Chem. Mater. 1994, 6, 1269-1281

Formation and Structure of a New Family of Organic Cocrystals[1]

Alison T. Ung, Roger Bishop,* Donald C. Craig, Ian G. Dance, and Marcia L. Scudder

School of Chemistry, The University of New South Wales, Kensington, New South Wales 2033, Australia

Received January 19, 1994. Revised Manuscript Received April 15, 1994®

Crystallization of the helical tubuland diols **1**, **2**, or **4** from solutions containing simple phenols has led to the discovery of a new family of stoichiometric diol–phenol cocrystalline solids. Sixteen such compounds have been prepared and characterized, and twelve of these shown to adopt the same lattice packing and symmetry in space group $P2_1/c$. The successful (and unsuccessful) diol–phenol combinations investigated are discussed in terms of their crystal lattice engineering characteristics. The structures of (**1**)·(*p*-chlorophenol), $(\mathbf{1})_2$·(hydroquinone), (**2**)·(*p*-chlorophenol), (**2**)·(*p*-methoxyphenol), (**2**)·(*p*-hydroxythiophenol), (**4**)·(phenol), and $(\mathbf{4})_2$·(phloroglucinol) have been fully determined by single-crystal X-ray methods. All except the last compound crystallise in space group $P2_1/c$ and their closely related lattice arrangements are compared and contrasted. The 3-fold hydrogen-bonded OH···OH···OH··· chains present in the helical tubuland structure of the diols are retained in these cocrystals. However, the phenolic molecules now occupy one of the three eclipsed arms of this motif, resulting in loss of the previous canal structure with concomitant change from a chiral to a centrosymmetric lattice. The different substitution and symmetry of 1,3,5-trihydroxybenzene (phloroglucinol) cannot be accommodated in this type of structure and $(\mathbf{4})_2$·(phloroglucinol) crystallizes as a quite different arrangement in space group *Fdd*2.

Introduction

The alicyclic diols **1–4** are examples of the helical tubuland diol family.[2,3] These compounds crystallize from ethyl acetate with a hydrogen-bonded structure containing parallel helical canals. As shown in Figure 1 for one canal only of **1–4**, the size and shape of the unobstructed canal cross section varies considerably for members of this series. For example, in the case of **1** it is almost triangular (side ca. 6.3 Å) with an area of ca. 22.4 Å^2.

Diols **1**,[4] **2**,[5] and **4**[6] are versatile hosts which include a wide range of small molecules in their canals; however, the canal in **3** is largely occupied by part of its own structure and thus guests cannot be included. During our screening of the inclusion properties of these diols we have monitored the possible inclusion of guests using techniques such as IR, NMR, microanalysis, X-ray powder diffraction (XRPD), and single-crystal X-ray structure determination. For diols **1**, **2**, and **4** all cocrystalline materials so far encountered (except hydrates), across a very wide range of different guest functional groups,[4-6] have proved to be conventional lattice inclusion compounds[7,8] with only van der Waals attractions between the two molecular components. Here we present details of the behavior of diols **1–4** with phenols, and show that when cocrystallinity is observed it is now due to an alternative type of lattice structure which gives rise to a new family of materials.[9]

Results

During the screening of diols **1**, **2**, and **4** for inclusion properties it was observed that the helical tubuland host lattice was retained even when polar, basic, acidic, or hydrogen-bonding guests were employed. Thus substances as diverse as dimethyl sulfoxide, diethylamine, acetic acid, and formamide were included as guests within the canals without disruption of the host hydrogen bonding.[10] In marked contrast, the behavior of phenols was quite distinct and unique. They either were not included at all or gave cocrystalline combinations with the diols which had quite different powder diffraction patterns to those found for the helical tubulate inclusion compounds. The first two examples discovered were 1:1 combinations of *p*-chlorophenol with either diol **1** or **2**, the structures of both compounds being determined by single-crystal X-ray crystallography.

Structure of (2)·(*p*-Chlorophenol). In the initial experiment, 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol[11] **2** was dissolved in a small volume of warm

---

® Abstract published in *Advance ACS Abstracts*, August 15, 1994.

[1] This paper is dedicated to the memory of the late Professor Margaret Etter.

[2] Bishop, R.; Dance, I. G. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 4, Chapter 1, pp 1–26.

[3] Bishop, R.; Dance, I. G. *Top. Curr. Chem.* **1988**, *149*, 137.

[4] Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G. Scudder, M. L. *J. Chem. Soc., Perkin Trans. 2* **1992**, 861.

[5] Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *Struct. Chem.* **1992**, *3*, 59.

[6] Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Rae, A. D.; Scudder, M. L. *J. Inclus. Phenom.* **1993**, *15*, 385.

[7] Goldberg, I. *Top. Curr. Chem.* **1988**, *149*, 1.

[8] *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D.; MacNicol, D. D., Eds.; Academic Press: London, 1984; Vols. 1–3; and Oxford University Press: Oxford, 1991; Vols. 4–5.

[9] A preliminary account of two of the sixteen compounds has been published: Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1993**, 322.

[10] Ung, A. T. Ph.D. Thesis, UNSW, 1993.

[11] Dance, I. G.; Bishop, R.; Hawkins, S. C.; Lipari, T.; Scudder, M. L.; Craig, D. C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1299.

0897-4756/94/2806-1269$04.50/0

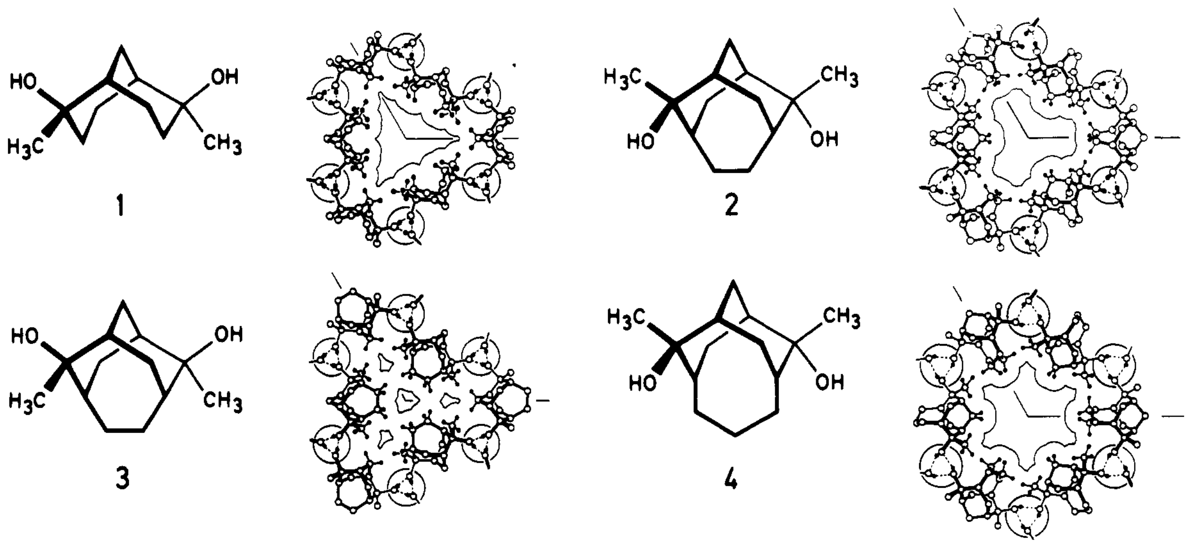

Figure 1. Molecular structures of the helical tubuland diols 1–4 showing for each a slice through one canal only. The van der Waals surface of each canal is defined by key hydrogen atoms shown as filled circles. The helical spines are circled and hydrogen bonds indicated by dashed lines.

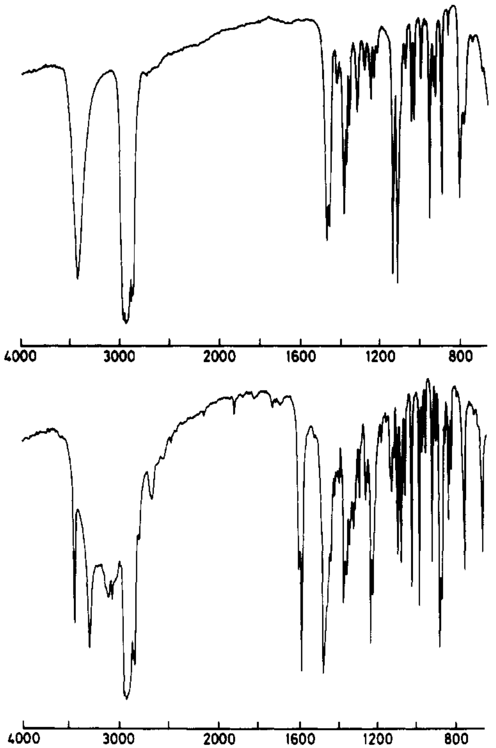

Figure 2. Comparison of the IR spectra (paraffin mull) of (top) a typical helical tubulate inclusion compound $(2)_3\cdot(CCl_4)_{1.2}$, and (below) the cocrystalline solid (2)·(*p*-chlorophenol).

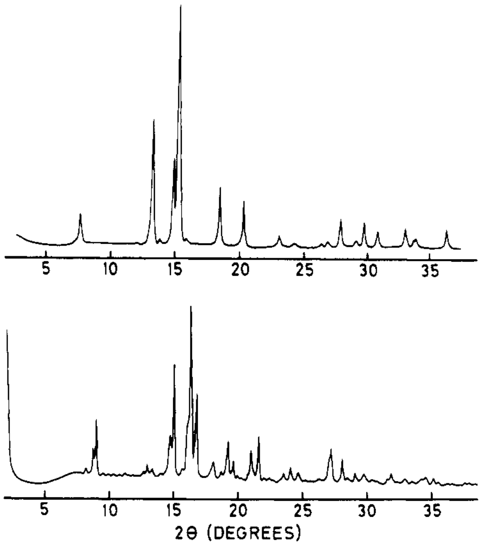

Figure 3. Comparison of the X-ray powder diffraction patterns of (top) a typical helical tubulate inclusion compound $(2)_3\cdot(CCl_4)_{1.2}$ and (below) the cocrystalline solid (2)·(*p*-chlorophenol).

p-chlorophenol and crystalline material allowed to form by slow evaporation. Investigation of this material using IR spectroscopy revealed the presence of both molecular components, while ^{1}H NMR studies and microanalysis indicated a 1:1 stoichiometry which is not that normally encountered in helical tubulate inclusion compounds.[4–6] The IR spectrum (especially in the hydroxylic stretch region) was markedly different (Figure 2). Wavenumber values for pure diol 2 and *p*-chlorophenol are 3420 and 3380 cm^{-1}, respectively, but in the cocrystalline material these are replaced by absorptions at 3450, 3300, 3110, and 3070 cm^{-1}. The XRPD pattern was also of a type not previously observed in our earlier work (Figure 3), thus suggesting a different lattice structure.

An X-ray structural determination was carried out on this compound, confirming the composition and revealing that the material was a cocrystalline substance in space group $P2_1/c$. In this material the molecules of *p*-chlorophenol and diol 2 in the lattice are linked together by hydrogen bonds with 1:1 stoichiometry.

In the crystal lattices of the helical tubuland diols, the fundamental structural core is a series of helical hydrogen-bonded spines. These 3-fold spirals of continuous hydrogen bonds OH···OH···OH··· subtend three arms of eclipsed diol molecules. Identical parallel spines at the other diol –OH positions lead to buildup of the three-dimensional network.[11]

The trigonal hydrogen-bonded spines present in helical tubulate compounds of 2 (Figure 4) are retained in this new cocrystalline material but molecules of *p*-chlorophenol now occupy one of the three eclipsed arms (Figure 5). Consequently the hydrogen-bonding network changes from a three- to a two-dimensional layer-type structure since the *p*-chlorophenol molecules cannot propagate the hydrogen-bonding network in the third dimension. Each

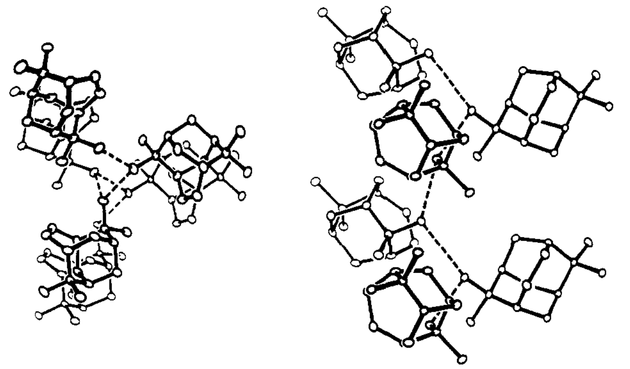

Figure 4. Part of the helical hydrogen bonded spine structure of diol **2** molecules which comprises the structural core of its helical tubuland lattice. Hydrogen bonds are shown as dashed lines, and hydrogen atoms are omitted for clarity. Left: projection close to the *ab* plane showing the trigonal hydrogen bonding arrangement with eclipsed columns of diol molecules. Right: the substructure with the axis *c* vertical.

