

THE FLEXIBILITY AND CONFORMATION OF POLYCYCLOALKANES WITH TWO-CARBON BRIDGES

by

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The eclipsed (D_{3h}) or twisted (D_3) nature of the structure of bicyclo[2.2.2]octane (I) presented a challenging problem which has been solved only recently.^{1,2} Both theoretical calculations and experimental results indicate that I possesses a broad energy minimum for twisting around the C_1-C_4 axis. Both eclipsed and twisted conformers were found to be of similar energy, the latter being favored by only ~ 0.1 kcal/mole.^{1,2}

The conformations of bicyclo[3.2.2]nonane (II),^{3,4} bicyclo[3.3.2]decane (III),^{4,5} and homoadamantane (IV)^{6,7} pose similar problems, which have not been fully appreciated in the literature. For example, Dreiding models have been used to assign a twisted conformation to II.³ Unfortunately, Dreiding models are known to be misleading for such purposes,⁶ since they over-emphasize angle strain and do not represent torsional and nonbonded interactions. We wish to report the results of quantitative conformational analysis calculations⁸ which suggest that the flexibility observed in I appears to be a more general phenomenon to be expected in a number of other polycycloalkanes with two-carbon bridges including II, III and IV.

Calculations on I, II, IV and the chair-boat (IIIa), boat-boat (IIIb), and chair-chair (IIIc) conformations of III were performed using a molecular mechanics program with a force field described previously.^{9,10} All of these systems (except IIIc) behave exceptionally

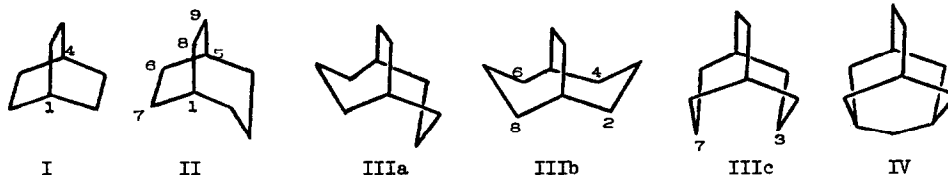


Table 1. Calculated Enthalpies and Torsional Angle (ϕ) Ranges

Compound	$\Delta H_f^{25^\circ}$ (calc, gas) kcal/mole	Torsional Angle (ϕ) Ranges ^a
Bicyclo[2.2.2]octane (I)	-24.3 (-23.8) ^b	0 \pm 10 $^\circ$ (0 \pm 12 $^\circ$) ^c
Bicyclo[3.2.2]nonane (II)	-29.5	0 \pm 15 $^\circ$ C ₁ C ₇ C ₆ C ₅ 0 \pm 24 C ₁ C ₈ C ₉ C ₅
Bicyclo[3.3.2]decane (III)		
boat-chair conformer (IIIa)	-32.8	0 \pm 18 $^\circ$
boat-boat conformer (IIIb)	-30.1	0 \pm 15 $^\circ$
chair-chair conformer (IIIc)	-32.3	22 $^\circ$ ^d
Homoadamantane (IV)	-34.5	0 \pm 33 $^\circ$

^aDefined as the estimated range of C-CH₂-CH₂-C dihedral angles where the calculated enthalpies do not vary more than ca. 0.3 kcal/mole. See text. ^bExperimental value: R. H. Boyd, S. V. Sanwal, S. Shay-Tehany, and D. McNally, J. Phys.Chem., 75, 1264 (1971). ^cExperimental range. See refs. 1,2. ^dNot flexible; staggered conformation ($\phi = 22^\circ$) more stable than eclipsed conformation ($\phi = 0^\circ$).

on minimization; no unique geometries are found, rather a number of conformations with closely similar energies. This indicates the presence of broad potential wells retarding movement along the energy surface during minimization. Hence, it is necessary to vary the torsional angles, ϕ , in the C-CH₂-CH₂-C bridges in order to probe the energy surface correctly.

The "flexibility" of I-IV can be gauged by the breadth of the potential well, that is the range of values of ϕ which correspond to the minimum energy (within 0.3 kcal/mole) (Table 1). Eclipsed conformations ($\phi = 0^\circ$) of I, II, IIIa, IIIb, and IV are indicated to have essentially the same energies as twisted arrangements. Contrary to the implications of Dreiding models,³ variations of angle strain with changes in ϕ are insignificant, and the same holds for the torsional and non-bonded strain components. Thus, relieving the two-carbon bridge torsional strain when $\phi = 0^\circ$ by twisting is accompanied by a compensating increase in the torsional strain to the two adjacent bridgehead positions.¹¹ Table 2 illustrates this balance among conformational energy components for widely differing geometries of homoadamantane (IV).

Table 2. Conformational Energy Components for Homoadamantane (IV)

Strain Component	$\phi = 0^\circ$	$\phi = 13^\circ$	$\phi = 33^\circ$
	Strain energies, kcal/mole		
Angle Strain	3.55	3.30	3.23
Bond Stretching	0.55	0.50	0.59
Torsional Strain	3.33	3.28	3.02
Nonbonded Strain	3.51	3.54	4.08
Total Strain	10.74	10.62	10.92

In bicyclo[3.3.2]decane, three types of conformations with respect to the two 3-carbon bridges are possible (III a-c).^{4, 5} Both the boat-chair (IIIa) and boat-boat (IIIb) conformers exhibit broad energy minima; however, in the chair-chair structure (IIIc) the staggered conformation (with $\phi = 22^\circ$) is some 2.4 kcal/mole more stable than the eclipsed form ($\phi = 0^\circ$). The inflexibility of IIIc originates from unfavorable H...H nonbonded interactions between C₃ and C₇ present in the eclipsed conformation. By twisting, this interaction is relieved. Recently, the observed high frequency absorption at 1484 cm⁻¹ for III has been suggested as arising from methylene-methylene interactions between C₃ and C₇ in the chair chair conformer (IIIc) or between C₂ and C₆ (or C₄ and C₈) in the twist boat-boat conformation (IIIb).^{5c} Our calculations indicate IIIb to be about 2.5 kcal less stable than either IIIa or IIIc.

That the inflexibility in IIIc is due to unfavorable H...H nonbonded interactions between hydrogens on C₃ and C₇ is strengthened by the finding of a very broad energy well in homoadamantane (IV), a model system for IIIc in which these unfavorable H...H interactions have been removed by connecting C₃ and C₇ with a methylene unit.

In summary, I, II, IIIa, IIIb, and IV may be added to the list of flexible ring systems whose intimate conformations are determined largely by the substituents present rather than by the carbon skeleton. Therefore, it is not surprising that conflicting reports concerning the preferred conformations of these systems, derived from data on derivatives, have appeared in the literature.³⁻⁷ The balance between strain components in the parent hydrocarbon can not be expected to be maintained when substituents are present.

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