Structural Investigation of Pyribenzoxim Using X-ray Crystallography

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Introduction

Pyribenzoxim, benzophenone *O*-[2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]benzoyl]oxime (Figure 1), is a new post-emergence herbicide developed by LG Chem Investment (Korea), providing broad-spectrum weed control in rice fields.[1,2] As do the sulfonylurea and imidazolinone herbicides, this pyrimidinyloxybenzoate is known to inhibit acetolactate synthase (ALS), the enzyme involved in the biosynthesis of the branched amino acids in plants.[3] There was also no significant maternal or embryonic toxicity,[4] and no phytotoxicity was observed.[1] The bioavailability was negligible in rats by the elimination of radioactivity with feces (~88%) and urine (~8%) after 7 days of treatment.[5] In the aquatic environment Seo *et al.*[6] suggested that the possibility of pyribenzoxim bioconcentration is not likely to occur. Since structural details of pyribenzoxim were not yet known, knowing the related information could pave a way to designing more efficient and potent herbicidal compounds. For these reasons, in the present study the structure of pyribenzoxim was determined unambiguously with single crystal X-ray crystallography.

Experimental Section

Small crystals were obtained by slow evaporation in a mixture of dichloromethane and hexane. The size of the data crystal is approximately $0.30 \times 0.20 \times 0.14$ mm^3. Data collection was performed with MoKα on an MXC3 Diffractometer (Mac Science, Japan) equipped with an incident beam graphite monochromator. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares refinement using the setting angles of 15 reflections in the range $20^\circ < 2\theta(\text{MoK}\alpha_1) < 28^\circ$. The triclinic cell parameters and calculated volumes are a = 10.421(3) Å, b = 12.555(4) Å, c = 14.799(4) Å, α = 100.32(2)°, β = 106.00(2)°, γ = 110.96(2)°, and 1652.6 (8) Å^3. Intensity data were collected with the ω-2θ scan techniques. The intensities of two standard reflections, showed no significant deviations during the data collection. A summary of the crystallographic data, data collection and structure refinement for the pyribenzoxim is given in Table 1.

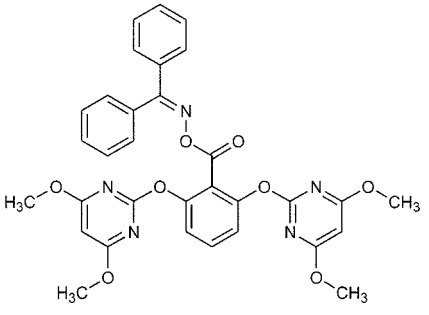

Figure 1. The structural formula of pyribenzoxim.

The centrosymmetric space group $P\bar{1}$ was assumed and the satisfactory refinement confirmed the choice of this space group. The initial position for all non hydrogen atoms were obtained by using direct methods of the SHELXS-86 program.[7] The structure was refined by full matrix least-squares technique with the use of the SHELXL-93 pro-

Table 1. Crystal data, data collection details and structure refinement results

Chemical formula	$C_{32}H_{32}N_8O_8 \cdot CH_2Cl_2$
Formula weight	694.51
Temperature (K)	292(2)
Wavelength (Å)	0.71070
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
Unit cell dimensions (a, b, c (Å), α,β,χ (°))	a=10.421(3), b=12.555(4), c=14.799(4) α=100.32(2), β=106.00(2), χ=110.96(2)
Volume (Å^3)	1652.6(8)
Z	2
Density (calculated) (Mg m^{-3})	1.396
Absorption coefficient (mm^{-1})	0.256
F(000)	720
Crystal size (mm)	$0.30 \times 0.20 \times 0.14$
θ range for data collection (°)	1.51 to 25.00
Index ranges	$-12 \le h \le 0$, $-13 \le k \le 14$, $-16 \le l \le 17$
Reflections collected	5848
Completeness to 2θ=25.00° (%)	93.9
Refinement method	Full-matrix least-squares on F^2
Data/restraints parameters	5472 / 0 / 438
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	R_1=0.0379, wR_2=0.0985
R indices (all data)	R_1=0.0460, wR_2=0.1034
Extinction coefficient	0.0134(12)
Largest diff. Peak and hole (e Å^{-3})	0.499 and 0.145

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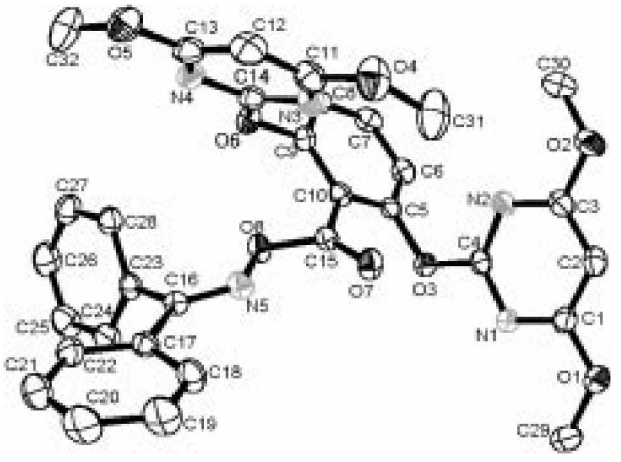

Figure 2. ORTEP diagram and numbering scheme for pyribenzoxim.

