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A New Strategy To Achieve Perfectly Planar Carbon Tetracoordination

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Nearly a century transpired before the concept that tetracoordinate carbon adopts tetrahedral arrangements[1] was challenged. The 1970 Hoffmann, Alder, Wilcox[2] analysis and the 1976 ab initio computational survey of the Schleyer−Pople group[3] showed how the seemingly prohibitive strain energy of planar tetracoordinate carbon (ptC) arrangements (~130 kcal/mol for D_{4h} vs T_d methane)[4] could be overcome. Two strategies, “electronic” and “mechanical,” generally are combined to achieve compounds with a ptC.[5] The “mechanical” approach constrains the putative ptC structurally, for example, by incorporation into three- or four-membered rings with their smaller CCC bond angles. By further constricting a ptC in an “alkaplane” cage,[5c,6] Rassmussen and Radom recently computed the first (and only) successful example, dimethanospiro[2,2]octaplane, based solely on this approach.[5c,7] This achievement is remarkable, since the many other alkaplanes studied, for example, octaplane (**1**, Figure 1), do not achieve the goal of having “perfect” ptC’s.[5c]

The alternative, “electronic” strategy, based on Hoffmann’s qualitative analysis of the electronic structure of planar methane,[2,3] has been applied more widely.[5] The D_{4h} CH_4 HOMO, p-orbital lone pair on the ptC, can be stabilized by π acceptor substituents or by aromatic delocalization. In addition, the electron-deficient in-plane bonding can benefit from σ donation by electropositive groups. Many ptC compounds, designed using such “electronic” approaches, have now been characterized theoretically and experimentally.[5] It is important in the present context to note that CH_4^{2+}, the simplest ptC molecule, prefers to be planar because the perpendicular carbon p-orbital is vacant. As in CH_3^+, the six valence electrons in CH_4^{2+} bind best in planar, sp^2 hybridization.[8]

We now report the computational discovery of a novel family of ptC molecules, the “boraplanes,” which utilize basically new electronic structural features, unprecedented in *neutral* molecules, to help planarize the central carbon coordination in derivatives of Radom’s alkaplanes.[5c,6] As in CH_4^{2+}, the perpendicular carbon p-orbitals in this new set are vacant, rather than occupied. Thus, when four boron atoms replace the four central CH groups in octaplane (**1**, S_4),[6] a minimum with a “perfect” ptC arrangement (**2**, D_{4h}, see Figure 1) results. This finding is remarkable, since, contrary to the coplanar sustituent orientations shown to be best earlier,[3] the conformations of the boron units in **2** are *perpendicular*. Moreover, neither the cage nor the new electronic effects, taken separately, suffice to result in ptC’s. Neither octaplane (**1**) nor $C(BH_2)_4$, in perpendicular (D_{4h} (**3**) or C_{2v} (**4**)) symmetries, have ptC energy minima.

Using GAUSSIAN 98,[9] structures were optimized and characterized by frequency computations and wave function stability checks at B3LYP/6-31G* initially, and then refined at B3LYP/6-311+G**. The latter results will be discussed, unless stated otherwise. For comparison, some of Radom’s HF/6-31G* alkaplane geometries[5c,7] were recomputed at B3LYP/6-31G*.

The structure of **2** is compared with **1** (the S_4 octaplane minimum) in Figure 1. The perfect ptC D_{4h} equilibrium structure of **2** was confirmed by frequency analysis (the smallest real value is 119.7 cm^{-1}). In contrast, the C_{4h} octaplane structure (related to **1**, but with a ptC) is a saddle point with one imaginary frequency. The S_4 equilibrium geometry (**1**) is 19.0 kcal/mol (B3LYP/6-31G*) more stable and has central dihedral angles of 169.7° rather than 180.0°.

