

PLANAR TETRACOORDINATE CARBON IN ORGANOBORON COMPOUNDS: *ab initio* COMPUTATIONAL STUDYTatyana N. GRIBANOVA, Ruslan M. MINYAEV^{1,*} and Vladimir I. MINKIN^{2,*}

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This paper is dedicated to Professor Otto Exner in recognition of his outstanding contributions in the area of physical organic chemistry and chemometrics and on the occasion of his 75th birthday.

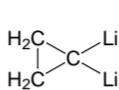
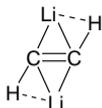
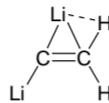
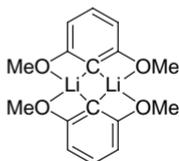
Ab initio MP2(full)/6-311++G** calculations revealed that 1,2-diborasp[2.2]pent-4-ene (**11**) and two of its isomers **14** and **15** possess stable structures with planar tetracoordinate carbon. These compounds and some of their derivatives, **21** and **22**, can be regarded as the first computationally found organoboron compounds with the planar tetracoordinate carbon.

Key words: Planar tetracoordinate carbon; *Ab initio* calculations; 1,2-Diborasp[2.2]-pent-4-ene; Boron; Boranes.

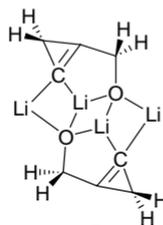
The concept of stereoelectronic stabilization of a planar tetracoordinate carbon advanced by Hoffmann *et al.*^{1,2} has been a great challenge for both theoretically oriented and experimental chemists. The analysis of the orbital pattern of the hypothetical planar methane allowed understanding principal electronic and structural factors contributing to stabilization of the planar tetracoordinate carbon. These factors include: (i) electropositive σ -donor substituents, (ii) π -acceptor substituents, and (iii) incorporation of the carbon into a small ring or an aromatic system. An alternative "brutal force" approach is based on locking a carbon atom into an appropriately strained polycyclic environment. These strategies used as the basis of the theoretical and experimental studies and the results achieved in both directions have been extensively reviewed³⁻⁶.

In accordance with the rules of stereoelectronic stabilization, the planar singlet *cis*-dilithiomethane was found by B3LYP/6-311++G** calculations⁵ to lie only 2.5 kcal mol⁻¹ higher in energy than the global minimum tetrahedral structure. Inclusion of the central carbon into the strained cyclopropane

ring of 1,1-dilithiocyclopropane (**1**) provides for further stabilization of the planar tetracoordinate carbon structure **2**, which, at various levels of approximation⁵, represents the global energy minimum for $C_3H_4Li_2$. Other organolithium compounds whose computationally predicted ground state structures contain planar tetracoordinate carbon centers comprise dilithiated ethylenes **2** and **3** (ref.⁵) and diverse dimeric structures, such as **4** and **5** (refs^{5,7}), in which planar tetracoordination is additionally favoured by intramolecular solvation.

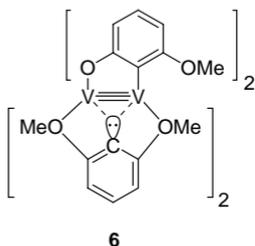
1, C_{2v} 2, C_{2h} 3, C_s 

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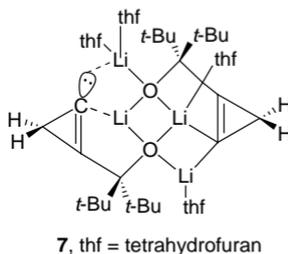


5

The structures **4** and **5** are simplified models of the isolated compounds **6** (ref.⁸) and **7** (ref.⁹), respectively, in which the planar tetracoordination of the carbon atom, confirmed by X-ray analysis, is due to formation of a σ -multicenter bond between the carbon atom of the aryl and cyclopropenyl anions¹⁰.



