

Supramolecular structures of 2-chloro-5-methylphenol and 4-chloro-3-methylphenol (chloro- cresol)

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Received 16 May 2003

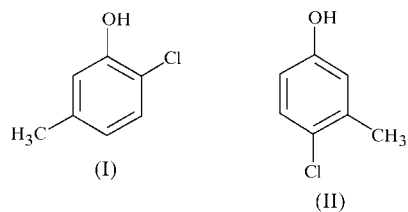
Accepted 5 June 2003

Online 23 August 2003

The crystal structures of the title compounds (both C_7H_7ClO) are characterized by two independent molecules in each of the asymmetric units and feature $O-H\cdots O$, $C-H\cdots\pi$ and $\pi-\pi$ interactions. In addition, intermolecular $C-H\cdots Cl$ and intramolecular $O-H\cdots Cl$ interactions are present in 2-chloro-5-methylphenol. For each crystal, the non-covalent interactions emphasize the different spatial environments for the two independent molecules.

Comment

4-Chloro-3-methylphenol (chlorocresol), (II), is a common antibacterial and antifungal agent that is used widely as a preservative in skin creams (British National Formulary, 2003). It can be detected and quantified by a variety of analytical methods, including high-pressure/high-performance liquid chromatography (Gatti *et al.*, 1997). Neither the crystal structure of (II) nor that of the structural isomer 2-chloro-5-methylphenol, (I), has been reported previously.



There are an increasing number of publications on non-covalent interactions, such as hydrogen bonding (Desiraju, 1996; Jeffrey, 1997; Desiraju & Steiner, 1999), and as the title small aromatic molecules are planar it is the determination of the supramolecular structure that is of interest.

Both compounds crystallize in space group $P2_1/c$, with similar unit-cell volumes, and each compound has two independent molecules in the unit cell. The atomic arrangements in the molecules are shown in Figs. 1 and 2.

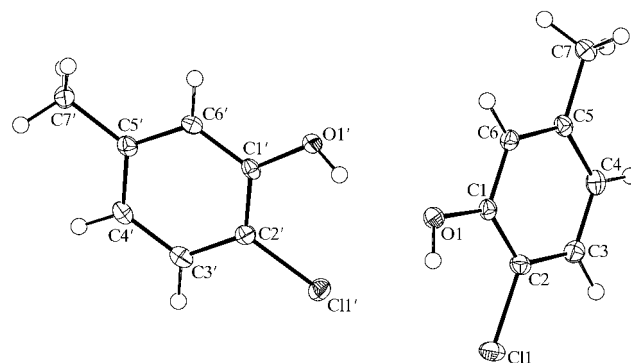


Figure 1

The atomic arrangement in (I). Displacement ellipsoids are shown at the 50% probability level.

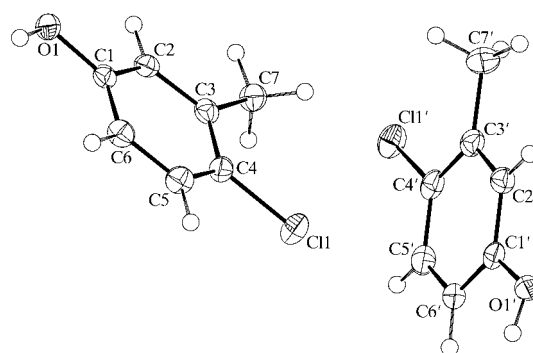


Figure 2

The atomic arrangement in (II). Displacement ellipsoids are shown at the 50% probability level.

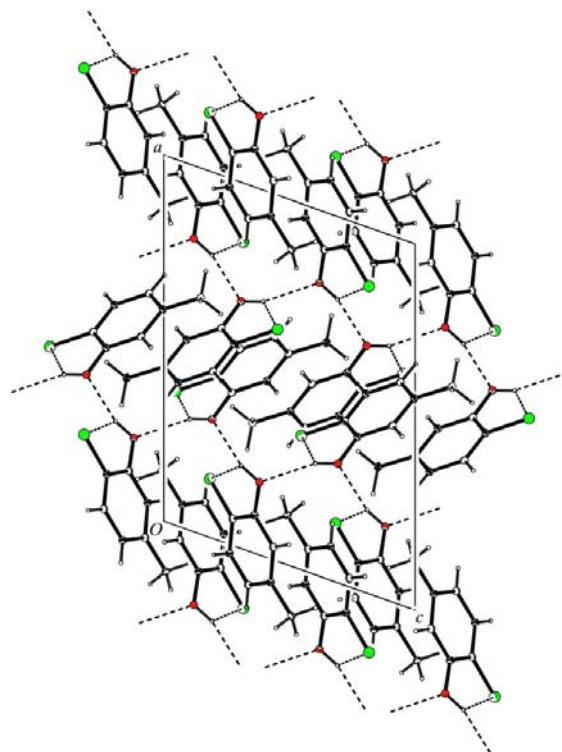


Figure 3

The molecular packing in (I).

