The Baylis–Hillman adduct of 4-nitrobenzaldehyde and cyclohex-2-en-1-one: 2-[hydroxy(4-nitrophenyl)methyl]-cyclohex-2-en-1-one

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In the title compound, $C_{13}H_{13}NO_4$, the cyclohexene ring has a sofa conformation, with the atom in position 5 of the cyclohex-2-en-1-one moiety displaced by 0.5699 (4) Å from the mean plane of the remaining atoms of the ring. A strong O—H⋯O hydrogen bond links the molecules into infinite chains running along the *b* axis of the crystal. Two weak C—H⋯O interactions involving CH groups of the aromatic ring and O atoms of the nitro or hydroxy group provide further intermolecular links, thus ensuring the formation of a three-dimensional framework in the crystal structure.

Comment

Like many other products of the Baylis–Hillman reaction, *i.e.* the coupling of activated alkenes with carbon electrophiles under the catalysis of tertiary amines, the title compound, (I), represents a useful intermediate in organic syntheses, leading to products having promising applications in biology (Kabat *et al.*, 1996; Kim *et al.*, 2002; Shi & Zhao, 2002; Smith *et al.*, 1980). Although the compound was synthesized and reported a few years ago (Shi *et al.*, 2002; Luo *et al.*, 2002), its crystal structure has not yet been published and is described in the present paper.

(I)
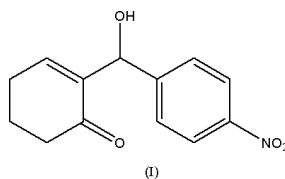
The selected geometric parameters of (I) are listed in Table 1. An ellipsoid plot of the molecule is shown in Fig. 1. Although the molecule contains a chiral atom, C7, the crystal belongs to a centrosymmetric space group and thus represents a racemate.

The cyclohexene ring C1–C6 has a sofa conformation, with atom C5 displaced by 0.5699 (4) Å from the C1/C2/C3/C4/C6 plane. The dihedral angle formed by the plane of the C8–C13
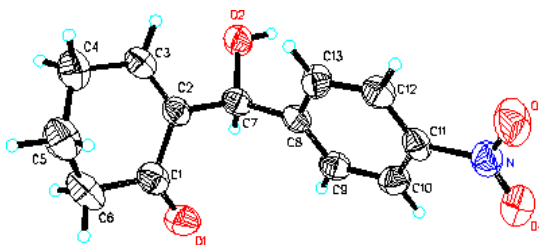

Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

benzene ring and the C1/C2/C3/C4/C6 plane is 70.44 (8)°.

There is one 'active' H atom in the structure which is responsible for the formation of a strong O2—H2···O1^i [symmetry code: (i) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$] hydrogen bond (Table 2), linking the molecules into infinite chains running along the *b* axis of the crystal. There are also two intermolecular and one weak intramolecular C—H···O interactions (Desiraju, 1996; Steiner, 1997). The intermolecular contacts involve the aromatic CH groups, whereas the olefinic H atom of the cyclohexene moiety participates in the intramolecular interaction. One of the intermolecular contacts [C12—H12···O3^{ii}; symmetry code: (ii) $2 - x$, $2 - y$, $2 - z$] involves one of the O atoms of the nitro group and links pairs of molecules into centrosymmetric dimers (Fig. 2) with a cyclic $R_2^2(10)$ pattern (Bernstein *et al.*, 1995). The other weak interaction, [C10—H10···O2^{iii}; symmetry code: (iii) $1 + x$, y, z] involves hydroxy atom O2 as acceptor; it links the molecules into chains along the *a* axis and has a $C(6)$ graph motif. The above mentioned O—H···O hydrogen bond and the two intermolecular C—H···O interactions produce an infinite three-dimensional framework in the crystal structure (Fig. 3).

The C3—H3···O2 intramolecular interaction closes the five-membered pseudo-ring O2—C7—C2—C3—H3 according to the $S(5)$ pattern; similar interactions involving olefinic CH groups were noted in a review of the structures of cinnamic acid derivatives (Pálinkó, 1999).

Experimental

The title compound was synthesized according to a method described in the literature (Shi *et al.*, 2002; Luo *et al.*, 2002) using the Baylis–Hillman reaction. At room temperature, a clear solution of 4-nitrobenzaldehyde (1 mmol), cyclohex-2-en-1-one (2 mmol) and imidazole (1 mmol) in 1.5 ml of tetrahydrofuran was mixed with 1.5 ml of deionized water. The mixture was stirred at ambient temperature for 20 h in order to bring the reaction to completion. The mixture was diluted with 10 ml of water and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure. After the usual work-up, chromatography of the crude product on silica gel, using ethyl acetate and petroleum ether (1:1) as eluant, gave a pure product in 95% yield. This compound (60 mg) was dissolved in ethyl acetate (1 ml) and petroleum ether (2 ml) was added. The solution was left to stand for 1–2 h at room temperature. Colorless crystals suitable for single-crystal X-ray diffraction were collected (m.p. 362 K). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.82–8.20 (*m*, H, ArH and CH), 5.60 (*d*, 1H, *CH), 3.57 (*br s*, 1H, OH), 2.42–2.48 (*m*, 4H, CH$_2$), 1.97–2.08 (*m*, 4H, CH$_2$).