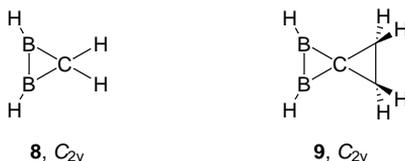
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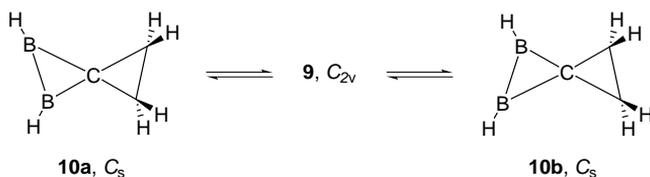
7, thf = tetrahydrofuran

In identical structural arrangements, substituents less electropositive than lithium reveal weaker stabilizing effects. No local minima for the C_{2v} structures with planar tetracoordinate carbons were computationally predicted⁵

for the disubstituted methanes CH_2X_2 ($\text{X} = \text{Na}, \text{BeH}, \text{BH}_2, \text{MgH}, \text{AlH}_2$) and the early claim¹¹ on the planar tetracoordinate carbon structure of 1,2-diboracyclopropane (**8**) has been recently dismissed^{5,12}. As was shown by B3LYP/6-311++G** calculations⁵, replacing both hydrogen atoms in the methylene group of **8** by a three-membered carbon ring results in an additional stabilization of the planar carbon structure in thus formed 1,2-diborasp[iro[2.2]pentane **9** (ref.⁵). The planar C_{2v} structure **9** was predicted to be a local energy minimum on the $\text{C}_3\text{B}_2\text{H}_6$ potential energy surface (PES), whereas the structure with the tetrahedral carbon conformed to a second-order stationary point ($\lambda = 2$, where λ stands for the number of negative eigenvalues of Hessian matrix) lying 9.4 kcal mol⁻¹ higher than **9**. Hereafter we use the term tetrahedral to describe distorted nearly tetrahedral C_{2v} arrangements of bonds around a carbon center.



We have calculated the structure of 1,2-diborasp[iro[2.2]pentane using *ab initio* MP2(full)/6-31G** method and found that at this level of approximation the C_{2v} structure **9** is not a minimum, but a saddle point ($\lambda = 1$) corresponding to the transition state for the very low-barrier (0.23 kcal mol⁻¹) in-plane interconversion of two equivalent C_s structures **10** (Fig. 1).



Even though the trapezoidal structures **10** are true minima ($\lambda = 0$) on the $\text{C}_3\text{B}_2\text{H}_6$ PES, the PES in the region of the planar tetracoordinate structures **9** and **10** is extremely flat and, therefore, they are weakly stabilized structures.

The present work has been aimed at computational search for other boron-containing structures incorporating a planar tetracoordinate carbon atom. The MP2(full)/6-311++G** method of calculation as a next higher level of approximation has been employed. Accounting for the promising results

obtained in calculations of 1,2-diborasp[2.2]pentane, our approach involved modification of its structure in an attempt to additionally stabilize the planar *versus* the tetrahedral arrangement of bonds around the spiro carbon. From the viewpoint of the concept of stereoelectronic stabilization, a possible step may consist in replacement of the cyclopropane ring in **9** by the unsaturated cyclopropene fragment in 1,2-diborasp[2.2]pent-4-ene (**11**). The results of the computational study of critical parts of the $C_3B_2H_4$ PES that include **11** and its various isomeric forms are discussed in the following sections of this paper.

COMPUTATIONAL METHODS

The geometries of molecules were optimized employing analytical gradients with polarized split-valence basis sets (6-31G** and 6-311++G**) at the MP2(full) level at which all electrons were included in the correlation energy calculations¹³. Inclusion of electronic correlation in the geometry optimization is regarded as a prerequisite for a reliable prediction of the geometries of nonclassic, particularly anti-van't Hoff structures¹⁴. The optimization of the structures, corresponding to the stationary points on the $C_3B_2H_4$ PES, was carried out up to the value of the energy gradients of 10^{-5} a.u./Bohr. The force-constant matrices were calculated numerically. All the calculations were performed with the Gamess program¹³ on a DEC Alpha-station 500. Three-dimensional PLUTO representations of the calculated structures were drawn with the use of the PD program incorporated into the PC MODEL package¹⁵.

