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Alkaplanes: A Class of Neutral Hydrocarbons Containing a Potentially Planar Tetracoordinate Carbon[1]

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The possibility of designing molecules containing a planar tetracoordinate carbon atom, a task that requires overcoming an inherent preference for tetrahedral bonding in methane of about 550 kJ mol^{-1}, has been actively pursued for some considerable time.[2-12] Two approaches to achieving this goal have been employed. The first, which may be described as electronic, involves selecting substituents that will preferentially stabilize a planar disposition of bonds at carbon over the normal tetrahedral-like arrangement.[3-5] The alternative approach may be described as mechanical, the aim in this case being to achieve planarity at the target carbon atom by constraining the bonds through appropriate linkages.[6-11] The latter would seem to be the only viable approach for obtaining a *neutral saturated hydrocarbon* containing a planar tetracoordinate carbon atom, but success in this direction to date has been quite limited. We report in this communication the design and theoretical characterization of a new class of neutral saturated hydrocarbons, the *alkaplanes*, that contain a potentially planar tetracoordinate carbon atom. Examples are presented with near-planar carbons.[13]

We have tackled the problem with the aid of ab initio molecular orbital calculations,[14] carried out using the TURBOMOLE[15] and GAUSSIAN 92[16] programs. Structures and harmonic vibrational frequencies were obtained at the Hartree–Fock level with the STO-3G and 6-31G* basis sets.[17] Improved relative energies were obtained through calculations on the HF/6-31G* optimized structures using second-order Møller–Plesset perturbation theory (MP2/6-31G*), employing the frozen-core approximation.

None of the hydrocarbons studied previously that show bonding arrangements approaching planarity at one or more tetracoordinate carbons (e.g., **1**–**3**) have the symmetry which would even allow the *possibility* of planarity at the quaternary carbon atom.

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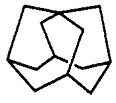

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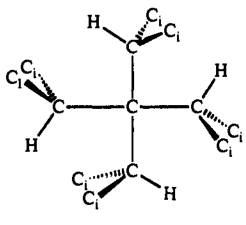
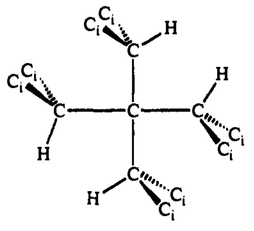
This would require a plane of symmetry containing the bonds at the quaternary carbon. Because the regions above and below the quaternary carbon in these molecules are different, planarity could only arise by accident or if the four attached carbon atoms are also planar tetracoordinate. Certainly the energy cost of the latter would be prohibitive.

Our design strategy is based on the skeletons **4** and **5** that *do* have the appropriate symmetry (C_{4h} and D_{2h}, respectively) to allow a planar disposition of bonds. Of course, the planar arrangement is not necessarily preferred. For example, if the four substituents are simply isopropyl groups, the molecule would be free to distort to a tetrahedral-type arrangement and undoubtedly does so. Our task, therefore, is to apply suitable constraints to the eight carbon atoms designated C_i in **4** and **5**.



4 (C_{4h})



5 (D_{2h})

In order to maintain the possibility of a planar tetracoordinate carbon in structures related to our basic skeletons **4** and **5**, we require the capping groups at the top and the bottom of structures **4** and **5** to be identical. Capping **4** by cyclobutane rings leads to **6**, which was found to be an equilibrium structure at HF/STO-3G but a second-order saddle point at HF/6-31G*; it is not discussed further here.

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[1] Presented in part at the Toronto International Conference on Reactive Intermediates, Toronto, Canada, July 1992.

[2] For reviews on this topic, see: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (c) Keese, R. *Nachr. Chem. Tech. Lab.* **1982**, *30*, 844. (d) Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399. (e) Agosta, W. C. In *The Chemistry of Alkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1992; Chapter 20.

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[12] We find total energies for planar and tetrahedral methane of −40.212 38 and −40.433 03 hartrees, respectively, leading to an energy difference of 579 kJ mol^{-1} at the QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* level. After incorporation of a scaled (by 0.93) MP2/6-31G* zero-point vibrational correction, the energy difference is 546 kJ mol^{-1}.

[13] Complete details will be reported in a subsequent full paper: McGrath, M. P.; Radom, L., to be published.

[14] For a description of the basis sets and theoretical methods used, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

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[17] Our 6-31G* calculations used five pure d functions rather than the set of six second-order Cartesian Gaussians of the standard 6-31G* basis set. The results are likely to be very similar to standard 6-31G* results.

