

## Allyl 4-hydroxybenzoate

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## Key indicators

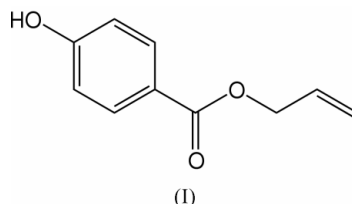
Single-crystal X-ray study  
T = 296 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
Disorder in main residue  
R factor = 0.052  
wR factor = 0.151  
Data-to-parameter ratio = 12.7

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

The crystal structure of the title compound,  $\text{C}_{10}\text{H}_{10}\text{O}_3$ , has two independent molecules in the asymmetric unit. In one of these molecules, the allyl group is disordered as a consequence of a degree of free rotation of *ca*  $15^\circ$  around the C—C  $\sigma$  bond of the allyl group.

## Comment

We are currently interested in the synthesis of allyl monomers (López-V *et al.*, 1995; López-V *et al.*, 1997). Some of them are potential precursors for organic glasses, like CR-39, which is used in the optical industry, or glass-like plastics (Dowbenko, 2003). Other allyl monomers (Schildknecht, 1973) deserve commercial interest as crosslinking agents, or as heat-resistant materials. Nowadays, various studies are carried out on allyl monomers due to their peculiar properties (Matsumoto *et al.*, 2000). The title compound, (I), is one of these compounds, including two functionalities, *viz.* hydroxy and allyl groups (Kusanagi *et al.*, 1977; Takahashi *et al.*, 1978). Because of the hydroxy group, (I) can easily be functionalized, to obtain multiallyl monomers (López-V & Herrera, 2003).

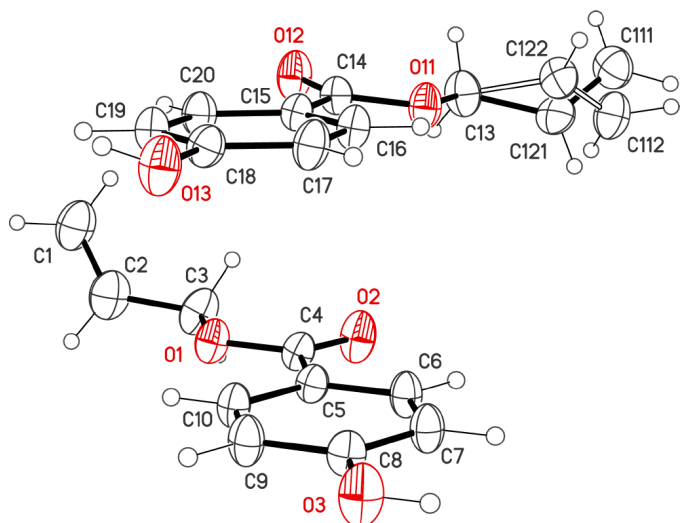


The title compound was synthesized by a classical condensation reaction (see *Experimental*) and its X-ray structure determined (Fig. 1 and Table 1). The asymmetric unit contains two independent molecules, one of which possesses an allyl group disordered over two positions. The 4-hydroxybenzoate moiety displays the expected planar geometry, very close to that reported for methyl and ethyl *p*-hydroxybenzoate (Xianti, 1983, 1986). The allyl moiety is mainly characterized by the non-conjugated  $\pi$  bond, C1=C2 (corresponding bonds for the disordered molecule: C111=C121 and C112=C122) with bond lengths in the range 1.280 (4) to 1.32 (3)  $\text{\AA}$ . The disorder in one molecule arises from a degree of free rotation around the  $\sigma$  bonds C2—C3 (corresponding bonds in the second molecule: C121—C13 and C122—C13) and C3—O1 (corresponding bond in the second molecule: C13—O11). This flexibility is reflected in the following torsion angles: the absolute value for  $\tau_1 = \text{C1}=\text{C2}-\text{C3}-\text{O1}$  and corresponding angles in the second molecule span the range 121.8 (3) to 136.7 (18) $^\circ$ ; the absolute value for  $\tau_2 = \text{C2}-\text{C3}-\text{O1}-\text{C4}$  and corresponding angles in the second molecule are in the range

