

The planar carbon story

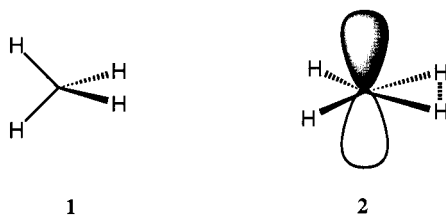
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Abstract: The events leading up to the design and characterization, through *ab initio* molecular orbital calculations, of dimethanospiro[2.2]octaplane, the first neutral saturated hydrocarbon containing a planar tetracoordinate carbon atom, are described. Dimethanospiro[2.2]octaplane is predicted to have bond lengths that are all less than 1.60 Å and a strain energy per carbon (46 kJ mol⁻¹) that is considerably less than that of cubane. These are both pointers to its likely stability. The calculated ionization energies of octaplane, spiro[2.2]octaplane and dimethanospiro[2.2]octaplane (4–5 eV) are comparable to those of the alkali metals, lithium and sodium, and the cations of these molecules are all found to contain planar tetracoordinate carbon atoms. Hemi-spiro[2.2]octaplane is found to have a proton affinity (1213 kJ mol⁻¹) greater than that of “proton sponge”. Several of these species are suggested as attractive synthetic targets.

INTRODUCTION

Attempts to design molecules containing a planar tetracoordinate carbon atom have been pursued for nearly 30 years since the initial seminal work on the subject by Hoffmann and coworkers.[†] Hoffmann wrote that “attempts to subvert something as basic to organic chemistry as the tetrahedral tetracoordinate carbon atom should perhaps be viewed as acts appropriately described by the Yiddish word *chutzpah* and/or the Greek word *hubris*. Nevertheless, in some recent work with R. Alder and C.F. Wilcox, this is precisely what we set out to do.” However, they cautioned that “it would seem too much to hope for a simple carbon compound to prefer a planar to a tetrahedral structure.” There is good reason for caution since making tetracoordinate carbon planar is energetically very expensive.^{1–4} For example, there is a cost of about 530 kJ mol⁻¹ involved in making methane planar (i.e. **1** → **2**)!⁴ So the task is certainly not trivial.



Over the years, two discrete approaches have been employed in attempts to achieve the goal of planar tetracoordinate carbon. The first, which may be described as electronic,^{1,5–9} involves selecting substituents that will preferentially stabilize a planar disposition of bonds at carbon over the normal tetrahedral arrangement. This approach can take advantage of the fact that planar carbon has a lone pair orbital as its highest occupied molecular orbital. It thus has two π electrons and is therefore π -electron rich. With only six electrons remaining to form the four in-plane σ bonds, it is σ -electron poor. It will therefore be stabilized by π -electron-accepting substituents and σ -electron-donating substituents. In addition, because the angles at a planar carbon are smaller than those at tetrahedral carbon, incorporation of the target carbon atom into a small ring is also favorable.

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In a landmark 1976 paper, Schleyer, Pople and co-workers⁵ took up the challenge of creating planar tetracoordinate carbon using the electronic approach. They examined theoretically a number of lithio- and bora- substituted systems and found the remarkable result that in several cases, including 1,1-dilithiocyclopropane and 3,3-dilithio-1,2-diboracyclopropane, a planar structure is predicted to actually lie lower in energy than the tetrahedral-type structure.

Designing a *neutral saturated hydrocarbon* containing a planar tetracoordinate carbon requires a different approach which 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 rings and cages.¹⁰⁻²² A well-known postulated example is [4.4.4]fenestrane.^{12,15} Although molecules with significant deviations from the normal tetrahedral arrangement at carbon have been constructed in this manner, they are still a long way from being completely planar.

Over the past six years, we have taken up the challenge of designing a neutral saturated hydrocarbon containing a planar tetracoordinate carbon atom. The events along the way and the successful outcome culminating in the identification of dimethanospiro[2.2]octaplane are described in this presentation.

