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n-Propyl gallate–chloroform (3/0.5)

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n-Propyl gallate (PG) is a charge-control agent used for toners in electrophotography, and shows pseudo-polymorphism. In the asymmetric unit of the title compound, 3 $C_{10}H_{12}O_5 \cdot 0.5CHCl_3$, there are three PG molecules and a half-molecule of chloroform, the solvent molecule being disordered over an inversion centre. There are intra- and intermolecular O—H···O hydrogen bonds, forming a two-dimensional hydrogen-bond network in the (421) plane.

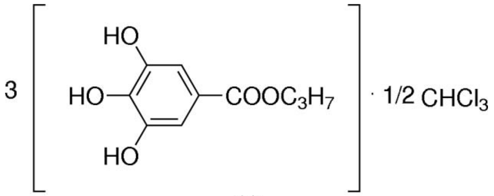
Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.063
wR factor = 0.201
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

PG is widely used as a charge-control agent (CCA) of the negative type for toners in electrophotograpy, as well as the colour former of leuco dyes, where the acidic nature of PG, due to the phenolic OH group, plays an important role (Suganami *et al.*, 2002). At first sight, the acidity of PG appears to be three times stronger than that of phenol because there are three hydroxyl groups in PG. However, it is often pointed out that the effective acidity appears considerably less in the solid state (Mizuguchi *et al.*, 2004). For this reason, the structure analysis of PG has been undertaken in order to gain more insight into its acidic nature from the standpoint of the crystal structure. The structure of PG dihydrate has already been investigated by Okabe & Kyoyama (2002) from a biological viewpoint. There are intra- and intermolecular O—H···O hydrogen bonds, forming a sheet-like hydrogen-bond network. Recently, we have isolated three kinds of solvated PG crystals, namely the title compound, (I), 3PG·0.5chloroform, compound (II), 3PG·0.5dichloromethane, and compound (III), 2PG·acetonitrile. In the present paper, the structure of (I) is reported. The structures of (II) (Hitachi *et al.*, 2005) and (III) (Mizuguchi *et al.*, 2005) will be reported in sequence, following this paper. Compounds (I) and (II) are isostructural.



(I)

Fig. 1 shows an *ORTEP* plot (Burnett & Johnson, 1996) of (I). There are three independent PG molecules and a half solvent molecule in the asymmetric unit. All OH groups in all molecules are bent in the same direction as the alkyl chain. In constrast, the bending direction of the OH groups in PG

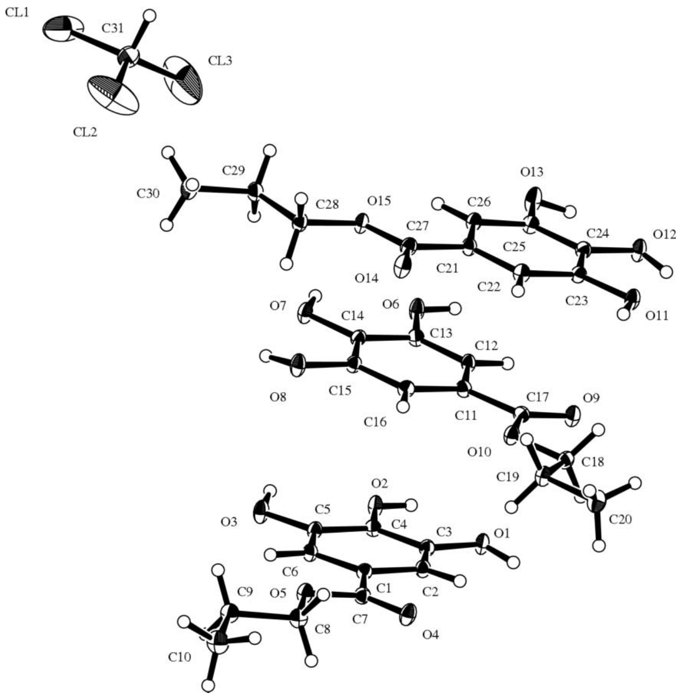


Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids. The solvent molecule is disordered around an inversion centre (occupancy 50%).

dihydrate is opposite to that of the alkyl chain (Okabe & Kyoyama, 2002).

There are two O—H···O intramolecular hydrogen bonds in each molecule, between one OH group and the O atom of another (Table 2), *e.g.* O13—H13O···O12 and O12—H12O···O11. There are also intermolecular O—H···O hydrogen bonds, as shown in Fig. 2. The pairs of symmetry-related molecules, as grouped by each brace, are dimerized in order to cancel the dipole moment of each molecule. On the other hand, if we draw six molecules surrounding the solvent molecule, this gives an interesting picture, as illustrated in Fig. 3, showing that the hydrophobic alkyl chains face the hydrophobic solvent molecule. All molecules are entirely planar (excluding alkyl H atoms), and they form a sheet-like layered structure in the (421) plane, as found in PG dihydrate.

It should also be mentioned that short intermolecular H···H contacts of less than 2.4 Å are found, as shown in Fig. 2, between atoms H12 and H12* [2.08 Å; symmetry codes (x, y, z) and ($-x$, $-y$, $2-z$), respectively], H22 and H22* [2.10 Å; symmetry codes ($1-x$, $1-y$, $1-z$) and ($1+x$, y, z), respectively], and H2 and H2* [2.15 Å; symmetry codes ($-x$, $1-y$, $1-z$) and (x, $1+y$, z), respectively]. This results from two intermolecular O—H···O hydrogen bonds which exist on each side of the H···H contact.

