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On the NMR Spectra of Some Substituted Pyridinium 2-Pyridylcarbonylmethylides

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Synopsis. The partial double-bond character of the ylide carbon–pyridinium nitrogen bond is discussed on the basis of the ^{1}H and ^{13}C NMR spectra of 4-cyano-(Y_{CN}), 4-methyl- (Y_{pic}), and 3,5-dimethylpyridinium 2-pyridylcarbonylmethylide (Y_{lut}). The α-proton signals of the 4-cyanopyridinium ring of Y_{CN} have been separately observed at low temperatures, indicating a hindered rotation around the ylide carbon-pyridinium nitrogen bond.

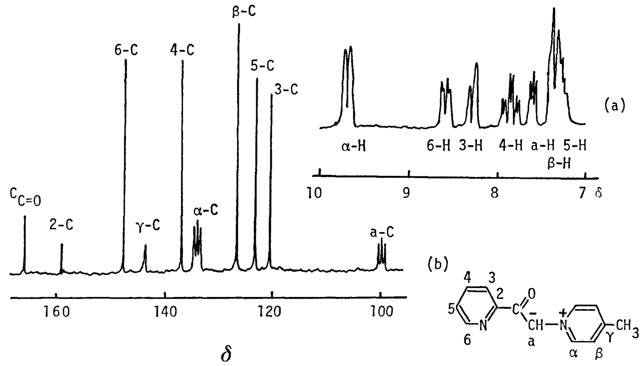
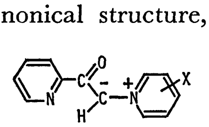


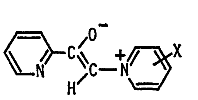
Fig. 1. The ^{1}H (a) and ^{13}C NMR (b) spectra of Y_{pic} in chloroform-*d*.

Sulfur and phosphorus ylides can be stabilized by the carbanion delocalization to d-orbitals of the sulfur and phosphorus atoms.[1,2] On the other hand, the same effect is usually unexpected in nitrogen ylides, because nitrogen has no d-orbitals available for bond formation. Pyridinium ylides, however, are unique in being stabilized by the carbanion participation in the resonance of the pyridinium ring.[3] In the course of an investigation of the nucleophilic reactivity of several 2-pyridylcarbonylmethylides, $C_5H_4NC(O)\overset{-}{C}H\overset{+}{Z}$ ($Z=\overset{+}{S}Me_2$, $\overset{+}{P}Ph_3$, and $\overset{+}{N}C_5H_4CH_3$-4), toward metal ions,[4–7] we have recently found some unique NMR spectral behavior of the substituted pyridinium 2-pyridylcarbonylmethylides. This paper will discuss the configurations of 4-cyano-(Y_{CN}), 4-methyl-(Y_{pic}), and 3,5-dimethylpyridinium 2-pyridylcarbonylmethylide (Y_{lut}) and the carbanion delocalization on the basis of the IR frequencies and the ^{1}H and ^{13}C NMR parameters.

The IR spectra of the 2-pyridylcarbonylmethylides gave ν(C=O) bands at fairly low frequencies compared with those of common organic carbonyl compounds: 1529, 1530, and 1530 cm^{-1} for Y_{pic}, Y_{lut}, and Y_{CN} respectively, indicating a considerable contribution of the canonical structure, **B**, besides **A**. Furthermore,



A



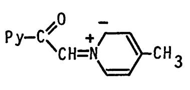
B

X=4-CH_3, 3,5-$(CH_3)_2$, and 4-CN

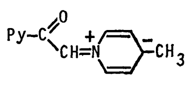
assuming that the 2-pyridylcarbonyl group is almost planar, the ylides are likely to adopt a configuration avoiding some electronic repulsion between the negatively polarized pyridine–nitrogen and carbonyl–oxygen atoms.

