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HINDERED ROTATION AROUND THE $\overset{+}{N}(sp^2)$-C(sp^3) SINGLE BOND IN 2,4,6-TRIMETHYL-N-ALKYLPYRIDINIUM CATIONS: ^{1}H DNMR ANALYSIS†

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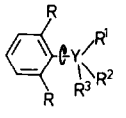
Abstract—Pairwise chemical shift nonequivalence of the 2,6-methyl and 3,5-protons in ^{1}H NMR spectra, as well as of the 2,6-methyl, 2,6-ring and 3,5-ring carbons in ^{13}C NMR spectra, was observed for N-alkyl-2,4,6-trimethylpyridinium salts **2**. Dynamic NMR spectroscopy demonstrates appreciably higher activation free energies $\Delta G^{\neq}$ for rotation around the $\overset{+}{N}(sp^2)$-C(sp^3) bond than $\Delta G^{\neq}$ for the analogously substituted mesityl derivatives, in agreement with the shorter $\overset{+}{N}$–C bond distance than for the C–C bond.

Hindered rotation around the C(sp^2)–Y(sp^3) single bond in compounds **1** was reported, where Y stands for a carbon atom,[1,2] a nitrogen atom,[3] phosphorus, arsenic, antimony or bismuth atom.[4]



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Y = C, N, P, As, Sb, Bi
R^3 = H or electron pair
R, R^1, R^2 = alkyl, aryl, alkoxy, halogen, etc.

In all cases cited above, both *ortho* positions of the aromatic ring are substituted by groups R ≠ H and the Y atom bears two groups R^1, $R^2 \neq$ H; the rate constant of this rotation is amenable to measurements by DNMR techniques. In a preliminary communication,[5] we added to this series another representative, namely 2,4,6-trimethyl-N-alkylpyridinium cations with general formula **2**, and we present now a more detailed description of these systems.

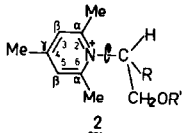

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Table 1 presents the compounds we have investigated and their notation according to the nature of the substituents R,R′. All compounds are crystalline perchlorates except the trifluoroacetoxy derivatives, which were obtained only as solutions in trifluoroacetic acid. In the experimental part, the synthetic procedure as well as the characterization of the compounds are presented.

Diastereotopic groups due to the restricted rotation

In the cations with general formula **2**, there are five pairs of atoms or groups of atoms which are diastereotopic and hence anisochronous at slow rotation on the NMR time-scale around the $\overset{+}{N}$–C single bond: the protons and the carbon atoms of the 2,6-methyl groups, the carbon atoms in the 2,6-positions, as well as the protons and the carbon atoms in the 3,5-positions of the pyridinium ring. The ^{1}H-NMR spectral data evidencing the hindered rotation are collected in Tables 2 and 3, displaying the results in the absence, or in the presence of Eu(fod)$_3$, respectively.

The protons of the 2,6-methyl groups are anisochronous in all compounds investigated. Even for the compound **3** where no splitting is indicated (Table 1), anisochronous signals for the 2,6-methyl groups were observed in a 100 MHz spectrum recorded at −10° in a mixture of pyridine-d_5/acetone-d_6(1:1).

The chemical shift differences of the 2,6-methyl protons in the cations **2** with R = alkyl (**3** and **4**) are

Table 1. Notation for pyridinium compounds with general formula **2**

R \ R′	H	$COCF_3$	$COCH_3$	COC_6H_5
Me	**3**	**3a**	**3b**	**3c**
Et	**4**	**4a**	**4b**	**4c**
Ph	**5**	**5a**	**5b**	**5c**

†Preliminary communication, Ref. 5.

Table 2. Chemical shifts (δ, ppm) of the 2,6-Me_2 and 3,5-H_2 in the ^1H NMR spectra (60 MHz) of the cations with general formula **2**

Compound	**3**	**3a**	**3b**	**3c**	**4**	**4a**	**4b**	**4c**	**5**	**5b**	**5c**
Solvent[a]	TFA	TFA	Me_2CO-d_6	Me_2CO-d_6	Py-d_5	TFA	Me_2CO-d_6	Me_2CO-d_6	Py-d_5	Py-d_5	Py-d_5
2,6-Me_2	3.02	2.98 3.05	3.05 3.11	3.10 3.19	2.93 2.99	3.05 3.11	3.04 3.08	3.07 3.17	2.40 3.22	2.44 3.22	2.56 3.33
3.5-H_2	7.66	7.70	7.94	*b*	7.53 7.60	7.83	7.92	*b*	*b*	*b*	*b*

[a]TFA = F_3CCOOH; Me_2CO-d_6 = D_3CCOCD_3; Py-d_5 = C_5D_5N.
[b]Signals obscured by other aromatic protons in the molecule.
[c]All spectra recorded at 30–32° except those for **5**, **5b**, **5c** recorded at $-3°$.

