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(1*R**,2*R**)-2-[(*S**)-1-Benzyloxyethyl]-1-cyclopropyl Methyl Ketone (*Z*)-2,4-Dinitrophenylhydrazone

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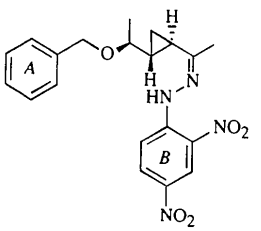
Abstract

The relative configuration of the *syn* isomer of the title compound, $C_{20}H_{22}N_4O_5$, has been determined. The configuration is stabilized by intramolecular stacking of the dinitrophenyl and benzyl π systems.

Comment

During the synthetic study of *trans*-disubstituted cyclopropanes (Nagasawa, Handa, Onoguchi, Ohba & Suzuki, 1995; Nagasawa, Handa, Onoguchi & Suzuki, 1996), the title compound, (I), was obtained. The X-ray analysis was performed in order to clarify the exocyclic chiral center. The relative configurations of the asymmetric C(18), C(19) and C(21) atoms were determined as shown below.



(I)

There is intramolecular stacking of the dinitrophenyl and benzyl π-electron systems. One of the nitro groups [O(2)—N(8)—O(3)] lies above the other terminal phenyl ring (*A*) [C(11)–C(16)]. The dihedral angle between the two phenyl rings is 24.9 (3)° and the nitro groups are nearly coplanar with the phenyl ring (*B*) to which they are attached. The O(2)···C(11) and O(3)···C(13) non-bonded distances are 3.328 (5) and 3.849 (8) Å, respectively. The dihedral angles between the cyclopropane ring and phenyl rings *A* and *B* are 82.7 (4) and 75.8 (4)°, respectively.

The N(6)—N(7) bond axis is nearly coplanar with the bonded phenyl ring, the N(6)—N(7)—C(24)—C(29) torsion angle being 1.2 (4)°. The coplanarity of the phenylhydrazone moiety and its orientation perpendicular to the cyclopropane ring has also been observed in the related compound (1*R**,2*R**)-2-[(6*R**)-2-oxo-6-tetrahydropyranyl]-1-cyclopropanecarbaldehyde (*E*)-2,4-dinitrophenylhydrazone (White & Jensen, 1993).

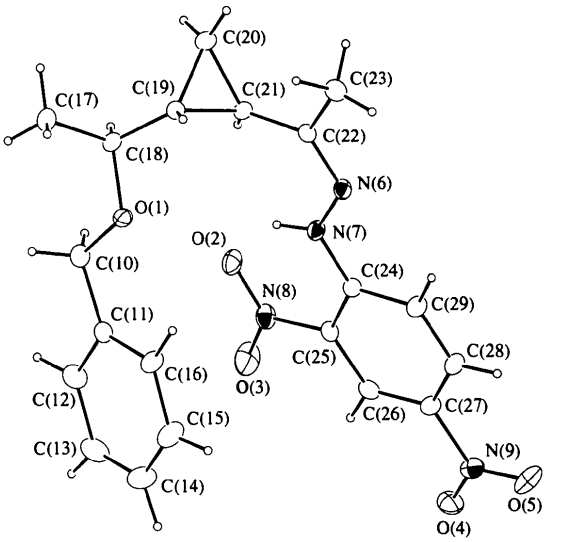


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 10% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

A *syn*/*anti* mixture of the title hydrazone was recrystallized from ethanol. The main product was the *anti* isomer which was obtained as thin orange plate-like crystals. Yellow prisms of the *syn* isomer were also obtained and were suitable for X-ray diffraction analysis.

Crystal data

$C_{20}H_{22}N_4O_5$
M_r = 398.42
Monoclinic
$P2_1/c$
a = 10.845 (1) Å
b = 7.773 (1) Å
c = 24.018 (1) Å
β = 97.37 (1)°
V = 2008.0 (3) Å^3
Z = 4
D_x = 1.318 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.5–15.0°
μ = 0.097 mm^{-1}
T = 299 K
Prism
0.60 × 0.40 × 0.20 mm
Yellow

