Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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1:1 Complex of 2-Aminobenzoic Acid and 3-Methyl-4-nitropyridine *N*-Oxide

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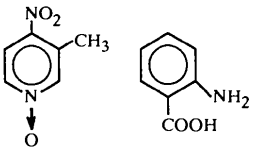
Abstract

The structure analysis of the title molecular complex, $C_7H_7NO_2.C_6H_6N_2O_3$, forms part of an ongoing study of the design of non-centrosymmetric systems based on 3-methyl-4-nitropyridine *N*-oxide. The title complex is held together by a hydrogen bond between the O atom of the *N*-oxide group and the O atom of the OH group of the 2-aminobenzoic acid molecule. In the crystal, the complexes overlap in the [100] direction.

Comment

A series of molecular complexes of 4-nitropyridine *N*-oxide and picoline *N*-oxide derivatives with diverse hydrogen-bond donors have been studied in recent years in order to obtain new materials with possible non-linear optical (NLO) properties (Moreno-Fuquen, De Almeida Santos & Lechat, 1996; Moreno-Fuquen, De Almeida Santos & Gambardella, 1996). Within the family of crystals having the *N*-oxide group, the 3-methyl-4-nitropyridine *N*-oxide (POM) molecular system is one of the best electro-optic materials in the visible range (Sapriel *et al.*, 1989). NLO properties of metal–halide complexes with the organic ligand POM have been reported (Hu *et al.*, 1992, 1994). In the present work, a molccular complex obtained from POM and one hydrogen-bond donor, namely 2-aminobenzoic acid (OABA), is described for the first time.



POM OABA

A *ZORTEP* (Zsolnai, 1995) diagram of the hydrogen-bonded complex is shown in Fig. 1. The complex is held together by a hydrogen bond between the O1 atom of the *N*-oxide group of the POM molecule and the O4 atom of the carboxylic group of the OABA molecule, with an O···O distance of 2.601 (3) Å and an O4—HO4···O1 angle of 160 (3)°.

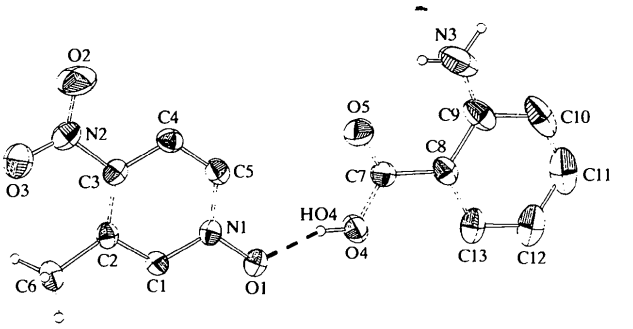


Fig. 1. A perspective view of the title complex with the atomic labelling scheme. Displacement ellipsoids are plotted at the 30% probability level. The ring H atoms have been omitted for clarity.

In the title structure, the O5 atom is intramolecularly hydrogen bonded to the amine HN31 atom, with an O5···N3 distance of 2.728 (4) Å. This distance is greater than the corresponding distances in free OABA molecules [2.688 (4) Å in the monoclinic form and 2.682 (7) Å in the orthorhombic form]. There is also an intermolecular hydrogen bond between the N3 atom (at x, y, z) and an O5 atom (symmetry code: $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$), with an N3···O5 distance of 3.121 (4) Å. The other bond lengths and angles observed in this complex are similar to those reported for free OABA molecules (Takazawa *et al.*, 1986; Boone *et al.*, 1977).

The internal parameters of POM in the complex are similar to those of the free molecule (Shiro *et al.*, 1977). They are also similar to those reported for metal–halide complexes in which POM is an organic ligand (Hu *et al.*, 1994).

A *ZORTEP* view (Zsolnai, 1995) of the crystal packing is presented in Fig. 2. The POM and OABA rings show an *ABAB* disposition and are overlapped with mean distances between the rings of 3.483 (3) (symmetry code: $x-1, y+1, z$) and 3.374 (3) Å (symmetry code: $x, y+1, z$) along the [100] direction. There are no nitro–amino interactions in this complex. This is contrary to what is observed in nitroanilines and their analogues (Panunto *et al.*, 1987).

The dihedral angle between the planes that essentially contain the rings of the molecules is 2.7 (1)°. The complex also shows a twist of 2.4 (4)° between the pyridine plane and the nitro group, which is very different from the twist of 16.7° reported for the free molecule (Shiro *et al.*, 1977).