Table 3. Molar induced shifts (MIS, ppm) by $Eu(fod)_3$ in the ^1H NMR spectra (60 MHz) of the cations with general formula **2**. Solvent: CH_2Cl_2. Temp 30–32°

Compound	3	3b	4	4b
2,6-Me_2	4.28	2.24	4.02	1.82
	3.41	1.76	3.40	1.38
3,5-H_2	2.44	1.58	2.31	1.31
	1.87	1.58	1.75	1.19

Table 4. Chemical shifts (δ, ppm) in ^{13}C NMR spectra (25.2 MHz) of the cations with general formula **2**. Solvent: F_3CCOOD. Temp 40°; TMS internal standard

Compound	3	3b	3c	4
2,6-Me_2	23.3	23.3	23.4	23.2
	24.2	23.9	24.0	24.7
2,6-C_2	157.3	157.3	157.5	157.3
	158.5	157.9	157.9	158.9
3,5-C_2	131.3	131.4	131.3	131.3
	133.1	133.2	133.2	133.1

small, 0.04 to 0.1 ppm. In the cations **2** with R = Ph (**5**), one of the signals is shifted upfield, leading to a remarkably high chemical shift difference for the 2,6-methyl groups (~ 0.8 ppm). This is due to an intramolecular shielding of one of the 2,6-methyl protons by the phenyl group. The aromatic 3,5-protons are in general accidentally isochronous (see Table 2). Pairwise chemical shift nonequivalence of 2,6-methyl protons and aromatic 3,5-protons was however attested in the presence of lanthanide shift reagents. Indeed, on modifying thus the NMR timescale,[6,7] one obtains increased chemical shift differences for the 2,6-methyl protons and different chemical shifts for the aromatic 3,5-protons. Table 3 presents the molar induced shift values (MIS, ppm) obtained in the presence of $Eu(fod)_3$ at room temperature.

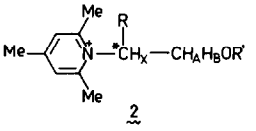
The ^{13}C NMR spectral data are in agreement with the ^1H NMR data: the carbon atoms in the 2,6-methyl groups as well as those in the 2,6-and 3,5-positions of the pyridinium ring are anisochronous (see Table 4). As expected for the larger ^{13}C chemical shift scale, all the diastereotopic carbon atoms present different chemical shifts at 40°C.

Dynamic NMR spectroscopic determinations

A rapid rotation around the $\overset{+}{N}$–C single bond leads to the averaging of the environments of the diastereotopic groups mentioned above and hence to the cancelling out of the chemical shift nonequivalence. As illustrated in Figs. 1 and 2 for two representative compounds, on raising the temperature the nonequivalent signals coalesce. The process is reversible, i.e. on returning to room temperature one obtains the initial aspect of the spectrum.

Diastereotopic protons due to the presence of an asymmetric carbon atom

The cations with general formula **2** possess an asymmetric carbon atom (designated by an asterisk



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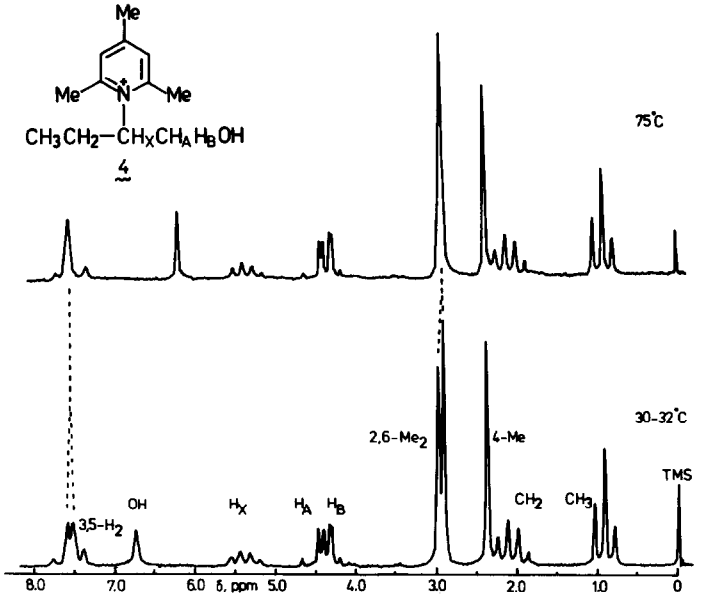


Fig. 1. The chemical shift nonequivalence of the 2,6-Me_2 groups and of 3,5-H_2 aromatic protons in the ^1H NMR spectrum (60 MHz) of the compound **4** at room temperature and the coalescence of the signals at higher temperatures. Solvent: C_5D_5N.

