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Small-Ring Geminanes−New Hypothetical Molecules with Inverted Carbon Atoms

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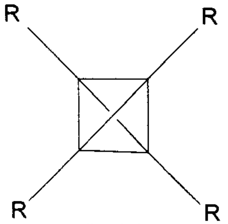
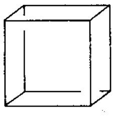
Details of the molecular structures and properties of three novel hypothetical hydrocarbons that could possess inverted carbon atoms are revealed through post-Hartree−Fock ab initio calculations. Their molecular geometries were optimized at the MP2 and DFT levels in conjunction with the 6-31G(d,p) and 6-311++G(d,p) basis sets. The calculated vibrational frequencies confirm that the predicted geometries represent minimum energy structures. The theoretically predicted chemical shifts reflect the unusual stereochemistry at the bridgehead atoms. All theoretical data indicate that for the studied molecules three carbon atoms are located approximately in a plane with the corresponding bridgehead atom.

Introduction

About 100 years after its formulation, the van't Hoff and LeBell hypothesis on the tetrahedral arrangement of substituents around a tetravalent carbon atom[1] ceased to be dogma. Several fascinating molecules with unusual stereochemistry have been synthesized, such as tetra-*tert*-butyltetrahedrane **1a**, cubane **2**, cyclohexane derivatives such as **3** having a planar six-membered ring,[2a] and small-ring propellanes **4** ($k = 1-3$; $l = 1, 2$; $m = 1, 2$)[3] to name but a few. They present a considerable challenge to the synthetic chemist trying to find a practical answer to the exciting question "To what extent can a carbon−carbon bond be distorted without being broken?" Hydrocarbons with an unusual spatial structure are also of considerable interest for theoretical chemists trying to elucidate the nature of a chemical bond. In addition, calculations allow one to predict whether a nonstandard structure represents a minimum on a potential energy surface, i.e., whether they represent thermodynamically stable structures. They also reveal the properties of such molecules.



1a R = C(CH$_3$)$_3$
1b R = H



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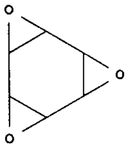

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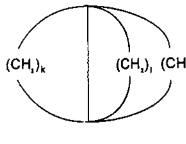

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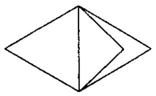

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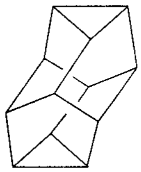

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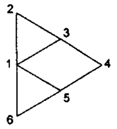

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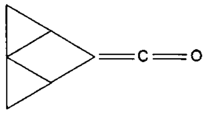

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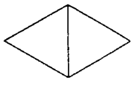

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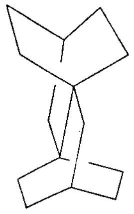

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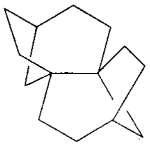

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Today, model calculations are an established tool enabling a study of hypothetical and inaccessible structures.[2b,4] One of the best examples of their effectiveness provides the Wiberg group proposal of the possibility of the existence of stable molecules possessing inverted carbon atoms on the basis of model calculations.[3] The synthesis of small-ring propellanes **4** was preceded by model calculations suggesting the feasibility of such nonstandard stereochemistry on a tetravalent carbon atom. Moreover, the predicted extraordinary stability of [1.1.1]propellane **5** and some other properties of this compound were later confirmed experimentally. Similarly, a quite unusual structure of dodecahedrane **6** having a highly puckered cyclohexane ring predicted by us[5] was established after its synthesis.[6] On the basis of high level quantum calculations,[7] we have recently

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(4) Reference 2a, Chapter 3.

10.1021/jo990040p CCC: $18.00

proposed that tricyclo[3.1.0^{1,3}]hexane **7** should represent a limiting case to the pyramidal carbon atom because the C2−C1−C6 bond angle in this molecule was found to assume a value of 180° for a tetravalent carbon atom. A recent synthesis of the highly unstable ketene derivative **8** by the Wiberg group[8] paves the way to a verification of the latter prediction.