METHODS

The method that we employ is *ab initio* molecular orbital theory.²³ The *ab initio* procedures, being non-empirical, are particularly well suited for examining molecules with unusual bonding characteristics, such as those that might occur in our planar carbon targets. Because the systems that we are dealing with are moderately large by *ab initio* standards (20–30 carbon atoms and more than that many hydrogens), we have used relatively modest levels of theory, namely, Hartree-Fock and MP2 theory with basis sets ranging from 6-31G(d) to 6-311+G(2d). Unless otherwise noted, structural parameters in the text refer to HF/6-31G(d) values and energies to MP2/6-31G(d)//HF/6-31G(d) values.

What we are doing could be regarded as an example of "designer chemistry" which represents an increasingly important application of theory these days. We ask the question: can we use the computer calculations to design new molecules? In the present case, we are designing a characteristic structure. It is likely that theory will increasingly be used to design new pharmaceutical products, new materials and so on.

Theory is ideal to use in this design mode. For example, in the present study, we might need to carry out calculations on a large set of possible target molecules before finding the molecule that contains a planar tetracoordinate carbon – *if* we happen to be successful. We are then in a position to suggest the best *single* target for organic synthesis and characterization. It would be much tougher to do this all experimentally, i.e. to synthesize many of these molecules. Synthesizing just one of them is a sufficient challenge!

DISCUSSION

Symmetry Considerations

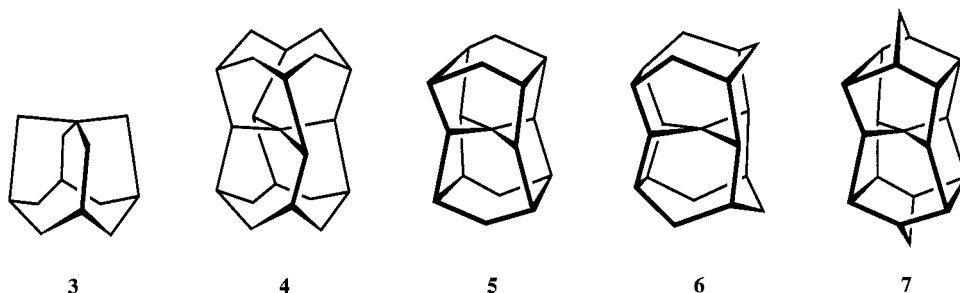
Our initial work in this area was concerned with the bowlane molecule (**3**).^{19,21} Unfortunately this molecule, like the paddlanes^{15,18,20,24} and fenestranes¹⁰⁻¹⁷ before it, does not have the correct symmetry to allow an exactly planar carbon. In order to permit exact planarity, the molecule must allow the possibility of having a plane of symmetry that passes through the target carbon atom and contains the four bonds that are required to be coplanar. Unless this possibility exists, symmetry does not permit exact planarity. This clearly does not hold for bowlane, nor for the fenestranes or paddlanes. Such molecules cannot achieve exact planarity at the central carbon.

Alkapanes

Our design strategy has been based on systems that *do* have the correct symmetry (e.g. **4–7**). They are characterized by having an equatorial plane containing the target carbon atom and capping groups at the

top and the bottom of the structure that are required to be identical. We have called this family of molecules *alkaplanes*,²² reflecting the cycloalkane caps and the potentially planar carbon.

Our most promising initial results were obtained for octaplane (4), with molecular formula $C_{21}H_{28}$, in which the capping groups are crown cyclooctane rings. The HF/6-31G(d) structure of octaplane has S_4 symmetry with $\angle CCC$ angles at the central carbon of 168.8° (see Figure 1). In an exactly planar form, the $\angle CCC$ angle would be 180° while for a tetrahedral carbon the angles are 109.5° . So with an angle of 168.8° , octaplane is not far from containing a planar carbon atom. However, despite the fact that the bonds at the quaternary carbon are each only 5.6° from the equatorial plane, the potential function for inversion at the quaternary carbon of octaplane indicates that there is quite a large barrier to inversion through the planar C_{4h} structure of about 70 kJ mol^{-1} at MP2/6-31G(d)//HF/6-31G(d).



