Thus, if one views the bond formation in two steps, (1) creation of valence-state atoms then (2) bond formation, the accumulation of density in the bond due to (2) is quite large even for F_2. In contrast to the F–F bond, the standard deformation densities of C–C and C–H bonds show quite large accumulations of density, since the density of the usual spherical atom reference is much closer to that of the valence state for C and H than it is for F.

Inverted Tricoordinate Carbon[1]

Koop Lammertsma

Contribution from the Department of Chemistry, University of Alabama at Birmingham, University Station, Birmingham, Alabama 35294. Received November 7, 1985

Abstract: Eleven four-membered ring structures (C_4, C_4H^+, $C_4H_2^{2+}$, C_3BH, $C_3BH_2^+$, $C_2B_2H_2$, C_3Be, C_3BeH^+, C_2BBeH, C_2Be_2, and B_4H_2) are discussed in terms of stability properties associated with inverted tricoordinate carbons. These minimum energy structures have short distances between the bridgehead carbons, averaging 1.484 Å (6-31G*), and short ring bonds, with average values for C–C, C–B, and C–Be bonds of 1.396, 1.487, and 1.576 Å, respectively. The stabilities of these molecules result from four-center, two-electron (aromatic) π bonding and a nonbonding σ HOMO between the bridgehead carbons. The Mulliken overlap population between these carbons ranges from −0.236 for $C_4H_2^{2+}$ to +0.495 for C_2Be_2. While there is no bridgehead–bridgehead bonding in $C_4H_2^{2+}$, there is in C_2Be_2. The beryllium isomers possess ionic character.

Strained hydrocarbons are of fundamental importance for understanding carbon–carbon bonding properties.[2] A particularly interesting feature is revealed in the series of saturated hydrocarbons: ethane,[3] cyclopropane,[3] bicyclo[1.1.0]butane (**1**),[4] and [1.1.1]propellane (**2**).[4g,5,6] In this series the geometry of the sp³

1   **2**
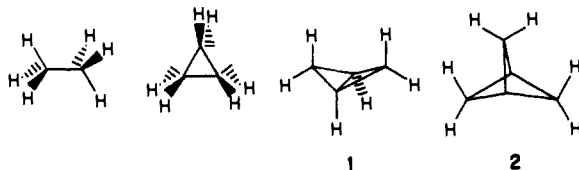
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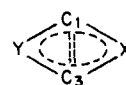
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Table I. 6-31G* Energies, Structural Parameters, and Mulliken Overlap Population Analysis for the Four-Membered Ring Structures **5–15**

5. X = Y = C
6. X = CH⁺; Y = C
7. X = Y = CH⁺
8. X = BH, Y = C
9. X = BH; Y = CH⁺
10. X = Y = BH
11. X = Be; Y = C
12. X = Be; Y = CH⁺
13. X = Be; Y = BH
14. X = Y = Be
15. X = Y = BH; C = B

compound	energy	geometry $r(C_1-C_3)$	geometry $r(C-X)$, $r(C-Y)$	overlap population
5,[a] C_4	−151.145 98	1.457	1.425	−0.063
6,[a] C_4H^+	−151.456 93	1.520	1.352, 1.472	−0.013
7,[a] $C_4H_2^{2+}$	−151.539 98	1.593	1.386	−0.236
8, C_3BH	−138.653 29	1.462	1.479, 1.418	0.138
9, $C_3BH_2^+$	−139.012 20	1.529	1.526, 1.345	0.060
10, $C_2B_2H_2$	−126.155 41	1.470	1.470	0.330
11, C_3Be	−127.983 66	1.418	1.563, 1.421	0.219
12, C_3BeH^+	−128.393 88	1.484	1.619, 1.345	0.107
13, C_2BBeH	−115.478 31	1.445	1.558, 1.473	0.389
14, C_2Be_2	−104.791 29	1.458	1.564	0.495
15 B_4H_2	−99.721 64	1.690[b]	1.604[b]	0.306

