Correlation of ^{13}C- and ^{15}N-NMR Chemical Shifts with Calculated Partial Charges in Pyridinium Bis(methoxycarbonyl)methylides

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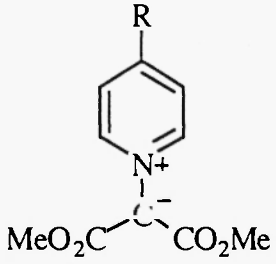
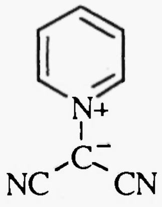
Abstract: Sufficiently good correlations were found between the ^{13}C- and ^{15}N-NMR chemical shifts and the partial charges, obtained by different computational methods, of some *p*-substituted pyridinium bis(methoxycarbonyl)methylides.

Pyridinium bis(methoxycarbonyl)methylides 1~10 and pyridinium dicyanomethylides 11 are of great synthetic utility for the preparation of novel heterocycles such as indolizines (1), cycl[2.2.3]azines (2), and 2-pyrones (3). Due to their interesting electronic properties and chemical reactivity, 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 we have already reported on some substituent effects on the ^{13}C-NMR and the ^{15}N-NMR chemical shifts of the ylidic nitrogen in the pyridinium bis(methoxycarbonyl)methylides (5) and dicyanomethylides (6). We now report the good correlation found between the ^{13}C-NMR and the ^{15}N-NMR chemical shifts and the calculated partial charges of some pyridinium bis(methoxycarbonyl)methylides 1~10.



1 ~ 10



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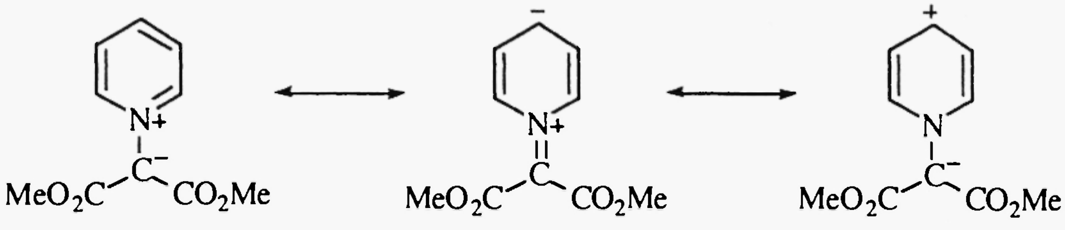
The ^{13}C-NMR spectra of the ylides 1~10 were obtained at 68 °C on a JEOL FX 90Q FT NMR spectrometer in dimethylsulfoxide-d_6 and the chemical shifts are reported in ppm downfield from internal tetramethylsilane. The natural-abundance ^{15}N-NMR spectra were obtained in dimethylsulfoxide-d_6 with Cr(acac)$_3$ at 68 °C on a JEOL FX 90Q FT NMR spectrometer and the chemical shifts are reported in ppm upfield from external nitromethane. The obtained chemical shifts are shown in Table 1 which summarizes the results of our work. A simple inspection of the table shows that the ^{13}C and ^{15}N chemical shifts of pyridinium bis(methoxycarbonyl)methylides 1~10 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 effect the contribution of resonance structures analogous to 1b becomes predominant and, in these pyridine *N*-ylides, the nitrogen-carbon bonds possess substantial double-bond character. Thus, substituents like CN, PhCO, and MeCO, cause deshielding of the ylidic carbons (C_7) while the ^{15}N chemical shifts are at higher fields. On the contrary, the alkyl-substituted pyridiniumbis(methoxycarbonyl)methylides have more upfield ^{13}C chemical shifts for C_7 and more downfield ^{15}N chemical shifts for N_1 as compared with the unsubstituted pyridinium bis(methoxycarbonyl)methylide 1.



1a 1b 1c

Table 1 : ^{13}C and ^{15}N Chemical Shifts and Partial Charges (Obtained with Semiempirical MO methods) of Pyridinium Bis(methoxycarbonyl)methylides 1-10

Chemical Sample	C^{13} Chemical Shift $(C_7)^a$	Partial Charge^b PM3	AM1	INDO	N^{15} Chemical Shift $(N_1)^c$	Partial Charge^d PM3	AM1	INDO
1 H	95.7	-0.677	-0.400	-0.241	160.3	0.919	0.187	0.057
2 Me	94.6	-0.679	-0.403	-0.242	166.6	0.911	0.180	0.042
3 Et	94.8	-0.680	-0.410	-0.241	166.3	0.910	0.170	0.043
4 *n*-Pr	94.7	-0.679	-0.404	-0.241	166.1	0.910	0.180	0.042
5 *i*-Pr	94.8	-0.679	-0.406	-0.242	165.9	0.914	0.175	0.041
6 *t*-Bu	94.6	-0.683	-0.408	-0.242	166.0	0.909	0.174	0.041
7 Ph	94.8	-0.675	-0.399	-0.240	165.1	0.909	0.182	0.046
8 MeCO	96.3	-0.654	-0.381	-0.231	152.7	0.932	0.199	0.061
9 PhCO	96.2	-0.653	-0.378	-0.231	156.5	0.933	0.196	0.061
10 CN	97.2	-0.647	-0.370	-0.233	152.9	0.924	0.203	0.058

[a] Chemical shifts are reported in δ scale from the internal standard, tetramethylsilane. [b] Partial charges in the carbon atoms are described in au unit. [c] Chemical shifts are reported in δ scale from the external standard, nitromethane. [d] Partial charges in the nitrogen atoms are described in au unit.

