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STUDIES IN MOLECULAR STRUCTURE, SYMMETRY AND CONFORMATION—IV

THE CONFORMATION OF THE CYCLOOCTANE RING SYSTEM FROM X-RAY STUDIES*

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Abstract—X-ray data of crystal structures have been analysed to reveal the conformation of the cyclooctane ring system. It is found to prefer predominantly a boat-chair conformation, but there is a tendency to adopt the crown form when there is either extensive replacement of ring C atoms or extensive substitution of the ring hydrogens.

INTRODUCTION

THE structure and conformation of molecules containing cycloalkane rings have been attacked (a) from a theoretical angle[1-7] using energy considerations to predict possible conformations, and (b) on the experimental side, by X-ray analyses undertaken only during the past few years. Our knowledge of the conformations of medium rings was recently reviewed by Dunitz.[8] Data from X-ray analyses of 8-membered ring and evidence from other physico-chemical studies such as NMR, IR and electron microscopy indicate a preference for the boat-chair form, but structure analyses of a wider range of derivatives of cyclooctane should be carried out before this conclusion can be accepted as firmly established.[8]

Recently, as part of a systematic X-ray analysis of compounds containing cycloalkane ring systems[12] undertaken in this laboratory, the crystal structure of another derivative of octane has been completed.[9-12] The conformational features of this and a number of other 8-membered ring compounds have been analysed and the significant results are presented in this paper.

ANALYSIS OF THE DATA AND DISCUSSION

The present analysis is based on data for the nine compounds listed in Table 1 and shown in Fig 1. The first six compounds (Group I, a–f) are in the boat-chair form and the last three (Group II, g–i) exist in the crown form. In the case of aza-cyclooctane hydrobromide (compound h) the evidence for the crown form is not unequivocal due to disorder in the structure[8] and hence little reliance is placed on this particular compound in our discussion.

In five of the six compounds in Group I all the ring atoms are carbon although substitutions by groups such as COOH, CH_3, OH, Cl, etc, occur. In compound (f), two of the ring carbons have been replaced by a nitrogen and a sulphur atom. In the second group of compounds, there are either numerous substitutions or ring replacements.

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Thus, disregarding the case of (h), it would appear that the cyclooctane ring prefers the boat-chair conformation except when there is extensive replacement and/or substitution in the ring. Replacements of up to two atoms in the ring or two substitutions on the same C atom (as in d) or at 1, 2 positions (as in a, b and c) or 1, 4 positions (as in e) or 1, 5 (as in f) seem tolerable from the point of view of the boat-chair conformation. If this is taken as a guide, it is doubtful whether compound (h) has the ring in the crown form, but the evidence in this case is not unequivocal and X-ray analyses of more compounds of this type are required.

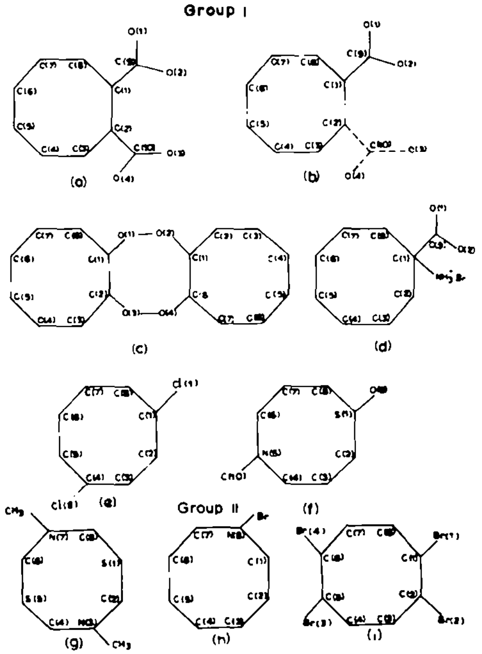

Fig 1. Structural formulae of compounds with an 8-membered ring system.

Details of the torsion angles are available only for the first six compounds, and are given in Table 2. For convenience, the theoretical values of the torsional angles predicted$^{2, 5, 7}$ are given as well as the calculated mean absolute deviation and the root-mean-square deviations of the angles. As the values of Bixon and Lifson^{7} show a consistently closer agreement between the experimental and theoretical values than those calculated by Hendrickson or Wiberg, and, as their treatment appears mathematically sound, we shall adopt their results as standard. The boat-chair conformation corresponds to the conformation I of Bixon and Lifson who also gave three other conformations, namely, conformations II, III and IV. They deduced that Conformations I to IV have energies of 9·43, 11·32, 12·34 and 13·05 kcal mole^{-1} respectively.

