$$\tfrac{1}{2}D_2O(g) + CH_3OH(g) \rightarrow \tfrac{1}{2}H_2O(g) + CH_3OD(g)$$
$$\Delta H^\circ = -147 \text{ cal/mol}$$

Combination of this result with standard heats of formation[13] of $H_2O(g)$, $D_2O(g)$, $H(g)$, and $D(g)$ gives

$$CH_3OH(g) + D(g) \rightarrow CH_3OD(g) + H(g)$$
$$\Delta H^\circ_{298.15} = -1.9_2 \text{ kcal/mol}$$

which represents the isotope effect on the enthalpy of the O-H bond in methanol. This is slightly larger than the average isotope effect on the O-H bond in water which can be calculated from standard heats of formation.[13]

$$\tfrac{1}{2}H_2O(g) + D(g) \rightarrow \tfrac{1}{2}D_2O(g) + H(g)$$
$$\Delta H^\circ_{298.15} = -1.77 \text{ kcal/mol}$$

**Acknowledgment.** We thank the Research Corporation for financial support of this work.

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# A Critical Examination of the Applicability of $J_{^{13}CH}$ as a Criterion for the Presence of $\sigma$ Bridging in Cyclopropylcarbinyl Cations

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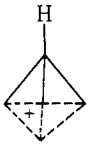
*Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907.* *Received November 24, 1974*

**Abstract:** The proposal that changes in the geometry caused by $\sigma$ bridging may be detected by increases in the value of $J_{^{13}CH}$ has been subjected to critical scrutiny in the cyclopropylcarbinyl cations. From comparisons of the methine coupling constants in such ions with the corresponding coupling constants in neutral compounds, it is concluded that the observed values are consistent with the presence of adjacent positive charge. However, the values of $J_{^{13}CH}$ for cyclopropylcarbinyl, 180, for methylcyclopropylcarbinyl, 190, and for dimethylcyclopropylcarbinyl, 187, fail to reveal the large increase in the value for the primary ion as anticipated for the formation of a $\sigma$ bridge. Consequently, of the two NMR criteria proposed as diagnostic for $\sigma$-bridged cations, one ($^{13}C$ chemical shifts) has been interpreted as supporting a $\sigma$-bridged structure for cyclopropylcarbinyl, whereas the other ($J_{^{13}CH}$) appears in better accord with the formulation as open equilibrating cations.

The fast rates of solvolysis of cyclopropylcarbinyl systems were originally attributed to the stabilization accompanying the formation of a $\sigma$ bridge through space with one or both of the far carbon atoms of the cyclopropane ring[2,3] (**1**, **2**).



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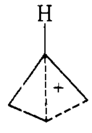

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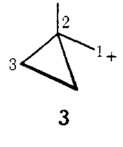
In the case of secondary (**4**) and tertiary cyclopropylcarbinyl cations (**5**), NMR studies[4] have led to the conclusion that these ions exist in the bisected arrangement, so that such $\sigma$ bridges must be absent. The formation of a $\sigma$ bridge from a bisected structure (**6**) requires rotation of the cationic group about the $C_1$-$C_2$ bond (**7**) with movement of the cationic carbon ($C_1$) toward the center of the $C_3$-$C_4$ bond (to form the tricyclobutonium ion (**1**)) or toward either $C_3$ or $C_4$ (to form a bicyclobutonium ion (**2**)).



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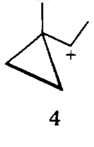

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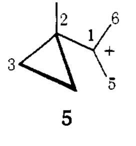

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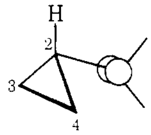

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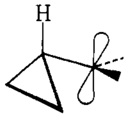
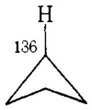


7

On the other hand, certain differences in the observed and calculated $^{13}C$ shifts for the primary ion (**3**)[5-7] have led to the conclusion that this ion exists as a $\sigma$-bridged species.[4c,8] Consequently, in this ion it is proposed that rotation of the cationic ethylene group occurs (**6** → **7**) with formation of a $\sigma$ bridge with one of the methylene carbons of the cyclopropane ring ($C_3$, $C_4$).