As evident from Fig. 2, the acid strength of the phenolic OH groups in PG appears considerably weakened due to the formation of intra- and intermolelcular O—H···O hydrogen bonds. This explains why the acidity of PG is relatively weak in the solid state, especially when used in toners.

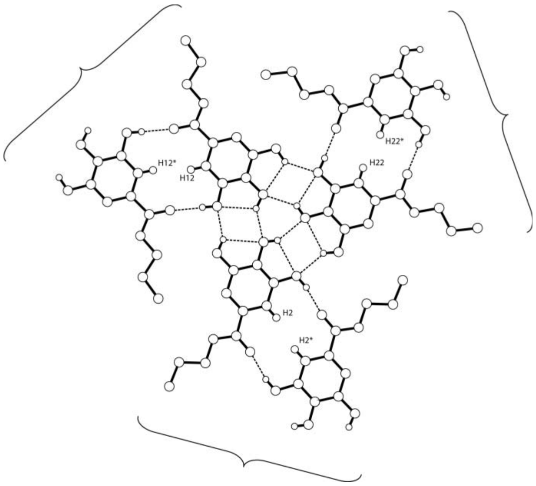


Figure 2
The six molecules involved in the intra- and intermolecular O—H···O hydrogen bonds. The hydrogen bonds are designated by dotted lines.

Experimental

PG was purchased from Kanto Chemicals Ltd. and used without further purification. Single crystals of (I) were grown from a chloroform solution by slow evaporation. After a week, a number of colourless transparent crystals were obtained in the form of blocks.

Crystal data

$3C_{10}H_{12}O_5\cdot0.5CHCl_3$
$M_r = 696.29$
Triclinic, $P\overline{1}$
$a = 9.9393$ (11) Å
$b = 12.7780$ (14) Å
$c = 13.9890$ (15) Å
$\alpha = 64.306$ (8)°
$\beta = 80.219$ (9)°
$\gamma = 87.010$ (9)°
$V = 1577.3$ (3) Å^3

$Z = 2$
$D_x = 1.466$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 13339 reflections
$\theta = 3.6$–68.2°
$\mu = 2.12$ mm^{-1}
$T = 93.1$ K
Block, colourless
0.50 × 0.50 × 0.50 mm

Data collection

Rigaku R-AXIS RAPID-F imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.339$, $T_{\max} = 0.347$
14658 measured reflections

5231 independent reflections
4533 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 68.2°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
$R = 0.063$
$wR = 0.201$
$S = 1.43$
5231 reflections
480 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + \{0.05[\max(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -0.94$ e Å^{-3}

Table 1
Selected bond lengths (Å, °).

O1—C3	1.367 (2)	O8—C15	1.367 (2)
O2—C4	1.365 (2)	O11—C23	1.372 (2)
O3—C5	1.364 (2)	O12—C24	1.371 (2)
O6—C13	1.374 (2)	O13—C25	1.366 (2)
O7—C14	1.373 (2)		

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O4^{i}	0.87	1.89	2.741 (2)	167
O2—H2O···O1	0.81	2.32	2.719 (2)	111
O2—H2O···O12^{ii}	0.81	2.09	2.809 (2)	148
O3—H3O···O2	0.89	2.33	2.753 (2)	109
O3—H3O···O6^{iii}	0.89	1.98	2.763 (2)	147
O6—H6O···O9^{ii}	0.85	1.88	2.729 (2)	177
O7—H7O···O2^{iii}	0.92	2.01	2.787 (2)	142
O7—H7O···O6	0.92	2.24	2.728 (2)	112
O8—H8O···O7	0.91	2.31	2.756 (2)	110
O8—H8O···O11^{iv}	0.91	2.02	2.777 (2)	140
O11—H11O···O14^{v}	0.91	1.85	2.742 (2)	166
O12—H12O···O7^{vi}	0.86	2.06	2.775 (2)	140
O12—H12O···O11	0.86	2.27	2.726 (2)	113
O13—H13O···O1^{ii}	0.90	2.07	2.794 (2)	138
O13—H13O···O12	0.90	2.29	2.753 (2)	112

Symmetry codes: (i) $-x, -y, 2-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $1+x, y, z$; (v) $-x, -y, 1-z$; (vi) $x-1, y, z$.

H atoms attached to O atoms were found in difference density maps and fixed during the least-squares refinement, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O). All other H atoms were positioned geometrically and included in a riding-model approximation, with C—H = 0.95 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The chloroform molecule is disordered over two possible sites around an inversion centre, each with occupancy 0.5.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2005).

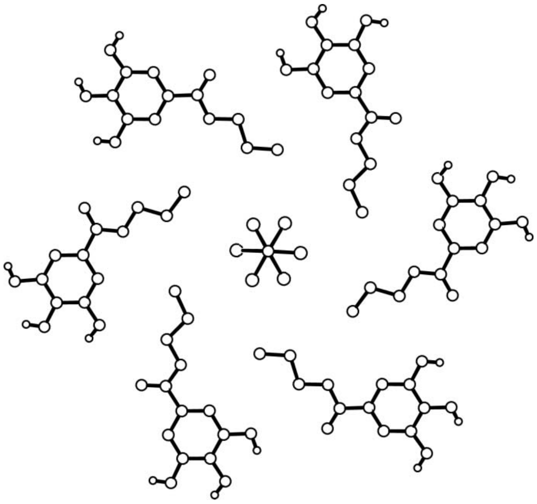

Figure 3
The six molecules which surround a disordered chloroform molecule. H atoms bonded to C atoms have been omitted for clarity.

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