

- Sakaino, Y., Kishi, K., Inouye, Y. & Yamanobe, T. (1996). *Mol. Cryst. Liq. Cryst.* **277**, 259–269.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). **C55**, 2087–2088

Methyl (*R,Z*)-(1-phenylethylimino)acetate *N*-oxide

YOSHINOBU INOUE AND TOMOYUKI ISHIMURA

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan. E-mail: inouye@staff.chem.tsukuba.ac.jp

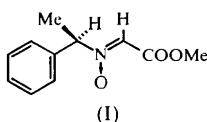
(Received 9 August 1999; accepted 7 September 1999)

Abstract

The geometry around the C=N bond of the title nitron, C₁₁H₁₃NO₃, is shown to be *Z*. The conformation around the chiral moiety shows that the benzene ring is more perpendicular to the nitron chromophore than to the methyl group.

Comment

Nitrones are widely used in 1,3-dipolar cycloaddition reactions (Tufariello, 1984) and methyl (alkylimino)-acetate *N*-oxides have been used as reagents to construct γ -hydroxyamino acids (Inouye *et al.*, 1979; Hara *et al.*, 1981). During the course of our investigation, we found that methyl (alkylimino)acetate *N*-oxides crystallize as the *Z* form but show a facile *Z*-*E* equilibrium in solution at ambient temperature (Inouye *et al.*, 1980, 1983, 1985). The *E*-configuration is predominant in non-polar solvents, but the *Z*-configuration is predominant in polar solvents. The crystal structures of methyl (benzylimino)-acetate *N*-oxide (Inouye, 1983) and methyl (diphenylmethylimino)acetate *N*-oxide (Inouye, 1984) have been reported previously. This paper describes the crystal structure of a chiral nitron, methyl (*R,Z*)-(1-phenylethylimino)acetate *N*-oxide, (I), in order to clarify the conformation around the chiral moiety which may control the stereochemistry in 1,3-dipolar cycloaddition reactions. Although (I) was first prepared by Tamura *et al.* (1994), details of the preparation and properties of (I) have not previously been reported.



The *Z* configuration of the nitron C=N bond of (I) is clearly shown in Fig. 1. The geometry around the nitron chromophore is similar to those of the *N*-benzyl (Inouye, 1983) and *N*-diphenylmethyl derivatives (Inouye, 1984). The best plane of the ester group (C1,O2,C3,O4) is inclined slightly [14.2(3)°] to the nitron plane (C5,N6,O7,C8). The ester carbonyl group (C3=O4) is in an *s-cis* conformation with respect to the C5=N6 bond. Selected torsion angles are given in Table 1.

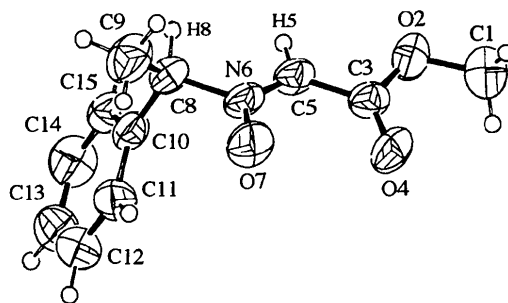


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as circles of an arbitrary radius.

The conformation around the chiral moiety is as follows. The C8—H8 bond eclipses the C5—H5 bond, while both the C8—C9 and the C8—C10 bonds are *gauche* to the N6—O7 bond. The comparison of the C5—N6—C8—C10 torsion angle with that of C5—N6—C8—C9 shows that the benzene ring is more perpendicular to the nitron chromophore than to the methyl group; thus, the *re*-face site at N6 may be protected more than *si*-face site from the incoming dipolarophile in the 1,3-dipolar cycloaddition reaction.

The molecular conformation in the crystal is in accord with the most desirable conformation estimated from the conformational analysis by semi-empirical molecular orbital (PM1) calculations. The shortest interatomic distance between non-H atoms is 3.222 (8) Å for O4...C1(1-x, 1/2+y, 2-z). Two other short distances of 3.254 (4) and 3.315 (4) Å were observed for O7...C8(x, y, 1+z) and O4...C5(x, y, 1+z), respectively.

Experimental

The title compound was prepared by condensation of methyl glyoxylate with (*R*)-(1-phenylethyl)hydroxylamine and then recrystallized slowly from hexane–benzene (10:1) as colourless plates (m.p. 351 K). Elemental analysis, found: C 63.70, H 6.42, N 6.72%; calculated for C₁₁H₁₃NO₃: C 63.75, H 6.32, N 6.76%.