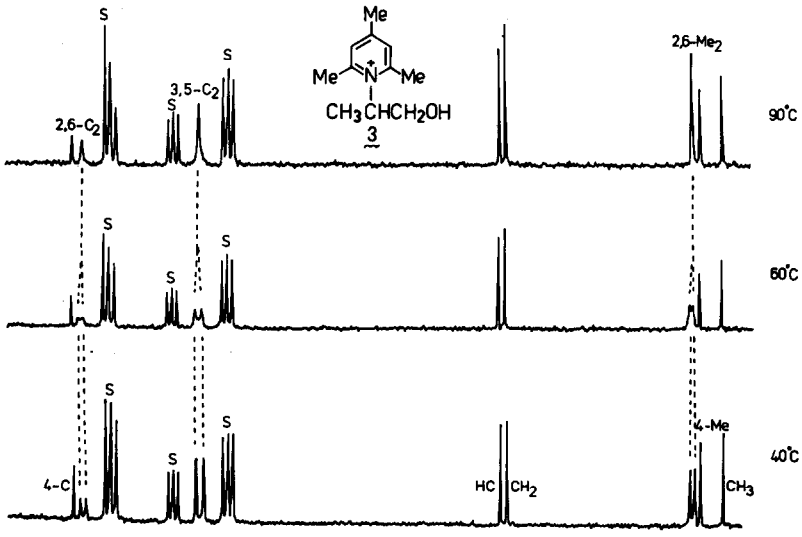


Fig. 2. The chemical shift nonequivalence of the 2,6-Me_2, 2,6-C_2 and 3,5-C_2 carbon atoms in the ^{13}C NMR spectrum (25.2 MHz) of the compound **3** at 40° and the coalescence of the signals at higher temperature in pyridine. S = solvent signals (pyridine carbon atoms). Peak assignments on the top spectrum are for signals which coalesce on heating; assignments for other peaks are indicated on the bottom spectrum.

in the formula). The two protons H_A, H_B of the hydroxymethylene group directly connected to *C are diastereotopic and present different chemical shifts in all the compounds investigated. They are spin-coupled to H_X, giving rise to a complex ABX pattern. As this chemical shift nonequivalence is not connected to the restricted rotation, it is not cancelled out at higher temperatures (see Fig. 1). Intriguingly, the methylenic protons of R = Et (in the compounds **4**, **4a**, **4b**, **4c**), which are also directly connected to *C, are accidentally isochronous. The attempts to remove this degeneracy by recording the spectra in the presence of a lanthanide shift reagent or by changing the solvent, failed.

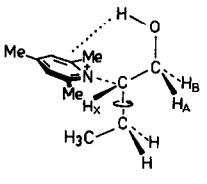
Determination of the rate constant and activation energy of the rotation

The rotation around the $\overset{+}{N}$–C single bond is equivalent to an exchange process of the 2,6-methyl groups between two nonequivalent positions. The kinetic parameter τ (the life-time of the exchanging nuclei) was determined by ^1H DNMR spectroscopy.[8-10] As the two nonequivalent positions are equally populated, the kinetic parameter τ is correlated to the rate constant of the rotation by $k = (2\tau)^{-1}$.[8] From the rate constant k at a given temperature T, the free energy of activation for the rotation ($\Delta G^{\neq}$) was calculated by using the Eyring equation at that temperature:

$$k = K(k_B T/k) \exp(-\Delta G^{\neq}/RT)$$

Determinations were performed with the compounds **3**, **3b**, **4** and **5** for determining the influence of the substituents R, R′ on the rotational barrier. The processing of the experimental data for the compounds **3**, **3b** and **4** is difficult because, on one hand, the chemical shift difference of the exchanging nuclei in the absence of the exchange ($\Delta\nu$) is small (of the same order of magnitude as the line-width) and, on the other hand, the static parameters $\Delta\nu$ and T_2 (the transverse relaxation time) are temperature-dependent in the absence of the exchange. Linear correlations $\Delta\nu$ vs T and T_2 vs T were obtained in the slow-exchange domain, and these correlations were extrapolated to the exchange domain. The temperature interval for kinetic determinations is small (10–25°), therefore a tentative correlation of $\Delta G^{\neq}$ with temperature was considered too risky to be taken into account.

