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X-ray crystallographic studies on 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole

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ABSTRACT

The activity of fungicides is intimately related to its chemical structure. Knowledge about the chemical structure of a chemical is useful for the synthesis of new compounds with more specific actions and fewer adverse reactions, to increase/decrease the duration of action of the original drug or to get a more potent compound, to restrict the action to a specific system of the body and to reduce the adverse reactions, toxicity and other disadvantages associated. We can understand the basic chemical groups responsible for drug action[1]. Recently it has been observed that some of the fungicides are loosing their effects. So 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. The composition of crystal 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole or Tricyclazole is confirmed by comparing the infra-red spectra of two components. The unit cell parameters are a=14.896(5) Å, b=7.410(5)Å, c=7.556(5) Å, α=90(5)°, β=90.000(5)°, γ=90.000(5)°.The Crystal system is Orthorhombic and space group is Pca21

KEYWORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure;
X-Ray diffraction.

INTRODUCTION

A systemic fungicide is defined as systemic fungi toxic compound that controls a fungus pathogen remote from the point of application and that can be detected or identified[2]. These compounds are absorbed by the plant and get trans located within it, thus providing protection as well as eradicating already established infection. Tricyclazole(TCE), a new systemic fungicide for the control of blast of rice (Pyricularia oryzae) is being developed under Code number EL-291(BEAM) by research and development division of Eli-Lilly and Co., Greenfield, Indiana, USA. Result from greenhouse and field studies show that TCE is readily absorbed by roots and translocated to leaves and provides residual disease control after a single soil or foliar application.

EXPERIMENTAL

First grow the crystals of existing fungicides 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

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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 Colorless well formed crystals of size 0.30×0.20×0.20 mm are obtained by slow evaporation from a solution of methanol at 297^{0}K temp. The crystals obtained are rectangular in shape. The density of crystal 1.587 Mg/m^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 .Chemical structure of 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole or Tricyclazole is given in figure 1.

Data collection and Structure Solution:The intensity data are collected on a computerized automatic CAD-4 Enraf Nonius 4-circled diffractometer. The data collection is done on ω-2θ scan mode. The hkl value varied from -23 to 23, -9 to 11 and -10 to 11, respectively. The total number of unique reflections is 3134. The observed reflections are 8479 correspond to the intensity limit I≥2σ. Each intensity measurement involved in a scan over the reflection peak, a back ground measurement at each end of the scan range and measurement of the peak height .The structure determination is carried out on VAX machine using SHELXS-97[3]. All the non-hydrogen atoms are located in the beginning itself.

TABLE 1: Crystal data of tricyclazole

Empirical formula	C9 H7 N3 S
Formula weight	189.24
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
space group	Pca21
a	14.896(5) A
alpha	90.000(5) deg.
b	7.410(5) A
beta	90.000(5) deg.
c	7.556(5) A
gamma	90.000(5) deg.
Volume	834.0(8) A^3
Z, Calculated density	4, 1.507 Mg/m^3
Absorption coefficient	0.335 mm^-1
F(000)	392
Crystal size	0.30 × 0.20 × 0.20 mm
Theta range for data collection	3.07 to 34.03 deg.
Limiting indices	-23<=h<=23, -9<=k<=11, -10<=l<=11
Reflections collected/unique	8479 / 3134 [R(int) = 0.0241]
Completeness to theta	34.03 99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9360 and 0.9062
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3134 / 1 / 126
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1=0.0433, wR2=0.1105
R indices (all data)	R1=0.0533, wR2=0.1187
Absolute structure parameter	0.00(8)
Largest diff. peak and hole	0.619 and -0.290 e.A^-3

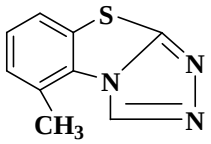

Figure 1: Chemical structure of 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole

Refinement

The positional co-ordinates, which were obtained from SHELXS 97 and isotropic temperature factors, were subjected to refinement by SHELXL[4] refinement program. After so many cycles of refinement the R factors dropped to 0.0533. Further refinement of the structure was carried out with individuals an isotropic temperature factors of the exponential form.

$$-2P_1\text{^}2[h\text{^}2a^*\text{^}2U_{11} + \text{-------} + 2hKa^*bxU_{12}$$

reduced R factor to 0.0511. The hydrogen atoms were fixed at this stage by geometrical considerations and were not refined.Refinement of the structure was terminated after two more cycles when all the deviations in parameters became much smaller than the corresponding estimated standard derivations. The final R value was 0.0432 for all 8479 reflections collected.

