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Studies on Molecules with Five-membered Rings

II. An Electron Diffraction Investigation of Gaseous Tetrahydrofuran

A. ALMENNINGEN, H. M. SEIP and T. WILLADSEN

Department of Chemistry, University of Oslo, Oslo 3, Norway

Gaseous tetrahydrofuran has been studied by electron diffraction. The five-membered ring is not planar. Evidence for essentially free pseudo-rotation has been found, but the possibility that the molecule exists in one conformation cannot be ruled out completely. However, a good agreement between experimental and theoretical intensity and radial distribution functions could not be obtained for a molecule with C_2 symmetry without unreasonable values for some of the molecular parameters.

The bond lengths (r_a) are $r(\mathrm{CO})=1.428$ (0.003) Å, $r(\mathrm{CC})=1.538$ (0.003) Å, and $r(\mathrm{CH})=1.110$ (0.005) Å.

The previous paper[1] gives conformational energies for tetrahydrofuran (THF) and 1,2,4-trioxacyclopentane (TOCP) calculated by the Westheimer-Hendrickson method. For THF these results indicate that the C_2 and C_s conformations (see Fig. 1) — and also intermediate conformations — have nearly the same energy.

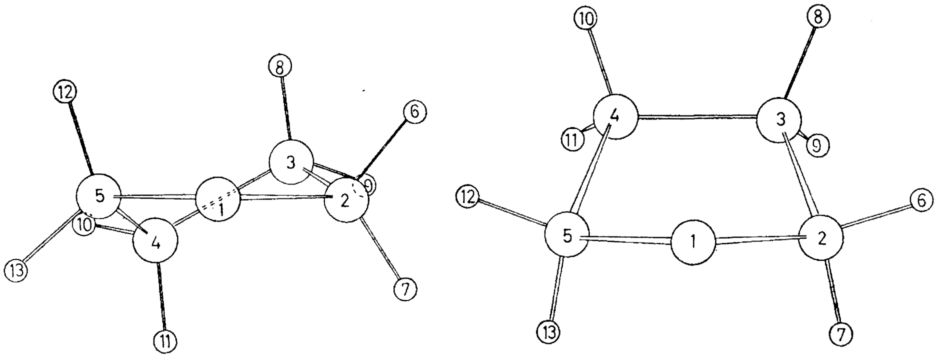

Fig. 1. a. The "half-chair" conformation (with C_2 symmetry) of tetrahydrofuran. Atom 3 is above and atom 4 below the plane through the atoms 1, 2, and 5.
b. The "envelope" conformation (with C_s symmetry). The atoms 3 and 4 are both above the plane through the atoms 1, 2, and 5.

The crystal structure of several compounds with five-membered rings has been studied.[2] For example, it is usually found that in the furanose ring either the four atoms C_5, O_1, C_2, and C_3 (see Fig. 1) or the atoms C_4, C_5, O_1, and C_2 are approximately in one plane, while C_4 or C_3 deviate from this plane. However, in these compounds the nonbonded intramolecular interactions are rather different from those in THF, and intermolecular forces may also be of importance.

THF was studied by electron diffraction by Beach[3] in 1941. He considered only planar models and obtained for the bond lengths $r(\mathrm{CO}) = 1.43 \pm 0.03$ Å and $r(\mathrm{CC}) = 1.54 \pm 0.03$ Å.

