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## Experimental and quantum chemical evidences for C-H···N hydrogen bonds involving quaternary pyridinium salts and pyridinium ylides

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#### Abstract

The rates of equilibrium of eight quaternary pyridinium salts containing activated methylene groups with the corresponding ylides have been measured in DMSO solution containing strong bases (DBU, MTBD and P1-tBu). The effect of the ring substituents on the deprotonation rate is greater than that of the methylene substituents. This observation is consistent with the energy of C–H···N hydrogen bonds and the elongation of the C–H bond participating in hydrogen bonds estimated by the PM3 and BLYP/6-31G(d,p) calculations. The UV spectra and <sup>1</sup>H NMR spectra of selected ylides have been measured. The solvent effect on the proton chemical shifts of quaternary pyridinium halides and ylides is discussed. Semiempirical and DFT calculations were carried out to investigate the structure of ylides. In ylides, the  $\alpha$ -pyridine protons are more acidic than the methine proton. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: N-quaternary cations; Ylides; Deprotonation; C-H...N hydrogen bond

### 1. Introduction

In quaternary ammonium halides of the type  $>N^+$ – CH<sub>2</sub>–Y, where Y is a strongly electron-withdrawing substituent, the methylene protons are acidic and their reactivity becomes comparable with that of the methylene group of  $\beta$ -ketoesters [1]. Strong bases can abstract one of such protons which may lead to the formation of ylides [2–7]. Most N-ylides are capable of only fleeting existence, but they may be stabilized by coordination with lithium halides [8]. On the other hand, in pyridinium-type ylides, a delocalization of charge into the heterocyclic ring may occur and the stability of such compounds is enhanced. Pyridine ylides with C=O or CN groups are so stable that their structures were determined by X-ray diffraction [6,9–13].

Ammonium ylides are important precursors in organic synthesis, due to their Stevens (1,2) and Sommelet-Hauser (2,3) rearrangement [14] under mild conditions to form highly substituted organic compounds and the possibility to prepare from them stereospecific compounds [15]. Heterocyclic N-ylides with five and six-membered rings are known as a mesoionic compounds and one of their most interesting properties is that they behave as 1,3-dipoles and undergo 1,3-dipolar additions with a great number of dipolarophiles (also known as 3 + 2 cycloaddition reactions) [2–7,16]. Another feature of N-ylides is

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their conversion to olefines or less substituted amines [17–22].

The ability of carbon atoms to act as proton donors in hydrogen bonds has been the subject of controversy for many years [23,24]. Spectroscopic studies [25] indicate that C–H···O and C–H···N occur in many systems, a conclusion that is supported by quantum chemical calculations [26–30].

In this paper, we investigate the deprotonation reactions of eight quaternary pyridinium halides, shown in Scheme 1, by strong bases in DMSO and perform semiempirical and DFT calculations in order to get information on the  $C-H\cdots N$  hydrogen bonds.

#### 2. Experimental

Quaternary pyridinium halides were prepared by treatment of the appropriate substituted pyridine (0.1 M) with the equimolar amounts of ClCH<sub>2</sub>COOEt, ClCH<sub>2</sub>CONH<sub>2</sub>, ClCH<sub>2</sub>CN, ClCH<sub>2</sub>COMe, or BrCH<sub>2</sub> COPh, respectively, in acetonitrile (AN) or acetone (30 cm<sup>3</sup>) (Scheme 1). The mixture was allowed to

Table 1

Reaction	of	<b>R</b> -pyridines	with	X-CH <sub>2</sub> -Y	ľ
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stand for 1–3 weeks at room temperature, until the solid was precipitated. The mixture containing BrCH<sub>2</sub>COPh required refluxing for 10 h. The excess of the solvent was removed under reduced pressure, the crude product was washed with diethyl ether and recrystallized (Table 1). The  $CH_2-N^+$  protons exchange slowly with D<sub>2</sub>O and in <sup>1</sup>H NMR spectrum the signal disappears.

1-(Phenacyl)pyridinium ylide (**3d**) was prepared by a slightly modified procedure described in Ref. [1]. A solution of potassium carbonate (3.5 g) in water (3 ml) was added with cooling to a solution of *N*-(4methylpyridinium)phenacyl bromide (2 g) in water (4 ml). The mixture was stirred for 20 min and then extracted with dichloromethane. The extract was dried for 1 h with Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated in vacuum. The red gun crystallized to orange crystals, m.p.  $104-106^{\circ}C$ .

Bases: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) ( $pK_a^{AN} = 23.9$  [35]; PA = 1047.9 kJ/mol [36]) 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) ( $pK_a^{AN} = 24.70$  [37]; PA = 1062.7 kJ/mol [32]); and

Comp.	Reaction conditions	Solvent for crystallization	M.p. (°C)	Yield crude (%)
1a	MeCOMe, 25°, 3 days	MeCN	226-227 <sup>a</sup>	75
1b	25°, 3 days	MeCN:MeOH (2:1)	157 <sup>b</sup>	93
1c	(Et) <sub>2</sub> O, reflux, 20 h	MeCN	64-67	65
1d	Steam-bath, 30 min	EtOH	245 <sup>°</sup>	99
2a	C <sub>6</sub> H <sub>6</sub> :MeCN (5:9), 25°, 4 days	MeCN	295-296	77
2b	$(Et)_2O:C_6H_6$ (9:1), rt, 4 days	MeCN:MeOH (2:1)	202-203	39
2c	MeCOMe, 25°, 4 days	MeCN	258-259	17
2d	MeCOMe, reflux, 12 h	MeCN:MeOH (2:1)	228-229 <sup>d</sup>	62
2e	MeCOMe, 25°, 2 weeks	MeCN:MeOH (2:1)	229-230	17

<sup>a</sup> M.p. 230–232°C [31].

