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Molecular and Crystal Structure of Metalaxyl, $C_{15}H_{21}NO_4$

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Metalaxyl, $C_{15}H_{21}NO_4$의 분자 및 결정구조

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Abstract

The molecular and crystal structure of metalaxyl, $C_{15}H_{21}NO_4$, was determined by single crystal x-ray diffraction study. Crystallographic data for title compound : $P2_1/c$, $a = 7.849(4)$ Å, $b = 13.081(5)$ Å, $c = 15.100(3)$ Å, $\beta = 101.8(2)°$, $V = 1517.6(3)$ Å^3, $Z = 4$. The molecular structure model was solved by direct methods and refined by full-matrix least- squares. The final reliable factor, R, is 0.067 for 1694 independent reflections ($F_o^2 > 4\sigma(F_o^2)$). The molecular structure of title compound shows an intramolecular hydrogen bond: C12-H12A···O1.

요 약

X-선 회절법을 이용하여 metalaxyl, $C_{15}H_{21}NO_4$의 분자 및 결정 구조를 규명하였다. 화합물의 결정학 자료 : 단사정계 공간군 $P2_1/c$, $a = 7.849(4)$ Å, $b = 13.081(5)$ Å, $c = 15.100(3)$ Å, $\beta = 101.8(2)°$, $V = 1517.6(3)$ Å^3, $Z = 4$. 분자 구조는 직접법으로 풀었고 완전최소자승법으로 정밀화하여 1694($F_o^2 > 4\sigma(F_o^2)$)인 독립회절반점에 대하여 최종 신뢰도 값 $R = 0.067$을 얻었다. 구조 해석 결과, C12-H12A···O1의 분자 내 수소 결합을 이루고 있었다.

1. Introduction

Metalaxyl, $C_{15}H_{21}NO_4$, methyl *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl) DL alanine,[1] a fungicide with a unique combination of residual and systematic properties, is highly active both *in vitro* and *in vivo* against Oomycetes, especially *Peronosporales* such as *Phytophthora Pseudoperonospora*, *Peronospora*, *Plasmopara*, *Erospora*, *Bremia* spp., and other species causing downy mildews, late blight, damping-off, and root, stem, and fruit rots. A high activity, at low rates of foliar or soil application against disease caused by air- or soil-borne Oomycetes, offers promise and performance for use in various crops, for example, potatoes, grape, tobacco, cereals, hops, and vegetables.[2]

The characteristic structure of this compound shown in this paper, which is the first report to our certain knowledge, might offer an important information to elucidate the relationship between the crystal structure and biological activity.

2. Experimental

Single crystals of this compound were grown from a saturated toluene solution. A transparent crystal of dimension 0.35×0.45×0.65 mm was mounted at the tip of a glass fiber. The accurate cell parameters were obtained by least-square refinement from 25 reflections in the range of $9° < \theta < 14°$ measured with graphite-monochromated Mo Kα radiation on an Enraf-Nonious CAD4 Diffractometer at 293±3 K.[3]

Table 1. X-ray data collection and structure refinement

*Crystal size	: 0.35×0.45×0.65 mm
*Lattice parameter determination	: 25 reflections of $\theta = 9^{\circ}$-14°
*Diffractometer	: Enraf Nonius CAD4 Diffractometer
*Radiation	: Graphate mono-chromated Mo-Kα ($\lambda = 0.7107$ Å)
*Data collection temperature	: 293 ± 3 K
*Index range	: $-9 \le h \le 9$, $0 \le k \le 15$, $0 \le l \le 17$ (Maximum $2\theta = 49.95^{\circ}$)
*Scane method	: ω-2 (ω-scane width = $0.8 + 0.35 \tan\theta^{\circ}$)
*Orientation	: Three standard reflections are used which has 3.0%/1 hr maximum variation
*Data	: 1694 unique reflections are collected
*Data conversion	: Correction of Lorentz and polarization is applied to intensity data
*Molecular formula	: $C_{15}H_{21}NO_4$
*Molecular weight	: 279.3 g/mol
*Density(calculated)	: 1.22 g/cm^3
*Crystal system	: Monoclinic
*Cell parameter	: $a = 7.849(4)$ Å, $b = 13.081(5)$ Å, $c = 15.100(3)$ Å, $\beta = 101.8(2)^{\circ}$
*Space group	: $P2_1/c$
*Volume	: 1517.6(3) Å^3
*Z	: 4
*Absorption coefficient	: 0.09/mm
*F(000)	: 600.0
*Structure	: Direct method (SHELXL-86 program)
*Refine	: Full-matrix least square method (SHELXL-93 program)
*Hydrogen atom	: Ideal geometry (SHELXL-93 program)
*Final R factor	: 0.067 for $F_o^2 > 4\sigma(F_o^2)$ data (1694)
*Goo. F.	: 1.065.

