

Comparison of the Structures of 1,5-Dichloro- and 1,5-Dibromonaphthalene-2,6-diol and Their Co-crystalline Compounds with Dioxane

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Abstract. The 1,5-dichloro- (**1**) and 1,5-dibromo- (**2**) naphthalene-2,6-diols form isostructural lattices incorporating $\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots$ hydrogen bonding surrounding 2_1 screw axes. Each phenolic hydroxy group participates in one donor and one acceptor hydrogen bond. When crystallised from dioxane, both compounds form new 1 : 1 co-crystalline materials whose lattices are closely related but not isostructural. All inter-phenolic hydrogen bonding is now absent with each hydroxy group acting instead as a donor to a dioxane oxygen atom. In consequence, the hydrogen bonded layer structures of pure **1** or **2** are now replaced by hydrogen bonded chain arrangements. All four crystal structures are analysed and compared in crystal engineering terms through discussion of the various types of other weak intermolecular attractions involved in their lattice constructions.

Key words. Phenols, dioxane, hydrogen bonding, screw axes, aromatic ring interactions, weak attractive forces.

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1. Introduction

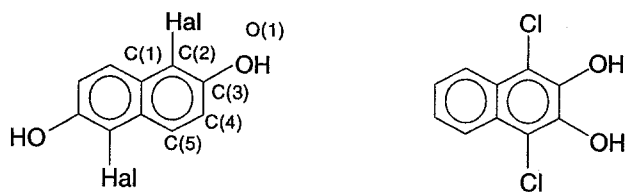
All six isomeric dichlorophenols form crystal structures where the molecules are linked by $\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots$ chains of hydrogen bonds which surround screw axes [1]. In particular the 2,5-, 3,5- and 2,6-dichloro compounds each adopt a 2_1 screw axis; the 2,4- a pseudo-threefold screw axis; the 2,3- a 3_1 screw axis; and the 3,4- isomer a 4_1 screw axis. In addition it is also known that hydrogen bonded 3_1 screw axes occur in the γ -form of 4-chlorophenol [2] and as part of the hydrogen bonded network present in α -hydroquinone [3].

Identical 3_1 hydrogen bonded spines are the core supramolecular element present in the C_2 symmetric helical tubuland family of alicyclic diol inclusion hosts and result in creation of an open lattice structure containing parallel canals [4]. This hydrogen bonding motif can be retained when these diols co-crystallise with phenols. The resulting hydrogen bonded pseudo 3_1 spines are similar except

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that one of the three eclipsed columns of diol molecules has been replaced by a column of phenolic molecules and the lattice void spaces are lost [5, 6].

Such observations are significant in crystal engineering terms [7] since they offer the possibility of designing new organic inclusion materials through control of their hydrogen bonding arrangements [8]. These considerations led us to examine the solid state behaviour of the halogenated phenols **1**, **2** which combine both C_2 symmetry and a second hydroxy group necessary for potential propagation of hydrogen bonding beyond one dimension



1 Hal = Cl

3

2 Hal = Br

2. Experimental

2.1. PREPARATIVE WORK

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using a Bruker AC300F instrument and are reported as chemical shifts (δ) relative to SiMe_4 . The substitution of carbon atoms was determined by the DEPT procedure. Melting points were determined with a Kofler instrument and are uncorrected. The IR spectra were recorded on a Perkin Elmer 298 spectrophotometer. Combustion analyses were carried out at UNSW by Dr. H.P. Pham.

2.1.1. 1,5-Dichloronaphthalene-2,6-diol **1**

A short burst of chlorine gas was passed through a solution of naphthalene-2,6-diol (0.20 g, 1.25 mmol) in glacial acetic acid (5 mL). The solution warmed, turned blue, and a precipitate formed. The solid was filtered off, washed with acetic acid and recrystallised from the same solvent to give the dichloride **1** (0.20 g, 69%), m.p. 204–208 °C (slow decomp.); lit. [9] 223.5 °C. (Found: C, 52.53; H, 2.90. $\text{C}_{10}\text{H}_6\text{Cl}_2\text{O}_2$ requires C, 52.43; H, 2.64%). ν_{max} (paraffin mull) 3240s, 1710 (acetic acid), 1610m, 1480s, 1290m, 1240w, 1210w, 980s, 810s, 760m cm^{-1} . ^1H NMR δ (DMSO- d_6) 10.3, s, 2H, —OH; 7.89, d, 2H, J 9.07 Hz; 7.35, d, 2H, J 9.07 Hz. ^{13}C NMR δ (DMSO- d_6) 149.6 (C), 126.9 (C), 122.7 (CH), 120.1 (CH), 113.4 (C). Crystals of pure **1** for X-ray investigation were grown from chloroform.

