A New Mesoionic Thia-Sydnone-arylimine System. Synthesis and Molecular Structure

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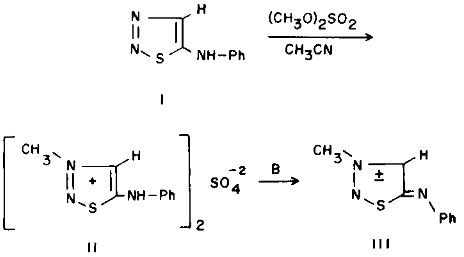
Received August 28, 1983

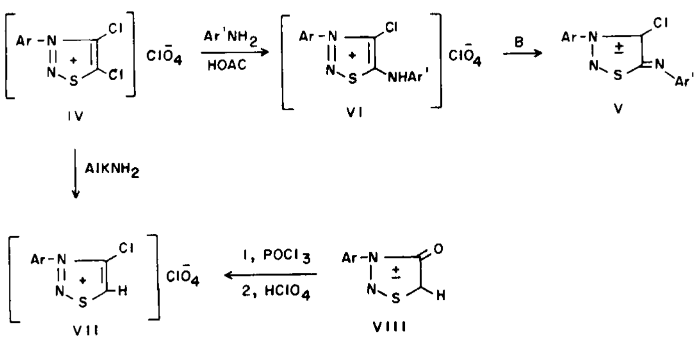
Methylation of 5-phenylamino-1,2,3-thiadiazole led regiospecifically to mesoionic 3-methyl-5-phenylimino-1,2,3-thiadiazole, its molecular structure was determined by X-ray diffraction analysis. 3-Aryl-5-arylimino-1,2,3-thiadiazoles were obtained by replacement of chlorine in 3-aryl-4,5-dichloro-1,2,3-thiadiazolium perchlorates with excess arylamine.

J. Heterocyclic Chem., **21**, 1889 (1984).

An unknown mesoionic system of 1,2,3-thiadiazole was synthesized in two ways. Alkylation of 5-phenylamino-1,2,3-thiadiazole (I) with dimethyl sulfate in boiling acetonitrile led with high regiospecificity to the salts of 3-methyl-5-phenylamino-1,2,3-thiadiazolium (II), the latter with bases gives mesoionic compound III.



Unlike 5-acylamino-1,2,3-thiadiazoles [1], no mesoionic III was detected with the diazomethane alkylation of I. The mesoionic 3-aryl-4-chloro-5-arylimino-1,2,3-thiadiazoles V were obtained from 3-aryl-4,5-dichloro-1,2,3-thiadiazolium perchlorates IV [2] *via* salts VI under boiling of IV with excess of arylamine in glacial acetic acid.



Reactions of dichloro compound IV with *ortho*-substituted amines failed, while those with *o*-aminophenols and alkylamines succeeded giving the salt VII by substitution of the chlorine atom in position 5 with hydrogen; this salt was also obtained from known mesoionic system of 3-aryl-1,2,3-thiadiazolium-4-olate VIII [3].

Treatment of ethanolic solutions of the salts II and VI with bases (ammonia, morpholine) gives orange and deep red crystals of III and V respectively.

The ir spectra of mesoionics III and V show the bands of an exocyclic C=N group at about 1520 cm^{-1} and 1545 cm^{-1} respectively, a characteristic doublet of the 1,2,3-thiadiazolium ring lying in the 1460-1495 cm^{-1} region.

Table 1

Fractional Atomic Coordinates ($\times\ 10^4$) and Equivalent Values B_{eq} (Å^2) of the Anisotropic Temperature Factors B_{ij} for Compound III

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_a \mathbf{a}_j$$

Atom	S	Y	X	B_{eq}
S	4277(1)	564(2)	3045(1)	3.5
N1	4129(1)	−1633(5)	3692(2)	4.32
N2	3528(1)	−1691(4)	3545(1)	2.93
N3	3242(1)	3127(4)	2001(2)	3.07
C1	3173(1)	−153(5)	2970(2)	2.85
C2	3499(1)	1442(5)	2566(2)	2.63
C3	3565(1)	4651(5)	1575(2)	2.87
C4	4177(1)	4416(6)	1561(2)	4.05
C5	4438(2)	6040(7)	1107(2)	4.75
C6	4104(2)	7978(6)	657(2)	4.78
C7	3503(2)	8216(6)	654(2)	4.58
C8	3231(1)	6597(6)	1094(2)	3.63
C9	3288(2)	−3562(5)	4031(2)	3.93
HC1	2738	−218	2862	
HC4	4409	3067	1858	
HC5	4850	5731	1094	
HC6	4295	9028	356	
HC7	3286	9415	312	
HC8	2811	6698	1093	
H1C9	3539	−3567	4612	
H2C9	3344	−5006	3790	
H3C9	2848	−3296	3988	

The nmr spectrum of III shows a C_4-signal (δ 8.38) shifted to a higher field with respect to that observed for non-mesoionic 5-phenylamino-1,2,3-thiadiazole (I), (δ 8.50). This is consistent with the partial negative charge on C_4-atom of III. In order to characterize completely the molecular structure of the new mesoionic system III we have undertaken an X-ray single crystal diffraction analysis.

