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SYNTHESIS AND STRUCTURE OF THE NEW MESOIONIC 1-THIASYDNONIMINE SYSTEM

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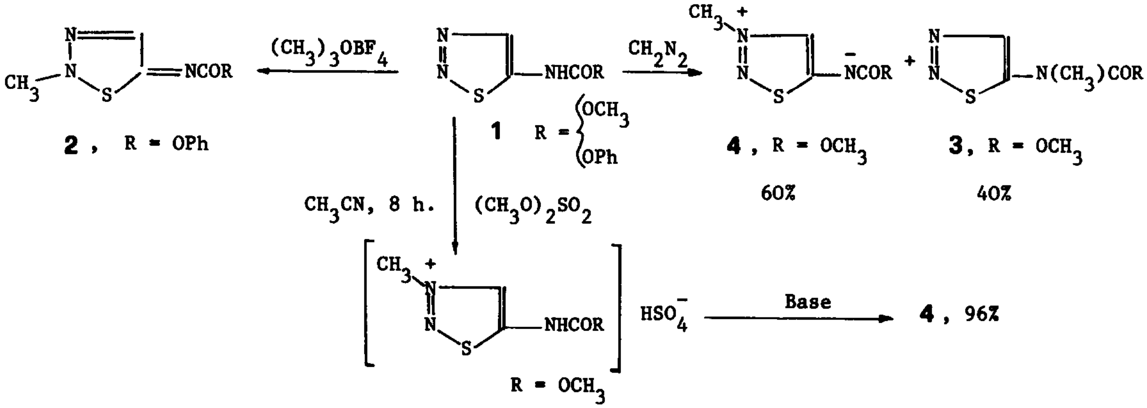
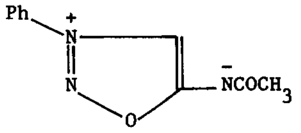
Summary: Synthesis of 5-acylimino-3-methyl-1,2,3-thiadiazole **4** is described and its molecular structure is confirmed by NMR and X-Ray diffraction analysis.

In a previous paper[1] we reported the synthesis of the new mesoionic system of 1-thiasydnone. As next step in synthesis of new mesoionic compounds we investigated the alkylation of 5-acylamino-1,2,3-thiadiazoles with dimethylsulphate and diazomethane. It has been reported that the alkylation of 5-acylamino-1,2,3-thiadiazole **1** yields, according to the Authors, the N-2-alkylated product **2** with $(CH_3)_3OBF_4$, or the thiadiazole **3** with diazomethane The mesoionic structure[3] **4** with the alkyl substituent in position 3 for the product of alkylation of **1** was excluded by the Authors[2] on the basis of the UV spectra and the melting point.



In the present study we have proved that the product of alkylation of 5-methoxycarbonyl-amino-1,2,3-thiadiazole with dimethylsulphate in acetonitrile has the mesoionic[4] structure **4** . The reaction with diazomethane yields two products, **3** and **4** , easily separable by column chromatography (silica gel, CH_2Cl_2 as eluent). Compound **4** has melting point 223-225°C and is easily soluble in water or ethanol; UV (methanol): λmax 218 nm (log ϵ 4.1), 244 nm (log ϵ 4.02), 342 nm (log ϵ 4.2).

The ^1H NMR spectrum of **4** in $CDCl_3$ showed three singlets at 3.87, 4.30 and 8.26 ppm corresponding to the OCH_3, $\overset{+}{N}CH_3$ and CH groups respectively. The signal at 4.30 ppm was assigned to the ring methyl group since decoupling experiments evidentiated that it is very weakly coupled with the hydrogen bonded to C(4). This value compares well with the $\overset{+}{N}CH_3$ chemical shift of other mesoionic systems[5]. The ^{13}C NMR spectrum of **4** was taken in DMSO-d_6; δ : 45.9 $\overset{+}{N}CH_3$, 52.8 OCH_3, 127.7 C(4), 165.4 CO, 174.7 C(5). The chemical shift of C(4) is at higher field than observed for the unsubstituted 1,2,3-thiadiazole (147.3 ppm)[6]. This is completely consistent with the mesoionic structure of **4** in which the delocalisation of the negative charge from the exocyclic nitrogen atom to the C(4) atom induces a high electron density at this carbon with the consequence of an upfield shift. From a comparison between **4** and the known[7] compound **5** it is evident that, whereas the C(5) chemical shift (173.8 ppm) remains practically unchanged, the C(4) carbon atom (105.2 ppm) in **5** is shielded by more than 20 ppm. This strong upfield shift is due to the presence in **5** of the ring oxygen atom which is a much stronger electron donor than the sulphur atom. In order to characterize completely the structure of compound **4** we have undertaken an X-ray single crystal diffraction analysis, carried out on a needle-shaped crystal obtained from a benzene/ethanol (10 : 1) solution.



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Crystal Data.- $C_5H_5N_3O_2S$, M = 171.2 . Monoclinic, a = 3.98(1), b = 14.07(2), c = 13.70(2) Å, V = 760.1 Å^3, D_c (for Z = 4) = 1.50, D_m (by flotation) = 1.49 g cm^{-3}, space group $P2_1/c$ (from systematic absences).

Intensity Measurements.- The intensities of 1003 reflections were collected up to 2θ = 110° (graphite monochromated Cu Kα radiation) with a PHILIPS PW1100 four-circle diffractometer and the $\theta/2\theta$ scan technique (scan speed 0.04° s^{-1}, scan range 1.0°). Two background counts (12.5 s each) for each reflection were averaged. Two standard reflections were measured every two hours to check stability. No significant variations were observed; no absorption or extinction corrections were applied. Reflections with $I > 3\sigma(I)$ were considered observed.

