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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.046

wR factor = 0.112

Data-to-parameter ratio = 6.6

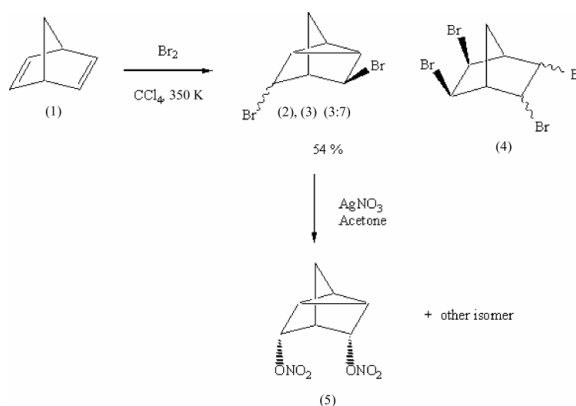
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.3,5-Dinitroxytricyclo[2.2.1.0^{2,6}]heptaneThe molecule of the title compound, $\text{C}_7\text{H}_7\text{N}_2\text{O}_6$, has a mirror plane through three common C atoms of two five-membered rings, which show distorted envelope conformations. The nitroso group is in a planar configuration.

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Comment

A convenient synthetic method for 3,5-disubstituted nortricyclane derivatives is not available in the literature. Most literature syntheses of 3,5-disubstituted nortricyclanes rely on the electrophilic addition to norbornadiene, yielding complex reaction mixtures in which normal addition and Wagner–Meerwein rearrangement stereoisomeric product mixtures are formed (Zefirov *et al.*, 1982).

3,5-Dibromonortricyclanes (2) and (3) (see *Scheme* above) constitute valuable precursors for the preparation of functionalized 3,5-disubstituted norbornadienes. We wish to demonstrate the synthetic potential of cyclopropyl bromides in nortricyclane structures for substitution reactions. Silver-induced nucleophilic substitution reactions of (2) and (3) may be prime tools for elusive 3,5-dibromonortricyclane derivatives. For this reason, a dibromonortricyclane mixture [(2) and (3)] in dry acetone was treated with two equivalents of AgClO_4 in dry acetone. After reaction, a 3,5-dinitroxy-nortricyclane product, (5), was obtained in 11% yield as a minor isomer. NMR spectra indicate symmetry in the structure. Two symmetrical structures are possible for the dinitroso structure. Therefore, it was not possible to establish the exact configuration of the nitroso groups from NMR investigations. The crystal structure determination established the conformation of (5) to be *endo,endo*.

It is interesting that both substituents in the structure are in the *endo* orientation, in which we expect strong dipole–dipole and van der Waals interactions as a consequence of the *cis* arrangement of the nitroso groups. As far as we know, no similar example of *endo,endo* substituents of nortricyclane is available in the literature (Chizhov *et al.*, 1987).

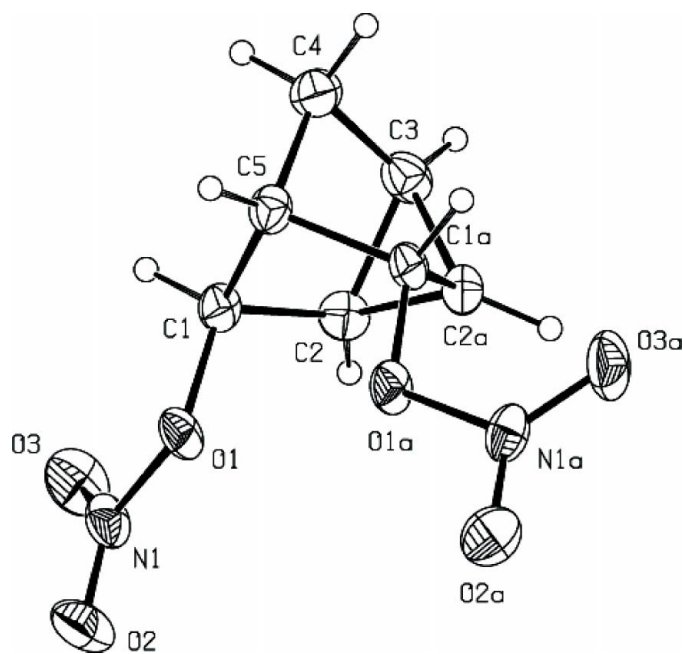


Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of the title compound, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Atoms with suffix 'a' are generated by reflection symmetry.

