

NITROGEN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF PYRIDINIUM  
DICYANOMETHYLIDS

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Abstract — The  $^{14}\text{N}$  and  $^{15}\text{N}$  chemical shifts of ylidic nitrogen of substituted pyridinium dicyanomethylids and related compounds have been measured. A linear correlation is obtained between the  $^{13}\text{C}$ -SCS and the  $^{15}\text{N}$ -SCS of the 4-substituted pyridinium dicyanomethylids. A comparison and/or correlation is made of these values with those of the related molecules such as pyridines and pyridine N-oxides and also by using several different scales of substituent parameters such as  $\sigma^*$ ,  $(\sigma_I, \sigma_R^o)$ , and  $(\sigma_R^+, \sigma_R^-)$ .

Because of the zwitterionic structure of cycloimmonium ylids, their electronic properties and chemical reactivities are of considerable interest. Specifically, cycloimmonium ylids, like pyridinium dicyanomethylids and bis(methoxycarbonyl)-methylids, having two electron-withdrawing groups covalently bonded to the ylidic carbon are stable and can be isolated. With regards to their electronic properties, we have reported on the trapping of the cation radicals of pyridinium bis(alkoxycarbonyl)methylids by formation of complexes with diphenylcyclopropenone<sup>1</sup> and also on the unusual E. S. R. spectrum of the anion radicals of pyridinium bis(alkoxycarbonyl)methylids<sup>2</sup>. Synthetically, these stable ylids have served as useful reagents for the preparation of novel heterocycles such as indolizines<sup>3</sup>, cycl[3.2.2]-azines<sup>4</sup>, and 2-pyrones<sup>5</sup>.

The use of  $^{14}\text{N}$ - and  $^{15}\text{N}$ -NMR as a tool for studying the electronic structure of nitrogenous system is well known<sup>6</sup>. To our knowledge, however, no nitrogen NMR study

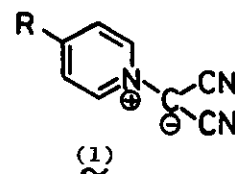


Table 1. The Chemical Shifts of Pyridinium Nitrogen of (1)

R	CN	CO <sub>2</sub> CH <sub>3</sub>	COCH <sub>3</sub>	COPh	H	CH <sub>2</sub> Ph	t-C <sub>4</sub> H <sub>9</sub>	i-C <sub>3</sub> H <sub>7</sub>	n-C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
N-14	154.1	154.4	155.0	156.1	162.3	167.4	167.9	167.8	168.1	167.8	162.3
N-15	N <sup>+</sup> 153.9	153.9	155.0	155.6	161.4	166.9	167.7	167.6	167.9	167.9	168.5
	(CN) 88.3	88.5	88.8	88.6	89.0	88.8	89.1	89.2	89.1	89.0	89.0)

In parenthesis, chemical shifts of the CN groups were shown.

Table 3. The SCS Values of Ylidic Carbon and Pyridinium Nitrogen of (1)

R	CN	CO <sub>2</sub> CH <sub>3</sub>	COCH <sub>3</sub>	COPh	H	CH <sub>2</sub> Ph	t-C <sub>4</sub> H <sub>9</sub>	i-C <sub>3</sub> H <sub>7</sub>	n-C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
C-13 <sup>1)</sup>	-3.7	-1.9	-1.9	-2.2	0	0.9	0.7	0.8	0.8	0.8	1.2
N-15 <sup>2)</sup>	-7.5	-7.5	-6.4	-5.8	0	5.5	6.3	6.2	6.5	6.5	7.1
N-15 <sup>3)</sup>	-10.1		-11.7	-10.7 <sup>4)</sup>	0	6.7	5.8	5.9	5.6 <sup>4)</sup>	6.6	8.0

1) The positive values show the upfield shifts. 2) The SCS of (1). 3) The SCS of a nitrogen of pyridines; calculated from the data in lit.<sup>8</sup> 4) This work.

Table 2. Effect of Substituents on Chemical Shifts at 3 and 4 Positions

Compd.	Sub.	x = 3			x = 4		
		Chem. Shifts	$\Delta^1$	$\Delta^2$	Chem. Shifts	$\Delta^1$	$\Delta^2$
Pyridinium	H	161.4		( 99.1)			
Dicyano-							
methylid	x-CH <sub>3</sub>	162.0	0.6	(100.2)	168.5	7.1	( 98.1)
	3,x-dimethyl	162.4	1.0		168.5	7.1	
	x-CO <sub>2</sub> CH <sub>3</sub>	160.2	-1.2		153.9	-7.5	
	x-CN	157.9	-3.5		153.9	-7.5	
Pyridine							
N-Oxide	H	87.6		( 25.3)			
	x-CH <sub>3</sub>	87.6	0	( 25.8)	96.4	8.8	( 26.1)
Pyridine							
	H	62.3					
	x-CH <sub>3</sub>	61.8	-0.5		70.3	8.0	

$\Delta^1$ : Difference from the non-substituted compound.

