A Hydrogen-bonded Complex. The Crystal Structure of 1,5,12,16,23,26,-29-Heptaoxa[$7^{3,14}$][5.5]orthocyclophane–Naphthalene-2,3-diol Monohydrate

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Reaction between the macrobicyclic ether, 223 (systematically named in the title), and naphthalene-2,3-diol in the presence of water has been shown, by crystal structure analysis, to yield a 1 : 1 : 1 complex. In a monoclinic unit cell having a = 9.014(1), b = 33.302(7), c = 9.663(1) Å, β = 95.42(1)°, space group $P2_1/a$ there are four molecules. Each consists of naphthalene-2,3-diol with the usual internal hydrogen bond and the second hydroxy hydrogen atom bonded to a water molecule (H · · · O 1.79 Å) which, in turn, forms hydrogen bonds to four oxygen atoms of the bicyclic molecule; one such bond is bifurcated (H · · · O 2.33 and 2.36 Å), while the other has unequal H · · · O distances 2.03 and 2.56 Å. Full matrix refinement with anisotropic vibration parameters for the oxygen atoms gave an R value of 0.069 for 3 006 observations from a CAD–4 diffractometer.

BRIDGED bicyclic polyethers have recently been synthesised and shown to have high complex formation constants with Group 1a salts.[1] The crystalline products of such reactions usually appear to contain several molecules of water of hydration. The crystal structure of the ligand 1,4,7,14,17,20,28,35-octaoxa[$2^{3,29}.2^{18,34}$]-[7.7]orthocyclophane (trivially called benzo-2,2,4) with potassium chloride contains approximately five molecules of water but these have been shown to be disordered, as are the chloride ions.[2] In an effort to exclude water from a similar complex of the ligand 1,5,12,16,23,26,29-heptaoxa[$7^{3,14}$][5.5]orthocyclophane (Figure 1) (trivial name 223) and sodium bromide (1 : 1), an excess of naphthalene-2,3-diol was added to an equimolar mixture of ligand and salt in benzene, to act as the molecule of crystallisation. After the mixture had been boiled and concentrated by evaporation, chunky crystals and an off-white powder were obtained.[3] On the hot stage microscope the crystals melted at 84—86° while the powder remained even at 250°. The crystals showed extinction under the polarising microscope and a suitable number was picked out to provide a sample for microanalysis. The i.r. spectrum of these crystals differed from that of a 1 : 1 mixture of the organic components particularly in the regions 3 100—3 600 and 1 000—1 100 cm^{-1}.

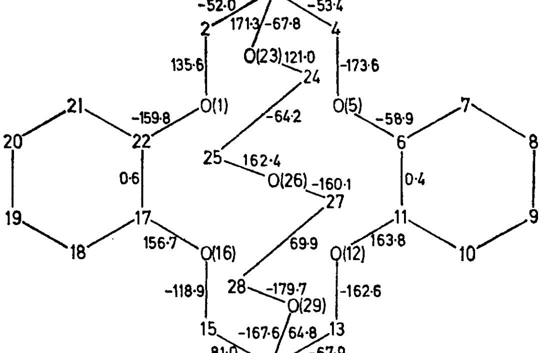

FIGURE 1 The bridged polyether showing designations of the atoms which correspond to the systematic name in the cyclophane numbering scheme. Hydrogen atoms are numbered to correspond to the carbon, those in CH_2 groups being distinguished as A or B. Also shown are most of the torsion angles (°); estimated standard deviations range from 0.8° at 0° to 0.4° at 180°. Torsion angles omitted are O(1)–C(2)–C(3)–O(23) 67.9°, O(23)–C(3)–C(4)–O(5) −172.3°, O(29)–C(14)–C(13)–O(12) 55.1°, and O(29)–C(14)–C(15)–O(16) −45.4°, and those round the benzene rings. The sign convention for the angle a–b–c–d is positive if the projection of c–d must be moved clockwise to eclipse the projection b–a viewed from c to b. In this connection atoms O(1) to C(22) inclusive run from a to d; the bridge from C(3) to C(14) runs from a to d

For X-ray measurements a piece was cut from a larger crystal. The power of modern techniques of crystal structure analysis is demonstrated by the fact that the determination, showing the complex to be 1 : 1 : 1 but of water (not sodium bromide!): 223 : naphthalene 2,3-diol, was completed before the microanalytical results were obtained.

Crystal Data.—$C_{32}H_{36}O_{10}$, M = 580.63. Monoclinic, a = 9.014(1), b = 33.302(7), c = 9.663(1) Å, β = 95.42(1)°, U = 2 887.4 Å^3, D_m = 1.31 (by flotation in KI), Z = 4, D_c = 1.336 g cm^{-3}; space group $P2_1/a$ uniquely determined; $F(000)$ = 1 232, $\lambda(\text{Mo-}K_{\alpha 1})$ = 0.709 26 Å, $\mu(\text{Mo-}K_{\alpha 1})$ = 0.93 cm^{-1}.

