

Inclusion of chlorophenols by 4,4'-(cyclohexane-1,1-diyl)-diphenol: structures and kinetics of decomposition

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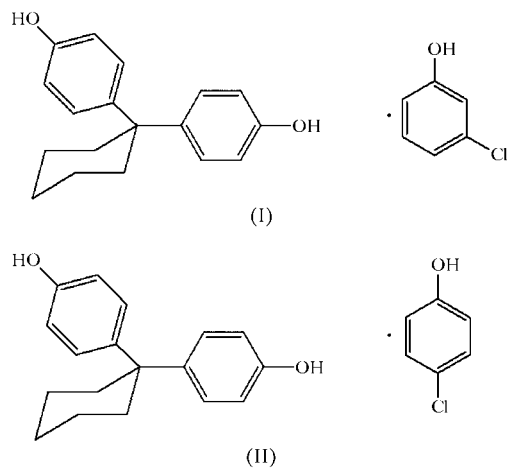
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The structures of the inclusion compounds 4,4'-(cyclohexane-1,1-diyl)diphenol-3-chlorophenol (1/1) and 4,4'-(cyclohexane-1,1-diyl)diphenol-4-chlorophenol (1/1), both $C_{18}H_{20}O_2 \cdot C_6H_5ClO$, are isostructural with respect to the host molecule and are stabilized by extensive host–host, host–guest and guest–host hydrogen bonding. The packing is characterized by layers of host and guest molecules. The kinetics of thermal decomposition follow the R2 contracting-area model, $kt = [1 - (1 - \alpha)^2]$, and yield activation energies of 105 (8) and 96 (8) kJ mol⁻¹, respectively.

Comment

The host compound 4,4'-(cyclohexane-1,1-diyl)diphenol forms inclusion compounds with a variety of guests. It enclathrates cyclohexanol and cyclohexanone (Goldberg *et al.*, 1987), as well as phenol and the isomers of cresol (Goldberg *et al.*, 1988). It has been employed to separate several mixtures of isomers, including phenyl diamines (Caira *et al.*, 1997),



picolines (Caira *et al.*, 1995) and aliphatic alcohols (Caira *et al.*, 1998a). The separation of lutidines and their kinetics of thermal decomposition have been studied (Caira *et al.*, 1998b).

We have demonstrated the use of controlled crystallization temperatures to obtain xylydine clathrates with differing host–guest ratios, a phenomenon of current interest (Nassimbeni & Su, 2002; Ibragimov, 2007). We now present the structures of the inclusion compounds formed by this host with *m*- and *p*-

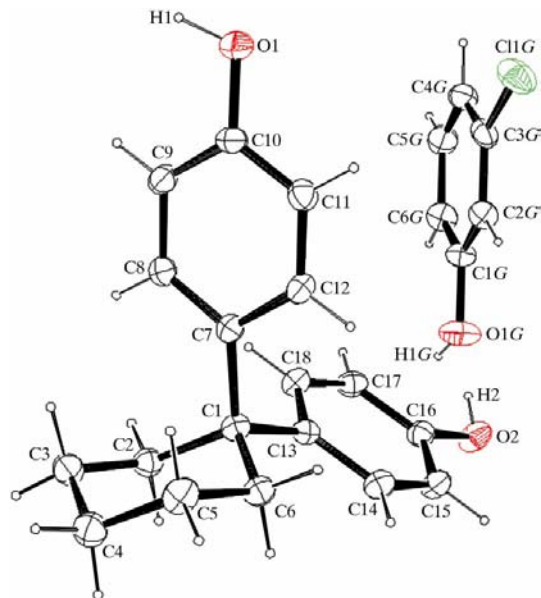


Figure 1

The structure of (I), showing the atom-numbering scheme; the suffix G denotes the guest molecule. Displacement ellipsoids are drawn at the 38% probability level and H atoms are shown as small spheres of arbitrary radii.

