

## Benzyl 2,6-dihydroxy-3-nitrobenzoate

Vijayakumar N. Sonar,<sup>a</sup> M. Venkatraj,<sup>a</sup> Sean Parkin<sup>b</sup> and Peter A. Crooks<sup>a\*</sup>

<sup>a</sup>Department of Pharmaceutical Sciences, College of Pharmacy, University of Kentucky, Lexington, KY 40536, USA, and <sup>b</sup>Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA

Correspondence e-mail: pccrooks@email.uky.edu

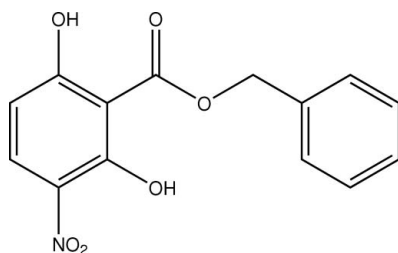
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Key indicators: single-crystal X-ray study;  $T = 90$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.041;  $wR$  factor = 0.114; data-to-parameter ratio = 14.5.

Crystals of the title compound,  $\text{C}_{14}\text{H}_{11}\text{NO}_6$ , were obtained by the reaction of benzyl 2,6-dihydroxybenzoate with nitric acid and crystallization of the product from ethyl acetate. In the molecule, the nitro group is essentially coplanar with the attached benzene ring [ $\text{O}-\text{N}-\text{C}-\text{C} = 176.75$  ( $11^\circ$ )], indicating conjugation with the  $\pi$ -electron system. The benzyloxy group of the ester group is *cis* with respect to the 2-hydroxy group. The crystal structure is stabilized by intra- and intermolecular hydrogen bonds. The 2-hydroxy group forms an intramolecular hydrogen bond with the nitro group, and the 6-hydroxy group forms an intramolecular hydrogen bond with the ester carbonyl function. In addition, there is intermolecular hydrogen bonding between the 2-hydroxy group of one molecule and the O atom of the 6-hydroxy group of another molecule.

### Related literature

For related literature, see: Herrmann (1989); Rushcig *et al.* (1973). For standard bond-length data, see: Allen *et al.* (1987).



### Experimental

#### Crystal data

$\text{C}_{14}\text{H}_{11}\text{NO}_6$   
 $M_r = 289.24$

Monoclinic,  $P2_1/c$   
 $a = 10.0050$  (3) Å

$b = 6.1633$  (2) Å  
 $c = 20.1048$  (6) Å  
 $\beta = 97.5817$  ( $12^\circ$ )  
 $V = 1228.90$  (7) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.12$  mm<sup>-1</sup>  
 $T = 90.0$  (2) K  
 $0.30 \times 0.25 \times 0.08$  mm

#### Data collection

Bruker Nonius KappaCCD area-detector diffractometer  
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.964$ ,  $T_{\max} = 0.990$

5320 measured reflections  
2791 independent reflections  
2280 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.017$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.114$   
 $S = 1.03$   
2791 reflections

192 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{O1}$	0.84	1.81	2.5478 (12)	145
$\text{O3}-\text{H3}\cdots\text{N1}$	0.84	2.42	2.8703 (14)	114
$\text{O3}-\text{H3}\cdots\text{O1}^{\dagger}$	0.84	2.56	3.2469 (13)	139
$\text{O4}-\text{H4}\cdots\text{O5}$	0.84	1.75	2.5034 (13)	148

Symmetry code: (i)  $-x, -y - 1, -z + 1$ .

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2412).

### References

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**supplementary materials**

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## Benzyl 2,6-dihydroxy-3-nitrobenzoate

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### Comment

Phenolic acids are widely distributed in plants and they have been the subject of a great number of chemical, biological, agricultural, and medicinal studies (Herrmann, 1989). Hydroxybenzoic acids occur in food plants as esters or glycosides conjugated with other natural compounds such as flavonoids, alcohols, hydroxfatty acids, sterols, and glucosides. The alkyl esters of *p*-hydroxybenzoic acids are used extensively in the preservation of pharmaceuticals, because they are relatively nonirritating and nontoxic and offer good antimicrobial coverage. 2,6-Dihydroxybenzoic acid derivatives are known to exhibit anthelmintic activity, especially the 3-nitro analogue (Rushcig *et al.*, 1973). In view of the biological activity associated with hydroxybenzoic acids, we have undertaken the synthesis of benzyl 2,6-dihydroxy-3-nitrobenzoate. In order to confirm the position of attachment of nitro group on the phenyl ring and to obtain more detailed information on the structural conformation of the molecule, its X-ray structure determination has been carried out.