A co-crystalline compound resulted when **1** was crystallised from acetic acid but crystals of this proved to be too unstable for X-ray structure determination. A

slightly more robust compound was obtained from dioxane. Solvents not trapped by **1**, as indicated by IR (mull) and ^1H solution NMR spectroscopy, include *n*-butanol, diethyl ether, *t*-butanol, ethanol, chloroform, benzene, ethyl acetate, methanol and toluene.

2.1.2. 1,5-Dibromonaphthalene-2,6-diol **2**

Bromine (0.64 g) in glacial acetic acid (1.3 mL) was added gradually to a stirred solution of naphthalene-2,6-diol (0.32 g, 2.0 mmol) in glacial acetic acid (9.6 mL). The solid produced was filtered and recrystallised from ethanol to yield the dibromide **2** (0.39 g, 61%), m.p. 220 °C; lit. [10] 223 °C. ν_{max} . (paraffin mull) 3280s, 1610m, 1490s, 1300w, 1280m, 1235w, 1200w, 975s, 810s cm^{-1} . ^1H NMR (DMSO- d_6) 10.39, s, 2H, —OH; 7.93, d, 2H, *J* 9.21 Hz; 7.31, d, 2H, *J* 9.21 Hz. ^{13}C NMR δ (DMSO- d_6) 150.9 (C), 128.2 (C), 126.3 (CH), 119.9 (CH), 105.2 (C). Crystals of pure **2** for X-ray investigation were grown from benzene.

Co-crystalline solids resulted when **2** was crystallised from acetic acid or dioxane. The structure of the latter was examined by single crystal X-ray techniques. Solvents not trapped by **2** include diethyl ether, ethyl acetate, methanol, ethanol, *t*-butanol, toluene, benzene and tetrahydrofuran.

2.2. X-RAY DATA COLLECTION, PROCESSING, AND REFINEMENT FOR THE STRUCTURES OF **1**, (**1**)·(DIOXANE), **2** AND (**2**)·(DIOXANE)

Data were recorded for all four structures using an Enraf-Nonius CAD4 X-ray diffractometer. Collection and processing procedures have been described elsewhere [11]. Corrections were made for absorption [12]. The crystallographic numbering system adopted for the phenols is shown against the structural formula, and the dioxane atoms were designated O(2), C(10), and C(11). Numerical details of the solution and refinement of these structures are presented in Table I. Atomic coordinates, bond lengths, bond angles, and dimensions associated with hydrogen bonding are contained in Tables II–V, respectively.

For the structure of pure **1** the positions of all seven non-hydrogen atoms were located using direct methods (MULTAN) [13]. The molecule is positioned about a centre of inversion. Full matrix least squares refinement (BLOCKLS) [14], with anisotropic thermal parameters for the non-hydrogen atoms converged with $R = 0.067$. The hydroxy hydrogen atom was included in the position in which it was located on a difference map, and its coordinates were refined. The other two hydrogen atoms were included in the refinement at calculated positions. They were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound and were not refined. Inspection of a difference Fourier map at this stage indicated that the structure was disordered, with a second disorder component being obtained by rotating the molecule by 180° about the intramolecular O...O vector. By keeping the position of the oxygen atom relatively unchanged, the hydrogen bonding network remains undisturbed by the disorder. Refinement was

Table I. Numerical details of the solution and refinement of the structures.

	1	(1)-(dioxane)
Formula, formula mass	C ₁₀ H ₆ Cl ₂ O ₂ , 229.1	(C ₁₀ H ₆ Cl ₂ O ₂) ·(C ₄ H ₈ O ₂), 317.2
Crystal description	{100}{10-2} (011)(1-1-1)(-1-11)	{111}{01-1}{100} (-122)(1-2-2)(010)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.054(2)	12.084(3)
<i>b</i> /Å	4.8267(5)	8.003(2)
<i>c</i> /Å	10.799(2)	7.427(2)
β /°	108.26(1)	92.31(1)
<i>V</i> /Å ³	448.2(1)	717.7(3)
Temp./°C	21(1)	21(1)
<i>Z</i>	2	2
<i>D</i> _{calc.} /g cm ⁻³	1.70	1.47
Radiation, λ /Å	CuK α , 1.5418	CuK α , 1.5418
μ /cm ⁻¹	63.8	42.4
Crystal dimensions/mm	~0.07 × 0.20 × 0.18	~0.16 × 0.40 × 0.30
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$ /°	140	140
ω scan angle	(0.60 + 0.15 tan θ)	(0.60 + 0.15 tan θ)
No. of intensity measurements	1013	1401
Criterion for observed reflection	<i>I</i> / σ (<i>I</i>) > 3	<i>I</i> / σ (<i>I</i>) > 3
No. of independent obsd. reflections	740	1109
No. of reflections (<i>m</i>) and variables (<i>n</i>) in final refinement	740, 89	1109, 94
$R = \Sigma^m \Delta F / \Sigma^m F_0 $	0.050	0.048
$R_w = [\Sigma^m w \Delta F ^2 / \Sigma^m w F_0 ^2]^{1/2}$	0.065	0.075
$s = [\Sigma^m w \Delta F ^2 / (m - n)]^{1/2}$	2.71	2.92
Crystal decay	None	1 to 0.56
Max., min. transmission coefficients	0.67, 0.34	0.55, 0.24
Largest peak in final diff.map/e Å ⁻³	0.49	0.25
<i>R</i> for multiple measurements	0.018	0.013

