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p-Nitrobenzaldehyde Nicotinoylhydrazone Monohydrate

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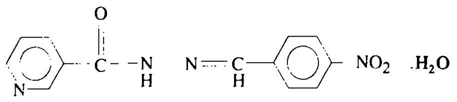
Abstract

The X-ray analysis revealed that the title compound, $C_{13}H_{10}N_4O_3.H_2O$, is a practically planar molecule which exists in the keto tautomeric form. The molecules lie parallel to (022) planes and form centrosymmetrically related dimers with possible π interactions. The water molecule bridges the hydrazone molecules of the adjacent stacks through hydrogen bonds and the crystal structure is stabilized by O—H···O, N—H···O and C—H···O hydrogen bonds.

Comment

The coordination of aroylhydrazines and related compounds, in addition to their medicinal properties, has been the subject of extensive studies (Ma, Zhang & Zhao, 1988; Dutta & Hossain, 1985; Wang, Deng, Wu & Chen, 1992; Constable & Holmes, 1987; Wester & Palenik, 1973). As part of our studies on the synthesis and characterization of aroylhydrazone derivatives, we have determined the structure of *p*-nitrobenzaldehyde nicotinoylhydrazone monohydrate, (I).



(I)

A displacement ellipsoid plot with the numbering scheme is shown in Fig. 1. The bonds and angles observed in this structure are normal and the molecule is in the keto form. The molecule is practically planar: the dihedral angle between the planes of the phenyl and pyridinyl rings is 3.68 (4)°; these two rings make angles of 2.99 (6) and 6.53 (6)° with the central hydrazone moiety (O1—C6—N2—N3—C7); the nitro group is tilted by 3.9 (1)° from the plane of the phenyl ring. The water molecule also lies in the plane of the hydrazone molecule.

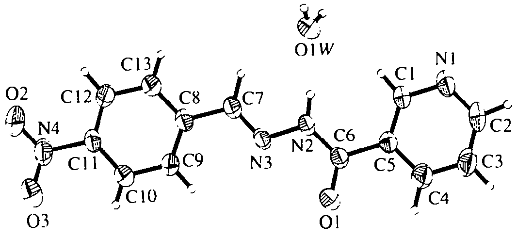


Fig. 1. Displacement ellipsoid plot (50% probability) of the title compound with numbering scheme.

In the crystal lattice, the hydrazone molecules are stacked in planes parallel to (022). The hydrazone molecules exist as centrosymmetrically related dimers, laid one over the other and separated by 3.42 Å, which suggests π-orbital interactions between them. The crystal structure is stabilized by a variety of hydrogen bonds between the hydrazone and water molecules (Table 3). The N2—H2N···O1*W* bond is weaker than that observed

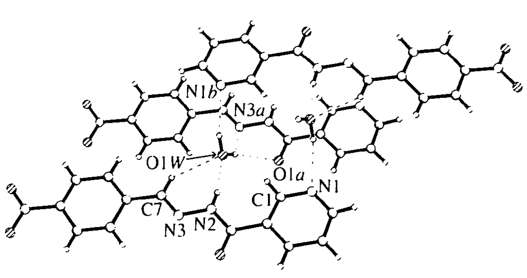


Fig. 2. Plot showing the hydrogen bonds between the hydrazone and water molecules.

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in the structure of a related compound, *p*-(dimethylamino)benzaldehyde isonicotinoylhydrazone monohydrate (N2···O1*W* 2.749 (3) Å) (Fun *et al.*, 1996), but in the present structure, the bonding between the hydrazone and the water molecule is strengthened by the surrounding C—H···O hydrogen bonds (Fig. 2).

Experimental

The synthesis of the compound was carried out by the reaction of *p*-nitrobenzaldehyde and nicotinoylhydrazine in ethanol solution, refluxing for 3 h. Single crystals were obtained by recrystallization from ethanol.