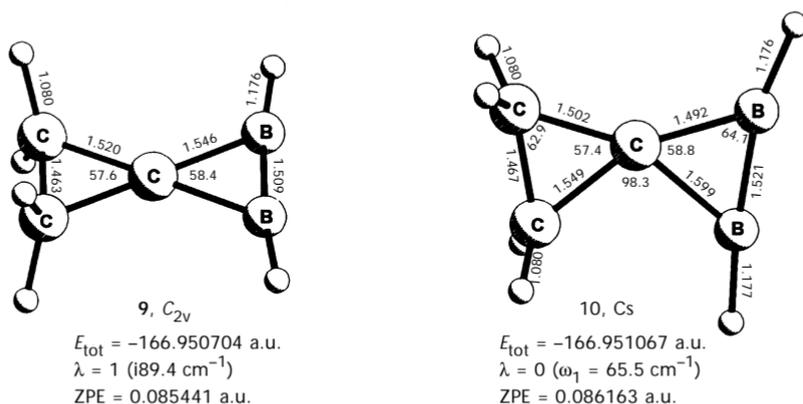


FIG. 1

Geometry parameters of the structures **9** and **10** calculated by MP2(full)/6-31G** method. Bond lengths and angles are given in Å and °, respectively

RESULTS AND DISCUSSION

It has been long recognized¹¹ that 1,2-diboracyclopropane ring possesses features favourable for stabilization of the incorporated planar carbon: borons bear vacant p_z orbitals capable of delocalization of the lone pair at carbon, possess σ -donor abilities and the small CB_2H_4 ring is of aromatic character similar to that of the cyclopropenium ion. The resemblance of the electronic structure of these two rings is due to the fact that π orbitals of both the rings are populated each by two ($4n + 2$) electrons. In the diboracyclopropylidene fragments in **9** and also **11**, the two electrons come from the carbon atom. Thus, the spiroannulated cyclopropen-1,1-diyl fragment of the planar conformation of the latter compound also contains only two π electrons and, consequently, possesses a certain degree of aromaticity

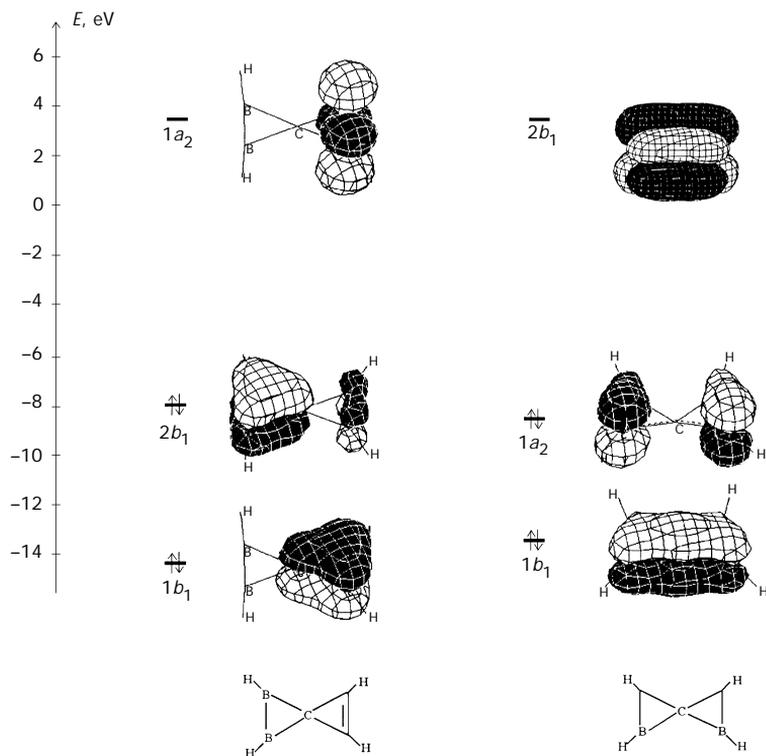
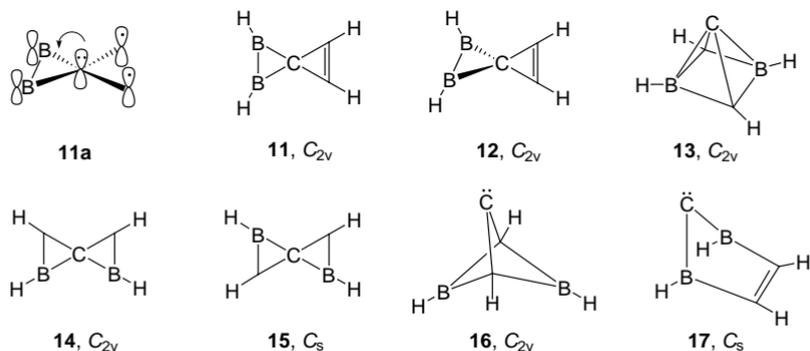