TABLE 2: Atomic coordinates (x 10∧4) and equivalent Isotropic displacement parameters (A^2 x 10^3) for tricyclazole U (eq) is defined as one third of the trace of the Orthogonalized Uij tensor

TOM	x	y	z	U(eq)
C(1)	7703(1)	3055(2)	1150(2)	30(1)
C(2)	8421(1)	1984(2)	651(2)	37(1)
C(3)	8239(1)	328(2)	-68(3)	41(1)
C(4)	7362(1)	-254(2)	-307(3)	37(1)
C(5)	6632(1)	784(2)	160(2)	31(1)
C(6)	6822(1)	2456(2)	895(2)	28(1)
C(7)	5312(1)	4074(3)	1675(3)	47(1)
C(8)	6598(1)	5273(2)	2187(3)	39(1)
C(9)	5685(1)	150(3)	-117(3)	46(1)
N(1)	6213(1)	3769(2)	1490(2)	33(1)
N(2)	5174(1)	5616(3)	2430(3)	62(1)
N(3)	6004(1)	6418(3)	2778(3)	56(1)
S(1)	7760(1)	5208(1)	2112(1)	42(1)

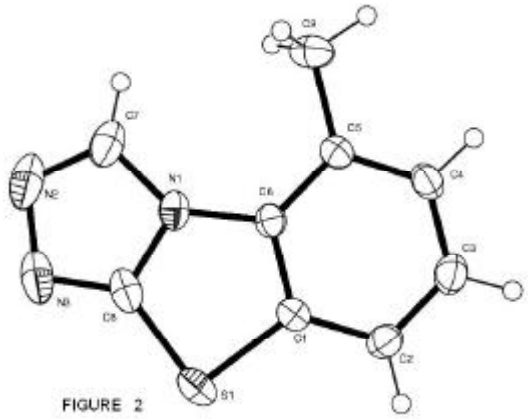

Figure 2: ORTEP diagram of 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole

RESULTS AND DISCUSSION

Atomic coordinates (x 104) and equivalent Isotropic displacement parameters (A^2 × 10^3) for tricyclazole is shown in TABLE 2. Bond lengths[A] Bond angles[deg] for Tricyclazole is shown in TABLE 3. Anisotropic displacement parameters (A∧2 × 10^3) for is shown in TABLE 4. The anisotropic displacement factor exponent takes the form: 2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]. Hydrogen coordinates (×10^4) and isotropic displacement parameters (A^2 ×10^3) for Tricyclazole is shown in TABLE 5. Torsion angles[deg] is shown in TABLE 6. The ORTEP[5] diagram is shown in figure 2. The average bond distances of C-H is 0.96(2)Å. The bond distances of C(7)-N(1) is 1.368Å, C(8)-N(1) is 1.360 Å. The bond distances of N (2)-N (3) is 1.396Å, C (8)-S (1)

