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Table S1 : ^1H NMR Data for the Cation **6** and the Related Carbon Base **C-6** in $(\text{CD}_3)_2\text{SO}$, and a 50:50 (v/v) H_2O - $(\text{CD}_3)_2\text{SO}$ Mixture^a

Solvent	Compound	$\delta(\text{H}_\alpha)$	$\delta(\text{H}_{3,5})$	$\delta(\text{H}_{2,6})$	$\delta(\text{H}_4)$	$\delta(\text{H}_{\text{Cp}}^*)$
$(\text{CD}_3)_2\text{SO}$	6	5.62	6.10 ^b	6.10 ^b	6.10 ^b	1.90
	C-6	6.27	5.75	6.35	5.70	1.85
	$\Delta\delta$	0.65	-0.35	0.25	-0.40	- 0.05
50:50 H_2O - $(\text{CD}_3)_2\text{SO}$	6	5.45	6.0 ^b	6.0 ^b	6.0 ^b	1.90
	C-6	6.49	5.79	6.36	5.70	1.90
	$\Delta\delta$	1.04	-0.21	0.36	-0.30	0

^a δ in ppm relative to internal reference SiMe_4 . ^b Broad signal.

Table S2 : ^{13}C NMR Data for the Cation **6** and the Related Carbon Base **C-6** in $(\text{CD}_3)_2\text{SO}$ and a 50:50(v/v) H_2O - $(\text{CD}_3)_2\text{SO}$ Mixture ^a

Solvent	Compound	$\delta(\text{C}_\alpha)$	$\delta(\text{C}_\text{I})$	$\delta(\text{C}_{2,6})$	$\delta(\text{C}_{3,5})$	$\delta(\text{C}_4)$	$\delta(\text{C}_{\text{CP}^+})$	$\delta(\text{C}_{\text{CH}_3})$	$\text{J}(\text{C}_\alpha\text{H}_\alpha)$
$(\text{CD}_3)_2\text{SO}$	6	75.8	89.7	89.2 ^b	87.9 ^b	87.6	96.7	10.0	150.5
	C-6	99.9	104.0	80.2 ^b	86.0 ^b	83.9	94.1	9.89	182.1
	$\Delta\delta$	23.9	14.3	-9.0	-1.9	-3.7	-2.6	-0.11	31.6
50:50 H_2O - $(\text{CD}_3)_2\text{SO}$	6	76.0	89.3	88.6 ^b	87.7 ^b	87.6	97.5	9.9	150.2
	C-6	106.0	97.7	83.0 ^b	86.3 ^b	85.4	95.8	9.8	184.4
	$\Delta\delta$	30.0	8.4	-5.6	-1.4	-2.2	-1.7	-0.1	34.2

^a δ in ppm relative to internal reference SiMe_4 ; J in Hz. ^b represent tentative assignments for ortho ($\text{C}_{2,6}$) and meta ($\text{C}_{3,5}$) carbons.

Table S3 Observed First-Order Rate Constants for the Ionization of **6** by amine buffers in 50:50(v/v) H₂O Me₂SO at 25°C.

Buffer (B)	pH	[B] (mol.L ⁻¹)	[BH] (mol.L ⁻¹)	k _{obsd} (s ⁻¹)
OH ⁻		0.0005		11.80
		0.00075		12.40
		0.0010		23.00
		0.0015		54.65
		0.0020		55.90
Butylamine	9.99	0.0040	0.0040	2.46
		0.0045	0.0045	2.79
		0.0050	0.0050	2.93
		0.0100	0.0100	4.86
		0.0150	0.0150	7.61
		0.0200	0.0200	9.73
N-Methylaminoethanol	9.39	0.004	0.004	2.33
		0.005	0.005	2.88
		0.010	0.010	5.73
		0.020	0.020	8.68
		0.025	0.025	12.07
		0.030	0.030	13.50
2-Methoxyethylamine	9.11	0.004	0.004	0.37
		0.005	0.005	0.43
		0.010	0.010	0.79
		0.020	0.020	1.46
		0.025	0.025	1.88
		0.030	0.030	2.37
Allylamine	9.08	0.004	0.004	0.51
		0.005	0.005	0.62
		0.010	0.010	0.98
		0.020	0.020	1.44
		0.030	0.030	2.17
		0.040	0.040	3.01
	8.78	0.004	0.008	0.50
		0.005	0.010	0.58
		0.010	0.020	1.13
		0.020	0.040	1.42
		0.030	0.060	2.17

