Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Toda, Fumio , Tanaka, Koichi , Okada, Toru , Bourne, Susan A. and Nassimbeni, Luigi R.(1994) 'Selective inclusion crystallization of phenol derivatives with tetraalkylammonium salts', Supramolecular Chemistry, 3: 4, 291 — 298

To link to this Article: DOI: 10.1080/10610279408034928

URL: http://dx.doi.org/10.1080/10610279408034928

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 291–298
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Selective inclusion crystallization of phenol derivatives with tetraalkylammonium salts

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(Received October 12, 1993)

The structures of four inclusion compounds of alkylammonium bromides with phenol derivatives are reported. Crystal data: (1) H1c.G4, monoclinic, $P2_1/m$ with $a = 5.5388(4)$, $b = 7.4464(9)$, $c = 32.421(5)$ Å, $\beta = 92.43°$, $Z = 2$, $D_C = 1.24\,g\,cm^{-3}$, $R = 0.082$ for 1556 observed reflections. (2) H1c.G2b, monoclinic, $P2_1/m$ with $a = 11.154(2)$, $b = 7.470(1)$, $c = 31.767(5)$ Å, $\beta = 91.42°$, $Z = 2$, $D_C = 1.13\,g\,cm^{-3}$, $R = 0.061$ for 2710 observed reflections. (3) H2b.G1, orthorhombic, P_{bca} with $a = 15.215(3)$, $b = 16.208(1)$, $c = 19.827(5)$ Å, $Z = 8$, $D_C = 1.13\,g\,cm^{-3}$, $R = 0.061$ for 1613 observed reflections. (4) H3.G6, monoclinic, $P2_1/c$ with $a = 9.472(2)$, $b = 18.345(2)$, $c = 16.384(3)$ Å, $\beta = 105.73°$, $Z = 4$, $D_C = 1.20\,g\,cm^{-3}$, $R = 0.050$ for 1783 observed reflections. The molecules are held in their aggregates by O...Br hydrogen bonding. The inclusion compounds can also be formed in the solid state by shaking together the powdered components. The reaction was followed by UV spectroscopy. Isomeric separation of the phenol derivatives was carried out using inclusion crystallization. The phenols were obtained in high purities in yields ranging from 20 to 60%.

INTRODUCTION

The molecular aggregation between alkylammonium salts and organic molecules is of importance in the mechanistic study of the role of membranes.[1] In a previous study,[2] hexadecamethylammonium bromide (H1c) was found to form a crystalline inclusion complex with phenol. We now report the inclusion complexation of phenol derivatives by various alkylammonium bromides and the X-ray structures of some of the inclusion complexes. We also report how isomers of phenol derivatives were separated by inclusion crystallization with ammonium salts.

RESULTS AND DISCUSSION

Scheme I shows the ammonium salts and phenol derivatives used in this study. The presence of strong hydrogen bonds in these complexes was observed in their infrared spectra. For example, **2** showed νOH at 3180 cm^{-1}, although in the free *p*-phenylphenol this stretch occurs at 3350 cm^{-1} in nujol mull (see Fig 1). The X-ray crystal structure disclosed that the hydrogen bond is formed between the hydroxyl group of the *p*-phenylphenol and the bromide ion of H1c, and this is described below.

CRYSTAL STRUCTURE ANALYSIS

The following inclusion compounds were chosen for X-ray structural studies:

1: H1c.G4 (1:1)
2: H1c.G2b (2:1)
3: H2b.G1 (1:1)
4: H3.G6 (1:2)

Details of data collection and structure refinement are given in Table 1. Final fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles and tables of observed and calculated structure factors have been deposited. Atomic labelling is according to Fig 2, which shows perspective views of the molecular structures.