Having found that octaplane (4) does not contain a fully planar carbon atom, we examined other alkaplanes including hexaplane (5), heptaplane (6) and biheptaplane (7). Somewhat surprisingly, the alkaplanes have structures that are all very similar, with $\angle CCC$ angles all in the vicinity of 168° . In some respects this is a disappointing result. It would seem that we cannot reach planarity simply by adjusting the caps. We need to try something else.

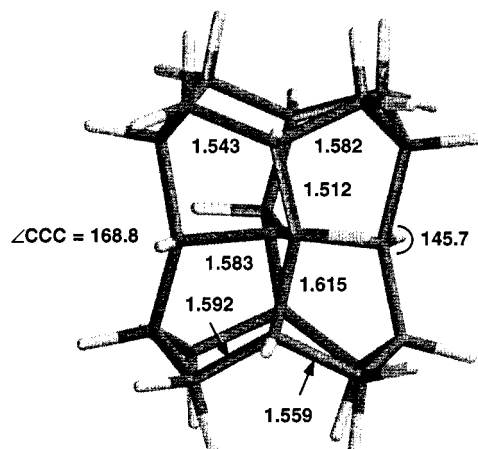


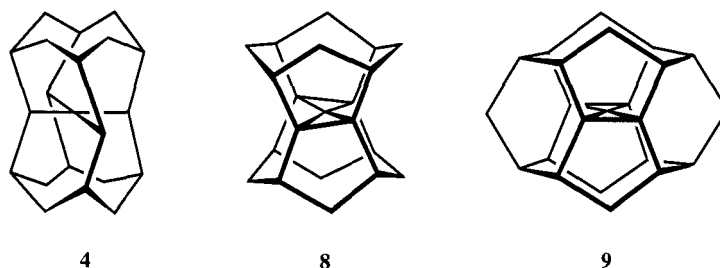
Figure 1. HF/6-31G(d) optimized structure of octaplane (4). Bond lengths are in Ångstrom, angles are in degrees.

Spiroalkaplanes

Linking up pairs of atoms in the equatorial plane, leading to the family of spiroalkaplanes, was our next structural variation.⁴ This set of molecules is exemplified by spiro[2.2]octaplane (8) which is closely related to octaplane (4) and basically consists of a flattened spiropentane moiety, capped at the top and the bottom by crown cyclooctane units.

The optimized geometry for spiro[2.2]octaplane (Figure 2) has D_2 symmetry. There are two notable features about this molecule that should be pointed out. In the first place, it is more flattened at the quaternary carbon atom than octaplane. The $\angle CCC$ angle is 172.1° compared with 168.8° in octaplane. The other striking feature is that the longest bond is just 1.572 \AA in length.²⁵ Spiro[2.2]octaplane appears to be a very respectable molecule.

The potential function for inversion in spiro[2.2]octaplane shows a barrier of just 11 kJ mol^{-1} . The large drop in the barrier from 70 kJ mol^{-1} in octaplane to 11 kJ mol^{-1} in spiro[2.2]octaplane is very striking.



We are now very close to planarity but are still not there yet. The best alkaplanes have out-of-plane angles of about $5\text{--}6^\circ$ and barriers to planarity of about $60\text{--}70 \text{ kJ mol}^{-1}$. The best spiroalkaplanes have out-of-plane angles of $3\text{--}4^\circ$ and barriers to becoming planar of $8\text{--}12 \text{ kJ mol}^{-1}$. How do we nudge the systems a little further and achieve an even closer approach to exact planarity?

