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X-Ray Crystallographic Studies of (β-4-(Iodophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol)

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Recently, it has been observed that some of these fungicides are lossing their effects and becoming resistant to them. Analogous compounds can be designed as substitute, if their structures are known. A rational approach to test these fungicides is to know the three dimensional structure of these compounds and macromolecular receptor sites as well as their molecular complex. In present studies, crystal and molecular structure of systemic fungicide (β-4-(iodophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol) is carried out. The unit cell parameters were determined by directly on CAD-4 Enraf Nonius 4-circle automatic diffractometer in ω-2θ scan mode using Ni-filtered CuK_α λ (1.5418 Å) radiations. The unit cell parameters are a = 8.136(2) Å, b = 16.762(1) Å, c = 21.979(1) Å, α = 90(1)°, β = 92.54(2)°, γ = 90(2)°. The space group was determined to be $P2_1/n$.

Key Words: X-Ray crystallography, Fungicide, Triazole.

INTRODUCTION

There are large numbers of chemicals compounds for the protection of crops, available commercially in the market but their effects dependent on the climate, type of soil and other physical parameters[1-3]. The interactions of proposed fungicides with the macromolecule of the parasite are dependent on the stereochemistry of these compounds. In order to design more effective synthetic fungicides, it is necessary to analyze the 3D structure of these compounds and if possible the receptor molecule. The structures of these compounds can be obtained by X-ray diffraction method in crystalline form and they will invariably be similar to their structures in solution.

EXPERIMENTAL

The determination of structural perturbation in fungicide derivatives and comparison of the result of their molecular association with other receptor sites were performed by X-Ray crystallography techniques. Thus, the structure of variety of such compounds and correlate their structure with biological activity, so that more safer and effective fungicides at reasonable price can be developed.

A fungicide, (β-4-(-iodophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol), colourless crystals are obtained by slow evaporation from a solution of propanol at 297 K. The crystals obtained are rectangular in shape. The composition of crystal is confirmed by comparing the infra-red spectra of two components. The density of crystal 1.7468 g/cm^3 is measured by floatation method the mixture of benzene and bromoform. The preliminary information about the crystal is listed in Table-1. The unit cell parameters are determined by directly on CAD-4 Enraf Nonius 4-circle automatic diffractometer in ω-2θ scan mode using Ni-filtered CuK$_\alpha$ λ(1.5418 Å) radiations. The unit cell parameters are a = 8.136(2) Å, b = 16.762(1) Å, c = 21.979(1) Å, α = 90(1)°, β = 92.54(2)°, γ = 90(2)°. The space group is determined to be P2$_1$/n.

TABLE-1
PRELIMINARY CRYSTAL DATA

Chemical name		(β-4-(Iodophenoxy)-α-(1,1-dimethylethyl)1*H*-1,2,4-triazole-1-ethanol)	
Mode of data collection		CAD Enraf-Nonius 4-circled automatic diffractometer	
m.f.	$C_{14}H_{18}IN_3O_2$	Structure refinement	SHELXL-97
m.w.	787.45	Intensity reflection	2 0 0
System	Monoclinic		0 4 4
Space	P2$_1$/n		0 4 0
A	8.136(2)Å	Mode of data collection	W-2θ
B	16.762(1) Å	λ(CuK$_\alpha$)	1.5418Å
C	21.979(1) Å	No. of reflections measured	8647
α	90(1)°	No. of unique reflections	6047
β	92.64(2)°	Temp. of crystal during data collection	293 K
γ	90(2)°	Theta range	1-73°
V	2994.2Å^3	Absorption coefficient	16.871 mm^{-1}
Dm	1.7328 g/cm^3	Symmetry element	X, Y, Z
Dc	1.7468 g/cm^3		½-X, ½+Y, ½-Z
Z	4		-X, -Y, -Z
			½+X, ½-Y, ½+Z
		Lp correction	Applied
		Absorption correction	Not applied

The intensity data are collected on a computerized automatic CAD-4 Enraf Nonius 4-circled diffractometer. The radiation used is CuK$_\alpha$ (1.5418 Å). The data are corrected for lorentz and polarization effects but not for absorption. The data collection is done on ω-2θ scan mode. Three reflections (2,0,0) (0,4,4) and (0,4,0) are selected for intensity reflection. The hkl value varied from 0 to 10, 0 to 15 and 0 to 16, respectively. The total number of unique reflections is 6074. The observed reflections correspond to the intensity limit $I \geq 2\sigma$. The structure determination is carried out on VAX machine using SHELXS-97. Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameters with estimated standard deviations in parentheses given in Table-2.

