The enol form of (+)-(1R,4R)-3-benzoylcamphor

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Key indicators

Single-crystal X-ray study
$T = 173$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.092
Data-to-parameter ratio = 9.3

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

In the crystalline state, the molecule of the title compound,
(+)-(1R,4R)-3-(hydroxybenzylidene)-1,7,7-trimethylbicyclo-
[2.2.1]heptan-2-one, $C_{17}H_{20}O_2$, exists in the enolized form,
with the H atom located on the phenyl-substituted C—O
fragment rather than on the camphoryl-substituted one. The
enolic H atom is involved in intramolecular hydrogen bonding
[O···O = 2.633 (2) Å].

Comment

The structure determination of the title compound, (I), was
performed as part of a project on the preparation of well
defined chiral cerium(III) β-diketonates (Niemeyer *et al.*,
2005) which might be used in enantioselective oxidation
reactions for the synthesis of the biologically important
α-hydroxy-β-dicarbonyl group (Christoffers & Werner, 2002;
Christoffers *et al.*, 2003, 2004; Rössle *et al.*, 2004).

(I)
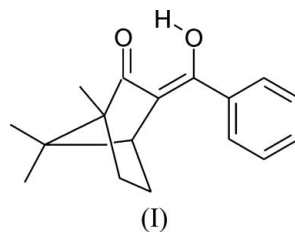
In the molecular structure of (I), monomeric units of the
enol form are observed (Fig. 1), in which the enolic atom H1 is
located on the benzoyl atom O1. The enol character of atom
O1 is supported by the bond-length pattern within the central
six-membered C_3HO_2 ring [C2—O2 = 1.234 (2), C2—C3 =
1.459 (2), C3—C11 = 1.352 (3) and C11—O1 = 1.350 (2) Å].
This ring is almost planar, with the deviations from the least-
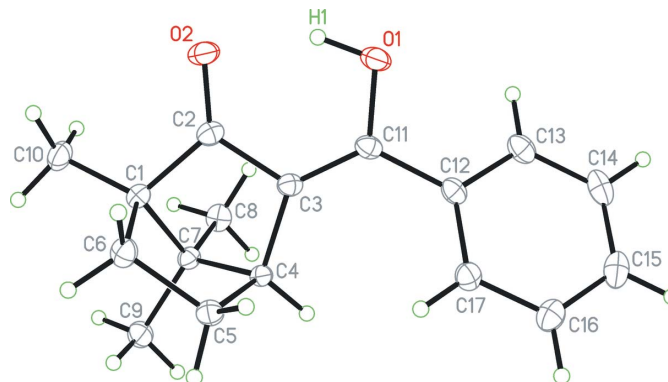

Figure 1
A drawing of the molecular structure of (I), with the atom-numbering
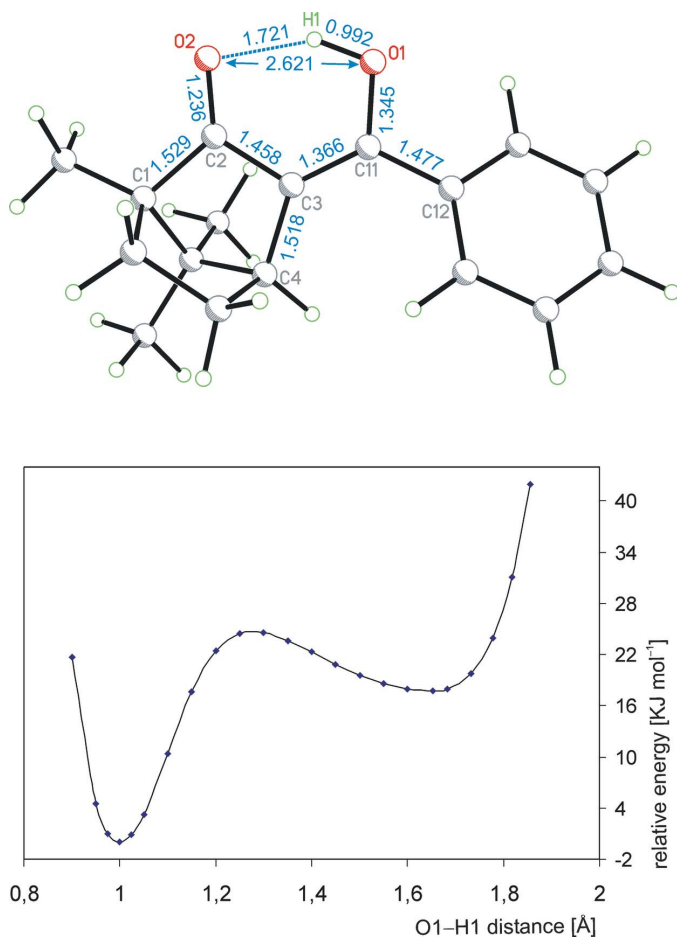scheme. Displacement ellipsoids are shown at the 30% probability level.

