

**<sup>17</sup>O NMR SPECTRA OF ACYLATED UREAS AND THIOUREAS**Josef JIRMAN<sup>a</sup> and Pavel PECH<sup>b</sup><sup>a</sup> Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví<sup>b</sup> Prague Institute of Chemical Technology, 166 28 Prague 6

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<sup>17</sup>O NMR spectra of ten acyl- and diacylureas (*I*–*V*) and thioureas (*VII*–*XI*) were measured. <sup>17</sup>O NMR chemical shifts of the ureido oxygen in the ureas range from 240 to 310 ppm, those of the acyl oxygens from 377 to 400 ppm (acetyl groups) and 359 to 389 ppm (benzoyl groups), the half-widths being tens to hundreds Hz. Acylation of urea to the diacyl stage has an almost twice as large effect on the chemical shift of the ureido oxygen than has the monoacetylation. From the viewpoint of <sup>17</sup>O NMR chemical shifts, no significant difference has been found in the influence of ureido and thioureido groups on the transfer of electronic effects in 1,3-diacylureas and 1,3-diacylthioureas.

Acylated ureas and thioureas are known already almost one hundred years. <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N studies<sup>1</sup> of structure of diacylated ureas and thioureas revealed interesting differences in the transmission of electron-acceptor effects of the acyl group to the nitrogen atoms via the C=O and C=S group. The aim of the present study is to find out whether similar differences also exist in the <sup>17</sup>O chemical shifts.

**EXPERIMENTAL**

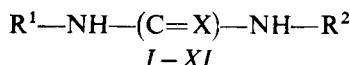
The <sup>17</sup>O NMR spectra were measured on a Bruker AM-400 instrument at 54.244 MHz. Compounds *I*–*XI* were measured in saturated solutions in acetonitrile at 345 K in 10 mm cells without cell rotation; <sup>2</sup>H<sub>2</sub>O in a coaxial sealed capillary was used both as a lock (deuterium signal) and as an external standard (oxygen signal). The values of the <sup>17</sup>O-chemical shifts were then referenced to the external H<sub>2</sub>O using the experimentally determined relation  $\delta^{17}\text{O}(\text{H}_2\text{O}) = -5.0$  ppm. Measurement parameters: spectral width 50 000 Hz, 4 k real data points, zero filling to 16 k, 90° pulse (13  $\mu\text{s}$ ), acquisition time 40 ms, preacquisition delay 100  $\mu\text{s}$ , relaxation time 50 ms, the number of accumulations for the individual compounds is given in Table I. Before Fourier transformation at least first eight points of FID were excluded and the residue was multiplied by exponential function for line broadening 150 Hz. This procedure corresponds to about 180  $\mu\text{s}$  preacquisition delay. Delays greater than 180  $\mu\text{s}$  result in signals of the same phase, shorter delays lead to "rolling base line" and phase artifacts<sup>2</sup>.

1-Acetylurea<sup>3</sup> (*I*), 1-benzoylurea<sup>4</sup> (*II*), 1,3-diacylurea<sup>5</sup> (*III*), 1,3-dibenzoylurea<sup>1</sup> (*IV*), 1-acetyl-3-benzoylurea<sup>1</sup> (*V*), 1-acetylthiourea<sup>3</sup> (*VII*), 1-benzoylthiourea<sup>6</sup> (*VIII*), 1,3-diacylthiourea<sup>3</sup> (*IX*), 1,3-dibenzoylthiourea<sup>7</sup> (*X*), and 1-acetyl-3-benzoylthiourea<sup>8</sup> (*XI*) were prepared according to the literature.

## RESULTS AND DISCUSSION

The <sup>17</sup>O NMR chemical shifts of the acylated ureas and thioureas are given in Table I.

The acyl oxygen signals in acylated thioureas are located up to 9 ppm downfield than those in the acylated ureas, an exception being the oxygen signals in *V* and *XI*; however, this value is negligible compared with the halfwidth of the signals of compound *XI*.



Compound	R <sup>1</sup>	R <sup>2</sup>	X
<i>I</i>	CH <sub>3</sub> CO	H	O
<i>II</i>	C <sub>6</sub> H <sub>5</sub> CO	H	O
<i>III</i>	CH <sub>3</sub> CO	CH <sub>3</sub> CO	O
<i>IV</i>	C <sub>6</sub> H <sub>5</sub> CO	C <sub>6</sub> H <sub>5</sub> CO	O
<i>V</i>	CH <sub>3</sub> CO	C <sub>6</sub> H <sub>5</sub> CO	O
<i>VI</i>	H	H	O
<i>VII</i>	CH <sub>3</sub> CO	H	S
<i>VIII</i>	C <sub>6</sub> H <sub>5</sub> CO	H	S
<i>IX</i>	CH <sub>3</sub> CO	CH <sub>3</sub> CO	S
<i>X</i>	C <sub>6</sub> H <sub>5</sub> CO	C <sub>6</sub> H <sub>5</sub> CO	S
<i>XI</i>	CH <sub>3</sub> CO	C <sub>6</sub> H <sub>5</sub> CO	S

This fact can be ascribed to the existence of *f* orbitals of the sulfur atoms which may be involved in the stabilization of resonance structures with partial negative charge on sulfur but not on the acyl oxygen atoms, decreasing thus the electron density on the acyl oxygens as compared with the acylated ureas. The same effect was observed for the <sup>15</sup>N NMR chemical shifts in the same compounds<sup>1</sup>.

