

The Molecular Structure of Gaseous Tetrahydropyran

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The molecular structure of tetrahydropyran has been studied by electron diffraction from the vapour. A simplified general valence force field has been derived from vibrational spectroscopic data taken from the literature, and used to give information about vibrational amplitude quantities and correction terms included in the structural analysis. The electron diffraction data are consistent with a chair form of C_s -symmetry. Several constraints were introduced and the derived bond distances (r_a) and valence angles (\angle_a) are: $r(\text{CH})=111.6(2)$ pm, $r(\text{CO})=142.0(2)$ pm, $r(\text{CC})=153.1(2)$ pm, $\angle \text{HCH}=110.1(9)^\circ$, $\angle \text{COC}=111.5(9)^\circ$, $\angle \text{CCC}(\text{C})=108.3(15)^\circ$, $\angle \text{OCC}=111.8(3)^\circ$, and $\angle \text{CCC}(\text{O})=110.9(12)^\circ$. The corresponding ring dihedral angles are: $\phi(\text{OCCC})=56.9(6)^\circ$, $\phi(\text{CCCC})=52.5(12)^\circ$ and $\phi(\text{COCC})=59.9(12)^\circ$. The parenthesized values are σ . Conjoint structural analysis of the diffraction data and experimental rotational constants reported in the literature showed that the quoted structural results are consistent with the microwave data. A combined refinement did not cause significant shifts in the parameter values, but yielded smaller standard deviations. However, problems due to non-obvious effects caused by the necessity of maintaining the many constraints on the molecular model have been discussed and related to the obtained correlation coefficients.

Results of spectroscopic studies have established that the chair form is the prevailing conformer for tetrahydropyran (pentamethylene oxide): it was concluded by NMR spectroscopy that the replacement of a CH_2 group in cyclohexane by an oxygen did not sensitively affect the conformational mobility;^{1,2} no rotational spectrum from the boat form was detected;^{3,4} and the vibrational spectra have been assigned in terms of a chair form of C_s -

symmetry.^{5,6} However, in connection with a planned conformational study of 2-hydroxytetrahydropyran, more detailed structural information about the parent molecule was wanted and an electron-diffraction study of gaseous tetrahydropyran was therefore initiated. Structural analysis of the electron-diffraction data should, when combined with the available information from rotational^{3,4} and vibrational^{5,6} spectroscopy, yield unambiguous structural results although some problems may be encountered as described in the electron-diffraction investigations of the related compounds 1,3-dioxan⁷ and 1,3,5-trioxan.⁸

EXPERIMENTAL AND DATA PROCESSING

A gas chromatographic analysis of a commercial sample of tetrahydropyran indicated a purity of about 99%, and it was used without further purification. Electron-diffraction photographs were made in a Balzers' Eldigraph KDG-2⁹ using Kodak Electron Image plates, nozzle-to-plate distances of 500.12 and 250.12 mm, an accelerating voltage of 42 kV, and sample-container and nozzle-tip temperatures of 8 and 20 °C, respectively. The ambient pressure during the sample run-in was $1.8-2.0 \times 10^{-6}$ Torr, and the exposure times were 1–3½ min. The electron wavelength was 5.862 pm as determined from electron-diffraction photographs of powdered thallos chloride and calibrated against diffraction patterns of gaseous benzene using $r_a(\text{CC})=139.75$ pm as a standard.¹⁰ The estimated uncertainty in the electron wavelength is 0.1%.

The optical densities of five plates from each of the two camera distances were recorded in a rectangular co-ordinate system using a Joyce-Loebl microdensitometer. For each of 40 equidistantly (0.6 mm) spaced lines, 600 data points were recorded in intervals of 0.25 mm. Using computer programs written by H. M. Seip and R. Seip data points between arcs about the center of the diagrams were