EXPERIMENT AND THEORY

Commercially supplied THF, filtered through aluminium oxide, was applied in this investigation. The diffraction photographs were obtained in the usual way with the Oslo apparatus.[4] The nozzle temperature was about 15°C, and the electron wave length 0.0648 Å corresponding to an accelerating potential of about 36 kV. Photographs were taken at two nozzle-to-plate distances, *i.e.* approximately 48 cm and 20 cm. Four plates from each distance were used in this investigation. The data were handled in the usual way.[5,6] By connecting the data from two plates, one from the long nozzle-to-plate distance and one from the short distance, four experimental intensity curves were obtained. These curves covered the s range 1.25 – 42.0 Å^{-1}, but the data below $s = 2.0$ Å^{-1} were discarded. The curves showed satisfactory mutual agreement. The average of the four curves was therefore used in the structure analysis. This experimental molecular intensity function is shown in Fig. 2 and the corresponding experimental radial distribution (RD) function[5-7] in Fig. 3. The inner peak corresponds to the C–H bond distances, the next peak to the C–C and C–O bond distances. The main contributions to the third peak come from the C···O and C···C distances, while the C···H and O···H distances give contributions in the same region as well as to the outer part of the curve.

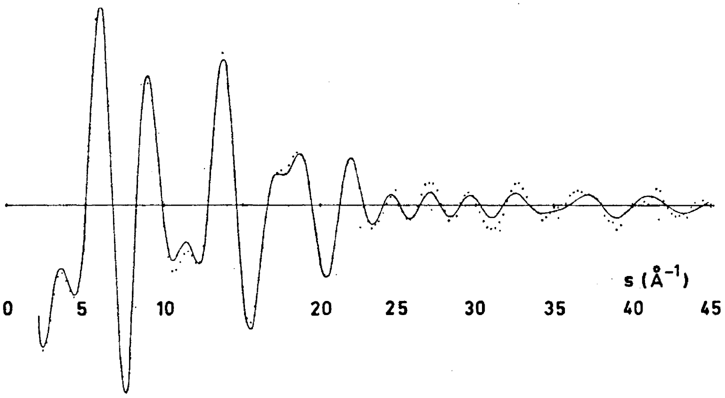

Fig. 2. The experimental (dotted) and theoretical intensity. The theoretical curve contains contributions from six conformations as described in the text.

Theoretical intensity and RD curves were calculated in the usual way.[5,6] The scattering amplitudes were calculated on a CDC 3300 computer by the "phase amplitude method" described by Peacher and Wills.[8] HF atomic potentials[9] were applied.

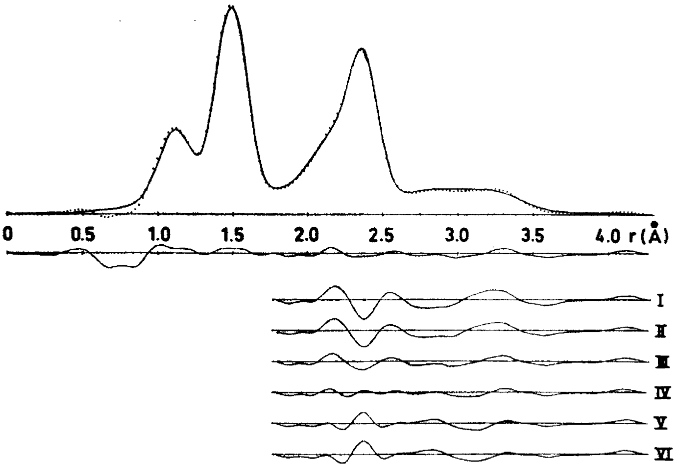

Fig. 3. The experimental (dotted) and theoretical RD curves corresponding to the intensity curves in Fig. 2. (An artificial damping constant $k=0.002$ Å^2 has been applied). The curve just below the RD curves shows the difference between the experimental and theoretical values. The curves marked I—VI show the difference between the experimental RD values and theoretical curves calculated from one conformation only. (The inner parts of all the difference curves are identical). The number on the curve shows which conformation has been used in the calculation of the theoretical curve. *Note that the ordinate scale for all the difference curves is twice the scale for the RD curves.*

STRUCTURE ANALYSIS

a. Results obtained with the assumption that the molecule exists in one conformation. First we tried to refine a model with C_2 symmetry by least-squares calculations with a diagonal weight matrix.[5,10] The model is shown in Fig. 1.* All the HCH angles were assumed equal and the H atoms were placed as described on p. 2744 of the previous paper.[1] A fairly good agreement between experimental and theoretical intensity values could be obtained, but only with some unreasonable molecular parameters. A model with C_s symmetry was also tried. The molecular parameters then refined to more reasonable values. However, the agreement between experimental and theoretical curves was not quite satisfactory. Some bond angles obtained in these two refinements are shown below. Standard deviations are given in parentheses.

