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X-ray crystallographic studies on tetra methyl thiram disulphide or bis (dimethyl thiocarbamoyl) disulphide

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ABSTRACT

It has been observed that some of the 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 Tetra methyl thiram disulphide or bis (dimethyl thiocarbamoyl) disulphide crystals are confirmed by comparing the infra-red spectra of the two components. The Unit cell parameters are $a=6.9130(10)\text{\AA}$, $b=6.9250(10)\text{\AA}$, $c=11.8020(10)\text{\AA}$ the space group is P1. © 2008 Trade Science Inc. - INDIA

KEYWORDS

X-ray crystallography;
Systemic fungicides;
Triazole structure.

INTRODUCTION

Thiram is the coined name for tetramethyl thiram disulphide or bis (dimethyl thiocarbamoyl) disulphide. The molecular weight of thiram is 240.4. It is white coloured substance which is essentially insoluble in water slightly soluble in alcohol and ether and completely soluble in acetone and chloroform. It is unstable in the presence of acids. Being carbamate fungicidal compound thiram is toxic if consumed orally. As a part of research, X-ray crystallographic analysis of this fungicidal compound was carried out to study the effect of substituents on the molecular geometry and conformation of fungicidal compound with the main object to understand their biological activity.

EXPERIMENTAL

It was developed by E.I. du Pont de Nemours and Co. in 1931. The crystals were grown at 20^o from its solution in acetone by slow evaporation method. The unit cell parameters were determined directly by automatic computerized 4 Enraf Nonious CAD-4 diffractometer in ω -2 θ scan mode using Nickel filtered CuK α , radiation with range of 3.8 to 69.94^o. These data showed $a=6.9130(10)\text{\AA}$, $b=6.9250(10)\text{\AA}$, $c=11.8020(10)\text{\AA}$. The space group is P1. The density of the crystal was measured by floatation method, in the mixture of benzene and carbon tetrachloride at room temp. Its calculated density is 1.469 mg/m³ and measured density is 1.454 mg/m³

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Data collection and structure solution

The three dimensional intensity data were collected on a computerized automatic 4-circled CAD-4 Enraf-Nonious diffractometer using Nickel filtered CuK α (1.5418Å) radiation at Deptt. of Biophysics AIIMS New Delhi. All these data were corrected for Lorentz and polarization effect, but no absorption correction was applied. The total number of reflection were 2247. The unique reflections corresponding to intensity limit were 2064. The hkl values varies from $0 \leq h \leq 8$, $-8 \leq k \leq 8$, $-14 \leq l \leq 14$ respectively. The crystal structure was solved using the SHELXS-97. The ORTEP Diagram is shown in figure 1 and packing diagram is shown in figure 2.

Refinement

For determination of structure of the crystal VAX machine using SHELXS-97^o was used. In the beginning all the non-hydrogen atom[']. are located The coordinates thus obtained are fed to SHELXL-97 for refinement The first three cycles of isotropic refinement gave on R value of 16.21%. To reduce R to 14.25% given form of refinement of structure with individual an isotropic temp. factors is in exponential form was implemented

$$2P^{[1 + 2hKa*b*U12]}$$

All the hydrogen atoms were fixed geometrically and not included in the refinement. The refinement was terminated when all the shifts indicated for parameters of non-hydrogen atoms were less than the corresponding standard deviation. The final R index was 13.46% for all the observed reflections.

RESULT AND DISCUSSION

The molecule consists of two diethyl, dithiocarbamato moieties connected through S(2)-S(3). The S(2)-S(3) bond length is of 2.0077(16)Å. 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 plan-

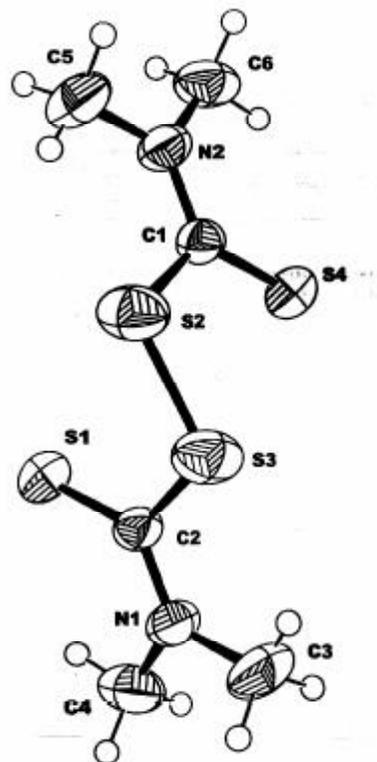


Figure 1: ORTEP drawing at 50% probability level

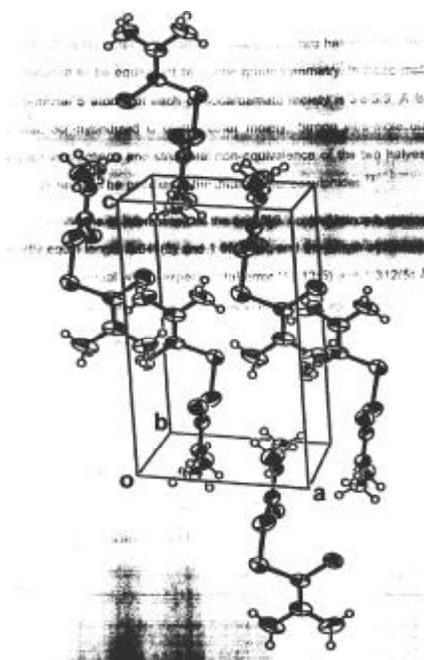
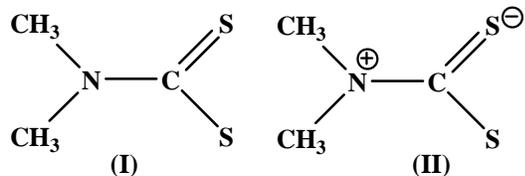


Figure 2 : The molecular pacing seen down b-axis

ner. The dihedral angle around S(2)-S(3) bond is -88.38(17)^o. 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 may be added that in tetramethylthiram disulphide the two halves of the molecules are required to be equivalent by space group-symmetry. In these molecules, the terminal S atoms of each dithiocarbamate crystal is 3.8-3.9 Å from the central, Sp 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] and 1.312(5) Å. Also the lengths of the four N-CH bonds are in reasonable agreement. It is well known that among the several factors affecting the values of bond angles is Sp Sp hybridized centres. 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 for in terms of varying repulsions between bonding electron pairs in valence cell of C.

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