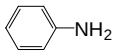
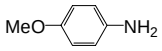
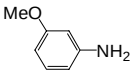
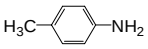
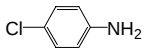
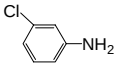
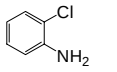
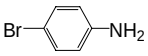
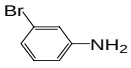
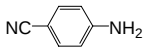
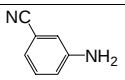
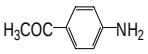
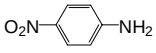
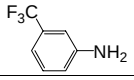
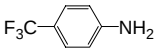
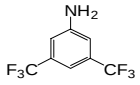
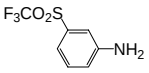
Computation of pK_a Values of Substituted Aniline Radical Cations in Dimethylsulfoxide Solution

*Ao Yu, Yuanhai Liu, Zucheng Li, Jin-Pei Cheng**

College of Chemistry, Nankai University, State Key Laboratory of Elemento-organic Chemistry, Tianjin 300071, China

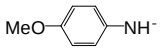
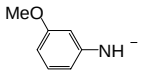
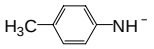
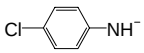
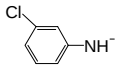
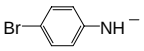
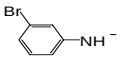
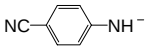
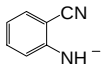
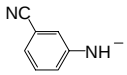
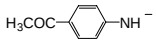
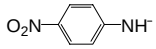
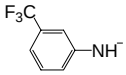
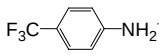
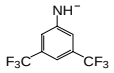
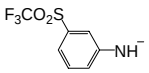
Table 1: Calculated Gas-Phase Thermodynamic Data for 18 Neutral Anilines. [a]

Compounds	E_{elec}	$G_{correct}$	$H_{correct}$	G	H
	-287.7066351	0.087918	0.123873	-287.6187171	-287.5827621
	-402.2674016	0.116643	0.159045	-402.1507586	-402.1083566
	-402.270677	0.117093	0.159122	-402.153584	-402.111555
	-327.0355324	0.112157	0.153187	-326.9233754	-326.8823454
	-747.3333249	0.076082	0.115516	-747.2572429	-747.2178089
	-747.334304	0.076178	0.115506	-747.258126	-747.218798
	-747.334785	0.076514	0.115634	-747.258271	-747.219151
	-2861.247463	0.075317	0.115722	-2861.172146	-2861.131741
	-2861.24824	0.075553	0.115758	-2861.172687	-2861.132482
	-379.9817908	0.083809	0.124271	-379.8979818	-379.8575198
	-379.9825203	0.083946	0.124288	-379.8985743	-379.8582323
	-379.9791979	0.083794	0.124241	-379.8954039	-379.8549569
	-440.409097	0.120355	0.164896	-440.288742	-440.244201
	-492.287529	0.086258	0.128904	-492.201271	-492.158625
	-624.8739408	0.085895	0.132018	-624.7880458	-624.7419228
	-624.8755497	0.085304	0.131961	-624.7902457	-624.7435887
	-962.0387316	0.082467	0.139985	-961.9562646	-961.8987466
	-1173.541032	0.091042	0.145251	-1173.44999	-1173.395781

[a] Units of Hartrees.

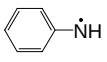
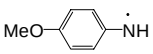
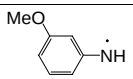
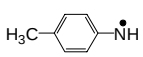
Table 2: Calculated Gas-Phase Thermodynamic Data for 18 Anilide Anions. [a]

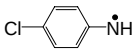
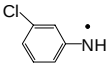
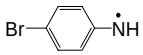
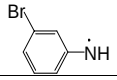
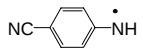
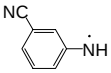
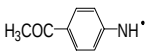
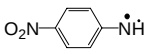
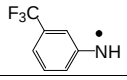
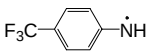
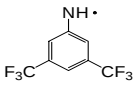
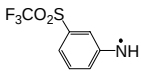
Compounds	E_{elec}	$G_{correct}$	$H_{correct}$	G	H
	-287.1085205	0.073088	0.108554	-287.0354325	-286.9999665