TABLE-2
FRACTIONAL COORDINATES OF NON-HYDROGEN ATOMS AND THE EQUIVALENT ISOTROPIC THERMAL PARAMETER WITH ESTIMATED STANDERD DEVIATION IN PARENTHESIS

Atoms	X	Y	Z	Ueq (Å)^2
I(1)	0.5076(1)	-0.1320(2)	0.3928(1)	0.1803(2)
O(1)	0.1073(1)	0.1561(1)	0.3972(2)	0.0370(1)
O(2)	-0.0952(2)	0.2959(2)	0.3996(1)	0.0482(1)
N(1)	0.1976(1)	0.3042(2)	0.3257(2)	0.0644(2)
N(2)	0.1133(2)	0.2372(1)	0.3106(2)	0.0306(1)
N(3)	0.2268(1)	0.2808(2)	0.2352(2)	0.0652(2)
C(1)	0.1975(2)	0.0863(2)	0.3916(1)	0.0301(1)
C(2)	0.2346(1)	0.0532(1)	0.3354(2)	0.0366(1)
C(3)	0.3321(2)	-0.0157(2)	0.3352(2)	0.0415(2)
C(4)	0.3842(2)	-0.0489(1)	0.3896(1)	0.0452(1)
C(5)	0.3439(1)	-0.0153(2)	0.4453(1)	0.0440(2)
C(6)	0.2530(2)	0.0512(2)	0.4451(2)	0.0385(2)
C(7)	0.0161(2)	0.1858(1)	0.3462(1)	0.0318(1)
C(8)	0.1347(1)	0.2206(1)	0.2503(2)	0.0402(2)
C(9)	0.2683(1)	0.3330(1)	0.2774(1)	0.0534(2)
C(10)	-0.1239(2)	0.2308(2)	0.3783(2)	0.0315(1)
C(12)	-0.2865(1)	0.1884(1)	0.3810(1)	0.0444(1)
C(13)	-0.3918(2)	0.2305(2)	0.4269(1)	0.0791(1)
C(14)	-0.3721(1)	0.1912(1)	0.3180(2)	0.0652(2)
C(15)	-0.2553(1)	0.0998(2)	0.4005(1)	0.0583(1)
I(2)	0.4942(1)	0.3710(1)	0.0911(1)	0.1790(1)
O(3)	0.8805(1)	0.0760(2)	0.0919(1)	0.0381(2)
O(4)	1.0978(2)	-0.0625(1)	0.0969(2)	0.0544(1)
N(4)	0.7998(1)	0.0671(2)	0.1691(1)	0.0678(2)
N(5)	0.8846(2)	0.0013(2)	0.1812(2)	0.0304(2)
N(6)	0.7844(1)	0.0399(2)	0.2612(1)	0.0790(2)
C(16)	0.7945(2)	0.1462(1)	0.0950(2)	0.0293(1)
C(17)	0.7590(1)	0.1846(2)	0.1498(1)	0.0365(2)
C(18)	0.6676(2)	0.2544(2)	0.1456(2)	0.0398(2)
C(19)	0.6127(2)	0.2814(1)	0.0914(2)	0.0429(1)
C(20)	0.6460(1)	0.2453(1)	0.0371(1)	0.0434(1)
C(21)	0.7389(2)	0.1781(2)	0.0390(2)	0.0427(2)
C(22)	0.9750(2)	0.0503(1)	0.1430(2)	0.0306(1)
C(23)	0.8753(1)	0.0168(2)	0.2428(1)	0.0402(2)
C(24)	0.7372(1)	-0.0956(1)	0.2180(1)	0.0482(1)
C(25)	1.1196(2)	0.0064(2)	0.1117(2)	0.0352(2)
C(27)	1.2777(2)	0.0502(1)	0.1042(2)	0.0493(1)
C(28)	1.3643(1)	0.0571(1)	0.1685(1)	0.0710(1)
C(29)	1.3930(1)	0.0035(1)	0.0656(1)	0.1044(1)
C(30)	1.2405(2)	0.1362(2)	0.0796(2)	0.0908(2)

Refinement: The positional co-ordinates which are obtained from SHELXS-97[4] and their isotropic temperature factors are fed to SHELXL-97[5] for refinement. The final R value of 0.089 is for 6074 reflections.

