Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3′-Isopropyl-8′,8′-dimethyl-2-benzofuran-1-spiro-7′-bicyclo[4.2.0]octa-1′(6′),2′,4′-trien-3-one

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.060
wR factor = 0.130
Data-to-parameter ratio = 17.6

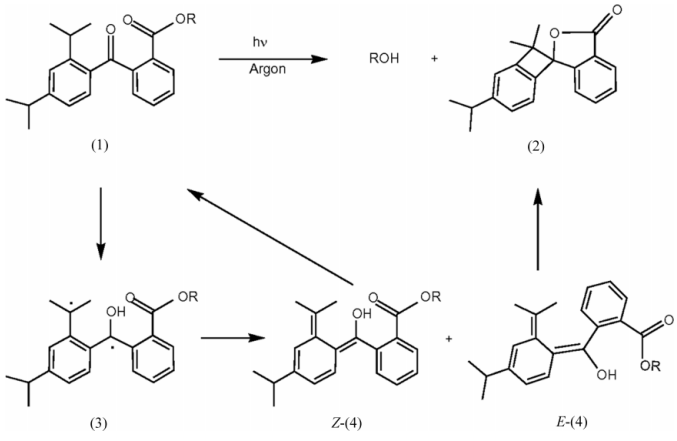
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 November 2004
Accepted 12 November 2004
Online 20 November 2004

Photolysis of a 2-(2-isopropyl-benzoyl)benzoate ester derivative in an oxygen-free environment results in the liberation of the alcohol from the ester and formation of the title spirolactone, $C_{20}H_{20}O_2$. The molecule of the title compound adopts the *syn* configuration with respect to the benzene rings, with a dihedral angle of 87.19 (5)° between the benzocyclobutene and isobenzofuranone ring planes. The cyclobutene ring is nearly planar, giving rise to ring distortion, as manifested in the bond distances and angles.

Comment

We have designed molecules which release alcohols upon exposure to UV light, independent of the reaction media, making it possible to liberate alcohols in a controlled manner in a variety of applications (Pika *et al.*, 2000). Photolysis of 2-(2-isopropylbenzoyl)benzoate ester derivatives, (1), in an oxygen-free environment results in the liberation of the alcohol from the ester and formation of spirolactone (2) (Pika *et al.*, 2003). The reaction mechanism for the release of the alcohol has been elucidated by time-resolved laser flash photolysis (see scheme). Upon irradiation, the triplet excited state of (1) is formed, which decays by efficient intramolecular H-atom abstraction to form a 1,4-biradical, (3). Radical (3) undergoes intersystem crossing to form photoenols *Z*-(4) and *E*-(4). Isomer *Z*-(4) returns to the starting material through a 1,5-intramolecular H-atom transfer mechanism, whereas isomer *E*-(4) releases the alcohol through an intramolecular lactonization reaction and undergoes conrotatory electrocyclic ring closure to form (2) (Wagner *et al.*, 1991). We present here the crystal structure of (2).



The molecular structure of (2) is shown in Fig. 1. The general geometric details (Table 1) are consistent with those of

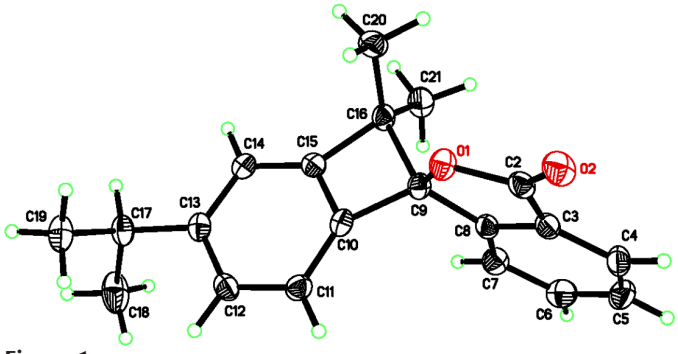


Figure 1
The molecular structure of (2), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

