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AB INITIO HEATS OF FORMATION OF MEDIUM-SIZED HYDROCARBONS.

6. PERISTYLANE[1]

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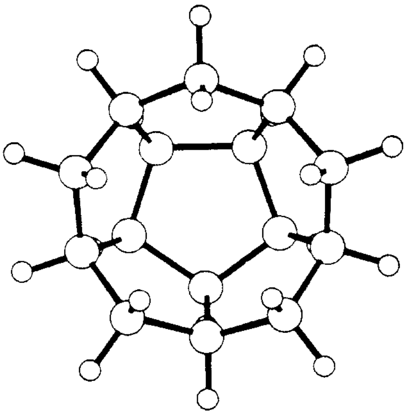
Summary: Peristylane is shown by calculations to be unstable with respect to methylene breathing motions about C_{5v} symmetry. Its ΔH_f is ca. 0.5 kcal/mol.

In the course of theoretical studies on dodecahedrane we have considered several $(CH_2)_m(CH)_n$ catacondensed cyclopentane-containing systems. By means of both ab initio[2] and molecular mechanics[3] calculations, the tricyclic molecule perhydrotriquinacene, $(CH_2)_6(CH)_4$, was shown to have C_3 rather than C_{3v} symmetry. We now have carried out a similar study of peristylane, the hexacyclic $(CH_2)_5(CH)_{10}$ hydrocarbon synthesized by Eaton and co-workers.[4] Full geometry optimization of peristylane in C_{5v} symmetry at the ab initio STO-3G(SCF) level using gradient techniques furnishes structure I, which has geometric parameters typical of such cyclopentane-containing systems, albeit with nearly unpuckered rings. However, study of the STO-3G(SCF) force constant matrix of this structure reveals that a degenerate pair of its eigenvectors of symmetry species E_2 has eigenvalues of essentially zero; the other ninety-seven eigenvalues are positive. This same behavior is found by means of the molecular mechanics method of Boyd, et al.[5]. Thus peristylane,



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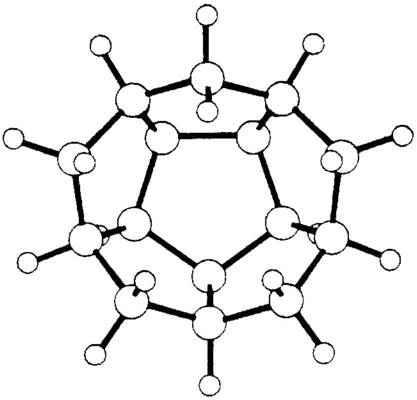

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like perhydrotriquinacene, eschews a more symmetrical, kinetically-unstable structure. Moreover, the distorted structure found in an X-ray study[6] of the diketoacetate of peristylane now can be ascribed, in part, to instabilities in the hydrocarbon moiety itself as well as to the effects of ring substitution.

In order to determine how flat the peristylane potential energy surface is, degenerate symmetry coordinates employed in the analysis of the force constant matrix were constructed as eigenvectors of a reflection of the group C_{5v}. Distortion along the unstable E_2 eigenvector which is symmetric with respect to this reflection reduces the symmetry to C_s and consists largely of methylene "breathing motions" both inward and outward from the periphery, with the basal cyclopentane plane largely unaffected. Distortion in this symmetry coordinate to a degree which moves some hydrogens by as much as 0.7 bohr, structure II, increases the energy by less than 1 kcal/mol.

The C_{5v} structure is useful in the calculation of the heat of formation as an energetically-representative average system. Its 6-31G*(SCF) energy at the STO-3G geometry is -579.6659 au; experience suggests that optimization in the 6-31G* basis set would yield an energy lower by ca. 0.7 kcal/mol. Using the vibrational frequencies obtained with the Boyd force field, the zero-point energy and enthalpy difference from 0 to 298 K are found to be 198.4 kcal/mol and 5.9 kcal/mol, respectively, with the two unstable modes making no contribution to the former and a classical contribution to the latter. The homodesmic reaction

5/2 adamantane --› 5/3 cyclohexane + peristylane

has a 6-31G*(SCF) heat of reaction of 33.3 kcal/mol, after corrections for zero-point energies and enthalpy conversions from 0 to 298 K. The heat of formation of peristylane is then found to be 0.5 kcal/mol. Similar values of 0.7 kcal/mol and 0.6 kcal/mol are obtained using the group equivalents of Wiberg[7] and the atom equivalents of Ibrahim and Schleyer[8], respectively. Somewhat lower and probably less accurate heats of formation are obtained by mechanics methods: -8.6 kcal/mol by Engler, et al.[9], -5.6 kcal/mol from MM2[10], and -6.5 kcal/mol from the Boyd force field[5]. The uncertainties in the ab initio heat of reaction and the zero-point energy are such that small negative heats of formation of -2 to -3 kcal/mol cannot be excluded.

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