



Trade Science Inc.

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 1(1), 2007 [20-26]

X-ray Crystallographic Studies On Systemic Fungicide β -4(-Chlorophenoxy)- α -(1,1-Dimethylethyl) 1H-1,2,4-Triazole-1-Ethanol

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Received: 3rd November, 2006Accepted: 18th November, 2006Web Publication Date : 21st December, 2006

ABSTRACT

In recent part it has been observed that some of these fungicides are losing 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 β -4(-chlorophenoxy)- α -(1,1 dimethylethyl)1H-1,2,4-triazole-1-ethanol. The composition of these crystals are confirmed by comparing the infra-red spectra of the two components. The unit cell parameters $a = 8.130(2) \text{ \AA}$ $b = 16.790(2) \text{ \AA}$ $c = 21.990 \text{ \AA}$. The space group is determined to be $P2_1/n$. The measured density is 1.3215 g/cm^3 and calculated density is 1.3102 g/cm^3 . The average bond distances of C-H and N-H types are $0.96(2) \text{ \AA}$ and $0.90(1) \text{ \AA}$ 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 $1.748(1) \text{ \AA}$ and $1.747(2) \text{ \AA}$ comparable to other structures although similar structures are not available for comparison. These distances are short and 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(21) are as usual shorter than single bond values. They may also appear to bear a partial double bond character. The C(7)-O(1) and C(21)-O(3) distances are $1.4028(1) \text{ \AA}$ and $1.4114(2) \text{ \AA}$ 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 $1.339(\text{ \AA})$.

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KEYWORDS

X-ray crystallography; Systemic fungicides; Triazole structure.

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 crystal-line form and they will invariably be similar to their structures in solution.

EXPERIMENTAL

Colorless well formed crystals were grown by slow evaporation technique from a solution of cyclohexanone at 278°K. The crystals have been found to be rectangular in shape. The composition of these crystals are confirmed by comparing the infra-red spectra of the two components. The unit cell parameters $a=8.130(2) \text{ \AA}$ $b=16.790(2) \text{ \AA}$ $c=21.990(1) \text{ \AA}$ were determined by automatic computerised 4-circled Enraf-Nonious CAD-4 diffractometer. The space group is determined to be $P2_1/n$. The density of the crystal was determined by floatation method in the mixture of benzene and carbon tetrachloride. The crystal was placed in RD bottle filled

TABLE 1: Preliminary crystal data

Chemical Name	β -4(- chlorophenoxy)- α -(1,1dimethylethyl)1H-1,2,4-trizole-1 Ethanol
Chemical formula	$C_{14} H_{18} Cl N_3 O_2$
Molecular weight	295.76
System	Monoclinic
Space group	$P2_1/n$
A	$8.130(2) \text{ \AA}$
B	$16.790(2) \text{ \AA}$
C	$21.990(1) \text{ \AA}$
α	$90(1)^\circ$
β	$92.52(1)^\circ$
γ	$90(1)^\circ$
V	2998.8 \AA^3
Dm	1.3215 g/cm^3
Dc	1.3102 g/cm^3
Mw	295.76
$\lambda_{Mok}(\alpha)$	0.71075 \AA
Z	4
Mode of data	CAD-4Enraf Nonious 4- circle automatic diffractometer
Structure solution	SHELXS-97
Structure refinement	SHELXL-97
Intensity reflection	400 06-6 060
Mode of Data collection	ω -2 θ
Theta range	$1-73^\circ$
No. of reflections measured	7542
No. of Unique reflections	6345
Temp. of crystal during	293°K
DataCollection μ	260 mm^{-1}
Lp correction	Applied
Absorption coefficient	Not applied
Symmetry element	X, Y, Z
	$1/2-X, 1/2+Y, 1/2-Z$
	$-X, -Y, -Z$
	$1/2+X, 1/2-Y, 1/2+Z$

with carbon tetrachloride. Benzene was added to the solution until the crystal floated in the middle of mixture. Thus the crystal and solution were of same density and the density of solution was measured

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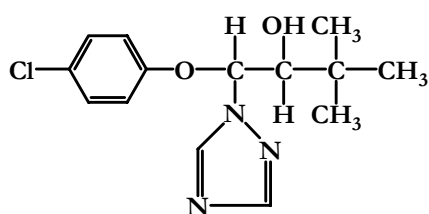


Figure 2.1: β -{4-Chlorophenoxy}- α -(1,1-dimethylethyl)1H-1,2,4-triazole-1-ethanol

with pycnometer. The measured density is 1.3215g/cm³ and calculated density is 1.3102g/cm³. More detailed information on this crystal is given in TABLE 1. Chemical structure of β -4(-chlorophenoxy)- α -(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol is given in figure 2.1.

