Myriad Planar Hexacoordinate Carbon Molecules Inviting Synthesis

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Molecules with planar hexacoordinate carbons (phC) are exciting prospects. They violate both the usual maximum tetracoordination of carbon and its proclivity for three-dimensional bonding. Two independent research groups discovered phC examples computationally in 2000. Exner and Schleyer's CB_6^{2-} (Figure 1, **1**) and the isoelectronic C_3B_4 isomers (e.g., **2**) have six aromatic π electrons.[1] Minyaev and Gribanova proposed heteroatomic extensions of **1** with eight-membered ring perimeters (Figure 1, **3**, X = NH and O).[2] We confirm these to be minima, despite having eight, rather than six π electrons (see Figure 14S for the π MO's of **3a**).

In contrast to this limited number of phC's, Wang and Schleyer predicted numerous molecules with planar pentacoordinate carbons (ppC) in 2001. They showed how ppC chemistry might offer unlimited possibilities for generalization and experimental realization.[3] Appropriate ppC structural units can be grafted onto virtually any arene or unsaturated ring having three adjacent CH groups. Likewise, generally applicable construction principles allow the incorporation of phC structural units, based on simple elaborations of **1** and **3**. The preparation of numerous planar tetracoordinate carbon compounds following theoretical predictions[4] offers hope for the realization of phC's.

Akin to principles devised for ppC's,[3] building block strategies facilitate the design of numerous molecules with phC's. The initial idea was based on the finding that C_{2v} $CH_2B_6^{2-}$ (**4**), the 1,2-dihydro derivative of **1**, retains the phC despite its ruptured BB ring bond[3] (albeit with somewhat elongated CB bond lengths). As in the design of ppC molecules,[3] the opened edge of **4** can be bridged and the ring closed by appropriate atoms and groups. The selection of phC examples in Figure 2 retains the planar hexacoordinate carbon CB_6 unit. Like **3**, more than one bridge is possible. Consequently, phC's can be grafted onto myriad systems.

The planar hypercoordinate bonding principles for phCs, like those for ppC's,[3] are general and are easily extended to other combinations of atoms, with elements other than carbon in the centers.[2] Thus, Minkin et al. computed examples of planar hexacoordinate boron species in 2001,[5] and the boron analogue of **4**, C_{2v} $H_2B_7^-$ (**S-4a**, see Figure 5S), was reported recently by Boldyrev and co-workers.[6] As in earlier studies of planar hypercoordination,[1,4] we focus here on carbon as the central element since violations of the conventional tetrahedral tetracoordinate bonding of carbon seem more unusual. While all our new phC molecules are local minima,[7] their isomers (e.g., with boron in the center and carbon on the outside) can be lower in energy. However, such species are no less interesting inherently and illustrate the generality of the bonding principles.

The two hydrogens in **4** provide substitution sites. Ring closure, for example, by replacing both the H's, as well as the two negative
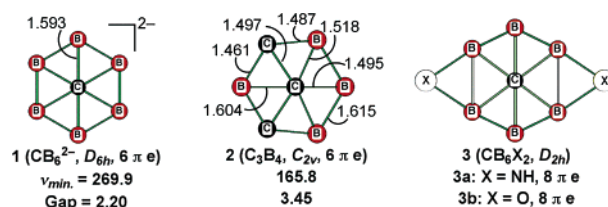
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Figure 1. Previously reported phC minima.[1] Bond lengths in Å, the lowest frequency (v_{min}) in cm^{-1}, HOMO−LUMO energy separation (Gap) in eV. See Supporting Information Figure 5S for the geometries of **3a** and **3b**.
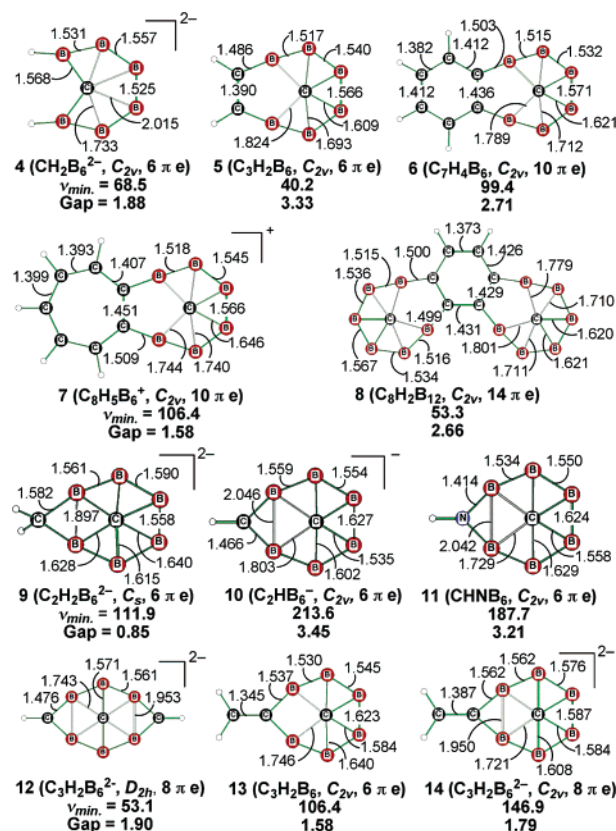