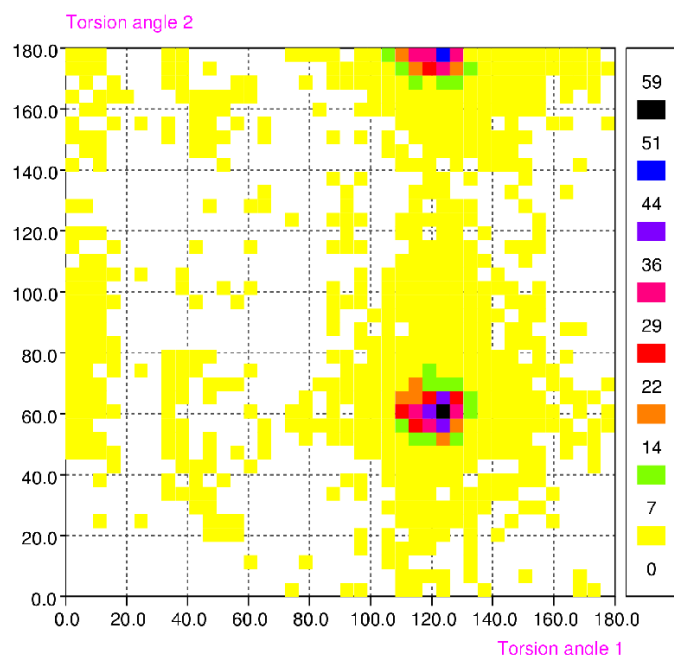
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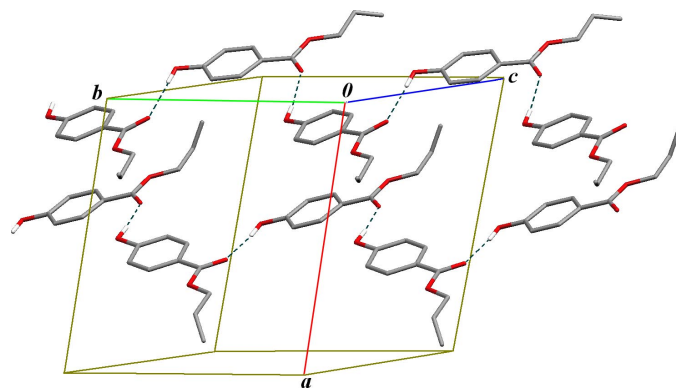


**Figure 1**  
The structure of the asymmetric unit of (I), with displacement ellipsoids drawn at the 25% probability level. Disordered components for the allyl group in the top molecule are displayed using different bond styles.



**Figure 2**  
 $\tau_1$ - $\tau_2$  correlation diagram (Allen & Motherwell, 2002) for 821 X-ray structures [CSD Version 5.24 updated April 2003 (Allen, 2002)], including an  $X-Y-CH_2-CH=CH_2$  fragment, where  $X$  and  $Y$  are any atom.  $\tau_1$  is the absolute value of torsion angle  $CH_2=CH-CH_2-Y$  while  $\tau_2$  corresponds to the absolute value of  $CH-CH_2-Y-X$ . The conformation adopted by (I) is close to the maximum at  $\tau_1, \tau_2 = 120, 180^\circ$ .

160.8 (8)–174.6 (8)°. In other words, the torsional flexibility of the allyl moiety in (I) is *ca* 15°. This conformation adopted by the allyl ester group in (I) is not uncommon and is consistent with numerous reported structures, including a  $X-Y-CH_2-CH=CH_2$  fragment, where  $X$  and  $Y$  are any atom (Fig. 2). At room temperature, this fluxional behaviour is probably retained in solution, in agreement with the  $^1H$  NMR data (see



**Figure 3**  
The hydrogen-bonding scheme observed in (I). H atoms not involved in the network have been omitted for clarity, as has the C112/C122 disordered component of the allyl group. The bottom chain is based on C1-containing molecules, while the top chain is formed using C111-containing molecules.

*Experimental*): for the five allyl protons, multiplets are observed rather than an *AMX* pattern expected for an allyl group with hindered rotation about its  $\sigma$  bonds. As expected, the hydroxy and carbonyl groups in (I) are involved in a hydrogen-bonding network (Table 2) through classical  $C=O \cdots H-O$  bonds. Each independent molecule forms independent one-dimensional chains running along the  $b$  axis (Fig. 3). Significant  $\pi$ - $\pi$  interactions between the benzene rings are avoided by steric hindrance of the allyl moieties, resulting in well separated chains without stacking interactions in the crystal.