<sup>b</sup> M.p. 151°C [32].

<sup>c</sup> M.p. 274–276<sup>o</sup>C [33].

<sup>d</sup> M.p. 215–217°C [34].

Solvent	$H_{lpha}$	$H_{eta}$	$Py^+CH_2$	R	Y
D <sub>2</sub> O	8.41(2H, d)	7.73(2H, d)	5.23(2H, s)	2.48(3H, s)	_
DMSO-d <sub>6</sub>	8.80(2H, d)	7.99(2H, d)	5.33(2H, s)	2.63(3H, s)	8.08(1H, b), 7.69(1H, b)
CD <sub>3</sub> CN	8.46(2H, d)	7.84(2H, d)	5.25(2H, s)	2.65(3H, s)	_
$D_2O$	8.44(2H, d)	7.74(2H, d)	5.29(2H, s)	2.49(3H, s)	4.11(2H, q), 1.09(3H, t)
DMSO-d <sub>6</sub>	8.94(2H, d)	8.07(2H, d)	5.66(2H, s)	2.65(3H, s)	4.23(2H, q), 1.26(3H, t)
CD <sub>3</sub> CN	8.92(2H, d)	7.88(2H, d)	5.72(2H, s)	2.65(3H, s)	4.26(2H, q), 1.28(3H, t)
$D_2O$	8.27(2H, d)	7.73(2H, d)	5.50(2H, s)	2.48(3H, s)	2.22(3H, s)
DMSO-d <sub>6</sub>	8.85(2H, d)	8.06(2H, d)	5.90(2H, s)	2.64(3H, s)	2.31(3H, s)
CD <sub>3</sub> CN	8.88(2H, d)	7.87(2H, d)	6.06(2H, s)	2.63(3H, s)	2.31(3H, s)
$D_2O$	8.37(2H, d)	7.81(2H, d)	6.14(2H, s)	2.52(3H, s)	7.87(2H <sub>o</sub> , d), 7.43(2H <sub>m</sub> , t), 7.60 (1H <sub>p</sub> , t)
DMSO-d <sub>6</sub>	8.90(2H, d)	8.12(2H, d)	6.50(2H, s)	2.68(3H, s)	$8.09(2H_0, d), 7.67(2H_m, t), 7.81(1H_p, t)$
CD <sub>3</sub> CN	8.59(2H, d)	7.91(2H, d)	6.31(2H, s)	2.69(3H, s)	$8.08(2H_0, d), 7.64(2H_m, t), 7.78(1H_p, t)$
CDCl <sub>3</sub>	9.09(2H, d)	7.82(2H, d)	7.09(2H, s)	2.74(3H, s)	$8.21(2H_0, d), 7.57(2H_m, t), 7.69(1H_p, t)$
$D_2O$	7.75(2H, d)	6.71(2H, d)	4.80(2H, s)	3.02(6H, s)	_
DMSO-d <sub>6</sub>	8.18(2H, d)	7.03(2H, d)	4.94(2H, s)	3.20(6H, s)	7.80(1H, b), 7.51(1H, b)
D <sub>2</sub> O	7.76(2H, d)	6.72(2H, d)	4.85(2H. s)	3.03(6H, s)	4.09(2H, q), 1.09(3H, t)
DMSO-d <sub>6</sub>	8.32(2H, d)	7.12(2H, d)	5.29(2H. s)	3.22(6H, s)	4.20(2H, q), 1.24(3H, t)
D <sub>2</sub> O	7.61(2H, d)	6.70(2H, d)	5.04(2H. s)	3.02(6H, s)	2.14(3H, s)
DMSO-d	8.16(2H, d)	7.09(2H d)	5.40(2H s)	3.21(6H_s)	2.23(3H_s)

5.67(2H. s)

6.04(2H, s)

5.14(2H, s)

5.58(2H, s)

6.79(1H, b)<sup>a</sup>

6.71(1H, b)<sup>a</sup>

3.03(6H, s)

3.24(6H, s)

3.05(6H, s)

3.23(6H, s)

2.40(3H, s)

2.43(3H, s)

<sup>1</sup>H NMR data (ppm) of the investigated compounds (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad)

<sup>a</sup>  $\delta CH^{-}$ .

 $D_2O$ 

D<sub>2</sub>O DMSO-d<sub>6</sub>

CD<sub>3</sub>CN

CDCl<sub>3</sub>

DMSO-d<sub>6</sub>

Table 2

Comp.

1b

1c

1d

2a 2b

2c

2d

2e

3d

Schwesinger base, phosphazene (P1-*t*Bu) (p $K_a^{AN}$  = 33.49; p $K_a^{DMSO}$  = 21.5 [38]; PA ~ 1100 kJ/mol [36]) were commercial materials purchased from Fluka and were used as received.

