ISSN : 0974 - 7435 Volume 5 Issue 3

Trade Science Inc.

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 5(3), 2011 [160-166]

X-ray crystallographic studies of systemic fungicide hexaconazole

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Received: 1st February, 2011 ; Accepted: 11th February, 2011

ABSTRACT

Triazoles compounds contain a ring composed of two carbon atoms and three nitrogen atoms. A systemic fungicide, RH-124(4-n-butyl-1, 2, 4-triazole, BT), has been introduced as an experimental fungicide, possessing high selective activity against brown rust of wheat. However, substitution on nitrogen atom in position 1 in the triazoles producing an amazing variety of compounds such as triadimefon, triadimenol, and biloxazol, have been discovered, which are known inhibitors of fungal sterol biosynthesis. These compounds possess a trityl carbon that can act as a carbonium ion, an organic ion carrying a positive at a carbon location. 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 (RS)-2-(2,4-dichlorophenyl)-1-(1H-1, 2,4-trizole-1-y1) hexane-2-ol or hexaconazole is confirmed by comparing the infra-red spectra of two components. The unit cell parameters are a=10. 9068(7) Å, b=10.9895(7) Å c=13.6124(8) Å, α=90°, β=106.554(2)°, γ=90.000(5)°. The Crystal system is Monoclinic, and space group P21/c

KEY-WORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure.

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. Hexaconazole is a new Triazole fungicide with low mammalian toxicity and an exceptionally broad-spectrum of antifungal activity. It was introduced by ICI Plant Protection Division Berkshire, UK[2]. The fungicide is a white crystalline solid with melting point 111°C, density1.29/cm^3 at 25°C and vapour pressure 2×10^{-8}kPa at 20°C[2]. The solubility of the compound in water is 0.017, methanol 246, acetone 164, toluene 59 and hexane 0.8 g 1^{-1} at 20°C. The compound has stability for at least 9 months at ambient temperature[2]. Hexaconazole has in vitro activity against Alternaria solani Helminthosporium oryzae, penicillium digitatum, sclerotinia sclerotiorum Sclerotium rolfsii, Pyricularia oryzae and Verticillium albo-atrum at 10 mg 1^{-1}[2]. The fungiside has outstanding activity against a wide variety of diseases, and its penetrant, curative, systemic and antisporulant properties provide a useful addition to the range of commercial fungicide[2]. The application rates of the control of early and late leaf spot of groundnut, apple, scab, powdery mildew of apples and black rot oh grapes ranged from 5 to 20g a.i. ha^{-1} According to Shephard, et al.[2], the rates of hexaconazole are expected to be lower than those for many trizoles. The fungicide is compatible to dithiocarbamates and chlorothalonil, and can be mixed with these or other suitable fungicide

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. Crystallization of hexaconazole was done by slow evaporation from a solution of methanol at 293°K temp. The crystals obtained were white and rectangular in shape. The density of crystal 1.334 Mg/m^3 is measured by floatation method the mixture of benzene and Bromoform. 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.

TABLE 1 : Preliminary crystal data

Identification code	shelxl
Empirical formula	C14 H17 Cl2 N3 O
Formula weight	314.21
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system,	Monoclinic,
space group	P21/c
a	10.9068(7) A
b	10.9895(7) A
c	13.6124(8) A
α	90 °
β	106.554(2) °
γ	90 °
Volume	1563.96(17) A^3
Z	4
Calculated density	1.334 Mg/m^3
Absorption coefficient	0.414 mm^-1
F(000)	656
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	2.42 to 25.00 deg.
Limiting indices	-12<=h<=12, -11<=k<=13, -16<=l<=10
Reflections collected / unique	14496 / 2746 [R(int) = 0.0205]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9218 and 0.8859

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Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2746 / 0 / 182
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0862
R indices (all data)	R1 = 0.0458, wR2 = 0.0935
Largest diff. peak and hole	0.344 and -0.352 e.A^-3

Data collection and structure solution

The three dimensional intensity data were collected on a computerized automatic 4-circle CAD-4 Enraf-Nonious diffractometer using graphite filtered MoKα (Å) radiation's at SAIF Madras.. Temperature of crystal during data collection was 293°K. All the data were corrected for Lorentz and Polarization effect. Three standard reflection were measured where h various -12to12, k varies from -11to13, l varies from -16to10. The total number of reflections were 14496 out of which unique reflection were 2746. 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 was solved using SHELXS- program for crystal structure solution.

