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## *p*-Nitrobenzyl Trichloroacetimidate

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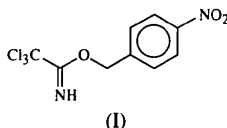
(Received 8 July 1994; accepted 19 September 1994)

### Abstract

The imidate group in the title compound, C<sub>9</sub>H<sub>7</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>3</sub>, is planar and approximately perpendicular to the *p*-nitrobenzyl group. The C=N bond is notably short for a double bond.

### Comment

In connection with our interest in the use of alkyl trichloroacetimidates for the preparation of ethers and esters from alcohols and carboxylic acids, respectively (Armstrong, Brackenridge, Jackson & Kirk, 1988), we have prepared the title compound, (I), by the base-promoted addition of *p*-nitrobenzyl alcohol to trichloroacetonitrile.



Unlike most other trichloroacetimidates (Cramer, Pawelzik & Baldauf, 1958) (the only exception appears to be benzhydryl trichloroacetimidate), the product was

crystalline above ambient temperature (m.p. 356–358K), and the structure was therefore determined crystallographically in order to ascertain the geometry of the imidate group. Other benzyl trichloroacetimidates have been prepared, notably the parent compound (Wessel, Iversen & Bundle, 1985) and also *p*-methoxybenzyl trichloroacetimidate (Nakajima, Horita, Abe & Yone-mitsu, 1988).

A search of the Cambridge Structural Database (Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991) yielded three structures containing acyclic imidate functionalities. Coordinates were not available for two of these (Kolakowski, 1973, 1979), so detailed geometry can not be assessed. For the third structure (Nakano, Yokota, Igarashi & Sato, 1988), the imidate group is essentially planar with bond lengths and angles similar to those observed here. In the present structure, the C<sub>3</sub>NO skeleton of the imidate group has an r.m.s. deviation from planarity of 0.006 Å. This group is approximately perpendicular to the aromatic ring [torsion angle C2—O1—C3—C4 80.3 (2)°], with the nitro substituent essentially in the plane of the ring [O—N—C—C torsion angles –5.5 (3), –6.5 (3), 173.7 (2) and 174.3 (2)°]. The NH group is involved in a weak bifurcated hydrogen bond, intramolecular to C13 [H1···C13 2.52 (5) Å, based on the freely refined position of H1] and intermolecular to O3 of the nitro group of an adjacent molecule [H1···O3(½–x, 1–y, z–½) 2.49 (9) Å], resulting in chains of hydrogen-bonded molecules running parallel to the *c* axis. The C=N bond is notably short for a double bond (typical values are in the range 1.27–1.32 Å), while the C—O bond lengths are typical for esters (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1992).

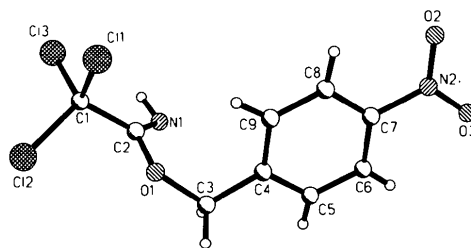


Fig. 1. The molecular structure of the title compound, showing the numbering scheme.

### Experimental

The compound was prepared by slow addition of trichloroacetonitrile to a solution of *p*-nitrobenzyl alcohol in tetrahydrofuran to which sodium hydride (10 mol%) had been added. After complete reaction, the solvent was evaporated and the residue dissolved in ethyl acetate. Filtration and removal of the solvent from the filtrate yielded the title compound (95% yield). A suitable crystal was obtained directly from this evaporation.

## Crystal data

C <sub>9</sub> H <sub>7</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>3</sub>	Mo K $\alpha$ radiation
$M_r = 297.52$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 32 reflections
$P2_12_12_1$	$\theta = 11.57\text{--}12.17^\circ$
$a = 7.0278 (3) \text{ \AA}$	$\mu = 0.764 \text{ mm}^{-1}$
$b = 10.8550 (5) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 15.6339 (7) \text{ \AA}$	Block
$V = 1192.66 (9) \text{ \AA}^3$	$0.52 \times 0.40 \times 0.32 \text{ mm}$
$Z = 4$	Colourless
$D_x = 1.657 \text{ Mg m}^{-3}$	