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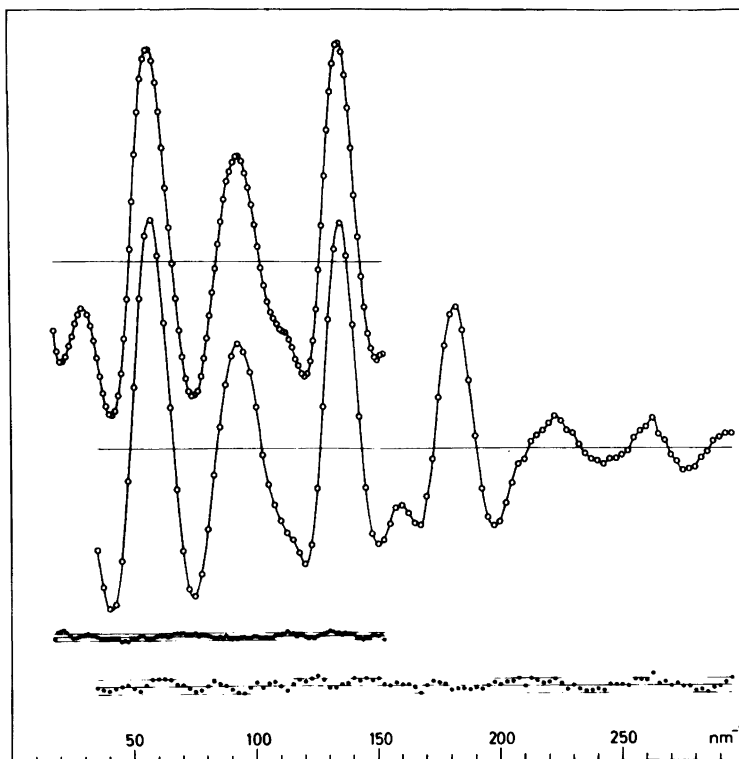


Fig. 1. Experimental molecular intensity data for tetrahydropyran obtained from electron-diffraction experiments at camera distances of 50 and 25 cm, and the corresponding differences between experimental and theoretical intensities computed according to the parameter values of Table 6 B. The full lines given along with the differences indicate the estimated uncertainties (three standard deviations) of the experimental intensity points.

averaged to give, in even intervals of R (0.5 mm), two co-centric branches of intensity data which consecutively were interpolated into even intervals of s . The further data reduction was carried out in routine fashion.¹¹ The applied blackness correction was $1.00 + 0D + 0.06D^2 + 0.06D^3$, and background corrections were carried out for the individual curves on the levelled¹¹ form. Averaged molecular intensity curves modified by $s/|f'_c|^2$, were calculated for each

of the two camera distances. The scattering amplitudes, $|f'_c|$, and phases, η ,¹¹ were calculated using the partial wave method¹² based upon analytical expressions for the HF potentials¹³ for the carbon and oxygen atoms and the best electron density for bonded hydrogen for the hydrogen atoms.¹⁴ The inelastic scattering factors used were those of Tavard *et al.*¹⁵

The modified molecular intensities upon which

Table 1. Ranges and weighting of the electron-diffraction data. The scattering angle parameters (s) in nm^{-1} : w_1 and w_2 in pm^2 ; and p_1 , p_2 and W dimensionless. Diagonal weight matrices for $p_2 = p_3 = 0$.

Curve (camera dist.)	Data range		Data interval	Constants of the weighting schemes ^{11,16}						
	s_{\min}	s_{\max}	Δs	s_1	s_2	w_1	w_2	p_2	p_3	W
50 cm	17.5	152.5	1.25	50.0	130.0	500	1000	-0.64	0.146	1.00
25 cm	35.0	295.0	2.50	50.0	210.0	4000	100	-0.60	0.125	1.00

