Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1-(4,6-Diethoxypyrimidin-2-yl)-2-thioxo-2,3-dihydropyrido[2,3-*d*]-pyrimidin-4(1*H*)-one

Si-Jia Xue,* Qing-Dong Wang*‡ and Jing-Zhi Li

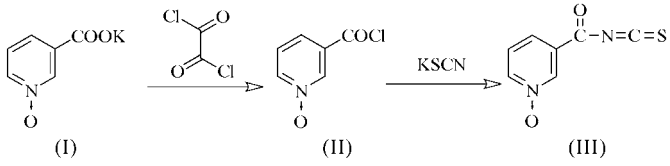
Department of Chemistry, College of Life and Environmental Science, Shanghai Normal University, Shanghai, 200234, People's Republic of China
Correspondence e-mail: sjxue@shnu.edu.com, wang_q_d@126.com

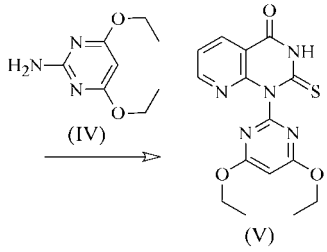
Received 7 September 2006
Accepted 5 October 2006
Online 31 October 2006

In the title compound, $C_{15}H_{15}N_5O_3S$, two parallel intermolecular N—H···S hydrogen bonds, forming an eight-membered ring, link two molecules into a dimer unit; these dimer units linked into a chain of edge-fused rings by weak C—H···O hydrogen bonds.

Comment

The title compound, (V), has been obtained in the course of our study of the biological activity of acylthiourea derivatives containing substituted pyrimidine. Many acylthiourea compounds show high herbicidal activity (Xue *et al.*, 2004), and investigation of acylthioureas as herbicides has become the subject of intensive research (Xue & Wang, 2003; Xue *et al.*, 2004; Xu *et al.*, 2005). We have developed the synthesis of (V) and report here its crystal structure.





The key feature of (V) is the two aromatic rings, namely a pyridine ring (C7–C11/N5), and a pyrimidine ring (C1–C4/N1/N2) with two ethoxy substituents (Fig. 1). The dihedral angle between the pyridine and pyrimidine ring planes is 78.3 (1)°.

‡ Additional address: Department of Chemistry, Yancheng Teachers College, Yancheng, Jiangsu 224002, People's Republic of China.

Instead of the catenarian structure usual in acylthiourea compounds, the acylthiourea bridge in (V) is embedded in a six-membered ring. The members of the ring are almost

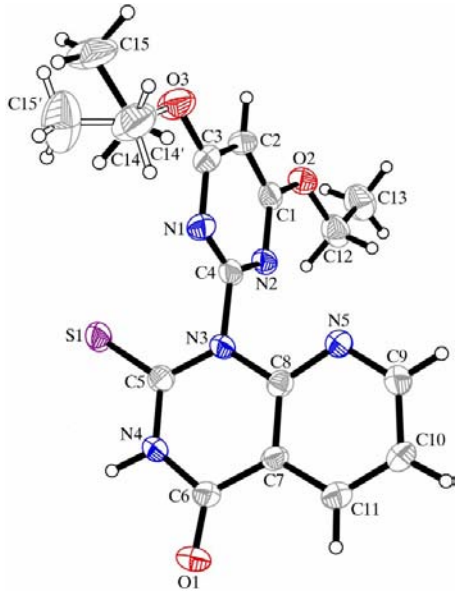


Figure 1
The molecular structure of (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms and H atoms are shown as small spheres of arbitrary radii. The two sites shown for the ethyl group bonded to O3 have occupancies of 0.672 (10) and 0.328 (10).

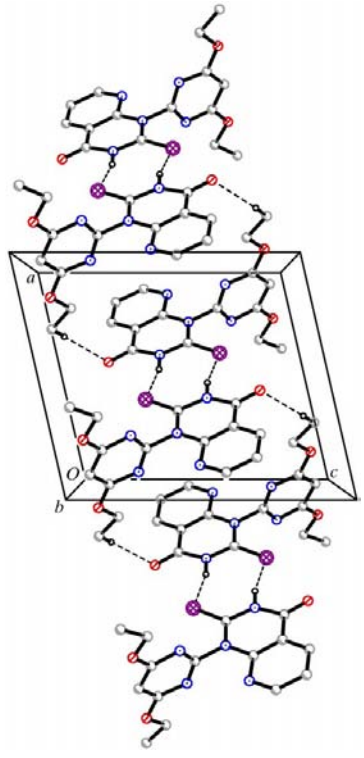


Figure 2
Part of the crystal structure of (V), showing the formation of a chain built from $R_2^2(8)$ and $R_2^2(24)$ rings. Only the major component of the disordered group is shown.

 © 2006 International Union of Crystallography DOI: 10.1107/S0108270106041151

coplanar, and the dihedral angle between this plane and that of the pyridine ring is 3.5 (7)°, while the dihedral angle between the plane and that of the pyrimidine ring is 79.5 (1)°.

In (V), the molecules are linked by two parallel independent N—H···S hydrogen bonds (Table 2). Atom N4 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom S1 in the molecule at $(1-x, -y, 1-z)$, linking the two molecules into a dimer unit, so generating a centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) ring centred at $(\frac{1}{2}, 0, \frac{1}{2})$ (Fig. 2). In the dimer, the two pyridine rings are parallel, with a distance between their planes of 0.16 (1) Å, and the pyrimidine rings are also parallel, with a separation of 6.48 (7) Å. In addition, atom C15 in the molecule at (x, y, z) acts as a donor to atom O1 in the molecule at $(-x, -y, 1-z)$, generating a centrosymmetric $R_2^2(24)$ ring centred at $(0, 0, \frac{1}{2})$. The combination of the $R_2^2(8)$ and $R_2^2(24)$ rings then generates a chain of edge-fused centrosymmetric rings.