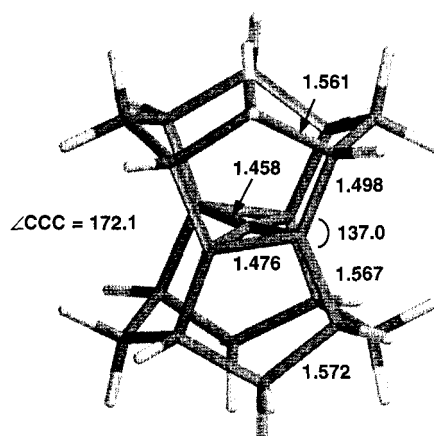


Figure 2. HF/6-31G(d) optimized structure of spiro[2.2]octaplane (8). Bond lengths are in ångstrom, angles are in degrees.

Dimethanospiroalkaplanes

The next thing that we tried was to strap the caps at the top and bottom with methano bridges.²⁶ This leads us to dimethanospiro[2.2]octaplane (9). Does this get us closer to planarity? The answer is a resounding yes! When we calculate the MP2/6-31G(d) potential curve at HF/6-31G(d) structures, as before, the $\angle CCC$ angle increases to 177.6° . Figure 3 shows the dramatic decrease in the barrier to planarity as we go from octaplane (70 kJ mol^{-1}) to spiro[2.2]octaplane (about 10 kJ mol^{-1}) to dimethanospiro[2.2]octaplane (0.3 kJ mol^{-1}).

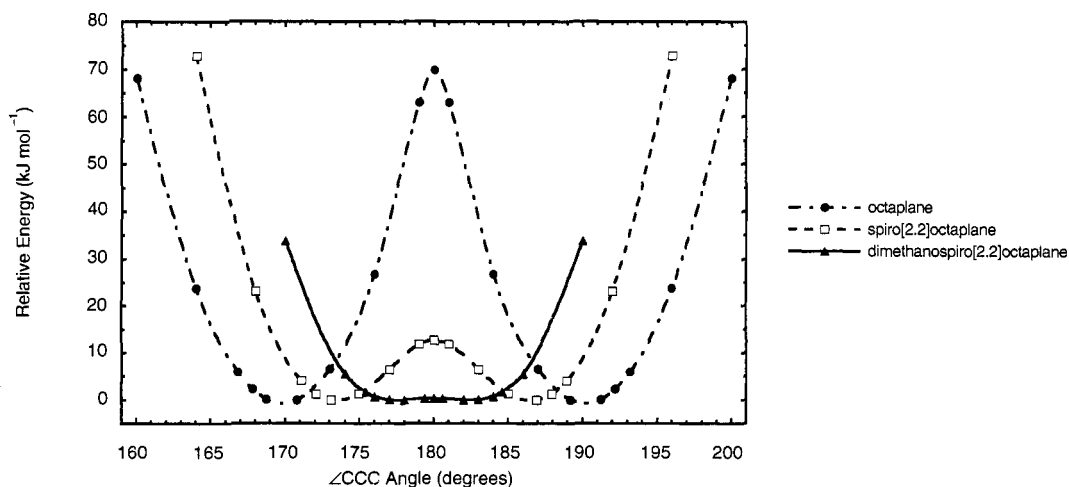


Figure 3. Inversion potentials for octaplane (4), spiro[2.2]octaplane (8) and dimethanospiro[2.2]octaplane (9) at the MP2/6-31G(d)//HF/6-31G(d) level. Structures were fully optimized on the HF/6-31G(d) surface at constrained values of the $\angle CCC$ angle (made by opposing α carbon atoms with the central atom).

We decided that dimethanospiro[2.2]octaplane looked sufficiently promising to warrant carrying out better calculations, namely MP2 calculations with a larger basis set. Specifically, we used 6-311+G(2d) on the central carbon, 6-311+G(d) on the α carbons and 6-31G(d) elsewhere — a total of 415 basis functions.

