C(5)—C(6)—S(1) and C(5)—C(4)—S(3) are both 111·0° which is significantly smaller than in PT (114·9 and 116·1°) but comparable with the values in cyclohexane itself (Geise, Buys & Mijlhoff, 1971). The angle S(1)—C(2)—S(3) (112·7°) is also smaller than in PT (115·3°). C(5) forms an sp^2 hybrid orbital, with C(4)—C(5)—C(6) 117·1°, similar to the values of 116 and 117° in cyclohexane-1,4-dione (Mossel & Romers, 1964; Groth & Hassel, 1964). The mean of the absolute values of the torsional angles S(3)—C(4)—C(5)—C(6) and S(1)—C(6)—C(5)—C(4) is 68·8° (Fig. 3), indicating that the C(4)—C(5)—C(6) part is more puckered than in PT (61·6°) or cis-2-chloro-4-tert-butylcyclohexanone (57·3°) (de Graaff, Giesen, Rutten & Romers, 1972). In 1,3-dioxane derivatives, the O—C—O part is more puckered than the C—C—C part (de Kok & Romers, 1970; Kobayashi & Iitaka, 1977) whereas in 1,3-dithiane derivatives, the C—C—C part is more puckered than the S—C—S part. In Figs. 4 and 5, the torsional angles along the C(4)—C(5) and C(5)—C(6) bonds of PTO and the C(1)—C(2) bond of cis-2-chloro-4-tert-butylcyclohexanone are given. In PTO, the carbonyl O atom lies between the S atom and the equatorial H atom while in the cyclohexanone derivative it lies between the equatorial Cl atom in the 2-position and the axial H atom. The average of the torsional angles O—C(5)—C(4)—S(3) and O—C(5)—C(6)—S(1) is 111·0° for PTO but the O—C(1)—C(2)—C(3) angle in cis-2-chloro-4-tert-butylcyclohexanone is 127·6°.

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(Z)-5-Isopropyl-2-phenyl-1,3-dioxan-5-ol*

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Abstract. $C_{13}O_3H_{18}$, $M_r = 222\cdot3$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9\cdot558$ (4), $b = 11\cdot336$ (5), $c = 5\cdot835$ (3) Å, $\alpha = 92\cdot61$ (4), $\beta = 107\cdot15$ (6), $\gamma = 89\cdot89$ (4)°. The final R value was 0·094. No intramolecular hydrogen bond was found in the crystal.

Introduction. The existence of intramolecular hydrogen bonds in 1,3-dioxan-5-ols in CCl_4 solution has been shown by IR spectra (Brimacombe, Foster & Stacey, 1958; Baker, Brimacombe, Foster, Whiffen & Zweifel, 1959; Bagget, Brimacombe, Foster, Stacey & Whiffen, 1960; Kobayashi, 1974). It has also been demonstrated by NMR that the OH group at C(5) in (Z)-2-phenyl-1,3-dioxan-5-ol is bonded equally to two

ring O atoms by a bifurcated hydrogen bond in dilute CCl_4 solution (Kobayashi, 1974; Jochims & Kobayashi, 1976).

In order to clarify the results of such studies, the crystal and molecular structure of (Z)-5-isopropyl-2-phenyl-1,3-dioxan-5-ol (Fig. 1) was determined by X-ray analysis. The reflexion data were collected on a Philips PW 1100 X-ray diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The intensities of 2227 independent reflexions were obtained within $\theta = 3 \sim 78°$. The crystal structure was solved by the multi-solution method (Germain, Main & Woolfson, 1971) based on 152 reflexions with $E \geq 2\cdot00$. The positions of all non-hydrogen atoms were located on an E map. The atomic parameters were refined by the block-diagonal least-squares method including anisotropic temperature factors. The positions of all the H atoms

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* This work forms part of the PhD thesis of Y. Kobayashi at the University of Konstanz, West Germany.

were determined on a difference Fourier map. The final refinement was carried out by the full-matrix least-squares method using anisotropic temperature factors for non-hydrogen atoms and isotropic ones for H atoms. The structure obtained is shown in Fig. 2. The atomic parameters are listed in Table 1.*

