

The Theoretical Design of Neutral Planar Tetracoordinate Carbon Molecules with C(C)₄ Substructures

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Received April 15, 2002

Abstract: Using a new charge-compensation strategy, we designed neutral molecules with perfectly planar C(C)₄-type tetracoordinate carbon arrangements (ptC) employing DFT computations. These designs, based on the planar preference of methane dications, replace two remote carbons in spiroalkaplanes by borons or two remote hydrogens by BH₃ groups; the two formally anionic boron units which result compensate the formal double positive charge on the central ptC's. The LUMOs correspond to the "wasted" lone pair HOMOs of the alkaplanes. As compared to the latter, π occupancies on the central carbon are much smaller (less than 0.7e), and the IPs are much larger. The newly predicted compounds utilize all of the electrons more effectively. There are no lone pairs, and the ptC–C bond lengths are ca. 1.50 Å. The Wiberg bond index sums of the ptC's are near 3.2, and the boron sums are close to 4.

1. Introduction

Since the stimulating suggestions of Hoffmann, Alder, and Wilcox (HAW)¹ in 1970, the computational design and experimental realization of molecules with planar tetracoordinate carbons (ptC) have made notable progress.^{2,3} Most of the successful examples involve boron^{2a,4,5} or metal^{2c–e,4,6} substituents. The achievement of C(C)₄-type ptC arrangements, where the central carbon is surrounded by four carbon-based groups, is more challenging. In 1999, Keese et al.⁷ stated that "despite considerable computational efforts, no structures with a planar-tetracoordinate C(C)₄ have been found."

The electronic structure of planar methane (that is, a p- π lone pair HOMO and σ electron-deficient C–H bonds) led HAW and later Keese et al.⁸ to propose an "electronic" strategy^{2,4} to delocalize the π lone pair by incorporating ptC's into aromatic

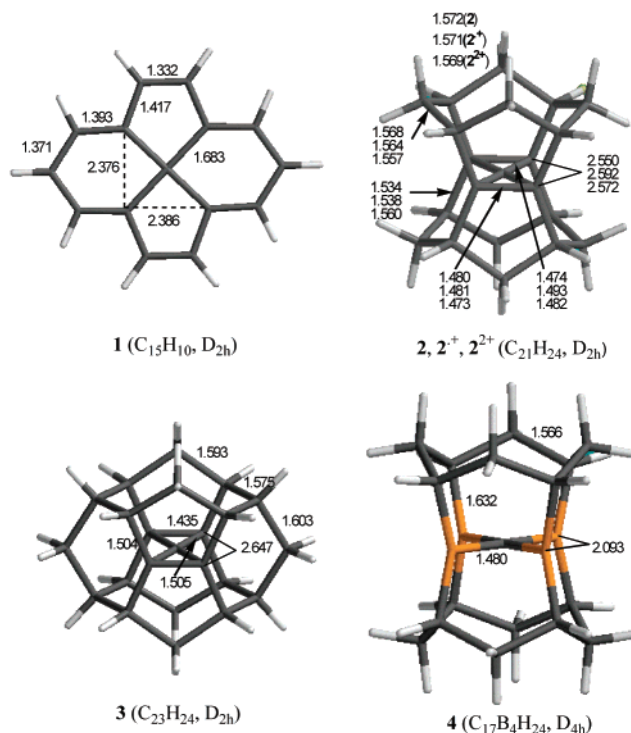


Figure 1. B3LYP/6-31G* geometries of **1** and **2** and B3LYP/6-311+G** geometries of **2**⁺–**4**.

annulene perimeters (for example, **1** in Figure 1). However, both computed⁹ and synthetic examples¹⁰ showed that such central carbon arrangements are far from being planar. The same has been true, until recently, of the results of "mechanical" strategies

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Table 1. Smallest Imaginary or Real Frequencies Freq (in cm^{-1}); π Occupation of ptC's; Wiberg Bond Indexes of ptC (WBI_{ptC}) Bonds and the Totals at Boron (WBI_{B}); NBO Charges on ptC (Q_{ptC}); Koopmans' Ionization Potentials (IP); and the Energy Difference between Singlet and Triplet ($\Delta E(\text{S-T})^c$)