Experimental

3-Carboxypyridine 1-oxide (13.9 g, 0.1 mol) was added to a 2% potassium hydroxide solution (200 ml) with stirring at room temperature and the mixture was stirred for 1 h. The precipitate was filtered off under suction and the filtrate was evaporated to dryness under vacuum. The product, potassium 1-oxidopyridine-3-carboxylate, (I), was dried under vacuum for another hour for further use. Excluding moisture, a solution of oxalyl dichloride (2.62 ml, 0.03 mol) in acetonitrile (5 ml) was added slowly to a stirred mixture of (I) (1.77 g, 0.01 mol) and acetonitrile (15 ml) at 273 K. The mixture was stirred for 1 h at 298 K and refluxed for another 1.5 h at 353 K. At the end of the reflux, the acetonitrile and the excess oxalyl dichloride were evaporated. The residue, 3-(chlorocarbonyl)pyridine 1-oxide, (II), was added to a solution of potassium thiocyanate in acetonitrile (20 ml). The mixture was refluxed for 1 h at 353 K and then filtered off to yield a clear yellow solution of 3-(isothiocyanatocarbonyl)pyridine 1-oxide, (III). To this solution, 4,6-diethoxypyrimidin-2-amine (1.55 g, 0.01 mol) was added; the mixture was refluxed and stirred for another 6 h at 343 K, and then allowed to stand at room temperature for 10 h. The separated precipitate, (V), was filtered off under suction and washed with 50% ethanol solution. The product was further purified by column chromatography on silica gel (hexane–ethyl acetate, 8:1) to give a white solid. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of (V) in hexane–ethyl acetate (6:1 *v*/*v*) at room temperature (m.p. 472–473 K). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.32 (*s*, 3H, CH_3), 4.25–4.34 (*q*, 2H, OCH_2), 6.41 (*s*, 1H, py–H), 7.47–8.65 (*m*, 4H, pyridine), 12.30 (*s*, 1H, NH); IR (KBr, cm^{-1}): ν 3436 (N—H), 1740 (C═O), 1254 (C═S). Analysis calculated for $C_{15}H_{15}N_5O_3S$: C 52.16, H 4.38, N 20.28, O 13.90%; found: C 53.02, H 4.08, N 19.28, O 14.10%.

Crystal data

$C_{15}H_{15}N_5O_3S$
M_r = 345.38
Monoclinic, $P2_1/n$
a = 9.0543 (10) Å
b = 17.884 (2) Å
c = 10.3365 (12) Å
β = 102.840 (2)°
V = 1631.9 (3) Å^3
Z = 4
D_x = 1.406 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 298 (2) K
Prism, colourless
0.10 × 0.09 × 0.07 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.989, T_{max} = 0.994
8352 measured reflections
2955 independent reflections
1651 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 25.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.081
S = 0.88
2955 reflections
232 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0122P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C5	1.661 (3)	N3—C4	1.456 (3)
O1—C6	1.213 (3)	N4—C5	1.362 (3)
N3—C5	1.362 (3)	N4—C6	1.384 (3)
N3—C8	1.394 (3)	C6—C7	1.453 (3)
C1—O2—C12	118.5 (2)	N4—C5—S1	121.7 (2)
C3—O3—C14	117.5 (3)	O1—C6—N4	120.4 (3)
C5—N4—C6	127.8 (3)	O1—C6—C7	125.7 (3)
N3—C5—N4	115.6 (3)	N4—C6—C7	114.0 (3)
C5—N3—C4—N2	−97.3 (3)	N4—C6—C7—C11	−176.7 (3)
C8—N3—C4—N2	79.8 (3)	O1—C6—C7—C8	−175.7 (3)
C5—N3—C4—N1	82.8 (3)	N4—C6—C7—C8	4.1 (4)
C8—N3—C4—N1	−100.1 (3)	C9—N5—C8—C7	3.7 (4)
O1—C6—C7—C11	3.5 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···S1^{i}	0.95 (3)	2.39 (3)	3.320 (3)	165 (2)
C15—H15A···O1^{ii}	0.96	2.48	3.379 (6)	156

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

The ethyl group bonded to O3 was found to be disordered over two sites. The coordinates of the C atoms of the disordered component were located in a difference Fourier map initially and refined with the occupancies tied to sum to unity. The site occupancies for the two components were refined freely to 0.672 (10) and 0.328 (10). The H atom bonded to the N atom was located in a difference Fourier map and refined isotropically. H atoms bonded to C atoms were positioned geometrically, with C—H distances in the range 0.93–0.97 Å, and refined as riding, with U_{iso}(H) values of 1.2 or 1.5 times U_{eq} of the parent C atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

This work was sponsored by the National Natural Science Foundation of China (grant No. 20672073). The authors also thank Professor Yong-Ge Wei of the Tsinghua University of China for his assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3022). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2000). *SADABS*, *SAINT*, *SHELXTL* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Xu, D. F., Li, J. Z., Guo, Y. L., Ke, S. Y. & Xue, S. J. (2005). *Chin. J. Org. Chem.* **25**, 1053–1056.
Xue, S. J., Duan, L. P., Ke, S. Y. & Zhu, J. M. (2004). *Chin. J. Org. Chem.* **24**, 686–690.
Xue, S. J. & Wang, J. P. (2003). *Chin. J. Appl. Chem.* **20**, 1111–1113.