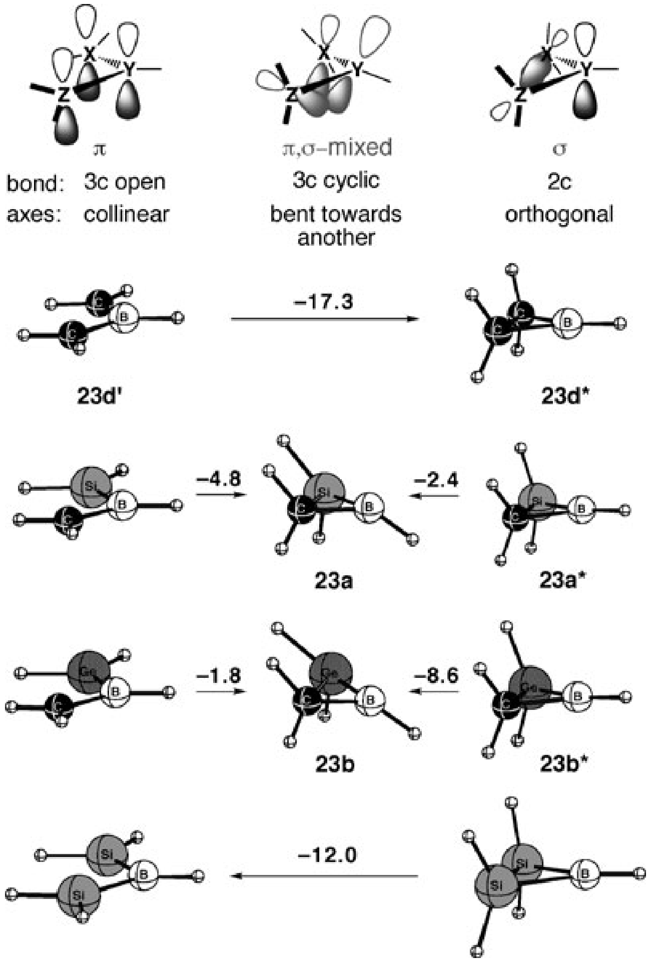
The General Building Principle of π,σ-Mixed Aromatics

The importance of the heteroatom in three-membered rings containing a tricoordinate boron for the π,σ-mixed aromatics to be preferred over classical structures is evident from the series as shown in Scheme 17 [57,58].

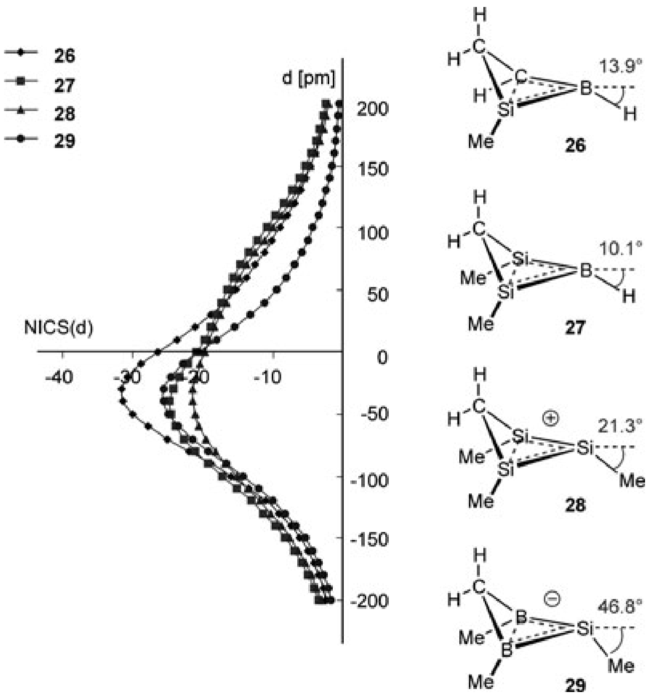
In classical borirane, **23d***, the 2c CC bond is orthogonal to the empty p-orbital at the boron center prohibiting any interaction between them. Disrotatory twist of the CH_2 groups weakens the C—C bond more than what participation of the boron atom can recover. 2-Boraallyl **23d**′ is therefore a transition state 17.3 kcal mol^{-1} higher in energy than **23d***. 3c orbital interaction becomes possible when the 2c CC bond is *forced* out of the CBC plane, e.g., by replacing two cis substituents by one methylene bridge as in homoborirene [38]. Pyramidalization at the boron atom generates a more favorably oriented boron acceptor orbital for better overlap with the carbon orbitals. However, this also leads to a smaller boron orbital lobe on the side of the overlap.

