

# $^{13}\text{C}$ -Nmr Spectra of Anhydro-3-mercapto-5-pyrazinyl-1,2,4-triazolium Hydroxides

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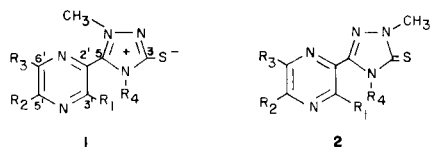
The complete assignment of the  $^{13}\text{C}$ -nmr spectra of some anhydro-3-mercapto-5-pyrazinyl-1,2,4-triazolium hydroxides (**1**) is reported. For purposes of comparison the spectra of some isomeric triazole-3-thiones (**2**) are also reported. Positions C-3 and C-5 of the triazole ring and 2' of the pyrazine moiety were found to be characteristic of each group of compounds.

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Besides being of synthetic interest as reactive intermediates, the class of heterocycles known as mesoionic compounds (**1**) is of theoretical interest because of the unequal distribution of  $\pi$ -electrons in the heterocyclic ring.

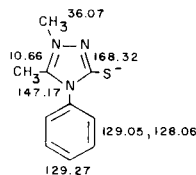
$^{13}\text{C}$ -nmr chemical shift data have been used in several instances to obtain information about the nature of  $\pi$ -electron densities in mesoionic compounds. Although  $^{13}\text{C}$  spectra did not give statistically significant correlations between  $^{13}\text{C}$ -chemical shifts and total charge densities in azolium salts (**2**)  $^{13}\text{C}$ -chemical shift studies were useful in determining the relative electron densities of the ring carbons of sydnone (**3**), sydnone conjugate acids (**4**), and trifluoroacetylated mesoionic oxazolines (**5**). In addition, a linear relationship has been shown between the calculated charge densities and the  $^{13}\text{C}$ -chemical shifts of some pyrimidinium betaines (**6**).

We have recently reported the synthesis of a series of anhydro-3-mercapto-1,2,4-triazolium hydroxides (**1**) and some isomeric triazole-3-thiones (**2**) (**7**). It proved to be difficult to reliably distinguish between **1** (**8**) and **2** by routine



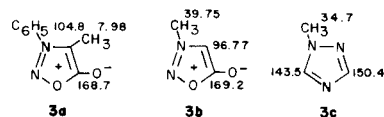
spectroscopic means, although differences in polarity were manifested in the different physical properties of **1** and **2** (melting points and solubilities). Therefore, we have recorded the  $^{13}\text{C}$ -nmr spectra of **1** and **2** with the goal of establishing a spectral method for structural assignment of these ring systems. The peak assignments for **1** and **2** are reported in Tables 1 and 2.

As a model compound, anhydro-3-mercapto-1,5-dimethyl-4-phenyl-1,2,4-triazolium hydroxide (**9**), **3**, was characterized by  $^{13}\text{C}$ -nmr using a variety of techniques

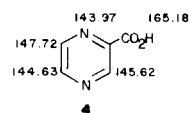


that have been reviewed by Wehrli and Wirthlin (**10**). The quaternary carbons were readily distinguished from the methines by a low power noise decoupling technique that we refer to as quaternary enhancement (**11**). The only possible ambiguity in the spectrum (other than the *ortho* and *meta* phenyl carbons) was between C-5 of the mesoionic ring and C-1 of the phenyl ring. Selective single frequency low power decoupling of the aromatic protons at 7.8 ppm in the  $^1\text{H}$ -nmr (**12**) caused the resonance at 147.17 ppm to collapse into a multiplet due to the 2-bond coupling from the adjacent methyl group. Under these conditions the resonance at 134.08 remained a singlet. This assignment made it possible to designate C-5 in compounds **1a-m** based on chemical shift arguments.