An increase in the $J_{^{13}CH}$ value of the methine group has also been proposed as a criterion diagnostic of the formation of a $\sigma$ bridge.[8] Such $\sigma$-bridge formation should result in movement of $C_1$ toward the cyclopropane ring. In neutral molecules, a similar decrease in the dihedral angle and increase in strain is reflected in major increases in the coupling constants[9] as shown by **8**, **9**, and bicyclobutane itself

(**10**).[9a] Consequently, it was proposed that the methine $J_{CH}$ in such a $\sigma$-bridged ion should exhibit a similar increase in value over those exhibited by related cations without $\sigma$ bridging.[10] Unfortunately, the $J_{CH}$ values could not be determined in the earlier study.[11] Accordingly, we undertook to confirm the proposed $\sigma$-bridged structure[8] for the primary cation (**1, 2**) by determining the coupling constant for the primary ion for comparison with the values for the secondary and tertiary ions and a number of related model compounds.



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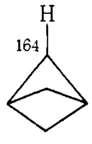

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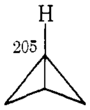
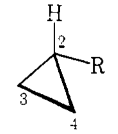


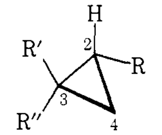
**10**

## Results

The one-bond $^{13}C$-H coupling constants were obtained from the proton-coupled $^{13}C$ spectra and are listed together with the chemical shifts in Table I. The values of $J_{C_2H}$ (Hz) are 180 for **3**, 190 for **4**, and 187 for **5**.[12] Thus the value for the primary ion is not only in the same region as those for the bisected secondary and tertiary ions, but it is actually somewhat lower.

In order to estimate the effect of adjacent positive charge alone on $J_{C_2H}$, we measured the values of the methine couplings in a number of neutral cyclopropylcarbinyl and related compounds. These values are 160–162 Hz for **11a–c** and **12a**, and 163–165 Hz for **12b,c**.

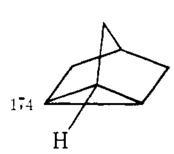




**11a**, R = $CH_2OH$
**b**, R = $CHOHCH_3$
**c**, R = $COH(CH_3)_2$

**12a**, R = R′ = R″ = $CH_3$
**b**, R = $COC^5H_3$; R′ = R″ = H
**c**, R = $CH{=}C^5H_2$; R′ = R″ = Cl

Since we were using $J_{C_2H}$ as a probe for movement of $C_1$ toward $C_{3,4}$, it seemed desirable to obtain corresponding coupling constants for a cyclopropylcarbinyl system in which nuclear movement was severely restricted. The 3-nortricyclyl system appeared to be an appropriate choice. The apical methine $J_{CH}$ for nortricyclene (**13**) and for the 3-nortricyclyl ions (**15a,b**) were available,[13,14] and we have measured the value for the ketone **14** as 186 Hz.



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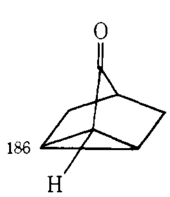
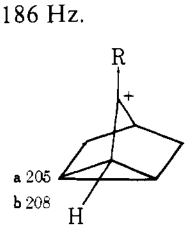


**14**



**15a**, R = H
**b**, R = $C_2H_5$[15]

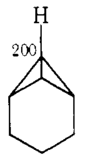
## Discussion

$^{13}C$-H coupling constants are affected by both the electronegativity of attached groups[9,16] (for example, a cationic carbon) and ring strain.[9,17] In the bicyclobutane derivatives, **16–18**, increasing strain by contraction of the ring structure increases the apical methine coupling from 200 Hz in **16** to 212 Hz in **18**.[17] It was on this basis that a value of ~200 Hz was predicted for the $\sigma$-bridged tricyclobutonium ion (**1**).[8] A similar value is expected for the bicyclobutonium ion (**2**), since (a) nuclear movement of $C_1$ occurs here also, in this case toward *either* $C_3$ or $C_4$ with a concomitant reduction in the angle between $C_2$-$C_1$ and the plane of the ring, (b) the methine $J_{CH}$ in bicyclobutane itself is 205 Hz,[9a,18] without any adjacent positive charge, and (c) $J_{C_7H}$ in the $\pi$-bridged 7-norbornenyl cation (**19**) is 219 Hz.

