Research Journal of Agriculture and Biological Sciences, 3(6): 990-993, 2007

Comparative X-Ray structure analysis of systemic fungicides Tetra Methyl Thiuram Disulphide And 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione

Jyotsna Chauhan

Physics Department, Rajeev Gandhi Technical University.

Abstract: The compositions of Tetra methyl thiuram disulphide crystals are confirmed by comparing the infra-red spectra of the two components. The Unit cell parameters are a=6.9130(10)Å, b=6.9250(10)Å c=11.8020(10)Å and α=96.57˚β=96.57˚ γ=91.61˚ with Z=2.The space group is P1 and system is Triclinic. The structures of 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione compounds can be obtained by X-ray diffraction method in crystalline form and they will invariably be similar to their structure in solutions. The Unit cell parameters are a=6.4270(10) Å, b=6.4270(10) Å, c=32.8890(10) Å and α=90˚ β=90˚ γ=120˚ with Z=6. Thus the space group is determined to be $P6_1$ and crystal of hexagonal system. We can see that there are some differences in unit cell parameters in both the crystals. We will see how these differences affect the systemic fungicides activity. We compare the structures of both the systemic fungicides. Thus we determine the three-dimensional structure, molecular dimensions, molecular geometry, electronic structure and the conformation of fungicides and analyze their crystal structures also. Then correlate the chemical activity by substituting the chemically active groups at the crucial sites of the model fungicide to enhance chemical affinity and introduce conformational changes in the fungicides to make than more effective, active and to some extent cheaper.

Key words: X-ray crystallography, Systemic fungicides, Triazole structure

INTRODUCTION

Recently 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

MATERIALS AND METHODS

Crystals of Tetra methyl thiuram disulphide are grown at 20^0 -$25^0$from its solution in acetone by slow evaporation method. The unit cell parameters are determined directly by automatic computerized 4 - circled Enraf Nonious CAD-4 diffractometer in ω-2θ scan mode. Crystals of 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione are obtained by slow evaporation from a solution of acetone at 303°K

Data Collection and Structure Solution: The three dimensional intensity data are collected on a computerized automatic 4-circled CAD-4 Enraf-Nonious diffractometer and the crystal structure is solved using the SHELXS-97.

Refinement: For determination of structure of the crystal VAX machine using SHELXS-97° is used. In the beginning all the non-hydrogen atom are located. The coordinates thus obtained are fed to SHELXL-97 for refinement. The final R index of is 13.46% for all the 2064 reflections collected for Tetra methyl thiuram disulphide. The final R value is 0.0310 for all 743 reflections collected for 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione.

RESULT AND DISCUSSION

The ORTEP diagram of Tetra methyl thiuram disulphide is shown in fig 1 and the ORTEP diagram of 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione is shown in fig 2. Bond length for THIRAM is given in Table 1 and Bond Angles in Table 2. Bond length for 3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione is given in Table 3 and Bond Angles in Table 4. The molecule of Tetra methyl thiuram disulphide consists of two diethyl, dithiocarbamato moieties connected through S(2)-S(3). The S (2)-S (3) bond length is of 2.0077(16) A. The conformation of the molecule is similar to that of

Corresponding Author: Jyotsna Chauhan, Physics Department, Rajeev Gandhi Technical University.
Email: jyotsnachauhan2006@gmail.com

Table 1: Bond length [Å] with estimated standard deviation in parenthesis for THIRAM

S (1) - C (2)	1.648 (3)
S (2) - C (1)	1.807 (4)
S (2) - S(3)	2.007 (16)
S (3) - C (2)	1.814(4)
S (4) - C (1)	1.652(4)
N (1) - C (2)	1.313 (5)
N (1) - C (4)	1.461(7)
N (1) - C (3)	1.471 (6)
N (2) - C (1)	1.312(5)
N (2) - C (6)	1.449(7)
N (2) - C (5)	1.463(6)

Table 2: Bond Angle [Degree] with estimated standard deviation in parenthesis for THIRAM

C (1) -S (2) - S(3)	104.21(9)
C (2) -S (3) - S(2)	104.16 (2)
C (2) -N (1) -C (4)	121.8(4)
C (4) -N (1) -C (3)	125.0 (4)
C (1) -N (2) -C (6)	124.6 (2)
C (1) -N (2) - C (5)	121.2(2)
C (6)- N (2) - C (5)	114.2(4)
N (2) - C (1) -S (4)	125.5(2)
N (2) - C (1) -S (2)	111.8(4)
S (4) - C (1) -S(2)	122.8(2)
N (1) - C (2) -S(1)	125.5(2)
N (1) - C (2) -S(3)	111.7(4)
H (3A) -C (3) - H (3B)	108.1(2)
S (1) - C (2) - S (3)	122.7(2)