completed using a program with rigid group capabilities (RAELS) [15] The second component was introduced into the refinement as a rigid group identical to the major component. Slack constraints were incorporated to ensure that the two symmetry related halves of the minor component remained coplanar and that the geometry about the carbon atoms was correct. The occupancies of the two components were allowed to refine, but their sum was maintained at 1.0. Thermal motion of the minor component was described as a *TLX* group (where *T* is the translation tensor, *L* is the libration tensor and *X* is the origin of libration) with 15 variables. The atoms of the major component were refined anisotropically in the usual way. *R* converged

Table I. Continued.

	2	(2)·(dioxane)
Formula, formula mass	C ₁₀ H ₆ Br ₂ O ₂ , 318.0	(C ₁₀ H ₆ Br ₂ O ₂) ·(C ₄ H ₈ O ₂), 406.1
Crystal description	{100}{10-2}{1-1-1}	{100}{-11-2} (-2 10 3)(-7 1 10)(8-7-8)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.362(2)	11.975(5)
<i>b</i> /Å	4.7835(7)	5.953(1)
<i>c</i> /Å	11.277(3)	10.195(4)
β /°	111.17(1)	96.34(2)
<i>V</i> /Å ³	470.9(2)	722.3(5)
Temp./°C	21(1)	21(1)
<i>Z</i>	2	2
<i>D</i> _{calc.} /g cm ⁻³	2.24	1.87
Radiation, λ /Å	MoK α , 0.7107	MoK α , 0.7107
μ /cm ⁻¹	84.9	55.6
Crystal dimensions/mm	~0.08 × 0.15 × 0.15	~0.11 × 0.15 × 0.16
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max.}$ /°	50	40
ω scan angle	(0.50 + 0.35 tan θ)	(0.50 + 0.35 tan θ)
No. of intensity measurements	998	1471
Criterion for observed reflection	$I/\sigma(I) \leq 3$	$I/\sigma(I) \leq 3$
No. of independent obsd. reflections	687	828
No. of reflections (<i>m</i>) and variables (<i>n</i>) in final refinement	687, 64	828, 94
$R = \Sigma^m \Delta F / \Sigma^m F_0 $	0.025	0.030
$R_w = [\Sigma^m w \Delta F ^2 \Sigma^m w F_0 ^2]^{1/2}$	0.036	0.035
$s = [\Sigma^m w \Delta F ^2 / (m - n)]^{1/2}$	1.41	1.15
Crystal decay	None	None
Max., min. transmission coefficients	0.45, 0.28	0.57, 0.32
Largest peak in final diff. map/e Å ⁻³	0.69	0.44
<i>R</i> for multiple measurements	0.015	0.044

to 0.050 with the occupancies refining to 0.952(1) and 0.048. The largest peak in the final difference Fourier map was 0.49 e Å⁻³.

For the structure of (1)·(dioxane) corrections were also made for decomposition of the crystal. The positions of all 10 non-hydrogen atoms of both the naphthalenediol and the dioxane were located using direct methods (MULTAN) [13]. Both molecules are positioned about centres of inversion. Initially all three atoms of the dioxane were included in the structure as carbon atoms. After isotropic refinement, the temperature factors of these three atoms made assignment of the oxygen atom unequivocal. This was supported by hydrogen bonding from the diol to the dioxane

Table II. Atomic coordinates for the non-CH atoms of structures **1**, **(1)**-(dioxane), **2** and **(2)**-(dioxane).

Atom	1		
	<i>x</i>	<i>y</i>	<i>z</i>
Cl	0.8259(1)	0.1901(2)	-0.0200(1)
O(1)	0.9367(2)	0.5628(5)	0.1975(2)
C(1)	0.5456(3)	0.4070(6)	-0.0242(3)
C(2)	0.7095(3)	0.4067(6)	0.0377(3)
C(3)	0.7790(3)	0.5760(6)	0.1405(3)
C(4)	0.6870(3)	0.7585(6)	0.1878(3)
C(5)	0.5291(3)	0.7676(6)	0.1302(3)
HO(1)	0.9733(50)	0.7004(62)	0.2418(37)
Cl'	0.7118(7)	0.8780(14)	0.2558(4)
O(1)'	0.9356(7)	0.5096(16)	0.2051(6)
C(1)'	0.5147(6)	0.6026(11)	0.0479(4)
C(2)'	0.6701(6)	0.6315(13)	0.1331(4)
C(3)'	0.7886(7)	0.4690(14)	0.1216(5)
C(4)'	0.7570(7)	0.2616(14)	0.0239(6)
C(5)'	0.6090(7)	0.2252(11)	-0.0586(5)
HO(1)'	0.9855(7)	0.3599(17)	0.2135(6)

[Major disorder component occupancy 0.952(12). Minor component, indicated by ', occupancy 0.048].