Conformation

The bond lengths and angles of the alkylammonium molecules are within the range of values normally found for such compounds. The values of selected bond lengths and angles may be found in Table 2. The guest molecules in **2**, **3** and **4** are also well-ordered (see Table 2 for selected lengths and angles). The β-naphthol molecule in **1**, however, showed an interesting mode of disorder. We found eight distinct peaks in the electron density map such that, when applying

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Alkylammonium salts :

$Me(CH_2)_n N^+Me_3 . Br^-$

H1

a : n = 5
b : n = 7
c : n = 15
d : n = 16
e : n = 17

$R_4 N^+ . Br^-$

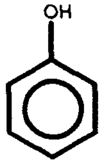
H2

a : R = Pr
b : R = Bu

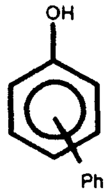
$Bu_3 N^+ (CH_2)_6 N^+ Bu_3 . 2Br^-$

H3

Phenol derivatives :

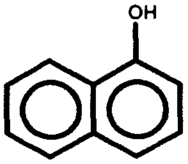


G1

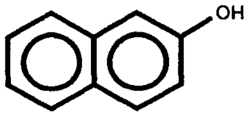


G2

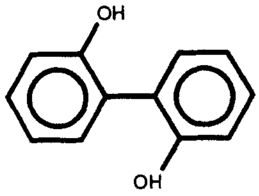
a : ortho
b : para



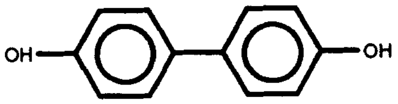
G3



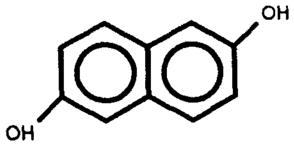
G4



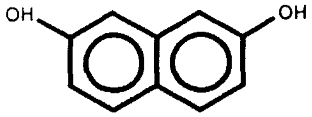
G5



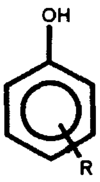
G6



G7



G8



G9

a : R = o-Cl
b : R = p-Cl
c : R = o-Me
d : R = m-Me
e : R = p-Me

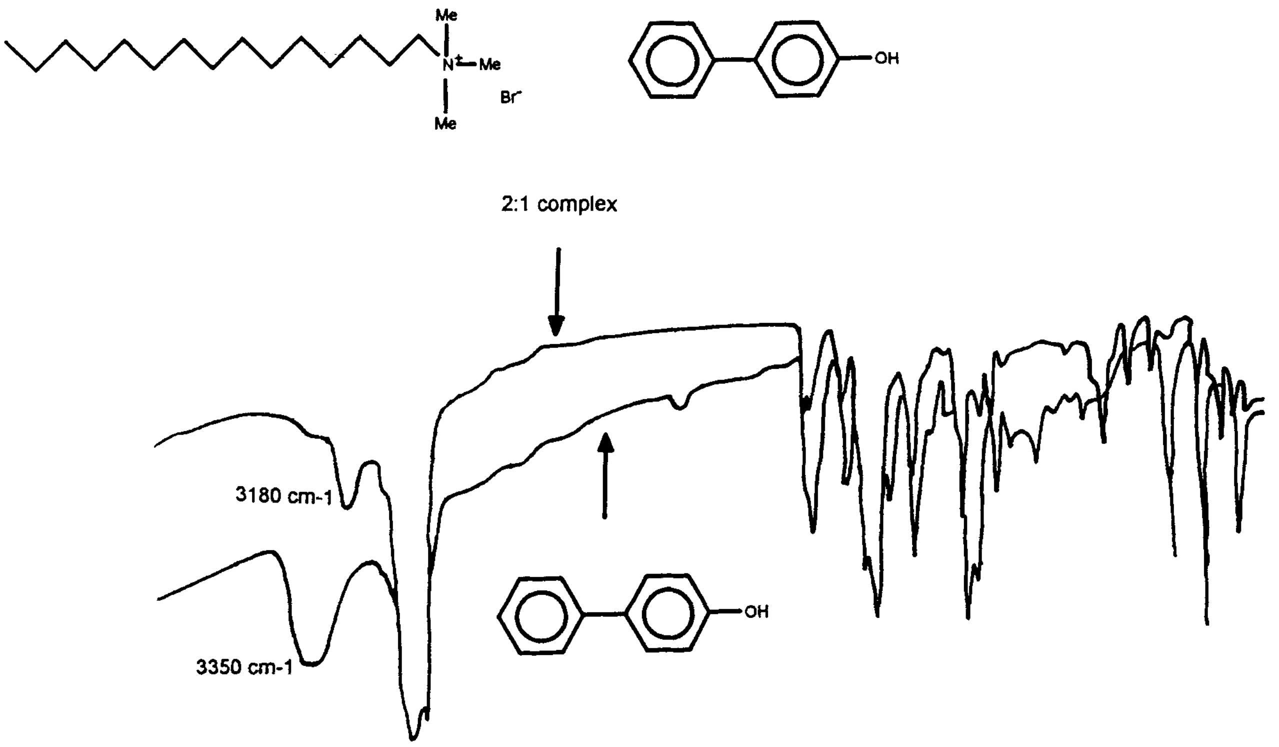


Figure 1 Infrared spectra of *p*-phenylphenol and its 2:1 complex with H1c, showing the shift in νOH on complexation.