Table 3: 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)

Table 4: 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)
C(2)-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(1)
N(1)-C(1)-H(1a)	108.8(2)
N(2)-C(1)-H(b)	108.2(2)
N(1)-C(1)-H(1b)	107.6(1)
H(1a)-C(1)-H(1b)	107.6(2)
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(1)
S(1)-C(3)-H(3a)	108.6(3)
N(2)-C(3)-H(3b)	109.2(3)
S(1)-C(3)-H(3b)	109.1(1)
H(3a)-C(3)-H(3b)	107.8(3)
N(1)-C(4)-H(4a)	109.2(3)
N(1)-C(4)-H(4b)	109.4(3)
H(4a)-C(4)-H(4a)	109.5(1)
H(4b)-C(4)-H(4c)	109.5(1)
N(2)-C(5)-H(5a)	109.3(2)
N(2)-C(5)-H(5b)	110.0(2)
H(5a)-C(5)-H(5b)	109.5(1)
N(2)-C(5)-H(5c)	109.0(2)
H(5)a)-C(5)-H(5c)	109.5(1)
H(5b)-C(5)0H(5c)	109.5(2)

thiram monosulphide and even more so that of several sulphides. This is also a good ideal system for the study of deformation density. For the reasons, the molecule contains various C-N, C-S, S-S bonds. If the molecule is dividing along S (2)-S (3) bond in two equal halves, it shows symmetry in parameters. Each of the two dimethyldithiocarbamato crystals approximately planner. The dihedral angle around S (2)-S (3) bond is - 88.38(17) °. The length of the C-N and terminal C-S bonds are intermediate between the values expected for single and double bonds, indicating that the canonical form II makes a substantial contribution of the structure. The high double bond character of these bonds also affects the C-N stretching frequencies of the infrared spectrum, which were shifted considerable towards higher frequency from the normal C-N region. It is interested to see that no difference greater than 3σ between corresponding bond angles at Sp^2- hybridized atoms is observed in tetraethyl-thiuram disulphide and dicyclopentamethylenethiuram disulphide. It may be. Added that in tetramethylthiuram disulphide the two halves of the molecules are required to be equivalent by space group-symmetry. In these molecules, the terminal 5 atoms of each dithiocarbamato crystal is 3.8-3.9 from the central, Sp^2 –hybridized C of the other moiety. Strong intra-molecular non- bonded interactions and structural non-equivalence of the two halves of the molecule seen to be peculiar of the thiuram monosculphides.It is of interest to see the two C-S 'double' bonds happen to have exactly equal length 1.648(3) and 1.652(4), and the length of two central C- N bonds are equal within experimental error [1.313(5) and 1.312(5)]. Also the lengths of the four N-CH_3 bonds are in reasonable agreement. It is well known that among the several factors affecting the values of bond angles is Sp^2= (and Sp^3) hybridized centers. An important role is played by the repulsions between bonding (non-bonding) electron pairs in the valence shell of the central atom. In a survey of the molecular geometries of urea derivatives the value of the N-C-N angles has been found to increase regularly with the length of opposite bond. C-O. This result is easily accounted in terms of varying repulsions between bonding electron pairs in valance cell of C.