Discussion. The bond lengths and bond angles of the molecule are listed in Tables 2 and 3. As in other reported structures of 1,3-dioxanes (de Kok & Romers, 1970; Nader, 1975a,b), the mean C—O distance (1·421 Å) is shorter than the mean C—C distance (1·524 Å) in the dioxane ring. The dioxane ring is in a chair confor-

mation as can be seen from the endocyclic torsional angles given in Fig. 3. However, the C—C—C part is more flattened than the O—C—O part. The mean of the absolute values of O(3)—C(4)—C(5)—C(6) and C(4)—C(5)—C(6)—O(1) is 49·6° while that of C(6)—O(1)—C(2)—O(3) and O(1)—C(2)—O(3)—C(4) is 63·6°. The former value is even smaller than the reported values

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32282 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
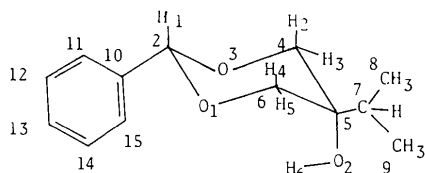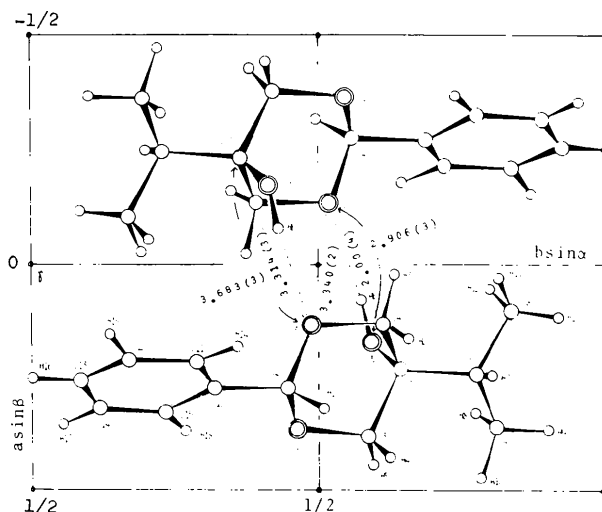

Fig. 1. Molecular structure of (Z)-5-isopropyl-2-1,3-dioxan-5-ol.

Fig. 2. c-Axis projection of the crystal structure.

Table 1. *Positional* ($\times 10^4$; $\times 10^3$ *for* H) *and thermal* ($\times 10^4$; $\times 10$ *for* H) *parameters*

The forms of the temperature factors are: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ and $\exp[-B(\sin\theta/\lambda)^2]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(2)	2756 (3)	4480 (3)	3751 (5)	107 (3)	101 (2)	303 (9)	16 (2)	70 (4)	−10 (4)
C(4)	1292 (3)	6107 (3)	2255 (5)	118 (3)	95 (2)	309 (9)	22 (2)	78 (4)	−19 (4)
C(5)	2289 (3)	6428 (2)	762 (4)	114 (3)	89 (2)	281 (8)	12 (2)	67 (4)	−22 (3)
C(6)	3769 (3)	5857 (3)	1854 (6)	105 (3)	97 (3)	404 (11)	13 (2)	73 (5)	4 (4)
C(7)	2469 (3)	7781 (3)	769 (6)	143 (4)	90 (3)	384 (11)	11 (2)	73 (5)	−19 (4)
C(8)	3581 (6)	8128 (4)	−452 (9)	200 (6)	109 (4)	580 (18)	−18 (4)	139 (8)	13 (6)
C(9)	1010 (5)	8381 (4)	−352 (13)	178 (6)	106 (4)	970 (30)	40 (4)	102 (11)	66 (9)
C(10)	2696 (3)	3202 (3)	4229 (5)	134 (4)	97 (2)	290 (9)	16 (2)	62 (4)	−12 (4)
C(11)	2130 (5)	2862 (4)	6009 (7)	225 (6)	120 (3)	433 (12)	25 (3)	165 (7)	12 (5)
C(12)	2058 (6)	1692 (4)	6473 (8)	298 (9)	135 (4)	457 (15)	11 (5)	163 (9)	48 (6)
C(13)	2561 (6)	825 (4)	5182 (8)	291 (8)	103 (3)	480 (14)	16 (4)	71 (9)	26 (6)
C(14)	3160 (6)	1169 (4)	3460 (9)	277 (8)	104 (3)	573 (17)	23 (4)	156 (9)	−29 (6)
C(15)	3231 (5)	2338 (3)	2976 (7)	219 (6)	104 (3)	440 (12)	13 (3)	159 (7)	−29 (5)
O(1)	3639 (2)	4642 (2)	2254 (4)	119 (3)	95 (2)	431 (8)	23 (2)	115 (4)	9 (3)
O(2)	1712 (2)	5939 (2)	−1640 (3)	145 (3)	116 (2)	272 (6)	0 (2)	79 (3)	−33 (3)
O(3)	1301 (2)	4864 (2)	2606 (4)	100 (2)	99 (2)	304 (6)	17 (1)	62 (3)	−20 (2)

