

$$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.504P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.023$

Absolute structure: assumed from synthetically related compounds with known configuration

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α -Naphthyl Phenyl Pinacols

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Abstract

Treatment of α -naphthyl phenyl ketone with Zn/acetic acid gives racemic α -naphthyl phenyl pinacol [1,2-di(1-naphthyl)-1,2-diphenylethane-1,2-diol], C₃₄H₂₆O₂, but reaction with Mg/MgI₂ gives a product which proves to be not a pinacol, but a tricyclic compound (with four chiral centers, formed by addition at the 2-position of one of the naphthalene groups), racemic 5-(1-naphthyl)-3,5-diphenyl-4-oxatricyclo[7.4.0.0^{2,6}]trideca-7,9,11,13-tetraen-3-ol, C₃₄H₂₆O₂. The aromatic ring in this tricyclic compound is planar, but the other six-membered ring, and the five-membered furano ring, are non-planar. Bond lengths and angles in both molecules correspond to the molecular formulations. In both structures, the OH groups are involved in only weak intermolecular interactions.

Comment

Glycols, which may be synthesized by the dissolving-metal reduction of ketones, undergo dehydration and skeletal rearrangement when treated with mineral acids, a process known as the pinacol rearrangement. A study of the rearrangement of benzpinacols was initiated, in order to obtain details of the geometrical parameters in solid-state reactions (*cf.* Jones *et al.*, 1989; Toda & Shigemasa, 1989; Chen *et al.*, 1991). For various reasons this study was discontinued, but some interesting results did emerge, which shed light on some long-outstanding ambiguities.

Reduction of α -naphthyl phenyl ketone (1-benzoyl-naphthalene), (1), with Zn/acetic acid is reported to produce a material with m.p. 431 K, while reduction with Mg/MgI₂ gives a different material, with m.p. 493 K (Bachmann & Shankland, 1929; Bergmann & Schuchardt, 1931). Although not specifically stated, the implication is that these materials are racemic, (2), and *meso* forms, respectively, of di- α -naphthyl diphenyl pinacol. These syntheses have been repeated, giving crystalline materials with m.p. 421 and 479 K (see supplementary material). X-ray analysis of the lower-melting

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

O1—C9	1.366 (5)	C5—C6	1.386 (6)
O1—C2	1.454 (5)	C6—C7	1.374 (6)
C2—C3	1.529 (6)	C7—C8	1.379 (6)
C3—O18	1.431 (6)	C8—C9	1.396 (6)
C3—C4	1.531 (6)	C9—C10	1.393 (6)
C4—N14	1.460 (6)	C15—O17	1.224 (5)
C4—C10	1.522 (6)	C15—C16	1.503 (7)
C5—C10	1.381 (6)		
C9—O1—C2	118.7 (3)	C7—C8—C9	120.5 (4)
O1—C2—C3	109.7 (4)	O1—C9—C10	123.8 (4)
O18—C3—C2	108.9 (4)	O1—C9—C8	115.2 (4)
O18—C3—C4	108.5 (4)	C10—C9—C8	121.0 (4)
C2—C3—C4	111.0 (4)	C5—C10—C9	117.8 (4)
N14—C4—C10	110.9 (4)	C5—C10—C4	122.3 (4)
N14—C4—C3	110.7 (4)	C9—C10—C4	119.8 (4)
C10—C4—C3	110.4 (4)	C15—N14—C4	122.8 (5)
C10—C5—C6	120.6 (4)	O17—C15—N14	121.9 (5)
C7—C6—C5	121.8 (4)	O17—C15—C16	123.1 (5)
C6—C7—C8	118.2 (5)	N14—C15—C16	115.0 (5)

The position and isotropic displacement parameters of three aromatic and 12 methyl H atoms were constrained using the AFIX43 and AFIX137 options in SHELXL93 (Sheldrick, 1993), respectively. Other H atoms were refined without constraints.

