An Investigation of the Molecular Structure and Conformation of 1,3,5,7-Tetraoxacyclooctane in the Gas Phase

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The molecular structure of 1,3,5,7-tetraoxacyclooctane has been investigated in the gas phase by the electron diffraction method. Satisfactory agreement between experimental and theoretical data is obtained for an equilibrium mixture of 32(6) % symmetric crown (D_{4d}) and 68(6) % BC (C_s) conformers.

The following parameters have been determined: $r(O-C) = 1.404(1)$ Å, $r(C-H) = 1.088(3)$ Å, $\angle$ HCH 112.4°, Crown: $\angle COC = 114.6(20)°$, $\angle OCO = 114.2(22)°$, $\delta OCOC = (\pm)90.2(36)°$; Boat-chair: $\angle COC = 114.4(22)°$, $\angle OCO = 114.3(2.1)°$, $\delta OCOC = (\pm)66.5(40)°/(\pm)46.2(28)°/(\pm)106.5(15)°$.

The structure and conformation of cyclooctane and several related compounds[1] have earlier been studied by different physical methods in the crystalline and gas phase, and in solution. Semi-empirical calculations of strain energy of static conformations of cyclooctane have been carried out.[2−5]

In the crystalline phase the X-ray investigation of cyclooctane[6] gave limited information because the structure is disordered. From an electron diffraction investigation in the gas phase[7] it is concluded that the experimental data are not consistent with any single conformer, and that a conformational mixture including high flexibility of the ring must exist.

Cyclooctane is reported to have small dipole moment in the gas phase.[8] From an NMR investigation[9] of cyclooctane any conformer with a C_2 axis passing through carbon atoms or a C_s plane passing only through bonds may be excluded. The infrared and Raman spectroscopic analysis[10] concludes that the molecular form is not centrosymmetric, other structural information cannot be drawn from this investigation. The difficulties in the

conformation determination of cyclooctane may be understood from the energy calculations of static conformers[2] where seven conformers are reported to have comparable energies.

However, the structure of cyclooctane derivatives and related compounds have been determined by X-ray diffraction.[11−17] From these investigations the preferred conformer of the cyclooctane ring system usually seems to be the boat-chair (BC) conformer, while heterocyclic eight-membered rings usually appear in the crown conformation when no other steric interactions influence the ring conformation. One exception is tetrathiacyclooctane, which is found in the boat-chair conformation.[18]

Proceeding from the crystalline phase, where packing effects may be responsible for the choice of conformation, to solution, the strong preference for only one conformer seems to be less pronounced.[19−21]

No strain-energy calculations for conformations of heterocyclic eight-membered rings in the cyclooctane class are available. In cyclooctane there are three main factors which contribute to the conformational strain energies. Those are the non-bonded transannular interaction, eclipsing strain and internal angle strain.

A replacement of CH_2 groups by oxygen atoms will most probably change the total strain energy of the different conformers relative to that of cyclooctane. A repulsive 1,5-CH···HC interaction across the ring in cyclooctane may become less repulsive or even attractive 1,5-O···O and 1,5-CH···O interactions in oxanes.

From an X-ray investigation of 1,3,5,7-tetra-oxacyclooctane[15] it is established that only the crown conformer exists in the solid state, while NMR investigations in solution[19−21] conclude

that two conformers are present: Crown + boat-chair.

The structure and conformation of 1,3,5,7-tetraoxacyclooctane in the gas phase were investigated in order to find out to what extent exchange of CH_2 groups by the much smaller and more electronegative oxygen atoms has a stabilizing effect on one certain conformer, and whether a conformer, which by calculations for cyclooctane is found to be less probable, could be preferred for 1,3,5,7-tetraoxacyclooctane due to reduction in the $H \cdots H$ transannular repulsions. This structure investigation is part of a study on cyclic [22] and acyclic ethers.[23-27]

EXPERIMENTAL

The sample of tetraoxacyclooctane used in the experiment was kindly supplied by cand.real. J. Krane, University of Trondheim.