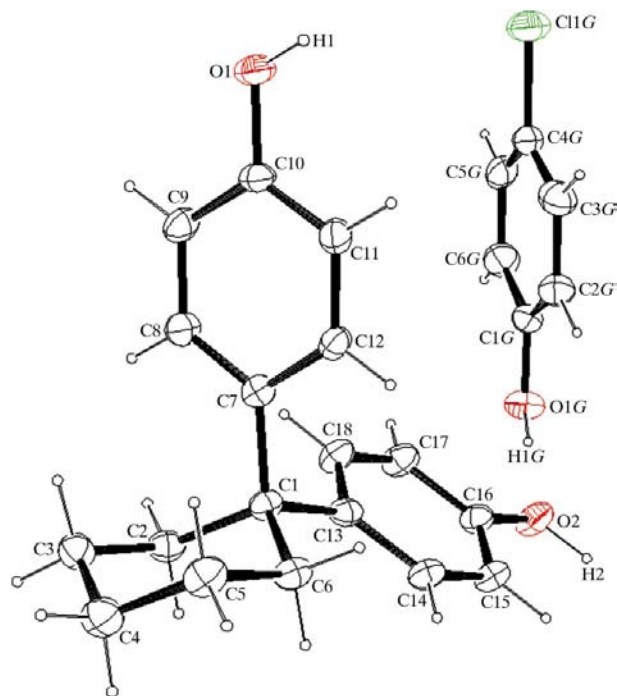


Figure 2

The structure of (II), showing the atom-numbering scheme; the suffix G denotes the guest molecule. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

chlorophenol, *viz.* (I) and (II), respectively (Figs. 1 and 2, respectively), their thermal characteristics and their kinetics of decomposition.

Compounds (I) and (II) both crystallize in the space group $P\bar{1}$ with $Z = 2$ and with similar unit-cell parameters and host-guest ratios of 1:1. They are isostructural with respect to the positions of the host atoms, except for the hydroxyl H atoms, which are located in positions governed by the requirements of the hydrogen bonding. The packing is characterized by ribbons of host molecules running in the [010] direction and linked by (host)O—H...O(H)(host) hydrogen bonds. These ribbons are in turn crosslinked by (host)O—H...O(H)(guest) and (guest)O—H...O(H)(host) hydrogen bonds, running in the [100] direction. The hydrogen-bonding network for (I) is

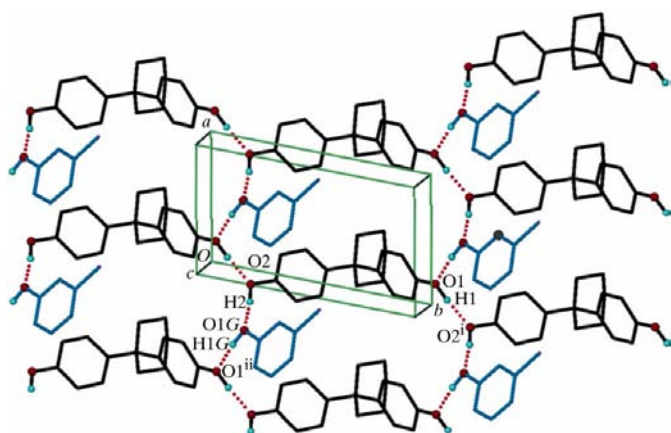


Figure 3
A partial packing diagram for structure (I), showing the hydrogen-bonding network. Host and guest molecules are represented with dark and light bonds, respectively. All H atoms, except the hydroxyl H atoms, have been omitted for clarity. Hydrogen bonds are shown as dotted lines. [Symmetry codes: (i) $x, 1 + y, z$; (ii) $x - 1, y - 1, z$.]

