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(1*S*,4*R*)-1,11,11-Trimethyl-1,2,3,4-tetrahydro-1,4-methanophenazine N^5-oxide

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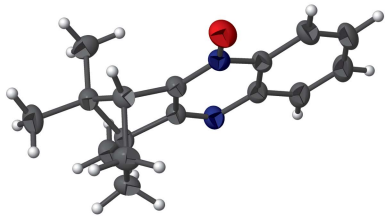
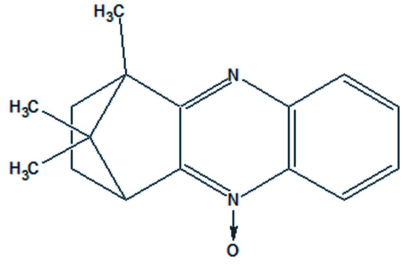
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{18}N_2O$, was synthesized *via* reaction of (1*S*,4*R*)-1,2,3,4-tetrahydro-1,11,11-trimethyl-1,4-methanophenazine with 3-chloroperbenzoic acid in dichloromethane. The absolute configuration for the product was assigned based on the stereochemistry of the camphorquinone reactant.

3D view



Chemical scheme



Structure description

In the molecule (Fig. 1), all bond lengths and angles are within expected values. The conformation of the product was assigned based upon the stereochemistry of the camphorquinone reactant. No classical hydrogen bonds are present.

Glisic *et al.* (2016) crystallized several chiral 1,2,3,4-tetrahydro-1,11,11-trimethyl-1,4-methanophenazine ligands with Au^{+3}. Steel & Fitchett (2000, 2006) illustrate the use of stereochemically active quinoxalines in extended metal–ligand networks.

Synthesis and crystallization

(1*S*,4*R*)-1,2,3,4-Tetrahydro-1,11,11-trimethyl-1,4-methanophenazine was synthesized by the condensation reaction of a diketone with a diamine in acid. To a 50 mL round-bottom flask were added (1*S*)-(+)-camphorquinone (3.1 g, 18.5 mmol), *o*-phenylenediamine (2.0 g, 18.5 mmol), and 20 ml of glacial acetic acid. This solution was then heated to boiling and held at reflux for 16 h. The resulting brown-colored solution was poured over 550 ml of cold water, neutralized with sodium carbonate, and isolated *via* vacuum filtration, which produced a light-brown solid. A hot gravity filtration with petroleum ether and activated charcoal, after evaporation of the petroleum ether, yielded 3.3 g of (1*S*,4*R*)-1,2,3,4-tetrahydro-1,11,11-trimethyl-1,4-methanophenazine (75%).

(1*S*,4*R*)-1,2,3,4-Tetrahydro-1,11,11-trimethyl-1,4-methanophenazine (3.3 g, 13.8 mmol) and 3-chloroperbenzoic acid (4.8 g, 27.6 mmol) were dissolved in dichloro-

