

However, Froimowitz's search also shows a second fairly stable rotamer for the β isomer, only 2.51 kJ mol⁻¹ higher than the most stable one, corresponding to C(2)–C(3)–C(9)–C(14) = –138°, but this rotamer is not found in the crystal structure.

The bond lengths and valence angles are listed in Table 3. Although most are comparable to those of the α isomer, three bond lengths have significant deviations of 0.30 (9) – 0.034 (9) Å, possibly due to low estimates for the standard deviations. Among corresponding valence angles in the two structures, the largest deviations occur in the two exocyclic angles at C(11) [6.2 (6) and 5.3 (6)°], two of the exocyclic angles at C(3) [3.9 (5) and 3.1 (4)°] and C(2)–N(1)–C(15) [4.0 (4)°]. It is quite plausible that these angular changes are caused by the differences in the configuration of the C(2) substituent, and the hydrogen-bonding environments in the two crystal structures.

Each Br forms two hydrogen bonds, N(1)–H(N)…Br…H(O)–O, to link the molecules into zigzag chains parallel to the *a* axis. The geometry of these bonds is given in Table 3.

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X-ray Structure Analysis of 1,4-Dioxane, Phase I at 279 K and Phase II at 153 K

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Abstract. Two crystalline phases of 1,4-dioxane, C₄H₈O₂, *M_r* = 88.105, were investigated. Phase I exists in the temperature region from 278 to 285 K, phase II from below 133 to 278 K. Both phases monoclinic, *P*2₁/*n*, *Z* = 2, *F*(000) = 96. Dioxane I at 279 K: *a* = 4.584 (7), *b* = 9.183 (13), *c* = 5.818 (10) Å, β = 99.63 (14)°, *V_c* = 241.5 (14) Å³. Dioxane II at 153 K: *a* = 5.736 (12), *b* = 6.507 (13), *c* = 6.144 (13) Å, β = 100.21 (18)°, *V_c* = 225.7 (18) Å³. *D_x* = 1.211 (7) (I), *D_x* = 1.296 (10) g cm⁻³ (II), room-temperature density of liquid *D_m* = 1.034 g cm⁻³. *Mo K α* , λ = 0.71069 Å, μ = 1.798 cm⁻¹ for I, 1.924 cm⁻¹ for II. *R* = 0.060 and 0.039 with 500 and 627 observed reflections. In both cases the molecule has its center on a crystallographic inversion center, and the ring geometry is that of a nearly ideal chair. The endocyclic C–O bond lengths range between 1.423 (3) and 1.432 (2) Å. They compare well with those of other dioxane and carbohydrate structures where the anomeric effect does not occur.

Introduction. In the course of the series of X-ray investigations on small cyclic ethers, we have previously reported the structures of non-substituted four- and five-membered rings, *i.e.* oxetane (Luger & Buschmann, 1984) and tetrahydrofuran (Luger & Buschmann, 1983). Our interest was directed towards tetrahydropyran and dioxane as the corresponding six-membered rings. Tetrahydropyran has two plastic crystalline phases with different cubic lattices below the melting point [phase I between 213 and 224 K, cubic, *Fm*3*m*, *a* = 8.34 (2) Å, *Z* = 4; phase II between 163 and 213 K, cubic, *P*43*n*, *a* = 10.42 (5) Å, *Z* = 8, see also Fig. 1] and a third non-plastic phase below 163 K for which only crystalline powder has been obtained up to now.

Dioxane has its melting point at 285 K and a transition point between ordinary crystalline phases at 278 K. This was discovered by a differential thermoanalysis run between 133 and 293 K on a Mettler thermoanalyzer TA1 (Fig. 1). The crystal and

molecular structures of the two phases of dioxane existing in this temperature range are reported here.

Experimental. Two separate low-temperature set-ups were used, one for X-ray film exposures, the other for X-ray diffractometer measurements. The first consists of a modified Enraf-Nonius camera with an N_2 -gas-stream system, the second is a Siemens four-circle diffractometer combined with an N_2 -gas-stream apparatus, which was designed and built in cooperation with Dietrich & Dierks (1970). Both temperature devices are continuously adjustable. The long-time stability is ± 0.5 K.

