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2-(*exo*-Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-*endo*-yl)acetaldehyde 2,4-dinitrophenylhydrazone

A. Abdul Ajees,[a]* N. Palani[b] and K. K. Balasubramanian[b]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and [b]Shasun Chemicals and Drugs Limited, R&D Centre, 60 Velachery Road, Chennai 600 042, India
Correspondence e-mail: alazeez34@yahoo.com

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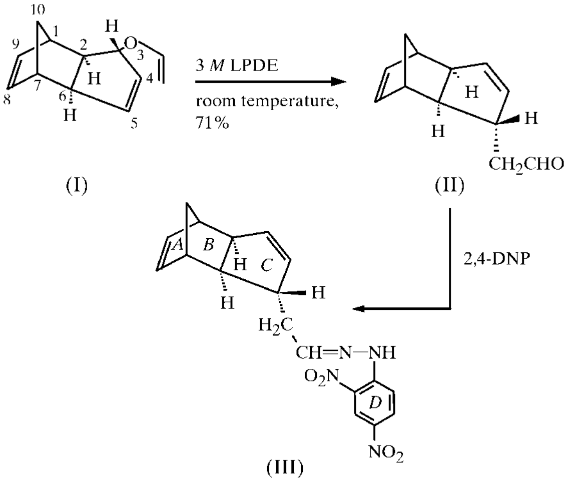
The six-membered ring of the norbornene moiety in the title compound, $C_{18}H_{18}N_4O_4$, is in a slightly distorted boat conformation, and the two five-membered rings within it adopt envelope conformations. The structure is stabilized by inter- and intramolecular N—H$\cdots$O hydrogen bonds.

Comment

It is known that norbornene derivatives, besides being biologically active by themselves, are used in the synthesis of other compounds possessing psychotropic, anticonvulsant and antimicrobial activities (Minoru, Morio & Hiroyuki, 1974; Minoru, Morio, Hiroyuki & Yasuo, 1974; Tasihiko & Syundzi, 1971). Norbornene derivatives are also used as efficient turn elements in the design of simple models of two-stranded parallel β sheets and hairpin cyclic peptides (Ranganathan *et al.*, 1998, 2000). In view of these features associated with the norbornene moiety, the present structure determination of the title compound, (III), was undertaken.

Another reason for undertaking a crystallographic study of (III) was to establish the configuration of the acetaldehyde chain in the rearrangement product, (II), since this was difficult to define from the ^{1}H NMR spectrum. In all the available literature, the γ-C atom of the vinyl ether is disubstituted, so that one can easily find out whether the product of the rearrangement of the allyl vinyl ether moiety of (I) is due to a formal 1,3 or 3,3 shift of its structure. However, in the case of (II) (Palani *et al.*, 1998), since the γ-C atom is not disubstituted and the starting material was racemic, it is difficult to establish whether the product is due to a 3,3 or a 1,3 shift. In order to establish the relative configuration of the acetaldehyde chain, the aldehyde was converted into its 2,4-dinitrophenylhydrazone derivative, *i.e.* the title compound, (III) (Fig. 1). The present X-ray crystal structure analysis showed that the acetaldehyde chain is in the α position.

The bond lengths and angles in (III) agree with normal values (Allen *et al.*, 1987). In particular, the bond lengths and angles of the norbornene moiety agree with the values in the literature (Milovac *et al.*, 2001; Beddoes *et al.*, 1993; Dvorkin *et al.*, 1987). The six-membered ring, C1/C2/C6–C9, is in a slightly distorted boat conformation with two local pseudo-mirrors, one along the midpoints of the C2—C6 and C8—C9 bonds, and the other along the C1—C7 direction. The ring puckering (Cremer & Pople, 1975) and asymmetry parameters (Nardelli, 1983) for this ring, calculated using *PARST*97 (Nardelli, 1995), are Q_T = 0.951 (4) Å, ΔC_s(C1) = 0.016 (2)° and ΔC_s(C6—C2) = 0.008 (2)°. The C1/C2/C6/C7/C10 and C1/C9/C8/C7/C10 rings are both in envelope conformations, with a pseudo-mirror running through atom C10. The total puckering amplitude and asymmetry parameter for the C1/C2/C6/C7/C10 ring are q_2 = 0.602 (4) Å and ΔC_s(C10) = 0.012 (2)°, respectively, and the corresponding values for the C1/C9/C8/C7/C10 ring are q_2 = 0.554 (4) Å and ΔC_s(C10) = 0.008 (2)°, respectively.



The five-membered ring *C* is planar. The two nitro groups are nearly coplanar with the phenyl ring, as shown by the C15—C16—N21—O22 [3.9 (4)°] and C17—C18—N24—O25 [2.9 (5)°] torsion angles. The angles between the plane of the three-atom bridge, C1/C10/C7, and the four-atom planes (C1/C9/C8/C7 and C1/C2/C6/C7) of the six-membered ring are 53.6 (2) and 58.1 (2)°, respectively. The dihedral angle

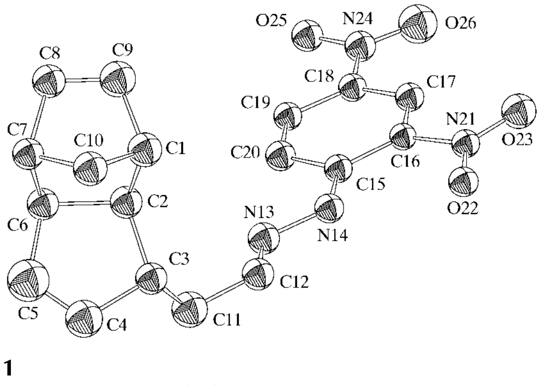


Figure 1
The molecular structure of (III), with displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

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between the norbornene ring and ring *C* is 30.2 (1)°. The C11—C12—N13—N14, C12—N13—N14—C15 and N13—N14—C15—C16 torsion angles are all (−)antiperiplanar [−178.8 (3), −178.9 (3) and −178.5 (3)°, respectively]. The torsion angles C3—C11—C12—N13 and C2—C3—C11—C12, which define the orientation of the tricycle substituent with respect to the central chain, are −111.7 (4) and 64.7 (4)°, respectively.