TABLE 3: Bond lengths [A] for tricyclazole

C(1)-C(2)	1.384(2)
C(1)-C(6)	1.3993(18)
C(1)-S(1)	1.7553(19)
C(2)-C(3)	1.369(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.387(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.379(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.387(2)
C(5)-C(9)	1.501(2)
C(6)-N(1)	1.4037(19)
C(7)-N(2)	1.294(3)
C(7)-N(1)	1.368(2)
C(7)-H(7)	0.92(3)
C(8)-N(3)	1.305(2)
C(8)-N(1)	1.360(2)
C(8)-S(1)	1.7316(19)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
N(2)-N(3)	1.396(3)
Bond angles [deg] for Tricyclazole	
C(2)-C(1)-C(6)	120.36(15)
C(2)-C(1)-S(1)	126.65(11)
C(6)-C(1)-S(1)	112.99(11)
C(3)-C(2)-C(1)	117.97(14)
C(3)-C(2)-H(2)	121.0
C(1)-C(2)-H(2)	121.0
C(2)-C(3)-C(4)	121.12(15)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	122.43(15)
C(5)-C(4)-H(4)	118.8
C(3)-C(4)-H(4)	118.8
C(4)-C(5)-C(6)	116.10(13)
C(4)-C(5)-C(9)	122.09(15)
C(6)-C(5)-C(9)	121.80(14)
C(5)-C(6)-C(1)	122.01(13)
C(5)-C(6)-N(1)	128.00(13)
C(1)-C(6)-N(1)	109.98(13)
N(2)-C(7)-N(1)	110.3(2)
N(2)-C(7)-H(7)	126.9(15)
N(1)-C(7)-H(7)	122.9(15)
N(3)-C(8)-N(1)	112.26(17)
N(3)-C(8)-S(1)	135.03(16)
N(1)-C(8)-S(1)	112.71(11)
C(5)-C(9)-H(9A)	109.5
C(5)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(5)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-N(1)-C(7)	103.83(15)
C(8)-N(1)-C(6)	114.82(13)
C(7)-N(1)-C(6)	141.32(16)
C(7)-N(2)-N(3)	108.59(16)
C(8)-N(3)-N(2)	105.06(17)
C(8)-S(1)-C(1)	89.47(7)

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TABLE 4: Anisotropic displacement parameters (A^2 x 10^3) for Tricyclazole The anisotropic displacement factor exponent takes the form: 2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
C(1)	34(1)	27(1)	29(1)	-1(1)	-1(1)	-2(1)
C(2)	29(1)	41(1)	40(1)	-1(1)	0(1)	1(1)
C(3)	37(1)	42(1)	45(1)	-4(1)	1(1)	10(1)
C(4)	42(1)	27(1)	40(1)	-7(1)	-1(1)	1(1)
C(5)	34(1)	28(1)	31(1)	0(1)	-2(1)	-2(1)
C(6)	31(1)	26(1)	27(1)	2(1)	-1(1)	2(1)
C(7)	41(1)	57(1)	43(1)	-1(1)	-2(1)	18(1)
C(8)	55(1)	30(1)	32(1)	-3(1)	-2(1)	8(1)
C(9)	40(1)	45(1)	55(1)	-1(1)	-5(1)	-13(1)
N(1)	37(1)	31(1)	31(1)	1(1)	1(1)	9(1)
N(2)	60(1)	69(1)	55(1)	-7(1)	-1(1)	35(1)
N(3)	74(1)	44(1)	49(1)	-11(1)	-3(1)	24(1)
S(1)	53(1)	30(1)	42(1)	-7(1)	-1(1)	-8(1)

TABLE 5 : Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x10^3) for tricyclazole

Atom	x	y	z	U(eq)
H(2)	9009	2377	800	44
H(3)	8711	-419	-402	49
H(4)	7264	-1387	-800	44
H(9A)	5691	-1056	-581	85(10)
H(9B)	5388	937	-938	59(8)
H(9C)	5371	164	992	67(10)
H(7)	4884(17)	3260(30)	1310(30)	50(6)

is 1.7316Å. The triazol ring is distorted in shape[6]. The average bond distances for C-N and N-N bonds are 1.354Å and 1.396Å. The bond lengths and angles in the benzene ring show regular features in the molecule.C-C distances are short and shortening may be due to delocalization of electrons from the benzene rings[7]. The whole molecules appeared to be twisted and folded and reason may be due to stacking constraints[8]. The bond distance around C(7) is as usual shorter than single bond value. This may also appears to bear a partial double bond character[9] The bond distances in the five member ring are comparable to corresponding distances in heterocyclic ring 1.339 (Å)[8]. The average value of bond lengths and angles in the rings derived from most reliable set of data by Spencer are 1.377Å and 119º, respectively[10]. The dimensions of the methyl groups are normal and comparable with those in 0-methyl obtusaquinone and moscaline hydrobromide[11]. The average bond angle around C(9) is 109.5°. The molecule is found to adopt a conformation such that the triazol ring is inc neq angle of 72.9(9)° to the aromatic ring[12]. The resulting arrangement 1ead approach of