REFINEMENT

The positional co-ordinates, which were obtained from SHELXS 97 and isotropic temperature factors, were subjected to refinement by SHELXL refinement program. After so many cycles of refinement the R factors dropped to 0.0458. Further refinement of the structure was carried out with individuals an isotropic temperature factors of the exponential form $-2P_1^2[h^2a^{*2}U_{11}+----------+2hKa^*bxU_{12}$ reduced R factor to 0.0354. 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 0.0354 for all 14496 reflections collected.

RESULTS AND DISCUSSION

Atomic coordinates (x 10^4) and equivalent Isotropic displacement parameters (A^2 x 10^3) for Hexaconazole is shown in TABLE 2. Bond lengths [A] Bond angles [deg] for Hexaconazole is shown in TABLE 3 and TABLE 4. Anisotropic displacement parameters (A^2 x 10^3) for Hexaconazole is shown in TABLE 5 The anisotropic displacement factor exponent takes the form:—2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]. Hydrogn coordinates (x 10^4) and isotropic displacement parameters (Ae^2 x 10^3) for hexaconazole is given in TABLE 6 Torsion angles [deg] is shown in TABLE 7. The ORTEP[5] diagram is shown in figure 2. Packing Diagram is shown in Figure 3. The average bond distances of C-H is 0. 96(2)Å. The bond distances of C(9)-N(1) is 1.325 Å, C(8)-N(1) is 1.346 Å. The bond distances of N (1)-N (3) is 1.349Å, C (7)-O (1) is 1.422Å. O(1)-H(1A) is .820Å . C(1)-Cl(1) is 1.7416(18) Å and C(3)-Cl(2) is 1.740(2) Å . The average C-Cl bond distance is 1.7408 Å. C(10)-N(3) is 1.305(3). C(9)-N(1)is 1.320(3). C(9)-N(2)is 1.313(3). C(10)-N(2) is 1.344(3). The average bond distances of C-N is 1.3205 Å The triazol ring is distorted in shape[6]. The average bond distances for C-N and N-N bonds are 1. 3205Å and 1.349Å. 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(8) is 109.5°. The bond angle C(9)-N(1)-C(8) is 130.03(19)The molecule is found to adopt a conformation such that the triazol ring is inclined angle of 72.9(9)° to the aromatic ring[12]. The resulting arrangement 1ead approach of 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]

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

atom	x	y	z	U(eq)
C(1)	1220(2)	1380(2)	-553(1)	42(1)
C(2)	863(2)	500(2)	-1306(2)	51(1)
C(3)	1791(2)	-73(2)	-1630(2)	54(1)
C(4)	3054(2)	216(2)	-1220(2)	57(1)
C(5)	3384(2)	1106(2)	-476(2)	49(1)
C(6)	2488(2)	1718(2)	-111(1)	39(1)
C(7)	2934(2)	2656(2)	748(1)	43(1)
C(8)	2641(2)	2222(2)	1734(1)	49(1)
C(9)	4335(2)	712(2)	2591(2)	64(1)
C(10)	3284(3)	-850(2)	2106(2)	73(1)
C(11)	2353(2)	3929(2)	479(2)	51(1)
C(12)	2420(3)	4430(2)	-539(2)	69(1)
C(13)	1959(3)	5742(2)	-721(2)	73(1)
C(14)	2856(3)	6652(2)	-72(2)	82(1)
N(1)	3169(2)	1028(2)	2053(1)	47(1)
N(2)	4456(2)	-477(2)	2646(2)	75(1)
N(3)	2467(2)	18(2)	1734(2)	63(1)
O(1)	4286(1)	2718(1)	956(1)	57(1)
Cl(1)	-39(1)	2021(1)	-182(1)	62(1)
Cl(2)	1343(1)	-1187(1)	-2574(1)	88(1)

The triozol ring is planner with C(8) 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(3) 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(1) [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 or intramolecular interactions.. The torsion angles of C(6)-C(1)-C(2)-C(3)is0.4°, C(4)-C(5)-C(6)-C(1)is -0.5(3)°, C(1)-C(2)-C(3)-C(4) is-0.1(3)°and Cl(1)-C(1)-C(2)-C(3)is -178.56(16)°, C(2)-C(1)-C(6)-C(7)is -177.92(18)°, C(1)-C(6)-C(7)-O(1)is-179.71(16). show that this ring is almost symmetric.