complexes which contain four- and five-membered rings at the spiro juncture. Examples of related structures are 1-acetyl-7a′-phenylspiro[3*H*-indole-3,2′(2a′*H*)-oxeto[2,3-*b*]benzofuran]-2(1*H*)-one (Usman *et al.*, 2001), 8-(indol-3-yl)-2,2,4-trimethylbicyclo[4.2.0]oct-4-ene-7-spiro-3′-indolin-2′-one (Wenkert *et al.*, 1987), (*E*)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole-1-spiro-1′-(3′,3′,4′-triphenyl)-2′,1′-oxathietane (Kawashima *et al.*, 1994), *trans*-4′-phenyl-3,3,3′,3′-tetrakis(trifluoromethyl)-3*H*-spiro(2,1)benzoxaselenole-1-λ-4,1′-(1,2)-selenazetidine (Kano *et al.*, 2001), [1,1-bis(trifluoromethyl)-2,3-benzoxathiolane]-3-spiro-2′-[3-phenyl-4,4-bis(trifluoromethyl)-1,2λ^4-oxathietane] and [1,1bis(trifluoromethyl)-2,3-benzoxathiolane]-3-spiro-2′-[3-phenyl-4,4-bis(trifluoromethyl-1,2λ^4-oxathietane 2-oxide] (Ohno *et al.*, 1996), (3*R*,3′*S*,4′*S*)-1-acetyl-1,2-dihydro-2-oxo-3′,4′-diphenylspiro(3*H*-indole-3,2′-oxetane), (3*R*,3′*R*)-1-acetyl-1,2-dihydro-2-oxo-3′-phenylspiro(3*H*-indole-3,2′-oxetane) and (3*R*,3′*R*)-1-acetyl-1,2-dihydro-3′-methyl-2-oxo-3′-phenyl-spiro(3*H*-indole-3,2′-oxetane) (Xue *et al.*, 2001), and 2,2′-di-*tert*-butyl-4′,5,6′,7-tetramethylspiro(1,2-disilaindan-1,1′(2′*H*)-1-silabenzocyclobutane (Weidenbruch *et al.*, 1990).

The molecule of (2) adopts a *syn* configuration with respect to the benzene rings, with a dihedral angle of 87.19 (5)° between the benzocyclobutene and isobenzofuranone ring planes. The cyclobutene ring is nearly planar, with torsion angles of −2.81 (15)° for C9—C10—C15—C16 and 2.66 (14)° for C16—C9—C10—C15. This in turn causes considerable ring distortion, with the C9—C16 bond lengthening to 1.615 (2) Å, while C10—C15 remains double-bond in character [1.379 (3) Å] to satisfy the bonding requirements imposed by the benzene ring. However, if the four-membered ring is an oxetane or substituted cyclobutane, as in (3*R*,3′*S*,4′*S*)-1-acetyl-1,2-dihydro-2-oxo-3′,4′-diphenyl-spiro-(3*H*-indole-3,2′-oxetane), (3*R*,3′*R*)-1-acetyl-1,2-dihydro-2-oxo-3′-phenylspiro(3*H*-indole-3,2′-oxetane) and (3*R*,3′*R*)-1-acetyl-1,2-dihydro-3′-methyl-2-oxo-3′-phenyl-spiro(3*H*-indole-3,2′-oxetane) (Xue *et al.*, 2001), and 8-(indol-3-yl)-2,2,4-trimethylbicyclo[4.2.0]oct-4-ene-7-spiro-3′-indolin-2′-one (Wenkert *et al.*, 1987), less distortion is observed. The degree of planarity of the four-membered ring appears to be, as expected, a function of the nature and bonding position of the substituent (analogous ring torsion angles for these complexes are approximately 9, 5, 10 and 17°, respectively).

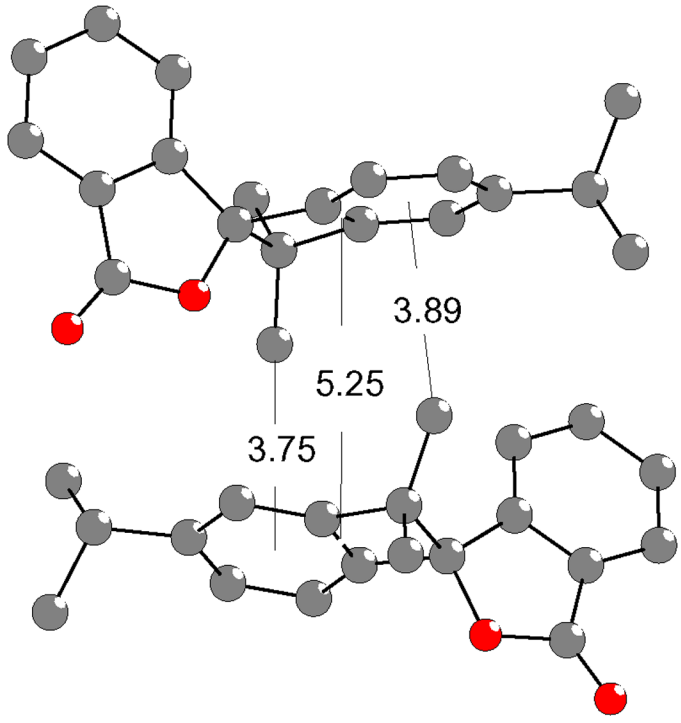


Figure 2
The stacking interactions of (2), indicating the separations between the molecules (Å).

Molecules of (2) pack in the typical ring-stacking motif (Fig. 2) in an attempt to maximize π-type interactions. However, the orientation of the isobenzofuranone ring makes this a little less efficient. A separation of 5.25 Å exists between the midpoints of the central C10—C15 bonds of neighboring stacked molecules, while the methyl groups are oriented towards the centroids of neighboring benzene rings (mean separation 3.82 Å). C—H···O intermolecular interactions (Fig. 3, Table 2) bind the molecules together in a columnar arrangement.