EXPERIMENTAL

A crystal 0.45 × 0.33 × 0.38 mm was mounted about the c axis. Preliminary Weissenberg and precession photographs gave unit cell dimensions and space group. Accurate unit cell dimensions were obtained from the positions of 25 high θ reflections on a CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation.

θ–ω Scans of diffracted beam peaks gave a maximum peak width of 0.113°. The long b axis led to peak overlap and the ω scan angle for an ω–2θ scan motion was reduced to (0.6 + 0.35 tan θ)°. Reflections were measured in the range 1.4 < θ < 20° with the scans in the bisecting position (ψ = 0). All reflections in the quadrant h = 8 to −8, k = 0—32, l = 0—9 were measured including those calculated to be absent. Pre-scan runs were made at a speed of 2° min^{-1}. Reflections were considered unobserved if $\sigma(I)/I > 2$ from pre-scan data and were flagged weak.

The final scan was made at a slower speed with the maximum time limit for the final scan of 90 s. Two intensity control reflections (1,20,0 and 2,8,3) were remeasured after every 7 200 s exposure time. No significant change in intensity was observed. Orientation control reflections were checked after each 100 reflections and the maximum allowed deviation of any scattering vector was 0.15.

After completion of this first shell (2 841 reflections) data from a second shell $20 \leqslant \theta \leqslant 22.5°$ were collected with a new pre-scan speed of 4° min^{-1}. This gave a total of 3 957 measured reflections.

Some $0kl$, $hk0$, and $\bar{1}kl$ reflections were remeasured when the original collection indicated uneven or unacceptably high background counts. The new scan angle for these measurements was $(0.4 + 0.35 \tan \theta)$, which was finally reduced to $(0.35 + 0.35 \tan \theta)$ for an acceptable scan of the 0,18,1 and 0,15,2 reflections. These data replaced the original scans of the same reflections. After omitting reflections for which $4\sigma(F) > F$ there were 3 008 unique observable reflections to which an Lp correction was applied.

Structure Determination.—A Patterson synthesis computed with SHELX[4] gave no clear solution so direct methods were employed. From 407 reflections [ε (min) = 1.5, $K_{\min} = 1.0$] a multisolution tangent refinement produced a convergence map which, in turn, gave three origin-determining reflections ($\bar{9}21$), (6,24,1), and 416) and nine phase-determining reflections to be used as input for the automatic centrosymmetric direct methods.

In the first run of direct methods an incorrect number of permutations, 2^6, was carried out instead of 2^9, but a recognisable solution was obtained. (Curiously, when this number was corrected, there was no identifiable solution.) The map showed the presence of the naphthalene-2,3-diol and 223 ligand molecules with all but three of the non-hydrogen atoms. The positions of the remaining atoms plus those of the hydrogen atoms on carbon were located in a series of difererence electron density maps with the 1 281 reflections having $\sin \theta < 0.275$ 6.

The atomic parameters were refined isotropically by the full-matrix least-squares refinement of SHELX with hydrogen atom positions at C–H 0.98 Å and their vibration parameters refined in groups. R fell to 0.06 and the hydrogen atoms of the water molecule, WAT(1) and WAT(2), and one of those of the diol were located. These were included in refinement with isotropic vibration parameters while the oxygen atoms were allowed anisotropic vibration. A difference synthesis following two cycles of refinement revealed the remaining hydrogen atom [H(531)]. For final refinement, oxygen atoms were anisotropic, hydrogen atoms on oxygen atoms and the carbon atoms were isotropic, while hydrogen atoms on carbon atoms were fixed as above. All observable reflections, except the two strongest, $\bar{1}61$($|F_o|$ 184, $|F_c|$ 201) and 132 ($|F_o|$ 173, $|F_c|$ 185), considered to be affected by extinction, were used. A weighting scheme was investigated but abandoned and the final refinement, including unit weights, converged at $R = 6.85\%$, $R_M = 6.32\%$ for 3 006 reflections. The maximum shift was 0.042 of the corresponding standard deviation, for the temperature factor of WAT2, and the final difference map showed no peaks greater than 0.772 e Å^{-3} [situated on the C(19)–C(20) bond].

The scattering factors were those of Cromer and Mann[5] for C and O and of Stewart *et al.*[6] for H.

The final atomic parameters are listed in Table 1. Observed and calculated structure factors are given in Supplementary Publication No. SUP 22792 (19 pp.).*

Computing.—Programs SHELX[4] and ORTEP[7] were run on the ICL System 4 in the Computer Department, Rothamsted Experimental Station. For calculations of molecular geometry the suite *X*-RAY ARC[8] was run on the IBM 1130 computer.