As discussed in ref 9, the Wiberg definition of an inverted carbon atom covers both inverted and pyramidal atoms. To make it more specific, we have defined an inverted carbon atom as one that has one CX bond “inverted,” that is, it has an opposite orientation in comparison to the standard tetrahedral geometry at this atom. As mentioned before, very few molecules having an inverted carbon atom are known. Except [1,1,0]-bicyclobutane **9**, all known molecules having inverted carbon atoms are small-ring propellanes.[3] They all possess symmetrical pairs of inverted carbon atoms. [2.2.2]-Propellane **4** ($k = l = m = 2$) represents a limiting case because its bridgehead carbon atoms lie approximately in a plane with their three neighbors. Looking for hypothetical hydrocarbons with nonstandard spatial structure,[5,7,9] we have previously proposed[10] on the basis of molecular mechanics calculations that molecules **10** and **11** and some higher analogues to the Paquette structures **12** and **13** (dubbed [2.2.2]- and *syn*-[3.2.1]-geminanes, respectively) should also possess inverted carbon atoms.[11] Moreover, in asymmetrical structures the inverted carbon atoms differ. Tricycloheptane **14**, (i.e., [1.1.1]geminane lacking one CC bond) and two other higher geminanes should exhibit isolated inverted carbon atoms. In this note, the results of high-level ab initio and DFT[12] calculations for molecules **12**−**14** are carried out to check the earlier predictions based on the primitive molecular mechanics model. Thus, a more sound basis for the possibility of the existence of these novel hydrocarbons possessing inverted carbon atoms is created. In particular, the possibility for the existence of nonsymmetrical pairs of inverted carbons or even an isolated carbon atom with such spatial bond arrangement is substantiated.

Method

All geometry optimizations were carried out using the GAUSSIAN 94 program package.[15] Initially they were performed at the HF/6-31G(d,p) level, and such optimized geometries were used as input parameters for the geometry optimizations at the MP2 approximation with two basis sets: 6-31G(d,p) and 6-311++G(d,p). In addition, the geometric parameters of all considered structures were reoptimized, and analytical harmonic vibrational frequencies were calculated at the B3LYP/6-31G(d,p) level.[15,16]

The CHF-GIAO (coupled Hartree−Fock gauge including atomic orbitals) approach[17,18] to the calculation of nuclear magnetic shielding tensors was used with the improvements of the calculation scheme introduced by Wolinski et al.[19] The basis set was of standard 6-31G-(d,p) quality. All the shielding calculations were performed using the TEXAS 95 program. Shielding constants σ and magnetic shielding anisotropies $\Delta\sigma$ were obtained as

$$\sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \qquad (1)$$

and

$$\Delta\sigma = (2\ \sigma_{11} - \sigma_{22} - \sigma_{33})/2 \qquad (2)$$

respectively, where σ_{ii} are diagonal terms of the shielding tensor and $\sigma_{11} > \sigma_{22}, \sigma_{33}$.

NMR chemical shifts were determined according to the IUPAC convention[20]

$$\delta_i = \sigma_{\mathrm{ref}} - \sigma_i \qquad (3)$$

In addition, Hansen and Bouman’s basis set of double-ζ quality[21] was used to verify our calculations of NMR chemical shifts. It was composed of (31/1) atomic orbitals contracted to [2s1p] for the hydrogen atom and (721/221/1) atomic orbitals contracted to [3s3p1d] for the carbon atom. The latter basis set has been found to be very efficient for the shielding calculations for carbon, nitrogen, and oxygen nuclei.[22]

Results of Calculation

The structures of molecules **10**, **11**, and **14** were optimized at the HF/6-31G(d,p), MP2/6-31G(d,p), MP2/6-311++G(d,p), and Becke3LYP/6-31G(d,p) levels of theory, and the frequency calculations were carried out using the 6-31G(d,p) basis set at the HF and DFT levels. The DFT calculations yielded the lowest frequency of 258, 280, and 321 cm^{-1} (Table 1) ensuring that all structures correspond to stationary points on the energy hypersurfaces. As expected, the frequencies calculated by the HF method are higher than those obtained in the DFT calculations.

