A neutral saturated hydrocarbon with a planar-tetracoordinate atom?

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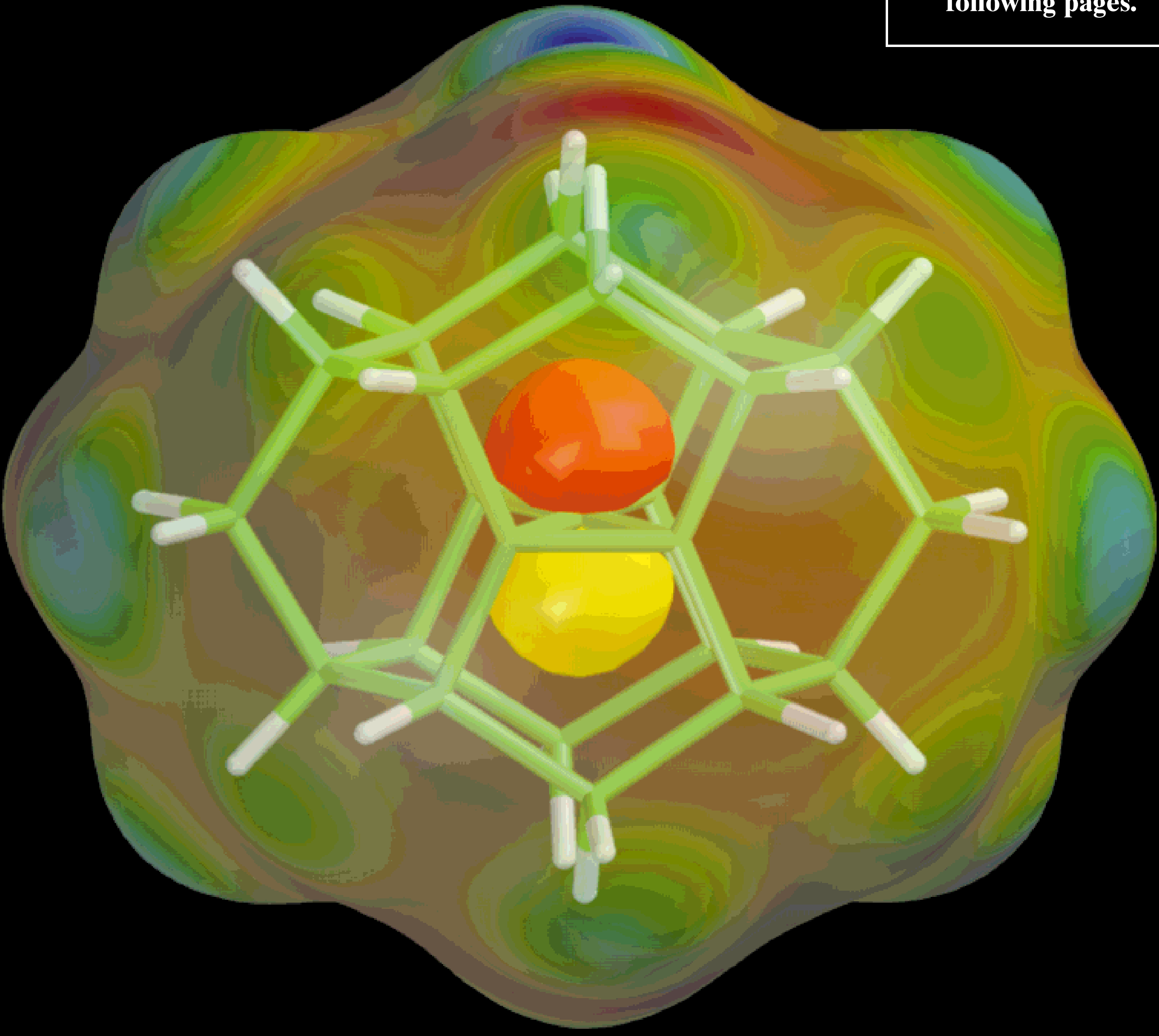


A saturated hydrocarbon with an ionization energy comparable to that of alkali metals?

