# SUBSTITUENT EFFECTS ON THE CARBON-13 CHEMICAL SHIFTS OF YLIDIC CARBONS IN PYRIDINIUM DICYANOMETHYLIDES

Kiyoshi Matsumoto,* Takane Uchida,† and Chizuko Uno†
College of Liberal Arts & Sciences, Kyoto University, Kyoto 606,
†Faculty of Education, Fukui University, Fukui 910, Japan

Abstract--A correlation between the carbon-13 chemical shifts of carbanions in 4-substituted pyridinium dicyanomethylides has been described. At present, best correlation coefficient (0.969) was obtained using the Inamoto-Masuda methods, i.e. ι and μ parameters.

Since cycloimmonium ylides are zwitterionic systems in which an anion is covalently bonded to a positively charged heteroatoms, their electronic properties[1] and reactivities[2] are of interest, and therefore experimental and theoretical studies of this class of compounds have been extensively performed.[3]
Specifically, cycloimmonium ylides, like pyridinium dicyanomethylides, possessing two electron-withdrawing groups covalently bonded to the ylidic carbon are stable and can be isolated. To our knowlegde, however, several theoretical calculations of pyridinium dicyanomethylide have been unsuccessful, being impossible to obtain a convergence to an energy minimum by successive iterations.[4,5] Furthermore, no $^{13}C$ NMR study of this system has been reported.[6] For these reasons, we have embarked on empirical treatments of these ylidic compounds, and now briefly describe a correlation between the carbon-13 chemical shifts of the ylidic carbons in 4-substituted pyridinium dicyanomethylides.

Table 1 contains the values for the chemical shifts and the $^{13}C$-SCS of the ylidic carbon atoms obtained in dimethyl sulfoxide-$d_6$ at 68 °C on a JEOL FX-60 FT NMR spectrometer. Their signals appear at 57-62 ppm downfield from tetramethylsilane, calculated by adding 39.6 ppm to the shifts relative to the center peak of DMSO-$d_6$.[7]
As expected, electron acceptors cause shielding of ylidic carbons.

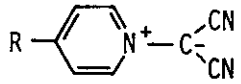

Table 1. $^{13}C$ Chemical shifts and SCS of the ylidic carbons of 4-substituted pyridinium dicyanomethylides

| R | Me | Et | i-Pr | t-Bu | H | MeCO | $CO_2Me$ | Ph | CN |
|---|---|---|---|---|---|---|---|---|---|
| $^{13}C$-Chemical shift | 57.2 | 57.6 | 57.6 | 57.7 | 58.4 | 60.3 | 60.3 | 61.5 | 62.1 |
| $^{13}C$-SCS | 1.2 | 0.8 | 0.8 | 0.7 | 0.0 | -1.9 | -1.9 | -3.1 | -3.7 |

The carbon-13 chemical shift data were correlated by the dual and multi parameter approaches employing the Taft (DSP equation),[8] Swain-Lupton,[9] Yukawa-Tsuno (LSFE or LArSR equation),[10] and Inamoto-Masuda[11] methods. Single parameter approaches either with $\sigma_p^+$, or $\sigma_p$ or $\chi_x$ gave poor correlations ($r < 0.75$). The results of the statistical treatment are listed in Table 2.

The ι, μ-parameter approach gave the best correlation, though the number of the data points is at present nine due to the preparative inaccessibility of the ylides or otherwise their instability in the measurement condition. Indeed, 4-bromo- and 4-chloropyridinium dicyanomethylides underwent decomposition at 68 °C in DMSO, which precluded us from obtaining the $^{13}C$ signals of the ylidic carbons with relatively weak intensity possibly due to long relaxation time. The best correlation by the Inamoto-Masuda methods apparently indicates the importance of resonance as well as electronegativity effects on $^{13}C$-SCS of the ylidic carbons in this systems. Intriguingly, there is significant improvement due to addition of ι when $\sigma_I$, $\sigma_R$ and ι are correlated.

Further $^{13}C$ and $N^{14}$ (or $N^{15}$) NMR studies of these and the related stable cycloimmonium ylides such as pyridinium bis(alkoxycarbonyl)methylides, indolizines, and azapentalenes are in progress.

This work was in part supported by the Japanese Ministry of Education (Grant-in-Aid, No.00554146 and 56430008).