[a]Reference 8. [b]The respective r(B–B) bonds are given.

hybridized carbons in ethane is inverted by the subsequent replacement of vicinal hydrogens for CH_2 groups with no significant effect on the (6-31G*) C–C distance. Moreover, while the carbons in ethane are bonded, this is not the case in [1.1.1]propellane.[5e] The intriguing bonding phenomena of the latter compound with its inverted tetracoordinate carbons are well documented.[5,7]

How are the bonding properties of unsatured hydrocarbons affected when the geometry of the neighboring tricoordinate carbons is inverted? There are two general deformations possible for sp² hybridized carbons, the out-of-plane and the in-plane deformations. The out-of-plane deformation has been subject to

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extensive study and include, for example, the anti-Bredt olefins,[8] bridgehead cations,[9] and bent aromatics.[10] The in-plane deformation has received relatively little attention[11] and is the subject of this study.

This paper illustrates by ab initio theory that the perfect trigonal geometry of a tricoordinate carbon (sp^2) indeed can be inverted, leading to compounds that have all three groups on one side of a plane through that carbon, while maintaining planarity. Taking

inverted geometries at carbon
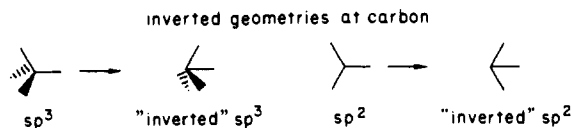
ethylene as the parent, two possibilities may be considered. First, the vicinal hydrogens in ethylene can be replaced by aliphatic CH_2 groups to give the series ethylene,[3] cyclopropene,[3,4a,12] and bicyclo[1.1.0]butene (3).[13] However, theory has shown that the latter
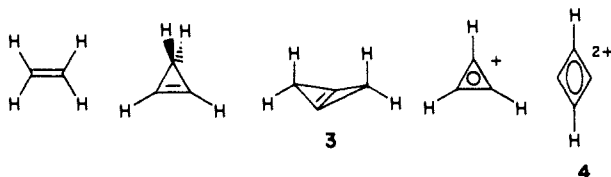
compound is a high-energy nonplanar species[13] and hence does not have inverted tricoordinate carbons. Second, the vicinal hydrogens of ethylene can be replaced stepwise by electron-deficient groups like CH^+, resulting in the series ethylene,[3] cyclopropenyl cation,[14] and cyclic $C_4H_2^{2+}$ (4).[15] Our recent calculational studies[15] have shown that the four-membered ring structure $C_4H_2^{2+}$ indeed is planar and possesses inverted tricoordinate carbons. To explore the generality as well as the special bonding phenomena associated with inverted tricoordinate carbons, we present here the new four-membered ring structures **8–15**. In these molecules the vicinal ethylene hydrogens are not only replaced with C: and CH^+ but also with Be and BH. The new species **8–15** are also of interest because they represent a new type of first-row carbides and carboranes.

Computational Methods

The ab initio calculations were performed by the spin-restricted Hartree–Fock method using the GAUSSIN 80 series of programs.[16] The

geometries were completely optimized within each assumed symmetry by using the standard 3-21G and 6-31G* basis sets;[17] a conjugate gradient method based on analytical first derivatives was used.[18] Population analyses were based on the Mulliken method.[19] The 3-21G force constant matrix was computed by numerical differentiation of the analytical energy gradient. None of the structures has a negative eigenvalue and hence all are equilibrium structures. The 6-31G* energies and geometrical parameters of these structures as well as the C_1–C_2 Mulliken overlap population are listed in Table I.

Results and Discussion

In maintaining the analogy of replacing the vicinal hydrogens of ethylene with a single group, we compare the influence of C:, CH^+, BH, and Be bridging in four-membered ring structures. These electron-deficient groups, which are isoelectronically or isolobally related, influence the character of the C–C bonding interaction. We focus on three important aspects in the four-membered ring structures: (a) the C–C transannular distance, (b) the peripheral (ring) bond distances, and (c) the electronic bonding features.