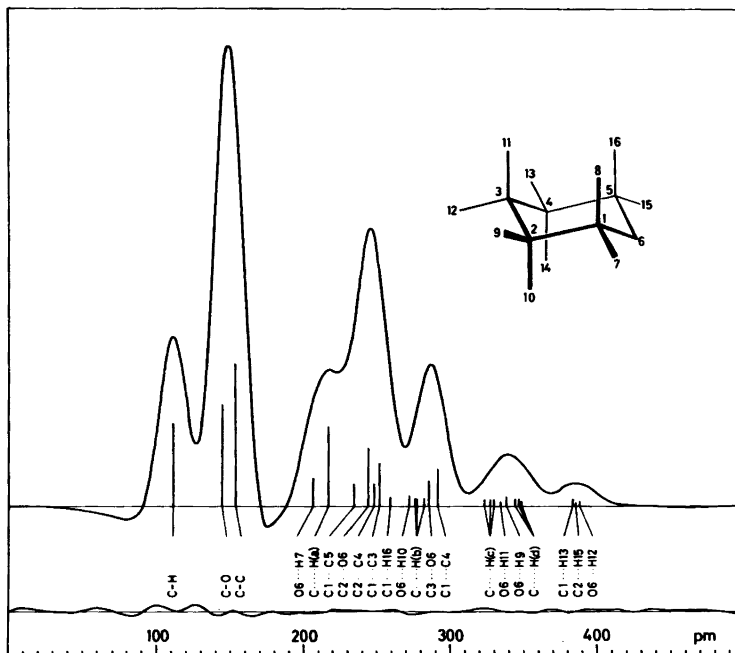


Fig. 2. Experimental radial distribution curve for tetrahydropyran calculated from the intensity data given in Fig. 1 using calculated intensity points for the unobserved inner region ($s \leq 17.5 \text{ nm}^{-1}$) and an artificial damping constant of $k=15 \text{ pm}^2$. The differences between experimental and theoretical curves calculated according to the parameter values of Table 6 B are given. A molecular model of the molecule ($\text{C}_5\text{H}_{10}\text{O}$) with the numbering of the atoms is shown. The vertical lines indicate the positions of the interatomic distances where $\text{C}\cdots\text{H}(a)$, $\text{C}\cdots\text{H}(b)$, $\text{C}\cdots\text{H}(c)$ and $\text{C}\cdots\text{H}(d)$ are composite and correspond to: a, $\text{C}1\cdots\text{H}9$, $\text{C}2\cdots\text{H}7$, $\text{C}2\cdots\text{H}11$ and $\text{H}3\cdots\text{H}9$; b, $\text{C}2\cdots\text{H}14$, $\text{C}3\cdots\text{H}8$ and $\text{C}1\cdots\text{H}11$; c, $\text{C}2\cdots\text{H}16$, $\text{C}1\cdots\text{H}14$ and $\text{C}1\cdots\text{H}15$; d, $\text{C}2\cdots\text{H}13$, $\text{C}3\cdots\text{H}7$ and $\text{C}1\cdots\text{H}12$.

the structural analysis of tetrahydropyran is based are shown in Fig. 1, and the intensity data are available upon request. The data ranges and intervals used are given in Table 1, which also contains the constants of the weighting schemes.^{11,16} All structural results quoted are obtained in least-squares refinements using diagonal weight matrices. However, the standard deviations obtained in this manner were augmented by a factor, f , to account for correlation among the electron-diffraction data. From the results of some comparative refinements using diagonal and non-diagonal weight matrices,¹⁶ appropriate estimates of f seem to be 2 for all quantities cited with the exception of the distance and amplitude parameters for the CH bond where a factor of 3 was preferable.

A composite intensity curve was computed from those of Fig. 1 by scaling and averaging intensity values in the overlap region, and the experimental radial distribution curve calculated from this con-

nected curve is presented in Fig. 2 together with a molecular model showing the numbering of the atoms.

TRIAL MODELS

In order to reduce the number of independent parameters, several constraints were introduced for the methylene groups: (a) all C–H distances are equal; (b) all HCH angles are equal; (c) the H–C–H planes are perpendicular to the planes defined by the carbon atom and its two adjacent ring atoms; and (d) the bisectors of the HCH angles and those of the corresponding angles of the ring are colinear. Assuming C_s -symmetry, nine parameters could then be used to describe the geometry of the molecule which could be chosen to be either in a chair form or a boat form. The

parameters are: $r(\text{CH})$, $r(\text{CO})$, $\overline{r(\text{CC})}$, $\Delta(\text{CC}) = r(\text{C1C2}) - r(\text{C2C3})$, $\angle \text{HCH}$, $\angle \text{COC}$, $\angle \text{C2C3C4}$, $\angle \text{OCC}$, $\angle \text{C1C2C3}$.

The boat and chair form were both tested assuming $\Delta(\text{CC}) = 0$, and using fixed sets of amplitudes of vibration computed for each of the two models from the simplified general force field given in the next section. The chair form of the molecule could be adjusted to fit the intensity data with a generalized weighted R -factor¹¹ of 4% as compared to 20% for the boat form which was found to be inconsistent with the experimental radial distribution curve in the 240–330 pm region. The further structure analysis was based on a chair conformation only. The interpretation of the radial distribution curve is seen from the line diagram of distances shown in Fig. 2, and it also demonstrates the presence of complex distance overlaps. The possibilities of false minima were therefore carefully considered. However, only one minimum was obtained as a result of several refinements where the start values and the refinement schemes for the geometrical parameters were systematically varied.

