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RE-EXAMINATION OF THE STRUCTURE OF ETHYLENETHIURAM MONOSULPHIDE

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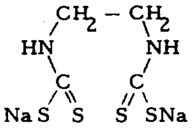
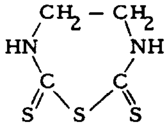
Aeration of dilute aqueous solutions of disodium ethylenebisdithiocarbamate (nabam, I) results in the formation of a yellow, insoluble, fungicidal material [1]. From this material a pale-yellow compound has been isolated, $C_4H_6N_2S_3$, m.p. 125-6°C, for which the ethylenethiuram monosulphide structure (ETM, II) was made plausible [2]. Despite severe criticism this structure was upheld, mainly on the basis of spectroscopical evidence [3].


(I)


(II)

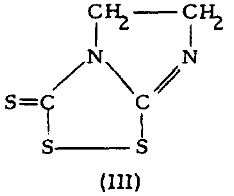
Renewed interest in the degradation products of nabam prompted a reevaluation of the ETM structure. A very pure sample of ETM was prepared by aeration of aqueous nabam solutions in the presence of manganese sulphate [4], and purification of the crude product on a silica gel column, using $CHCl_3$/EtOAc (1:1) as a solvent system. Analysis values point to $C_4H_4N_2S_3$ instead of $C_4H_6N_2S_3$:

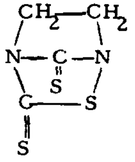
Found : C 27.25; H 2.42; N 15.71; S 54.81
Calcd. for $C_4H_4N_2S_3$: C 27.27; H 2.28; N 15.91; S 54.55
Calcd. for $C_4H_6N_2S_3$: C 26.97; H 3.37; N 15.73; S 53.93

Mass spectrography proved the molecular weight to be 176, which fits $C_4H_4N_2S_3$ rather than $C_4H_6N_2S_3$.

NMR spectra of $CDCl_3$ solutions of the compound reveal the presence of 4 H atoms as two triplets at 3.93 and 4.52 ppm downfield from tetramethyl silane. This points to two unequal pairs of hydrogen atoms and consequently rules out symmetrical structures like II.

The asymmetrical structure III, 5,6-dihydroimidazo [2,1-c]-1,2,4-dithiazole-3-thione, which has been considered earlier by Thorn [3] as an alternative ETM structure, appears to fit the analytical data presented above. Presumably this structure, or structure IV, one of the other early Thorn structures, was meant when "ethylene bis isothiocyanate sulphide" was mentioned among the decomposition products of mancozeb 5). It also offers an explanation for the formation of a CS_2-complex, which had been observed earlier by one of us (C. W. P.) when the compound was dissolved in CS_2 (cf. also 3) footnote).


(III)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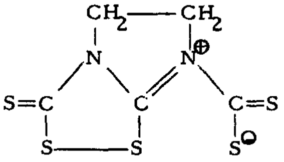
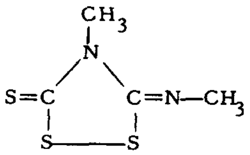

(V)


(VI)

The supposed ETM dissolves readily in CS_2 with a red colour and after a few minutes the complex separates as a voluminous orange-red precipitate. This is almost insoluble in H_2O and in most organic solvents, except DMSO. Apparently the complex is not stable in DMSO solution, since the initial orange colour gradually fades. The complex decomposes on heating and the decomposition product melts at 125°C, the m.p. of the original "ETM". An NMR spectrum in CD_3SOCD_3 shows a singlet at 4.50 ppm and two triplets at 3.84 and 4.38 ppm. The triplets most probably originate from "ETM", which is formed from the complex because of the instability of the latter in deutero-DMSO solution. The singlet at 4.50 ppm is thought to represent the four hydrogen atoms of the CS_2-complex, which requires a highly symmetrical structure. We propose structure V for the CS_2-complex, a structure which is thought to be stabilized by resonance. It resembles the structure of the no-bond resonance compounds, reviewed recently by Beer 6). Analysis values of the CS_2-complex are in agreement with the structure proposed:

Found : C 23.77; H 1.61
Calcd. for $C_5H_4N_2S_5$: C 23.79; H 1.60

Formation of the CS_2-complex from structure IV could also be envisaged. However, this requires cleavage of the N–S bond. The ease of formation of V and the mild conditions required for loss of CS_2 favour structure III. Furthermore the similarity of the UV-spectra of 4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione (VI) and "ETM" strongly favours structure III.3)

On account of the aforesaid data structure III is considered the correct structure of the pale-yellow compound isolated from the aeration product of nabam.

Acknowledgement. The authors wish to thank Mr. H.A.Selling for helpful discussions.

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