7.82(2H, d)

8.24(2H, d)

7.88(2H, d)

8.41(2H, d)

9.58 (2H,d)

9.50 (2H,d)

6.73(2H, d)

7.15(2H, d)

6.76(2H, d)

7.14(2H, d)

7.35(2H, b)

7.40(2H, d)

The <sup>1</sup>H NMR spectra were recorded on a Varian Gemini 300VT spectrometer, operating at 300.07 MHz, using TMS as the internal standard. 2D (H,H-COSY) and homodecoupling methods were used to verify proton chemical shifts in the investigated compounds. The UV spectroscopy was recorded in DMSO on a Diode Array Hewlett-Packard spectrophotometer.

The rates of proton transfer were measured spectrophotometrically in a Applied Photophysics stoppedflow apparatus with the cell block thermostated to  $\pm 1^{\circ}$ C. The reactions were monitored at maximum absorption of ylide (400–497 nm). The reactions were conducted by mixing a DMSO solution of **1a**– **e**–**2a**–**e** with the base in DMSO. The concentration of **1** and **2** was  $2 \times 10^{-4}$  M. The PM3 [39], AM1 [40] and SAM1 [41] semiempirical calculations were performed using the AMPAC 6.0 program [42]. In all cases, the PRECISE and GRAD keywords were used and the full geometry optimisation was carried out without any symmetry constraints. The ab initio calculations were run with the GAUSSIAN 98 [43] program packages. The molecular parameters of the complex were determined at the DFT [44] level using the standard 6-31 G(d,p) basis set [45] with two different functionals BLYP and B3LYP (the exchange functional of Becke (B) [46] and the gradient-corrected functional of Lee et al. (LYP) [47].

7.70(2Ho, d), 7.40(2Hm, t), 7.56 (1Hp, t)

8.05(2H<sub>o</sub>, d), 7.65(2H<sub>m</sub>, t), 7.78 (1H<sub>p</sub>, t)

7.78(2Ho, d), 7.35(2Hm,p, m)

7.83(2Ho, d), 7.35(3Hm,p, m)

#### 3. Results and discussion

# 3.1. <sup>1</sup>H NMR and UV–Vis spectra of quaternary pyridinium halides and pyridinium ylides

Pyridines have displayed pronounced substituent



Fig. 1. <sup>1</sup>H NMR spectrum of **1d** and **3d** in CDCl<sub>3</sub>.

and solvent effects [48,49]. Conversion of pyridine into pyridinium cation causes a downfield shift of all the hydrogens [50]. Table 2 summarises the chemical shifts of the protons in the investigated salts in several solvents. As expected, the chemical shifts are affected by substituents and solvents. The observed solvent effect on the chemical shifts (Table 2) may be explicable in terms of variation of ion pairing between the pyridinium ion and counterion and changes of the resonance hybrid. The chemical shifts of the pyridine ring protons in DMSO-d<sub>6</sub> solution of 4-NMe<sub>2</sub>-pyridinium salts are comparable to these 4-NMe<sub>2</sub>-pyridinium methiodide [51]. Fig. 1 shows spectra of **1d** and **3d** in CDCl<sub>3</sub>. Conversion of the quaternary salt into the ylide causes a downfield shift of  $\alpha$ -pyridine proton and an upfield shift of  $\beta$ -pyridine and CH<sub>3</sub> protons. Similar changes of chemical shifts have been observed by Phillips and Ratts [52] and by Matsuboyashi [53]. The methine proton appears as a broad signal at 6.71 ppm. All signals of phenyl protons are deshielding (compare values for **1d** and **3d** in Table 2). It is interesting to note that solvent has an influence on the multiplicity of the ylide protons. In CD<sub>3</sub>CN the pyridine ring protons appeared as broad singlets, whilst in CDCl<sub>3</sub> solution they were doublets (Fig. 1). These differences



Fig. 2. UV–Vis spectra of **1c**  $(2 \times 10^{-4} \text{M})$  and a mixture of **1c**  $(2 \times 10^{-4} \text{M})$  with MTBD  $(2 \times 10^{-3} \text{M})$  in DMSO; curve 1, 0 min; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 50 min; 7, 60 min; 8, 70 min.

may be explained in terms of dynamic aspects of solvation.  $CDCl_3$  as weak proton donor can form weak hydrogen bonds with the oxygen atom, electron pair of methine group and  $\pi$ -electrons of pyridine and phenyl rings.  $CD_3CN$  with ylides can form a dipole–dipole complex. The NMR data indicate that the life-time of solvated species in  $CD_3CN$  is comparable with the time of observation, while in  $CDCl_3$  it is longer [54]. Another explanation is given by entropy [55]. The NMR spectra reflect variation of structure and dynamics of solvated species.

Fig. 2 shows the UV–Vis spectrum of **1c** in DMSO and its time-dependent changes on addition of MTBD. The absorption in the 422–497 nm region (Table 3; Fig. 2) is due to an intramolecular charge-transfer transition [1,53,56]. The significant intensity

Table 3 UV–Vis absorption spectra of 4-R– $C_5H_4N^+$ – $C^-H$ –Y in DMSO-d<sub>6</sub>

Ylides	$\lambda$ (nm)	$\log \epsilon$	
3a	446	3.06	
3b	422	3.78	
3c	424	4.48	
3d	442	3.87	
4b	414	3.15	
4c	410	3.33	

decreasing of the 442 nm band (Fig. 2) reflects decomposition of the ylide.