RESULTS AND DISCUSSION

It is interesting to compare this structure with the structure β-4-(chlorophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol. In β-4-(chlorophenoxy)-α-1,1-dimethylethyl)1*H*-1,2,4-triazole-1-ethanol, the average bond distances of C-H and N-H types are 0.96(2) Å and. 090(1) Å, respectively. The bond lengths and angles in the benzene rings show regular features in both the molecules. The C(4)-Cl(1) and Cl(2)-C(18) distances are 1.748(1) Å and 1.747(2) Å. The whole molecules appeared to be twisted and folded and reason may be due to stacking constraints. The bond distances around C(7) and C(21) are as usual shorter than single bond values. They may also appears to bear a partial double bond character. The C(7)-O(1) and C(21)-O(3) distances are 1.4028(1) Å and 1.4114(2) Å, respectively. These distances do not change significantly in similar structures, despite variable intermolecular interactions through them. The bond distances in the five member rings are comparable to corresponding distances inheterocyclic rings 1.339 (Å). The average value of bond lengths and angles in the rings derived from most reliable set of data by Spencer are 1.377 Å and 119 °, respectively. The variations observed are within the limit of estimation errors. Similarly, in β-4-(iodophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol) the average bond distances of C-H and N-H types are 0.96 Å and 0.89 Å, respectively. The bond lengths and angles in the benzene rings show regular features in both the molecules. The C(19)-I(2) and C(4)-I(1) distances are 1.784(1) Å and 1.717(1) Å comparable to other structures. The whole molecules appeared to be twisted and folded and reason may be due to stacking constraints. The bond distances around C(7) and C(22) are as usual shorter than single bond values. They may also appears to bear a partial double bond character The C(7)-O(1) and C(22)-O(3) distances are 1.4057 and 3994 Å, respectively. These distances do not change significantly in similar structures, despite variable intermolecular interactions through them. The bond distances in the five member rings[6-24] are comparable to corresponding distances in heterocyclic rings 1.339 (Å).

The average value of bond lengths and angles in the rings derived from most reliable set of data by Spencer are1.377 Å and 119 °, respectively. The dimensions of the methyl groups are normal and comparable with those in *o*-methylobtusaquinone and moscaline hydrobromide. Around the carbon atoms C(7) and C(22) arrangement is only slightly distorted from the regular tetrahedral geometry, this distortion around C(7) and C(22) carbon atoms is because the substituents at carbon atoms are not alike. The angles vary from 111.38 ° to 118.67 °. Thus the substitution of iodine to chlorine does not change the structure or the molecular dimensions in general. The variations observed are within the limit of estimation errors. The equations of the least squares planes, calculated using Blow's method[25]. The benzene rings are practically planar. The five member rings are also planar. The two rings are inclined with respect to each other by an angle of 72.3° in both the molecules.

Hydrogen bonding and molecular packing: The hydrogen bond parameter and some other non-bonded contact distances up to 3.50 Å are given in Table-3. The crystal structure consists of parallel sheets stacked along a-axis. The molecules overlap while running along the a-axis. The parallel sheets are hydrogen bonded through the center of inversion where N(4) and N(1) works as donor while the symmetry related O(2) works as an acceptor.

TABLE-3
HYDROGEN BOND PARAMETERS AND INTERMOLECULAR DISTANCES LESS THAN 3.50 A

Hydrogen bonds				
D–H··A	D–H	H···A	D···A	D–H···A
N(1)-H(1A).O(4c)	0.899(2)	2.589(1)	3.222(2)	27.9(1)
N(4)-H(4A).O(2a)	0.900(1)	2.552(2)	3.175(1)	126.9(2)
Some Non-bonded contacts				
C(20)--H(20A)..O(1d)	0.9600	3.4915		
C(24)--H(24A)..O(2b)	0.9600	3.3242		

It is interesting to note that although there are minor differences in the cell parameters and growth conditions in the two independent studies, the molecular geometry, overall dimensions, crystal packing are almost same under the error limits whatever small differences are there, they are not really significant, which suggest that the molecular parameters remain unchanged even there is a change in growth condition the crystal forces, therefore, they don't alter the molecular geometry.

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