TABLE 3 : Bond lengths [A] of hexaconazole

C(1)-C(2)	1.382(3)
C(1)-C(6)	1.393(2)
C(1)-Cl(1)	1.7416(18)
C(2)-C(3)	1.368(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.368(3)
C(3)-Cl(2)	1.740(2)
C(4)-C(5)	1.379(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.390(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.530(3)
C(7)-O(1)	1.422(2)
C(7)-C(11)	1.536(3)
C(7)-C(8)	1.542(3)
C(8)-N(1)	1.448(2)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-N(2)	1.313(3)
C(9)-N(1)	1.320(3)
C(9)-H(9)	0.9300
C(10)-N(3)	1.305(3)
C(10)-N(2)	1.344(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.513(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.523(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.498(4)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
N(1)-N(3)	1.349(2)
O(1)-H(1A)	0.8200

TABLE 4 : Bond angles [A] of hexaconazole

C(2)-C(1)-C(6)	122.89(17)
C(2)-C(1)-Cl(1)	114.78(14)
C(6)-C(1)-Cl(1)	122.32(14)
C(3)-C(2)-C(1)	118.89(18)
C(3)-C(2)-H(2)	120.6

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C(1)-C(2)-H(2)	120.6
C(2)-C(3)-C(4)	120.84(19)
C(2)-C(3)-Cl(2)	118.91(17)
C(4)-C(3)-Cl(2)	120.25(17)
C(3)-C(4)-C(5)	119.12(19)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	122.84(19)
C(4)-C(5)-H(5)	118.6
C(6)-C(5)-H(5)	118.6
C(5)-C(6)-C(1)	115.40(17)
C(5)-C(6)-C(7)	119.77(16)
C(1)-C(6)-C(7)	124.79(16)
O(1)-C(7)-C(6)	105.63(14)
O(1)-C(7)-C(11)	109.78(16)
C(6)-C(7)-C(11)	114.29(15)
O(1)-C(7)-C(8)	107.62(15)
C(6)-C(7)-C(8)	110.91(15)
C(11)-C(7)-C(8)	108.41(15)
N(1)-C(8)-C(7)	112.18(16)
N(1)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8A)	109.2
N(1)-C(8)-H(8B)	109.2
C(7)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
N(2)-C(9)-N(1)	111.0(2)
N(2)-C(9)-H(9)	124.5
N(1)-C(9)-H(9)	124.5
N(3)-C(10)-N(2)	115.3(2)
N(3)-C(10)-H(10)	122.3
N(2)-C(10)-H(10)	122.3
C(12)-C(11)-C(7)	115.19(17)
C(12)-C(11)-H(11A)	108.5
C(7)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11B)	108.5
C(7)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
C(11)-C(12)-C(13)	113.15(19)
C(11)-C(12)-H(12A)	108.9
C(13)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12B)	108.9
C(13)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.8
C(14)-C(13)-C(12)	14.0(2)
C(14)-C(13)-H(13A)	108.8
C(12)-C(13)-H(13A)	108.8
C(14)-C(13)-H(13B)	108.8
C(12)-C(13)-H(13B)	108.8
H(13A)-C(13)-H(13B)	107.7
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(9)-N(1)-N(3)	109.30(18)
C(9)-N(1)-C(8)	130.03(19)
N(3)-N(1)-C(8)	120.51(15)
C(9)-N(2)-C(10)	101.97(19)
C(10)-N(3)-N(1)	102.37(19)
C(7)-O(1)-H(1A)	109.5