Data collection and structure solution

The three-dimensional intensity data were collected using a computerized automatic 4-circle CAD-4 Enraf-Nonius diffractometer using graphite filtered MoK α (.71075Å) radiations, Dept. of Biophysics AIIMS, New Delhi at 293°K. All the data were corrected for Lorentz and polarization effect, but no absorption correction was applied.

Three standard reflections (4,0,0) (0,6,-6), (0,6,0) were measured, where h varies from 0 to 10, k from 0 to 15 and l from 0 to 18 The total number of reflections measured was 7542. The crystal structure was solved 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

The perspective view of the molecule and numbering scheme are shown in figure 2.2. The ORTEP diagram is shown in figure 2.3.

RESULT AND DISCUSSION

The average bond distances of C-H and N-H types are 0.96(2)Å and 0.90(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 comparable to other structures although similar structures are not available for comparison.

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.(Å) ²
Cl(1)	-0.0086(2)	0.6334(1)	0.1091(2)	0.0987(1)
O(1)	0.3918(1)	0.3435(2)	0.1029(2)	0.0627(2)
O(2)	0.5955(1)	0.2037(2)	0.1002(1)	0.0778(2)
N(1)	0.3649(2)	0.2781(2)	0.2489(2)	0.0760(2)
N(2)	0.3876(2)	0.2623(1)	0.1898(2)	0.0606(2)
N(3)	0.2321(2)	0.1677(2)	0.2229(2)	0.0908(1)
C(1)	0.3045(1)	0.4139(2)	0.1088(1)	0.0530(2)
C(2)	0.2616(1)	0.4470(1)	0.1631(1)	0.0627(2)
C(3)	0.1695(2)	0.5155(2)	0.1642(2)	0.0638(2)
C(4)	0.1155(2)	0.5484(2)	0.1089(2)	0.0687(1)
C(5)	0.1559(2)	0.5159(2)	0.0544(2)	0.0655(1)
C(6)	0.2485(1)	0.4482(1)	0.0539(1)	0.0630(2)
C(7)	0.4845(1)	0.3132(1)	0.1530(2)	0.0564(2)
C(8)	0.6224(2)	0.2692(2)	0.1209(1)	0.0560(2)
C(9)	0.7865(2)	0.3115(2)	0.1175(2)	0.0666(1)
C(10)	0.7584(1)	0.3983(2)	0.0977(1)	0.0895(2)
C(11)	0.8902(2)	0.2694(1)	0.0726(2)	0.1101(1)
C(12)	0.8688(2)	0.3090(2)	0.1809(1)	0.0960(2)
C(13)	0.3037(2)	0.1957(1)	0.1753(2)	0.0757(1)
C(14)	0.2750(1)	0.2193(2)	0.2663(1)	0.0830(1)
Cl(2)	1.0063(2)	0.1301(1)	0.4109(1)	0.1000(1)
O(3)	0.6187(2)	0.4235(1)	0.4083(2)	0.0626(2)
O(4)	0.4030(1)	0.5624(2)	0.4026(1)	0.0776(2)
N(4)	0.7030(2)	0.5653(2)	0.3301(1)	0.1143(1)
N(5)	0.6172(2)	0.4990(1)	0.3179(1)	0.0545(2)
N(6)	0.7146(1)	0.5440(2)	0.2412(2)	0.1177(2)
C(15)	0.7059(2)	0.3536(2)	0.4047(2)	0.0550(1)
C(16)	0.7412(2)	0.3151(1)	0.3511(1)	0.0562(2)
C(17)	0.8321(2)	0.2462(2)	0.3532(2)	0.0665(2)
C(18)	0.8875(2)	0.2168(2)	0.4080(2)	0.0625(2)
C(19)	0.8540(2)	0.2535(2)	0.4615(1)	0.0628(2)
C(20)	0.7606(1)	0.3224(1)	0.4608(2)	0.0640(2)
C(21)	0.5232(2)	0.4494(2)	0.3569(2)	0.0539(1)
C(22)	0.3811(2)	0.4951(2)	0.3859(2)	0.0553(2)
C(23)	0.2250(1)	0.4497(2)	0.3958(2)	0.0752(2)
C(24)	0.2574(2)	0.3659(1)	0.4188(1)	0.1259(1)
C(25)	0.1101(2)	0.4948(2)	0.4339(2)	0.1378(2)
C(26)	0.1379(2)	0.4425(2)	0.3314(2)	0.1060(2)
C(27)	0.6267(1)	0.4834(2)	0.2586(1)	0.0537(2)
C(28)	0.7641(2)	0.5961(1)	0.2815(2)	0.0680(1)

