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X-ray structure analysis of 1-(4-chlorophenoxy) 3,3-dimethyl-1-H(1,2,4 triazole-1-Y-1) -2-butanone

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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 1-(4-chlorophenoxy) 3,3-dimethyl-1-H(1,2,4 triazole-1-Y-1)-2-butanone is given in figure 2. The composition of these crystals are confirmed by comparing the infra-red spectra of the two components. The unit cell parameters $a = 8.16(10)\text{\AA}$ $b = 16.81(3)\text{\AA}$ $c = 22.05(2)\text{\AA}$. The space group is determined to be $P2_1/n$. The measured density is $1.291\mu\text{g}/\text{cm}^3$ and calculated density is $1.295\mu\text{g}/\text{cm}^3$.

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KEYWORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure.

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 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 1-(4-chlorophenoxy)3,3-dimethyl-1-H(1,2,4 triazole-1-Y-1)-2-butanone sample synthesized by Meiser at research center of Bayer AG in Wuppertal Elerfeld, West Germany which was initially tested under the code Bay MEB 6467.. Crystallization was done by slow evaporation from a solution of cyclohexanone at 287°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 TABEL 1.

Data collection and Structure Solution: The three

TABLE 1

Preliminary	Crystal data
Chemical name	1-(4-chlorophenoxy) 3, 3-dimethyl-1-H(1,2,4 triazole-1-Y-1)-2-butanone
Chemical formula	C ₁₄ H ₁₆ C ₁ N ₃ O ₂
System	Monoclinic
Space	P2 ₁ /n
A	8.16260(10)Å
B	16.8106(3)Å
C	22.0520(2)Å
α	90(1)°
β	92.37(1)°
γ	90(2)°
V	3023.35Å ³
Dm	1.291µg/cm ³
Dc	1.295µg/cm ³
Mw	293.75
Z	8
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(MoKα)	71073Å
No. of reflections measured	20912
No. of unique reflections	7542
Tempo crystal during data collection	03°K
Theta range	1.52-29.48°
absorption coefficient	257mm ⁻¹
Lp correction	Applied
Absorption correction	Not applied

dimensional intensity data were collected on a computerized automatic 4-circle CAD-4 Enraf-Nonious diffractometer using graphite filtered MoKα (Å) radiation's at Deptt. of Biophysics AIIMS, New Delhi. Temperature of crystal during data collection was 303°K. All the data were corrected for lorentz and polarization effect, but no absorption correction were applied.

Three standard reflection were measured where h various -7 to 11, K from -21 to 21 and I from -26 to 28. The total number of reflections were 20912, out of which unique reflection were 7542. 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. The crystal is monoclinic having space group P2₁/n

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)
Cl(1A)	-80(1)	6330(1)	1095(1)	90(1)
O(1A)	3916(2)	3437(1)	1028(1)	51(1)
O(2A)	5953(2)	2041(1)	1004(1)	64(1)
N(1A)	3876(2)	2622(1)	1898(1)	46(1)
N(2A)	3675(3)	2790(1)	2494 (1)	61(1)
N(3A)	2306(3)	1670(1)	2225(1)	80(1)
C(1A)	3027(2)	4131(1)	1087(1)	41(1)
C(2A)	2635(3)	4468(1)	1634(1)	50(1)
C(3A)	1691 (3)	5156(1)	1636(1)	55(1)
C(4A)	1145(3)	5488(1)	1097(1)	53(1)
C(5A)	1556(3)	5156(1)	551(1)	55(1)
C(6A)	2495(3)	4480(1)	544(1)	51(1)
C(7A)	4853(2)	3134(1)	1535(1)	42(1)
C(8A)	3040(3)	1958(1)	1753(1)	69(1)
C(9A)	2750(4)	2195(2)	2656(1)	74(1)
C(10A)	6245(3)	2685(1)	1217(1)	46(1)
C(11A)	7866(3)	3113(1)	1179(1)	57(1)
C(12A)	8705(3)	3096(2)	1812(1)	80(1)
C(13A)	7585(4)	3982(2)	977(1)	80(1)
C(14A)	8935(4)	2690(2)	725(2)	103(1)
Cl(1B)	60(1)	1302(1)	4111(1)	91(1)
O(1B)	-3826(2)	4234(1)	4083(1)	52(1)
O(2B)	-5981(2)	5624(1)	4026(1)	68(1)
N(1B)	-3838(2)	4991(1)	3183(1)	44(1)
N(2B)	-3753(3)	4827(1)	2583(1)	62(1)
N(3B)	-2356(3)	5949(1)	2819(1)	81(1)
C(1B)	-2944(3)	3531(1)	4047(1)	42(1)
C(2B)	-2586(3)	3153(1)	3513(1)	48(1)
C(3B)	-1673(3)	2461(1)	3536(1)	52(1)
C(4B)	-1111(3)	2166(1)	4085(1)	51(1)
C(5B)	-1463(3)	2540(1)	4619(1)	56(1)
C(6B)	-2388(3)	3226(1)	4602(1)	51(1)
C(7B)	-4779(2)	4493(1)	3572(1)	42(1)
C(8B)	-2864(4)	5427(2)	2398(1)	76(1)
C(9B)	-2984(3)	5653(1)	3310(1)	69(1)
C(10B)	-6189(3)	4946(1)	3870(1)	48(1)
C(11B)	-7764(3)	4493(1)	3953(1)	63(1)
C(12B)	-8625(4)	4421(2)	3314(1)	94(1)
C(13B)	-8879(4)	4958(2)	4347(2)	125(2)
C(14B)	-7432(4)	3657(2)	4187(2)	110(1)