The electron diffraction diagrams were taken on a Balzers Eldigraph KDG2. The nozzle temperature was kept at about 100 °C during the exposures, and the pressure in the apparatus was approximately 1×10^{-5} Torr. The diffraction diagrams were recorded at 188.79 and 578.55 mm nozzle-to-plate distances, the electron wavelengths being 0.05859 and 0.05851 Å, respectively. Four selected plates were analysed for each nozzle-to-plate distance. The intensity was recorded on a photometer for each 0.25 mm on the photographic plates. Each plate was oscillated about the center of the diffrac-tion diagrams and the intensity integrated over the arc. The data were treated in the usual way.[28]

An experimental background was subtracted on each plate before averaging the intensity data. The intensities were modified by $s/|f'_C||f'_O|$, where $|f'|$ is the scattering amplitude[29,30] for carbon and oxygen. The experimental data obtained cover scattering angles corresponding to an s-range of $1.00 - 36.25$ Å^{-1}. The molecular intensity curve is shown in Fig. 1. A least-squares procedure was used to refine the distances and vibrational amplitudes estimated from the experimental radial distribution (RD) curve. The RD curve has been obtained by Fourier transformation of the molecular intensity curve.

The calculations have been carried out on CDC 3300 and CDC 7400 (CYBER) computers.[28]

STRUCTURE AND DISCUSSION

Based on strain energy calculations for cyclooctane Hendrickson[2] and Wiberg[3] have presented data and arguments indicating that energy minima will occur in symmetrical conformations. This investigation is therefore restricted to symmetric conformers. In principle there exsist a large number of conformations of the eight-membered ring system having either planes or axes of symmetry. Among these forms (Fig. 2) according to Hendrickson seven appear to have about the same energy (within 11.7 kJ/mol), while three (C,B,TC) are highly strained
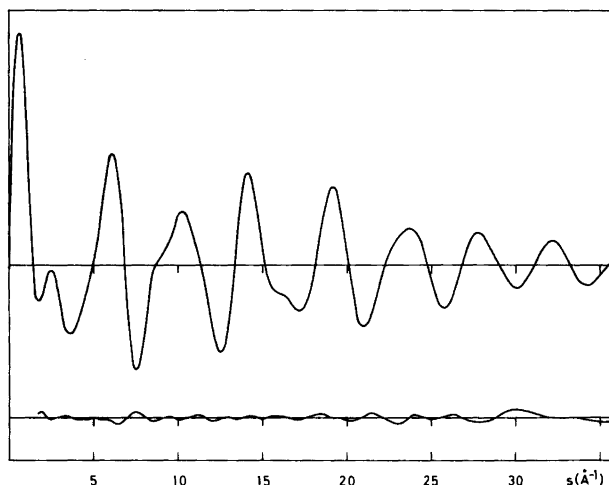

Fig. 1. 1,3,5,7-Tetraoxacyclooctane. Theoretical molecular intensity curve for an equilibrium mixture of crown (32 %) and BC (68 %) conformers. The lower curve shows the difference between experimental and theoretical values.

Table 1. Structure parameters for 1,3,5,7-tetraoxacyclooctane obtained by least-squares refinement on the intensity data. Distances (r_a-values) are given in Å, angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation. The uncertainty arising from error in the electron wavelength is included. (For numbering of the atoms see Fig. 3).

