Structure and Energetics of [4.4.4.4]Fenestrane

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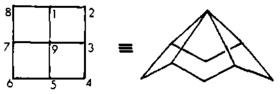
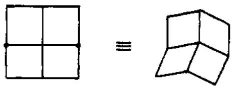
Abstract: The energetics of the D_{2d} and C_{4v} forms of [4.4.4.4]fenestrane were explored by ab initio calculation. Geometries were optimized in the STO-3G basis set and relative energies, heats of formation and strain energies were calculated at the SCF level in the 6-31G* basis set and to second order in electron correlation in the 4-31G basis set. The strain energy of the more stable D_{2d} form is found to be 160 kcal/mol. The C_{4v} form is estimated to be less stable than the D_{2d} form by 48.3 kcal/mol.

Introduction

A highly strained organic molecule of synthetic[1] and theoretical[2,3] interest is tetracyclo[$3.3.1.0^{3,9}.0^{7,9}$]nonane, also known as [4.4.4.4]fenestrane. Liebman and Greenberg[2] speculated that the most stable conformer would be IA; on the other hand, MINDO/3[3] and MNDO[4] calculations predicted the isomer IB to be more stable than IA by 28.5 and 50.8 kcal/mol, respectively. In order to obtain further insight into the energetics of this system, we have carried out ab initio molecular orbital calculations for both IA and IB: geometry optimization in the STO-3G basis[5a] with respect to all parameters followed by calculation of the energies of the optimized structures in the 4-31G basis[5b] accurate to second order in electron correlation (RMP2)[6,7] (within the frozen-core approximation). In order to assess the role of d-orbitals on carbon we have also performed 6-31G* basis set[5c] calculations at these same geometries. Geometry searches in the STO-3G basis were carried out using the program GAUSSIAN 80;[8] all other results were obtained by means of optimized machine-dependent programs developed by us.



IA



IB

Results and Discussion

The optimized geometric parameters of IA and IB are given in Table I. For IA a structure of C_{4v} symmetry was found, the angles $C_1C_9C_5$ and $C_1C_9C_7$ being 118.9° and 75.0°, respectively. The latter is remarkably small for a cyclobutane CCC angle. MINDO/3 furnishes 128° for $C_1C_9C_5$. The cyclobutane rings are puckered toward the pyramidal carbon with a dihedral angle $C_1C_9C_7C_8$ equal to −1.5°.

For IB a structure of D_{2d} symmetry was found (Figure 1). The exterior angle $C_1C_9C_5$ is 131.7° and the interior angle $C_1C_9C_7$ is 99.6°. The central carbon and the four methylene carbon atoms are coplanar. There is no puckering of the cyclobutane rings. However, each set of methylene protons in IB is slightly twisted, such that the angle between planes HC_8H and $C_1C_8C_7$ differs from a right angle by ca. 5°. This twisting brings the methylene protons closer to their cis neighboring methine protons and farther from their neighboring cis carbon–carbon bonds.

The small degree of ring puckering found in IA and its absence in IB are consistent with the slight puckering of cis-fused cyclobutanes: 8.1° in bicyclo[2.2.0]hexane,[10] and essentially zero in the planar central cyclobutane ring of the tricyclo[$4.2.0.0^{1,4}$]octane derivative reported by Wiberg et al.[11] The latter is the tricyclic analogue of fenestrane IB. The CC bond lengths of IB are C_1C_9

Table I. Bond Lengths (Å) and Bond Angles (deg) for Fenestranes (IA and IB) Optimized in the STO-3G Basis Set

bond length[a]	IA	IB
C_1C_9	1.728	1.487
C_1C_8	1.529	1.603
C_1H_1	1.088	1.083
C_8H_a	1.085	1.089
C_8H_b	1.085	1.089
bond angle	IA	IB
$C_1C_9C_5$	118.9	131.7
$C_1C_9C_7$	75.0	99.6
$C_9C_1C_8$	98.9	85.1
$C_1C_8C_7$	87.0	90.3
$H_1C_1C_9$	105.3	119.7
$H_aC_8C_1$	115.3	111.3
$H_bC_8C_1$	114.3	117.7

[a] H_1 is the hydrogen on C_1. In IA, the cyclobutane rings are puckered, with the methylene carbon atoms displaced toward C_9. H_a and H_b are the hydrogens on C_8 pointing away from and toward C_9, respectively. In IB, H_a and H_b are methylene hydrogens with dihedral angles $H_aC_8C_9C_1$ = −85.0° and $H_bC_8C_9C_1$ = +95.0°, respectively.