X-ray crystallography confirmed the molecular structure and atom connectivity as illustrated in Fig. 1. In the title molecule the nitro group shows normal geometrical parameters. The torsion angles [O1—N1—C1—C6 =  $-176.75$  (11) and O2—N1—C1—C2 =  $-177.50$  (11) Å] indicate that there is not much deviation of nitro group plane from the plane of phenyl ring, facilitating conjugation with  $\pi$  electrons of the phenyl ring. Furthermore, the observed length of the N1—C1 bond [1.4329 (16) Å] is shorter than the theoretical length for a C<sub>ar</sub>—NO<sub>2</sub> bond of [1.468 (14) Å; Allen *et al.*, 1987], which indicates the formation of a conjugated  $\pi$ -electron system along this bond. There is an asymmetry of the exocyclic angles at C1, C2, C3, C4, and C9 atoms.

The mode of packing of the title compound along the *b* direction is illustrated in Fig. 2. In addition to O—H $\cdots$ O intra and intermolecular hydrogen bonding and C—H $\cdots$ O interactions contribute to the stabilization of the crystal structure.

### Experimental

The title compound was prepared by nitration of benzyl 2,6-dihydroxybenzoate and recrystallization of the resultant product from ethyl acetate afforded pale yellow coloured crystals. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, p.p.m.):  $\delta$  5.31 (s, 2H), 6.57 (d, 1H), 7.32–7.44 (m, 5H), 8.03 (d, 1H), 10.95(s, 1H), 11.70 (s, 1H).

### Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 0.95 Å (C<sub>ar</sub>—H), 0.99 Å (CH<sub>2</sub>) and 0.84 Å (O—H). *U*<sub>iso</sub>(H) values were set to 1.5*U*<sub>eq</sub>(OH only) or 1.2*U*<sub>eq</sub> of the attached atom.

## Figures

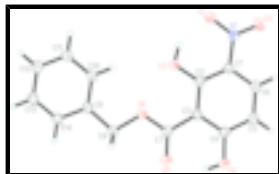


Fig. 1. A view of the title molecule, with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

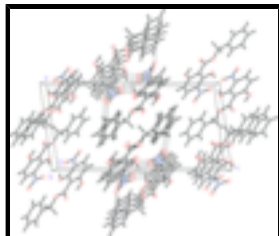


Fig. 2. The packing diagram of the title compound, viewed down the *b* axis; showing the hydrogen-bonding interactions (dashed lines).

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### Crystal data

$C_{14}H_{11}NO_6$

$M_r = 289.24$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 10.0050\ (3)\ \text{\AA}$

$b = 6.1633\ (2)\ \text{\AA}$

$c = 20.1048\ (6)\ \text{\AA}$

$\beta = 97.5817\ (12)^\circ$

$V = 1228.90\ (7)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 600$

$D_x = 1.563\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3037 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 90.0\ (2)\ \text{K}$

Cut plate, pale yellow

$0.30 \times 0.25 \times 0.08\ \text{mm}$

### Data collection

Bruker Nonius KappaCCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution:  $18\ \text{pixels mm}^{-1}$

$T = 90.0\ (2)\ \text{K}$

$\omega$  scans at fixed  $\chi = 55^\circ$

Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)