Crystal data

$C_{13}H_{10}N_4O_3.H_2O$
$M_r = 288.27$
Triclinic
$P\bar{1}$
$a = 6.417 (1)$ Å
$b = 8.378 (1)$ Å
$c = 12.503 (2)$ Å
$\alpha = 94.02 (1)°$
$\beta = 92.19 (1)°$
$\gamma = 91.66 (1)°$
$V = 669.7 (2)$ Å^3
$Z = 2$
$D_x = 1.430$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–25°$
$\mu = 0.109$ mm^{-1}
$T = 293 (2)$ K
Needle
0.58 × 0.30 × 0.26 mm
Light yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3889 measured reflections
3071 independent reflections
2263 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0175$

$\theta_{\rm max} = 27.5°$
$h = -1 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0486$
$wR(F^2) = 0.1599$
$S = 1.108$
3071 reflections
238 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.0238P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.216$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.243$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.7752 (2)	0.2829 (2)	0.38998 (9)	0.0626 (4)
O2	0.8515 (3)	−0.2510 (2)	1.03387 (11)	0.0916 (5)
O3	1.1264 (2)	−0.2490 (2)	0.94209 (11)	0.0867 (5)
N1	0.1535 (2)	0.5304 (2)	0.27664 (11)	0.0533 (3)
N2	0.4940 (2)	0.25626 (13)	0.49092 (9)	0.0381 (3)
N3	0.6097 (2)	0.17162 (13)	0.56121 (8)	0.0396 (3)
N4	0.9452 (2)	−0.2174 (2)	0.95489 (10)	0.0547 (4)
C1	0.2637 (2)	0.4455 (2)	0.34451 (12)	0.0456 (3)
C2	0.2484 (3)	0.5738 (2)	0.18923 (12)	0.0532 (4)
C3	0.4507 (3)	0.5396 (2)	0.16849 (12)	0.0571 (4)
C4	0.5648 (3)	0.4544 (2)	0.24043 (12)	0.0512 (4)
C5	0.4675 (2)	0.4041 (2)	0.32992 (10)	0.0379 (3)
C6	0.5931 (2)	0.3098 (2)	0.40571 (10)	0.0392 (3)
C7	0.5154 (2)	0.1229 (2)	0.64125 (11)	0.0403 (3)
C8	0.6289 (2)	0.0335 (2)	0.72032 (10)	0.0376 (3)
C9	0.8316 (2)	−0.0167 (2)	0.70431 (11)	0.0439 (3)
C10	0.9354 (2)	−0.0995 (2)	0.78060 (12)	0.0453 (3)
C11	0.8340 (2)	−0.1323 (2)	0.87240 (10)	0.0413 (3)
C12	0.6328 (2)	−0.0896 (2)	0.88944 (11)	0.0478 (4)
C13	0.5307 (2)	−0.0048 (2)	0.81285 (12)	0.0461 (4)
O1*W*	0.0854 (2)	0.2829 (2)	0.56506 (12)	0.0616 (4)

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

O1—C6	1.217 (2)	N3—C7	1.274 (2)
O2—N4	1.221 (2)	N4—C11	1.468 (2)
O3—N4	1.214 (2)	C5—C6	1.501 (2)
N2—C6	1.358 (2)	C7—C8	1.466 (2)
N2—N3	1.3764 (15)		
C6—N2—N3	117.1 (1)	O1—C6—C5	120.7 (1)
C7—N3—N2	116.5 (1)	N2—C6—C5	117.0 (1)
O1—C6—N2	122.3 (1)	N3—C7—C8	119.7 (1)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O1*W*	0.90 (2)	1.93 (2)	2.824 (2)	171 (2)
O1*W*—H1*W*···O1$^{\rm i}$	0.85 (3)	2.14 (3)	2.902 (2)	149 (3)
O1*W*—H1*W*···N3$^{\rm i}$	0.85 (3)	2.46 (3)	3.164 (2)	139 (2)
O1*W*—H2*W*···N1$^{\rm ii}$	0.84 (3)	2.14 (3)	2.942 (2)	158 (3)
C1—H1···O1*W*	0.92 (2)	2.49 (2)	3.384 (2)	162 (2)
C7—H7···O1*W*	1.03 (2)	2.41 (2)	3.242 (2)	137 (2)
C10—H10···O1$^{\rm iii}$	0.89 (2)	2.54 (2)	3.220 (2)	134 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, 1-z$; (iii) $2-x, -y, 1-z$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93. Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:2 Host–Guest Complex of Diaza-15-crown-5 with Picric Acid