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Table 1. Calculated Becke3LYP/6-31G(d,p) Level Frequencies (cm^{-1}) and Intensities (km/mol in Parentheses)

compound		
14	**10**	**11**
280.0 (0.06)	321.1 (0.06)	257.7 (0.09)
359.1 (0.68)	430.0 (0.06)	327.6 (0.09)
420.8 (2.86)	486.8 (12.94)	406.7 (0.08)
547.5 (0.82)	566.0 (0.0)	485.9 (4.97)
583.3 (1.88)	570.0 (8.82)	518.5 (3.92)
854.4 (2.33)	579.1 (0.0)	549.6 (2.24)
898.7 (1.78)	587.7 (0.0)	568.7 (0.33)
931.2 (0.69)	786.6 (0.67)	589.6 (1.51)
978.6 (0.25)	792.3 (0.0)	693.7 (1.04)
988.1 (0.62)	814.4 (0.0)	773.8 (0.03)
1011.9 (1.33)	818.6 (1.16)	798.5 (0.80)
1024.4 (0.65)	863.2 (13.56)	823.0 (1.22)
1048.7 (0.90)	895.6 (0.0)	833.2 (3.89)
1094.2 (1.51)	944.9 (0.0)	860.7 (0.40)
1114.9 (0.21)	957.1 (1.39)	887.6 (0.59)
1011.9 (1.12)	978.5 (0.0)	912.0 (3.14)
1115.6 (0.97)	1000.9 (0.03)	929.7 (0.64)
1149.9 (4.92)	1011.7 (0.0)	942.1 (0.19)
1092.8 (2.61)	1042.5 (6.20)	963.4 (1.86)
1209.1 (1.07)	1081.4 (1.45)	981.6 (0.56)
1135.7 (1.26)	1084.3 (0.0)	996.9 (0.49)
1148.6 (0.28)	1084.5 (1.06)	1013.2 (0.24)
1190.5 (1.21)	1105.4 (0.0)	1038.8 (0.75)
1202.6 (0.39)	1109.3 (0.0)	1076.0 (1.06)
1206.4 (4.01)	1141.6 (0.32)	1090.5 (0.35)
1211.6 (1.74)	1154.4 (0.0)	1098.1 (1.10)
1234.0 (8.27)	1172.2 (0.0)	1122.1 (1.24)
1242.2 (0.80)	1200.7 (0.0)	1133.1 (0.05)
1257.9 (9.05)	1200.9 (5.19)	1163.8 (0.60)
1278.5 (4.91)	1208.3 (0.33)	1176.9 (1.24)
1371.7 (2.94)	1229.9 (0.0)	1189.8 (0.92)
1485.1 (1.11)	1233.7 (37.38)	1201.6 (1.39)
1498.2 (0.19)	1251.0 (1.58)	1211.2 (1.69)
1516.5 (0.55)	1261.1 (0.0)	1217.4 (4.44)
1561.0 (0.40)	1504.3 (0.0)	1239.4 (7.82)
3044.8 (52.83)	1538.1 (0.60)	1247.1 (8.67)
3053.6 (22.44)	1539.8 (0.43)	1267.6 (3.19)
3055.9 (110.59)	1572.4 (0.0)	1281.4 (0.20)
3060.1 (64.12)	3039.6 (225.08)	1306.2 (0.82)
3072.9 (84.51)	3040.7 (0.0)	1317.4 (2.70)
3083.6 (16.10)	3067.6 (0.0)	1503.1 (0.72)
3111.5 (13.45)	3073.2 (55.05)	1506.1 (0.89)
3121.4 (33.92)	3073.4 (171.0)	1529.0 (2.18)
3129.9 (50.64)	3084.2 (0.0)	1544.6 (1.93)
3144.8 (44.77)	3142.3 (0.0)	1572.1 (0.04)
	3146.4 (55.4)	3053.9 (83.83)
	3168.3 (77.68)	3057.7 (27.79)
	3168.6 (0.22)	3064.9 (33.40)
		3069.1 (56.59)
		3072.3 (83.07)
		3080.9 (82.70)
		3090.4 (54.00)
		3101.5 (10.14)
		3121.1 (44.70)
		3152.8 (28.83)
		3156.9 (35.94)
		3185.3 (32.31)

The bond lengths and some bond angles calculated for the studied species at the MP2/6-31G(d,p), MP2/6-311++G(d,p), and Becke3LYP/6-31G(d,p) levels of theory are collected in Tables 2−6. The bond lengths obtained sometimes differ by more than 0.1; however, the corresponding bond angle values are very close and do not differ by more than 1°.

