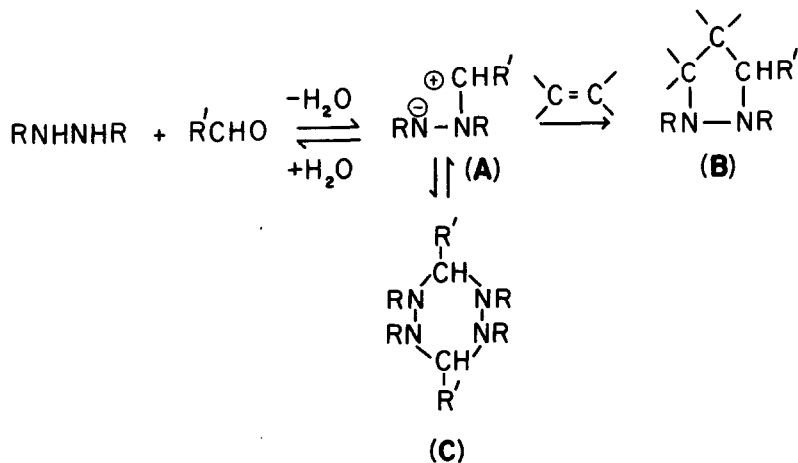


THE STRUCTURE AND STEREOCHEMISTRY OF 2-p-METHOXYPHENYL-
 3,4-DIBENZYL-1,3,4-THIAZOLIDINE-5-THIONE BY X-RAY ANALYSIS

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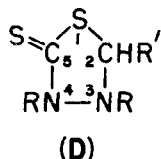
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The reaction of N,N'-dialkylhydrazines with aromatic aldehydes and an unsaturated compound (a dipolarophile) represents a versatile and useful heterocyclic synthesis via 1,3-dipolar cycloaddition (1). In this three component system, reaction of the aldehyde and hydrazine yields an equilibrium concentration of the 1,3-dipolar azomethine-imine intermediate (A). Subsequent addition to the dipolarophile completes the cycloaddition (A→B). Support for this description of the reaction was provided by the



observation that the hydrazine and aldehyde, in the absence of a dipolarophile, yielded the corresponding hexasubstituted hexahydro-1,2,4,5-tetrazine (C); thermal decomposition of (C) in the presence of the dipolarophile yielded the same adduct as was obtained in the three component system.

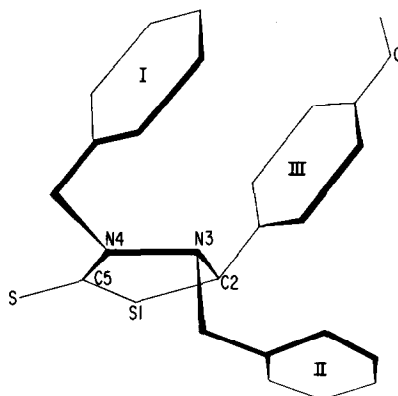
In the case of carbon disulfide as dipolarophile, the resulting product of 1,3-dipolar cycloaddition is a 1,3,4-thiadiazolidine-5-thione (2) (D). While considerable chemical and physical evidence was



adduced in favor of the 1,3,4-thiadiazolidine-5-thione structure for these adducts, the possibility existed of addition of the dipolarophile in the reverse sense to yield a 1,2,3-thiadiazolidine-5-thione derivative. Also an unexpected AB quartet pattern was observed in the NMR for the N(3) methylene group of a number of these derivatives with the large chemical shift difference of $\delta_{AB} = 1.00-1.20$ p.p.m., $J_{AB} = 14-15$ c.p.s.⁽²⁾. This result could be due to asymmetry at either C₂ or N₃. In the light of these unresolved and unusual features and also due to the versatility of this 1,3-dipolar heterocyclic synthesis, an x-ray diffraction study of 2-p-methoxyphenyl-3,4-dibenzyl-1,3,4-thiadiazolidine-5-thione was undertaken in order to establish unequivocally the structure of this representative compound.

The material crystallizes in the triclinic system with unit cell dimensions: $a = 7.74 \text{ \AA}$, $b = 12.07 \text{ \AA}$, $c = 12.32 \text{ \AA}$, $\alpha = 111^{\circ}20'$, $\beta = 88^{\circ}10'$, $\gamma = 100^{\circ}43'$, and contains two molecules per unit cell. Statistical tests on the full sphere of x-ray data obtained with $\text{CuK}\alpha$ radiation strongly indicated the presence of a center of symmetry in the cell. Phases for the x-ray reflections determined directly by the symbolic addition procedure (3) led to an electron density map which displayed the configuration and stereochemistry of the molecule. A least squares refinement of 3780 data with anisotropic temperature factors results in an R factor of 10.7%.

FIG. 1



The determination of the crystal structure confirmed the structural formula (D). Fig. 1 illustrates the configuration of the molecule. In the SCNNC ring, atoms $\text{S}_1, \text{N}_3, \text{N}_4,$ and C_5 lie in a plane whereas atom C_2 is displaced from the plane by 0.58 \AA . The other sulfur atom and the carbon atom attached to N_4 lie nearly in the same plane as $\text{S}_1, \text{N}_3, \text{N}_4, \text{C}_5$. Of particular

interest is the fact that the three bonds to N₃ form a pyramid with angles of $\sim 110^\circ$ while the three bonds to N₄ lie in a plane. Furthermore, the C₂-N₃ distance is 1.51 Å, a single bond value, while the C₅-N₄ distance is 1.36 Å, close to a double bond value. The proximity of the C = S bond to N₄ has undoubtedly a large effect on the bonding system. Rings I and III are in planes nearly parallel to each other. These planes make an angle of $\sim 80^\circ$ with the plane of SNNC. The constituents attached to C₂ and N₃ are trans to each other. The plane of ring II makes an angle of $\sim 112^\circ$ with the planes of rings I and III.

A detailed description of the structure determination will be published elsewhere

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