DISCUSSION

An ORTEP[7] diagram of the asymmetric unit is shown in Figure 2 illustrating that it is discrete and consists of one molecule of the 223 ligand linked through

TABLE 1

(a) Fractional atomic co-ordinates (× 10^4) with standard deviations in the least significant digits in parentheses. Isotropic vibration parameters, U_{iso} × 10^3 Å^2

Atom	X	Y	Z	U_{iso}
WAT	4 720(5)	1 991(1)	−1 068(4)	*
O(1)	5 048(3)	1 103(1)	−402(3)	*
C(2)	6 507(5)	996(1)	189(5)	48(1)
C(3)	7 631(5)	1 176(1)	−696(4)	43(1)
C(4)	7 267(5)	1 066(1)	−2 226(4)	41(1)
O(5)	7 136(4)	635(1)	−2 289(3)	*
C(6)	6 959(5)	476(1)	−3 619(4)	39(1)
C(7)	7 971(5)	189(1)	−3 967(5)	50(1)
C(8)	7 824(6)	9(2)	−5 272(5)	56(1)
C(9)	6 672(5)	116(2)	−6 217(5)	56(1)
C(10)	5 642(5)	402(1)	−5 888(5)	48(1)
C(11)	5 773(5)	582(1)	−4 582(4)	38(1)
O(12)	4 779(3)	856(1)	−4 156(3)	*
C(13)	3 804(5)	1 048(1)	−5 199(5)	47(1)
C(14)	3 144(5)	1 422(1)	−4 608(5)	43(1)
C(15)	2 077(5)	1 348(2)	−3 518(5)	53(1)
O(16)	2 875(3)	1 276(1)	−2 187(3)	*
C(17)	2 737(4)	919(1)	−1 503(4)	37(1)
C(18)	1 498(5)	672(1)	−1 663(5)	48(1)
C(19)	1 464(6)	322(2)	−880(5)	58(1)
C(20)	2 636(6)	226(2)	42(5)	58(1)
C(21)	3 888(5)	475(1)	237(5)	51(1)
C(22)	3 935(5)	826(1)	−535(4)	40(1)
O(23)	7 578(3)	1 604(1)	−539(3)	*
C(24)	8 730(6)	1 826(2)	−1 151(5)	57(1)
C(25)	8 062(6)	2 118(2)	−2 213(5)	59(1)
O(26)	7 288(4)	1 905(1)	−3 335(3)	*
C(27)	6 267(5)	2 142(2)	−4 183(5)	56(1)
C(28)	5 171(5)	1 866(2)	−4 970(5)	53(1)
O(29)	4 242(3)	1 694(1)	−4 012(3)	*
C(51)	246(5)	2 125(1)	2 947(5)	49(1)
C(52)	1 227(5)	2 319(1)	2 197(5)	45(1)
O(521)	1 359(5)	2 728(1)	2 240(4)	*
C(53)	2 131(5)	2 098(1)	1 335(5)	44(1)
O(531)	3 022(4)	2 334(1)	619(4)	*
C(54)	2 038(5)	1 692(1)	1 271(5)	44(1)
C(541)	1 010(5)	1 480(1)	2 038(4)	39(1)
C(55)	868(5)	1 059(1)	2 001(5)	47(1)
C(56)	−103(5)	865(2)	2 765(5)	56(1)
C(57)	−989(6)	1 084(2)	3 619(5)	59(1)
C(58)	−889(5)	1 489(1)	3 683(5)	52(1)
C(581)	104(5)	1 702(1)	2 895(4)	41(1)

(b) Anisotropic vibration parameters × 10^3 Å^2 of the form $\exp\{-2\pi^2[U_{(11)}h^2a^{*2} + 2U_{(12)}hka^*b^* + U_{(22)}k^2b^{*2} + 2U_{(23)}klb^*c^* + 2U_{(13)}hla^*c^* + U_{(33)}l^2c^{*2}]\}$

Atom	$U_{(11)}$	$U_{(22)}$	$U_{(33)}$	$U_{(12)}$	$U_{(13)}$	$U_{(23)}$
WAT	55(2)	58(2)	57(2)	8(2)	13(2)	−7(2)
O(1)	41(2)	51(2)	55(2)	6(2)	−1(2)	6(2)
O(5)	62(2)	37(2)	37(2)	8(1)	−2(1)	0(2)
O(12)	44(2)	52(2)	32(2)	12(1)	−3(1)	−3(1)
O(16)	50(2)	52(2)	37(2)	−6(2)	−1(1)	11(2)
O(23)	45(2)	53(2)	45(2)	1(2)	3(1)	−14(2)
O(26)	57(2)	50(2)	47(2)	−3(2)	9(2)	−8(2)
O(29)	48(2)	49(2)	35(2)	0(1)	12(1)	8(1)
O(521)	68(3)	52(2)	80(3)	−5(2)	27(2)	−18(2)
O(531)	62(2)	55(2)	62(2)	0(2)	25(2)	−3(2)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

TABLE 1 (*Continued*)

(c) Fractional co-ordinates for the hydrogen atoms and their isotropic vibration parameters $\times 10^3$ Å^2. Individual parameters were refined for those attached to oxygen atoms. Positions were calculated for those on carbon atoms and isotropic vibration parameters refined in groups

