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Planar Tetracoordinate Carbon

Sir:

The tetracoordinate tetrahedral carbon has magnificently served biological systems for millions of years and our imaginations for but a century.[1] We here open the problem of stabilizing tetracoordinate planar carbon. It would seem too much to hope for a simple carbon compound to prefer a planar to a tetrahedral structure. Our more modest goal is to consider how to stabilize a planar geometry so that it could serve as a thermally accessible transition state for a classical racemization experiment.

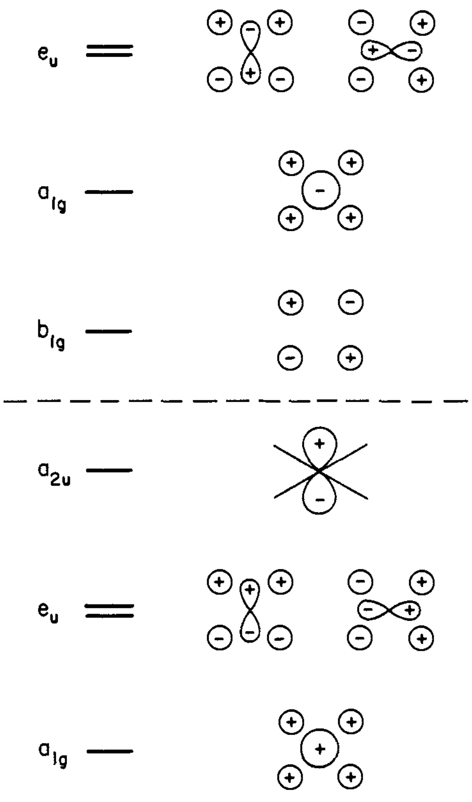

Figure 1. The molecular orbitals of planar methane. Levels below the dashed line are occupied. The representation of the e_u levels is of course not unique.

A rational procedure begins with an analysis of the electronic structure of planar methane. We form a normal set of sp^2 hybrids at the carbon. Two hybrids engage in normal two-electron two-center bonds with two hydrogens, using up two of the four carbon valence electrons. The third hybrid participates in a two-electron three-center bond[2] with the remaining two hydrogens. *This three-center bond utilizes only the hydrogen* electrons. The remaining two valence electrons of carbon are placed in the 2p orbital perpendicular to the molecular plane (**1**). Resonance among equivalent structures with different relative placement of three-center and two-center C–H bonds achieves equivalence of all hydrogens. Alternatively the molecular orbitals of planar CH_4 are shown in Figure 1.

1

The following characteristics of a planar methane emerge from either picture. (1) All C–H bonds are weaker than in tetrahedral methane. (2) Since the three-center bonding uses only H electrons there is considerable electron transfer from H to C. (3) The planar carbon atom possesses a pure 2p lone pair perpendicular to the molecular plane. (4) The transformation of tetrahedral to planar methane is a symmetry-allowed process for either a twisting ($T_d \rightarrow D_2 \rightarrow D_{4h}$) or a squashing ($T_d \rightarrow D_{2d} \rightarrow D_{4h}$) pathway.

An extended Hückel (EH) calculation[3] makes tetrahedral CH_4 more stable than a square-planar geometry with identical bond lengths of 1.10 Å by 5.5 eV. A CNDO[4] computation yields 8.1 eV for the same quantity. An approximate *ab initio* calculation[5] produces a barrier of 10.8 eV. To reduce lifetimes for racemization from eons to the experimentally accessible scale the planar geometry must be stabilized or the tetrahedral destabilized. The electronic structure of planar CH_4 suggests the ways in which stabilization may be achieved.

Delocalization of the lone pair may be accomplished by attaching substituents to carbon which are good electron acceptors, as in $C(CN)_4$. The planar–tetrahedral energy difference, ΔE, is reduced to 3.4 eV.[6] Alternatively we may incorporate the lone pair as part of a $4n + 2\pi$ electron system, as in the planar geometry of cyclopentadiene, **2**. ΔE for **2** is 4.2 eV[7] and the planar geometry is best described as a σ cation of an aromatic anion, **3**. In a model benzenonium ion **4**, ΔE is reduced to 2.9 eV. Substitution of H by less electronegative groups lowers ΔE still further—in $C(BH_2)_4$ to 1.8 eV, in $C(SiH_3)_4$ to 2.9 eV. In the latter case 3d orbitals on Si were included; Si then acts as a σ donor and π ac-

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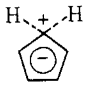

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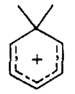

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[1] J. H. van't Hoff, "Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte strukuurformules in de ruimte," Utrecht, 1874; J. A. LeBel, *Bull. Soc. Chim. Fr.*, **22**, 337 (1874).

[2] W. N. Lipscomb "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 27.

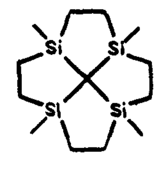
[3] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1963); *Tetrahedron*, **22**, 521, 539 (1966). A Slater exponent of 1.3 for hydrogen was used in the present work.

[4] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

[5] H. J. Monkhorst, *Chem. Commun.*, 1111 (1968). This calculation predicts approximately equal bond lengths in T_d and D_{4h} methane.

[6] This and all subsequent values of ΔE quoted are from extended Hückel calculations.