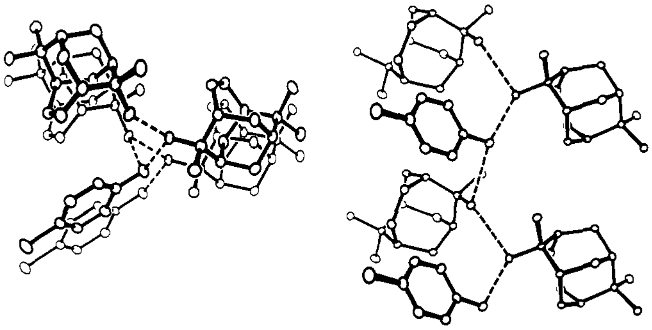

Figure 5. Comparable views to Figure 4 of the hydrogen bonded spine structure present in the cocrystalline compound (**2**)·(*p*-chlorophenol). It can be seen that the phenol molecules have replaced diol molecules in one of the eclipsed columns, but otherwise the two arrangements are remarkably similar.

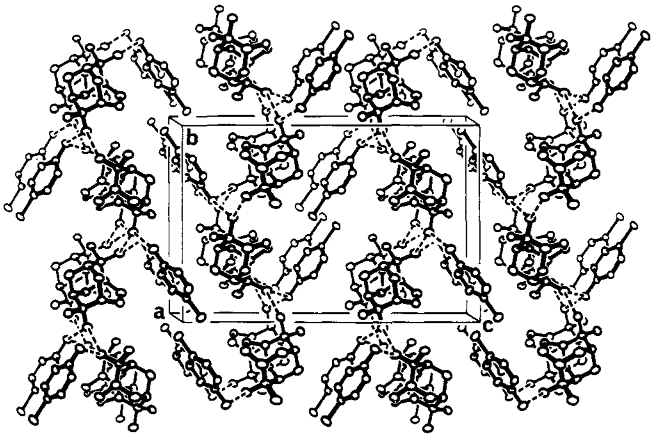

Figure 6. Unit cell of the cocrystalline compound (**2**)·(*p*-chlorophenol) showing eclipsed stacks of diol **2** molecules, *p*-chlorophenol molecules, and chlorine atoms. Hydrogen bonds are shown as dashed lines and hydrogen atoms are omitted for clarity. The narrow tubes of pseudomacrocyclic cross section formed between adjacent enantiomeric layers are prominent.

layer incorporates molecules of **2** with the same chirality around the helical spines, but these layers alternate with those of opposite chirality yielding a centrosymmetric lattice (Figure 6). Therefore, unlike the helical tubuland diols which crystallize as a conglomerate,[12] members of this family of cocrystals are achiral.

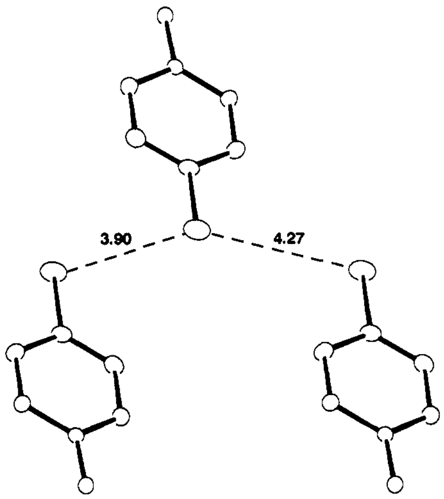

Figure 7. Arrangement of the Cl- - -Cl associations present in the structure (**2**)·(*p*-chlorophenol). Inter-chlorine distances are quoted in angstroms.

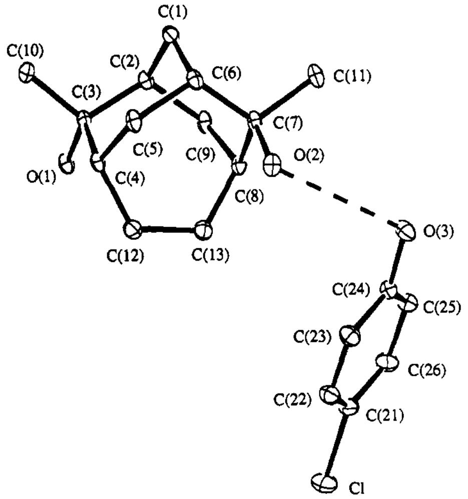

Figure 8. Crystallographic numbering system used for the cocrystalline solid (**2**)·(*p*-chlorophenol). Hydrogen atoms are omitted for clarity, and the hydrogen bond is represented as a dashed line separating two of the oxygen atoms.

In this structure the enantiomeric layers cannot associate by means of hydrogen bonding and instead utilize multiple Cl···Cl···Cl··· interactions between two adjacent vertical columns of aryl chlorides. Thus viewing in the *bc* plane the layers are associated into long narrow tubes along *a*. These tubes have a cross section resembling a pseudomacrocycle assembled from four molecules of **2** and four of *p*-chlorophenol (Figure 6).

Chlorine interactions, such as those present here, are favorable attractive forces documented across a wide range of chlorinated compounds. Desiraju[13] has commented that chlorine substituents are excellent steering groups in the assembly of crystalline lattices.[14] Indeed, in a number of structures the Cl···Cl separations lie in the range 3.37–3.49 Å, which is less than the sum of the van der Waals radii (3.60 Å).[15]

In crystalline (**2**)·(*p*-chlorophenol) there is a center of inversion midway between adjacent pairs of chlorine atoms,

---

[12] Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981; Chapter 2.

[13] Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

[14] Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222.

[15] Bavoux, C.; Perrin, M.; Thozet, A. *Acta Crystallogr., Sect. B*, **1980**, *36*, 741.

Table 1. Numerical Details of the Solution and Refinement of Structures

	(1)·(*p*-chlorophenol)	$(1)_2$·(hydroquinone)	(2)·(*p*-chlorophenol)	(2)·(*p*-methoxyphenol)	(2)·(*p*-hydroxythiophenol)	(4)·(phenol)	$(4)_2$·(phloroglucinol)
formula	$C_{11}H_{20}O_2\cdot C_6H_5OCl$	$(C_{11}H_{20}O_2)_2\cdot C_6H_6O_2$	$C_{13}H_{22}O_2\cdot C_6H_5OCl$	$C_{13}H_{22}O_2\cdot C_7H_8O_2$	$C_{13}H_{22}O_2\cdot C_6H_6OS$	$C_{14}H_{24}O_2\cdot C_6H_6O$	$(C_{14}H_{24}O_2)_2\cdot C_6H_6O_3$
formula mass	312.84	478.6	338.87	334.46	336.49	318.45	574.8
crystal description	{100}{010}{001}	{001}{011}-{01−1} (10−2)(−101)	{100}{001}-{1−1−1} {11−1}{012}-{0−12}	{001}(−100)-(11−1) (1−1−1){011}-{01−1}	{001}{1−1−1}-{11−1}	{011}{01−1}-{100}	{010}{1−10}{110} (00−1)(−101)-(3−32)
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Fdd2$
a/Å	6.927(1)	6.8637(5)	6.8747(5)	6.8964(4)	6.8717(8)	6.9077(9)	26.132(1)
b/Å	12.696(1)	12.8289(5)	13.2443(4)	13.1445(3)	13.2552(6)	13.7541(6)	45.337(2)
c/Å	19.286(4)	15.974(1)	19.878(2)	20.598(1)	20.021(3)	19.561(3)	10.7267(4)
β/deg	94.825(8)	103.099(3)	97.562(3)	97.210(3)	96.643(6)	102.797(6)	90
V/Å^3	1690.1(4)	1370.0(2)	1794.2(2)	1852.4(2)	1811.3(3)	1812.3(4)	12708.2(8)
temp/°C	21(1)	21(1)	21(1)	21(1)	21(1)	21(1)	21(1)
Z	4	2	4	4	4	4	16
D_{calc}/g cm^{-3}	1.23	1.16	1.25	1.20	1.23	1.17	1.20
radiation, λ/Å	Cu Kα, 1.5418	Cu Kα, 1.5418	Cu Kα, 1.5418	Cu Kα, 1.5418	Cu Kα, 1.5418	Cu Kα, 1.5418	Cu Kα, 1.5418
μ/cm^{-1}	20.71	6.05	19.89	6.21	16.39	5.70	6.23
crystal dimensions/mm	0.59 × 0.24 × 0.07	0.25 × 0.25 × 0.11	0.21 × 0.30 × 0.23	~0.40 × 0.35 × 0.23	~0.17 × 0.17 × 0.10	0.36 × 0.15 × 0.15	~0.30 × 0.17 × 0.30
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$/deg	100	140	140	120	140	120	140
ω scan angle	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$	$(0.60 + 0.15 \tan\theta)$
no. of intensity measurements	2028	2825	3871	2755	3865	2684	3303
criterion for observed refln	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
no. of independent obsd reflns	1375	2065	2357	2240	1605	1851	2745
no. of reflections (m) and variables (n) in final refinement	1375, 199	2065, 164	2357, 209	2240, 248	1605, 208	1851, 226	2745, 391
$R = \Sigma_m\lvert\Delta F\rvert/\Sigma_m\lvert F_o\rvert$	0.035	0.046	0.043	0.055	0.046	0.044	0.038
$R_w = [\Sigma_m w\lvert\Delta F\rvert^2/\Sigma_m w\lvert F_o\rvert^2]^{1/2}$	0.047	0.075	0.060	0.083	0.055	0.058	0.055
$s = [\Sigma_m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	1.74	2.75	2.09	3.28	1.74	1.99	2.04
crystal decay	1 to 0.83	none	1 to 0.83	1 to 0.92	1 to 0.80	1 to 0.83	none
max, min transmission coefficients	0.86, 0.58	0.94, 0.85	0.77, 0.60	0.88, 0.80	0.87, 0.77	0.93, 0.82	0.91, 0.83
R for 276 multiple measurements	0.021	0.011	0.039	0.016	0.018	0.009	
largest peak in final diff map/eÅ^{-3}	0.13	0.24	0.36	0.37	0.16	0.16	0.08
extinction coefficient		1.83×10^{-4}	4.21×10^{-4}				7.54×10^{-5}

and the corresponding Cl···Cl distances are 3.899(2) and 4.274(2) Å as shown in Figure 7. These separations are longer than the sum of the van der Waals radii but nonetheless represent significant interlayer lattice stabilization. Thus from a crystal engineering point of view this structure can be recognized as involving two well-known types of structural motif, namely, the intermolecular chlorine–chlorine interaction and the 3-fold hydrogen-bonded spine. Furthermore, the latter arrangement (which is the key to formation of the helical tubuland diol lattice) is retained in the mixed crystal when one eclipsed arm is replaced by the eclipsed stack of *p*-chlorophenol molecules.

The crystallographic numbering system employed is shown in Figure 8, and numerical details of the solution and refinement of the structure (2)·(C_6H_5ClO) are shown in Table 1. Atomic positional parameters for the non-C–H atoms are listed in Table 2; bond lengths and angles are given in Tables 3 and 4. Dimensions associated with the hydrogen bonding are presented in Table 5.

Structure of (1)·(*p*-Chlorophenol). The structure of the cocrystalline substance of 1:1 stoichiometry obtained by crystallization of 2,6-dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol[11] 1 from *p*-chlorophenol was also determined by X-ray crystallography.

This compound also crystallizes in space group $P2_1/c$ and is isostructural with the first (Figure 9). Once again the major structural features are the mixed hydrogen-bonded spines and the chlorine–chlorine interactions. This time these interatomic separations are shorter [3.648(2) and 3.772(2) Å, respectively].