$\Delta^2$ : Difference from pyridine with the same substituents.

of the pyridinium dicyanomethylids has been reported. We now report a preliminary study of the effect of polar substituents on the <sup>15</sup>N-NMR chemical shifts of the pyridinium dicyanomethylids(1) which are briefly compared with those of the related heterocycles such as pyridines and pyridine N-oxides.

<sup>14</sup>N-NMR spectra were obtained in a sealed tube of DMSO-d<sub>6</sub> solution at 68 °C and

<sup>15</sup>N-NMR spectra were obtained in DMSO-d<sub>6</sub> with Cr(acac)<sub>3</sub> at 68 °C on a JEOL FX 90Q FT NMR spectrometer and chemical shifts are reported in ppm upfield from external nitromethane.

In the <sup>14</sup>N-NMR spectra of pyridinium dicyanomethylids the signal of the N-ylid function can be clearly distinguished from those of the other nitrogen atoms by its much smaller width and the characteristic range of shielding, ca. 150 to 170 ppm from neat nitromethane external standard. Table 1 shows that the <sup>15</sup>N shifts are almost the same as those derived from the <sup>14</sup>N-NMR data. Some of the variations

probably arise from uncertainties in the  $^{14}\text{N}$  resonance-line positions because of quadrupole-induced relaxation.

An examination of the  $^{15}\text{N}$  data in Table 2 indicates that replacement of the lone pair of electrons on the nitrogen atom of pyridine by a bond to another atom leads to an upfield shift of the  $^{15}\text{N}$  resonance. The magnitude of the  $^{15}\text{N}$ -shielding change for the pyridinium ylids (ca. 100 ppm) is comparable to that observed for protonation or N-methylation (ca. 115 ppm)<sup>7</sup>, and is much larger than that observed for the N-oxide (ca. 25 ppm). Such difference between N-oxides and dicyanomethylids is probably due to back donation effect by oxygen in the N-oxides. The  $^{15}\text{N}$  chemical shifts of the substituted pyridinium dicyanomethylids are sensitive to the position of the substituent group on the pyridine ring (Table 2). Methyl, methoxycarbonyl, and cyano substituents exert the larger effects in the 4-position (ca.  $\pm 7$  ppm), whereas the increments for 3-position are small. The similar phenomenon has been observed in pyridines<sup>8</sup> and pyridine N-oxides<sup>7</sup>.

For a discussion of the increments of individual substituents it is interesting to compare the substituent effects of the ylidic  $^{15}\text{N}$  nucleus with those of the ylidic  $^{13}\text{C}$  nucleus<sup>9</sup>. A correlation of this type has now been established from the SCS values in Table 3 [Eqn. (1)]. It is concluded that shielding of the ylidic  $^{15}\text{N}$

$$^{13}\text{C SCS} = 0.25(^{15}\text{N SCS}) - 0.66 \quad (r = 0.956, n = 11) \quad (1)$$

and  $^{13}\text{C}$  nuclei is governed by the analogous factors whereby, on the ppm scale, the nitrogen chemical shift is ca. 4 times more sensitive towards substituents than the carbon shift.

A good linear correlation between the  $^{15}\text{N}$  SCS in pyridines and pyridinium dicyanomethylids has also been observed as shown in Eqn. (2), supporting that shielding of

$$^{15}\text{N SCS}(\text{Pyridines}) = 1.31(^{15}\text{N SCS}) - 1.57 \quad (r=0.990, n=8) \quad (2)$$

$^{15}\text{N}$  in these aromatic systems is governed by the same factors.

Finally, the ylidic  $^{15}\text{N}$  chemical shift data have been correlated by the single ( $\sigma^*$ )<sup>10,11</sup>, dual ( $\sigma_{\text{I}}$ ,  $\sigma_{\text{R}}^{\pm}$ )<sup>11</sup>, and multi ( $\sigma_{\text{I}}$ ,  $\sigma_{\text{R}}^+$ ,  $\sigma_{\text{R}}^-$ )<sup>11,12</sup> parameter approaches as exemplified by Eqns. (3), (4), and (5).

$$^{15}\text{N SCS} = -6.8\sigma^* + 5.4 \quad (r=0.977, n=9) \quad (3)$$

$$^{15}\text{N SCS} = -10.9\sigma_{\text{I}} - 36.0\sigma_{\text{R}}^{\pm} - 6.4 \quad (r=0.987, n=9) \quad (4)$$

$$^{15}\text{N SCS} = -10.9\sigma_{\text{I}} - 38.9\sigma_{\text{R}}^+ - 6.23\sigma_{\text{R}}^- + C \quad (r=0.988, n=9) \quad (5)$$

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