	x	y	z	B		x	y	z	B
H(1)	317 (4)	507 (3)	521 (7)	54 (7)	H(10)	471 (11)	784 (8)	34 (19)	144 (32)
H(2)	163 (4)	656 (3)	375 (6)	53 (7)	H(11)	29 (6)	816 (4)	57 (10)	109 (13)
H(3)	24 (5)	628 (4)	138 (7)	61 (9)	H(12)	51 (10)	803 (8)	−183 (18)	108 (30)
H(4)	425 (5)	626 (4)	330 (9)	75 (11)	H(13)	117 (5)	920 (4)	−28 (8)	76 (10)
H(5)	439 (5)	596 (4)	67 (8)	72 (9)	H(14)	181 (6)	360 (5)	677 (10)	84 (13)
H(6)	76 (4)	574 (3)	−180 (6)	65 (7)	H(15)	154 (9)	137 (7)	775 (16)	106 (25)
H(7)	283 (4)	805 (3)	249 (7)	51 (8)	H(16)	251 (5)	−4 (4)	559 (8)	89 (9)
H(8)	328 (7)	779 (5)	−220 (12)	81 (15)	H(17)	352 (8)	54 (6)	257 (13)	100 (18)
H(9)	365 (5)	903 (4)	−59 (8)	75 (11)	H(18)	364 (6)	268 (5)	167 (11)	135 (14)

(53·2 ~ 55°) (de Kok & Romers, 1970; Nader, 1975a,b), indicating that the flattening at C(4)–C(5)–C(6) is more remarkable in this crystal. Consequently the mean torsional angles Hax–C(4)[and C(6)]–C(5)–C(7) and Heq–C(4)[and C(6)]–C(5)–C(7) are 48 and 71° respectively (Fig. 4).

The orientation of the phenyl ring is not perpendicular to the heterocyclic ring (de Kok & Romers, 1970) but is rather twisted [torsional angle: O(3)–C(2)–C(10)–C(11) = 72°, Fig. 5]. The OH does not form an intramolecular hydrogen bond with the ring O atoms but does form an intermolecular hydrogen bond to a ring O atom of the adjacent molecule. The bond distances 2·906 Å for O(2)···O(3′) and 2·00 Å for
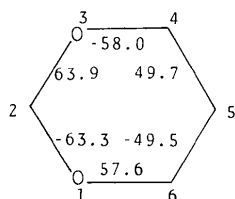
Table 4. *Angles around* H(6) (°)

O(2)–H(6)–O(3′)	171 (3)	O(3)–H(6)–O(3′)	89 (1)
O(1)–H(6)–O(3)	44 (0·5)	O(3)–H(6)–O(2)	96 (3)
O(1)–H(6)–O(2)	56 (2)		

H(6)···O(3′) are reasonable values for an O–H···O hydrogen bond. O(2), H(6) and O(3′) deviate slightly from a straight line, as seen in Table 4. The intramolecular distances from O(2) to the ring O atoms [2·937 (3) Å for O(2)···O(3) and 2·923 (3) Å for O(1)···O(2)] seem reasonable for hydrogen-bonded O···O distances but the H···O distances are too long

Fig. 3. Endocyclic torsional angles in the 1,3-dioxane ring.
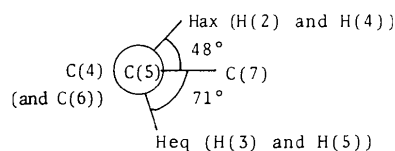

Fig. 4. Newman projection along the bonds C(4)–C(5) and C(5)–C(6). The torsional angles shown are the mean values of H(2)–C(4)–C(5)–C(7) and H(4)–C(6)–C(5)–C(7) (= 48°), and H(3)–C(4)–C(5)–C(7) and H(5)–C(6)–C(5)–C(7) (= 71°).

