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

O1—C7	1.353 (2)	O5—C16	1.433 (3)
O1—C4	1.414 (2)	O6—C2	1.352 (3)
O2—C7	1.219 (2)	O7—C18	1.212 (3)
O3—C13	1.355 (2)	O8—C18	1.343 (3)
O4—C11	1.369 (2)	O8—C19	1.456 (3)
O4—C15	1.431 (3)	O9—C6	1.362 (3)
O5—C9	1.360 (2)		
C7—O1—C4—C5	−82.2 (2)	O2—C7—C8—C13	−11.1 (3)
C4—O1—C7—C8	179.5 (2)	C19—O8—C18—O7	2.6 (4)
O1—C7—C8—C9	−12.8 (3)	C6—C1—C18—O8	2.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1O3···O2	0.94 (3)	1.69 (3)	2.554 (2)	151 (3)
O6—H1O6···O7	0.94 (4)	1.71 (4)	2.579 (3)	153 (4)
O9—H1O9···O8	0.88 (5)	1.76 (4)	2.570 (3)	152 (4)
C5—H5···O4^{i}	0.91 (3)	2.57 (3)	3.409 (3)	154 (3)

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4.023 cm and the detector swing angle was −35°. Coverage of the unique set is over 91% complete to at least 25° in θ. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996*b*). Cell refinement: *SAINT* (Siemens, 1996*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1218). Services for accessing these data are described at the back of the journal.

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2-Crotonoyl-5,8-dihydro-1-naphthol, (I), and 4-(1-Naphthoyl)-5,8-dihydro-1-naphthol, (II)†

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Abstract

In (I), $C_{14}H_{14}O_2$, the dihydrobenzene ring adopts a flattened boat conformation and the hydroxyl group is involved in an O—H···O intramolecular hydrogen bond. In (II), $C_{21}H_{16}O_2$, the dihydronaphthalene ring system is planar and makes a dihedral angle of 70.06 (7)° with the naphthalene ring system; the hydroxyl group forms O—H···O intermolecular hydrogen bonds.

Comment

The hydroxyketone derivatives of naphthalene are useful in the synthesis of the subunits of daunomycinone and adriamycin anticancer drugs (Crouse *et al.*, 1981). The dihydronaphthalene derivatives are useful intermediates in the synthesis of cyclic polymethylene phenols, which are useful antifibrillatory agents, disinfectants and water softeners (Hauck *et al.*, 1977). The crystal structure determinations of the title compounds, (I) and (II), were carried out in order to elucidate the molecular conformation and packing arrangements.

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† IUPAC names: 1-(1-hydroxy-5,8-hydro-2-naphthyl)but-2-en-1-one and 1-hydroxy-5,8-dihydro-4-naphthyl 1-naphthyl ketone.

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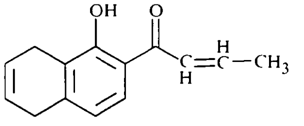
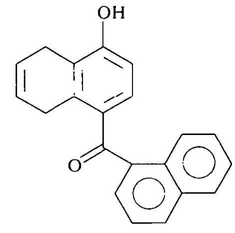


(I)



(II)

In both structures, the C_{sp^2}–C_{sp^3} distances, C5—C10 and C8—C9, are longer than the C5—C6 and C7—C8 distances, due to steric interactions, as also observed in related structures (Chinnakali *et al.*, 1998*a*, *b*). The C6—C7 bond shows double-bond nature. In the dihydronaphthalene moiety of (I), the mean planes through the benzene and dihydrobenzene rings form a dihedral angle of 3.30 (8)°, and the dihydrobenzene ring adopts a flattened boat conformation, with both α values equal to 6.3 (3)° (Marshall *et al.*, 1977). In (II), the dihydronaphthalene ring system is planar to within ±0.021 (4) Å and the naphthalene ring system is planar, with C16 deviating by a maximum of 0.029 (5) Å; the dihedral angle between these two ring systems is 70.06 (7)°. The small α values [1.6 (3) and 1.9 (3)°] for the dihydrobenzene ring of (II) indicate that this ring is slightly distorted from planarity.