		Freq ^a	π	WBI_{ptC}	WBI_{B}	Q_{ptC}	IP	$\Delta E(\text{S-T})^c$
1	D_{2h}	592i	1.24	0.90		-0.32	5.1	
2	D_{2h}	529i	1.68	0.72		-0.51	2.8	34.3
2⁺	D_{2h}	187	1.04	0.74		-0.01	9.1	
2²⁺	D_{2h}	174	0.50	0.80		0.35	15.4	50.3
3	D_{2h}	298i	1.68	0.71		-0.48	2.8	34.3
4	D_{4h}	119	0.59	0.68	3.2	-0.70	4.5	11.1
5	C_{2h}	147	0.52	0.78	3.7	0.34	6.3	25.2
6	D_{2h}	233	0.59	0.78	3.6	0.30	6.3	24.4
7	C_{2h}	106	0.68	0.80	3.8	0.23	6.3	22.1
7a^b	C_{2h}	63	0.58	0.80	2.9	0.18	6.4	8.1
8	C_{2h}	77	0.59	0.77	3.9	0.31	6.3	13.1
9	C_{2h}	236	0.48	0.79	3.7	0.23	6.5	16.6
10	C_{2h}	145	0.60	0.80	3.8	0.31	6.3	29.2
11	C_{2h}	228	0.53	0.80	3.7	0.32	6.2	23.6
12	C_{2h}	119	0.64	0.81	3.8	0.31	6.1	14.8

^a At B3LYP/6-31G*. ^b Like **7**, but with AlH_3 in place of BH_3 groups. ^c Vertical energy difference at the singlet geometry.

(employing strain in nonaromatic hydrocarbons to hold the valences in place).^{10,11}

Radom et al.^{2b,12,13} designed a family of alkaplane molecules (for example, spirooctaplane, **2**) which incarcerate the ptC candidate in hydrocarbon cages. Although approaching a planar $\text{C}(\text{C})_4$ -type ptC more closely than ever before, such “mechanical” designs without “electronic” assistance must struggle hard to overcome the enormous strain of a ptC with a p - π lone pair HOMO.¹⁴ More buttresses were needed to achieve planarity (for example, in **3**).¹³ As Radom et al. noted, **3** is a minimum at MP2 but not quite at the B3LYP/6-311+G(3df,2p) level. (At B3LYP/6-31G*, **3** has a 279i cm^{-1} imaginary frequency, Table 1). The lone pair HOMO of **3** is shown in Figure 2.

The ptC lone pair is absent in the “electronically assisted” alkaplans we describe here (see **4** and **6** in Figure 2). Our computationally designed family with perfectly planar $\text{C}(\text{C})_4$ -type ptC arrangements is achieved by an unconventional “charge-compensation” strategy¹⁵ that has considerable potential in other applications.

2. Computational Methods

Using Gaussian 98,¹⁶ we optimized and characterized structures by frequency computations at B3LYP/6-31G* initially, and then refined

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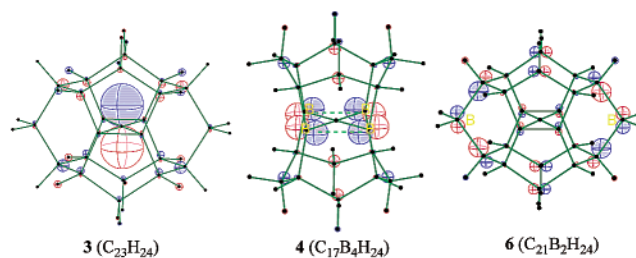


Figure 2. B3LYP/6-311+G** geometries of **5**–**12**.

them at B3LYP/6-311+G**. The latter results will be discussed, unless stated otherwise. The B3LYP/6-311+G** structures with key geometrical parameters are displayed in Figures 1, 3, and 4, and the Cartesian coordinates and energies are given in the Supporting Information.

