

On the Structure of Gaseous 3-Bromotetrahydrofuran

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Gaseous 3-bromotetrahydrofuran has been studied by electron diffraction and its conformational energies have been calculated by the Westheimer-Hendrickson method. The best agreement between theoretical and experimental electron diffraction data is obtained when one assumes that the ring undergoes nearly free pseudorotation. The bond distances (r_a) and standard deviations determined are: $r(\text{CO}) = 1.428(0.005)$ Å, $r(\text{CC}) = 1.527(0.008)$ Å, and $r(\text{CBr}) = 1.954(0.008)$ Å. The low energy difference between different conformations, calculated to be about 0.5 kcal mol⁻¹, confirms the results obtained by electron diffraction.

In the previous papers of this series¹⁻⁶ the influence of heteroatoms on the pseudorotation of five-membered saturated rings was studied. It appeared that a heteroatom in the ring tends to restrict the ring pseudorotation and to stabilize the conformation with C_2 symmetry, the effect increasing with the size of the heteroatom.

Several studies have been made⁷⁻⁹ to determine the effect of halogens on the conformational arrangement of the five-membered rings. Reisse *et al.*⁷ calculated the barrier for pseudorotation of chloro- and bromocyclopentane to be only 1.1 kcal mol⁻¹ which would allow the presence of all pseudorotational conformations in the gas and liquid phases. From a temperature study of the Raman spectra, Durig *et al.*⁸ estimated the enthalpy difference between the axial and the equatorial orientations of the halogen atom in chloro- and bromocyclopentane to be 0.34 and 0.61 kcal mol⁻¹, respectively. From an IR study⁸ they concluded that both molecules exist in a mixture of the different conformers and suggested that the barrier to pseudorotation is smaller than 4 kcal mol⁻¹. 3-Halotetrahydrofurans,⁹ however, were re-

ported to be less flexible, despite the fact that tetrahydrofuran itself undergoes pseudorotation. Buys *et al.*⁹ interpreted infrared spectra and dipole-moment measurements of 3-halotet-

Table 1. Structural parameters with standard deviations referring to the last digit given for 3-bromotetrahydrofuran.^a

Distances	r^b (Å)	u (Å)
C—O	1.428 (5)	0.040 (5)
C—C	1.527 (8)	0.045 (5)
C—Br	1.954 (8)	0.052 (5)
C—H	1.105 (8)	0.080 (8)

^a Standard deviations include estimate of systematic errors. ^b r_a values.¹³

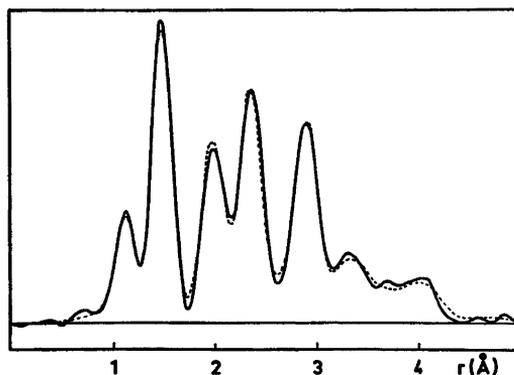


Fig. 1. The experimental (—) and calculated (---) radial distribution function for 3-bromotetrahydrofuran (data in the s -ranges 2.0–15.5 Å⁻¹ and 7.0–30.0 Å⁻¹ were used for nozzle-to-plate distance of 50 cm and 25 cm, respectively). The damping constant used was $k = 0.0015$ Å². The calculated radial distribution function for model 6 (see text for definition) was used.

Table 2. Conformational energies E (in kcal mol⁻¹) and the corresponding angle parameters (in degrees) in 3-bromotetrahydrofuran. Constants used in the calculations: (k is given in kcal mol⁻¹ degree⁻² and V° in kcal mol⁻¹). Bond distances: $r(\text{C}-\text{O})=1.428$ Å, $r(\text{C}-\text{C})=1.527$ Å, $r(\text{C}-\text{Br})=1.951$ Å, $r(\text{C}-\text{H})=1.10$ Å, $\angle\text{HCB}r=107^\circ$, and $\angle\text{HCH}=110^\circ$. $\theta^\circ_{\text{COC}}=109^\circ$, $\theta^\circ_{\text{OCC}}=\theta^\circ_{\text{CCC}}=112^\circ$; $k_{\text{COC}}=k_{\text{OCC}}=k_{\text{CCC}}=0.030$, $k_{\text{CC}(\text{Br})\text{C}}=0.035$; $V^\circ_{\text{CO}}=2.0$, $V^\circ_{\text{CC}}=2.9$; $V^\circ_{\text{CC}(\text{Br})}=3.1$ (Set I),¹⁴ $V^\circ_{\text{CC}(\text{Br})}=3.6$ (Set II).¹⁵