Experimental

The synthetic procedure for the preparation of (2) and the photochemical reactivity of the compound are described in detail in the paper by Pika *et al.* (2003). Single crystals of (2) were obtained from a solution in pentane.

Crystal data

$C_{20}H_{20}O_2$
M_r = 292.36
Monoclinic, $P2_1/c$
a = 11.8742 (4) Å
b = 10.0738 (3) Å
c = 13.3550 (4) Å
β = 96.375 (1)°
V = 1587.62 (9) Å^3
Z = 4
D_x = 1.223 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6130 reflections
θ = 2.5–27.0°
μ = 0.08 mm^{-1}
T = 150 (2) K
Block, colorless
0.24 × 0.20 × 0.17 mm

Data collection

Bruker SMART6000 PLATFORM CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.922, T_{max} = 0.987
11 970 measured reflections
3496 independent reflections
2920 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.1°
$h = -15 \rightarrow 15$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.130
S = 1.12
3496 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 1.3492P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C9—C10	1.514 (2)	C10—C15	1.379 (3)
C9—C16	1.615 (2)	C15—C16	1.531 (2)
C10—C9—C16	86.29 (13)	C10—C15—C16	94.58 (15)
C15—C10—C9	94.23 (15)	C15—C16—C9	84.77 (13)
C16—C9—C10—C15	2.66 (14)	C9—C10—C15—C16	−2.81 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O2^{i}	0.95	2.45	3.375 (2)	164
C12—H12···O2^{ii}	0.95	2.46	3.372 (2)	160

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$.

H atoms were either located directly or calculated based on geometric criteria, and were treated with a riding model, with C—H = 1.00, 0.99, 0.98 and 0.95 Å for —CH, —CH_2, —CH_3 and aromatic H, respectively, and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL*.

JAKB thanks Dr Alan Pinkerton, Department of Chemistry, University of Toledo, Ohio, USA, for the use of the SMART6000 diffractometer.

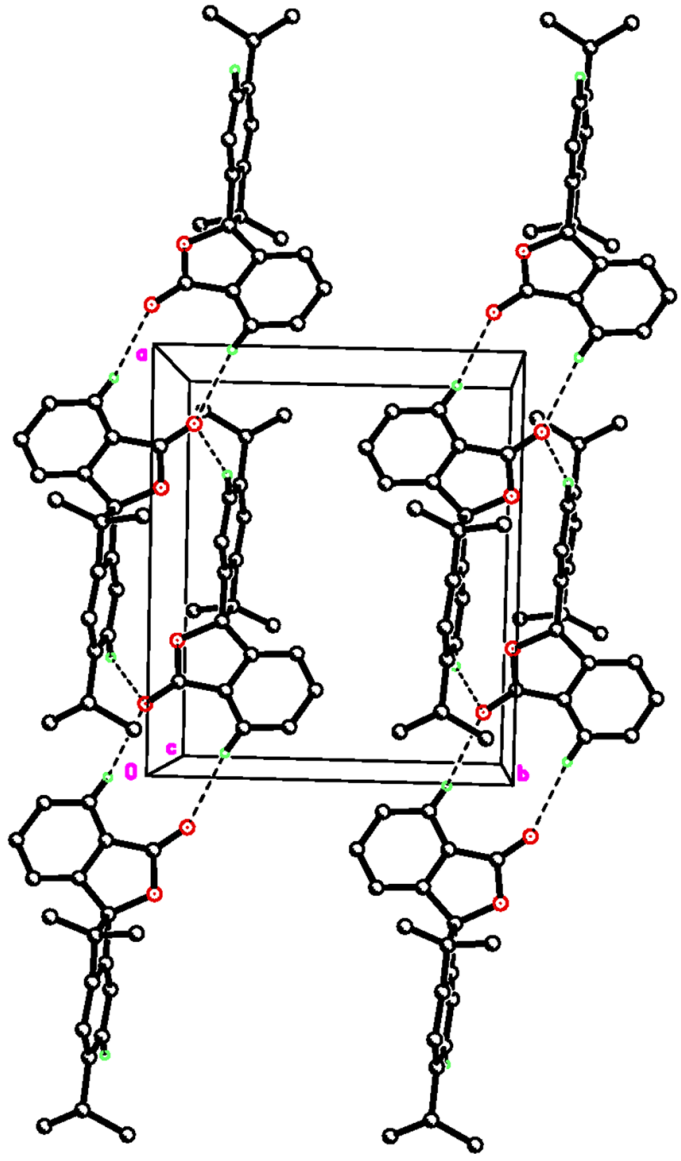


Figure 3
The C—H···O intermolecular interactions (dashed lines) of (2). H atoms not involved in hydrogen bonding have been omitted.

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