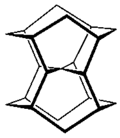
Planar-Tetracoordinate Carbon in a Neutral Saturated Hydrocarbon: Theoretical Design and Characterization**

Danne R. Rasmussen and Leo Radom*

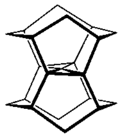
It is more than a century since van't Hoff and Le Bel independently concluded that the four bonds to tetracoordinate carbon in organic molecules are oriented in an approximately tetrahedral arrangement.[1] About 30 years ago, however, Hoffmann and co-workers[2] raised the question of whether it would be possible to design and synthesize compounds with a planar arrangement of bonds at tetracoordinate carbon. This has been achieved both theoretically[3] and experimentally[4, 5] in systems where the planar-tetracoordinate carbon atom has metal substituents. In contrast, as noted in a recent important paper by Keese et al.,[6] "despite considerable computational efforts no structures with a planar-tetracoordinate $C(C)_4$ substructure have been found."[7] We report here the design of the first neutral saturated hydrocarbon containing a planar-tetracoordinate carbon and its theoretical characterization through molecular orbital calculations.

Ab initio molecular orbital calculations[8] show that the energy cost of constraining the bonds at tetracoordinate carbon to be planar is enormously high.[9] For example, the lowest energy planar structure of methane is found to lie approximately 520 kJ mol^{-1} higher in energy than the normal tetrahedral form.[10] However, the energy needed to break the H_3C-H bond is approximately 100 kJ mol^{-1} lower than this. Clearly, methane will fall apart before it can be flattened. A similar situation is seen for the central carbon of neopentane,[10] where we estimate flattening to cost 880 kJ mol^{-1}. It appears that a very high energy difference between planar and tetrahedral geometries is the norm for tetracoordinate carbon in organic molecules. One important consequence of this high energy barrier is that it ensures that racemization of chiral compounds through planar bonding arrangements at carbon is generally energetically prohibitive, and this leads to preservation of enantiomeric integrity. As has been indicated previously,[2, 3, 5c, 9] the large energy penalty is a consequence of the unusual bonding arrangement for planar carbon, in which the highest occupied molecular orbital (HOMO) is a *p*-type lone pair of loosely bound electrons, leaving only six electrons to bind the four substituents.

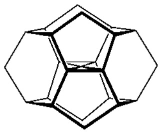
We have been interested in recent years in designing a neutral saturated hydrocarbon containing a planar-tetracoordinate carbon atom, the driving force necessarily being structural rather than electronic. Our strategy to achieve this end has been based on variants of the alkaplane family of molecules,[11] which may be described as strained hydrocarbon cage compounds. We have used ab initio molecular orbital calculations,[8] carried out with the Gaussian 94[12] and GAMESS programs,[13] to investigate the structures and properties of these molecules. The geometries of alkaplanes **1**–**5** were determined by optimization at the MP2 level using an enhanced 6-31G(d) basis;[14] energies were calculated at the MP2/6-311+G(2d,p) level.



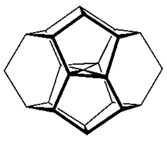
1 (S_4)



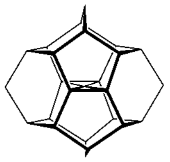
2 (D_2)



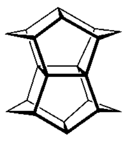
3 (D_{2h})



4 (D_2)



5 (D_{2h})



6 (D_{2h})

The simplest alkaplanes may be described in terms of an equatorial plane that contains the potentially planar quaternary carbon atom and is capped above and below by cycloalkane moieties (e.g. octaplane **1**).[11a] The angle δ between the bonds at the quaternary carbon atom and the best plane through that carbon atom is found to be 5.1° in octaplane, compared with 35.3° in a perfectly tetrahedral arrangement and 0.0° in an exactly planar arrangement. Thus, octaplane contains a nearly but not exactly planar tetracoordinate carbon atom.

Modification of the equatorial plane in octaplane by forming two new C–C bonds between opposite pairs of adjacent α-carbon atoms leads to spiro[2.2]octaplane (**2**)[10] with a δ angle of 3.1°. This indicates an even closer approach to planarity, but there is still some deviation from an exactly planar arrangement.

However, if the top and bottom caps in **2** are linked by methylene bridges, leading to dimethanospiro[2.2]octaplane (**3**), our calculations indicate that exact planarity at the central quaternary carbon atom is achieved. The calculated potential functions[15] corresponding to out-of-plane bending in **1**–**3** (Figure 1) show the clear progression from a distinctly nonplanar situation with a moderately large inversion barrier in **1** to exact planarity in **3**.[16] Compound **3** is the first neutral saturated hydrocarbon to be found either theoretically or experimentally to contain a planar-tetracoordinate carbon atom.

