References

Clark, P. D., Mesher, S. T. E. & Hinman, A. S. (1996). *J. Chem. Soc. Chem. Commun.* In the press.

Clark, P. D., Mesher, S. T. E. & Primak, A. (1996). *Phosphorus Sulfur Silicon.* In the press.

Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Parvez, M., Mesher, S. T. E. & Clark, P. D. (1996*a*). *Acta Cryst.* C**52**, 905–907.

Parvez, M., Mesher, S. T. E. & Clark, P. D. (1996*b*). *Acta Cryst.* C**52**, 1248–1250.

Williams, J. M., Ferraro, J. R., Thorn, R. J., Carlson, K. D., Geiser, U., Wang, H. H., Kini, A. M. & Whangbo, M. (1992). In *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory.* New Jersey, USA: Prentice Hall.

Acta Cryst. (1996). C**52**, 1505–1507

p-(Dimethylamino)benzaldehyde Isonicotinoylhydrazone Monohydrate

Hoong-Kun Fun,[a] Kandasamy Sivakumar,[a]† Zhong-Lin Lu,[b] Chun-Ying Duan,[b] Yu-Peng Tian[b] and Xiao-Zeng You[b]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and* [b]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: hkfun@usm.my*

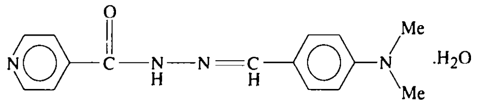
(*Received 11 October 1995; accepted 4 January 1996*)

Abstract

The single-crystal X-ray structure determination of the title compound, $C_{15}H_{16}N_4O.H_2O$, reveals that the molecule is in the keto tautomeric form and that the azomethine C=N double bond has the *E* configuration. The water molecule is hydrogen bonded to the hydrazone molecules to form a network structure in the crystal lattice. The crystal structure is stabilized by N—H···O, O—H···O and C—H···O hydrogen bonds.

Comment

The chemical and pharmacological properties of aroylhydrazones have been investigated extensively, owing to their chelating ability with metal ions and to their antineoplastic, antiviral and anti-inflammatory activities (Lu, Wu, Liang, Song & Ma, 1994; Dutta & Hossain, 1985; Rao & Gopal, 1991; Constable & Holmes, 1987; Wester & Palenik, 1973). In this paper we report the structure of *p*-(dimethylamino)benzaldehyde isonicotinoylhydrazone monohydrate, (I).



(I)

Fig. 1 shows an *ORTEP*II (Johnson, 1976) plot of the title compound with the atom-numbering scheme. It can be seen that the molecule is in the keto tautomeric form and that the configuration of the N3—C7 bond is *E*. The bond lengths and angles in the pyridine and dimethylaminophenyl rings are in agreement with those of related structures reported earlier (Wang, Deng, Wu & Chen, 1992; Lu *et al.*, 1995). While the hydrazone moiety is in the plane of the phenyl ring, the pyridine ring makes an angle of 48.08 (7)° with the phenyl ring, and the dimethylamino group is tilted 4.3 (2)° from the plane of the phenyl ring. As a whole, the molecule has an almost planar conformation with the plane of the molecule parallel to the *bc* plane and its axis parallel to the *c* axis. The water molecule lies almost in the plane of the central hydrazone group.

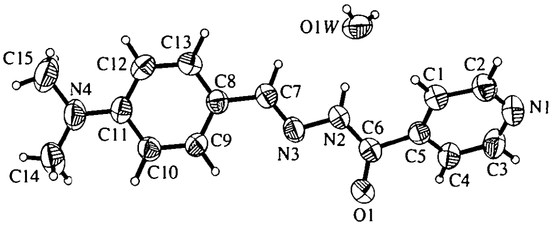


Fig. 1. Displacement ellipsoid plot (50% probability) of the title compound with numbering scheme.