Comparison of Figures 6 and 9 reveals the extreme similarity of the two structures but the narrow tubes are less crowded in this case. Numerical details of the solution and refinement of (1)·(C_6H_5ClO) are shown in Table 1. All other crystallographic data are available in the supplementary material (see paragraph at end of paper).

A Family of Diol–Phenol Compounds? The observation that either diol 1 or 2 and *p*-chlorophenol could participate together in a helical spine arrangement immediately suggested the possibility of obtaining further compounds of this general type. It seemed most likely that the use of other helical tubuland diols and/or other phenols would result in closely related lattice structures based on the same structural core. In other words it should be possible to develop a family of diol–phenol cocrystalline

Table 2. Positional Parameters (with Standard Deviations) for the Non-C–H Atoms of the Structure (2)·(*p*-Chlorophenol)

	x/a	*y/b*	*z/c*
O(1)	0.1085(2)	−0.0307(1)	0.6763(1)
O(2)	0.2041(2)	0.3449(1)	0.7919(1)
C(1)	0.1167(4)	0.2374(2)	0.6160(1)
C(2)	0.1904(3)	0.1296(2)	0.6326(1)
C(3)	0.0248(3)	0.0677(1)	0.6572(1)
C(4)	−0.0532(3)	0.1165(2)	0.7187(1)
C(5)	−0.0937(3)	0.2300(2)	0.7075(1)
C(6)	0.0718(3)	0.2890(2)	0.6809(1)
C(7)	0.2601(3)	0.2999(1)	0.7305(1)
C(8)	0.3622(3)	0.1976(1)	0.7473(1)
C(9)	0.3789(3)	0.1368(2)	0.6824(1)
C(10)	−0.1427(4)	0.0506(2)	0.5995(1)
C(11)	0.4004(3)	0.3748(2)	0.7032(1)
C(12)	0.0682(4)	0.0960(2)	0.7872(1)
C(13)	0.2791(4)	0.1341(2)	0.8009(1)
HO(1)	0.0009	−0.0773	0.6884[a]
HO(2)	0.3324	0.3566	0.8299[a]
Cl	0.7530(2)	0.0355(1)	0.0507(0)
O(3)	0.5884(2)	0.3936(1)	−0.1195(1)
C(21)	0.7074(5)	0.1412(2)	−0.0010(1)
C(22)	0.5367(5)	0.1929(2)	0.0007(1)
C(23)	0.5005(4)	0.2788(2)	−0.0386(1)
C(24)	0.6348(3)	0.3104(2)	−0.0797(1)
C(25)	0.8063(4)	0.2575(2)	−0.0810(1)
C(26)	0.8421(4)	0.1722(2)	−0.0414(1)
HO(3)	0.7123	0.4193	−0.1373[a]

[a] Errors have not been estimated since these hydrogen atom positions were not refined.

Table 3. Interatomic Distances and Standard Deviations (Å) for the Structure (2)·(*p*-Chlorophenol)

O(1)–C(3)	1.455(2)	Cl–C(21)	1.740(3)
O(2)–C(7)	1.456(2)	O(3)–C(24)	1.370(3)
C(1)–C(2)	1.537(3)	C(21)–C(22)	1.363(4)
C(1)–C(6)	1.528(3)	C(22)–C(23)	1.384(4)
C(2)–C(3)	1.534(3)	C(23)–C(24)	1.376(3)
C(2)–C(9)	1.527(3)	C(24)–C(25)	1.375(3)
C(3)–C(4)	1.540(3)	C(25)–C(26)	1.381(3)
C(3)–C(10)	1.532(3)	C(26)–C(21)	1.366(3)
C(4)–C(5)	1.540(3)	O(3)–HO(3)	1.02(3)
C(4)–C(12)	1.525(3)		
C(5)–C(6)	1.530(3)		
C(6)–C(7)	1.527(3)		
C(7)–C(8)	1.543(3)		
C(7)–C(11)	1.532(3)		
C(8)–C(9)	1.537(3)		
C(8)–C(13)	1.525(3)		
C(12)–C(13)	1.526(3)		
O(1)–HO(1)	1.02(3)		
O(2)–HO(2)	1.09(3)		

Table 4. Interatomic Angles and Standard Deviations (deg) for the Structure (2)·(*p*-Chlorophenol)

C(2)–C(1)–C(6)	109.3(2)	Cl–C(21)–C(22)	118.5(2)
C(1)–C(2)–C(3)	109.1(2)	Cl–C(21)–C(26)	120.4(2)
C(1)–C(2)–C(9)	108.0(2)	C(22)–C(21)–C(26)	121.1(2)
C(3)–C(2)–C(9)	115.4(2)	C(21)–C(22)–C(23)	119.3(2)
O(1)–C(3)–C(2)	106.1(2)	C(22)–C(23)–C(24)	120.0(2)
O(1)–C(3)–C(4)	109.6(2)	O(3)–C(24)–C(23)	117.6(2)
O(1)–C(3)–C(10)	107.2(2)	O(3)–C(24)–C(25)	122.3(2)
C(2)–C(3)–C(4)	112.3(2)	C(23)–C(24)–C(25)	120.1(2)
C(2)–C(3)–C(10)	110.9(2)	C(24)–C(25)–C(26)	119.7(2)
C(4)–C(3)–C(10)	110.5(2)	C(21)–C(26)–C(25)	119.8(2)
C(3)–C(4)–C(5)	111.7(2)	C(24)–O(3)–HO(3)	109(2)
C(3)–C(4)–C(12)	115.3(2)		
C(5)–C(4)–C(12)	111.7(2)		
C(4)–C(5)–C(6)	114.8(2)		
C(1)–C(6)–C(5)	107.8(2)		
C(1)–C(6)–C(7)	109.8(2)		
C(5)–C(6)–C(7)	115.6(2)		
O(2)–C(7)–C(6)	106.5(2)		
O(2)–C(7)–C(8)	109.9(2)		
O(2)–C(7)–C(11)	106.3(2)		
C(6)–C(7)–C(8)	112.3(2)		
C(6)–C(7)–C(11)	110.7(2)		
C(8)–C(7)–C(11)	110.9(2)		
C(7)–C(8)–C(9)	111.1(2)		
C(7)–C(8)–C(13)	115.7(2)		
C(9)–C(8)–C(13)	111.9(2)		
C(2)–C(9)–C(8)	115.2(2)		
C(4)–C(12)–C(13)	119.7(2)		
C(8)–C(13)–C(12)	119.6(2)		
C(3)–O(1)–HO(1)	109(1)		
C(7)–O(2)–HO(2)	111(1)		

Table 5. Dimensions Associated with Hydrogen Bonding in the Structure (2)·(*p*-Chlorophenol)

O(1)···O(2)[a]	2.844(2)	HO(1)···O(2)[a]	1.83(2)
O(1)···O(3)[b]	2.691(2)	HO(2)···O(3)[c]	1.97(2)
O(2)···O(3)[c]	3.045(2)	HO(3)···O(1)[e]	1.68(2)
C(3)–O(1)···O(2)[a]	107.0(1)		
C(3)–O(1)···O(3)[b]	121.7(1)		
O(2)[a]···O(1)···O(3)[b]	121.8(1)		
O(1)–HO(1)···O(2)[a]	176(3)		
C(7)–O(2)···O(3)[c]	105.5(1)		
C(7)–O(2)···O(1)[d]	135.6(1)		
O(2)–HO(2)···O(3)[c]	166(3)		
O(3)–HO(3)···O(1)[e]	171(3)		
O(3)[c]···O(2)···O(1)[d]	111.8(1)		
O(2)[e]···O(3)···O(1)[f]	119.8(1)		

[a] $-x, -1/2 + y, 1\,1/2 - z$. [b] $1 - x, -1/2 + y, 1/2 - z$. [c] $x, y, 1 + z$. [d] $-x, 1/2 + y, 1\,1/2 - z$. [e] $x, y, -1 + z$. [f] $1 - x, 1/2 + y, 1/2 - z$.

solids by utilization of crystal engineering concepts and by analogy with the known first structure. These ideas have now been fully substantiated.

A total of 16 diol–phenol combinations have been found by crystallizing the diol from the pure liquid phenol or, alternatively, from a solution of the diol and the phenol in mesitylene (which is too bulky to be incorporated as a guest in the helical inclusion compound). These materials have been fully characterized, and their properties are reported in Table 6. Formation of each diol–phenol compound was detected by microanalysis, IR and ^{1}H NMR spectroscopy, and the XRPD pattern of the solid. The characteristic changes in the IR –O–H group vibrational region (see Figure 2) were especially useful during screening of potential combinations.

The crystal structures of seven of these compounds have been determined by X-ray methods. All of these substances are stoichiometric cocrystals with hydrogen-bonding networks incorporating intimate combinations of both molecular components. Six of these adopt a similar lattice packing arrangement with identical symmetry in space group $P2_1/c$, and (on the basis of X-ray powder diffraction patterns) it is believed that a total of 12 of the 16 compounds belongs to this new family of materials.

Structure of (2)·(*p*-Methoxyphenol). Diol 2 and *p*-methoxyphenol also formed a 1:1 cocrystalline compound, with melting point 80–81 °C. The structure of this material in space group $P2_1/c$ shows a remarkable similarity to the previous cases. The methoxy groups are arranged in a similar manner to the chlorine atoms in the *p*-chlorophenol compounds except that they protrude more into the centers of the long narrow tubes (Figure 10). Furthermore this structure suffers from disorder: a major component (0.78) as shown in Figure 10, and a minor component (0.22) with the orientation of the methoxy group rotated through 180° about the phenol C(21)–C(24) axis and accompanied by a small shift in the ring position, being present. This reflects the loss of the stabilizing influence of the chlorine atoms in this new structure. Despite the greater bulk of the methoxy group compared with the chloro atom of the first two compounds, the closest

Table 6. Summary of Diol–Phenol Cocrystal Combinations[a]

diol	*phenol*	*stoichiometry*	*mp (°C)*	*crystal structure*
1	phenol	1:1	181–182	$P2_1/c$ XRPD
1	*p*-chlorophenol	1:1	105–106	$P2_1/c$ structure
1	*m*-chlorophenol	1:1	117–120	$P2_1/c$ XRPD
1	*o*-chlorophenol	1:1	110–112	$P2_1/c$ XRPD
1	hydroquinone	2:1	189–190	$P2_1/c$ structure
2	*p*-chlorophenol	1:1	104–105	$P2_1/c$ structure
2	*p*-methoxyphenol	1:1	80–81	$P2_1/c$ structure
2	*p*-hydroxythiophenol	1:1	100–101	$P2_1/c$ structure
2	hydroquinone	2:1	160–161	$P2_1/c$ XRPD
2	phloroglucinol	1:1 (+CH_3CN)	175–176	unknown
2	2,6-dihydroxynaphthalene	2:1	178–179	unknown
4	phenol	1:1	91–92	$P2_1/c$ structure
4	*p*-hydroxythiophenol	1:1	82–83	$P2_1/c$ XRPD
4	hydroquinone	2:1	159–160	$P2_1/c$ XRPD
4	2,6-dihydroxynaphthalene	2:1 (+C_6H_6)	145–146	unknown
4	phloroglucinol	2:1	167–168	*Fdd*2 structure

[a] "Structure" designates full X-ray structural determination performed; "XRPD" indicates that the space group is presumed from similarity of the powder pattern with those of known structures. The three combinations with unknown space groups gave material unsuited for single-crystal X-ray structural determination, but with a different powder pattern to the main family of compounds.

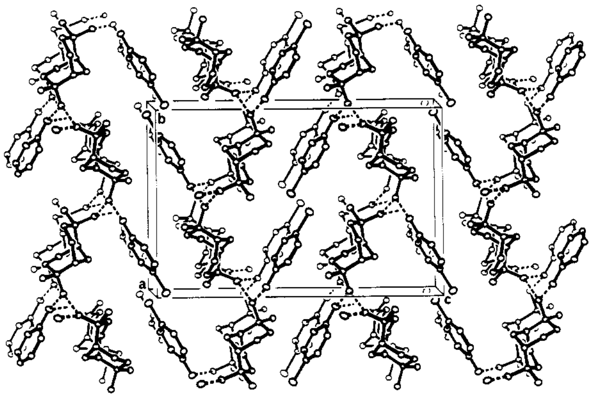

Figure 9. Unit cell of the cocrystalline compound (1)·(*p*-chlorophenol).[9] Hydrogen bonds are shown as dashed lines, and hydrogen atoms are omitted for clarity. The close similarity to the structure shown in Figure 6 should be noted.

approach of two inversion-related methoxy carbon atoms (including both disorder components) is 3.7 Å.