Atom	X	Y	Z	U_{iso}
WAT(1)	551(7)	185(2)	−71(6)	96(24)
WAT(2)	429(7)	186(2)	−166(7)	88(26)
H(2)A	667	110	114	51(4)
H(2)B	661	70	21	51(4)
H(3)	863	107	−40	51(4)
H(4)A	807	116	−277	51(4)
H(4)B	633	119	−259	51(4)
H(7)	880	11	−329	71(5)
H(8)	855	−19	−551	71(5)
H(9)	657	−1	−714	71(5)
H(10)	482	48	−658	71(5)
H(13)A	436	112	−598	51(4)
H(13)B	300	86	−552	51(4)
H(14)	259	154	−543	51(4)
H(15)A	146	111	−379	51(4)
H(15)B	144	158	−346	51(4)
H(18)	65	74	−232	71(5)
H(19)	59	15	−99	71(5)
H(20)	261	−2	58	71(5)
H(21)	472	40	91	71(5)
H(24)A	933	197	−42	76(6)
H(24)B	937	164	−160	76(6)
H(25)A	886	228	−256	76(6)
H(25)B	737	229	−179	76(6)
H(27)A	574	232	−360	76(6)
H(27)B	680	230	−484	76(6)
H(28)A	571	165	−542	76(6)
H(28)B	456	202	−568	76(6)
H(51)	−37	228	353	85(7)
H(521)	193(6)	280(2)	173(6)	72(21)
H(531)	364(7)	221(2)	20(7)	108(26)
H(54)	268	154	69	85(7)
H(55)	148	90	141	85(7)
H(56)	−18	57	272	85(7)
H(57)	−168	94	417	85(7)
H(58)	−151	164	428	85(7)

hydrogen bonding *via* a water molecule to naphthalene-2,3-diol. The bond lengths and angles, including those involved in hydrogen bonding, are in Table 2. A check on the standard deviations, as obtained by deviations from the mean values of chemically equivalent bonds, suggested that those from full matrix refinement are underestimates and that C–C and C–O bond lengths have e.s.d. values of 0.01 Å, *i.e.* double those of Table 2.

The dimensions involving the hydrogen bonding in Table 2 show the usual internal hydrogen bond of *ortho*-substituted aromatic derivatives, from H(521) to O(531). OH(531) acts as a donor to the water molecule; the distances and the angle at H(531) are indicative of strong hydrogen bonding. The water molecule in turn is a multiple donor to the 223 molecule, WAT(2) forms a symmetrical bifurcated bond to O(16) and O(29), while WAT(1) forms a stronger bond to O(23) with a very weak interaction to O(1). Adjustment of the hydrogen positions to give O–H distances of 0.97 Å by extrapolation along the present O–H bonds, does not change but reinforces these conclusions.

The structure found is consistent with the i.r. spectrum which, in the hydroxy region, shows one band at 3 500 cm^{-1} with shoulders on each side, whereas naphthalene-2,3-diol has sharp bands at 3 500 and 3 450 cm^{-1} and a broad band at 3 250 cm^{-1}. In the region 1 000—1 100 cm^{-1} the complex showed fewer bands than 223 itself, indicative of a change in conformation. There are two significant changes in conformation compared with that of the uncomplexed molecule[9] in which the torsion angle C(22)–O(1)–C(2)–C(3) is 153.7(1)° and C(14)–C(15)–O(16)–C(17) is −151.9(1)° (*cf.* Figure 1); these involve the aromatic oxygen atoms which are acceptors of hydrogen bonds. The torsion angle of −119° in the complex is equivalent to an eclipsed arrangement of substituents but does not lead to unfavourably short H ··· H contacts; the minimum is 2.06 Å for H(15A) ··· H(18). The complexed ligand was examined for possible intramolecular H ··· O interactions and O(12) ··· H(4B) was found to be 2.25 Å which is shorter than the sum of the van der Waals' radii for hydrogen and oxygen, but the O(12) ··· H(4B)C(4) angle, 119°, is not indicative of hydrogen bonding.

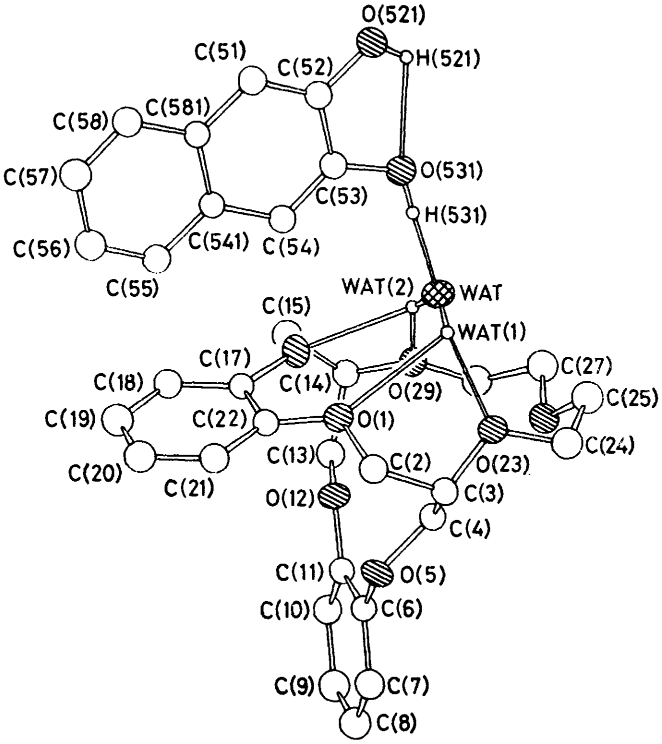

FIGURE 2 One complete molecule showing the designations of the atoms in naphthalene-2,3-diol and of the water molecule; hydrogen atoms on carbon atoms are omitted. The ellipsoids for anisotropically refined atoms correspond to the 50% confidence level