FIG. 2

Shape and energy levels of π MOs of the structures **11** and **14** as given by the 6-31G** basis set

as an additional, as compared with **9**, factor favouring the planar coordination of the spiro carbon center. The aromatic character of **11** is well illustrated by the orbital pattern **11a** shown in Fig. 2. Two π MOs next to σ MO of **11** strictly correspond to bonding π MOs of the cyclopropenium ion.

Thus, the structure **11** of 1,2-diborospiro[2.2]pent-4-ene comprises all the above mentioned stereoelectronic features beneficial for the planar tetracoordinate carbon.



The calculations performed have shown, indeed, that the C_{2v} structure **11** with a planar tetracoordinate carbon corresponds to a true minimum on the $C_3B_2H_4$ PES, whereas the structures **12** with the tetrahedral carbon and **13** with pyramidal configuration of the apical carbon represent the higher-order stationary points ($\lambda \geq 2$) and do not conform to stable molecular forms. The stationary points related to **12** and **13** on the PES lie 59.7 and 54.5 kcal mol⁻¹, respectively, higher than that of **11**. The calculations revealed the existence of two other stable isomers of 1,2-diborospiro[2.2]pent-4-ene with planar tetracoordinate carbon centres – **14** (C_{2v} symmetry) and **15** (C_s symmetry). On the level of approximation employed, the structure **14** is the most stable isomer of $C_3B_2H_4$ with a planar tetracoordinate carbon. As portrayed by Fig. 2, filled π MOs of **14** are of well-pronounced bonding type.

The planar structure **14** is only by 3.0 (MP2/6-31G**) and 3.7 (MP2/6-311++G**) kcal mol⁻¹ less favourable than the structure of the carbene **16** which corresponds to the global minimum on the $C_3B_2H_4$ PES. Another carbene with the classic structure **17** is less stable than the structures **14** and **15** with the planar tetracoordinate carbon. Calculated energies of all the structures discussed above are given in Table I. The geometries of the optimized $C_3B_2H_4$ species are shown in Fig. 3.

