Gerrit L'abbé, Suzanne Toppet, André Willocx, and Georges Mathys*

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

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The usefulness of ^{13}C nmr spectroscopy in the tautomeric assignment of 5-(monosubstituted)-amino-1,2,3,4-thiatriazoles is demonstrated. The reaction products, derived therefrom by alkylation, acylation and sulfonylation, are also readily characterized by an inspection of the $^{13}C_5$ signal shift. For thiatriazolinethione, the ^{13}C nmr spectrum indicates the presence of a thioketone function (**6**, δ 193.1 ppm) instead of a thiol function (**7**).

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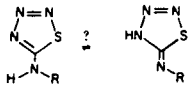
The long unsolved and confusing problem of prototropic tautomerism of 1-monosubstituted tetrazoline-5-thiones has recently been settled definitively by ^{13}C nmr analysis (1). For the isomeric 5-(monosubstituted)amino-1,2,3,4-thiatriazoles, the available spectroscopic evidences (2) favor the amino form **1** over the imino form **2**, and it would be desirable to corroborate this by ^{13}C nmr spectroscopy. Indeed, the C_5 atoms in **1** and **2** are



1 **2**

expected to resonate at different places in the ^{13}C nmr spectra, allowing for an easy diagnosis of this tautomeric aspect. In order to locate the C_5 absorptions of **1** and **2**, we have prepared the known model compounds **3a,b** and **4a,b** (3,4). The C_5 atom in **3a** absorbed at δ 180.4 ppm, comparable with the values found for 5-phenyl-1,2,3,4-thiatriazole (δ 178.5 ppm) (5) and *S*-alkylated thiatriazolinethiolates (δ 179 ppm) (1). In contrast, **4a** exhibited a significant upfield chemical shift for the C_5 atom at δ 156 ppm. As expected (6), the tosyl derivatives **3b** and **4b** resonated respectively at higher and lower field than **3a** and **4a**.

3a: R = Ph, δ 180.4 (deuteriochloroform)
3b: R = Ts, δ 173.1 (deuteriochloroform)

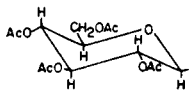
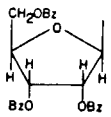
4a: R = Ph, δ 156 (deuteriochloroform)
4b: R = Ts, δ 166.3 (deuteriochloroform)

With these values at hand, we can conclude that all the monosubstituted aminothiatriazoles **1b-g** recorded in Table 1 exist exclusively (at least in solution by nmr) in the amino form, even when a strong electron-withdrawing group is present on the exocyclic nitrogen atom (see **1e**). Further confirmation comes from the ^{1}H nmr spectrum of **1b** which showed a triplet NH absorption at δ 8.6 ppm and a methylene doublet at δ 4.6 ppm. Note also that the unsubstituted 5-aminothiatriazole **1a**, whose amino form was accepted on the basis of firm ir and uv data (2), exhibited a C_5 absorption (δ 178.2 ppm) at the expected position in the ^{13}C nmr spectrum.

The ^{13}C nmr data of model compounds **3** and **4** can also be used to elucidate the structure of any substitution product. Thus, methylation of **1f** with diazomethane furnished a mixture of two products in a ration of 70:30.

Table 1

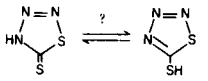
^{13}C Nmr Data of 5-Aminothiatriazoles (ppm from TMS)

Compound	R	M.p., °C	C_5	solvent
1a	H	128-130	178.2	DMSO-d_6
1b	$PhCH_2$	80-81	179.4	deuteriochloroform
1c	t-C_4H_9	113-114	176	deuteriochloroform, DMSO-d_6, perdeuterioacetone
1d	C_6H_5	142-143	174.2	DMSO-d_6
1e	Ts	142-144	173.1	DMSO-d_6
1f		126-127 dec.	177.5	deuteriochloroform
1g		121-122 dec.	177.4	deuteriochloroform

They were readily identified as **3** and **4** (R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) on the basis of their ^{13}C nmr spectra which showed C_5 absorptions respectively at δ 181.2 and 156.4 ppm (deuteriochloroform). Treatment of **1d** with *p*-methoxybenzoyl chloride and tosyl chloride in the presence of triethylamine furnished single products which exhibited C_5 absorptions respectively at δ 171.5 (deuteriochloroform) and 174.3 ppm (DMSO-d_6), pointing to structures **5a** and **5b** (7).