Table I. $^{13}C$ NMR Parameters for Cyclopropylcarbinyl Cations and Model Compounds[a]

| Compd | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|---|---|---|---|---|---|---|
| **3**[b] | 57.6 | 108.2 | 57.6 | 57.6 | | |
| | t, 180 | d, 180 | t, 180 | t, 180 | | |
| **4**[b] | 250.0 | 66.7 | 59.1 | 59.1 | 32.1 | |
| | d, 166 | d, 190 | t, 178 | t, 178 | q, 133 | |
| **5**[b] | 281.7 | 56.4 | 53.4 | 53.4 | 28.8 | 38.7 |
| | | d, 187 | t, 176 | t, 176 | q, 132 | q, 132 |
| 11a | 67.4 | 13.5 | 2.7 | 2.7 | | |
| | t, 142 | d, 162 | t, 162 | t, 162 | | |
| 11b | 72.4 | 19.1 | (2.2)[c] | (3.2)[c] | 22.6 | |
| | d, 141 | d, 160 | t, 162 | t, 162 | q, 126 | |
| 11c | 69.5 | 22.5 | 0.9 | 0.9 | 28.6 | 28.6 |
| | | d, 160 | t, 162 | t, 162 | q, 124 | q, 124 |
| 12a | 14.1 | 18.4 | 15.2 | 20.9 | 19.6[e] | 27.4 |
| | q, 125[d] | d, 160[d] | | t, 160[d] | q, 125[d] | q, 125[d] |
| 12b | *f* | 21.2 | 10.6 | 10.6 | 30.0 | |
| | | d, 163 | t, 165 | t, 165 | q, 127 | |
| 12c | 133.9 | 34.0 | 60.7 | 27.6 | 118.8 | |
| | d, 160 | d, 165 | | d,d, 165,169[g] | t, 160 | |
| 14 | 19.4 | 17.3 | 214.3 | 37.8 | 31.7[h] | 19.4 |
| | d, 181 | d, 186 | | d, 156 | t, 136 | d, 181 |

[a] Chemical shifts are ±0.1 ppm from internal TMS for all compounds except **3, 4**, and **5**, which are from external TMS (converted from external benzene at 128.5 ppm). Coupling constants are ±1 Hz; d = doublet, t = triplet, q = quartet. [b] Olah has recently obtained similar shifts[23] but slightly different coupling constants.[12] [c] Assignments may be reversed. [d] ±3 Hz, complex multiplets. [e] $C_1$ and $C_5$ are cis. [f] Not measured. [g] Nonequivalent protons give rise to doublet of doublets.[12] [h] $C_5 \equiv C_7$



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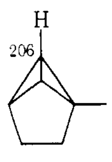
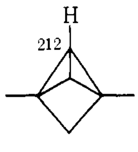
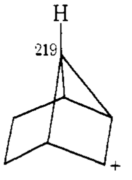


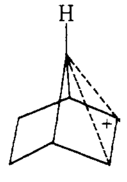
**17**



**18**

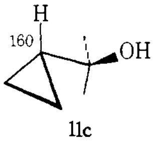


or

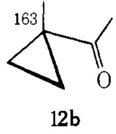


**19**

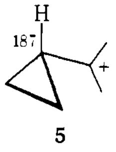
The effect of adjacent positive charge on $J_{C_2H}$ for cyclopropylcarbinyl cations can be estimated from the following series **11c–12b–5**. The introduction of an $sp^2$ center at $C_1$ increases $J_{C_2H}$ by 3 Hz, and a positive charge by a further 24–27 Hz[20] for the bisected ions **4** and **5**, and by 17 Hz for **3**. In the case of the nortricyclyl systems, **13–15**, the apical coupling constant increases by 12 Hz from **13** to **14**, which can be attributed mainly to increasing ring strain brought about by the introduction of an $sp^2$ center at $C_3$, since a similar introduction in acyclic and unstrained cyclic sys-