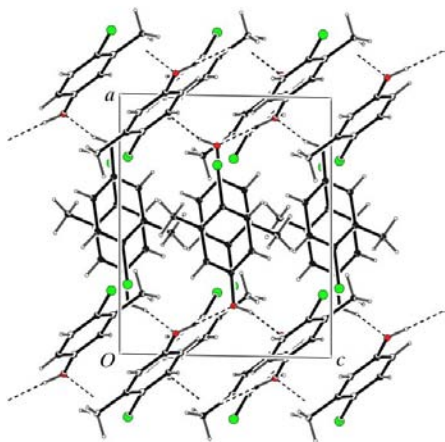


Figure 4
The molecular packing in (II).

Bond lengths, valence angles and torsion angles [Table 1 for (I) and Table 5 for (II)] are as expected for these chloromethylphenols. Very small differences between the geometries of the two independent molecules in each asymmetric unit are ascribed to the differences in non-covalent interactions at each molecule.

In (I), short H···Cl intramolecular and intermolecular attractions (Aullón *et al.*, 1998; Aakeroy *et al.*, 1999; Brammer *et al.*, 2001) are present. An intramolecular O—H···Cl interaction stabilizes the molecular structure (Table 2), and the O—H···Cl—C torsion angles in the two independent molecules are 22 (2) (unprimed atoms) and -23 (2) $^\circ$ (primed atoms). In addition, the displacements of atoms H1 and H1' from the planes of the benzene rings are -0.28 (3) and 0.30 (3) Å, respectively, which demonstrates a conformational difference between the two independent molecules in (I). If this was the only non-covalent interaction associated with the

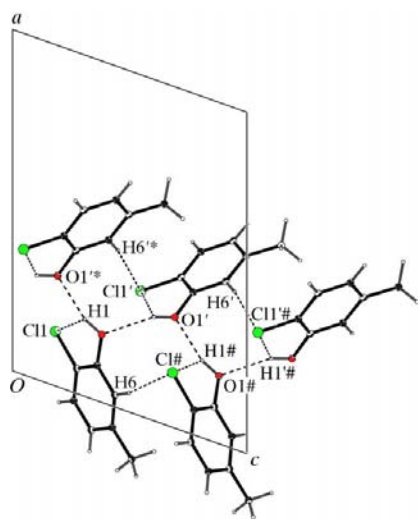


Figure 5
Part of the molecular packing in (I), showing the O—H···O, O—H···Cl and C—H···Cl interactions. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

O atom, the H atoms might be expected to lie in the planes of the benzene rings, pointing towards the $3p_y$ orbital of the Cl atom. There is also only a small indication that the C—O bond is shorter in (I) than in (II), in which there are no O—H···Cl interactions. In addition, weak, but nearly linear, C6—H6···Cl1 and C6'—H6'···Cl1' interactions are present (Table 2).

The shortest Cl···Cl separations in (I) and (II) are 3.573 (2) and 4.775 (1) Å, respectively, while the sum of the van der Waals radii (Bondi, 1964) is 3.50 Å. The role of Cl···Cl contacts in crystal engineering has been discussed previously (Sarma & Desiraju, 1985; Csöregi *et al.*, 2001).

The molecular-packing diagrams of (I) (Fig. 3) and (II) (Fig. 4) show that the molecules pack in a head-to-tail fashion, forming sheets of molecules running parallel to the *c* axis. Classical O—H···O hydrogen bonding is present and the geometric parameters are given in Tables 2 and 6. Figs. 5 and 6 show that in both (I) and (II) the O atom acts as both a donor and an acceptor, and this situation is also observed in the closely related chloroxenol molecule (Cox, 1995), where $Z' = 2$. If the H···Cl contacts in (I) are considered as hydrogen bonds then eight-membered $R_4^4(8)$ rings are formed and bifurcated hydrogen bonding is present at atoms H1 and H1'.

Both supramolecular structures are supported by edge-to-face C—H··· π interactions (also known as T-shaped conformations); the geometric parameters are given in Tables 3 and 7. The differences between the two independent molecules in each crystal are clearly shown. The C—H··· π interactions that involve both molecules in (I) are not identical, while for (II), only one of the two molecules is involved in these interactions.