It is instructive to compare the assignments for **3** with 4-methyl-3-phenylsydnone (**3a**) (**3**), 3-methylsydnone (**3b**) (**3**) and 1-methyl-1,2,4-triazole (**3c**) (**13**). The methyl group attached to nitrogen in **3**, although more deshielded than the methyl group of **3c**, was not as deshielded as the methyl group of the **3b**. This reflects, perhaps, a more even distribution of the positive charge in the triazolium ring, with less localization on the nitrogen in the 1-position. The carbon at the 5-position of **3** is significantly deshielded by the two adjacent nitrogens (compare with **3c**). Accordingly, the C-5 methyl group of **3** does not display the strong shielding observed for the methyl group of **3a**.

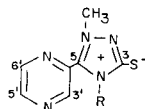


The spectrum of pyrazine-2'-carboxylic acid, **4** (**8**), was



assigned by selective decoupling experiments. Since the  $^1\text{H}$ -nmr spectrum could be assigned (**14**) by close examination, the closely spaced methine carbons could be assigned in this way. In the case of each decoupling experiment, the

Table 1  
<sup>13</sup>C-Nmr Assignments for Some Anhydro-3-mercapto-1,2,4-triazolium Hydroxides

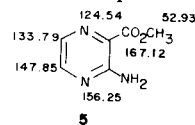


Compound No.	CH <sub>3</sub>	C-5	C-3	C-2'	C-3' (subst.)	C-5' (subst.)	C-6' (subst.)	R
<b>1a</b>	37.51	143.25	169.32	137.45	146.29 (H)	145.34 (H)	147.39 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (40.16), CH <sub>2</sub> CH <sub>3</sub> (13.59)
<b>1b</b>	37.68	143.47	170.53	137.39	146.07 (H)	144.85 (H)	146.67 (H)	C <sub>6</sub> H <sub>5</sub> : C-1" (133.85); C-4" (129.38); C-2", C-3" (128.99, 128.39)
<b>1c</b>	36.96	143.36	169.32	138.16	146.73 (H)	145.29 (H)	147.83 (H)	c-C <sub>6</sub> H <sub>11</sub> : C-1" (57.40), C-2" (30.22), C-3" (25.25), C-4" (24.53)
<b>1d</b>	37.01	144.96	169.32	128.61	145.95 (NHCOCH <sub>3</sub> )	140.82 (H)	145.95 (H)	C <sub>6</sub> H <sub>5</sub> : C-1" (133.58), C-4" (129.10), C-2", C-3" (128.61, 127.17), COCH <sub>3</sub> (169.15), COCH <sub>3</sub> (22.76)
<b>1e</b>	36.72	144.33	170.64	119.85	154.56 (NH <sub>2</sub> )	146.68 (H)	132.87 (H)	C <sub>6</sub> H <sub>5</sub> : C-1" (134.11), C-4" (129.30), C-2", C-3" (128.84, 127.86)
<b>1f</b>	36.63	144.46	168.93	129.55	146.45 (NHCOCH <sub>3</sub> )	141.31 (H)	146.45 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (40.22), CH <sub>2</sub> CH <sub>3</sub> (13.04), COCH <sub>3</sub> (169.10), COCH <sub>3</sub> (22.65)
<b>1g</b>	36.59	143.64	169.27	119.84	154.77 (NH <sub>2</sub> )	147.13 (H)	133.29 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (40.91), CH <sub>2</sub> CH <sub>3</sub> (13.56)
<b>1h</b>	36.64	144.20	169.28	103.85	153.44 (152.89) (NH <sub>2</sub> )	152.89 (153.44) (NH <sub>2</sub> )	119.68 (Cl)	CH <sub>3</sub> : CH <sub>3</sub> (31.55)
<b>1i</b>	36.76	143.81	169.28	103.79	153.16 (152.78) (NH <sub>2</sub> )	152.78 (153.16) (NH <sub>2</sub> )	119.21 (H)	CH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> O: CH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> O (36.76), C-2" (148.35), C-3" (108.77), C-4" (110.54), C-5" (142.93)
<b>1j</b>	36.70	143.86	169.22	103.79	153.16 (152.78) (NH <sub>2</sub> )	152.78 (153.16) (NH <sub>2</sub> )	119.34 (H)	CH <sub>2</sub> CH=CH <sub>2</sub> : CH <sub>2</sub> (46.11), CH=CH <sub>2</sub> (117.57), CH=CH <sub>2</sub> (137.69)
<b>1k</b>	36.53	143.81	168.72	103.62	153.38 (152.94) (NH <sub>2</sub> )	152.94 (153.38) (NH <sub>2</sub> )	119.51 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (40.91), CH <sub>2</sub> CH <sub>3</sub> (13.51)
<b>1l</b>	36.63	144.41	169.87	103.42	153.02 (152.31) (NH <sub>2</sub> )	152.31 (153.02) (NH <sub>2</sub> )	119.00 (Cl)	4-FC <sub>6</sub> H <sub>4</sub> : C-1" (130.70, J <sub>CCCCF</sub> = 3.3 Hz), C-2" (130.12, J <sub>CCCF</sub> = 9.1 Hz), C-3" (115.46, J <sub>CCF</sub> = 23.2 Hz), C-4" (161.70, J <sub>CF</sub> = 245.7 Hz)
<b>1m</b>	36.52	144.30	169.82	103.53	152.97 (152.25) (NH <sub>2</sub> )	152.25 (152.97) (NH <sub>2</sub> )	118.78 (Cl)	C <sub>6</sub> H <sub>5</sub> : C-1" (134.35), C-4" (128.77), C-2", C-3" (128.44, 127.78)