The bond lengths and angles in the complexed and uncomplexed ligand do not differ significantly except for C(14)–C(15)–O(16) 107.8(1)° and C(28)–O(29)–C(14) 117.5(1)° which are respectively 2.9° smaller and 2.5° larger in the uncomplexed molecule ($\Delta/\sigma = 7$).

Other macrocyclic polyether derivatives exhibit conformational changes induced by co-ordination from water. 18-crown-6 has only a centre of symmetry in the free form[10] but in its solvate of bisaquobisnitratodioxouranium(VI)[11] hydrogen bonding from co-ordinated water molecules induces a qualitative change in torsion angles (C–C from *gauche* to *trans* and C–O from *trans* to *gauche*) to give the cyclic ether D_{3d} symmetry, as in its complex with potassium.[12] Co-ordination by water to 12-crown-4 results in a quantitative change in conformation; it is centrosymmetrical in both crystals,[13,14] the changes are in two pairs of C–O torsion angles, one of 23° and one of 26°. Benzo-15-crown-5, with an approximate plane of symmetry, shows a change in a pair of C–O torsion angles from *ca.* 80° in the uncomplexed molecule[15] to 159° in the hydrated form.[16]

TABLE 2

Bond lengths (Å) and angles (°)

(i) The 223 ligand

O(1)–C(2)	1.429(5)	C(14)–O(29)	1.422(5)
C(2)–C(3)	1.510(6)	C(15)–O(16)	1.434(5)
C(3)–C(4)	1.528(6)	O(16)–C(17)	1.371(5)
C(3)–O(23)	1.432(5)	C(17)–C(18)	1.383(6)
C(4)–O(5)	1.443(5)	C(17)–C(22)	1.395(6)
O(5)–C(6)	1.385(5)	C(18)–C(19)	1.391(7)
C(6)–C(7)	1.384(6)	C(19)–C(20)	1.354(7)
C(6)–C(11)	1.395(6)	C(20)–C(21)	1.398(7)
C(7)–C(8)	1.390(7)	C(21)–C(22)	1.391(6)
C(8)–C(9)	1.363(7)	C(22)–O(1)	1.360(5)
C(9)–C(10)	1.387(6)	O(23)–C(24)	1.447(6)
C(10)–C(11)	1.392(6)	C(24)–C(25)	1.498(7)
C(11)–O(12)	1.369(5)	C(25)–O(26)	1.422(6)
O(12)–C(13)	1.423(5)	O(26)–C(27)	1.414(6)
C(13)–C(14)	1.517(6)	C(27)–C(28)	1.501(7)
C(14)–C(15)	1.512(6)	C(28)–O(29)	1.426(5)

C(22)–O(1)–C(2)	120.8(3)	O(29)–C(14)–C(15)	106.7(4)
O(1)–C(2)–C(3)	108.4(4)	C(14)–C(15)–O(16)	110.7(4)
C(2)–C(3)–C(4)	111.0(4)	C(15)–O(16)–C(17)	121.1(3)
C(2)–C(3)–O(23)	107.7(4)	O(16)–C(17)–C(18)	124.7(4)
O(23)–C(3)–C(4)	109.5(3)	O(16)–C(17)–C(22)	114.6(4)
C(3)–C(4)–O(5)	106.8(3)	C(22)–C(17)–C(18)	120.6(4)
C(4)–O(5)–C(6)	114.9(3)	C(17)–C(18)–C(19)	119.7(4)
O(5)–C(6)–C(7)	117.9(4)	C(18)–C(19)–C(20)	120.0(5)
O(5)–C(6)–C(11)	122.4(4)	C(19)–C(20)–C(21)	121.2(5)
C(11)–C(6)–C(7)	119.6(4)	C(20)–C(21)–C(22)	119.4(5)
C(6)–C(7)–C(8)	120.5(5)	C(21)–C(22)–C(17)	119.1(4)
C(7)–C(8)–C(9)	119.8(5)	C(21)–C(22)–O(1)	125.4(4)
C(8)–C(9)–C(10)	120.6(5)	C(17)–C(22)–O(1)	115.5(4)
C(9)–C(10)–C(11)	120.2(4)	C(3)–O(23)–C(24)	115.7(3)
C(6)–C(11)–C(10)	119.2(4)	O(23)–C(24)–C(25)	110.8(4)
C(6)–C(11)–O(12)	116.8(4)	C(24)–C(25)–O(26)	109.6(4)
C(10)–C(11)–O(12)	123.9(4)	C(25)–O(26)–C(27)	114.2(4)
C(11)–O(12)–C(13)	117.6(3)	O(26)–C(27)–C(28)	108.3(4)
O(12)–C(13)–C(14)	109.9(4)	C(27)–C(28)–O(29)	108.4(4)
C(13)–C(14)–C(15)	115.1(4)	C(28)–O(29)–C(14)	115.0(3)
C(13)–C(14)–O(29)	113.1(4)		

