Acta Chemica Scandinavica A 36 (1982) 513–515

Equilibrium Geometry and Conformational Preference of Tricyclo[3.1.0.0^{2,4}]hexane

PER N. SKANCKE

Department of Chemistry, Institute for Mathematical and Physical Sciences, University of Tromsø, P.O. Box 953, N-9001 Tromsø, Norway

A complete geometry optimization of the chair and the boat form of tricyclo[3.1.0.0^{2,4}]hexane has been performed using the gradient technique of Pulay. The structural differences between the two molecular forms are consistent with severe strain in the boat form which is 20.7 kcal/mol less stable than the observed chair form.*

In a previous paper[1] we have carried through *ab initio* calculations on bicyclic hydrocarbons of the type [*n*.1.0] with $n = 1$, 2 and 3. The purpose of those calculations was to obtain a detailed knowledge of the molecular ground state structures of these molecules using a complete geometry relaxation. In the discussion of the bonding characteristics of these systems special attention was paid to the properties of the transannular bonds of the rings.

The present paper is a natural extension of the work referred to above.[1] The molecule tricyclo-[3.1.0.0^{2,4}]hexane (TCH) has two intraannular bonds and is expected to have more ring strain than the corresponding bicyclic system. The nature of the intraannular bonds in this molecule as compared to the one in bicyclohexane is of interest in the present context.

The ground state structure of TCH has been examined in an electron diffraction investigation by Geise *et al.*.[2] Their work also included *ab initio* calculations using an STO-3G basis. The analysis of the diffraction data was based on an assumed chair form of the molecule. Due to near degeneracy of bond distances which always complicates experimental structure analyses of this kind, only average values of C–C and C–H bond distances were determined.

In a very recent paper that appeared after the initiation of the present study a complete geometry relaxation of the chair form of TCH has been given.[3] We decided to complete the present study for two reasons.

Firstly our basis, 4–31G, is slightly different from the 4–21 basis used in that paper. However, more important is the fact that we have also included in our study a complete relaxation of the boat form of the molecule. To our knowledge this form of the molecule has not been observed. This has been done in order to get information on possible structural differences between the two molecular forms, and also to obtain an estimate of their relative energies.

COMPUTATIONAL METHOD

The geometry optimizations were performed by means of the program TEXAS written by Pulay.[4] This program uses a force-relaxation method in the optimizations.[5]

The basis set applied was the 4–31G basis of Pople *et al.*[6] As demonstrated previously this basis is particularly suitable for the prediction of differences between related bond distances.[1] However, predicted absolute values using this basis have to be corrected in order to bring them in accordance with experimental values.[7]

The end points in the geometry variations were defined by changes less than 0.002 Å in bond distances and less than 0.5° in valence angles when reasonable values of the appropriate force constants were used.

* 1 kcal = 4.184 kJ.

0302-4377/82/060513-03$02.50
© 1982 Acta Chemica Scandinavica

Table 1. Optimized geometries of the chair and boat forms of tricyclo[3.1.0.0^{2,4}]hexane. The structural parameters are defined with reference to the labelling of atoms given in Fig. 1. Distances in Å, angles in degrees.

Parameter	Chair			Boat
	This work	Ref. 2	Ref. 3	This work
R(C1 – C2)	1.515		1.520	1.557
R(C2 – C3)	1.505	1.508	1.516	1.507
R(C1 – C5)	1.543		1.550	1.520
R(C1 – H7)	1.075		1.069	1.074
R(C3 – H9)	1.079	1.080	1.073	1.080
R(C3 – H10)	1.080		1.072	1.074
A(C1C2C3)	110.1	109.9	109.6	113.8
A(C3C2C4)	59.2	60.0	59.2	59.7
A(C5C1H7)	128.6	127.8		129.3
A(C2C1H7)	125.3	128.8		122.3
A(C2C3H9)	119.9			114.2
A(C2C3H10)	116.0	120.0		123.0
A(H9C3H10)	113.8	110.0		112.5

RESULTS AND DISCUSSION

Predicted molecular structures for the chair form and the boat form of the molecule are given in Table 1. Experimental results[2] and previously obtained theoretical results[3] for the chair form are included for comparison.

In the refinement of the geometries we assumed C_{2h} symmetry for the chair and C_{2v} symmetry for the boat. This implies that the 4-membered ring is constrained to be planar in both isomers. This assumption is in accordance with experimental findings for the chair form.[2]

The labelling of atoms and definition of structural parameters are presented in Fig. 1.

From the data in Table 1 the redundant parameters α and τ defined in Fig. 1 can be evaluated. For the chair form we find $\alpha = 66.3°$ whereas $\alpha = 62.1°$ for the boat form. The CH_2 groups do not exhibit local C_{2v} symmetry. In the chair form the rocking angle τ has a value of 2.4°. In the boat form this angle has increased to 5.4°. An increase in both the α- and the τ-value is to be expected in going from the chair to the boat form due to the steric contact between atoms H10 and H13. Even at the equilibrium geometry of the boat form this distance is only 1.02 Å.

A more interesting structural deviation between the two molecular forms is represented by the differences in the carbon – carbon bond distances

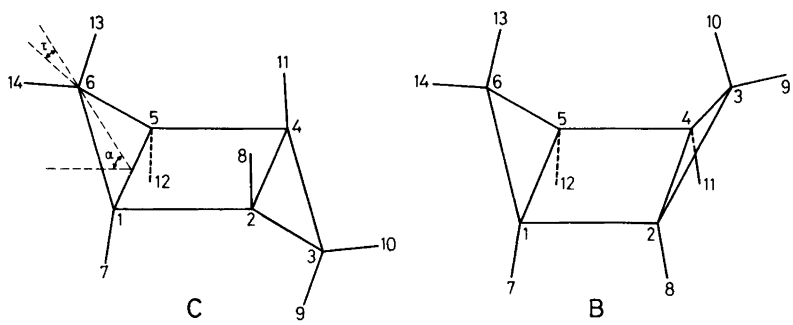

Fig. 1. Atomic arrangements and labelling in the chair (C) and boat (B) form of tricyclo[3.1.0.0^{2,4}]-hexane.

C1 – C2 and C1 – C5. The latter being a transannular bond is significantly shortened in the boat form as compared to the chair form. This shortening is coupled to an even more pronounced lengthening of the C1 – C2 bond. These structural features are compatible with a high energy model consisting of two cyclopropene units that interact more weakly than in the ground state chair form. The energy difference between the two forms is predicted to be 20.7 kcal/mol.

REFERENCES

1. Skancke, P. N. *Theochem. 86* (1982) 255.
2. Van den Enden, L., Geise, H. J., Figeys, H. P., Geerlings, P. and van Alsenoy, C. *J. Mol. Struct. 33* (1976) 69.
3. Scarsdale, J. N., van Alsenoy, C., Schäfer, L., van den Enden, L. and Geise, H. J. *Tetrahedron Lett. 22* (1981) 147.
4. Pulay, P. *Theor. Chim. Acta 50* (1979) 299.
5. Pulay, P. *Mol. Phys. 17* (1969) 197.
6. Ditchfield, R., Hehre, W. H. and Pople, J. A. *J. Chem. Phys. 54* (1971) 724.
7. Pulay, P., Fogarasi, G., Pang, F. and Boggs, J. E. *J. Am. Chem. Soc. 101* (1979) 2550.
8. Boys, S. E. In Löwdin, P. O., Ed., *Quantum Theory of Atoms, Molecules and the Solid State*, Academic, New York 1966, p. 253.

Received October 23, 1981.