Numerical details of the solution and refinement of (2)·($C_7H_8O_2$) are shown in Table 1. All other crystallographic data are available in the supplementary material.

Structure of (2)·(*p*-Hydroxythiophenol). Diol 2 and *p*-hydroxythiophenol also form a cocrystalline compound, this phenol being chosen since it has two potential hydrogen bonding functional groups. The X-ray structural determination shows that this material is a further example of the family of cocrystalline solids in space group $P2_1/c$ (Figure 11). The general arrangement of the two components in the unit cell is almost indistinguishable from that of (2)·(*p*-chlorophenol) (cf. Figure 6).

It is known that –S–H groups do not usually form hydrogen bonds as effectively as –O–H or –N–H functional groups.[13] However, 4-*p*-mercaptophenyl-2,2,4-trimethylchroman (the mercapto analogue of Dianin's compound) is reported[16,17] to exhibit a $(\text{–S–H})_6$ cycle analogous to the $(\text{–O–H})_6$ cycle of the parent compound.[18]

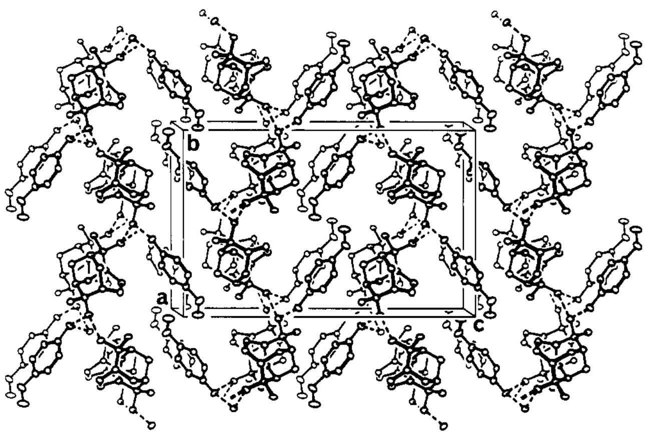

Figure 10. Unit cell of the cocrystalline compound (2)·(*p*-methoxyphenol) showing the major disorder component (0.78). Hydrogen bonds are shown as dashed lines and hydrogen atoms are omitted for clarity.

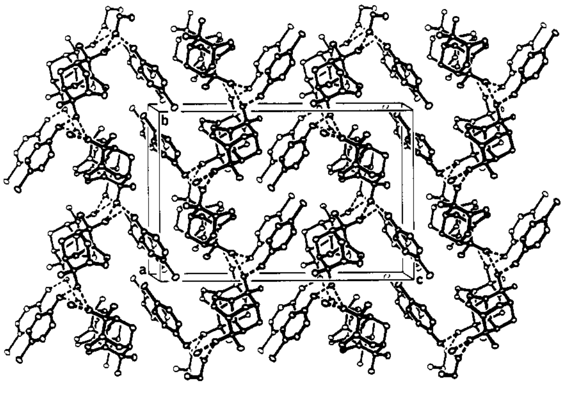

Figure 11. Unit cell of the cocrystalline compound (2)·(*p*-hydroxythiophenol). Hydrogen bonds are shown as dashed lines, and hydrogen atoms are omitted for clarity. The remarkable similarity of this structure to that of (2)·(*p*-chlorophenol) shown in Figure 6 should be noted.

The –S–H stretching vibration is normally observed[19] as a weak signal in the range 2600–2550 cm^{-1} though, in the above case,[16,17] the absorption was noted at 2506 cm^{-1}. The compound (2)·(*p*-hydroxythiophenol) showed very weak peaks at 2720, 2660, and 2590 cm^{-1}. However, closer examination of other diol–phenol compounds discussed in this paper revealed that almost identical weak signals were present and therefore these peaks are almost certainly not due to the thiol group.

Only the hydroxy groups hydrogen bond as part of the spines, with the thiol groups uninvolved. However, the sulfur atoms of the thiol groups are stacked in a similar manner as the chlorine atoms in the previous *p*-chlorophenol structures. Alternate S···S distances are 3.94 and 4.13 Å in this structure. Interaction between the thiol groups is suggested by the material being a yellow solid, with the color vanishing when it is redissolved.

Numerical details of the solution and refinement of (2)·(C_6H_6OS) are shown in Table 1. All other crystallographic data are available in the supplementary material.

---

(16) Hardy, A. D. U.; MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *J. Chem. Soc., Chem. Commun.* **1977**, 292.

(17) Hardy, A. D. U.; MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 729.

(18) MacNicol, D. D. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 2, Chapter 1, pp 1–45.

(19) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed., Holden-Day: San Francisco, 1977.

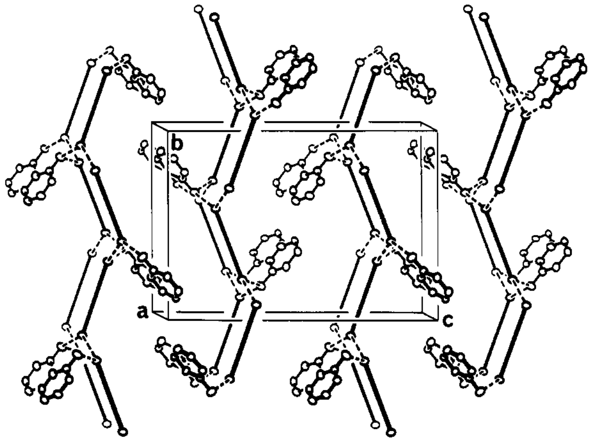

Figure 12. Unit cell of the cocrystalline compound (4)·(phenol). Hydrogen bonds are shown as dashed lines, hydrogen atoms are omitted for clarity, and the diol 4 molecules are shown here simply as solid tie rods linking two oxygen atoms.

Structure of (4)·(Phenol). Diol 4 behaves similarly to 1 and 2. The 1:1 combination of 4 and phenol melts at 91–92 °C and its structure in space group $P2_1/c$ is shown in Figure 12. Due to lack of a para substituent, the aromatic rings move inward toward each other, but at the same time are displaced slightly toward the interior of the long, narrow tubes.

Numerical details of the solution and refinement of (4)·(C_6H_6O) are shown in Table 1. All other crystallographic data are available in the supplementary material.

Structure of $(\mathbf{1})_2$·(Hydroquinone). We anticipated that use of hydroquinone as the phenolic partner would also result in formation of a cocrystalline substance but where two of the adjacent monohydric phenol units would be replaced by one hydroquinone molecule. A three-dimensional hydrogen-bonded lattice would thus result. To test this crystal engineering concept, crystals were grown from a solution of diol 1 and hydroquinone in mesitylene.

Microanalysis confirmed that this material had the anticipated (different) stoichiometry $(1)_2$·(hydroquinone). This solid also had a considerably higher melting point (189–190 °C) than the previous compounds. The crystal structure fully confirmed our expectations, revealing that the solid was a cocrystalline substance adopting the same lattice packing and symmetry (space group $P2_1/c$) as the previous five compounds (Figure 13). The hydroquinone units now directly link the enantiomeric helical spines producing an achiral hydrogen-bonded network lattice. The long narrow tubes along *a* are now fully hydrogen bonded. These tubes have a cross section resembling a pseudomacrocycle assembled from four molecules of 1 and two of hydroquinone. There is a concomitant major shortening of the *c* dimension [15.974(1) Å, compared with 19.286(4) Å for (1)·(*p*-chlorophenol)] and contraction of the unit cell volume [1370(2) Å^3, compared with 1690.1(4) Å^3].

Numerical details of the solution and refinement of $(1)_2$·($C_6H_6O_2$) are shown in Table 1. All other crystallographic data are available in the supplementary material.

Structure of $(\mathbf{4})_2$·(Phloroglucinol). It was anticipated that use of the trihydric phenol phloroglucinol (1,3,5-trihydroxybenzene) would force any resulting cocrystalline product to have a different lattice arrangement to the previous examples and this proved to be the case.

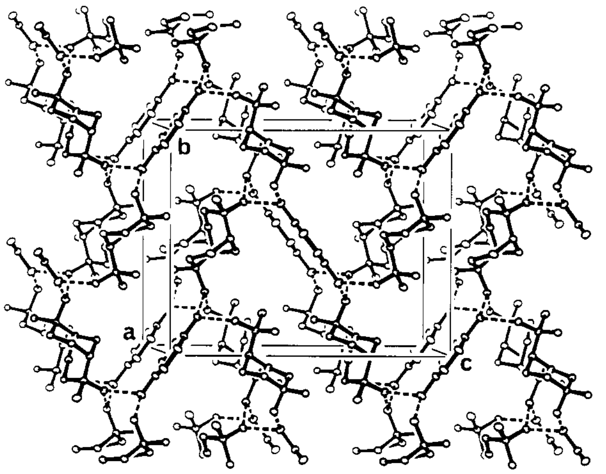

Figure 13. Unit cell of the cocrystalline compound $(1)_2$·(hydroquinone). Hydrogen bonds are shown as dashed lines, and hydrogen atoms are omitted for clarity. A three-dimensional hydrogen bonding lattice is now present since the hydroquinone molecules now directly link the enantiomeric layers.[9] The concomitant shortening of the *c* dimension is quite apparent, but the same lattice packing and symmetry is present.

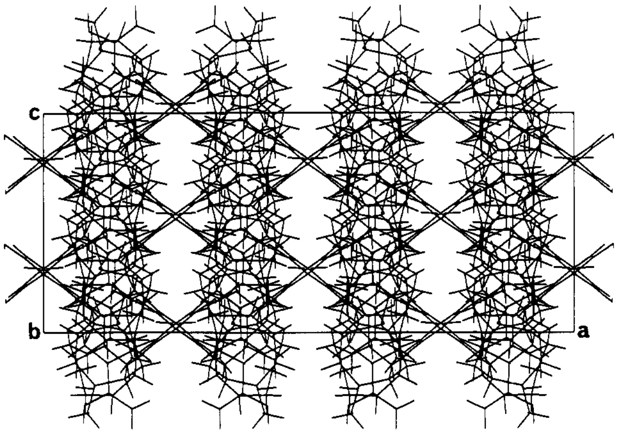

Figure 14. Unit cell of the cocrystalline compound $(4)_2$·(phloroglucinol) viewed down the *b* axis, showing the molecular frameworks only and with hydrogen atoms included. Four vertical parallel layers of diols are present, linked by bridging phloroglucinol molecules.

The compound $(4)_2$·(phloroglucinol) crystallizes in space group *Fdd*2. The asymmetric unit consists of two independent diol molecules (**4A** and **4B**) and one molecule of phloroglucinol (**P**). There are distinct layers in the crystal, perpendicular to *a*. In each unit cell there are four layers composed of diol molecules. Wedged in between these layers are the phloroglucinol molecules. There are two distinct orientations of phloroglucinol molecules making an angle of 74.2° with each other, as shown in Figure 14 which is a view down the long *b* axis. In Figure 15, a view down the *c* axis, the layers run across the unit cell.

There is a complex network of hydrogen bonding between the three components of the asymmetric unit. There are seven independent hydroxy groups and each takes part in two hydrogen bonds, one as donor and one as acceptor (Table 10). Each phloroglucinol molecule takes part in two four-membered hydrogen bonded structures (Figure 16), seen commonly by us in previously reported diol structures.[20]

Each cycle is made up of **4A---P---4B--P** with O(2)A, O(2)B, O(1)C, and O(2)C being the hydroxy oxygen atoms involved. These cycles lie on the surface of the diol layer.

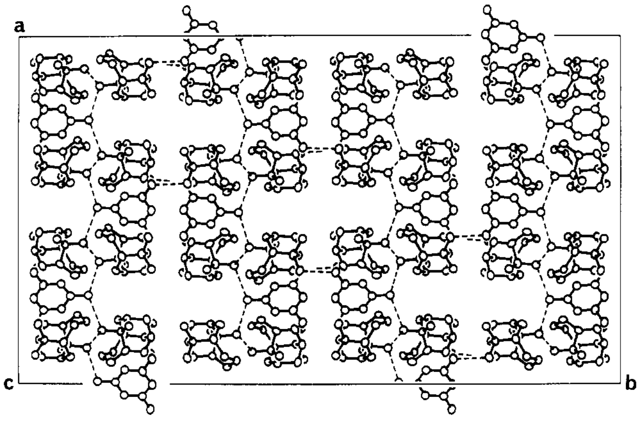

Figure 15. Unit cell of the cocrystalline compound $(4)_2$·(phloroglucinol) viewed down the *c* axis. Hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. In this view the layers of diol molecules run horizontally across the cell.