Conformation	BC (C_s)	Crown (D_{4d})
Distances		
O$-$C	1.404(1)	1.404(1)
C$-$H	1.088(3)	1.088(3)
O(1)···O(3)	2.359(18)	2.357(35)
O(1)···O(5)	3.236(24)	} 3.334(50)
O(3)···O(7)	2.780(18)	
C(2)···C(4)	2.361(17)	2.364(42)
C(2)···C(6)	3.339(26)	3.342(59)
O(1)···C(4)	2.747(18)	
O(5)···C(2)	3.284(16)	} 3.139(11)
O(7)···C(2) }		
O(3)···C(8) }	2.922(12)	
Angles		
COC	114.4(22)	114.6(20)
OCO	114.3(21)	114.2(22)
HCH	112.4	112.4
δ_1	66.5(40)	-90.2(36)
δ_2	46.2(28)	90.2(36)
δ_3	-106.5(15)	-90.2(36)
δ_4	66.5(40)	90.2(36)
δ_5	-66.5(40)	-90.2(36)
δ_6	106.5(15)	90.2(36)
δ_7	-46.2(28)	-90.2(36)
δ_8	-66.5(40)	90.2(36)
Mixture (%)	68(6)	32(6)

and consequently considerably less stable. Only the seven conformers of lower energy for cyclooctane have been studied in this investigation, as the remaining three will be strained also for tetraoxacyclooctane.

Approximate values for the structure parameters used in the least-squares analysis are determined from the experimental RD curve in Fig. 3.

The bond distances in the molecule are represented by the two first peaks in the RD curve. The peak at 1.1 Å corresponds to the eight C$-$H bond distances, and the peak at 1.4 Å to the C$-$O bond distances.
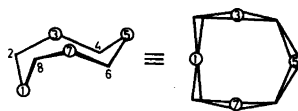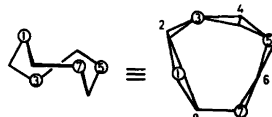
CROWN FAMILY

CROWN (D_{4d})

CC (C_{2v})
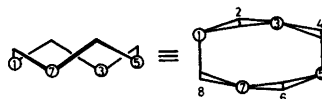
TCC (D_2)
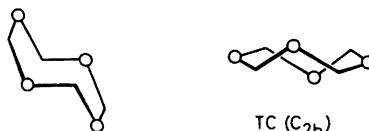
C (C_{2h})

TC (C_{2h})

BOAT FAMILY
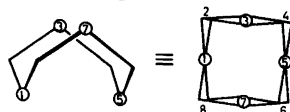
BB (D_{2d})

TB (S_4)

B (D_{2d})

BOAT$-$CHAIR FAMILY

BC (C_s)

TBC (C_2)

Fig. 2. The different conformers of the eight-membered ring system having either planes or axes of symmetry.
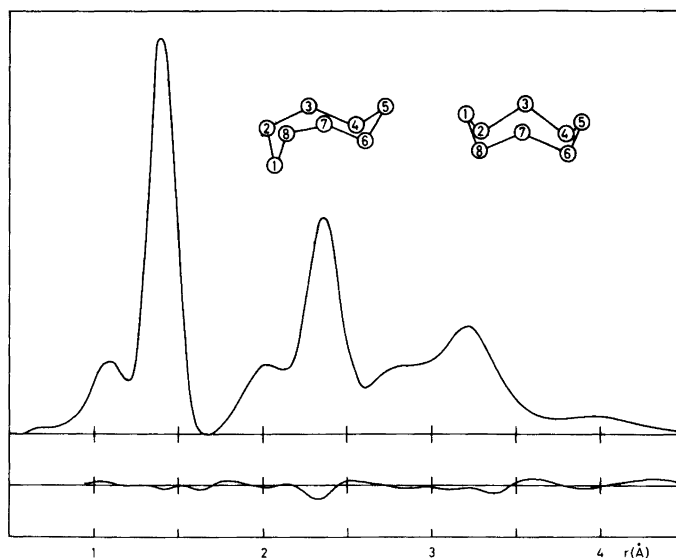
Fig. 3. 1,3,5,7-Tetraoxacyclooctane. Experimental radial distribution curve. The lower curve shows the difference between the experimental and theoretical values for a mixture of crown (32 %) and BC (68 %) conformers. Artificial damping constant $k = 0.002$ Å.