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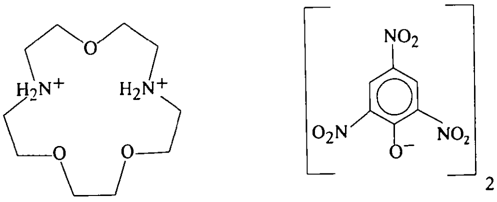
Abstract

In $C_{10}H_{24}N_2O_3^{2+}.2C_6H_2N_3O_7^-$, the crown ether, 1,4,10-trioxa-7,13-diazacyclopentadecane (diaza-15-crown-5), exists as a dication by accepting protons from two 2,4,6-trinitrophenol (picric acid) molecules. The crown ether shows disorder due to the two uniangular conformations at C3 and C4. The anions are stacked between the dications and are connected to them by N—H···O hydrogen bonds to form columns of interleaved ions. The crystal structure is stabilized by N—H···O and C—H···O hydrogen bonds.

Comment

The interaction between crown ethers and neutral organic molecules has been reviewed by several authors (Vogtle, Sieger & Muller, 1981; Watson, Galloy, Grossie, Vogtle & Muller, 1984; Goldberg, 1984). Replacement of ether O atoms by —NH— groups provides sites that can act as either electron or proton donors; such diaza-crown ether molecules form stable complexes with neutral organic molecules containing proton donors and have been found useful in selectively precipitating some polyhydroxy guests from mixtures of oligohydroxy phenols (Watson, Nagl & Eduok, 1989). It is well known that picric acid (PicH) forms charge-transfer complexes, but little has been reported on its complexes with crown ethers. We have investigated the reaction of PicH with diaza-15-crown-5 and obtained single crystals of the title complex, (I), in which the host–guest ratio is 1:2, as is the case for many crown ether complexes with organic compounds. The structural results are presented in Fig. 1 and Tables 1, 2 and 3.



(I)

The crown ether ring shows disorder of atoms C3 and C4. Such disorder is common in 15-crown-5 molecules because of the two uniangular conformations at C3 and C4 (Wei, Tinant, Declercq, Van Meerssche & Dale, 1988; Rogers, 1988). The *gauche* O—C—C—O torsion angle sequences in the ether ring are + + − − for C3*A* and C4*A* and + + + − − for C3*B* and C4*B*; the disordered region occupies a corner in each conformation. The forced *gauche* angles are −82.3 (4) (C5—O2—C4*A*—C3*A*) and 84.3 (6)° (C2—O1—C3*B*—C4*B*), which are (always) greater than 70° as a result of non-bonded H···H repulsion (Rogers, Kurihara & Benning, 1987). The ether has near mirror symmetry with the mirror plane passing through atom O3 and the C3—C4 bond and adopts a sofa-like conformation; all non-H atoms except O1, O2, C3 and C4 lie approximately in one plane [the mean deviation is 0.182 (3) Å and the maximum is 0.554 (3) Å for C9]. Atoms O1, O2, C3 and C4 lie well above this plane. Both N1 and N2 have acquired additional protons from the two PicH molecules and hence the crown exists as a dication. The two anions sit on either side of the dication.

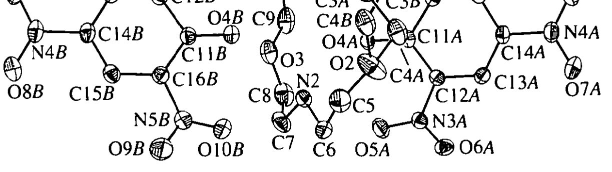


Fig. 1. Displacement ellipsoid plot (30% probability) of the title compound with the numbering scheme; H atoms are excluded for clarity.

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