

$\omega/2\theta$ scans
 Absorption correction:
 ψ scan (North *et al.*,
 1968)
 $T_{\min} = 0.094$, $T_{\max} = 0.176$
 2552 measured reflections
 2388 independent reflections

$R_{\text{int}} = 0.014$
 $\theta_{\max} = 25.46^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = -11 \rightarrow 11$
 3 standard reflections
 frequency: 30 min
 intensity decay: 0.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.078$
 $S = 1.085$
 2388 reflections
 112 parameters
 H-atom parameters
 constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 1.5688P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.776 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.764 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
SHELXL97 (Sheldrick,
 1997)
 Extinction coefficient:
 0.0085 (7)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-------------|-------------------------|------------|
| Te1—C1 | 2.092 (6) | C1—C2 | 1.308 (9) |
| Te1—C4 | 2.134 (7) | C2—C3 | 1.523 (9) |
| Te1—Br2 | 2.6115 (10) | C4—C5 | 1.445 (10) |
| Te1—Br1 | 2.7295 (10) | C5—C6 | 1.502 (11) |
| Br3—C2 | 1.889 (6) | C6—C7 | 1.425 (13) |
| O1—C3 | 1.403 (8) | | |
| C1—Te1—C4 | 99.7 (3) | Br2—Te1—Br1 | 176.59 (3) |
| C1—Te1—Br2 | 88.87 (19) | C2—C1—Te1 | 124.1 (5) |
| C4—Te1—Br2 | 89.0 (3) | Br1—Te1—O1 ¹ | 82.5 (1) |
| C1—Te1—Br1 | 89.65 (19) | Br2—Te1—O1 ¹ | 98.5 (1) |
| C4—Te1—Br1 | 88.2 (3) | C4—Te1—O1 ¹ | 72.6 (2) |

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

H atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they are attached. The hydroxyl H atom was found in a difference Fourier map and the torsion around the O atom refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1481). Services for accessing these data are described at the back of the journal.

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7-Methoxy-1-[1-(6-methoxy-2-naphthoyl)-ethyl]-2-methyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalen-3-one

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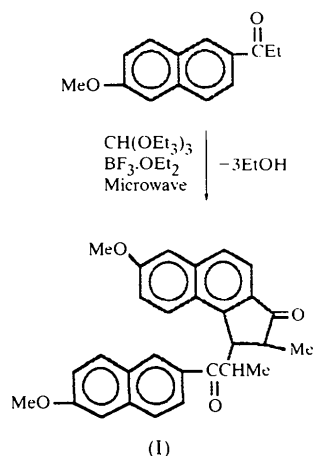
(Received 27 May 1997; accepted 6 July 1998)

Abstract

The structure of the title compound, $\text{C}_{29}\text{H}_{26}\text{O}_4$, prepared from 1-(6-methoxy-2-naphthyl)propan-1-one and ethyl *ortho*-formate in the presence of boron trifluoride under microwave irradiation, consists of connected 7-methoxy-2-methyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalen-3-one and 1-(6-methoxy-2-naphthyl)propan-1-one units. The space group, *Pc*, is non-centrosymmetric but achiral; three chiral centres exist in the molecule, but both enantiomers are present in the crystal.

Comment

The structure of the title compound, (I), has been determined as part of our studies on the condensation of aryl ketones with ethyl *ortho*-formate in the presence of boron trifluoride under microwave irradiation. Usually, ketals are obtained when ethyl *ortho*-formate reacts with various ketones under acid conditions (Abrahams *et al.*, 1949; Alazard *et al.*, 1977; Patwardhand & Dev, 1974), but when 1-(6-methoxy-2-naphthyl)propan-1-one was mixed with ethyl *ortho*-formate in the presence of an ethereal solution of boron trifluoride and irradiated for 10 min, an abnormal reaction took place, resulting in a new compound, *i.e.* (I).



The title compound has not been described previously and its structure could not be elucidated easily from classical spectroscopic data (IR, UV, MS, ¹H/¹³C NMR); it was therefore determined by X-ray analysis.

The molecule consists of connected 7-methoxy-2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-3-one and 1-(6-methoxy-2-naphthyl)propan-1-one moieties. We tentatively propose that it was formed as follows: under microwave irradiation, ethyl *ortho*-formate pyrolyzed to give a methenyl group, which attacked the α -carbon of the carbonyl groups of two 1-(6-methoxy-2-naphthyl)-

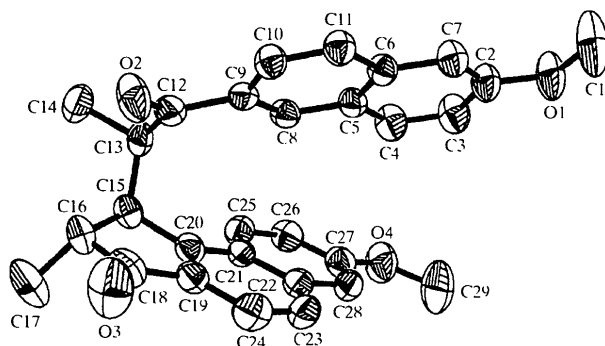


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

propan-1-one molecules, with subsequent electrophilic attack on an α position of a naphthalene group to give a fused cyclopentenone ring.

Bond lengths and angles of the naphthalene units are typical of such systems (Abrahams *et al.*, 1949; Robertson, 1953), ranging from 1.356 (4) to 1.425 (4) Å, and from 117.2 (3) to 121.8 (3)°, respectively. The differences in the C=O bond lengths of the cyclopentenone and open-chain ketones are insignificant.