SIMPLIFIED GENERAL VALENCE FORCE FIELD (SGVFF)

A valence force field with as few interaction force constants as possible was derived from a more extensive one reported by Snyder and Zerbi⁵ and from a simplified one for cyclohexane.¹⁷ A normal coordinate program written by D. W. Gwinn¹⁸ was used to adjust the force constants so as to give calculated normal frequencies in satisfactory agreement with the observed values reported by Vedal *et al.*⁶ The obtained overall fit was 1.2% which corresponds to a mean deviation of 17 cm^{-1} . There are slight discrepancies in the two spectroscopic studies^{5,6} regarding the value of ν_{13} and the assignment of ν_{17-19} and $\nu_{38,39}$ and our calculations compare more favourably with the results of Snyder and Zerbi.⁵ The values for the nine different groups of centrifugal distortion coefficients (τ) calculated from the derived force field were further reduced to the six Kivelson-Wilson coefficients (τ')¹⁹ and consecutively to the quartic distortion constants,²⁰ τ''_{aaaa} , τ_1 , τ_2 and τ_3 . As seen from the comparisons in Table 2 the calculated values reproduce the sign and magnitude of the values obtained from the microwave spectral data.⁴ The final force constants of the derived SGVFF are given in Table 3.

Table 2. Quartic distortion constants²⁰ in kHz calculated from the derived SGVFF of Table 3 and values computed from microwave spectral data.⁴

	Calc.	Obs. ⁴
τ''_{aaaa}	-4.76	-3.99 ± 0.83
τ''_{bbbb}	-4.43	-4.22 ± 0.83
τ''_{cccc}	-0.78	-0.849 ± 0.844
τ_1	-6.75	-5.209 ± 2.488
τ_2	-1.88	-1.441 ± 0.829
τ_3	-231	-300 ± 50

Table 3. Simplified general valence force field (SGVFF) for tetrahydropyran. The number of contributions for each type is given in parentheses. The interaction force constants k_{rr} and $k_{r\theta}$ should be doubled when used in Gwinn's program,¹⁸ and the torsional force constants have three and nine contributions, respectively, for torsion about each CO and CC bond.

k_r (nN nm ⁻¹)		k_{rr} (nN nm ⁻¹)	
CH(10)	458.	CO/CO(1)	28.
CO(2)	454.	CC/CO(2)	28.
CC(4)	410.	CC/CC(3)	28.
k_θ (nN nm rad ⁻²)		$k_{r\theta}$ (nN rad ⁻¹)	
$\angle \text{CC2C}(2)$	0.99	CO/COC(2)	3.6
$\angle \text{CC3C}(1)$	0.79	CO/OCC(2)	3.6
$\angle \text{COC}(1)$	0.89	CC/OCC(2)	3.6
$\angle \text{OCC}(2)$	0.80	CC/CC2C(4)	3.6
$\angle \text{HCH}(5)$	0.48	CC/CC3C(2)	3.6
$\angle \text{OC1H}(4)$	0.75	CO/OC1H(4)	3.5
$\angle \text{CC1H}(4)$	0.83	CC/CC1H(4)	3.5
$\angle \text{CCH}(12)$	0.70	CC/CCH(12)	3.5
$\phi(\text{COCC})(2)$	0.045		
$\phi(\text{CCCC})(2)$	0.015		
$\phi(\text{OCCC})(2)$	0.015		

CONVERSIONS TO R_a , R_a^* AND R_z STRUCTURES

The various vibrational amplitude quantities and correction terms required in the combined analysis were computed from the derived force field of Table 3 using geometrical parameters consistent with those of the final results.

Conversion from the operational parameter for electron diffraction, r_a , to the quantity which represents the distance between average positions of atoms at thermal equilibrium, r_a^* , and to the

corresponding quantity extrapolated to 0 K, r_a° , may be carried out according to the following two relations²¹⁻²³

$$r_a = r_a + l_T^2/r_a - K_T + \delta r_{\text{cent}} \quad (1)$$

$$r_a^\circ = r_a - \frac{3}{2}a_3(l_T^2 - l_0^2) + (K_T - K_0) \quad (2)$$

The root-mean-square amplitudes of vibration (l) and the perpendicular amplitude correction coefficients (K) were calculated as described by Stølevik *et al.*²⁴ and the centrifugal stretching of the distances^{25,26} (δr_{cent}) as in the pertinent part of Hilderbrandt's MSAV-program.²⁷ Obtained values