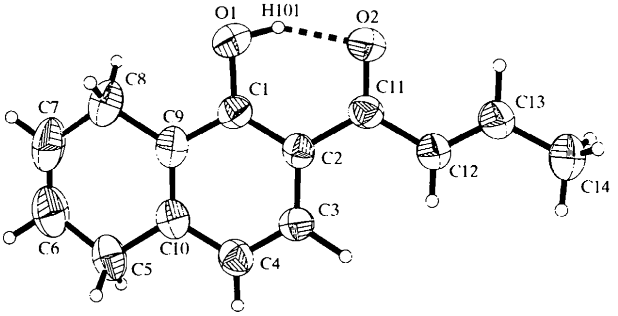


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are displayed as small circles of arbitrary radii.

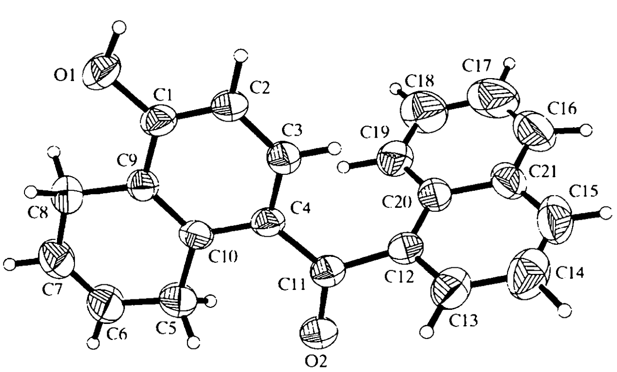


Fig. 2. The structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are displayed as small circles of arbitrary radii.

In the structure of (I), the hydroxyl group is involved in an O—H···O intramolecular hydrogen bond: within the crystal, centrosymmetrically related molecules lie in parallel planes at a distance of 3.496 (5) Å. The glide-related pairs lie at an angle of 72.0 (1)°, with a minimum non-bonding distance of 3.760 (6) Å between C2 and C6($\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$). This geometry indicates the possible π–π stacking interactions in the sets of parallel planes, and the side-on interactions in the glide-related pairs. These pairs extend to form layers parallel to the (111) plane (Fig. 3). As well as participating in the intramolecular hydrogen bond, the carbonyl O2 atom is also involved in C—H···O intermolecular hydrogen bonds, which link the glide-related molecules in different layers along the [101] direction (Fig. 3).

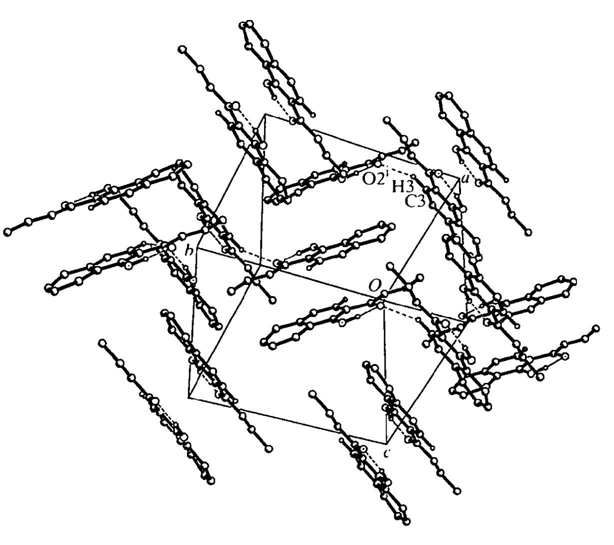


Fig. 3. Packing of the molecules of (I), viewed normal to the (111) plane. Dashed lines indicate hydrogen bonds. As the C—H···O contacts involve molecules in different layers, only one pair of molecules from the layers above and below is shown. [Symmetry code: (i) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$.]

In the crystal of (II), the hydroxyl groups form O—H···O intermolecular hydrogen bonds, to give a linear chain of dihydronaphthalene rings, which pack as layers parallel to the ($\bar{2}02$) planes. In the adjacent layers, the benzene ring of the dihydronaphthalene moiety is separated by a minimum non-bonding distance of 3.596 (5) Å between C2 and C10(x, $\frac{3}{2} - y$, $\frac{1}{2} + z$).