Table 1 Crystal data and experimental parameters

	1	*2*	*3*	*4*
Molecular formula	$C_{19}H_{42}NBr.C_{10}H_8O$	$(C_{19}H_{42}NBr)_2.C_{12}H_{10}O$	$C_{16}H_{36}NBr.C_6H_6O$	$C_{30}H_{66}N_2Br_2.C_{12}H_{10}O_2$
Mass (g mol^{-1})	508.634	899.133	416.493	493.546
Space group	$P2_1/m$	$P2_1/m$	Pbca	$P2_1/c$
a (Å)	5.5388(4)	11.154(2)	15.215(3)	9.472(2)
b (Å)	7.4464(9)	7.470(1)	16.208(1)	18.345(2)
c (Å)	32.421(5)	31.767(5)	19.827(5)	16.384(3)
β (°)	92.43(1)	91.42(1)	90	105.73(1)
Volume (Å^3)	1335.9(6)	2646(1)	4889(2)	2740(10)
Z	2	2	8	4
F(000)	548	972	1792	1052
μ (MoKα) (cm^{-1})	15.40	15.11	16.72	15.04
D_c (g cm^{-3})	1.24	1.13	1.13	1.20
Crystal dimensions (mm)	0.28 × 0.28 × 0.31	0.60 × 0.31 × 0.41	0.41 × 0.50 × 0.50	0.35 × 0.40 × 0.40
θ limit (°)	25	25	25	25
Max h, k, l	6, 8, ±38	±13, 8, 37	18, 19, 23	11, −21, −19
N (measured)	2827	5122	4791	3197
N (observed)	1556	2710	1613	1783
Number of parameters	163	342	240	299
Max l.s. shift/e.s.d.	0.36	0.10	0.05	0.2
Max, min residual electron density (e Å^{-3})	b, −0.40	0.14, −0.15	0.32, −0.43	0.44/−0.39
R	0.082	0.061	0.061	0.050
Rw	0.082	0.055	0.049	0.044
w[a]	1	0	0	0
Absorption correction				
Minimum transmission (%)	82.66	75.39	81.90	84.71
Maximum transmission (%)	99.93	99.97	99.91	100.0
Average transmission (%)	94.60	94.86	91.56	93.17

[a] Weighting scheme: $(\sigma^2F + wF^2)^{-1}$.

[b] Several peaks ca. 1 eÅ^{-3} close to the guest.