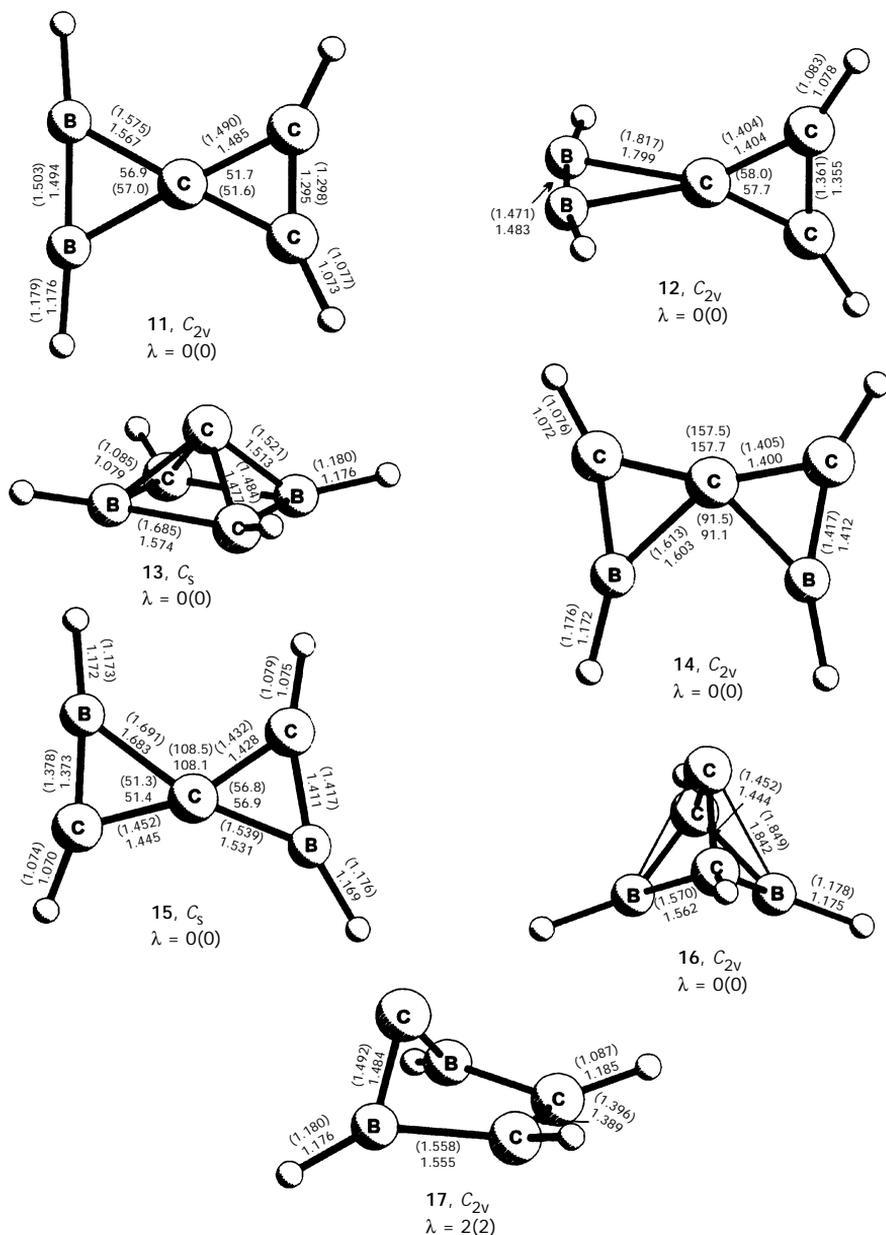


FIG. 3

Geometry parameters of the structures 11–17 calculated by MP2(full)/6-31G** and MP2(full)/6-311++G** (numbers in parentheses) methods. Bond lengths and angles are given in Å and $^\circ$, respectively

The most important feature of the geometries of the planar tetracoordinate carbon structures **11**, **14**, and **15** is significant shortening of the B–C bonds as compared with those in the tetrahedral carbon structure **12**. This effect is due to the cyclopropenium-ion like bonding pattern **11a**. At the same time, no expected equalization of lengths of the C–C bonds was found in the calculations. The HC–CH bond in **11** is closer to a normal C=C double bond.

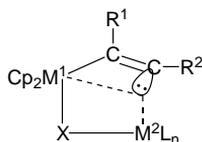
It should be noted that structural motifs of all the previously computed planar-tetracoordinate carbon species basically reproduce those found in experimentally studied transition metal compounds incorporating carbon atoms with anti-van't Hoff configurations⁶. Thus, as shown above, the structures **4** and **5** closely resemble **6** and **7**, the dilithiated ethenes **2** and **3**

TABLE I

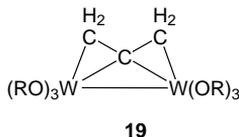
Total energies (E_{tot}), relative energies (ΔE), the number of the negative hessian eigenvalues (λ), harmonic zero-point correction (ZPE), relative energy including harmonic zero-point correction (ΔE_{ZPE}), and the smallest or imaginary vibration frequency ($\omega_1/i\omega$) for the structures **11–17**, **21** and **22** calculated by MP2(full)/6-31G** and MP2(full)/6-311++G** (numbers in parentheses) methods