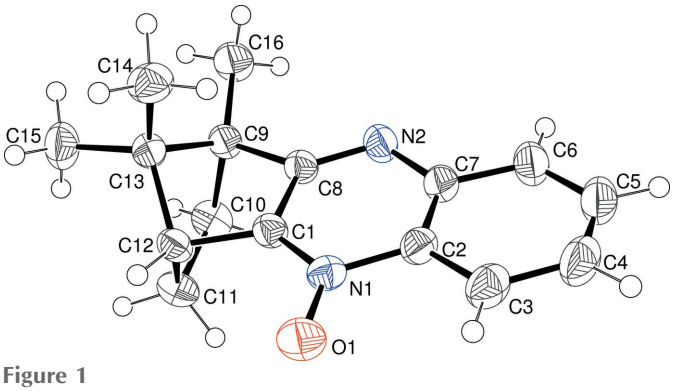


Figure 1
A view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

methane and stirred at room temperature for 24 h. Several spots were observed during TLC, suggesting the other possible oxide was also formed. The product was isolated *via* column chromatography (SiO_2, 50% dichloromethane/50% ethyl acetate, R_f = 0.5) to yield 1.77 g of the title compound (50%), m.p. 433.2 K. ATR–IR (cm^{-1}): 2971, 1496, 780; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.653 (*dd*, 1H, *J* = 8.3 Hz, 1.5 Hz), 8.113 (*dd*, 1H, *J* = 7.7 Hz, 1.7 Hz), 7.763 (*dt*, 1H, *J* = 7.6 Hz, 1.8 Hz), 7.701 (*dt*, 1H, *J* = 7.6 Hz, 1.8 Hz), 3.674 (*d*, 1H, *J* = 4.17 Hz), 2.310 (*m*, 1H), 2.087 (*m*, 1H), 1.498 (*m*, 2H), 1.459 (*s*, 3H), 1.142 (*s*, 3H), 0.756 (*s*, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.06, 144.26, 130.15, 129.30, 128.40, 118.71, 77.23, 76.51, 55.00, 54.71, 47.92, 32.37, 23.78, 20.32, 18.40, 10.14; UV/Vis (CH_2Cl_2; λ_{max}) 315 nm.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Reflections affected by the beam stop were omitted from the refinement.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{18}N_2O$
M_r	254.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	298
a, *b*, *c* (Å)	10.6779 (3), 10.7120 (3), 11.5207 (3)
V (Å^3)	1317.76 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.34 × 0.28 × 0.15
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.801, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33091, 4925, 4043
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.779
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.132, 0.93
No. of reflections	4925
No. of parameters	175
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.14
Absolute structure	Flack *x* determined using 1516 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter	0.1 (4)

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *OLEX2* (Bourhis *et al.*, 2015).

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full crystallographic data

IUCrData (2018). **3**, x180531 [https://doi.org/10.1107/S241431461800531X]