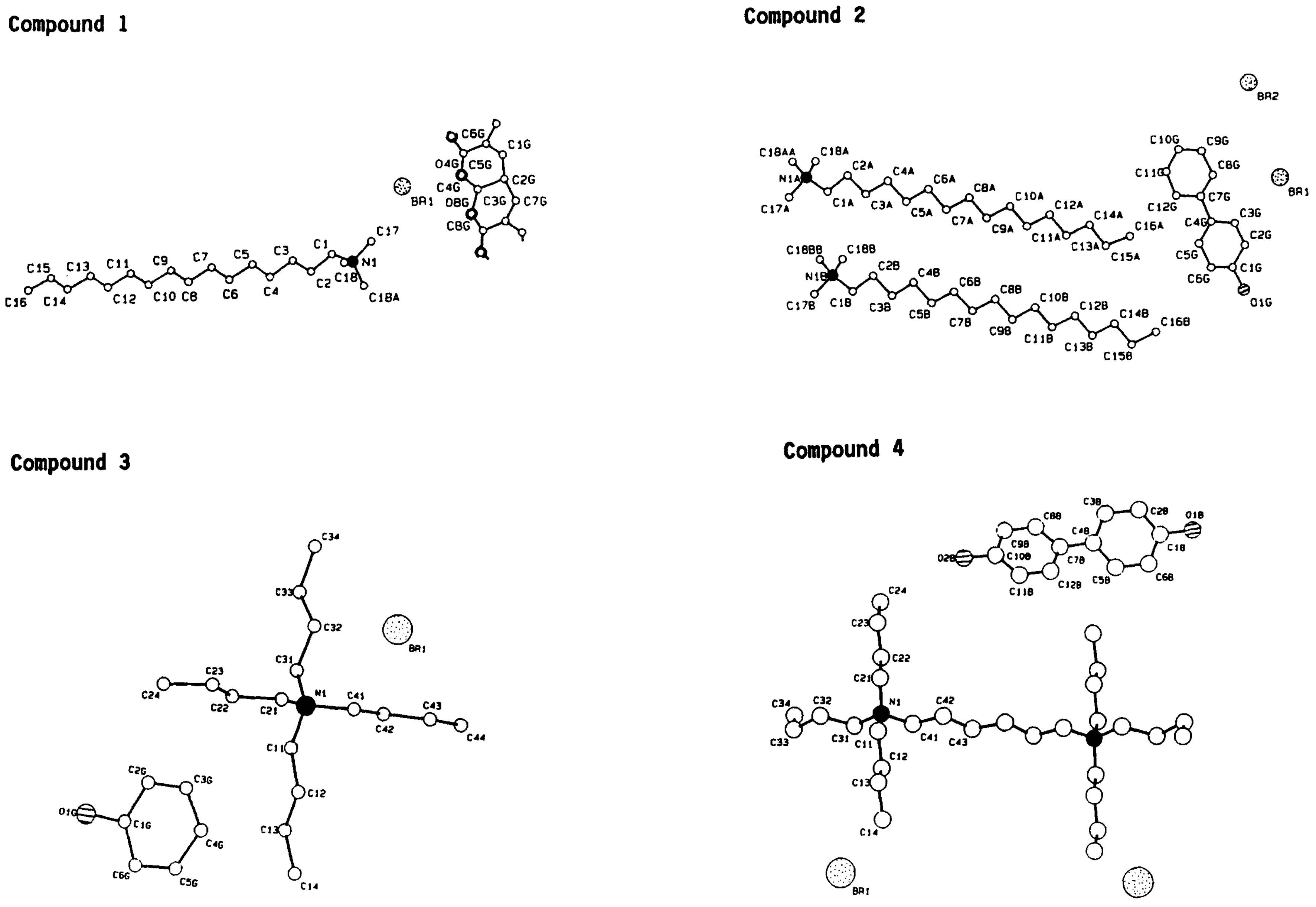


Figure 2 Perspective views and atomic labelling of the molecular structures of **1–4**.