Table 2. Correlation results[a]

| Constants | | | a[b] | b[b] | c[b] | i[c] | r[d] | n |
|---|---|---|---|---|---|---|---|---|
| $\sigma_I$, | $\sigma_R^\circ$ | | -8.89 | 3.92 | | 0.230 | 0.882 | 9 |
| $\sigma_I$, | $\sigma_R$ | | -10.4 | 6.65 | | 0.429 | 0.896 | 9 |
| $\sigma_I$, | $\sigma_R$, | ι | -1.73 | -3.40 | -6.40 | 13.88 | 0.933 | 9 |
| ι , | $\sigma_R^\circ$ | | -7.78 | -5.45 | | 16.81 | 0.930 | 9 |
| ι , | $\sigma_R$ | | -7.43 | -5.56 | | 16.01 | 0.932 | 9 |
| ι , | μ | | -12.28 | 11.60 | | 25.75 | 0.969 | 9 |
| | | | -12.50 | 11.99 | | 26.22 | 0.966 | 8[e] |
| *F* , | *R* | | -6.79 | 6.48 | | 0.550 | 0.852 | 8[e] |
| $\sigma_i$ | $\sigma_\pi^{+(or-)}$ | | -14.70 | 7.83 | 5.24 | 0.24 | 0.941 | 8[e] |
| $\sigma^\circ$ | $\Delta\sigma_R^{+(or-)}$ | | -12.80 | 6.78 | 12.29 | -0.10 | 0.930 | 8[e] |

[a] The results of least-square fit of the data expression $\Delta\delta = a\sigma_I + b\sigma_R + i$ and the similar expressions in other constants.
[b] Regression coefficients.
[c] Calculated intercept.
[d] Correlation coefficient.
[e] iso-Propyl group is not included.

REFERENCES


1. For instance, H. Fujita, J. Yamauchi, K. Matsumoto, H. Ohya-Nishiguchi, and Y. Deguchi, J. Magn. Res., 35, 171 (1979).
2. For example, K. Matsumoto and T. Uchida, J. Chem. Soc., Perkin I, 1981, 73.
3. G. Surpateau, J.P. Catteau, P. Karafiloglou, and A. Lablache, Tetrahedron, 32, 2647 (1976); I. Zugravescu and M. Petrovanu, 'N-Ylide Chemistry', McGraw-Hill International, New York, 1976.
4. J.P. Catteau, A. Lablache-Combier, J. Grimblot, M. Nastasi, and J. Streith, Tetrahedron, 31, 2909 (1975).
5. S. Kako and K. Matsumoto, unpublished results.
6. Unstable pyridinium ylides in situ generated, and the related phosphonium and sulphonium ylides have been investigated by $^{13}$C-NMR: G. Fronza, P. Bravo, and C. Ticozzi, J. Organomet. Chem., 157, 299 (1978); K.O. Startweski and H. Bock, J. Am. Chem. Soc., 98, 8486 (1976); G.A. Gray, ibid., 95, 5092, 7736 (1973); H. Matsuyama, H. Minato, and M. Kobayashi, Bull. Chem. Soc. Jpn., 50, 3393 (1977).

7. G. C. Levy and J. D. Cargioli, J. Magn. Res., 6, 143 (1972). The higher temperature, e,g, 68 °C was employed because of the low solubility of the ylides at room temperature.
8. S. Ehrenson, R.T.C. Browlee, and R.W. Taft, Prog. Phy. Org. Chem., 10, 1 (1973).
9. C.G. Swain and E.C. Lupton, Jr., J. Am. Chem. Soc., 90, 4328 (1968).
10. LSFE equation: Y. Tsuno, M. Fujino, and Y. Yukawa, Bull. Chem. Soc. Jpn., 48, 3324 (1975); LArSR equation: Y. Yukawa and Y. Tsuno, Nippon Kagaku Zasshi, 86, 873 (1965).
11. N. Inamoto and S. Masuda, Kagaku no Ryoiki, 33, 4, 105, 198 (1979) and references cited therein. See also, Y. Tsuno, Kagaku, 36, 412 (1981) and W.F. Reynolds, J. Chem. Soc., Perkin II, 1980, 985.

Received, 18th June, 1982