To save diffractometer time a two-step experimental strategy was followed. First dioxane was crystallized on the Weissenberg camera. After suitable crystallization conditions and preliminary cell data were known, the experiment was repeated on the diffractometer. Crystal growth was achieved by cooling the sample far below the transition point, returning to a temperature just below the transition point, partially transforming and/or melting the solid material in the direction against the cold gas stream and reducing the temperature again very slowly (Luger & Buschmann, 1984). A cylindrical

single crystal ~ 2 mm long was obtained within sealed glass tube (0.5 mm diameter, 0.01 mm thickness).

The quality of the crystal intended for diffractometer measurement was examined by scans over different reflections and by displaying the profiles on a graphic screen. D_m given by supplier (Merck).

Phase I of dioxane is stable only over a temperature range of 7 K; data collection was performed at 279 K, 6 K below the dioxane melting point. The phase II crystal was cooled to 153 K to obtain less-temperature-affected intensity data. In contrast to tetrahydropyran where both high-temperature phases consist of plastic crystals, dioxane I and II are both ordinary crystalline phases with the same monoclinic space group $P2_1/n$.

Precise lattice parameters and orientation matrix from screen-controlled centering of 10 three-dimensional high-order reflections. For each phase one set of independent reflections measured in θ - 2θ scan mode up to $(\sin\theta/\lambda)_{\max} = 0.704 \text{ \AA}^{-1}$ with Zr-filtered $Mo K\alpha$ radiation. Number of reflections 707 [207 unobserved with $I < 2\sigma(I)$] for dioxane I with h,k,l 0 to 6, 0 to 12, -8 to 8, and 665 (38 unobserved) for dioxane II with h,k,l -8 to 8, -9 to 1, -2 to 8. Standard reflections, 330 and $00\bar{4}$ in dioxane I and $0\bar{2}\bar{2}$ and 400 in dioxane II, measured every 30 reflections and showed statistical intensity variation of 2% for dioxane I and 1.5% for dioxane II. Reflection intensities corrected by Lorentz and polarization factor and for change in crystal volume hit by X-ray beam, which depended on angle between the 'endless' crystal cylinder and X-ray beam. This correcting factor varied between 1.00 and 0.89 (Luger, 1984). No absorption correction. Structure solution in both cases easily obtained with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Usual parameters, including isotropic extinction parameter, submitted to full-matrix least-squares refinement with *XRAY* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) from which atomic scattering factors and anomalous-dispersion values f' , f'' applied. Quantity minimized $\sum(|F_o| - |F_c|)^2$. Unobserved reflections included if $|F_c| > |F_o|$. Extinction correction factor for calculated structure factors $F_c(hkl)$ varied between 1.00 and 0.75 for dioxane I and between 1.00 and 0.60 for dioxane II. Distribution of ΔF versus F_o and $\sin\theta$ showed little variation, so unit weights used in refinements. $\Delta/\sigma \leq 0.04$. Final R values for observed reflections 0.060 for dioxane I, 0.039 for dioxane II.* Final difference Fourier map gives for dioxane I residual peaks below 0.27 e \AA^{-3} . For dioxane II residual density below 0.33 e \AA^{-3} and three highest peaks positioned near centers of the three independent ring bonds, largest on the C-C bond.