Buffer (B)	pH	[B] (mol.l ⁻¹)	[BH] (mol.l ⁻¹)	k _{obs} (s ⁻¹)
Glycinamide	8.31	0.008	0.004	0.18
		0.010	0.005	0.22
		0.040	0.020	0.75
		0.060	0.030	1.10
		0.080	0.040	1.43
	7.71	0.004	0.008	0.09
		0.005	0.010	0.12
		0.010	0.020	0.20
		0.020	0.040	0.37
		0.030	0.060	0.63
		0.040	0.080	0.79
Glycine ethyl ester	7.54	0.020	0.010	0.40
		0.030	0.015	0.61
		0.040	0.020	0.88
		0.050	0.025	0.96
		0.060	0.030	1.19
		0.070	0.035	1.40
	7.24	0.010	0.010	0.21
		0.015	0.015	0.30
		0.020	0.020	0.63
		0.025	0.025	0.50
		0.030	0.030	0.42
		0.035	0.035	0.70
	6.94	0.010	0.020	0.23
		0.015	0.030	0.33
		0.020	0.040	0.45
		0.030	0.060	0.69
		0.035	0.070	0.79

Table S4 Observed First-Order Rate Constants for the Ionization of **6** by carboxylic buffers in 50:50(v/v) H₂O-Me₂SO at 25°C

Buffer (BH)	pH	[B] (mol.L ⁻¹)	[BH] (mol.L ⁻¹)	k _{obsd} (s ⁻¹)
Acetic acid	6.32	0.0150	0.0050	0.090
		0.0300	0.0100	0.173
		0.0450	0.0150	0.265
		0.0600	0.0200	0.365
		0.0900	0.0300	0.56
	6.14	0.0400	0.0200	0.280
		0.0500	0.0250	0.355
		0.0600	0.0300	0.425
		0.0700	0.0350	0.510
	5.84	0.0100	0.0100	0.105
		0.0200	0.0200	0.200
		0.0250	0.0250	0.246
		0.0300	0.0300	0.305
		0.0400	0.0400	0.405
		0.0500	0.0500	0.490
	5.54	0.0100	0.0200	0.093
		0.0200	0.0400	0.18
		0.0300	0.0600	0.28
		0.0400	0.0800	0.36
		0.0500	0.1000	0.46
		0.0600	0.1200	0.55
	5.36	0.0100	0.0300	0.255
		0.0133	0.0400	0.33
		0.0167	0.0500	0.42
		0.0200	0.0600	0.51
		0.0233	0.0700	0.59

Buffer (BH)	pH	[B] (mol.L ⁻¹)	[BH] (mol.L ⁻¹)	k _{obsd} (s ⁻¹)
Methoxyacetic acid	4.95	0.0200	0.0100	0.65
		0.0400	0.0200	1.125
		0.0500	0.0250	1.625
		0.0600	0.0300	1.85
		0.0700	0.0350	1.97
		0.0800	0.0400	2.29
	4.65	0.0100	0.0100	0.603
		0.0200	0.0200	1.25
		0.0250	0.0250	0.78
		0.0300	0.0300	1.67
		0.0400	0.0400	2.27
		0.0500	0.0500	3.02
	4.35	0.0100	0.0200	1.38
		0.0200	0.0400	2.345
		0.0250	0.0500	2.58
		0.0300	0.0600	3.54
		0.0350	0.0700	3.755
		0.0400	0.0800	4.43
Formic acid	4.75	0.0100	0.0050	0.32
		0.0200	0.0100	0.51
		0.0300	0.0150	0.75
		0.0400	0.0200	1.04
		0.0500	0.0250	1.25
		0.0600	0.0300	1.49
	4.15	0.0050	0.0100	0.47
		0.0100	0.0200	0.91
		0.0150	0.0300	1.275
		0.0200	0.0400	1.74
		0.0250	0.0500	2.06
		0.0300	0.0600	2.68

