Standard Enthalpies of Formation of *cis*- and *trans*-Bicyclo[6.1.0]nonanes

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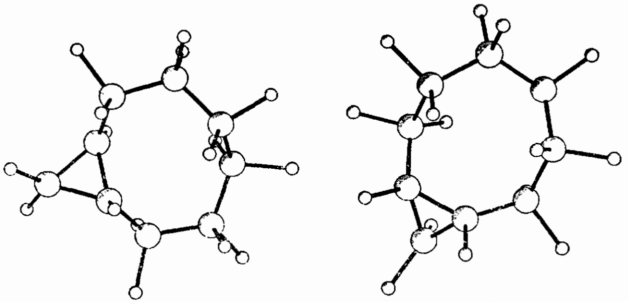
Summary The standard enthalpies of formation of both *cis*- and *trans*-bicyclo[6.1.0]nonane have been determined in the liquid and gas phases: the results show that these are the smallest bicycloalkanes for which the *trans*-fused isomer is more stable than the corresponding *cis*-isomer.

IN the course of experiments designed to investigate the stereochemistry of a cyclopropane ring-opening reaction,[1] we became interested in the *trans*-bicyclo[6.1.0]nonane system. No reliable thermochemical data were available for *trans*-bicyclo[6.1.0]nonane (I),[2] but it was envisaged that the *trans* fusion would impart a strain energy appreciably greater than that in cyclopropane itself. To obtain evidence for this, force field calculations were carried out on (I).[3] From these, the calculated value for the gas-phase enthalpy of formation, ΔH_f°(g), of (I) was estimated to be −40·0 kJ mol^{-1}; parallel calculations on the *cis*-isomer (II) gave a value of −29·8 kJ mol^{-1}. Surprisingly, therefore, the *trans*-isomer seemed *more* stable than the *cis*-isomer, with a calculated strain energy of 155·8 kJ mol^{-1}. This is only 28·7 kJ mol^{-1} greater than that in cyclopropane itself and is considerably less than the sum of the strain energies in cyclopropane and cyclo-octane (174·3 kJ mol^{-1}).



(I) (II)

FIGURE. Computer generated drawings of the most stable conformations calculated for *trans*-bicyclo[6.1.0]nonane (I) and *cis*-bicyclo[6.1.0]nonane (II)

In order to obtain experimental verification for these results, the hydrocarbons (I) and (II) were prepared. Compound (I) was obtained by making the pyrazoline from *trans*-cyclo-octene and diazomethane and pyrolysing it. This gave predominantly the *trans*-product (63% yield after preparative g.l.c.). Compound (II) was prepared by conventional Simmons–Smith cyclopropanation of *cis*-cyclo-octene. Both compounds were rigorously purified by fractional distillation and preparative g.l.c. Their standard energies of combustion were then determined using the aneroid static bomb microcalorimeter described previously.[4]

The bomb calorimetry yielded the following standard enthalpies of formation: ΔH_f° {*trans*-bicyclo[6.1.0]nonane, (I), l} = − 82·4 ± 3·2 kJ mol^{-1} and ΔH_f° {*cis*-bicyclo[6.1.0]nonane, (II), l} = − 80·3 ± 3·7 kJ mol^{-1} where the uncertainties are twice the standard errors of the mean.[4] The corresponding standard enthalpies of vaporization, ΔH_v° (I) = 42·7 ± 0·6 kJ mol^{-1} and ΔH_v° (II) = 49·8 ± 0·8 kJ mol^{-1}, were derived from vapour pressure *vs.* temperature data obtained by a semimicro-ebulliometer method[5] in excellent agreement with previously reported values.[6,7] From the above results ΔH_f° (*trans*-bicyclo[6.1.0]nonane, g) = − 39·7 ± 3·3 kJ mol^{-1} and ΔH_f° (*cis*-bicyclo[6.1.0]nonane, g) = − 30·5 ± 3·8 kJ mol^{-1} in excellent agreement with the force field calculations. The value for (II) is also in close accord with the earlier experimental results of Chang *et al.*[7]

Substantiation of the unexpected value for (I) was obtained by conventional static bomb calorimetry at Leeds.[8] A gas-phase enthalpy of formation of (I) of −49·1 ± 4·4 kJ mol^{-1} is calculated from their calorimetric data. Although this is very slightly less than the microcalorimetric result, it fully supports the conclusion that the *trans*-isomer is less strained than the *cis*.

That the *trans*-bicyclo[6.1.0]nonane should be more stable than the *cis*-isomer by 9·2 ± 5·0 kJ mol^{-1} in the gas phase is rather unexpected. In the liquid phase both isomers are of similar stability. The extra stability of the *trans* isomer in the force field calculations arose mainly in a decrease in the torsional strain energy term. In an attempt to obtain true global minima, the energies of several conformations of both molecules were minimized in the programme.†

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† A referee states that the pre-1977 force fields are known to contain errors in the non-bonded potential functions which can give rise to serious error under certain circumstances, a comment with which one of us (W.V.S.) wholeheartedly agrees and has tried to show in earlier work (ref. 4). Here the non-bonded strain contribution did not vary very much between (I) and (II) and hence can be neglected in any comparison.

[1] R. P. Corbally, A. P. Elnitski, and M. J. Perkins, *J.C.S. Perkin I*, in the press.

[2] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London **1970**.

[3] E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Amer. Chem., Soc.*, 1973, **95**, 8005.

[4] W. Parker, W. V. Steele, W. Stirling, and I. Watt, *J. Chem. Thermodynamics*, 1975, **7**, 795.

[5] R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, 1971, **75**, 1264.

[6] R. M. Varushchenko, N. A. Belikova, S. M. Skurator, and A. F. Plate, *Russ. J. Phys. Chem.*, 1970, **44**, 1722.

[7] S-J. Chang, D. McNally, S. Sharry-Tehrany, Sister M. J. Hickey, and R. H. Boyd, *J. Amer. Chem. Soc.*, 1970, **92**, 3109.

[8] See *e.g.* A. S. Carson and B. R. Wilmshurst, *J. Chem. Thermodynamics*, 1971, **3**, 251.