Experimental data on C_4 and $C_4H_2^{2+}$ suggest the possible existence of rhombic forms beside the (triplet) linear cumulenes.[20] This is supported by a series of recent theoretical studies on these species.[15,21] Inspection of the 6-31G* MO framework of the structures C_4 (**5**), C_4H^+ (**6**), and $C_4H_2^{2+}$ (**7**) reveals that the two highest MOs are important in reducing the anticipated large strain.[15] The HOMO (orbital 12, a_g) displays nonbonding or σ-bond-deficient character between C_1–C_3 with the electron density mainly located outside the molecule. The next highest occupied

orbital 11, b_{3u}

HOMO orbital 12, a_g
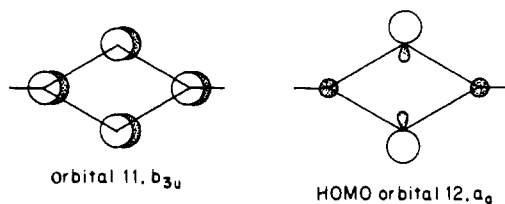
MO (11, b_{3u}) displays four-center (aromatic) π bonding, and therefore the C_1–C_3 interaction is also π bond deficient. Thus, despite the short distances beteen C_1 and C_3 of 1.457 Å in C_4, 1.520 Å in C_4H^+, and 1.593 Å in $C_4H_2^{2+}$, there is no direct bonding between these carbons, which is in accord with the negative Mulliken C_1–C_3 overlap populations of −0.063, −0.013, and −0.236, respectively. The elongation of the C_1–C_3 distance in the series C_4, C_4H^+, and $C_4H_2^{2+}$ suggests some influence of Coulombic repulsion. The aromatic nature of these compounds is supported by their relatively short peripheral bonds, which range between 1.425 Å for C_4 and 1.386 Å for $C_4H_2^{2+}$.

The bonding distances in the boron derivatives **8–10** are remarkably similar to those in the carbon analogues **5–7**. Comparing the C_1–C_3 distance in the neutral species **5**, **8**, and **10** gives a maximum difference of only 0.013 Å with an average distance of 1.462 Å. For the monocations **6** and **9** this difference is 0.009 Å with a slightly larger average C_1–C_3 distance of 1.525 Å. Also

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Inverted Tricoordinate Carbon

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the peripheral C–C bonds in the boron compounds are nearly identical with those in the corresponding carbon ring structures, i.e., 1.418 Å in **8** vs. 1.425 Å in **5** and 1.345 Å in **9** vs. 1.352 Å in **6**. The C–B bond lengths average 1.492 Å and are substantially shorter than 1.575 Å, calculated (6-31G*) for the single bond length of methylborane.[3a] Hence, the structural properties of **8–10** appear to be in full agreement with the concept of inverted tricoordinated carbons outlined for **5–7**.

Although the C_1–C_3 distances are very similar, the electronic properties of the boron derivatives **8–10** are, however, slightly different from their carbon analogues. In contrast to **5–7**, the Mulliken C_1–C_3 overlap populations are positive for all boron isomers. Exchange of C: and CH^+ for BH results in an average change in the C_1–C_3 overlap population of +0.197 and suggests increased bonding between C_1 and C_3. Since the HOMO in **8–10** remains of essentially nonbonding σ character (like in **5–7**), it follows that the C_1–C_3 interaction in the boron derivatives must be of π nature. Indeed, the next highest occupied MO shows enhanced π overlap between C_1 and C_3. In this aromatic π orbital the coefficients on the carbons are slightly larger than those on the borons.