Full MP2 optimization of the planar structure with this enhanced basis set yields the beautifully symmetric (D_{2h}) structure shown in Figure 4. All the bond lengths have reasonable values, the longest being 1.591 Å, which is an encouraging sign for the possible synthesis of this molecule.²⁵

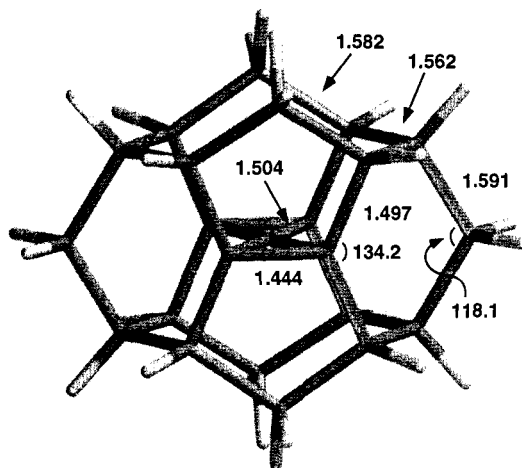


Figure 4. MP2 optimized structure of dimethanospiro[2.2]octaplane (9) using an enhanced 6-31G(d) basis set (see text). Bond lengths are in ångstrom, angles are in degrees.

Demonstrating rigorously whether our molecule corresponds to a stable structure requires the calculation of vibrational frequencies. If all the frequencies are real, then we are at a true minimum. If one or more frequencies are imaginary, then we are at a first-order or higher-order saddle point on the surface. At the MP2 level this is a massive computational task but this calculation has recently been carried out with the

enhanced 6-31G(d) basis set by Gordon.²⁷ It took 256 hours on 128 nodes of a Cray T3E Supercomputer, equivalent to 32,768 hours on a single processor of this computer ... about 3.7 years. It is indeed a very big calculation!

This giant calculation shows that all the frequencies of dimethanospiro[2.2]octaplane are real! The result confirms the planarity at the central carbon. Dimethanospiro[2.2]octaplane is thus the *first neutral saturated hydrocarbon containing a planar tetracoordinate carbon atom*.

We have calculated strain energies using the method of homodesmotic reactions.^{4,28} The results show that, although the absolute values of the strain energies in octaplane, spiro[2.2]octaplane and dimethanospiro[2.2]octaplane are quite high, this strain is shared among many carbon atoms. So the strain energy per carbon is quite low, particularly for spiro[2.2]octaplane (41 kJ mol⁻¹) and dimethanospiro[2.2]octaplane (46 kJ mol⁻¹). These values compare very favorably with that for cubane (86 kJ mol⁻¹) which is of course a stable molecule. So this is again very encouraging.

Alkaplane Cations

A striking electronic feature of dimethanospiro[2.2]octaplane (as well as octaplane and spiro[2.2]octaplane) is the highest occupied molecular orbital (HOMO). This has b_{2u} symmetry and is essentially a lone pair on the quaternary carbon that lies within the cage formed by the remaining carbon atoms (Figure 5). The HOMO lone pair is of course in keeping with the HOMO of planar methane (2).

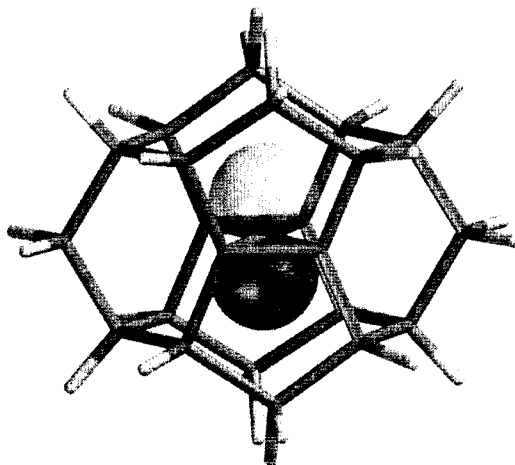


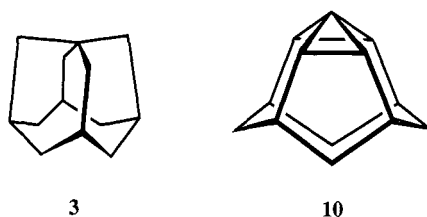
Figure 5. Highest occupied molecular orbital (HOMO) of dimethanospiro[2.2]octaplane (9) shown at the $0.08 e\text{\AA}^{-3}$ iso-surface.