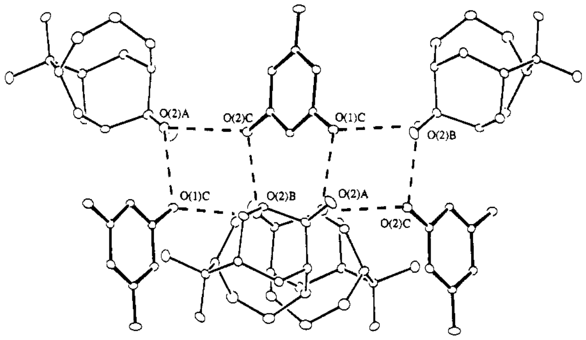

Figure 16. Arrangement of four-membered hydrogen bonded cycles $(\text{-O-H})_4$ present between molecules of diol and phloroglucinol in $(4)_2$·(phloroglucinol). Hydrogen atoms are omitted for clarity and hydrogen bonds shown as dashed lines.

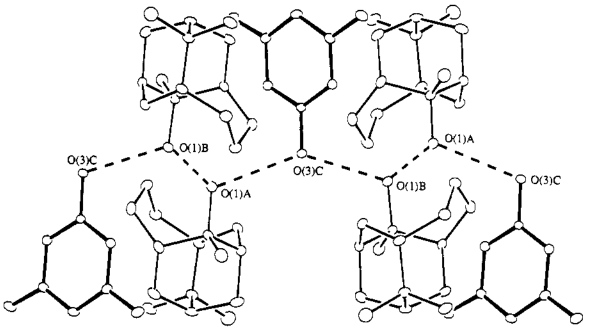

Figure 17. Arrangement in a hydrogen-bonded chain present between molecules of diol and phloroglucinol in $(4)_2$·(phloroglucinol). Hydrogen atoms are omitted for clarity and hydrogen bonds shown as dashed lines.

Linking layers and running through the crystal in the direction of the *ac* diagonal is a continuous chain of hydrogen bonding, where each phloroglucinol molecule once again hydrogen bonds to one **4A** molecule and one **4B** molecule: ---**4A**---**4B**---**P**---**4A**---**4B**---**P**---. The hydroxy oxygen atoms O(1)A, O(1)B and O(3)C take place in this chain (Figure 17).

The crystallographic numbering system employed is shown in Figure 18, and numerical details of the solution and refinement of the structure $(4)_2$·$(C_6H_6O_3)$ are shown in Table 1. Atomic positional parameters for the non-C–H atoms are listed in Table 7; bond lengths and angles are given in Tables 8 and 9. Dimensions associated with the hydrogen bonding are presented in Table 10.

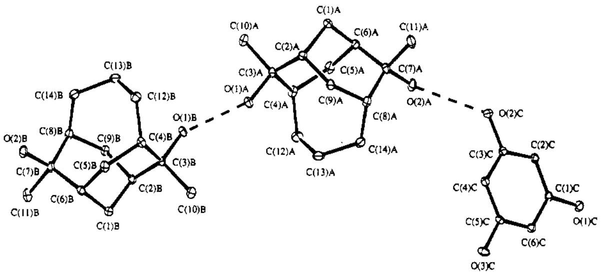

Figure 18. Crystallographic numbering system used for the two independent molecules (**4A** and **4B**) of the diol and phloroglucinol (suffix C) in the cocrystalline compound $(4)_2$·(phloroglucinol). Hydrogen atoms are omitted for clarity, and hydrogen bonds represented as dashed lines separating oxygen atoms.

Table 7. Positional Parameters (with Standard Deviations) for the Non-Hydrogen Atoms of the Structure $(4)_2$·(Phloroglucinol)[a]

	x/a	*y/b*	*z/c*
O(1)A	0.4059(1)	0.1099(0)	0.2446
O(2)A	0.3367(1)	0.0295(1)	0.6227(4)
C(1)A	0.4365(1)	0.0347(1)	0.3765(4)
C(2)A	0.4400(1)	0.0685(1)	0.3616(4)
C(3)A	0.4027(1)	0.0781(1)	0.2596(4)
C(4)A	0.3462(1)	0.0700(1)	0.2889(4)
C(5)A	0.3416(1)	0.0393(1)	0.3519(4)
C(6)A	0.3852(1)	0.0280(1)	0.4369(4)
C(7)A	0.3852(1)	0.0390(1)	0.5714(4)
C(8)A	0.3922(1)	0.0730(1)	0.5797(4)
C(9)A	0.4359(1)	0.0831(1)	0.4917(4)
C(10)A	0.4179(1)	0.0650(1)	0.1331(4)
C(11)A	0.4269(2)	0.0239(1)	0.6474(5)
C(12)A	0.3137(1)	0.0949(1)	0.3457(5)
C(13)A	0.3313(1)	0.1101(1)	0.4625(5)
C(14)A	0.3420(1)	0.0912(1)	0.5754(4)
O(1)B	0.6053(1)	0.1147(0)	1.2907(3)
O(2)B	0.6735(1)	0.0325(1)	0.9184(3)
C(1)B	0.5771(1)	0.0392(1)	0.1736(4)
C(2)B	0.5740(1)	0.0724(1)	1.1854(4)
C(3)B	0.6116(1)	0.0831(1)	1.2850(4)
C(4)B	0.6679(1)	0.0744(1)	1.2550(4)
C(5)B	0.6723(1)	0.0434(1)	1.1913(4)
C(6)B	0.6281(1)	0.0319(1)	1.1108(4)
C(7)B	0.6265(1)	0.0426(1)	0.9745(4)
C(8)B	0.6197(1)	0.0764(1)	0.9648(4)
C(9)B	0.5773(1)	0.0869(1)	1.0556(4)
C(10)B	0.5966(1)	0.0709(1)	1.4138(4)
C(11)B	0.5826(2)	0.0275(1)	0.9037(5)
C(12)B	0.7003(1)	0.0990(1)	1.1949(5)
C(13)B	0.6820(1)	0.1144(1)	1.0778(5)
C(14)B	0.6707(1)	0.0938(1)	0.9677(4)
O(1)C	0.1755(1)	0.0295(0)	0.1534(3)
O(2)C	0.3228(1)	0.0270(1)	−0.1148(3)
O(3)C	0.2570(1)	0.1177(0)	0.0415(3)
C(1)C	0.2141(1)	0.0423(1)	0.0891(4)
C(2)C	0.2486(1)	0.0266(0)	0.0188(4)
C(3)C	0.2869(1)	0.0419(1)	−0.0442(4)
C(4)C	0.2904(1)	0.0721(1)	−0.0402(4)
C(5)C	0.2554(1)	0.0875(0)	0.0324(4)
C(6)C	0.2173(1)	0.0733(1)	0.0974(4)

[a] The suffixes A and B indicate the two independent molecules of 4 in the structure, while C indicates atoms of the phloroglucinol molecule.

Characteristics of the Other Diol–Phenol Compounds. A further six diol–phenol combinations were prepared and characterized (Table 6 and Experimental Section) which are believed also to crystallize in space group $P2_1/c$ on the basis of the similarity of their XRPD patterns to the previous examples. These compounds were

---

(20) Hawkins, S. C.; Scudder, M. L.; Craig, D. C.; Rae, A. D.; Abdul Raof, R. B.; Bishop, R.; Dance, I. G. *J. Chem. Soc., Perkin Trans. 2* **1990**, 855.

Table 8. Interatomic Distances and Standard Deviations (Å) for the Structure $(4)_2$·(Phloroglucinol)[a]

	diol A	diol B
O(1)–C(3)	1.454(3)	1.441(3)
O(2)–C(7)	1.447(4)	1.443(4)
C(1)–C(2)	1.541(4)	1.513(4)
C(1)–C(6)	1.520(5)	1.531(4)
C(2)–C(3)	1.528(4)	1.530(4)
C(2)–C(9)	1.548(4)	1.542(4)
C(3)–C(4)	1.554(4)	1.559(4)
C(3)–C(10)	1.533(5)	1.539(5)
C(4)–C(5)	1.552(4)	1.564(4)
C(4)–C(12)	1.539(5)	1.540(4)
C(5)–C(6)	1.546(5)	1.533(5)
C(6)–C(7)	1.527(5)	1.541(5)
C(7)–C(8)	1.553(4)	1.543(4)
C(7)–C(11)	1.522(5)	1.538(5)
C(8)–C(9)	1.551(4)	1.551(4)
C(8)–C(14)	1.550(5)	1.551(5)
C(12)–C(13)	1.503(6)	1.515(5)
C(13)–C(14)	1.509(6)	1.534(5)
O(1)–HO(1)	0.93(4)	1.00(5)
O(2)–HO(2)	0.90(5)	0.85(6)
O(1)C–C(1)C	1.353(3)	
O(2)C–C(3)C	1.383(3)	
O(3)C–C(5)C	1.371(2)	
C(1)C–C(2)C	1.376(4)	
C(2)C–C(3)C	1.393(4)	
C(3)C–C(4)C	1.371(4)	
C(4)C–C(5)C	1.389(4)	
C(5)C–C(6)C	1.376(4)	
C(6)C–C(1)C	1.409(3)	
O(1)C–HO(1)C	0.76(5)	
O(2)C–HO(2)C	0.86(4)	
O(3)C–HO(3)C	0.81(4)	

[a] The designators A and B indicate the two independent molecules of 4 in the structure, while the suffix C indicates atoms of the phoroglucinol molecule.

Table 9. Interatomic Angles and Standard Deviations (deg) for the Structure $(4)_2$·(Phloroglucinol)

	diol A	diol B
C(2)–C(1)–C(6)	107.3(2)	107.3(2)
C(1)–C(2)–C(3)	108.6(3)	109.9(2)
C(1)–C(2)–C(9)	109.1(2)	110.2(2)
C(3)–C(2)–C(9)	118.6(2)	117.3(2)
O(1)–C(3)–C(2)	109.1(2)	105.8(2)
O(1)–C(3)–C(4)	108.2(2)	111.6(2)
O(1)–C(3)–C(10)	105.7(3)	107.0(2)
C(2)–C(3)–C(4)	113.1(2)	112.4(2)
C(2)–C(3)–C(10)	111.0(3)	110.4(2)
C(4)–C(3)–C(10)	109.4(3)	109.4(2)
C(3)–C(4)–C(5)	112.0(3)	112.8(2)
C(3)–C(4)–C(12)	115.6(2)	114.9(2)
C(5)–C(4)–C(12)	116.2(3)	115.2(2)
C(4)–C(5)–C(6)	119.9(2)	119.7(2)
C(1)–C(6)–C(5)	109.3(3)	109.6(3)
C(1)–C(6)–C(7)	109.7(3)	109.0(3)
C(5)–C(6)–C(7)	116.6(3)	116.6(3)
O(2)–C(7)–C(6)	105.2(3)	105.7(3)
O(2)–C(7)–C(8)	112.0(3)	112.6(3)
O(2)–C(7)–C(11)	106.9(3)	106.7(3)
C(6)–C(7)–C(8)	112.2(3)	112.3(2)
C(6)–C(7)–C(11)	111.0(3)	110.4(3)
C(8)–C(7)–C(11)	109.3(3)	108.9(3)
C(7)–C(8)–C(9)	110.2(3)	110.2(3)
C(7)–C(8)–C(14)	115.4(2)	113.8(2)
C(9)–C(8)–C(14)	116.5(3)	116.4(3)
C(2)–C(9)–C(8)	118.2(2)	118.4(2)
C(4)–C(12)–C(13)	119.8(3)	120.6(3)
C(12)–C(13)–C(14)	117.7(3)	114.7(3)
C(8)–C(14)–C(13)	118.9(3)	119.4(3)
C(3)–O(1)–HO(1)	108(2)	104(2)
C(7)–O(2)–HO(2)	113(3)	112(3)
O(1)C–C(1)C–C(2)C	123.0(2)	
O(1)C–C(1)C–C(6)C	116.1(3)	
C(2)C–C(1)C–C(6)C	120.9(2)	
C(1)C–C(2)C–C(3)C	118.5(2)	
O(2)C–C(3)C–C(2)C	120.6(2)	
O(2)C–C(3)C–C(4)C	117.3(3)	
C(2)C–C(3)C–C(4)C	122.1(3)	
C(3)C–C(4)C–C(5)C	118.4(2)	
O(3)C–C(5)C–C(4)C	121.5(3)	
O(3)C–C(5)C–C(6)C	116.9(3)	
C(4)C–C(5)C–C(6)C	121.6(2)	
C(1)C–C(6)C–C(5)C	118.5(2)	
C(1)C–O(1)C–HO(1)C	107(4)	
C(3)C–O(2)C–HO(2)C	111(3)	
C(5)C–O(3)C–HO(3)C	103(3)	

(1)·(phenol), (1)·(*m*-chlorophenol), (1)·(*o*-chlorophenol), $(2)_2$·(hydroquinone), (4)·(*p*-hydroxythiophenol), and $(4)_2$·(hydroquinone).

