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Isopropyl 2-(3-nitrobenzylidene)-acetoacetate

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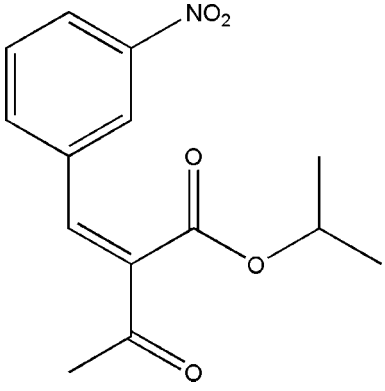
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.058; wR factor = 0.156; data-to-parameter ratio = 15.0.

The title compound, $C_{14}H_{15}NO_5$, is an intermediate in the synthesis of azelnidipine. The dihedral angle between the aromatic ring and the enone fragment is 15.33 (8)°. The crystal packing is consolidated by a weak C—H···O interaction.

Related literature

For related literature, see: Takashi *et al.* (1995).



Experimental

Crystal data

$C_{14}H_{15}NO_5$
M_r = 277.27
Triclinic, $P\overline{1}$
a = 7.545 (4) Å
b = 9.240 (5) Å
c = 11.055 (6) Å
α = 103.598 (8)°
β = 101.898 (8)°
γ = 105.876 (8)°
V = 689.7 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 294 (2) K
0.22 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.980, T_{max} = 0.984
3816 measured reflections
2754 independent reflections
1499 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.156
S = 1.02
2754 reflections
184 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O3	0.93	2.49	3.302 (4)	147
C4—H4···O5^{i}	0.93	2.48	3.308 (5)	150

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2448).

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supplementary materials

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Isopropyl 2-(3-nitrobenzylidene)acetoacetate

P.-F. Deng, G.-B. Chen, Y.-Q. Feng and J. Song

Comment

The title compound (I) is an intermediate in a synthesis of azelnidipine, which is a calcium antagonist for the treatment of hypertension (Takashi *et al.*, 1995) and we report its crystal structure here (Fig. 1).

C1—C6, N1 and O2—O3 are almost coplanar, with an r.m.s. deviation from the mean plane of 0.008 (8) Å. C7—C9, C13—C14 and O5 are also almost coplanar, with an r.m.s. deviation of 0.055 (4) Å, forming a dihedral angle of 15.33 (8)° with the above plane. In addition, C8—C10 and O3—O4 are almost coplanar, with an r.m.s. deviation from the mean plane of 0.018 (7) Å, which is nearly orthogonal to the second plane (C7—C9, C13—C14 and O5) with a dihedral angle of 87.27 (9)°.

In the crystal of (I), the packing is consolidated by weak C—H···O interactions (Table 1).

Experimental

A solution of 3-nitrobenzaldehyde and isopropyl acetoacetate in 2-propanol containing a catalytic amount of piperidinium acetate was stirred at 323–328 K for 1 h and left at room temperature for 48 h. The product was collected by filtration and was recrystallized from 2-propanol to yield colourless blocks of (I). Yield was 77%. m.p.: 365 K.

Refinement

The H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Figures

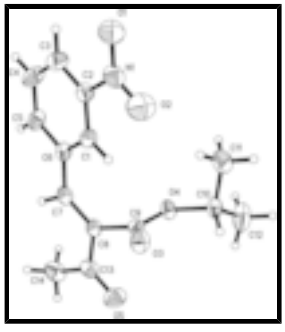

Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level (arbitrary spheres for the H atoms).

