

## Multinuclear NMR Study of some Mesoionic 3-Phenyl-1-thia-2,3,4-triazol-3-ium-5-ylmethanides with Various Exocyclic Groups

Wojciech Bocian,<sup>a</sup> Jarosław Jaźwiński,<sup>a</sup> Lech Stefaniak<sup>\*a</sup> and Graham A. Webb<sup>b</sup>

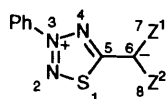
<sup>a</sup> Institute of Organic Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland

<sup>b</sup> Department of Chemistry, University of Surrey, Guildford, Surrey, UK GU2 5XH

Six mesoionic 3-phenyl-1-thia-2,3,4-triazol-3-ium-5-ylmethanides (**3**–**9**) have been synthesized for the first time. <sup>13</sup>C, <sup>14</sup>N and <sup>15</sup>N NMR data have been collected and interpreted in terms of molecular structure. The <sup>1</sup>J<sub>C-5-C-6</sub> coupling constants of the ring-exocyclic group bond have been determined and are discussed.

Mesoionic compounds form a class of heterocyclic structures with interesting properties.<sup>1,2</sup> It has been demonstrated that <sup>13</sup>C, <sup>14</sup>N and <sup>15</sup>N NMR techniques are very useful tools for the structural investigation of this class of compounds. Thus, the NMR techniques have been applied to the study of some mesoionic thia- and oxa-triazoles,<sup>3–5</sup> tetrazoles<sup>6–8</sup> and diazoles.<sup>9</sup>

Previously<sup>5</sup> three mesoionic 3-phenyl-1-thia-2,3,4-triazol-3-ium-5-ylmethanides **1**, **2** and **4** have been investigated by NMR techniques. The NMR data indicate that two non-equivalent CN groups are present in **1**. Similarly, two non-equivalent COEt groups are present in **4**, due to the stereochemistry around the C-5–C-6 bond which is like a C=C double bond.



- 1 Z<sup>1</sup> = Z<sup>2</sup> = CN
- 2 Z<sup>1</sup> = CN, Z<sup>2</sup> = CO<sub>2</sub>Et
- 3 Z<sup>1</sup>, Z<sup>2</sup> = –CO<sub>2</sub>C(Me)<sub>2</sub>CO<sub>2</sub>–
- 4 Z<sup>1</sup> = Z<sup>2</sup> = CO<sub>2</sub>Et
- 5 Z<sup>1</sup> = COMe, Z<sup>2</sup> = COEt
- 6 Z<sup>1</sup> = Z<sup>2</sup> = COMe
- 7 Z<sup>1</sup> = COMe, Z<sup>2</sup> = COPh
- 8 Z<sup>1</sup> = Z<sup>2</sup> = COPh
- 9 Z<sup>1</sup> = COMe, Z<sup>2</sup> = CONHPh

We now present the NMR data of some new 1-thia-2,3,4-triazol-3-ium-5-ylmethanides and some results concerning the nature of the C-5–C-6 ring-exocyclic group bond.

### Results and Discussion

<sup>14</sup>N And <sup>15</sup>N NMR Data.—(Table 1). A nitrogen atom bearing a formal positive charge is expected to produce a relatively sharp <sup>14</sup>N signal as observed for the Type A mesoionic heterocycles.<sup>3–5</sup> Thus, the N-3 signals of compounds **1**–**9** are easily assigned by means of the <sup>14</sup>N NMR technique. The high-frequency signals within the range –30 to –50 ppm, are assigned to the N-2 atom (due to the vicinity of a heteroatom). The signals within the range –80 to –90 ppm are assigned to the N-4 atom. Generally, the assignments are made on the basis of the rules observed for the mesoionic thiazoles previously described.<sup>3–5</sup> The signals of the exocyclic groups (CN, CONHPh) are identified due to typical values of their chemical shifts.

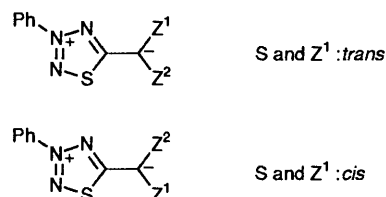
It is interesting that a quite strong solvent effect (*ca.* 10 ppm) is observed for the nitrogen chemical shifts of compounds **1**, **2** and **4**. Thus, the <sup>15</sup>N chemical shifts of **1**, **2** and **4** observed in DMSO solution<sup>5</sup> (Table 2) are different from those observed in

CDCl<sub>3</sub> solution (Table 1). The solvent dependence of the nitrogen chemical shifts is probably a reflection of the highly polar nature of the compounds studied.