Table 4. Values for l , K and δr_{cent} (in pm) calculated from the force field of Table 3 at $T=298$ K, excluding results for the hydrogen, hydrogen interactions. The curly brackets and the identifications $l1$ to $l6$ describe the grouping of l -values in the structure refinement.

		l_T	K_T	δr_{cent}
C1-H7	} (l1)	7.91	1.64	0.00
C1-O6		4.93	0.37	0.02
C1-C2	} (l2)	5.30	0.35	0.02
C2-C3		5.31	0.36	0.02
C2-O6	} (l3)	6.70	0.18	0.06
C1-C5		6.65	0.20	0.05
C2-C4		6.99	0.17	0.06
C1-C3		6.80	0.16	0.05
C3-O6		7.17	0.07	0.06
C1-C4		7.21	0.08	0.06
O6-H7	} (l4)	10.41	1.08	0.02
C1-H9		10.72	1.05	0.02
C2-H7		10.51	1.04	0.02
C2-H11		10.71	1.04	0.02
C3-H9		10.72	1.07	0.02
O6-H10		14.74	0.66	0.07
C1-H16	} (l5)	14.75	0.69	0.06
C1-H11		14.78	0.61	0.08
C2-H14		15.19	0.63	0.08
C3-H8		14.80	0.62	0.07
O6-H9		10.36	0.63	0.05
C1-H15		10.24	0.64	0.04
C1-H12	} (l6)	10.40	0.58	0.05
C2-H13		10.43	0.60	0.05
C3-H7		10.32	0.58	0.05
O6-H11		14.67	0.41	0.08
C1-H14		15.03	0.43	0.07
C2-H16		15.07	0.42	0.07
O6-H12	} (l6)	11.09	0.42	0.05
C1-H13		11.02	0.44	0.05
C2-H15		10.87	0.42	0.05

for $T=298$ K, l_T , K_T and δr_{cent} , are entered in Table 4 where averaged values are given for symmetrically different distances taken to be equal by the molecular model used, and where the values corresponding to the hydrogen, hydrogen interactions are omitted. Eqn. 2 was used only for the bond distances for which the calculated amplitude quantities at $T=0$ K, l_0 and K_0 , are respectively: C-H, 7.91 and 1.49 pm; C-O, 4.89 and 0.28 pm; and C-C, 5.25 and 0.26 pm. The anharmonicity constants for the bond stretching vibrations (a_3) are taken to be 0.0198, 0.0239 and 0.0213 pm⁻¹, respectively for the C-H, C-O and C-C bonds.^{23,28}

For small amplitude motions, shrinkage effects may be accounted for by the use of an r_a° -model, *i.e.* the geometrically inconsistent set of r_a° -values demanded by the electron-diffraction intensity expression,¹¹ are obtained from the geometrically consistent set of r_a° -values by using eqn. 1. Neglecting temperature effects in the angle parameters,^{22,29} eqn. 2 in combination with eqn. 1 may be used to calculate the coordinates for an r_a° -structure, and from these the rotational constants A_a° , B_a° and C_a° which correspond to the average position of the atoms in the ground vibrational state. The uncertainties originating from the various correction terms used to obtain the r_a° rotational constants are assumed to be negligible compared to those originating from the uncertainties in the geometrical parameters.

A_a° , B_a° and C_a° represent the same physical quantity as A_z , B_z and C_z which may be derived from the effective rotational constants A_0 , B_0 and C_0 obtained from the microwave experiments^{29,30}

$$B_z = B_0 + \delta B_{\text{vib}} + \delta B_{\text{cent}} + \delta B_{e1} \quad (3)$$

For tetrahydropyran the corrections due to electronic contribution, δB_{e1} , were neglected since such corrections seem to be appreciable only for molecules with a π -electron system.³⁰ The vibrational corrections to the rotational constants,^{21,22,26,30} δB_{vib} , were computed²⁷ from the force field in Table 3 which also gave the τ -values used to calculate the centricentrifugal correction, δB_{cent} . The uncertainty in the δB_{vib} correction is relatively large and its standard deviation was taken to be 10% of the calculated value. This means that δB_{cent} is also negligible and the only significant contribution to the standard deviation of B_z (σ_z) is the standard deviation of δB_{vib} . The experimental

Table 5. Observed rotational constants (B_0),⁴ correction terms ∂B_{vib} and ∂B_{cent} calculated from the force field of Table 3, and derived r_z rotational constants (B_z) in MHz for tetrahydropyran.