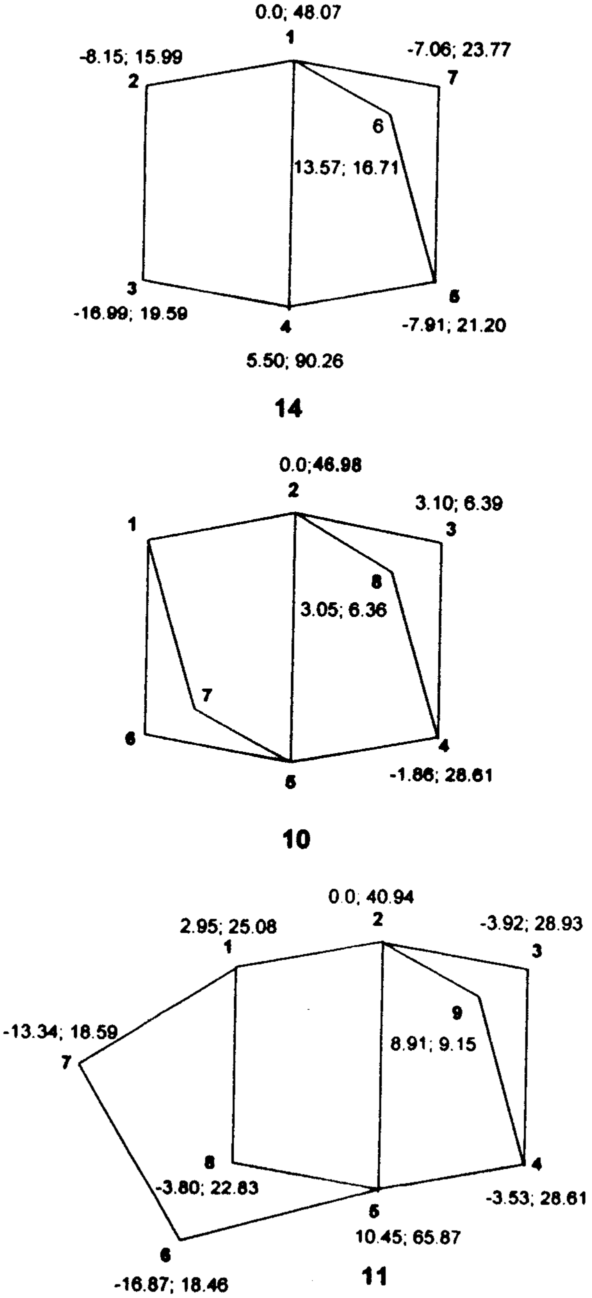

Figure 1. The calculated values of relative ^{13}C NMR chemical shifts and magnetic anisotropies for **10**, **11**, and **14**.

The calculated chemical shifts and magnetic shielding anisotropies (cf. eqs 1−3) in the ^{13}C NMR spectra of **10**, **11**, and **14** will be useful not only for confirming the structures when the molecules are synthesized. As will be discussed later, they also reflect unusual stereochemistry at the bridgehead atoms. It should be stressed that the ^{13}C NMR chemical shifts and magnetic anisotropies collected in Figure 1 (the shifts of a bridgehead atom involved in bicyclopentane fragment (C1 in **14** and C2 in **10** and **11**) were taken as reference) are calculated with sufficient accuracy[21] to support future experimental studies of the molecules under investigation since, for instance, the values of the chemical shifts cover a wide range changing from −17.0 ppm for C3 in **14** to 10.5 ppm for C5 in **11**. All metine carbon atoms in these fragments

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Table 2. Calculated Bond Lengths for Tricycloheptane 14 (Å)

level	bond								
	1,4	1,6	1,7	4,5	5,6	5,7	1,2	2,3	3,4
MP2/6-31G(d,p)	1.526	1.556	1.556	1.563	1.534	1.583	1.540	1.577	1.569
MP2/6-311++G(d,p)	1.534	1.562	1.562	1.570	1.541	1.590	1.545	1.584	1.575
Becke3LYP/6-31G(d,p)	1.528	1.564	1.568	1.577	1.560	1.539	1.548	1.588	1.577

