Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N-[5-(1-Naphthyl)pyrimidin-4-yl]acetamide oxime

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Key indicators

Single-crystal X-ray study
T = 250 K
Mean σ(C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.182
Data-to-parameter ratio = 20.3

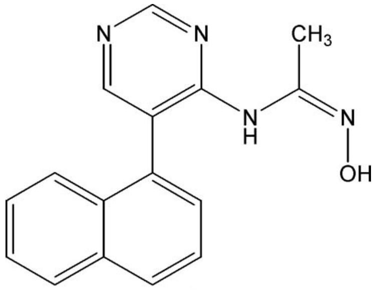
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 1 December 2006
Accepted 3 December 2006

In the asymmetric unit of the title compound, $C_{16}H_{14}N_4O$, there are two crystallographically independent molecules, which are connected to each other by O—H···N hydrogen bonds, forming a molecular chain. The neighboring chains are linked into a layer through π–π stacking interactions.

Comment

As part of our investigation to prepare anti-advanced glycation end-product (AGEs) agents, we have developed a pyrimidine ring-opening reaction accompanied by the formation of a 1,2,4-oxadiazole ring by the reaction of various 4-pyrimidinylamidines or amide oximes with hydroxylamine hydrochloride (Sasaki *et al.*, 2001). The title compound, (I), was prepared as a reaction substrate of this reaction. A methanol solution of the compound on silica gel thin-layer chromatography (TLC) gave a single spot but it changed to two spots gradually, suggesting that the compound changed to an equilibrium mixture of two compounds. In order to obtain fundamental information about this phenomenon, an X-ray crystal structure analysis of (I) was undertaken.



(I)

In the asymmetric unit of (I), there are two crystallographically independent molecules, A and B (Fig. 1). Each molecule has an intramolecular N—H···O hydrogen bond (Table 1), which makes non-H atoms in the acetamide oxime unit coplanar; the r.m.s. deviations are 0.007 and 0.006 Å for molecule A and B, respectively. The geometries of both molecules are essentially the same; the dihedral angles between the naphthalene and pyrimidine rings are 67.40 (7) and 69.35 (7)° for molecules A and B, respectively, and those between the pyrimidine ring and the acetamide oxime plane are 19.98 (8) and 14.57 (9)°, respectively.

Molecules A and B are connected to each other by O—H···N (Table 1) hydrogen bonds to form a molecular chain running along the $[1\bar{1}1]$ direction. Neighboring chains related by an inversion center are linked *via* π–π stacking interactions between pyrimidine rings of A and B, and between naphtha-

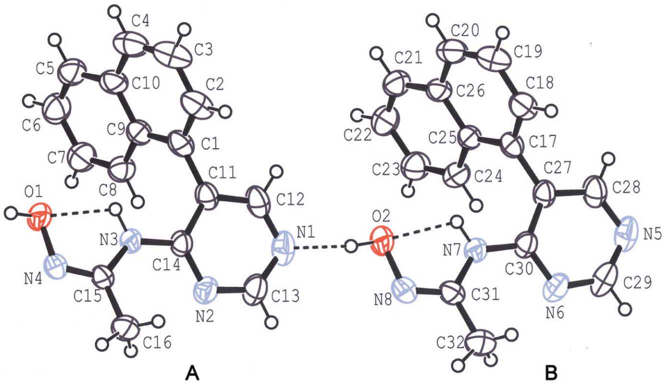


Figure 1
The asymmetric unit of (I), showing two independent molecules designated by A and B. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level. Dashed lines indicate hydrogen bonds.

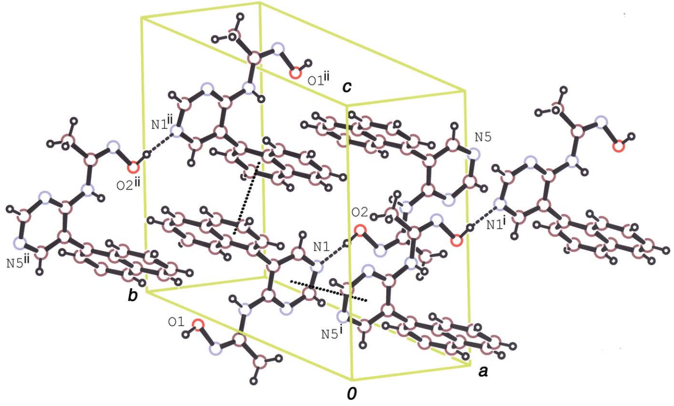


Figure 2
Packing diagram of (I), showing the hydrogen bonds (dashed lines) and the π-π stacking interactions (dotted lines). [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, 1 - y, 1 - z$].

lene rings of A, giving a molecular layer extending parallel to the (110) plane. The centroid–centroid and interplanar distances are 3.9212 (11) and 3.404 (5) Å, respectively, for the prymidine rings, and 4.2445 (11) and 4.086 (2) Å for the naphthalene rings.

The TLC phenomenon mentioned above might be explained in terms of the molecular structure. In the molecule, three distinct planes, *viz.* naphthalene, pyrimidine and acetamide oxime, are connected by single bonds, around which the rotation of these planes is hindered by intramolecular interactions. In a methanol solution, one single bond may cause a set of atropisomers by these interactions, so that the two single bonds cause two diastereomers. We suggest the new spot on silica gel TLC is derived from another diastereomer.

Experimental

Hydroxylamine hydrochloride (83.4 mg, 1.2 mmol) was dissolved in a solution of N^1,N^1-dimethyl-N^2-[5-(1-naphthyl)pyrimidin-4-yl]acetamidine (290 mg, 1.0 mmol) in methanol (4 ml) at *ca* 283 K, then stirred at the same temperature for 1.5 h. The mixture was cloudy within a few minutes after the addition of hydroxylamine hydrochloride. Filtering and washing with H_2O gave white crystals (yield 221 mg, 79.5%; m.p. 412–416 K). Single crystals suitable for X-ray diffraction were obtained from a methanol solution.

Crystal data

$C_{16}H_{14}N_4O$
$M_r = 278.31$
Triclinic, $P\overline{1}$
$a = 10.8011$ (6) Å
$b = 11.6051$ (6) Å
$c = 12.8489$ (8) Å
$\alpha = 63.3951$ (16)°
$\beta = 76.8282$ (16)°
$\gamma = 89.5278$ (19)°
$V = 1394.00$ (14) Å^3
$Z = 4$
$D_x = 1.326$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 250$ (2) K
Plate, colorless
0.38 × 0.30 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID-II diffractometer
ω scans
Absorption correction: none
24844 measured reflections
8057 independent reflections
4461 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.065$
$\theta_{\rm max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.182$
$S = 0.98$
8057 reflections
396 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0969P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N5$^{\rm i}$	0.86 (2)	1.89 (2)	2.744 (2)	175.4 (19)
O2—H2O···N1	0.88 (2)	1.89 (2)	2.762 (2)	172.7 (18)
N3—H3N···O1	0.90 (2)	2.064 (19)	2.4878 (17)	107.5 (15)
N7—H7N···O2	0.870 (19)	2.097 (18)	2.5068 (18)	108.0 (14)

Symmetry code: (i) $x - 1, y + 1, z - 1$.

O-bound and N-bound H atoms were found in a difference Fourier map and refined isotropically (refined distances given in Table 1). Other H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}$(methyl C).

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

This work was partly supported by a Grant-in-Aid for Scientific Research (C) (No. 16550014) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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