Figure 2. Examples of phC minima optimized at B3LYP/6-311+G**. Bond distances are shown in Å, the lowest frequency (v_{min}) in cm^{-1}, HOMO−LUMO energy separation (Gap) in eV.

charges, of **4** with a CH=CH bridge, results in the neutral six π electron $C_3H_2B_6$ (**5**). The appreciable vertical ionization potentials (VIP) of **5** and other neutral species imply stability (Table 1S). The six Wiberg bond indices (WBI) to the central carbon in **5**, ranging from 0.46 to 0.80, document the hexacoordination to the B_6 ring. The total WBI (3.86) of the central carbon does not violate octet rule expectations. Exchanging the central carbon with the three

unique borons resulted in isomers (with hexacoordinate borons in the center and carbons in the perimeter) ranging between 18.5 and 30.8 kcal/mol lower in energy (see Figure 4S). However, a Born−Oppenheimer molecular dynamics simulation[8] (BOMD, Figure 3S for the trajectory), using the deMon 2004 program,[9] demonstrates the viability of **5** as a local minimum and its resistance toward isomerization. Searches only located high-energy transition states for isomerization.

Benzannulation of **5** gives **6**, the 10 π electron analogue of naphthalene. Similarly, the replacement of vicinal hydrogens in benzene and essentially all arenes by a CB_6 group (i.e., **4** without its H's) can yield new phC candidates. The tropylium ion derivative, $C_8H_5B_6^+$ (**7**), exemplifies other bicyclic systems. The tricyclic minimum, C_{2v} $C_8H_2B_{12}$ (**8**), has two CB_6 units, each with a phC, grafted *meta* onto benzene.

Elaborations of **4** with single-atom bridges result in phC minima with seven-membered ring perimeters. For example, a methylene group can replace the two H's in **4** and bridge the CB_6^{2-} unit to give C_s $C_2H_2B_6^{2-}$ (**9**). While the methylene carbon in **9** deviates slightly from the CB_6 plane, the planarity of the CB_6 moiety is nearly exact. Replacing the two H's in **4** with CH^- results in C_{2v} $C_2HB_6^-$ (**10**); planarity is retained. Heteroatomic bridging groups such as NH can result in favorable neutral phC minima, such as $CHNB_6$ (**11**).

The phC units in **4−11** have $4n + 2$ π electrons. Their aromaticity is demonstrated by refined nucleus-independent chemical shift (NICS) indices, such as the perpendicular tensor components, 1 Å above the central carbons (NICS(1)$_{\pi zz}$).[13] The NICS(1)$_{zz}$ grid of **5** and the large negative value (−45.0) above the ring center indicate the presence of a strong induced diatropic ring current, with a shielding zone inside and a deshielding zone outside (see Figure 7S). Dissection of NICS(1)$_{zz}$ shows that the shielding tensor contributions from the π MO and from the in-plane radial σ MO sets are both diatropic (NICS(1)$_{\pi zz}$ = −18.5; NICS(1)$_{radialzz}$ = −14.3. See Supporting Information Figure 10S and Table 1S for NICS(1) and dissected NICS(1) results). Schleyer et al. coined the term "doubly aromatic"[10] for such situations. The NICS(1)$_{zz}$ results for **5** indicate that both π and radial MO's help to achieve the planar geometry with a phC. Planar hypercoordination may benefit even more from σ MO stabilization than from the π MO system. **S-4a**,[6] with only four π electrons, also illustrates this point.