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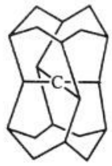

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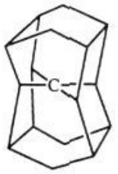

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More promising results are obtained when **4** is capped by crown cyclooctane rings, leading to **7** with the molecular formula $C_{21}H_{28}$. A (local) minimum energy structure with C_{4h} symmetry, i.e., containing an exactly planar tetracoordinate carbon atom, was found for **7** at HF/STO-3G. However, there is a lower energy structure corresponding to distortion to S_4 symmetry. At HF/6-31G*, the S_4 structure is the *only* local minimum found in this vicinity. The CCC angles at the quaternary carbon, which would be 180° for a planar carbon, are 168.8° in the HF/6-31G* structure (Figure 1). *This represents the closest approach to planarity for a tetracoordinate carbon atom in a neutral saturated hydrocarbon* reported to date.[18]

We suggest the name *octaplane* for **7**, reflecting the cyclooctane caps and the near-planar carbon. The systematic name is octacyclo$[9.7.1.1^{5,17}.1^{7,13}.0^{3,14}.0^{6,15}.0^{9,16}.0^{15,19}]$heneicosane. More generally, we suggest the name *alkaplanes* for the class of compounds formed by capping the potentially planar carbon arrangments in **4** and **5** with cycloalkanes. For example, if the capping groups in **5** are [2.2.1]bicycloheptane rings, we obtain the *biheptaplane* molecule.

Some of the more interesting structural features for octaplane (**7**), as calculated at HF/6-31G*, are shown in Figure 1. The C–C lengths are, at worst, only marginally longer than normal and are comparable to those determined experimentally for some of the fenestranes.[2d,e] This is certainly an encouraging first sign as to the stability of this molecule.[19]

The HF/6-31G* structure for *hexaplane* (**8**), constructed from **5** with boat cyclohexane capping groups, has D_2 symmetry and shows features around the quaternary carbon similar to those of octaplane, e.g., C–C bond lengths of 1.574 Å and CCC angles of 168.6°. However, the other C–C bonds range up to 1.632 Å in length.

It is interesting to note that despite the relatively small geometric distortions from planarity in **7** and **8**, the energy cost for achieving planarity in these molecules is moderately large at 70 and 68 kJ mol^{-1}, respectively (MP2/6-31G*//HF/6-31G*).

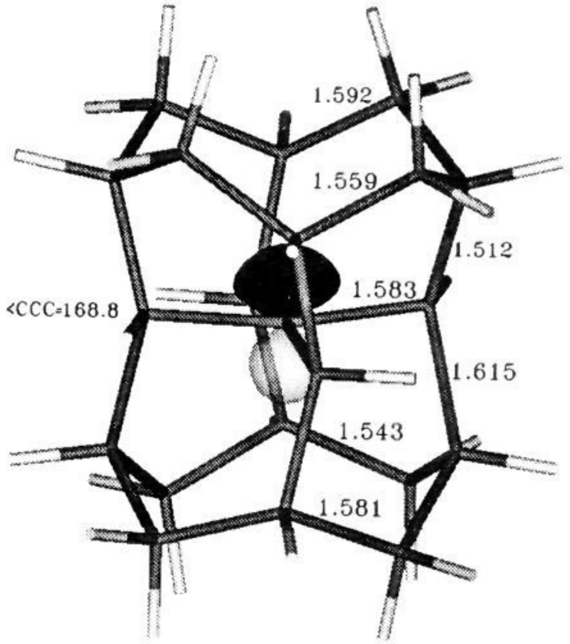

Figure 1. Selected structural features including CCC bond angle at the quaternary carbon (HF/6-31G*) and highest occupied molecular orbital for octaplane (**7**). Bond lengths in angstroms, bond angles in degrees.

Striking electronic features for octaplane (**7**) and hexaplane (**8**) are the highest occupied molecular orbitals (e.g., the 19b orbital of octaplane shown in Figure 1), which are basically lone pair orbitals localized on the quaternary carbon atoms. Intriguingly, these lone pairs lie within the cage formed by the remaining carbon atoms, a feature that may have interesting consequences on some of the chemical properties of these and other alkaplanes.

In summary, we have identified alkaplanes as a class of neutral saturated hydrocarbons containing potentially planar tetracoordinate carbon atoms. We have characterized two examples with near-planar carbons, octaplane (**7**) and hexaplane (**8**), presenting ab initio predictions of some of their structural properties. The predictions that the bonds in **7** and **8** are only marginally longer than normal C–C bonds and their strain energies per carbon atoms are comparable to those of known strained hydrocarbons suggest that octaplane and hexaplane represent reasonable prospects for experimental observation. Calculations on a variety of additional alkaplanes are in progress.

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(18) CCC angles of 178° at the quaternary carbon have been reported[2c] from AM1 calculations on the highest energy isomer of [5.5.5.5]fenestrane. However, we obtain 163.6° for these angles at HF/6-31G*.

(19) In addition, the calculated strain energies per carbon atom in **7** and **8** (63 and 90 kJ mol^{-1}, respectively, at MP2/6-31G*) are comparable to those of known strained hydrocarbons.[11,13]