Structure	E_{tot}	ΔE	λ	ZPE	ΔE_{ZPE}	$(\omega_1/i\omega)$
11 , C_{2v}	-165.70199	48.48	0	0.05856	45.83	72.7
	(-165.83476)	(47.77)	(0)	(0.05745)	(45.26)	(77.6)
12 , C_{2v}	-165.60119	111.74	3	0.05590	107.42	i1241.2; i517.4; i200.4
	(-165.73960)	(107.48)	(3)	(0.05505)	(103.47)	(i1036.3; i492.7; i82.4)
13 , C_{2v}	-165.61440	103.45	2	0.05793	100.40	i4887.9; i697.4
	(-165.74785)	(102.31)	(2)	(0.05648)	(99.19)	(i5186.5; i690.4)
14 , C_{2v}	-165.77308	3.87	0	0.06141	3.01	166.9
	(-165.90382)	(4.44)	(0)	(0.06022)	(3.67)	(166.6)
15 , C_s	-165.75031	18.16	0	0.06041	16.67	185.6
	(-165.88164)	(18.35)	(0)	(0.05911)	(16.89)	(180.1)
16 , C_{2v}	-165.77926	0	0	0.06279	0	494.3
	(-165.91089)	(0)	(0)	(0.06145)	(0)	(477.5)
17 , C_s	-165.73775	26.05	0	0.06241	25.81	226.1
	(-165.87083)	(25.14)	(0)	(0.06110)	(24.92)	(220.3)
21 , C_{2v}	-241.769987	-	0	0.07494	-	255.2
22 , C_{2v}	-241.77333	-	0	0.07776	-	226.2

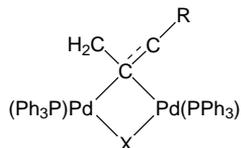
are associated with the structures of mono- and dinuclear complexes of Groups 4 and 13, e.g., **18** (refs^{6,16}). In a certain way, allenic or heteroallenic complexes exemplified by the structures **19** (ref.¹⁷) and **20** (ref.¹⁸) serve as analogues of **10**, **11**, **14**, and **15** and also of recently computed pentaatomic molecules CSi_2Ga_2 and CGe_2Al_2 containing the planar tetracoordinate carbon¹⁹.



18 $M^1 = \text{Ti, Zr, Hf}$
 $M^2 = \text{BEt}_2, \text{AlMe}_2, \text{GaMe}_2$
 $X = \text{H, alkyl, Cl}$
 $R = \text{alkyl, aryl}$



19



20 $X = \text{Cl, SPh}$
 $R = \text{H, Ph}$

An important feature of the structure **11** considered in this work is that it can be easily modified by attaching proper substituents to the ring carbon or by fusing rings. Thus, according to our MP2(full)/6-31G** calculations, the tricyclic derivatives of 1,4-diborasp[iro[2.2]pentane, **21** and **22**, represent sufficiently deep local minima on the $\text{C}_5\text{B}_2\text{H}_4$ PES (Table I, Fig. 4).

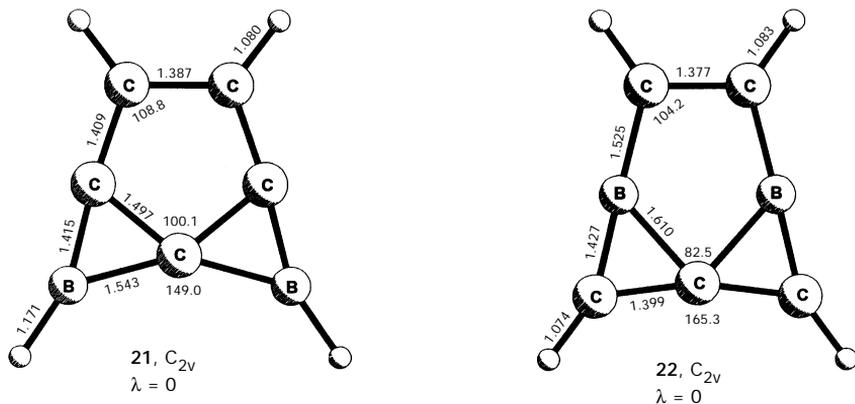
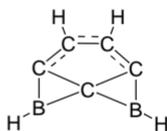
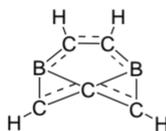


FIG. 4

Geometry parameters of the structures **21** and **22** calculated by MP2(full)/6-31G** method. Bond lengths and angles are given in Å and °, respectively



21



22

It can be concluded that the calculations performed on the structures **11**, **14**, **15**, **21**, and **22** make these a possible synthetic target for organoboron compounds with a planar-tetracoordinate carbon.

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