TABLE 6: Torsion angles [deg] for tricyclazole

C(6)-C(1)-C(2)-C(3)	-0.9(3)
S(1)-C(1)-C(2)-C(3)	179.43(15)
C(1)-C(2)-C(3)-C(4)	0.6(3)
C(2)-C(3)-C(4)-C(5)	-0.1(3)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(3)-C(4)-C(5)-C(9)	179.49(19)
C(4)-C(5)-C(6)-C(1)	0.0(2)
C(9)-C(5)-C(6)-C(1)	-179.75(16)
C(4)-C(5)-C(6)-N(1)	-179.71(16)
C(9)-C(5)-C(6)-N(1)	0.6(3)
C(2)-C(1)-C(6)-C(5)	0.6(2)
S(1)-C(1)-C(6)-C(5)	-179.68(12)
C(2)-C(1)-C(6)-N(1)	-179.67(15)
S(1)-C(1)-C(6)-N(1)	0.06(16)
N(3)-C(8)-N(1)-C(7)	0.7(2)
S(1)-C(8)-N(1)-C(7)	179.82(14)
N(3)-C(8)-N(1)-C(6)	-177.61(16)
S(1)-C(8)-N(1)-C(6)	1.5(2)
N(2)-C(7)-N(1)-C(8)	-0.6(2)
N(2)-C(7)-N(1)-C(6)	177.01(19)
C(5)-C(6)-N(1)-C(8)	178.74(17)
C(1)-C(6)-N(1)-C(8)	-1.0(2)
C(5)-C(6)-N(1)-C(7)	1.3(3)
C(1)-C(6)-N(1)-C(7)	-178.4(2)
N(1)-C(7)-N(2)-N(3)	0.3(2)
N(1)-C(8)-N(3)-N(2)	-0.6(3)
S(1)-C(8)-N(3)-N(2)	-179.4(2)
C(7)-N(2)-N(3)-C(8)	0.2(2)
N(3)-C(8)-S(1)-C(1)	177.6(3)
N(1)-C(8)-S(1)-C(1)	-1.17(15)
C(2)-C(1)-S(1)-C(8)	-179.67(16)
C(6)-C(1)-S(1)-C(8)	0.62(13)

the ortho-H, H(2A) to the triazol, atoms N(1) and N (2) such that both N-H distances lie within the Sum of the Vander Walls radii of N and H[13]. 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[14].

The triozol ring is planner with C(7) lying only O.063(7)A from the mean plane. All four C-N distances are shorter than a normal single bond (1.47A). The N(1)-N(2) bond is also shorter than a normal single bond (1.45A). The three atoms bonded to N(1) are almost co planer with it. Taken together these data indicate extensive delocalization within the hetrocyclic ring. The most note worthy feature of the hetrocyclic ring.is the asymmetry of the exocyclic angles at N(1A) [130.80°1. We have observed a similar pattern in related triazole systems and it appear to be a function of a triazolyl ring itself rather than the influence Of any inter

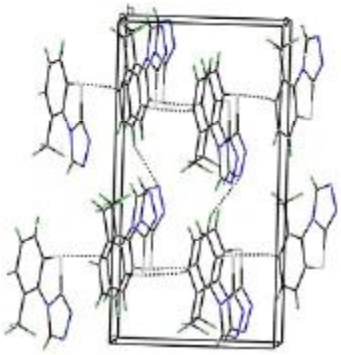

Figure 3: Packing diagram of 5-methyl-1, 2, 4-triazolo (3,4b)-benzothiazole

or intramolecular interactions.. The torsion angles of C(6)-C(1)-C(2)-C(3) is -0.9(3)°. The torsion angles of S(1)-C(1)-C(2)-C(3) is 179.43(15)° and C(3)-C(4)-C(5)-C(9) is 179.49(19) show that this ring is almost symmetric.

The packing diagram is shown in figure 3. The crystal structure consists of parallel sheets stacked along a-axis. The molecules overlap while running along the a-axis. It is interesting to note that when 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

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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