(ii) The naphthalene-2,3-diol

C(51)–C(52)	1.359(6)	C(541)–C(581)	1.424(6)
C(52)–O(521)	1.367(6)	C(541)–C(55)	1.409(6)
O(521)–H(521)	0.78(6)	C(55)–C(56)	1.361(6)
C(52)–C(53)	1.424(6)	C(56)–C(57)	1.407(7)
C(53)–O(531)	1.359(5)	C(57)–C(58)	1.354(7)
O(531)–H(531)	0.83(7)	C(58)–C(581)	1.418(6)
C(53)–C(54)	1.357(6)	C(581)–C(51)	1.412(6)
C(54)–C(541)	1.426(6)		

C(581)–C(51)–C(52)	121.1(4)
C(51)–C(52)–O(521)	121.2(4)
C(51)–C(52)–C(53)	120.2(4)
C(53)–C(52)–O(521)	118.7(4)
C(52)–O(521)–H(521)	111(4)
C(52)–C(53)–O(531)	113.4(4)
C(52)–C(53)–C(54)	120.4(4)
C(54)–C(53)–O(531)	126.2(4)
C(53)–O(531)–H(531)	114(5)
C(53)–C(54)–C(541)	120.6(4)
C(54)–C(541)–C(55)	122.7(4)
C(54)–C(541)–C(581)	118.9(4)
C(581)–C(541)–C(55)	118.4(4)
C(541)–C(55)–C(56)	121.4(5)
C(55)–C(56)–C(57)	120.1(5)
C(56)–C(57)–C(58)	120.4(5)
C(57)–C(58)–C(581)	121.1(5)
C(58)–C(581)–C(51)	122.6(4)
C(58)–C(581)–C(541)	118.6(4)
C(541)–C(581)–C(51)	118.8(4)

TABLE 2 (*Continued*)

(iii) Water and hydrogen bonding

WAT–WAT(1)	0.88(6)	WAT · · · O(16)	3.046(5)
WAT–WAT(2)	0.79(6)	WAT · · · O(23)	2.883(5)
O(521)–H(521)	0.78(6)	WAT · · · O(29)	3.005(5)
O(531) · · · H(521)	2.18(6)	WAT(1) · · · O(1)	2.56(6)
O(531)–H(531)	0.83(7)	WAT(1) · · · O(23)	2.03(6)
WAT · · · H(531)	1.79(7)	WAT(2) · · · O(16)	2.36(6)
WAT · · · O(531)	2.603(6)	WAT(2) · · · O(29)	2.33(6)
WAT · · · O(1)	3.036(5)		

WAT(1)–WAT–WAT(2)	109(6)
C(52)–O(521)–H(521)	111(4)
O(521)–H(521) · · · O(531)	116(5)
H(521) · · · O(531)–H(531)	163(5)
O(531)–H(531) · · · WAT	165(7)
H(531) · · · WAT–WAT(1)	114(5)
H(531) · · · WAT–WAT(2)	117(5)
WAT–WAT(1) · · · O(1)	115(5)
WAT–WAT(1) · · · O(23)	159(6)
WAT–WAT(2) · · · O(16)	146(6)
WAT–WAT(2) · · · O(29)	143(6)
WAT(1) · · · O(1)–C(2)	98(1)
WAT(1) · · · O(1)–C(22)	141(1)
WAT(1) · · · O(23)–C(3)	116(2)
WAT(1) · · · O(23)–C(24)	116(2)
WAT(2) · · · O(16)–C(15)	106(2)
WAT(2) · · · O(16)–C(17)	133(2)
WAT(2) · · · O(29)–C(14)	120(2)
WAT(2) · · · O(29)–C(28)	125(2)

TABLE 3

Mean planes through groups of atoms with respect to orthogonal axes, and deviations (Å) of atoms from the planes (non-weighted planes)

Plane 1

$$-0.3701x + 0.8203y + 0.4359z - 1.3890 = 0$$

Atoms in plane

O(1), O(16), O(23), O(26), O(29)

Deviations (Å)

O(1)	−0.242(3)	O(26)	−0.128(3)
O(16)	0.146(3)	O(29)	0.005(3)
O(23)	0.219(3)	WAT	1.992(4)

Plane 2

$$0.5994x + 0.7202y - 0.3491z - 6.3102 = 0$$

Atoms in plane

C(6), C(7), C(8), C(9), C(10), C(11)

Deviations

C(6)	0.005(4)	O(5)	−0.038(3)
C(7)	−0.001(5)	C(4)	1.044(4)
C(8)	−0.001(5)	O(12)	−0.050(3)
C(9)	0.001(5)	C(13)	0.289(5)
C(10)	0.002(5)		
C(11)	−0.005(4)		