	-401.6648466	0.102637	0.142613	-401.5622096	-401.5222336
	-401.674008	0.102003	0.143785	-401.572005	-401.530223
	-326.4354854	0.097251	0.137613	-326.3382344	-326.2978724
	-746.745662	0.061369	0.100588	-746.684293	-746.645074
	-746.7486945	0.061483	0.100493	-746.6872115	-746.6482015
	-746.7483487	0.06206	0.100887	-746.6862887	-746.6474617
	-2860.661692	0.06092	0.100907	-2860.600772	-2860.560785
	-2860.663741	0.060921	0.100733	-2860.60282	-2860.563008
	-379.4146772	0.069946	0.109861	-379.3447312	-379.3048162
	-379.4112599	0.070113	0.109918	-379.3411469	-379.3013419
	-379.4033542	0.069431	0.109392	-379.3339232	-379.2939622
	-439.8376927	0.106164	0.150325	-439.7315287	-439.6873677
	-491.7318696	0.073122	0.114811	-491.6587476	-491.6170586
	-624.2920781	0.07122	0.116924	-624.2208581	-624.1751541
	-624.2994482	0.071144	0.116958	-624.2283042	-624.1824902
	-961.4720348	0.069256	0.125095	-961.4027788	-961.3469398
	-1172.97298	0.07652	0.130267	-1172.89646	-1172.842713

[a] Units of Hartrees

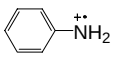
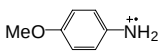
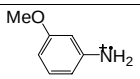
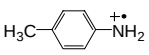
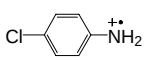
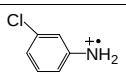
Table 3: Calculated Gas-Phase Thermodynamic Data for 18 Aniline Radicals. [a]

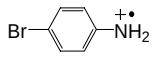
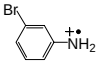
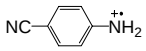
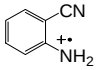
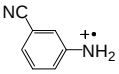
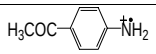
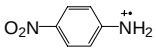
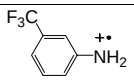
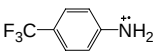
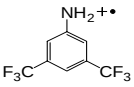
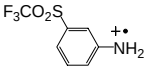
Compounds	E_{elec}	$G_{correct}$	$H_{correct}$	G	H
	-287.0520077	0.074242	0.110128	-286.9777657	-286.9418797
	-401.6194173	0.103574	0.145611	-401.5158433	-401.4738063
	-401.6168559	0.103474	0.145369	-401.5133819	-401.4714869
	-326.3833678	0.098637	0.139479	-326.2847308	-326.2438888

	-746.6794679	0.062445	0.101786	-746.6170229	-746.5776819
	-746.6778973	0.062332	0.10165	-746.6155653	-746.5762473
	-746.6789855	0.062683	0.101876	-746.6163025	-746.5771095
	-2860.593176	0.061688	0.101968	-2860.531488	-2860.491208
	-2860.591579	0.061695	0.101868	-2860.529884	-2860.489711
	-379.3230681	0.069922	0.11041	-379.2531461	-379.2126581
	-379.322805	0.070133	0.110517	-379.252672	-379.212288
	-379.3207518	0.069948	0.11039	-379.2508038	-379.2103618
	-439.7510137	0.106425	0.151072	-439.6445887	-439.5999417
	-491.6261427	0.072179	0.115032	-491.5539637	-491.5111107
	-624.2166917	0.072287	0.118198	-624.1444047	-624.0984937
	-624.2167839	0.071767	0.1182	-624.1450169	-624.0985839
	-961.3789246	0.06936	0.126160	-961.3095646	-961.2527646
	-1172.880872	0.07703	0.131335	-1172.803842	-1172.749537

[a] Units of Hartrees

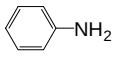
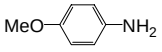
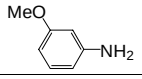
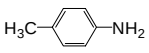
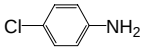
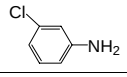
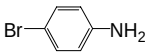
Table 4: Calculated Gas-Phase Thermodynamic Data for 18 Aniline Radical Cations. [a]

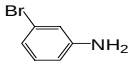
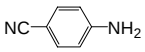
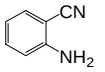
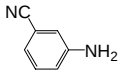
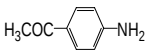
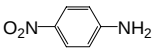
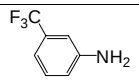
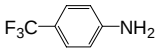
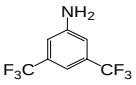
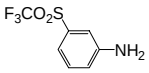
Compounds	E_{elec}	$G_{correct}$	$H_{correct}$	G	H
	-287.4300462	0.088023	0.124470	-287.3420232	-287.3055762
	-402.015843	0.117657	0.160248	-401.898186	-401.855595
	-402.0059168	0.117177	0.159670	-401.8887398	-401.8462468
	-326.7700243	0.111792	0.153713	-326.6582323	-326.6163113
	-747.0575881	0.076427	0.116249	-746.9811611	-746.9413391
	-747.0501577	0.075964	0.115810	-746.9741937	-746.9343477
	-747.0528796	0.076381	0.116049	-746.9764986	-746.9368306