Figure 2
(Top) The structure of (I), calculated using density functional theory, at the B3LYP/6-311+G(d,p) level of theory, showing pertinent bond lengths (Å), and (bottom) the shape of the potential-energy surface at the B3LYP/6-31 G(d) level of theory.

squares plane defined by the non-H atoms being less than 0.0148 (12) Å. The angle between the normals to the mean plane and to the phenyl ring is 35.78 (7)°.

On the basis of the O1···O2 separation, the intramolecular OHO hydrogen bonding in (I) (details in Table 2) is classified as being medium strong (Emsley, 1984). Bond parameters for (I) calculated using density functional theory are in excellent agreement with the experimentally determined values (Fig. 2, top). According to further quantum-chemical calculations, the enolic form, where atom H1 is bonded to the (phenyl-C)—O1 fragment, is energetically favoured by 17.1 kJ mol^{-1} [at the B3LYP/6-311+G(d,p) level of theory, with zero-point energy correction] over the tautomer with atom H1 located near atom O2 (Fig. 2, bottom). The destabilization of the latter isomer is mainly due to the greater double-bond character for the endocyclic C2—C3 bond and the resulting ring strain.

Experimental

The title compound was prepared as described previously by Cullen *et al.* (1988) from (1R,4R)-(+)-3-bromocamphor and ethyl benzoate.

Crystals of (I) suitable for X-ray study were grown from petroleum ether at 273 K (m.p.: 360–362 K). Spectroscopic analysis: ^{1}H NMR (C$_6$D$_6$, 250 MHz, δ, p.p.m.): 0.59 (s, 3H), 0.64 (s, 3H), 0.97 (s, 3H), 1.22–1.50 (m, 3H), 1.68–1.85 (m, 1H), 2.66 (d, 1H), 7.10–7.16 (m, 3H, m- + p-C$_6$H$_5$), 7.70 (d, 2H, o-C$_6$H$_5$), 13.15 (s, 1H, OHO); ^{13}C NMR (C$_6$D$_6$, 62.9 MHz, δ, p.p.m.): 9.1, 18.6, 20.2, 27.2, 30.8, 48.7, 50.0, 57.7, 115.6, 128.2, 128.4, 130.4, 134.8, 162.2, 212.8.

The *GAUSSIAN03* package (Frisch *et al.*, 2003) was used for all energy and frequency calculations. Starting from the experimentally determined positions, the geometry of (I) was optimized using density functional theory with the functional B3LYP, GDIIS algorithm with TIGHT convergence criterion, and 6-311+G(d,p) (single point energies for the two tautomers) or 6-31 G(d) (OHO potential scan and frequency calculations) basis sets for C, H and O atoms. The sum of the electronic energy and the zero-point energy was used to calculate the energy difference between the H1—O1 and H1–O2 tautomers.

Crystal data

C$_{17}$H$_{20}$O$_2$	Mo $K\alpha$ radiation
$M_r = 256.35$	Cell parameters from 48
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.520$ (2) Å	$\theta = 6.5$–12.5°
$b = 12.646$ (3) Å	$\mu = 0.08$ mm^{-1}
$c = 12.917$ (3) Å	$T = 173$ (2) K
$V = 1391.7$ (6) Å^3	Plate, colourless
$Z = 4$	$0.75 \times 0.70 \times 0.25$ mm
$D_x = 1.223$ Mg m^{-3}	

Data collection

Rebuilt Syntex $P2_1$/Siemens $P3$	$\theta_{max} = 27.5°$
four-circle diffractometer	$h = -1 \rightarrow 11$
Wyckoff ω scans	$k = -1 \rightarrow 16$
2435 measured reflections	$l = -1 \rightarrow 16$
1836 independent reflections	2 standard reflections
1697 reflections with $I > 2\sigma(I)$	every 198 reflections
$R_{int} = 0.020$	intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.243P]$
$wR(F^2) = 0.092$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1836 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
198 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.350 (2)	C3—C11	1.352 (3)
O2—C2	1.234 (2)	C3—C4	1.509 (2)
C1—C2	1.517 (3)	C11—C12	1.475 (3)
C2—C3	1.459 (2)		
C11—O1—H1	106.0 (17)	C11—C3—C4	133.82 (17)
O2—C2—C3	126.38 (17)	C2—C3—C4	104.69 (14)
O2—C2—C1	126.90 (16)	O1—C11—C3	120.41 (17)
C3—C2—C1	106.72 (14)	O1—C11—C12	112.68 (16)
C11—C3—C2	121.43 (16)	C3—C11—C12	126.88 (16)
O1—C11—C12—C13	−33.7 (2)	C3—C11—C12—C17	−37.6 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O2	0.94 (3)	1.77 (3)	2.633 (2)	151 (3)

The H atoms were positioned geometrically at C—H distances of 1.00 (CH), 0.99 (CH$_2$) and 0.98 Å (CH$_3$) and refined in a riding-model approximation, including free rotation for methyl groups and variable isotropic displacement parameters. The position of atom H1 was located in a difference Fourier map and was allowed to refine freely. The absolute configuration was assigned on the basis of the known absolute configuration of the starting material, (1R,4R)-(+)-3-bromocamphor. Because of negligible anomalous scattering effects, Friedel pairs were averaged in the final refinement.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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