**11c**



**12b**



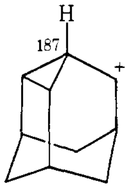
**5**

tems causes only minor (~3 Hz) increases in $J_{C_2H}$.[21] A positive charge at $C_3$ results in a further increase in $J_{C_2H}$ of 22 Hz for the tertiary ion (**15b**)[15] and 19 Hz for the secondary ion (**15a**).

These data indicate that the introduction of a positive charge adjacent to the methine carbon in the flexible cyclopropylcarbinyl systems **3–5** has approximately the same effect on $J_{C_2H}$ as it does in the case of the rigid 3-nortricyclyl system where there is little, if any, nuclear movement.

We therefore conclude that although the upfield shift of $C_1$ in the series **5–4–3** may indicate increasing $\sigma$ delocalization,[4c,8] application of the $J_{CH}$ criterion indicates that such delocalization does not occur by movement of $C_1$ toward $C_3$, $C_4$, or both, as required by the formation of a $\sigma$ bridge.

In an examination of 8,9-dehydroadamantyl cations, Olah and coworkers[23] used the fact that the apical methine $J_{CH}$ values (and the chemical shifts) were very similar in **20** and **21** to conclude that $\sigma$ bridging was not important in the secondary ion (**20**), in contrast to that proposed by Baldwin and Foglesong from solvolytic studies.[24]



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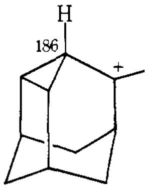

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In the parent cyclopropylcarbinyl cation **3**, the apical $J_{CH}$ value is also not substantially different from that for the bisected ions **6** and **7** ($\leq$10 Hz)[25] and is *lower* than either of them, in contrast to that predicted for increasing strain.

These results therefore support structures without a $\sigma$ bridge for the parent cyclopropylcarbinyl cation, in contrast to the $^{13}C$ chemical shift results,[4c,8] but in agreement with recent molecular orbital calculations,[26] stability considerations,[27] and solvolytic[28] and stereochemical studies.[29]

## Conclusion

The present results have a further important implication. Two major NMR criteria have been proposed to distinguish the formation of $\sigma$-bridged nonclassical ions in super acids. The first is the agreement between calculated and observed values for $^{13}C$ shifts. A failure to obtain agreement has been used as a basis to argue for the formation of a $\sigma$-bridged species.[4c] The second has been an increase in the $^{13}C$–H coupling constant postulated to accompany an increase in strain with the formation of the $\sigma$ bridge.[8] Failure to observe a substantially different coupling constant has been used to argue for a classical cationic intermediate.[23]

In the case of the cyclopropylcarbinyl cation, these criteria now lead to conflicting interpretations. The earlier chemical shift data led to a preference for the $\sigma$-bridged structure.[4c,8] The present coupling constant data appears in better accord for a structure without such a $\sigma$ bridge. Clearly it is necessary to proceed with caution before using either criterion as a basis for a decision in this difficult area.

## Experimental Section

**Materials.** Dimethylcyclopropylcarbinol was prepared by the addition of methyllithium to methyl cyclopropyl ketone according to the method of Buhler[30] and purified by preparative GLC. 1,1-Dichloro-2-vinylcyclopropane was prepared by Dr. M. Ravindranathan according to the method of Woodworth and Skell.[31] 3-Nortricyclone was available from another study[32] and all other compounds were commercially available.

