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(8*RS*,5*SR*,7*SR*)-7-Benzoyl-8-hydroxy-8-phenylspiro[4.5]decan-1-one

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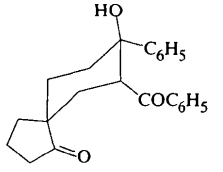
Abstract

In the title compound, $C_{23}H_{24}O_3$, the five-membered ring adopts a half-chair conformation and the cyclohexane ring is in a chair conformation. The benzoyl group and the phenyl ring are equatorially attached. The hydroxyl group and the benzoyl O atom are involved in an intramolecular O—H···O hydrogen bond. In the crystal, the phenyl rings of the inversion- and screw-related molecules are involved in C—H···π interactions.

Comment

While attempting to develop a facile route to azagonanes, we have isolated not only the expected 1,5-diketone 2-(3-oxo-3-phenylpropyl)-1-cyclopentanone, but also the title compound, (I), in 7% yield from the reaction of phenyl vinyl ketone and cyclopentanone in the presence of barium hydroxide. The importance of this compound comes from the fact that from simple starting materials, such as phenyl vinyl ketone and cyclopentanone, a complex product can be formed which has three stereogenic centres. The stereoselectivity in the reaction is very high, since only one product out of the four enantiomeric pairs has resulted from the reaction. A possible mechanism involves sequential Michael addition, Michael addition and aldol condensation. The X-ray structure determination of (I) was carried out in order to elucidate its molecular conformation.



(I)

Except for C—C bonds involving C17, all bond lengths in (I) show normal values (Allen *et al.*, 1987). The C7—C17 [1.521 (2) Å] and C17—C18 [1.491 (2) Å] bond lengths are longer than normal Csp^2—Csp^3 and Csp^2—Csp^2 bond lengths, which may be due to steric interactions. The bond angles around the spiro-C atom (C5) vary from 99.8 (1) to 113.8 (1)°. Such large deviations from normal sp^3 bond angles have been reported for the spiran junction by Selladurai *et al.* (1995) and Ianelli *et al.* (1992). The spiro planes, C1—C5—C4 and C6—C5—C10, are inclined at 89.6 (1)° to each other. The five-membered ring adopts a half-chair conformation, with C4 and C5 twisted out of the mean plane by 0.229 (2) and −0.234 (2) Å, respectively; asymmetry parameter ΔC_2(C2) = 3.6 (2)° (Duax *et al.*, 1976). The cyclohexane ring adopts a chair conformation, with the C4—C5 bond, the benzoyl group and the phenyl ring attached to it equatorially. The mean plane through the cyclohexane ring forms dihedral angles of 78.1 (1) and 82.68 (9)°, respectively, with the mean planes through the five-membered ring and the phenyl ring. The conformation of the attachment of the benzoyl substituent to the cyclohexane ring is described by the C6—C7—

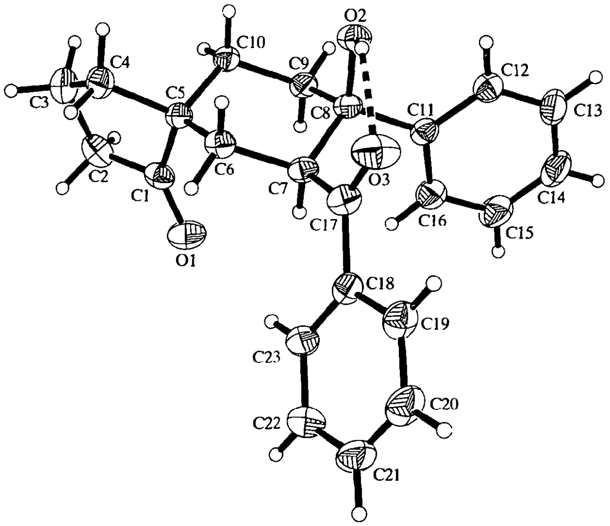


Fig. 1. The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

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C17—C18 torsion angle of 97.5 (2), while the C7—C17—C18—C19 torsion angle of 170.0 (2)° shows how the benzoyl phenyl is oriented. The hydroxyl group and the carbonyl O3 atom are involved in an O2—H2*A*···O3 intramolecular hydrogen bond. Also, a very weak O2—H2*A*···O1(*x*, *y* + 1, *z*) contact exists between the hydroxyl group and the other carbonyl atom (O1), leading to the formation of an infinite one-dimensional chain along [101]. In the crystal, the phenyl rings (excluding the benzoyl phenyl) of the inversion- and screw-related molecules are involved in C—H···π interactions (Table 2).

