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X-ray structure analysis of β-(phenoxy)-α-(1,1dimethylethyl) 1H-1,2,4-triazole-1-ethanol

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ABSTRACT

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. Crystal and molecular structure of β-(phenoxy)-α(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol is given in figure 1.The composition of these crystals are confirmed by comparing the infra-red spectra of the two components. The unit cell parameters a = 8.136(2)Å b = 16.790(2)Å c=21.990Å. The space group is determined to be $P2_1/n$. The measured density is 1. 3215g/cm^3 and calculated density is 1. 3102g/cm^3. The average bond distances of C-H and N-H types are 0. 96(2)Åand 0. 90(1)Å respectively.

KEYWORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure.

EXPERIMENTAL

First grow the crystals of existing fungicids available and synthesize their derivatives in lab. The determination of structural perturbation in fungicide derivatives and comparison of the result of their molecular association with other receptor sites by X-Ray crystallography techniques will be done. In parallel with these structural studies, spectroscopic studies carried out on them. The goal is then to tie together the structural and spectroscopic studies to have more comprehensive account of the precise shape of these molecules, the non-covalent interaction which are likely to be involved in and the changes introduced in molecular geometry and electronic structure of these compounds as a result of their molecular association with other compounds. Thus we study 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. In that particular fungicide β-(phenoxy)-α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol sample synthesized by Meiser at research center of Bayer A G in Wuppertal Elerfeld, West Germany was obtained directly from the market in powdered form. Crystallization was done by slow evaporation from a solution of cyclohaxenone at 282°K temp.The crystals obtained were white and rectangular in shape.The unit cell parameters were determined by automatic computerized 4-circled enraf-Nonius CAD-4 Diffractometer. The preliminary information about crystal is given in TABLE 1.

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TABLE 1

Preliminary	Crystal data
Chemical name	β-(phenoxy)-α-(1,1-di methyl ethyl)1H-1,2,4-trizole-1-ethanol
Chemical formula	C14 H_{19} N3 O2
System	monoclinic
Space	$P2_1/n$
A	8.136(2)Å
B	16.762(1)Å
C	21.979(2)Å
α	90(1) °
β	92.64(1) °
γ	90(2)°
V	2994.2Å^3
Dm	1.1529g/cm^3
Dc	1.1594g/cm³
Mw	261.32
Z	4
Mode of data collection	CAD-4 enraf-nonius 4-
Circled automatic diffractometer	
Structure solution	SHELXS-97
Structure refinement	SHELXL-97
Mode of data collection	ω-2θ
λ(Cukα)	1.5418Å
No. of Reflections measured	6856
No. of unique reflections	6742
Tempo crystal during data Collection	293°K
Theta range	1-73°
Intensity reflections	4 0 0 0 8 8 0 8 0
(absorption coefficient)	0.641mm^{-1}
Symmetry element	X,Y, Z 1 /2-X, 1/2+Y, 1/2-Z -X,-Y, -Z ½+X, 1/2-Y, 1/2+Z
Lp correction	Applied
Absorption correction	Not applied

TABLE 2 : Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameter with standard deviations in parenthesis