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
3730 measured reflections
3529 independent reflections
1929 observed reflections [$|F_o| > 3\sigma(|F_o|)$]
R_{int} = 0.015
θ_{max} = 25.0°
h = 0 → 12
k = 0 → 9
l = −28 → 28
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F
$R = 0.0566$
$wR = 0.0541$
$S = 1.89$
1929 reflections
350 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.002F^2]$
$(\Delta/\sigma)_{max} = 0.13$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	0.1584 (2)	0.0805 (3)	0.1942 (1)	0.061 (1)
O(2)	−0.0358 (3)	0.4174 (4)	0.1262 (1)	0.082 (1)
O(3)	−0.2320 (3)	0.4592 (6)	0.1139 (1)	0.134 (2)
O(4)	−0.4770 (3)	0.3910 (5)	−0.0612 (1)	0.106 (2)
O(5)	−0.3975 (3)	0.2834 (4)	−0.1319 (2)	0.100 (1)
N(6)	0.1732 (3)	0.2069 (4)	0.0228 (1)	0.056 (1)
N(7)	0.0739 (3)	0.2696 (4)	0.0478 (1)	0.057 (1)
N(8)	−0.1373 (3)	0.4137 (5)	0.0966 (1)	0.074 (1)
N(9)	−0.3908 (3)	0.3294 (4)	−0.0825 (2)	0.073 (1)
C(10)	0.0712 (4)	0.1231 (7)	0.2313 (2)	0.069 (2)
C(11)	−0.0572 (3)	0.0724 (5)	0.2065 (2)	0.060 (1)
C(12)	−0.1578 (4)	0.1251 (6)	0.2323 (2)	0.083 (2)
C(13)	−0.2776 (5)	0.0751 (8)	0.2104 (3)	0.099 (2)
C(14)	−0.2969 (5)	−0.0247 (8)	0.1642 (3)	0.102 (2)
C(15)	−0.1996 (5)	−0.0751 (8)	0.1387 (3)	0.101 (3)
C(16)	−0.0807 (4)	−0.0251 (7)	0.1591 (2)	0.079 (2)
C(17)	0.3522 (5)	0.0595 (9)	0.2582 (2)	0.085 (2)
C(18)	0.2792 (3)	0.1536 (5)	0.2098 (2)	0.056 (1)
C(19)	0.3425 (3)	0.1477 (5)	0.1584 (2)	0.052 (1)
C(20)	0.4290 (4)	0.2857 (6)	0.1448 (2)	0.066 (2)
C(21)	0.3016 (3)	0.2727 (5)	0.1115 (2)	0.053 (1)
C(22)	0.2790 (3)	0.2096 (5)	0.0536 (2)	0.053 (1)
C(23)	0.3848 (4)	0.1356 (8)	0.0262 (2)	0.078 (2)
C(24)	−0.0395 (3)	0.2844 (4)	0.0175 (1)	0.051 (1)
C(25)	−0.1445 (3)	0.3515 (5)	0.0394 (1)	0.053 (1)
C(26)	−0.2577 (3)	0.3652 (5)	0.0067 (2)	0.061 (1)
C(27)	−0.2705 (3)	0.3147 (5)	−0.0476 (2)	0.058 (1)
C(28)	−0.1704 (4)	0.2469 (5)	−0.0708 (2)	0.065 (2)
C(29)	−0.0577 (4)	0.2330 (6)	−0.0392 (2)	0.062 (1)

Table 2. *Selected geometric parameters (Å, °)*

O(1)—C(10)	1.419 (5)	C(17)—C(18)	1.509 (8)
O(1)—C(18)	1.434 (5)	C(18)—C(19)	1.487 (6)
N(6)—N(7)	1.385 (5)	C(19)—C(20)	1.489 (6)
N(6)—C(22)	1.283 (5)	C(19)—C(21)	1.510 (6)
N(7)—C(24)	1.351 (5)	C(20)—C(21)	1.509 (6)
N(8)—C(25)	1.450 (5)	C(21)—C(22)	1.466 (6)
N(9)—C(27)	1.462 (6)	C(22)—C(23)	1.507 (7)
C(10)—C(11)	1.496 (6)		
C(10)—O(1)—C(18)	113.8 (3)	C(20)—C(19)—C(21)	60.4 (3)
N(7)—N(6)—C(22)	115.7 (3)	C(19)—C(20)—C(21)	60.5 (3)
N(6)—N(7)—C(24)	120.1 (3)	C(19)—C(21)—C(20)	59.1 (3)
O(1)—C(10)—C(11)	110.4 (4)	C(19)—C(21)—C(22)	119.3 (4)
O(1)—C(18)—C(17)	112.4 (4)	C(20)—C(21)—C(22)	123.7 (4)
O(1)—C(18)—C(19)	105.9 (3)	N(6)—C(22)—C(21)	125.4 (4)
C(17)—C(18)—C(19)	111.9 (4)	N(6)—C(22)—C(23)	114.7 (4)
C(18)—C(19)—C(20)	122.0 (4)	C(21)—C(22)—C(23)	119.9 (4)
C(18)—C(19)—C(21)	118.4 (4)		

The structure analysis was carried out using *CRYSTAN-GM* software (Edwards, Gilmore, Mackay & Stewart, 1995) on a SUN SPARC10 workstation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1995). *CRYSTAN-GM*. Version 6.2. *A Computer Program for the Solution and Refinement of Crystal Structures*. Japan: MacScience.

Nagasawa, T., Handa, Y., Onoguchi, U., Ohba, S. & Suzuki, K. (1995). *Synlett*, pp. 739–741.

Nagasawa, T., Handa, Y., Onoguchi, U. & Suzuki, K. (1996). *Bull. Chem. Soc. Jpn*, **69**, 31–39.

White, J. D. & Jensen, M. S. (1993). *J. Am. Chem. Soc.* **115**, 2970–2971.