#### 3.2. Kinetics of proton transfer to amine bases

When quaternary pyridinium halide (AH) is treated by an excess of a strong base (B)  $\{[B_o] \gg [AH_o]\}$  the following processes can occur:

$$AH + B \underset{k_{-}}{\overset{k}{\rightleftharpoons}} (A^{+/-} \cdots H - B^{+}); \quad k_{obs} = k[B_o] + k_{-} \quad (1)$$

$$\mathbf{A}\mathbf{H} + \mathbf{B} \stackrel{k}{\underset{k_{-}}{\cong}} \mathbf{A}^{+/-} + \mathbf{B}^{+}\mathbf{H}; \ k_{\text{obs}} = k[\mathbf{B}_{\text{o}}] + k_{-}[\mathbf{B}^{+}\mathbf{H}]$$
(2)

$$AH + B \stackrel{k}{\underset{k_{-}}{\rightleftharpoons}} (A^{+/-} \cdots H - B^{+}) \stackrel{k_{D}}{\rightleftharpoons} A^{+/-} + B^{+}H;$$
(3)

$$k_{\rm obs} = k[B_{\rm o}] + k_{\rm -}[B^{\rm +}H]/K_{\rm D}$$

where k is the rate constant for the deprotonation (forward) reaction,  $k_{-}$  is the rate constant for the protonation (backward) reaction,  $[B_0]$  is the initial base concentration, [B<sup>+</sup>H] is the concentration of the cation and  $K_{\rm D}$  is the dissociation constant of the ion pair ( $A^- \cdots H - B^+$ ). The  $k_{obs}$  values were calculated from the traces of absorbance (400-497 nm) vs. time and are listed in Table 4. When  $k_{obs}$  was plotted vs.  $[B_0]$ , excellent straight lines were obtained (r > 0.99), where the slope gives k values and the intercept  $k_{-}$ values (Table 4), which means that the reaction studied was correctly described by Eq. (1). Note that in the case of Eq. (2), term  $[B^+H]$  is not constant; for the forward reaction the process is of the first order, but for the backforward reaction is of the second order.

Although Eq. (1) correctly fitted the experimental data, model (3) cannot be completely neglected. The dissociation of the hydrogen bonded ion pairs into ions increases with dilution and increasing temperature. It seems that the contribution of solvated ions can be neglected in the range of concentration and temperature applied in this work.

The rate of deprotonation, as expected, is primary affected by the substituent in the pyridine ring. All salts with 4-NMe<sub>2</sub> substituent show ca 4–6 order of magnitude slower reactivity than the corresponding salts with 4-Me group. The unsubstituted pyridine

Table 4	
Kinetic data (standard deviation) for the deprotonation of $4-R-C_5H_4N^+-CH_2-YX^-$	

Comp.	Base	$B_{\rm o}$ (M)	$k_{obs} (s')$									
			30°C	35°C	40°C	45°C	50°C					
1a	MTBD	0.05	140(20)	190(10)	240(30)	300(20)						
		0.1	260(20)	350(20)	420(30)	480(30)						
		0.125	330(20)	420(20)	510(20)	620(20)						
1b	DBU	0.015	417(6)	529(6)	640(8)	750(9)						
		0.03	580(5)	750(6)	920(7)	1080(8)						
		0.05	760(2)	1030(3)	1303(4)	1600(6)						
	MTBD	0.015	147(2)	174(3)	200(4)	240(1)						
		0.03	198(3)	230(4)	259(5)	249(5)						
		0.05	260(1)	298(2)	333(3)	372(1)						
1c	DBU	0.0015	358(2)	480(3)	580(7)	700(8)						
		0.003	518(1)	690(3)	800(5)	950(10)						
		0.005	695(3)	905(2)	1060(7)	1250(12)						
	MTBD	0.0015	123(1)	140(3)	162(4)	180(5)						
		0.003	144(2)	166(4)	189(3)	230(7)						
		0.005	177(3)	207(5)	242(5)	275(6)						
1d	MTBD	0.0015	210(10)	300(10)	380(10)	490(10)						
		0.003	290(10)	400(10)	490(10)	670(20)						
		0.005	372(20)	510(10)	660(20)	910(20)						
2b	DBU	0.1	0.00055	0.00082	0.00157	0.00281	0.00381					
		0.2	0.00173	0.00263	0.00428	0.00613	0.00827					
		0.3	0.00295	0.00413	0.00651	0.00924	0.01210					
	MTBD	0.05	0.00066	0.00126	0.00208	0.00288	0.00413					
		0.075	0.00161	0.00252	0.00383	0.00532	0.00697					
		0.1	0.00227	0.00368	0.00561	0.00811	0.01010					
	P₁-tBu	0.005	0.0129	0.0276	0.0430	0.0429	0.0532					
	1	0.015	0.0295	0.0551	0.0880	0.1260	0.1610					
		0.025	0.0466	0.0832	0.1300	0.1900	0.2560					
2c	DBU	0.1	0.00221	0.00268	0.00296	0.00322	0.00343					
		0.2	0.00266	0.00324	0.00361	0.00410	0.00444					
		0.3	0.00291	0.00375	0.00435	0.00499	0.00562					
	MTBD	0.050	0.00339	0.00509	0.00642	0.00732	0.00833					
		0.075	0.00423	0.00644	0.00813	0.00971	0.01130					
		0.100	0.00511	0.00793	0.00971	0.01150	0.01430					
	P <sub>1</sub> -tB <sub>11</sub>	0.005	0.00590	0.00680	0.00785	0.00891	0.01010					
	1100	0.015	0.00625	0.00718	0.00872	0.00992	0.01140					
		0.025	0.00685	0.00805	0.00977	0.01140	0.01280					
2d	DBU	0.1	0.00116	0.00145	0.00172	0.00194	0.00235					
20	DDC	0.2	0.00148	0.00184	0.00226	0.00258	0.00233					
		0.2	0.00145	0.00216	0.00220	0.00256	0.00314					
	MTRD	0.05	0.00150	0.00179	0.00211	0.00268	0.00299					
	MIDD	0.075	0.00156	0.00192	0.00234	0.00208	0.00235					
		0.075	0.00150	0.00192	0.00234	0.00224	0.00355					
	P. tBu	0.005	0.00103	0.00155	0.00245	0.00250	0.00305					
	1   tDu	0.005	0.00157	0.00105	0.00198	0.00294	0.00200					
		0.015	0.00155	0.00195	0.00221	0.00234	0.00344					
20	DBU	0.025	0.00108	0.00214	0.00270	0.00342	0.00401					
20	DBU	0.05	0.00220	0.00240	0.00233	0.00274	0.00288					
		0.1	0.00200	0.00200	0.00304	0.00340	0.00300					
		0.15	0.00290	0.00317	0.00308	0.00387	0.00410					
	MTRD	0.2	0.00320	0.00500	0.00398	0.00423	0.00432					
		0.05	0.00000	0.00044	0.00050	0.010.00	0.01200					

