THE CONFORMATIONAL EQUILIBRIUM IN BICYCLO(3.3.1)NONANE AT 65-400°C BY ELECTRON DIFFRACTION AND MOLECULAR MECHANICS

V. S. Mastryukov*, M. V. Popik, O. V. Dorofeeva,
A. V. Golubinskii, L. V. Vilkov and N. A. Belikova
Department of Chemistry, Moscow State University,
Moscow 117234, USSR

N. L. Allinger#
Department of Chemistry, University of Georgia
Athens, GA 30602, USA

Abstract: The amount of boat-chair conformation (5-25 %) in equilibrium with the chair-chair has been measured and calculated.

It is widely known that in cyclohexane the energy difference between chair (C) and boat (B) forms is quite large, approximately 5-6 kcal/mol.[1] This value becomes much smaller for the cyclohexane moiety of bicyclo-(3.3.1)nonane because in the chair-chair form (CC) there are the severe interactions between the endo hydrogens at C_3 and C_7 which significantly destabilize this conformer with respect to the boat-chair form (BC)[2].

The easier accessibility of the boat conformation in bicyclononane than in cyclohexane itself has attracted a great deal of attention to the chemistry of this compound and its derivatives.[3] Although there are no direct measurements reported so far of the energy difference between the CC and BC conformers for parent hydrocarbon, values ranging from 2.1 to 2.7 kcal/mol were reported for several derivatives.[3] Theoretical estimates of ΔE for bicyclononane based on molecular mechanics calculations gave the following results, depending on the force field used: $1.5^{[4]}$, $2.5^{[5]}$ and 3.8 kcal/mol[6]. Calculations in the present work using the recently improved force field (MM2)[7] lead to the value of 2.31 kcal/mol, and also give correctly the heat of formation of the compound (Calcd. -30.50 kcal/mol, reported[8] -30.5 ± 0.6 kcal/mol).

These data imply that one may hope to obtain a detectable amount of BC conformer in an appropriate high-temperature experiment. There are many recent successful applications of electron diffraction to the study of conformational equilibria at elevated temperatures by Hedberg et al.[9] Accordingly, in an attempt to detect experimentally the BC form we have undertaken an electron diffraction study of the hydrocarbon at 400°C, the highest temperature at which the compound is stable under the experimental conditions.

Diffraction patterns were recorded at Moscow State University using the gas standard method recently described.[10] The usual experimental procedure and calculation techniques were in general employed.[11] An important experimental modification, however, consisted in the construction of a special nozzle system with a

needle valve which can be heated up to about $900^\circ C$[12]. This significantly extends the applicability of electron diffraction to studies of conformational equilibria which normally are carried out at temperatures not higher than $250^\circ C$ (see ref. 9).

The molecular structure and conformational ratio were refined by least squares calculations on the intensity data. This was done by incorporation in the structural analysis of a special geometrical subroutine which permitted the refinement of a mixture of two conformations (with one average C-C distance) identical in all respects except for several dihedral angles. After a number of refinements, all of the geometrical parameters together with the ratio of the conformers were allowed to vary simultaneously. The results are shown in the Table. In

Table	The amount of BC conformer according to different molecular mechanics calculations and experiment.		
		$t = 65^\circ$	$t = 400^\circ C$
Experiment[a]		$5 \overset{+}{-} 4 \%$	$25 \overset{+}{-} 3 \%$
Theory	Ref.		
$\Delta E = 1.5$ kcal/mol	4	17.7 %	39.5 %
2.3 kcal/mol	present work	6.1 %	26.4 %
3.8 kcal/mol	6	1.0 %	10.5 %

a) The errors quoted are estimated standard deviations.

parallel, the geometries of CC and BC calculated by the MM2 force field were introduced into the analysis, and only the conformational ratio was refined.