The optimized structure for **3** is displayed in Figure 2. This D_{2h} structure is verified by numerical frequency analysis using double differencing to be a minimum on the potential energy surface.[17] This calculation confirms that **3** indeed prefers an exactly planar bonding arrangement at the central carbon atom. An examination of the structure reveals that the longest

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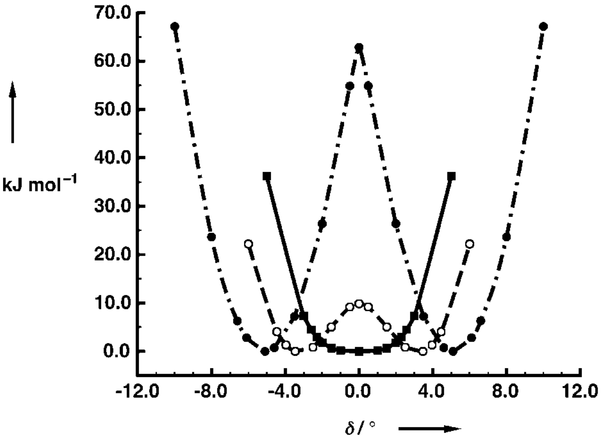

Figure 1. Calculated potential energy curves[15] describing the lowest mode for distortion from planarity at the central quaternary carbon atom. The relative energy E_{rel} [kJ mol^{-1}] is plotted against the angle of distortion from planarity δ [°] for octaplane (**1**, ●), spiro[2.2]octaplane (**2**, ○), and dimethanospiro[2.2]octaplane (**3**, ■).

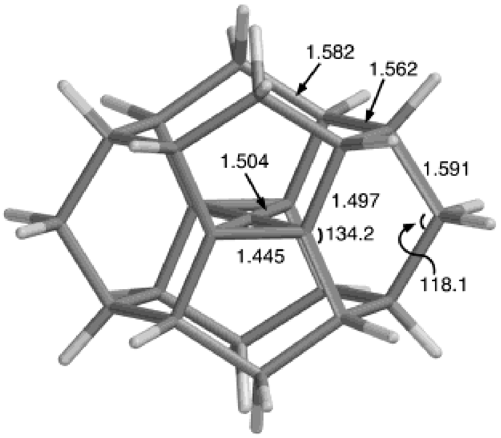

Figure 2. Calculated structure for **3** with bond lengths [Å] and angles [°].

C–C bonds are 1.582 and 1.591 Å. This suggests that there are no glaringly long C–C bonds, which might have reflected inherent instability in the molecule. In fact, the structure shows some correspondence to a synthetically known [4.4.4.5]fenestrane derivative that bears the most flattened tetracoordinate carbon atom (δ = 11.5°) observed experimentally in an organic molecule to date.[18] The internal bonds to the central carbon atom in this fenestrane system are about 1.50 Å, while some peripheral bonds are as long as 1.60 Å.

The fact that the calculated vibrational frequencies for **3** are all real shows that there are finite barriers to any decomposition mode. However, it does not indicate the size of these barriers. This would require explicit calculations of possible reaction pathways, which is a major undertaking for a system the size of **3**.[19, 20] We have nevertheless carried out a preliminary exploration of a number of the lowest vibrational modes of **3**. We find that, despite the high degree of strain particularly at the central carbon atom, **3** appears to lie in a relatively deep potential well.

We have examined structures for two other members of the dimethanospiroalkaplane family, dimethanospiro[2.2]bioctaplane (**4**) and dimethanospiro[2.2]binonaplane (**5**). Both molecules are closely related to **3** but may prove more accessible synthetic targets. The bioctaplane **4** is particularly interesting because of its similarity to pagodane (**6**), a well-known cage hydrocarbon involved in the synthesis of dodecahedrane from isodrin.[21] Our calculations indicate that **4** is slightly nonplanar at the central carbon atom (δ = 2.2°), with a difference in energy between the planar and tetrahedral forms of only 4.4 kJ mol^{-1}. On the other hand, the binonaplane **5** is found, according to a potential curve analysis like that used for **3**, to contain an exactly planar tetracoordinate carbon atom, as does **3**, and has the advantage from a synthetic point of view of not containing any eight-membered rings.

The HOMO of **3** is predominantly a *p*-type lone pair orbital at the central quaternary carbon atom, which is surrounded by the hydrocarbon cage (Figure 3). As a consequence, **3**, like the simpler members of the alkaplane family **1**[11] and **2**,[10] has an extremely low predicted ionization energy[22] of about 5 eV, which is comparable to that of the alkali metals lithium (5.39 eV) and sodium (5.14 eV). Our calculations suggest in addition that the electron is removed from the central atom with little change to the surrounding cage, thus protecting the ionized atom in a lipophilic sphere.