The packing of the molecules of (III) viewed down the *a* axis is shown in Fig. 2 and details of the hydrogen bonds are given in Table 1. The weak N14—H14···O22^{i} interaction joins the molecules into centrosymmetric dimers, causing an O22···O22^{i} contact of 2.69 (4) Å, a little shorter than the sum of the van der Waals radii (2.80 Å; Pauling, 1960).

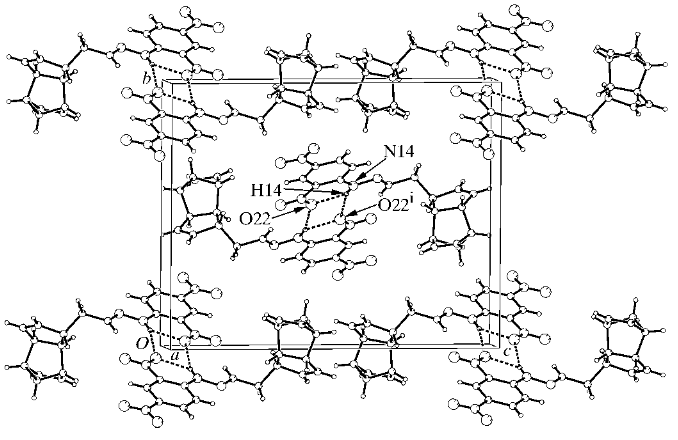

Figure 2
A packing diagram for (III), viewed down the *a* axis, showing the N—H···O hydrogen bonds [symmetry code: (i) $-x$, $1 - y$, $1 - z$].

Experimental

Vinyl ether, (I) (348 mg, 0.2 mmol) was treated with 3 *M* LPDE (anhydrous lithium perchlorate/diethyl ether) (10 ml) and stirred at room temperature for 3 h. The reaction mixture was quenched with ice water and extracted with dichloromethane (3 × 10 ml). The combined organic extracts were washed with water, dried over anhydrous sodium sulfate and purified using flash column chromatography, yielding 0.25 g of aldehyde (II). A sample of (II) was treated with 2,4-dinitrophenylhydrazine in methanol, and the hydrazine derivative, (III), precipitated out. Crystals of (III) suitable for X-ray diffraction studies were grown by slow evaporation from an ethyl acetate–hexane (2:1) solution. Spectroscopic analysis, IR (pure sample, cm^{-1}): 2720 (C—H, aldehydic), 1710 (C═O); ^{1}H NMR (400 MHz, C_6D_6, *δ*, p.p.m.): 9.1 (*t*, *J* = 1.46 Hz, 1H), 5.7 (*dd*, *J* = 5.87 and 2.93 Hz, 1H), 5.65 (*dd*, *J* = 5.87 and 2.93 Hz, 1H), 5.15 (*dt*, *J* = 5.85 and 2.92 Hz, 1H), 5.1 (*dt*, *J* = 585 and 2.93 Hz, 1H), 2.3 (*m*, 2H), 2.13 (*m*, 2H), 1.60 (*m*, 2H), 1.3 (*m*, 2H), 1.2–1.0 (*m*, 1H); ^{13}C NMR (100.5 MHz, C_6D_6, *δ*, p.p.m.): 200.43 (*d*), 137.97 (*d*), 137.72 (*d*), 136.53 (*d*), 133.60 (*d*), 54.53 (*d*), 51.03 (*t*), 50.41 (*d*), 48.20 (*d*), 46.11 (*d*), 44.36 (*d*), 42.62 (*t*).

Crystal data

$C_{18}H_{18}N_4O_4$
M_r = 354.36
Monoclinic, $P2_1/c$
a = 6.412 (1) Å
b = 14.569 (2) Å
c = 19.144 (3) Å
β = 105.02 (1)°
V = 1727.4 (4) Å^{3}
Z = 4
D_x = 1.363 Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 14–30°
μ = 0.82 mm^{-1}
T = 293 (2) K
Needle, yellow
0.30 × 0.25 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.880, T_{max} = 0.899
3300 measured reflections
3206 independent reflections
1973 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 69.9°
h = −7 → 7
k = 0 → 17
l = −7 → 23
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.214
S = 1.02
3306 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1180P)^2 + 0.5657P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0047 (8)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N14—H14···O22	0.86	2.01	2.618 (3)	127
N14—H14···O22^{i}	0.86	2.57	3.395 (4)	162

Symmetry code: (i) $-x$, $1 - y$, $1 - z$.

All H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.98 Å, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent C atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *SDP* (Frenz, 1978); data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *PARST*97 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1574). Services for accessing these data are described at the back of the journal.

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