The validity of inverted geometries of tricoordinate carbon was tested by substitution of these carbons for borons. If indeed the HOMO does not contribute to bonding in the carbon derivatives, then analogues with these two fewer electrons should maintain essentially the same orbital structure.[5e] This is indeed the case on comparing **10** with the all-boron compound B_4H_2, **15**. In **15** both the ring and the bridgehead–bridgehead B–B bonds remain short, 1.604 and 1.690 Å, respectively, whereas typical B–B single bond distances are 1.65–1.90 Å.[22] Further, the bond order between the bridgehead atoms in **15** and **10** are nearly identical, 0.306 and 0.330, respectively.

The bonding distances in the beryllium derivatives **11–14** are surprisingly similar to those of the isolobal carbon and boron analogues **5–10**. The C_1–C_3 distance in C_2Be_2 (1.458 Å) differs by only 0.001 Å (!) from that in C_4 but is shorter by 0.039 Å in C_3Be. Again the monocation has the longest C_1–C_3 distance (1.484 Å) but is shorter than in both the boron and carbon analogues. The peripheral C–C bond in neutral **11** is nearly identical with that in **5** and **8**, while this C–C bond in cation **12** compares well with that in **6** and **9**. Even the ring C–B bond in **13** is of nearly the same length as that in **8** and **10**. The average C–Be bond length of 1.576 Å in the structures **11–14** is substantially shorter than 1.699 Å, calculated (6-31G*) for the single bond length of methylberyllium hydride.[3a] The structural parameters of **11–14** suggest that also these structures have inverted tricoordinated carbons.

Despite the similarity in bond length in the four-membered ring structures, beryllium substitution has an even larger impact on the electronic properties of the carbon derivatives than boron. This evident from the Mulliken C_1–C_3 overlap populations, which are

significantly more positive for all beryllium isomers. For example, exchange of BH for Be results in an average change in the C_1–C_3 overlap population of +0.073. Illustrative is the series C_4, $C_2B_2H_2$, and C_2Be_2 with respective C_1–C_3 overlap populations of –0.063, 0.330, and 0.495. This suggests that on substitution of C: for BH and for Be, the C_1–C_3 bonding increases. The contribution of Be to the π molecular orbital is very small, resulting in a three-center, two-electron (CCC) π interaction in **11–13** and an even stronger two-center C_1–C_3 π overlap in **14**.

Also in **14** (and to a lesser extent in **13**) the σ orbital shows more bonding character between C_1 and C_3 and is no longer the HOMO but the next highest occupied MO. Consequently, when C: or CH^+ is substituted for B and for Be, the π and σ bonding between the bridgehead carbons increases, resulting in significant ionic character in the C–Be interaction in **14**. A recent ab initio study on the related three-membered ring structure berylliryne (cyclic C_2Be) also showed ionic character for the C–Be bond.[23] Similarly, magnesium dicarbide (C_2Mg) was shown to be ionic.[24]

In conclusion, the bonding phenomena in inverted trigonal geometries of tricoordinate carbons (sp^2) compare well with those of the recently reviewed[7] inverted tetrahedral geometries of tetracoordinated carbons (sp^3). Thus, the HOMO of the highly strained [1.1.1]propellane (**2**), elegantly synthesized by Wiberg and Walker,[5a] is of σ-deficient character with no appreciable electron density between the bridgehead carbons (C_1 and C_3)[5,6] and is similar to the HOMOs of the four-membered ring structures **5–14**. The short C_1–C_3 distance in **2** of 1.543 Å (HF/6-31G*)[5a] was shown to result from *two three-center two-electron interactions* with the CH_2 bridges,[5] also termed σ-bridged π bonds.[5e] The short C_1–C_3 distance in **5–12** results from *one four-center, two-electron π interaction*.[25] The increased C_1–C_3 overlap in **14**, as compared to **5**, is in agreement with Epiotis' qualitative study[26] on σ-deficient molecules and is the result of the more ionic nature of the beryllium dicarbides.[27]

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