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 0.123. Further refinement of the structure was carried out with individuals an isotropic temperature factors of the exponential form.

$-2P_1 \wedge 2[h \wedge 2a \wedge 2U_{11} + \dots + 2hKa \wedge bxU_{12}$
reduced R factor to 0.101. The hydrogen atoms were

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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 0.0569 for all 20912 reflections collected. Fractional coordinates of non-hydrogen atoms and the equivalent isotropic thermal parameter are listed in TABLE 2

RESULTS AND DISCUSSION

The perspective view of the molecule and numbering scheme is shown in figure 2 and ORTEP drawing is shown in figure 3.

The average bond distance of C-H is 0.95Å. The bond lengths and angles in the benzene ring show regular features in both the molecules. The Cl(1A)-C(4A) and Cl(1B)-C(4B) distances are 1.733Å and 1.738Å 'comparable to other structure'. These distances are short and this may be due to delocalization of electrons from the benzene rings. The whole molecules appeared to be twisted and folded and reason may be stacking-constraint. The bond distances around C(7A) and C(7B) are usual shorter than single bond values. They may also appear to bear a partial double bond character. The O(1A)-C(7A) and O(2B)-C(7B) distances are 1.423(2)Å and 1.411(2)Å respectively. These distances do not change significantly in similar structures, despite variable intermolecular interactions through them. The bond distances in the triazol rings are comparable to corresponding distances in heterocyclic rings 1.339(Å). The average set of data by Spencer are 1.377Å and 119° respectively.

The dimensions of the methyl groups are normal and comparable with those in 0-methyl obtusaquinone and moscaline hydrobromide.

The molecule is found to adopt a conformation such that the triazolyl ring is inclined at an angle of 72.9(9)° to the aromatic ring and at an angle of 61.5(9)° to the O(1A), C(7A) group. The resulting arrangement leads to the approach of the ortho-H, H(2A) to the triazolyl ring, atoms N(1A) and N(2A) such that both N...H distances lie within the sum of the Van der Waals radii of N and H. There was an accompanying distortion of the exocyclic angles at C(1A) with the C(2A)-C(1A)-O(1A) bond

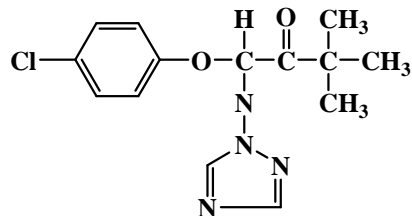


Figure 1: 1-(4-Chlorophenoxy) 3,3-dimethyl-1-H(1,2,4-triazole-1Y-1)-2butanone

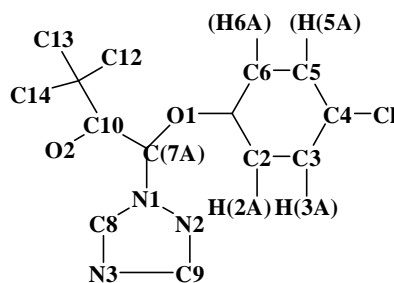


Figure 2: Molecular numbering scheme of triadimafon



Figure 3: ORTEP drawing at 50% probability level

angle of 124.65(17)° being considerably larger than the value found for O(1A)-C(1A)-C(6A) 114.97(17)°.

