Supporting Information for:

Solvent Effects on Charge Transfer Bands of Nitrogen-centered Intervalence Compounds

Stephen F. Nelsen, Dwight W. Trieber, II, Rustem F. Ismagilov, and Yoshio Teki

Table 8. Room Temperature (296-298 K) solvent parameters employed in this work[a]

Solvent	code	10^3 d*d*/d*T*[b]	ε_s	*n*	f(*n*)[c]	10^3 d*n*/dT	γ	*DN*
acetonitrile	MeCN	-1.10	35.94	1.3416	.914	-0.490	0.528	14.1
butyronitrile	PrCN	-0.909	24.83	1.3820	.902	-0.424	0.483	16.6
Me_2NCHO	DMF	-0.871	36.71	1.4282	.887	-0.460	0.463	26.6
Me_2SO	DMSO	-0.970	46.45	1.4775	.872	-0.358	0.437	29.8
benzonitrile	PhCN	-0.881	46.45	1.5257	.856	-0.460	0.390	11.9
CH_2Cl_2	CH_2Cl_2	-1.80	8.93	1.4212	.890	-0.601	0.387	0.0
acetone	Acet	-	20.56	1.3560	.910	-	0.495	17.0
nitromethane	NM	-	35.87	1.3796	.903	-	0.497	2.7

a. Data from ref. 31. b. Temperature coefficient for *d*ensity change in g mL^{-1} K^{-1} c. f(*n*) = $3n^{-1/2}/(n^2+2)$.

Note: The numbers in Tables 9 and 10 are copied from simulation program outputs, and have not been rounded to probable reproducability. For example, E° data are probably only good to 0.01 V, and E_{op} data to 100 cm^{-1}. For both voltammograms and optical spectra, simulations were superimposed on a computer screen with the experimental curves, and the parameters adjusted for best fit.

Table 9. Cyclic Voltammetry data

Compound	Solvent	$E°_1$ V	$E°_2$ V	ΔE° kcal/mol	K_{eq}[a]	fraction rad.cat.
sBI4T(ref. 6)	MeCN	-0.210	0.030	5.5	11600	0.98
aBI4T "	MeCN	-0.200	0.040	5.5	11600	0.98
sB4T (ref.7)	MeCN	-0.745	-0.410	8.0	69600	1.00
aB4T "	MeCN	-0.755	-0.410	8.0	69600	1.00
sBI6σ	MeCN	-0.212	-0.131	1.9	23.5	0.71
	PrCN	-0.128	-0.063	1.5	12.6	0.64
	DMF	-0.087	-0.018	1.6	14.7	0.66
	PhCN	-0.124	-0.057	1.5	13.7	0.65
	CH_2Cl_2	-0.111	-0.050	1.4	10.8	0.62
aBI6σ	MeCN	-0.216	-0.133	1.9	25.4	0.72
	PrCN	-0.118	-0.042	1.8	19.4	0.69
	DMF	-0.095	-0.014	1.9	23.5	0.73
	PhCN	-0.125	-0.050	1.7	18.6	0.68
	CH_2Cl_2	-0.112	-0.049	1.5	11.7	0.63

Table 9. Cyclic Voltammetry data (cont.)

Compound	Solvent	E°_1 V	E°_2 V	ΔE° kcal/mol	K_{eq}[a]	fraction rad.cat.[b]
sBP4T	MeCN	0.255	0.434	4.1	1070	0.94
	Acetone	0.375	0.513	3.2	217	0.88
	PrCN	0.330	0.470	3.4	334	0.90
	DMF	0.352	0.494	3.3	254	0.89
	CH_2Cl_2	0.348	0.513	3.8	623	0.93
sBP6σ	MeCN	0.194	0.263	1.6	14.7	0.66
	PrCN	0.269	0.313	1.0	5.7	0.54
	DMF	0.293	0.360	1.5	13.6	0.65
	DMSO	0.256	0.319	1.5	11.7	0.63
	CH_2Cl_2	0.265	0.312	1.1	6.3	0.56
aBP6σ	MeCN	0.185	0.257	1.7	16.6	0.67
	PrCN	0.270	0.316	1.1	6.0	0.55
	DMF	0.295	0.359	1.5	13.6	0.65
	DMSO	0.261	0.320	1.4	10.0	0.61
	CH_2Cl_2	0.291	0.327	0.8	4.1	0.50
$P_2$6σ	MeCN	0.422	0.492	1.6	15.3	0.66
	Acetone	0.496	0.557	1.4	10.8	0.62
	PrCN	0.494	0.555	1.4	10.8	0.62
	DMF	0.507	0.582	1.7	18.6	0.68
	CH_2Cl_2	0.506	0.562	1.3	8.9	0.60
sB6σ	MeCN	-0.807	-0.690	2.7	95.8	0.83
	DMF	-0.735	-0.623	2.6	78.8	0.82
	DMSO	-0.750	-0.637	2.6	82.0	0.82
	CH_2Cl_2	-0.702	-0.605	2.2	43.9	0.77
aB6σ	MeCN	-0.801	-0.685	2.7	92.1	0.83
	PrCN	-0.742	-0.642	2.3	49.4	0.78
	DMF	-0.728	-0.622	2.4	62.4	0.80
	DMSO	-0.749	-0.638	2.6	75.8	0.81
	CH_2Cl_2	-0.707	-0.617	2.1	33.4	0.74

