

C6—C1—P	121.6 (4)	C6'—C1'—P'	123.1 (3)
C5—C6—C1 ⁱ	117.3 (3)	C1'—C6'—C1' ⁱⁱ	125.5 (6)
C5—C6—C1	117.3 (3)	C1'—C6'—C5'	117.3 (3)
C1 ⁱ —C6—C1	125.5 (6)	C1' ⁱⁱ —C6'—C5'	117.3 (3)
P—C1—C2—C3	167.6 (3)	P'—C1'—C2'—C3'	169.6 (3)
P—C1—C6—C5	-162.00 (14)	P'—C1'—C6'—C1' ⁱⁱ	11.88 (15)
P—C1—C6—C1 ⁱ	18.00 (14)	P'—C1'—C6'—C5'	-168.12 (15)

Symmetry codes: (i) 2 - x, -y, z; (ii) 1 - x, -y, z.

The absolute structure was determined by the method of Flack (1983) and the origin was fixed by the method of Flack & Schwarzenbach (1988).

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1288). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1122–1124

Methyl 8-Hydroxy-1,2,3,4-tetrahydro-naphthalene-5-carboxylate

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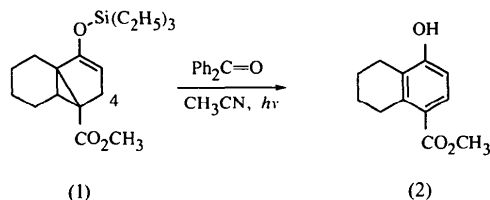
(Received 9 October 1996; accepted 18 February 1997)

Abstract

All non-H atoms in the two identical molecules of the title compound, C₁₂H₁₄O₃, lie on a crystallographic mirror plane, except for C2 and C3, which lie equally above and below the plane by approximately 0.4 Å. Intermolecular hydrogen bonds between the phenol group and the carboxylate O atom link the molecules into chains which lie along the *a* axis.

Comment

During the course of our studies of the photochemical [2+2] cycloaddition of carbonyl compounds with cyclopropyl-substituted silyl enol ethers, a mixture of the tricyclic silyl enol ether, (1), and benzophenone were subjected to UV irradiation. Only one product of this type, (2), in 28% yield, was isolated from the reaction mixture. The ¹H and ¹³C NMR spectra were insufficient for unequivocal structural assignment of this material and so an X-ray structural analysis was carried out on (2).



Compound (2) was formed from initial H4-atom abstraction by photoexcited triplet biradical benzophenone, followed by cyclopropylmethyl radical fragmentation; this gave a radical intermediate that underwent subsequent oxidation and hydrolysis. This product is unusual, since such reactions normally result in an oxetane product by way of the well known Paterno–Büchi reaction (Porco & Schreiber, 1991).

Essentially, there are two identical molecules in the asymmetric unit. For both molecules, all of the non-H atoms lie on a mirror plane, except for C2 and

C3, which are equally disordered across the plane. The bond between C2 and C3 involves atoms which lie on opposite sides of the mirror plane [C2 0.414(10), C3 -0.461(7) Å; C2' 0.433(8), C3' -0.412(7) Å]. This conformation of the alicyclic ring is in contrast to that found for compounds with ring substituents, such as 5,8-dimethoxy-1-(1'-methoxycarbonylethyl)-4-methyl-1,2,3,4-tetrahydronaphthalene (Beckwith, Ghisalberti, Jefferies, Raston & White, 1988), where the only atom out of the plane of the aromatic ring, by about 0.7 Å, is the atom opposite to the point of fusion of the two rings, adjacent to the most sterically demanding pair of substituents. The other geometric parameters of (2) are similar to those of the above compound.

Intermolecular hydrogen bonds between the phenol group and the carboxylate O atom (Table 3) link the molecules into chains which lie along the *a* axis.

