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RESEARCH ARTICLE

BIO CHEMISTRY

X-RAY CRYSTALLOGRAPHIC STUDIES OF SYSTEMIC FUNGICIDE DIMETHOMORPH

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ABSTRACT

There are large numbers of chemical compounds for the protection of crops available commercially in the market but their effects depends 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. Recently it has been observed that some of the fungicides are loosing their effects. if their structures are known we can design analogous compounds as a substitute. 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 **Dimethomorph** is confirmed by comparing the infra-red spectra of two components. The unit cell parameters are a=8.593(5) Å, b=11.220(5)Å, c=11.712 (5) Å, α=63.50 (5)^o, β=72.17 (5)^o, γ=85.39(5)^o. The Crystal system is ***Triclinic*** and space group is ***P-1***

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KEYWORDS

X-ray crystallography, Systemic fungicides, Triazole structure

INTRODUCTION

Dimethomorph ,a Local systemic fungicide with good protectant and antisporulant function. Only the (Z)- isomer is intrinsically active, but, because of rapid inter conversion of isomers in the light, it has no advantage over the (E)-isomer in practice. Fungicide is effective against Oomycetes, especially Peronosporaceae and Phytophthora spp. (but not Pythium spp.) in vines, potatoes, tomatoes and other crops. It is readily absorbed by roots and translocated to leaves and provides residual disease control after a single soil or foliar application. The activity of fungicides is intimately related to its chemical structure. It is always advisable to have knowledge about the structure of a chemical for the synthesis of new compounds with more specific actions and fewer adverse reactions. It is also useful to know about the effect of it when the duration of action is increased/decreased over the original drug or fungi 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 action.

EXPERIMENTAL

(This line needs restructuring) **First grow the crystals of available fungicides and synthesize their derivatives in lab**.. Then determine the structural perturbation in fungicide derivatives by X-Ray crystallography techniques. After that we try to understand their molecular association with other receptor sites. In parallel with these structural studies, spectroscopic studies also carried out on them. [3] 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.. . White well formed crystals of size *0.30 x 0.20 x 0.20 mm* are obtained by slow evaporation from a solution of Toluene at 297□K temp. The preliminary information about the crystal is listed in**Table1**. The unit cell parameters are determined by directly on CAD-4 Enraf Nonius 4-circle automatic Diffractometer .

Table 1

Identification code	*ShelxI*
Empirical formula	***C21 H22 Cl N O4***
Formula weight	***387.85***
Temperature	***293(2) K***
Wavelength	***0.71073 A***

Crystal system, space group	*Triclinic, P-1*
Unit cell dimensions	*a = 8.593(5) A alpha = 63.504(5) deg.*
	b = 11.220(5) A beta = 72.177(5) deg.
	c = 11.712(5) A gamma = 85.391(5) deg.
Volume	*960.0(8) A^3*
Z, Calculated density	*2, 1.342 Mg/m^3*
Absorption coefficient	*0.226 mm^-1*
F(000)	*408*
Crystal size	*0.30 x 0.20 x 0.20 mm*
Theta range for data collection	*2.03 to 26.00 deg.*
Limiting indices	*-10<=h<=10, -13<=k<=13, -14<=l<=14*
Reflections collected / unique	*19752 / 3767 [R(int) = 0.0256]*
Completeness to theta =	*26.00 100.0 %*
Absorption correction	*Semi-empirical from equivalents*
Max. and min. transmission	*0.967 and 0.912*
Refinement method	*Full-matrix least-squares on F^2*
Data / restraints / parameters	*3767 / 0 / 251*
Goodness-of-fit on F^2	*1.034*
Final R indices [I>2sigma(I)]	*R1 = 0.0372, wR2 = 0.0973*
R indices (all data)	*R1 = 0.0448, wR2 = 0.1038*
Extinction coefficient	*0.032(3)*
Largest diff. peak and hole	*0.229 and -0.270 e.A^-3*

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.T*heta range for data collection is 2.03 to 26.00 deg.* The hkl value varied from -10 to10, -13 to 13 and -14 to 14, respectively. *Reflections collected is 19752* The total number of unique reflections is 3767. *[R(int) = 0.0256]*.The structure determination is carried

out on VAX machine using SHELXS-97[4]. All the non-hydrogen atoms are located in the beginning itself.