A^a	Set I $\angle\text{C}_5\text{O}_1\text{C}_5$	$\angle\text{O}_1\text{C}_2\text{C}_3$	$\angle\text{C}_2\text{C}_3\text{C}_4$	$\phi(\text{O}_1-\text{C}_2)$	$\phi(\text{O}_1-\text{C}_5)$	E	Set II E
0	108.0	107.2	101.2	12.5	13.0	9.57	9.97
36	107.8	107.9	102.1	0.5	24.0	9.67	10.21
72	107.0	108.0	103.2	-12.5	34.0	9.78	10.50
108	105.9	107.7	103.9	-22.6	40.0	9.87	10.77
144	105.1	105.5	104.9	-36.5	44.0 ^b	9.94	10.89
180	103.5	104.7	104.0	-43.0	43.0 ^b	9.85	10.73
216	104.2	103.7	103.3	-43.5	35.0	9.72	10.40
252	105.6	103.5	102.2	-40.5	25.0	9.65	10.11
288	106.9	104.2	101.2	-34.1	13.0	9.60	9.96
324	107.7	105.5	100.8	-24.8	0.0	9.55	9.89
360	107.9	106.7	101.2	-13.3	-13.0	9.55	9.93
396	107.7	107.3	101.9	-4.0	-22.0	9.61	10.16
432	106.9	107.7	103.2	11.1	-34.0	9.80	10.55
468	105.9	107.6	103.9	21.5	-40.0	9.93	10.83
504	104.0	106.0	104.9	36.0	-45.0 ^b	10.00	10.89
540	103.2	104.6	104.0	43.0	-42.0	9.82	10.77
576	104.2	103.8	103.2	43.6	-35.0	9.69	10.37
612	105.6	103.7	102.1	40.4	-25.0	9.60	10.07
648	106.9	104.5	101.1	33.9	-13.0	9.54	9.91
684	107.7	105.8	100.7	24.4	0.0	9.52	9.87

^a Approximate phase angle of pseudorotation. ^b Not optimized.

rahydrofurans in the liquid phase as favouring the presence of only one conformer, the halogen atom being in an axial position on the most puckered part of the ring.

Due to the presence of the bromine, which is a strong scatterer, one would expect the possible multiple conformers in 3-bromotetrahydrofuran to be detectable by electron diffraction. Therefore an investigation of this compound was undertaken, and the electron-diffraction study was complemented by calculations (Westheimer-Hendrickson method) of the conformational energies and by recording IR spectra. The nozzle temperature was about 75 °C; further experimental details are given in Ref. 10.

Altona *et al.*^{9,11} have described the pseudorotation by

$$\phi_j = \phi_m \cos (\Delta/2 + j \times 144^\circ), \quad j=0, 1, 2, 3, 4$$

where ϕ_j is the torsional angle around the j -th bond in the ring, ϕ_m is a constant equal to the maximum possible torsional angle, and Δ is called "the phase angle of pseudorotation" (see

also Ref. 12). In order to estimate the barrier to pseudorotation, the energy of the conformer as a function of the phase angle must be calculated. The phase angle increment chosen was 36°, and the modified Westheimer-Hendrickson method¹ was used to calculate the conformational energies. The bond lengths were obtained from this electron-diffraction experiment (see Table 1). The planes through the atoms HCH and HCB r were assumed to be perpendicular to the planes through XCC (where X is O or C) and to bisect the XCC angle. Dipole-dipole interactions were not included in the calculations since the effect was expected to be small.