Experimental

To a stirred suspension of freshly activated barium hydroxide (0.343 g, 2 mmol) in 7 ml of absolute ethanol, cyclopentanone (0.942 g, 11 mmol) was added at room temperature and stirring continued for 10 min. Phenyl vinyl ketone (1.32 g, 10 mmol) was added dropwise to the reaction mixture, which was then allowed to stand for 12 h at room temperature to give a mixture of two products. The reaction mixture was diluted with dichloromethane (10 ml), washed with iced water (2 × 10 ml), then brine (2 × 10 ml), dried with anhydrous sodium sulfate and concentrated. The crude mixture of products was then separated by column chromatography using silica gel (100–200 mesh) with hexane/ethyl acetate solutions (99:1 to 90:10), to give the 1,5-diketone and the title spiro alcohol, (I). Single crystals of (I) were grown by slow evaporation from a solution of methanol/chloroform (1:1).

Crystal data

$C_{23}H_{24}O_3$
$M_r = 348.42$
Monoclinic
$P2_1/c$
$a = 13.4416\ (4)$ Å
$b = 6.4787\ (2)$ Å
$c = 21.7352\ (6)$ Å
$\beta = 104.065\ (1)°$
$V = 1836.05\ (9)$ Å^3
$Z = 4$
$D_x = 1.260$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5066 reflections
$\theta = 1.56$–$28.29°$
$\mu = 0.082$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.38 × 0.24 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
11 803 measured reflections
4526 independent reflections
2836 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\rm max} = 28.29°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 28$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.142$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

$S = 1.051$
4526 reflections
236 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.3146P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.208 (2)	C7—C17	1.521 (2)
O2—C8	1.426 (2)	C17—C18	1.491 (2)
O3—C17	1.223 (2)		
C1—C5—C6	113.7 (1)	C4—C5—C10	110.0 (1)
C1—C5—C4	99.8 (1)	O3—C17—C18	119.9 (2)
C6—C5—C4	113.8 (1)	O3—C17—C7	119.9 (2)
C1—C5—C10	109.0 (1)	C18—C17—C7	120.1 (2)
C6—C5—C10	110.1 (1)		
O1—C1—C5—C6	−20.7 (2)	C3—C4—C5—C10	75.6 (2)
O1—C1—C5—C4	−142.3 (2)	C11—C8—C9—C10	−179.6 (1)
C3—C4—C5—C6	−160.4 (2)	C7—C8—C11—C16	52.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O1$^{\rm i}$	0.82	2.52	2.963 (2)	115
O2—H2*A*···O3	0.82	2.10	2.773 (2)	140
C2—H2*C*···π(phenyl)$^{\rm ii}$	0.97	2.97	3.829 (2)	148
C21—H21*A*···π(phenyl)$^{\rm iii}$	0.93	3.05	3.979 (2)	176

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

After checking their presence in the difference map, all H atoms were placed at their geometrically calculated positions and a riding model was used for their refinement.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1274). Services for accessing these data are described at the back of the journal.

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3-Cyclopropyl-1,2,4-triazolo[3,4-*b*]benzothiazole monohydrate†

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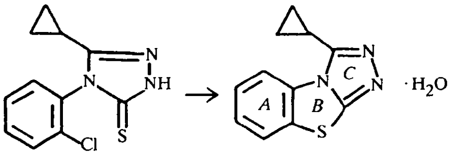
Abstract

The title structure, $C_{11}H_9N_3S{\cdot}H_2O$, contains two crystallographically independent molecules, each consisting of a 1,2,4-triazolo[3,4-*b*]benzothiazole-fused ring fragment substituted with a cyclopropyl ring, and a water molecule. The geometry of both molecules differs slightly. Both molecules are planar within 0.041 and 0.03 Å. The dihedral angle between triazole and the cyclopropyl ring is 60.0 (1) and 61.7 (1)° for molecules *A* and *B*, respectively, and the cyclopropyl ring is inclined at an angle of 2.0 (1) and 1.2 (1)° to the benzothiazole moiety for molecules *A* and *B*, respectively. The packing of the molecules is stabilized by O—H···N-type hydrogen bonds.

