Equilibration of Biadamantane Isomers

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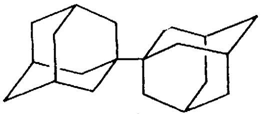
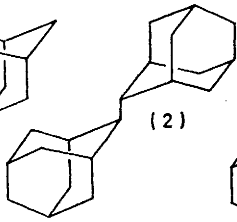
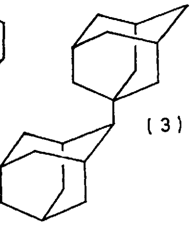
Summary In agreement with molecular mechanics calculations, 2,2′-biadamantane (**2**) is more stable than 1,1′-biadamantane (**1**): (**1**) $\rightleftharpoons$ (**2**), $\Delta G^{\circ}_{\mathrm{I}}$ (298) = − 0·51 ± 0·21 kcal mol^{-1}, $\Delta H^{\circ}_{\mathrm{I}}$ = 1·11 ± 0·12 kcal mol^{-1}, and $\Delta S^{\circ}_{\mathrm{I}}$ = 5·4 ± 0·3 cal deg^{-1} mol^{-1}.

Treatment of 1,1′-biadamantane (**1**)[1] with aluminium bromide in cyclohexane at 60° leads to an equilibrium mixture consisting of 25·4 ± 0·2% (**1**), 69·8 ± 0·2% 2,2′-biadamantane (**2**),[2] and *ca.* 4·8% 1,2′-biadamantane (**3**).[3]†


(1)


(2)


(3)

Isomerization starting from (**2**) gave the same results. This is the first example in which a 2-substituted adamantane is the major constituent at equilibrium. Small amounts of disproportionation products with shorter retention times were also observed.

Table 1.

Equilibrium constants (**1**) $\rightleftharpoons$ (**2**)

Temperature (K)	Equilibrium constant
323·2	2·75 ± 0·03
331·1	2·89 ± 0·03
348·3	3·08 ± 0·03
363·1	3·32 ± 0·03

Equilibrium constants for (**1**) $\rightleftharpoons$ (**2**) were determined as a function of temperature by g.l.c. (Table 1). Relative isomer distribution was corrected for differences in flame ionization detector response against known mixtures of (**1**) and (**2**). The derived thermodynamic parameters are $\Delta G^{\circ}_{\mathrm{I}}$ = − 0·51 ± 0·21 kcal mol^{-1}, $\Delta H^{\circ}_{\mathrm{I}}$ = 1·11 ± 0·12 kcal mol^{-1} and $\Delta S^{\circ}_{\mathrm{I}}$ = 5·4 ± 0·3 cal deg^{-1} mol^{-1}. Molecular mechanics

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† 1,2′-Biadamantane (**3**) was identified by comparison of g.l.c. retention times with a mixture of (**1**) and (**2**) prepared by treatment of equimolar amounts of 1- and 2-bromoadamantanes with sodium under reflux. Compound (**3**) has been excluded from the analysis presented here due to the difficulty in accurately measuring its change as a function of temperature. Based on the relative calculated enthalpies and entropies in Table 2 for the isomeric biadamantanes, 4—5% (**3**) is predicted at equilibrium (60°).

calculations support the experimental findings (Table 2).[4–6][‡]

TABLE 2.

Relative calculated energies for isomeric biadamantanes

	ΔH°_I (gas, 25°)[a]		Rel. strain (25°)[a]		ΔS°_I[b]
	Calc. 1[c]	Calc. 2[d]	Calc. 1[c]	Calc. 2[d]	Calc.
(**1**)	0	0	1·76	1·22	0
(**2**)	0·46	1·10	0	0	5·3
(**3**)	2·69	2·87	3·34	2·93	5·1

[a] kcal mol^{-1}. [b] cal deg^{-1} mol^{-1}. Calculated from differences in symmetry numbers and in substitution pattern (ref. 8). [c] Calculated using force field described in ref. 5. [d] Calculated using force field described in ref. 6.

On the basis of strain (Table 2), (**2**) is the most stable isomer, but this is compensated somewhat by the higher degree of branching in (**1**) [and in (**3**)]. While (**1**) and (**2**) have the same number of *gauche* interactions, those in (**1**), a molecule of the hexamethylethane type, are higher in energy.[7] The dominant factor controlling the position of equilibrium is the appreciable entropy which shifts the isomerization in favour of (**2**). The experimental entropy difference (5·4 cal deg^{-1} mol^{-1}) is in excellent agreement with the value (5·3 cal deg^{-1} mol^{-1}) expected on the basis of the difference in symmetry numbers ($R\ln 6/2 = 2{\cdot}2$ cal deg^{-1} mol^{-1}) and in substitution type (3·1 cal deg^{-1} mol^{-1})[8] between (**1**) and (**2**).

The agreement between calculated and experimental enthalpy differences (despite the comparison of gas and liquid values), for (**1**) → (**2**) increases confidence in the molecular mechanics method for predicting the stabilities of complex hydrocarbons.

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[‡] To increase confidence in the calculated results, our standard procedure is to compare the results of two independent calculations using different force fields (refs. 5 and 6).

[1] H. F. Reinhardt, *J. Org. Chem.*, 1962, **27**, 3258.

[2] J. H. Wieringa, H. Wynberg, and J. Strating, *Synthetic Comm.*, 1971, **1**, 7.

[3] The mechanism interconverting the biadamantanes, (**1**) → (**3**) presumably involves 1,2-alkyl shifts to give protoadamantyl-type intermediates (*cf.* the skeletal rearrangements of substituted adamantanes: A. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5731; Z. Majerski, S. H. Liggero, P. v. R. Schleyer, and A. P. Wolf, *Chem. Comm.*, 1970, 1596).

[4] For a review see J. E. Williams, jun., P. J. Stang, and P. v. R. Schleyer, *Ann. Rev. Phys. Chem.*, 1968, **19**, 531.

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[6] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. N. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637.

[7] *E.g.*, a *gauche* interaction in n-butane raises the energy by 0·77 kcal mol^{-1} relative to the staggered conformation (P. B. Woller and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 5310). In hexamethylethane each *gauche* interaction is worth 1·27 kcal mol^{-1} (strain energy/6, P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, 1970, **92**, 2377).

[8] Liquid phase values: S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.