Atom	(1) -(dioxane)		
	<i>x</i>	<i>y</i>	<i>z</i>
Cl	0.3409(1)	0.1402(1)	0.8298(1)
O(1)	0.1877(2)	-0.0577(2)	0.5862(3)
C(1)	0.4863(2)	0.0418(2)	0.5805(3)
C(2)	0.3766(2)	0.0367(2)	0.6347(3)
C(3)	0.2941(2)	-0.0474(3)	0.5399(3)
C(4)	0.3227(2)	-0.1308(3)	0.3809(4)
C(5)	0.4273(2)	-0.1282(3)	0.3223(4)
HO(1)	0.1721(37)	-0.0218(54)	0.6874(51)
O(2)	0.0724(2)	0.0513(3)	0.8696(3)
C(10)	0.0840(4)	0.1043(7)	1.0524(5)
C(11)	0.0399(3)	-0.0116(6)	1.1735(4)

oxygen atoms. Full matrix least squares refinement (BLOCKLS) [14] was carried out with anisotropic thermal parameters for the non-hydrogen atoms. The hydroxy hydrogen atom was included in the refinement at the position found from a differ-

Table II. Continued.

Atom	2		
	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.8290(0)	0.1908(1)	-0.0264(0)
O(1)	0.9334(3)	0.5698(7)	0.1963(3)
C(1)	0.5428(4)	0.4111(8)	-0.0248(3)
C(2)	0.7068(4)	0.4164(9)	0.0371(4)
C(3)	0.7767(4)	0.5779(9)	0.1391(4)
C(4)	0.6896(5)	0.7541(8)	0.1861(4)
C(5)	0.5331(4)	0.7610(8)	0.1298(4)
HO(1) ^a	0.9665	0.7318	0.2471

Atom	(2)·(dioxane)		
	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.1720(0)	0.2180(1)	0.2510(1)
O(1)	0.3039(3)	0.6230(7)	0.1581(4)
C(1)	0.0163(4)	0.4172(7)	0.0493(4)
C(2)	0.1252(4)	0.4330(7)	0.1192(4)
C(3)	0.1985(4)	0.5993(9)	0.0935(5)
C(4)	0.1660(4)	0.7576(8)	-0.0049(5)
C(5)	0.0626(4)	0.7495(7)	-0.0738(5)
HO(1)	0.3135(53)	0.5523(85)	0.2213(64)
O(2)	0.4217(3)	0.4828(6)	0.3866(3)
C(10)	0.4429(5)	0.3014(9)	0.4753(5)
C(11)	0.4804(5)	0.3782(10)	0.6101(5)

^aErrors not estimated since the hydrogen atom position was not refined.

ence map and its coordinates were refined. All other hydrogen atoms were included in the refinement at calculated positions; they were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound and were not refined. The dimensions of the dioxane ring at this stage gave the C(10)—C(11) bond length as 1.41 Å, and the angles at the two carbon atoms at approximately 113°. As in the case of (1,4-dichloronaphthalene-2,3-diol **3**)₂·(dioxane) [16] there is clearly some disorder of the dioxane ring with the resulting average structure having a shortened C—C bond and enlarged O—C—C angles. However, in this case, it was not considered warranted to include both components in the refinement. *R* converged to 0.048. The largest peak in the final difference Fourier map was 0.25 e Å⁻³.

For structure **2** the position of the bromine atom was determined using direct methods (MULTAN) [13] and the remainder of the non-hydrogen atoms were located

Table III. Bond lengths and standard deviations (Å) for the structures **1**, (1)-(dioxane), **2**, and (2)-(dioxane).