Table 2 Selected bond lengths and angles

Compound	*1*	*2*	*3*	*4*
N-C	1.50(1)–1.54(1)	1.51(2)–1.51(2)	1.50(1)–1.52(1)	1.493(9)–1.53(1)
Csp^3-Csp^3	1.47(2)–1.55(1)	1.35(4)–1.52(2)	1.44(2)–1.53(2)	1.43(1)–1.53(1)
O-Car	1.38(1)	1.44(3)–1.51(4)	1.37(2)	1.36(1)–1.37(1)
Car-Car	1.35(2)–1.39(2)	1.44(7)–1.61(6)	1.27(3)–1.50(3)	1.36(1)–1.40(1)
Csp^3-N-Csp^3	104.2(6)–112.5(7)	105.9(9)–110.7(4)	105.7(7)–111.5(3)	105.7(6)–112.2(6)
N-Csp^3-Csp^3	113.7(7)–114.2(7)	117.6(9)	116.3(7)–117.9(7)	113.8(7)–115.1(6)
Csp^3-Csp^3-Csp^3	105.85(7)–113.6(9)	110(1)–130(2)	108.4(7)–122.3(2)	110.4(7)–114.5(8)
O-Car-Car	115.2(9)–121(1)	111.8(30)–121.8(32)	118.6(13)–121.3(13)	119.0(8)–121.4(7)
Car-Car-Car	116(1)–123(1)	93(4)–146(4)	114.7(12)–125.6(18)	116.5(7)–122.8(8)

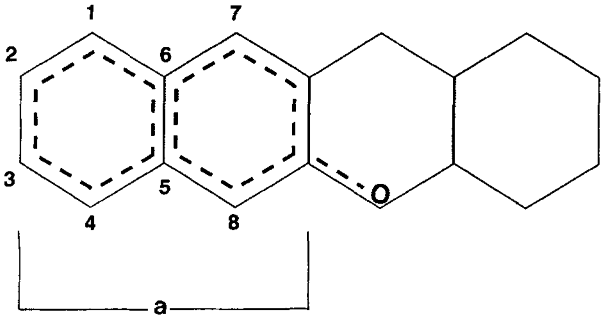


Figure 3 Model of the disordered β-naphthol in 1.

translation along *a*, they yielded a continuous chain of fused hexagons. The structure of β-naphthol can be imposed on these hexagons as shown by the dashed lines in Fig 3. The bond lengths and angles for this molecule therefore deviate somewhat from expected values. The values obtained in the final model are listed in Table 2. The fact that the β-naphthol (compound **1**) and *p*-phenylphenol (compound **2**) are found on the mirror plane forces these molecules to be planar. In **3**, the phenol molecule is also planar, with a maximum deviation from the least squares plane of 0.01 Å. The aromatic rings of the biphenyl in **4** are also planar with a maximum deviation from the plane of 0.004 Å. The dihedral angle between the two rings is 22.7(3)°.

Crystal packing and host-guest interactions

The β-naphthol and *p*-phenylphenol guests (compounds **1** and **2**, respectively) form sheets parallel to *a*, as shown in Fig 4(a) for compound **1**. In **1**, the oxygen atoms modelled at positions 4 and 8 (Fig 3) are 3.54 and 3.81 Å from the bromide ion. Thus a system of hydrogen bonding can be inferred. There is also a close contact of 3.32 Å between the hydroxyl moiety of the *p*-phenylphenol and Br(2) in **2**. Figure 4(b) is a packing diagram of **2** showing the projection down [010] with $0 \leqslant b \leqslant \frac{1}{2}$. The positions of the molecules on the mirror plane are clearly seen.

In compound **3**, the phenol molecules are located in zigzag channels running approximately parallel to *b*. There is a close contact between the hydroxyl oxygen of the phenol and the bromide ion (the O…Br distance is 3.15 Å). The packing of **3** is illustrated in Fig 4(c).

The ammonium bromide in **4** is placed about a centre of inversion at $(0, 0, \frac{1}{2})$, Wyckoff position *c*. The [1,1′-biphenyl]-4,4′-diol is located in a general position. The structure is packed in stacks of ammonium ions and biphenyl molecules along [100] and [010] as shown in Fig 4(d).