Table 2. *Bond lengths* (Å)

C(2)–O(1)	1·399 (4)	C(2)–O(3)	1·430 (4)	C(4)–O(3)	1·433 (4)	C(6)–O(1)	1·420 (4)
C(5)–O(2)	1·432 (3)	C(4)–C(5)	1·522 (4)	C(5)–C(6)	1·525 (4)	C(5)–C(7)	1·544 (4)
C(7)–C(8)	1·505 (7)	C(7)–C(9)	1·528 (6)	C(2)–C(10)	1·493 (4)	C(10)–C(11)	1·374 (6)
C(10)–C(15)	1·381 (5)	C(11)–C(12)	1·372 (6)	C(12)–C(13)	1·381 (7)	C(13)–C(14)	1·366 (8)
C(14)–C(15)	1·373 (8)	C(1)–H(1)	1·04 (3)	C(4)–H(2)	0·96 (3)	C(4)–H(3)	1·01 (4)
C(6)–H(4)	0·94 (5)	C(6)–H(5)	1·05 (5)	O(2)–H(6)	0·92 (4)	C(7)–H(7)	0·99 (4)
C(8)–H(8)	1·03 (7)	C(8)–H(9)	1·03 (5)	C(8)–H(10)	1·10 (10)	C(9)–H(11)	1·03 (7)
C(9)–H(12)	0·93 (9)	C(9)–H(13)	0·94 (5)	C(11)–H(14)	1·02 (6)	C(12)–H(15)	1·08 (10)
C(13)–H(16)	1·03 (5)	C(14)–H(17)	0·98 (8)	C(15)–H(18)	1·04 (7)		

Table 3. *Bond angles* (°)

C(2)–O(1)–C(6)	110·9 (2)	C(2)–O(3)–C(4)	110·6 (2)	O(1)–C(2)–O(3)	109·8 (2)
O(1)–C(2)–C(10)	109·7 (2)	O(3)–C(2)–C(10)	108·6 (2)	O(3)–C(4)–C(5)	111·5 (2)
C(4)–C(5)–C(6)	107·7 (2)	C(4)–C(5)–O(2)	110·0 (2)	C(6)–C(5)–O(2)	107·4 (2)
C(4)–C(5)–C(7)	110·6 (2)	C(6)–C(5)–C(7)	110·4 (4)	C(5)–C(6)–O(1)	112·6 (2)
C(5)–C(7)–C(8)	112·1 (3)	C(5)–C(7)–C(9)	111·8 (3)	C(11)–C(10)–C(15)	118·2 (3)
C(10)–C(11)–C(12)	120·7 (4)	C(11)–C(12)–C(13)	121·1 (5)	C(12)–C(13)–C(14)	118·0 (5)
C(13)–C(14)–C(15)	121·3 (4)	C(14)–C(15)–C(10)	120·7 (4)		
O(1)–C(2)–H(1)	105 (2)	O(3)–C(2)–H(1)	105 (2)	C(10)–C(2)–H(1)	118 (2)
C(5)–O(2)–H(6)	106 (2)	O(3)–C(4)–H(2)	112 (2)	O(3)–C(4)–H(3)	105 (3)
H(2)–C(4)–H(3)	112 (3)	C(5)–C(4)–H(3)	111 (3)	C(5)–C(4)–H(2)	107 (2)
C(5)–C(6)–H(4)	109 (3)	H(4)–C(6)–H(5)	108 (4)	C(5)–C(6)–H(5)	107 (2)
O(1)–C(6)–H(4)	110 (3)	O(1)–C(6)–H(5)	110 (2)	C(5)–C(7)–H(7)	105 (2)
C(8)–O(7)–H(7)	109 (2)	C(9)–C(7)–H(7)	109 (2)	C(7)–C(8)–H(8)	110 (4)
C(7)–C(8)–H(9)	113 (3)	C(7)–C(8)–H(10)	117 (6)	H(8)–C(8)–H(9)	105 (5)
H(8)–C(8)–H(10)	105 (7)	H(9)–C(8)–H(10)	106 (6)	C(7)–C(9)–H(11)	108 (3)
C(7)–C(9)–H(12)	112 (6)	C(7)–C(9)–H(13)	109 (3)	H(11)–C(9)–H(12)	98 (7)
H(11)–C(9)–H(13)	112 (4)	H(12)–C(9)–H(13)	118 (7)	C(10)–C(11)–H(14)	109 (3)
C(12)–C(11)–H(14)	131 (3)	C(11)–C(12)–H(15)	124 (5)	C(13)–C(12)–H(15)	115 (5)
C(12)–C(13)–H(16)	119 (3)	C(14)–C(13)–H(16)	123 (3)	C(13)–C(14)–H(17)	117 (4)
C(15)–C(14)–H(17)	122 (4)	C(10)–C(15)–H(18)	113 (3)	C(14)–C(15)–H(18)	126 (3)