The small peak at 2.0 Å shows the shortest non-bonded $O \cdots H$ distances. The main contributions to the peak at 2.4 Å are from the four $O \cdots O$ and the four $C \cdots C$ distances over one valence angle (*i.e.* OCO and COC angles) in the ring. In the structure determination it is assumed that all COC angles and OCO angles, respectively, are equal within one conformer, although this may not be strictly correct. A satisfactory fit between experimental and theoretical RD curves for this peak may, therefore, be obtained in different ways: (i) $\angle COC \approx \angle OCO$ ($\sim 114.5°$), (ii) $\angle COC \neq \angle OCO$ (one angle about 112° and the other about 116°). However, the alternative possibility of valence angles does not influence the conformational dependent part of the theoretical RD curve for the single conformers to any importance, and only a mean value for the valence angles can be determined.

The different possibilities for the valence angles will, however, result in different vibrational amplitudes for the non-bonded distances over one angle. Assuming that the vibrational amplitudes for the $C \cdots C$ and $O \cdots O$ distances across one valence angle are equal, the following vibrational amplitudes are obtained from least-squares refinement: (i) 0.077 Å for $C \cdots C \approx O \cdots O$, (ii) 0.066 Å for $C \cdots C \neq O \cdots O$.

It is assumed that the HCH plane of each

methylene group is perpendicular to the OCO plane and bisecting the OCO angle.

The part of the RD curve which gives information about the conformation of the molecule is the region outside 2.6 Å. The determination of the conformation is based mainly on the lengths of the $O \cdots C$ and $O \cdots O$ distances across the ring in the different conformers. As may be seen from Fig. 4, curve A, this part of the experimental curve is not well-resolved. The most pronounced peak in this region is found at 3.2 Å, with a shoulder at about 2.8 Å.

For further argumentation it is convenient to assort the conformers into three groups, often referred to as "families", around the crown, the BC and the BB conformers (Fig. 2). Within one family, an interconversion between different conformers may take place by passing over relatively small barriers, while a transition to another family involves higher energy.

Crown family. In Hendrickson's calculations[2] the symmetric crown formation of cyclooctane is 11.7 kJ/mol less stable than the conformer with minimum energy. This is assumed to be due to eclipsing strain of the bonds in the crown conformer. From the calculations the eclipsing strain is found to be somewhat reduced by introducing a distortion of
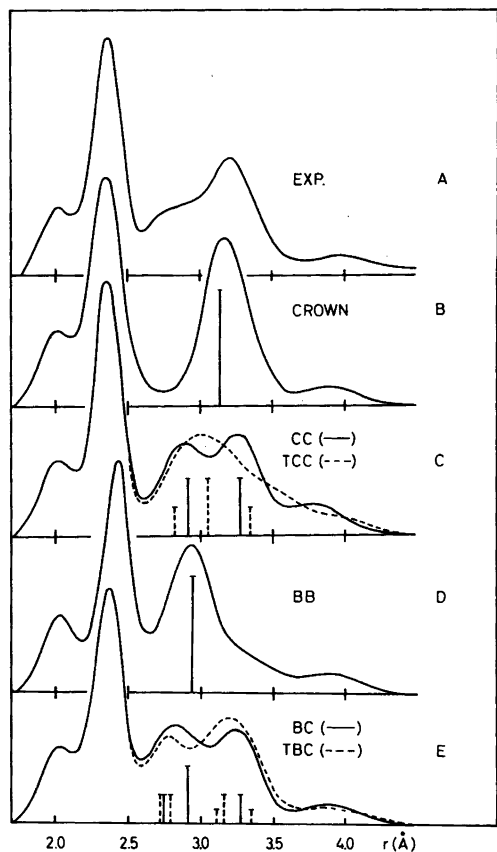
EXP.   A

CROWN   B

CC (——)
TCC (- - -)   C

BB   D

BC (——)
TBC (- - -)   E

2.0   2.5   3.0   3.5   4.0   r (Å)

Fig. 4. 1,3,5,7-Tetraoxacyclooctane. The outer part of the experimental (A) radial distribution curve compared with the corresponding part of theoretical radial distribution curves for the conformers crown (B), CC and TCC (C), BB (D) and BC and TBC (E). The position of the conformation dependent O···C distances are indicated for each conformer. ($k = 0.002$ Å).