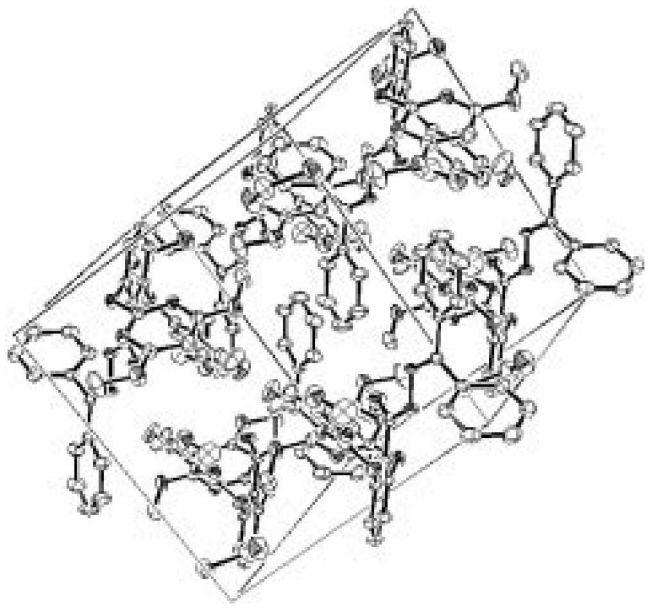

Figure 3. Packing diagram for pyribenzoxim.

gram.[8] Anisotropic thermal motion for non-hydrogen atoms and extinction parameters were included. The final cycle of refinement performed on Fo^2 with all 5848 unique reflections afforded residuals $wR_2 = 0.1034$ and the conventional R index based on the reflections having $Fo > 2\sigma(Fo^2)$ is 0.0379.

Results and Discussion

An ORTEP diagram and numbering scheme for pyribenzoxim are shown in Figure 2. Two benzene rings of benzophenone oxime ester group of pyribenzoxim were nearly perpendicular to each other. Also, two dimethoxypyrimidine rings were not in the same plane. X-ray crystallography revealed that pyribenzoxim cocrystallizes with one molecule of dichloromethane. The mean C-C single bond length is 1.49 Å, in good agreement with the expected range for a C-C single bond. Single bond length of nitrogen-oxygen and double bond length of carbon-oxygen are about 1.43, and 1.20 Å, respectively. Bond lengths among the phenyl ring

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for pyribenzoxim

Bond (Å)		Angle (°)		Dihedral angle (°)	
C1-N1	1.335(3)	N1-C1-O1	118.98(18)	N1-C1-C2-C3	-2.0(3)
C1-O1	1.344(2)	N1-C1-C2	123.96(18)	O1-C1-C2-C3	178.57(18)
C3-O2	1.349(2)	C3-C2-C1	115.13(18)	C1-C2-C3-O2	-177.11(18)
C4-N1	1.329(2)	N2-C4-N1	129.17(17)	O3-C5-C6-C7	176.18(16)
C4-O3	1.363(2)	N2-C4-O3	117.75(16)	C7-C8-C9-O6	-175.49(16)
C5-O3	1.401(2)	C6-C5-O3	118.70(17)	C6-C5-C10-C15	-179.17(17)
C15-O8	1.370(2)	C5-C10-C15	119.85(16)	O3-C5-C10-C15	5.8(2)
C16-N5	1.287(2)	O7-C15-O8	125.01(17)	C5-C10-C15-O7	39.9(3)
C29-O1	1.439(3)	O7-C15-C10	125.22(17)	C9-C10-C15-O7	-137.7(2)
C30-O2	1.435(3)	N5-C16-C17	115.42(16)	C5-C10-C15-O8	-138.50(17)
		N5-C16-C23	125.86(16)	C9-C10-C15-O8	43.9(2)
		C16-N5-O8	110.33(14)	N5-C16-C17-C18	-13.0(3)
		C4-O3-C5	116.27(14)	C23-C16-C17-C18	168.36(18)
		C15-O8-N5	111.64(13)	N5-C16-C17-C22	164.02(18)
				C23-C16-C17-C22	-14.6(3)
				N5-C16-C23-C24	114.1(2)
				C17-C16-C23-C24	-67.4(2)
				N2-C4-O3-C5	-10.7(2)
				N1-C4-O3-C5	170.02(15)
				C6-C5-O3-C4	92.0(2)
				C10-C9-O6-C14	67.3(2)
				O7-C15-O8-N5	9.8(3)
				C10-C15-O8-N5	-171.85(14)

carbons are around 1.39 Å. in the expected range. Bond angles of sp^2 hybrid of benzene ring are around 120°. The values of selected bond lengths, angles and torsion angles are given in Table 2. Figure 3 shows the packing mode of molecules in the unit cell. Two molecules of pyribenzoxim were packed with an inversion symmetry. The arrangement of the molecular units suggests that the packing should be stabilized by a network of intermolecular hydrophobic interactions between the benzene groups of benzophenone oxime groups of pyribenzoxim.

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