March 2008 Volume 7 Issue 5

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ 7(5) 2008 [328-331]

X-ray crystallographic studies on 3,5-dimethyl 1,3,5-thiadiazine-2-thione

Rachna Tiwari[1], Jyotsna Chauhan*[1], R.K.Tiwari[2]

[1]Lecturer in physics department in Rajeev Gandhi Technical University, Airport Bypass Road, Gandhi Nagar, Bhopal-462036, (INDIA)

[2]Reader in Physics Department in Jiwaji University, Airport Bypass Road, Gwalior, (INDIA)

Phone: 0755-2677343, 0755-2678812; Fax: 0755:2742006/2

E-mail: jyotsnachauhan2006@gmail.com

Received: 23rd June, 2007 ; Accepted: 28th June, 2007

ABSTRACT

It has been observed that some of these fungicides are loosing their effects and becoming resistant to them. 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 3, 5-dimethyl 1,3,5-thiadiazine-2-thione crystals are confirmed by comparing the infra-red spectra of the two components. The Unit cell parameters are a=6.4270(10)Å, b=6.4270(10)Å, c=32.8890(10) Å and Z=6. Thus the space group is determined to be $P6_1$ and crystal of hexagonal system.

© 2008 Trade Science Inc. - INDIA

KEYWORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure.

INTRODUCTION

Basamid a fungicidal compound is classified as a chemical soil sterile. It's IUPAC name is 3,5-dimethyl 1,3,5-thiadiazine-2-thione or tetrahydro-3, 5-dimethyl-1, 3, 5-thiadiazine-2-thione, it's molecular formula is $C_5H_{10}N_2S_2$ and molecular weight is 162.3. Basamid granular, when worked into the soil, nematicidal, fungicidal and herbicidal effects. It possesses a broad spectrum of activity and is almost equivalent in its effect to steam sterilization. It's solubility in water is 3gm/kg (20°C), in cyclohexane 400, in chloroform 391, in acetone 173, in benzene 51, in ethanol 15(all in g/kg, 20°C). Basamid is stable at temperature up to 35°C, sensitive to temperature >50°C, and to moisture. It hydrolyzed in acidic medium to carbon disulfide, formaldehyde and methyl amine The chemical structure of Basamid is shown in figure 1.

EXPERIMENTAL

Basamid was originally prepared by M. Delepine later introduced as a soil fumigant. 3.5-dimethyl-1,3,5-thiadiazinane is developed under the code N-521 by

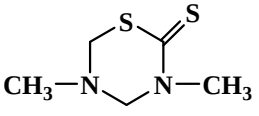

Figure 1: 3,5-dimethyl 1,2,5-thiadiazine-2-thione

TABLE 1 : Crystal data and structure refinement for Basamid

Identification code	Basamid	
Empirical formula	$C_5H_{10}N_2S_2$	
Formula weight	162.27	
Temperature	293(2)K	
Wavelength	1.54178A	
Crystal system, space group	Hexagonal, P61	
Unit cell dimensions	a=6.4270(10)A b=6.4270(10) A c=32.8890(10) A	alpha=90deg. beta=90deg. gamma=120deg.
Volume	1176.5 (3)A^3	
z, Calculated density	6, 1.374mg/m^3	
Absorption coefficient	5.478mm^-1	
F(000)	516	
Crystal size	0.3×0.2×0.1 mm	
Theta range for data collection	7.96 to 69.77 deg.	
Limiting indices	O<=h<=6,O<=k<=6, O<=1<=38	
Reflections collected/unique	743/743 [R (int) =0.0000]	
Completeness to theta = 69.77	98.7	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/ parameters	743/1/83	
Goodness-of-fit on F^2	0.927	
Final R indices [I>2sigma(I)]	R1=0.0310, wR2=0.0993	
R indices (all data)	R1=0.0328, wR2=0.1019	
Absolute structure parameter	0.28(4)	
Extinction coefficient	0.0035 (13)	
Largest diff. peak and holes	0.190 and -0.345e.A^-3	

Staufter Chemical Company. Commercially it is known as Dazomet, DMTT and BASF. Crystals were obtained by slow evaporation from a solution of acetone at 303°K. The crystals were colourless and hexagonal in shape. The unit cell parameters were determined by automatic computerized 4-circle Enraf-Nonious CAD=4 diffractometer. The parameters are a=6.4270 (10)Å b=6.4270(10)Å, c=32.8890(10)Å γ= 20º and Z=6. The space group is P6 and crystal belongs to hexagonal crystal system. The density of the crystal is determined by floatation method at room temperature. The measured and calculated density was 1.298 mg/m^3 and 1.374 mg/m^3 The preliminary information about the crystal is given in TABLE 1.