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Crystal data

$C_{16}H_{18}N_2O$
M_r = 254.32
Orthorhombic, $P2_12_12_1$
a = 10.6779 (3) Å
b = 10.7120 (3) Å
c = 11.5207 (3) Å
V = 1317.76 (6) Å^3
Z = 4
$F(000)$ = 544
D_x = 1.282 Mg m^{-3}
Melting point: 433.2 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9304 reflections
θ = 5.1–31.4°
μ = 0.08 mm^{-1}
T = 298 K
Plate, yellow
0.34 × 0.28 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
T_{min} = 0.801, T_{max} = 1.000
33091 measured reflections
4925 independent reflections
4043 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 33.6°, θ_{min} = 5.2°
h = −16→15
k = −16→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.132
S = 0.93
4925 reflections
175 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0978P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Absolute structure: Flack x determined using 1516 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.1 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms were included in calculated positions with C—H distances of 0.93 Å, 0.96 Å, 0.97 Å, and 0.98 Å based upon type of carbon and were included in the refinement in riding motion approximation with U_{iso} = 1.2 U_{eq} for CH and CH_2 and 1.5 U_{eq} for CH_3 groups, respectively. of the carrier atom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.39348 (13)	0.85071 (12)	0.83151 (13)	0.0297 (3)
C2	0.20009 (13)	0.95167 (14)	0.82727 (14)	0.0332 (3)
C3	0.07772 (15)	0.96131 (18)	0.78408 (17)	0.0435 (4)
H3	0.0479	0.9039	0.7302	0.052*
C4	0.00214 (16)	1.0572 (2)	0.82275 (19)	0.0510 (4)
H4	−0.0782	1.0660	0.7926	0.061*
C5	0.04485 (18)	1.14087 (18)	0.9064 (2)	0.0499 (4)
H5	−0.0086	1.2027	0.9339	0.060*
C6	0.16511 (17)	1.13333 (16)	0.94883 (18)	0.0439 (4)
H6	0.1926	1.1901	1.0044	0.053*
C7	0.24709 (14)	1.03897 (13)	0.90783 (14)	0.0343 (3)
C8	0.43617 (13)	0.94590 (12)	0.90722 (13)	0.0301 (3)
C9	0.56940 (13)	0.91155 (13)	0.93723 (14)	0.0312 (3)
C10	0.55122 (17)	0.79711 (15)	1.01944 (15)	0.0401 (3)
H10A	0.6299	0.7736	1.0555	0.048*
H10B	0.4906	0.8158	1.0797	0.048*
C11	0.50284 (17)	0.69165 (14)	0.93913 (15)	0.0400 (3)
H11A	0.4211	0.6624	0.9637	0.048*
H11B	0.5606	0.6217	0.9377	0.048*
C12	0.49567 (13)	0.75654 (13)	0.81835 (12)	0.0308 (3)
H12	0.4898	0.7012	0.7508	0.037*
C13	0.61140 (13)	0.84520 (13)	0.82243 (13)	0.0316 (3)
C14	0.61709 (19)	0.93181 (18)	0.71758 (16)	0.0450 (4)
H14A	0.6400	0.8847	0.6500	0.068*
H14B	0.6783	0.9958	0.7311	0.068*
H14C	0.5365	0.9695	0.7057	0.068*
C15	0.73576 (16)	0.77619 (18)	0.8335 (2)	0.0483 (4)
H15A	0.7303	0.7162	0.8953	0.073*
H15B	0.8012	0.8349	0.8503	0.073*
H15C	0.7540	0.7340	0.7620	0.073*
C16	0.64970 (16)	1.01615 (17)	0.98404 (18)	0.0445 (4)
H16A	0.6561	1.0811	0.9269	0.067*
H16B	0.7318	0.9848	1.0016	0.067*
H16C	0.6123	1.0491	1.0534	0.067*
N1	0.27666 (11)	0.85118 (11)	0.79122 (11)	0.0314 (3)
N2	0.36923 (12)	1.03772 (12)	0.94822 (12)	0.0356 (3)
O1	0.23308 (12)	0.76566 (11)	0.72480 (12)	0.0454 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0288 (6)	0.0278 (6)	0.0326 (6)	−0.0004 (5)	−0.0027 (5)	−0.0014 (5)
C2	0.0283 (6)	0.0345 (7)	0.0368 (7)	0.0008 (5)	0.0002 (5)	0.0076 (6)
C3	0.0321 (7)	0.0500 (9)	0.0484 (9)	0.0001 (7)	−0.0059 (6)	0.0099 (8)
C4	0.0306 (7)	0.0597 (11)	0.0628 (11)	0.0084 (7)	−0.0004 (7)	0.0196 (9)
C5	0.0402 (8)	0.0477 (10)	0.0619 (11)	0.0136 (8)	0.0118 (8)	0.0140 (8)
C6	0.0418 (8)	0.0401 (9)	0.0498 (9)	0.0100 (7)	0.0081 (7)	0.0017 (7)
C7	0.0329 (6)	0.0318 (6)	0.0382 (7)	0.0030 (6)	0.0032 (6)	0.0030 (5)
C8	0.0287 (6)	0.0277 (6)	0.0341 (6)	−0.0005 (5)	−0.0021 (5)	−0.0030 (5)
C9	0.0280 (6)	0.0299 (6)	0.0356 (7)	0.0004 (5)	−0.0046 (5)	−0.0040 (5)
C10	0.0475 (8)	0.0399 (7)	0.0330 (7)	0.0005 (7)	−0.0067 (6)	0.0036 (6)
C11	0.0495 (9)	0.0295 (6)	0.0409 (8)	−0.0024 (6)	−0.0027 (7)	0.0049 (6)
C12	0.0331 (6)	0.0254 (6)	0.0341 (6)	−0.0002 (5)	−0.0021 (5)	−0.0032 (5)
C13	0.0295 (6)	0.0298 (6)	0.0355 (6)	0.0002 (5)	0.0003 (5)	−0.0022 (5)
C14	0.0498 (9)	0.0449 (8)	0.0404 (8)	−0.0058 (7)	0.0075 (7)	0.0051 (7)
C15	0.0342 (7)	0.0510 (10)	0.0598 (11)	0.0100 (7)	−0.0009 (7)	−0.0119 (8)
C16	0.0372 (7)	0.0410 (8)	0.0553 (10)	−0.0044 (6)	−0.0104 (7)	−0.0125 (7)
N1	0.0298 (5)	0.0319 (6)	0.0324 (6)	−0.0039 (4)	−0.0026 (4)	0.0014 (5)
N2	0.0346 (6)	0.0318 (6)	0.0404 (6)	0.0032 (5)	−0.0012 (5)	−0.0060 (5)
O1	0.0430 (6)	0.0453 (6)	0.0480 (6)	−0.0082 (5)	−0.0101 (5)	−0.0100 (6)