The kinetic parameter τ was determined by line-shape analysis using a program for the exchange between two uncoupled singlets, establishing by an iterative process the optimum fit of the experimental and theoretical spectra. This program gave meaningful results for temperatures lower than the coalescence temperature T_c; the information contained by the spectra recorded at temperatures above T_c is too poor to ensure a successful analysis. At the coalescence temperature T_c, the rate constant k_c was calculated by means of the formula[11] $k_c = \pi\Delta\nu/\sqrt{2}$. The kinetic results and the free activation energy of the rotation $\Delta G^{\neq}$ are presented in Table 5. An inspection of the results from Table 5 reveals that $\Delta G^{\neq}$ values are practically constant within the restricted temperature range in the exchange domain. Consequently, for the comparison of the compounds, a mean $\Delta G^{\neq}$ value ($\Delta G^{\neq}$) was calculated for this particular temperature interval. The individual $\Delta G^{\neq}$



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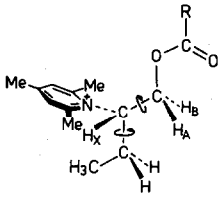
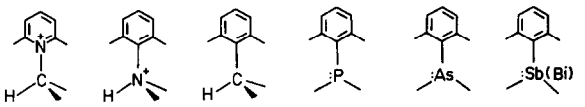


4a - 4c

values not taken into account for the calculation of this mean value are given in parenthesis in Table 5. The mean value was affected by a statistical error σ, estimated[9] from the possible errors in the rate constant determinations and considering a $\pm 2°$ error in the temperature determination. The results are presented in Table 6. Taking into account the modest precision in the rate constant as well as of temperature determinations, the errors affecting the $\Delta G^{\neq}$ values are in the normal range for ^{1}H DNMR determinations. Nevertheless, the $\Delta G^{\neq}$ values for the investigated compounds are significantly different as to enable their comparison, evidencing the influence of the nature of the substituents R, R′ on the rotational barrier.

Temperature-dependent ^{13}C NMR spectra recorded for the compounds **3** and **4** (solvent pyridine) revealed the following: for the compound **3**, coalescence of the 2,6-Me_2 and 2,6-C_2 signals was observed in the temperature interval 60–70° and of the 3,5-C_2 signals in the temperature interval 70–80°. For compound **4**, the coalescence of the signals of any pair of diastereotopic carbon atoms in the molecule was not observed even at 110° (the maximum temperature permitted by the solvent).

The most interesting feature of the system **2** seems to be its high rotational barrier around the $\overset{+}{N}$–C single bond. Indeed, it was surprising that the rotation around a single bond should still be hindered at temperatures as high as 100° so as to observe anisochronous signals in the NMR spectra. Comparing the actual results for the cations **2** with those reported in the literature for compounds **1** with similar substitution, one may work out the following $\Delta G^{\neq}$ values series:



$\Delta G^{\neq}$ (kcal/mol)	16	16	13	12	9	<7
Ref.	this paper	3	1	4	4	4

Table 5. Calculated data from ^{1}H DNMR spectra by line-shape analysis

Compound	Parameters						
	T(°C)	6.7	15.0	21.4	25.0(T_c)		
	τ(sec)	0.28	0.16	0.14	0.11		
3	k(sec^{-1})	1.8	3.2	3.6	4.4		
	$\Delta G^{\neq}$ (kcal/mol)	(16.0)	16.2	16.5	16.6		
	T(°C)	50.5	56.0	59.0	60.2	63.7	66.0	67.0(T_c)
	τ(sec)	0.41	0.39	0.32	0.34	0.32	0.26	0.082
4	k(sec^{-1})	1.2	1.3	1.6	1.5	1.5	1.9	6.1
	$\Delta G^{\neq}$ (kcal/mol)	(18.9)	19.2	19.2	19.3	19.5	19.5	(18.8)
	T(°C)	18.7	24.5	32.0(T_c)				
	τ(sec)	0.014	0.008	0.004				
5	k(sec^{-1})	35.7	62.5	115.3				
	$\Delta G^{\neq}$ (kcal/mol)	15.0	15.0	15.0				
	T(°C)	28.5	34.0	37.5	40.0	41.0(T_c)		
	τ(sec)	0.23	0.13	0.082	0.076	0.062		
3b	k(sec^{-1})	2.1	3.8	6.1	6.6	8.1		
	$\Delta G^{\neq}$ (kcal/mol)	17.2	17.2	17.1	17.2	17.1		