The perfect ptC arrangement in **2** results from its unusual bonding, which does not correspond to either of the two known types of electronic structures for the ground states of planar isoelectronic XH_4 ($X = B^-$, C, N^+, Al^-, Si, and P^+) molecules.[10] The species with more electronegative central atoms and shorter XH bond lengths, that is, X = C and N^+, have a_{2u} (π) HOMOs dominated by the occupied p-orbital of the central atoms, and a b_{1g} (δ) LUMO, combining the four hydrogen s orbitals in “delta” symmetry. This HOMO−LUMO order is reversed when the central atoms are more electropositive and have larger hydrogen separations, that is, when $X = B^-$, Al^-, Si, and P^+. For D_{4h} CH_4, the π state (rCH = 1.090 Å) is 111.7 kcal/mol more stable than the δ state (B3LYP/6-311+G**). In the later, the hydrogen repulsion due to the occupation of the b_{1g} HOMO, which is responsible for this large energy difference, also is evident in the elongated CH distance, 1.265 Å. Note that CH_4^{2+}, the simplest ptC molecule, prefers to be planar because **BOTH** this unfavorable δ orbital and the perpendicular carbon p-orbital are vacant.

The same is true in **2** and in the simple model, $C(BH_2)_4$ (**3**, D_{4h}), with *perpendicular* BH_2 groups, although both are neutral species and have two more valence electrons to accommodate! The equatorial C−B distances, 1.480 Å in **2** and 1.510 Å in **3**, are unexpectedly short (cf. the normal C−B single length,1.554 Å in CH_3-BH_2). This shows that both **2** and **3** do not utilize δ-type MOs. But if both also have formally *vacant* p-orbitals on the central carbons (see the **2** LUMO in Figure 2), where are the “missing” electron pairs? These reside in a “perimeter” multicenter HOMO, as shown for **2** in Figure 2.[11]

The perpendicular arrangements at the boron groups in **2** and in **3** result in a favorable combination of their in-plane B p orbitals. The relatively short CB bond lengths result in B••B separations of only ~2.1 Å in **2** and **3** and permit substantial overlap (the Wiberg BB bond indexes are ~0.3). The accommodation of two electrons in the resulting 4c-2e BBBB bonding MO is energetically more favorable than in the nonbonding carbon p(π) MO.

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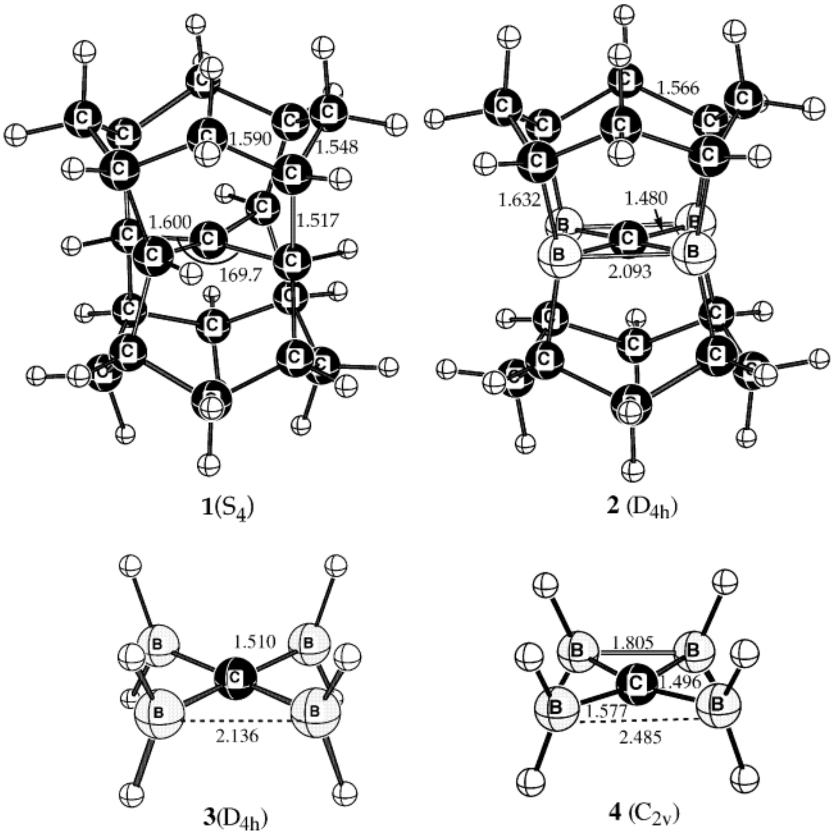

1(S_4) **2** (D_{4h}) **3**(D_{4h}) **4** (C_{2v})

Figure 1. B3LYP/6-311+G** structures of **1**, **2**, **3**, and **4**.