On the basis of the crystal structures of the above family of materials we anticipated that if a dihydric phenolic component were used which was longer than hydroquinone then this might lead to enlargement of the narrow tubes and production of a more open hydrogen bonded network which might have sufficient void space to enclose solvent molecules thus producing a three-component solid. 2,6-Dihydroxynaphthalene was tested as the phenolic component and the compounds $(2)_2$·(2,6-dihydroxynaphthalene), and $(4)_2$·(2,6-dihydroxynaphthalene)·(benzene) were obtained.

An additional compound, (2)·(phloroglucinol)·$(\text{acetonitrile})_n$ [where n = ca. 0.33 from ^{1}H NMR data], was also produced using the trihydric phenol phloroglucinol.

All three cocrystalline compounds were unstable and X-ray crystal structures could not be determined. However, these further three cocrystalline compounds have different powder diffraction patterns to the main family of compounds. Therefore, although three-component solids were formed, these probably have different structural arrangements from the main family of substances.

Unsuitable Diol–Phenol Combinations. No cocrystals were formed with the following: diol **1** using *p*-methoxyphenol, catechol, resorcinol, phloroglucinol, 2,6-dihydroxynaphthalene, 2,2-bis(*p*-hydroxyphenyl)propane,[21] β-naphthol, or Dianin's compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman);[18] diol **2** using catechol, resorcinol, *p*-phenylphenol, or 2,2-bis(*p*-hydroxyphenyl)propane; 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*anti*-2,*anti*-7-diol[11] **3** with a variety of phenols including *p*-chlorophenol or hydroquinone; and diol **4** using *p*-methoxyphenol or *p*-chlorothiophenol.

It is particularly noteworthy that no evidence of helical tubulate inclusion compounds was obtained for any of these cases. In other words the only favorable *binary* materials are the cocrystalline solids.

Discussion

It is already known that a number of simple phenols suffer surprising problems in forming simple, close-packed lattices. Such compounds often form cocrystalline materials of various types[18] and show polymorphic behavior.[22] In the case of *p*-chlorophenol, inclusion compounds are

---

[21] Toda, F. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: London, 1991; Vol. 4, pp 140–141.

[22] Perrin, R.; Lamartine, R.; Perrin, M.; Thozet, A. In *Organic Solid State Chemistry*, Desiraju, G. R., Ed.; *Studies in Organic Chemistry*; *32*; Elsevier; Amsterdam, 1987; Chapter 8, pp 271–329.

Table 10. Dimensions Associated with Hydrogen Bonding in the Structure (4)$_2$·(Phloroglucinol)[m]

O(1)A···O(1)B[a]	2.803(2)	HO(1)A···O(3)C[b]	1.96(2)
O(1)A···O(3)C[b]	2.875(3)	HO(2)A···O(2)C[d]	1.98(2)
O(2)A···O(1)C[c]	2.715(3)	HO(1)B···O(1)A[e]	1.82(2)
O(2)A···O(2)C[d]	2.842(4)	HO(2)B···O(1)C[g]	2.02(2)
O(1)B···O(3)C[e]	2.691(3)	HO(1)C···O(2)A[h]	1.98(2)
O(2)B···O(2)C[f]	2.725(3)	HO(2)C···O(2)B[j]	1.86(2)
O(2)B···O(1)C[g]	2.847(4)	HO(3)C···O(1)B[a]	1.89(2)
C(3)A–O(1)A···O(1)B[a]	117.9(2)		
C(3)A–O(1)A···O(3)C[b]	112.5(2)		
O(1)B[a]···O(1)A···O(3)C[b]	115.2(2)		
O(1)A–HO(1)A···O(3)C[b]	170(4)		
C(7)A–O(2)A···O(1)C[c]	116.1(2)		
C(7)A–O(2)A···O(2)C[d]	120.0(2)		
O(1)C[c]···O(2)A···O(2)C[d]	79.9(2)		
O(2)A–HO(2)A···O(2)C[d]	166(4)		
C(3)B–O(1)B···O(3)C[e]	113.8(1)		
C(3)B–O(1)B···O(1)A[e]	112.8(2)		
O(3)C[e]···O(1)B···O(1)A[e]	109.0(2)		
O(1)B–HO(1)B···O(1)A[e]	166(4)		
C(7)B–O(2)B···O(2)C[f]	113.5(2)		
C(7)B–O(2)B···O(1)C[g]	116.6(2)		
O(2)C[f]···O(2)B···O(1)C[g]	79.7(2)		
O(2)B–HO(2)B···O(1)C[g]	155(4)		
C(1)C–O(1)C···O(2)A[h]	116.7(2)		
C(1)C–O(1)C···O(2)B[i]	120.1(2)		
O(2)B[i]···O(1)C···O(2)A[h]	99.7(2)		
O(1)C–HO(1)C···O(2)A[h]	165(5)		
C(3)C–O(2)C···O(2)B[j]	115.9(2)		
C(3)C–O(2)C···O(1)A[k]	127.5(2)		
O(2)A[k]···O(2)C···O(2)B[j]	99.5(2)		
O(2)C–HO(2)C···O(2)B[j]	173(5)		
C(5)C–O(3)C···O(1)B[a]	109.0(1)		
C(5)C–O(3)C···O(1)A[l]	108.2(1)		
O(1)A[l]···O(3)C···O(1)B[a]	140.5(2)		
O(3)C–HO(3)C···O(1)B[a]	169(4)		

[a] $-\frac{1}{4} + x, \frac{1}{4} - y, -1\frac{1}{4} + z$. [b] $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$. [c] $\frac{1}{2} - x, -y, \frac{1}{2} + z$. [d] $x, y, 1 + z$. [e] $\frac{1}{4} + x, \frac{1}{4} - y, 1\frac{1}{4} + z$. [f] $1 - x, -y, 1 + z$. [g] $\frac{1}{2} + x, y, \frac{1}{2} + z$. [h] $\frac{1}{2} - x, -y, -\frac{1}{2} + z$. [i] $-\frac{1}{2} + x, y, -\frac{1}{2} + z$. [j] $1 - x, -y, -1 + z$. [k] $x, y, -1 + z$. [l] $-\frac{1}{4} + x, \frac{1}{4} - y, -\frac{1}{4} + z$. [m] The suffixes A and B indicate the two independent molecules of **4** in the structure, while C indicates atoms of the phloroglucinol molecule.

formed with noble gases and low molecular weight hydrocarbons.[23,24] Molecular 2:1 and 1:1 complexes are also produced with *p*-benzoquinone.[25]

Many of the phenols used here are liquids or low-melting solids at room temperature and crystal structure data are unavailable. However, pure *p*-chlorophenol crystallizes in two polymorphic structures[26] both of which are in space group $P2_1/c$. The stable α-form[27-29] has a structure involving hydrogen-bonded chains along the *c* axis, whereas the metastable β-form has the *p*-chlorophenols linked as cyclic hydrogen-bonded tetramers.[30] We have frequently encountered this latter type of arrangement in the crystal structures of alicyclic diols which are close in molecular structure to the helical tubuland diols.[20] *p*-Chlorophenol can adopt a further crystal arrangement which is not stable.[31] This γ-form is in space group $C2/c$ and contains the 3-fold hydrogen-bonded spine motif discussed earlier in this paper.

Another simple phenol with considerable packing difficulties is hydroquinone itself. It forms both inclusion compounds and different crystal modifications,[18] and its most stable form at room temperature (α-hydroquinone) contains 54 molecules per unit cell.[32] For such a small and highly symmetrical molecule this complexity is quite astonishing if only close-packing arguments are considered.[33]

As revealed in this work, a further manner in which *p*-chlorophenol, hydroquinone, and other simple phenols, can solve their packing difficulties is to cocrystallize with one of the helical tubuland diols **1**, **2**, or **4**.

In contrast to this behavior we have been unable to obtain cocrystalline materials using diol **3**. This latter result is easily rationalized by considering the efficiency with which the canals of crystalline **3** are largely filled by its own structure (Figure 1). Consequently the melting point of **3** (245–247 °C) is 100 °C higher than its isomeric double epimer **2** (146–148 °C).[11] It is therefore only those helical tubuland diols which pack poorly by themselves and crystallize with a substantial canal cross section[34] which are expected to form mixed crystals with simple phenols.

Other more complex phenols also tend to produce unusual crystal lattices.[18] However, in this context, there is a size restriction because the phenolic material must occupy one eclipsed arm of the helical hydrogen-bonded spine without causing steric problems. This is probably self-evident from consideration of Figure 5; however, some rather qualitative evidence in its support is available from comparing the melting points of (**1**)·(phenol) (181–182 °C) and (**4**)·(phenol) (91–92 °C) or (**2**)·(*p*-hydroxythiophenol) (100–101 °C) and (**4**)·(*p*-hydroxythiophenol) (82–83 °C), where the increase in diol size causes a concomitant decrease in value.

In this context it should also be noted that the compounds (**1**)·(*o*-chlorophenol) and (**1**)·(*m*-chlorophenol) were considerably less stable than the structure involving the para isomer. Although some stabilization by means of chlorine interactions may still be possible for these two isomers, it is likely that steric factors are the main cause of their instability relative to *p*-chlorophenol. Phenolic candidates such as 2,2-bis(*p*-hydroxyphenyl)propane[21,35] or Dianin's compound[18] are simply too bulky to occupy the helical spine arrangement.

Conclusions

A new family of helical tubuland diol–phenol cocrystaline solids has been discovered and the crystal engineering factors involved in its construction have been investigated. In these materials the trigonal helical hydrogen-bonded spine, which is the structural core of the helical tubuland diol lattice, is retained. However, molecules of the phenol have infiltrated one of its three arms by replacing an eclipsed stack of diol molecules. Consequently, a centrosymmetric and achiral lattice results in space group $P2_1/c$.

---

(23) Nikitin, B. A.; Ioffe, E. M. *Dokl. Akad. Nauk SSSR* **1952**, *85*, 809. [*Chem. Abstr.* **1953**, *47*, 394a].

(24) Barrer, R. M.; Shanson, V. H. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2348.

(25) Shipley, G. G.; Wallwork, S. C. *Acta Crystallogr.* **1967**, *22*, 585, 593.

(26) Perrin, M.; Michel, P.; Perrin, R. *J. Chim. Phys.* **1975**, *72*, 851.

(27) Wu, V. Y. *Z. Kristallogr.* **1968**, *126*, 66.

(28) Perrin, M.; Michel, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 253.

(29) Shiono, R.; Wu, V. Y. *Acta Crystallogr., Sect. A* **1972**, *28*, S17.

(30) Perrin, M.; Michel, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 258.

(31) Lamartine, R.; Decoret, C.; Royer, J.; Vicens, J. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 197.

(32) Wallwork, S. C.; Powell, H. M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 641.

(33) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

(34) Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1012.

(35) Goldberg, I.; Stein, Z.; Tanaka, K.; Toda, F. *J. Inclus. Phenom.* **1991**, *10*, 97.

Not all helical tubuland diols or all phenols behave in this manner, and the reasons for this have been explored. There is a delicate balance of factors operating in the crystal packing. The position of the substituent groups of the phenol plays an active role in stabilizing the crystal structure and likewise weak attractive forces between these groups are an important factor.

