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EMPIRICAL FORCE FIELD CALCULATIONS—V[1]

BICYCLO[2.2.0]HEXANE AND ITS SEVEN 1,2,3,4,5,6-HEXAMETHYL DERIVATIVES

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Abstract—The calculations reveal that the equilibria of 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexanes with four or three *endo*-Me groups shift completely to the invertomers with four or three *exo*-Me groups. The strain introduced by the Me substitution of bicyclo[2.2.0]hexane is rather low for the Engler force field. Geometrical details of the calculated energy minima are discussed briefly.

Recently, skeletal inversions of 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexanes were reported from this laboratory.[2] In spite of the increase of the number of pairs of almost eclipsed Me groups, isomer **2** is more stable than invertomer **1** and **4** is more stable than **3** (Scheme 1). Apparently, the steric interactions of *endo*-Me groups are rather unfavourable. An extensive study of the invertomer equilibria is prevented by thermal cleavage reactions and heats of formation are not determined easily. Therefore, we carried out empirical force field calculations to study the enthalpy differences and steric interactions of these and some related compounds.

RESULTS

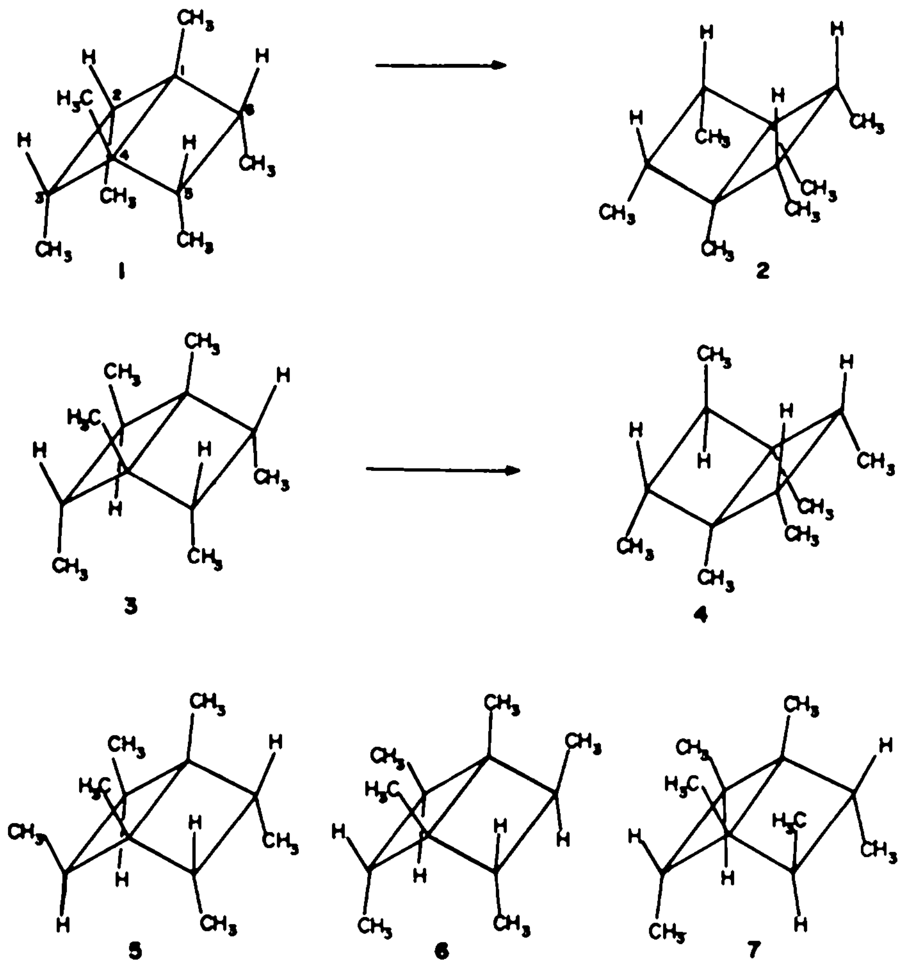
The heats of formation and the strain energies of cyclobutane and of bicyclo[2.2.0]hexane and its seven 1,2,3,4,5,6-hexamethyl derivatives were calculated using the Engler force field[3] (EAS) and the Allinger MM1 force field.[4] The heats of formation of cyclobutane and cubane can be reproduced, among that of a great number of (cyclo)alkanes, with both force fields so that good reliance is expected for the results on the present compounds. The heats of formation and strain energies are given in Table 1, the values of some internal coordinates relevant for the discussion are summarized in Table 2.[5]