* Lists of structure factors and bond angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42829 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

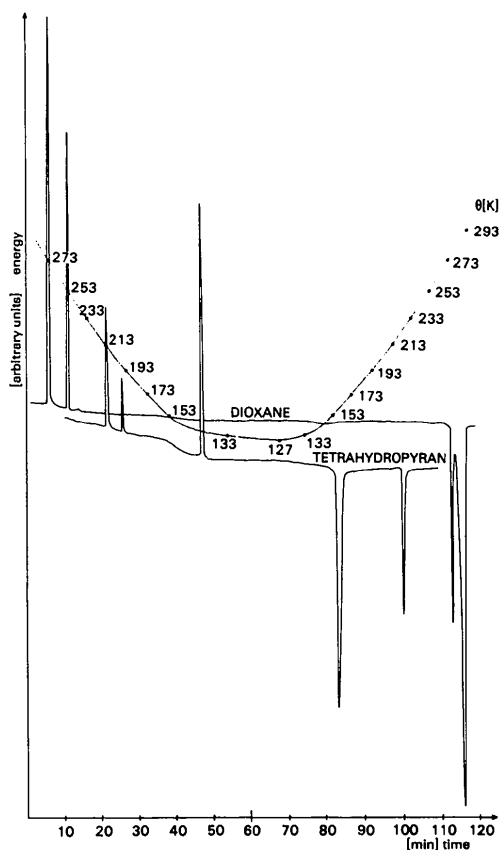


Fig. 1. Differential-thermal-analysis curves of 1,4-dioxane and tetrahydropyran.

Fig. 2 shows stereo representations of the two dioxane crystal structures and Table 1 presents the final atomic parameters.

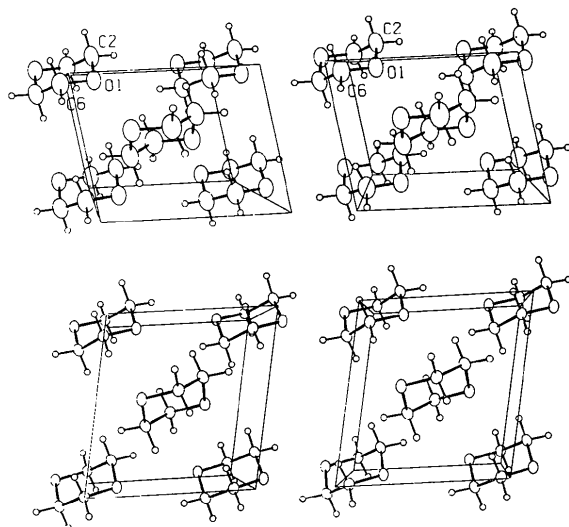


Fig. 2. Stereoviews of the cell of 1,4-dioxane I at 279 K (top) and 1,4-dioxane II at 153 K (bottom).

Table 1. Atomic parameters (U_{ij} , U_{eq} and U in $\text{\AA}^2 \times 10^2$)

U_{eq} values were calculated according to Hamilton (1959).

(a) 1,4-Dioxane, phase I, at 279 K

	x	y	z	U_{eq} or U
O(1)	0.9454 (3)	0.0852 (2)	0.1902 (2)	7.97 (6)
C(2)	1.1547 (7)	-0.0306 (3)	0.2186 (4)	8.9 (1)
C(6)	0.9263 (7)	0.1438 (3)	-0.0388 (4)	9.0 (1)
H(21)	1.365 (8)	-0.001 (4)	0.203 (5)	15.4 (12)
H(22)	1.157 (5)	-0.077 (3)	0.379 (5)	10.8 (8)
H(61)	1.123 (6)	0.180 (3)	-0.074 (5)	12.2 (10)
H(62)	0.783 (5)	0.220 (3)	-0.055 (4)	10.0 (8)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	10.13 (11)	7.70 (10)	5.88 (8)	1.15 (8)	1.48 (7)	-0.70 (7)
C(2)	10.67 (19)	9.68 (17)	5.83 (12)	1.80 (15)	0.53 (12)	0.27 (11)
C(6)	12.42 (23)	6.77 (13)	7.54 (14)	1.78 (14)	1.86 (14)	0.57 (11)

