ORGANIC COMPOUNDS

Acta Cryst. (1999). C**55**, 1666–1667

8-Isopropyl-7,10-dimethoxy-3-phenyl-1-oxa-2,6,9-triazaspiro[4.5]deca-2,6,9-triene†

MARTIN NIEGER[a] AND MICHAEL BOLTE[b]

[a]*Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany, and* [b]*Institut für Organische Chemie, Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany. E-mail: bolte@chemie.uni-frankfurt.de*

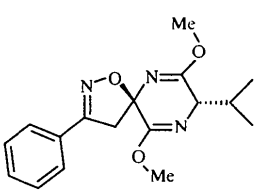
(*Received 5 October 1998; accepted 26 November 1998*)

Abstract

The title compound, $C_{17}H_{21}N_3O_3$, is an intermediate in an asymmetric synthesis of amino acids. It has an essentially planar central bis-lactim ether ring, with both methoxy groups lying in the plane of the heterocycle. The isopropyl group adopts the same conformation as found in similar structures. The phenyl substituent is nearly coplanar with the isoxazoline ring.

Comment

Biological activity is usually displayed by only one enantiomer of a compound, the other enantiomer might even be toxic, so it is desirable to synthesize enantiomerically pure compounds. This is especially true for amino acids which are used in large quantities by the pharmaceutical industry, and in medical science and biochemistry, *e.g.* as building blocks for peptides (Schöllkopf, 1983*a*). In recent years, Schöllkopf and co-workers have developed a generally applicable stereospecific synthesis of amino acids *via* metallated bis-lactim ethers of 2,5-diketopiperazines (Schöllkopf, 1983*b*). In order to understand the reasons for the observed stereospecificity, a series of structural investigations has been performed (Bolte *et al.*, 1999). We report here the crystal structure of one intermediate product, (I).



(I)

† Dedicated to Professor Dr E. Egert on the occasion of his 50th birthday.

The geometrical parameters of the bis-lactim ether heterocycle are in excellent agreement with those of all structures published previously (Bolte *et al.*, 1999). The essentially planar heterocycle (r.m.s. deviation = 0.035 Å) is nearly perpendicular [89.17 (9)°] to the isoxazoline ring, which is also planar (r.m.s. deviation = 0.048 Å). The phenyl substituent is nearly coplanar [3.1 (3)°] with the isoxazoline ring. Both methoxy groups lie in the plane of the bis-lactim ether ring. The isopropyl group adopts the same conformation as observed in all other bis-lactim ethers (Bolte *et al.*, 1999), with the tertiary H atom directed towards the methoxy O51 atom. The same preferred conformation of the isopropyl group had been observed in comparable structures, *e.g.* lactides (Bolte *et al.*, 1994) and dihydro-oxazinones (Bolte, 1995).

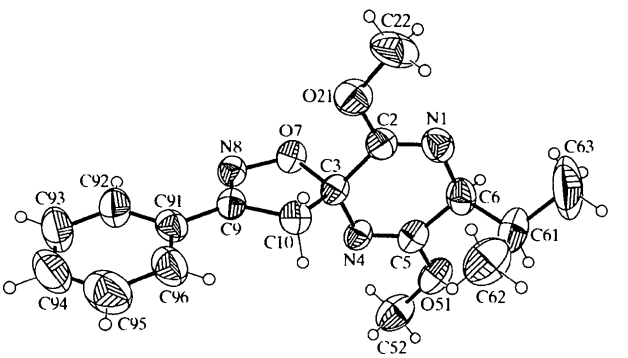


Fig. 1. Perspective view of the title compound with the atom-numbering scheme and displacement ellipsoids at the 40% probability level.

Experimental

The title compound was prepared by a 1,3-dipolar cycloaddition reaction (Huisgen, 1963*a*,*b*) between 5-isopropyl-3,6-dimethoxy-5*H*-pyrazin-2-one and benzonitrile *N*-oxide.