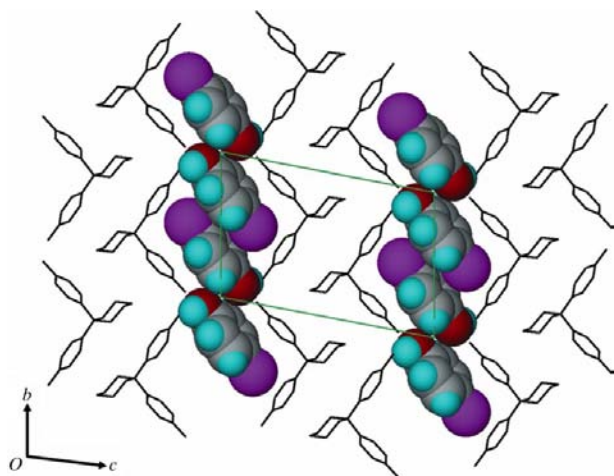


Figure 4
A projection of the structure of (II), viewed along [100], showing the double ribbons of host molecules forming layers perpendicular to c and the guest molecules located between the host layers. All H atoms of the host molecules have been omitted for clarity. The guest *p*-chlorophenol molecules are represented by their van der Waals radii.

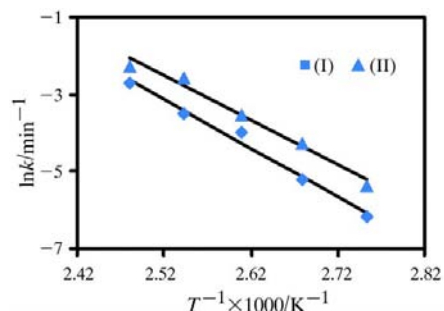


Figure 5
Arrhenius plots of $\ln k$ versus $1/T$ for the decomposition reactions of (I) and (II).

shown in Fig. 3 as an example. Details of the hydrogen bonds for structures (I) and (II) are given in Tables 1 and 2, respectively. Double ribbons of host molecules form layers perpendicular to c , with the guest chlorophenols interleaving the hydrophilic side of the host layers which contain the hydroxyl groups. This is shown in Fig. 4. The narrowest interlayer host spacings are approximately 2.1 Å for (I) and 2.3 Å for (II). This packing is common for this host and reoccurs in the structures with phenyl diamines (Caira *et al.*, 1997), picolines (Caira *et al.*, 1997), aliphatic alcohols (Caira *et al.*, 1998a) and lutidines (Caira *et al.*, 1998b).

The conformation of the host molecule is governed by the torsion angles C2—C1—C7—C8 and C6—C1—C13—C14, and the dihedral angle between rings C7—C12 and C13—C18. In both structures, the host conformations are very similar (Table 3).

The results of the thermal analysis are given in Table 4. The measured and calculated values for the mass loss are in excellent agreement, confirming the host-guest ratios and justifying the use of full site-occupancy factors for the guest atoms in the crystallographic refinement. Differential scanning calorimetry showed a single endotherm for guest loss for both compounds, and the onset temperatures occur at values well below the normal boiling points of the guests. This is an indication of relatively weak interactions between host and guest.

The kinetics of thermal decomposition were determined for both compounds by performing a series of isothermal thermogravimetric experiments between 363 and 403 K. For both compounds, the plots of the resultant extent of reaction α versus time are deceleratory and fit the R2 contracting-area model, $kt = [1 - (1 - \alpha)^2]$ (Brown, 1988), over a wide range of α from 0.05 to 0.95. Arrhenius plots of $\ln k$ versus $1/T$, shown in Fig. 5, yield activation energies of 105 (8) kJ mol⁻¹ for (I) and 96 (8) kJ mol⁻¹ for (II).

Experimental

The 4,4'-(cyclohexane-1,1-diyl)diphenol host compound was dissolved in excess amounts of 1:1 (mol/mol) mixtures of ethyl acetate-*o*-chlorophenol, ethyl acetate-*m*-chlorophenol and ethyl acetate-*p*-chlorophenol. The resulting solutions were allowed to stand open at room temperature. Colourless needle-like crystals

appeared after between a few days and a little more than a week. The crystalline products were subjected to thermogravimetry, differential scanning calorimetry and X-ray analysis. The title inclusion compounds (I) and (II) were obtained from their respective mother liquors. *o*-Chlorophenol was not included and the resultant crystals were those of the apohost.