$T_{\min} = 0.964$ ,  $T_{\max} = 0.990$

5320 measured reflections

2791 independent reflections

2280 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -12 \rightarrow 12$

$k = -7 \rightarrow 7$

$l = -26 \rightarrow 25$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.114$	$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.3636P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2791 reflections	$(\Delta/\sigma)_{\max} < 0.001$
192 parameters	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	-0.10725 (11)	-0.29419 (18)	0.39249 (5)	0.0213 (2)
O1	-0.06977 (9)	-0.40479 (15)	0.44407 (4)	0.0240 (2)
O2	-0.20301 (10)	-0.35119 (16)	0.35140 (5)	0.0287 (2)
O3	0.12549 (9)	-0.14652 (14)	0.47955 (4)	0.0217 (2)
H3	0.0773	-0.2569	0.4824	0.033*
O4	0.13652 (10)	0.48223 (15)	0.34164 (5)	0.0245 (2)
H4	0.2018	0.5127	0.3708	0.037*
O5	0.30779 (9)	0.43345 (15)	0.44313 (5)	0.0252 (2)
O6	0.31031 (9)	0.13490 (15)	0.50629 (4)	0.0209 (2)
C1	-0.03792 (12)	-0.0967 (2)	0.38146 (6)	0.0194 (3)
C2	0.07555 (12)	-0.0302 (2)	0.42602 (6)	0.0180 (3)
C3	0.13804 (12)	0.1685 (2)	0.41310 (6)	0.0186 (3)
C4	0.08403 (13)	0.2913 (2)	0.35642 (6)	0.0202 (3)
C5	-0.02761 (13)	0.2183 (2)	0.31257 (6)	0.0227 (3)
H5	-0.0613	0.3018	0.2743	0.027*
C6	-0.08734 (13)	0.0270 (2)	0.32527 (6)	0.0218 (3)
H6	-0.1631	-0.0229	0.2958	0.026*
C7	0.25843 (13)	0.2571 (2)	0.45507 (6)	0.0197 (3)

## supplementary materials

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C8	0.43003 (13)	0.2209 (2)	0.54614 (6)	0.0220 (3)
H8A	0.4099	0.3632	0.5654	0.026*
H8B	0.5027	0.2413	0.5177	0.026*
C9	0.47396 (12)	0.0615 (2)	0.60144 (6)	0.0198 (3)
C10	0.40299 (13)	-0.1265 (2)	0.61159 (6)	0.0232 (3)
H10	0.3224	-0.1593	0.5828	0.028*
C11	0.44938 (14)	-0.2668 (2)	0.66366 (6)	0.0256 (3)
H11	0.4000	-0.3949	0.6703	0.031*
C12	0.56721 (14)	-0.2217 (2)	0.70606 (6)	0.0245 (3)
H12	0.5984	-0.3179	0.7416	0.029*
C13	0.63878 (13)	-0.0346 (2)	0.69588 (7)	0.0251 (3)
H13	0.7198	-0.0026	0.7244	0.030*
C14	0.59223 (13)	0.1064 (2)	0.64395 (6)	0.0246 (3)
H14	0.6416	0.2345	0.6374	0.029*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0200 (5)	0.0208 (6)	0.0230 (5)	-0.0004 (4)	0.0030 (4)	-0.0026 (4)
O1	0.0264 (5)	0.0213 (5)	0.0240 (5)	-0.0030 (4)	0.0022 (4)	0.0032 (4)
O2	0.0254 (5)	0.0280 (5)	0.0306 (5)	-0.0072 (4)	-0.0043 (4)	-0.0016 (4)
O3	0.0225 (5)	0.0179 (5)	0.0237 (4)	-0.0032 (4)	-0.0009 (4)	0.0039 (4)
O4	0.0250 (5)	0.0206 (5)	0.0271 (5)	-0.0031 (4)	0.0005 (4)	0.0054 (4)
O5	0.0258 (5)	0.0209 (5)	0.0282 (5)	-0.0054 (4)	0.0004 (4)	0.0037 (4)
O6	0.0200 (5)	0.0199 (5)	0.0217 (4)	-0.0028 (3)	-0.0021 (3)	0.0014 (4)
C1	0.0193 (6)	0.0175 (6)	0.0217 (6)	0.0001 (5)	0.0043 (5)	-0.0019 (5)
C2	0.0184 (6)	0.0180 (6)	0.0178 (6)	0.0027 (5)	0.0031 (4)	-0.0011 (5)
C3	0.0178 (6)	0.0186 (6)	0.0197 (6)	0.0001 (5)	0.0030 (5)	-0.0006 (5)
C4	0.0205 (6)	0.0184 (6)	0.0223 (6)	0.0017 (5)	0.0053 (5)	0.0006 (5)
C5	0.0229 (6)	0.0237 (7)	0.0210 (6)	0.0022 (5)	0.0010 (5)	0.0025 (5)
C6	0.0195 (6)	0.0245 (7)	0.0208 (6)	0.0013 (5)	0.0009 (5)	-0.0024 (5)
C7	0.0205 (6)	0.0189 (6)	0.0201 (6)	0.0014 (5)	0.0040 (5)	-0.0003 (5)
C8	0.0202 (6)	0.0221 (6)	0.0229 (6)	-0.0044 (5)	-0.0005 (5)	-0.0007 (5)
C9	0.0188 (6)	0.0220 (7)	0.0189 (6)	-0.0005 (5)	0.0031 (5)	-0.0023 (5)
C10	0.0212 (6)	0.0243 (7)	0.0233 (6)	-0.0039 (5)	-0.0002 (5)	-0.0015 (5)
C11	0.0274 (7)	0.0232 (7)	0.0257 (7)	-0.0043 (5)	0.0017 (5)	0.0007 (5)
C12	0.0246 (7)	0.0268 (7)	0.0218 (6)	0.0028 (5)	0.0015 (5)	0.0019 (5)
C13	0.0182 (6)	0.0334 (8)	0.0232 (6)	-0.0016 (5)	0.0001 (5)	-0.0013 (5)
C14	0.0212 (6)	0.0279 (7)	0.0243 (6)	-0.0060 (5)	0.0018 (5)	0.0003 (5)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

