Equilibration of Diamantan-1-ol and Diamantan-4-ol. Conformational Enthalpy of the Hydroxy-group, and an Unusual Example of how Entropy and Symmetry Factors can Influence Relative Thermodynamic Stabilities

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Summary The isomeric diamantan-1- and -4-ols establish an equilibrium in 98% sulphuric acid at 273—473 K *via* a hydride transfer mechanism, and are equally thermodynamically stable at 321 K owing to differences in entropy values due to symmetry factors; the conformational enthalpy of the hydroxy-group is found to be 1·1 kcal mol^{-1}.

An interesting structural distinction exists between diamantan-1-ol (**1**) and diamantan-4-ol (**2**). In isomer (**1**) the substituent is axially disposed with respect to one cyclohexane ring of the diamantane skeleton whereas in isomer (**2**) the substituent is exclusively equatorial. One can visualise these molecules as formal analogues of the axially and equatorially substituted chair conformations of cyclohexanol (denoted by the heavy lines). Of course the diamantane skeleton totally precludes the process of ring inversion whereby the cyclohexanol conformers are interconverted. Nevertheless, we now show that interconversion of alcohols (**1**) and (**2**) can easily be achieved by another mechanism and that entropy differences between the isomers can be explained by symmetry considerations.

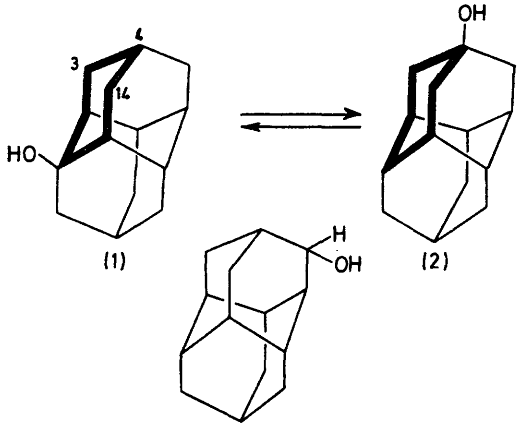
The alcohols[1] rapidly establish an equilibrium in 98% sulphuric acid probably *via* an intermolecular hydride transfer mechanism.[2] Isomer distributions at seven temperatures were determined by g.l.c. (see Table). At the lower temperatures the equilibrium mixtures were relatively uncomplicated: small amounts of diamantane, diamantanone, and diamantan-3-ol (**3**) were produced. [The 3-ol (**3**) is actually present at equilibrium with isomers (**1**) and (**2**) but it has been excluded from this analysis because within the range of temperatures studied it amounted to not more than 1·0—4·0% of the mixture.] At higher temperatures particularly over 423 K, large amounts of diamantanone were present.

Table

*Relative equilibrium concentrations of diamantan-*1*-ol* (**1**) *and diamantan-*4*-ol* (**2**)

T/K	273	313	321	341	371	423	473
(**1**)	44·0	46·5	50·0	50·5	53·7	60·0	65·0
(**2**)	56·0	53·5	50·0	49·5	46·3	40·0	35·0

The 1-ol (**1**) possesses unfavourable 1,3-interactions between the axial hydroxy-group and the axial 3- and 14-protons. No such interactions exist in the 4-ol (**2**). Consequently, on this steric argument alone, isomer (**2**) should be of lower energy than isomer (**1**). However, at temperatures above 321 K the equatorial isomer (**2**) is actually the less thermodynamically stable of the two. The thermodynamic data for the isomerisation of (**2**) to (**1**) are derived from the temperature dependence of the equilibrium by a linear least-squares analysis: $\Delta H = 1{\cdot}1 \pm 0{\cdot}1$ kcal mol^{-1} and $\Delta S = 3{\cdot}4 \pm 0{\cdot}3$ cal deg^{-1} mol^{-1}. Thus, the 4-isomer (**2**) is indeed of lower enthalpy than the 1-isomer (**1**) by 1·1 kcal mol^{-1}, but above 321 K this is overwhelmed by the higher entropy of the 1-isomer (**1**).



(1) (2) (3)

It seems highly unlikely with such rigid molecules as (**1**) and (**2**) that flexibility differences could be responsible for the observed entropy difference. But entropy differences can result from differing symmetry properties,[3] and this appears to be the situation here. Consideration of the symmetry properties of the two isomers reveals that the 1-isomer (**1**) has C_s symmetry and the 4-isomer (**2**) C_{3v} symmetry. Since a molecule with C_{3v} symmetry has a symmetry number of 3 compared with 1 for C_s symmetry, the entropy of the 4-isomer (**2**) should be lower by (Rln3) or 2·18 cal deg^{-1} mol^{-1} whereas the entropy of the 1-isomer (**1**) will be unaffected by the symmetry effect. Thus, the entropy change (**2**) → (**1**) is 2·18 cal deg^{-1} mol^{-1}, a value in reasonable agreement with that found experimentally, considering that terms for the entropy of mixing of the various accessible rotational conformations of the hydroxy-group in the two isomers have not been taken into account. This complicating factor does not arise when the substituent is spherically symmetrical, and we are currently studying the temperature dependence of the equilibration of the corresponding chloro- and methyl-diamantanes.

The conformational enthalpy of the hydroxy-substituent obtained with the diamantyl system is identical, within the combined limits of experimental error, with the values of 1·09 and 1·18 kcal mol^{-1} (for hydrogen-donor solvents) derived from equlibration of *cis*- and *trans*-4-t-butylcyclohexanol.[4] This agreement is noteworthy, considering the large differences in flexibility between the cyclohexyl and diamantyl systems and the theoretical objections which have been raised regarding the use of the t-butyl group as a conformation-fixing device.[5]

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[1] The alcohols were synthesised by aluminium chloride-catalysed isomerisation of 1-chlorodiamantane and subsequent hydrolysis of the mixture of 1- and 4-chlorodiamantane produced (see D. Faulkner, R. A. Glendinning, D. E. Johnston, and M. A. McKervey, *Tetrahedron Letters*, 1970, 1671).

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[3] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962: for a similar situation in a hydrocarbon rearrangement see: P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Amer. Chem. Soc.*, 1963, **85**, 1358.

[4] E. L. Eliel and E. C. Gilbert, *J. Amer. Chem. Soc.*, 1969, **87**, 5487.

[5] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, 1969, **91**, 337.