Aromatic π - π -stacking interactions (Janiak, 2000) are also present in both isomers, as shown in Tables 4 and 8. Fig. 7 shows the stacking of the rings about the centres of symmetry. The interplanar separation between the aromatic rings for the unprimed atoms in (II) is 3.422 (2) Å, but the offset of the ring centres, $Cg1 \cdots Cg1$, is 3.10 Å. Direct overlap is unfavourable and a small offset is desirable, but as this distance is greater than the length of the benzene ring, π - π interactions are absent. Again, this observation shows the differences between the environments of the independent molecules in (II).

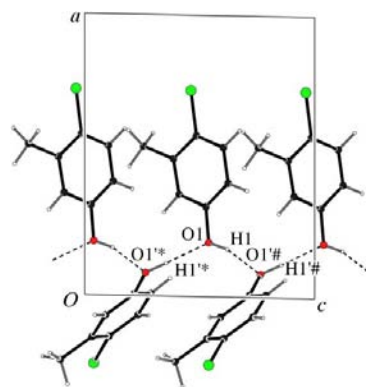


Figure 6
Part of the molecular packing in (II), showing the O—H···O bonding. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x - 1, y, z)$ and $(x - 1, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

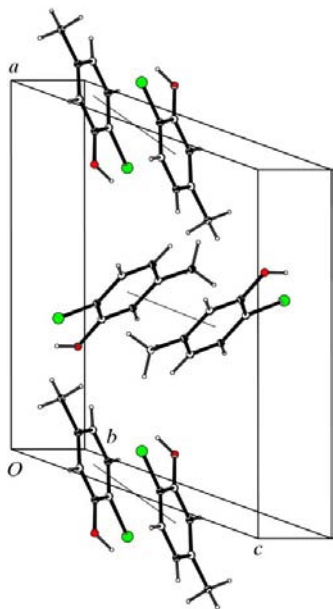


Figure 7
Part of the molecular packing for (I), showing the π - π interactions (thin lines) between molecules stacked across centres of symmetry.

The crystal structure of a complex containing the 4-chloro-3-methylphenol molecule has been published previously (Iimura *et al.*, 1999).

Experimental

Both compounds were purchased from Sigma-Aldrich and were recrystallized from ethanol.

Compound (I)

Crystal data

C_7H_7ClO	$D_x = 1.443 \text{ Mg m}^{-3}$
$M_r = 142.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8054 reflections
$a = 12.951 (3) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 11.430 (2) \text{ \AA}$	$\mu = 0.49 \text{ mm}^{-1}$
$c = 9.4079 (19) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 109.51 (3)^\circ$	Block, colourless
$V = 1312.7 (5) \text{ \AA}^3$	$0.40 \times 0.32 \times 0.26 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD area-detector diffractometer	2998 independent reflections
φ and ω scans to fill Ewald sphere	2571 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$R_{\text{int}} = 0.088$
$T_{\text{min}} = 0.560$, $T_{\text{max}} = 0.882$	$\theta_{\text{max}} = 27.5^\circ$
11 902 measured reflections	$h = -15 \rightarrow 16$
	$k = -14 \rightarrow 14$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 1.6312P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.81 \text{ e \AA}^{-3}$
2998 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
204 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.047 (5)

Table 1
Selected geometric parameters (\AA , $^\circ$) for (I).

C11—C2	1.746 (2)	C11'—C2'	1.743 (2)
O1—C1	1.373 (3)	O1'—C1'	1.375 (3)
C5—C7	1.508 (3)	C5'—C7'	1.507 (3)
O1—C1—C2	124.2 (2)	O1'—C1'—C2'	124.1 (2)
O1—C1—C6	116.7 (2)	O1'—C1'—C6'	116.8 (2)
C1—C2—C11	119.31 (18)	C1'—C2'—C11'	119.26 (18)
O1—C1—C2—C11	0.0 (3)	O1'—C1'—C2'—C11'	−0.5 (3)
C6—C1—C2—C11	−178.57 (16)	C6'—C1'—C2'—C11'	179.16 (17)
C11—C2—C3—C4	178.87 (18)	C11'—C2'—C3'—C4'	−179.81 (18)

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1 \cdots C11	0.88 (2)	2.62 (3)	3.040 (2)	110 (3)
O1'—H1' \cdots C11'	0.81 (3)	2.64 (4)	3.033 (2)	112 (3)
C6—H6 \cdots C11 ⁱ	0.98 (3)	2.86 (3)	3.830 (3)	169 (2)
C6'—H6' \cdots C11' ⁱ	0.97 (3)	2.83 (3)	3.784 (3)	170 (2)
O1—H1 \cdots O1 ⁱⁱⁱ	0.88 (2)	1.99 (2)	2.798 (2)	152 (3)
O1'—H1' \cdots O1	0.81 (3)	2.09 (3)	2.843 (3)	155 (3)

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 3
C—H $\cdots\pi$ interactions (\AA , $^\circ$) for (I).