Atom	X	Y	Z	Ueq(A)2
O(1)	0.10490(1)	0.15592(2)	0.39822(1)	0.07026(1)
O(2)	-0.09297(1)	0.29770(1)	0.39985(2)	0.08486(2)
N(1)	0.19504(1)	0.30281(2)	0.33089(1)	0.09998(1)
N(2)	0.11560(1)	0.23643(1)	0.31239(2)	0.05761(2)
N(3)	0.23157(1)	0.28211(1)	0.23717(1)	0.11409(1)
C(1)	0.19563(1)	0.08476(1)	0.39146(2)	0.04807(2)
C(2)	0.24060(2)	0.05056(2)	0.33795(1)	0.06868(1)
C(3)	0.32876(1)	-0.01484(1)	0.33737(2)	0.06482(1)
C(4)	0.38710(2)	-0.04941(2)	0.38894(1)	0.06635(2)
C(5)	0.33916(1)	-0.01782(1)	0.44655(2)	0.07224(1)
C(6)	0.25877(2)	0.05361(2)	0.44850(1)	0.06323(2)
C(7)	0.01255(1)	0.18860(1)	0.34629(2)	0.06809(1)
C(8)	0.13014(2)	0.22226(2)	0.25070(1)	0.06297(2)
C(9)	0.28016(1)	0.33106(1)	0.27808(2)	0.07414(1)
C(10)	-0.12506(1)	0.23299(2)	0.37696(1)	0.06744(2)
C(12)	-0.28233(1)	0.19213(1)	0.37819(2)	0.08210(1)
C(13)	-0.39175(1)	0.23735(2)	0.42802(1)	0.10446(2)
C(14)	-0.37324(2)	0.19034(1)	0.31967(2)	0.07715(1)
C(15)	-0.26078(1)	0.11564(2)	0.40706(1)	0.11142(2)
O(3)	0.88678(1)	0.07782(2)	0.09394(2)	0.07193(2)
O(4)	1.09694(2)	-0.06205(1)	0.09812(1)	0.08882(2)
N(4)	0.79966(1)	-0.06697(2)	0.16930(2)	0.08640(1)
N(5)	0.87922(2)	0.00256(1)	0.18140(2)	0.05900(2)
N(6)	0.78905(1)	-0.04715(2)	0.26401(1)	0.09169(1)
C(16)	0.78925(2)	0.14307(1)	0.09148(2)	0.06134(2)
C(17)	0.75879(1)	0.18267(2)	0.14753(1)	0.06760(1)
C(18)	0.66812(2)	0.25442(1)	0.14569(2)	0.06053(2)
C(19)	0.60675(2)	0.28421(2)	0.09071(2)	0.06589(1)
C(20)	0.64846(1)	0.24548(1)	0.03924(1)	0.07753(2)
C(21)	0.73885(2)	0.17567(2)	0.03986(2)	0.06642(1)
C(22)	0.97617(1)	0.04777(2)	0.14192(2)	0.06489(1)
C(23)	0.86807(2)	0.01424(1)	0.24096(1)	0.06806(2)
C(24)	0.72576(1)	-0.09240(2)	0.21459(2)	0.10582(1)
C(25)	1.11744(2)	0.00524(1)	0.11258(2)	0.06273(1)
C(27)	1.26856(2)	0.05097(2)	0.10330(2)	0.08152(1)
C(28)	1.35366(1)	0.06651(2)	0.17269(1)	0.11178(1)
C(29)	1.39834(2)	0.00879(1)	0.06711(2)	0.17858(2)
C(30)	1.25459(1)	0.13038(2)	0.07788(1)	0.10550(1)

Data collection and structure solution

The three -dimensional intensity data are collected on a computerized automatic 4-circle CAD-4 Enraf-Nonius Diffractometer using graphite filtered MoKα (Å) radiation's .All the data were corrected for lorentz and polarization effect, but no absorption correction was applied. Attenuation of the beam for measuring the strong reflection is accomplished by inserting calibrated pack varying from 3 to 10 as required.Three standard reflections (4,0,0) (0,8,8), (0,8,0) were measured, where h varies from 0 to10, k from 0 to15 and l from 0 to 18 The total number of unique reflections measured was 6742. The crystal belongs to the Monoclinic system and space group$P2_1/n$. The crystal structure was solved using SHELXS-97, program for crystal structure solution.

Refinement

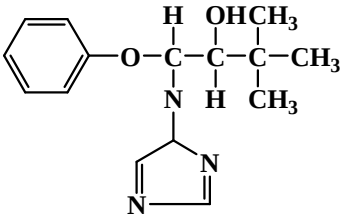
The positional co-ordinates which were obtained from SHELXS-97 and their isotropic temperature factors were subjected to refinement by SHELXL-97 refinement program. The final R value was 0.09 for all the 6742 observed reflections. Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameter is given in TABLE 2.

TABLE 3: Bond Lengths (Angstrom). - (Bonds are ordered on the first label, left to right and top to bottom) involving non hydrogen atom with estimated standard deviations in parentheses