As an additional datum, we have reanalyzed in the same way our previous experiment,[13] which was carried out at $65^\circ C$. Both sets of experimental results are compared in the Table with the theoretical estimates calculated from three different force field values for the energy difference using the equation

$$N_{BC} / N_{CC} = 2 \exp(-\Delta E / RT).$$

In the Figure are shown the radial distribution function and the differences between the calculated and observed functions at $400^\circ C$. Curve A is the best fit, and yields an equilibrium containing $25 \overset{+}{-} 10 \%$ of the boat chair. Curves B and C show the corresponding difference functions corresponding to 5 and 50 % boat chair, respectively. Also shown is the difference curve (D) obtained using the structures obtained by molecular mechanics, and optimizing only the conformational composition. Note that the % BC from experiment and from molecular mechanics are in very good agreement.

Boat conformations in cyclohexanoid moieties are frequently found in polycyclic hydrocarbons as a consequence of some geometrical constraints (see some examples in ref. 1, 10). For unconstrained systems, there are few examples in which the boat or twist boat conformation has been detected. Our results demonstrate the existence of the conformational equilibrium for bicyclo(3.3.1)nonane as determined by electron diffraction, and confirm that the amount of BC conformer increases as the temperature is raised. From these measurements at two temperatures a rough estimate of ΔS° and ΔE° can be made from the equation

$$K = N_{BC} / N_{CC} = 2 \exp(\Delta S^\circ / R) \exp(-\Delta E^\circ / RT).$$

It gives $\Delta S^\circ = 0.14$ e.u. and $\Delta E = 2.48$ kcal/mol. Since the difference in the symmetry numbers of the conformations is allowed for by the pre-exponential factor, a ΔS° of approximately zero is anticipated here.
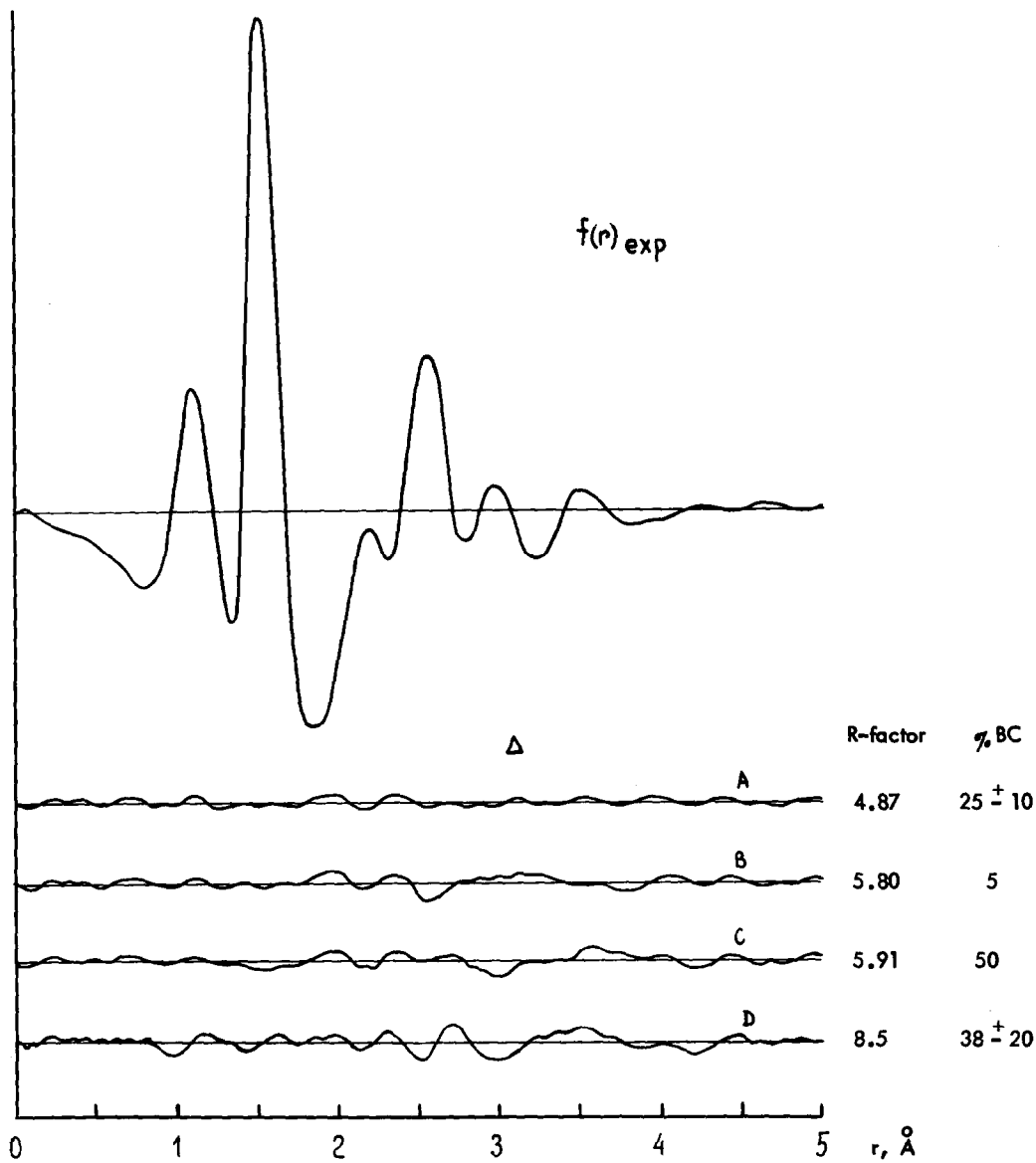
Figure – The Radial Distribution Function of Bicyclo(3.3.1)nonane at 400°C, and the Differences Between the Calculated and Experimental Curves. (The errors listed correspond to 3 esd.)

