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# Interesting Errors in Sulfur Chemistry, 2

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# INTERESTING ERRORS IN SULFUR CHEMISTRY, 2

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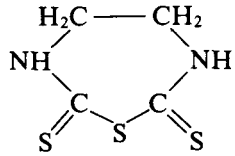
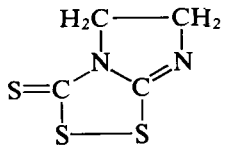
## Ethylenethiuram Monosulfide

Beside polymeric material and sulfur the air oxidation of aqueous solutions of disodium ethylenebisdithiocarbamate (the commercial fungicide Nabam) yields approximately 20% of ethylenethiuram monosulfide which was recognized as $C_4H_6N_2S_3$ and assigned the structure **1,** tetrahydro-1,3,6-thiadiazepine-2,7-dithione, CAS Registry No. [5782-83-2].[1,2]



**1**

In 1960 Thorn discussed a number of spectral and chemical inconsistencies between ethylenethiuram monosulfide and the assigned structure **1,** but concluded nevertheless that **1** (in equilibrium with its enethiol tautomers) was the correct structure and rejected the alternative structure **2.**[3] One of the more interesting arguments in favor of **1** was that the slope of the dose-response curve in a fungicidal activity test for ethylenethiuram monosulfide was significantly different from the corresponding slopes for model compounds containing ring systems related to **2.**



**2**

Eleven years later Pluijgers, Vonk, and Thorn[4] reanalyzed ethylenethiuram monosulfide and found closer agreement with the formula $C_4H_4N_2S_3$, corresponding to, *inter alia,* **2.** Noting the non-equivalence of the two methylene groups in the $^1H$ NMR spectrum of ethylenethiuram monosulfide the authors concluded that the compound has indeed the structure **2,** 5,6-dihydro-3H-imidazo[2,1-c]-1,2,4-dithiazole-3-thione, CAS Registry No. [33813-20-6]. This structural assignment was further supported by

UV spectral and chemical arguments,[4] and, in parallel investigations[5,6] by MS, Raman, $^{1}H$ NMR, and $^{13}C$ NMR data. Thus, although no X-ray structure determination of **2** is on record, there appears to exist an unchallenged consensus that the structure of "ethylenethiuram monosulfide" is **2** rather than **1**.

Nevertheless, the equivalent names ethylenethiuram monosulfide and tetrahydro-1,3,6-thiadiazepine-2,7-dithione **1** have been used throughout the seventies just about as frequently as the correct name 5,6-dihydro-3H-imidazo[2,1-c]-1,2,4-dithiazole-3-thione **2**. A recent Chemical Abstracts index[7] contains 20 references using the obsolete name and molecular formula and even later examples can be found.[8,9]

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