<sup>1</sup>H and <sup>13</sup>C NMR data are presented in Table 3. Generally, the <sup>1</sup>H NMR data are less useful for the structural analysis than are the <sup>13</sup>C and <sup>15</sup>N results. However, the <sup>1</sup>H and <sup>13</sup>C signals of the exocyclic groups can be used as an easy and simple means of compound identification. Especially, the signals of the C-5 and -6 atoms are quite characteristic. The chemical shift of the C-6 atom depends strongly on the kind of exocyclic group and its value varies within the range from *ca.* 40 ppm for the compound **1** to *ca.* 108 ppm for the compound **6**.

As demonstrated previously,<sup>5</sup> two non-equivalent exocyclic groups (CN groups) are observed for compound **1**, as well as for compound **4** (2 CO<sub>2</sub>Et groups). Similar effects are observed for the compounds **3**, **6** and **8** containing 'symmetrical' exocyclic groups (*i.e.* Z<sup>1</sup> = Z<sup>2</sup>).

By analogy, two isomers are expected for the compounds **2**, **5**,

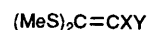


**7** and **9** (*i.e.* isomers in which the exocyclic substituents are either *cis* or *trans* in relation to the ring sulfur atom). However only one isomer has been separated from the crude reaction mixture of each synthesis. These results indicate that only one isomer (*cis* or *trans*) seems to be stable and it is formed as the major product in the preparation process.

<sup>13</sup>C–<sup>13</sup>C Coupling Constant.—The magnitude of <sup>13</sup>C–<sup>13</sup>C coupling constants depends strongly on the structure of the compound in question due to various electronic effects depending upon substituents and molecular geometries.<sup>10</sup> Thus, the value of <sup>1</sup>J<sub>C-5-C-6</sub> can be used as a probe for the nature of bond investigations.

The <sup>13</sup>C–<sup>13</sup>C coupling constants of some mesoionic compounds are presented in Table 4. The values of <sup>1</sup>J<sub>C-5-C-6</sub> are observed to change within the range 75.1 to 92.7 Hz.

The compounds **10**–**12**, with C=C bonds, are used as model



- 10 X = Y = CN
- 11 X = CN, Y = CO<sub>2</sub>Et
- 12 X = Y = CO<sub>2</sub>Et

**Table 1**  $^{15}\text{N}$  and  $^{14}\text{N}$  NMR data of some mesoionic 1-thia-2,3,4-triazoliumylmethanides<sup>a</sup>

Compound	$\delta_{15\text{N}}$ ( $^{14}\text{N}$ Line width/Hz) { $^{15}\text{N}$ - $^1\text{H}$ Coupling constant with PhHs/Hz}			
	N-2	N-3	N-4	exo-Group
<b>1</b>	-50.6	-70.9 ( $\approx 700$ ) { $^3J$ 2.1}	-81.6	-116.6, -110.5
<b>2</b>	-39.9	-76.9 (287) { $^3J$ 2.0}	-85.9	-119.6
<b>3</b>	-38.3	-78.2 (368) { $^3J$ 2.1}	-81.1	—
<b>4</b>	-40.3	-78.2 (420) { $^3J$ 2.1}	-83.3	—
<b>5</b>	-32.1	-80.9 (377) { $^3J$ 2.2}	-78.2 { $^4J$ 1.5}	—
<b>6</b>	-31.3	-82.8 (217) { $^3J$ 2.3}	-83.2 { $^4J$ 1.3}	—
<b>7</b>	-37.1	-82.3 (430) { $^3J$ 2.0}	-81.5	—
<b>8</b>	-35.9	-80.6 (452) { $^3J$ 2.0}	-80.0	—
<b>9</b>	-31.2	-82.1 (334) { $^3J$ 2.6}	-87.4 { $^4J$ 1.5}	-257.6 { $^1J$ 88.6} <sup>b</sup>

<sup>a</sup> Measurements were taken on  $\text{CDCl}_3$  solutions with external nitromethane as a standard. <sup>b</sup>  $^1J_{15\text{N}-1\text{H}}$  from NH group.