Experimental

An ethereal solution of boron trifluoride (0.26 ml, 0.001 mol) was added to a mixture of 1-(6-methoxy-2-naphthyl)propan-1-one (2.14 g, 0.01 mol) and ethyl *ortho*-formate (3.32 ml, 0.02 mol). After microwave irradiation and refluxing for 10 min, the reaction mixture was cooled to room temperature and poured into vigorously stirred water (20 ml), and then extracted with CH₂Cl₂ (3 × 15 ml). The organic phase was washed with water (3 × 5 ml), dried (MgSO₄), filtered and concentrated. The solid residue was purified *via* silica-gel column chromatography with petroleum ether–dichloromethane (4:1) as eluent. The pure title compound (1.61 g, 78.6%) was obtained as colourless prismatic crystals (m.p. 460 K). Well-shaped single crystals of this compound were obtained by slow diffusion of *n*-hexane into a solution of the compound in CH₂Cl₂.

Crystal data

C₂₉H₂₆O₄
M_r = 438.50
 Monoclinic
Pc
a = 12.204 (2) Å
b = 14.957 (2) Å
c = 6.527 (1) Å
 β = 102.41 (1)°
V = 1163.6 (3) Å³
Z = 2
D_s = 1.252 Mg m⁻³
D_m not measured

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 2287 measured reflections
 2017 independent reflections
 1443 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

Refinement on *F*²
R(*F*) = 0.034
wR(*F*²) = 0.069
S = 0.997
 2015 reflections
 303 parameters
 H atoms riding

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 24 reflections
 θ = 3.22–13.23°
 μ = 0.082 mm⁻¹
T = 296 (2) K
 Tabular prism
 0.78 × 0.37 × 0.18 mm
 Colourless

θ_{\max} = 24°
 h = -13 → 13
 k = -17 → 1
 l = 0 → 7
 3 standard reflections
 every 97 reflections
 intensity decay: 1.83%

$\Delta\rho_{\max}$ = 0.142 e Å⁻³
 $\Delta\rho_{\min}$ = -0.127 e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0157 (19)

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$ Scattering factors from
 where $P = (F_o^2 + 2F_c^2)/3$ *International Tables for*
 $(\Delta/\sigma)_{\max} = -0.001$ *Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|-----------|-------------|-----------|
| O2—C12 | 1.222 (4) | C15—C20 | 1.516 (4) |
| O3—C18 | 1.212 (4) | C15—C16 | 1.555 (4) |
| C9—C12 | 1.496 (4) | C16—C18 | 1.510 (5) |
| C12—C13 | 1.518 (5) | C18—C19 | 1.467 (5) |
| C13—C15 | 1.548 (4) | C19—C20 | 1.366 (4) |
| O2—C12—C9 | 118.4 (3) | C13—C15—C16 | 113.9 (3) |
| O2—C12—C13 | 119.3 (3) | C18—C16—C15 | 105.0 (3) |
| C9—C12—C13 | 122.3 (3) | O3—C18—C19 | 126.1 (4) |
| C12—C13—C14 | 110.0 (3) | O3—C18—C16 | 126.0 (3) |
| C12—C13—C15 | 112.2 (3) | C19—C18—C16 | 107.8 (3) |
| C14—C13—C15 | 110.7 (3) | C20—C19—C18 | 109.9 (3) |
| C20—C15—C13 | 111.9 (2) | C19—C20—C15 | 111.7 (3) |
| C20—C15—C16 | 102.9 (3) | | |

Intensities above 2θ in θ were very weak and not measured.

Data collection: XSCANS (Siemens, 1993). Cell refinement: XSCANS. Data reduction: SHELXTL (Sheldrick, 1994). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1195). Services for accessing these data are described at the back of the journal.

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Four *N*-Benzyl-Substituted 2-Ethyl-3-hydroxypyridin-4-ones

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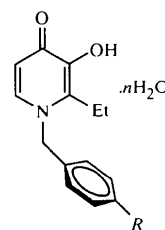
(Received 27 March 1998; accepted 19 June 1998)

Abstract

The molecular structures of 1-benzyl-2-ethyl-3-hydroxypyridin-4-one hydrate [(1), $C_{14}H_{15}NO_2 \cdot H_2O$], 2-ethyl-3-hydroxy-1-(4-methylbenzyl)pyridin-4-one [(2), $C_{15}H_{17}NO_2$], 2-ethyl-1-(4-fluorobenzyl)-3-hydroxypyridin-4-one [(3), $C_{14}H_{14}FNO_2$] and 2-ethyl-3-hydroxy-1-(4-trifluoromethylbenzyl)pyridin-4-one hemihydrate [(4), $C_{15}H_{14}F_3NO_2 \cdot 0.5H_2O$] have been determined. The compounds all exhibit mutually hydrogen-bonded dimeric pairs. In the case of (1) and (2), the molecules of the dimer are symmetry related, while in (3) and (4), two independent molecules of the asymmetric unit are linked. For the hydrates (1) and (4), the dimeric pairs are linked by further hydrogen bonds through the water molecules.

Comment

The title structures form dimeric units through mutual O1—H1...O2 hydrogen bonds (Figs. 1, 2, 3 and 4). This type of dimeric structure is commonly found for the anhydrous 3-hydroxypyridin-4-ones (Hider *et al.*, 1990; Chan *et al.*, 1992; Xiao *et al.*, 1992; Burgess *et al.*, 1993, 1998) and 3-hydroxypyran-4-ones, which have also been reported as hydrogen-bonded chains (Burgess *et al.*, 1996; Brown *et al.*, 1995). Important bond distances in compounds (1), (2), (3) and (4) are essentially the same within experimental error.



- (1) $R = H; n = 1$
 (2) $R = Me; n = 0$
 (3) $R = F; n = 0$
 (4) $R = CF_3; n = 0.5$

In the case of (1) and (2), the dimeric pair is related by a centre of symmetry at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, 0$, respectively,