Crystal data

C₁₁H₁₃NO₃
M_r = 207.22

Mo K α radiation
 λ = 0.71073 Å

Monoclinic
P2₁
a = 12.653 (3) Å
b = 8.0849 (6) Å
c = 5.5247 (9) Å
β = 95.408 (8)°
V = 562.7 (2) Å³
Z = 2
D_x = 1.223 Mg m⁻³
D_m not measured

Cell parameters from 25 reflections
θ = 9.78–14.03°
μ = 0.089 mm⁻¹
T = 293 (2) K
Plate
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2062 measured reflections
1891 independent reflections
1243 reflections with I > 2σ(I)

R_{int} = 0.018
θ_{max} = 30.98°
h = -18 → 18
k = 0 → 11
l = 0 → 7
3 standard reflections
frequency: 120 min
intensity decay: 0.8%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.054
wR(F²) = 0.188
S = 0.801
1891 reflections
138 parameters
H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.1P)²]
where P = (F_o² + 2F_c²)/3

(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.31 e Å⁻³
Δρ_{min} = -0.32 e Å⁻³
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected torsion angles (°) for (I)

C1—O2—C3—O4	-2.1 (7)	C5—N6—C8—C9	-138.8 (4)
O4—C3—C5—N6	13.2 (6)	C5—N6—C8—C10	96.5 (4)
O2—C3—C5—N6	-168.4 (4)	O7—N6—C8—C9	42.3 (5)
C3—C5—N6—O7	2.6 (6)	O7—N6—C8—C10	-82.5 (4)
C3—C5—N6—C8	-176.2 (3)		

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1021). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1989). CAD-4 Software. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). MolEN. An Interactive Intelligent System for Crystal Structure Analysis. Enraf–Nonius, Delft, The Netherlands.
Hara, J., Inouye, Y. & Kakisawa, H. (1981). Bull. Chem. Soc. Jpn. **52**, 3763–3764.
Inouye, Y. (1983). Bull. Chem. Soc. Jpn. **56**, 244–247.
Inouye, Y. (1984). Acta Cryst. **C40**, 140–142.
Inouye, Y., Hara, J. & Kakisawa, K. (1980). Chem. Lett. pp. 1407–1410.

- Inouye, Y., Takaya, K. & Kakisawa, K. (1983). Bull. Chem. Soc. Jpn. **56**, 3541–3542.
Inouye, Y., Takaya, K. & Kakisawa, K. (1985). Magn. Reson. Chem. **23**, 101–103.
Inouye, Y., Watanabe, Y., Takahashi, S. & Kakisawa, H. (1979). Bull. Chem. Soc. Jpn. **52**, 3763–3764.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1990). Acta Cryst. **A46**, 467–473.
Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
Tamura, O., Yamaguchi, T., Okabe, T. & Sakamoto, M. (1994). Synlett, pp. 620–622.
Tufariello, J. J. (1984). 1,3-Dipolar Cycloaddition Chemistry, Vol. 2, edited by A. Padwa, pp. 83–168. New York: John Wiley & Sons.

Acta Cryst. (1999). **C55**, 2088–2090

Mirror symmetry in 7,9-dibenzyl-1-tert-butoxycarbonyl-1,7,9-triazaspiro[4.5]dec-3-en-2-one

YONGKWAN DONG,^a HOSEOP YUN,^a JANG-MIN SUH,^b
YOUNG-GIL AHN^b AND HYUN-JOON HA^b

^aDepartment of Molecular Science and Technology, Ajou University, Suwon 442-749, Republic of Korea, and
^bDepartment of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Republic of Korea. E-mail: hsyun@madang.ajou.ac.kr

(Received 11 March 1999; accepted 6 September 1999)

Abstract

The crystal structure of tert-butyl 7,9-dibenzyl-2-oxo-1,7,9-triazaspiro[4.5]dec-3-ene-1-carboxylate, C₂₆H₃₁N₃O₃, is reported. The molecule has imposed mirror symmetry and the hexahydropyrimidine ring adopts a chair conformation with two benzyl substituents bonded equatorially to the ring N atoms. The 3-pyrrolin-2-one is attached as a spiro-skeleton to the hexahydropyrimidine ring by one axial C—C and one equatorial C—N bond.

Comment

During the course of synthetic studies with N-methylenamine equivalents generated from 1,3,5-trialkylhexahydro-1,3,5-triazines, the spiro product 1-tert-butoxycarbonyl-7,9-dialkyl-1,7,9-triazaspiro[4.5]dec-3-en-2-one, was obtained from their reaction with 1-tert-butoxycarbonyl-2-tert-butyl-dimethylsilyloxypyrrole (Ha *et al.*, 1999). When the alkyl substituent is benzyl, the product is 1-tert-butoxycarbonyl-7,9-dibenzyl-1,7,9-triazaspiro[4.5]dec-3-en-2-one, (I), and its structure was determined by X-ray diffraction. In this title compound,