(b) 1,4-Dioxane, phase II, at 153 K

	x	y	z	U_{eq} or U
O(1)	0.7145 (2)	0.6138 (2)	0.5250 (2)	3.16 (3)
C(2)	0.4997 (2)	0.7057 (2)	0.5662 (2)	3.02 (4)
C(6)	0.6612 (2)	0.4555 (2)	0.3625 (2)	3.34 (4)
H(21)	0.547 (3)	0.807 (2)	0.683 (3)	3.1 (4)
H(22)	0.421 (3)	0.778 (3)	0.433 (3)	3.6 (4)
H(61)	0.583 (3)	0.517 (3)	0.219 (3)	3.8 (4)
H(62)	0.812 (3)	0.397 (3)	0.342 (3)	3.9 (4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2.41 (5)	3.04 (5)	3.93 (5)	-0.31 (3)	0.60 (3)	-0.48 (4)
C(2)	2.73 (6)	2.62 (6)	3.59 (6)	0.01 (4)	0.41 (5)	-0.28 (5)
C(6)	3.04 (6)	3.38 (7)	3.60 (7)	-0.20 (5)	1.14 (5)	-0.51 (5)

Table 2. Geometric data (bond lengths in \AA , valence and dihedral angles in degrees)

	1,4-Dioxane, phase I, at 279 K		1,4-Dioxane, phase II, at 153 K	
O(1)—C(2)	1.423 (3)	1.445*	1.432 (2)	1.441*
O(1)—C(6)	1.426 (3)	1.446	1.429 (2)	1.436
C(2)—C(3)	1.478 (3)	1.495	1.513 (2)	1.522
C(2)—H(21)	1.02 (4)		0.97 (2)	
—H(22)	1.03 (3)		0.98 (2)	
C(6)—H(61)	1.02 (3)		1.00 (2)	
—H(62)	0.95 (3)		0.97 (2)	
C(2)—O(1)—C(6)	109.0 (2)	108.6	109.9 (1)	109.86
O(1)—C(2)—C(3)	111.0 (2)	110.8	110.5 (1)	110.51
O(1)—C(6)—C(5)	111.4 (2)	111.1	111.3 (1)	111.16
C(6)—O(1)—C(2)—C(3)	57.0 (3)		56.8 (1)	
O(1)—C(2)—C(3)—O(4)	-58.3 (3)		-57.6 (1)	
C(2)—C(3)—O(4)—C(5)	57.2 (3)		57.3 (1)	
Cremer-Pople puckering parameters				
$Q(\text{\AA})$	0.564 (6)		0.562 (1)	
$\varphi(^{\circ})$	0		0	
$\theta(^{\circ})$	0		0	

* Values corrected for rigid-body librations.

Discussion. Intramolecular bond lengths, angles and dihedral angles are listed in Table 2. For both phases the dioxane ring center is on a crystallographic inversion center. The dihedral angles and the Cremer-Pople puckering parameters (Cremer & Pople, 1975; Luger & Bülow, 1983) show that in both cases the molecular structure is close to an ideal chair conformation. The average dihedral angles of 57.5° (I) and 57.2° (II) agree well with the theoretical $\varphi_{av} = 57.9^{\circ}$ calculated by Romers, Altona, Buys & Havinga (1969). The mean C—O bond length derived from some 105 crystal structures in the Cambridge Crystallographic Data File, version of 1982 (Kennard, Watson & Town, 1972), that contain dioxane as solvent molecule is $1.43(3) \text{\AA}$, the C—C value is $1.52(3) \text{\AA}$. All C—O bonds and the C—C bond for dioxane II found in this analysis agree with these values, but the C—C bond of the 279 K measurement is significantly shorter. A rigid-body libration correction on bond lengths and angles according to Schomaker & Trueblood (1968) and Scheringer (1972, 1978) performed for both structures produces enlarged values for all bond lengths, but the high-temperature C—C bond is still short. It has to be remembered that the 279 K structure was measured close to the dioxane melting point so that temperature effects may not have been sufficiently corrected for.