We predict that other helical tubuland diols not yet tested, but which are known to have substantial canal cross sections,[36] will produce similar cocrystalline combinations with phenols. The most likely phenolic compounds will be those simple phenols which are known to have the packing problems discussed earlier.[18,22]

In the longer term, the increased understanding of hydrogen bonding and weak intermolecular forces pioneered by Etter[37] is likely to lead chemists into exciting new and unconventional fields of organic synthesis.

Experimental Section

Diols 1–4 were prepared as described previously.[11] ^{1}H NMR spectra were recorded at 300 MHz using a Bruker AC300F instrument. Spectra of the cocrystals showed a superposition of the diol and phenol signals, and peaks are reported as chemical shifts (δ) relative to $SiMe_4$. IR spectra were recorded using a Hitachi 260-10 instrument. Melting points were measured on a Kofler instrument and are uncorrected. X-ray powder diffraction (XRPD) patterns were recorded on a Siemens D500 X-ray diffractometer and are quoted as 2θ degrees (relative intensity). Microanalyses were performed at UNSW by Dr. H. P. Pham.

Synthesis. (1)·(Phenol). 2,6-Dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol (1, 0.05 g, 0.27 mmol) was slowly dissolved upon warming in a mixture of phenol and mesitylene (3 mL). The platelike crystals which had formed overnight were filtered and dried, mp 181–182 °C. Anal. Calcd for $(C_{11}H_{20}O_2)\cdot(C_6H_6O)$: C, 70.34; H, 9.41. Found: C, 70.10; H, 9.46. IR (paraffin mull) 3420 (s), 3280 (s), 3050 (m), 1600 (s), 1250 (s), 1110 (m), 1090 (m), 1040 (m), 1000 (m), 930 (w), 900 (m), 750 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.26 (t, 2H), 6.97 (t, 1H), 6.88 (d, 2H), plus diol signals. XRPD 9.5 (100), 14.2 (12), 15.9 (53), 16.7 (51), 17.0 (34), 18.4 (8), 20.3 (94), 24.8 (26), 32.1 (12). Single crystals suitable for X-ray structural determination could not be obtained.

(1)·(*p*-Chlorophenol). Diol 1 (0.05 g, 0.27 mmol) and *p*-chlorophenol (0.07 g, 0.54 mmol) were dissolved with warming in mesitylene (5 mL). The resulting solution was left at room temperature overnight, then the needlelike crystals which had formed were filtered and air dried, mp 105–106 °C. Anal. Calcd for $(C_{11}H_{20}O_2)\cdot(C_6H_5ClO)$: C, 65.27; H, 8.06. Found: C, 65.62; H, 7.80. IR (paraffin mull) 3425 (m), 3270 (m), 1585 (m), 1490 (m), 1260 (s), 1245 (s), 1160 (w), 1100 (m), 1080 (m), 1030 (m), 985 (w), 895 (m), 820 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.20 (d, 2H), 6.75 (d, 2H), plus diol signals. XRPD 9.2 (20), 15.4 (57), 16.4 (100), 19.8 (54), 21.4 (12), 24.3 (100), 25.9 (10), 28.4 (17), 31.2 (19).

(1)·(*m*-Chlorophenol). Diol 1 (0.050 g, 0.27 mmol) was first dissolved upon warming in mesitylene (2 mL), and then *m*-chlorophenol (1 mL) was added and mixed well. The needlelike crystals which had formed overnight were filtered and dried, mp 117–118 °C. Anal. Calcd for $C_{11}H_{20}O_2)\cdot(C_6H_5OCl)$ C, 65.27; H, 8.06. Found: C, 65.30; H, 8.15. IR (paraffin mull) 3450 (s), 3125 (m), 3075 (m), 1580 (s), 1240 (m), 1100 (w), 1080 (w), 1030 (m), 990 (m), 920 (w), 880 (s), 820 (w), 760 (m), 680 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.28 (t, 2H), 6.93–6.80 (m, 2H), plus signals of diol. XRPD 8.7 (26), 11.5 (9), 15.2 (68), 17.0 (17), 17.4 (13), 19.1 (27), 20.0 (47), 23.2 (23), 24.3 (11), 26.4 (14), 26.7 (19), 27.6 (38), 30.6 (15). Crystals of this compound decompose slowly on standing.

(1)·(*o*-Chlorophenol). Diol 1 (0.50 g, 0.27 mmol) was dissolved on warming in *o*-chlorophenol (3 mL, freshly redistilled). The resulting solution was allowed to cool to room temperature and then stored at 0 °C. The unstable needlelike crystals which formed overnight were filtered and dried, mp 110–112 °C. Anal. Calcd for $(C_{11}H_{20}O_2)\cdot(C_6H_5OCl)$: C, 65.27; H, 8.06. Found: C, 66.00; H, 8.23. IR (paraffin mull) 3500 (m), 3300 (s), 1600 (m), 1300 (m), 1220 (m), 1105 (m), 1040 (w), 1030 (w), 1000 (w), 930 (w), 900 (s), 840 (w), 750 (s), 680 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.42 (d, 2H), 7.25 (m, 1H), 7.05 (d, 1H), 6.86 (dd, 1H), and peaks due to the diol. XRPD 8.5 (24), 9.3 (33), 14.2 (30), 15.7 (52), 16.0 (33), 17.2 (30), 20.1 (100), 23.4 (12), 24.4 (14), 25.2 (13), 25.6 (13), 27.6 (10), 28.6 (12). Crystals of this compound decompose slowly on standing, though less rapidly than for the case of the meta isomer.

(1)$_2$·(Hydroquinone). Diol 1 (0.05 g, 0.27 mmol) and hydroquinone (0.06 g, 0.54 mmol) were slowly dissolved under heating in mesitylene (3 mL). The prismatic crystals which had formed after 3 weeks at room temperature were filtered and dried, mp 189–190 °C. Anal. Calcd for $(C_{11}H_{20}O_2)_2\cdot(C_6H_6O_2)$: C, 70.26; H, 9.69. Found: C, 70.37; H, 9.56. IR (paraffin mull) 3400 (s), 3375 (s), 3125 (s), 1510 (m), 1340 (m), 1240 (s), 1110 (w), 1030 (m), 990 (w), 900 (m), 820 (m), 760 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 8.71 (s, 2H), 6.65 (s, 4H) and signals of the diol. XRPD 10.5 (12), 10.8 (13), 11.6 (13), 13.6 (14), 14.1 (25), 14.2 (24), 14.6 (14), 16.4 (95), 17.2 (91), 17.8 (16), 18.3 (22), 19.2 (70), 19.9 (22), 23.6 (93), 25.6 (14), 26.6 (12), 27.7 (19), 29.5 (12), 34.9 (11).

(2)·(*p*-Chlorophenol). 2,7-Dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol (2, 0.05 g, 0.238 mmol) was added to a solution of *p*-chlorophenol (0.06 g, 0.475 mmol) and mesitylene (4 mL) and warmed until solution was complete. The crystals which had formed after standing at room temperature for 2 days were filtered and dried, mp 104–105 °C. Anal. Calcd for $(C_{13}H_{22}O_2)\cdot(C_6H_5OCl)$: C, 67.34; H, 8.03. Found: C, 67.36; H, 7.90. IR (paraffin mull) 3450 (s), 3300 (s), 3110 (m), 3070 (m), 1580 (s), 1380 (m), 1360 (m), 1240 (s), 1230 (m), 1100 (m), 1080 (m), 1030 (m), 1000 (m), 930 (m), 890 (s), 880 (m), 850 (w), 760 (m), 680 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.18 (d, 2H), 6.78 (d, 2H), and signals of the diol. XRPD 8.8 (18), 9.0 (20), 14.8 (24), 15.0 (52), 16.3 (75), 16.8 (40), 18.1 (13), 19.2 (22), 19.6 (14), 21.0 (19), 21.6 (24), 24.1 (12), 27.2 (19), 28.1 (15).

(2)·(*p*-Methoxyphenol). Diol 2 (0.05 g, 0.24 mmol) was dissolved on warming with a solution containing *p*-methoxyphenol (0.85 g, 0.70 mmol) and mesitylene (3 mL). The prismatic crystals which had formed after standing overnight at 0 °C were filtered and dried, mp 80–81 °C. Anal. Calcd for $(C_{13}H_{22}O_2)\cdot(C_7H_8O_2)$: C, 71.82; H, 9.04. Found: C, 72.00; H, 9.25. IR (paraffin mull) 3450 (w), 3350 (m), 3150 (m), 1510 (s), 1310 (w), 1240 (s), 1120 (m), 1100 (m), 1040 (m), 940 (m), 920 (w), 880 (m), 740 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 4H), 3.72 (s, 3H), plus peaks for the diol. XRPD 8.55 (11), 8.8 (82), 13.3 (91), 13.4 (33), 14.7 (48), 15.7 (27), 16.0 (70), 16.5 (34), 18.5 (44), 26.6 (30).

(2)·(*p*-Hydroxythiophenol). Diol 2 (0.05 g, 0.238 mmol) and *p*-hydroxythiophenol (0.06 g, 0.5 mmol) wre dissolved in mesitylene (2 mL) to give a colorless solution. The yellow prismatic crystals which had formed overnight were filtered and dried, mp 100–101 °C. Anal. Calcd for $(C_{13}H_{22}O_2)\cdot(C_6H_6OS)$: C, 67.82; H, 8.39. Found: C, 67.75; H, 8.26. IR (paraffin mull) 3460 (m), 3340 (s), 3100 (s), 1600 (m), 1590 (s), 1495 (s), 1460 (s), 1310 (w), 1270 (s), 1240 (s), 1225 (s), 1175 (m), 1125 (s), 1105 (s), 1035 (w), 1020 (w), 940 (m), 910 (w), 870 (m), 820 (s), 640 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.20 (d, 2H), 6.72 (d, 2H), and diol peaks. XRPD 9.0 (20), 13.2 (10), 15.0 (41), 16.2 (32), 16.6 (10), 17.8 (10), 19.0 (15), 19.5 (8), 20.8 (8), 23.2 (7), 27.0 (17), 36.4 (7).

(2)$_2$·(Hydroquinone). Diol 2 (0.05 g, 0.238 mmol) and hydroquinone were slowly dissolved on warming in mesitylene (4 mL). The needlike crystals which had formed overnight were filtered and dried, mp 160–161 °C. Anal. Calcd for $(C_{13}H_{22}O_2)_2\cdot(C_6H_6O_2)$: C, 72.42; H, 9.50. Found: C, 72.60; H, 9.21. IR (paraffin mull) 3440 (s), 3350 (s), 3150 (s), 1250 (s), 1130 (s), 1110 (s), 940 (m), 920 (w), 890 (m), 830 (m), 760 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 8.57 (s, 2H), 6.52 (s, 4H), plus diol peaks. XRPD 10.95 (48), 12.85 (76), 13.3 (46), 14.8 (10), 15.55 (24), 16.4 (56), 17.8 (39), 18.8 (13), 25.8 (9), 27.3 (12).

(2)$_2$·(2,6-Dihydroxynaphthalene). Diol 2 (0.50 g, 0.238 mmol) and 2,6-dihydroxynaphthalene (0.05 g, 0.31 mmol) were dissolved in acetonitrile (3 mL) on warming. The fine needlelike crystals which had formed after standing overnight were filtered and dried, mp 178–179 °C. Anal. Calcd for $(C_{13}H_{22}O_2)_2\cdot$

---

(36) Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L.; Marchand, A. P.; Wang, Y. *J. Chem. Soc., Perkin Trans. 2* **1993**, 937.

(37) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.

($C_{10}H_8O_2$): C, 74.45; H, 9.02. Found: 74.66; H, 8.77. IR (paraffin mull) 3475 (s), 3350 (s), 3140 (s), 1600 (s), 1260 (w), 1220 (s), 1120 (m), 1100 (s), 940 (m), 920 (w), 880 (m), 860 (m) cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$) δ 9.3 (s, 2H), 7.49 (d, 2H), 6.95 (m, 4H), plus diol signals. XRPD 10.0 (45), 12.3 (30), 14.5 (65), 15.1 (41), 16.5 (67), 17.0 (47), 21.15 (82), 22.1 (23), 25.2 (17), 26.0 (17), 27.3 (17), 38.7 (14). Crystals of this compound were unstable and decomposed rapidly on standing at room temperature.