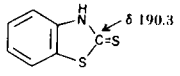
5a: R = *p*-$CH_3OC_6H_4CO$ (61%, m.p. 115° dec.)
5b: R = *p*-$CH_3C_6H_4SO_2$ (20%, m.p. 142-144°)

In contrast with **1**, thiatriazolinethione exists in acetone-d_6 solution in the thione form **6**, and not in the thiol form **7** as claimed by Jensen and Pedersen (2). Indeed, at 0° its ^{13}C nmr spectrum manifested a low-field



6 **7**

C=S absorption at δ 193.1 ppm, comparable with reference compound **8** (8) whereas the C-atom in **7** would be expected to resonate in the region δ 175-180 ppm (1).



8 (DMSO-d_6)

EXPERIMENTAL

The ir spectra were taken on a Perkin-Elmer 157G spectrometer. Proton nmr spectra were recorded with a Jeol MH-100 or Varian XL-100 spectrometer. For ^{13}C nmr spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation. The known thiatriazoles were prepared as reported (2,3,4,9).

Synthesis of 5-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosylamino)thiatriazole (**1g**).

This compound was synthesized by treatment of 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl isothiocyanate (10) (2.5 g.) with an excess of hydrazoic acid in ether (120 ml.) at room temperature for one week. Compound **1g** precipitated in 78% yield and was recrystallized from dichloromethane-ether to give white needles, m.p. 121-122° dec.; ir (potassium bromide): 3400-3200, 1720, 1540 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.4 (NH, exchangable with deuterium oxide), 8.0-7.8 (6H, m), 7.7-7.2 (9H, m), 5.95-5.7 (3H, m), 4.8-4.5 (3H, m); ^{13}C nmr (deuteriochloroform): δ 177.4 (*C*=N), 166.7, 166 (*C*=O), 89.4 (C_1), 80.1, 74.8, 71.9, 64 (C_5).

Anal. Calcd. for $C_{27}H_{22}N_4O_7S$ (547): C, 59.33; H, 4.05. Found: C, 59.28; H, 4.16.

Methylation of 5-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosylamino)thiatriazole (**1f**).

A saturated solution of diazomethane in ether (30 ml.) was added to a suspension of **1f** (3 g.) in ether (30 ml.). After one week, the solvent was removed to give a white solid composed of the two methylated products **3** and **4** (R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) in a ratio of 70:30 (overall yield 90%). They were separated by fractional crystallization from ether and recrystallized from ether. Compound **3** (R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl), m.p. 102-104°; ir (potassium bromide): 1750, 1540, 1230, 1040 cm^{-1}; ^1H nmr (deuteriochloroform): δ 5.67 (1H, d, J = 9 Hz), 5.5-5.0 (3H, m), 4.4-4.2 (2H, m), 4.2-3.8 (1H, m), 3.18 (3H, s), 2.08, 2.02 and 2.00 (9H, three s), 1.84 (3H, s); ^{13}C nmr (deuteriochloroform): δ 181.2 (*C*=N), 88 (C_1), 74.5, 72.9, 68.7, 68.1, 62 (C_6), 36.8 (CH_3N).

Anal. Calcd. for $C_{16}H_{22}N_4O_9S$ (446): C, 43.07; H, 4.93. Found: C, 42.99; H, 4.94.

Compound **4** (R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl), had m.p. 102-104°; ir (potassium bromide): 1760, 1650 (C=N), 1235, 1040 cm^{-1}; ^1H nmr (deuteriochloroform): δ 5.4-4.9 (3H, m), 4.64 (1H, d, J = 9 Hz), 4.25 (CH_2, m), 3.8 (1H, m), 3.73 (3H, s), 2.12 (3H, s), 2.08 and 2.00 (9H, three s); ^{13}C nmr (deuteriochloroform): δ 156.4 (*C*=N), 88.7 (C_1), 74.1, 73.3, 72.6, 68.8, 62.2 (C_6), 34.4 (CH_3N).

Anal. Calcd. for $C_{16}H_{22}N_4O_9S$ (446): C, 43.07; H, 4.93. Found: C, 42.71; H, 4.84.

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(6) Although it is logical that **4b** resonates at lower field than **4a**, the upfield chemical shift of **3b** with respect to **3a** cannot be rationalized, but was indeed expected by comparison with other systems; see, for instance, G. L'abbé, G. Verhelst, L. Huybrechts, and S. Toppet, *J. Heterocyclic Chem.*, **14**, 515 (1977).

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