## Data collection

Stoe Siemens diffractometer	$R_{\text{int}} = 0.0239$
$\omega/\theta$ scans with on-line profile fitting (Clegg, 1981)	$\theta_{\text{max}} = 24.98^\circ$
Absorption correction: none	$h = -8 \rightarrow 8$
3906 measured reflections	$k = -12 \rightarrow 12$
2098 independent reflections	$l = -18 \rightarrow 18$
1992 observed reflections [ $I > 2\sigma(I)$ ]	3 standard reflections
	frequency: 60 min
	intensity decay: none

## Refinement

Refinement on $F^2$	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.0228$	<i>SHELXL93</i> (Sheldrick, 1993)
$wR(F^2) = 0.0623$	Extinction coefficient:
$S = 1.041$	0.0170 (16)
2097 reflections	Atomic scattering factors
183 parameters	from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0320P)^2 + 0.2219P]$	Absolute configuration:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983) parameter,
$(\Delta/\sigma)_{\text{max}} = 0.001$	$x = -0.03 (6)$
$\Delta\rho_{\text{max}} = 0.170 \text{ e \AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.191 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
C11	0.99911 (9)	0.31196 (5)	0.57317 (4)	0.0624 (2)
C12	1.22786 (7)	0.48565 (5)	0.47767 (4)	0.0581 (2)
C13	0.96329 (10)	0.32843 (6)	0.39029 (4)	0.0684 (2)
N1	0.7031 (3)	0.5310 (2)	0.45281 (13)	0.0556 (5)
N2	0.0801 (3)	0.5283 (2)	0.76184 (11)	0.0533 (4)
O1	0.8898 (2)	0.57606 (13)	0.56784 (9)	0.0480 (3)
O2	0.0589 (3)	0.4194 (2)	0.77976 (12)	0.0759 (5)
O3	-0.0354 (3)	0.6082 (2)	0.77958 (12)	0.0718 (5)
C1	1.0016 (3)	0.4134 (2)	0.48483 (12)	0.0438 (4)
C2	0.8467 (3)	0.5116 (2)	0.49717 (11)	0.0410 (4)
C3	0.7617 (3)	0.6749 (2)	0.5893 (2)	0.0516 (5)
C4	0.5844 (3)	0.6314 (2)	0.63425 (12)	0.0416 (4)
C5	0.4401 (3)	0.7166 (2)	0.64829 (14)	0.0476 (5)
C6	0.2749 (3)	0.6847 (2)	0.69002 (13)	0.0478 (5)
C7	0.2555 (3)	0.5647 (2)	0.71759 (11)	0.0429 (4)
C8	0.3950 (3)	0.4779 (2)	0.70470 (13)	0.0497 (5)
C9	0.5609 (3)	0.5125 (2)	0.66406 (14)	0.0503 (5)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C11—C1	1.766 (2)	O1—C3	1.440 (2)
C12—C1	1.777 (2)	C1—C2	1.536 (3)
C13—C1	1.763 (2)	C3—C4	1.506 (3)
N1—C2	1.242 (3)	C4—C9	1.382 (3)
N1—H1	0.89 (3)	C4—C5	1.390 (3)
N2—O3	1.220 (3)	C5—C6	1.377 (3)
N2—O2	1.225 (3)	C6—C7	1.378 (3)
N2—C7	1.468 (3)	C7—C8	1.375 (3)
O1—C2	1.343 (2)	C8—C9	1.379 (3)
C2—N1—H1	113.0 (16)	O1—C2—C1	107.77 (15)
O3—N2—O2	123.6 (2)	O1—C3—C4	113.1 (2)
O3—N2—C7	118.3 (2)	C9—C4—C5	118.8 (2)
O2—N2—C7	118.0 (2)	C9—C4—C3	123.3 (2)
C2—O1—C3	116.0 (2)	C5—C4—C3	117.9 (2)
C2—C1—C13	111.11 (13)	C6—C5—C4	121.5 (2)
C2—C1—C11	109.10 (13)	C5—C6—C7	118.0 (2)
C13—C1—C11	109.16 (10)	C8—C7—C6	122.1 (2)
C2—C1—C12	109.63 (12)	C8—C7—N2	118.9 (2)
C13—C1—C12	108.35 (10)	C6—C7—N2	119.0 (2)
C11—C1—C12	109.47 (11)	C7—C8—C9	118.9 (2)
N1—C2—O1	123.7 (2)	C8—C9—C4	120.7 (2)
N1—C2—C1	128.6 (2)		
N1—C2—C1—C13	3.8 (3)	O3—N2—C7—C8	173.7 (2)
O2—N2—C7—C6	174.3 (2)	C13—C1—C2—N1	3.8 (3)
O3—N2—C7—C6	-6.5 (3)	C1—C2—N1—H1	-3.1 (17)
O2—N2—C7—C8	-5.5 (3)		