CROWN
$\delta = (\pm)90.1°$

CC
$\delta = (\pm)81.1°, (\pm)97.9°$

CC
$\delta = (\pm)70.9°, (\pm)104.4°$

CC
$\delta = (\pm)59.8°, (\pm)109.6°$

3.0   3.5   4.0   r (Å)

Fig. 5. The outer part of theoretical radial distribution curves showing the step-by-step distortion from symmetric crown (D_{4d}) to CC (C_{2v}) conformations.

the ring, which leads to the chair-chair (CC) or twist-chair-chair (TCC) conformer. The total strain energy of the crown conformer may further be reduced by exchange of CH_2 groups by oxygen atoms, because of the somewhat lower barrier to eclipsing for $-O-CH_2-$ than for $-CH_2-CH_2-$.

Because of the high symmetry of the crown conformation, all the eight O(1)···C(4) distances across the ring are equal. These distances are found in the peak at 3.2 Å in the RD curve. As may be seen from Fig. 4, curve B, the area underneath the theoretical RD curve in this region is much too
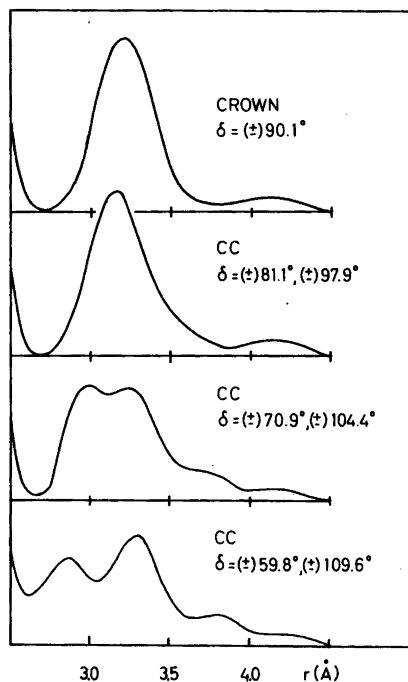
large, while there are no distances at about 2.8 Å. However, an interconversion of the crown to the less symmetric CC conformer will result in four longer ($\sim$3.3 Å) and four shorter ($\sim$2.9 Å) O···C distances (Fig. 3, curve C). The oxygen atoms in the distorted CC ring system must be at position 1, 3, 5 and 7. Otherwise the CH···HC transannular repulsion between CH_2 groups in position 3 and 7 would be appreciable. Depending on the degree of deviation from the symmetrical crown conformation, the outer part of the theoretical RD curve for the CC conformer will change. In Fig. 5 is shown a step-by-step distortion from a symmetric crown conformation. This corresponds to a change of the dihedral angles in the ring from about 90° in the symmetric crown conformer to 66 and 107° in the CC conformer in Fig. 4, curves B and C.

With the oxygen atoms in 3 and 7 positions repulsion between the lone pair electrons in the CC conformer must be expected. The O(1)···O(5) distance is increased due to the distortion of the crown and the repulsion between lone pair electrons

will be unimportant. Fig. 4 shows that none of the crown family conformers alone can be present.

By introducing a twist of the CC conformer into a twist-chair-chair (TCC) conformer (Fig. 2), the transannular $O(3) \cdots O(7)$ distances will be increased while the $O(7) \cdots C(2)$ will be somewhat shorter. A repulsion between oxygen atoms in positions 3 and 7 in the CC conformer will be reduced in the TCC conformer. An essential difference between the twisted and non-twisted conformers in the crown family is the increase in the dihedral angles $O(1)C(2)-O(3)C(4)$ ($\sim 116°$) and thereby increased $O(1) \cdots C(4)$, $O(1) \cdots O(5)$, and $C(4) \cdots C(8)$ lengths in the TCC conformer. The TCC conformer can, therefore, be excluded in this investigation.