	1	(1)-(dioxane)	2	(2)-(dioxane)
Hal—C(2)	1.732(3)	1.738(2)	1.891(4)	1.895(4)
O(1)—C(3)	1.368(3)	1.347(3)	1.374(4)	1.366(5)
C(1)—C(1) ^a	1.425(5)	1.421(5)	1.415(8)	1.431(8)
C(1)—C(2)	1.424(3)	1.401(4)	1.440(5)	1.419(6)
C(2)—C(3)	1.363(4)	1.373(3)	1.343(6)	1.367(6)
C(3)—C(4)	1.413(4)	1.412(4)	1.403(6)	1.400(6)
C(4)—C(5)	1.369(4)	1.353(4)	1.371(6)	1.354(7)
C(5)—C(1) ^a	1.412(4)	1.424(3)	1.406(6)	1.412(6)
O(1)—HO(1)	0.82(3)	0.83(4)	0.95(2)	0.77(2)
O(2)—C(10)		1.424(4)		1.414(6)
C(10)—C(11)		1.411(5)		1.471(7)
O(2)—C(11) ^b		1.418(4)		1.432(6)

1: Hal = Cl **2**: Hal = Br

Equivalent position indicators:

1 a $1 - x, 1 - y, -z$ (1) · (dioxane) a $1 - x, -y, 1 - z$; b $-x, -y, 2 - z$
2 a $1 - x, 1 - y, -z$ (2) · (dioxane) a $-x, 1 - y, -z$; b $1 - x, 1 - y, 1 - z$

by Fourier techniques. This structure is isomorphous with the analogous chloro compound **1** with the molecule positioned about a centre of inversion. Full matrix least squares refinement (BLOCKLS) [14], with anisotropic thermal parameters for the non-hydrogen atoms converged with $R = 0.025$. The hydroxy hydrogen atom was included in the position in which it was located on a difference map and the other two hydrogen atoms were included in the refinement at calculated positions. All hydrogen atoms were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound and were not refined. The largest peak in the final difference Fourier map was $0.69 \text{ e } \text{Å}^{-3}$.

For (2)-(dioxane) the position of the bromine atom was determined using direct methods (MULTAN) [13] and the remainder of the non-hydrogen atoms were located by Fourier techniques. This structure is not isomorphous with the analogous chloro compound (1)-(dioxane) although it is structurally closely related. The molecule of **2** and that of dioxane are both positioned about a centre of inversion. Full matrix least squares refinement (BLOCKLS) [14], with anisotropic thermal parameters for the non-hydrogen atoms, converged with $R = 0.030$. The hydroxy hydrogen atom was included in the position in which it was located on a difference map and its position was refined. The other hydrogen atoms were included in the refinement at calculated positions and were not refined. These hydrogen atoms were assigned

Table IV. Bond angles and standard deviations ($^{\circ}$) for the structures **1**, (**1**)·(dioxane), **2** and (**2**)·(dioxane).

	1	(1)·(dioxane)	2	(2)·(dioxane)
Hal—C(2)—C(1)	119.6(2)	119.7(2)	119.4(3)	119.7(3)
Hal—C(2)—C(3)	118.5(2)	117.5(2)	118.6(3)	118.7(3)
C(2)—C(1)—C(1) ^a	117.8(3)	118.9(2)	117.0(4)	118.2(5)
C(2)—C(1)—C(5) ^a	123.0(2)	123.4(2)	123.0(4)	123.7(4)
C(1) ^a —C(1)—C(5) ^a	119.2(2)	117.6(3)	122.0(4)	118.1(5)
C(1)—C(2)—C(3)	121.9(2)	122.8(2)	122.0(3)	121.7(4)
O(1)—C(3)—C(2)	119.3(2)	125.5(2)	119.5(4)	124.1(4)
O(1)—C(3)—C(4)	121.1(2)	116.9(2)	120.5(4)	116.4(4)
C(2)—C(3)—C(4)	119.6(2)	117.6(3)	120.0(3)	119.5(4)
C(3)—C(4)—C(5)	120.4(3)	121.6(2)	120.6(4)	120.8(4)
C(4)—C(5)—C(1) ^a	121.0(3)	121.3(2)	120.4(4)	121.7(4)
C(3)—O(1)—HO(1)	113(3)	118(3)	109(3)	113(2)
C(10)—O(2)—C(11) ^b		109.7(3)		109.7(3)
O(2)—C(10)—C(11)		112.8(3)		112.0(5)
C(10)—C(11)—O(2) ^b		112.7(3)		111.5(5)

1: Hal = Cl **2**: Hal = Br

Equivalent position indicators:

1 $a \ 1 - x, 1 - y, -z$ (**1**)·(dioxane) $a \ 1 - x, -y, 1 - z; \ b \ -x, -y, 2 - z$
2 $a \ 1 - x, 1 - y, -z$ (**2**)·(dioxane) $a \ -x, 1 - y, -z; \ b \ 1 - x, 1 - y, 1 - z$

isotropic temperature factors equivalent to those of the atoms to which they were bound. The largest peak in the final difference Fourier map was $0.44 \text{ e } \text{Å}^{-3}$.

The material deposited for each structure comprises atomic coordinates, thermal parameters, and structure factors.