O(1)	C(1)	1.4142(1)	O(3)	C(16)	1.3509(1)
O(1)	C(7)	1.4451(2)	O(3)	C(22)	1.3506(2)
O(2)	C(10)	1.2189(2)	O(4)	C(25)	1.1816(1)
N(1)	N(2)	1.3405(1)	N(4)	N(5)	1.3536(2)
N(1)	C(9)	1.4578(2)	N(4)	C(24)	1.2606(1)
N(2)	C(7)	1.3994(1)	N(5)	C(22)	1.4186(2)
N(2)	C(8)	1.3869(2)	N(5)	C(23)	1.3308(2)
N(3)	C(8)	1.3411(1)	N(6)	C(23)	1.3262(1)
N(3)	C(9)	1.2670(2)	N(6)	C(24)	1.4031(2)
C(1)	C(2)	1.3731(1)	C(16)	C(17)	1.4310(2)
C(1)	C(6)	1.4314(1)	C(16)	C(21)	1.3081(1)
C(2)	C(3)	1.3104(2)	C(17)	C(18)	1.4105(2)
C(3)	C(4)	1.3402(1)	C(18)	C(19)	1.3796(2)
C(4)	C(5)	1.4427(2)	C(19)	C(20)	1.3608(1)
C(5)	C(6)	1.3659(1)	C(20)	C(21)	1.3818(2)
C(7)	C(10)	1.5268(2)	C(22)	C(25)	1.5210(1)
C(10)	C(12)	1.4527(1)	C(25)	C(27)	1.4710(1)
C(12)	C(13)	1.6298(2)	C(27)	C(28)	1.6661(2)
C(12)	C(14)	1.4542(1)	C(27)	(29)	1.5247(1)
C(12)	C(15)	1.4377(2)	C(27)	C(30)	1.4460(2)

TABLE 4 : Bond (Degrees) -(Angles are ordered on the middle label, left to right and top to bottom) involving non hydrogen atoms with estimated standard deviations in parenthesis

C(1)	O(1)	C(7)	119.45(1)	C(7)	C(10)	C(12)	116.29(1)
N(2)	N(1)	C(9)	105.56(2)	C(13)	C(12)	C(14)	109.43(2)
N(1)	N(2)	C(7)	127.33(1)	C(13)	C(12)	C(15)	100.22(1)
N(1)	N(2)	C(8)	112.15(2)	C(14)	C(12)	C(15)	114.75(2)
C(7)	N(2)	C(8)	120.17(1)	C(16)	O(3)	C(22)	128.86(2)
C(8)	N(3)	C(9)	120.14(2)	N(5)	N(4)	C(24)	112.16(1)
O(1)	C(1)	C(2)	127.09(1)	N(4)	N(5)	C(22)	127.89(2)
O(1)	C(1)	C(6)	112.56(2)	N(4)	N(5)	C(23)	105.44(1)
C(2)	C(1)	C(6)	119.92(1)	C(22)	N(5)	C(23)	126.02(2)
C(1)	C(2)	C(3)	121.68(2)	C(23)	N(6)	C(24)	106.90(1)
C(2)	C(3)	C(4)	121.75(1)	O(3)	C(16)	C(17)	117.76(1)
C(3)	C(4)	C(5)	118.95(2)	O(3)	C(16)	C(21)	122.21(1)
C(4)	C(5)	C(6)	119.90(1)	C(17)	C(16)	C(21)	119.54(2)
C(1)	C(6)	C(5)	116.44(1)	C(16)	C(17)	C(18)	118.81(2)
O(1)	C(7)	N(2)	109.59(2)	C(17)	C(18)	C(19)	120.10(1)
O(1)	C(7)	C(10)	101.61(2)	C(18)	C(19)	C(20)	117.48(1)
N(2)	C(7)	C(10)	115.17(1)	C(19)	C(20)	C(21)	123.28(2)
N(2)	C(8)	N(3)	99.77(2)	C(16)	C(21)	C(20)	120.51(2)
N(1)	C(9)	N(3)	102.16(1)	O(3)	C(22)	N(5)	112.47(1)
O(2)	C(10)	C(7)	117.93(2)	O(3)	C(22)	C(25)	103.53(2)
O(2)	C(10)	C(12)	125.73(2)	N(5)	C(22)	C(25)	117.47(1)



β-(phenoxy)-α-(1,1-dimethylethyl) 1H-1,2,4-triazole-1-ehtanol

Figure 1

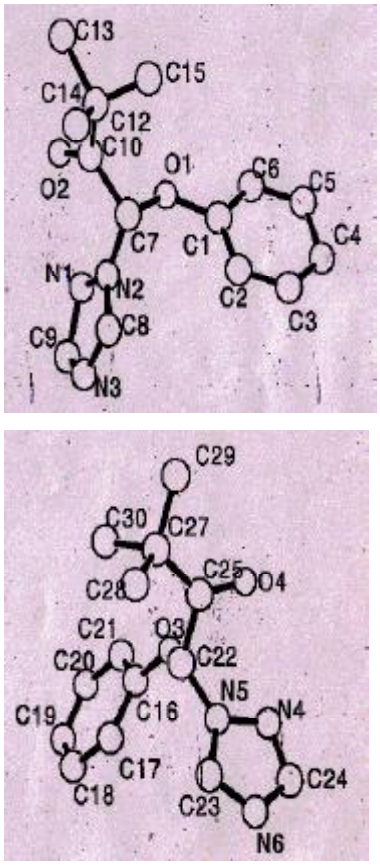


Figure 2: The perspective view and numbering scheme of β-(phenoxy)-α-(1,1-dimethylethyl)1H-1,2,4 triazole-1-ethanol