Plane 3

$$-0.4905x + 0.5047y + 0.7103z + 0.7491 = 0$$

Atoms in plane

C(17), C(18), C(19), C(20), C(21), C(22)

Deviations

C(17)	−0.011(4)	O(16)	0.030(3)
C(18)	0.006(5)	C(15)	−0.465(5)
C(19)	0.003(5)	O(1)	0.078(3)
C(20)	−0.006(5)	C(2)	−0.317(4)
C(21)	0.001(5)		
C(22)	0.008(4)		

TABLE 3 (*Continued*)

Plane 4

$$-0.6179x - 0.4098y + 0.6709z + 6.0966 = 0$$

Atoms in plane

WAT, WAT(1), WAT(2)

Deviations

O(1)	1.498(3)	O(23)	−0.692(3)
O(16)	1.220(3)	O(29)	−1.394(3)
		H(531)	1.19(7)

Plane 5

$$0.6433x - 0.0786y + 0.7615z - 1.5766 = 0$$

Atoms in plane

C(51), C(52), O(521), C(53), O(531), C(54), C(541), C(55), C(56), C(57), C(58), C(581)

Deviations

C(51)	−0.005(5)	H(521)	−0.028(56)
C(52)	0.007(4)	H(531)	0.094(66)
O(521)	0.006(4)		
C(53)	0.008(4)		
O(531)	−0.019(4)		
C(54)	0.019(4)		
C(541)	−0.006(4)		
C(55)	−0.003(4)		
C(56)	0.000(5)		
C(57)	0.005(5)		
C(58)	−0.000(5)		
C(581)	−0.011(4)		

Planes	1	2	3	4
2	77.48			
3	25.14	100.28		
4	79.34	154.14	55.05	
5	88.32	86.38	79.30	81.62

The C–C bond lengths of the naphthalene-2,3-diol do not differ significantly from those of naphthalene itself [17] or from those in the molecular complexes of naphthalene-2,3-diol with flavins studied by Fritchie and his co-workers.[18-20] In each of these complexes there are two independent naphthalene-2,3-diol molecules, one intercalating flavin molecules in extensive π overlap and the other only hydrogen bonded; all six show no changes in bond lengths and angles from those in the present compound.

The naphthalene-2,3-diol molecule is planar (Table 3, plane 5) and approximately perpendicular to the plane 1, formed by O(1), O(16), O(23), O(26), and O(29); the hydrogen atom H(55) sits above the centre of the C(17)–C(22) benzene ring (plane 3) with the average C–H(55) distance being 2.99 Å. Plane 2 of the other benzene ring of the 223 ligand is approximately perpendicular to planes 1 and 5. As the compound crystallises from a solution containing an equimolar concentration of sodium bromide, and apparently acquires the water from the solvent or the atmosphere, it is presumably less soluble than the sodium complex. The hydrogen bonding is purely intramolecular, intermolecular contacts are of the van der Waals' type.

Figure 3 illustrates the packing of the molecules. The reflections rejected because of suspected extinction can be visualised; $\bar{1}61$ is nearly parallel to plane 1 defined by the oxygen atoms of the 223 ligand, while 132 passed through O(521), O(531), and WAT. Table 4 gives intermolecular distances. Possible attractive interactions are parallel stacking of entities with π electrons, and CH • • • O hydrogen bonds; other considerations are that each planar group is likely to have neighbours on each side and that some of its hydrogen atoms will be making contacts. We refer to a contact of CH • • • C normal to the plane of the recipient ring as a ' mesh '. The benzene ring atoms C(9)—C(11) stack against those of the ring related by the centre of symmetry at $\frac{1}{2}$, 0, $-\frac{1}{2}$ (II), and the nearest contact on the other side is H(57^{V}); the hydrogen atom H(9) meshes to C(19^{II}). The other benzene ring butts onto the molecule related by the centre of symmetry at the origin to give the H(19) • • • H(19^{III}) contact; the bond C(20)–H(20) points towards O(5^{I}), the H • • • O distance does not indicate a hydrogen bond, while H(21) is 2.43 Å from H(10^{VIII}). This ring is meshed on one side by H(55) in the molecule of naphthalene-2.3-diol, contact on the other is from H(9^{II}) only to C(19). The naphthalene-2,3-diol plane, 5 of Table 3, is nearly normal to the *b* axis so that the same entity in the glide-related molecules

