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THE MESOIONIC SYSTEM
3-METHYL-4-PHENYL-1,2,3-THIADIAZOLIUM-5-THIOLATE
SYNTHESIS AND X-RAY STRUCTURE DETERMINATION.

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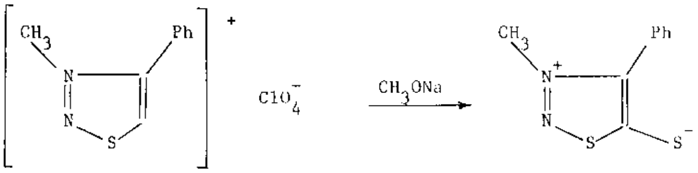
We report the synthesis and the crystal structure determination of 3-methyl-4-phenyl-1,2,3-thiadiazolium-5-thiolate which belongs to a mesoionic system which has only recently been investigated.

Following the studies on methylation of 4-phenyl-1,2,3-thiadiazole[1] we have investigated the reaction of N-methyl-1,2,3-thiadiazolium salts with sodium methoxide. When a solution of 3-methyl-4-phenyl-1,2,3-thiadiazolium perchlorate in methanol was added to a methanolic solution of sodium methoxide (molar ratio 1 : 2) a reaction occurred. After evaporation of the solvent the remaining oil let separate a crystal compound which was recrystallized from chloroform or petroleum ether, yield 50%, m.p. 140°C. NMR($CDCl_3$)δppm: 7.55(5H, s); 4.05(3H, s). Mass : M^+ cluster, m/z : 207 (100); 208 (91); 209 (19); 210 (9). The data of NMR and Mass spectra suggested that this compound is the 3-methyl-4-phenyl-1,2,3-thiadiazolium-5-thiolate.



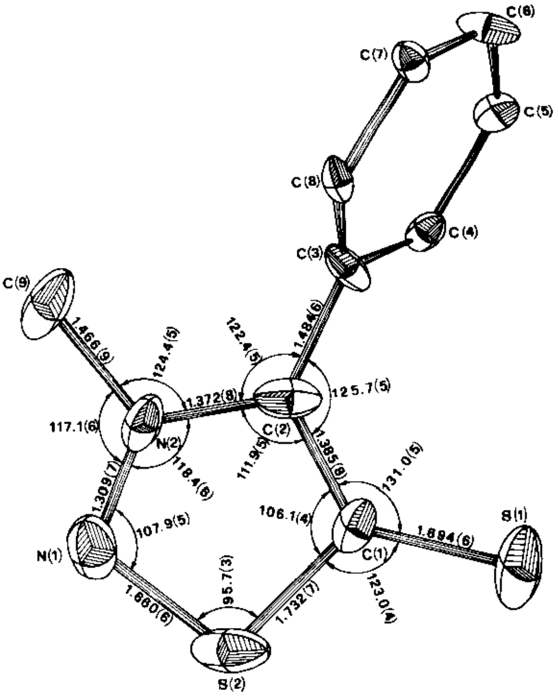
In a recent paper of Masuda et al.[2] the synthesis of compounds which belong to the same mesoionic system is reported.

The structure was confirmed by X-ray crystallographic analysis.

Crystal data: $S_2N_2C_9H_8$, M = 208.3, orthorhombic, space group $Pna2_1$, with a = 18.46(2), b = 7.03(1), and c = 7.59(1) A, Z = 4, μ(Mo Kα) = 0.436 mm^{-1}.

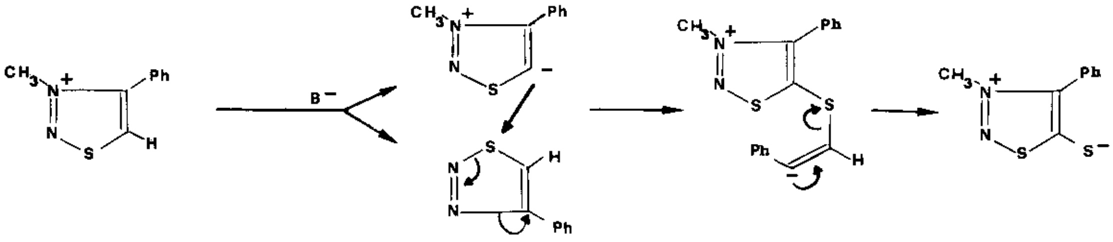
The 1208 observed reflections $[I > 3\,\sigma(I)]$ having $2\theta \leq 60°$ were measured with a fully automated Philips PW1100 diffractometer. Data were corrected for Lorenz and polarization factors but not for absorption or extinction.

The structure was solved by direct methods using the MULTAN 74[3] programme package. Full-matrix anisotropic refinement, with the benzene ring refined as rigid group, gave a final R of 0.065. The hydrogen atoms which belong to the methyl group did not clearly appear on the difference map, therefore their contribution has been ignored throughout the refinement procedure.
A perspective view of the molecule is shown in figure with bond lengths and angles. The five-membered ring is planar (max. displacement from the least-squares plane 0.005 Å). The ring distances indicate that there are no true single or double bonds, while the C-S bond length (1.694 Å) suggests a residual negative charge to lie on sulphur. The relative orientation of the two rings may be defined by the rotational angle C(1)-C(2)-C(3)-C(4) whose value is 64.1°.



A perspective view of the molecule with the numbering scheme. Bond lengths and angles within the six-membered ring are 1.395 Å and 120° respectively.

In analogy with the mechanism proposed for the formation of the 1,4-dithiafulven from 1,2,3-thiadiazoles and base[4], a mechanism can be envisaged which would account for the formation of 5-thiolate.



References

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2) K. Masuda, J. Adachi, K. Nomura, J. Chem. Soc. Perkin I, 1979, 956.

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