Of special interest is the endocyclic C—O bond length compared with previously studied non-substituted cyclic ethers and with some halogen-substituted dioxane derivatives investigated with respect to the anomeric effect. Table 3 shows that for dioxane and

tetrahydrofuran the C—O lengths are in the same range, whereas for oxetane they are somewhat larger. This is further support for the assumption of Mastyukov, Osina & Vilkov (1975) that in corresponding four-membered rings the C—O bond should be enlarged. The dioxane derivatives with axial halogens at C(2) show the well known shortening of a C—O bond next to a halogen-substituted carbon atom as a consequence of back donation (Romers, Altona, Buys & Havinga, 1969).

Table 3. Comparison of endocyclic C—O bonds in various cyclic ethers and derivatives

ED = electron diffraction, MW = microwave spectroscopy.

Compound	Ring C—O bond (Å)	Reference
1,4-Dioxane I (279 K)	1.423 (3)	(a)
	1.426 (3)	
1,4-Dioxane II (153 K)	1.432 (2)	(a)
	1.429 (2)	
1,4-Dioxane (ED)	1.423 (3)	(b)
Tetrahydrofuran (148 K)	1.435 (5)	(c)
Tetrahydrofuran (100 K)	1.429 (6)	(c)
Tetrahydrofuran (ED)	1.428 (3)	(d), (e)
Oxetane (140 K)	1.443 (2)	(f)
Oxetane (90 K)	1.460 (1)	(f)
Oxetane (MW)	1.449 (2)	(g)
<i>trans</i> -2,5-Dichloro-1,4-dioxane (148 K)	1.388 (7) [O(1)—C(2)]	(h)
	1.428 (7) [O(1)—C(6)]	
<i>trans</i> -2,3-Dichloro-1,4-dioxane (128 K)	1.382 (12) [O(1)—C(2)]	(h)
	1.428 (12) [O(1)—C(6)]	
<i>cis</i> -2,3-Dichloro-1,4-dioxane (133 K)	1.394 (10) [O(1)—C(2)]	(h)
	1.466 (10) [O(1)—C(6)]	
<i>trans</i> -2,3-Dibromo-1,4-dioxane (173 K)	1.37 (3) [O(1)—C(2)]	(h)
	1.47 (3) [O(1)—C(6)]	

References: (a) This work; (b) Davis & Hassel (1963); (c) Luger & Buschmann (1983); (d) Geise, Adams & Bartell (1969); (e) Almenningen, Seip & Willadsen (1969); (f) Luger & Buschmann (1984); (g) Chan, Zinn & Gwinn (1961); (h) Altona (1964).

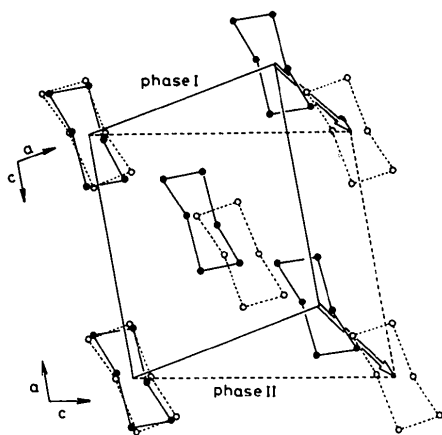


Fig. 3. Illustration of the phase I → phase II transition of dioxane. Both cells are projected down the monoclinic *b* axis, the phase I structure is drawn with full lines, phase II with dashed lines.

Fig. 3 gives a superimposed picture of the high- and low-temperature dioxane structures both projected down the monoclinic *b* axis. It is easy to see how the lattice of phase I is transformed to that of phase II. It is obvious that the general orientation of the dioxane ring remains almost constant. Moreover, one axis is the same, the *c* axis of phase I corresponds to the *a* axis of phase II. The transition moves the phase I molecules situated at $x = 1$ in the *a* + *c* direction by somewhat less than $\frac{1}{2}$. This enlarges the *ac* plane and allows the molecules at the inversion center ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) to move closer to the center of the *ac* plane, shortening the *b* axis. In total, however, the cell volume changes little (a volume loss of 6.5% occurs on going from phase I to phase II and on reducing temperature from 279 to 153 K).

In both crystal structures no intermolecular contacts of interest are present.

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