Enhanced Axial–Equatorial Enthalpy Differences in the Methyl Adamantanes

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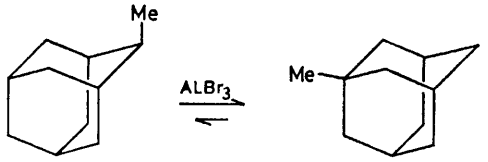
Summary Analysis of the thermodynamic parameters for the isomerization with $AlBr_3$ of 2-methyl- to 1-methyladamantane, $\Delta G^{0}_{\mathrm{I}}$ (298) $-2{\cdot}47 \pm 0{\cdot}19$ kcal mol^{-1}, $\Delta H^{0}_{\mathrm{I}}$ $-3{\cdot}37 \pm 0{\cdot}11$ kcal mol^{-1}, $\Delta S^{0}_{\mathrm{I}}$ $-3{\cdot}0 \pm 0{\cdot}3$ cal mol^{-1} deg^{-1}, reveals an enhancement of the total axial methyl strain of $0{\cdot}9$ kcal mol^{-1} in the rigid adamantane system over that typical of cyclohexanes.

Adamantane is an assembly of fused-chair cyclohexane rings.[1] Positional isomers, such as 1- and 2-methyladamantane [equation (1)], are related in much the same way as equatorial and axial methylcyclohexane [equation (2)].



(2) (1)

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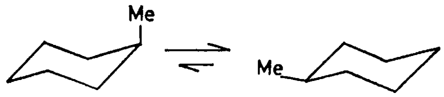


(2)

However, the more flexible nature of cyclohexane enables it to adopt somewhat flattened geometries [∠ CCC (ring) *ca.* 111·5°] in which the best balance between angle, nonbonded, and torsional strain is achieved.[2] The rigidity of the adamantane skeleton prevents any comparable relaxation.[1] Hence, 2-substituents should suffer from enhanced *axial* nonbonded repulsions, and the heat of reaction of equation (1) should be greater than that of equation (2).[1b]

TABLE 1

Equilibrium constants for 1- *and* 2-*methyladamantane interconversion*

Temperature /K	Equilibrium constant [equation (1)]
308·0$_1$	52·9 ± 2·8
317·3$_8$	45·2 ± 2·4
331·7$_5$	34·8 ± 2·0
344·2$_2$	30·1 ± 1·7

The aluminium bromide-catalysed equilibration of 1- and 2-methyladamantanes[1] was carried out at four temperatures in the 35—70 °C range and the (**1**) : (**2**) ratios evaluated by g.l.c. (Table 1). The derived thermodynamic values for the equilibrium are: $\Delta H^0_\mathrm{I} = -3{\cdot}37 \pm 0{\cdot}11$ kcal mol^{-1}, $\Delta S^0_\mathrm{I} = -3{\cdot}0 \pm 0{\cdot}3$ cal mol^{-1} deg^{-1}, $\Delta G^0_\mathrm{I}(298) = -2{\cdot}47 \pm 0{\cdot}19$ kcal mol^{-1}.[3]† The experimental entropy difference is in reasonable agreement with the value (2·1 cal mol^{-1} deg^{-1}) expected on the basis of the differences in symmetry numbers of (**1**) and (**2**).

TABLE 2

Experimental and calculated strain energy differences between axial and equatorial methyl on a six-membered ring

Equilibrium	Δ Strain/(kcal/mol)			ΔΔ Strain/(kcal/mol)[a]		
	Expt.	Calc. 1[b]	Calc. 2[c]	Expt.	Calc. 1[b]	Calc. 2[c]
Eq. (2)	1·7[d], 1·9[e]	1·0	1·7	0	0	0
Eq. (1)	2·6[d,f]	1·9	2·7	0·9	0·9	1·0
(**3**) $\rightleftarrows$ (**5**)	2·14[e]	2·2	3·0	0·2	1·2	1·3
(4) $\rightleftarrows$ (5)	1·7[e,f]	1·9	2·8	−0·2	0·9	1·1

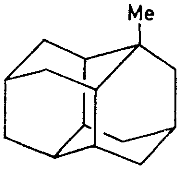
[a] Strain energy relative to the energy difference for methylcyclohexane [eq. (2)]. [b] Calculated using force field described in ref. 9. [c] Calculated using force field described in ref. 10. [d] Liquid-phase value. [e] Gas-phase value, ref.6. [f] Corrected for difference in substitution type by subtracting 0·7 kcal mol^{-1} (liquid phase) or 1·0 kcal mol^{-1} (gas phase) from ΔH^0_I; see refs. 3 and 4 for further details.

The enthalpy difference between 1- and 2-methyladamantane does not correspond directly to the axial methyl strain because of a difference in substitution pattern, *i.e.* (**1**) has a quaternary carbon and an extra CH$_2$ group. Application of a correction of 0·7$_2$ kcal mol^{-1} based on equation (3) and group increments for the liquid phase[3,4] yields an energy of 2·6 kcal mol^{-1}, *ca.* 0·9 kcal mol^{-1} higher than

$$2\,\mathrm{CH} \rightarrow \mathrm{C} + \mathrm{CH_2} \qquad (3)$$

that found in the cyclohexyl system.[5]

In a related study, the methyl isomers of diamantane (**3**)—(**5**) have been equilibrated in the gas phase.[6] The experimental enthalpy difference of 2·14 kcal mol^{-1} is closer to the gas-phase value of 1·9 kcal mol^{-1} for methylcyclohexane[7] [equation (2)] than that found for adamantane (2·6 kcal mol^{-1}).



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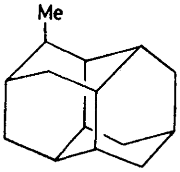

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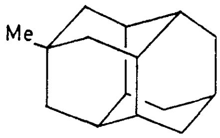

(5)

These experimental results were checked by molecular mechanics calculations.[8] Our recently published force field[9] tends to underestimate the axial methyl strain in cyclohexane (Table 2). However, such defects are minimized when differences in energies between closely related processes are considered [*e.g.*, equation (1) *vs.* equation (2), ΔΔ strain in Table 2] and agreement with experiment is excellent. The validity of this procedure was checked by repeating the computer conformational analysis using Allinger's 1968 force field,[10] known to give good absolute axial–equatorial energy differences. The results (Table 2) confirm our conclusion that axial methyl strains in adamantane and diamantane should be enhanced over those in the more flexible cyclohexane systems.

Thus, we differ with McKervey *et al.*,[6] who concluded that diamantyl systems are good models for corresponding cyclohexanes. This view is supported by experimental equilibration data of polymethyladamantanes.[11] Better agreement between calculated and experimental results can be achieved if our value of 1·3 instead of 0·9 kcal mol^{-1} is used for each axial methyl *gauche* interaction.[12] Perhaps the (**3**)—(**5**) enthalpy differences determined in the range 130–290 °C do not correspond to values at 25 °C owing to non-linearity of log K *vs.* $1/T$ plots.[13] Actually, ΔG values for (**3**)—(**5**) and (**1**)—(**2**) are in excellent agreement when corrections for differences in substitution type and entropy of mixing are made; experimental ΔH and ΔS

† Data quoted in ref. 1a were preliminary and inaccurate. A revised statistical treatment leads here to slightly different values from those cited in ref. 1b.

values are much more difficult to determine accurately.[13]

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