a. K_{eq} is that for the conproportionation equilibrium: designating the compounds only by their charge, $[2+] + [0] \rightleftharpoons 2\cdot[1+]$, $K_{eq} = [1+]^2/[0][2+]$. b. Equilibrium fraction of cation present = $[1+]/([1+]+2[2+]) = 1/(1+2/(K_{eq})^{1/2})$.

Table 10. Variable temperature optical data

Cmpd.	Solvent	T	E_{op}	ε_{max}	$\Delta\tilde{\nu}_{1/2}$	Q	d_{ab}	$H_{ab}(n)$[a]
aBI6σ⁺	MeCN	258	21350	343	8510	0.22	5.93	647
		271	21270	228	8610	0.21		646
		284	21180	224	8710	0.20		644
		296	21090	220	8790	0.19		641
		309	20980	216	8850	0.18		637
		322	20860	212	8830	0.16		630
	PrCN	258	20940	237	8410	0.22		636
		270	20840	234	8500	0.21		635
		284	20750	230	8620	0.20		634
		296	20660	227	8700	0.19		632
		309	20540	223	8760	0.18		629
		322	20460	220	8740	0.16		623
	DMF	261	21880	203	8570	0.21		598
		270	21810	201	8620	0.20		597
		283	21710	199	8720	0.19		597
		296	21630	197	8810	0.18		596
		309	21540	194	8880	0.17		595
		322	21470	192	8950	0.16		594
	PhCN	270	20190	293	8380	0.21		658
		284	20090	289	8480	0.20		658
		296	20010	287	8560	0.19		658
		309	19930	283	8640	0.18		658
		322	19860	280	8610	0.17		653
	CH_2Cl_2	259	18250	228	7800	0.21		552
		270	18200	225	7880	0.20		552
		284	18100	221	7970	0.19		550
		296	18050	217	8050	0.18		549
		305	18020	215	8070	0.17		547
sBI6σ⁺	MeCN	261	21370	227	8560	0.22	5.93	642
		270	21290	224	8610	0.21		639
		284	21190	220	8710	0.20		637
		296	21110	216	8790	0.19		635
		310	20990	212	8780	0.17		628
		322	20880	208	8740	0.15		620
	PrCN	259	20970	229	8440	0.22		627
		270	20850	227	8520	0.21		625
		283	20750	223	8610	0.20		623
		296	20660	220	8700	0.19		622
		309	20540	217	8760	0.18		619
		322	20420	214	8730	0.16		612

Table 10. Variable temperature optical data (cont.)

