

CORRELATION OF ^{13}C - AND ^{15}N -NMR CHEMICAL SHIFTS OF
YLIDIC CARBON AND NITROGEN WITH CALCULATED PARTIAL
CHARGES IN PYRIDINIUM DICYANOMETHYLIDES

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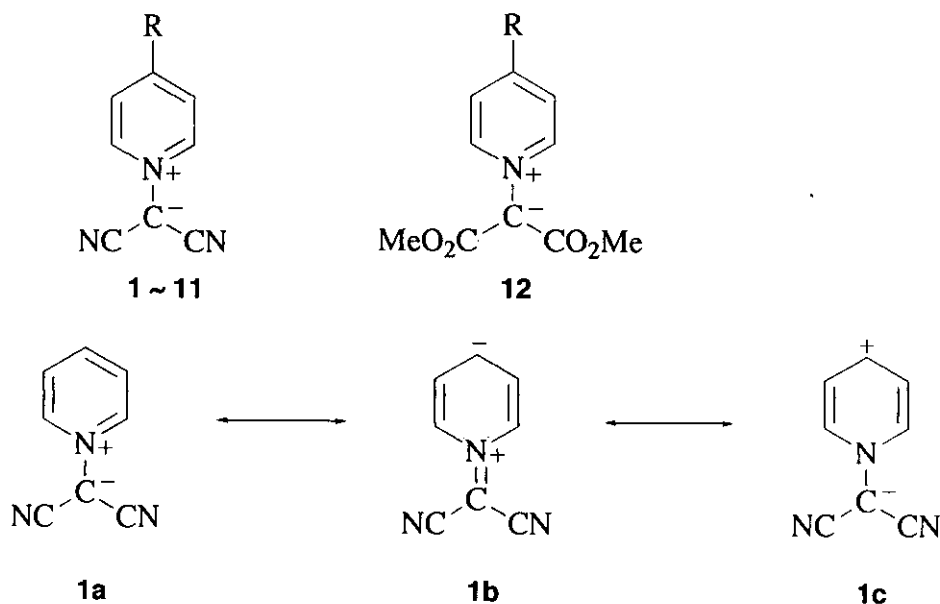
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Abstract- Good correlations were found between the ^{13}C - and ^{15}N -NMR chemical shifts of ylidic carbon and nitrogen and their partial charges, obtained by different semiempirical molecular orbital (MO) methods, of some 4-substituted pyridinium dicyanomethylides.

Pyridinium dicyanomethylides (**1-11**) and pyridinium *bis*(methoxycarbonyl)methylides (**12**) are of synthetic utility for the preparation of novel heterocycles such as indolizines,¹ cycl[3.2.2]azines,² and 2-pyrones.³ Due to their interesting electronic properties and chemical reactivities, these stable cycloimmonium ylides have been the subject of extensive theoretical and experimental studies.⁴ We have also embarked on empirical treatments of these ylidic compounds and have reported on some substituent effects

on the ^{13}C -NMR and the ^{15}N -NMR chemical shifts of the ylidic carbon and nitrogen in the pyridinium dicyanomethylides⁵ and *bis*(methoxycarbonyl)methylides.⁶

We now report the good correlations found between the ^{13}C -NMR and the ^{15}N -NMR chemical shifts of the ylidic atoms and the calculated partial charges of some pyridinium dicyanomethylides (**1**).



The ^{13}C -NMR (relative to internal tetramethylsilane) and ^{15}N -NMR chemical shifts (relative to external nitromethane) of the ylides (**1-11**) were obtained at 68 °C on a JEOL FX 90Q FT NMR spectrometer in dimethyl sulfoxide- d_6 . The results are shown in Table 1. A simple inspection of the Table shows that the ^{13}C and ^{15}N chemical shifts of the ylidic carbon and nitrogen of **1-11** are very sensitive to the nature of substituents at the 4-position of the pyridine ring. As expected, when the substituents have a strong electron-withdrawing group, the contribution of resonance structures (**1b**) becomes predominant and thus the nitrogen-carbon bonds possess substantial double-bond character. Thus, the substituents like CN, PhCO, MeCO_2 , and MeCO cause deshielding shift of the ylidic carbons (C_7) in **8-11**, while the ^{15}N chemical shifts are at higher fields. On the contrary, the alkyl-substituted pyridinium *N*-ylides (**2-7**) have more

Table 1. ^{13}C and ^{15}N Chemical Shifts and Partial Charges (Obtained with Semiempirical MO methods) of Pyridinium Dicyanomethylides (1-11).