Crystal data

$C_{17}H_{21}N_3O_3$
M_r = 315.37
Orthorhombic
$P2_12_12_1$
a = 10.087 (1) Å
b = 12.454 (2) Å
c = 14.177 (3) Å
V = 1781.0 (5) Å^3
Z = 4
D_x = 1.176 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 10.0–12.5°
μ = 0.082 mm^{-1}
T = 293 (2) K
Block
0.40 × 0.31 × 0.23 mm
Colourless

Data collection

Stoe–Siemens AED diffractometer	$R_{int} = 0.021$
$\omega/2\theta$ scans with profile fitting (Clegg, 1981)	$\theta_{max} = 25°$
Absorption correction: none	$h = -11 \rightarrow 2$
2171 measured reflections	$k = 0 \rightarrow 14$
2131 independent reflections	$l = 0 \rightarrow 16$
1241 reflections with $I > 2\sigma(I)$	3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.13$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
$wR(F^2) = 0.117$	Extinction correction: *SHELXL*97
$S = 1.005$	Extinction coefficient: 0.013 (2)
2131 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
209 parameters	
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.249 (5)	N4—C5	1.263 (4)
N1—C6	1.453 (5)	C5—O51	1.346 (4)
C2—O21	1.353 (4)	C5—C6	1.496 (5)
C2—C3	1.498 (5)	O7—N8	1.412 (3)
C3—N4	1.436 (4)	N8—C9	1.267 (4)
C3—O7	1.465 (4)	C9—C10	1.500 (4)
C3—C10	1.523 (4)		
C2—N1—C6	118.1 (4)	N1—C6—C5	113.6 (3)
N1—C2—C3	127.6 (4)	N8—O7—C3	109.4 (2)
N4—C3—C2	114.5 (3)	C9—N8—O7	109.8 (3)
O7—C3—C10	104.1 (3)	N8—C9—C10	114.1 (4)
C5—N4—C3	117.6 (3)	C9—C10—C3	101.5 (3)
N4—C5—C6	128.0 (4)		

The absolute configuration of the title compound could not be determined experimentally, but was established from the known configuration at C6 (*S*). All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [U_{iso}(H) = 1.5U_{eq}(C_{methyl}) or 1.2U_{eq}(C)], using a riding model with C—H(aromatic) = 0.93, C—H(tertiary) = 0.98, C—H(secondary) = 0.97 or C—H(methyl) = 0.96 Å. Atom C63 shows slightly high anisotropic displacement parameters, but there is no disorder present and the C61—C63 bond is of normal length.

Data collection: *DIF*4 (Stoe & Cie, 1984*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1984*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*97.

We thank the late Professor Dr U. Schöllkopf (University of Göttingen) for providing the sample of the title compound.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1299). Services for accessing these data are described at the back of the journal.

References

Bolte, M. (1995). *Acta Cryst.* C**51**, 2587–2593.
Bolte, M., Beck, H., Nieger, M. & Egert, E. (1994). *Acta Cryst.* C**50**, 1717–1721.
Bolte, M., Benecke, B. & Egert, E. (1999). *Acta Cryst.* C**55**, 964–968.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Huisgen, R. (1963*a*). *Angew. Chem.* **75**, 604–637.
Huisgen, R. (1963*b*). *Angew. Chem.* **75**, 742–754.
Schöllkopf, U. (1983*a*). *Top. Curr. Chem.* **109**, 65–84.
Schöllkopf, U. (1983*b*). *Pure Appl. Chem.* **55**, 1799–1806.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stoe & Cie (1984*a*). *DIF*4. *Data Collection Program*. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1984*b*). *REDU*4. *Data Reduction Program*. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1999). C**55**, 1667–1669

1-(2,4-Dinitrophenyl)-3-(2-hydroxyphenyl)-1*H*-pyrazole-4-carbaldehyde

S. Shanmuga Sundara Raj,[a] J. Jeyakanthan,[b] S. Selvi,[c] D. Velmurugan,[b] H.-K. Fun[a] and P. T. Perumal[c]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,* [b]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and* [c]*Organic Division, Central Leather Research Institute, Chennai 600 020, India. E-mail: hkfun@usm.my*

(*Received 21 June 1999; accepted 28 June 1999*)

Abstract

In the crystal of the title compound, $C_{16}H_{10}N_4O_6$, the dinitrophenyl and hydroxyphenyl groups are oriented at angles of 43.8 (1) and 28.0 (1)°, respectively, with respect to the pyrazole ring. The internal C—C—C ring angles at the *o*- and *p*- positions, where NO_2 is bonded, are 121.6 (2) and 122.3 (2)°. The crystal structure and packing are stabilized by O—H···N and C—H···O hydrogen bonds.

Comment

Pyrazole and several of its N-substituted derivatives are used as inhibitors and deactivators of liver alcohol dehydrogenase and many pyrazole derivatives have pharmaceutical applications such as analgesic, antipyretic and anti-inflammatory effects (Potts, 1996). Pyrazole