Table II. Ab Initio Energies of Fenestranes IA and IB, Cyclobutane, Cubane, and Neopentane

	energy, au			
molecule	STO-3G (SCF)	4-31G (SCF)	4-31G (RMP2)	6-31G* (SCF)
fenestrane (IA)[a]	−343.3205	−346.9396	−347.7747	−347.4706
fenestrane (IB)[a]	−343.4657	−347.0346	−347.8537	−347.5635
cyclobutane[b]		−155.8661	−156.2295	−156 0970
cubane[b]		−306.9289	−307.6211	
neopentane[a]	−194.0468	−196.0510		

[a] Optimized geometry in STO-3G; T_d symmetry was assumed for neopentane. [b] Optimized geometry in 4-31G.

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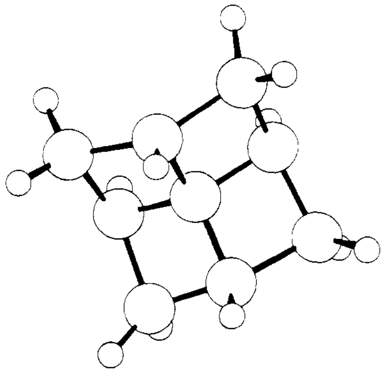

Figure 1. Perspective drawing of fenestrane (IB) in the STO-3G geometry.

= 1.487 Å and C_1C_8 = 1.603 Å. These are rather different from the corresponding lengths found in the tricyclo[4.2.0.$0^{1,4}$]octane: 1.552–1.571 Å and 1.525–1.534 Å, respectively. A 4-31G SCF calculation using 1.545 Å for both CC bond lengths in IB gave an energy some 20 kcal/mol higher than the STO-3G minimum-energy structure.

Energies in the 4-31G basis set show IB to be 59.6 kcal/mol more stable than IA; when the correlation correction is included, the difference drops to 49.6 kcal/mol. The effect of including d-orbitals on the nine carbons of each isomer is apparently negligible since the 6-31G* SCF energy difference decreased by only 1.3 kcal/mol. (Relevant energies are given in Table II.) Thus, the best estimate is that IB is more stable than IA by 48.3 kcal/mol. This is in good agreement with the MNDO result, 50.8 kcal/mol.

An isodesmic reaction for which all carbon atoms are in four-membered rings can be used to estimate $\Delta H_f(0\ K)$ for IB

$$(^3/_4)(\text{cubane}) + (^3/_4)(\text{cyclobutane}) \rightarrow (\text{fenestrane}) \quad (1)$$

It was necessary to obtain the RMP2 energies of cyclobutane and cubane in the 4-31G basis for the accurate evaluation of ΔH of reaction 1. Minimization of the 4-31G energy of cubane with respect to the two independent bond lengths in O_h symmetry yields R_{CC} = 1.573 Å and R_{CH} = 1.075 Å. For cyclobutane we used the 4-31G geometry given by Newton[12] and computed the RMP2 energy (Table II). The heats of reaction 1 at the SCF and RMP2 levels of approximation are 38.7 and 21.5 kcal/mol, respectively. Using the known $\Delta H_f(0\ K)$ of cyclobutane and cubane[12] and ignoring a net zero-point energy correction, $\Delta H_f(0\ K)$ for fenestrane is found to be 165 (SCF) and 148 (RMP2) kcal/mol. The heat of formation of IB was also computed using the "homodesmotic" reaction 2, in which the reactants and products