Data collection: local program (Yoon *et al.*, 1994). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

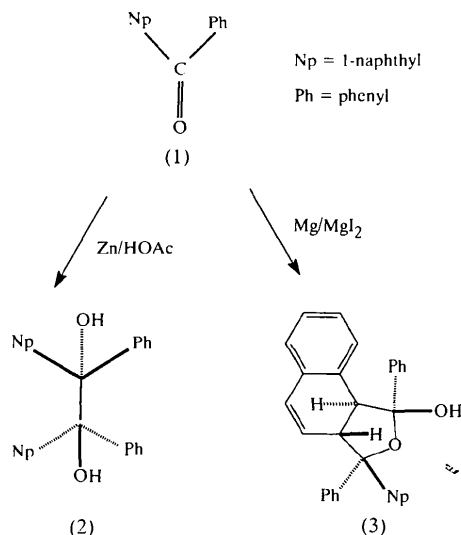
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1040). Services for accessing these data are described at the back of the journal.

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crystals indicates that the compound is racemic (2). The higher-melting material proves to be racemic (3), a tricyclic compound (with four chiral centers), formed as a result of addition at the 2-position of one of the naphthalene groups.



Room-temperature Rigaku AFC-6 data for (2) yielded a structure which did not refine satisfactorily. The structure of (3) was determined initially with room-temperature Rigaku AFC-6 diffractometer data (University of British Columbia, UBC), and later with Rigaku R-axis II image-plate data (Chinese University of Hong Kong, CUHK). Cell parameters showed differences of $8\text{--}18\sigma$, suggesting typical underestimation of errors (Taylor & Kennard, 1986). Differences between the two sets of positional and displacement parameters were examined by half-normal probability plots (Abrahams & Keve, 1971), which gave reasonably straight lines through the origin, slopes of 1.3–1.5, again suggesting some underestimation of errors. The main difference was that U_{22} (CUHK) were nearly all greater than U_{22} (UBC), by a mean of 1.9σ and maximum of 4.5σ ; this suggested possible errors in (or a need for) absorption corrections for the needle-shaped crystals. To establish both crystal structures definitively, new data had been measured at 180 K with a Rigaku/ADSC CCD area detector (UBC).

Compound (2) is racemic α -naphthyl phenyl pinacol, the molecule having approximate (non-crystallographic) C_2 symmetry (Fig. 1 shows the *R,R* enantiomer). The molecular dimensions are close to normal, except for a long central C1—C2 bond of 1.618(2) Å. In the tricyclic ring system of (3) (Fig. 2), the aromatic ring is planar, but the other two rings show deviations from planarity (roughly C_3 envelopes). Bond lengths and angles correspond to the molecular formulation (3), with C10=C11 definitely a double bond [1.336(3) Å]. Neither structure exhibits strong hydrogen bonds: (2)

has a weak O1—H···O2 intermolecular interaction [$O\cdots O = 2.937(2)$ Å and $O\text{—}H\cdots O = 116(2)^\circ$], and possible O2—H··· π and C—H···O interactions; (3) exhibits possible O—H··· π and C—H···O interactions (*cf. e.g.* Ferguson *et al.*, 1995). The C—H···O interactions are all weak, with $C\cdots O = 2.7\text{--}2.9$, $H\cdots O =$

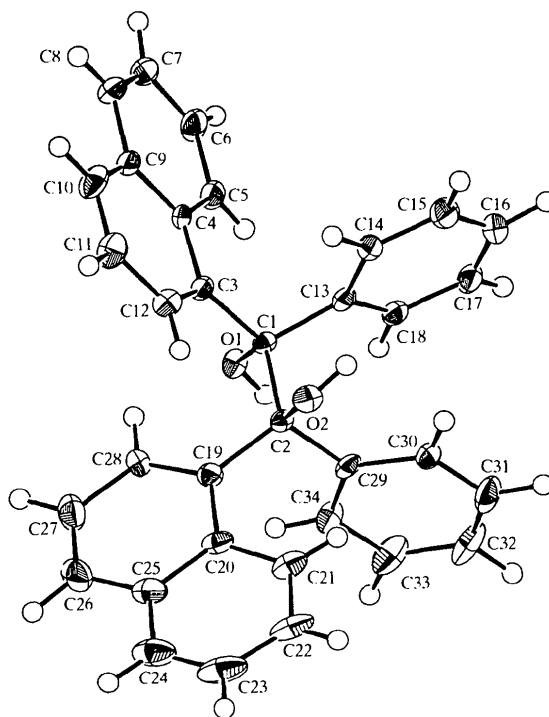


Fig. 1. View of the molecule of (2). Displacement ellipsoids are shown at 50% probability.