Comp.	Base	$B_{\rm o}$ (M)	$k_{\rm obs}~({\rm s}^{-1})$							
			30°C	35°C	40°C	45°C	50°C			
		0.1	0.00577	0.00850	0.01170	0.01410	0.01610			
		0.15	0.00842	0.01170	0.01520	0.01730	0.02050			
		0.2	0.01030	0.01450	0.01770	0.02130	0.02500			
	P <sub>1</sub> -tBu	0.025	0.129	0.161	0.196	0.223				
		0.035	0.142	0.178	0.217	0.265				
		0.05	0.160	0.203	0.254	0.319				
		0.065	0.177	0.234	0.299	0.369				

salts react ca 90-fold faster than 4-Me-pyridine salts [57]. In the case of 4-CN-pyridine salts, deprotonation was too fast to be measured in our stopped-flow apparatus. These data indicate that electron-withdrawing substituents accelerate deprotonation, while electrondonating ones decelerate it down. Similar effect of substituents on the reaction of abstraction of  $\beta$ -proton from N-(2-cyanoethyl) pyridinium cations in aqueous solution was observed by Bunting et al. [21]. The effect methylene substituents on the rate of of proton abstraction is much weaker than that of ring substituents. Abstraction of proton by MTBD in 4-Me–C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>–CH<sub>2</sub>COMe is ca 20-fold faster than in 4-Me- $C_5H_4N^+$ -CH<sub>2</sub>CONH<sub>2</sub>. In the case of 4-NMe<sub>2</sub>- $C_5H_4N^+$ –CH<sub>2</sub>Y the difference between the fastest and

the slowest reaction is 12 and 140-fold, respectively, in MTBD and P1-tBu. The effect of the base strength varies with the type of salt. In 4-NMe<sub>2</sub>-C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>- CH<sub>2</sub>Y, the rate of proton abstraction, as expected, increases with increasing  $pK_a$  value of the super base applied. However, this trend is broken in the case of 4-Me-C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>-CH<sub>2</sub>Y salts.

The activation parameters (Table 5) were calculated from the Eyring equation in form (4) [58,59]:

$$\log \frac{k}{T} = \log \frac{k_{\rm B}}{\hbar} + \frac{\Delta S^{\neq}}{2.303 \rm R} - \frac{\Delta H^{\neq}}{2.303 \rm RT}$$
$$= 10.319 + \frac{\Delta S^{\neq}}{19.137} + \frac{1000 \Delta H^{\neq}}{19.137 \rm T}$$
(4)

Table 5 Activation parameters for proton abstraction from 4-R–C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>–CH<sub>2</sub>–Y X<sup>-</sup> in DMSO at 30°C