In order to elucidate the effect of silicon on the structure of homoaromatics, we computed the structures of **26–29** (Scheme 18).

Pyramidalization at the boron center is very similar in **26** and **23a** (13.9 vs. 14.1) which both contain



SCHEME 17 The heteroatom in three-membered rings containing a tricoordinate boron is essential for π,σ-mixed aromatic isomers to be energetically preferred over classical structures: for borirane **23d*** any pyramidalization is endergonic (3.7 kcal mol^{-1} in **23d** forced to have the same degree of pyramidalization as in **23a**).



SCHEME 18 The effect of silicon on pyramidalization at tricoordinate boron and silicon centers of π,σ-mixed aromatics. Note that the formal combination of the very strong donor B-B^{2-} with a silicon cation as the acceptor leads to an especially strong pyramidalization.

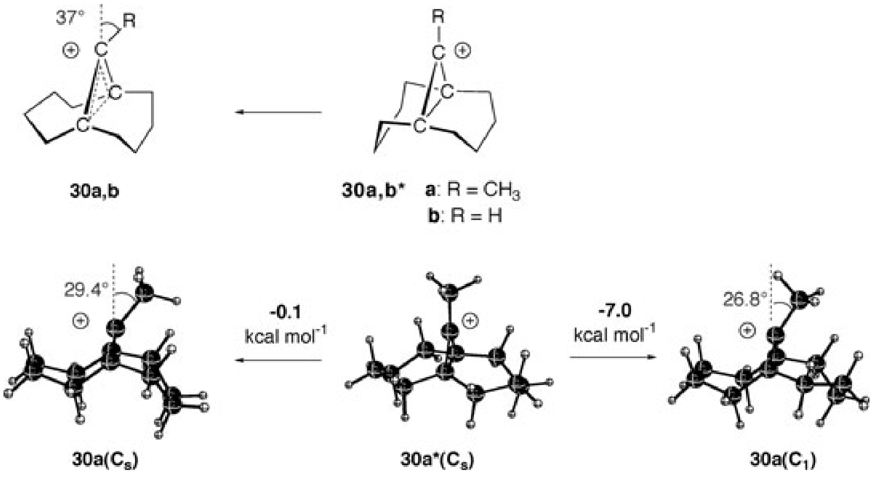
the same centers of cyclic delocalization. The same is true for their NICS patterns. Replacement of a carbon center of **26** by silicon leads to slightly reduced pyramidalization in **27** [59].

Especially effective is the replacement of the acceptor center boron by a silicon cation: pyramidalization in **28** is twice that of **27**. With the very strong B-B^{2-} donor instead of Si—Si in **28**, pyramidalization at the tricoordinate silicon in **29** is increased to not less than 46.8°. It may be further enhanced by σ-donating substituents at the boron centers and electron-withdrawing substituents at the silicon atom. To the best of our knowledge, the homoaromatics **28** and **29** are the first molecules computed to contain pyramidal-tricoordinate silicon centers. However, pyramidal-*penta*coordinate silicon centers are well-known units in bishomoaromatic silicon cations [60] and their pyramidalizations are due to the same building principle as those at tricoordinate centers. This principle, "improvement of overlap by pyramidalization," was introduced by Haddon [61] for bridged annulenes, C_{60} and six-electron homoaromatics. However, it operates also in two-electron homoaromatics, more precisely, in π,σ-mixed aromatics. Even more general, this building principle governs all strong interactions of an electron deficient center with a two-electron donor bond [62–65]. All these pyramidalizations of a center refer to its three neighbors, which are connected classically, i.e., by 2c,2e bonds. Pyramidalization is caused by the additional nonclassical 3c,2e π,σ-mixed bond. If this is generated between centers which are not bound to each other by classical bonds, their coordination number is increased: to four of two centers of homoaromatics and bishomoaromatics, to five for bishomoaromatics. *Tricoordinate* in spite of additional *3c-2e bonding* do remain only those pyramidal centers, which are already connected by classical 2c-2e bonds to the two remaining centers of the 3c-2e bond. Thus, the additional bonding via the 3c,2e bond is responsible for pyramidalizations at centers which are all tricoordinate in the classical sense. Since this additional bonding is not π but π,σ-mixed, pyramidalization improves the overlap.