[3·34 (4), 2·71(4) Å] for hydrogen bonds and the O—H· · ·O angles also deviate too much from linearity (Table 4). Thus, contrary to the solution studies, it is evident that there exist only intermolecular hydrogen bonds in the crystal. The torsional angle H(6)—O(2)—C(5)—C(4) (16°) indicates that H(6)—O(2) almost eclipses C(4)—C(5).
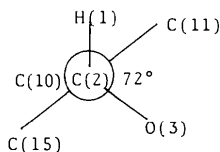

Fig. 5. Newman projection along C(2)—C(10).

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4-Hydroxy-4H-furo[3,2-c]pyran-2(6H)-one (DL-Patulin)

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Abstract. $C_7H_6O_4$, $M_r = 154 \cdot 1$, monoclinic, $P2_1/n$, $a = 9 \cdot 008(2)$, $b = 9 \cdot 549(2)$, $c = 7 \cdot 786(2)$ Å, $\beta = 94 \cdot 80(2)°$, $Z = 4$, $D_m = 1 \cdot 53(2)$ (flotation), $D_x = 1 \cdot 535$ g cm^{-3}. The structure has been solved by direct methods and refined by least-squares techniques to a final R value of 0·05, based on 1365 reflections. Centrosymmetrically related molecules form dimers via a pair of hydrogen bonds connecting the hydroxyl H atom to the pyran ring O atom. The hydrogen-bond O· · ·O distance is 2·810(2) Å and the OH· · ·O angle is 167(2)°.

Introduction. Crystals of DL-patulin were prepared from the natural product by one of the authors (GW). Details of the isolation and crystallization procedure will be given in a subsequent publication. A pyramidal colorless crystal was selected for film and diffractometer work (maximum dimension 0·2 mm). Precession photographs revealed $2/m$ symmetry. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) observed on the films and verified on the diffractometer indicated that the space group is $P2_1/n$. 3013 reflections were measured on a diffractometer out to $\theta = 75°$ with

Cu $K\alpha$ X-radiation ($\lambda = 1 \cdot 54188$ Å).* The θ–2θ scan technique was used with a scan range of $(2 \cdot 0 + 1 \cdot 0 \tan\theta)°$ and scan speed of 4° min^{-1}. Three standard reflections, measured at regular intervals, showed only statistical fluctuations about the average intensity throughout the course of data collection. The intensities were corrected for Lorentz–polarization effects, but not for absorption ($\mu = 11 \cdot 2$ cm^{-1}). $\sigma(I)$ was estimated by combining a counting statistics term with a factor proportional to scan count: $S^{1 \cdot 2} + (t_s/t_b)B^{1 \cdot 2} + 0 \cdot 01S$, where S = scan count (time t_s) and B = background count (time t_b). Equivalent reflections were then averaged ($R = 0 \cdot 024$) to yield a data set of 1471 unique reflections of which 93 were systematically extinct. The estimated standard deviation of F_{avg} was calculated from the individual $\sigma(F)$'s and the r.m.s. deviation from the average. A trial model containing all C and O atoms was obtained with MULTAN (Germain, Main & Woolfson, 1971). After preliminary refinement, a difference map was calculated and all H atoms in the

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