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2-Acetylamino-6-methylpyridine *N*-oxide monohydrate

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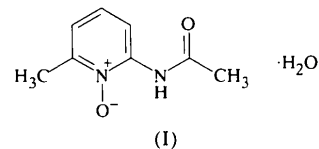
Abstract

In the title molecule, C₈H₁₀N₂O₂·H₂O, the acetylamino group forms a dihedral angle of 6.05 (6)° with the pyridine ring. The N—H···O, O—H···O and C—H···O hydrogen bonds, along with π–π stacking interactions, are involved in the formation of a supramolecular assembly, with the water molecule acting as a bridging ligand.

Comment

Hydrogen bonds play an important role in all biological recognition and assembly processes (Jeffrey & Saenger, 1991). They are widely used for the development of synthetic receptors (Seel *et al.*, 1995; Meissner *et al.*, 1997) and for the design of supramolecular crystals (McDonald & Whitesides, 1994). Most of the supramolecular crystals originate from strong N—H···X and O—H···X (X = O or N) hydrogen bonds. Besides these conventional hydrogen bonds, unconventional C—H···O hydrogen bonds are also involved in the formation of supramolecular assemblies (Krishnamohan Sharma *et al.*, 1992). These bonds are much weaker than the X—H···X (X = O or N) hydrogen bonds. Work performed on C—H···O hydrogen bonds reveals that they play important functional and structural roles in biological macromolecules, including nucleic acids (Sussman *et al.*, 1972), proteins (Derewenda *et al.*, 1995) and carbohydrates (Steiner & Saenger, 1992). More interestingly, water molecules can complement their incomplete tetrahedral co-ordination through such C—H···O contacts. These C—H···O contacts involving water molecules are observed in layered biological structures *e.g.* vitamin B₁₂ and the enzyme actindin (Steiner & Saenger,

1993*a,b*). The study of similar weak C—H···O interactions between small organic molecules is also of great interest; they often determine the molecular packing. In this paper, the title molecule, (I), provides such an example, where all the weak forces such as π-stacking, C—H···O, X—H···X (X = O or N) hydrogen bonding interactions and water encapsulation *via* C—H···O contacts, *etc.*, are involved in building a supramolecular assembly from a dimeric entity.



The mean plane through the acetylamino group makes a dihedral angle of 6.05 (6)° with the pyridine plane. In the crystal, the inversion related molecules are linked

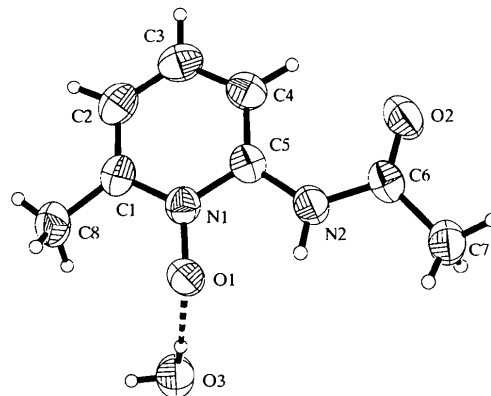


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

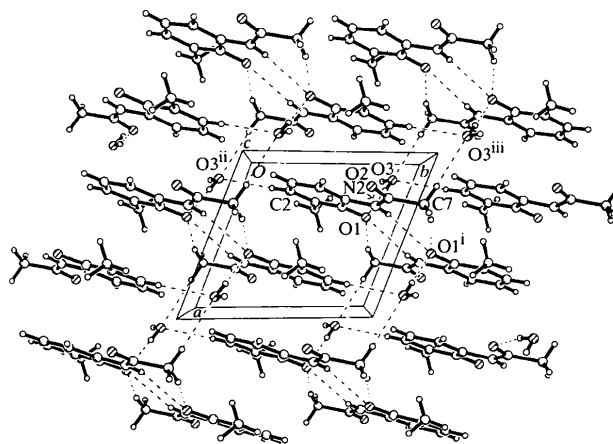


Fig. 2. A view of the supramolecular assembly of (I) viewed down the *c* axis. Symmetry codes are as in Table 2.

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by N2—H···O1ⁱ and C7—H···O1ⁱ hydrogen bonds to form a dimeric pair. Neighbouring pairs along the *a* direction are connected through water molecules by O3—H···O1 and C7—H···O3ⁱⁱⁱ hydrogen bonds to form a column. Neighbouring columns of molecules along the *b* direction are linked by C2—H···O3ⁱⁱ hydrogen bonds (Fig. 2). Their pyridine rings are interleaved and stacked 3.473 (2) Å apart along the *a* direction, an optimum arrangement for π - π stacking interactions. This molecular network is interlinked by O3—H···O2^{iv} hydrogen bonds to form a supramolecular structure [symmetry codes: (i) 1 - *x*, 2 - *y*, 1 - *z*; (ii) *x*, *y* - 1, *z*; (iii) -*x*, 2 - *y*, 1 - *z*; (iv) *x*, *y*, *z* - 1].

Experimental

The title compound was prepared from 2-(*N*-acetylamino)-6-methylpyridine by reaction with 48% H₂O₂ in glacial acetic acid at 353 K. Single crystals were obtained by slow evaporation from a chloroform solution of the compound.