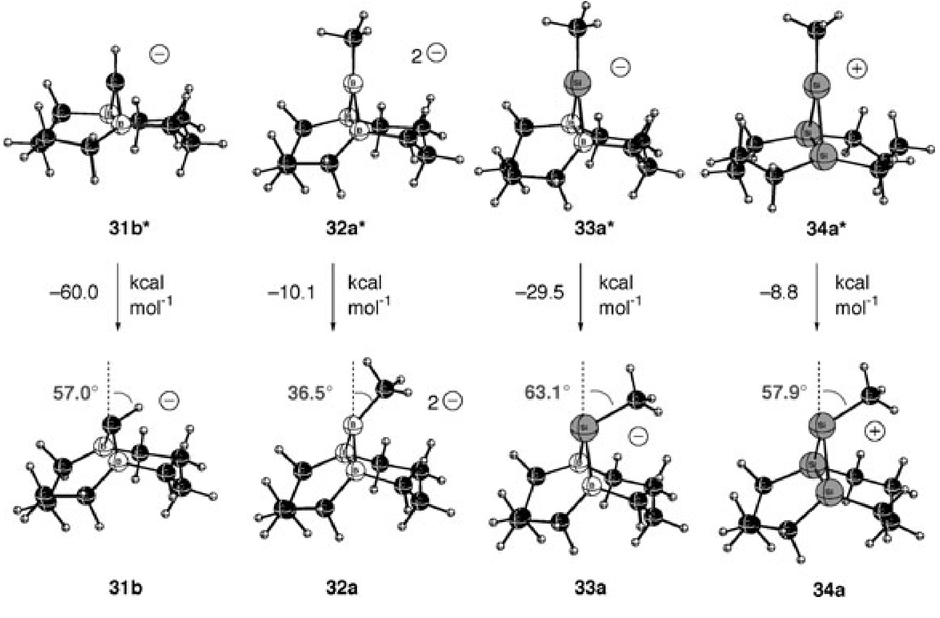
The remarkable increase of pyramidalization upon replacement of a boron by a silicon center (11° for **27** → **28**, 28° for **14u** → **29**) can also be explained by this building principle. Due to the considerably bigger (by 35 pm) covalent radius of silicon as compared to boron, the long distance of the silicon center from the remaining centers of the 3c,2e bond to be formed requires an especially strong tilt at the tricoordinate silicon center. Pyramidalization angles at tricoordinate silicon centers up to 63° presented in the next section can be explained on the same basis. In addition, the pyramidalization angles of centers of homoaromatics are in general bigger at silicon than at carbon, i.e., also for tetracoordinate (**26**: 40.4° at Si, 13.7° at C) as well as for pentacoordinate centers [60].

Aromatic Stabilization Energies of π,σ-Mixed Aromatics

The NICS patterns clearly show that silaborirane **23a** as well as germaborirane **23b** and stannaborirane **23c** are aromatics in the magnetic sense. However, the stabilization energies of **23a** and **23b** upon cyclic delocalization, 2.4 and 8.5 kcal mol^{-1}, respectively, are rather poor. Low aromatic stabilization energies of π-aromatics have been explained by unsymmetric delocalization due to different electronegativities



SCHEME 19 Cyclopropyl cations with a pyramidal tricoordinate carbon center as computed at the MINDO/3 (**30b**) and the B3LYP/6-311+G**//B3LYP/6-31G* level of theory (**30a**).