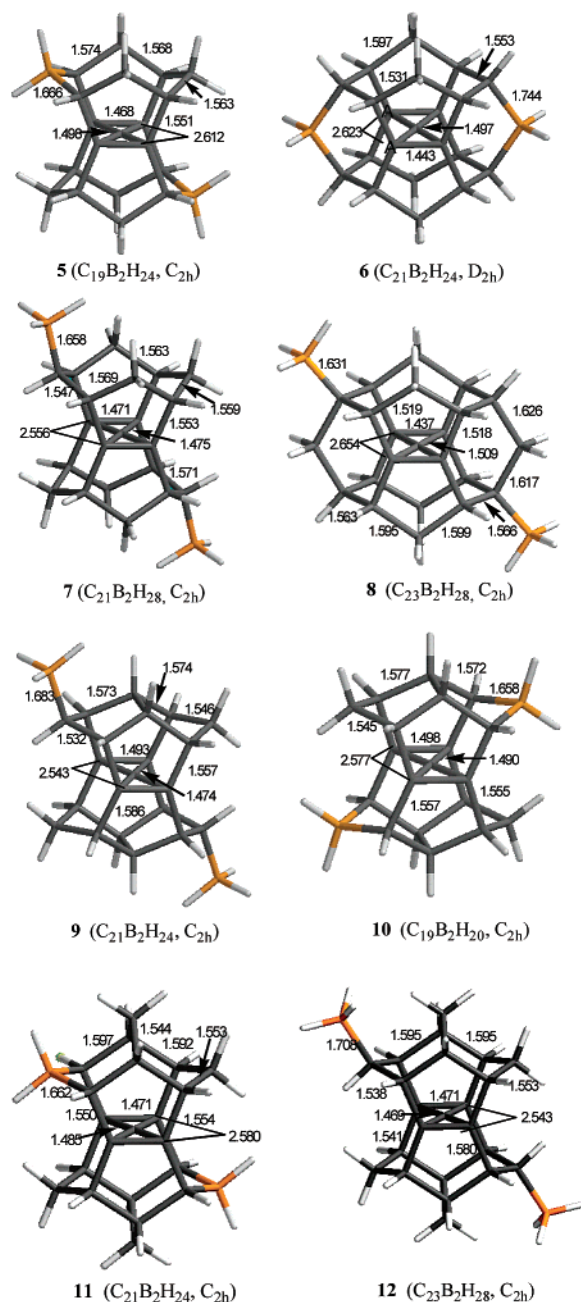
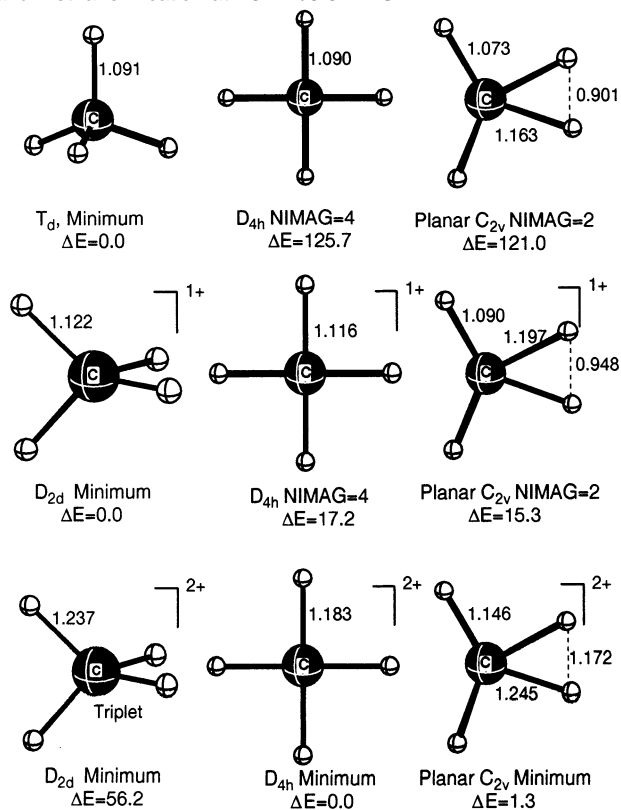


Figure 3. Comparison of HOMOs of **3**, **4**, and **6**.

Scheme 1. Energy Differences (ΔE in kcal/mol) between Planar and Tetrahedral Structures of Methane, Methane Radical Cation, and Methane Dication at B3LYP/6-311+G** + ZPE^a



^a NIMAG gives the number of imaginary frequencies.

3. Results and Discussion

Removal of the destabilizing ptC lone pair electrons planarizes the central carbon arrangement. As shown in Scheme 1, the planar methane dication is a minimum,¹⁷ and the planar methane radical cation is only modestly less stable than its tetrahedral alternatives.¹⁸ Like Radom et al.'s¹⁹ result on the octaplane radical cation, we find that the spirooctaplane radical cation, 2^{+} , with only a single p electron in its HOMO, has a planar ptC. Likewise, the spirooctaplane dication, 2^{2+} , also is a minimum in D_{2h} symmetry (Table 1); the p- π orbital on the central carbon is now the LUMO rather than the HOMO. On the basis of a similar design, we achieved ptC arrangements recently in a family of neutral compounds, the boraplanes²⁰ (for example, **4**; the borons are shown in orange in **4**–**12**). Instead of a ptC lone pair, the HOMO is a 4c-2e BBBB σ MO (Figure 2). Although 2^{2+} and **4** utilize the same basic principle to achieve their ptC arrangements, these compounds are not isoelectronic: 2^{2+} has two more electrons than **4**. This extra pair of electrons goes into one of a pair of degenerate orbitals, and 2^{2+} distorts from D_{4h} to D_{2h} symmetry. Therefore, there are two perimeter 2c-2e C–C bonds at the equator of 2^{2+} , whereas there is only one pair of electrons for the 4c-2e bonding of the central BBBB perimeter in **4**.