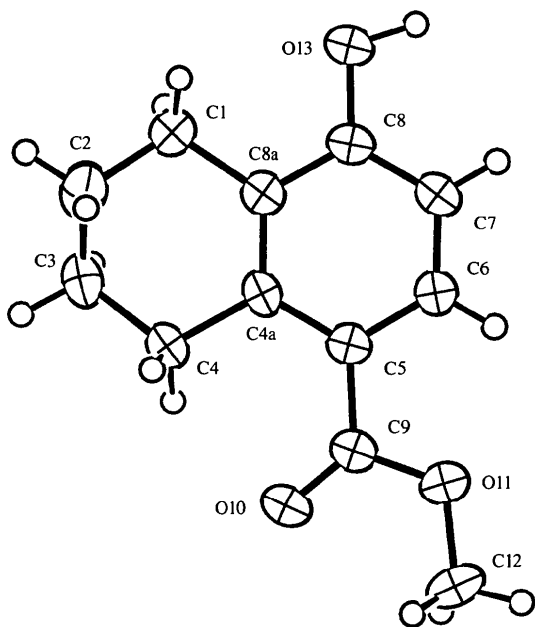


Fig. 1. ORTEP (Johnson, 1976) drawing of one of the two identical molecules of (2). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of radius 0.1 Å.

Experimental

Silyl ether (1) was prepared by enolization of the known parent ketone (Hagiwara, Abe & Uda, 1993) and trapping with triethylsilyl chloride. The title compound was prepared by UV irradiation of a solution of the tricyclic silyl enol ether [(1), 70 mM] and benzophenone (72 mM) in acetonitrile at 298 K for two days. It was isolated by concentration of the reaction mixture followed by preparative thin-layer chromatography of the oily residue. Crystals were obtained by vapour diffusion of a chloroform solution with petroleum spirit (b.p. 373–393 K).

Crystal data

C₁₂H₁₄O₃
M_r = 206.23
 Orthorhombic
Pnma
a = 15.2699 (9) Å
b = 6.833 (2) Å
c = 19.9199 (13) Å
V = 2078.4 (6) Å³
Z = 8
D_x = 1.318 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4-MachS diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian by integration (Sheldrick, 1976)
T_{min} = 0.841, *T_{max}* = 0.975
 3067 measured reflections
 2333 independent reflections

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.151
S = 1.027
 2333 reflections
 327 parameters
 H atoms refined geometrically, except for H13 and H13'
 $w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 0.22P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cu *K*α (nickel filtered) radiation
 $\lambda = 1.54180$ Å
 Cell parameters from 25 reflections
 $\theta = 18.1\text{--}45.3^\circ$
 $\mu = 0.770$ mm⁻¹
T = 293 (1) K
 Thin plate
 0.57 × 0.11 × 0.03 mm
 Colourless

1347 reflections with *I* > 2σ(*I*)
R_{int} = 0.027
 $\theta_{\text{max}} = 74.94^\circ$
h = -1 → 19
k = -1 → 8
l = -24 → 1
 3 standard reflections
 frequency: 160 min
 intensity decay: none

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\text{max}} = 0.293$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.122$ e Å⁻³
 Extinction correction: *SHELXL96* (Sheldrick, 1996)
 Extinction coefficient: 0.00046 (13)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C1†	-0.1028 (2)	1/4	0.42503 (17)	0.0516 (10)
C2‡	-0.0096 (5)	0.3105 (15)	0.4399 (3)	0.063 (2)
C3‡	0.0508 (3)	0.1825 (10)	0.3968 (2)	0.060 (2)
C4†	0.0378 (2)	1/4	0.3224 (2)	0.0486 (14)
C4a†	-0.0572 (2)	1/4	0.30119 (17)	0.0367 (8)
C5†	-0.08085 (19)	1/4	0.23319 (19)	0.0344 (7)
C6†	-0.16946 (18)	1/4	0.21573 (15)	0.0387 (7)
C7†	-0.23386 (18)	1/4	0.26314 (16)	0.0410 (8)
C8†	-0.21027 (18)	1/4	0.33068 (15)	0.0381 (7)
C8a†	-0.12232 (18)	1/4	0.35023 (15)	0.0376 (7)
C9†	-0.0155 (3)	1/4	0.17829 (16)	0.0387 (8)
O10†	0.06353 (17)	1/4	0.18456 (12)	0.0583 (8)
O11†	-0.05293 (14)	1/4	0.11765 (10)	0.0542 (7)
C12‡	0.0063 (3)	1/4	0.06126 (17)	0.0597 (12)
O13†	-0.27245 (14)	1/4	0.37979 (11)	0.0504 (7)
C1B§	0.375 (2)	1/4	0.4197 (14)	0.108 (16)
C2B¶	0.467 (3)	0.303 (15)	0.438 (3)	0.19 (6)
C3B¶	0.530 (3)	0.185 (13)	0.394 (2)	0.14 (3)
C4B§	0.521 (2)	1/4	0.319 (2)	0.08 (3)