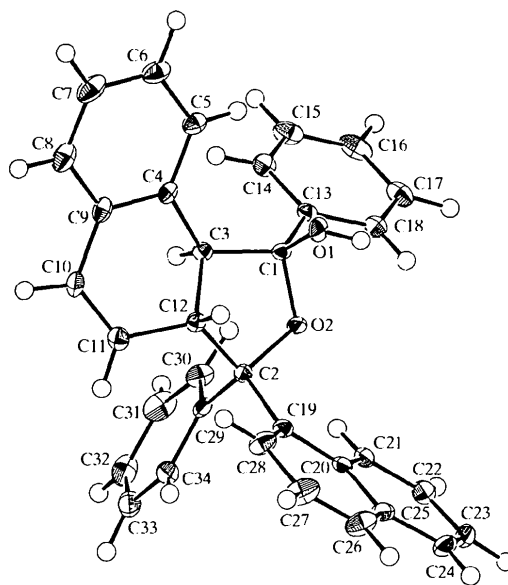


Fig. 2. View of the molecule of (3). Displacement ellipsoids are shown at 50% probability.

2.3–2.6 Å, and C—H···O = 90–120°. The O—H··· π interactions also do not appear to be particularly strong, with H···C=C_{aromatic} distances in the range 2.3–2.5 Å and O—H··· π angles of 120–147°.

Experimental

The title compounds were synthesized by reduction of 1-benzoylnaphthalene (details in supplementary material).

Compound (2)

Crystal data

C₃₄H₂₆O₂ Mo *K* α radiation
M_r = 466.58 λ = 0.7107 Å
 Orthorhombic Cell parameters from 16 454 reflections
*Pna*2₁ θ = 1.95–30.16°
a = 12.5595 (3) Å μ = 0.077 mm⁻¹
b = 18.7907 (7) Å *T* = 180 K
c = 10.375 (2) Å Prism
V = 2448.5 (5) Å³ 0.50 × 0.35 × 0.30 mm
Z = 4 Colorless
D_x = 1.266 Mg m⁻³
D_m not measured

Data collection

Quantum CCD diffractometer 5357 reflections with *I* > 3 σ (*I*)
 ω scan *R*_{int} = 0.047
 Absorption correction: θ _{max} = 30.16°
 symmetry analysis of *h* = -12 → 16
 redundant data (*d***TREK*; *k* = -21 → 24
 Molecular Structure *l* = -12 → 14
 Corporation, 1997) Intensity decay: none
*T*_{min} = 0.949, *T*_{max} = 0.977
 20 342 measured reflections
 5964 independent reflections
 (Friedel pairs not merged)

Refinement

Refinement on *F*² (Δ/σ)_{max} = 0.004
R(*F*) = 0.044 $\Delta\rho$ _{max} = 0.32 e Å⁻³
wR(*F*²) = 0.113 $\Delta\rho$ _{min} = -0.32 e Å⁻³
S = 1.30 Extinction correction: none
 5964 reflections Scattering factors from
 428 parameters *International Tables for*
 All H atoms refined *Crystallography* (Vol. C)
w = 1/[$\sigma^2(F_o^2)$]

Table 1. Selected geometric parameters (Å, °) for (2)

O1—C1	1.431 (2)	C1—C2	1.618 (2)
O2—C2	1.441 (2)		
O1—C1—C2	108.8 (1)	O2—C2—C1	107.6 (1)

Compound (3)

Crystal data

C₃₄H₂₆O₂ Mo *K* α radiation
M_r = 466.58 λ = 0.7107 Å

Orthorhombic

*P*2₁2₁2₁

a = 11.072 (2) Å

b = 11.4926 (3) Å

c = 18.9075 (7) Å

V = 2405.9 (3) Å³

Z = 4

D_x = 1.288 Mg m⁻³

D_m = 1.27 Mg m⁻³

D_m measured by flotation
 in aqueous KI at room
 temperature

Data collection

Quantum CCD diffractometer 5402 reflections with *I* > 3 σ (*I*)
 ω scan *R*_{int} = 0.051
 Absorption correction: θ _{max} = 30.04°
 symmetry analysis of *h* = -12 → 14
 redundant data (*d***TREK*; *k* = -15 → 12
 Molecular Structure *l* = -26 → 22
 Corporation, 1997) Intensity decay: none
*T*_{min} = 0.963, *T*_{max} = 0.986
 20 354 measured reflections
 6629 independent reflections
 (Friedel pairs not merged)

