X-Ray Crystal Structure of 3,5-Bis(thiocarbamoyl)-1,2,4-dithiazolidines

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Summary Single-crystal *X*-ray analyses have been performed on two 3,5-bis(thiocarbamoyl)-1,2,4-dithiazolidines; the molecules are planar with sulphur–sulphur distances of 2·2 and 2·8 Å.

Goerdeler and Ulmen[1] reported that 1,1,5-trisubstituted-2,4-dithiobiurets were autoxidised in solution to 3,5-bis(thiocarbamoyl)-1,2,4-dithiazolidines (**3**).[2] During a recent study by one of us[3] on the air oxidation of 1,1,5,5-tetramethyl-2,4-dithiobiuret,[4] a house fly (*Musca domestica L.*) sterilant, a minor product was identified as the pentamethyl derivative (**3a**) of the same dithiazolidine system. The compounds (**3a**) and (**3b**) were prepared by the route in the Scheme from the isothiocyanate (**2**).[3] It was recognized[2,3] that 'no-bond resonance'[5] may exist in this system, but it was not certain whether (**3**) or (**4**) represent the actual structure. Single crystal *X*-ray analyses were therefore performed on (**3a**) and (**3b**).

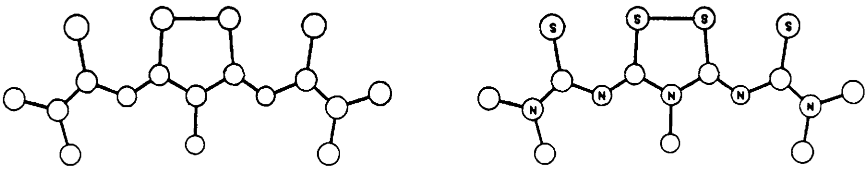
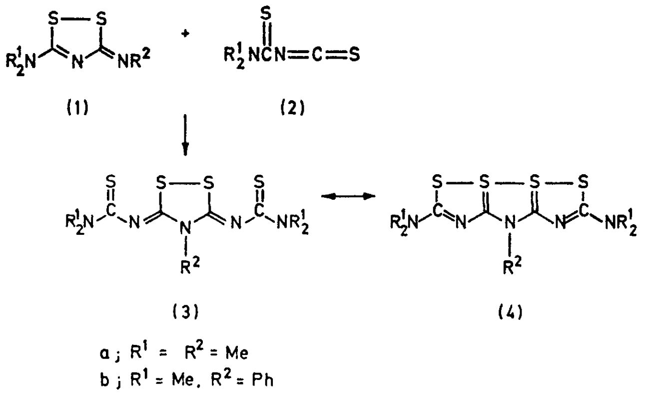


Figure 1. *Stereodrawing of the methyl derivative* (**3a**).

Both materials crystallise in the monoclinic space group *C*2/*c*. For the methyl derivative (**3a**), $a = 11{\cdot}34(2)$, $b = 9{\cdot}04(2)$, $c = 27{\cdot}53(6)$ Å, and $\beta = 97{\cdot}9(1)°$; for the phenyl derivative (**3b**), $a = 17{\cdot}80(2)$, $b = 10{\cdot}83(1)$, $c = 9{\cdot}66(1)$,



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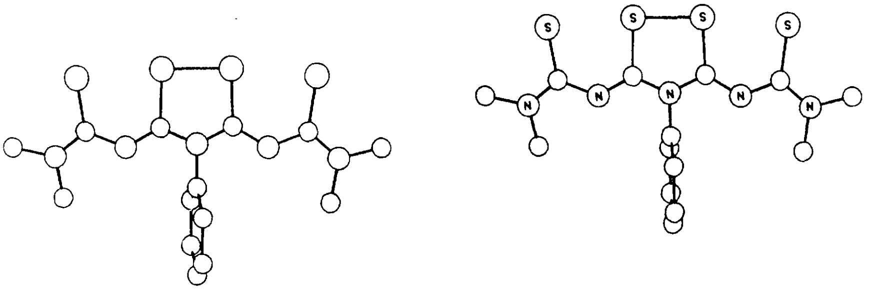
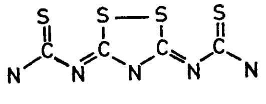


FIGURE 2. *Stereodrawing of the phenyl derivative* (**3b**). *Both drawings were made by a computer from a program written by C. K. Johnson, Oak Ridge National Laboratory.*

and $\beta = 100(1)°$. The structures were solved using the symbolic addition procedure[6] and are currently being refined. The phenyl derivative possesses a 2-fold axis of rotation. Fragment (A) in both molecules is essentially planar with the four sulphur atoms arranged collinearly (see Figure 1 and 2) as would be required for either (**3**) or (**4**). However, the central S–S distance, in both molecules, is *ca.* 2·2 Å indicating a central 1,2,4-dithiazole ring with a normal S–S single bond,[7] and the outer S–S distances are *ca.* 2·8°. These distances indicate that (**3**) is the predominant isomer in both molecules. The outer S–S distances are too long for sulphur–sulphur bonds, but are considerably less than twice the sum of their van der Waals radii (3·7 Å)[8] and indicate that some sort of strong sulphur–sulphur interaction is present.[5]



(A)

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