X-ray intensity data were collected by ω-2θ scan method (ω-scan width = $0.8 + 0.35 \tan\theta^{\circ}$) with $2\theta = 49.94^{\circ}$ in the ranges of $-9 \le h \le 9$, $0 \le k \le 15$, and $0 \le l \le 17$. Three standard reflections monitored every 100 reflections showed maximum 3% deviation of intensity during the course of data collection. All reflections were corrected for Lp effect[4] but not for absorption effect because of the small linear absorption coefficient (0.09/mm). Crystallographic details and data collection parameters are given in Table 1. The structure was solved by the application of direct methods using SHELXS-86[5] and refined by full-matrix least-squares on F_o^2 using SHELXL-93[6] with anisotropic displacement factors for all 20 non-H atoms. The H atoms were located by geometrical calculations. The final R value was 0.067 with 1694 ($F_o^2 > 4\sigma(F_o^2)$) observed reflections and 193 variables. The final positions and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2. In the Table 3, crystal geometric properties are listed.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atom of metalaxyl, $C_{15}H_{21}NO_4$

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

Atom	x	y	z	U_{eq}
C1	0.8832(4)	0.1031(2)	0.2918(2)	0.0463(8)
C2	1.0401(4)	0.1341(3)	0.2715(2)	0.0539(8)
C3	1.1897(5)	0.0810(3)	0.3117(3)	0.068 (1)
C4	1.1811(5)	0.0000(3)	0.3669(3)	0.076 (1)
C5	1.0258(6)	−0.0296(3)	0.3865(3)	0.071 (1)
C6	0.8714(5)	0.0215(3)	0.3494(2)	0.058 (8)
C7	1.0542(5)	0.2220(3)	0.2105(3)	0.083 (3)
C8	0.7020(6)	−0.0118(4)	0.3714(3)	0.084 (1)
C9	0.6050(4)	0.1168(2)	0.1717(2)	0.0503(8)
C10	0.6793(6)	0.0259(3)	0.1299(3)	0.074 (1)
C11	0.5563(4)	0.1978(3)	0.1007(2)	0.0540(8)
C12	0.3403(6)	0.2406(4)	−0.0272(3)	0.085 (1)
C13	0.6644(4)	0.2344(3)	0.2970(2)	0.0567(9)
C14	0.7806(5)	0.2671(3)	0.3863(3)	0.080 (1)
C15	0.7943(9)	0.4376(4)	0.3823(5)	0.145 (3)
N	0.7253(3)	0.1573(2)	0.2518(2)	0.0461(7)
O1	0.6444(4)	0.2679(2)	0.0859(2)	0.0793(8)
O2	0.3999(3)	0.1771(2)	0.0509(2)	0.0666(7)
O3	0.5211(3)	0.2719(2)	0.2687(2)	0.0734(8)
O4	0.7323(4)	0.3606(2)	0.4174(2)	0.092 (1)

Table 3. Bond distances (Å), bond angles (°), selected torsion angles (°) and intramolecular hydrogen bond. The e.s.d.'s are in parentheses. Metalaxyl, $C_{15}H_{21}NO_4$

Bond distances (Å)			
C1-C2	1.389(4)	C1-C6	1.391(4)
C1-N	1.448(3)	C2-C3	1.392(4)
C2-C7	1.492(5)	C3-C4	1.357(5)
C4-C5	1.367(5)	C5-C6	1.396(5)
C6-C8	1.499(5)	C9-C10	1.517(4)
C9-C11	1.501(4)	C9-N	1.472(3)
C11-O1	1.197(4)	C11-O2	1.330(3)
C12-O2	1.438(4)	C13-C14	1.526(5)
C13-N	1.357(3)	C13-O3	1.221(4)
C14-O4	1.391(5)	C15-O4	1.279(7)
Bond angles (°)			
C3-C2-C1	117.6(3)	C4-C3-C2	121.0(3)
C5-C4-C3	120.8(3)	C5-C6-C1	117.1(3)
C6-C1-C2	122.5(2)	C6-C5-C4	121.1(3)
C7-C2-C1	122.9(3)	C7-C2-C3	119.5(3)
C8-C6-C1	122.4(3)	C8-C6-C5	120.5(3)
C9-N-C1	121.1(2)	C11-C9-C10	108.6(2)
C12-O2-C11	116.9(2)	C13-N-C1	120.8(2)
C13-N-C9	116.6(2)	C15-O4-C14	113.5(4)
N-C1-C2	119.1(2)	N-C1-C6	118.3(2)
N-C9-C10	112.8(2)	N-C9-C11	111.1(2)
N-C13-C14	116.4(3)	O1-C11-C9	127.1(3)
O2-C11-C9	109.4(2)	O2-C11-O1	123.5(3)
O3-C13-C14	122.4(3)	O3-C13-N	121.1(3)
O4-C14-C13	113.1(3)		
Torsion angles (°)			
N-C1-C2-C3	179.5(4)	C10-C9-N-C13	−175.7(3)
N-C1-C2-C7	.5(3)	C11-C9-N-C1	−131.4(3)
N-C1-C6-C5	179.7(4)	C13-N-C9-C10	62.1(3)
N-C1-C6-C8	−.2(3)	C9-C11-O2-C12	−173.3(3)
C2-C1-N-C9	99.2(3)	O1-C11-O2-C12	3.3(3)
C2-C1-N-C13	−94.8(3)	N-C13-C14-O4	165.4(4)
C6-C1-N-C9	−80.7(3)	O3-C13-C14-O4	−17.7(3
C6-C1-N-C13	85.3(3)	C14-C13-N-C1	6.1(3)
C10-C9-C11-O1	−93.5(4)	C14-C13-N-C9	172.7(4)
C10-C9-C11-O2	82.9(3)	O3-C13-N-C1	−170.9(4)
N-C9-C11-O1	31.1(3)	O3-C13-N-C9	−4.4(3)
N-C9-C11-O2	−152.5(3)	C13-C14-O4-C15	−83.7(5)
C10-C9-N-C1	−9.2(2)		
Intramolecular hydrogen bond			
C12-H12A···O1			
C12-H12A	: 0.96(4) Å,		
H12A···O1	: 2.496(5) Å,		
C12-C12A-O1	: 89.0(5)°		