Experimental

Compound (I) was prepared as follows: 5,8-dihydro-1-naphthyl crotonate was prepared from 5,8-dihydro-1-naphthol and crotonyl chloride in the presence of pyridine, using dry benzene as solvent. Irradiation of 5,8-dihydro-1-naphthyl crotonate at 254 nm in dry ethyl acetate furnished two rearranged products. The major product was found to be the *ortho* rearranged compound, while the *para* rearranged compound was the minor product. Structures of both isomers have been confirmed by the spectroscopic data (Sriraghavan, 1998). Single crystals of (I), the major isomer, were obtained by slow evaporation of the compound in methanol. Compound (II) was prepared according to the method of Chinnakali *et al.* (1998*b*). Single crystals of (II) were grown by slow evaporation of the compound in a methanol–chloroform (1:1) solvent system. Spectroscopic data for (I): m.p. 399–341 K; IR (KBr): 3400, 2950, 2900, 2800, 2750, 1640, 1580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), p.p.m.: 13.27 (*s*, 1H, OH, exchanged with D_2O), 7.57 [*d*, 1H, Ar (C4-H) J = 8.31 Hz], 6.2 [*d*, 1H, Ar (C3-H) J = 8.34 Hz], 7.20–7.00 (*m*, 2H, C12-H and C13-H), 5.92–5.83 (*m*, 2H, C7-H and C8-H), 3.37 (*d*, 2H C8-H, J = 2.67 Hz), 3.30 (*d*, 2H C5-H, J = 2.70 Hz) and 2.02 (*dd*, 3H, C14, J = 6.15 and 1.02 Hz); ^{13}C NMR (22.5 MHz), p.p.m.: 193.5, 161.6, 144.9, 143.1, 126.6, 125.7, 112.4, 122.8, 118.6, 30.1, 23.7 and 18.5; MS (*m/e*): 214 (18), 199 (100), 173 (25), 115 (20), 91 (7); analytical data for $C_{14}H_{14}O_2$ = 214.266: calculated C 78.48, H 6.58%; found C 78.10, H 6.54%. Spectroscopic data for (II): m.p. 479–481 K; IR (KBr): 3390, 3000, 2900, 2850, 1620, 1560, 1450 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6), p.p.m.: 10.43 (*s*, 1H, OH exchanged with D_2O), 8.09–7.96 (*m*, 3H, Ar-H), 7.55–7.51 (*m*, 4H, Ar-H), 7.06–7.2 (*m*, 1H, Ar-H), 6.68–6.45 (*m*, 1H, Ar-H), 5.91–5.85 (*m*, 2H, C6-H, C7-H), 3.72–3.70 (*m*, 2H, C5-H), 3.26–3.23 (*m*, 2H, C8-H); ^{13}C NMR (100 MHz, DMSO-d_6): p.p.m. 158.4, 138.3, 137.1, 137.0, 133.1, 132.5, 130.6, 130.1, 128.4, 128.1, 127.3, 127.1, 126.3, 125.2, 124.1, 122.2, 122.1, 111.0, 28.2, 23.9; MS (*m/e*): 300 (100), 281 (13), 171 (90), 155 (77), 127 (82), 115 (37), 77 (16); analytical data for $C_{21}H_{16}O_2$ = 300.359: calculated C 83.97, H 5.36%; found C 83.90, H 5.25%.

Compound (I)

Crystal data

$C_{14}H_{14}O_2$
M_r = 214.25
Monoclinic
$P2_1/n$
a = 9.735 (3) Å
b = 12.7753 (8) Å
c = 9.735 (3) Å
β = 110.580 (2)°
V = 1133.50 (12) Å^3
Z = 4
D_x = 1.255 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 2829 reflections
θ = 3–25°
μ = 0.083 mm^{-1}
T = 293 (2) K
Parallepiped
0.30 × 0.28 × 0.16 mm
Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
5477 measured reflections
1986 independent reflections