In Table 1 we report the atomic fractional coordinates.

In Figure 1 we show bond lengths and angles together with e.s.d.'s and the numbering scheme.

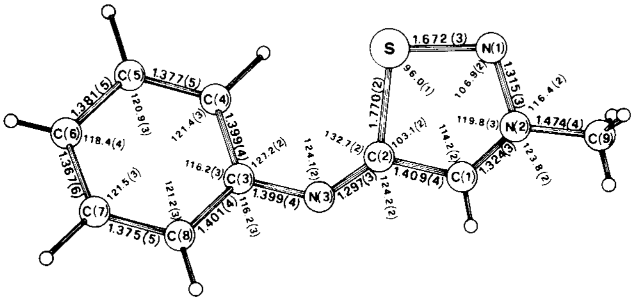


Figure 1. Perspective view of a molecule of III.

A comparison may be drawn between the geometric features of the title compound III and those of 5-methoxycarbonylimino-3-methyl-1,2,3-thiadiazole (henceforth IX) whose synthesis and structure is described in reference [1].

The greatest difference concerns the valence angle on the imino nitrogen atom, this being 124.1(2)° in III while it is 113.0(2)° in IX. This difference may be accounted for by observing that in IX there is an attraction between the cyclic S atom and the carbonyl oxygen atom in the exocyclic group while in III this interaction is absent, since there is a different type of π-electronic conjugation in mesoions III and IX. The different conjugation involves a rearrangement of bond lengths, in fact we see that bond lengths involving the S atom are significantly longer in III than in IX while C(2)-N(3) becomes shorter and N(3)-C(3) longer than the corresponding distances in compound IX. Compound III is nearly planar, the calculated least-squares planes through the five-membered and the six-membered rings showing an angle of 13.5(3)°.

π-Bonds orders of the mesoionic 3-methyl-5-phenylimino-1,2,3-thiadiazole (III) were calculated using Höffelinger's [4] equations and are shown in Figure 2.

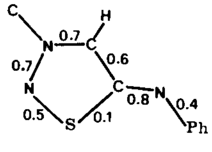


Figure 2. Calculated π-bond order of the mesoionic system III.

The low π-order of S_1-C_5 bond and high order of the exocyclic C_5-N bond is evidence against the cyclic delocalization of π-electrons with a negative charge on the excocyclic nitrogen (structure **3a**); on the contrary a significant non-cyclic conjugation (structure **3b**) for the mesoionic system III is postulated.

An analogous type of electronic structure may be proposed for sydnones according to their physical and chemical properties. The π-order of S_1-N_2 in mesoionic III is 0.5, while that of $O_1 = N_2$ in sydnones is 0.2. This difference may be explained by the interaction of the excess of electron density on N_2 (or on N_2-N_3-C_4-C_5-N_{exo} conjugated system) with vacant d-orbitals of sulfur, this increasing the stability of molecule III.

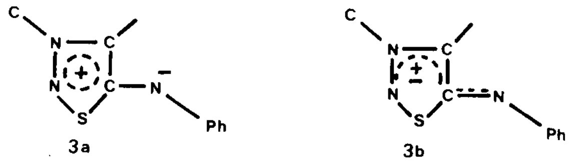


Figure 3

EXPERIMENTAL

1. 5-Phenylamino-1,2,3-thiadiazole (I).

This compound was obtained by the Wolf procedure [5] from diazomethane and phenylisothiocyanate, yield 45%, mp 183-185°.

2. 3-Methyl-5-phenylamino-1,2,3-thiadiazolium Sulfate (II).

A solution of 0.885 g (0.005 mole) of I in 15 ml of acetonitrile was added to 0.95 ml (0.01 mole) of dimethyl sulfate and the mixture was refluxed on a water bath for 2 hours. After cooling yellow crystals of salt II were filtered off and washed with 2-propanol. Recrystallization from water/2-propanol (1:10) gave 1 g of II (83% yield), mp 200-202°; uv (2-propanol): λ max, nm (log ϵ) 250 (3.97), 265 (3.85); ir (potassium bromide): 3050 cm^{-1} (NH).

Anal. Calcd. for $C_{18}H_{20}N_6S_3O_4$: C, 44.99; H, 4.19; N, 17.49; S, 20.02. Found: C, 45.17; H, 4.28; N, 17.52; S, 20.13.

3. 3-Methyl-5-phenylimino-1,2,3-thiadiazole (III).