Comp.	Base	$k (1 \text{ mol}^{-1} \text{ s}^{-1})$	Int $(s^{-1})$	$\Delta H^{\neq} (\mathrm{kJ} \mathrm{mol}^{-1})$	$\Delta S^{\neq}$ (J mol <sup>-1</sup> deg <sup>-1</sup> )	$\Delta G^{\neq} (\text{kJ mol}^{-1})$
1a	MTBD	2530 (180)	13 (7)	24.5(0.8)	-99	54.5(0.8)
1b	DBU	9760 (520)	277 (18)	46.1(2.9)	-17	51.3(2.9)
	MTBD	3220 (80)	100 (3)	6.19(2.5)	-157	53.8(2.5)
1c	DBU	95870 (5100)	220 (18)	23.1(2.5)	-73	45.2(2.5)
	MTBD	15490 (700)	99 (2)	26.9(1.3)	-76	49.9(1.3)
1d	MTBD	45620(1420)	144 (4)	47.3(2.3)	0.2	47.2(2.3)
2b	DBU	0.0120(1)	~0	48.7(2.2)	-121	85.4(2.2)
	MTBD	0.032 (3)	$\sim 0$	53.0(4.3)	-99	83.0(4.3)
	P <sub>1</sub> -tBu	1.69 (1)	0.0044(2)	71.9(2.5)	-3	72.8(2.5)
2c	DBU	0.0035 (6)	0.0019(1)	42.9(3.3)	-150	84.4(3.3)
	MTBD	0.0344 (5)	0.0017(1)	44.2(4.7)	-127	82.7(4.7)
	P <sub>1</sub> -tBu	0.048 (7)	0.0056(1)	43.1(4.6)	-128	81.9(4.6)
2d	DBU	0.0025 (4)	0.0009(1)	42.8(3.2)	-154	89.5(3.2)
	MTBD	0.0026 (1)	0.0014(1)	63.7(2.4)	-84	89.2(2.4)
	P <sub>1</sub> -tBu	0.0155 (14)	0.0013(1)	51.9(4.2)	-108	84.6(4.2)
2e	DBU	0.0066 (3)	0.0019(1)	17.4(2.9)	-229	86.8(2.9)
	MTBD	0.044 (2)	0.0015(3)	22.2(3.6)	-198	82.2(3.6)
	$P_1$ -tBu	1.197 (23)	0.010(1)	57.0(2.1)	-55	72.4(2.1)



Scheme 2.

Table 6

Heats of formation (kcal), dipole moments (Debye), hydrogen bond energies (kcal) and selected distances (Å) calculated by the PM3 method of compounds from Scheme 2 (heats of formation for  $NH_2^-$ , 38.3;  $NH_3$ , -3.1;  $NH_4^+$ , 153.4;  $C_5H_5N$ , 30.4;  $C_5H_5N^+H$ , 187.3; 4- $NH_2-C_5H_5N$ , 27.5; 4- $NH_2-C_5H_5N^+H$ , 175.2 kcal)

Comp.	$\Delta H$	$\mu$	$E_{\rm HB}$	$C{\cdots}N^a$	$(C)H{\cdots}N$	$C{\cdots}H(N)$	$C{-}H^{\mathfrak{b}}$	$C-H^c$	$N^+\!\!\cdots\!O$	$C_8-O$	$N^+\!\!-\!C_7$	C <sub>7</sub> -C <sub>8</sub>	$C_2 - N^+ - C_7 - C_8$
Comple	xes												
7ak	131.4	5.0	-10.1	2.914	1.748		1.169	1.111	2.767	1.213	1.481	1.527	-86.0
8ak	137.5	8.8	-16.3	2.702		1.605		1.107	2.893	1.220	1.430	1.484	-52.3
9ak	-4.01	4.4	-1.3	3.753	2.506		(1.123)	1.098	2.893	1.234	1.365	1.446	-0.0
7am	162.3	5.3	-12.7	2.917	1.752		1.167	1.111	2.767	1.213	1.481	1.526	-84.0
8am	175.7	5.8	-12.0	2.725		1.579		1.106	2.911	1.221	1.428	1.483	-51.5
7an	157.2	5.5	-14.9	2.911	1.741		1.170	1.111	2.762	1.214	1.481	1.525	-86.4
8an	165.1	8.0	-10.5	2.752		1.676		1.103	2.888	1.228	1.414	1.469	-21.4
7bk	174.9	6.8	-10.5	2.912	1.745		1.170	1.111	2.762	1.213	1.481	1.528	-86.1
8bk	178.2	12.4	-11.2	2.729		1.648		1.105	2.886	1.223	1.422	1.478	-24.0
9bk	31.2	5.3	-1.7	3.520	2.423		(1.124)	1.098	2.896	1.231	1.357	1.453	-0.1
7ck	119.7	4.8	-9.8	2.916	1.740		1.167	1.111	2.767	1.213	1.482	1.526	-86.0
8ck	125.4	9.0	-19.0	2.710		1.619		1.105	2.889	1.227	1.431	1.477	23.9
9ck	-13.6	4.3	-1.5	3.575	2.507		(1.104)	(1.124)	2.897	1.234	1.367	1.445	0.0
7dk	117.9	4.6	-8.3	2.927	1.770		1.160	1.110	2.779	1.214	1.482	1.524	-89.8
8dk	127.4	8.4	-23.5	2.693		1.583		1.105	2.889	1.227	1.444	1.477	-24.7
9dk	-7.1	4.5	-1.5	3.598	2.505		(1.125)	1.097	2.896	1.236	1.371	1.441	-0.2
Ylides													
6a	0.39	3.4						1.097	2.856	1.233	1.364	1.448	0.0
6b	36.0	4.0						1.098	2.894	1.231	1.357	1.455	0.0
6c	-9.0	3.6						1.097	2.895	1.234	1.365	1.447	0.0
6d	-2.5	4.3						1.096	2.894	1.235	1.369	1.444	0.0
Cations													
5a	144.6	4.4						1.113	2.768	1.210	1.489	1.538	-89.4
5b	188.5	5.9						1.113	2.765	1.211	1.489	1.539	-89.1
5c	132.6	4.1						1.113	2.771	1.211	1.489	1.537	-89.0
5d	129.3	3.9					1.112		2.783	1.212	1.487	1.533	-88.7

<sup>a</sup> Distance between  $C(7) \cdots N$  bond and between  $C(2) \cdots N$  in parenthesis.