**Table 2**  $^{15}\text{N}$  NMR data of some methanides in [ $^2\text{H}_6$ ]DMSO solution<sup>5</sup>

Compound	$\delta_{15\text{N}}$			
	N-2	N-3	N-4	exo-Group
<b>1</b>	-39.3	-70.4	-78.6	-113.4, -108.1
<b>2</b>	-34.8	-75.0	-83.4	-113.9
<b>4</b>	-40.2	-77.5	-97.6	—

structures. The values of some  $^1J_{\text{C}-\text{C}}$  coupling constants are presented in Table 5. These values are similar to those observed for the mesoionic compounds **1–9**. Thus, the data suggest that the C-5–C-6 bond has a large amount of double bond character.

A linear correlation [ $J = (-0.266 \pm 0.026)\delta + (104.9 \pm 2.4)$ ;  $R = -0.9676$ ] is observed between the  $^1J_{\text{C}-5-\text{C}-6}$  coupling constants and the C-6 chemical shifts for compounds **1–9**. It is very interesting that only compound **9** appears as an exception, probably due to the presence of the amide group PhNHCO and the possibility of hydrogen bonding.

Two different coupling constants are observed for the C-6–CN bond in the exocyclic groups of **1**. Thus, the C-5–C-6 coupling constant is 92.7 Hz, the C-6–CN coupling constant is either 97.2 or 99.1 Hz, depending upon whether the CN group is *cis* or *trans* in relation to the S atom. A similar effect is observed for the other structures investigated which have 'symmetric' exocyclic groups (*i.e.* for compounds **4**, **6** and **8**).

## Experimental

**NMR Measurement.**—All NMR measurements were recorded on a BRUKER AM 500 machine. Typically a saturated solution of a compound in  $\text{CDCl}_3$  was used, with a concentration *ca.* 1–1.5 mol  $\text{dm}^{-3}$ . The 5 mm  $^1\text{H}/^{13}\text{C}$  dual probe, 10 mm  $^{14}\text{N}$  broad band probe and 10 mm  $^{15}\text{N}$  probe were used. The  $\text{Me}_4\text{Si}$  signal (0.0 ppm) was used as an internal standard for the  $^1\text{H}$  NMR measurements; the solvent peak ( $\delta_{\text{C}} = 77.0$ ) was used as the internal standard for the  $^{13}\text{C}$  measurements. The neat nitromethane ( $\delta = 0$ ) was used as an external reference for the  $^{14}\text{N}$  and  $^{15}\text{N}$  measurements.

**$^{13}\text{C}$  NMR Measurements.** The standard spectra were recorded at 125.76 MHz, with a relaxation delay of 2 s, an acquisition time of 1.2 s, a flip angle of *ca.* 45°, and *ca.* 100–1000 scans were taken.

The  $^{13}\text{C}$ – $^{13}\text{C}$  coupling constants were recorded either by the INADEQUATE technique, or by recording the standard  $^{13}\text{C}$  NMR spectra and investigating their satellite signals. A relaxation delay of 8 s, an acquisition time of 1.5 s and 15 000–20 000 scans were applied. Alternatively, 0.5 mol  $\text{dm}^{-3}$  solutions were used, with the addition of 2–3% molar ratio of  $\text{Cr}(\text{acac})_3$  as a relaxation reagent. In this case, the relaxation delay

was decreased to 1.5 s, and 20 000–40 000 scans were collected.

The spectral digital resolution of 0.7 Hz/Pt typically was applied.

**$^{14}\text{N}$  NMR Measurements.** The frequency of 36.118 MHz was used, and typical parameter values were 0 s (relaxation delay), 0.2 s (acquisition time), *ca.* 50° (flip angle) and 1000–2000 scans.

**$^{15}\text{N}$  NMR Measurements.** The frequency of 50.698 MHz was employed, flip angle *ca.* 40°, acquisition time 2.0 s and a relaxation delay of 4–10 s were applied. Typically, 1000–3000 scans were collected.

**Syntheses.**—The mesoionic compounds **1**, **2** and **4** were obtained according to published procedures,<sup>5,11</sup> as well as the 5-ethoxy-3-phenyl-1,2,3,4-thiaziazolium tetrafluoroborate **13**<sup>12</sup> and the model structures **10–12**.<sup>13,14</sup> Acetonitrile was dried over  $\text{P}_2\text{O}_5$  and distilled. All remaining reagents were commercially available.