N1—O2	1.2308 (14)	C5—H5	0.9500
N1—O1	1.2563 (14)	C6—H6	0.9500
N1—C1	1.4329 (16)	C8—C9	1.5051 (18)
O3—C2	1.3339 (15)	C8—H8A	0.9900
O3—H3	0.8400	C8—H8B	0.9900
O4—C4	1.3381 (15)	C9—C10	1.3879 (18)
O4—H4	0.8400	C9—C14	1.3929 (17)

O5—C7	1.2303 (16)	C10—C11	1.3897 (19)
O6—C7	1.3253 (15)	C10—H10	0.9500
O6—C8	1.4507 (15)	C11—C12	1.3887 (18)
C1—C6	1.3977 (18)	C11—H11	0.9500
C1—C2	1.4109 (17)	C12—C13	1.387 (2)
C2—C3	1.4147 (18)	C12—H12	0.9500
C3—C4	1.4144 (17)	C13—C14	1.3904 (19)
C3—C7	1.4809 (17)	C13—H13	0.9500
C4—C5	1.4026 (18)	C14—H14	0.9500
C5—C6	1.3614 (19)		
O2—N1—O1	121.36 (11)	O6—C7—C3	116.02 (11)
O2—N1—C1	119.24 (11)	O6—C8—C9	107.98 (10)
O1—N1—C1	119.40 (10)	O6—C8—H8A	110.1
C2—O3—H3	109.5	C9—C8—H8A	110.1
C4—O4—H4	109.5	O6—C8—H8B	110.1
C7—O6—C8	115.57 (10)	C9—C8—H8B	110.1
C6—C1—C2	121.62 (12)	H8A—C8—H8B	108.4
C6—C1—N1	117.47 (11)	C10—C9—C14	119.01 (12)
C2—C1—N1	120.91 (11)	C10—C9—C8	123.25 (11)
O3—C2—C1	122.74 (11)	C14—C9—C8	117.73 (11)
O3—C2—C3	119.06 (11)	C9—C10—C11	120.26 (12)
C1—C2—C3	118.20 (11)	C9—C10—H10	119.9
C4—C3—C2	118.69 (11)	C11—C10—H10	119.9
C4—C3—C7	117.21 (11)	C12—C11—C10	120.66 (13)
C2—C3—C7	124.10 (11)	C12—C11—H11	119.7
O4—C4—C5	116.47 (11)	C10—C11—H11	119.7
O4—C4—C3	122.01 (11)	C13—C12—C11	119.27 (12)
C5—C4—C3	121.52 (12)	C13—C12—H12	120.4
C6—C5—C4	119.52 (12)	C11—C12—H12	120.4
C6—C5—H5	120.2	C12—C13—C14	120.13 (12)
C4—C5—H5	120.2	C12—C13—H13	119.9
C5—C6—C1	120.44 (12)	C14—C13—H13	119.9
C5—C6—H6	119.8	C13—C14—C9	120.67 (13)
C1—C6—H6	119.8	C13—C14—H14	119.7
O5—C7—O6	121.84 (11)	C9—C14—H14	119.7
O5—C7—C3	122.14 (11)		
O2—N1—C1—C6	2.73 (17)	C2—C1—C6—C5	-0.95 (19)
O1—N1—C1—C6	-176.75 (11)	N1—C1—C6—C5	178.81 (11)
O2—N1—C1—C2	-177.50 (11)	C8—O6—C7—O5	-1.20 (17)
O1—N1—C1—C2	3.01 (18)	C8—O6—C7—C3	178.63 (10)
C6—C1—C2—O3	-179.24 (11)	C4—C3—C7—O5	2.46 (18)
N1—C1—C2—O3	1.01 (19)	C2—C3—C7—O5	-178.09 (12)
C6—C1—C2—C3	0.95 (18)	C4—C3—C7—O6	-177.38 (10)
N1—C1—C2—C3	-178.81 (11)	C2—C3—C7—O6	2.08 (18)
O3—C2—C3—C4	-179.70 (11)	C7—O6—C8—C9	179.99 (10)
C1—C2—C3—C4	0.12 (17)	O6—C8—C9—C10	-3.07 (17)
O3—C2—C3—C7	0.85 (18)	O6—C8—C9—C14	176.59 (11)
C1—C2—C3—C7	-179.33 (11)	C14—C9—C10—C11	0.3 (2)