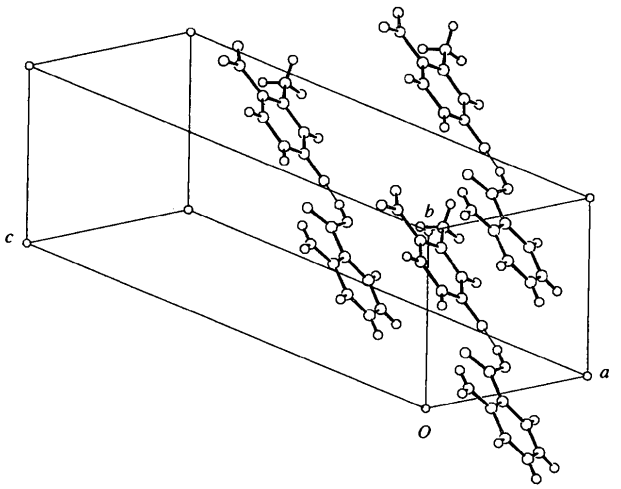


Fig. 2. Packing view showing the overlapped rings along the [100] direction.

Experimental

The synthesis of the title complex was carried out by slow evaporation of an equimolecular solution of POM and OABA in acetonitrile. The crystals have a melting point of 382 (1) K.

Crystal data

$C_7H_7NO_2.C_6H_6N_2O_3$
M_r = 291.26
Monoclinic
$P2_1/n$
a = 7.5011 (14) Å
b = 7.1875 (13) Å
c = 24.917 (2) Å
β = 92.90 (2)°
V = 1341.7 (4) Å^3
Z = 4
D_x = 1.442 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.09–16.45°
μ = 0.113 mm^{-1}
T = 243 K
Transparent prism
0.25 × 0.18 × 0.10 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2927 measured reflections
2717 independent reflections
1955 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 26.33°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = -31 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity decay: 1.84%

Refinement

Refinement on F^2
$R(F)$ = 0.055
$wR(F^2)$ = 0.149
S = 1.04
2717 reflections
195 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.7887P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.002 (2)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—N1	1.309 (2)	O5—C7	1.227 (3)
O2—N2	1.200 (3)	N3—C9	1.326 (5)
O3—N2	1.197 (3)	C2—C6	1.493 (3)
O4—C7	1.317 (3)	C7—C8	1.458 (4)
O4—HO4	0.83 (3)	O1···HO4	1.76 (3)
O1—N1—C1	119.0 (2)	C3—C2—C6	127.8 (2)
O1—N1—C5	120.4 (2)	O5—C7—O4	120.9 (3)
O3—N2—O2	123.1 (3)	O5—C7—C8	125.5 (2)
O3—N2—C3	119.6 (2)	O4—C7—C8	113.6 (2)
O2—N2—C3	117.3 (3)	N3—C9—C8	123.0 (3)
C1—C2—C6	116.8 (2)	N3—C9—C10	119.2 (3)

The ring, methyl and amine H atoms were added at calculated positions and included using a riding model; C—H = 0.93–0.96 and N—H = 0.86 Å, and U_{iso}(methyl/amine H) = $1.5U_{eq}$(parent C) and U_{iso}(aromatic H) = $1.2U_{eq}$(parent C). The HO4 atom was located from a difference Fourier map and its coordinates were refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP-VAX* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SDP-VAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1358). Services for accessing these data are described at the back of the journal.

References

Boone, C. D. G., Derissen, J. L. & Schoone, J. C. (1977). *Acta Cryst.* B**33**, 3205–3206.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.

Hu, S.-Z., Shi, D.-S., Huang, Y.-Q., Li, S.-X. & Yang, Y.-C. (1992). *Acta Cryst.* C**48**, 1597–1599.
Hu, S.-Z., Shi, D.-S., Li, S.-X. & Yang, Y.-C. (1994). *Acta Cryst.* C**50**, 893–895.
Moreno-Fuquen, R., De Almeida Santos, R. H. & Gambardella, M. T. (1996). *Acta Cryst.* C**52**, 1745–1747.
Moreno-Fuquen, R., De Almeida Santos, R. H. & Lechat, J. R. (1996). *Acta Cryst.* C**52**, 220–222, and references therein.
Panunto, T. W., Urbanczyk-Lipkowska, Z., Johnson, R. & Etter, M. C. (1987). *J. Am. Chem. Soc.* **109**, 7786–7797.
Sapriel, J., Hierle, R., Zyss, J. & Boissier, M. (1989). *Appl. Phys. Lett.* **55**, 2594–2596.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Shiro, M., Yamakawa, M. & Kubota, T. (1977). *Acta Cryst.* B**33**, 1549–1556.
Takazawa, H., Ohba, S. & Saito, Y. (1986). *Acta Cryst.* C**42**, 1880–1881.
Zsolnai, L. (1995). *ZORTEP*. University of Heidelberg, Germany.