Refinement

Refinement on *F*² (Δ/σ)_{max} = 0.019
R(*F*) = 0.048 $\Delta\rho$ _{max} = 0.37 e Å⁻³
wR(*F*²) = 0.121 $\Delta\rho$ _{min} = -0.40 e Å⁻³
S = 1.16 Extinction correction: none
 6629 reflections Scattering factors from
 429 parameters *International Tables for*
 All H atoms refined *Crystallography* (Vol. C)
w = 1/[$\sigma^2(F_o^2)$]

Table 2. Selected geometric parameters (Å, °) for (3)

O1—C1	1.408 (2)	O2—C2	1.459 (2)
O2—C1	1.436 (2)	C10—C11	1.336 (3)
C1—O2—C2	112.4 (1)		

Attempts to refine the Flack parameter (Flack, 1983) with *TEXSAN* (Molecular Structure Corporation, 1992–97) and with *SHELXL97* (Sheldrick, 1997) were unsuccessful (not surprising, with light-atom structures and Mo radiation). Hence, the polarity of the crystal of (2) and the absolute configuration of the crystal of (3) are undetermined. The bulk sample of (3) presumably contains equal amounts of both enantiomers.

For both compounds, data collection: *d***TREK* (Molecular Structure Corporation, 1997); cell refinement: *d***TREK*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997); program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1438). Services for accessing these data are described at the back of the journal. Synthesis and spectroscopic analysis details have also been deposited.

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10-Ethyl-3-nitrophenothiazine

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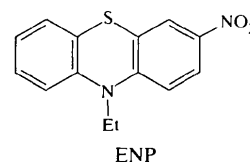
Abstract

The title compound, C₁₄H₁₂N₂O₂S (ENP), is a precursor in the synthesis of antipsychotic drugs based on 3-nitro-

phenothiazines. The structure analysis confirms the expected 3-nitro derivative. The nitro group flattens the tricycle; the dihedral angle between the phenyl rings is 157.2(1)°, compared with a value of 135.2(1)° in the non-nitrated compound.

Comment

Phenothiazines having different substituents have been systematically synthesized in order to find new antipsychotic drugs. The title compound, ENP, is an intermediate in the synthesis of active 3-nitrophenothiazinic compounds.



The structural study of ENP was undertaken in order to confirm the position of the nitro group and the transposition of the phenyl group corresponding to the Smiles rearrangement (Levy *et al.*, 1931).

The folding of the molecule is characterized by the angle between the phenyl planes, whose value is 157.2(1)°. In the non-nitrated compound, 10-ethylphenothiazine (Chu & van der Helm, 1975), the corresponding angle is 135.2(1)°, which suggests that addition of groups to the phenyl rings flattens the tricycle. This tendency is also observed in the structure of the dibromo-substituted compound, 3,7-dibromo-10-ethylphenothiazine (Meester *et al.*, 1986), in which the folding angles are 156.3(2) and 145.3(2)° in the two independent molecules.

In ENP, the ethyl group is almost orthogonal to the thiazine ring, the torsion angle C9—N10—C11—C12 being –84.9(2)°; the corresponding angle is 146.1(4)° in the non-nitrated compound (Chu & van der Helm, 1975). The nitro group is almost coplanar with its

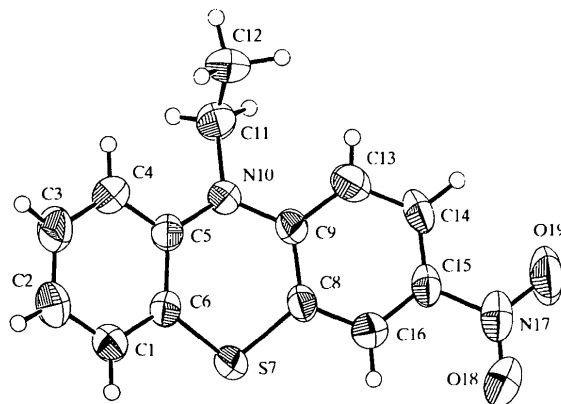


Fig. 1. The molecular structure of ENP shown with 50% probability displacement ellipsoids.