$Cg1$ and $Cg2$ represent the centres of gravity of the aromatic rings of unprimed and primed atoms, respectively. The symmetry applies to the CgI ($I = 1$ or 2) position.

C—H	CgI	Symmetry code	$H\cdots CgI$	C—H $\cdots CgI$	C $\cdots CgI$
C4—H4	1	$-x, -y, 1 - z$	3.37 (4)	87 (2)	3.453 (3)
C7—H7B	1	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.73	166	3.692 (3)
C7'—H7X	2	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.09	112	3.579 (3)
C7'—H7Z	2	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.15	108	3.579 (3)

Table 4
 π - π interactions (\AA , $^\circ$) for (I).

$Cg1$ and $Cg2$ represent the centres of gravity of the aromatic rings of unprimed and primed atoms, respectively. The symmetry applies to the CgI ($I, J = 1$ or 2) position.

CgI	CgJ	Symmetry code	$Cg\cdots Cg$	Dihedral angle	Interplanar distance	Offset distance
1	1	$-x, -y, 1 - z$	3.941 (2)	0.0	3.387 (2)	2.02
2	2	$1 - x, -y, 2 - z$	3.904 (2)	0.0	3.461 (2)	1.81

Compound (II)

Crystal data

C_7H_7ClO	$D_x = 1.422 \text{ Mg m}^{-3}$
$M_r = 142.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 36 420 reflections
$a = 10.6998 (4) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 14.2926 (5) \text{ \AA}$	$\mu = 0.48 \text{ mm}^{-1}$
$c = 8.7105 (3) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 91.152 (2)^\circ$	Block, colourless
$V = 1331.81 (8) \text{ \AA}^3$	$0.18 \times 0.14 \times 0.10 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD area-detector diffractometer	3003 independent reflections
φ and ω scans to fill Ewald sphere	2032 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$R_{\text{int}} = 0.068$
$T_{\text{min}} = 0.982$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 27.5^\circ$
15 691 measured reflections	$h = -13 \rightarrow 13$
	$k = -18 \rightarrow 18$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
3003 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{\AA}^{-3}$
203 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 5
Selected geometric parameters (\AA , $^\circ$) for (II).

C1—C4	1.744 (2)	C11'—C4'	1.751 (2)
O1—C1	1.379 (2)	O1'—C1'	1.386 (2)
C3—C7	1.497 (3)	C3'—C7'	1.505 (3)
O1—C1—C2	116.79 (18)	C2'—C1'—O1'	116.87 (19)
O1—C1—C6	122.64 (18)	C6'—C1'—O1'	122.19 (19)
C5—C4—C11	119.43 (17)	C5'—C4'—C11'	118.44 (18)
C1—C2—C3—C7	-178.04 (19)	C1'—C2'—C3'—C7'	-179.7 (2)
C7—C3—C4—C11	-1.8 (3)	C7'—C3'—C4'—C11'	-0.5 (3)
C11—C4—C5—C6	-179.58 (17)	C11'—C4'—C5'—C6'	-179.30 (15)

Table 6
Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O1 ⁱⁱⁱ	0.877 (17)	1.854 (19)	2.711 (2)	165 (3)
O1'—H1' \cdots O1' ^{iv}	0.870 (17)	1.846 (18)	2.714 (2)	175 (3)

Symmetry codes: (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 + x, y, z$.

Table 7
C—H $\cdots\pi$ interactions (\AA , $^\circ$) for (II).

$Cg1$ represents the centre of gravity of the aromatic ring of unprimed atoms. The symmetry applies to the $Cg1$ position.

C—H	Symmetry code	$H \cdots Cg1$	C—H $\cdots Cg1$	$C \cdots Cg1$
C6—H6	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.00 (3)	147 (2)	3.823 (3)
C7—H7B	$1 - x, -y, 1 - z$	2.67	141	3.492 (3)

Table 8
 π — π interactions (\AA , $^\circ$) for (II).

$Cg2$ represents the centre of gravity of the aromatic ring of primed atoms. The symmetry applies to the CgJ position.

CgI	CgJ	Symmetry code	$Cg \cdots Cg$	Dihedral angle	Interplanar distance	Offset
2	2	$2 - x, -y, -z$	3.885 (2)	0.0	3.500 (2)	1.69

Non-methyl H atoms were initially placed in calculated positions and thereafter were allowed to refine freely, with independent isotropic displacement parameters. Methyl H atoms were located from difference maps and allowed to ride on their attached atoms (C—H = 0.98 \AA), with independent isotropic displacement parameters.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003).

We thank the EPSRC for use of the National Crystallographic Service at Southampton University (X-ray data collection) and for the use of the Chemical Database Service at Daresbury (Fletcher *et al.*, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1535). Services for accessing these data are described at the back of the journal.

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