3. Results and Discussion

3.1. DESCRIPTION OF THE STRUCTURES OF **1** AND **2**

The solvent-free forms of **1** and **2** are isostructural. In each case, the asymmetric unit consists of half of one molecule, with a centre of inversion relating its two identical halves. Molecules of both **1** and **2** are planar with the maximum deviation from the plane of best fit being 0.02 Å for **1** and 0.03 Å for **2**. The two molecules of the naphthalenediol in the unit cell pack in columns with the normal to the molecular plane making an angle of about 45° with the b axis (44.8° for **1**, and 42.5° for **2**). Adjacent columns in the c direction tilt in opposite directions and are displaced by half a unit cell in b . Each molecule takes part in edge-face (ef) $\text{CH} \cdots \text{C}$ interactions with four other molecules and also in offset aromatic face-face (ff) interactions with two other molecules. The shortest ef $\text{H} \cdots \text{C}$ distance is 2.83

Table V. Dimensions associated with hydrogen bonding in structures **1**, **(1)**·(dioxane), **2** and **(2)**·(dioxane). The minor disorder component of **1** has been omitted.

	1	2
O(1)··O(1) ^a	2.758(2)	2.766(3)
HO(1)··O(1) ^a	1.95(3)	1.86(3)
C(3)—O(1)··O(1) ^a	112.6(2)	114.7(2)
O(1)··O(1) ^a —C(3) ^a	117.8(2)	117.8(2)
O(1)—HO(1)··O(1) ^a	165(4)	159(3)
	$a\ 2 - x, 1/2 + y, 1/2 - z$	$a\ 2 - x, 1/2 + y, 1/2 - z$
	(1) ·(dioxane)	(2) ·(dioxane)
O(1)··O(2)	2.714(3)	2.718(5)
HO(1)··O(2)	1.94(4)	2.05(6)
C(3)—O(1)··O(2)	134.7(1)	138.3(3)
O(1)··O(2)—C(10)	143.3(2)	145.4(3)
O(1)··O(2)—C(11) ^a	105.6(2)	100.9(3)
O(1)—HO(1)··O(2)	155(4)	145(7)
	$a - x, -y, 2 - z$	$a\ 1 - x, 1 - y, 1 - z$

Å for **1** and 2.95 Å for **2**; the shortest H··C distance for the ff interaction is 3.41 Å for **1** and 3.49 Å for **2**. These distances can be compared with those found in the planar aromatic molecule coronene where the shortest CH··C ef distance is 2.78 Å and the shortest H··C ff distance is 3.46 Å [17].

The naphthalenediol molecules are linked together by hydrogen bonding to produce layers perpendicular to the *ac* plane and at an angle of approximately 45° to *a*. Each hydroxy group takes part in two hydrogen bonds, one as donor and one as acceptor. These hydrogen bonded molecules are related by 2_1 screw axes parallel to *b* and are nearly orthogonal. These features are illustrated by the structure of **1** in Figure 1.

3.2. DESCRIPTION OF THE STRUCTURES OF **(1)**·(DIOXANE) AND **(2)**·(DIOXANE)

When **1** or **2** is crystallised from dioxane, the resulting co-crystalline structures are no longer isostructural. However, in each case the asymmetric unit comprises half a molecule of the naphthalenediol and half a molecule of dioxane. There are centres of inversion relating the two halves of both molecules and the maximum deviation from the plane of best fit through either naphthalenediol is 0.01 Å. The molecules of **1** are orientated so that the normal to the plane through the molecule makes an angle of 34.3° with the *b* axis, while for **2** the corresponding angle is 54.4°. In both structures, the aromatic molecules still form columns as found for the

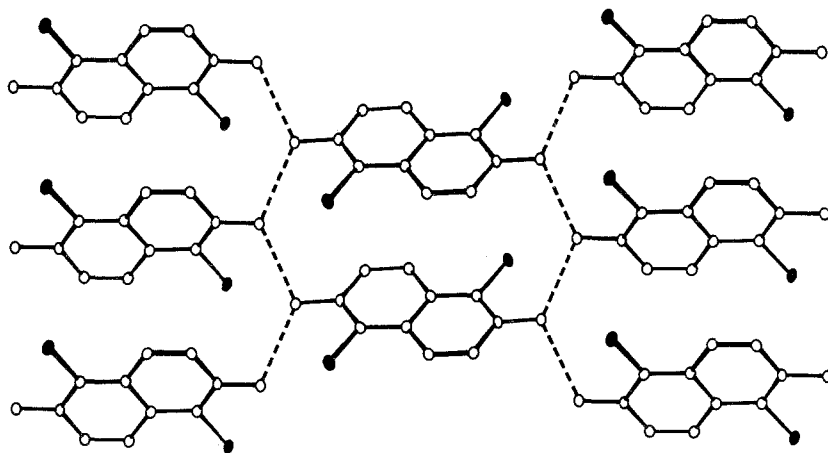


Figure 1. A layer of **1** viewed down c with the $\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots$ hydrogen bonded chains represented by dashed lines. Chlorine atoms are shaded black and hydrogen atoms have been omitted.

pure compounds above, but these are now separated by columns of dioxane. Closer inspection of the aromatic columns shows that the ff interactions have become so offset as to be almost non-existent. (For **2** there remains one $\text{H}\cdots\text{C}$ contact of 3.52 Å). The four ef interactions are maintained with the minimum $\text{CH}\cdots\text{C}$ distances being 2.92 Å for **1** and 2.97 Å for **2**.