TABLE 5 : Anisotropic displacement parameters (A^2 x 10^3) for hexaconazole. 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)	41(1)	39(1)	45(1)	4(1)	12(1)	5(1)
C(2)	50(1)	48(1)	49(1)	1(1)	5(1)	-5(1)
C(3)	71(1)	43(1)	46(1)	-5(1)	13(1)	-1(1)
C(4)	67(1)	52(1)	59(1)	-7(1)	27(1)	10(1)
C(5)	45(1)	48(1)	56(1)	-3(1)	16(1)	3(1)
C(6)	42(1)	34(1)	41(1)	3(1)	13(1)	3(1)
C(7)	41(1)	40(1)	48(1)	-4(1)	12(1)	-1(1)
C(8)	53(1)	48(1)	46(1)	-5(1)	11(1)	5(1)
C(9)	44(1)	76(2)	65(1)	14(1)	3(1)	-3(1)
C(10)	81(2)	51(1)	84(2)	13(1)	20(1)	3(1)
C(11)	60(1)	39(1)	58(1)	-4(1)	23(1)	1(1)
C(12)	101(2)	50(1)	64(1)	3(1)	35(1)	12(1)
C(13)	103(2)	50(1)	70(2)	10(1)	31(1)	12(1)
C(14)	86(2)	54(2)	116(2)	10(2)	43(2)	3(1)
N(1)	44(1)	50(1)	42(1)	2(1)	6(1)	0(1)
N(2)	62(1)	75(2)	89(2)	31(1)	21(1)	19(1)
N(3)	59(1)	52(1)	69(1)	8(1)	4(1)	-6(1)
O(1)	44(1)	54(1)	72(1)	-15(1)	12(1)	-9(1)
Cl(1)	41(1)	69(1)	76(1)	-6(1)	17(1)	7(1)
Cl(2)	117(1)	68(1)	73(1)	-31(1)	18(1)	-7(1)

TABLE 6 : Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for hexaconazole

	x	y	z	U(eq)
H(2)	5	301	-1588	61
H(4)	3681	-182	-1439	69

	x	y	z	U(eq)
H(5)	4244	1306	-208	59
H(8A)	2992	2801	2280	59
H(8B)	1721	2197	1618	59
H(9)	4985	1258	2891	77
H(10)	3070	-1669	2004	87
H(11A)	1463	3901	476	61
H(11B)	2791	4489	1015	61
H(12A)	1903	3925	-1086	83
H(12B)	3298	4386	-568	83
H(13A)	1836	5941	-1436	88
H(13B)	1136	5808	-585	88
H(14A)	2913	6516	637	124
H(14B)	2541	7459	-264	124
H(14C)	3687	6564	-172	124
H(1A)	4562	3291	1341	69

TABLE 7 : Torsion angles [deg] for hexaconazole

C(6)-C(1)-C(2)-C(3)	0.4(3)
Cl(1)-C(1)-C(2)-C(3)	-178.56(16)
C(1)-C(2)-C(3)-C(4)	-0.1(3)
C(1)-C(2)-C(3)-Cl(2)	179.68(15)
C(2)-C(3)-C(4)-C(5)	-0.6(3)
Cl(2)-C(3)-C(4)-C(5)	179.70(16)
C(3)-C(4)-C(5)-C(6)	0.9(3)
C(4)-C(5)-C(6)-C(1)	-0.5(3)
C(4)-C(5)-C(6)-C(7)	177.38(18)
C(2)-C(1)-C(6)-C(5)	-0.1(3)
Cl(1)-C(1)-C(6)-C(5)	178.76(14)
C(2)-C(1)-C(6)-C(7)	-177.92(18)
Cl(1)-C(1)-C(6)-C(7)	1.0(3)
C(5)-C(6)-C(7)-O(1)	2.6(2)
C(1)-C(6)-C(7)-O(1)	-179.71(16)
C(5)-C(6)-C(7)-C(11)	123.39(19)
C(1)-C(6)-C(7)-C(11)	-58.9(2)
C(5)-C(6)-C(7)-C(8)	-113.70(19)
C(1)-C(6)-C(7)-C(8)	64.0(2)
O(1)-C(7)-C(8)-N(1)	-60.6(2)
C(6)-C(7)-C(8)-N(1)	54.4(2)
C(11)-C(7)-C(8)-N(1)	-179.31(15)
O(1)-C(7)-C(11)-C(12)	69.5(2)
C(6)-C(7)-C(11)-C(12)	-48.9(2)
C(8)-C(7)-C(11)-C(12)	-173.16(19)
C(7)-C(11)-C(12)-C(13)	-174.0(2)
C(11)-C(12)-C(13)-C(14)	71.7(3)
N(2)-C(9)-N(1)-N(3)	0.3(3)
N(2)-C(9)-N(1)-C(8)	-174.95(19)
C(7)-C(8)-N(1)-C(9)	83.2(3)
C(7)-C(8)-N(1)-N(3)	-91.6(2)
N(1)-C(9)-N(2)-C(10)	0.0(3)
N(3)-C(10)-N(2)-C(9)	-0.3(3)
N(2)-C(10)-N(3)-N(1)	0.5(3)
C(9)-N(1)-N(3)-C(10)	-0.4(2)
C(8)-N(1)-N(3)-C(10)	175.34(19)