Crystal data

C₈H₁₀N₂O₂·H₂O

M_r = 184.20

Triclinic

P $\bar{1}$

a = 7.1276 (6) Å

b = 7.8860 (6) Å

c = 8.9938 (7) Å

α = 100.143 (2)°

β = 91.493 (2)°

γ = 110.972 (1)°

V = 462.47 (6) Å³

Z = 2

D_x = 1.323 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 2224 reflections

θ = 2.82–33.13°

μ = 0.102 mm⁻¹

T = 293 (2) K

Block

0.46 × 0.42 × 0.38 mm

Colourless

Table 1. Selected geometric parameters (Å, °)

O1—N1	1.3271 (14)	N1—C5	1.3683 (17)
O2—C6	1.2171 (18)	N2—C6	1.3682 (17)
N1—C1	1.3654 (18)	N2—C5	1.3845 (18)
C6—N2—C5—C4	−6.3 (2)	C5—N2—C6—O2	5.5 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H1O3···O1	0.86 (3)	1.96 (3)	2.817 (2)	175 (3)
C4—H4···O2	0.95 (2)	2.24 (2)	2.849 (2)	121 (1)
N2—H1N2···O1 ⁱ	0.90 (2)	2.54 (2)	3.321 (2)	146 (2)
C7—H7C···O1 ⁱ	0.91 (3)	2.40 (4)	3.276 (2)	161 (3)
C2—H2···O3 ⁱⁱ	0.95 (2)	2.46 (2)	3.380 (2)	161 (2)
C7—H7A···O3 ⁱⁱⁱ	0.93 (4)	2.51 (4)	3.443 (3)	177 (3)
O3—H2O3···O2 ^{iv}	0.86 (4)	2.06 (4)	2.898 (2)	167 (3)

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

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm ($2\theta_{\max}$ = 66.27°) and the detector swing angle was -35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. Only reflections having 2θ less than 64° were used for structure solution and refinement, as only a few reflections were found to be observed at higher angles.

All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1243). Services for accessing these data are described at the back of the journal.

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

Absorption correction: none

3579 measured reflections

2541 independent reflections

1808 reflections with

$I > 2\sigma(I)$

R_{int} = 0.018

θ_{\max} = 30°

$h = 0 \rightarrow 12$

$k = -11 \rightarrow 10$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.161$

S = 1.044

2541 reflections

166 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0933P)^2 + 0.0223P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.224 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.172 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

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3-(2-Chlorophenyl)-4-phenyl-1,2,4-triazole-5-thione

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Abstract

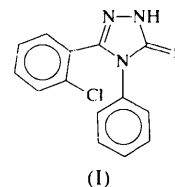
In the title compound, C₁₄H₁₀ClN₃S, the triazole ring is planar. The chlorophenyl and phenyl rings are oriented at angles of 60.3 (1) and 59.0 (1)°, respectively, to the triazole ring. The structure is stabilized by hydrogen bonds of the N—H···S type, in addition to van der Waals forces.

Comment

The 4-substituted 1,2,4-triazoles form predominantly binuclear species with three bridging triazoles. The ability of triazoles to form a bridge between transition metal ions makes these complexes particularly interesting from the magnetochemical point of view (Groeneveld *et al.*, 1982). The recent finding indicated that the 1,2,4-triazole nucleus is associated with diverse pharmacological properties such as analgesic, anti-asthmatic, diuretic, antifun-

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gal, antibacterial, pesticidal and anti-inflammatory activities (Mohamed *et al.*, 1993; Heubach *et al.*, 1980; Bennur *et al.*, 1976; Sharma & Bahel, 1982). In view of these important factors, the crystal structure determination of the title compound, (I), has been carried out.



The bond lengths and bond angles of the triazole ring are comparable with related structures (Groeneveld *et al.*, 1982; Gorter & Engelfriet, 1981; Kokkou & Rentzeperis, 1975). The triazole ring is planar with a maximum deviation of $-0.005(1)$ Å for the atom N2. The C=S [C3=S1 1.680(2) Å] and C—Cl [C11—Cl1 1.735(3) Å] bond lengths are comparable with the values reported in the literature (Allen *et al.*, 1987).

The phenyl and chlorophenyl rings are planar and subtend at angles of 60.3 (1) and 59.0 (1)°, respectively, with the triazole ring. Also these two rings orient at an angle of 63.7 (1)° with respect to each other.

Interestingly, a linear N—H···S type of hydrogen bonding is observed [N2···S1($-x, -y + 1, -z$) = 3.273(2) Å, N2—H2 = 0.81(4) Å, N2—H2···S1 = 176(3)°]. The packing of the molecules in the unit cell is van der Waals in nature.

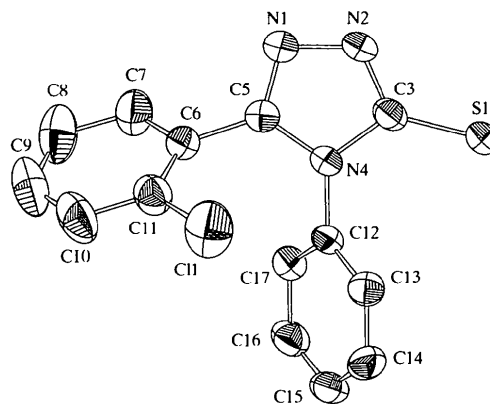


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

The title compound was synthesized by refluxing *o*-chlorophenyl hydrazide and phenyl isothiocyanate in NaOH solution (Jayanthi *et al.*, 1997).