Data collection and structure solution

TABLE 2 : Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2×10^3) for Basamid. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atom	x	y	z	U (eq)
S (1)	5509 (2)	68 (2)	1330 (1)	53 (1)
S (2)	5586 (2)	1886 (2)	2130 (1)	56 (1)
N (1)	9586 (5)	2606 (6)	1767 (1)	40 (1)
N (2)	9732 (6	149 (7)	1207 (1)	48 (1)
C (1)	10995 (7)	2260 (8)	1441 (1)	47 (1)
C 92)	7229 (7)	1698 (7)	1761 (1)	41 (1)
C (3)	7781 (7)	133 (9)	994 (1)	54 (1)
C (4)	11063 (8)	4120 (8)	2102 (1)	52 (1)
C (5)	9054 (10)	-2078 (9)	1426 (2)	68 1)

A computerized 4-circled CAD-4 Enraf-Nonious diffractometer was used to collect the three dimensional intensity data. This diffractometer used graphite filter at the department of Biophysics, AIIMS, New Delhi. During the data collection temperature of the crystal was 293(2)ºK. All the data were corrected for Lorentz and polarization effect, but no. absorption correction was applied. The total numbers, of reflection were 743. The unique reflections corresponding to limit were 743. Some standard reflections were measured for which h varies from 0 to 6, k from 0 to 6 and I varies from 0 to 36. Each intensity measurement involved in a scan over the reflection peak, a background' measurement at each end of the scan range,and a measurement of the peak height. The crystal belongs to hexagonal system having space group P61: SHELX-97 programme was used to solve the structure of the crystal.

Refinement

The positional co-ordinates obtained from the SHELX-97 programme for the crystal structure solution, were subjected to refinement by SHELXL-97 refinement programme with their isotropic temperature factor. After so many cycles of refinement the R factor dropped to 0.0328. Further refinement of the structure was carried out with individuals anisotropic temperature factors of the exponential form

-2PiA2 [+2hka*b*U12]

reduced R factor to 0.0310. The hydrogen atoms were fixed at this stage by geometrical consideration and were not refined. Refinement of the structure was terminated after two more cycles when all the deviations in parameters became much smaller the corresponding estimated standard deviations. The final R value was 0.0310 for

Full Paper

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

Atom	U11	U22	U33	U23	U13	U12
S (1)	39 (1)	73 (1)	51 (1)	- 11 (1)	- 10 (1)	30 (1)
S (2)	54 (1)	77 (1)	51 (1)	- 4(1)	2 (1)	45 (1)
N (1)	35 (1)	46 (2)	40 (2)	-1 (1)	- 4(1)	21 (1)
N (2)	39 (2)	53 (2)	50 (2)	- 1 (2)	7 (1)	22 (1)
C (1)	38 (2)	56 (2)	44 (2)	- 1 (2)	3 (2)	22 (2)
C (2)	41 (2)	46 (2)	44 (2)	0 (2)	- 5 (2)	28 (1)
C (3)	47 (2)	63 (3)	44 (2)	-5 (2)	0 (2)	20 (2)
C (4)	47 (2)	53 (2)	54 (2)	-9 (2)	- 9(2)	23 (2)
C (5)	67 (3)	59 (3)	88 (40	9 (3)	15 (3)	39 (2)