	C_2 model	C_s model
∠COC	115.4° (0.2°)	106.2° (0.4°)
∠OCC	104.1° (0.2°)	105.0° (0.1°)
∠HCH	122.0° (2.0°)	110.8° (1.1°)

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* Note that the numbering of the atoms in the ring is not the same as in Ref. 1.

It is seen that both the COC and the HCH angles became unreasonably large in the C_2 model. These refinements seemed to lead to the conclusion that the molecule cannot exist in a C_2 conformation only. The C_s model may probably also be rejected, but with less certainty.

Table 1. Final values for the bond lengths (r_a values[13]) and the corresponding mean amplitudes of vibration. Standard deviations are given in parentheses.

	r (Å)	u (Å)
C–O	1.428 (0.003)	0.0519 (0.003)
C–C	1.538 (0.003)	0.0539 (0.003)
C–H	1.110 (0.005)	0.0845 (0.005)

The values obtained for the bond lengths were very nearly the same irrespective of the assumed symmetry. Table 1 gives our results for the bond distances and the corresponding mean amplitudes. All the values are seen to be normal. The standard deviations obtained by least-squares refinement with a diagonal weight matrix are usually too small.[11,12] Inclusion of the proper off-diagonal elements may increase the standard deviations for the best determined parameters by a factor of about 2. The factor is usually smaller for larger standard deviations. To obtain more realistic standard deviations than those given by the least-squares calculations, refinements were also carried out on the four experimental intensity curves separately. The standard deviations given in Table 1 have been estimated taking the results of these calculations into account.

b. *Results obtained when mixtures of conformations are considered.* The conformational energies given in Table 1 of the previous paper[1] indicate that the C_2 and the C_s conformations (and also intermediate conformations) of THF have nearly the same energy. As mentioned in Ref. 1 recent spectroscopic investigations have also given evidence for nearly free pseudo-rotation in THF. The fact that neither a C_2 nor a C_s model with reasonable parameters gives satisfactory agreement between experimental and theoretical intensity functions is in accordance with this conclusion. By synthesising a theoretical intensity or RD function with appropriate contributions from a series of conformations, it should be possible to obtain satisfactory agreement with the experimental curves. The results given in Table 1 of the previous paper[1] were used in the calculation of the theoretical curves. The contributions from six conformations were included, *i.e.* the models with nearly C_2 symmetry (conformation I), with nearly C_s symmetry (conformation VI), and the intermediate conformations II—V described on p. 2746 of the previous paper.[1] Inclusion of more intermediate conformations did not change the final RD curve significantly. The RD curve with contributions from the conformations I—VI can therefore be regarded as a good approximation to the RD curve corresponding to THF with free or restricted pseudo-rotation according to the weights given to the conformations.

Theoretical RD curves were calculated for a series of molecular models with the bond lengths and the corresponding u values given in Table 1. HCH angles equal to 110° and 112° were tried. The u values for the non-bonded, C···O and C···C distances were assumed equal and varied from 0.055 Å to 0.075 Å. Fig. 3 shows difference curves [RD(exp)−RD(theor)] calculated for the conformations I—VI with the angles given in Table 1 column b of the previous paper and the u values for the non-bonded distances given in Table 2.

Table 2. Mean amplitudes of vibration (in Å) for the non-bonded distances applied in the calculations of the theoretical curves shown in Figs. 2 and 3.