While **4** has a perfect ptC, it is not of the $C(C)_4$ -type; 2^{+} and 2^{2+} do have perfect $C(C)_4$ -type ptC's but are not neutral. Our goal, a perfect $C(C)_4$ ptC in neutral molecules, can be realized by simply replacing two carbons *remote from the central position* of **2** by borons (Figure 3). As illustrated by **5** (C_{2h}) which has the requisite symmetry for perfect ptC planarity, the two new formal BH₂ anion groups compensate the formal double positive charge on the ptC. Indeed, **5** is a minimum at B3LYP/6-31G*; the smallest frequency is 146.7 cm⁻¹ (Table 1). Compound **6** shows that the BH₂ groups also can function as tetracoordinated bridges. Furthermore, many types of pendant anionic groups can achieve the charge compensation; this is illustrated here most simply by the BH₃ substituents in **7** and **8**, as well as the AlH₃'s in **7a** (not shown, but like **7**; see Table 1).²¹ Compounds **9**–**12** illustrate that other placements also achieve the desired goal. The usual p- π lone pairs on ptC's are accommodated instead by the four adjacent boron atoms in the boraplanes (for example, **4**); the HOMOs involve multicenter 4c-2e BBBB bonding. The same principle is utilized, but the HOMOs of **5**–**12** involve BC bonds (for example, in **5**) and BH bonds (for example, in **7**). Despite the different types of HOMOs, all LUMOs correspond to the lone pair HOMOs of the alkylanes. As an illustration, Figure 2 compares the HOMOs of **3**, **4**, and **6**. As described above for **4** (relative to 2^{2+}), the one extra electron pair of **5**–**12** results in two central 2c-2e C–C bonds. (Note that there is only one electron pair for the equatorial 4c-2e BBBB bonds in the boraplanes, for example, **4**.) The charge-compensation principle we employ here to achieve ptC arrangements also differs from that in metal-containing ptC complexes where the ptC carbon is sp²-hybridized and the electronic interactions between the metal(s) and the central carbon stabilize the ptC arrangements.^{2c–e,4,6}

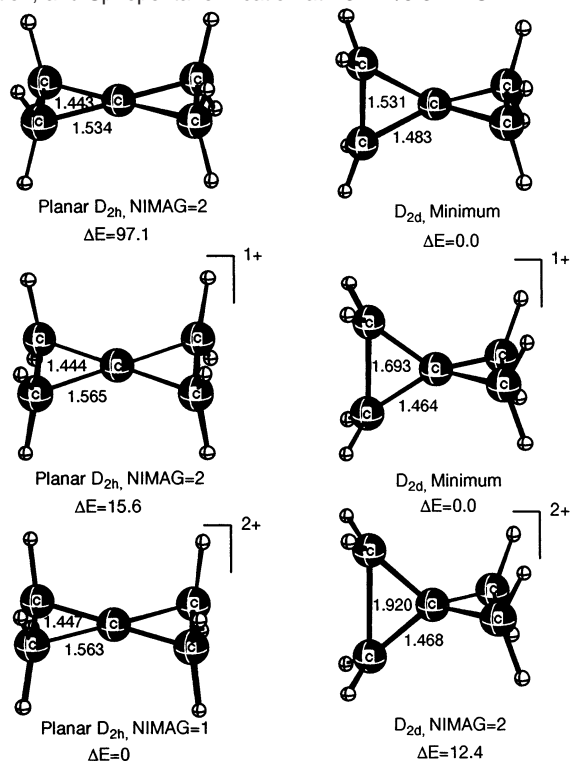
Compounds **2**, **3**, and **5**–**12** all contain a common, formally dicationic $C(C)_4$ planar spiro-pentane substructure. Note that the planar D_{2h} form of the parent, neutral spiro-pentane, is 97.1 kcal/mol less stable than the normal “tetrahedral” D_{2d} structure (Scheme 2). The removal of two electrons from spiro-pentane results in a planar D_{2h} structure, which is 12.0 kcal/mol more stable than the D_{2d} form. However, the planar spiro-pentane dication also has a $C(C)_4$ substructure like **5**–**12**, but it is a first-order saddle point. This shows that the additional cage effect is needed to achieve the ptC arrangement.