Table 6. Mean calculated free energies of activation for rotation around the $\overset{+}{N}$–C bond

Compound (R,R′)	**3** (Me, H)	**4** (Et, H)	**5** (Ph, H)	**3b** (Me, $COCH_3$)
Solvent	Py-d_5/Me_2CO-d_6(1:1)	Py-d_5	Py-d_5	Me_2CO-d_6
Temperature range (°C)	15–25	55–65	20–30	30–40
$\Delta G^{\neq}$ (kcal mol^{-1})	16.4 ± 0.2	19.3 ± 0.3	15.0 ± 0.3	17.2 ± 0.2

The $\Delta G^{\neq}$ values obtained for the cations with general formula **2** are among the highest in this series; they are, within the experimental error limits, of the same order of magnitude as those obtained by Mannschreck and Münsch[3] for protonated N,N-dialkylanilines and considerably higher than those obtained[1] for the corresponding mesitylene derivatives. Most probably, this is due to shorter $\overset{+}{N}$–C (respectively, C–$\overset{+}{N}$) bond lengths than the C–C bond length.

The series of $\Delta G^{\neq}$ values in Table 6 reveals a strong influence of the substituents on the rotational barrier; the order in this series is that corresponding to the increase of the van der Waals radii of the substituents (for the phenyl substituent, the sp^2 carbon atomic radius is considered). The replacement of a phenyl group by a methyl leads to an increase in the $\Delta G^{\neq}$ value of 1.4 kcal mol^{-1}, a value quite close to that of 1.6 kcal mol^{-1} observed by Mannschreck and Ernst[1] for the similar replacement in the series of mesitylene derivatives. The replacement of methyl by ethyl leads to a substantial increase of $\sim$ 3 kcal/mol in the $\Delta G^{\neq}$ value. Actually, the value $\Delta G^{\neq} = 19.3 \pm 0.3$ kcal mol^{-1} obtained for compound **4** is among the highest ever observed in such systems. If the increase in the substituent volume is due to a flexible, remote fragment (such as on going from hydroxymethylene in **3** to acetoxymethylene in **3b**), the increase in the $\Delta G^{\neq}$ value is less significant.

CONCLUSIONS

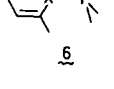
Pyridinium salts **2** (possessing 2- and 6-methyl groups and a group with a secondary N-bonded carbon atom as the 1-substituent) present NMR spectra having chemical shift nonequivalent 2,6-methyl groups owing to hindered rotation around the $\overset{+}{N}(sp^2)$–$C(sp^3)$ single bond. This nonequivalence exists in ^{1}H NMR spectra around room temperature, and in ^{13}C NMR spectra at temperatures ranging between 50° and over 100°.

By dynamic NMR spectroscopy and line-shape analysis it was possible to calculate free energies of activation for this rotation around an $\overset{+}{N}(sp^2)$–$C(sp^3)$ single bond. The values $\Delta G^{\neq} \cong 16$ kcal mol^{-1} for compounds **2** with R = Ph or Me are comparable to those found earlier[3] for rotation barriers in salts of 2,6,N,N-tetramethylaniline derivatives involving rotation around an $\overset{+}{N}(sp^3)$–$C(sp^2)$ single bond, whereas for compounds **2** with R = Et we find $\Delta G^{\neq} \cong 19$ kcal mol^{-1}, higher than for any other C–$\overset{+}{N}$ bond. In fact, compounds **2** present rotation barriers which are among the most substantial from all compounds **6** (where one of the bonds of atom Y may be an unshared electron pair). This is probably due to the short $\overset{+}{N}(sp^2)$–$C(sp^3)$ bond distance.

EXPERIMENTAL

Synthesis of N-(1′-*hydroxyisopropyl*)-2,4,6-*trimethylpyridinium perchlorate* (**3**)

To an alcoholic solution (isopropanol or ethanol) of



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2,4,6-trimethylpyrylium perchlorate **7**, 2-aminopropanol **8** was added (using an excess of 2 moles **8**/mole **7**). The solution was heated at the reflux of the solvent for 30 minutes. The pyridinium perchlorate **3** precipitated on cooling or on cooling and addition of ether. The crude product was recrystallized from isopropanol. The yields are 50–65%.