Crystal data

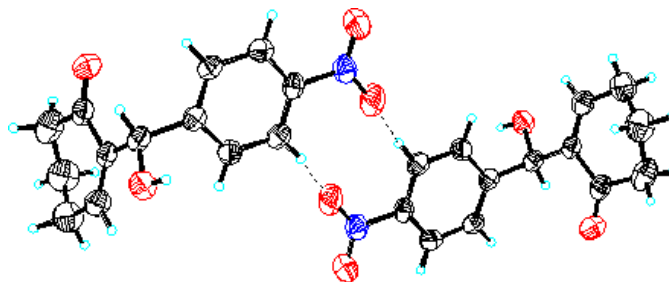|	
C$_{13}$H$_{13}$NO$_4$	$D_x = 1.367$ Mg m^{-3}
$M_r = 247.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6932
$a = 6.7202$ (16) Å	reflections
$b = 10.131$ (3) Å	$\theta = 2.3$–22.2°
$c = 17.813$ (4) Å	$\mu = 0.10$ mm^{-1}
$\beta = 97.884$ (4)°	$T = 298$ (2) K
$V = 1201.2$ (5) Å^3	Pillar, colorless
$Z = 4$	$0.20 \times 0.20 \times 0.10$ mm

Figure 2
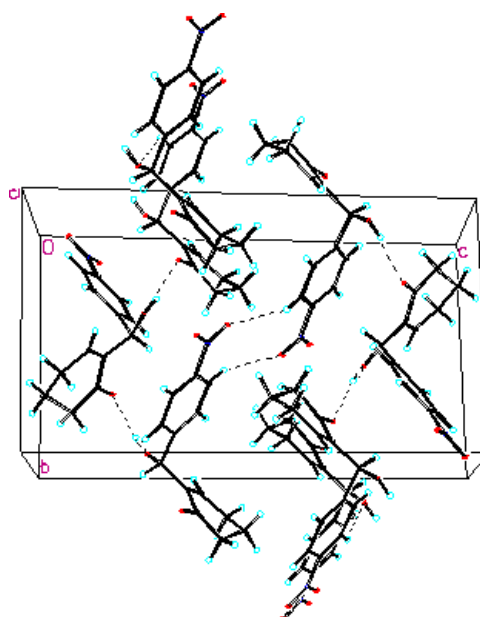Two molecules, related by the inversion centre, linked *via* C—H···O interactions (dashed lines).

Figure 3
A packing diagram of the title compound, viewed approximately along the *a* axis. The O—H···O hydrogen bonds and intermolecular C—H···O interactions are shown as dashed lines.

Data collection

Bruker SMART 1K CCD area-detector diffractometer	2102 independent reflections
	1396 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.087$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
	$h = -7 \rightarrow 7$
$T_{min} = 0.98$, $T_{max} = 0.99$	$k = -11 \rightarrow 12$
5777 measured reflections	$l = -16 \rightarrow 21$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$
$wR(F^2) = 0.146$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2102 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
164 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.214 (3)	C2—C7	1.514 (3)
O2—C7	1.413 (3)	C3—C4	1.491 (3)
C1—C2	1.477 (3)	C4—C5	1.472 (4)
C1—C6	1.510 (4)	C5—C6	1.507 (4)
C2—C3	1.313 (3)	C7—C8	1.532 (3)
O1—C1—C2	121.3 (2)	C3—C4—C5	113.1 (2)
O1—C1—C6	121.7 (2)	C4—C5—C6	111.8 (2)
C2—C1—C6	116.8 (2)	C1—C6—C5	114.2 (2)
C1—C2—C3	119.9 (2)	O2—C7—C2	108.08 (19)
C1—C2—C7	115.9 (2)	O2—C7—C8	111.29 (18)
C3—C2—C7	124.0 (2)	C2—C7—C8	112.12 (19)
C2—C3—C4	125.1 (2)	C7—C8—C9	121.1 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O2—H2$\cdots$O1[i]	0.82	2.02	2.834 (2)	171
C10—H10$\cdots$O2[iii]	0.93	2.51	3.208 (3)	132
C12—H12$\cdots$O3[ii]	0.93	2.53	3.376 (3)	152
C3—H3$\cdots$O2	0.93	2.36	2.722 (3)	103

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $2 - x, 2 - y, 2 - z$; (iii) $1 + x, y, z$.

H atoms were placed in calculated positions and allowed to ride on their parent atoms, with U_{iso}(H) values set at $1.5U_{eq}$(parent atom) for the hydroxyl H atom and $1.2U_{eq}$(parent atom) for the remaining H atoms. The O—H distance was fixed at 0.82 Å and the C—H distances were fixed in the range 0.93–0.98 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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