3-Methyl-5-phenylamino-1,2,3-thiadiazolium sulfate (II) (4.8 g, 0.01 mole) was dissolved in 10 ml of water and a little excess of ammonia was added. An orange product was filtered off and 1.5 g (80% yield) of mesoionic III was obtained, mp 94-96° (ethanol); uv (2-propanol): λ max, nm (log ϵ) 280 (4.03), 410 (3.89); ir (potassium bromide): 1520 cm^{-1} (exocyclic C=N); nmr (DMSO-d_6): δ 8.38 (s, 1H, C_4-H), 7.05-7.38 (m, 5H, Ph-), 4.15 (s, 3H, N-CH_3).

Anal. Calcd. for $C_9H_9N_3S$: C, 56.52; H, 4.74; N, 21.97; S, 16.76. Found: C, 56.71; H, 4.91; N, 21.88; S, 16.58.

4. 3-Phenyl-4,5-dichloro-1,2,3-thiadiazolium Perchlorate (IV).

This compound was obtained according to our second procedure, yield 38%, mp 250° dec.

5. 3-Phenyl-4-chloro-5-phenylamino-1,2,3-thiadiazolium Perchlorate (VI).

Perchlorate IV (1.65 g, 0.005 mole) was dissolved in 20 ml of hot acetic acid and 1.5 ml (0.015 mole) of aniline was added and the mixture was refluxed 1.5 hours. After cooling a yellow solid was obtained (0.8 g, yield 42%), mp 230° dec; ir (potassium bromide): 3135 cm^{-1} (NH).

6. 3-Phenyl-4-chloro-1,2,3-thiadiazolium Perchlorate (VII).

a) Perchlorate IV (1.5 g, 0.0045 mole) was dissolved in hot acetic acid (15 ml) and 1.5 ml (0.0015 mole) of *n*-butylamine was added. After 1.5

hours refluxing and cooling, 0.72 g (yield 54%) of crystalline VII was obtained, mp 250° dec.

b) 3-Phenyl-1,2,3-thiadiazol-4-olate (1.78 g, 0.01 mole) was boiled with 10 ml of phosphorus oxychloride (0.5 hour) and poured on crushed ice, then an excess of 70% perchloric acid was added. The solid which formed was identical with the sample prepared following procedure a); ir (potassium bromide): 3135 cm^{-1} (C_5-H).

7. 3-Phenyl-4-chloro-5-phenylimino-1,2,3-thiadiazole (V).

Perchlorate VI (0.58 g, 0.002 mole) was dissolved in aqueous ethanol (20 ml) and an excess of ammonia was added. After 6 hours deep red crystals were collected and recrystallized from ethanol (0.3 g, yield 73%), mp 122-124°; ir (potassium bromide): 1540 cm^{-1} (exo C=N).

Anal. Calcd. for $C_{14}H_{10}ClN_3S$: C, 58.71; H, 3.98; N, 15.01; S, 11.17. Found: C, 58.52; H, 4.21; N, 14.73; S, 11.14.

X-Ray Data Collection.

Orange crystals of mesoionic III were obtained by slow evaporation from a solution in a hexane-acetone mixture. Unit cell parameters and intensities data were measured on a Philips PW 1100 automatic four-cycles diffractometer with graphite monochromated MoKα radiation, up to $\vartheta = 28°$, with the $\vartheta/2\vartheta$ scan technique (scan speed 0.04° s^{-1}, scan range 1.5°). During the data collection two reflections were monitored for crystal and instrument stability. The crystal system appeared to be monoclinic and systematically absent reflections were consistent with two possible space groups: Cc and C2/c. A total of 2317 reflections were recorded of which 1441 were considered observed having $I > 3\sigma(I)$.

The intensities were corrected for Lorentz and polarization factors but not for absorption.

Crystal data:

$C_9H_9N_8S$, monoclinic C2/c, a = 22.635(9), b = 5.544(2), c = 15.491(7) Å, β = 106.81(5)°, F(000) = 744, Z = 8, V = 1861(1) Å^3, D_x = 1.36 Mgm^{-3}, μ(MoKα) = 0.254 mm^{-1}.

Structure Solution and Refinement.

The structure was solved with MULTAN 74 [6] using 130 normalized structure factors with $|E| > 1.9$ and 588 phase relationships. Intensity statistics indicated the space group to be centrosymmetric (C2/c) with 8 molecules in the unit cell. The first E map revealed all non-hydrogen atoms. After a block-diagonal least-squares refinement with anisotropic temperature factors, a difference map showed all 9 H atoms. The refinement of non H (anisotropic) and H atoms (isotropic thermal parameters) was stopped when a final R = 0.044 and Rw = 0.045 were obtained for all observed reflections. In the final cycles the weighting scheme was $w = 2.2602/(\text{sigma}^2|F| + 0.000597|F|^2)$. The atomic scattering factors for non hydrogen atoms were taken from Comer and Mann [7], while the values used for H are those of Stewart *et al.* [8]. Refinement and subsequent calculations were performed with SHELX 76 program system [9].

A list of structure factors and any other crystallographic detail may be obtained from the authors on request.

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