Two-fold bridging of **1** on opposite edges results in an eight-membered ring perimeter exemplified by Minyaev's phC molecules, **3** (X = NH and O), which have eight π electrons (see Figure 15S). The isoelectronic **12** (i.e., D_{2h} $C_3H_2B_6^{2-}$ where X = CH^- in **3**) also has eight π electrons, but two of these (in HOMO-1) are nonbonding due to remoteness of the CH units; the remaining six π electrons are delocalized in the central CB_6 moiety (see Figure 11S; neutral D_{2h} $C_3H_2B_6$ is a triplet).

Replacing two H's in **4** with an exocyclic C=CH_2 results in C_{2v} $C_3H_2B_6$ (**13**), a phC minimum. Although **13** has a total of six π electrons, two of these are localized as a C=C π bond (HOMO-4; see Figure 10S). Four π electrons remain for the CB_6 moiety, and a +66.2 paratropic NICS(1)$_{zz}$ value for **13** results. The C_{2v} $C_3H_2B_6^{2-}$ dianion (**14**), with six of the eight π electrons on the CB_6 unit, results in a −53.4 diatropic NICS(1)$_{zz}$ value, thus **14** may be more viable than **13**. Double C=CH_2 bridging gives the eight π electron phC minimum, D_{2h} $C_5H_4B_6$ (**S-15**; see Figure 5S for details). However, akin to **13**, **S-15** has four π electrons localized on exocyclic C=C bonds (HOMO-3 and HOMO-5; see Figure 14S); only four π electrons remain on the CB_6 unit. As expected, the 10 π electron dianion D_{2h} $C_5H_4B_6^{2-}$ (**S-16**; see Figures 5S and 15S) has six π electrons on the CB_6 unit and a diatropic NICS(1)$_{zz}$

(−55.8). Molecules like **3** (X = NH and O), **12**, and **14** demonstrate that the total π electron count is less important than the number of π electrons associated with the phC moiety. Evidently, delocalized bonding of the σ system is needed to achieve planar hypercoordination.

CB_6 units with planar hexacoordinate carbons (or borons) can be grafted onto olefins, arenes, or saturated carbon systems. Most of these new phC candidates are doubly aromatic with delocalized σ as well as π systems, but a total of $4n + 2$ π electrons is not required. All these phC derivatives provide additional examples of deltahedral bonding involving carbon and offer many opportunities for experimental realization.

Supporting Information Available: Optimized geometries of phC and selected isomers, NICS$_{zz}$ grids of **5**, CMO−NICS$_{zz}$ of selected molecules, MO figures, MD trajectory of **5**, a summary of NICS(1)$_{zz}$, and dissected NICS(1)$_{zz}$ results and Gaussian archive files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) All the phC's, optimized with Gaussian 03 (see ref 11) at the B3LYP/6-311+G** DFT level, were minima, and their wavefunctions were stable. Magnetic shieldings—a good measure of aromaticity or antiaromaticity—were evaluated by nucleus-independent chemical shift methods (NICS, see ref 12). In particular, out-of-plane (*zz*) tensor component contribution from individual canonical molecular orbitals to NICS (CMO−NICS; see ref 13) computed using the NBO 5.0g program (ref 14) at the GIAO/PW91PW91/6-311G* level was used to analyze the behavior of the radial and π MO's.

(8) BOMD was carried out on **5** for 10 ps after 2 ps of equilibration with the interval of 0.5 fs at 300 K at the PBE/DZVP/Gen-A2* level.

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