The ^{1}H and ^{13}C NMR spectra of Y_{pic} in chloroform-*d* are depicted in Fig. 1. The proton signals have easily been assigned by comparison with the spectra of *N*-substituted 2-pyridylmethanimines[8] and 2,2′-bipyridine.[9] The ^{13}C-signal assignment has been performed by comparing the chemical shifts with those of 2-substituted pyridines[10] and the coupling constants between ^{13}C and directly bonded hydrogen atoms ($^1J(^{13}C–H)$).

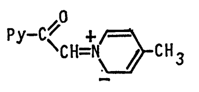
The ylide-carbon signal is observed at an extremely low field (99.1 δ) compared with those of other related phenacylides and 2-pyridylcarbonylmethylides: $PhC(O)\overset{-}{C}H\overset{+}{P}Ph_3$ (50.4 δ),[11] $PhC(O)\overset{-}{C}H\overset{+}{As}Ph_3$ (53.13 δ),[12] and $PyC(O)\overset{-}{C}H\overset{+}{S}Me_2$ (53.8 δ).[13] This may be due to the strongly electron-withdrawing property of the 4-methylpyridinium group, as is shown in the resonance contributions, **C**—**E**.



C



D



E

The ylide-proton signal of Y_{pic} appears at a fairly low field compared with that of 4-methylpyridinium phenacylide (6.64 δ);[14] this is because of the paramagnetic anisotropy effect of the lone-pair electrons of the pyridine nitrogen in the configurations, **A** and **B**, with the almost planar 2-pyridylcarbonyl group. Essentially the same situation was noticed in Y_{lut} (7.46 δ) and 3,5-dimethylpyridinium phenacylide (6.56 δ).

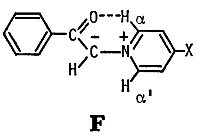
A characteristic feature is the clear appearance of a triplet signal of the ylide proton resulting from spin-spin coupling with the ^{14}N nucleus ($^2J(^{14}N–H_{ylide})=2.5$ Hz). Furthermore, it is notable that the α-carbon signal, as well as the ylide-carbon signal, appears as a well-resolved triplet because of the ^{14}N coupling. In Y_{lut} and 3,5-dimethylpyridinium phenacylide, these carbon signals have also been observed as triplets ($^1J(^{14}N–^{13}C)=8.8$ and 8.3 Hz respectively). The relevant ^{1}H and ^{13}C NMR parameters of the ylides are summarized in Table 1.

Previously Phillips and Ratts[15] showed that the signals of the α-protons of the pyridinium ring of 4-substituted pyridinium phenacylides are shifted fairly downfield compared to those of the α-protons of the HBr salts of the phenacylides. These downfield shifts were attributed to the deshielding of α-H by the carbonyl function, as is depicted in **F**. This explanation may be based on the planarity of both the pyridinium ring and the phenacyl group. However, no separated

Table 1. Relevant NMR chemical shifts (δ) of the ylides$^{a)}$

	6-H	a-H	α-H	6-C	a-C	α-C
Y_{pic}	8.52	7.50$^{b)}$	9.61	147.2$^{c)}$ (178)	99.1$^{c)}$ (183)	133.4 (189)
Y_{lut}	8.49	7.46$^{b)}$	9.31	147.6$^{c)}$ (178)	99.2$^{c)}$ (185)	131.3 (189)
Y_{CN}	8.56	7.82	9.39	d)	d)	d)

a) Measured in chloroform-d at 24 °C (^{1}H NMR) and at 34 °C (^{13}C NMR). The spin-spin couplings ($^1J(^{13}C\text{-}^1H)$, Hz) are shown in parentheses. b) $^2J(^{14}N\text{-}^1H) = 2.5$ Hz. c) $^1J(^{14}N\text{-}^{13}C) = 8.8$ Hz. d) Not measured because of its poor solubility.