The conformational energies were calculated for two sets of parameters and the differences between maxima and minima were about 0.5 kcal mol⁻¹ in set I and 1.0 kcal mol⁻¹ in set II (see Table 2). In both sets the minima were found at phase angles 324 and 684°, both conformers having "nearly" C_s symmetry (neglecting the difference between CH₂ and O) with the "plane of symmetry" passing through

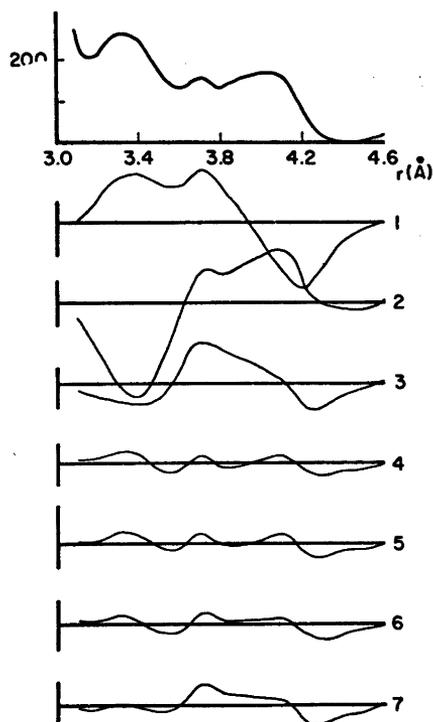


Fig. 2. Comparison of the experimental and calculated radial distribution functions in the region which exhibits the conformational effects. The top curve is the experimental function, the lower curves are differences between experimental and theoretical curves. The numbers correspond to the models defined in the text.

the carbon atom to which the bromine is bonded. The bromine is in the equatorial position at 324° and axial position at 684° . At both maxima the ring has "nearly" C_2 symmetry, with the axis of symmetry passing through the brominated carbon. The results of these calculations show that the most favourable conformations are those with maximum puckering on the brominated carbon. When the puckering moves away from this carbon the energy of the conformers increases until it reaches a maximum when the puckering is on the opposite side of the ring.

Buys *et al.*⁹ calculated the barrier to be considerably higher, $2.9 \text{ kcal mol}^{-1}$, considering only torsional energy contributions. These authors⁹ used a value for the barrier to rotation of $V^\circ_{\text{CO}} = 1.07 \text{ kcal mol}^{-1}$ in comparison

to $2.00 \text{ kcal mol}^{-1}$ used in the present calculations and also kept the maximum torsional angle constant at 39° , while in this work all torsional angles were varied. As can be seen from the calculations,¹⁰ the contributions of the bending energy have just the opposite trend from the torsional energy, and this tends to cancel the energy differences between the conformations.

The experimental radial distribution function is shown in Fig. 1 (the solid line). All bond angles and torsional angles in the ring constantly change so that any refinement of angles from electron-diffraction data is impossible. Except for the bond lengths and amplitudes of vibrations, all of the structural parameters for different models were obtained from the calculations. These models were used to construct radial distribution functions for comparison with the experimental function. The agreement for the outer part of the radial distribution function, which is most sensitive to the conformational arrangement, is shown in Fig. 2 for the following models:

1. The conformation with a phase angle of 324° of set I, which corresponds to a minimum on the potential curve.
2. The conformation with a phase angle 684° of set I, which corresponds to a minimum on the potential curve.
3. The 1:1 mixture of models 1 and 2.
4. An equally-weighted mixture of all 20 conformers with parameters from set I.
5. An equally-weighted mixture of all 20 conformers with parameters from set II.
- 6,7. A mixture of all 20 conformers, each conformer weighted by the Boltzmann factor $f_i = \exp(E_{\text{min}} - E_i)/RT$, where E_i is the energy of i -th conformer, E_{min} is the energy minimum, R is the gas constant, and T is the temperature. Model 6 uses the angles and energies of set I, model 7 of set II.

From Fig. 2 one can see that the best agreement between the experimental and the calculated radial distribution functions is obtained with models 4, 5, and 6. The radial distribution function for model 6 is shown in Fig. 1 (dashed line).

Despite the lack of perfect agreement between the calculated and experimental molecular intensity, it is clear that 3-bromotetra-

hydrofuran undergoes hindered pseudorotation. The location of the bromine and the barrier to pseudorotation are less certain, but it appears that bromine prefers to be on the puckered part of the ring and that the barrier is about 0.5 kcal mol⁻¹.

The electron diffraction results are contradictory to those reported in the IR and Raman study of liquid 3-halotetrahydrofurans;⁹ IR spectra of *gaseous* 3-bromotetrahydrofuran were therefore recorded at three different temperatures, namely 72, 85, and 105 °C. The C-Br stretching frequencies for the axial and the equatorial bromine were previously assigned to 535 and 728 cm⁻¹, respectively. The infrared spectra of the gaseous sample showed the presence of both bands with the intensity of the peaks about equal. This is consistent with a small energy difference between the two forms having equatorial and axial bromine. However, two peaks would also be consistent with the picture of free or slightly-hindered interchange of conformations by pseudorotation in the gas-phase.

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