References and Notes

1. a) E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, Conformational Analysis, Wiley-Interscience, N.Y. (1965).

   b) M. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, J. Am. Chem. Soc., 97, 3244 (1975).

2. These interactions are geometrically characterized by the drastic flattening of six-membered rings at the periphery of the molecular as is shown from an electron diffraction study by V. S. Mastryukov, E. L. Osina, O. V. Dorofeeva, M. V. Popik, L. V. Vilkov and N. A. Belikova, J. Mol. Struct., in press.

3. See for references an excellent review by N. S. Zefirov, Uspekhi Khim., 44, 413 (1975).

4. N. L. Allinger, M. T. Tribble, M. A. Miller and D. H. Wertz, J. Am. Chem. Soc., 93, 1637 (1971).

5. E. M. Engler, J. D. Andose and P. v. R. Schleyer, J. Am. Chem. Soc., 95, 8005 (1973).

6. V. K. Mikhailov, E. N. Aredova, V. V. Sevostianova and V. A. Shlyapochnikov, Izv. Akad. Nauk, ser. Khim., 2455 (1978).

7. N. L. Allinger, J. Am. Chem. Soc., 99, 8127 (1977).

8. W. Parker, W. V. Steele, and I. Watt, J. Chem. Thermo, 9, 307 (1977).

9. See K. Hagen, B. V. Bondybey and K. Hedberg, J. Am. Chem. Soc., 99, 1365 (1977) and references therein on earlier publications of this series.

10. V. S. Mastryukov, E. L. Osina, L. V. Vilkov, and R. L. Hilderbrandt, J. Am. Chem. Soc., 99, 6855 (1977).

11. V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, and A. V. Golubinskii, J. Mol. Struct., 32, 161 (1976).

12. M. V. Popik, L. V. Vilkov, V. S. Mastryukov and A. V. Golubinskii, Prib. Tekhn. Eksp., in press.

13. E. L. Osina, V. S. Mastryukov, L. V. Vilkov and N. A. Belikova, J. C. S. Chem. Comm., 12 (1976).