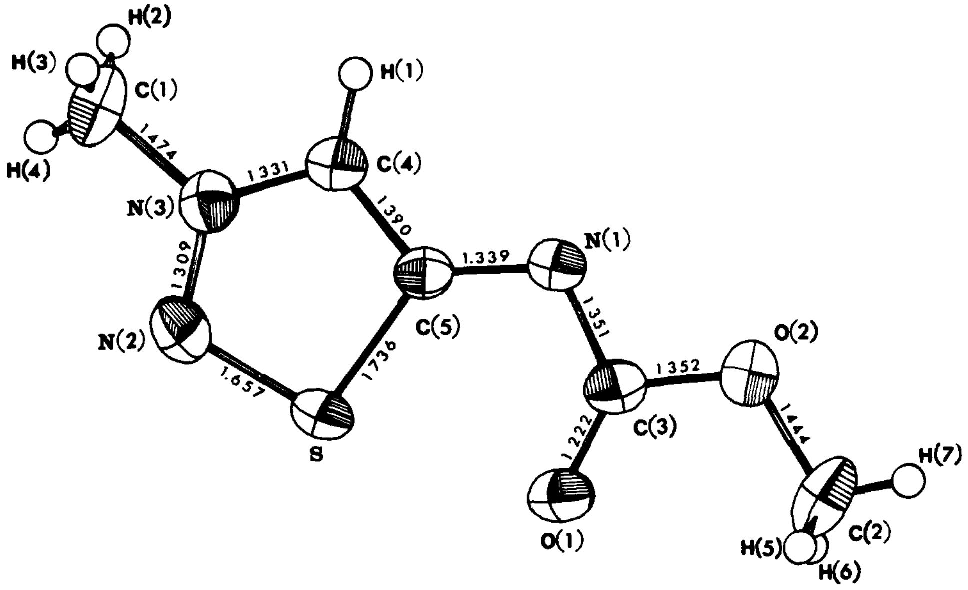

Fig. 1 .- An ORTEP view of the molecule with the numbering scheme and bond lengths. We estimate a standard deviation of 0.005 Å for all bonds between non-hydrogen atoms.

Determination of the structure.- The structure was routinely solved with MULTAN 74[8]. All non-hydrogen atoms were found on the E-map while all hydrogen atoms were found on a difference map calculated at R = 0.08. Full-matrix refinement with anisotropic temperature factors for the non-hydrogen atoms and weights chosen after Cruickshank et al.[9] gave a final R of 0.063 for observed reflections.

Description of the Structure.- The view of an ORTEP[10] drawing of the molecule is shown in Fig. 1 together with bond lengths. A list of bond angles is reported in Table 1.

Table 1. - Bond angles (°)

N(3)-C(4)-C(5)	112	C(1)-N(3)-C(4)	123	N(1)-C(3)-O(1)	127
C(4)-C(5)- S	106	C(1)-N(3)-N(2)	119	N(1)-C(3)-O(2)	110
C(5)- S -N(2)	94	C(4)-C(5)-N(1)	126	O(1)-C(3)-O(2)	122
S -N(2)-N(3)	109	S -C(5)-N(1)	128	C(3)-O(2)-C(2)	116
N(2)-N(3)-C(4)	119	C(5)-N(1)-C(3)	113		

Within the thiasydnone ring the C(5)-C(4), C(4)-N(3) and N(3)-N(2) bond lengths compare quite well with distances in the sydnone rings (see Table VI of ref. 11 for a wide collection of available data) while bond angles are systematically larger owing to the presence of the sulphur atom. The molecule is essentially planar, only C(2) being appreciably (0.039 Å) out of the least-squares plane which passes through all non-hydrogen atoms.

Distances in the ring and those involving N(1), C(3) and O(1) show the foreshortening of single bonds and a small increase in length of double bonds found in conjugated systems. It is interesting to note that the distance S···O(1) is 2.52 Å, far shorter than the sum of the van der Waals radii of the two atoms, thus indicating some interaction.

References and Notes

1. S.I.Burmistrov, V.A.Kozinski, Zh. Org. Khim., 10, 891 (1974); CA 81, 13444v (1974).
2. J.Goerdeler, G.Gnad, Chem. Ber., 99, 1618(1966).
3. M.Ohta, H.Kato in "Nonbenzenoid Aromatics" (J.P.Snyder, ed. 1, pp 117-248), Academic Press, New York, 1969.
4. Upon the referee's remark we wish to acknowledge that an example of this type of mesoionic system has recently been prepared by another route (K.Masuda, J.Adachi, and K.Nomura, J. Chem. Soc. Perkin I, 956 (1979); K.Masuda, J.Adachi, and K.Nomura, J. Chem. Soc. Perkin I, 2349 (1979)).
5. K.D.Lawson, W.S.Brey Jr., and L.B.Kier, J. Am. Chem. Soc., 86, 463 (1964).
6. J.H.Looker, N.A.Khatri, R.B.Patterson, and C.A.Kingsbury, J. Heterocyclic Chem., 15, 1383 (1978).
7. M.T.W.Hearn and K.T.Potts, J. Chem. Soc. Perkin II, 875 (1974).
8. P.Main, M.M.Woolfson, L.Lessinger, G.Germain, and J.P.Declercq. MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures. Univs. of York, England, and Louvain, Belgium (1974).
9. D.W.J.Cruickshank, D.E.Pilling, A.Bujosa, F.M.Lovell, and M.R.Truter in "Computing Methods and the Phase Problem in X-ray Crystal Analysis". Oxsford: Pergamon Press (1961).
10. C.K.Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee (1965).
11. G.D.Andreetti, G.Bocelli, L.Cavalca, and P.Sgarabotto, Gazz. Chim. Ital., 102, 23 (1972).

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