3. Results and Discussion

The ORTEP-drawing[7] of the molecule with the numbering and packing are presented in Fig. 1 and Fig. 2. This compound is composed of 2,6-dimethylphenyl, alaninate and methoxyacetyl bonded to nitrogen of alaninate.

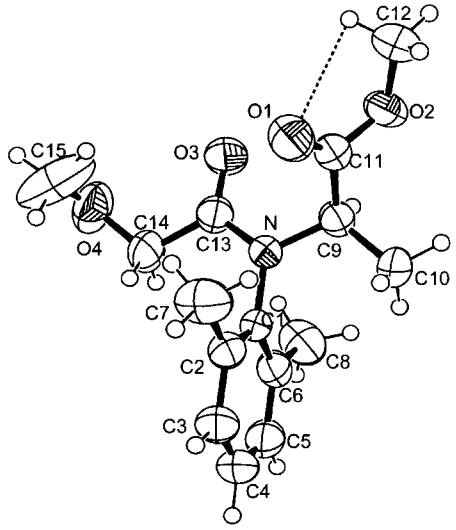

Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids.

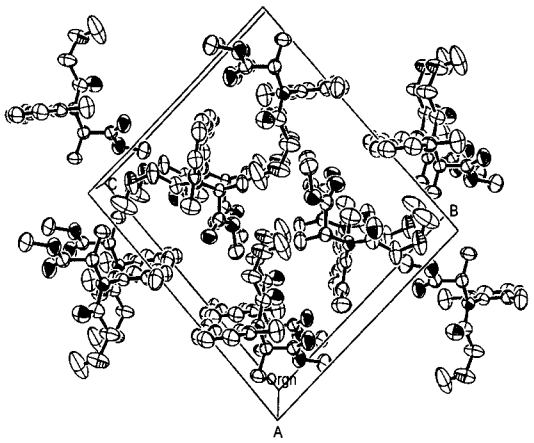

Fig. 2. Packing diagram viewed down the *a* axis.

The molecule appears to be stabilized by interactions between 2,6-dimethylphenyl ring and other two functional group. It is shown in structural conformation of torsion angles: C2-C1-N-C13: −94.8(3)°, C2-C1-N-C9: 99.2(3)°. Lone pair effect of nitrogen (N) can be deduced as the torsion angle is not perfectly 90°.

The length between C7 of 2,6-dimethylphenyl

and C14 of methoxyacethyl is 3.787(3) Å, C8 of 2,6-dimethylphenyl and C10 of alaninate is 3.612(3) Å, and O1 of alanilate and O2 of methoxyacetyl is 3.107(3) Å. These values are shorter than any other molecular interaction length in spite of electric repulsion groups. It can be deduced that strong repulsions between C7 and C14, C8 and C10, on the reverse direction, and O1 and O2 may be exist.

The torsion angle for the end group of alaninate indicate a gauche conformation (O1-C11-O2-C12: 3.3(3)°) and has a strong intramolecular hydrogen bond (C12-H12A···O1; C12-H12A: 0.96(4) Å, H12A···O1: 2.496(5) Å, C12-C12A-O1: 89.0(5)°). The torsion angle of methoxyacetyl indicate also a gauche conformation (O3-C14-C15: −83.7(5)°).

Acknowledgemen

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