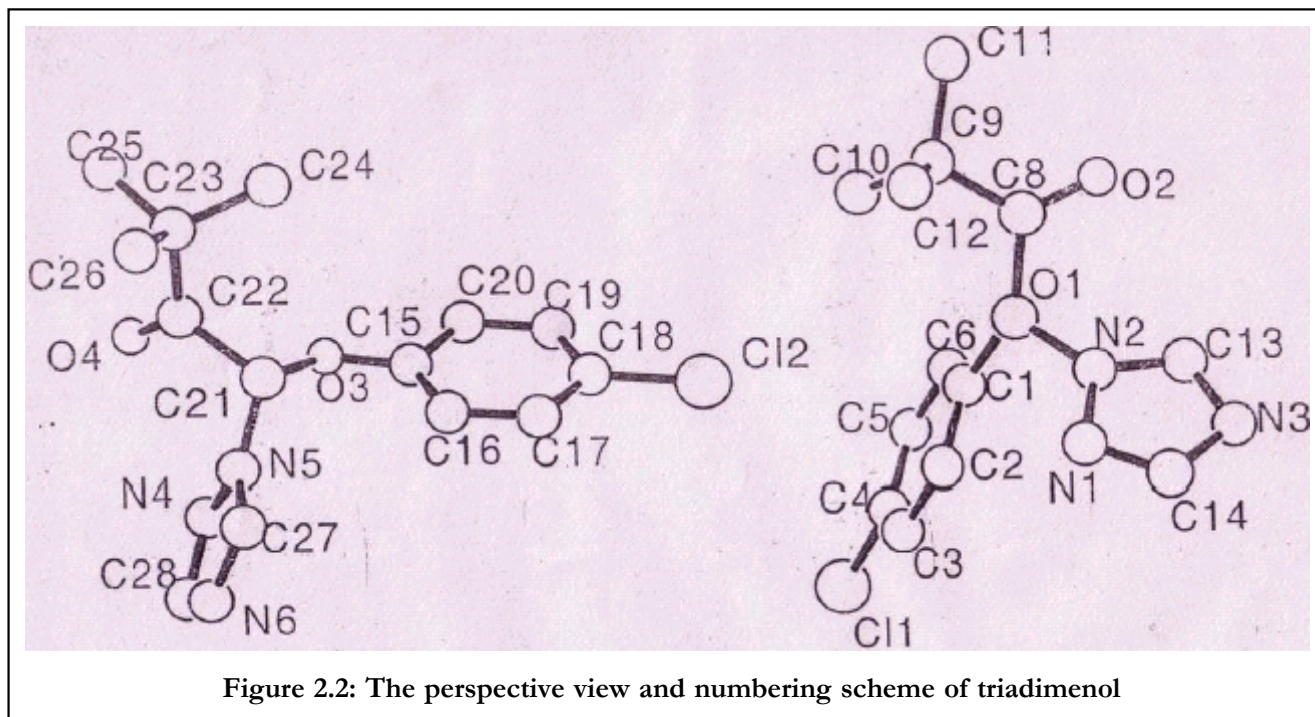


Figure 2.2: The perspective view and numbering scheme of triadimenol

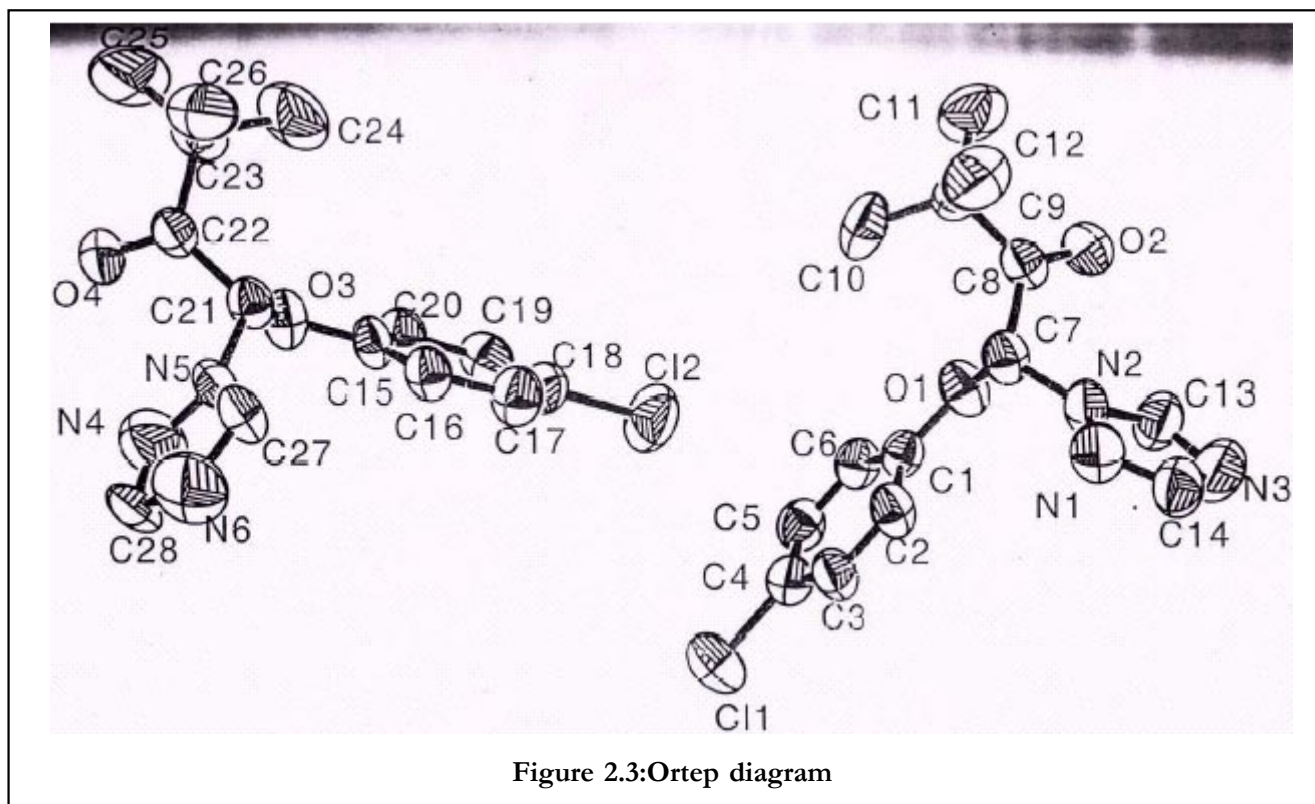


Figure 2.3: Ortep diagram

These distances are short and 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(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 vari-

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able 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 are 1.377 Å and 119°, respectively.

Comparison of two molecules

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(21) the arrangement is only slightly distorted from the regular tetrahedral geometry. This distortion around C(7) and C(21) carbon atoms is because of the substituents at carbon atoms are not alike. The angles vary from

100.96(2)° to 113.64(1)°.

The equations of the least squares planes, calculated using Blow's method. The benzene rings are practically planar. Since the atomic displacements are much less than their e.s.d's. The five member rings are also planar. The two rings are inclined with respect to each other by an angle of 66.52(1)° in molecule 1 and 68.36(2)° in molecule 2.