Geometric parameters (Å, º)

C1—N1	1.3310 (17)	C10—C11	1.549 (2)
C1—C8	1.4172 (19)	C10—H10A	0.9700
C1—C12	1.4937 (19)	C10—H10B	0.9700
C2—C3	1.402 (2)	C11—C12	1.557 (2)
C2—C7	1.410 (2)	C11—H11A	0.9700
C2—N1	1.4142 (19)	C11—H11B	0.9700
C3—C4	1.380 (3)	C12—C13	1.559 (2)
C3—H3	0.9300	C12—H12	0.9800
C4—C5	1.393 (3)	C13—C14	1.524 (2)
C4—H4	0.9300	C13—C15	1.525 (2)
C5—C6	1.376 (3)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—C7	1.418 (2)	C14—H14C	0.9600
C6—H6	0.9300	C15—H15A	0.9600
C7—N2	1.385 (2)	C15—H15B	0.9600
C8—N2	1.3045 (18)	C15—H15C	0.9600
C8—C9	1.5095 (19)	C16—H16A	0.9600
C9—C16	1.510 (2)	C16—H16B	0.9600
C9—C10	1.561 (2)	C16—H16C	0.9600
C9—C13	1.567 (2)	N1—O1	1.2811 (15)
N1—C1—C8	120.89 (12)	C12—C11—H11A	111.2
N1—C1—C12	130.68 (13)	C10—C11—H11B	111.2

C8—C1—C12	108.26 (11)	C12—C11—H11B	111.2
C3—C2—C7	121.10 (15)	H11A—C11—H11B	109.1
C3—C2—N1	119.38 (15)	C1—C12—C11	104.29 (12)
C7—C2—N1	119.50 (12)	C1—C12—C13	99.47 (11)
C4—C3—C2	119.03 (18)	C11—C12—C13	101.89 (12)
C4—C3—H3	120.5	C1—C12—H12	116.3
C2—C3—H3	120.5	C11—C12—H12	116.3
C3—C4—C5	120.72 (16)	C13—C12—H12	116.3
C3—C4—H4	119.6	C14—C13—C15	109.07 (14)
C5—C4—H4	119.6	C14—C13—C12	112.23 (12)
C6—C5—C4	120.90 (17)	C15—C13—C12	113.41 (12)
C6—C5—H5	119.6	C14—C13—C9	113.84 (12)
C4—C5—H5	119.6	C15—C13—C9	113.47 (13)
C5—C6—C7	119.96 (18)	C12—C13—C9	94.29 (11)
C5—C6—H6	120.0	C13—C14—H14A	109.5
C7—C6—H6	120.0	C13—C14—H14B	109.5
N2—C7—C2	123.37 (13)	H14A—C14—H14B	109.5
N2—C7—C6	118.45 (15)	C13—C14—H14C	109.5
C2—C7—C6	118.18 (15)	H14A—C14—H14C	109.5
N2—C8—C1	126.10 (13)	H14B—C14—H14C	109.5
N2—C8—C9	128.12 (13)	C13—C15—H15A	109.5
C1—C8—C9	105.59 (11)	C13—C15—H15B	109.5
C8—C9—C16	115.85 (12)	H15A—C15—H15B	109.5
C8—C9—C10	102.30 (12)	C13—C15—H15C	109.5
C16—C9—C10	115.88 (14)	H15A—C15—H15C	109.5
C8—C9—C13	100.78 (11)	H15B—C15—H15C	109.5
C16—C9—C13	118.38 (13)	C9—C16—H16A	109.5
C10—C9—C13	101.04 (11)	C9—C16—H16B	109.5
C11—C10—C9	104.58 (12)	H16A—C16—H16B	109.5
C11—C10—H10A	110.8	C9—C16—H16C	109.5
C9—C10—H10A	110.8	H16A—C16—H16C	109.5
C11—C10—H10B	110.8	H16B—C16—H16C	109.5
C9—C10—H10B	110.8	O1—N1—C1	123.09 (12)
H10A—C10—H10B	108.9	O1—N1—C2	120.65 (12)
C10—C11—C12	102.98 (12)	C1—N1—C2	116.25 (12)
C10—C11—H11A	111.2	C8—N2—C7	113.68 (13)