RESULT AND DISCUSSION

The perspective view of the molecule and numbering scheme are shown in figure 2. The ORTEP drawing is shown in figure 3. The bond lengths and angles in the two benzene rings have characteristics values and do not merit significant comments.The average C-H and N-H distances in the structure are 0.96Å and 0.90Å, respectively. The triazole rings are distorted in shapes.The average bond distances for N-N and C-N bonds are 1.340Å and 1.354Å. The angles show unusual variations. In Molecule 1 the angles vary from 99.8º to 120.1º, whereas in molecule 2, the variation is from 104.9º to 112.1º. The C(7) and C(22) atoms have usual geometry. It is of interest to see that the effect of steric hindrances. In molecule 1, the angle C(6)-C(1)-

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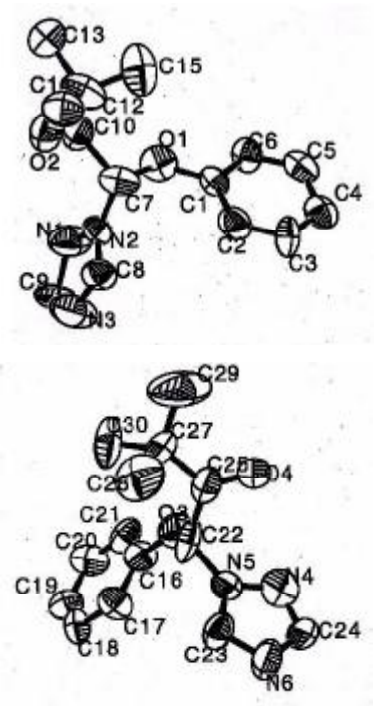

Figure 3 : Ortep diagram

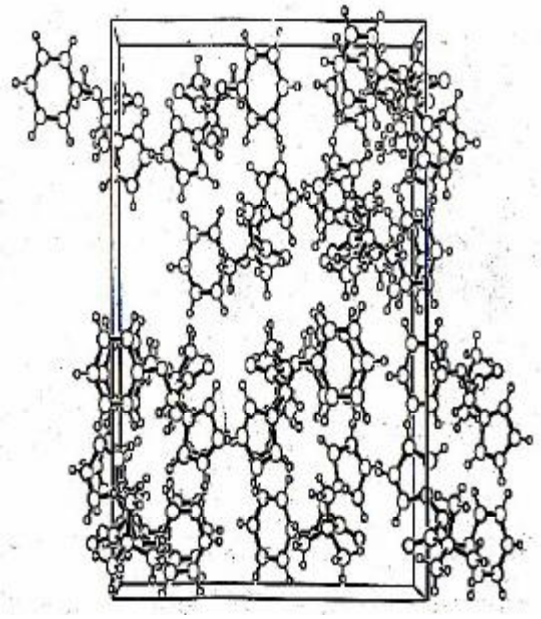

Figure 4 : The packing seen down a-axis

O(1) is 112.6º whereas C(2)-C(1)-O(1) is 127.1º. On comparing to molecule 2,these angles are just 122.2º and 117.8º, respectively. The geometry of phenoxy and methylethyl groups bears not attention as they are comparable to other organic structures. Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameter is shown in TABLE 2

TABLE 5: Hydrogen bond parameters and intermolecular distances less than 3.50(Å)

Hydrogen bonds				
Donor- H…..A	**D - H**	**H...A**	**D...A**	**∠D - H...A**
N(1)-H(1A)..O(4a)	0.900(2)	2.592(1)	3.191(1)	124.6(1)
N(4)-H(4A)..O(2b)	0.900(1)	2.541(2)	3.169(2)	127.3(2)
Some non bonded contacts				
C(9) .. O(4a)			3.3709	
C(24) .. O(2b)			3.2614	
Symmetry codes				
[a] = 3/2-x,1/2+y,1/2-z				
[b] = 1/2-x,-1/2+y,1/2-z				