C···C		0.063
C···O		
O···H		0.12−0.15
C···H		0.12−0.15
H···H	(bounded to the same C)	0.12
H···H	(otherwise)	0.20

The HCH angle was 110°. Fig. 3 shows that of these six conformations the best agreement between the experimental and theoretical RD curves is obtained for number IV; none of the others give satisfactory agreement. The theoretical curve calculated by averaging the six theoretical curves is also shown in Fig. 3. The curves corresponding to the C_2 and C_s conformations (I and VI) were given equal weights, the curves for the conformations II—V twice the weight (see p. 2746 of Ref. 1). Finally the difference between the average curve and the experimental one is shown. The agreement is seen to be quite satisfactory.

The average theoretical intensity curve is compared to the experimental intensity in Fig. 2.

Table 3 gives the range of the non-bonded distances (except H···H) as well as of the angles in the ring for all the conformations I—VI used in the calculation of the theoretical curves in Figs. 2 and 3.

The conformational energies given in Table 1 column b of the previous paper[1] indicate that the C_s conformation should be given less weight than the C_2 conformation. However, the agreement between the experimental and theoretical RD curves was not as good as in Fig. 3 if the weights were calculated from the conformational energies.

Similar calculations were also carried out using the angle parameters given in the other columns (a, c—f) of Table 1 in the previous paper.[1] In all cases it was necessary to give conformation VI (C_s symmetry) about the same weight as conformation I (C_2 symmetry) to obtain the best agreement. If the data in the columns a, c, or d were used, it was possible to obtain an agreement between the average theoretical curve and the experimental one similar to the agreement obtained with the angles given in column b (see Fig. 3). The angles in the columns e and f gave theoretical RD curves where the peak centred around 2.35 Å was slightly displaced towards smaller r-values for all reasonable choices of the HCH angles and the u values.

Table 3. Range of non-bonded distances and angles in the conformations used to calculate the RD curves shown in Fig. 3. The distances given on one line cover together the given range.

	Range (Å)
$C_2 \cdots C_4$, $C_3 \cdots C_5$	2.362 – 2.431
$C_2 \cdots C_5$	2.287 – 2.334
$O_1 \cdots C_4$, $O_1 \cdots C_3$	2.333 – 2.390
$O_1 \cdots H_6$, $O_1 \cdots H_{12}$	2.085 – 2.096
$O_1 \cdots H_8$, $O_1 \cdots H_9$, $O_1 \cdots H_{10}$, $O_1 \cdots H_{11}$	2.776 – 3.312
$C_2 \cdots H_8$, $C_3 \cdots H_6$, $C_3 \cdots H_{10}$, $C_4 \cdots H_{12}$	2.181 – 2.203
$C_2 \cdots H_{11}$, $C_5 \cdots H_8$	2.793 – 3.194
$C_2 \cdots H_{10}$, $C_5 \cdots H_9$	3.165 – 3.348
$C_2 \cdots H_{12}$, $C_2 \cdots H_{13}$, $C_5 \cdots H_6$, $C_5 \cdots H_7$	2.713 – 3.261
$C_3 \cdots H_{12}$, $C_3 \cdots H_{13}$, $C_4 \cdots H_6$, $C_4 \cdots H_7$	2.775 – 3.356
	Range (degrees)
∠COC	106.4 – 109.7
∠OCC	103.7 – 107.4
∠CCC	100.3 – 104.1
	Max. value (degrees)
φ (O_1-C_2)	41.0
φ (O_1-C_5)	
φ (C_2-C_3)	39.5
φ (C_4-C_5)	
φ (C_3-C_4)	38.0

CONCLUSION

Satisfactory agreement between the experimental and theoretical curves cannot be obtained for a model with C_2 symmetry and reasonable molecular parameters. A C_s model may probably also be rejected. A good fit may be obtained with a less symmetric model (*cf.* curve IV in Fig. 3), but it seems much more likely that the molecule exhibits nearly free pseudorotation, *i.e.* that the energy difference between the C_s and C_2 models is small (say 0.0 ± 0.3 kcal/mole).

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