DISCUSSION

The two force fields give similar heats of formation for the bicyclic compounds except for compounds **2** and **5**. In both force fields the all-*endo* compound **1** has by far the highest enthalpy and the 1,2-*exo*,3-*endo*,4,5-*exo*,6-*endo* isomer **7** is the most stable. The relative energies of the compounds **1** and **2** and **3** and **4** are in accord with the experimental course of the inversion reactions and the energy differences point to very minor amounts of the least stable invertomers in the case of equilibration. An estimate of the enthalpy difference between the compounds **1** and **2** can be obtained from the experimental difference between the enthalpies of activation[2] of the thermal cleavage reactions to *erythro*-(*E*,*Z*) - 3,4,5,6 - tetramethylocta - 2,6 - diene if both reactions proceed *via* a common intermediate (e.g. the 1,4-π-bonded intermediate A depicted in Ref. 2*). This difference amounts to 8.9 ± 0.5 kcal $mole^{-1}$ as compared with differences between the heats of formation of **1** and **2** of 5.7 and 7.1 kcal $mole^{-1}$ calculated with the EAS and MM1 force fields, respectively.[6]

The strain energies of the hexamethyl derivatives can be compared directly with that of cyclobutane and bicyclo[2.2.0]hexane. The latter differences reflect the strain due to the additional Me groups. The strain energy of the unsubstituted bicyclic system is almost twice that of cyclobutane and the Me substitution gives a further increase of the strain. This increase, however, is rather low. For instance, three times the interaction of two almost eclipsed Me groups in compound **7** gives a rise in the calculated strain energy of only 2.5 kcal $mole^{-1}$ using the EAS force field as compared with a difference between the strain energies of eclipsed ethane and n-butane[7] of 2.0 kcal $mole^{-1}$.

Most notable on the geometries of the minima is that both force fields give bicyclo[2.2.0]hexane a structure with two planar 4-membered rings, although they also yield a puckered cyclobutane with ring torsion angles of 3.6° (EAS) and 10.9° (MM1), respectively. The experimental value of the torsion angle $C_3C_1C_2C_4$ in bicyclo[2.2.0]hexane amounts to 8.1°.[8] The valency angles $C_2C_1C_6$ and $C_3C_4C_5$ at the bridgehead C atoms differ about 5° from the experimental value and the HCH valency angles about 6°. It seems therefore proper to look at the geometries of the hexamethyl derivatives in a comparative way only. None of the minima of the derivatives has a planar 4-membered ring; the ring torsion angles are generally less than 15°. The comparison of the $C_2C_1C_6$ and $C_3C_4C_5$ valency angles is interesting (Table 2). A relatively small value (about 115°) is calculated if two H atoms are present in the adjacent *endo*-positions, an intermediate value (about 119°) is found for one H atom and one Me group and the largest value (about 125°) is calculated in the case that two *endo*-Me groups flank the bridgehead C atom. The value at one bridgehead is almost independent from that at the other one. These values demonstrate the repulsive interactions between the groups on 2- and 6- (or 3- and 5-) *endo*-positions. The fact that this valency angle with two



Scheme 1.