(2)·(Phloroglucinol). Diol **2** (0.05 g, 0.238 mmol) and anhydrous 1,3,5-trihydroxybenzene (phloroglucinol, 0.063 g, 0.50 mmol) were dissolved in acetonitrile (2 mL) upon warming. The square plate-shaped crystals which had formed after standing at room temperature overnight were filtered and dried, mp 175–176 °C. The crystals turned opaque after about 3 days at room temperature corresponding to loss of included acetonitrile. Anal. Calcd for ($C_{13}H_{22}O_2$)·($C_6H_6O_3$): C, 67.83; H, 8.39. Found: C, 67.45; H, 8.40. IR (paraffin mull) 3500 (m), 3440 (s), 3280 (s), 3160 (s), 2150 (vw, –CN), 1620 (s), 1500 (s), 1370 (m), 1320 (m), 1300 (m), 1160 (s), 1140 (s), 1120 (s), 1000 (s), 940 (m), 910 (w), 810 (m), 760 (w), 680 (w) cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$) δ 8.91 (s, 3H), 5.66 (s, 3H), and 2.06 (s, CH_3CN), plus diol signals. XRPD 13.0 (88), 14.8 (25), 15.3 (71), 16.0 (62), 16.5 (84), 17.5 (25), 18.0 (42), 18.8 (34), 20.8 (22), 21.9 (26), 23.0 (20), 24.5 (37), 25.0 (18), 27.8 (19), 33.7 (13).

(4)·(Phenol). 2,8-Dimethyltricyclo[5.3.1.1^{3,9}]dodecane-*syn*-2,*syn*-8-diol (**4**, 0.05 g, 0.23 mmol) was slowly dissolved on heating in a solution of phenol in mesitylene. The needlelike crystals which had formed overnight were filtered and dried, mp 91–92 °C. Anal. Calcd for ($C_{14}H_{24}O_2$)·(C_6H_6O): C, 75.43; H, 9.50. Found: C, 75.68; H, 9.45. IR (paraffin mull) 3450 (m), 3350 (s), 3140 (br s), 1600 (s), 1260 (m), 1240 (m), 1170 (w), 1130 (w), 1100 (s), 1030 (w), 1000 (w), 930 (m), 900 (w), 870 (m), 810 (w), 750 (s), 690 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 2H), 6.90 (t, 1H), 6.85 (d, 2H), plus diol signals. XRPD 8.0 (10), 9.2 (51), 13.2 (11), 13.7 (15), 14.4 (10), 14.6 (34), 18.9 (11), 19.7 (16), 24.0 (10).

(4)·(*p*-Hydroxythiophenol). Diol **4** (0.05 g, 0.23 mmol) and *p*-hydroxythiophenol (0.058 g, 0.46 mmol) were dissolved in mesitylene (2 mL) with warming to give a colorless solution. The bright yellow blocklike crystals formed after 1 week at room temperature were filtered, washed with a little hexane and dried over P_2O_5 to give the product, mp 82–83 °C. Anal. Calcd for ($C_{14}H_{24}O_2$)·(C_6H_6OS): C, 68.53; H, 8.63. Found: C, 69.00; H, 8.65. IR (paraffin mull) 3490 (s), 3390 (s), 3160 (s), 1590 (m), 1500 (s), 1265 (s), 1230 (s), 1170 (w), 1130 (w), 1100 (s), 1030 (w), 1000 (w), 935 (m), 900 (m), 880 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.20 (d, 2H), 6.73 (d, 2H), plus diol signals. XRPD 8.8 (73), 13.1 (31), 14.7 (45), 16.05 (68), 16.2 (30), 17.45 (25), 18.65 (40), 19.1 (16), 20.4 (16), 23.4 (20), 25.5 (15), 26.3 (26).

(4)$_2$·(Hydroquinone). Diol **4** (0.05 g, 0.23 mmol) and hydroquinone (0.025 g, 0.22 mmol) were dissolved in acetonitrile (2 mL) with warming. The needlelike crystals which had formed overnight were filtered and dried, mp 159–160 °C. Anal. Calcd for ($C_{14}H_{24}O_2$)$_2$·($C_6H_6O_2$): C, 73.08; H, 9.74. Found: C, 73.35; H, 10.00. IR (paraffin mull) 3440 (s), 3350 (s), 3150 (s), 1600 (w), 1510 (m), 1240 (s), 1220 (s), 1120 (m), 1100 (s), 1020 (w), 990 (w), 930 (m), 900 (w), 850 (w), 820 (m), 760 (m) cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$) δ 8.57 (s, 2H), 6.52 (s, 4H), plus diol signals. XRPD 10.8 (26), 11.4 (33), 12.8 (73), 14.7 (24), 15.8 (68), 16.5 (49), 18.0 (21), 18.6 (28), 20.0 (13), 23.3 (13), 26.0 (15), 29.2 (16), 29.8 (14).

(4)$_2$·(2,6-Dihydroxynaphthalene). Diol **4** (0.05 g, 0.23 mmol) was dissolved in a warm concentrated solution of 2,6-dihydroxynaphthalene in benzene/diethyl ether (1:1, 2 mL). The cubic crystals which formed on standing at room temperature were filtered and dried, mp 145–146 °C. These unstable crystals rapidly turned opaque corresponding to loss of included benzene at room temperature, and even slowly at 0 °C. IR (paraffin mull) 3460 (s), 3345 (s), 3120 (br s), 1605 (s), 1270 (w), 1230 (s), 1135 (m), 1120 (m), 1100 (s), 1025 (w), 1000 (w), 950 (w), 940 (s), 680 (m, benzene) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.24 (br s, 2H), 7.52 (s, 2H), 7.10–7.00 (m, 4H), and 7.33 (s, C_6H_6), plus diol peaks. The NMR integration suggested the composition (**4**)$_2$·(2,6-dihydroxynaphthalene)·(benzene). XRPD 7.25 (22), 7.5 (21), 7.75 (29), 10.25 (71), 13.0 (23), 13.5 (24), 14.5 (27), 16.0 (30), 17.0 (31), 17.5 (33), 18.2 (32), 22.7 (14), 23.6 (22), 24.6 (14).

(4)$_2$·(Phloroglucinol). Diol **4** (0.05 g, 0.23 mmol) was dissolved in a solution of anhydrous phloroglucinol in acetonitrile (2 mL). The crystals which formed on standing overnight were filtered and dried. Needle-shaped and diamond-shaped crystals were observed. Both had mp 167–168 °C and identical IR, NMR, and XRPD data. Anal. Calcd for ($C_{14}H_{24}O_2$)$_2$·($C_6H_6O_3$): C, 71.05; H, 9.47. Found: C, 71.26; H, 9.51. IR (paraffin mull) 3410 (s), 3250 (m), 3100 (m), 1600 (s), 1490 (m), 1370 (m), 1360 (m), 1340 (w), 1300 (w), 1140 (s), 1120 (s), 1090 (s), 1010 (w), 1000 (s), 920 (m), 820 (m) cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$) δ 8.88 (s, 3H), 5.62 (s, 3H), plus diol peaks. XRPD 8.0 (62), 9.2 (12), 13.4 (25), 13.8 (40), 14.4 (15), 15.8 (14), 16.3 (23), 27.4 (12).

Solution and Refinement of the Structures. Reflection data for all seven structures were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized copper radiation (λ 1.5418 Å). Data were corrected for absorption and any decomposition. Reflections with $I > 3\sigma(I)$ were considered observed. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[38]

For most of the structures, solution and refinement were straightforward. The positions of all non-hydrogen atoms of the diol and phenol molecules were located using direct methods (MULTAN[39]) and Fourier techniques. The asymmetric unit comprised one diol and one phenol molecule. Exceptions were the hydroquinone structure, where the asymmetric unit consisted of one diol and half a phenol molecule; and the phloroglucinol structure, where the asymmetric unit consisted of two diol molecules and one phenol molecule. Full-matrix least-squares refinement (BLOCKLS[40]) followed. Hydroxy hydrogen atoms were included in the refinement at positions in which they were located on a difference Fourier map and their positions were allowed to vary while all other hydrogen atoms were included in calculated positions and were not refined. All hydrogen atoms were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound. Refinement for the non-hydrogen atoms was standard with anisotropic thermal parameters. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04l_o)^2]^{1/2}$. An IBM 3090 computer was used for calculations, while diagrams were drawn using ORTEP-II[41] running on a Macintosh IIcx. Individual variations from this procedure are outlined below.

(1)·(*p*-Chlorophenol). Refinement converged with $R = 0.035$. The largest peak in the final difference Fourier map was 0.13 e Å^{-3}.

(1)$_2$·(Hydroquinone). An extinction correction was included in the refinement and its final value was 1.83×10^{-4}. Refinement converged with $R = 0.046$. The largest peak in the final difference map was 0.24 e Å^{-3}.

(2)·(*p*-Chlorophenol). An extinction correction was included in the refinement, and hydroxy hydrogen positions were not refined. At convergence, R was 0.043. The largest peak in the final difference Fourier map was 0.36 e Å^{-3}.

(2)·(*p*-Methoxyphenol). Standard refinement converged with $R = 0.096$, and there were residual peaks on a difference Fourier map which indicated that there was an alternate position for the *p*-methoxyphenol molecule. The position of the hydroxy group (which is involved in hydrogen bonding) was almost unchanged, but the molecule was effectively flipped over. Refinement was transferred to a program capable of rigid-body least-squares analysis (RAELS[42]), and the O–Ar–OH portion of the major component was used as a template to overlay the peaks found in the difference map. The minor component was refined as a rigid group, the variables refined being its position and orientation. The methyl group of the minor component was included as a separate atom with the C–O distance slack constrained to be 1.35 Å. The thermal motion of the minor component was refined as a 12-variable TL group (where T is the

---

(38) *International Tables for X-Ray Crystallography*; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch Press: Birmingham, 1974; Vol. 4.

(39) Main, P. MULTAN80, University of York, England, 1980.

(40) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS, Oak Ridge National Laboratory, TN, 1962, (BLOCKLS is a local version of this program).

(41) Johnson, C. K. ORTEP-II, Oak Ridge National Laboratory, TN, 1976.

(42) Rae, A. D. RAELS, A comprehensive constrained least squares refinement program, University of New South Wales, Australia, 1989.

translation tensor, and L is the libration tensor). The hydrogen atoms of the minor component were included in calculated positions, and they were included in the thermal group. The minor component of the phenolic hydrogen atom was not included. The occupancies of the major and minor components of the phenol were refined and were constrained to total 1. The final value of the occupancy of the major component was 0.780(2). Refinement converged with $R = 0.055$. The largest peak in the final differrence map was 0.37 e Å^{-3}.

(2)·(*p*-Hydroxythiophenol). The thiol hydrogen atom was disordered and was included in two positions of equal occupancy. Surprisingly, these two positions did not represent alternate directions for possible –S–H···S–H··· hydrogen-bonding chains. Instead, both hydrogen atoms lay between pairs of sulfur atoms with the smaller inter-sulfur-atom separation. It is possible that this represents some phenomenon giving rise to the yellow color of this solid and the absence of the IR absorption band discussed earlier. Disorder of –S–H hydrogen atoms was noted previously in the structure of 4-*p*-mercaptophenyl-2,2,4-trimethylchroman.[17]

The hydroxy and thiol hydrogen atoms were not refined, and refinement converged with $R = 0.046$. The largest peak in the final difference Fourier map was 0.16 e Å^{-3}.

(4)·(Phenol). The central carbon atom of the propano bridge of the diol was disordered. Two alternate positions were included in the refinement. The occupancies were refined and final values were 0.65(1) and 0.35. Refinement converged with $R = 0.044$. The largest peak in the final difference map was 0.16 e Å^{-3}.

(4)$_2$·(Phloroglucinol). An extinction correction was included in the refinement and its final value was 7.54×10^{-5}. Refinement converged with $R = 0.038$. The largest peak in the final difference map was 0.08 e Å^{-3}.

Supplementary Material Available: Details of solution and refinement, positional parameters, thermal parameters for the non-hydrogen atoms, interatomic distances and angles, dimensions associated with hydrogen bonding (49 pages); list of structure factors (56 pages). Ordering information is given on any current masthead page.

Acknowledgment. We thank Mrs. H. Stender for recording the NMR data and the Australian Research Council for financial support.