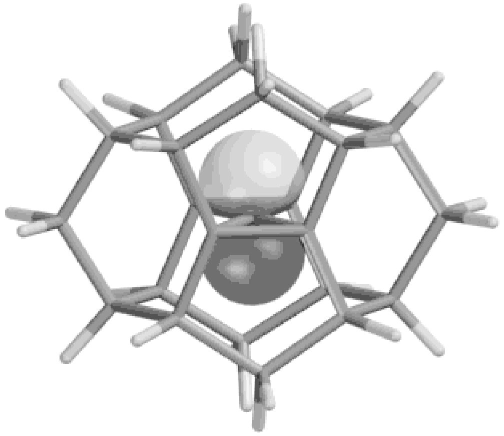

Figure 3. An isosurface of the HOMO of **3** (0.08 e Å^{-3}).

The unusual bonding at the central planar-tetracoordinate carbon atom in **3** gives rise to a new organic moiety which can be expected to have remarkable properties and functions. Advantage might be taken in this respect of the unique combination of metallike properties (such as readily ionizable electrons) and organic properties (such as strong covalent bonding, which helps preserve integrity). We hope that such considerations will add impetus to attempts to synthesize dimethanospiro[2.2]octaplane (**3**).

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[1] a) J. H. van't Hoff, *Arch. Neerl. Sci. Exactes Nat.* **1874**, *9*, 445–454; English translation: J. H. van't Hoff in *Classics in the Theory of Chemical Combinations*, *Vol. I* (Ed.: O. T. Benfey), Dover, New York, **1963**, pp. 151–160; b) J. A. Le Bel, *Bull. Chim. Soc. Fr.* **1874**, *22*, 337–

347; English translation: J. A. Le Bel in *Classics in the Theory of Chemical Combinations*, *Vol. I* (Ed.: O. T. Benfey), Dover, New York, **1963**, pp. 161–171.

[2] a) R. Hoffmann, R. Alder, C. F. Wilcox, Jr, *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993; b) R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181–194.

[3] See, for example, a) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. von R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419–5427; b) K. Krogh-Jesperson, D. Cremer, D. Poppinger, J. A. Pople, P. von R. Schleyer, J. Chandrasekhar, *J. Am. Chem. Soc.* **1979**, *101*, 4843–4851; c) K. Sorger, P. von R. Schleyer, *J. Mol. Struct. Theochem.* **1995**, *338*, 317–346.

[4] See, for example, a) F. A. Cotton, M. Millar, *J. Am. Chem. Soc.* **1977**, *99*, 7886–7891; b) H. Dietrich, W. Mahdi, W. Storck, *J. Organomet. Chem.* **1988**, *349*, 1–10; c) S. Harder, J. Boersma, L. Brandsma, A. van Heteren, J. A. Kanters, W. Bauer, P. von R. Schleyer, *J. Am. Chem. Soc.* **1988**, *110*, 7802–7806; d) S. L. Buchwald, E. A. Lucas, W. M. Davies, *J. Am. Chem. Soc.* **1989**, *111*, 397–398; e) S. T. Chacon, M. H. Chisholm, K. Folting, J. C. Huffman, M. J. Hampden-Smith, *Organometallics* **1991**, *10*, 3722–3735; f) A. D. Horton, A. G. Orpen, *Angew. Chem.* **1992**, *104*, 912; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 876–878.

[5] See also a) M. Albrecht, G. Erker, C. Krüger, *Synlett* **1993**, 441–448; b) R. Gleiter, I. Hyla-Kryspin, S. Niu, G. Erker, *Angew. Chem.* **1993**, *105*, 753; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 754–756; c) D. Röttger, G. Erker, *Angew. Chem.* **1997**, *109*, 840–856; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 813–827; d) J. Schottek, G. Erker, R. Fröhlich, *Eur. J. Inorg. Chem.* **1998**, 551–558.

[6] B. W. Ding, R. Keese, H. Stoeckli-Evans, *Angew. Chem.* **1999**, *111*, 387–388; *Angew. Chem. Int. Ed.* **1999**, *38*, 375–376.

[7] For representative studies, see a) K. B. Wiberg, *Tetrahedron Lett.* **1985**, *26*, 5967–5970; b) W. C. Agosta in *The Chemistry of Alkanes and Cycloalkanes* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1992**, pp. 927–962; c) M. Thommen, R. Keese, *Synlett* **1997**, 231–240.

