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X-Ray Crystallographic Studies On Systemic Fungicide
β-4 (-Iodophenoxy)-α-(1,1dimethylethyl)1H-1,2,4-Triazole-1-Ethanol

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ABSTRACT

In recent part it has been observed that some of these fungicides are loosing 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 The structures of these compounds can be obtained by X-ray diffraction method in crystalline form and they will invariably be similar to their structure in solutions. Crystal and molecular Structure of systemic fungicide(β-4(-Iodophenoxy)α-(1,1dimethylethyl)1H-1,2,4- triazole-1-ethanol) The unit cell parameters were determined by directly on CAD-4 Enraf Nonius 4-circle Automatic Diffract meter in ω-2θ scan mode using Ni-filtered CuKα λ(1.5418Å) 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)°, ϒ=90(2)°. The space group was determined to be P2$_1$/n . The average bond distances of C-H and N-H types are 0.96Å and 0.89Å respectively . The bond lengths and angles in the benzenerings 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 . These distances are short and this shortening may be due to delocalization of electrons from the benzene rings. 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 1.4057Å and1.3994Å, respectively. These distances do not change significantly in similar structures.   © 2007 Trade Science Inc. - INDIA

KEYWORDS

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INTRODUCTION

The word fungicide has originated from two Latin words: namely, fungus and caedo. The word caedo means 'to kill'. Thus literally speaking a fungicide would be any agency which has the ability to kill a fungus. Some chemicals do not kill fungi but they inhibit fungus growth temporarily. If the fungus is freed from such substances, it would revive. Such a chemical is called a 'Fungistat' and the phenomenon of temporarily inhibiting the growth is called 'Fungistasis'. Even though fungistats do not 'kill' fungi, they are broadly termed as fungicide. Normally the word fungicide is defined as a chemical substance which can prevent damage caused to plants and their product by a fungi. 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. 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 three dimensional 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

Colorless well formed crystals were obtained by slow evaporation from a solution nof propropanol at 297^0K temp. The crystals obtained were rectangular in shape. The composition of crystal was confirmed by comparing the infrared spectra of two components. The density of crystal 1.7468 g cm³ was 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 were determined by directly on CAD-4 Enraf Nonius 4-circle automatic Diffracto-meter in ω-2θ scan mode using Ni-filtered CuKα λ(1.5418Å) radiations. The unit cell parameters are a=8.136(2)Å, b=16.762(1)Å, c=21.979(1) Å, α=90

TABLE 1: Preliminary crystal data

Chemical name	β-4(- Iodophenoxy)-α-(1,1dimethylethyl)1H-1,2, 4-trizole-1 ethanol
Chemical formula	$C_{14} H_{18} lN_3 O_2$
Mw	787.45
System	Monoclinic
Space	$P2_1/n$
A	8.136(2)Å
B	16.762(1)Å
C	21.979(1)Å
α	90 (1)°
β	92.64 (1) °
γ	90(2) °
V	2994.2 Å³
Dm	1.7328 g/cm³
Dc	1.7468 g/cm³
Z	4
Mode of data collection	CAD-4Enraf Nonious 4-circle automatic diffractrometer
Structure refinement	SHELXL-97
Intensity reflection	200 044 040
Mode of data collection	ω-2θ
λ(CuKα)	1.5418 Å
No. of reflections measured	8647
No. of Unique reflections	6074
Temp. of crystal during data collection	293^0K
Theta range	$1-73^0$
Absorption coefficient	$16.871mm^{-1}$
Symmetry element	X, Y, Z
	1/2-X, 1/2+Y,1/2-Z
	-X, -Y, -Z
	1/2+X , 1/2-Y, 1/2+Z
Lp correction	Applied
Absorption correction	Nor applied

(1)°, β=92.54(2)°, γ=90(2)°. The space group was determined to be $P2_1/n$. Chemical structure of (b-4(-Iodophenoxy) α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol) is given in figure 1.

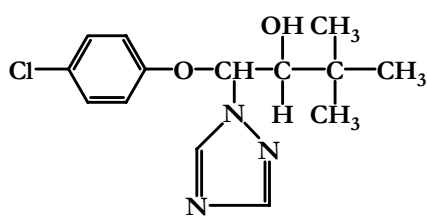## Data collection and structure solution

Figure 1: β-{4-Iodophenoxy}-α-(1,1-dimethy-lethyl)1H-1,2,4-triazole-1-ethanol

The intensity data were collected on a computerized automatic CAD-4 Enraf Nonius 4-circled diffractometer national facility of DST, Dept. of Biophysics, AIIMS, New Delhi. The radiation used was Cukα λ(1.5418Å). The data were corrected for Lorentz and Polarization effects but not for absorption. The data collection was done on ω-2θ scan mode. Three reflections(2,0,0) (0,4,4) and (0,4, 0) were 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 were 6074. The observed reflections correspond to the intensity limit |³2σ. The structure determination was carried out on VAX machine using SHELXS-97. All the non-hydrogen atoms were located in the beginning itself.

Fractional coordinates of Non-Hydrogen atoms and the equivalent isotropic thermal parameters with estimated standard deviations in parentheses given in TABLE 2.