<sup>b</sup> Length of C(7)–H (C(2)–H) bond engaged in hydrogen bond.

<sup>c</sup> Length of C(7)–H bond non-engaged in hydrogen bond and in parenthesis C(6)–H bond.

Table	7
rabic	/

Comp.	Energy	$\mu$	$E_{\rm HB}$	$C{\cdots}N^a$	$(C)H{\cdots}N$	$C{-}H^b$	$C-H^c$	$N^+\!\!\cdots\!O$	$C_8-O$	$N^+\!\!-\!\!C_7$	C <sub>7</sub> -C <sub>8</sub>	$C_2 - N^+ - C_7 - C_8$	$q\mathrm{N}^+$	qO	qC
Comple	xes														
7ak	-497.0016536	3.94	-12.87	3.220	2.104	1.121	1.098	2.762	1.224	1.482	1.563	-65.1	-0.3311	-0.3737	-0.1940
7ak <sup>d</sup>	-497.0015812	4.00	-12.87	3.211	2.092	1.121	1.098	2.763	1.224	1.482	1.563	-65.5	-0.3310	-0.3740	-0.1956
9ak	-496.5854357	6.3	-3.2	(3.463)	(2.969)	(1.094)	1.091	2.978	1.265	1.396	1.426	-0.0	-0.3603	-0.5290	0.0405
7bk	-589.214939	7.16	-12.94	3.193	2.070	1.124	1.098	2.761	1.223	1.479	1.567	-63.5	-0.3345	-0.3692	-0.1970
7bk <sup>d</sup>	-589.214981	7.12	-12.95	3.194	2.074	1.123	1.098	2.760	1.223	1.479	1.567	-64.1	-0.3347	-0.3694	-0.1964
9bk	-588.8190129	7.40	-5.96	(3.412)	(2.317)	(1.095)	1.087	2.971	1.261	1.387	1.435	-0.0	-0.3651	-0.5070	-0.0226
7dk	-630.931716	3.77	-10.16	3.283	2.172	1.116	1.099	2.760	1.225	1.479	1.557	-69.0	-0.3510	-0.3836	-0.1868
Ylides															
6a	-440.0491485	4.31					1.089	2.976	1.262	1.392	1.431	0.0	-0.3561	-0.5094	-0.0186
							(1.089)								
6b	-532.2812866	4.53					1.089	2.968	1.259	1.383	1.439	-0.2	-0.3612	-0.4902	-0.0031
							(1.089)								
6d	-573.9548516	7.55					1.088	2.969	1.270	1.406	1.420	0.0	-0.3634	-0.5446	-0.0442
							(1.089)								
Cations															
5a	-440.4528046	3.60					1.100	2.713	1.220	1.485	1.578	-85.8	-0.3236	-0.3600	-0.1722
							(1.089)								
5b	-532.66601	6.40					1.098	2.758	1.221	1.482	1.581	62.2	-0.3408	-0.3554	-0.1700
							1.102								
							(1.089)								
5d	-574.3872828	3.13					1.099	2.765	1.223	1.478	1.568	-64,8	-0.3571	-0.3707	-0.1590
							1.103								
							(1.088)								

Energies (a.u), dipole moments (Debye), hydrogen bond energies (kcal/mol) and selected distances (Å) calculated by the BLYP/6-31G(d,p) method of compounds from Scheme 2 (energy of  $NH_{3}$ , -56.5282252 and  $NH_{4}^{-}$  -56.8753721 a.u.)

<sup>a</sup> Distance between C(7)···NH<sub>3</sub> and between C(2)···NH<sub>3</sub> in parenthesis.
<sup>b</sup> Length of C(7)–H (C(2)–H) bond engaged in hydrogen bond.
<sup>c</sup> Length of C(7)–H (C(6)–H) bond non-engaged in hydrogen bond
<sup>d</sup> Values obtained for calculations started with C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>CH<sup>-</sup>OMe·H–NH<sub>3</sub><sup>+</sup> geometry.



Scheme 3.

where  $k_B$  is the Boltzman constant and  $\hbar$  is the Planck constant.

#### 3.3. Semiempirical and DFT calculations

Enthalpy, energy, dipole moment and selected results of geometry optimisation at the PM3 and BLYP/6-31G(d,p) level for carbocation **5**, ylides **6** and their complexes with NH<sub>3</sub>, pyridine and 4-NH<sub>2</sub>pyridine (Scheme 2) are collected in Tables 6 and 7, respectively. The atom numbering is given in Scheme 3. The rotational isomers shown in Fig. 3 were found to correspond to the global minima for complexes. As data given in Tables 6 and 7 show, there is essential difference between the PM3 and BLYP results. The PM3 method reproduces shorter C–O, C–H bonds and N…O distance in comparison to the corresponding BLYP values. However, geometrical differences between cations and ylides are comparable in both methods.

The data in Tables 6 and 7 show that formation of ylide **6** from cation **5** caused the following geometry changes: (i) the  $N^+-C_7$  and  $C_7-C_8$  bonds become shorter ca 0.1 and 0.15 Å, respectively; (ii) the C–O



Fig. 3. The optimised BLYP/6-31 G(d,p) structures of **5a**, **6a**, **7ak** and **9ak**.