remaining two signals appeared as doublets whose residual splittings reflected the proton chemical shifts with respect to that of the irradiated proton (15). This observation was helpful in assigning the methines of **1a-c** and **2a,b** when H-5' and H-6' were too closely spaced in the <sup>1</sup>H-nmr to be selectively decoupled.

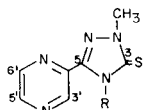
After **4** and **1a-c** were assigned it was possible to determine the shielding effects of the mesoionic group. The mesoionic triazolium group shielded C-2' in compounds **1a-c** 7.0-7.8 ppm compared to pyrazine itself (16). Carbons C-3' and C-6' were deshielded 0.9-1.5 ppm and 1.5-2.6 ppm respectively. Carbon C-5' was shifted less than 0.5 ppm. These effects are similar to those observed in the phenyl group of 1,3-dimethyl-2-phenylimidazolium bromide (17).

Methyl 3'-aminopyrazine-2'-carboxylate, **5** (8), was a suitable model for compounds **1e,g** and **2c,d**. The methines were again assigned by selective decoupling techniques. It was clear from published data (18) that the



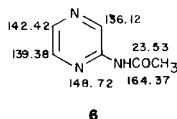
shielding effects of the amino group on pyrazine were qualitatively similar to its effects on benzene (19). Taking into account the observed shielding effects of the mesoionic group around the pyrazine ring, the assignment of the widely separated quaternary carbons was essentially trivial.