In these co-crystals there are insufficient hydrogen bond donors for the number of potential acceptors. Consequently the total number of hydrogen bonds present is halved and all inter-naphthalenediol hydrogen bonding is lost. Each hydroxy group now takes part in only one hydrogen bond where the dioxane molecules link two naphthalene diols in the manner $\text{OH}\cdots\text{OC}_4\text{H}_8\text{O}\cdots\text{HO}$. The resulting hydrogen bonded chain arrangements for the two co-crystalline structures are illustrated in Figures 2 and 3.

3.3. FURTHER COMMENT ON THE STRUCTURES

Desiraju and Gavezzotti have investigated and classified the packing of a wide range of polynuclear aromatic hydrocarbons [18, 19]. They describe various packing motifs which result from the size and shape of particular molecules. Even though **1** and **2** are functionalised aromatic molecules and, indeed, take part in hydrogen bonding and co-crystallisation in the structures described here, these naphthalenediols fit surprisingly well into the Desiraju and Gavezzotti definitions.

They found that the type of packing depended on the unit cell dimension in the direction of the screw axis — in their work this was invariably the shortest axis (sa). Packing was described as a herringbone structure if the principal aromatic intermolecular interactions were ef rather than ff, and this was observed to occur

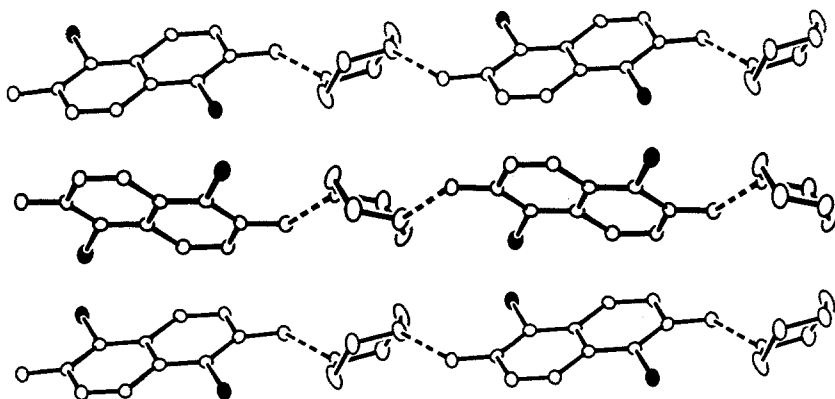


Figure 2. The structure of (1)-(dioxane) viewed approximately down c showing strands of the hydrogen bonded molecules: dioxane \cdots naphthalenediol \cdots dioxane \cdots naphthalenediol. Hydrogen bonds are indicated by dashed lines, halogen atoms are shaded black, and hydrogen atoms have been omitted.

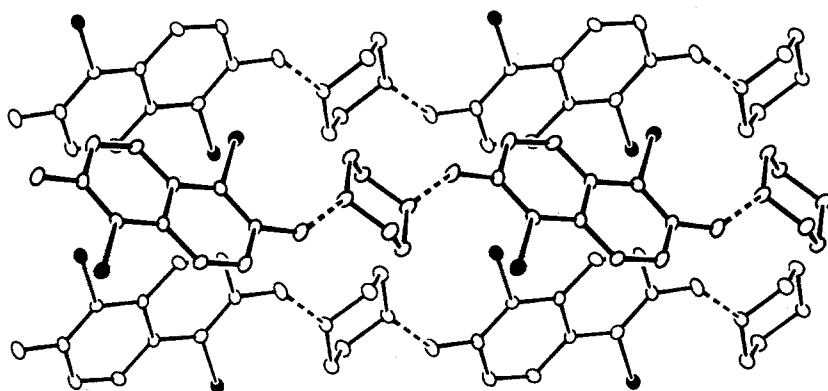


Figure 3. The structure of (2)-(dioxane) viewed approximately down c as above. Whereas 1 and 2 are isostructural, the difference between (1)-(dioxane) and (2)-(dioxane) is apparent on comparison of Figures 2 and 3.

for $5.4 < s_a < 8.0 \text{ \AA}$. When $4.6 < b < 5.4 \text{ \AA}$ the packing was termed a γ -structure and ff interactions were now significant.