## Experimental

The title compound was synthesized by heating, at reflux for 24 h, a solution of 4-hydroxybenzoic acid (2 g, 15 mmol) and sulfuric acid (5 drops) in a large excess of allyl alcohol. After cooling, the excess of allyl alcohol was distilled under reduced pressure. The remaining solid was washed with a 5%  $NaHCO_3$  solution, then with water, and finally recrystallized from ethanol/water (2:3), giving 2.26 g (12 mmol, 88% yield) of colorless thin crystals, m.p. 370 K. Analysis: found C 67.3%, H 5.7%, O 27.0%. Calcd. for  $C_{10}H_{10}O_3$ : C 67.4%, H 5.7%, O 26.9%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ,  $\delta$ , p.p.m. relative to TMS): 4.80 (*m*,  $J = 5.6, 2.8$  Hz, 2H, O- $CH_2$ ), 5.27 (*m*,  $J = 2.8, 1.6$  Hz, 1H,  $C=CH_2$ ), 5.42 (*m*,  $J = 2.8, 1.6$  Hz, 1H,  $C=CH_2$ ), 6.04 (*m*,  $J = 5.6, 5.5$  Hz, 1H,  $CH_2=C-H$ ), 6.61 (*s*, 1H, OH), 6.88 (*d*,  $J = 8.8$  Hz, 2H, Ph), 7.99 (*d*,  $J = 8.8$  Hz, 2H, Ph).

## Crystal data

$C_{10}H_{10}O_3$	$D_x = 1.287$ Mg $m^{-3}$
$M_r = 178.18$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 78 reflections
$a = 12.6682$ (12) Å	$\theta = 4.7$ – $12.4^\circ$
$b = 13.2891$ (10) Å	$\mu = 0.10$ mm $^{-1}$
$c = 11.5196$ (10) Å	$T = 296$ (1) K
$\beta = 108.450$ (7)°	Irregular, colorless
$V = 1839.6$ (3) Å $^3$	0.40 × 0.40 × 0.22 mm
$Z = 8$	

Data collection

Bruker P4 diffractometer	$\theta_{\max} = 25.0^\circ$
$\omega$ scans	$h = -14 \rightarrow 15$
Absorption correction: none	$k = -15 \rightarrow 1$
5486 measured reflections	$l = -13 \rightarrow 5$
3231 independent reflections	3 standard reflections
1854 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.023$	intensity decay: 1%

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.089P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.151$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
3231 reflections	$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
255 parameters	Extinction correction:
H-atom parameters constrained	<i>SHELXTL-Plus</i>
	Extinction coefficient: 0.0063 (14)

**Table 1**  
Selected geometric parameters (Å).

O1—C4	1.328 (3)	O11—C13	1.456 (3)
O1—C3	1.460 (3)	O12—C14	1.215 (3)
O2—C4	1.214 (3)	O13—C18	1.360 (3)
O3—C8	1.358 (3)	C111—C121	1.32 (3)
C1—C2	1.280 (4)	C121—C13	1.469 (15)
C2—C3	1.420 (4)	C112—C122	1.28 (3)
C4—C5	1.473 (3)	C122—C13	1.506 (15)
O11—C14	1.334 (3)	C14—C15	1.467 (3)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3 $\cdots$ O2 <sup>i</sup>	0.84	1.88	2.716 (2)	171
O13—H13 $\cdots$ O12 <sup>ii</sup>	0.77	2.00	2.763 (2)	173

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

Atoms C111 and C121 were found to be disordered with, respectively, C112 and C122. Site-occupancy factors (SOFs) were refined in two parts, with the sum of the SOFs for the two disordered components constrained to 1, and converged to 0.50 (2). H atoms for the hydroxyl groups, H3 and H13, were found in difference maps, while other H atoms were placed at idealized positions. All H atoms were treated as riding atoms, with C—H distances constrained to 0.93 (aromatic CH, allyl CH and CH<sub>2</sub>) or 0.97 Å (methylene CH<sub>2</sub>), and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent C})$ . Hydroxyl groups were constrained using O—H distances determined from difference maps and  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{parent O})$ .

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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