Table 3. Selected Calculated Bond Angles (deg) for 14

level	angle				
	2,1,4	4,1,6	4,1,7	2,1,6	2,1,7
MP2/6-31G(d,p)	90.8	88.6	88.3	119.5	153.4
MP2/6-311++G(d,p)	90.8	88.6	88.3	119.6	153.4
Becke3LYP/6-31G(d,p)	91.1	88.8	88.5	119.1	153.9

exhibit negative values while the corresponding value for remaining metine C1 carbon atom in **11** is positive. The carbon atoms of methylene bridges in asymmetric molecules **14** (C6 and C7) and **11**(C3 and C9) exhibit chemical shifts of different signs, with the positive value approximately twice as large as the negative one. Interestingly, the corresponding shifts in symmetrical [1.1.1]-geminane **10** are practically equal. These calculated chemical shifts correlate with the magnitudes of the bond angles at the bridgehead carbon atoms equal to 119.5° and 153.4° for C2C1C6 and C2C1C7, respectively, for **14**; 133.7° for both C1C2C3 and C1C2C8 bond angles for **10**; and 128.9° and 143.5° for C1C2C3 and C1C2C9, respectively, for **11**. The bridgehead−bridgehead carbon atoms that lie very close to the planes of their three neighbors (see below) exhibit considerable anisotropies. They assume intermediate values of 47−90 ppm between those for carbon atoms with sp^3 hybridization (10−30 ppm) and the corresponding values for sp^2 hybridization (180 ppm for ethylene).[21] The calculated anisotropy values compare favorably with the experimental ones (46 ppm for bridgehead carbon atoms and 88 ppm for those in methylene bridges[22]) for [1.1.1]propellane that possesses inverted carbon atoms and with the value 52 ppm calculated for the carbon atoms in hypothetical tetrahedrane **1b**. We believe that this increase in magnetic shielding anisotropy reflects unusual stereochemistry at the bridgehead−bridgehead carbon atoms.

Tricyclo[3.1.1.0^{1,4}]heptane 14. The bond lengths and bond angles for **14** calculated at the MP2/6-31G(d,p), MP2/6-311++G(d,p), and Becke3LYP/6-31G(d,p) levels are collected in Tables 2 and 3. The central bridgehead−bridgehead bond is the shortest at all levels of calculation, and the relative ordering of all CC bonds is the same in all but the DFT method. There are considerable differences between the C5C6 and C5C7 bond lengths and the C2C1C6 and C2C1C7 bond angles (119.5° and 153.4°) at all levels of the calculations. These differences parallel those involving the chemical shifts and magnetic anisotropies of C6 and C7 shown in Figure 1. The value of the sum of bond angles C4C1C2 + C4C1C6 + C4C1C7 is equal to 267.9°, which indicates that the configuration at the C1 atom is very close to the limiting case when the bridgehead atom C1 lies in one plane with its three neighbors C1, C6, and C7 (for which the sum should be equal to 270°). Interestingly, the analogous sum for the C4 atom involving its connected hydrogen atom (C1C4C3 + C1C4C5 + C1C4H4 = 275.2°) is only slightly larger than the value corresponding to a planar arrangement of the C3, C5, and H4 atoms. This shows that the configuration of the latter atom is constricted although the C4H4 bond does not participate in the cage structure. As mentioned above, the calculated values of the bond angles do not depend significantly on the level of calculations used. Therefore, the same conclusions concerning the bond configurations at the C1 and C4 atoms hold for all calculations.

Tetracyclo[3.1.1.1^{2,4}.0^{1,5}]octane 10 ([1.1.1]Geminane). At all levels, the optimum structure exhibits *C*1 symmetry that has not been imposed on the calculations. The bond lengths and bond angles for **10** calculated at the MP2/6-31G(d,p), MP2/6-311++G(d,p), and Becke3LYP/6-31G(d,p) levels are collected in Table 4. The same ordering of the bond lengths has been obtained using the last two methods. However, this ordering does not agree with that calculated using the first method. In agreement with the finding for **14**, the bond angles involving the C2 and, by symmetry, the C5 atoms in molecule **10** indicate that the bridgehead atoms assume an inverted configuration, with the value of the sum of the bond angles C1C2C5 + C5C2C3 + C5C2C8 equal to 250.0°. The difference of the latter value from 270.0° shows that the bridgehead atom C2 lies very close to but not in the plane formed by the C1, C3, and C8 atoms. The lengths of the C2C3 and C2C8 bonds and the magnitudes of the C1C2C3 and C1C2C8 bond angles are very close at all levels of the calculations, and practically the same values of chemical shifts and magnetic anisotropies have been obtained for the C3 and C8 atoms.

