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THE [4.4.4.4] FENESTRANES AND [2.2.2.2] PADDLANE. PROSPECTS FOR THE REALIZATION OF PLANAR TETRACOORDINATE CARBON?

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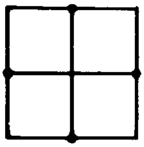
Summary. Semi-empirical (MINDO/3 and MNDO) MO calculations on highly strained planar tetracoordinate carbon candidates indicate the central carbons in cis-[4.4.4.4]fenestrane (1) to have pyramidal (1a) and in trans-[4.4.4.4]fenestrane (2) to have distorted tetrahedral (2a) geometries. In [2.2.2.2]paddlane (3), the two central carbons are pentacoordinate. Each is nearly coplanar with four carbon neighbours; additionally, the two bridgehead carbons are connected by a single bond (3a).

How might planar tetracoordinate carbon geometries be achieved in molecules containing only carbon and hydrogen? Strained polycyclic compounds with extreme angular distortions, such as the "fenestranes" (1 and 2)[1,2] and [2.2.2.2]paddlane (3),[2,3] have been suggested as possibilities. It is much easier to gain information about the structures and energies of such molecules calculationally than experimentally.[4] The strain energies of 1-3 may be too high for their syntheses ever to be achieved. The Table summarizes the heats of formation and strain energies of 1-3 and of the D_{4h} and C_{4v} distortions of methane, calculated by the semi-empirical MINDO/3[5] and MNDO[6] methods.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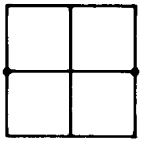
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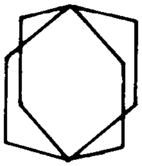
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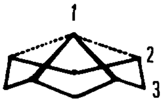
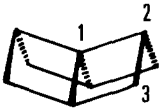
Two stereochemical forms of [4.4.4.4]fenestrane are of interest.[2] All cis 1 is calculated to prefer C_{4v} symmetry (1a) with the central carbon having pyramidal coordination.
Such pyramidal distortions of tetracoordinate carbon are known to be be preferred energetically over planar D_{4h} arrangements.[4,7] Of course, tetrahedral geometries are a great deal more favorable![4] The long C_1-C_2 bonds involving the pyramidal carbon in 1a, 1.60 Å, are noteworthy. Otherwise, the calculated geometry is unexceptional. Any flattening of the central carbon in 1a is strongly resisted energetically.

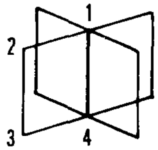
The all trans isomer, **2**, might achieve a square planar geometry (**2b**) at the central carbon. Instead, our calculations indicate a distorted tetrahedral arrangement (**2a**) to be strongly preferred. If planarity at the central carbon (**2b**) is imposed calculationally, the MNDO energy increases by nearly 200 kcal/mol!



1a



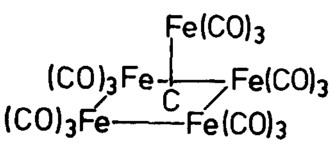
2a



3a

Which isomer, cis **1a** or trans **2a**, is more stable? The two calculational methods do not agree (Table), but there is no doubt that the large strain energies in these molecules (Table), resulting in high reactivity, would present formidable obstacles to their experimental realization. Neither **1a** nor **2a** can be expected to have a planar tetracoordinate carbon.

In this last respect, [2.2.2.2]paddlane (**3**) is a much better prospect: both bridgehead carbons are indicated to lie very nearly in the same plane as their four CH_2 carbon neighbours. Pyramidal distortion, as in **1a**, has been predicted for **3**.[2,3c] This is *not* what we find. The reason is interesting. The two bridgehead carbons are actually *bound* to one another (**3a**) (the MNDO bond order is 0.99). A remarkably similar pentacoordinate carbon with local C_{4v} symmetry is found in the iron carbonyl complex, **4**.[9] Planar tetracoordinate carbon is sp^2-hybridized, with a lone pair of electrons in the p-orbital perpendicular to the molecular plane and a LUMO with δ symmetry localized on the substituents. In **3a**,with two such planar units face to face, both p-type (HOMO-1) and δ-type (HOMO) orbitals are occupied. The p-orbital interaction in **3a**(seen in HOMO-1) results in the short C_1-C_4 bond (1.56 Å). The HOMO, C_2-C_3 bonding but C_1-C_2 nonbonding, is responsible for the other calculated C-C bond lengths, shortened for C_2-C_3 (1.51 Å) but lengthened for C_1-C_2 (1.71 Å). In localized orbital terms, C_1 is bound to C_4 by a two-electron bond and to the other four immediate carbon neighbours by a total of only six electrons.



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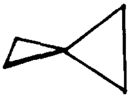

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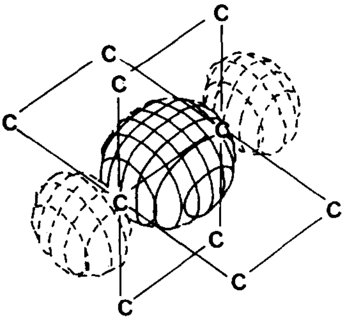
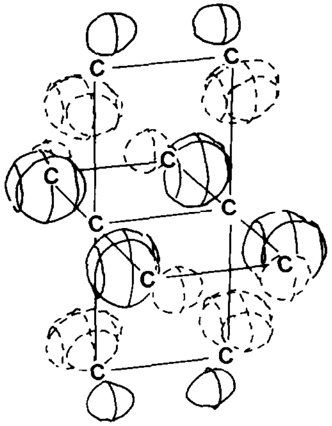
Unfortunately, **3** is also indicated to be highly unstable thermodynamically. **3a** can be regarded as the combination of two planar tetramethylenemethane units. "Tetramethylenemethane" is more familiar in quite a different geometrical arrangement, viz. spiropentane, **5**. Spiropentane, already a highly strained molecule, is calculated to have a dimerization energy to 3 endothermic by 250 kcal/mol. Even rotation around the central carbon of spiropentane (via planar 6) is indicated to be much more favorable, requiring "only" 60 (MINDO/3) to 80 (MNDO) kcal/mol.

Alas, 1-3 do not appear to be realistic prospects for experimental realization.



HOMO-I



HOMO

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Table. Calculated Heats of Formation and Strain Energies (kcal/mol)

Molecules	Symmetry	Heats of Formation (kcal/mol)		Strain Energies[a]	
		MINDO/3	MNDO	MINDO/3	MNDO
CH_4	T_d	-6.3	-11.9	0.0	0.0
	D_{4h}	113.4	128.8	119.7[b]	140.7[b]
	C_{4v}	93.8	c	100.1[b]	-
1a	C_{4v}	137.9	146.5	166.6	175.3
2a	D_{2d}	108.5	150.6	137.3	179.4
2b[d]	D_{2d}	273.7	341.0	302.5	369.8
3a	D_{4h}	303.3	311.5	341.7	349.9
5	D_{2d}	28.7	33.7	47.9	52.9
6[d]	D_{2h}	89.8	111.6	109.0	130.8

[a] Estimated using group enthalpy increments from ref. 8, unless otherwise indicated.

[b] Energy differences from tetrahedral. These values are in reasonable agreement with high level ab initio data; see ref. 4.

[c] Optimizes to the D_{4h} structure.

[d] The carbon skeleton was constrained to be planar.

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