The triazolyl ring is planar with C(7A) lying only 0.063(7)Å from the mean plane. Although the C(8A) and C(9A)-N(3A) distances are somewhat larger than C(8A)-N(3A) and C(9A)-N(2A), in keeping with the uncharged canonical valence form. All four C-N dis-

TABLE 3: Torsion angles [deg] for TRIMEEFON

C(8A)---N(1A)---N(2A)---C(9A)	1.2 (3)
C(7A)—N(1A)—N(2A)—C(9A)	-179.4 (2)
C(7A)—O(1A)—C(1A)—C(2A)	-16.5 (3)
C(7A)---O(1A)—C(1A)—C(6A)	164.77 (17)
O(1A)—C(1A)—C(2A)—C(3A)	-178.10 (19)
C(6A)—C(1A)—C(2A)—C(3A)	0.5 (3)
C(1A)—C(2A)—C(3A)—C(4A)	0.7 (3)
C(2A)---C(3A)—C(4A)---C(5A)	-1.5 (4)
C(2A)—C(3A)—C(4A)—C(1A)	178.23 (17)
C(3A)—C(4A)—C(5A)—C(6A)	1.1 (3)
Cl(1A)—C(4A)—C(5A)—C(6A)	-178.63 (17)
C(4A)—C(5A)—C(6A)—C(1A)	0.1 (3)
C(2A)—C(1A)---C(6A)---C(5A)	-0.9 (3)
O(1A)—C(1A)—C(6A)—C(5A)	177.82 (18)
C(1A)—O(1A)—C(7A)—N(1A)	87.8 (2)
C(1A)—O(1A)—C(7A)—C(10A)	-151.70 (17)
C(8A)—N(1A)—C(7A)—O(1A)	57.8 (3)
N(2A)—N(1A)—C(7A)—O(1A)	-121.47 (19)
C(8A)—N(1A)—C(7A)—C(10A)	-55.5 (3)
N(2A)—N(1A)—C(7A)—C(10A)	125.2 (2)
C(9A)—N(3A)—C(8A)—N(1A)	0.0 (3)
N(2A)—N(1A)--C(8A)—N(3A)	-0.8 (3)
C(7A)—N(1A)—C(8A)—N(3A)	179.9 (2)
N(1A)-N(2A)--C(9A)-N(3A)	-1.3 (3)
C(8A)—N(3A)—C(9A)—N(2A)	0.8 (3)
O(1A)--C(7A)—C(10A)—O(2A)	-78.6 (2)
N(1A)—C(7A)—C(10A)—O(2A)	40.4 (3)
O(1A)—C(7A)—C(10A)—C(11A)	99.17 (19)
N(1A)---C(7A)---C(10A)---C(11A)	-141.81 (19)
O(2A)-C(10A)---C(11A)--C(12A)	-108.0 (3)
C(7A)—C(10A)—C(11A)—C(12A)	74.3 (2)
O(2A)—C(10A)—C(11A)—C(14A)	11.6 (3)
C(7A)—C(10A)—C(11A)---C(14A)	-166.0 (2)
O(2A)—C(10A)---C(11A)---C(13A)	132.4 (2)
C(7A)—C(10A)---C(11A)---C(13A)	-45.2 (2)
C(9B)—N(1B)—N(2B)—C(8B)	-1.2 (3)
C(7B)—N(1B)—N(2B)—C(8B)	177.4 (2)
C(7B)—O(1B)—C(1B)—C(2B)	16.8 (3)
C(7B)—O(1B)—C(1B)—C(6B)	-164.68 (18)
C(6B)—C(1B)—C(2B)—C(3B)	0.4 (3)
O(1B)—C(1B)—C(2B)—C(3B)	178.92 (19)
C(1B)—C(2B)—C(3B)—C(4B)	-1.1 (3)
C(2B)—C(3B)—C(4B)—C(5B)	1.1 (3)
C(2B)—C(3B)—C(4B)—C(1B)	-179.17 (16)
C(3B)—C(4B)—C(5B)—C(6B)	-0.4 (3)
C(1B)—C(4B)—C(5B)—C(6B)	179.84 (17)
C(4B)—C(5B)—C(6B)—C(1B)	-0.2 (3)
C(2B)—C(1B)—C(6B)—C(5B)	0.2 (3)
O(1B)—C(1B)—C(6B)—C(5B)	-178.40 (19)
C(1B)—O(1B)—C(7B)---N(1B)	-89.6 (2)
C(1B)—O(1B)—C(7B)—C(10B)	149.76 (17)
C(9B)—N(1B)—C(7B)—O(1B)	-54.7 (3)
N(2B)—N(1B)—C(7B)—O(1B)	127.01 (19)
C(9B)—N(1B)—C(7B)—C(10B)	59.3 (3)

tances are shorter than a normal single bond (1.47Å).

The N(1A)-N(2A) bond is also shorter than a normal single bond (1.45Å). 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) [$\pm 30.80^\circ$]. 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 C(11A), C(10A), C(7A), O(1A), C(1A) backbone is rather compressed resulting in the main from the orientation of the tert-butyl group, the C(11A)-C(10A)-C(7A)-O(1A) torsion being only $99.17(19)^\circ$. From the least square plane equation by Blow's method, the benzene and triazolyl rings are partially planner since the atomic displacements are much less than their e.s.d's. The triazolyl ring is inclined to the aromatic ring at an angle of $72.9(9)^\circ$. Torsion angles calculated are given in TABLE 3.

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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