REFINEMENT: The positional co-ordinates, which were obtained from SHELXS 97 and isotropic temperature factors, were subjected to refinement by SHELXL[5] refinement program. After so many cycles of refinement the R factors dropped to 0.0372. Further refinement of the structure was carried out with individuals isotropic temperature factors of the exponential form.
$-2P_1$^ 2[h^2a*^2U_{11}+----------+2hKa*bxU_{12} reduced to*R indices [I>2sigma(I)] R1 = 0.0372, wR2 = 0.0973*. 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. .

RESULTS AND DISCUSSION

Atomic coordinates (x 10^4) and equivalent Isotropic displacement parameters (A^2 x 10^3) for Dimethomorph is shown in Table 2. Bond lengths [A] Bond angles [deg] for Dimethomorph is shown in Table 3.Anisotropic displacement parameters (A^2 x 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 (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Dimethomorph is shown in Table 5. Torsion angles [deg] is shown in Table 6.In Table *7Hydrogen bonds for* Dimethomorph (*deg) are shown].* The ORTEP[6] diagram is shown in fig.1. The average bond distances of C-H is 0. 9700Å. The bond distances of *C(1)-O(1) is 1.415(3)and* C(7)-N(1) is 1.368Å , C(8)-N(1) is 1.360 Å. The triazol ring is distorted in shape[6]. The Bond distances in Benzene Ring are *C(14)-C(15) is 1.380(2),.C(15)-C(16)is 1.386(2)*, *C(16)-C(17) is 1.374(2),C(17)-C(18)is ,C(18)-C(19)is 1.377(2) 1.405(2).*The Bond Angles in benzene ring are *C(15)-C(14)-C(19) is 118.12(14),C(15)-C(14)-C(7)is 120.34(14),C(19)-C(14)-C(7)is 121.47(13) and) C(14)-C(15)-C(16) is 121.40(15).*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. The whole molecules appeared to be twisted and folded and reason may be due to stacking constraints.. The equations of the Least squares planes, calculated using [7]Blow method .The torsion angles of *O(1)-C(1)-C(2)-N(1) is 55.1(3)* , *N(1)-C(3)-C(4)-O(1) is 55.7(2)* , *O(2)-C(5)-C(6)-C(7) is -106.2(2)* and *N(1)-C(5)-C(6)-C(7) is 75.0(2)* . The torsion angles of *C(5)-C(6)-C(7)-C(8) is -1.5(3)* and *C(5)-C(6)-C(7)-C(14) is 176.11(15)* . show that this ring is almost symmetric.The packing diagram is shown in Fig2. The crystal structure consists of parallel sheets stacked along *a-axis*. The molecules overlap while running along the *a-axis*. 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

Table 2
***Bond lengths Á] and angles [deg] for* Dimethomorph**

Bond lengths Á	
C(1)-O(1)	***1.415(3)***

C(1)-C(2)	1.483(4)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-N(1)	1.456(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-N(1)	1.460(2)
C(3)-C(4)	1.489(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-O(1)	1.417(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-O(2)	1.2251(19)
C(5)-N(1)	1.336(2)
C(5)-C(6)	1.493(2)
C(6)-C(7)	1.333(2)
C(6)-H(6)	0.892(19)
C(7)-C(8)	1.488(2)
C(7)-C(14)	1.490(2)
C(8)-C(13)	1.387(2)
C(8)-C(9)	1.388(2)
C(9)-C(10)	1.377(2)
C(9)-H(9)	0.9300
C(10)-C(11)	1.373(2)
C(10)-H(10)	0.9300
C(11)-C(12)	1.373(2)
C(11)-Cl(1)	1.7418(17)
C(12)-C(13)	1.381(2)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-C(15)	1.380(2)
C(14)-C(19)	1.399(2)
C(15)-C(16)	1.386(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(2)
C(16)-H(16)	0.9300
C(17)-O(4)	1.3584(19)
C(17)-C(18)	1.405(2)
C(18)-O(3)	1.359(2)
C(18)-C(19)	1.377(2)
C(19)-H(19)	0.9300