For pure 1 and 2 ff interactions are present as shown in Figure 4 (a) and (c) respectively, and $4.6 < b < 5.4 \text{ \AA}$. In contrast, for the structures (1)-(dioxane) and (2)-(dioxane), where $5.4 < b < 8.0 \text{ \AA}$, ef interactions dominate as shown in Figure 4 (b) and (d) respectively. Hence using the Desiraju and Gavezzotti classification both naphthalenediol-dioxane compounds crystallise in a herringbone array, while the lattices of pure 1 and 2 adopt the γ -structural type.

Several other weak intermolecular forces can be recognised as providing additional stabilisation to the crystal lattices of these four structures. There are short Cl \cdots Cl contacts [20] in pure 1 of 3.55 \AA , but when dioxane is incorporated the

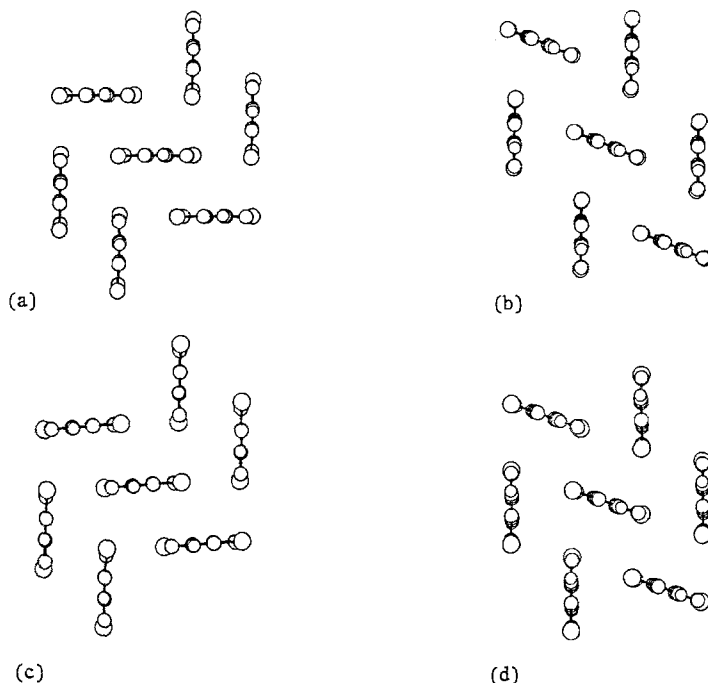


Figure 4. View of seven molecules of the naphthalenediol in (a) **1**, (b) **(1)·(dioxane)**, (c) **2**, and (d) **(2)·(dioxane)**, showing the herringbone packing. In (a) and (c) the stacks are nearly orthogonal with parallel molecules suitably positioned to take part in offset face-face interaryl interactions. In (b) and (d) the stacks are canted and parallel molecules are now too far offset for significant face-face interaction. Edge-face interactions occur in all four cases. Hydrogen atoms have been omitted for clarity.

shortest Cl···Cl interaction lengthens to 4.11 Å. For **2**, Br···Br contacts [7] of 3.54 Å exist in the pure compound but there are none shorter than 5.08 Å when dioxane is present

However, the halogen atoms also take part in some relatively short X···H interactions [21, 22]. In pure **1** there are Cl···HC distances of 3.03 Å and in **(1)·(dioxane)** these fall to 2.91 Å. For pure **2**, Br···HC is 3.04 Å but in the co-crystal this increases to 3.18 Å.

In both dioxane compounds there are some relatively short CH···O contacts [21, 23, 24] which provide additional stabilisation of these co-crystalline products. For **1** and **2** the shortest values are 2.97 and 3.04 Å respectively. However, in **(1)·(dioxane)** there are now CH···O contacts of 2.73 Å (Ar—H···O—Ar), 2.80 Å (dioxane H···O—Ar), and 2.95 Å (dioxane H···O dioxane). For **(2)·(dioxane)** the shortest such contacts are 2.69 Å (dioxane H···O—Ar) and 2.84 Å (dioxane H···O dioxane).

The two pure phenolic compounds **1**, **2** proved to favour a layer lattice involving chains of hydrogen bonds surrounding a 2_1 screw axis. We have previously

observed this hydrogen bonded motif in the structure of (1,4-dichloronaphthalene-2,3-diol)₂·(dioxane) [15]. As anticipated both naphthalenediols also exhibited inclusion properties, on this occasion through forming co-crystalline compounds with dioxane.

Other reported X-ray structures of phenol-ether adducts include the molecular adducts (hydroquinone)·(cineole)₂ [25] and (pentafluorophenol)₂·(dioxane) [26], the one-dimensional chain structure (hydroquinone)·(dioxane) [27], and the two-dimensional layer structure (1,4-dichloronaphthalene-2,3-diol)₂·(dioxane) [16]. The present materials have many similarities to the hydroquinone-dioxane compound.

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