Isopropyl 2-(3-nitrobenzylidene)acetoacetate

Crystal data

$C_{14}H_{15}NO_5$	$Z = 2$
$M_r = 277.27$	$F_{000} = 292$
Triclinic, $P\overline{1}$	$D_x = 1.335$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 365 K
$a = 7.545$ (4) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 9.240$ (5) Å	Cell parameters from 1113 reflections
$c = 11.055$ (6) Å	$\theta = 2.6$–24.9º
$\alpha = 103.598$ (8)º	$\mu = 0.10$ mm^{-1}
$\beta = 101.898$ (8)º	$T = 294$ (2) K
$\gamma = 105.876$ (8)º	Block, colorless
$V = 689.7$ (6) Å^3	0.22 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD diffractometer	2754 independent reflections
Radiation source: fine-focus sealed tube	1499 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 294$(2) K	$\theta_{max} = 26.4$º
ω scans	$\theta_{min} = 2.0$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 7$
$T_{min} = 0.980$, $T_{max} = 0.984$	$k = -7 \rightarrow 11$
3816 measured reflections	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.156$	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2485P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
2754 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
184 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.2135 (3)	0.4164 (3)	0.0034 (2)	0.0825 (8)
O2	−0.1935 (4)	0.6589 (3)	0.0411 (2)	0.0917 (8)
O3	0.0432 (3)	1.1048 (2)	0.30423 (18)	0.0577 (6)
O4	0.3410 (3)	1.1135 (2)	0.29935 (16)	0.0479 (5)
O5	0.3443 (3)	1.3493 (3)	0.5663 (2)	0.0745 (7)
N1	−0.1550 (4)	0.5522 (4)	0.0740 (2)	0.0612 (7)
C1	0.0380 (4)	0.7413 (3)	0.2841 (2)	0.0443 (7)
H1	0.0055	0.8195	0.2543	0.053*
C2	−0.0298 (4)	0.5891 (3)	0.2048 (3)	0.0456 (7)
C3	0.0137 (4)	0.4697 (3)	0.2429 (3)	0.0615 (8)
H3	−0.0329	0.3668	0.1864	0.074*
C4	0.1277 (5)	0.5056 (4)	0.3664 (3)	0.0703 (10)
H4	0.1584	0.4262	0.3951	0.084*
C5	0.1969 (4)	0.6570 (3)	0.4482 (3)	0.0570 (8)
H5	0.2736	0.6789	0.5322	0.068*
C6	0.1554 (4)	0.7794 (3)	0.4089 (2)	0.0431 (6)
C7	0.2365 (4)	0.9379 (3)	0.5013 (2)	0.0445 (7)
H7	0.2807	0.9420	0.5875	0.053*
C8	0.2577 (3)	1.0773 (3)	0.4828 (2)	0.0408 (6)
C9	0.1986 (4)	1.0990 (3)	0.3518 (2)	0.0403 (6)
C10	0.3134 (4)	1.1453 (3)	0.1732 (3)	0.0534 (8)
H10	0.2163	1.1969	0.1626	0.064*
C11	0.2471 (6)	0.9911 (4)	0.0685 (3)	0.0818 (11)
H11A	0.3449	0.9430	0.0772	0.123*
H11B	0.2224	1.0083	−0.0147	0.123*
H11C	0.1311	0.9225	0.0756	0.123*
C12	0.5033 (5)	1.2548 (5)	0.1801 (4)	0.0909 (12)
H12A	0.5370	1.3512	0.2496	0.136*
H12B	0.4962	1.2780	0.0993	0.136*
H12C	0.5994	1.2061	0.1958	0.136*
C13	0.3435 (4)	1.2283 (4)	0.5895 (3)	0.0508 (7)
C14	0.4305 (5)	1.2290 (4)	0.7243 (3)	0.0683 (9)
H14A	0.4829	1.3358	0.7816	0.103*

H14B	0.5311	1.1841	0.7241	0.103*
H14C	0.3332	1.1675	0.7534	0.103*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0826 (17)	0.0679 (16)	0.0576 (14)	−0.0046 (13)	0.0022 (12)	−0.0004 (12)
O2	0.109 (2)	0.0929 (19)	0.0554 (14)	0.0409 (16)	−0.0158 (13)	0.0165 (13)
O3	0.0493 (12)	0.0763 (15)	0.0531 (12)	0.0249 (11)	0.0096 (10)	0.0302 (10)
O4	0.0483 (11)	0.0634 (12)	0.0365 (10)	0.0210 (9)	0.0122 (9)	0.0213 (9)
O5	0.0934 (18)	0.0521 (13)	0.0608 (14)	0.0202 (12)	0.0027 (12)	0.0086 (11)
N1	0.0585 (16)	0.0657 (18)	0.0432 (15)	0.0086 (14)	0.0065 (12)	0.0090 (14)
C1	0.0443 (15)	0.0486 (17)	0.0428 (15)	0.0169 (13)	0.0099 (12)	0.0200 (13)
C2	0.0422 (15)	0.0473 (17)	0.0435 (16)	0.0109 (13)	0.0107 (13)	0.0135 (13)
C3	0.063 (2)	0.0455 (18)	0.067 (2)	0.0124 (15)	0.0152 (17)	0.0115 (15)
C4	0.084 (2)	0.051 (2)	0.075 (2)	0.0245 (18)	0.0067 (19)	0.0304 (18)
C5	0.0620 (19)	0.059 (2)	0.0505 (17)	0.0179 (16)	0.0072 (14)	0.0295 (16)
C6	0.0417 (15)	0.0499 (16)	0.0400 (15)	0.0141 (13)	0.0114 (12)	0.0203 (13)
C7	0.0414 (15)	0.0585 (18)	0.0328 (14)	0.0161 (13)	0.0078 (12)	0.0161 (13)
C8	0.0380 (14)	0.0478 (16)	0.0354 (14)	0.0135 (12)	0.0087 (11)	0.0135 (12)
C9	0.0462 (16)	0.0354 (14)	0.0340 (14)	0.0116 (12)	0.0071 (13)	0.0078 (11)
C10	0.0618 (19)	0.0653 (19)	0.0381 (15)	0.0212 (16)	0.0131 (14)	0.0266 (14)
C11	0.108 (3)	0.080 (2)	0.048 (2)	0.023 (2)	0.0173 (19)	0.0163 (18)
C12	0.085 (3)	0.103 (3)	0.071 (2)	0.001 (2)	0.017 (2)	0.046 (2)
C13	0.0442 (16)	0.0572 (19)	0.0421 (17)	0.0140 (14)	0.0077 (13)	0.0074 (14)
C14	0.066 (2)	0.082 (2)	0.0420 (17)	0.0256 (18)	0.0004 (15)	0.0051 (16)