SOLID STATE REACTIONS AND ISOMERIC SEPARATION

Inclusion compounds of ammonium salts with phenol derivatives can also be formed simply by mixing the two powdered components and the process may be monitored by measurement of the solid-state UV spectrum. For example, the UV spectrum of a 2:1 molar mixture of powdered H1c and G2b shows the fast and efficient complexation between them. The powdered solids were shaken for 1 min and kept at room temperature for 6 h. The UV spectrum was measured in the solid state every 10 min. Because the population of the coplanar form of the biphenyl increases as the complexation proceeds, the absorption coefficient of this population increases in the UV spectrum, as shown in Fig 5. The complexation is complete within 6 hours.

Because the complexation between the ammonium salt and the phenol derivative occurs selectively, isomeric phenol derivatives can be separated. For example, G2a and G2b are easily separated by complexation with H1c, since the former does not form a complex with H1c. When a solution of a 1:1 mixture of *o*- and *p*-phenylphenol in MeOH was added to a solution of H1c and allowed to stand, **2** was formed

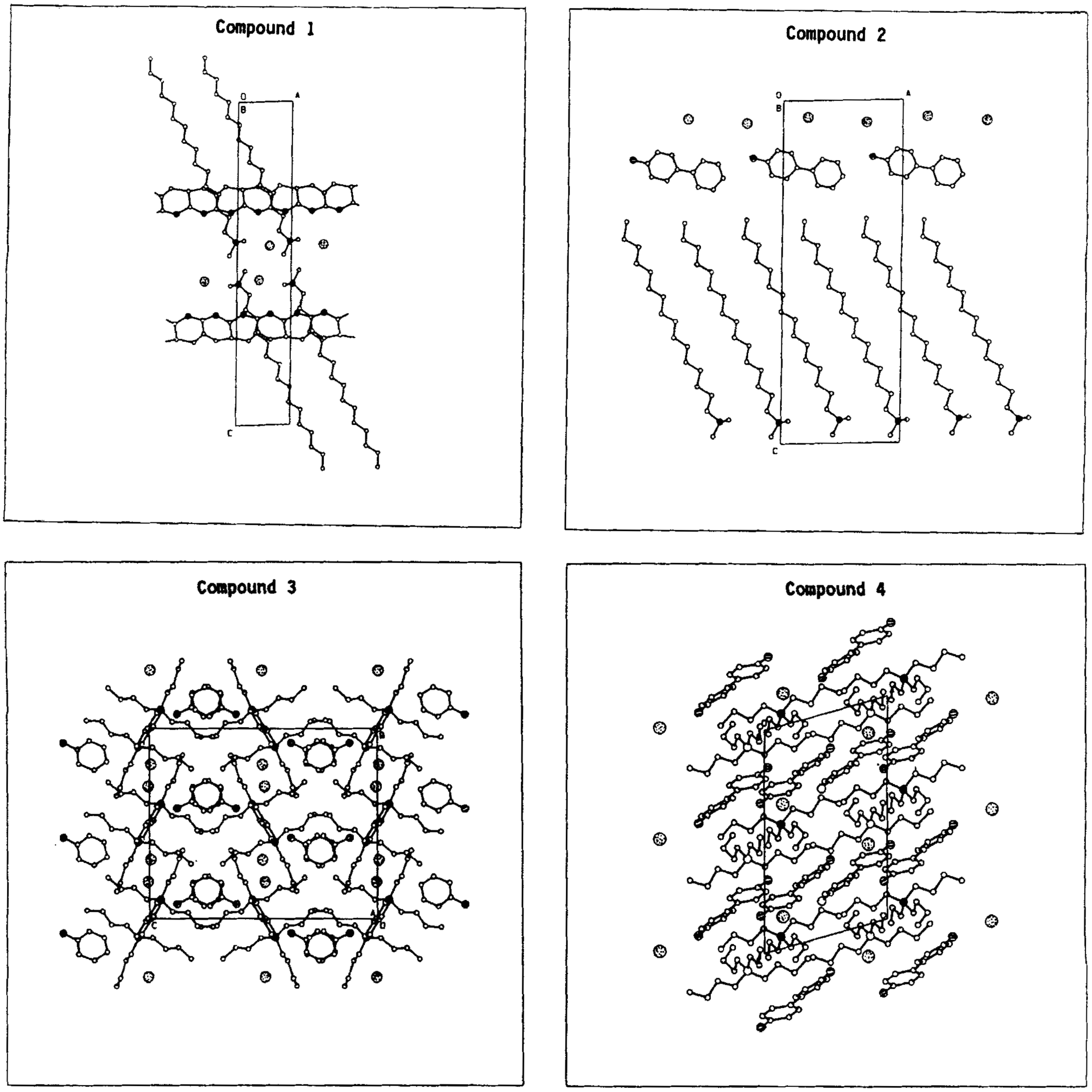


Figure 4(a)–(d) Packing diagrams of the four inclusion compounds. Bromide ions are represented by dotted circles, nitrogen and oxygen atoms by shaded and striped circles respectively and carbons are shown as open circles

and *p*-phenylphenol of 98% purity was isolated from the inclusion compound in 54% yield. This, and other examples of isomeric separation, are listed in Table 3. Separation of 2,2′-dihydroxy- and 4,4′-dihydroxybiphenyl (G5 and G6 respectively) was achieved by complexation with H1d and with H3. Separation of 2,6-dihydroxy- and 2,7-dihydroxynaphthalene (G7 and G8) was achieved using the ammonium salt H2a, since this salt does not form a complex with G8. 2,6-dihydroxynaphthalene was isolated in 94% purity from a 1:1 mixture, although the yield was rather poor. *p*-Chlorophenol (G9b) was efficiently separated from a mixture with its *o*-isomer (G9a) using H1a which has a relatively short alkyl chain. However, attempts at separating G3 and G4, *o*-cresol (G9c) and *p*-cresol (G9e) and *m*- and *p*-cresol (G9d and G9e) were not very successful (see Table 3).