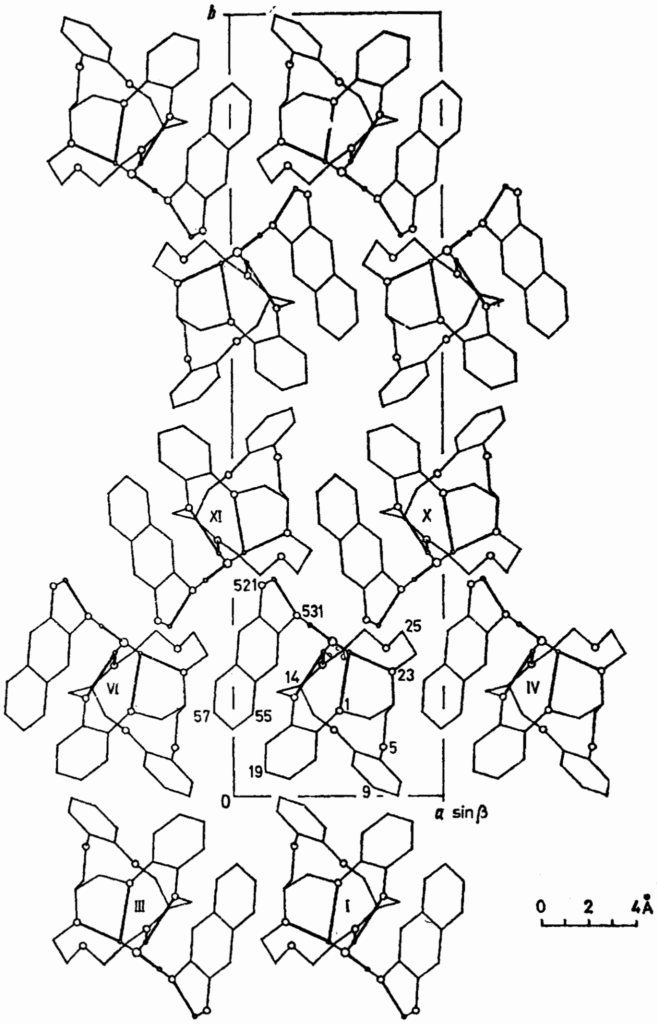

FIGURE 3 The structure projected on to (001). Some atoms in the crystal chemical unit are designated; C–H hydrogen atoms have been omitted. Roman numerals correspond to symmetry related positions defined in Table 4; II is below I, V is below IV, VIII is above and IX below the crystal chemical unit, XII is above XI and XIII below X.

TABLE 4

Intermolecular distances, less than 3.5 Å for C · · · C and C · · · O contacts, less than 3.0 Å for C · · · H and O · · · H contacts, and less than 2.6 Å for H · · · H contacts. A few additional distances are shown

a	*b*		*a*→*b*	*b*→*a*
H(2B)	H(20)	2.51	I	I
O(5)	H(20)	2.62	I	I
O(5)	C(20)	3.59	I	I
C(9)	C(11)	3.34	II	II
C(10)	C(10)	3.44	II	II
H(9)	C(19)	2.92	II	II
H(19)	H(19)	2.48	III	III
H(3)	C(55)	2.93	IV	VI
H(24A)	C(53)	2.94	IV	VI
H(24A)	C(54)	2.96	IV	VI
C(6)	H(57)	2.99	V	VII
C(11)	H(57)	2.94	V	VII
O(26)	H(58)	2.78	V	VII
O(26)	C(58)	3.72	V	VII
H(28A)	H(58)	2.55	V	VII
H(13B)	C(55)	3.00	IX	VIII
H(14)	C(541)	2.72	IX	VIII
H(14)	C(581)	2.69	IX	VIII
H(10)	H(21)	2.43	IX	VIII
H(24A)	O(531)	2.82	X	XI
C(25)	O(531)	3.29	X	XI
C(24)	O(531)	3.37	X	XI
H(25B)	O(531)	2.65	X	XI
O(531)	C(51)	3.39	X	XI
O(531)	C(52)	3.34	X	XI
O(531)	O(521)	3.26	X	XI
H(531)	O(521)	3.00	X	XI
H(25A)	H(27A)	2.44	X	XI
H(25A)	WAT	2.89	X	XI
H(28B)	H(51)	2.46	XIII	XII
H(28B)	O(521)	2.83	XIII	XII
C(27)	O(521)	3.49	XIII	XII
H(27B)	O(521)	2.82	XIII	XII
C(28)	O(521)	3.28	XIII	XII

Roman numerals denote the equivalent positions, the coordinates of the crystal chemical unit in Table 1 being taken as x, y, z

I $1 - x, -y, -z$
II $1 - x, -y, -1 - z$
III $-x, -y, -z$
IV $x + 1, y, z$
V $x + 1, y, z - 1$
VI $x - 1, y, z$
VII $x - 1, y, z + 1$
VIII $x, y, z + 1$
IX $x, y, z - 1$
X $\frac{1}{2} + x, \frac{1}{2} - y, z$
XI $-\frac{1}{2} + x, \frac{1}{2} - y, z$
XII $-\frac{1}{2} + x, \frac{1}{2} - y, z + 1$
XIII $\frac{1}{2} + x, \frac{1}{2} - y, z - 1$

X—XIII is nearly parallel (9°) to it; this is reason for the overlapping contacts, X and XI, in the region of O(521) and O(531). H(57) meshes into the C(6)—C(11) benzene ring, H(58) may be involved in a weak C–H · · · O(26) hydrogen bond. The CH_2 groups on C(24), C(25), C(27), and C(28) are in van der Waals contact with the hydroxy oxygen atoms of molecules X and XIII. Contacts into the two sides of the naphthalene rings arise from $H(14^{VIII})$ and from $H(24A^{VI})$.

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