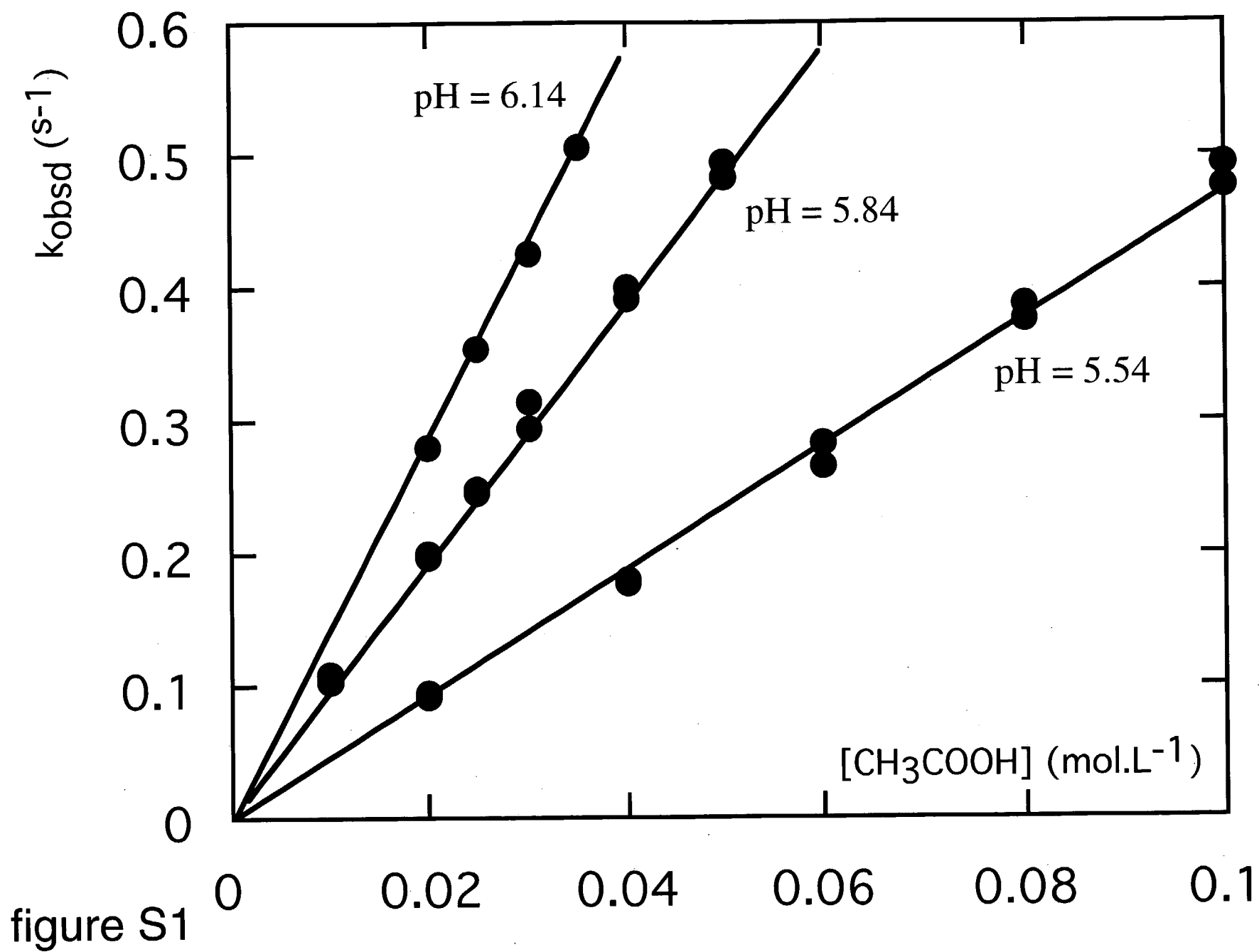
Buffer (BH)	pH	[B] (mol.L ⁻¹)	[BH] (mol.L ⁻¹)	k _{obsd} (s ⁻¹)
Chloroacetic acid	4.19	0.0090	0.0030	0.28
		0.0120	0.0040	0.48
		0.0150	0.0050	0.55
		0.0300	0.0100	1.00
		0.0450	0.0150	1.51
		0.0600	0.0200	1.98
	4.01	0.0060	0.0030	0.34
		0.0080	0.0040	0.42
		0.0100	0.0050	0.55
		0.0300	0.0150	1.38
		0.0400	0.0200	2.00
	3.71	0.0030	0.0030	0.370
		0.0040	0.0040	0.481
		0.0050	0.0050	0.572
		0.0100	0.0100	1.06
		0.0150	0.0150	1.475
		0.0200	0.0200	1.96
	3.41	0.0030	0.0060	0.630
		0.0040	0.0080	0.77
		0.0045	0.0090	0.855
		0.0050	0.0100	0.920
		0.0100	0.0200	1.68
	3.23	0.0030	0.0090	0.860
		0.0035	0.0110	0.905
		0.0040	0.0120	0.99
		0.0045	0.0140	1.10
		0.0050	0.0150	1.25
		0.0100	0.0300	2.15
H ₃ O ⁺			9.5x10 ⁻⁴	0.27
			1.05x10 ⁻³	0.28
			1.15x10 ⁻³	0.30
			1.25x10 ⁻³	0.31
			1.35x10 ⁻³	0.33
			2.43x10 ⁻³	0.41
			3.93x10 ⁻³	0.44
			4.93x10 ⁻³	0.46

Supplementary material

FIGURE CAPTIONS

Figure S1 : Effect of buffer concentration and pH on the observed rate constant, k_{obsd} , for protonation of **C-6** in acetic acid buffers in 50% H_2O / 50% Me_2SO (v/v) ; $T = 25^\circ\text{C}$; $I = 0.5 \text{ mol.L}^{-1}$.