TABLE 4 : Bond lengths (Å) with estimated standard deviation in parenthesis

S (1) -C (2)	1.781 (4)
S (1) -C (3)	1.815 (4)
S (2) -C (2)	1.653 (4)
N (1) -C (2)	1.323 (5)
N (1) -C (4)	1.464 (5)
N (1) -C (1)	1.489 (5)
N (2)-C (1)	1.411 (6)
N (2)-C (3)	1.431 (5)
N (2)-C (5)	1.461 (6)
C (1)-H (1a)	0.9599
C (1)-H (1b)	0.9600
C (3)-H (3a)	0.9599
C (3)-H (3b)	0.9601
C (4)-H (4a)	0.9599
C (4)-H (4b)	0.9599
C (4)-H (4c)	0.9600
C (5)-H (5a)	0.9599
C (5)-H (5b)	0.9599
C (5)-H (5c)	0.9600

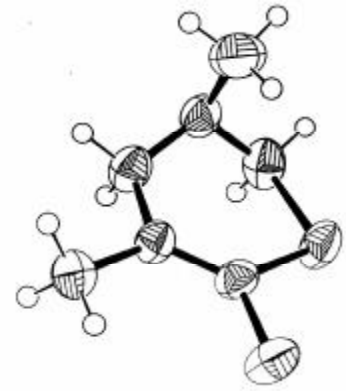

Figure 2: ORTAP diagram for figure 1

all 743 reflections collected. The final positional and thermal parameters of non-hydrogen atoms with fixed isotropic temperature factors listed in TABLES 2 and 3 respectively. The TABLES 4 and 5 list the bond lengths and angles respectively. The torsion angles are given in TABLE 6.

TABLE 5: Bond angles (degree) with estimated standard deviation in parenthesis

C(2)-S(1)-C(3)	102.43(18)
C(2)-N(1)-C(4)	121.5(3)
2(C)-N(1)-C(1)	124.9*(3)
C(4)-N(1)-C(1)	113.6(3)
C(1)-N(2)-C(3)	110.7(3)
C(1)-N(2)-C(5)	114.8(4)
C(3)-N(2)-C(5)	113.8(4)
N(2)-C(1)-N(1)	115.8(3)
N(2)-C(1)-H(1a)	108.5
N(1)-C(1)-H(1a)	108.8
N(2)-C(1)-H(b)	108.2
N(1)-C(1)-H(1b)	107.6
H(1a)-C(1)-H(1b)	107.6
N(1)-C(2)-S(2)	126.2(3)
N(1)-C(2)-S(1)	120.5(3)
S(2)-C(2)-S(1)	113.4(2)
N(2)-C(3)-S(1)	113.2(3)
N(2)-C(3)-H(3a)	108.8
S(1)-C(3)-H(3a)	108.6
N(2)-C(3)-H(3b)	109.2
S(1)-C(3)-H(3b)	109.1
H(3a)-C(3)-H(3b)	107.8
N(1)-C(4)-H(4a)	109.2
N(1)-C(4)-H(4b)	109.4
H(4a)-C(4)-H(4a)	109.5
H(4b)-C(4)-H(4c)	109.5
N(2)-C(5)-H(5a)	109.3
N(2)-C(5)-H(5b)	110.0
H(5a)-C(5)-H(5b)	109.5
N(2)-C(5)-H(5c)	109.0
H(5)a)-C(5)-H(5c)	109.5
H(5b)-C(5)0H(5c)	109.5

TABLE 6: Torsion angles (deg) for Basamid

C(3)-N(2)-C(1)-N(1)	61.8(5)
C(5)-N(2)-C(1)-N(1)	-68.7(5)
C(2)-N(1)-C(1)-N(2)	-26.(6)
C(4()-N(1)-C(1)-N(2)	154.8(4)
C(4)-N(1)-C(2)-S(2)	-5.7(5)
C(1)-N(1)-C(2)-S(2)	175.4(3)
C(4)-N(1)-C(2)-S(1)	174.9(3)
C(1)-N(1)-C(2)-S(1)	-4.0(5)
C(3)-S(1)-C(2)-N(2)	0.7(24)
C(3)-S(1)-C(2)-S(2)	-178.8(2)
C(1)-N(2)-C(3)-S(1)	-63.8(4)
C(5)-N(12)-C(3)-S(1)	67.3(5)
C(2)-S(1`)-C(3)-N(2)	31.9(4)

