

1,4,4-Trimethyl-9-phenyl-8-oxa-9-aza-bicyclo[3.2.2]non-6-en-2-one

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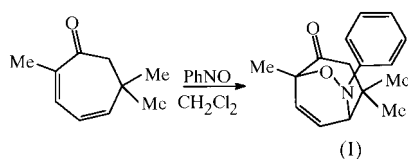
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The structure of the adduct of eucarvone with nitrosobenzene, $\text{C}_{16}\text{H}_{19}\text{NO}_2$, is reported. The [3.2.2] bicyclic system corresponds to two seven-membered rings in boat and distorted chair conformations and a six-membered ring that adopts a distorted boat conformation. No conjugation is observed between the phenyl group and the N—O system. The packing is directed mainly by a $\text{C}\cdots\text{O}$ hydrogen bond, $\text{C—H}\cdots\text{O}$ ($1 - x, -y, z$) and by intermolecular $\text{C—H}\cdots\pi$ interactions.

Comment

Diels–Alder reactions using NO compounds as dienofiles constitute a flexible key for natural products synthesis, especially for alkaloids such as lycorine. Reactions between nitroso compounds and dienes are strongly dependent on stereo-electronic factors which direct the regiochemistry of the cycloaddition reaction. Although the orientation of the cycloaddition can be determined by spectroscopic methods, crystal-structure determination of the final product of the reaction is necessary for a complete analysis of the conformation of the molecule. This communication reports the structure of the adduct of the eucarvone (a rearranged monoterpene derived from carvone, possessing a diene system) with nitrosobenzene, (I) (Hart *et al.*, 1979), as part of the research into the synthesis of amaryllidaceas alkaloids.



The title compound contains a [3.2.2] bicyclic system with the endocyclic torsion angles listed in Table 1. The six-membered ring shows a distorted boat conformation as could be predicted by the presence of the bridge. The puckering

parameters (Cremer & Pople, 1975) for this ring are $q_2 = 0.624 \text{ \AA}$, $q_3 = 0.070 \text{ \AA}$, $\varphi_2 = 108.67^\circ$, $\theta_2 = 83.6^\circ$ and $Q_T = 0.628 \text{ \AA}$. The conformations that the two seven-membered rings adopt are different from those of other similar compounds previously reported (Tinant & Declercq, 1991a). The ring with the C6–C7 double bond has a distorted chair conformation and the ring containing the N–O bond is a slightly distorted boat, as evidenced by the puckering parameters $q_2 = 0.668$ and $1.189 \text{ \AA}$, $q_3 = 0.596$ and $0.082 \text{ \AA}$, $\varphi_2 = 163.59$ and 316.1° , $\varphi_3 = 229.11$ and 287.78° , $Q_T = 0.895$ and $1.191 \text{ \AA}$, respectively, for the two rings. These different conformations can be explained by the presence of methyl-group substituents which could introduce steric effects. There is no conjugation between the phenyl group and the N9–O8 bond as can be deduced from the N–O bond length [$1.446(2) \text{ \AA}$], which is longer than in other similar compounds (Tinant & Declercq, 1991b). The distance of atom O8 from the phenyl group plane [$0.299(1) \text{ \AA}$] confirms this conclusion.

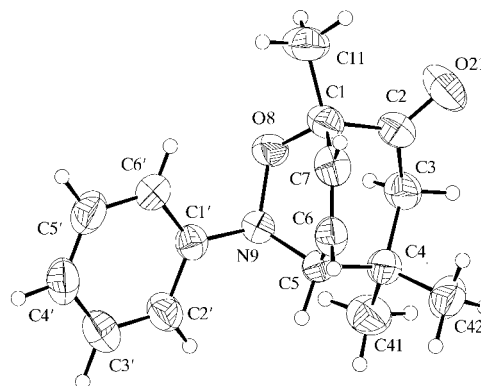


Figure 1
ZORTEP (Zsolnai & Pritzkow, 1995) drawing of the molecular structure of (I) showing 30% probability displacement ellipsoids.

The packing is directed mainly by intermolecular contacts involving the H atoms bonded to C6 and C7. C7—H7...O21-(1 - x, -y, z) appears to be a hydrogen bond where the distances C7—H7, H7...O21 and C7...O21 are 0.92 (2), 2.50 (2) and 3.326 (2) Å [the angle C7—H7...O21 is 150 (2)°], respectively. C6—H6 interacts with the phenyl group of a neighboring molecule at (-x, -y, -z) with the characteristic distances (H6...ring centroid, C6...ring centroid and H6...ring mean plane) of 2.749, 3.665 and 2.725 Å, respectively; the C6—H6...ring centroid angle is 153.64°.

The structure has also been used to determine the regiochemistry of the cycloaddition reaction. The O atom of the dienophile adds to C1, α to the carbonyl exclusively, yielding only one adduct. The stereoelectronic structure of the adduct also accounts for some of the signals detected in the ^1H NMR spectrum. The most relevant are the deshielding of the proton bonded to C5 by an anisotropic effect due to the orientation of the phenyl group, and the nonequivalent, diastereotopic protons, belonging to C3, where the proton lying equatorial is shielded by the carbonyl group.