The equations of the Least squares planes, calculated using Blow method and the displacements of the relevant atoms from the mean planes for different planer groups together with the respective. The two Benzene rings are essentially planar as the deviations of atoms from the planes are of 0.002. The triazole rings are also planar but the average deviations of atoms are 0.06. The two rings in Molecule 1 and 2 are inclined to each other by angles of 70.32º and 66.56º. The dihedral angles between the rings in two molecules along C(7)-O(1) and C(22)-O(3) bonds are -85.39º and 80.0º. It means the orientation or angle of twist in both the molecules is opposite with the approximate same amount. Bond Lengths (Angstrom) involving non-hydrogen atoms is shown in TABLE 3. Bond Angles (Degrees)-(Angles are ordered on the middle label, left to right and top to bottom) involving non-hydrogen atoms is shown in TABLE 4.

Hydrogen bonding and molecular packing

The Hydrogen bond parameters and some other non-bonded contacts are listed in TABLE 5. The molecular packing viewed down a-axis is shown in figure 4. The molecules are stacked along the a-axis and held firmly through hydrogen bonds. There are two hydrogen bonds. The N(1) is bonded to O(4) and N(4) to O(2) of symmetry related molecules. There are no intermolecular bonds between molecule1 and Molecule 2. So they are held together by weak Vander-Walls forces between them. In general, the Molecules appear to be under heavy constraints. Thus we study 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.

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REFERENCES

[1] S.R.Gautam; Ph.D THESIS G.B Pant Univ. of Agriculture and Technology U.P, **(1981)**.
[2] G.M.Sheldrich; SHELXS-97. Program for the solution of Crystal Structure, **(1997)**.
[3] G.M.Sheldrich; SHELXSL-97. Program for Crystal Structure determination, **(1997)**.
[4] C.K.Johnson; ORTEP. Report ORNL-3794.OAK Ridge National Lab, Tennessee, U.S.A, **(1965)**.
[5] M.Alleaume, J.Decap; Acta.Cryst, **B24**, 214 **(1968)**.
[6] M.Alleaume, J.Morena; Compt.Rend.Acad D.Sc., **267**, 64 **(1968)**.
[7] A.K.Basak, S.K.Majumdar; Cryst Struct.Comm., **11**, 1609 **(1987)**.
[8] A.K.Basak, S.Chaudhury, S.K.Majumdar; Acta. Cryst, **B40**, 1848 **(1984)**.
[9] G.P.Bettinetti, F.Giordano, A.La Manne, G. Guiseppetti, C.Todini; Cryst.Struct.Comm., **11**, 821 **(1982)**.
[10] C.Chatterjee, J.K.Dattagupta, N.N.Saha; Acta. Cryst, **B38**, 1845 **(1982)**.
[11] M.Haridas, N.R.Kulkarni, R.K.Tiwari, T.P.Singh; Curr.Sci., India, **51(23)**, 1111 **(1982)**.
[12] V.V.Joshi, R.K.Tiwari, T.C.Patel, T.P.Singh; Indian Journal Phys., **57A**, 79 **(1983)**.
[13] A.Kalman, M.Czugler, G.Y.Argay; Acta.Cryst., **B37**, 868 **(1981)**.
[14] H.P.Klug; Acta.Cryst., **B24**, 792 **(1968)**.
[15] G.J.Kruger, G.Gafner; Acta.Cryst., **B27**, 326 **(1971)**.
[16] J.M.Leger, S.Alberola, A.Carpy; Acta.Cryst., **B33**, 1455 **(1977)**.
[17] R.K.Tiwari, M.Haridas, T.P.Singh; Acta.Cryst., **C40**, 658 **(1984)**.
[18] A.M.O'Connel, E.N.Maslen; Acta.Cryst., **B22**, 134 **(1967)**.
[19] N.Rodier, A.Chauvet, Masse; J.Acta.Cryst., **B34**, 218 **(1978)**.
[20] M.Spencer; Acta.Cryst., **12**, 50 **(1959)**.
[21] K.J.Palmer, R.Y.Wang, L.Jurd; Acta.Cryst., **B29**, 1509 **(1973)**.
[22] D.M.Blow; Acta.Cryst., **13**, 168 **(1960)**.
[23] 'Hand book of Indian Agriculture Journal of Mycology and Plant Patheology, **26**, **(1996)**.