

1,4,4-Trimethyl-9-phenyl-8-oxa-9-aza-
bicyclo[3.2.2]non-6-en-2-oneSilvia Russi,^a Helena Pardo,^a Horacio Heinzen,^b Eduardo
Dias,^b Patrick Moyna,^b Raúl A. Mariezcurrena,^a Leopoldo
Suescun^a and Alvaro W. Mombru^{a*}^aLaboratorio de Cristalografía y Química del Estado Sólido, Facultad de Química,
Universidad de la República, Av. Gral Flores 2124, Casilla de Correos 1157,
Montevideo, Uruguay, and ^bCátedra de Farmacognosia, Facultad de Química,
Universidad de la República, Av. Gral Flores 2124, Casilla de Correos 1157,
Montevideo, Uruguay
Correspondence e-mail: amombru@bilbo.edu.uy

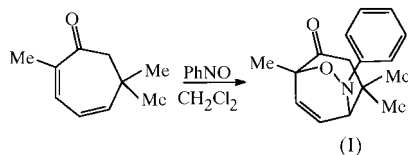
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The structure of the adduct of eucarvone with nitrosobenzene, C₁₆H₁₉NO₂, is reported. The [3.2.2] bicyclic system corresponds to two seven-membered rings in boat and distorted chair conformations and a six-membered ring that adopts a distorted boat conformation. No conjugation is observed between the phenyl group and the N—O system. The packing is directed mainly by a C···O hydrogen bond, C—H···O-(1 - x, -y, z) and by intermolecular C—H···π interactions.

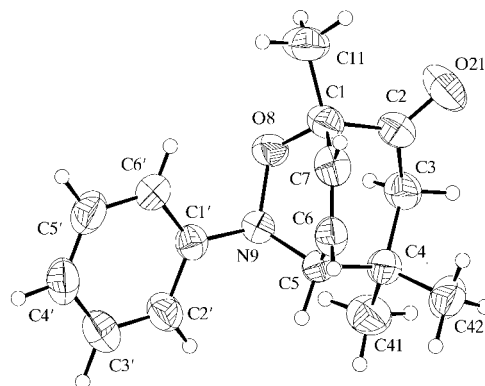
Comment

Diels–Alder reactions using NO compounds as dienophiles 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 amaryllidaceae 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 \AA , $q_3 = 0.596$ and 0.082 \AA , $\varphi_2 = 163.59$ and 316.1° , $\varphi_3 = 229.11$ and 287.78° , $Q_T = 0.895$ and 1.191 \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.



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	$\theta = 20.17$ – 25.40°
$b = 8.263$ (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 (Molecular Structure Corporation, 1993)	$h = -7 \rightarrow 13$
$T_{\text{min}} = 0.964$, $T_{\text{max}} = 1.000$	$k = -8 \rightarrow 10$
3571 measured reflections	$l = -21 \rightarrow 21$
3254 independent reflections	3 standard reflections
1819 reflections with $I > 2\sigma(I)$	every 150 reflections
	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 $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.027$	$\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{Å}^{-3}$
3254 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{Å}^{-3}$
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.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
 Corey, E. J. & Burke, H. J. (1956). *J. Am. Chem. Soc.* **78**, 174–180.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Hart, H., Ramaswami, S. K. & Willer, R. (1979). *J. Org. Chem.* **44**, 1–6.
 Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (1998). *PLATON98*. University of Utrecht, The Netherlands.
 Tinant, B. & Declercq, J.-P. (1991a). *Acta Cryst.* **C47**, 1266–1269.
 Tinant, B. & Declercq, J.-P. (1991b). *Acta Cryst.* **C47**, 827–829.
 Zsolnai, L. & Pritzkow, H. (1995). *ZORTEP*. University of Heidelberg, Germany.