The perchlorates **4** and **5** were similarly prepared from the pyrylium salt **7** and 2-aminobutanol **9** or α-phenylglycinol **10**, respectively.

In all these preparations, and in all derivatisations which follow, optically active aminoalcohols were used. The pyridinium salt **4** was obtained from both the optically active and the racemic 2-aminobutanol **9**. As expected, the corresponding optically active and racemic pyridinium salt **4** had the same behaviour with respect to hindered rotation evidenced in the NMR spectra, therefore all experimental details which follow refer to the optically active salt **4** and its derivatives **4a–4c**.

Acetylations were effected by heating the perchlorates **3**, **4** or **5** with excess acetic anhydride (2–4 moles Ac_2O/mol pyridinium salt) for 2–3 h at 80–90°. The mixture was left overnight; from the resulting oil, the salts **3b**, **4b** or **5b** precipitated on addition of ether. The crude products were recrystallized from isopropanol or isopropanol/ether. The yields are 80–90%.

Benzoylations were effected by heating the perchlorates **3**, **4** or **5** with excess benzoyl chloride (4–6 moles PhCOCl/mol pyridinium salt) for 1–2 h at 80–90°. The mixture was left overnight and then was triturated with ether to remove the excess benzoyl chloride. The resulting oil was dissolved in isopropanol at the reflux of the solvent (active charcoal was added). From the filtered solution, the benzoylated derivatives **3c**, **4c** or **5c** precipitated on cooling and addition of ether. The yields are 50–60%.

The trifluoroacetoxy derivatives **3a**, **4a** and **5a** were prepared directly in the NMR vials by leaving overnight the solutions of the corresponding alcohols **3**, **4** and **5** in trifluoroacetic acid. For these derivatives, which were not isolated since they hydrolyze rapidly, only ^{1}H NMR spectral data are indicated.

Physical constants, elemental analysis and NMR data are given below. Chemical shifts in ^{1}H NMR (60 MHz) and ^{13}C NMR (25.2 MHz) spectra are given in δ scale in ppm from internal TMS.

N-(1′-*Hydroxyisopropyl*)-2,4,6-*trimethylpyridinium perchlorate* **3**. M.p. 117°; ^{1}H NMR (solvent TFA, room temp.) δ = 1.85 (d, J = 7.5 Hz, 3H, 3′-CH_3) 2.62 (s, 3H, 4-Me) 3.02 (s, 6H, 2,6-Me_2) 4.39, 4.70 (m, 2H, 1′-CH_2) 5.55–5.90 (m, 1H, 2′-CH) 7.66 (s, 2H, 3,5-H_2); ^{13}C NMR (solvent CF_3COOD, 40°) δ = 16.9 (3′-CH_3) 21.8 (4-Me) 23.3, 24.2 (2,6-Me_2) 65.4 (1′-CH_2) 65.8 (2′-CH_2) 131.3, 133.1 (3,5-C_2) 157.3, 158.5 (2,6-C_2) 162.0 (4-C). Found: N, 4.83. $C_{11}H_{18}NClO_5$ requires N, 5.01%.

N-(1′-*Trifluoroacetoxyisopropyl*)-2,4,6-*trimethylpyridinium perchlorate* **3a**. ^{1}H NMR (solvent TFA, room temp) δ = 1.95 (d, J = 7.5 Hz, 3H, 3′-CH_3) 2.62 (s, 3H, 4-Me) 2.98, 3.05 (s, s, 6H, 2,6-Me_2) 4.91, 5.26 (m, 2H, 1′-CH_2) 5.70–6.04 (m, 1H, 2′-CH) 7.70 (s, 2H, 3,5-H_2).

N-(1′-*Acetoxyisopropyl*)-2,4,6-*trimethylpyridinium perchlorate* **3b**. M.p. 109°; ^{1}H NMR (solvent TFA, room temp) δ = 1.92 (d, J = 7.5 Hz, 3H, 3′-CH_3) 1.99 (s, 3H, O.CO.CH_3) 2.62 (s, 3H, 4-Me) 3.05, 3.11 (s, s, 6H, 2,6-Me_2) 4.59, 5.02 (m, 2H, 1′-CH_2) 5.69–6.05 (m, 1H, 2′-CH) 7.94 (s, 2H, 3,5-H_2); ^{13}C NMR (solvent CF_3COOD, 40°C) δ = 17.4 (3′-CH_3) 21.0 ($\underline{C}H_3CO.O$) 21.9 (4-Me) 23.3, 23.9 (2,6-Me_2) 62.7 (1′-CH_2) 67.7 (2′-CH) 131.4, 133.2 (3,5-C_2) 157.3, 157.9 (2,6-C_2) 162.5 (4-C) 177.7 (O.CO). (Found: C, 48.59; H, 6.39; Cl, 11.32 $C_{13}H_{20}NClO_6$ requires C, 48.53; H, 6.27; Cl, 11.02%).