Table 8

Calculated heat of formation (kcal), dipole moment (Debye), selected bond lengths (Å), bond angles, some torsial angles (deg) and some distances (Å) for *N*-acetyl-4-methyl-pyridinium ylide (**6a**)

Method	B3LYP	BLYP	AM1	PM3	SAM1
$\Delta H$	а	b	17.46	0.39	10.40
$\mu$	5.21	4.31	3.94	3.40	3.90
$N_1 - C_7$	1.386	1.392	1.362	1.364	1.389
$C_7 - C_8$	1.416	1.431	1.441	1.448	1.453
$C_8 - O_9$	1.247	1.262	1.247	1.233	1.272
C <sub>2</sub> -H	1.081	1.090	1.109	1.124	1.109
C <sub>6</sub> -H	1.080	1.089	1.103	1.099	1.090
$C_2H\cdots O_9$	1.972	1.980	2.073	1.840	1.778
$C_2 \cdots O_9$	2.800	2.828	2.867	2.702	2.659
$N_1 \cdots O_9$	2.942	2.976	2.983	2.896	2.903
$C_2-N-C_7$	123.0	122.7	123.4	121.8	121.7
$H-C_6-N_1$	115.3	115.1	116.5	118.4	116.1
$H-C_2-N_1$	114.2	113.4	116.8	115.1	114.8
$C_2-H-O_9$	130.7	132.0	125.9	129.9	132.8
$C_2 - N_1 - C_7 - C_8$	0.0	0.0	0.0	0.0	0.0
$N_1 - C_7 - C_8 - O_9$	0.0	0.0	0.0	0.0	0.0

<sup>a</sup> E = -440.3298074 a.u.

<sup>b</sup> E = -440.0491485 a.u.

bond becomes longer ca 0.04 Å (BLYP) and 0.02 Å (PM3); (iii) the intramolecular N<sup>+</sup>···O distance elongates ca 0.25 Å (BLYP) and 0.01 Å (PM3); and (iv) the N<sup>+</sup>-C<sub>7</sub>-C<sub>8</sub>-O unit in **5** is perpendicular, while in **6** is coplanar with the pyridine ring plane. These data indicate that in ylides, there is strong electron coupling between the pyridine ring and the oxygen atom through bonds, while in carbocations there is electrostatic interaction between the positively charged nitrogen atom and the oxygen atom via space. Conformation of *N*-(carbamoyl)pyridinium perchlorate in crystal is similar to that in **5** [60].

In ylides 6 there is a contact between the  $\alpha$ -proton of pyridine ring and the oxygen atom. The question arises is if this contact can be classified as a hydrogen



Fig. 4. The optimised PM3 structures of 7ak and 8ak.

bond. The difference between the length of C<sub>2</sub>–H and C<sub>6</sub>–H bonds vary with the method of calculation. The smallest difference is predicted by the B3LYP and the largest by the PM3 methods. The data collected in Table 8 suggest that this interaction is not hydrogen bond. The O<sub>9</sub>…H–C<sub>2</sub> angle (126–133°) is smaller than the analogous angle in the enol form of  $\beta$ -diketones with intramolecular hydrogen bond (147.6°) [61]. The second  $\alpha$ -pyridine proton interacts with NH<sub>3</sub> and pyridines (Fig. 3, **9ak**). This suggests that the methine proton.

The PM3 method predicts two types of complexes, a molecular 7 and an ion-pair 8 (Fig. 4). The former is more stable by ca 6-10 kcal/mol. According to BLYP results only molecular complexes are formed. This indicates that in the gas phase ammonium is not a strong enough base to abstract proton from 5. However, in the case of molecular complexes several rotamers can be formed, which differ slightly in energy and geometry (see Table 7). Formation of molecular complexes 7 elongates the C-H bond engaged in hydrogen bonds by ca 0.02 Å relatively to the non-bonded ones. The energy of the C-H···N bond is ca 12 kcal/mol. The NH<sub>2</sub><sup>-</sup> anion is strong enough to abstract the proton from 5, which leads to the formation of 9. In 9, NH<sub>3</sub> interacts with the  $\alpha$ proton of the pyridine ring (Fig. 3), causing its slight elongation (compare  $C_2$ -H and  $C_6$ -H in Table 7). The geometry of 9 only slightly differs from that of 6.

#### 4. Summary

The rate constants for deprotonation of  $N-CH_2$ groups in eight quaternary pyridinium cations by DBU, MTBD and P1-tBu in DMSO solution have been determined. The rate constant is extremely sensitive to the ring substituent and less to the methylene substituent. The pyridine-ring electron-withdrawing substituents accelerate the reaction while the electron-donating ones slow it down.

The PM3 and BLYP/6-31G(d,p) calculations confirmed that the investigated pyridinium cations form  $C-H\cdots N$  hydrogen bonds with nitrogen bases. The estimated energy of hydrogen bonds and elongation of the C-H bond participating in hydrogen bond are consistent with the rate constants measured. The <sup>1</sup>H NMR spectra of the investigated quaternary pyridinium salts and ylides are strongly affected by substituents and solvents. Ylides have planar structures and the  $\alpha$ -pyridine proton has contact with the oxygen atom and this caused its downfield shift relative to the quaternary salts. Ammonium and pyridines interact with the second  $\alpha$ -pyridine proton of ylides but not with the methine proton.

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