C4aB§	0.427 (2)	1/4	0.2953 (14)	0.077 (17)
C5B§	0.403 (2)	1/4	0.2278 (13)	0.12 (2)
C6B§	0.313 (2)	1/4	0.2107 (18)	0.20 (3)
C7B§	0.248 (2)	1/4	0.2579 (17)	0.20 (3)
C8B§	0.272 (2)	1/4	0.3254 (16)	0.121 (19)
C8aB§	0.3601 (19)	1/4	0.3445 (14)	0.15 (2)
C9B§	0.469 (2)	1/4	0.1742 (14)	0.067 (13)
O10B§	0.547 (2)	1/4	0.182 (3)	0.13 (2)
O11B§	0.436 (2)	1/4	0.1118 (16)	0.157 (18)
C12B§	0.502 (3)	1/4	0.060 (2)	0.031 (12)
O13B§	0.210 (2)	1/4	0.3753 (17)	0.145 (16)
C1'†	0.1313 (2)	1/4	0.91955 (15)	0.0504 (10)
C2'‡	0.2247 (3)	0.3134 (11)	0.9348 (2)	0.060 (2)
C3'‡	0.2856 (3)	0.1896 (10)	0.8930 (2)	0.061 (2)
C4'†	0.2732 (3)	1/4	0.81847 (18)	0.0490 (11)
C4a'†	0.17850 (18)	1/4	0.79720 (17)	0.0341 (7)
C5'†	0.15428 (17)	1/4	0.72760 (15)	0.0339 (7)
C6'†	0.0663 (2)	1/4	0.71036 (16)	0.0397 (8)
C7'†	0.0009 (2)	1/4	0.7582 (2)	0.0393 (8)
C8'†	0.02469 (18)	1/4	0.82537 (15)	0.0379 (7)
C8a'†	0.11238 (18)	1/4	0.84486 (14)	0.0352 (7)
C9'†	0.2214 (2)	1/4	0.67384 (16)	0.0390 (8)
O10'†	0.2991 (3)	1/4	0.68109 (19)	0.064 (2)
O11'†	0.18518 (15)	1/4	0.61254 (11)	0.0550 (7)
C12'†	0.2457 (3)	1/4	0.5570 (2)	0.0676 (18)
O13'†	-0.03715 (13)	1/4	0.87486 (11)	0.0512 (7)
C1'B§	0.646 (3)	1/4	0.9244 (15)	0.14 (2)
C2'B¶	0.741 (3)	0.299 (14)	0.940 (3)	0.13 (3)
C3'B¶	0.799 (3)	0.175 (11)	0.895 (2)	0.13 (3)
C4'B§	0.788 (2)	1/4	0.822 (2)	0.06 (3)
C4a'B§	0.6924 (17)	1/4	0.8016 (12)	0.049 (10)
C5'B§	0.6694 (17)	1/4	0.7320 (12)	0.050 (11)
C6'B§	0.5817 (19)	1/4	0.7141 (17)	0.19 (3)
C7'B§	0.519 (2)	1/4	0.7637 (16)	0.066 (17)
C8'B§	0.5393 (19)	1/4	0.8309 (16)	0.15 (5)
C8a'B§	0.6274 (18)	1/4	0.8499 (14)	0.13 (2)
C9'B§	0.7374 (17)	1/4	0.6801 (12)	0.056 (13)
O10'B§	0.8148 (17)	1/4	0.6871 (17)	0.102 (14)
O11'B§	0.702 (2)	1/4	0.6185 (13)	0.127 (13)
C12'B§	0.758 (4)	1/4	0.562 (2)	0.11 (3)
O13'B§	0.479 (2)	1/4	0.8815 (16)	0.144 (16)

† Site occupancy = 0.895 (4). ‡ Site occupancy = 0.447 (2). § Site occupancy = 0.105 (4). ¶ Site occupancy = 0.053 (2).