C(20)-O(3)	1.420(2)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-O(4)	1.420(2)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

Table of Bond Angles for Dimethomorph in Degree

O(1)-C(1)-C(2)	112.2(2)
O(1)-C(1)-H(1A)	109.2
C(2)-C(1)-H(1A)	109.2
O(1)-C(1)-H(1B)	109.2
C(2)-C(1)-H(1B)	109.2
H(1A)-C(1)-H(1B)	107.9
N(1)-C(2)-C(1)	110.0(2)
N(1)-C(2)-H(2A)	109.7
C(1)-C(2)-H(2A)	109.7
N(1)-C(2)-H(2B)	109.7
C(1)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
N(1)-C(3)-C(4)	109.61(16)
N(1)-C(3)-H(3A)	109.7
C(4)-C(3)-H(3A)	109.7
N(1)-C(3)-H(3B)	109.7
C(4)-C(3)-H(3B)	109.7
H(3A)-C(3)-H(3B)	108.2
O(1)-C(4)-C(3)	111.9(2)
O(1)-C(4)-H(4A)	109.2
C(3)-C(4)-H(4A)	109.2
O(1)-C(4)-H(4B)	109.2
C(3)-C(4)-H(4B)	109.2
H(4A)-C(4)-H(4B)	107.9
O(2)-C(5)-N(1)	122.17(15)
O(2)-C(5)-C(6)	119.32(15)
N(1)-C(5)-C(6)	118.50(14)
C(7)-C(6)-C(5)	125.43(15)
C(7)-C(6)-H(6)	119.4(12)
C(5)-C(6)-H(6)	115.0(12)
C(6)-C(7)-C(8)	121.17(14)

C(6)-C(7)-C(14)	121.83(14)
C(8)-C(7)-C(14)	116.95(13)
C(13)-C(8)-C(9)	117.97(14)
C(13)-C(8)-C(7)	121.33(14)
C(9)-C(8)-C(7)	120.69(13)
C(10)-C(9)-C(8)	121.32(14)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
C(11)-C(10)-C(9)	119.23(15)
C(11)-C(10)-H(10)	120.4
C(9)-C(10)-H(10)	120.4
C(10)-C(11)-C(12)	121.11(15)
C(10)-C(11)-Cl(1)	118.82(13)
C(12)-C(11)-Cl(1)	120.04(12)
C(11)-C(12)-C(13)	119.09(14)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-H(12)	120.5
C(12)-C(13)-C(8)	121.27(15)
C(12)-C(13)-H(13)	119.4
C(8)-C(13)-H(13)	119.4
C(15)-C(14)-C(19)	118.12(14)
C(15)-C(14)-C(7)	120.34(14)
C(19)-C(14)-C(7)	121.47(13)
C(14)-C(15)-C(16)	121.40(15)
C(14)-C(15)-H(15)	119.3
C(16)-C(15)-H(15)	119.3
C(17)-C(16)-C(15)	120.47(15)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
O(4)-C(17)-C(16)	125.92(15)
O(4)-C(17)-C(18)	115.23(15)
C(16)-C(17)-C(18)	118.85(14)
O(3)-C(18)-C(19)	124.90(14)
O(3)-C(18)-C(17)	114.82(14)
C(19)-C(18)-C(17)	120.28(14)
C(18)-C(19)-C(14)	120.80(14)
C(18)-C(19)-H(19)	119.6
C(14)-C(19)-H(19)	119.6
O(3)-C(20)-H(20A)	109.5
O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(3)-C(20)-H(20C)	109.5

H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(4)-C(21)-H(21A)	109.5
O(4)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(5)-N(1)-C(2)	124.77(15)
C(5)-N(1)-C(3)	121.78(14)
C(2)-N(1)-C(3)	113.09(15)
C(1)-O(1)-C(4)	109.91(16)
C(18)-O(3)-C(20)	117.84(13)
C(17)-O(4)-C(21)	118.15(15)