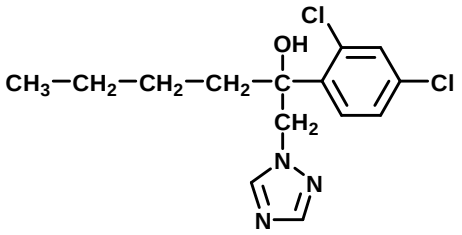

Figure 1 : Chemical structure of hexaconazole

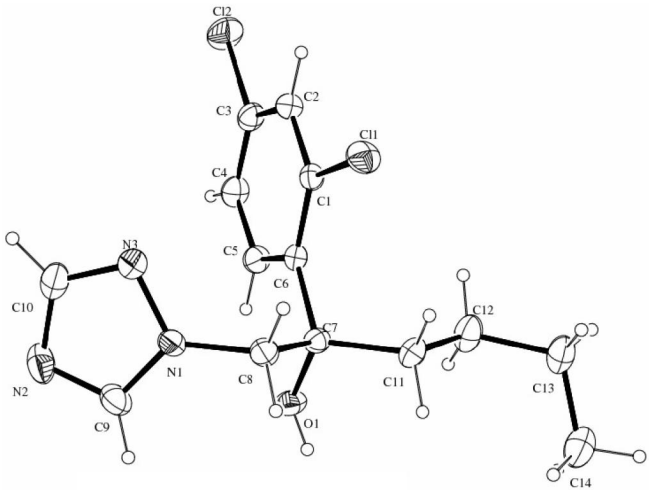

Figure 2 : ORTEP diagram of hexaconazole

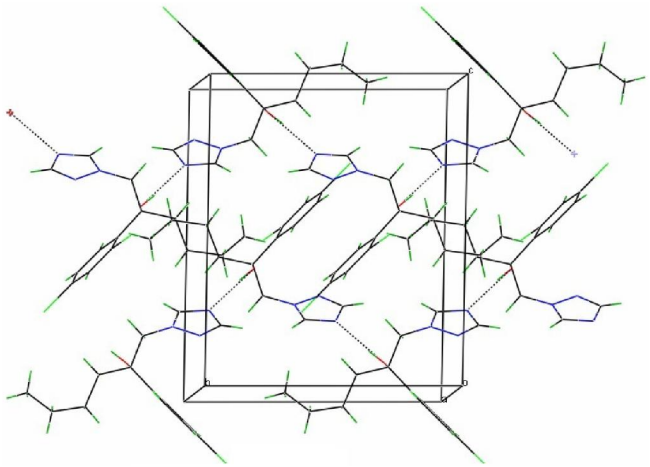

Figure 3 : Packing diagram of hexaconazole

Hydrogen bonding and molecular packing

The hydrogen bond parameters are given in

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TABLE 8. 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.

TABLE 8 : Hydrogen bonds for hexaconaxzole

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

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.

ACKNOWLEDGEMENT

I am thankful to SAIF IIT MADRAS for providing me Facility CAD-4Diffractometer and Lab and valuable help in Data collection.

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