Fig. 3. An *ORTEP* (Johnson, 1976) drawing of four molecules (the contents of two unit cells) with one unit cell outlined, viewed down the *b* axis. H atoms are not shown.

There are six contacts between symmetry-related molecules of less than 3.6 Å, all from methyl, methylene or benzene C atoms to O atoms, although only one of these [C16···O4 at $x - 1$, $y - 1$, $z - 1$, 3.294 (7) Å] is short enough to imply a weak C—H···O hydrogen bond. The other contacts represent weaker interactions. Some of these interactions can be seen in Fig. 3.

Discussion. This oxazolidinone has structural features that are comparable to those of similar compounds. Individual bond distances and angles (Table 2) fall within normal ranges and, for the oxazolidinone system, the geometry is like that seen by others (Walba, Thurmes & Haltiwanger, 1988; Abdel-Magid, Pridgen, Eggleston & Lantos, 1986; Nakai, 1988; Baker, Cooke, Humphrey, Wright & Hirshfield, 1987; Molander & Kenny, 1989; Herold, Duthaler, Riks & Angst, 1989). For these compounds, distances in the oxazolidinone system are shown in Fig. 1 (with sample standard deviations in brackets), along with the distances observed for this structure. The atoms involved in these distances are nearly planar: ±0.11 Å for the structure reported by Nakai (1988) (better for all other reference compounds), ±0.14 Å for the present structure. There is a twist of about −13° about the N—C4 bond that is primarily responsible for the departures from planarity, but even the fragment O1, C1, N, C3, C4 has atoms up to ±0.09 Å from their plane, so the situation is not a simple one. Fig. 2 shows the complete molecule.

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Structure of 1,2,3,5,6,7-Hexahydro-1,5:3,7-dimethano-4-benzoxonin-3,5-diol Monohydrate

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Abstract. $C_{14}H_{16}O_3.H_2O$, $M_r = 250.30$, monoclinic, $P2_1/c$, $a = 10.582$ (3), $b = 6.864$ (1), $c = 17.786$ (5) Å, $\beta = 101.84$ (1)°, $V = 1264.4$ (6) Å^3, $Z = 4$, $D_m = 1.32$, $D_x = 1.31$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.7107$ Å (graphite monochromated), $\mu = 0.89$ cm^{-1}, $F(000) = 536$, $T = 294$ K, $R = 0.040$ for 1599 observed $[I/\sigma(I) > 3]$

reflections out of 2508 measured, and for 163 variables. Diol molecules form centrosymmetric dimeric units by means of two identical hydrogen bonds. Dimers are linked by lattice water molecules to form layers with interlocking benzo groups.

Introduction. As part of our studies of chemical cocrystallization properties (Bishop & Dance, 1988), we have recently reported the structures of several organic hydrates (Bishop, Craig & Scudder, 1989; Amini, Bishop, Burgess, Craig, Dance & Scudder, 1989; Bong, Ung, Craig, Scudder & Bishop, 1989). We report here the quite different behaviour shown by 1,2,3,5,6,7-hexahydro-1,5:3,7-dimethano-4-benzoxonin-3,5-diol monohydrate [(I).H₂O], which may be regarded as a two-stage hydrate of 5,6,8,9-tetrahydro-5,9-propano-7H-benzocycloheptene-7,11-dione (II) (Föhlisch, Novotny & Schmidt, 1972).

