Instrumental Achievements

Crystal Structure of 3-Ethoxy-6-cyano-5-[2-(4-ethoxycarbonyl)thiazolyl]pyridine

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Nosiheptide¹ is a peptide antibiotic whose acid hydrolysis gave heterocyclic compounds called Fragments A, C, D, E and two kinds of amino acids. Among them, Fragment A has a pyridine skeleton substituted with three thiazole rings. In the course of the synthesis of Fragment A, cyanation of 3-ethoxy-5-[2-(4-ethoxycarbonyl)thiazolyl]pyridine (1) by Reissert-Henze method gave two isomers (main, mp. 158 – 159°C; minor, mp. 159.5 – 160.5°C). The structures of them are deduced to be 2-cyano (2) and 6-cyano (3) derivatives, but they couldn't be distinguished by usual analytical methods. The minor compound can be separated by silica gel column chromatography and the single crystal was obtained by slow recrystallization from an ethanol/ethyl acetate solution covered with hexane vapor. Here, we wish to report that the minor compound was determined to be

Scheme 1 Synthetic route.

Table 1 Crystal data and experimental details

Formula	C ₁₄ H ₁₃ N ₃ O ₅ S
Formula weight	303.33
Temperature	173 K
Crystal size	0.40×0.30×0.05 mm
Crystal color	transparent
Crystal description	plate
Crystal system	triclinic
Space group	P1 Z=2
a	9.685(2) Å
b	16.718(2) Å
c	4.4015(4) Å
α	91.51(1)°
β	94.12(1)°
γ	99.555(5)°
V	700.5(2) Å ³
D _x	1.438 Mg m ⁻³
Radiation	0.71069 Å (Mo K _α)
Diffractionmeter	Rigaku R-AXIS-II-CS
Monochromator	graphite
No. of reflections measured	5931
No. of reflections observed [≥2σ(I)]	2379
No. of parameters	229
R(F)	0.0500
wR(F)	0.1354
Structure determination	TEXSAN ²
Refinement	SHELX-93 ³

Table 2 Positional and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	U _{eq}
S1	0.67500(5)	0.15741(3)	0.9102(1)	0.0362
O1	0.3531(2)	0.41981(9)	0.2237(4)	0.0390
O2	0.2271(2)	0.1459(1)	1.3144(4)	0.0430
O3	0.3160(2)	0.0333(1)	1.4294(4)	0.0488
N1	0.7092(2)	0.3893(1)	0.3387(5)	0.0373
N2	0.9363(2)	0.2850(1)	0.6905(6)	0.0521
N3	0.4335(2)	0.1980(1)	0.9538(4)	0.0302
C1	0.5937(2)	0.4173(1)	0.2480(6)	0.0359
C2	0.4606(2)	0.3846(1)	0.3382(5)	0.0326
C3	0.4489(2)	0.3200(1)	0.5281(5)	0.0314
C4	0.5698(2)	0.2890(1)	0.6276(5)	0.0296
C5	0.6974(2)	0.3265(1)	0.5253(5)	0.0319
C6	0.2124(2)	0.3864(1)	0.3033(7)	0.0411
C7	0.1158(3)	0.4415(2)	0.1771(7)	0.0426
C8	0.8302(2)	0.3023(1)	0.6195(6)	0.0392
C9	0.5519(2)	0.2195(1)	0.8279(5)	0.0303
C10	0.4388(2)	0.1308(2)	1.1221(5)	0.0309
C11	0.5610(2)	0.1001(1)	1.1241(5)	0.0346
C12	0.3212(2)	0.0966(1)	1.3039(5)	0.0337
C13	0.1097(3)	0.1232(2)	1.5024(7)	0.0514
C14	-0.0228(3)	0.1092(2)	1.3008(8)	0.0622

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i^* a_j).$$

Fig. 1 ORTEP⁴ drawing with the numbering of the atoms. Thermal ellipsoids scaled to enclose 50% probability.

6-cyanate by X-ray analysis.

Crystal and experimental data are given in Table 1 and the final atomic parameters for non-hydrogen atoms are listed in Table 2. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were located on a difference Fourier map and isotropically refined. The molecular structure drawn by ORTEP⁴ with atomic numbering is shown in Fig. 1 and indicates that the minor compound is 6-cyanate. Since the torsion angles are almost 0° or 180° ($C7-C6-O1-C2=173.9(2)^\circ$, $C6-O1-C2-C3=-0.9(3)^\circ$, $C3-C4-C9-N3=-12.7(3)^\circ$, $N3-C10-C12-O2=-9.4(3)^\circ$, $C10-C12-O2-C13=-176.0(2)^\circ$) except for the terminus of the ethoxycarbonyl group ($C12-O2-C13-C14=-116.8(3)^\circ$), the molecular structure becomes planar in the crystal structure.

The crystal structure is shown in Fig. 2. The molecules are packed as sheets almost parallel to the (021) plane. The short contacts such as $C1\cdots O1=3.461(3)$ Å, $S1\cdots C14=3.508(4)$ Å and $C7\cdots C7=3.522(5)$ Å may be

Fig. 2 Crystal structure viewed along *a* axis.

responsible to the sheet formation. The crystal structure is constructed by stacking the sheets. The distance between the sheets is about 3.5 Å. There are two short contacts between the sheets $N3\cdots C4=3.305(3)$ Å and $N3\cdots C14=3.374(5)$ Å.

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