

Solvent effect in β -phosphorylated nitroxides. Part 4: detection of traces of water by Electron Paramagnetic Resonance

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Table 1SI. a_N^a and a_P^a values of **1** and **2** in 45 solvents as well as the corresponding normalized Reichardt polarity solvent constant E_T^{Nb} .

entry	solvent ^c	E_T^N	$a_{N,1}^d$	$a_{N,2}^d$	$a_{P,2}^d$	$a_{N,4c}$	$a_{P,4c}$	$a_{N,4t}$	$a_{P,4t}$
1	pentane	0.009	15.15	- ^e	- ^e	13.67	47.75	13.58	51.80
2	<i>n</i> -hexane	0.009	15.219	14.8	40.8	13.69	47.75	13.77	51.41
3	CHex	0.006	15.19	- ^e	- ^e	13.96	47.85	13.77	51.61
4	<i>n</i> -octane	0.012	15.22	- ^e	- ^e	13.58	47.95	13.67	51.70
5	benzene	0.111	15.53	14.4	35.8	14.44	40.44	14.06	50.93
6	toluene	0.099	15.461	14.4	36.6	14.25	40.92	13.96	51.12
7	<i>t</i> -BuPh	0.099	15.47	14.4	36.6	13.86	43.33	13.86	51.22
8	PhBr	0.182	15.565	- ^e	- ^e	14.44	40.15	14.06	50.45
9	Pyridine	0.302	15.66	14.9	32	15.31	25.23	14.15	49.87
10	AcPh	0.306	15.639	- ^e	- ^e	15.11	27.82	14.15	50.26
11	<i>t</i> -BuPH/CH ₂ Cl ₂	- ^f	15.61	- ^e	- ^e	14.63	36.20	14.06	49.97
12	CH ₂ Cl ₂	0.309	15.77	- ^e	- ^e	14.73	33.89	14.15	50.26
13	DCE	0.327	15.71	- ^e	- ^e	14.73	33.89	14.15	50.26
14	CHCl ₃	0.259	15.77	- ^e	- ^e	14.83	33.79	14.25	50.83
15	CCl ₄	0.052	15.404	14.7	38.2	13.77	44.96	13.96	51.51
16	DME	0.231	15.265	- ^e	- ^e	14.92	27.83	13.96	50.55
17	Et ₂ O	0.117	15.241	- ^e	- ^e	14.73	33.31	13.96	51.22
18	<i>i</i> -Pr ₂ O	0.105	15.23	- ^e	- ^e	14.63	35.05	13.67	51.03
19	<i>n</i> -Bu ₂ O	0.071	15.36	- ^e	- ^e	14.54	33.89	13.96	50.83
20	Met-BuO	0.124	15.32	- ^e	- ^e	14.44	31.29	13.86	50.93
21	14D	0.164	15.45	- ^e	- ^e	15.02	26.96	14.15	51.03
22	THF	0.207	15.47	14.8	35.9	14.92	29.65	14.15	51.03
23	AcOEt	0.228	15.6	- ^e	- ^e	15.02	29.27	13.96	50.83
24	acetone	0.355	15.62	- ^e	- ^e	15.31	27.15	14.15	50.45
25	ACN	0.46	15.76	15	31	15.40	26.09	14.15	49.87
26	MeNO ₂	0.481	15.86	16	28.6	15.31	26.86	14.25	49.78
27	DMSO	0.444	15.77	- ^e	- ^e	15.40	24.55	14.15	50.16