**Preparation of Ions.** The ions **3–5** were prepared from the corresponding alcohols in $SbF_5/SO_2ClF$ at −78° in a manner similar to that previously described[4c,8] but utilizing techniques which more fully protect the solutions from the atmosphere.[33] The ions were prepared under nitrogen in calibrated centrifuge tubes and transferred to NMR tubes via a cooled, double-ended syringe needle.[33] Complete dissolution of the precursor alcohols was achieved to yield clear yellow solutions which exhibited NMR spectra free of spurious peaks: 3, 1.13 *M;* $SbF_5$, 4.60 *M;* **4**, 0.93 *M;* $SbF_5$, 4.43 *M;* 5, 0.90 *M;* $SbF_5$, 4.19 *M*.

**NMR Spectra.** Spectra of the ions were recorded at −70° on a Varian CFT-20 spectrometer using 8 mm tubes containing a concentric 3 mm (o.d.) capillary tube of acetone-$d_6$ plus a trace of benzene for reference. Spectra of the neutral compounds were recorded at 30° in $CDCl_3$ solutions (~3.5 *M*). The coupled spectra were obtained using the gated decoupling facility, 8K data points, and between 4000 and 7000 transients. The reported coupling constants are ±1 Hz. Long range coupling of the apical carbons prevented us from obtaining more accurate values of $J_{C_2H}$. Chemical shifts are ±0.1 ppm from internal TMS except for **3–5**, which are from external TMS.

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(5) The methylene carbon shift estimated for a set of rapidly equilibrating classical cyclopropylcarbinyl ions is 115 ppm (TMS)[4c,8] as compared to the observed value of 57.6 ppm.

(6) The differentiation between equilibrating classical and $\sigma$-bridged ions relies on a discrepancy between the observed $^{13}C$ shift and that calculated from a model static structure.[7] In **3** this requires an estimated $^{13}C$ shift for the primary cationic carbon with only **4** and **5** as a guide. Since it is not possible to estimate the shift for a static $\sigma$-bridged ion, it is not possible to support the conclusion by making a similar comparison between the calculated and observed values for the nonclassical structure.

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(10) A value of ~200 Hz was predicted for a $C_{3v}$ tricyclobutonium ion based on the data for bicyclobutanes.[8]

(11) The low intensity of the methine proton signal of the primary ion precluded the measurement of this value by the INDOR technique.[8] A similar problem occurred for the secondary and tertiary ions where the methine proton and methylene proton resonances overlapped.

(12) After this work was completed, Professor George Olah informed us that, from his recent work, *J. Am. Chem. Soc.*, in press, $J_{C_2H}$ (Hz) was 186.8 for **4** and 185.0 for **5**, and that the methylene carbons ($C_{3,4}$) all appeared as doublets of doublets, $J_{C_{3,4}H}$ = 177.5 and 180.0 Hz for **3**, 175.5 and 177.3 Hz for **4**, and 175.0 and 177.0 Hz for **5**. Under our conditions (Varian CFT-20 spectrometer, 4000 Hz spectral width, 8K data points, ca. 1 *M* solutions in ca. 4 *M* $SbF_5$ in $SO_2ClF$, −70°) the methylene carbons appeared as triplets, and for **4**, the width at half-height (6 Hz) was identical for each of the three lines. In the case of **3** and **5**, slightly broader central lines were observed (**3**, 12, 15, and 12 Hz; **5**, 6, 7.5, and 6 Hz) indicating a slight nonequivalence of the coupling constants. However, the differences were of the order of the experimental uncertainty in the measurement of the couplings. In the case of **12c**, we could clearly distinguish nonequivalent $J_{CH}$ values for the methylene

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(21) Compare $J_{C_2H}$ for propanone (126), 3-pentanone (124), and 2,4-dimethyl-3-pentanone (128)[22] with that for propane ($CH_3$, 125; $CH_2$, 128),[9a] and that for cyclohexanone (129, this work) with cyclohexane (126).[9a]

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# The Rates of Ionization of Arylamino Ketones Possessing the Potentiality for Intramolecular Imine Formation and Intramolecular Proton Abstraction

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**Abstract:** The rates of ionization of a series of compounds of the general structure $Ar(CH_2)_nNHCH_2CH_2CH_2COCH_3$ where Ar is phenyl or 2-pyridyl and *n* is 0, 1, or 2 have been measured by deuterium exchange methods. On the basis of the results it is concluded that (a) the formation of the cyclic pyrrolinium compounds enhances the rate of ionization by ca. $10^7$ when pyridine is the proton acceptor, (b) the proximity to the pyrrolinium ring of a second positive charge (i.e., the protonated pyridine ring in the 2-pyridyl compounds) enhances the ionization rate via an inductive effect, a field effect, or both, and (c) intramolecular proton transfer occurs to a small but probably real extent in the ionization of the 2-pyridyl compounds in which *n* is 1 and 2.