(I) H₂O   (II)
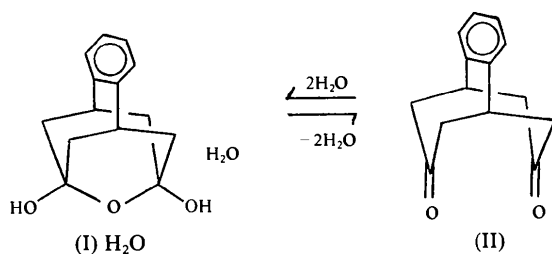
Experimental. The hydrate (I).H₂O was prepared as previously reported (Föhlisch et al., 1973) and recrystallized from acetic acid and water (9:1) giving prisms suitable for X-ray analysis. Heating at approximately 448 K caused double dehydration to the diketone (II). This latter material also resulted from azeotropic removal of water from benzene solutions of (I).H₂O. It is already known that the diketone (II) undergoes quantitative reaction with water to regenerate (I).H₂O (Föhlisch et al., 1973). The ^{13}C NMR spectrum of (I).H₂O was recorded on a Bruker AM-500 instrument (126 MHz): $\delta_C(d_6\text{-DMSO})$ 145.5 (C), 128.6 (CH), 126.9 (CH), 97.5 (C), 39.5 (CH₂) and 38.8 (CH). Crystal density was measured as 1.32 g cm⁻³ by flotation in carbon tetrachloride/cyclohexane.

Data collection was performed using a crystal of size 0.18 × 0.18 × 0.19 mm, on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters were determined by least squares from setting angles of 23 reflections with $35 < 2\theta < 46°$. Data collection: $\theta/2\theta$ scan, scan width $(0.5 + 0.35\tan\theta)°$ to $2\theta_{max} = 50°$ $(-12 \le h \le 12, \ 0 \le k \le 8, \ 0 \le l \le 21)$. A standard reflection monitored every 2000 s showed no indication of crystal decay. 2508 measured reflections gave 1599 independent observed reflections $[I/\sigma(I) > 3]$. Absorption corrections were carried out using a 6

× 6 × 6 Gaussian grid; maximum, minimum transmission coefficients 0.99, 0.98. Merging R for 59 reflections measured twice was 0.007.

The structure was solved using direct methods (MULTAN80; Main et al., 1980) and Fourier techniques. Least-squares refinement (BLOCKLS; Busing, Martin & Levy, 1962) based on F, used weights $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$; anisotropic temperature factors for non-H atoms. H atoms on O atoms were placed at positions determined from difference Fourier syntheses, those on C at calculated positions; H atoms were not refined and were given B_{eq} values of the atoms to which they were bonded. Final $R = 0.040$, $wR = 0.059$, $S = 2.2$]. $(\Delta/\sigma)_{max} = 0.01$. The largest residual peak in the difference map was 0.17 e Å⁻³, with a minimum of 0.2 e Å⁻³. No extinction correction was applied. Scattering factors for neutral atoms and anomalous-dispersion terms were taken from International Tables for X-ray Crystallography (1974, Vol. IV). Computation was performed on an IBM3090 computer.

Discussion. Atomic coordinates are listed in Table 1, bond lengths and angles are given in Table 2,* and the atom-labelling system of (I).H₂O is shown in Fig. 1.

In solution (I).H₂O has the C_{2v} symmetry expected of the parent ring system (I), as indicated by the ^{13}C NMR spectrum of only six lines. However, this is not so in the solid state where each molecule of (I) is chiral as a consequence of the orientation of its hydroxyl H atoms and the resultant hydrogen-bonding network.

Pairs of centrosymmetrically related molecules of (I) are linked by two hydrogen bonds between the ether O atom O(1) and the hydroxyl H atom HO(3) to form the dimeric building block of the crystal structure (Fig. 1). Two orientations of the dimer are present (Fig. 2) with alternate rows (parallel to b) of dimeric units having their benzo groups tilted at ±16.5° to the $a*b$ plane. This results in an angle of 33° between rings of adjacent rows of dimers. Layers of dimeric units in the bc plane are linked together by hydrogen-bonding lattice water molecules. Each water molecule takes part in three hydrogen bonds: two in which it is the donor [to O(2) and O(3) of two different dimers], and one in which it is the acceptor [from HO(2) of a third dimer]. Hydrogen-bond dimensions are included in Table 2.