Thermogravimetry and differential scanning calorimetry experiments were performed using a Perkin Elmer PC series System. Programmed analyses were carried out at a heating rate of 10 K min⁻¹ under a dry nitrogen gas purge with a flow rate of 30 ml min⁻¹ over a temperature range from 303 to 553 K.

Compound (I)

Crystal data

C ₁₈ H ₂₀ O ₂ ·C ₆ H ₅ ClO	$\gamma = 101.247 (2)^\circ$
$M_r = 396.89$	$V = 994.89 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.2254 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.7538 (3) \text{ \AA}$	$\mu = 0.22 \text{ mm}^{-1}$
$c = 15.3703 (6) \text{ \AA}$	$T = 183 (2) \text{ K}$
$\alpha = 98.214 (1)^\circ$	$0.18 \times 0.10 \times 0.04 \text{ mm}$
$\beta = 93.370 (1)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	17286 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	3613 independent reflections
$T_{\min} = 0.908, T_{\max} = 0.992$	2527 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
3613 reflections	
263 parameters	
3 restraints	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O2 ⁱ	0.97 (1)	1.72 (1)	2.684 (2)	173 (3)
O2—H2 \cdots O1G	0.97 (1)	1.71 (1)	2.672 (2)	172 (3)
O1G—H1G \cdots O1 ⁱⁱ	0.97 (1)	1.71 (1)	2.681 (2)	172 (3)

Symmetry codes: (i) $x, y + 1, z$; (ii) $x - 1, y - 1, z$.

Compound (II)

Crystal data

C ₁₈ H ₂₀ O ₂ ·C ₆ H ₅ ClO	$\gamma = 105.376 (2)^\circ$
$M_r = 396.89$	$V = 1004.99 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.2593 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.8408 (3) \text{ \AA}$	$\mu = 0.21 \text{ mm}^{-1}$
$c = 15.6476 (6) \text{ \AA}$	$T = 183 (2) \text{ K}$
$\alpha = 99.705 (1)^\circ$	$0.20 \times 0.12 \times 0.08 \text{ mm}$
$\beta = 92.366 (1)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	19130 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	3773 independent reflections
$T_{\min} = 0.913, T_{\max} = 0.983$	2425 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.119$	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
3773 reflections	
263 parameters	
3 restraints	

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O1G ⁱ	0.97 (1)	1.73 (1)	2.695 (2)	170 (2)
O2—H2 \cdots O1 ⁱⁱ	0.96 (1)	1.71 (1)	2.671 (2)	173 (3)
O1G—H1G \cdots O2	0.97 (1)	1.70 (1)	2.665 (2)	174 (2)

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $x, y - 1, z$.

Table 3

Host conformations for (I) and (II) ($^\circ$).

δ is the dihedral angle between rings C7–C12 and C13–C18.

	(I)	(II)
C2—C1—C7—C8	−17.1 (3)	−18.6 (3)
C6—C1—C13—C14	0.9 (3)	3.9 (3)
δ	87.66 (6)	88.01 (6)

Table 4

Results of the thermal analyses.

	(I)	(II)
Host–guest ratio	1:1	1:1
Calculated thermogravimetric mass loss (%)	32.4	32.4
Experimental thermogravimetric mass loss (%)	33.0	33.1
Onset temperature of guest loss (K)	396.55	410.75
Normal boiling point of guest (K)	487.45	493.35

For both structures, the host hydroxyl H atoms and the *m*- and *p*-chlorophenol hydroxyl H atoms were all located in difference electron-density maps and refined with simple bond-length restraints, O—H = 0.98 (1) \AA , and with $U_{\text{iso}}(\text{H})$ values refined independently for (II), but fixed at $1.5U_{\text{iso}}(\text{O})$ for (I) (due to its relatively high thermal motion). The remainder of the H atoms were placed in idealized positions in a riding model, with C—H = 0.95 or 0.99 \AA , and refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: COLLECT (Nonius, 2000); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-SEED (Barbour, 2001) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3095). Services for accessing these data are described at the back of the journal.

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