Geometric parameters (Å, °)

O1—N1	1.214 (3)	C7—C8	1.324 (3)
O2—N1	1.212 (3)	C7—H7	0.9300
O3—C9	1.203 (3)	C8—C13	1.474 (4)
O4—C9	1.313 (3)	C8—C9	1.501 (4)
O4—C10	1.477 (3)	C10—C12	1.486 (4)
O5—C13	1.203 (3)	C10—C11	1.488 (4)
N1—C2	1.459 (4)	C10—H10	0.9800
C1—C2	1.360 (4)	C11—H11A	0.9600
C1—C6	1.382 (4)	C11—H11B	0.9600
C1—H1	0.9300	C11—H11C	0.9600
C2—C3	1.365 (4)	C12—H12A	0.9600
C3—C4	1.364 (4)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C4—C5	1.362 (4)	C13—C14	1.497 (4)
C4—H4	0.9300	C14—H14A	0.9600
C5—C6	1.391 (4)	C14—H14B	0.9600
C5—H5	0.9300	C14—H14C	0.9600
C6—C7	1.453 (4)		
C9—O4—C10	118.1 (2)	O3—C9—C8	124.0 (2)

O2—N1—O1	123.5 (3)	O4—C9—C8	110.4 (2)
O2—N1—C2	118.4 (3)	O4—C10—C12	105.3 (2)
O1—N1—C2	118.1 (3)	O4—C10—C11	108.0 (2)
C2—C1—C6	119.7 (2)	C12—C10—C11	114.0 (3)
C2—C1—H1	120.1	O4—C10—H10	109.8
C6—C1—H1	120.1	C12—C10—H10	109.8
C1—C2—C3	122.7 (3)	C11—C10—H10	109.8
C1—C2—N1	118.5 (3)	C10—C11—H11A	109.5
C3—C2—N1	118.8 (3)	C10—C11—H11B	109.5
C4—C3—C2	118.0 (3)	H11A—C11—H11B	109.5
C4—C3—H3	121.0	C10—C11—H11C	109.5
C2—C3—H3	121.0	H11A—C11—H11C	109.5
C5—C4—C3	120.6 (3)	H11B—C11—H11C	109.5
C5—C4—H4	119.7	C10—C12—H12A	109.5
C3—C4—H4	119.7	C10—C12—H12B	109.5
C4—C5—C6	121.6 (3)	H12A—C12—H12B	109.5
C4—C5—H5	119.2	C10—C12—H12C	109.5
C6—C5—H5	119.2	H12A—C12—H12C	109.5
C1—C6—C5	117.4 (3)	H12B—C12—H12C	109.5
C1—C6—C7	124.4 (2)	O5—C13—C8	119.3 (3)
C5—C6—C7	118.2 (2)	O5—C13—C14	121.1 (3)
C8—C7—C6	130.5 (2)	C8—C13—C14	119.6 (3)
C8—C7—H7	114.8	C13—C14—H14A	109.5
C6—C7—H7	114.8	C13—C14—H14B	109.5
C7—C8—C13	123.2 (2)	H14A—C14—H14B	109.5
C7—C8—C9	123.9 (2)	C13—C14—H14C	109.5
C13—C8—C9	112.9 (2)	H14A—C14—H14C	109.5
O3—C9—O4	125.6 (2)	H14B—C14—H14C	109.5
C6—C1—C2—C3	−0.3 (4)	C5—C6—C7—C8	162.8 (3)
C6—C1—C2—N1	179.4 (2)	C6—C7—C8—C13	179.7 (3)
O2—N1—C2—C1	0.1 (4)	C6—C7—C8—C9	−0.7 (4)
O1—N1—C2—C1	179.3 (2)	C10—O4—C9—O3	2.3 (4)
O2—N1—C2—C3	179.7 (3)	C10—O4—C9—C8	−176.4 (2)
O1—N1—C2—C3	−1.0 (4)	C7—C8—C9—O3	91.8 (3)
C1—C2—C3—C4	1.0 (5)	C13—C8—C9—O3	−88.6 (3)
N1—C2—C3—C4	−178.7 (3)	C7—C8—C9—O4	−89.5 (3)
C2—C3—C4—C5	−0.6 (5)	C13—C8—C9—O4	90.1 (3)
C3—C4—C5—C6	−0.4 (5)	C9—O4—C10—C12	143.2 (3)
C2—C1—C6—C5	−0.8 (4)	C9—O4—C10—C11	−94.7 (3)
C2—C1—C6—C7	179.7 (2)	C7—C8—C13—O5	−174.3 (3)
C4—C5—C6—C1	1.1 (4)	C9—C8—C13—O5	6.1 (4)
C4—C5—C6—C7	−179.3 (3)	C7—C8—C13—C14	6.6 (4)
C1—C6—C7—C8	−17.6 (4)	C9—C8—C13—C14	−173.0 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O3	0.93	2.49	3.302 (4)	147
C4—H4···O5^{i}	0.93	2.48	3.308 (5)	150

Symmetry codes: (i) *x*, *y*−1, *z*.

Fig. 1