Refinement

The positional co-ordinates which were obtained from SHELXS-97 and their isotropic temperature factors were fed to SHELXL-97 for refinement. The final R value of 0.089 was for 6074 reflections.

RESULTS AND DISCUSSION

The perspective view of the molecule and numbering scheme are shown in figure 2 The ORTEP diagram is shown in figure 3. It is interesting to compare this structure with the structure β-4(-chlorophenoxy)-α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol. The substitution of Iodine to chlorine does not change the structure or the molecular dimensions in general. The variations ob-

TABLE 2: Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameters with estimated standard deviations in parentheses

| Atoms	x	y	z	Ueq.(A)^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)	-0.157(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(1)	0.3783(2)	0.0315(1)
C(12)	-0.2865(2)	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(1)
O(4)	1.0978(2)	-0.0625(1)	0.0969(2)	0.0544(1)
N(4)	0.7998(1)	-0.671(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(1)	0.0064(2)	0.1117(2)	0.0352(1)
C(27)	1.277(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(1)	0.1362(2)	0.0796(2)	0.0908(2)

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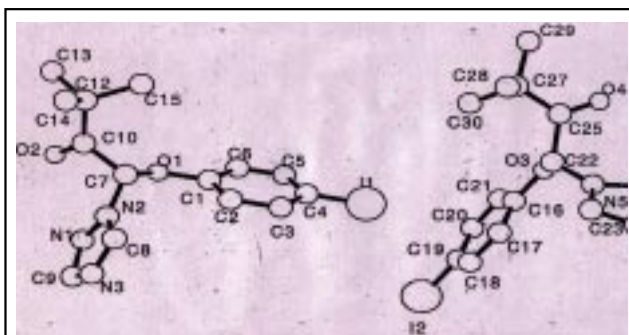
Figure 2: The perspective view and numbering scheme of β-{4-Iodophenoxy}-α-(1,1-dimethylethyl)1H-1,2,4-triazole-1-ethanol
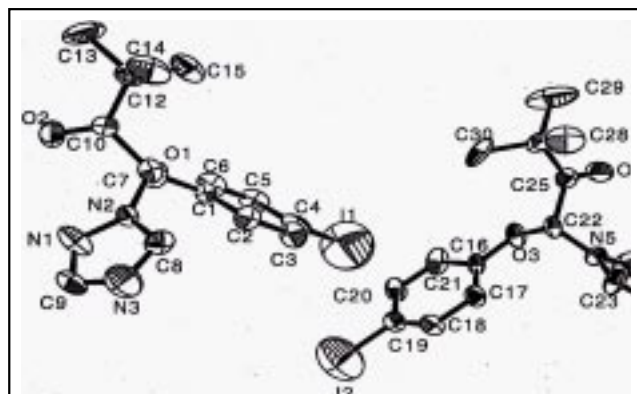

Figure 3: Ortep diagram

served are within the limit of estimation errors The average bond distances of C-H and N-H types are 0.96Å and 0.89Å 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.

These distances are short and this shortening may be due to delocalization of electrons from the benzene rings. 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 1.4057Å and 3994Å, 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 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 are1.377Å and119⁰ respectively. The dimensions of the methyl groups are normal and comparable with those in O-methyl obtusaquinone 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 111.38^0 to118.67^0.

The equations of the least squares planes, calculated using Blow's method. 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 72.3^0 in both the molecules.

Hydrogen bonding and molecular packing

The hydrogen bond parameter and some other non-bonded contact distances up to 3.50Å are given in TABLE 3. The packing diagram is shown in figure 4. 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.

A note on the comparison of two molecules

It is interesting to note that although there are minor differences in the cell parameters and growth conditions in the two independent studies, the moleculargeometry, 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.

TABLE 3: Hydrogen bond parameters and intermolecular distances less than 3.50(Å)

(1) 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)

(2) Some Non Bonded contacts:		
C(20) -- H(20A).. O(1d)	0.9600	3.4915
C(24) -- H(24A).. O(2b)	3.9600	3.3242

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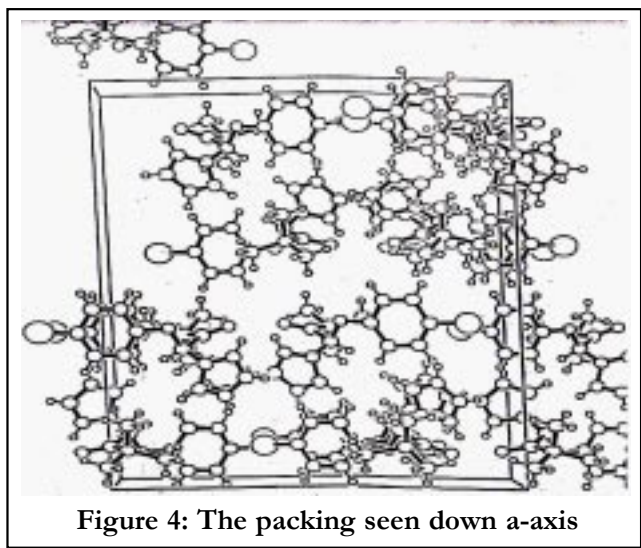
Figure 4: The packing seen down a-axis

ACKNOWLEDGMENT

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