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 demonstrate explicitly that there are rather good linear correlations (correlation coefficients, $r^2 = 0.752\sim0.883$ for ^{13}C 0.847~0.898 f(0.847~0.898 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 (correlation coefficients, $r^2 = 0.879$ for ^{13}C shifts and $r^2 = 0.898$ for ^{15}N shifts).

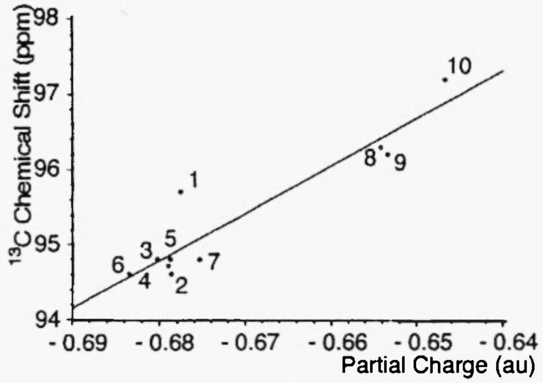


Figure 1. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with PM3 Method ($r^2 = 0.883$).

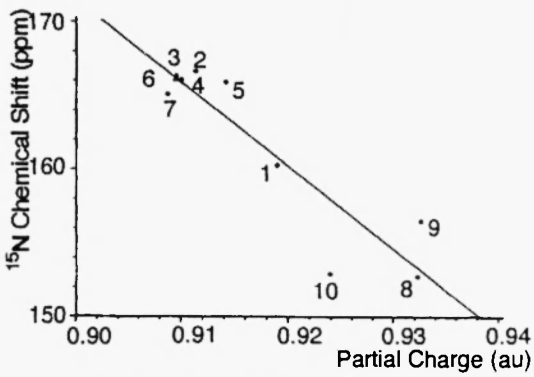


Figure 2. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with PM3 Method ($r^2 = 0.847$).

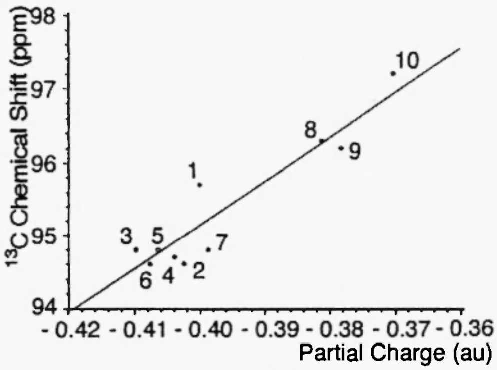


Figure 3. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with AM1 Method ($r^2 = 0.879$).

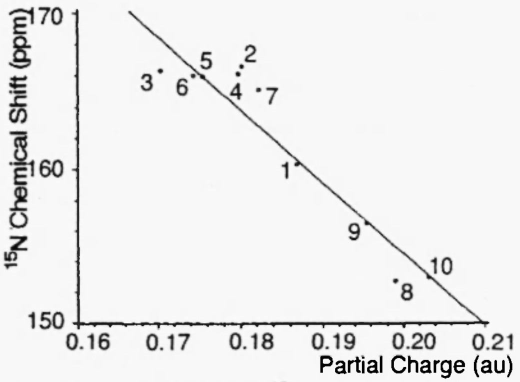


Figure 4. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with AM1 Method ($r^2 = 0.898$).

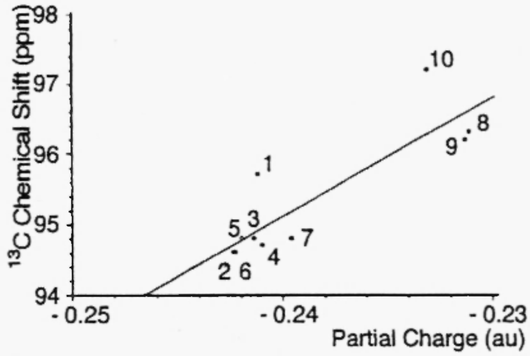


Figure 5. Correlation of ^{13}C Chemical Shifts versus Partial Charges Calculated with INDO Method ($r^2 = 0.752$).

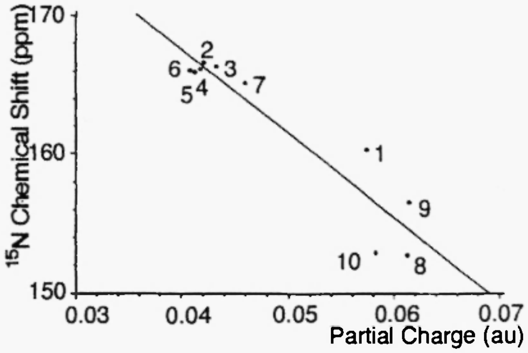


Figure 6. Correlation of ^{15}N Chemical Shifts versus Partial Charges Calculated with INDO Method ($r^2 = 0.887$).

In summary, we have found linear correlations between the ^{13}C and ^{15}N chemical shifts and partial charges of the ylidic carbon and the nitrogen nuclei in pyridinium bis(methoxycarbonyl)methylides (8). 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 .

Acknowledgments

This work was supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (No. 08221214 to KM).

References and Notes

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Received on August 18, 1997