In the crystal lattice, the molecules create a network structure through hydrogen bonds. The water molecule acts as both acceptor and donor in the hydrogen bonds. The keto O1 atom is involved in both O—H···O and C—H···O hydrogen bonds. The details are: N2···O1$W^{\rm i}$ 2.749 (3) Å, N2—H2N···O1$W^{\rm i}$ 172 (2)°; O1*W*···O1$^{\rm ii}$ 2.741 (3) Å, O1*W*—H1*W*···O1$^{\rm ii}$ 150 (4)°; O1*W*···N1$^{\rm iii}$ 2.839 (3) Å, O1*W*—H2*W*···N1 170 (4)°;

---

† On leave from the Department of Physics, Anna University, Madras 600 025, India.

C7···O1^{ii} 3.419 (3) Å, C7—H7···O1^{ii} 143 (2)° [symmetry codes: (i) x, y, z; (ii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, 2-z$].

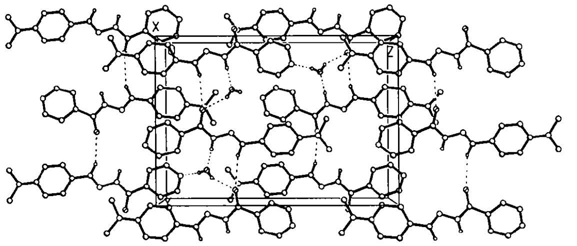


Fig. 2. Packing of the molecules viewed down the *a* axis. The hydrogen bonds are shown as dashed lines.

Experimental

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

Crystal data

$C_{15}H_{16}N_4O.H_2O$
$M_r = 286.33$
Orthorhombic
$P2_12_12_1$
$a = 7.386 (1)$ Å
$b = 11.810 (1)$ Å
$c = 17.197 (2)$ Å
$V = 1500.1 (3)$ Å^3
$Z = 4$
$D_x = 1.268$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–25°$
$\mu = 0.087$ mm^{-1}
$T = 293 (2)$ K
Plate
0.56 × 0.48 × 0.16 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2631 measured reflections
1985 independent reflections
1396 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0166$

$\theta_{\rm max} = 27.48°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 15$
$l = -1 \rightarrow 22$
3 standard reflections monitored every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0336$
$wR(F^2) = 0.0864$
$S = 0.928$
1984 reflections
263 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.112$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.089$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0113 (14)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.4 (18) (indeterminate)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.0703 (3)	1.06805 (13)	0.81808 (8)	0.0652 (5)
N1	0.0845 (3)	0.8514 (2)	1.06437 (11)	0.0674 (6)
N2	−0.0149 (3)	0.8940 (2)	0.77507 (9)	0.0497 (5)
N3	−0.0116 (3)	0.92712 (15)	0.69751 (9)	0.0511 (5)
N4	−0.0858 (3)	0.9090 (2)	0.32331 (11)	0.0729 (6)
C1	0.1073 (3)	0.8156 (2)	0.92809 (13)	0.0535 (6)
C2	0.1286 (4)	0.7855 (2)	1.00536 (14)	0.0634 (7)
C3	0.0162 (4)	0.9528 (2)	1.04730 (13)	0.0667 (7)
C4	−0.0061 (3)	0.9915 (2)	0.97234 (13)	0.0542 (6)
C5	0.0402 (3)	0.9215 (2)	0.91144 (11)	0.0441 (5)
C6	0.0313 (3)	0.9683 (2)	0.83003 (11)	0.0474 (5)
C7	−0.0781 (3)	0.8539 (2)	0.65054 (12)	0.0497 (5)
C8	−0.0798 (3)	0.8709 (2)	0.56626 (11)	0.0469 (5)
C9	−0.0090 (3)	0.9674 (2)	0.53103 (11)	0.0498 (5)
C10	−0.0088 (3)	0.9788 (2)	0.45108 (11)	0.0520 (5)
C11	−0.0814 (3)	0.8949 (2)	0.40259 (12)	0.0503 (5)
C12	−0.1501 (3)	0.7975 (2)	0.43849 (13)	0.0548 (6)
C13	−0.1501 (3)	0.7871 (2)	0.51860 (13)	0.0505 (5)
C14	−0.0268 (5)	1.0114 (3)	0.2869 (2)	0.0750 (8)
C15	−0.1505 (7)	0.8201 (4)	0.2728 (2)	0.0900 (11)
O1*W*	−0.1779 (4)	0.6907 (2)	0.80911 (12)	0.0887 (8)