Boat family. The boat-boat (BB) is the only conformer which represents the diamond-lattice. Also this conformer has a high symmetry with eight equal non-bonded $O \cdots C$ distances across the ring. Relatively large valence angles ($\sim 118°$) are necessary in order to avoid transannular $O \cdots O$ distances which are shorter than the sum of van der Waals radii.[31] This is also the case for the twist-boat (TB) conformer. Therefore, neither the BB nor the TB conformer fit the experimental data.

Boat-chair family. Owing to the lower symmetry of the boat-chair (BC) conformer the eight non-bonded $O \cdots C$ distances across the ring are split into three different lengths, *i.e.* two distances at about 2.8 Å, four at about 2.9 Å and two at about 3.3 Å. However, even if the BC conformer shows a number of different distances in the outer part of the RD curve outside 2.6 Å, it does not give a satisfactory fit between experimental and theoretical curves.

If a twist of the BC conformer into a twist-boat-chair (TBC) is introduced, the symmetry will be changed from C_s to C_2, as shown in Fig. 2, and there will be even more different interatomic distances. The best correspondence between the TBC conformer and the experimental data is shown in Fig. 4, E (stippled). Even if the distribution of non-bonded distances between the peak at 2.8 Å and the peak at 3.2 Å gives a better correspondence with experimental curves for the TBC conformer than for the BC, the agreement is not satisfactory.

Mixtures of conformers. In the further analysis equilibrium mixtures of conformers are discussed. The bond distances and HCH angles are kept at the values determined for the single conformers. The valence angles and dihedral angles of the ring have been determined for each conformer in the

mixtures by trial and error or by least-squares refinement of a few parameters in each cycle, as convergency could not be obtained by simultaneous refinement of several independent parameters.

All the conformers shown in Fig. 4, except the symmetric crown, lead to too small area at about 3.2 Å compared to the experimental RD curve. Therefore, the symmetric crown conformer must exist in the conformational mixture. Further, all the conformers except the crown show too large area at about 2.8 Å.

The boat family may be excluded also in a mixture because of too large valence angles. A mixture of a boat and a crown conformer with small valence angles would have to have unreasonably small vibrational amplitudes for the $C \cdots C$ and $O \cdots O$ distances over one valence angle in order to fit the experimental peak at 2.4 Å.

A mixture of crown and CC conformers shows that the conformational dependent peak at 2.9 Å for the CC conformer (Fig. 4, curve C) appears at a too long distance to give a good correspondence with the experimental RD curve. A further deformation of the CC conformer (Fig. 5) will indeed shift the main contribution (the four $O(7) \cdots C(2)$ distances) in the mentioned peak towards shorter distances, but this means that the shortest $O(3) \cdots O(7)$ distance will be considerably shorter than the van der Waals distance, which is assumed to be unreasonable.

A mixture of crown and BC conformers shows a good agreement for a distribution of 32 % crown and 68 % BC conformers (Fig. 3). In the BC conformer the maximum of the first conformation dependent peak is found at 2.8 Å, *i.e.* at a somewhat shorter distance than in the CC conformer. This is because the shortest $O \cdots C$ distances across the ring may be shorter in the BC conformer than in the CC conformer without causing a too short $O \cdots O$ distance. The reason for this is that the oxygen atoms in positions 1 and 5 in the BC conformer are situated on different sides of the CCCC plane, so that a decrease in the $O(1) \cdots C(4)$ distances results in an increase in the $O(3) \cdots O(7)$ distance, and *vice versa*. In the CC conformer, a decrease of the shortest $O \cdots C$ distances will result in a simultaneous decrease of the shortest $O \cdots O$ distance.

Even if the theoretical RD curve for the TBC conformer is the one most similar to the experimental RD curve, it has a somewhat too large peak at 2.75 Å and a too small at about 3.2 Å. In a

mixture with the crown conformer, a relatively large portion of the TBC must be present in order to give acceptable agreement with the experimental curve for the region at about 2.8 Å. However, this will result in a too large area about 2.6−2.7 Å, and a good fit is not obtained.