1517 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034
$\theta_{\rm max}$ = 25°
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.134
S = 1.096
1986 reflections
202 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.2366P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.17 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C5—C6	1.476 (5)	C7—C8	1.478 (5)
C5—C10	1.500 (4)	C8—C9	1.513 (4)
C6—C7	1.305 (5)		
C6—C5—C10	114.2 (3)	C7—C8—C9	113.1 (3)
C10—C5—C6—C7	−7.6 (6)	C7—C8—C9—C10	7.4 (4)
C5—C6—C7—C8	−0.1 (7)	C8—C9—C10—C5	0.0 (4)
C6—C7—C8—C9	7.6 (6)	C6—C5—C10—C9	7.4 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H101···O2	0.94 (5)	1.66 (5)	2.540 (3)	154 (4)
C3—H3···O2$^{\rm i}$	1.11 (3)	2.39 (4)	3.422 (3)	155 (3)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_{21}H_{16}O_2$
M_r = 300.34
Monoclinic
$P2_1/c$
a = 12.2964 (2) Å
b = 16.2109 (3) Å
c = 7.8517 (2) Å
β = 103.197 (2)°
V = 1523.79 (5) Å^3
Z = 4
D_x = 1.309 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 1837 reflections
θ = 3–25°
μ = 0.083 mm^{-1}
T = 293 (2) K
Thin plate
0.26 × 0.18 × 0.02 mm
Light yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
7933 measured reflections
2681 independent reflections

1275 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.082
$\theta_{\rm max}$ = 25°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.134
S = 1.005
2679 reflections
272 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.14 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.16 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

C5—C6	1.477 (5)	C7—C8	1.476 (4)
C5—C10	1.512 (4)	C8—C9	1.504 (4)
C6—C7	1.302 (5)		
C6—C5—C10	115.2 (3)	C7—C8—C9	114.2 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O2^{i}	1.00 (4)	1.75 (5)	2.740 (3)	173 (4)

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm for (I) and 3.99 cm for (II); the detector swing angle was −30°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of the data collection and analysing the duplicate reflections, and was found to be negligible. Both structures were solved by direct methods and refined by full-matrix least-squares techniques; all H atoms were located from successive difference Fourier maps and refined isotropically. Though all the atoms in the structure of (I) had been located, the refinement did not converge and showed an *R* value of 0.174 (*wR* = 0.507). Nearly equal lengths for the *a* [9.7322 (6) Å] and *c* [9.7382 (6) Å] axes suggested the possibility of a rotational twin, with the *a* and *c* axes interchanged. Accordingly, the structure was refined with *TWIN* 001, 0$\bar{1}$0, 100 and *BASF* instructions, with equal values for *a* and *c* lengths, and it converged to the present *R* value with twin components of 0.720 (2) and 0.280 (2). The slightly low reflection-to-parameter ratios of 9.8 are due to the fact that the H-atom parameters were refined.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1234). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1499–1501

The 3,3,6,6-Tetramethyl *cis-transoid-cis*-Photocyclodimer of *tert*-Butyl 2,5-Dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate

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(Received 23 January 1998; accepted 8 April 1998)

Abstract

The X-ray structure of di-*tert*-butyl *cis-transoid-cis*-perhydro-3,3,6,6-tetramethyl-1,4-dioxocyclobuta[1,2-*c*:3,4-*c*′]dipyrrole-2,5-dicarboxylate, $C_{22}H_{34}N_2O_6$, which is the major photocyclodimer obtained on hexadeuterioacetone-sensitized irradiation of the monomeric *tert*-butyl 2,5-dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate, was determined in order to establish its constitution and configuration unambiguously.

Comment

The photochemical behaviour of 5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (Ihlefeld & Margaretha, 1992) parallels that of the pyrimidine bases of DNA, such as uracil or thymine. Direct irradiation (Ihlefeld & Margaretha, 1992) or hexadeuterioacetone-sensitized irradiation (Wrobel & Margaretha, 1997) affords a mixture of two dimers, (*A*) (major) and (*B*) (minor), whose structures were previously assigned on the basis of their ^{1}H NMR spectra only, because suitable single crystals could not be obtained. We have prepared the title compound,