Table 1. *Non-H atomic coordinates and equivalent isotropic temperature factors ($\AA^2$) with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)(a^2\beta_{11} + ... + 2ab\beta_{12} + ...).$$

	x	y	z	B_{eq}
O(1)	0.0889 (1)	0.1890 (2)	0.0581 (1)	3.31 (4)
O(2)	0.0642 (1)	0.2806 (2)	0.1765 (1)	4.11 (4)
O(3)	0.0939 (1)	0.0929 (2)	−0.0641 (1)	3.95 (4)
C(1)	0.1585 (2)	0.2410 (3)	0.1347 (1)	3.21 (5)
C(2)	0.2326 (2)	0.0631 (3)	0.1714 (1)	3.48 (6)
C(3)	0.3210 (2)	−0.0275 (3)	0.1227 (1)	3.44 (6)
C(4)	0.2469 (2)	−0.0510 (3)	0.0395 (1)	3.45 (6)
C(5)	0.1745 (2)	0.1309 (3)	0.0071 (1)	3.21 (5)
C(6)	0.2574 (2)	0.3036 (3)	−0.0040 (1)	3.71 (6)
C(7)	0.3323 (2)	0.3892 (3)	0.0717 (1)	3.65 (6)
C(8)	0.2410 (2)	0.4193 (3)	0.1271 (1)	3.64 (6)
C(9)	0.4486 (2)	0.0805 (3)	0.1293 (1)	3.68 (6)
C(10)	0.5628 (2)	−0.0147 (4)	0.1600 (1)	4.69 (7)
C(11)	0.6826 (3)	0.0785 (5)	0.1679 (2)	5.79 (9)
C(12)	0.6876 (3)	0.2692 (5)	0.1457 (2)	5.70 (9)
C(13)	0.5731 (2)	0.3668 (4)	0.1156 (1)	4.84 (7)
C(14)	0.4537 (2)	0.2751 (3)	0.1062 (1)	3.64 (6)
WO	0.0252 (2)	0.1393 (3)	0.3179 (1)	6.34 (7)

Table 2. *Bond lengths ($\AA$), bond angles (°) and hydrogen-bond geometry ($\AA$, °) with e.s.d.'s in parentheses*

O(1)—C(1)	1.455 (2)	C(7)—C(8)	1.529 (3)
O(1)—C(5)	1.462 (2)	C(7)—C(14)	1.523 (3)
O(2)—C(1)	1.388 (2)	C(9)—C(10)	1.384 (3)
O(3)—C(5)	1.399 (2)	C(10)—C(11)	1.401 (4)
C(1)—C(2)	1.523 (3)	C(11)—C(12)	1.371 (4)
C(1)—C(8)	1.525 (3)	C(12)—C(13)	1.392 (4)
C(2)—C(3)	1.531 (3)	C(13)—C(14)	1.390 (3)
C(3)—C(4)	1.535 (3)	C(14)—C(9)	1.401 (3)
C(3)—C(9)	1.524 (3)	O(2)—HO(2)	0.963 (2)
C(4)—C(5)	1.516 (3)	O(3)—HO(3)	1.064 (1)
C(5)—C(6)	1.512 (3)	WO—H1WO	0.85 (1)
C(6)—C(7)	1.533 (3)	WO—H2WO	0.96 (1)