Substrate	^{13}C Chemical Shift (C_7) ^a	Partial Charge ^b			^{15}N Chemical Shift (N_1) ^f	Partial Charge ^g		
		PM3 ^c	AM1 ^d	INDO ^e		PM3 ^h	AM1 ⁱ	INDO ^j
1. R = H	58.4	-0.360	-0.205	-0.108	161.4	0.868	0.190	0.043
2. R = Me	57.2	-0.366	-0.211	-0.114	168.5	0.860	0.184	0.031
3. R = Et	57.6	-0.368	-0.213	-0.114	167.9	0.860	0.184	0.031
4. R = <i>n</i> -Pr	57.6	-0.368	-0.213	-0.114	167.9	0.860	0.184	0.031
5. R = <i>i</i> -Pr	57.6	-0.366	-0.212	-0.116	167.6	0.864	0.186	0.030
6. R = <i>t</i> -Bu	57.7	-0.368	-0.214	-0.116	167.7	0.864	0.186	0.030
7. R = Bz	57.5	-0.367	-0.212	-0.113	166.9	0.861	0.185	0.031
8. R = MeCO	60.3	-0.331	-0.167	-0.086	155.0	0.878	0.198	0.043
9. R = MeCO ₂	60.3	-0.324	-0.159	-0.085	153.9	0.879	0.199	0.043
10. R = PhCO	60.6	-0.336	-0.172	-0.119	155.6	0.877	0.198	0.019
11. R = CN	62.1	-0.319	-0.162	-0.089	153.9	0.868	0.194	0.040

^aChemical shifts are reported in δ scale from the internal standard, tetramethylsilane. ^bPartial charges in the carbon atoms are described in au unit. ^cCorrelation coefficient: $r^2 = 0.941$.

^dCorrelation coefficient: $r^2 = 0.908$. ^eCorrelation coefficient: $r^2 = 0.838$. ^fChemical shifts are reported in δ scale from the external standard, nitromethane. ^gPartial charges in the nitrogen atoms are described in au unit. ^hCorrelation coefficient: $r^2 = 0.808$. ⁱCorrelation coefficient: $r^2 = 0.935$. ^jCorrelation coefficient: $r^2 = 0.875$.

upfield ^{13}C chemical shifts for C_7 and more downfield ^{15}N chemical shifts for N_1 as compared with the unsubstituted pyridinium dicyanomethylide (1).

The partial charges on the carbon and nitrogen atoms were calculated with precise option by MO (PM3, AM1, and INDO) methods.⁷ Figures 1~6 show the correlations between the chemical shifts and the partial charges. These figures demonstrate explicitly that there are good linear correlations (correlation coefficients, $r^2 = 0.838 \sim 0.941$ for ^{13}C shifts and $r^2 = 0.808 \sim 0.935$ for ^{15}N shifts) in all three cases. Particularly when AM1 method was used good correlations were obtained for both ^{13}C and ^{15}N shifts

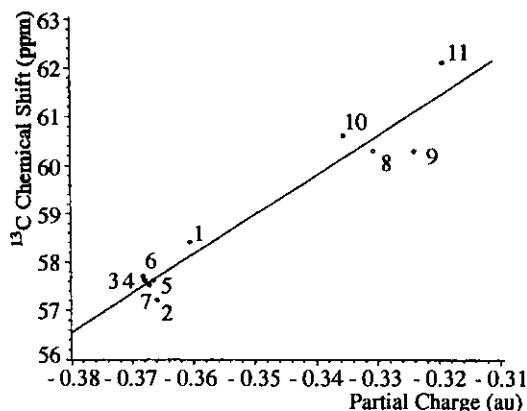


Figure 1. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with PM3 Method ($r^2 = 0.941$).

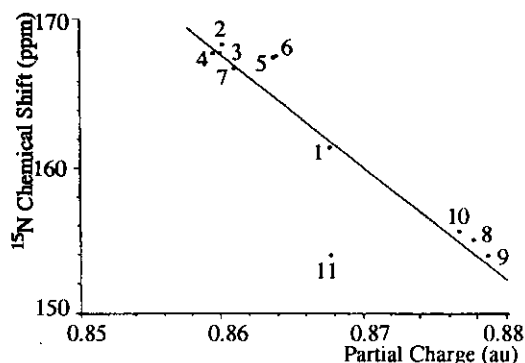


Figure 2. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with PM3 Method ($r^2 = 0.808$).