	B_0	∂B_{vib}	∂B_{cent}	B_z
A	4673.506 ± 0.009	-0.958	+0.002	4672.55(10)
B	4495.071 ± 0.009	-1.652	+0.002	4493.42(16)
C	2601.282 ± 0.009	-0.558	+0.002	2600.72(6)

B_0 -values, and ∂B_{vib} and ∂B_{cent} corrections, and the resulting B_z -values which correspond to a r_z -structure are given in Table 5.

LEAST-SQUARES REFINEMENTS OF THE STRUCTURE

The least-squares program written by H. M. Seip,^{11,16} was slightly modified to provide possibilities for calculations of rotational constants from the independent geometrical parameters used to describe the molecule, and to include options for refinements based on experimental values for the rotational constants in combination with the electron-diffraction intensity data.^{22,23} When the experimental rotational constants are included in the basis for the refinement, the estimates of their standard deviations are used to compute the relative weights among the rotational constants ($w_k = \sigma_z^{-2}$). The weighting of the data originating from the two methods may be arranged in various ways by the program, and the weight on the rotational data should be increased gradually until, for example, the standard deviations for the B_z -values are within the values for the corresponding σ_z -estimates. However, prior to such escalation of the weight, possible scale problems should be considered. In addition, attention should be paid to the various constraints imposed on the molecular model used, since such constraints may cause significant distortion in the rotational constants in spite of their small impact on the results of the structural analysis based on electron-diffraction data alone.

The final structural refinements for tetrahydropyran were based upon electron-diffraction intensity expressions which account for anharmonicity in the bond distances,¹¹ using the a_3 - and l -values given in the previous section to calculate κ according to the relation^{23,31} $\kappa = \frac{1}{6}a_3l^4$. Six groups of l -values were arranged as shown in Table 4. When refined

Table 6. Results of least-squares structural refinements of tetrahydropyran based on electron-diffraction intensity data (A, B) and on experimental spectroscopic rotational constants in combination with the intensity data (C). Distances (r_a) and amplitude parameters (l , defined in Table 4) in pm, angles (\angle_a , ϕ_a) in degrees, rotational constants (B_z) in MHz, and agreement factors (R) in %. The parenthesized standard deviations refer to the last digit given, and they include effects of correlations, but do not account for uncertainty in the s -scale of 0.1 %.

	A	B	C
$r(\text{CH})$	111.57(24)	111.61(21)	111.63(19)
$r(\text{CO})$	142.09(11)	142.01(17)	142.01(16)
$r(\text{CC})$	153.01(8)	153.05(10)	153.05(9)
$\Delta(\text{CC})$	0	0	0
$\angle \text{HCH}$	110.1(9)	110.1(9)	109.4(7)
$\angle \text{COC}$	111.8(5)	111.5(9)	112.3(6)
$\angle \text{C2C3C4}$	107.9(6)	108.3(15)	109.6(4)
$\angle \text{OCC}$	111.8(3)	111.8(3)	112.0(4)
$\angle \text{C1C2C3}$	111.0(3)	110.9(12)	110.0(4)
l_1	7.9	7.8(2)	7.8(2)
l_2	4.9	4.7(3)	4.7(2)
l_3	6.7	6.7(7)	7.2(2)
l_4	10.4	11.3(3)	11.0(3)
l_5	10.4	10.7(10)	11.2(6)
l_6	11.1	11.2(13)	11.0(13)
$\phi(\text{OCCC})$	56.9(4)	56.9(6)	56.1(2)
$\phi(\text{CCCC})$	53.2(8)	52.5(12)	53.0(10)
$\phi(\text{COCC})$	59.1(11)	59.9(12)	59.3(10)
A	4722(13)	4721(49)	4672.55(10)
B	4458(13)	4457(45)	4493.42(15)
C	2606(5)	2605(5)	2600.73(6)
$R(\text{ED})$	3.91	3.59	3.68
$R(\text{MW})$	0.79	0.78	$\sim 10^{-5}$

the differences between the values within each group were maintained at those established by the calculated values of Table 4. The values for the first ones given in each group are included in Table 6. In addition to the independent parameters in the structural refinement this table also contains the three dependent ring torsional angles (ϕ) and the r_z rotational constants which should be compared to the experimental counterparts, B_z of Table 5. The generalized weighted R -factors¹¹ for the electron-diffraction data, $R(\text{ED})$, and for the microwave

Table 7. Comparison of the larger elements of the correlation matrices ($100|\rho_{ij}| \geq 60$) for the least-squares structural results given in Table 6 B and C.