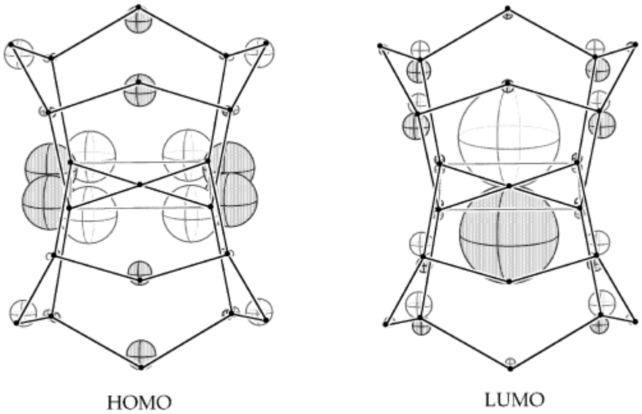

Figure 2. HOMO (left) and LUMO (right) of **2**.

While **2** and **3**, like CH_4^{2+}, have formally vacant p(π)-orbitals on the central carbons (see Figure 2), hyperconjugation provides stabilization. This results in lengthening of the eight axial C−B bonds (1.635 Å) in **2** as well as a significant carbon p(π)-orbital electron occupancy (∼0.60 in **2** and **3**).

Despite such favorable features, **3** is a third-order saddle point (NIMAG = 3) but is 34.3 kcal/mol stable than the planar D_{4h} conformer considered earlier[3,5a] (which stabilizes a ptC with a filled rather than an empty p-orbital). Like CH_4^{2+} and planar CH_4, $C(BH_2)_4$ with perpendicular BH_2 groups prefers C_{2v} (**4**) over D_{4h} (**3**) symmetry (but only by 0.83 kcal/mol). While having an electronic structure similar to **3**, **4** is only a first-order saddle point (the vectors of the imaginary frequency lead to an approximately "tetrahedral" geometry, only 38.3 kcal/mol more stable than **3** (compared with 122 kcal/mol[4] for planar C_{2v} vs T_d methane).[4] These facts emphasize the importance of the cage effect in achieving the perfect D_{4h} ptC arrangement in **2.** The four-fold symmetry preference of the caps not only forces the boron moieties into perpendicular geometries but also prevents distortion into C_{2v} symmetry.[12]

In summary, we have foreseen a new family of planar tetracoordinate carbon compounds combining an unprecedented "electronic" with "mechanical" stabilization strategies. Although based on alkaplanes, the electronic structures of these boraplanes are quite different, and possess a vacant, rather than a filled p-orbital on the planar tetracoordinate carbon. The cage effect, augmented by in-plane BB bonding and hyperconjugation, is needed to complete the perfect ptC arrangements. As we will show in subsequent papers, planar tetracoodination involving other elements can be achieved using similar strategies.

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Supporting Information Available: Figure 3: B3LYP/6-311+G** structure of **5** and its HOMO; the B3LYP/6-311+G** Cartesian coordinates of 2 and 5 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) When lower symmetry caps are present, the $C(B)_4$ moiety does adopt a C_{2v} configuration. This is found when the eight-membered ring caps in **3** are replaced by cyclopentane, cyclohexane, cycloheptane, and bicyclic moieties (e.g., as explored in Radom's alkaplane studies).[6] All of these "boraplanes" have perfectly planar tetracoordinate carbons. An example, (**5**) with cyclopentane caps, is shown in Figure 3 (see Supporting Information). Instead of the 4c-2e BBBB multicenter bond in **2** (Figure 2), the HOMO of **5** is better described as having a three-membered ring with a rather localized B−B bond. However, the in-plane exocyclic boron p orbitals stabilize the adjacent CB bonds hyperconjugatively.