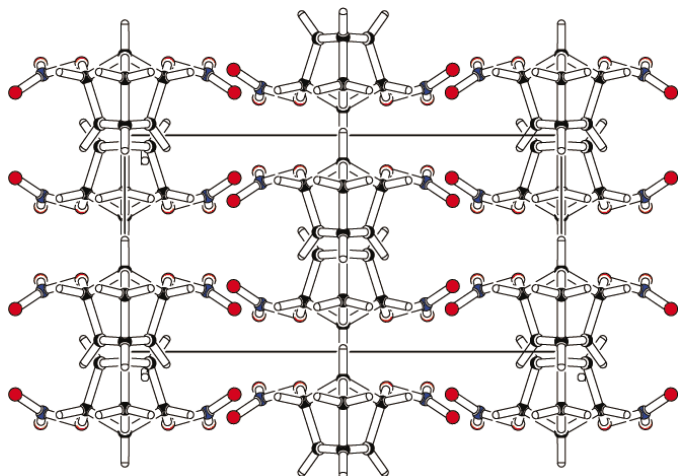


Figure 2

A view of the crystal packing along the *c* axis.

The values of the bond distances and angles agree with the literature values (Allen *et al.*, 1987). The five-membered ring (C1–C5) adopts a distorted envelope conformation. The molecule possesses a mirror plane, passing through atoms C3, C4 and C5. The torsion angle C1–C2–C3–C4 is 1.8 (3)°. The nitroxy group is planar configuration and the N1–O1 distance [1.391 (3) Å] is in agreement with electron delocalization of the nitro group.

Experimental

Recently, we have succeeded in the preparation of 3,5-dibromonortricyclane by the selective bromination of norbornadiene (Tutar *et al.*, 1996). After completion of the reaction shown in the Scheme above, the reaction mixture was subjected to silica-gel chromatography by eluting with hexane–ethyl acetate. Five fractions were obtained, including compound (5) in a yield of 11%. This was dissolved in boiling acetone and *n*-hexane was added. The clear solution was cooled slowly to room temperature. After about one day, colourless prism-shaped crystals had formed.

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Crystal data

C₇H₇N₂O₆
M_r = 215.15
 Orthorhombic, *Cmc2₁*
a = 13.4146 (9) Å
b = 6.6414 (5) Å
c = 10.0118 (6) Å
V = 891.97 (10) Å³
Z = 4
D_x = 1.602 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 2626 reflections
 θ = 3–26°
 μ = 0.14 mm⁻¹
T = 293 (2) K
 Prism, colorless
 0.32 × 0.22 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 2626 measured reflections
 485 independent reflections

423 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.072
 θ_{\max} = 26.0°
h = –12 → 16
k = –8 → 7
l = –12 → 11

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.112
S = 1.13
 485 reflections
 74 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.023 (5)

Table 1

Selected geometric parameters (Å, °).

O1–N1	1.391 (3)	C1–C5	1.525 (4)
O1–C1	1.451 (4)	C2–C3	1.504 (6)
O2–N1	1.191 (4)	C3–C4	1.538 (7)
O3–N1	1.210 (4)	C4–C5	1.540 (8)
C1–C2	1.489 (4)		
N1–O1–C1	114.9 (2)	C2–C1–C5	98.8 (3)
O1–N1–O2	113.1 (3)	C1–C2–C3	105.7 (3)
O1–N1–O3	117.7 (3)	C2–C3–C4	106.1 (4)
O2–N1–O3	129.2 (3)	C3–C4–C5	97.0 (4)
O1–C1–C2	114.6 (3)	C1–C5–C4	99.2 (3)
O1–C1–C5	109.4 (3)		
C1–O1–N1–O2	176.9 (3)	C2–C1–C5–C4	55.1 (3)
C1–O1–N1–O3	–3.9 (4)	O1–C1–C2–C3	–150.8 (2)
N1–O1–C1–C2	–82.8 (3)	C1–C2–C3–C4	1.8 (3)
N1–O1–C1–C5	167.4 (2)	C2–C3–C4–C5	31.27 (18)
C5–C1–C2–C3	–34.7 (3)	C3–C4–C5–C1	–52.7 (2)
O1–C1–C5–C4	175.1 (2)		

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The Flack (1983) parameter was indeterminate and so the Friedel data were merged before the refinement.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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3,5-Dinitroxytricyclo[2.2.1.0^{2,6}]heptane. Erratum

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In the paper by Öztürk *et al.* [*Acta Cryst.* (2003), E59, o550–o552], the author list is incorrect. The correct list is given here.