The aldolization reaction of dihydroxyacetone has been shown to be susceptible to pyridine catalysis,[1] and its in vivo counterpart with dihydroxyacetone phosphate is known to involve imine intermediates.[2] As part of a program dealing with the synthesis of polyfunctional catalysts for this process, a series of arylamino ketones has been studied to assess the consequences of (a) the intramolecular imine formation, (b) the proximity of positive charge to the imine moiety, and (c) the proximity of a pyridyl moiety to the site of carbanion formation, employing the rate of deuterium exchange as the assay procedure.

**Synthesis of Arylamino Ketones.** By means of the reaction sequence shown in Figure 1, compounds of the general structure $Ar(CH_2)_nNHCH_2CH_2CH_2COCH_3$ were synthesized in which the aryl group is a pyridyl or a phenyl moiety and *n* has values of 0, 1, and 2. The starting material in every instance was 5-chloro-2-pentanone[3] which was converted to the ketal with methyl orthoformate, alkylated with the appropriate arylalkylamine, and hydrolyzed to the product **1–5**. Except for compound **1**, the isolated compounds exist primarily in the cyclic iminium form (**2b–5b**) rather than the amino ketone form (**2a–5a**).

The assignment of structure to compounds **2b–5b** is based on the elemental analysis of the perchlorate salts and on the ir and NMR characteristics. For additional verification, two alkyl-substituted pyrrolinium perchlorates of known structure[4,5] were prepared, and their spectral characteristics were compared with those of compounds **2b–5b.**

**p$K_a$ Values of Compounds 1–5.** Using titrimetric (for **1a, 3b, 4b,** and **5b**) and spectrophotometric (for **2b**) techniques, the p$K_a$ values of compounds **1–5** were determined (see Table I). The value for the pyridylamino ketone **1** agrees well with the reported values for 2-aminopyridine of 6.82[6] and 6.51,[7] supporting the open chain structure (**1a**). The phenyl analog (**4**) of compound **1** has a p$K_a$ that is approximately 3 p*K* units greater than that of aniline (p$K_a$ = 4.62), commensurate with the cyclic iminium structure (**4b**). The greater tendency for the phenylamino ketone **4a** to cyclize, compared with the pyridylmethyl ketone **1a**, is probably attributable to the greater basicity of the nitrogen atom in **4a;** although the macroscopic p$K_a$ of 2-aminopyridine exceeds that of aniline by ca. 2 p*K* units, the amino group of 2-aminopyridine behaves as a less basic entity than the amino group of aniline. In fact, the p$K_1$ of 2-ammoniumpyridinium dication has been determined to be −7.6.[8]

The p$K_a$ values for the pyrrolinium moiety of **2b, 3b,** and **5b** are 11.00, 11.87, and 11.76, respectively, in agreement with the reported values of 11.94 for 1,2-dimethyl-$\Delta^1$-pyrrolinium perchlorate, 11.92 for 1-ethyl-2-methyl-$\Delta^1$-pyrrolinium perchlorate, and 11.90 for 1-butyl-2-methyl-$\Delta^1$-pyrrolinium perchlorate;[9] the group attached to the nitrogen atom of the pyrrolinium ring has relatively little effect on its p$K_a$. The pyrrolinium moiety, however, has a considerable influence on the p$K_a$ value of the pyridinium moiety, reducing it to 1.41 in **2b** and 3.42 in **3b.**[10]

Of interest with respect to the rate of proton exchange