Symmetry transformations used to generate equivalent atoms:

Table 4

Anisotropic displacement parameters (A^2x10^3) **Dimethomorph.** ***The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]***

	U11	U22	U33	U23	U13	U12
C(1)	171(3)	58(1)	65(1)	-27(1)	4(2)	-27(2)
C(2)	84(1)	79(1)	60(1)	-33(1)	6(1)	-33(1)
C(3)	69(1)	70(1)	45(1)	-23(1)	-3(1)	-1(1)
C(4)	98(2)	76(1)	70(1)	-41(1)	-7(1)	8(1)
C(5)	44(1)	48(1)	40(1)	-10(1)	-13(1)	7(1)
C(6)	45(1)	46(1)	45(1)	-15(1)	-12(1)	9(1)
C(7)	39(1)	39(1)	42(1)	-14(1)	-9(1)	0(1)
C(8)	39(1)	44(1)	37(1)	-16(1)	-9(1)	2(1)
C(9)	39(1)	46(1)	49(1)	-11(1)	-5(1)	-2(1)
C(10)	52(1)	42(1)	51(1)	-10(1)	-10(1)	5(1)
C(11)	43(1)	56(1)	42(1)	-23(1)	-13(1)	12(1)
C(12)	37(1)	58(1)	45(1)	-20(1)	-7(1)	-3(1)
C(13)	44(1)	42(1)	43(1)	-12(1)	-9(1)	-1(1)
C(14)	39(1)	39(1)	41(1)	-15(1)	-11(1)	2(1)

C(15)	*39(1)*	*61(1)*	*49(1)*	*-22(1)*	*-16(1)*	*5(1)*
C(16)	*52(1)*	*62(1)*	*46(1)*	*-23(1)*	*-21(1)*	*2(1)*
C(17)	*50(1)*	*46(1)*	*42(1)*	*-21(1)*	*-11(1)*	*2(1)*
C(18)	*38(1)*	*46(1)*	*48(1)*	*-22(1)*	*-13(1)*	*4(1)*
C(19)	*41(1)*	*45(1)*	*42(1)*	*-19(1)*	*-15(1)*	*3(1)*
C(20)	*43(1)*	*69(1)*	*71(1)*	*-33(1)*	*-25(1)*	*11(1)*
C(21)	*97(2)*	*74(1)*	*55(1)*	*-39(1)*	*-25(1)*	*9(1)*
N(1)	*55(1)*	*55(1)*	*43(1)*	*-19(1)*	*-1(1)*	*-7(1)*
O(1)	*161(2)*	*68(1)*	*74(1)*	*-42(1)*	*-2(1)*	*-14(1)*
O(2)	*81(1)*	*49(1)*	*49(1)*	*-9(1)*	*-2(1)*	*-6(1)*
O(3)	*41(1)*	*92(1)*	*64(1)*	*-47(1)*	*-17(1)*	*16(1)*
O(4)	*63(1)*	*87(1)*	*53(1)*	*-42(1)*	*-16(1)*	*13(1)*
Cl(1)	*51(1)*	*82(1)*	*65(1)*	*-27(1)*	*-19(1)*	*24(1)*

Table 6
***Torsion angles [deg] for* Dimethomorph**

Bond	*Torsion Angle [deg]*
O(1)-C(1)-C(2)-N(1)	***-55.1(3)***
N(1)-C(3)-C(4)-O(1)	***55.7(2)***
O(2)-C(5)-C(6)-C(7)	***-106.2(2)***
N(1)-C(5)-C(6)-C(7)	***75.0(2)***
C(5)-C(6)-C(7)-C(8)	***-1.5(3)***
C(5)-C(6)-C(7)-C(14)	***176.11(15)***
C(6)-C(7)-C(8)-C(13)	***58.4(2)***
C(14)-C(7)-C(8)-C(13)	***-119.32(16)***
C(6)-C(7)-C(8)-C(9)	***-123.11(17)***
C(14)-C(7)-C(8)-C(9)	***59.2(2)***
C(13)-C(8)-C(9)-C(10)	***0.0(2)***
C(7)-C(8)-C(9)-C(10)	***-178.61(15)***
C(8)-C(9)-C(10)-C(11)	***1.0(3)***
C(9)-C(10)-C(11)-C(12)	***-1.3(3)***
C(9)-C(10)-C(11)-Cl(1)	***177.12(13)***
C(10)-C(11)-C(12)-C(13)	***0.6(3)***