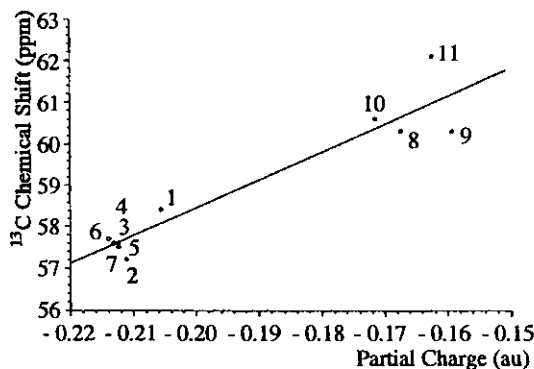


Figure 3. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with AM1 Method ($r^2 = 0.908$).

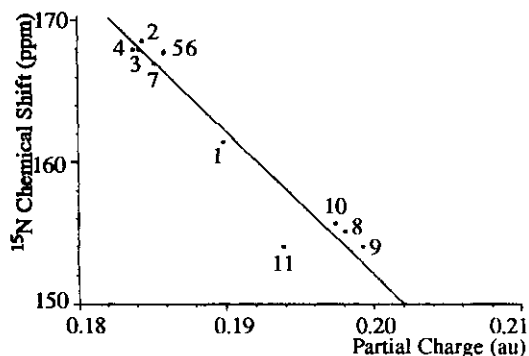


Figure 4. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with AM1 Method ($r^2 = 0.935$).

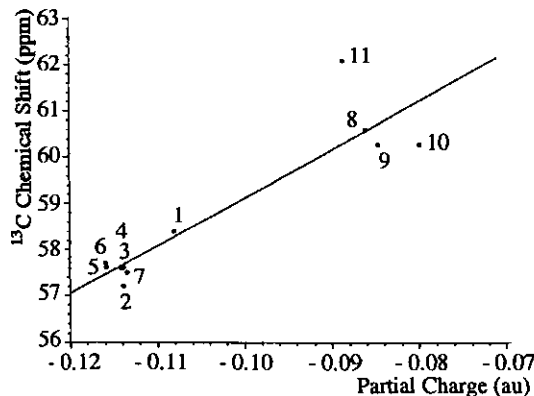


Figure 5. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with INDO Method ($r^2 = 0.838$).

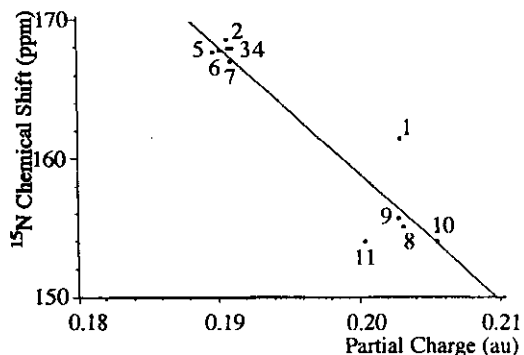


Figure 6. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with INDO Method ($r^2 = 0.875$).

(correlation coefficients, $r^2 = 0.908$ for ^{13}C shifts and $r^2 = 0.935$ for ^{15}N shifts).

In summary, we have found that there are linear correlations between the ^{13}C and ^{15}N chemical shifts and partial charges of the ylidic carbon and the nitrogen nuclei in pyridinium dicyanomethylides. Therefore, semiempirical molecular orbital calculations such as AM1, PM3, and INDO methods which are readily and commercially available have proven useful to predict the ^{13}C and ^{15}N chemical shifts of heteroaromatic *N*-ylides.

EXPERIMENTAL

Dicyanomethylides (**1-11**) were prepared according to the method of Linn *et al.*⁸ and some of the physical properties of the ylides (**1-11**) have been described.¹ The ^{13}C -NMR spectra of the ylides (**1-11**) were obtained at 68 °C on a JEOL FX 90Q FT NMR spectrometer in dimethyl sulfoxide- d_6 and the chemical shifts are reported in ppm downfield from internal tetramethylsilane. The natural-abundance ^{15}N -NMR spectra were obtained in dimethyl sulfoxide- d_6 with $\text{Cr}(\text{acac})_3$ at 68 °C on a JEOL FX 90Q FT NMR spectrometer and the chemical shifts are reported in ppm upfield from external nitromethane.

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