The data set consisted of a unique octant of reflections together with their Friedel opposites; the index limits given above are overall and do not indicate a whole sphere of data. H atoms were freely refined with individual isotropic displacement parameters.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**(Z)-12-Hydroxy-14,15-dinorlabda-8(17),11-dien-13-one, C<sub>18</sub>H<sub>28</sub>O<sub>2</sub>**

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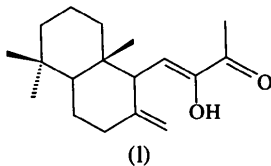
(Received 18 October 1994; accepted 13 December 1994)

**Abstract**

The stereochemistry of the diosphenol moiety of the title compound [alternative systematic name: 4-(decahydro-5,5,8a-trimethyl-2-methylene-1-naphthyl)-3-hydroxy-3-buten-2-one] was confirmed to have the *Z* configuration. The diosphenol moiety is approximately planar with an intramolecular hydrogen bond existing between the alcohol and the keto group.

**Comment**

As part of investigations to prepare potential odorants from labda-8(17),14-dien-13-ol (Grant, Hanton, Lynch, Robinson & Wong, 1994), we isolated a series of stereochemically related diosphenols (Wong, 1990). The crystal structure determination of (*Z*)-12-hydroxy-14,15-dinorlabda-8(17),11-dien-13-one, (1), determined the stereochemistry of these diosphenols to be the *Z* configuration.



In (1), the six-membered rings adopt flattened chair conformations. Me groups C19 and C20 adopt 1,3-diaxial positions and are splayed outwards from the rings by 13(1)°. The diosphenol moiety C9,C11,C12,C13,C16,O1,O2 is approximately planar [average deviation 0.052(6) Å] and makes an angle of

86.7(3)° with the mean plane through all the C atoms of both rings. The planarity is in part facilitated by an intramolecular hydrogen bond: O2...H1 distance 2.102 Å and O1—H1...O2 angle 117.0°. Close intermolecular contacts, which range from 2.412 to 2.780 Å, exist between both O atoms and various alkyl protons.

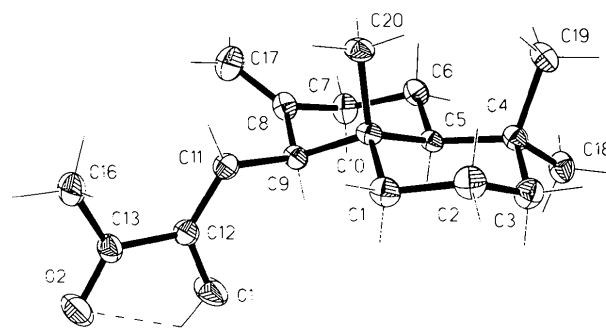


Fig. 1. Molecular structure of (1); displacement ellipsoids are drawn with boundary surfaces at the 50% level (Johnson, 1965).

**Experimental**

14,15-Dinorlabd-8(17)-en-13-one (2.5 g) in 1M <sup>t</sup>BuOK/<sup>t</sup>BuOH (100 ml) was shaken with oxygen until the uptake was complete. Acidification with 2M HCl followed by standard workup procedures and radial chromatography (5% ether/hexane) gave (1) (1.17 g, 44%) (Wong, 1990). Crystals were obtained by slow evaporation from hexane.

*Crystal data*

C<sub>18</sub>H<sub>28</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 276.4  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 7.353(9) Å  
*b* = 10.805(7) Å  
*c* = 9.959(11) Å  
 $\beta$  = 93.2(1)°  
*V* = 790(2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.162 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 12–31°  
 $\mu$  = 0.073 mm<sup>-1</sup>  
*T* = 148(2) K  
 Rectangular plate  
 0.82 × 0.56 × 0.20 mm  
 Colourless

*Data collection*

Nicolet R3m diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 2983 measured reflections  
 2983 independent reflections  
 2361 observed reflections  
 [*I* > 2σ(*I*)]

$\theta_{\max}$  = 32.49°  
*h* = -11 → 11  
*k* = 0 → 16  
*l* = 0 → 15  
 3 standard reflections monitored every 97 reflections  
 intensity decay: 5%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0517  
*wR*(*F*<sup>2</sup>) = 0.1357

$\Delta\rho_{\max}$  = 0.244 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.243 e Å<sup>-3</sup>  
 Extinction correction: none