	B	C
$\overline{r}(\text{CO}), \overline{r}(\text{CC})$	-51	-74
$\angle \text{HCH}, \angle \text{OCC}$	-57	-64
$\angle \text{HCH}, \angle \text{C1C2C3}$	0	+74
$\angle \text{COC}, \angle \text{C2C3C4}$	+56	-96
$\angle \text{COC}, \angle \text{C1C2C3}$	-67	+32
$\angle \text{C2C3C4}, \angle \text{C1C2C3}$	-93	-24
$\angle \text{OCC}, \angle \text{C1C2C3}$	-50	-97
$\overline{r}(\text{CO}), l_2$	+76	+83
$\overline{r}(\text{CC}), l_2$	-60	-61
$\angle \text{COC}, l_3$	+75	+26
$\angle \text{C2C3C4}, l_3$	+92	-33
$\angle \text{C1C2C3}, l_3$	-96	-31
$\angle \text{C2C3C4}, l_5$	+70	-7
l_3, l_5	+74	+4

data, $R(\text{MW})$, are included in Table 6, and they reflect the goodness of the least-squares fit for the structural results to the two sets of experimental data. The results of refinements based on r_α -models showed the same trends for variations in the least-squares fits, parameter-values, standard deviations and correlation coefficients as obtained in comparable refinements neglecting shrinkage effects, and all results are presented and discussed in terms of those obtained in the r_α -refinements.

The results of refinements based on electron-diffraction data are given in Table 6 A and B, and they were obtained for $\Delta(\text{CC})=0$. with fixed l -values and with simultaneous adjustments of the six groups of l -values, respectively. Attempts to determine $\Delta(\text{CC})$ indicated no significant deviation from zero.

The parameter-values of column B in Table 6 represent the final structural results based on electron-diffraction data including information from vibrational spectroscopy in the analysis. The larger elements of the corresponding correlation matrix (ρ_{ij}) are given in Table 7, whereas the correlation matrix corresponding to results A contained no elements with absolute values larger than 0.60. The structural results give excellent agreement with the electron-diffraction data as seen from the small $R(\text{ED})$ value of 3.59% and from the differences between experimental and calculated counterparts shown for the molecular intensities in Fig. 1 and for the radial distribution curves in Fig. 2.

The obtained A_α° -, B_α° - and C_α° -values in Table 6 A and B compare favourably with the corresponding

B_z -values of Table 5, and the condition for conjoint structural analysis based on the experimental spectroscopic rotational constants in combination with the electron-diffraction data should be present. In particular, scale problems could be ignored since no systematic discrepancies are apparent. Refinements corresponding to A and B in Table 6 were carried out giving gradually increased weight on the spectroscopic data until the standard-deviation estimates for the calculated rotational constants were of the same magnitude as the corresponding σ_z -estimates of Table 5. The better fit to the rotational constants was accompanied by somewhat poorer fit to the electron-diffraction data. $R(\text{ED})$ was 4.25% for fixed l -values, whereas simultaneous refinements of the l -value groups compensated for most of this loss in agreement as seen from Table 6 C where the results are given for the latter refinement. However, the combined refinement led to new problems in the correlation among the variables. Table 7 contains the larger coefficients corresponding to the results of Table 6 C, and correlations of about -95% between the two pairs of ring bond angles were obtained even for refinements with fixed l -values. The problems are possibly associated with the various constraints imposed on the molecular model which may be discussed in terms of three types: *i*, $\Delta(\text{CC})=0$; *ii*, the assumptions *a-d* for the methylene groups; and *iii*, the imposed C_s -symmetry. $\Delta(\text{CC})$ was included in the refinement. For fixed l -values $R(\text{ED})=4.14\%$ and $\Delta(\text{CC})=1.6(11)$ pm were obtained and the two large correlation coefficients disappeared. However, subsequent refinements including the l -values diverged, and $\Delta(\text{CC})$ fixed at 1.6 pm rather than zero gave as compared to the results of Table 6 C and 7 C slightly poorer fit and similar correlation coefficients. Relaxation of constraints of types *ii* and *iii* was not implemented. This would have necessitated introduction of several new variables which seems not to be justified by the inclusion of three rotational constants in the data basis for the refinement.