N-(1′*Benzoyloxyisopropyl*)-2,4,6-*trimethylpyridinium perchlorate* **3c**. M.p. 84–85°; ^{1}H NMR (solvent acetone-d_6, room temp) δ = 2.03 (d, J = 7.5 Hz, 3H, 3′-CH_3) 2.59 (s, 3H, 4-Me) 3.10, 3.19 (s, s, 6H, 2,6-Me_2) 4.92, 5.32 (m, 2H,

1'-CH_2) 5.80–6.28 (m, 1H, 2'-CH) 7.50–8.17 (m, 7H, aromatic protons and β-hydrogens in pyridinium ring); ^{13}C NMR (solvent CF_3COOD, 40°) δ = 17.4 (3'-CH_3) 21.9 (4-Me) 23.4, 24.0 (2,6-Me_2) 63.1 (1'-CH_2) 67.6 (2'-CH) 131.3, 133.2 (3,5-C_2) 157.5, 157.9 (2,6-C_2) 162.4 (4-C) 171.5 (O.CO) 137.1 (*p*-C) 129.2 (*m*-C_2) 130.9 (*o*-C_2) 131.5 (*ipso*-*C*-CO). (Found: N, 3.80 $C_{18}H_{22}NClO_6$ requires N, 3.65%).

N-(1'-*Hydroxy*-*sec*(2')-*butyl*)-2,4,6-*trimethylpyridinium perchlorate* **4**. M.p. 100°; ^{1}H NMR (solvent TFA, room temp) δ = 1.08 (t, J = 7.5 Hz, 3H, 4'-CH_3) 2.30 (quintet, J = 7.5 Hz, 2H, 3'-(CH_2) 2.65 (s, 3H, 4-Me) 3.05 (s, 6H, 2,6-Me_2) 4.44, 4.72 (m, 2H, 1'-CH_2) 5.30–5.80 (m, 1H, 2'-CH) 7.68 (s, 2H, 3,5-H_2); ^{13}C NMR (solvent CF_3COOD, 40°) δ = 11.5 (4'-CH_3) 21.8 (4-Me) 23.2, 24.7 (2.6-Me_2) 25.5 (3'-CH_2) 64.5 (1'-CH_2) 72.4 (2'-CH) 131.3, 133.1 (3,5-C_2) 157.3, 158.9 (2,6-C_2) 162.0 (4-C). (Found: C, 49.06; H, 7.18; Cl, 12.03, $C_{12}H_{20}NClO_5$ requires C, 49.07; H, 6.86; Cl, 12.07%).

N-(1'-*Trifluoroacetoxy*-*sec*(2')-*butyl*)-2,4,6-*trimethylpyridinium perchlorate* **4a**. ^{1}H NMR (solvent TFA, room temp) δ = 1.13 (t, J = 7.5 Hz, 3H, 4'-CH_3) 2.45 (quintet, J = 7.5 Hz, 2H, 3'-CH_2) 2.69 (s, 3H, 4-Me) 3.05, 3.11 (s, s, 6H, 2,6-Me_2) 5.03, 5.37 (m, 2H, 1'-CH_2) 5.54–5.96 (m, 1H, 2'-CH) 7.83 (s, 2H, 3,5-H_2).

N-(1'-Acetoxy-sec(2')-butyl)-2,4,6-trimethylpyridinium perchlorate **4b**. M.p. 104–105°; ^{1}H NMR (solvent acetone-d_6, room temp) δ = 1.02 (t, J = 7.5 Hz, 3H, 4'-CH_3) 1.98 (s, 3H, O.$COCH_3$) 2.38 (quintet, J = 7.5 Hz, 2H, 3'-CH_2) 2.62 (s, 3H, 4-Me) 3.04, 3.08 (s, s, 6H, 2,6-Me_2) 4.63, 5.02 (m, 2H, 1'-CH_2) 5.39–5.88 (m, 1H, 2'-CH) 7.92 (s, 2H, 3,5-H_2). (Found: C, 50.29; H, 6.90; Cl, 10.88 $C_{14}H_{22}NClO_6$ requires C, 50.08; H, 6.60; Cl, 10.56%).