[8] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

[9] a) M. S. Gordon, M. W. Schmidt, *J. Am. Chem. Soc.* **1993**, *115*, 7486–7492; b) M. J. M. Pepper, I. Shavitt, P. von R. Schleyer, M. N. Glukhovtsev, R. Janoschek, M. Quack, *J. Comput. Chem.* **1995**, *16*, 207–225.

[10] Detailed results and more extensive references will be published elsewhere: D. R. Rasmussen, M. P. McGrath, L. Radom, unpublished results.

[11] a) M. P. McGrath, L. Radom, *J. Am. Chem. Soc.* **1993**, *115*, 3320–3321; b) J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, *Angew. Chem.* **1994**, *106*, 1722; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1667–1668.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision E.2*, Gaussian, Inc., Pittsburgh PA, **1995**.

[13] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, Jr., *J. Comput. Chem.* **1993**, *14*, 1347–1363.

[14] With the 6-31G(d) basis, we have used five pure d functions rather than the usual six cartesian functions. Detailed calculations on model systems (methane, neopentane, and spiropentane) indicate that the binding at the central $C(C)_4$ substructure is not well described by small basis sets.[10] In particular, we find that diffuse functions on the central atom significantly lower the relative energies of the planar versus the tetrahedral species. The 6-311+G(2d,p) basis was found to be the smallest basis set which adequately approaches the basis set limit for this energy difference. As might have been expected, calculations on alkaplanes indicate that the full 6-311+G(2d,p) basis can be well approximated by using a 6-31G(d) basis which is enhanced to 6-311+G(2d) level at the central carbon atom and to the 6-311+G(d) level at the four α-carbon atoms, thus significantly reducing the size of the calculations. Optimization in the full 6-311+G(2d,p) basis (765 basis functions for **3**) is beyond our current computational resources.

[15] Energies for the potential functions were calculated at the MP2/6-311+G(2d,p) level using the full 6-311+G(2d,p) basis on all atoms. Geometries were optimized at the HF/6-31G(d) level.

[16] Calculations at the B3-LYP/6-311+G(3df,2p) level predict a double-well potential for **3**, but with a barrier of just 0.1 kJ mol^{-1}.

[17] This 435 basis function calculation took 32000 node hours on a Cray T3E at the CEWES High Performance Computing Center! D. R. Rasmussen, M. S. Gordon, L. Radom, unpublished results.

[18] V. B. Rao, C. F. George, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1985**, *107*, 5732–5739.

[19] A noteworthy potential decomposition pathway involves opening of the central spiropentane unit to give allene- and ethylene-type moieties.[20] However, it would seem difficult for this to occur within the extremely rigid constraints of the cage system.

[20] a) R. Herges, personal communication; b) R. Herges, *Angew. Chem.* **1994**, *106*, 261; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 255–276.

[21] H. Prinzbach, K. Weber, *Angew. Chem.* **1994**, *106*, 2329; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2239–2257, and references therein.

[22] Ionization energies for the alkaplanes **1**–**3** were obtained at the RMP2/6-31G(d)//RHF/6-31G(d) level and found to be 4.6, 4.3, and 4.2 eV, respectively. Test calculations on molecules where experimental data are available suggest that ionization energies calculated at this level of theory are generally underestimated by about 0.3–0.7 eV.[11b]

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meso Myths: What Drives Assembly of Helical versus *meso*-[M_2L_3] Clusters?[**]

Jide Xu, Tatjana N. Parac, and Kenneth N. Raymond[*]

Metallohelicates are the simplest supramolecular structures formed by the self-assembly of metal centers and bridging ligands.[1, 2] With each metal center viewed as a polyhedral vertex, metallohelicates [M_2L_3] are two-vertex structures. Currently the scope and power of the supramolecular chemistry of metal coordination compounds is being explored, particularly with regard to the selective preparation of more complex architectures based on the structures containing multiple vertices.[3]

Triple helicates of M_2L_3 stoichiometry may be formed by bridging bis-bidentate ligands bound to two octahedral metal centers. This generates chiral (Λ or Δ) metal centers.[2] If there is mechanical coupling between the two centers, the chirality at one can be transmitted to the second, thereby generating the homochiral ($\Lambda\Lambda$ or $\Delta\Delta$) helicate. The magnitude of this coupling has been measured in one case.[4] In contrast, the

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