## supplementary materials

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C2—C3—C4—O4	178.95 (11)	C8—C9—C10—C11	179.95 (12)
C7—C3—C4—O4	-1.57 (18)	C9—C10—C11—C12	-0.2 (2)
C2—C3—C4—C5	-1.20 (19)	C10—C11—C12—C13	-0.1 (2)
C7—C3—C4—C5	178.28 (11)	C11—C12—C13—C14	0.4 (2)
O4—C4—C5—C6	-178.91 (11)	C12—C13—C14—C9	-0.3 (2)
C3—C4—C5—C6	1.2 (2)	C10—C9—C14—C13	-0.1 (2)
C4—C5—C6—C1	-0.14 (19)	C8—C9—C14—C13	-179.75 (12)

### Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O3—H3 $\cdots$ O1	0.84	1.81	2.5478 (12)	145
O3—H3 $\cdots$ N1	0.84	2.42	2.8703 (14)	114
O3—H3 $\cdots$ O1 <sup>i</sup>	0.84	2.56	3.2469 (13)	139
O4—H4 $\cdots$ O5	0.84	1.75	2.5034 (13)	148

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



Fig. 1

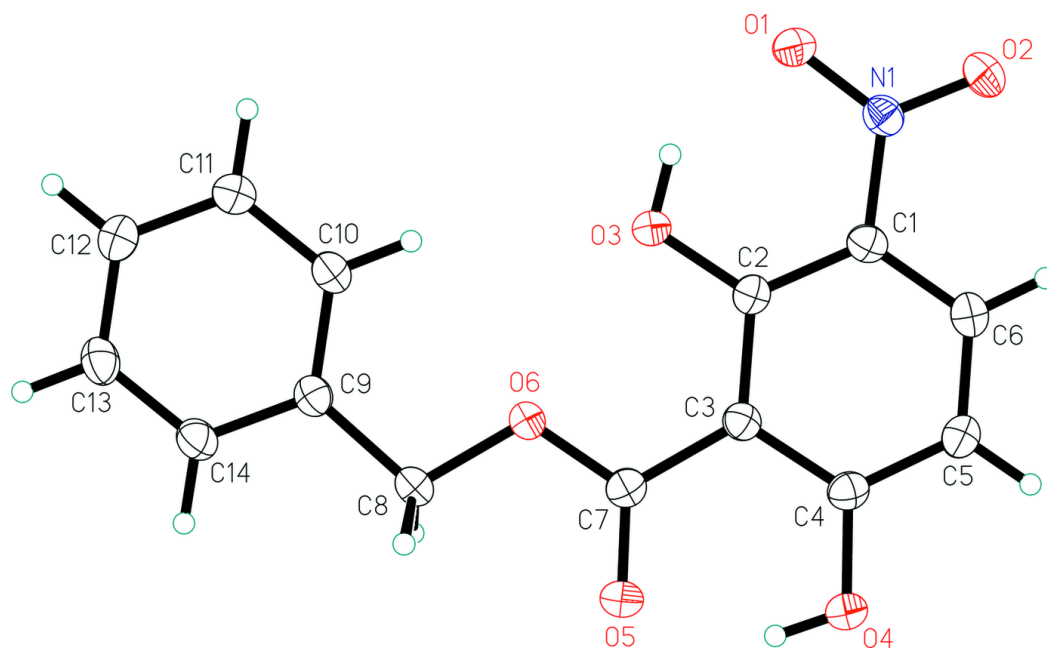


Fig. 2