Tetracyclo[3.2.1^{2,4}.0^{2,5}]nonane 11. The calculated bond lengths and bond angles for **11** are collected in Tables 5 and 6, respectively. The C4C9 bond length is found to be the biggest for all levels of calculations, whereas the C5C6 bond is the shortest. Similarly to tricycloheptane **14**, there are considerable differences between the calculated C3C4 and C4C9 bond lengths and the C2C1C6 and C2C1C7 bond angles (128.9° and 143.5°) at all levels of the calculations. Consequently, there are considerable differences in the calculated chemical shifts and magnetic anisotropies of the atoms C3 and C9 (Figure 1). The values analogous to the correspoding values for **10** and **14** are equal to 260.9° and 264.5° for the C2 and C5 bridgehead atoms, respectively. The latter values indicate that both atoms lie very close to the planes of their three neighbors, with a very small difference in their positions relative to the respective planes. Similarly to the finding for **14**, there are considerable differences between the C3C4 and C4C9 bond lengths and the C1C2C3 and C1C2C9 bond angles (128.9° and 143.5°) at all levels of the calculations.

4. Conclusions

The results of the calculations at the MP2/6-31G(d,p), MP2/6-311++G(d,p), and Becke3LYP/6-31G(d,p) levels for **10**, **11**, and **14** indicate that configurations at the bridgehead carbon atoms in these molecules should be

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[22] Jackowski, K. *Bull. Pol. Acad. Sci., ser. Chem.* **1998**, *46*, 91.

Table 4. Calculated Bond Lengths (Å) and Selected Bond Angles (deg) for 10

	bond						angle				
level	1,2	2,3	2,5	2,8	3,4	4,8	1,2,5	5,2,3	5,2,8	1,2,3	1,2,8
MP2/6-31G(d,p)	1.568	1.564	1.551	1.563	1.559	1.559	74.5	87.8	87.8	133.7	133.7
MP2/6-311++G(d,p)	1.573	1.567	1.566	1.566	1.562	1.565	74.2	87.8	87.7	133.7	133.7
Becke3LYP/6-31G(d,p)	1.576	1.571	1.547	1.571	1.569	1.569	74.6	88.2	88.2	134.0	133.0

Table 5. Calculated Bond Lengths (Å) for 11

	bond											
level	1,2	1,7	1,8	2,3	2,5	2,9	3,4	4,5	4,9	5,6	5,8	6,7
MP2/6-31G(d,p)	1.546	1.542	1.571	1.566	1.546	1.557	1.542	1.568	1.578	1.530	1.576	1.565
MP2/6-311++G(d,p)	1.550	1.547	1.576	1.566	1.556	1.563	1.549	1.574	1.585	1.532	1.582	1.571
Becke3LYP/6-31G(d,p)	1.556	1.550	1.583	1.568	1.547	1.540	1.550	1.576	1.588	1.540	1.583	1.575

Table 6. Selected Calculated Bond Angles (deg) for 11

	angle				
level	1,2,5	5,2,3	5,2,9	1,2,3	1,2,9
MP2/6-31G(d,p)	84.1	88.2	88.8	128.9	143.6
MP2/6-311++G(d,p)	84.1	88.1	88.7	128.9	143.5
Becke3LYP/6-31G(d,p)	84.1	88.5	89.1	128.8	143.8

very close to the limiting case with their respective three neighbors lying approximately in a plane with the corresponding bridgehead atom. The strongest, however small, departure from planarity (i.e., the most pronounced inverted character of the bridgehead atoms) should exhibit [1.1.1]geminane **5**. Thus, our earlier predictions based on a primitive molecular mechanics model with the MM2 parametrization (developed for standard hydrocarbons)[11] were only qualitatively correct because those calculations yield much more pronounced inverted character of the bridgehead carbon atoms in the geminanes under study. However, the calculated configurations at the bridgehead carbon atoms are so unusual that the synthesis of these molecules seems worth pursuing.

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