Table 2  
<sup>13</sup>C-Nmr Assignments for Some Triazole-3-thiones



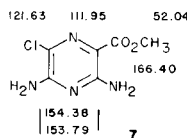
Compound No.	CH <sub>3</sub>	C-5	C-3	C-2'	C-3'	C-5'	C-6'	R
					(subst.)	(subst.)	(subst.)	
<b>2a</b>	36.30	145.23	167.22	141.43	143.86 (H)	143.86 (H)	145.62 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (41.43), CH <sub>2</sub> CH <sub>3</sub> (13.37)
<b>2b</b>	36.52	145.68	168.49	140.82	144.41 (H)	143.80 (H)	145.68 (H)	C <sub>6</sub> H <sub>5</sub> : C-1" (135.18); C-4" (129.10); C-2", C-3" (128.88, 128.22)
<b>2c</b>	36.18	145.62	166.45	123.25	153.30 (NH <sub>2</sub> )	144.19 (H)	131.31 (H)	C <sub>2</sub> H <sub>5</sub> : CH <sub>2</sub> CH <sub>3</sub> (41.82), CH <sub>2</sub> CH <sub>3</sub> (13.31)
<b>2d</b>	36.41	145.78	167.72	123.36	153.91 (NH <sub>2</sub> )	144.24 (H)	131.20 (H)	C <sub>6</sub> H <sub>5</sub> : C-1" (135.73), C-4" (128.66), C-2", C-3" (128.66, 127.95)
<b>2e</b>	36.68	146.07	167.11	108.11	152.31 (150.98) (NH <sub>2</sub> )	150.98 (152.31) (NH <sub>2</sub> )	116.95 (Cl)	C <sub>6</sub> H <sub>5</sub> : C-1" (136.51), C-4" (128.50), C-2", C-3" (128.50, 128.17)

Unfortunately, the methines of the acetamide compounds **1d** and **1f** were not separated in the <sup>1</sup>H-nmr. Acetamidopyrazine (20), **6** (8) was easily assigned, however, using selective heteronuclear decoupling. Carbons C-5' and C-6' of **1d** and **1f** were assigned on the basis of **6**. Carbons C-2' and C-3' were widely enough separated to be designated on the basis of chemical shift arguments similar to **1e,g** and **2c,d**. The acetamido carbonyl carbon



was distinguished from C-3 by obtaining the fully proton coupled spectrum. Under these conditions C-3 remained a singlet, while the carbonyl was a quartet.

Finally, methyl 3',5'-diamino-6'-chloropyrazinecarboxylate, **7** (8), **1h-m**, and **2e** were assigned solely on chemical shift arguments. Again taking into consideration the observed shielding effect of the triazolium group on the

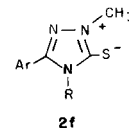


pyrazine C-2' position and the lack of shielding at the other carbons, it was plain that C-6' in **7**, **1h-m**, and **2e** resonated in the range of 117-120 ppm and that C-2' gave rise to a peak at 112 ppm in **7**, 103-104 ppm in **1h-m** and 108 ppm in **2e**. Positions C-3' and C-5' in this group of compounds remained ambiguous.

The triazol-3-thione moiety (Table 2) was less shielding than the mesoionic group. Position C-2' was shielded only about 4 ppm compared to pyrazine instead of about 7.5

ppm. Carbons C-3' and C-5' were deshielded by the triazol-3-thione group, although only to the extent of 0.8-1.4 ppm, while C-6' was shifted less than 0.5 ppm.

In comparing the mesoionic ring with the triazol-3-thione ring, there was very little difference in the <sup>13</sup>C-chemical shift of the methyl groups. They were shielded slightly in **2a-d** compared to **1a,b,g**, and **1e**, respectively, but the methyl groups of **2e** and **1m** had virtually identical chemical shifts. This most likely reflects the tendency of **2** to exist as the aromatic tautomer **2f**, as suggested by Begtrup (17) for pyrazolinthiones. Thus, the methyl groups in **1** and **2** are in similar environments. Positions C-3 and C-5 proved to be characteristic of **1** and **2**, however. Position C-3, bearing the sulfur, was uniformly shielded by 2-3 ppm in **2a-e** compared to **1a-m**. Conversely, C-5 was deshielded 1.5-2.2 ppm in **2a-e**.



## EXPERIMENTAL

<sup>13</sup>C-nmr spectra were recorded as DMSO-d<sub>6</sub> solutions at 15.03 MHz using a JEOL FX-60 spectrometer equipped with an internal deuterium lock. Operating parameters were: pulse width, 3 μs; tip angle, 30°; pulse repetition, 2.0 sec; sweep width, 3.4 kHz; data size, 8K. All chemical shifts are given in parts per million relative to internal tetramethylsilane.

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