5-(3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**3**). 2,2-Dimethyl-1,3-dioxane-4,6-dione (1.44 g; 0.01 mol) was dissolved in acetonitrile (50  $\text{cm}^3$ ), then sodium methanoate (0.54 g; 0.01 mol) and the thiaziazolium tetrafluoroborate **13** (1.5 g; 0.005 mol) were added. The mixture was heated (reflux) for 2 h, then the solvent was evaporated under reduced pressure, the residue was dissolved in a mixture of chloroform (100  $\text{cm}^3$ ) and water (50  $\text{cm}^3$ ). The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent was evaporated under reduced pressure. The crude product was purified by crystallisation (ethanol–heptane, 1:1); yield 0.7 g (0.0023 mol) 46%. Crystallisation from ethanol gave red needles, m.p. 205 °C (Found: C, 51.3; H, 3.7; N, 13.8; S, 10.35.  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_4\text{S}$  requires C, 51.14; H, 3.63; N, 13.76; S, 10.50%).

3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl(acetyl)ethoxycarbonylmethanide (**5**). Ethyl acetylacetate (1.7 g; 0.013 mol) was dissolved in acetonitrile (10  $\text{cm}^3$ ), then sodium methanoate (0.7 g; 0.013 mol) and the thiaziazolium tetrafluoroborate **13** (2 g; 0.0068 mol) were added. The mixture was heated (reflux) for 4 h, then the solvent was evaporated under reduced pressure, the residue was dissolved in a mixture of chloroform (100  $\text{cm}^3$ ) and water (20  $\text{cm}^3$ ). The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent was evaporated under reduced pressure. The crude product was purified by crystallisation (heptane); yield 0.6 g (0.002 mol) 34%. Crystallisation (acetonitrile) gave red needles, m.p. 139–140 °C (Found: C, 53.8; H, 4.6; N, 14.4; S, 11.1.  $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$  requires C, 53.61; H, 4.47; N, 14.42; S, 11.01%).

3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl(di(acetyl)methanide) (**6**). Acetylactone (1.0 g; 0.01 mol) was dissolved in acetonitrile (40  $\text{cm}^3$ ), then sodium methanoate (0.54 g; 0.01 mol) was added. The thiaziazolium tetrafluoroborate **13** (1.5 g; 0.005 mol) was added; the mixture was heated (reflux) for 2 h, then the solvent

**Table 3**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of some mesoionic 1-thia-2,3,4-triazoles<sup>a</sup>

Compound	$\delta^{13}\text{C}$ ( $\delta^1\text{H}$ )		exo-Group <sup>b</sup>			
	C-5	C-6	>C=O	CN	CH <sub>2</sub>	CH <sub>3</sub>
	<b>1</b>	182.0	40.8	—	116.7, 114.1	—
<b>2</b>	177.9	65.4	169.5	115.2	61.8 (4.371)	14.3 (1.393)
<b>3</b>	176.1	80.1	167.5, 158.1	—	—	26.3 (1.787)
<b>4</b>	177.1	85.3	170.3, 163.1	—	61.0 (4.395), 59.2 (4.367)	14.0 (1.430), 14.0 (1.415)
<b>5</b>	174.6	98.1	191.2, 164.1	—	59.3 (4.421)	25.5 (2.715), 14.2 (1.479)
<b>6</b>	175.4	108.3	192.6, 192.3	—	—	31.9 (2.848), 26.4 (2.726)
<b>7</b>	174.4	106.8	192.0, 191.1	—	—	24.8 (2.612)
<b>8</b>	175.1	106.2	192.6, 186.5	—	—	—
<b>9</b>	176.7	96.7	192.4, 167.0	—	—	31.7 (2.850)

Measurements were taken on  $\text{CDCl}_3$  solutions with TMS as standard. <sup>b</sup> Two inequivalent signals occur in the order C-7, C-8.

**Table 4**  $^{13}\text{C}$ - $^{13}\text{C}$  Coupling constants of some mesoionic 1-thia-2,3,4-triazoles<sup>a</sup>

Compound	$J^{13}\text{C}-^{13}\text{C}/\text{Hz}$			
	C-5-C-6	C-6-C-7	C-6-C-8	CO-Me
<b>1</b>	92.7	97.2	99.1	—
<b>2</b>	89.2 (89.1) <sup>b</sup>	94.2	88.8	—
<b>3</b>	83.1	74.4	80.9	—
<b>4</b>	82.0	83.0	86.2	—
<b>5</b>	78.6 (78.7) <sup>b</sup>	62.6 (62.3) <sup>b</sup>	82.9 (82.8) <sup>b</sup>	44.5
<b>6</b>	75.1	60.2	60.5	44.3, <sup>c</sup> 42.6 <sup>d</sup>
<b>7</b>	75.6	60.4	62.2	44.1
<b>8</b>	75.6	61.3	63.7	—
<b>9</b>	82.6	—	—	—

<sup>a</sup> The measurements were taken on  $\text{CDCl}_3$  solutions with 2%  $\text{Cr}(\text{Acac})_3$  as a relaxation reagent. <sup>b</sup> The measurements were taken on  $\text{CDCl}_3$  solutions with not used  $\text{Cr}(\text{Acac})_3$ . <sup>c</sup> C-7. <sup>d</sup> C-8.