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

O1—C6	1.230 (3)	N4—C11	1.374 (3)
N1—C2	1.320 (3)	N4—C14	1.430 (4)
N1—C3	1.332 (3)	N4—C15	1.444 (4)
N2—C6	1.333 (3)	C5—C6	1.506 (3)
N2—N3	1.390 (2)	C7—C8	1.463 (3)
N3—C7	1.281 (3)		
C6—N2—N3	119.4 (2)	O1—C6—C5	119.7 (2)
C7—N3—N2	114.1 (2)	N2—C6—C5	115.4 (2)
O1—C6—N2	124.8 (2)	N3—C7—C8	122.4 (2)

The structure was solved by direct methods and refined by full-matrix least-squares technique. The 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).

The authors would like to thank the Malaysian Government and the Universiti Sains Malaysia for research grant R&D No. 123-3417-2201, and the State Science and Technology Commission and the National Nature Science Foundation of China for a Major Key Research Project. KS thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Constable, E. C. & Holmes, J. M. (1987). *Inorg. Chim. Acta*, **126**, 187–193.

Dutta, R. L. & Hossain, Md. M. (1985). *J. Sci. Ind. Res.* **44**, 635–674.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1995). *Acta Cryst.* C**51**, 2078–2080.

Lu, Z.-L., Wu, X.-L., Liang, Y.-M., Song, Q.-B. & Ma, Y.-X. (1994). *Bull. Soc. Chim. Belg.* **103**, 47–57.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Rao, K. R. & Gopal, E. R. (1991). *Acta Cienc. Indica. Phys.* **17**(4), 341–346.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wang, X., Deng, R.-W., Wu, J.-G. & Chen, Z.-N. (1992). *Acta Cryst.* C**48**, 1295–1297.

Wester, D. & Palenik, G. J. (1973). *J. Am. Chem. Soc.* **95**, 6506–6509.

Acta Cryst. (1996). C**52**, 1507-1509

p-Nitrobenzaldehyde Nicotinoylhydrazone Monohydrate

Zhong-Lin Lu,[a] Chun-Ying Duan,[a] Yu-Peng Tian,[a] Xiao-Zeng You,[a] Hoong-Kun Fun[b] and Kandasamy Sivakumar[b]†

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

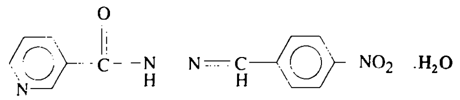
(*Received 13 October 1995; accepted 11 December 1995*)

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.

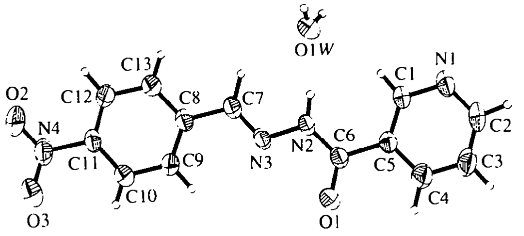


Fig. 1. Displacement ellipsoid plot (50% probability) of the title compound with numbering scheme.

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

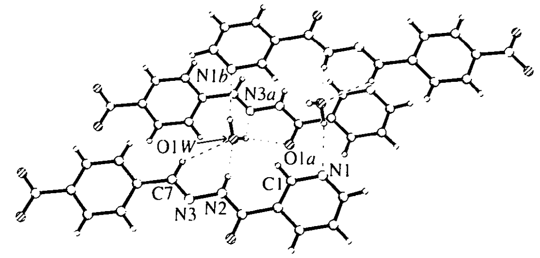


Fig. 2. Plot showing the hydrogen bonds between the hydrazone and water molecules.

---

† On leave from the Department of Physics, Anna University, Madras 600 025, India.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996