Electron-diffraction Investigation of the Molecular Structure of Bicyclo[3,3,1]nonane

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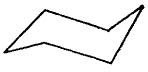
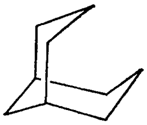
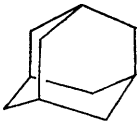
Summary The geometry of the title compound was determined by electron diffraction in the gas phase.

Cyclohexane (**1**), bicyclo[3,3,1]nonane (**2**), and adamantane (**3**) are interesting molecules with a diamond-like arrangement of carbon atoms. Accurate geometries of (**1**)[1] and (**3**)[2] are known in the gas phase, but the structure of (**2**) can be constructed only on the basis of several derivatives studied in the crystal[3] or by molecular mechanics calculations.[4] In view of the lack of experimental data for (**2**) we undertook an electron diffraction study of this molecule.

The structure of (**2**) (refined by a least-squares analysis to *R* 0·06) is shown in the Figure. The twin-chair conformation gives the best agreement with the intensity and radial distribution curves. This is in accord with a conclusion by Laszlo[5] and a quantitative analysis for the conformation which has the minimum energy.[4]


(1)


(2)


(3)

The average C–C bond length is fairly reliable but the individual differences are not well established. The average C–C bond distance in (**2**) of 1·536(2) Å is closer to that in (**1**) [1·534 Å] than to that in (**3**) [1·540 Å]. This is also true for the average C–C–C bond angle of 111·5° in (**2**) which can be compared with 111·4° in (**1**) and 109·3° in (**3**). Both these facts can be rationalized on the basis of unfavourable gauche interactions relieved by bond angle and torsion angle deformations in (**1**) and (**2**). However, in (**3**) only the C–C bond lengthening leads to relief of strain.[6] A similar model was suggested to account for the differences observed in C–C bond distances in n-hydrocarbons and diamond.[7]

The six-membered ring in (**2**) shows a rather drastic flattening compared with that in (**1**), which is probably due to C(3)–C(7) methylene non-bonded interactions.[8] The dihedral angle between the planes C(9)–C(1)–C(2) and C(1)–C(2)–C(3) in (**2**) (53°) is significantly less than in (**1**) (54·9°) or in (**3**) (60·5°). A similar flattening has been indicated in the crystal.[8]

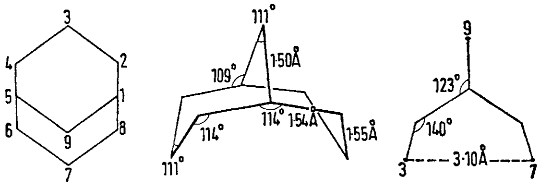


FIGURE Bond lengths and angles in bicyclo[3,3,1]nonane. The uncertainties in molecular parameters are believed to be 0·015 Å, 1·0° and 2·0° for internuclear distances, bond angles and dihedral angles respectively.

With the value of the angle C(1)–C(9)–C(5) now available for (**2**) it can be seen that the angle between the two bridging carbons in symmetrical bicyclo[*m*,*m*,1]alkanes opens linearly with increasing ring size; $n = m + 3$, $\angle\mathrm{CCC} = 0{\cdot}12 + 18{\cdot}55n^\circ$ ($n = 4,5,6$). Experimental results are: 74·2° for bicyclo[1,1,1]pentane,[9] 93·1° for bicyclo[2,2,1]heptane,[10] and 111.3° for (**2**). This trend can be reproduced by molecular mechanics calculations.

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[1] O. Bastiansen, L. Fernholt, H. M. Seip, H. Kambara, and K. Kuchitsu, *J. Mol. Struc.*, 1973, **18**, 163.

[2] I. Hargittai and K. Hedberg, *Chem. Comm.*, 1971, 1499; 'Molecular Structures and Vibrations,' ed. S. J. Cyvin, Elsevier, Amsterdam, 1972, p. 340.

[3] N. S. Zefirov, *Uspekhi Khim.*, 1975, **44**, 413.

[4] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637; E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[5] I. Laszlo, *Rec. Trav. chim.*, 1965, **84**, 251.

[6] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, 1970, **92**, 2377.

[7] L. S. Bartell, *J. Amer. Chem. Soc.*, 1959, **81**, 3497.

[8] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1965, 1844.

[9] A. Almenningen, B. Andersen, and B. A. Nyhus, *Acta Chem. Scand.*, 1971, **25**, 1217.

[10] A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Japan*, 1971, **44**, 2356.