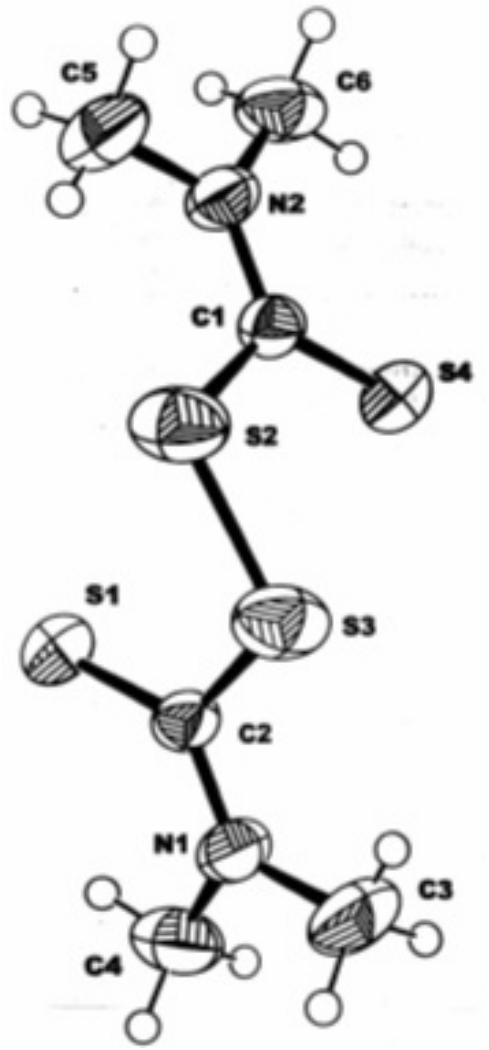

Fig. 1: ORTEP Drawing at 50% probability level.

3, 5-dimethyl 1, 3, 5-thiadiazine-2-thione have not been subjected to experimental 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 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.*[8]. As expected the inner ring angles vary from 102.4(2) ° to 124.9(3) °. The bond lengths show usual character throughout the structure R. Perez *et al.*[8] 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.

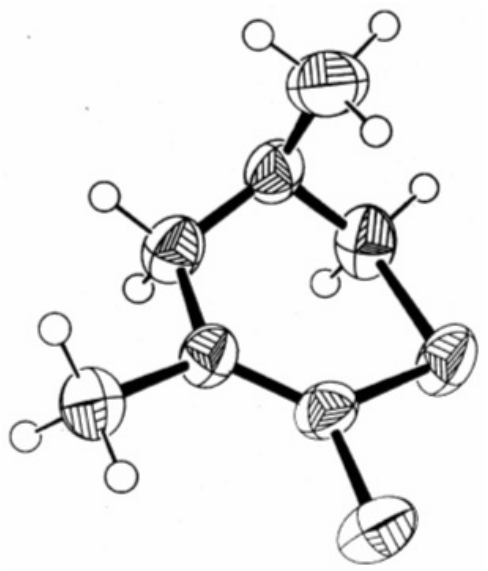

Fig. 2: 3,5-dimethily 1,3,5 thiadiazine-2-thione

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

Thus we compare 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.

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. Maroy, K., 1965. Acta Chern Scand., 19: 1509.
2. Mareello, C, D. Aldo and V Hessandro, 1976. Acta Cryst., B32, 2581.
3. Domenicano, A., J.A. and C.A. Coulson, 1974. Second Eur. Crystallogr. Meet., Kerzlney. Hungary. Abstracts, 436-438.
4. Bandoli, G., DA Clemente, E. Tondello and A. Dondoni, 1974. J. Chem. Soc. Perkin II, 157-160.

5. Heijden, S.P., N. Vander, W.D. Chandler and Robertson, B.E. Canad, 1975. J. Chem., 53: 2102-2107.
6. Stephens, F.S., 1970. J Chem. Soc. (A), 843-1846.
7. Delepine M., 1897. Bull. Soc. Chim. Fr., 15: 891.
8. Perez, R., *et al.,* 2001. Tetrahedron, 57: 7361-7367.
9. Kolbe, W., 1976. Poflanzenschutz - Nachnchten Bayer, 31: 163-180.
10. Clark. T., D.R. Clifford, A.H Deas, P. Gendle and D.A.M. Watkins, 1978. Pestic. Sci, 9: 497-506.
11. Sheldrich, G.M., 1997. SHELXS-97, Program for the solution of crystal structure.
12. Sheldrich, G.M., 1997. SHELXL-97, Program for crystal structure determination.
13. Jolmson, C.K., 1965. ORTEP, Report ORNL-3794. Oak Ridge National laboratory, Temessee, U.S.A.
14. Nowell, l.W. and P.E. Walker, 1982. Acta Cryst., B38: 1857-1859
15. Bucheuauer, H., Z.P. llanzeskar, 1976. Pflanzenschutz., B3: 368-367.
16. Martin, T.J. and D.B. Morris, 1979. Pflanzenschutz Nachr. Am. Ed., 32: 31-79.
17. Senger, Jyotsna, Ph.D. Thesis, Jiwaji University, Gwalior India (2002).
18. Blow, O.M., 1960. Acta Cryst., 13: 168.