The start-values of the parameters were varied also in the combined refinement of the structure. Special attention was paid to the relative magnitude of the highly correlated ring bond angles, and the results of Table 6 C were reproduced in all cases.

DISCUSSION

The electron-diffraction data have been found to be consistent with a chair form of C_s -symmetry.

The final structural results are presented in Table 6 B. They were obtained in analysis of the electron-diffraction data combined with information gained from vibrational spectroscopy. Provided that the l -values calculated from the derived force field are reliable, it appears that unambiguous structural results have been obtained. Effects of changes in the relative magnitude of the l -values have not been examined. However, the calculated l -values agree well with corresponding amplitudes calculated for related molecules such as, for example, cyclohexane³² and 1,3,5-trioxan.⁸ It is also reassuring that the l -values obtained in grouped refinements are rather close to the calculated ones. Conjoint analysis including experimental spectroscopic rotational constants in the databasis for the refinement did not cause significant shifts in the parameter values, but smaller standard deviations were obtained (Table 6 C). However, these results should probably not be viewed with full confidence due to the behaviour of the parameter correlations and the fact that possible effects from the imposed structural constraints are rather obscure. In spite of these problems, it is seen from the agreement between calculated (Table 6) and experimental (Table 5) values for the rotational constants that the information from rotational spectroscopy corroborate the presented structural results.

The standard deviations for the bond distances are 0.2 pm when corrected for uncertainty in the s -scale. The CH bond of 111.6(2) pm agrees well with the corresponding r_s bond distances of 111.5 ± 0.4 and 111.0(5) pm in cyclohexane³² and tetrahydrofuran,³³ respectively. The CC bonds in these two compounds and in 1,3-dioxan⁷ are respectively 153.4 ± 0.4 , 153.8(3) and 152.8(9) pm as compared to the average of 153.1(2) pm in tetrahydropyran. The CO bond lengths in the monoethers tetrahydrofuran,³³ dimethylether³⁴ and dipropylether³⁵ are, respectively, 142.8(3), 141.6(3) and 140.4(6) pm, as compared to 142.0(2) pm for tetrahydropyran. In related six-membered heterocyclic compounds the CO bonds are 141.1(2) and 141.0(4) pm in 1,3,5-trioxan⁸ and 2,4,6-trimethyltrioxan,³⁶ respectively, and for 1,3-dioxan⁷ an average of 141.6(5) pm may be calculated from the reported values for the two types of CO bonds and their correlation coefficient (143.9(28), 139.3(18) pm and 99.7 %, respectively). The $C(sp^3)$ -O bond lengths are known to be sensitive to their surroundings, in particular to the number of adjacent C-O bonds.^{37,38} The trend observed in the presented series of six-membered

cyclic ethers is hardly significant, and the variation of the CO bonds of monoethers suggests that, if real, the variation of the CO bond lengths should be discussed in terms of several effects.

The C2-C3-C4 bond angle of 108.3(15)° is comparable with $\angle CCC = 107.7(11)^\circ$ of 1,3-dioxan⁷ as compared to $111.4 \pm 0.2^\circ$ for cyclohexane.³² The other ring bond angles of tetrahydropyran (Table 6 B) compare more closely to the value in cyclohexan. The C-O-C angle of 111.5(9)° is in the range of the values obtained for the ethers previously referred to: 111.5(15), 116.1(36), 112.3(8), 109.2(10) and 109.2(8)°, respectively, for dimethylether,³⁵ dipropylether,³⁶ 2,4,6-trimethyltrioxan,³⁴ 1,3,5-trioxan⁸ and 1,3-dioxan.⁷ Possible distortion of the cyclohexane ring by introduction of the oxygen heteroatoms is most easily seen from the obtained ring torsional angles. It has been pointed out⁷ that no flattening of the ring seems to occur for 1,3,5-trioxan and 1,3-dioxan where the torsional angles are $\phi(\text{OCOC}) = 58.6^\circ$ and $\phi(\text{OCOC}) = 58.9^\circ$, $\phi(\text{COCC}) = 56.0^\circ$ and $\phi(\text{OCCC}) = 57.4^\circ$, respectively. The torsional angles obtained for tetrahydropyran (Table 6 B) provide a basis for extending this statement to cover also the monoether.

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