**Table 5** Some  $^1J^{13}\text{C}-^{13}\text{C}$  couplings for model compounds containing a C=C double bond

Compound	$^1J^{13}\text{C}-^{13}\text{C}/\text{Hz}$		
	>C=C<	C-CN	C-CO <sub>2</sub> Et
<b>10</b>	83.3	94.9	—
<b>11</b>	79.0	88.3	83.1
<b>12</b>	78.4	—	80.0

was evaporated under reduced pressure. The residue was dissolved in chloroform-water 100:10  $\text{cm}^3$ . The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent evaporated under reduced pressure. The crude product was crystallised (benzene-hexane, 1:1); yield 0.4 g (0.0016 mol) 31%. Crystallisation (acetonitrile) yielded orange needles, m.p. 173 °C (Found: C, 55.2; H, 4.3; N, 16.1; S, 12.3.  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  requires C, 55.16; H, 4.24; N, 16.08; S, 12.27%).

**3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl(acetyl)benzoylmethanide (7).** Benzoylacetone (2.1 g; 0.013 mol) was dissolved in acetonitrile (80  $\text{cm}^3$ ), then sodium methanoate (0.7 g; 0.013 mol) was added and the mixture was stirred for 20 min. Then thiaziazolium tetrafluoroborate **13** (2 g; 0.0068 mol) was added; the mixture was heated (reflux) for 5 h, then the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform-water, 70:30  $\text{cm}^3$ . The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent was evaporated under reduced pressure. The crude product was crystallised (benzene-heptane, 1:1); yield 1.4 g (0.043 mol) 64%. Crystallisation from ethanol yielded red plates, m.p. 190–191 °C (Found: C, 63.0; H,

3.9; N, 13.0; S, 9.8.  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$  requires C, 63.14; H, 4.05; N, 13.01; S, 9.91%).

**3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl(benzoyl)methanide (8).** Dibenzoylmethane (2.9 g; 0.013 mol) was dissolved in acetonitrile (80  $\text{cm}^3$ ), then sodium methanoate (0.7 g; 0.013 mol) was added, and the mixture was stirred for 30 min. The thiaziazolium tetrafluoroborate **13** (2 g; 0.0068 mol) was added; the mixture was heated (reflux) for 5 h, then the solvent was evaporated under reduced pressure. The residue was dissolved in a mixture of chloroform-water 70:30  $\text{cm}^3$ . The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent was evaporated under reduced pressure. The crude product was crystallised (benzene-heptane, 1:1); yield 1.7 g (0.0044 mol) 65%. Crystallisation (ethanol) gave yellow needles, m.p. 206–207 °C (Found: C, 68.3; H, 3.9; N, 10.7; S, 8.3.  $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$  requires C, 68.56; H, 3.92; N, 10.91; S, 8.32%).

**3-Phenyl-1,2,3,4-thiaziazol-3-ium-5-yl(acetyl)phenylcarbamoylmethanide (9).** Acetylacetanilide (2.3 g; 0.013 mol) was dissolved in acetonitrile (30  $\text{cm}^3$ ), then sodium methanoate (0.7 g; 0.013 mol) was added, the mixture was stirred for 20 min. The thiaziazolium tetrafluoroborate **13** (2 g; 0.0068 mol) was added; the mixture was heated (reflux) for 1 h, then the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform-water 80:80  $\text{cm}^3$ . The organic layer was separated, dried ( $\text{MgSO}_4$ ) and the solvent was evaporated under reduced pressure. The crude product was crystallised (benzene-hexane, 2:1); yield 1 g (0.003 mol) 44%. Crystallisation (acetonitrile) yielded yellow fine needles, m.p. 208–209 °C (Found: C, 60.3; H, 3.9; N, 16.5; S, 9.5.  $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$  requires C, 60.34; H, 4.17; N, 16.56; S, 9.42%).

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