SCHEME 20 Pyramidalization at tricoordinate carbon, boron, and silicon centers induced by formation of π,σ-mixed aromatics and corresponding aromatic stabilization energies. The centers of the 2e-aromatics are B_2C (**31b**), B_3 (**32a**), B_2Si (**33a**), and Si_3 (**34a**).

of the centers of delocalization [21]. To find out, whether the same effects are operating in π,σ-mixed aromatics like **23a**, we started computations for a type of π,σ-mixed aromatics which was investigated only for carbon as centers of cyclic delocalization. May heteroatoms lead to new π,σ-mixed aromatics with large aromatic stabilization energies as shown before for bishomoaromatics [19]? Closely related to the electronic structure of **20u** is that of cation **30a** characterized by Olah et al. as early as 1977 using ^{13}C-NMR spectroscopy [66]. **30a** was described as "showing significant homoaromatic nature" and to be a "bent cyclopropyl cation" i.e., to contain a pyramidal-tricoordinate carbon atom. Computations for **30b** at the MINDO/3 level by Schleyer et al. revealed a pyramidalization angle at the tricoordinate carbon atom of 37° and a stabilization of 15 kcal mol^{-1} with respect to **30b*** with a planar tricoordinate carbon center [67].

Our own computations at the B3LYP/6-311+G**//B3LYP/6-31G* level showed **30a** with C_s-symmetry to be a transition state. In spite of its pyramidalization (29.4°), it has about the same energy as **30a*** with C_s-symmetry containing a planar-tricoordinate carbon center. The minimum **30a**(**C$_1$**) with a tricoordinate carbon center bent by 26.8° is stabilized by 7 kcal mol^{-1} with respect to **30a***(**C$_s$**) (see Scheme 19). Evidently, conformational effects are of the same order of magnitude as stabilization by π,σ-mixed aromaticity in **30a** with C_s-symmetry.

Increasing the strength of the 2e-donor by replacing the C—C bond of **30b** by the isoelectronic B—B bond carrying two negative charges, i.e., by a very strong donor, leads to **31b** with an extremely strong (57°) pyramidalization at the tricoordinate carbon atom. Even with a weak acceptor, the isoelectronic boron, a very strong pyramidalization (36.5°) results in **32a**. Remarkable pyramidalizations upon formation of π,σ-mixed aromatics like **31b** and **33a** can be accompanied by aromatic stabilization energies of not less than 60 and 29.5 kcal mol^{-1}, respectively (see Scheme 20). Charge separation in the classical isomers, as elucidated in the case of bishomoaromatics [19], explains the main part of these stabilization energies.

CONCLUSION AND OUTLOOK

The power of two-electron aromaticity is the key to understanding unusual structures of small rings containing boron atoms. $(\pi + \sigma)$-Double aromaticity is supported by enhanced NICS values, the now widely accepted measure of aromaticity. In contrast to π-, σ-, and $(\pi + \sigma)$-aromatics, π,σ-mixed aromatics show unsymmetric NICS patterns due to unsymmetric overlapping in the orbital of the cyclically delocalized electrons. This allows us to reveal that recently described sila-, germa-, and stannaboriranes are the first members of the class of π,σ-mixed aromatics which are not homoaromatics. The pyramidalization at their tricoordinate boron centers is shown to be another consequence of the general building principle "improvement of overlap by pyramidalization" introduced by Haddon in 1988. Combining a strong two-electron donor with a strong acceptor in a geometry which allows the formation of a three-center-two-electron bond leads to new π,σ-mixed aromatics with remarkable big aromatic stabilization energies and pyramidalizations at tricoordinate boron, carbon, and silicon centers. To experimentally verify their derivatives as well as of a double aromatic containing a planar-tetracoordinate carbon atom not coordinated to metal centers is a challenge to synthetic chemists.

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