Introduction of acyl to the N-1 nitrogen in urea results in a downfield shift of the ureido oxygen, 24 ppm for acetyl and 27 ppm for benzoyl group. On introduction of a second acyl to the N-3 nitrogen this effect is almost doubled (37 ppm and 46 ppm for acetyl and benzoyl, respectively). It is known that the length of the O—C bond in urea lays between the values for the single and double bond between these atoms. We may therefore assume that electron-accepting acyl groups on the nitrogen atoms in urea will increase the C—O bond order and thus shorten the bond. This assumption agrees with the observation that the chemical shift of the ureido oxygen is more affected by diacylation than monoacylation since in diacylurea the electronic effects of the acyl groups are transmitted to the ureido oxygen atom across the bond of higher order than in a monoacylurea.

Introduction of the second acyl to the N-3 nitrogen in an N-1 acylated urea or thiourea results in a downfield shift of the  $^{17}\text{O}$  NMR signal of the N-1 acyl group. This effect is more pronounced for the acetyl ( $\text{R}^2 = \text{CH}_3$ ) than for the benzoyl group ( $\text{R}^2 = \text{C}_6\text{H}_5$ ), see Eq. (1), Table II). In acylated thioureas this effect is somewhat lower:

$$\Delta\delta = \delta^{17}\text{O}(\text{R}^1-\text{CONH}(\text{CX})\text{NHCO}-\text{R}^2) - \delta^{17}\text{O}(\text{R}^1-\text{CONH}(\text{CX})\text{NH}_2); \quad (1)$$

this could indicate that the  $\text{C}=\text{S}$  group is not so good a transmitter of electron acceptor effects than the  $\text{C}=\text{O}$  group. A diametrically different conclusion based on

TABLE I

$^{17}\text{O}$  NMR chemical shifts  $\delta$  and halfwidths of  $^{17}\text{O}$  signals ( $W_{1/2}$ ) for compounds *I*–*XI* in acetonitrile at 345 K

Compound	NHCONH	COCH <sub>3</sub>	COC <sub>6</sub> H <sub>5</sub>	<i>n</i> <sup>a</sup>
<i>I</i>	264 (100)	377 (70)	—	313 000
<i>II</i>	267 (130)	—	359 (160)	459 000
<i>III</i>	301 (130)	402 (160)	—	28 800
<i>IV</i>	<sup>b</sup>	—	377 (c)	1 775 000
<i>V</i>	310 (180)	401 (140)	385 (150)	796 000
<i>VI</i>	240 (50)	—	—	10 000
<i>VII</i>	—	386 (130)	—	26 100
<i>VIII</i>	—	—	367 (180)	477 800
<i>IX</i>	—	409 (160)	—	4 100
<i>X</i>	—	—	383 (160)	160 900
<i>XI</i>	—	400 (380)	386 (210)	74 300

<sup>a</sup> Number of accumulations; <sup>b</sup> no signal was detected; <sup>c</sup> value was not determined owing to the fact that signal was too low and halfwidth could be strongly affected by noise.

TABLE II

Values of differences of chemical shifts  $\Delta\delta^{17}\text{O}$  according to Eq. (1)

$\text{R}^1$	$\text{R}^2 = \text{CH}_3$		$\text{R}^2 = \text{C}_6\text{H}_5$	
	$\text{X} = \text{O}$	$\text{X} = \text{S}$	$\text{X} = \text{O}$	$\text{X} = \text{S}$
$\text{CH}_3$	25	23	24	14
$\text{C}_6\text{H}_5$	26	19	18	16

by far more convincing differences between the acylated ureas and thioureas has been made from evaluation of <sup>15</sup>N NMR spectra of the same series of compounds<sup>1</sup>. Taking into account the halfwidths of the <sup>15</sup>N and <sup>17</sup>O NMR signals and thus the accuracy of reading the chemical shifts, the differences between the values for X = O and X = S in Table II are of low significance; moreover, the <sup>17</sup>O NMR signals of compounds *I*–*XI* can also be affected by the conformation which may be different for the acyl and diacyl ureas and thioureas. We can thus conclude that the effect of ureido and thioureido groups on the transfer of electron acceptor effects in 1,3-diacylureas and thioureas has no marked effect on the <sup>17</sup>O NMR chemical shifts of the acyl oxygen atoms.

The halfwidths of the <sup>17</sup>O NMR signals in the spectra of acylated ureas and thioureas are tens to hundreds of Hz and depend substantially on the viscosity of the sample. Since the solubility of the compounds was different, the viscosity of the measured saturated solutions was not comparable. Therefore the halfwidths together with the number of accumulations (both in Table I), have only an informative value about the time required for obtaining the spectrum (4 100 accumulations correspond to 6 min, 1 775 000 accumulations to 45.8 h of the measurement time). Compound *IV* is the least soluble one and has a relatively high molecular weight: therefore the measurement of the ureidic grouping signal was unsuccessful. Using another solvent was of no advantage because acetonitrile was chosen as the optimal dipolar aprotic solvent, compromising between solubility of the compounds, viscosity of the solvent, and absence of oxygen atoms in its molecule.

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