N-(1'-*Benzoyloxy*-*sec*(2')-*butyl*)-2,4,6-*trimethylpyridinium perchlorate* **4c**. Oily product; ^{1}H NMR (solvent acetone-d_6, room temp) δ = 1.07 (t, J = 7.5 Hz, 3H, 4'-CH_3) 2.48 (quintet, J = 7.5 Hz, 2H, 3'-CH_2) 2.61 (s, 3H, 4-Me) 3.09, 3.17 (s, s, 6H, 2, 6-Me_2) 4.96, 5.33 (m, 2H, 1'-CH_2) 5.61–6.07 (m, 1H, 2'-CH) 7.44–8.11 (m, 7H, aromatic protons and β-hydrogens in pyridinium ring). (Found: N, 3.62 $C_{19}H_{24}NClO_6$ requires N, 3.52%).

N-(2'-*Hydroxy*-1'-*phenyl*-1'-*ethyl*)-2,4,6-*trimethylpyridinium perchlorate* **5**. M.p. 157°; ^{1}H NMR (solvent pyridine-d_5, temp −3°C) δ = 2.40, 3.22 (s, s, 6H, 2,6-Me_2) 2.43 (s, 3H, 4-Me) 4.94, 5.18 (m, 2H, 2'-CH_2) 6.83–7.17 (m, 1H, 1'-CH) 7.28–7.78 (m, 7H, aromatic protons and β-hydrogens in pyridinium ring). Found: C, 56.19; H, 5.69; Cl, 10.62; N, 4.07 $C_{16}H_{20}NClO_5$ requires C, 56.23; H, 5.90; Cl, 10.37; N, 4.10%.

N-(2'-*Trifluoroacetoxy*-1'-*phenyl*-1'-*ethyl*)-2,4,6-*trimethylpyridinium perchlorate* **5a**. ^{1}H NMR (solvent TFA, room temp) δ = 2.32–3.37 (very broad signal due to the exchange, 6H, 2,6-Me_2) 2.72 (s, 3H, 4-Me) 5.81, 5.57 (m, 2H, 2'-CH_2) 6.92–7.17 (m, 1H, 1'-CH) 7.20–7.92 (m, 7H, aromatic protons and β-hydrogens in pyridinium ring).

N-(2'-*Acetoxy*-1'-*phenyl*-1'-*ethyl*)-2,4,6-*trimethylpyridinium perchlorate* **5b**. M.p. 167°; ^{1}H NMR (solvent pyridine-d_5, temp −3°C) δ = 2.07 (s, 3H, O.$COCH_3$) 2.44, 3.22 (s,s, 6H, 2,6-Me_2) 2.47 (s, 3H, 4-Me) 5.33–5.83 (m, 2H, 2'-CH_2) 6.93–7.30 (m, 1H, 1'-CH) 7.30–8.10 (m, 7H, aromatic protons and β-hydrogens in pyridinium ring). Found: C, 56.54; H, 6.05; Cl, 8.94. $C_{18}H_{22}ClNO_6$ requires: C, 56.33; H, 5.78; Cl, 9.24%.

N-(2'-*Benzoyloxy*-1'-*phenyl*-1'*ethyl*)-2,4,6-*trimethylpyridinium perchlorate* **5c**. M.p. 67–70°; ^{1}H NMR (solvent pyridine-d_5, temp −3°) δ = 2.56, 3.33 (s,s, 6H, 2,6-Me_2) 2.47 (s, 3H, 4-Me) 5.62–6.17 (m, 2H, 2'-CH_2) 7.17–8.33 (m, 13H, 1'-CH, aromatic protons and β-hydrogens in pyridinium ring). Found: N, 3.07 $C_{23}H_{24}NClO_6$ requires N, 3.14%.

Dynamic NMR spectra

The experimental dynamic ^{1}H NMR spectra were recorded with a Varian A60-A spectrometer, using the variable temperature unit of this spectrometer. For temperature determinations, the temperature-dependent chemical shift differences of protons in CH_3OH and in $HOCH_2CH_2OH$ were used (the "NMR thermometer liquid" in a replacement tube). The precision in the temperature determinations was estimated to ± 2°. For line-shape analysis, a HP 9830A computer was used.

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