Synthesis and *X*-Ray Molecular Structure of a Mesoionic 2-Methylene-1,3,4-thiadiazole

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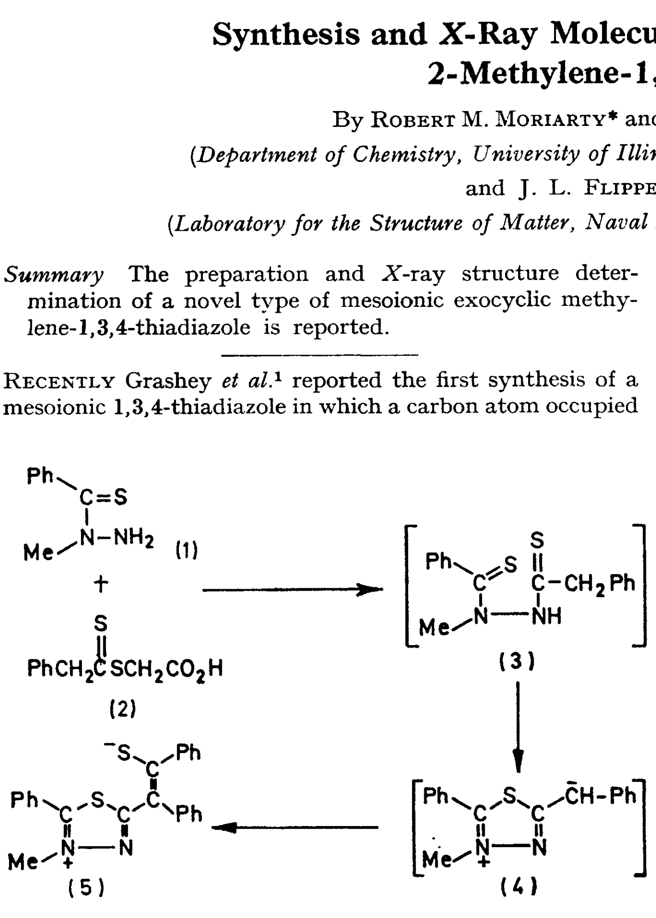
Summary The preparation and *X*-ray structure determination of a novel type of mesoionic exocyclic methylene-1,3,4-thiadiazole is reported.

RECENTLY Grashey *et al.*[1] reported the first synthesis of a mesoionic 1,3,4-thiadiazole in which a carbon atom occupied the exocyclic position at C(2) [*e.g.* C(2)=C(CN)$_2$; C(2)=C·CN·CO$_2$Me]. A compound bearing a CHPh group at this position would be of theoretical and synthetic interest. We attempted the synthesis of (**4**) *via* combination of the hydrazine (**1**) with the dithioate (**2**)[3] in the presence of pyridine as catalyst. The deep-red product (**5**) (65% yield) had m.p. 238—239°; M^+ 400 ($C_{24}H_{20}N_2S_2$); λ_{max} (MeCN) 263, 358, and 430 nm (log ϵ 5·44, 4·97, and 5·17) (bands shift in a similar way to those of other mesoionic 1,3,4-thiadiazoles in solvents of increasing polarity);[4] δ ($CF_3 \cdot CO_2H$) 3·47 (s, CH$_2$), 4·34 (s, NMe), and 7·01, 7·27, and 7·47 (all m, ArH) p.p.m. Its methiodide had m.p. 140—145° (decomp.) Intense ions at $M - 118$, (PhC≡NMe$^+$) and M—121 (PhC=S$^+$) in the mass spectrum of (**5**)† are characteristic of the mesoionic 1,3,4-thiadiazoles.[5]



The 1,3,4-thiadiazole (**5**) may be regarded as a derivative of the sought after (**4**) or as a more highly substituted analogue of the type of exocyclic carbanionic type compounds reported by Grashey *et al.*[1]

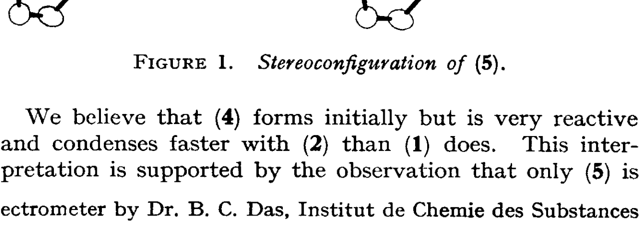


FIGURE 1. *Stereoconfiguration of* (**5**).

We believe that (**4**) forms initially but is very reactive and condenses faster with (**2**) than (**1**) does. This interpretation is supported by the observation that only (**5**) is

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† High resolution mass spectra were obtained on an AE1 MS9 spectrometer by Dr. B. C. Das, Institut de Chemie des Substances Naturelles, 91-Gif-sur-Yvette, France.

obtained even when a three-fold excess of (**1**) over (**2**) is used.

An *X*-ray analysis was undertaken to confirm the molecular formula as well as to establish the stereochemistry of (**5**) and show that the sulphur atoms are in a *syn* configuration with respect to each other. The material crystallizes in space group $P2_1/n$; $a = 14{\cdot}673$, $b = 11{\cdot}037$, $c = 12{\cdot}955$ Å, $\beta = 102{\cdot}1°$. The structure was solved by the symbolic addition procedure[6] and refined to an R factor of 0·061.

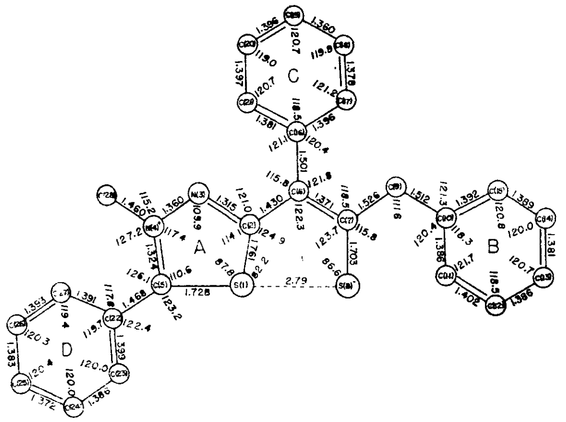
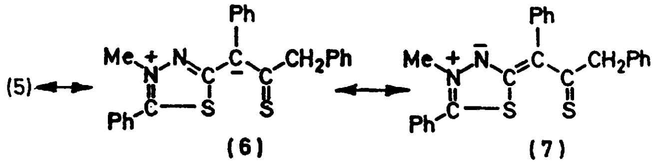


FIGURE 2. *Bond lengths and angles for* (**5**).

The stereoconfiguration of the molecule is shown in Figure 1 and the bond lengths and angles in Figure 2. Atoms 1—9 and C(28) are planar to within 0·2 Å. This implies that resonance forms such as (**6**) and (**7**) do not contribute significantly to the structure since as they involve single bond character and a concomitantly low torsional barrier of the 2,6 and 6,7 bonds.



The benzylic protons in the n.m.r. spectra of (**5**) were unaffected upon raising the temperature to 150°. Hence (**5**) is firmly locked in the configuration indicated.

The S–S distance in (**5**) is 2·79 Å, much longer than that (2·00—2·12 Å) in disulphides,[7] and greater than the 'long' S–S bond (2·23—2·57 Å) in thiathiophthens[8] but considerably shorter than the sum of the van der Waals radii (3·70 Å) for two sulphur atoms.[9] The distances in ring A and those for the bonds involving C(6), C(7), and S(8) show the foreshortening of single bonds and the small increase in length of double bonds found in conjugated systems. These alterations are considerable but not sufficient to imply significant bicycloaromaticity in (**5**).

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