Table 1. Heats of formation and strain energies (kcal mole^{-1})

No.	Compound[a]	H_f° 25° gas		Strain energy[b]	
		EAS	MM1	EAS	MM1
	Cyclobutane	5.73[c]	5.86[d]	26.25[c]	25.80[d]
	Bicyclo[2.2.0]hexane	25.78[e]	27.42	50.62[e]	50.23
1	1,2n,3n,4,5n,6n-HMBCH	-7.02	-7.48	62.52 (9.41)	60.66 (8.22)
2	1,2x,3x,4,5x,6x-HMBCH	-12.70	-14.57	56.84 (3.74)	53.57 (1.13)
3	1,2x,3n,4,5n,6n-HMBCH	-11.94	-11.71	57.60 (4.49)	56.43 (3.99)
4	1,2n,3x,4,5x,6x-HMBCH	-14.68	-15.33	54.86 (1.76)	52.81 (0.37)
5	1,2x,3x,4,5n,6n-HMBCH	-12.69	-13.84	56.85 (3.75)	54.31 (1.87)
6	1,2x,3n,4,5n,6x-HMBCH	-14.00	-13.85	55.54 (2.44)	54.30 (1.86)
7	1,2x,3n,4,5x,6n-HMBCH	-16.44	-15.71	53.10 (0.00)	52.44 (0.00)

[a] HMBCH = hexamethylbicyclo[2.2.0]hexane, n = -*endo*, x = -*exo*, numbers according to Scheme 1. [b] Differences with respect to the most stable isomer between parentheses. [c] Ref. 3: 5.78 and 26.30, respectively. [d] Ref. 4: 6.16 and 25.8, respectively, the former value possibly including 0.3 kcal mole^{-1} for the heat content of the excitation of the pseudo-rotation energy levels at room temperature. [e] Ref. 3: 25.83 and 50.67, respectively.

adjacent *exo*-Me groups is much smaller than that in the unsubstituted compound illustrates that unfavourable steric interactions between a bridgehead Me group and the adjacent *exo*-Me groups are also operative.

EXPERIMENTAL

The calculations were performed using an IBM 370/158 computer. Each energy minimum was characterized by six eigenvalues from the final force constant matrix equal to zero.[9]

Table 2. Data on the geometries of the energy minima

Compound[a]	Point group	EAS		MM1	
		$< C_2C_1C_6$	$< C_3C_4C_5$	$< C_2C_1C_6$	$< C_3C_4C_5$
[illegible][b]	C_{2v}	118.3	118.3	118.4	118.4
1	C_2	126.5	126.5	125.0	125.0
2	C_2	114.8	114.8	115.7	115.7
3	C_1	119.5	126.0	119.7	124.3
4	C_1	119.2	114.8	118.9	116.0
5	C_1	119.1	119.6	118.9	119.3
6	C_1	115.0	125.7	116.4	123.6
7	C_2	119.1	119.1	118.9	118.9

[a]See note a of Table 1. [b]Experimental value (Ref. 8): 113.5°.

Vibration frequencies and statistical thermodynamic parameters are not given because of the fact that the force fields used are not designed to reproduce this information.[5]

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[5] Full details on the geometries, partial energies, vibration frequencies and thermodynamic parameters of all minima can be obtained from the authors on request.

[6] It must be noted that the enthalpies of activation were measured at temperatures between 140° and 250° for solns in heptane or decane.

[7] Eclipsed ethane: strain energy $-0.49 + 2.8$ kcal mole^{-1} from Ref. 3; eclipsed n-butane with *syn*-periplanar Me groups: strain energy 4.32 kcal mole^{-1} from our calculation (a calculation similar to that for ethane with values from Ref. 3 gives a strain energy of 5.12 kcal mole^{-1}; however, see also E. Osawa, J. B. Collins and P. v. R. Schleyer, *Tetrahedron* 33, 2667 (1977)). The difference between the strain energies of eclipsed ethane and propane is neglected in this comparison.

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