RESULT AND DISCUSSION

The ORTEP Diagram is shown in figure 2. Since thiadiazine-2-tiones have not been subjected to experi-

TABLE 7: Torsion angles(R>Perez et al 2001) present work

(R>Perez et al 2001)	Present work		Torsion angles
	X-ray	AM1	
C(3)-S(1)-C(23)-S(2)	178.3(2)	174.6	-178.8(2)
C(3)-S(10-C(2)-N(1)	-1.1(3)	-6.9	0.7(4)'
C(2)-S(1)-C(3)-N(2)	-25.8(2)	-20.2)	31.9(4)
S(1)-C(2)-N(1)-C(1)	-4.8(4)	2.8	-4.0(5)
S(1)-C(2)-N(1)-C(4)	177.1(2)	177.3	174.9(3)
S(2)-C(2)-N(1)-C(1)	175.8(12)	-178.8	175.4(3)
S(2)-C(2)-N(1)-C(4)	-2.3(4)	-4.3	-5.7(5)
C(2)-N(1)-N(2)	39.1(3)	30-.1	-26.3(6)
C(4)-N(1)-C(1)-N(2)	-142.8(2)	-144.7	154.(8)
N(1)-C(1)-N(2)-C(3)	-67.4(3)	-57.8	61.8(5)
C(1)-N(2)-C(3)-S1)	59.3(3)	50.7	-63.8(4)

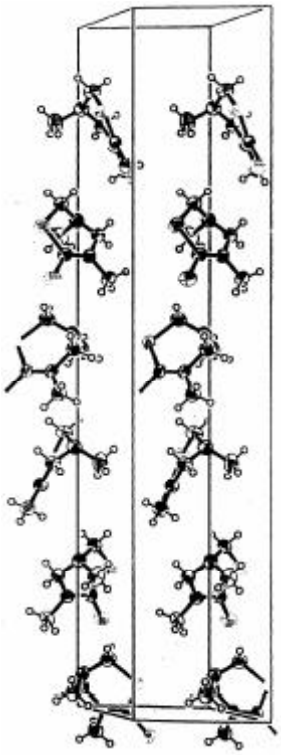

Figure 3 : The molecular packing seen down b-axis

mental structure examinations; we could locate only one similar work. We can obtain reliable structural information for this type of compounds by using theoretical calculations at the semi empirical AM1 quantum-chemical calculations and experimental X-ray analysis and NMR spectroscopic measurement: Also, we carried out ab.initio Hartee-Fock. Calculations taking into account the AM1 results. The bond distances and angles in our measurement are well in agreement what have been Observed by R.Perez et al. (2001). We have tabulated our results along with their findings, in TABLE 7. As expected the inner ring angles vary from 102.4(2)° to 124.9(3)c. The bond lengths show usuai character throughout the structure R.Perez et al.[4] have shown that in thiadiazine-2-thione ling shows an envelope conformation in which the N atom lies out of the plane while the rest of the atoms are co-planner. The most important conformational changes that the given an envelope conformation can undergo are concerned with ring inversion, where N can be either above or below the mean plane, as well as the N inversion which leads to situation in which the substituents attached at N can be either in an axial or in equivatorical position.The packing diagram is shown in figure 3.

ACKNOWLEDGMENT

The financial assistance provided by Deptt of Science and Technology (D. S. T), New Delhi in form Junior Research Fellow is gratefully acknowledged. Iam thankful to Prof T. P Singh Head Deptt of Biophysics, AIIMS, New Delhi for providing me National Facility CAD-4Diffractometer and Lab. Iam also thankful to Prof. D. Vellmurgan, UNIV OF MADRAS for his valuable help in Data collection

REFERENCES

[1] M.Delepine; Bull.Soc.Chim.Fr., **15**, 891 **(1897)**.
[2] G.M.Sheldrich; SHELXS-97 Programme for The Solution of Crystal Structure, **(1997)**.
[3] G.M.Sheldrich; SHELXL-97, Programme for Crystal Refinement, **(1997)**.
[4] R.Perez et al.; Tetrahedron, **57**, 7361-7367 **(2001)**.