28	F	0.775	16.2	- ^e	- ^e	15.69	23.11	14.63	48.14
29	NMF	0.722	- ^e	- ^e	- ^e	15.50	23.11	14.44	47.27
30	DMF	0.386	15.67	14.8	32	15.50	25.13	14.06	50.06
31	MeOH	0.762	16.2	15.7	21.9	15.40	24.07	14.53	48.43
32	EtOH	0.654	16.08	15.6	24	15.40	24.26	14.54	48.72
33	TFE	0.898	16.78	- ^e	- ^e	15.89	24.55	14.73	51.13
34	<i>i</i> -PrOH	0.546	16.04	15.2	27.6	15.21	25.03	14.35	49.58
35	<i>n</i> -BuOH	0.586	16.038	15.4	24.8	15.31	24.55	14.35	48.43
36	<i>t</i> -BuOH	0.389	15.91	- ^e	- ^e	15.31	25.61	14.25	51.41
37	BnOH	0.608	16.286	- ^e	- ^e	15.60	24.07	14.44	49.58
38	EG	0.79	16.3	- ^e	- ^e	15.60	23.49	14.54	49.29
39	TEG	0.682	-	15.5	22.9	15.11	24.26	14.35	49.10
40	water/MeOH	0.71	16.72	- ^e	- ^e	15.79	23.97	14.92	49.68
41	water	1	16.99	16.5	22.8	16.08	23.97	15.21	49.68
42	Tampon	- ^f	- ^e	- ^e	- ^e	16.08	23.97	15.21	49.78
43	AcOH	0.648	16.189	- ^e	- ^e	15.50	24.45	14.44	49.97
44	Et ₃ N	0.043	15.32	- ^e	- ^e	13.78	30.91	13.86	51.61
45	<i>i</i> -Pr ₂ NH	0.145	15.36	- ^e	- ^e	14.70	29.56	13.86	51.22
46	<i>i</i> -PenOH	0.565	15.961	- ^e	- ^e				
47	CS ₂	0.065	15.374	- ^e	- ^e				
48	Mecyc	- ^f	- ^e	14.5	39.8				
49	PhCl	0.108	15.563	- ^e	- ^e				
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^a a_N and a_P are given in G (1 G = 0.1 mT). ^b E_T^N values are given in ref. [1] unless otherwise mentioned. ^c CHex: *cyclo*-hexane, *t*-BuPh: *tert*-butylbenzene, PhBr: bromobenzene, AcPh: acetophenone, DCE: 1,2-di-chloroethane, DME: 1,2-dimethoxyethane, 14D: 1,4-dioxane, THF: tetrahydrofuran, AcOEt: ethyl acetate, ACN: acetonitrile, DMSO: dimethylsulfoxide, F: formamide, NMF: *N*-methylformamide, DMF: *N,N*-dimethylformamide, TFE: 2,2,2-trifluoroethanol, EG: ethylene glycol, TEG: triethylene glycol, AcOH: acetic acid, BnOH: benzylic alcohol. *i*-PenOH: *iso*-pentanol,

Mecyc: Methyl *cyclo*-hexane, PhCl: chlorobenzene. ^d a_N values for **1** are given in refs. [2] and [3]. a_N and a_P values for **2** are given in ref. [4] ^e Not measured. ^f Not available.

Table 2SI. % water in THF, mole fraction x_{water} , nitrogen and phosphorus hyperfine coupling constants a_{N} and a_{P} , respectively, of **4c** for different % of water.

entry	% water	x_{water}	a_{N} (G)	a_{P} (G)
1	0	0	14.94	29.56
2	0.1	0.0045	15.05	29.47
3	0.2	0.0090	15.05	29.38
4	0.3	0.0134	15.00	29.14
5	0.4	0.0178	15.06	29.06
6	0.5	0.0221	15.04	28.78
7	0.6	0.0265	15.04	28.64
8	0.7	0.0308	15.10	28.48
9	0.8	0.0350	15.04	28.30
10	0.9	0.0393	15.04	28.00
11	1	0.0435	15.14	27.82
12	2	0.0840	15.21	27.28
13	3	0.1220	15.24	26.76
14	4	0.1580	15.34	26.00
15	5	0.1920	15.34	25.82
16	10	0.3334	15.38	25.36
17	20	0.5295	15.56	24.82
18	30	0.6586	15.62	24.52
19	40	0.7501	15.68	24.4
20	50	0.8182	15.80	24.22
21	60	0.8710	15.86	24.12
22	70	0.9131	15.98	24.12
23	80	0.9474	16.16	24.12
24	90	0.9759	16.22	24.12
25	100	1	16.22	24.18

$$a_N = y_0 + \alpha_1 \cdot E_T^N$$

(1)

Table 3SI. Correlations for a_N vs E_T^N for **1**, **2**, and **4c,t** in various solvents

Eq.	Nitroxide	Slope α_1	Error ^a	y-intercept	Error ^a	R^{2b}	N^c	outliers
(1a)	1•	1.55	8	15.20	3	0.90	44	29,39 ^d
(1b)	2•	2.12	15	14.16	8	0.96	12	2,15,26
(1c)	4c•	1.35	13	14.62	7	0.77	32	1-8,15,20,44
(1d)	4t•	1.12	7	13.77	3	0.86	43	none

^a Error given on the last digit. ^b Square of the regression coefficient. ^c Number of data. ^d Not displayed in Figure 3.

$$a_p = y_0 + \alpha_2 \cdot E_T^N$$

(2)

Table 4SI. Correlations for a_p vs E_T^N for **2** and **4t** in various solvents.

eq.	nitroxide	Slope α_2	error ^a	y-intercept	error ^a	R^{2b}	N^c	outliers
(2a)	2•	-23.84	107	39.96	45	0.98	16	41
(2b)	4t•	-3.87	27	51.57	11	0.85	40	33,36,41

^a Error given on the last digit. ^b Square of the regression coefficient. ^c Number of data

References

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