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Some 1,3-Dipolar Adducts from Benzodiazepine. I. Condensation of Nitrilimines with 2-Methyl-4-phenyl-1,5-benzodiazepines

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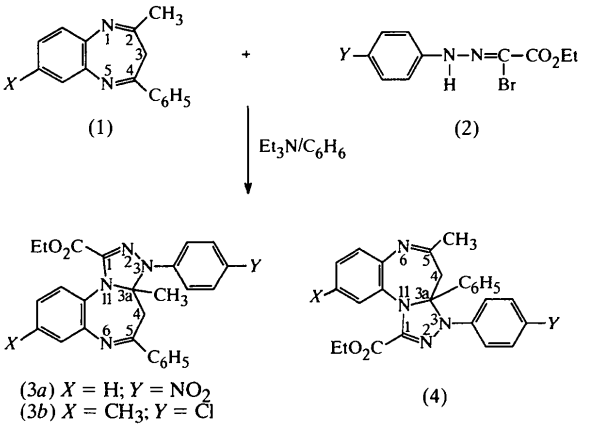
Abstract

The condensation reaction of *N*-*p*-nitrophenyl-*C*-ethoxycarbonyl nitrilimine or *N*-*p*-chlorophenyl-*C*-ethoxycarbonyl nitrilimine with 7-*X*-2-methyl-4-phenyl-1,5-benzodiazepine (*X* = H or CH_3) is regio- and periselective. The 1,3-dipolar cycloaddition occurs in a unique way on the N1=C2 double bond of the 1,5-benzodiazepine and leads to ethyl 3a-methyl-3-(4-nitrophenyl)-5-phenyl-3a,4-dihydro-3*H*-[1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine-1-carboxylate, $C_{26}H_{23}N_5O_4$, (3*a*), or ethyl 3-(4-chlorophenyl)-3a,8-dimethyl-5-phenyl-3a,4-dihydro-3*H*-[1,2,4]triazolo[4,3-*a*][1,5]benzodiazepine-1-carboxylate, $C_{27}H_{25}ClN_4O_2$, (3*b*).

Comment

In recent publications (Hasnaoui *et al.*, 1991; El Messaoudi *et al.*, 1992, 1994; Baouid *et al.*, 1996), we have emphasized the noteworthy regio- and periselectivity of 1,3-dipolar cycloadditions on 1,2(1,4)-diazepines and 1,5-benzodiazepine. Developing our work concerning the synthesis of bi- and triheterocyclic systems from seven-membered nitrogen heterocycles, we describe here the cycloaddition of nitrilimines to 1,5-benzodiazepines.



According to the scheme above, the condensation reaction of the 2-methyl-4-phenyl-1,5-benzodiazepines, (1) (*X* = H or CH_3) (Barltrop *et al.*, 1959), with *N*-*p*-nitro(or chloro)phenyl-*C*-ethoxycarbonyl nitrilimine, prepared *in situ* by the action of triethylamine on ethyl α-bromo-α-[*p*-nitro(or chloro)phenylhydrazono]-acetate, (2) (Huisgen & Koch, 1955; Sharp & Hamilton, 1946), produces the monocyclo adducts (3) or (4). The structures were assigned by X-ray crystallography analysis, which showed that these adducts are (3*a*) and (3*b*): the N1=C2 double bond of the benzodiazepine is the site of the addition. The reaction is periselective, as only the N1=C2 double bond of (1) is affected. The N atom of the dipole is linked to the C atom of the N1=C2 dipolarophile, making the reaction regioselective.

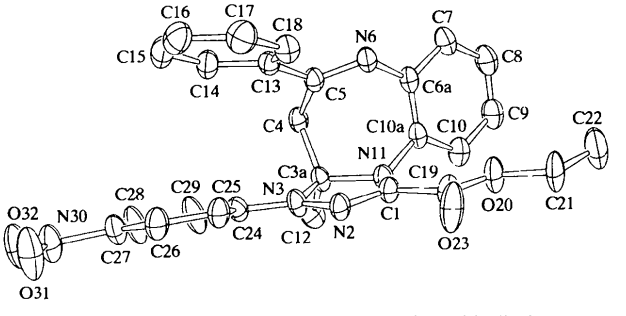


Fig. 1. The molecular structure of compound (3*a*) with displacement ellipsoids at the 50% probability level.