One immediate consequence of the HOMO lone pair is that the ionization energy of dimethanospiro[2.2]octaplane might be expected to be particularly low. Indeed, our calculated MP2/6-31G(d)//HF/6-31G(d) + ZPVE value is just 4.6 eV. For comparison, the value for a typical paraffin such as *n*-decane is 9.6 eV. The lowest value for a saturated hydrocarbon recorded in a recent compendium²⁹ is 7.1 eV for tetra-*tert*-butyltetrahedrane. Indeed, the predicted ionization energy of dimethanospiro[2.2]octaplane is even slightly lower than the experimental values for the alkali metals lithium and sodium (5.39 and 5.14 eV, respectively)! Comparably low ionization energies of around 4.5 to 5 eV are predicted for octaplane and spiro[2.2]octaplane.

The cations of octaplane, spiro[2.2]octaplane and dimethanospiro[2.2]octaplane are all predicted to contain planar carbon atoms. This is also unprecedented. Indeed, we have recently reported octaplane cation as the first singly-charged saturated hydrocarbon to contain a planar tetracoordinate carbon.³⁰

Hemialkapanes

A feature of the alkapanes, spiro[2.2]alkapanes and dimethanospiro[2.2]alkapanes is the lone pair HOMO which, as noted above, leads to ionization energies that are exceptionally low and comparable to those of alkali metals. The HOMO lone pair might in principle have led to these molecules also being very basic, i.e. to have very high proton affinities. However, the caps on the top and bottom of the cage are likely to protect the lone pair and impede protonation. We have therefore removed one of the caps, generating so-called hemialkapanes and hemispiro[2.2]alkapanes (e.g. **3** and **10**), with a view to determining their proton affinities.³¹



A picture of hemispiro[2.2]octaplane showing the highest occupied molecular orbital is displayed in Figure 6. It really looks like an orbital that should be readily protonated, so we might expect hemispiro[2.2]octaplane to have a high proton affinity.

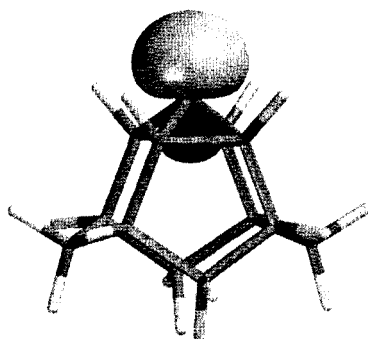


Figure 6. Highest occupied molecular orbital (HOMO) of hemispiro[2.2]octaplane (**10**) shown at the $0.08 e\text{\AA}^{-3}$ iso-surface.

The calculated proton affinity for hemispiro[2.2]octaplane of 1213 kJ mol^{-1} (MP2/6-31G(d)//HF/6-31G(d) + ZPVE) is indeed remarkably high. It is in fact higher than that for the well-known “proton sponge” (1,8-bis(*N,N*-dimethylamino)naphthalene) (1012 kJ mol^{-1}), which has the greatest proton affinity of any molecule in a recent compendium.³²

CONCLUSIONS

Our results to date show that the alkapanes, spiro[2.2]alkapanes and dimethano[2.2]spiroalkapanes are exciting families of molecules. Most importantly, dimethanospiro[2.2]octaplane is the first neutral saturated hydrocarbon to contain a planar tetracoordinate carbon atom. All the alkaplane variants contain a lone pair in a cage, leading to ionization energies that are comparable to those of alkali metals. The alkaplane cations all contain planar tetracoordinate carbon atoms at their centers. And the hemialkapanes have proton affinities that are greater than that of “proton sponge”. We are encouraged by the various results from our calculations – the reasonable bond lengths and strain energies – to believe that some of these species may well be synthesizable. We consider that they are attractive synthetic targets.

ACKNOWLEDGEMENTS

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