$$(\text{neopentane}) + (4)(\text{isobutane}) + (4)(\text{cyclobutane}) \rightarrow (\text{fenestrane, IB}) + (6)(n\text{-butane, trans}) + (2)(\text{ethane}) \quad (2)$$

contain equal numbers of CH_3, CH_2, and CH groups as well as quaternary carbons and four-membered rings. For this purpose we minimized the STO-3G energy of neopentane in T_d symmetry, obtaining CC and CH bond lengths of 1.550 and 1.086 Å, respectively, and an HCH angle of 108.3°. Energies for this geometry are given in Table II. Using the 4-31G energies of neopentane, isobutane,[13] n-butane,[13] cyclobutane,[12] and ethane,[12] the heat of reaction 2 is found to be 69.6 kcal/mol. The $\Delta H_f(0\ K)$ of IB found from this heat of reaction and the known heats of formation of reactants and products, corrected to 0 K and ignoring zero-point energy corrections, is 159 kcal/mol. Since the 4-31G heats of formation of IB are within 6 kcal/mol, there is essential agreement between the isodesmic and homodesmotic derived values. The best estimate of $\Delta H_f(0\ K)$, including second-order correlation corrections, is 148 kcal/mol obtained from reaction 1. It is significantly larger than the 108.5 and 95.7 kcal/mol values furnished by MINDO/3[3] and MNDO,[4] respectively.

Franklin's group equivalents[14] furnish $\Delta H_f(0\ K) = -12.2$ kcal/mol for a hypothetical unstrained fenestrane. Thus, the strain energy of IB obtained in the present work is 160 kcal/mol. This is in fair agreement with the molecular mechanics value, 183 kcal/mol, reported by Wiberg et al.[11] It is noteworthy that the bond angles of fenestrane reported by these authors are within 2° of the ab initio values obtained here. The strain energy of IA is 209 kcal/mol.

While the strain energy of cubane, 155 kcal/mol,[12] is ca. six times that of cyclobutane, 27 kcal/mol, the strain energy of fenestrane is significantly greater than four times that of cyclobutane. Fenestrane is therefore much more strained (on a per-ring basis) than cubane. How much of that strain is attributable to bond-angle distortions at C_9? A symmetrically distorted D_{2d} methane with the fenestrane C_9 bond angles has a 6-31G* energy only 20 kcal/mol greater than tetrahedral methane. (This value is similar to a 4-31G result obtained in a study of distorted methanes by Wiberg et al.[15]) For the analogue to IA, the situation is rather different. A C_{4v} methane with the bond angles of C_9 in IA has a 6-31G* distortion energy of 139 kcal/mol (in agreement with values obtained by Palalikit and Shavitt[16]). The difference in strain energies between the C_{4v} and D_{2d} methanes is 119 kcal/mol, which far exceeds the 58.3 kcal/mol (SCF) found for the difference in energy between IA and IB. The extra stabilization of IA can be attributed to its unusual electronic structure, in which the four CC bonds are actually formed from three electron pairs, the other pair residing in a nonbonding a_1 orbital pointing away from the pyramid. This zwitterionic character of IA confers upon it an unusually large electric dipole moment for a hydrocarbon, 3.2 D (4-31G). For a discussion of the relationship of this bonding scheme to that of the $(CH_5)^+$ ion, see ref 3.

As a final remark, we point out that the 4-31G SCF energy of fenestrane having a square planar C_9 is found to be ca. 130 kcal/mol greater than that of IB; this is not surprising in view of the 168.3 kcal/mol distortion energy of D_{4h} methane in the 4-31G basis.[16] Clearly, for distortions of the order of that found at C_9 of structure IB, the bond-angle strain of that atom does not make a dominant contribution to the total strain energy. Only when the distortions become much more pronounced, as in IA or square-planar fenestranes, is the effect of angle strain at the central carbon atom predominant.

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Registry No. Fenestrane, 40220-30-2; cyclobutane, 287-23-0; cubane, 277-10-1; neopentane, 463-82-1.

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