Experimental

Eucarvone (Corey & Burke, 1956) (0.1 g, 0.67 mmol) and nitrosobenzene (0.071 g, 0.67 mmol) were dissolved in dichloromethane (30 ml). After stirring in the darkness for 10 h, the green colour disappeared. The solvent was distilled at reduced pressure and the oil was dissolved in pentane. Leaving the solution overnight at 261 K yielded colourless crystals suitable for X-ray diffraction (m.p. 329–331 K). MS (Shimadzu GC–MS QP 1100 EX, id, 20 eV): m/z = 257 (M^+ , 89.7%); 214 (37%); 174 (64.5%); 172 (43.6%); 130 (89.4%); 107 (PhNO^+ , 100%); 95 (72.7%); 77 (Ph^+ , 89.3%). ^1H NMR (CDCl_3 , 400 MHz, Bruker Avance DPX400, δ p.p.m.): 7.28 (*dd*, 2H, J = 8.6, 7.3 Hz, H'3, H'5); 7.04 (*dd*, 2H, J = 8.6, 1.0 Hz, H'2, H'6); 6.99 (*tt*, 1H, J = 7.3 $\times$ 2, 1.0 $\times$ 2 Hz, H'4); 6.17 (*dd*, 1H, J = 9.1, 7.3 Hz, H6); 6.07 (*d*, 1H, J = 9.1 Hz, H7); 4.02 (*d*, 1H, J = 7.3 Hz, H5); 3.46 (*d*, 1H, J = 13.4 Hz, H3); 2.32 (*d*, 1H, J = 13.4 Hz, H3 gem); 1.67 (*s*, 3H, CH_3 bridge); 1.47, 1.11 (*s*, 3H each, CH_3 gem). ^{13}C NMR (CDCl_3 , p.p.m., 400 MHz): 206.4 (C2); 152.7 (C'1); 132.6 (C6); 129.0 (C7); 128.5 $\times$ 2 (C'3, C'5); 122.1 (C'4); 117.3 $\times$ 2 (C'2, C'6); 82.6 (C1); 71.4 (C5); 53.7 (C3); 35.6 (C4); 29.6, 26.2 (CH_3 gem); 19.9 (CH_3 bridge).

Crystal data

$\text{C}_{16}\text{H}_{19}\text{NO}_2$	$D_x = 1.205 \text{ Mg m}^{-3}$
$M_r = 257.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 10.417$ (3) Å	$\theta = 20.17\text{--}25.40^\circ$
$b = 8.263$ (2) Å	$\mu = 0.079 \text{ mm}^{-1}$
$c = 16.5049$ (12) Å	$T = 293$ (2) K
$\beta = 92.746$ (11)°	Prismatic, colourless
$V = 1419.0$ (5) Å ³	$0.20 \times 0.17 \times 0.13 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.017$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 27.49^\circ$
Absorption correction: ψ scan	$h = -7 \rightarrow 13$
(Molecular Structure Corporation, 1993)	$k = -8 \rightarrow 10$
$T_{\text{min}} = 0.964$, $T_{\text{max}} = 1.000$	$l = -21 \rightarrow 21$
3571 measured reflections	3 standard reflections
3254 independent reflections	every 150 reflections
1819 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.0281P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.027$	$\Delta\rho_{\text{max}} = 0.15 \text{ e Å}^{-3}$
3254 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e Å}^{-3}$
230 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure:

Table 1

Selected geometric parameters (Å, °).

O8—N9	1.4461 (17)	C6—C7	1.313 (3)
O8—C1	1.4669 (19)	C3—C2	1.497 (3)
N9—C5	1.486 (2)	C3—C4	1.548 (2)
C5—C6	1.496 (2)	C2—C1	1.535 (3)
C5—C4	1.547 (2)	C1—C7	1.501 (3)
N9—O8—C1	117.69 (11)	C5—C4—C3	112.31 (14)
O8—N9—C5	111.19 (11)	C3—C2—C1	117.15 (14)
N9—C5—C6	109.20 (13)	O8—C1—C7	111.57 (13)
N9—C5—C4	111.23 (13)	O8—C1—C2	106.88 (13)
C6—C5—C4	115.28 (13)	C7—C1—C2	105.79 (14)
C2—C3—C4	116.65 (15)	C6—C7—C1	117.48 (17)
C1—O8—N9—C5	−16.70 (18)	C4—C3—C2—C1	−53.0 (2)
O8—N9—C5—C6	55.29 (16)	N9—O8—C1—C7	−31.29 (19)
O8—N9—C5—C4	−73.06 (16)	N9—O8—C1—C2	83.91 (15)
N9—C5—C6—C7	−46.37 (19)	C3—C2—C1—O8	−29.4 (2)
C4—C5—C6—C7	79.7 (2)	C3—C2—C1—C7	89.66 (19)
N9—C5—C4—C3	50.25 (19)	C5—C6—C7—C1	−3.5 (2)
C6—C5—C4—C3	−74.76 (19)	O8—C1—C7—C6	43.1 (2)
C2—C3—C4—C5	40.3 (2)	C2—C1—C7—C6	−72.72 (19)

SHELXL97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON98* (Spek, 1998) and *CSD* (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1097). Services for accessing these data are described at the back of the journal.

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