C7—C2—C3—C4	−0.9 (2)	C10—C11—C12—C1	−67.26 (15)
N1—C2—C3—C4	177.78 (15)	C10—C11—C12—C13	35.86 (15)
C2—C3—C4—C5	−2.2 (3)	C1—C12—C13—C14	−66.52 (15)
C3—C4—C5—C6	2.8 (3)	C11—C12—C13—C14	−173.42 (13)
C4—C5—C6—C7	−0.3 (3)	C1—C12—C13—C15	169.31 (15)
C3—C2—C7—N2	−176.30 (15)	C11—C12—C13—C15	62.41 (16)
N1—C2—C7—N2	5.0 (2)	C1—C12—C13—C9	51.42 (12)
C3—C2—C7—C6	3.2 (2)	C11—C12—C13—C9	−55.48 (13)
N1—C2—C7—C6	−175.42 (14)	C8—C9—C13—C14	65.83 (15)
C5—C6—C7—N2	176.95 (16)	C16—C9—C13—C14	−61.56 (18)
C5—C6—C7—C2	−2.6 (2)	C10—C9—C13—C14	170.79 (13)

N1—C1—C8—N2	2.7 (2)	C8—C9—C13—C15	−168.62 (13)
C12—C1—C8—N2	−173.03 (15)	C16—C9—C13—C15	63.99 (18)
N1—C1—C8—C9	177.97 (13)	C10—C9—C13—C15	−63.66 (15)
C12—C1—C8—C9	2.21 (16)	C8—C9—C13—C12	−50.78 (12)
N2—C8—C9—C16	−24.0 (2)	C16—C9—C13—C12	−178.17 (13)
C1—C8—C9—C16	160.86 (15)	C10—C9—C13—C12	54.18 (12)
N2—C8—C9—C10	102.99 (17)	C8—C1—N1—O1	−178.35 (13)
C1—C8—C9—C10	−72.13 (14)	C12—C1—N1—O1	−3.7 (2)
N2—C8—C9—C13	−153.07 (15)	C8—C1—N1—C2	0.7 (2)
C1—C8—C9—C13	31.82 (14)	C12—C1—N1—C2	175.35 (14)
C8—C9—C10—C11	69.77 (15)	C3—C2—N1—O1	−3.8 (2)
C16—C9—C10—C11	−163.24 (14)	C7—C2—N1—O1	174.85 (13)
C13—C9—C10—C11	−33.97 (15)	C3—C2—N1—C1	177.13 (14)
C9—C10—C11—C12	−0.94 (17)	C7—C2—N1—C1	−4.19 (19)
N1—C1—C12—C11	−105.67 (18)	C1—C8—N2—C7	−2.1 (2)
C8—C1—C12—C11	69.52 (14)	C9—C8—N2—C7	−176.23 (14)
N1—C1—C12—C13	149.38 (16)	C2—C7—N2—C8	−1.8 (2)
C8—C1—C12—C13	−35.42 (14)	C6—C7—N2—C8	178.64 (14)