EXPERIMENTAL

The inclusion complexes of the phenol derivatives and

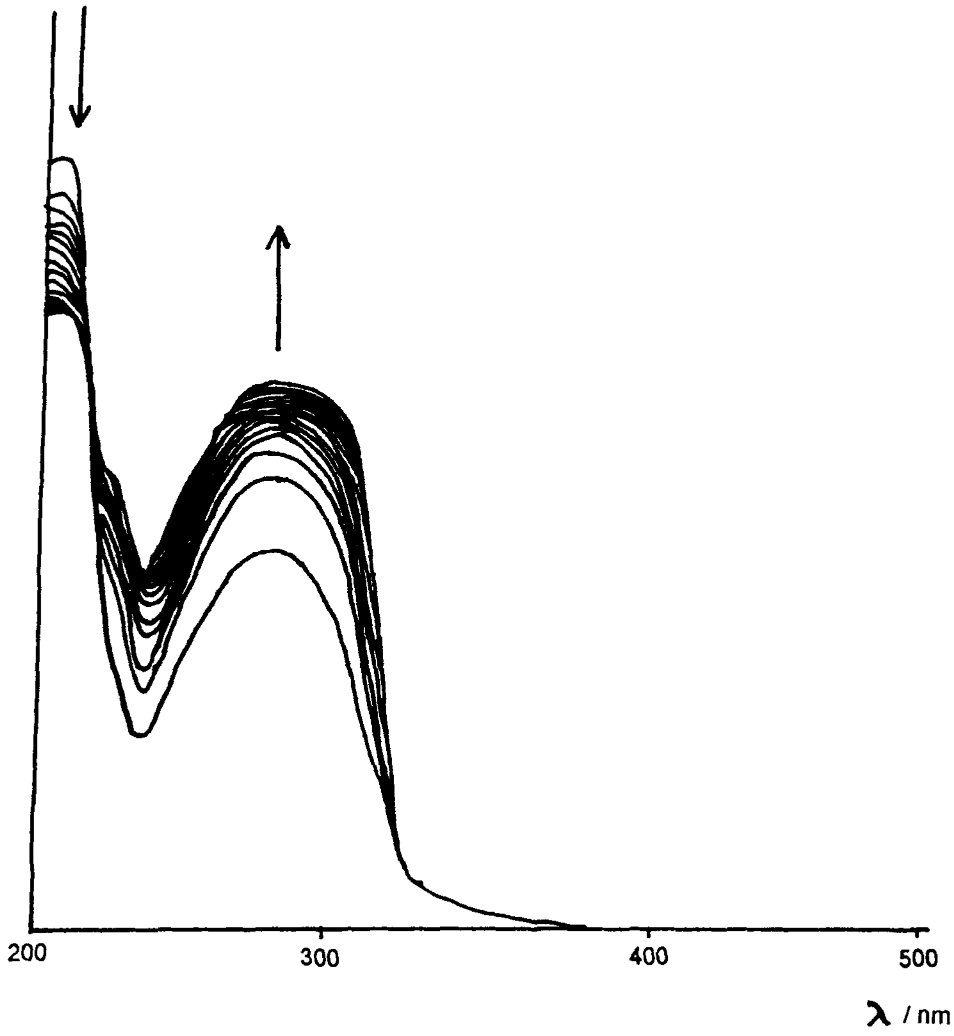


Figure 5 Solid state UV spectra measured every 10 min to monitor the complexation of H1c and G2b. The reaction was complete within 6 h.

Table 3 Separation of isomers of phenol derivatives by complexation with ammonium salts

1:1 Mixture of phenols	*Ammonium salt*	*Product*	*Isolated phenol derivative yield (%)*	*Purity (%)*
G2a and G2b	H1c	G2b	54	98
G5 and G6	H3	G6	75	99
G5 and G6	H1d	G6	37	98
G7 and G8	H2a	G7	23	94
G9a and G9b	H1a	G9b	18	82
G3 and G4	H1a	G4	60	62
G9c and G9e	H1b	G9e	23	62
G9d and G9e	H1e	G9e	75	65

ammonium salts were prepared by recrystallizing both components from a common solvent. Accurate cell dimensions were obtained by at least squares analysis of 24 reflections measured in the range $16 \leqslant \theta \leqslant 17°$ on an Enraf Nonius CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å). During data collection, three reference reflections were monitored periodically for intensity and orientation control. The ω-2θ method was used with a scan width of $(0.85 + 0.35 \tan\theta)°$, an aperture length of 4 mm and an aperture width of $(1.12 + 1.05 \tan\theta)$ mm. Lorentz-polarisation and absorption[3] corrections were applied to the data. The structures were solved by direct methods (**1** and **3**) and by the automatic Patterson function (**2** and **4**) using SHELXS-86.[4] Compounds **1** and **2** were similar in that the cetrimonium bromide and the β-naphthol and *p*-phenylphenol molecules were all found on the mirror plane at (x, $\frac{1}{4}$, z) (Wyckoff position *e*). Refinement of all four structures was by full-matrix least squares using SHELX76.[5] The non-hydrogen atoms of the alkylammonium bromide molecules were refined anisotropically. The guest molecules in **2**–**4** were also refined anisotropically and the aromatic hydrogens restrained to 1.00 Å from their parent atoms. The naphthol guest in compound **1** was disordered as previously described. The final refinement required the use of constrained bond lengths and of isotropic temperature factors. The atoms at positions 4 and 8 were modelled as carbon and oxygen atoms, each with a site occupancy factor of one half of that of the carbon atoms at positions 1–3 and 5–7. No hydrogens were modelled on the naphthol. The hydroxyl hydrogens could not be located in the difference Fourier maps of **1–4** and they were thus omitted.

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