F

signals due to α-H and α'-H were observed, and only one signal occurred at an averaged field, because of the fast rotation around the ylide carbon-pyridinium nitrogen bond. This is the same as with the α-H signals of the pyridinium rings of both Y_{pic} and Y_{lut}, which exhibited the averaged chemical shifts of the α-H and α'-H signals at approximately 9.5 δ even at −70 °C in dichloromethane.

In Y_{CN} broad α-H signals are observed at 9.39 δ in chloroform-*d* at room temperature. At −50 °C, two widely separated α-H signals are noticed, as is illustrated in Fig. 2. This indicates the magnetic non-equivalence of the two α-protons, which seems to be attributable to the slow hindered rotation around the ylide carbon-pyridinium nitrogen bond on the NMR time scale. The Gibbs energy of activation ($\Delta G_{Tc}{}^*$) for the rotation at the coalescence temperature (−20±5 °C) has been estimated to be 11.4(±0.3) kcal/mol using the approximate equation.[16] The hindered rotation may be caused by the partial double-bond character of the ylide carbon-pyridinium nitrogen bond, which is ascribed to the contribution of the canonical structures, **C**—**E**.

Experimental

Preparation of 4-Cyanopyridinium 2-Pyridylcarbonylmethylide (Y_{CN}). 4-Cyanopyridine (1.25 g, 12 mmol) was added to a benzene (50 ml) solution of 2-(bromoacetyl)pyridine[17] (2.0 g, 10 mmol), and the mixture was refluxed for 10 h to give white precipitates of Y_{CN}·HBr, which were subsequently collected by filtration (1.98 g, 66% yield). To an aqueous solution (10 ml) of the product was added a 30% K_2CO_3 aqueous solution (50 ml) to separate out red solids immediately. They were collected and recrystallized from a mixture of dichloromethane/diethyl ether (1/1 vol. ratio) to afford red crystals of Y_{CN} (0.59 g, 26% yield); mp 168 °C (dec). Found: C, 69.95; H, 4.06; N, 18.82%. Calcd for $C_{13}H_9N_3O$: C, 70.28; H, 3.77; N, 18.65%.

The preparation of Y_{pic} and Y_{lut} is described elsewhere.[5)]

Spectral Measurements. The IR and ^{1}H NMR spectra were measured as has been described previously.[14] The ^{13}C NMR spectra were recorded in chloroform-*d* at 15.03 MHz, using the pulse Fourier transform technique on a JEOL FX 60 spectrometer at 34 °C. The chemical shifts were measured relative to TMS as the internal standard.

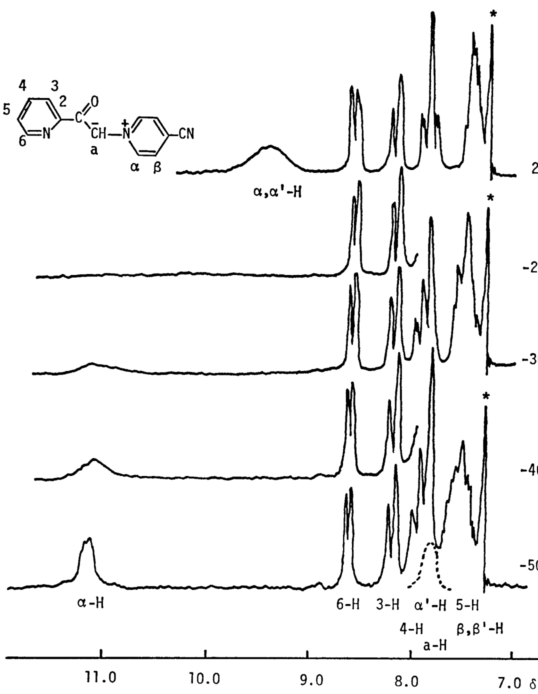


Fig. 2. Temperature-dependent ^{1}H NMR spectra of Y_{CN} in chloroform-*d* (*; $CHCl_3$).

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