C(1)—O(1)—C(5)	112.9 (1)	C(5)—C(6)—C(7)	113.3 (2)
O(2)—C(1)—O(1)	105.6 (1)	C(6)—C(7)—C(8)	109.7 (2)
O(1)—C(1)—C(2)	108.7 (2)	C(6)—C(7)—C(14)	113.5 (2)
O(1)—C(1)—C(8)	107.6 (2)	C(8)—C(7)—C(14)	113.7 (2)
O(2)—C(1)—C(2)	106.9 (2)	C(7)—C(8)—C(1)	113.4 (2)
O(2)—C(1)—C(8)	112.2 (2)	C(3)—C(9)—C(10)	119.3 (2)
C(2)—C(1)—C(8)	115.3 (2)	C(14)—C(9)—C(3)	121.9 (2)
C(1)—C(2)—C(3)	113.8 (2)	C(14)—C(9)—C(10)	118.9 (2)
C(2)—C(3)—C(4)	109.8 (2)	C(9)—C(10)—C(11)	121.5 (3)
C(2)—C(3)—C(9)	113.2 (2)	C(10)—C(11)—C(12)	119.6 (3)
C(4)—C(3)—C(9)	113.2 (2)	C(11)—C(12)—C(13)	119.2 (2)
C(3)—C(4)—C(5)	113.4 (2)	C(12)—C(13)—C(14)	121.7 (3)
O(3)—C(5)—O(1)	105.8 (2)	C(7)—C(14)—C(9)	121.9 (2)
C(4)—C(5)—O(1)	108.6 (2)	C(13)—C(14)—C(7)	119.1 (2)
O(1)—C(5)—C(6)	108.5 (2)	C(13)—C(14)—C(9)	119.0 (2)
C(4)—C(5)—O(3)	110.9 (2)	C(1)—O(2)—HO(2)	113.5 (1)
O(3)—C(5)—C(6)	106.9 (2)	C(5)—O(3)—HO(3)	110.2 (1)
C(4)—C(5)—C(6)	115.7 (2)	H1WO—WO—H2WO	110 (1)

O(1)···O(3^i)	2.754 (2)	C(1)—O(1)···O(3^i)	111.1 (1)
O(2)···WO^{ii}	2.647 (2)	C(5)—O(1)···O(3^i)	111.2 (1)
O(2)···WO	2.804 (2)	C(1)—O(2)···WO	131.8 (1)
O(3)···WO^{iii}	2.772 (2)	C(1)—O(2)···WO^{ii}	120.3 (1)
		C(5)—O(3)···WO^{iii}	125.3 (1)
		O(2)···WO···O(2^{iv})	118.4 (1)
		O(2)···WO···O(3^v)	112.7 (1)
		O(2^{iv})···WO···O(3^v)	128.9 (1)

Symmetry code: (i) $-x$, $-y$, $-z$; (ii) $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (iv) $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (v) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

Packing between the hydrogen-bonded layers of (I).H_2O involves only van der Waals forces. Benzo groups protrude from both sides of the plane, resulting in deep undulations in the surface. Layers interlock, so that the benzo groups of one layer penetrate the cavities of the two adjacent layers.
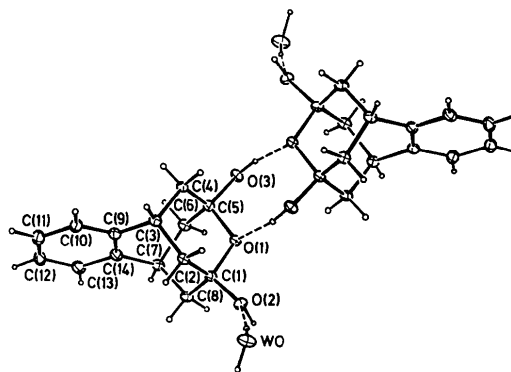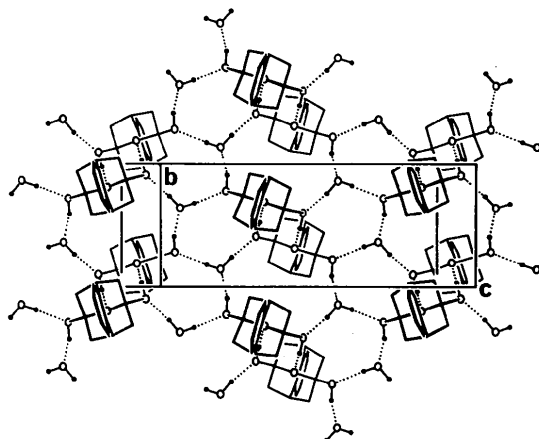

Fig. 1. Molecular structure of (I).H_2O and its centrosymmetric hydrogen-bonded dimer showing the crystallographic numbering system used.

Fig. 2. Molecules of (I).H_2O projected onto the *bc* plane showing the layer hydrogen-bonding network.

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