The NBO²² π occupancies on all of the central carbons of **4**–**12** (Table 1) are small and are comparable to the value (0.5) of dication 2^{2+} . These nonzero occupancies are due to hyperconjugation between the formally vacant central carbon p orbitals and the eight adjacent perpendicular C–C bonds. In contrast, the π occupancies are 1.68e in both **2** and **3** and 1.04e in radical cation 2^{+} . While the C–C_{ptc}(ptC) Wiberg bond indexes (all around 0.8) are less than that in ethane (1.04), the C–C_{ptc} bond lengths (ca. 1.49 Å) are actually slightly shorter than those of normal single C–C bonds (for example, 1.53 Å in ethane). The borons in **4**–**12** have Wiberg bond index totals close to 4. This demonstrates that these boron groups, in effect, attract electrons from the central ptC carbons of **2** and **3**. The

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Scheme 2. Energy Differences (ΔE in kcal/mol) between Planar and Tetrahedral Structures of Spiropentane, Spiropentane Radical Cation, and Spiropentane Dication at B3LYP/6-311+G** + ZPE^a



^a NIMAG gives the number of imaginary frequencies.

2.93 total Wiberg bond index for aluminum in **7a** reflects the partially ionic bonding.

The unfavorable electronic structures of the alkplanes also are responsible for their exceptionally low Koopmans' ionization potentials (IP), for example, 2.8 eV for both **2** and **3**.¹³ The larger IPs (6.1–6.3 eV) of **5–12** resemble those of benzene (6.7 eV), naphthalene (5.8 eV), and azulene (5.2 eV). As shown by the $\Delta E(S-T)$ in Table 1, all of the singlets are more stable than the corresponding triplets.

As indicated in Scheme 2, the removal of one electron from spiropentane is not enough to planarize spiropentane. Yet **2⁺** has a perfect ptC arrangement due to the cage effect. This indicates that the unfavorable LUMO can be singly occupied without losing the ptC arrangement. Figure 4 shows that this also is true for the present systems. At B3LYP/6-31G*, the smallest frequencies of **5^{•-}** and **7^{•-}** are 159.0 and 112.0 cm^{-1} , respectively.

Our new ptC stabilization strategy results in charge delocalization, but not of the conventional type. The positive charges on the central carbons of **5–12** (Table 1) and the similar negative charges on the boron groups are much less than the formal +2 (ptC) and -1 (boronate) charges of the conceptual model. Note that the charge on the central carbon in dication **2²⁺** is only +0.35. In contrast, the charges on the central carbons of **1–3** are negative.

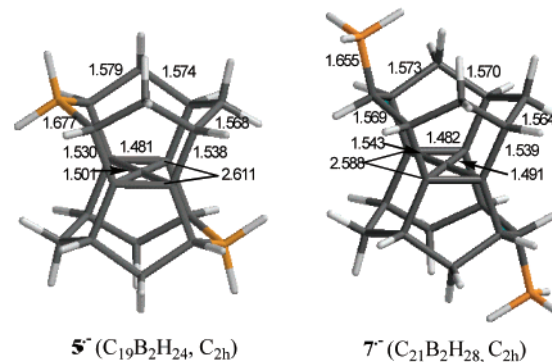


Figure 4. B3LYP/6-311+G** structures of the radical anions of **5^{•-}** and **7^{•-}**.

We also were interested in the bond shifting processes in the equatorial perimeter, and we studied **2²⁺** as an example. Although we failed to locate a transition state for the bond shifting, the barrier appears to be very high because of the large difference in the initial CC distances in the perimeter. This differs from the situation in cyclobutadiene.

4. Conclusions

We have employed a charge-compensation strategy to design a family of neutral molecules with C(C)₄-type planar tetracoordinate carbons. In the alkplanes, for example, **2** and **3**, the lone pair electrons on the central carbons are “wasted” in nonbonding HOMOs. As in the boraplanes (for example, **4**), the ptC p- π orbitals are the LUMOs in the present charge-compensated compounds (**5–12**) (see Figure 1). The “missing” electrons are utilized effectively for bonding. In contrast to the alkplanes, these new species have unambiguous, perfectly planar tetracoordinate C(C)₄ minima, positively charged ptC's with much lower p- π occupancies, and much larger Koopmans' ionization potentials. Although **5–12** can be considered to be zwitterions, none of the atoms have large positive or negative charges. The charges are “spread out” over the whole molecule. Consequently, in conceiving ptC candidates, it is more fruitful to base designs on the inherently planar methane dication as the parent, rather than on methane itself.

In subsequent papers, we will apply the charge-compensation strategy to the solution of a wide range of structural problems.

Acknowledgment. This paper is dedicated to Professor Walter Siebert on the occasion of his 65th birthday. We thank the University of Georgia for financial support.

Supporting Information Available: B3LYP/6-311+G** geometries (in the form of Gaussian archive entries) of **1–12** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0265310