It should be noticed that dihedral angles and valence angles in an eight-membered ring are interdependent. Consequently it is not possible to change some distances in the molecule without a simultaneous change of most other distances.

Thus, the mixture of 32 % crown + 68 % BC is the combination which is found to give best agreement between experimental and theoretical data. As already shown, small deviations from the symmetric crown, i.e. to a C_{2v} symmetry, do not influence the RD curve significantly. However, such deviation will shift the distances at 3.2 Å somewhat towards shorter r-values (Fig. 5). This is not in accordance with the experimental data, and the symmetric crown is found to be preferred to the CC conformer in the equilibrium mixture in the gas phase.

The dihedral angles determined for the symmetric crown and BC conformers of 1,3,5,7-tetraoxacyclooctane (i.e. $(\pm)90.2°$ and $(\pm)66.5°/(\pm)46.2°/(\pm)106.5°$, respectively) are in good agreement with those calculated[2] for cyclooctane (i.e. $(\pm)87.5$ and $(\pm)65.0°/(\pm)44.7°/(\pm)102.2°$, respectively).

The vibrational amplitudes listed in Table 2 have been grouped according to distance type and lengths and refined in separate cycles, as con-

vergency could not be obtained if the geometric parameters were refined simultaneously. There is a large correlation between valence angles and dihedral angles for the crown ($\rho = 0.91$) and BC ($\rho = 0.62$) conformers. Also the correlation between the percentage population and the valence angles is considerable for both conformers ($\rho = 0.69 - 0.74$).

CONCLUSION

Based on arguments from semi-empirical energy calculations for cyclooctane,[2-5] there are indications that energy minima will occur in symmetrical conformations. The following seven conformers have been studied in this investigation: Crown, CC and TCC in the crown-family, BB and TB in the boat-family and BC and TBC in the boat-chair-family. Owing to severe steric repulsions in the B, C and TC conformers, these have been excluded in this work. From the calculations of cyclooctane by Hendrickson, some of the twist-forms are found to be more stable than the corresponding non-twisted conformers. The electron diffraction investigation of 1,3,5,7-tetraoxacyclooctane shows no preference for the twisted conformers compared to the non-twisted.

Compared to cyclooctane, 1,3,5,7-tetraoxacyclooctane is released from transannular 1,5-CH···HC repulsion, due to exchange of CH_2 groups by oxygen atoms. The corresponding interaction between lone pair electrons on oxygen atoms (1,5-O···O interaction) in 1,3,5,7 positions are probably less important.

From the present investigation it may be concluded that no single conformer gives satisfactory agreement between experimental and theoretical data.

Conformers from the crown, boat-chair and boat-families have been studied in conformation mixtures.

A conformational mixture of the crown (32 %) and the BC (68 %) conformers (~ 100 °C on the nozzle) is shown to result in an acceptable solution (Fig. 3). The results are in fairly good agreement with those of NMR investigations in solution.[19-20]

Probably the minima of the potential curves for various existing conformers are rather flat. This would result in large amplitude motion, an effect which is more pronounced in the gas phase than in solids and solutions. A further study of large amplitude motion may lead to better agreement between experimental and theoretical electron diffraction data.

Table 2. Vibrational amplitudes (u-values) for 1,3,5,7-tetraoxacyclooctane. The u-values are given in Å. The values are determined by refinements in separate cycles of a small number of parameters.

Distances	BC	Crown
O−C	0.049(1)	0.049(1)
C−H	0.068(4)	0.068(4)
O(1)···O(3)	0.077	0.077
O(1)···O(5)	0.116	} 0.107
O(3)···O(7)	0.120	
C(2)···C(4)	0.077	0.077
C(2)···C(6)	0.169	0.179
O(1)···C(4)	0.120	
O(5)···C(2)	0.116	} 0.129
O(7)···C(2) } O(3)···C(8) }	0.136	

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