Reference to Table 2 shows that the minimum absolute deviation is found for compound (b), namely the 1,2-*trans* cyclooctane dicarboxylic acid while the maximum absolute deviation of 5·8° occurs for compound (c). In the latter case, the molecule contains bridging oxygens which impose strain not found in the other examples.

TABLE 1

X-RAY CRYSTALLOGRAPHIC DATA OF CYCLOOCTANE DERIVATIVES

Ring systems Name of compound	Space group	*R*-factor	Conformation	Reference
(a) 1,2-*cis*-Cyclooctane dicarboxylic acid	$P2_1/c$	6·1%	Boat-chair	13
(b) 1,2-*trans*-Cyclooctane dicarboxylic acid	$C2/c$	5·5%	Boat-chair	14
(c) 3,6-Spiro-dicyclo octylidene 1,2,4,5-tetraoxycyclohexane	$P2_1/c$	5·7%	Boat-chair	15
(d) 1-Amino-cyclooctane carboxylic acid hydrobromide	$P2_12_12_1$	8·6%	Boat-chair	12
(e) *trans*-1,4-Dichlorocyclooctane (−180°)	$P2_1/c$	8·8%	Boat-chair	16
(f) 5-Methyl-1-thia-2-aza-cyclooctane-1-oxide perchlorate	$P2_1/c$	9·2%	Boat-chair	17
(g) Dimethyl-3-7-dithia-1,5-diaza-3,7-cyclooctane	$Fdd2$	12%	Crown	18
(h) Aza-cyclooctane hydrobromide	$Abmm$	9·1%	Crown*	19
(i) *trans-syn-trans*-1,2,5,6,Tetrabromocyclooctane	$P2_1/c$	10·8%	Crown	20

* The evidence for crown form is not unequivocal (see Dunitz)[8]

TABLE 2

THEORETICAL AND OBSERVED TORSIONAL ANGLES OF THE CYCLOOCTANE RING BOAT-CHAIR FORMS AS FOUND IN THE VARIOUS CRYSTAL STRUCTURES

Theoretical values (θ_0)			Observed values in compounds(θ) (in degrees)					
Bixon and Lifson	Hendrickson	Wiberg	(a)	(b)	(c)	(d)	(e)	(f)
64	77·1	73·3	68·8	62·2	69·7	67·2	67·5	64·2
46	42·9	44·8	38·0	46·8	36·5	40·5	40·9	54·7
255	247·8	254·8	263·9	254·1	261·6	261·9	260·0	250·6
70	50·7	49·4	65·7	70·8	66·1	67·2	62·6	65·8
288	309·3	310·6	292·6	289·7	296·0	294·6	299·7	287·4
106	112·2	95·2	104·8	100·9	101·3	97·9	100·6	98·7
316	317·1	315·2	311·8	316·6	311·0	313·6	311·8	318·2
296	282·9	286·7	299·9	297·0	298·9	296·5	297·8	292·6
Bixon and Lifson		m.d.*	5·0	1·5	5·8	4·5	5·5	3·6
		r.m.s.*	5·5	2·1	6·1	5·1	6·2	4·7
Hendrickson		m.d.	11·5	11·4	11·2	11·1	11·7	9·6
		r.m.s.	12·5	13·2	11·8	12·2	13·3	10·4
Wiberg		m.d.	10·1	9·2	9·1	9·4	10·0	7·4
		r.m.s.	12·1	12·1	10·1	11·3	12·0	8·2

* m.d. stands for mean absolute deviation, i.e. $<|\theta - \theta_0|>$ and r.m.s. stands for root-mean-square deviation $<(\theta - \theta_0)^2>^{\frac{1}{2}}$ where θ_0 is the theoretically predicted value of Bixon and Lifson, Hendrickson or Wiberg

Thus, evidence from X-ray analyses seems to indicate[8] that the cyclooctane ring prefers the boat-chair conformation except when there is extensive substitution and/or replacement in the ring system.

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