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Acta Cryst. (1999). C55, 1920–1921

2-(3,5-Dinitropyridyl-2-oxy)-3,5,7-trimethylcyclohepta-2,4,6-trien-1-one

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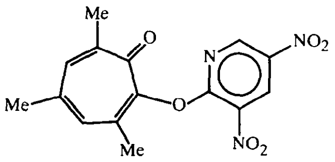
(*Received 24 May 1999; accepted 5 July 1999*)

Abstract

The molecules of the title compound, $C_{15}H_{13}N_3O_6$, exist in the ring-opened form. The seven-membered ring is considerably twisted with respect to the pyridine ring, the angle between the least-squares planes of these rings being 66.51 (8)°.

Comment

Compounds such as the title compound, (I), are of great interest because of their ability to undergo acylotropic tautomerism (Knyazev & Drozd, 1995; Kurbatov *et al.*, 1997). For example, in solution, (I) exhibits fast and reversible migration of the heteroaryl group (Olekhnovich *et al.*, 1985). The intermediate in this nucleophilic rearrangement is a dipolar spirocyclic Meisenheimer complex containing tropylium (cycloheptatrienylium) as an intramolecular cation. Such a situation gives rise to an equilibrium between the ring-opened and ring-closed isomers in solution and their interrelation is determined by many factors (Olekhnovich *et al.*, 1994). In several cases in the literature, the ring-closed form of such zwitterionic Meisenheimer complexes was observed in the crystal phase (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982). The aim of the present X-ray study is to establish the structural isomer of (I) in the crystal.



(I)

In the crystal phase, molecules of (I) exist in the ring-opened form. The seven-membered ring is considerably twisted with respect to the pyridine ring, probably due to the presence of short intramolecular contacts: N1···C7 = 2.947 (3) and O6···C1 = 2.722 (3) Å (the corresponding sums of the van der Waals radii are 3.21 and 3.00 Å, respectively; Zefirov & Zorky, 1989). The angle between the least-squares planes of these rings is 66.51 (8)°.

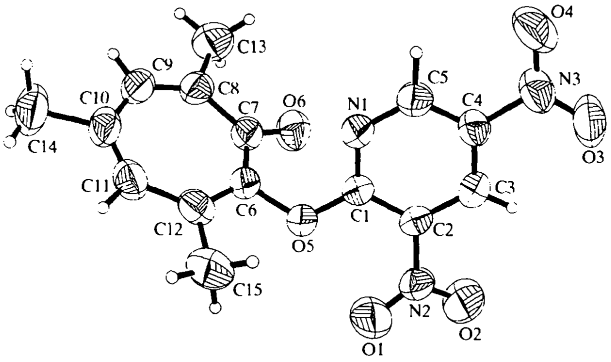


Fig. 1. View of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small circles of arbitrary radius.

The nitro groups in (I) are somewhat twisted with respect to the plane of the pyridine ring: the O1—N2—C2—C1 and O4—N3—C4—C5 torsion angles are −16.3 (4) and −14.1 (4)°, respectively.

According to the bond-length distribution, no conjugation is present within the seven-membered ring. The C8—C9 [1.356 (4)], C10—C11 [1.349 (4)] and C6—C12 [1.359 (3) Å] distances are considerably shorter than the other bonds of the ring, indicating that the double bonds are localized.

Experimental

Compound (I) was prepared according to the procedure of Olekhnovich *et al.* (1985), and crystals suitable for X-ray analysis were obtained by isothermal evaporation from a solution of (I) in nitromethane.

Crystal data

$C_{15}H_{13}N_3O_6$
$M_r = 331.28$
Monoclinic
$P2_1/c$
$a = 12.996\,(5)$ Å
$b = 10.106\,(5)$ Å
$c = 12.717\,(11)$ Å
$\beta = 110.35\,(6)°$
$V = 1566.0\,(16)$ Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10–11°$
$\mu = 0.111$ mm^{-1}
$T = 293\,(2)$ K
Square prism
$0.50 \times 0.25 \times 0.25$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2878 measured reflections
2752 independent reflections
2051 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 14$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.131$
$S = 1.14$
2686 reflections
237 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.4754P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.019$

$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXTL/PC* (Sheldrick, 1994)
Extinction coefficient: 0.112 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N2—C2	1.457 (3)	C7—C8	1.462 (3)
N3—C4	1.447 (3)	C8—C9	1.356 (4)
O5—C1	1.330 (3)	C9—C10	1.411 (4)
O5—C6	1.410 (3)	C10—C11	1.349 (4)
C6—C12	1.359 (3)	C11—C12	1.434 (4)
C6—C7	1.454 (3)		
C1—O5—C6	117.9 (2)		

Atoms H3, H5, H9 and H11 were refined isotropically. All methyl-H atoms were located from a difference Fourier synthesis and thereafter allowed to refine as part of a rigid group which was allowed to rotate but not tip or distort. The high value of U_{11} for atom O1 is attributed to the considerable thermal motion in which this atom is involved, the data having been acquired at room temperature. However, there is no evidence for disorder in the relevant nitro group.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Strel'tsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by the Russian Foundation for Basic Research (grant Nos. 97-03-33783 and 96-15-97367) and the Scientific Training Centre of the Chemistry of Organometallic Compounds (grant 234, Federal Target Programme 'Integration').

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1347). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1921–1923

2,2′-Bipyridine-5-sulfonic acid

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(Received 29 March 1999; accepted 26 July 1999)

Abstract

The title compound, $C_{10}H_8N_2O_3S$, exists as a zwitterion, 6-(2-pyridinio)pyridine-3-sulfonate, following deprotonation of the sulfonic acid group and protonation of the N

Acta Crystallographica Section C
ISSN 0108-2701 © 1999