[7] The actual value could be lower. We did not optimize the position of the sterically hindered hydrogens in the planar geometry.



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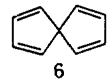
ceptor. The hypothetical molecule **5** combines these factors with destabilization of the tetrahedral form. Further favorable effects of an electronegativity differential are observed on Li substitution or replacement of C by N^+.[8]

New types of stabilization in planar systems with tetracoordinate carbon may be probed with standard Hückel calculations. Thus the neutral spirononatetraene **6** and the cations **7** and **8** in their planar geometries are stabilized 10-, 8-, and 10π-electron systems, respectively, superimposed on a positively charged σ core. Their highest occupied and lowest unoccupied MO's are at +0.62 and −0.62β for **6**, +0.37 and −1.00 for **7**, +0.62 and −0.29 for **8**. In an extended Hückel calculation on **7** we find the tetrahedral form favored by only 1.1 eV. Chiral derivatives of **6** are known but do not racemize readily;[9] in these cases benzo fusion makes worse the steric problems apparent in a planar geometry of **6**.



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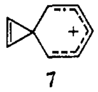

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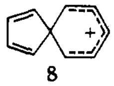

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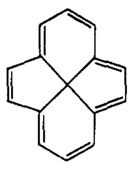
Still more promising systems are created when a central carbon atom is fused to an annulene perimeter. For example, the chiral molecules **9** and **10**, highly strained in their normal geometries, possess stable 16π-electron systems when planar. The porphyrin-like hydrocarbon **11** is also stabilized.[10]



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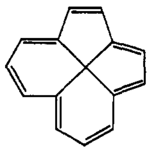

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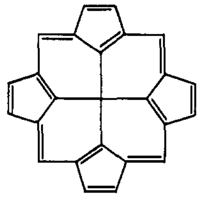

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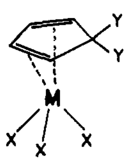
For further prospects we turn to model transition metal complexes for the type **12**, *e.g.*, M = Fe, X = CO.



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The cyclopentadiene is acting as a four-electron ligand. If the group X is modified or removed, so that a six-electron donor is needed to satisfy the electronic demands of M, there could occur a rotation of the CY_2 group to fulfill this requirement.

Acknowledgment. We are grateful to H. Wynberg for the stimulus to this work, to M. Gheorghiu for some preliminary studies, to P. Klosterman for help with the calculations, to W.-D. Stohrer for the suggestion of **4**, and to R. B. Woodward and C. Levin for discussions. This work was supported by the National Science Foundation (GP 8013, GP 6180) and the National Institutes of Health (GM 13468).

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[8] In any practical example a planar transition state for racemization must compete with pathways such as facilitated heterolytic or homolytic cleavage followed by recombination. The relative merits of the various mechanisms are, we feel, too delicate a question to evaluate given the available computational schemes. They must, of course, be considered in practice.

[9] Vespirenes: G. Haas and V. Prelog, *Helv. Chim. Acta*, **52**, 1202 (1969). The substituted achiral system **6** is also known: E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, **31**, 4260 (1966).

[10] As a preliminary criterion for stability we take the absence of nonbonding molecular orbitals, the occupation of only bonding orbitals, and the presence of a sizable gap between highest filled and lowest unfilled molecular orbitals. Criteria for stabilization may be derived (C. F. Wilcox, to be published); it suffices to say at this time that most likely candidates fail these tests. If we denote these molecules by the rings involved (for example **6** would be [5,5], **7** = [3,6], **9** = [5,6,5,6], **10** = [5,5,6,6]) then other stabilized species we have found are [5,3,5], [5,7,5], [5,6,7], [3,5,5,5], [3,5,6,5], and [5,6,6,6].

Preparation and Crystallographic Characterization of the $[B_9C_2H_{11}\cdot Co\cdot B_8C_2H_{10}\cdot Co\cdot B_8C_2H_{10}\cdot Co\cdot B_9C_2H_{11}{}^{3-}]$ Anion. A System with Four Fused Icosahedra

Sir:

We wish to report the preparation and crystallographic characterization of a fused polyhedral system which contains three formal d^6 Co(III) ions sandwich bonded to two $B_8C_2H_{10}{}^{4-}$ π-bidentate ligands and two π-monodentate $B_9C_2H_{11}{}^{2-}$ ligands which serve as chain caps (Figure 1).

Recently,[1,2] the complex ion $[B_9C_2H_{11}CoB_8C_2H_{10}CoB_9C_2H_{11}{}^{2-}]$ was reported to arise from the base degradation of the $(B_9C_2H_{11})_2Co^-$ ion in aqueous media. The new tricobaltate complex reported here has been isolated from among the products of this reaction. Details of the preparation and unusual chemical properties of this new complex ion will be reported elsewhere.

The tetraethylammonium salt, $[(C_2H_5)_4N^+]_3[B_9C_2H_{11}\cdot Co\cdot B_8C_2H_{10}\cdot Co\cdot B_8C_2H_{10}\cdot Co\cdot B_9C_2H_{11}{}^{3-}]$, crystallizes from an acetone–water solution as deep red parallelepipeds belonging to the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1, no. 2) with unit cell parameters a = 12.248, b = 26.733, c = 20.428 Å, α = 113.34, β =

[1] J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

[2] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969).