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.510 (7)	C1'—C2'	1.522 (5)
C1—C8a	1.520 (4)	C1'—C8a'	1.516 (4)
C2—C3	1.535 (9)	C2'—C3'	1.508 (7)
C3—C4	1.564 (6)	C3'—C4'	1.553 (5)
C4—C4a	1.510 (5)	C4'—C4a'	1.507 (5)
C4a—C8a	1.394 (4)	C4a'—C8a'	1.386 (4)
C5—C9	1.480 (5)	C5'—C9'	1.483 (4)
C8—O13	1.363 (3)	C8'—O13'	1.365 (3)
C9—O10	1.214 (6)	C9'—O10'	1.196 (5)
C9—O11	1.336 (4)	C9'—O11'	1.341 (4)
O11—C12	1.442 (4)	O11'—C12'	1.442 (4)
C2—C1—C8a	112.2 (4)	C2'—C1'—C8a'	112.0 (3)
C1—C2—C3	107.5 (5)	C1'—C2'—C3'	107.9 (4)
C2—C3—C4	106.6 (4)	C2'—C3'—C4'	107.7 (4)
C4a—C4—C3	112.8 (3)	C4a'—C4'—C3'	112.7 (3)
C8a—C4a—C4	119.3 (3)	C8a'—C4a'—C4'	120.4 (3)
C4a—C8a—C1	123.1 (3)	C4a'—C8a'—C1'	122.3 (3)
O10—C9—O11	121.2 (3)	O10'—C9'—O11'	121.3 (4)
O10—C9—C5	126.5 (3)	O10'—C9'—C5'	126.8 (3)
O11—C9—C5	112.3 (3)	O11'—C9'—C5'	111.9 (3)
C9—O11—C12	115.9 (3)	C9'—O11'—C12'	115.7 (3)
C8a—C1—C2—C3	-52.0 (6)	C8a'—C1'—C2'—C3'	-52.2 (5)
C1—C2—C3—C4	70.2 (6)	C1'—C2'—C3'—C4'	69.1 (5)
C2—C3—C4—C4a	-53.1 (5)	C2'—C3'—C4'—C4a'	-51.0 (4)
C3—C4—C4a—C8a	18.7 (3)	C3'—C4'—C4a'—C8a'	16.7 (3)
C4—C4a—C8a—C1	0.0	C4'—C4a'—C8a'—C1'	0.0
C2—C1—C8a—C4a	17.2 (4)	C2'—C1'—C8a'—C4a'	17.9 (3)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O13—H13...O10 ⁱ	0.96 (4)	1.85 (4)	2.814 (3)	180 (2)
O13'—H13'...O10' ⁱⁱ	1.05 (4)	1.69 (4)	2.737 (4)	176 (3)

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

The crystals were thin plates, many of which could be seen to be composed of several crystals stacked on top of each other. Even though the selected crystal appeared to be single, the refinement indicated that it was either not single or, less likely, was a single crystal that was disordered. Each molecule was found to be distributed over two different positions, with occupancy factors of 0.895 (4) and 0.105 (4). The two components can be described as being related by a translation of approximately $0.48 + x, y, z$ (Le Page, 1987) or, since this translation results in the minor component being superimposed on a symmetry-related molecule of the major component along the *a* glide, by a mirror situated close to $c = \frac{1}{4}$ for one molecule and $c = \frac{3}{4}$ for the second. All non-H atoms of the major component were refined with anisotropic displacement parameters; H atoms were constrained to geometric estimates, except for H13 and H13' where the *x* and *z* coordinates were allowed to refine, and were assigned individual isotropic displacement parameters. The positions of 23 non-H atoms of the minor component were located from the difference map (peak heights $0.3\text{--}0.6 \text{ e \AA}^{-3}$), while the other atoms were located geometrically. All non-H atoms of the minor component were assigned individual isotropic displacement parameters, while the displacement parameters of the H atoms were assigned to be either 1.1 (CH), 1.3 (CH₂) or 1.5 (CH₃) times that of the parent C atom. During the refinement, the minor component was constrained to have the same geometric parameters as the major component.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL96*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1143). Services for accessing these data are described at the back of the journal.

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