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 packing diagram is shown in figure 2.4. The crystal structure consists of parallel sheets stacked along *a*-axis. The molecules overlap while running along the *a*-axis. The parallel sheets

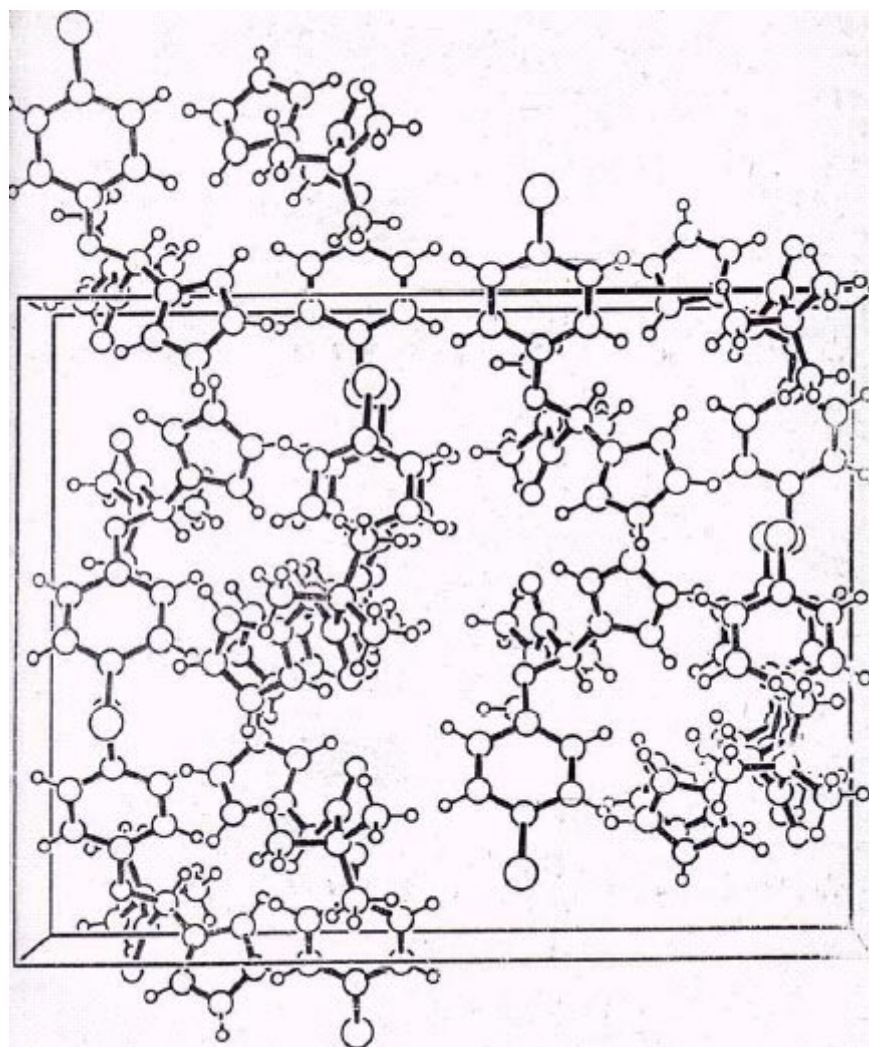


Figure 2.4: The packing seen down *a*-axis

TABLE 3: Hydrogen bond parameters and intermolecular distances less than 3.50(Å) with estimated standard deviations in parentheses

3. 50(Å) with estimated standard deviations in parentheses :-	
D - H.... A. D - H H... A D... A DD - H... A	
N(4)- H(1A).. O(2b) 0. 9001(1) 2. 5688(2) 3. 1937(1)	127. 12(2)
(B)Some Non Bonded contacts :-	
C(13) -- H(13A).. O(4a) 3. 2425(1)	
C(28) -- H(28).. O(2b) 3. 3246(2)	
Symmetry codes:-	
[a] = 1/2-x,-1/2+y,1/2-z	
[b] = 3/2-x,1/2+y,1/2-z	

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.

ACKNOWLEDGEMENT

The Financial assistance provided by Deptt. of Science and Technology (D.S.T), New Delhi in form Junior Research Fellow is gratefully acknowledged. I am thankful to Prof T.P.Singh Head Deptt of BioPhysics, AIIMS, New Delhi for providing me National Facility CAD-4Diffractometer and Lab. I am also thankful to Prof. D.Vellmurgan, UNIV OF MA-DRAS for his valuable help in Data collection.

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