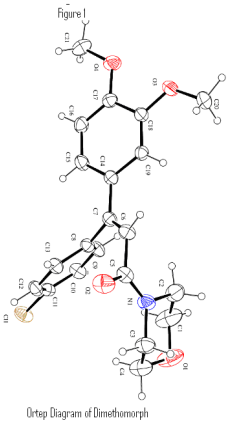
Cl(1)-C(11)-C(12)-C(13)	*-177.71(12)*
C(11)-C(12)-C(13)-C(8)	*0.3(2)*
C(9)-C(8)-C(13)-C(12)	*-0.6(2)*
C(7)-C(8)-C(13)-C(12)	*177.97(15)*
C(6)-C(7)-C(14)-C(15)	*-149.96(16)*
C(8)-C(7)-C(14)-C(15)	*27.7(2)*
C(6)-C(7)-C(14)-C(19)	*27.1(2)*
C(8)-C(7)-C(14)-C(19)	*-155.22(14)*
C(19)-C(14)-C(15)-C(16)	*-2.7(2)*
C(7)-C(14)-C(15)-C(16)	*174.43(15)*
C(14)-C(15)-C(16)-C(17)	*1.5(3)*
C(15)-C(16)-C(17)-O(4)	*-179.65(16)*
C(15)-C(16)-C(17)-C(18)	*1.2(2)*
O(4)-C(17)-C(18)-O(3)	*-2.6(2)*
C(16)-C(17)-C(18)-O(3)	*176.65(15)*
O(4)-C(17)-C(18)-C(19)	*178.12(14)*
C(16)-C(17)-C(18)-C(19)	*-2.7(2)*
O(3)-C(18)-C(19)-C(14)	*-177.82(14)*
C(17)-C(18)-C(19)-C(14)	*1.4(2)*
C(15)-C(14)-C(19)-C(18)	*1.2(2)*
C(7)-C(14)-C(19)-C(18)	*-175.87(13)*
O(2)-C(5)-N(1)-C(2)	*-169.37(19)*
C(6)-C(5)-N(1)-C(2)	*9.4(3)*
O(2)-C(5)-N(1)-C(3)	*3.3(3)*
C(6)-C(5)-N(1)-C(3)	*-177.88(16)*
C(1)-C(2)-N(1)-C(5)	*-135.2(2)*
C(1)-C(2)-N(1)-C(3)	*51.6(2)*
C(4)-C(3)-N(1)-C(5)	*134.69(19)*
C(4)-C(3)-N(1)-C(2)	*-51.8(2)*
C(2)-C(1)-O(1)-C(4)	*59.5(3)*
C(3)-C(4)-O(1)-C(1)	*-59.8(3)*
C(19)-C(18)-O(3)-C(20)	*-3.4(2)*
C(17)-C(18)-O(3)-C(20)	*177.35(14)*
C(16)-C(17)-O(4)-C(21)	*4.9(3)*
C(18)-C(17)-O(4)-C(21)	*-175.99(15)*

Symmetry transformations used to generate equivalent atoms:

Table 7
Hydrogen bonds for Dimethomorph *[A and deg.].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...N(2)#1	0.82	2.01	2.820(2)	169.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2)



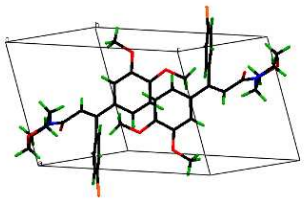


Figure 2
Packing diagram of dimethomorph

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