	-2860.972654	0.075679	0.116416	-2860.896975	-2860.856238
	-2860.964824	0.075336	0.116029	-2860.889488	-2860.848795
	-379.6857572	0.083447	0.124547	-379.6023102	-379.5612102
	-379.6845586	0.083585	0.124520	-379.6009736	-379.5600386
	-379.6808554	0.083396	0.124457	-379.5974594	-379.5563984
	-440.1234194	0.118096	0.164958	-440.0053234	-439.9584614
	-491.9818417	0.085123	0.128879	-491.8967187	-491.8529627
	-624.5820035	0.086173	0.132466	-624.4958305	-624.4495375
	-624.5813555	0.085539	0.132492	-624.4958165	-624.4488635
	-961.7326988	0.082852	0.140407	-961.6498468	-961.5922918
	-1173.23842	0.090312	0.145481	-1173.148108	-1173.092939

[a] Units of Hartrees

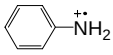
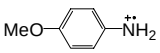
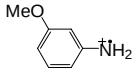
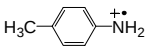
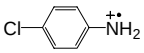
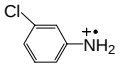
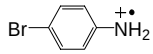
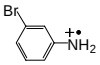
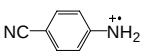
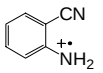
Table 5: Calculated Solvation Free Energies of 18 Anilines and Their Corresponding Anions, Radicals, Radical Cations. [a]

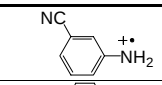
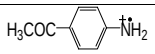
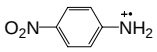
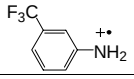
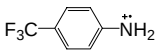
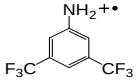
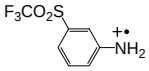
Compounds	$\Delta G^*_{solv}(HA)$	$\Delta G^*_{solv}(A^-)$	$\Delta G^*_{solv}(A^\bullet)$	$\Delta G^*_{solv}(HA^{+\bullet})$	
	f=1.10	*f*=1.10	*f*=1.10	*f*=1.10	*f*=1.025
	-2.57	-52.08	-2.79	-49.93	-55.03
	-0.88	-51.21	-1.22	-42.53	-47.52
	-1.05	-50.26	-0.71	-43.5	-52.36
	-0.14	-50.24	-0.67	-44.96	-50.07
	-3.32	-48.21	-2.39	-50	-55.65
	-3.09	-47.93	-2.37	-51.35	-57.25
	-1.93	-48.98	-1.46	-48.19	-53.43
	-3.49	-47.82	-2.56	-49.37	-55.03

	-3.26	-48.11	-2.91	-51.07	-56.95
	-7.21	-44.99	-4.55	-57.93	-65.32
	-4.24	-46.81	-3.5	-53.65	-60.26
	-5.75	-45.51	-4.62	-59.19	-67
	-5.02	-45.23	-2.24	-50.63	-57.32
	-8.36	-45.58	-4.58	-59.43	-67.01
	-1.92	-44.47	-1.1	-53.08	-59.12
	-2.53	-43.09	-1.12	-53.2	-59.41
	-0.73	-37.41	0.77	-54.48	-61.62
	-3.97	-41.45	-3.25	-56.22	-63.91

[a] Units of kcal/mol.

Table 6: Experimental and Theoretical pK_a's for Aniline Radical Cations in DMSO.

Compounds	$pK_a(\text{exp.})$	$pK_a(calc.)^a$	$pK_a(calc.)^b$	Ref.
	6.4	4.7	4.7	1
	10	8.7	8.6	1
	7.2	6.5	6.6	1
	8.5	6.9	6.8	1
	5	5.5	5.4	1
	3.4	4.2	4.0	1
	3.9	2.6	2.6	1
	5	5.3	5.4	1
	3.8	3.9	3.8	1
	2.6	4.1	4.0	1
	2.8	0.7	0.6	1

	2.1	4	4.0	1
	3.9	5.1	5.1	1
	2	2.2	2.2	1
	4.6	3.1	3.0	1
	4.7	3	2.9	1
	1.2	1.1	1.1	1
	1.9	1.8	1.6	1
me[c]	--	0.31	0.40	--
sd[d]	--	1.22	1.2	--

[a] Calculated by indirect protocol. [b] Calculated by direct protocol [c] Mean error between the experimental and theoretical data. [d] Standard deviation between the experimental and theoretical data.

$G(H_2O) = -76.459705$ Hartrees $G(OH^-) = -75.837636$ Hartrees

$\Delta G^*_{solv}(H_2O) = -4.47$ kcal/mol $\Delta G^*_{solv}(OH^-) = -77.53$ kcal/mol

Ref:

(1) Bordwell, F. G.; Zhang, X.-M.; Cheng, J. –P. *J. Org. Chem.* **1993,** *58*, 6410.