Cmpd.	Solvent	T	E_{op}	ε_{max}	$\Delta\tilde{\nu}_{1/2}$	Q	d_{ab}	$H_{ab}(n)$[a]
	DMF	258	21930	203	8620	0.22		600
		270	21840	201	8720	0.21		600
		284	21750	199	8820	0.20		600
		296	21670	197	8910	0.19		599
		309	21580	194	8990	0.18		599
		322	21500	192	8960	0.16		594
	PhCN	270	20220	282	8380	0.21		645
		284	20120	278	8490	0.20		645
		296	20030	275	8560	0.19		644
		309	19940	272	8640	0.18		644
		322	19840	269	8700	0.17		642
	CH_2Cl_2	259	18300	222	7890	0.22		547
		270	18270	218	7970	0.21		547
		284	18230	215	8000	0.19		544
		296	18190	211	8080	0.18		543
		305	18170	209	8100	0.17		541
aBP6σ⁺	MeCN	257	17650	306	7710	0.22	6.04	632
		270	17610	301	7750	0.20		629
		284	17520	296	7840	0.19		627
		296	17410	291	7900	0.18		624
		309	17340	286	7890	0.16		618
		322	17270	281	7950	0.15		615
	PrCN	257	17410	291	7660	0.22		602
		270	17370	287	7700	0.20		600
		284	17280	282	7790	0.19		598
		296	17160	278	7850	0.18		596
		309	17060	274	7820	0.16		589
		322	16960	270	7870	0.15		586
	DMF	257	18090	280	7810	0.22		598
		270	18050	277	7840	0.20		597
		284	17970	274	7940	0.19		597
		296	17780	271	7980	0.18		593
		309	17620	267	7950	0.16		587
		322	17480	264	7990	0.15		584
	DMSO	296	17910	263	8010	0.18		577
		305	17770	261	8010	0.17		573
		313	17650	259	8010	0.16		570
		322	17520	257	8000	0.15		566

Table 10. Variable temperature optical data (cont.)

Cmpd.	Solvent	T	E_{op}	ε_{max}	$\Delta\tilde{\nu}_{1/2}$	Q	d_{ab}	$H_{ab}(n)$[a]
	CH_2Cl_2	260	15010	351	7160	0.22		584
		273	14940	346	7230	0.21		583
		285	14850	340	7310	0.20		581
		296	14790	335	7370	0.19		579
		306	14760	331	7390	0.18		581
sBP6σ⁺	MeCN	260	18100	301	7850	0.22	6.04	641
		270	18030	296	7840	0.20		636
		284	17960	291	7940	0.19		634
		296	17870	286	7920	0.17		628
		309	17790	282	7990	0.16		624
		322	17650	276	8030	0.15		619
	PrCN	259	17590	300	7740	0.22		619
		270	17550	297	7730	0.20		615
		284	17490	292	7830	0.19		615
		296	17380	288	7810	0.17		609
		309	17290	284	7880	0.16		607
		322	17650	276	8030	0.15		611
	DMF	261	18330	300	7920	0.22		628
		270	18280	297	7890	0.20		624
		284	18180	294	7990	0.19		624
		296	18110	290	7970	0.17		620
		309	18010	287	8040	0.16		618
		322	17890	283	8080	0.15		615
	DMSO	296	18540	263	8150	0.18		593
		305	18430	261	8160	0.17		590
		313	18340	259	8160	0.16		587
		322	18160	257	8140	0.15		587
	CH_2Cl_2	259	15440	358	7240	0.22		602
		270	15360	353	7310	0.21		600
		284	15280	346	7320	0.19		595
		296	15220	340	7390	0.18		594
		305	15180	336	7410	0.17		591
sB6σ⁺	MeCN	253	13470	307	8040	0.44	5.65	603
		268	13400	301	8010	0.40		596
		283	13290	296	7950	0.36		588
		298	13190	290	8010	0.34		583
		313	13120	285	8120	0.33		582
		329	13010	289	8220	0.32		578

Table 10. Variable temperature optical data (cont.)

Cmpd.	Solvent	T	E_{op}	ε_{max}	$\Delta\tilde{\nu}_{1/2}$	Q	d_{ab}	$H_{ab}(n)$[a]
DU^{+} [b]	MeCN	255	14260	1030	6920	0.22	4.67	1276
		270	14210	1010	7040	0.21	"	1275
		284	14160	990	7170	0.21	"	1275
		298	14110	970	7290	0.20	"	1273
		312	14050	955	7370	0.19	"	1270
		326	13990	942	7490	0.19	"	1272
BI^{+} [b]	MeCN	256	15410	2868	6000	0.06	8.52	1130
		270	15340	2877	5990	0.04	"	1131
		284	15290	2686	6040	0.03	"	1099
		298	15210	2600	6090	0.02	8.51	1085
		312	15170	2544	6130	0.01	"	1078
		326	15110	2505	6160	0.00	"	1073

a. $H_{ab}(n) = 3n^{1/2}/(n^2+2)H_{ab}$(Hush) (eq. 3a); H_{ab}(Hush) = $(0.0206/d_{ab})(E_{op}\varepsilon_{max}\Delta\nu_{1/2})^{1/2}$ (eq. 1). b. Data of ref. 4c with d_{ab} (obtained from eq. 5) and $H_{ab}(n)$ recalculated using the AM1 d_{12} values (Table 1).