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Comparative X-ray Analysis of systemic fungicides bis (dim ethyl thiocarbamoyl) disulphide and β-(phenoxy)—α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol

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Abstract: 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.

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

Keywords: X-ray crystallography, Systemic fungicides, Triazole structure

Introduction

Fungicides are the important class of chemicals used widely for the protection of crops. 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. These compounds are absorbed by the plant and get trans located within it, thus providing protection as well as eradicating already established infection. The structure is determined by X-Ray Crystallography. The composition of **bis (dim ethyl thiocarbamoyl) disulphide** crystals are confirmed by comparing the infra-red spectra of the two components. The Unit cell parameters are a=6.91 30(10) Å,b=6.9250(10.) Å c=11.8020(10) Å and γ=91.61° with Z=2.The space group is P1. The composition of **β-(phenoxy)—α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol** crystals are confirmed by comparing the infra-red spectra of the two components. The unit cell parameters a = 8. 136(2) Å b = 16. 790(2) Å c=21. 990Å. The space group is determined to be P2_1/n. The measured density is 1. 3215g/cm^3 and calculated density is 1. 3102g/cm^3.

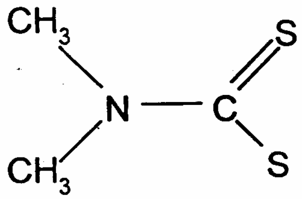
Experimental

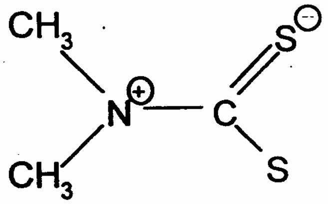
The crystals of **bis (dim ethyl thiocarbamoyl) disulphide** are grown at 20^0 -$25^0$from its solution in acetone by slow evaporation method. The unit cell parameters are determined directly by automatic computerized 4 - circled Enraf Nonious CAD-4 diffractometer in ω-2θ scan mode using Nickel filtered CuKα, radiation with range of 3.8° to 69.94°. The density of the crystal is measured by floatation method, in the mixture of benzene and carbon tetrachloride at room temp. Its calculated density is 1.469 mg/m^3 and measured density is 1.454 mg/m^3

Crystallization of **β-(phenoxy)—α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol** is done by slow evaporation from a solution of cyclohaxenone at 282°K temp.The crystals obtained are white and rectangular in shape. The density of the crystal is determined by floatation method at room temp.The Crystal is placed in RD bottle with carbontetrachloride.Benzene is added to the solution untill the crystal floated in the middle of the mixture. Thus the crystal and solution are of same density and the density of solution is measured with Pyknometer. The measured density is 1. 3215g/cm^3 and calculated density is 1. 3102g/cm^3. 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

Result and Discussion

The molecule of **bis (dim ethyl thiocarbamoyl) disulphide** consists of two diethyl, dithocarbamato 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 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 divide 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.


(I)


(II)

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 tetramethyithiuram disulphide the two halves of the molecules are required to be equivalent by space group-symmetry. In these molecules, the terminal 5 atom of each dithiocarbamato crystal is 3.8-3.9 Å 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 monosulphides. It is of interest to see the two C-S 'double' bonds happen to have exactly equal length 1.648(3) Å and 1.652(4) Å, and the length of two central C- N bonds are equal within experimental error [1.313(5) and 1.312(5) Å]. 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. The ORTEP drawing of bis (dim ethyl thiocarbamoyl) disulphide is shown in Fig..1. The ORTEP drawing of β-(phenoxy)—α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol is shown in Fig.2 The bond lengths and angles of β-(phenoxy)—α-(1,1dimethylethyl)1H-1,2,4-triazole-1-ethanol in the two benzene rings have characteristics values and do not merit significant comments.The average C-H and N-H distances in the structure are 0.96Å and 0.90Å, respectively. The triazole rings are distorted in shapes.The average bond distances for N-N and C-N bonds are 1.340Å and 1.354Å. The angles show unusual variations. In Molecule 1 the angles vary from 99.8° to 120.1°,whereas in Molecule 2, the variation is from 104.9°to 112.1°. The C(7) and C(22) atoms have usual geometry. It is of interest to see that the effect of steric hindrances. In molecule 1, the angle C(6)-C(1)-O(1) is 112.6° whereas C(2)-C(1)-O(1) is 127.1°.On comparing to molecule 2,these angles are just 122.2° and 117.8°, respectively. The geometry of phenoxy and methylethyl groups bears not attention as they are comparable to other organic structures.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. The two Benzene rings are essentially planar as the deviations of atoms from the planes are of 0.002. The triazole rings are also planar but the average deviations of atoms are 0.06. The two rings in Molecule 1 and 2 are inclined to each other by angles of 70.32° and 66.56° .The dihedral angles between the rings in two molecules along C (7)-O (1) and C (22)-O (3) bonds are - 85.39° and 80.0°.It means the orientation or angle of twist in both the molecules is opposite with the approximate same amount.

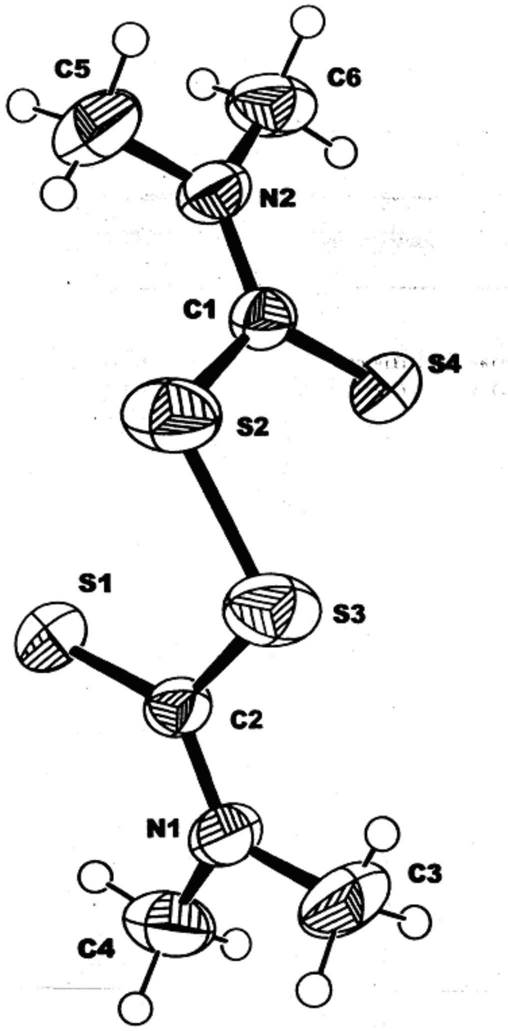


Fig. 1 : ORTEP Drawing at 50% probability level

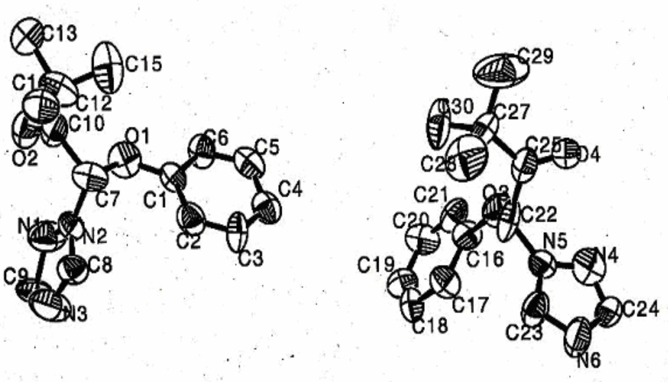


Fig 2 ORTEP DIAGRAM

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