Figure S2 : UV-VIS absorption spectra of the carbon base **C-6** and the related nitronic acid **C-6aH** in a $5 \times 10^{-2} \text{ mol.L}^{-1}$ HCl solution in 50% H_2O / 50% Me_2SO (v/v) ; $T = 25^\circ\text{C}$; $I = 0.5 \text{ mol.L}^{-1}$.



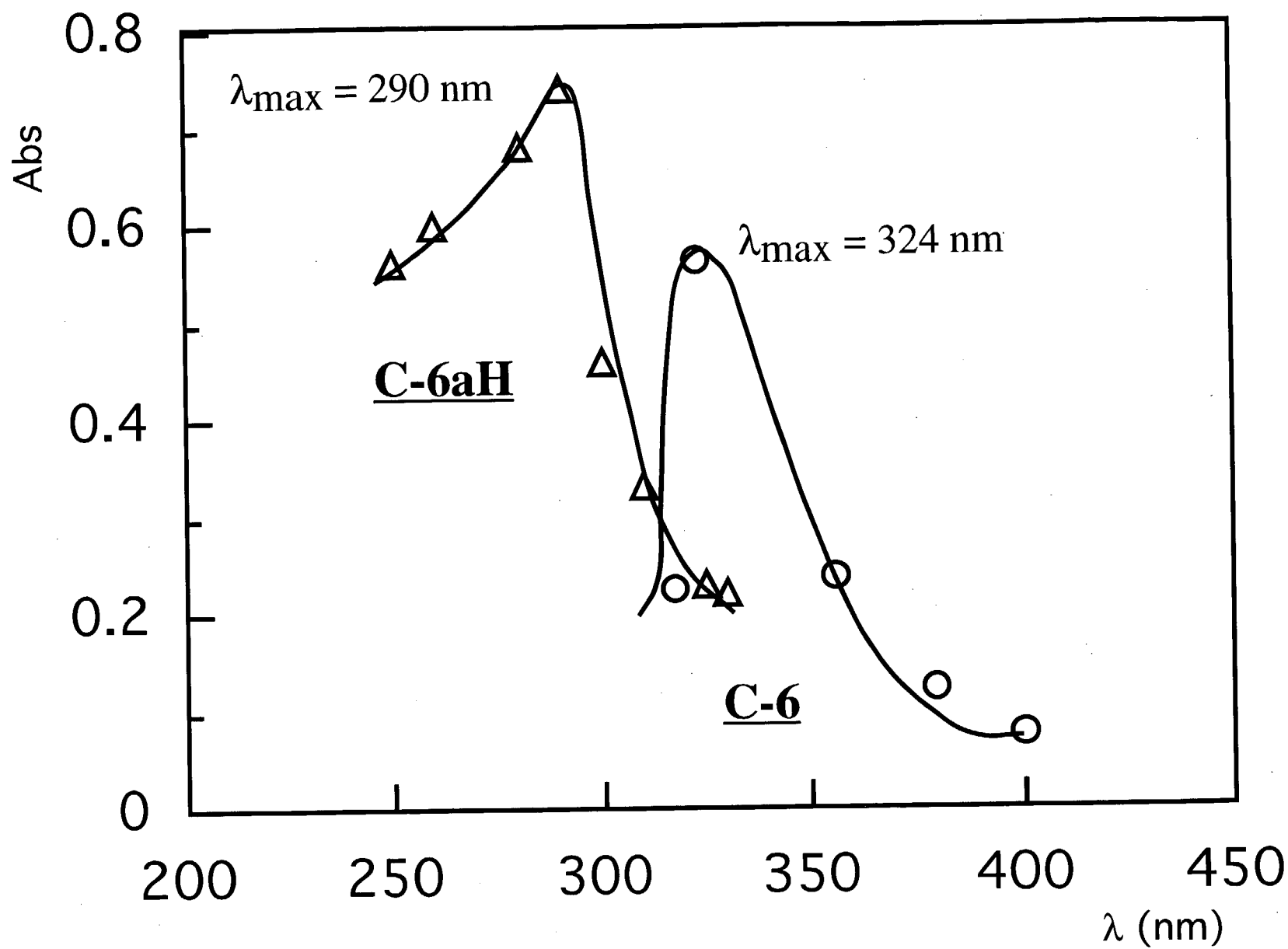


figure S2