Comment

The triazole part of the title compound is used as an antimicrobial (Habib *et al.*, 1997), potential antiviral (Ergen *et al.*, 1996), anti-HIV-1 (Invidiata *et al.*, 1996), antifungal, antimycobacterial and anticonvulsant (Gülerman *et al.*, 1997) agent. It is also a highly potent eosinophilia inhibitor (Naito *et al.*, 1996) and is used as a fungicide (Crofton, 1996) and a herbicide (Tada *et al.*, 1995). Some of the 1,2,4-triazolo[3,4-*b*] derivatives have been evaluated for their antibacterial activity against both Gram-positive and Gram-negative bacteria (Bs *et al.*, 1996). Benzothiazoles are extremely important heterocycles from an industrial, agricultural, biological and pharmaceutical point of view. Benzothiazoles are used as antineoplastic agents and show antinociceptive, anti-inflammatory and antitumour activities (Bradshaw *et al.*, 1998; Dögruer *et al.*, 1998). The fused benzothiazole–triazole fragment may have useful medicinal properties. Some Schiff bases derived from thiazole and benzothiazoles (Dash *et al.*, 1980) and several derivatives of the styryl–benzothiazoles have shown biological activity (Cox *et al.*, 1982).

In view of the above biological activities associated with the benzothiazole and triazole moieties, we focused our interest on the structure determination of 1,2,4-triazolo[3,4-*b*]benzothiazole, incorporating both the units. Substituted 1,2,4-triazolo[3,4-*b*]benzothiazoles were prepared from the respective triazole-3-thiones by photochemical methods. In order to confirm the identity and to study the stereochemistry, a single-crystal X-ray structure determination was carried out. It was found that the asymmetric unit of the title compound, (I), consists of two crystallographically unique but structurally similar molecules, along with two water molecules.



(I)

In both molecules (Fig. 1), the average C—N, C—S and C—C distances (1.370, 1.730 and 1.390 Å, respectively) for the benzothiazole are similar to those found in a related structure (Muir *et al.*, 1987; Ruiwu *et al.*, 1997). It should be mentioned that the large size of the S atom compared with the N atom results in a reduction of the average C—S—C angle [89.24 (7)°] compared with the C—N—C angle [114.74 (12)°] and the other internal angles [111.64° (N—C—C, C—C—S)] within the thiazole ring. This suggests that the S atom might be using unhybridized *p* orbitals for bonding (Muir *et al.*, 1987; Cox *et al.*, 1997). In the triazole rings in both molecules, the average N—C distances [1.313 (2) Å] agree well with those found in 3,5-bis(2-pyridyl)-4-*p*-chlorophenyl-4*H*-1,2,4-triazole (Wang *et al.*, 1998). The average N—N distance [1.411 (2) Å] is slightly greater than the literature value (Cromer & Storm, 1991).

Both the benzene and thiazole rings in the benzothiazole moiety are essentially planar, with no atom deviating from the plane by more than 0.027 (2) Å (C7*A*) in molecule *A* and 0.026 (2) Å in molecule *B*. The orientation of the cyclopropyl ring is explained by the torsion angles N1*A*—C8*A*—C9*A*—C10*A* of 154.57 (17) and N3*A*—C8*A*—C9*A*—C11*A* of −95.2 (2)° in molecule *A*, and N1*B*—C8*B*—C9*B*—C10*B* of −159.59 (17) and N3*B*—C8*B*—C9*B*—C11*B* of 89.5 (2)° in molecule *B*.

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† DCB contribution No. 886.