Species with negative electron affinity and standard DFT methods. Finding the valence anions.

Marcelo Puiatti, D. Mariano A. Vera and Adriana B. Pierini
INFIQC, Departamento de Química Orgánica. Facultad de Ciencias Químicas, Universidad Nacional de Córdoba

Electronic Supporting Information (ESI). Supplementary Material

Table of Contents

Part 1. Calculations Details

1.1 Gas phase calculations

TABLE S1. Gas phase calculation details: total energies and zero point energy corrections [a]

Species	E(neutral)	ZPE	Anion type	E(anion)	ZPE
Adenine	-467.3399	0.1120	*V*	-467.3100	
Chloroethylene	-538.2480	0.0428	*V*	-538.1995	
Cytosine	-395.0575	-0.0984	*V*	-395.0550	
Cytosine [b]			*V*	-395.0687	0.0944
Ethylene	-78.6192	0.0511	*V*	-78.5565	
Ethyl radical	-79.1879	0.0595	*V*	-79.1769	0.0578
Thiophene	-553.0895	0.0667	*V*	-553.0438	
Thymine	-454.3001	0.1149	*V*	-454.2890	
Uracil	-414.9689	0.0871	*V*	-414.9588	
Acetone	-193.2267	0.0838	*N*	-193.1882	
Cis-butene	-157.2778	0.1079	*N*	-157.2341	
Furan	-230.1010	0.0700	*N*	-230.0560	
Propene	-117.9509	0.0798	*N*	-117.9020	
Pyrrole	-210.2417	0.0825	*N*	-210.2060	
Trans-butene	-157.2815	0.1081	*N*	-157.2301	
Trimethylethylene	-196.6068	0.1356	*N*	-196.5657	
Guanine	-542.7286	0.1168	*N*	-542.7297	

a) All energies in Hartrees
b) Optimized geometry of the anion (for adiabatic EAs)

1.2 $\Delta E(1/\varepsilon)$ extrapolation details.

The overall free energy of the process

(S1) $A(sol) + e \rightarrow A^{\cdot -}(sol)$

can be obtained by desolvating the species, ionizing in gas phase and re-solvating:

(S2) $\Delta G = -EA + \Delta\Delta G_{solv}$

where

(S3) $\Delta\Delta G_{solv} = \Delta G_{solv}(anion) - \Delta G_{solv}(neutral)$

If the solvation energies are computed by the IEF-PCM model, they can be easily separated in their electrostatic (reaction field) and non-electrostatic (cavitation enthropic term, dispersion and repulsion van der Waals terms) contributions.[28a,36]

(S4) $\Delta\Delta G_{solv} = \Delta\Delta G_{solv;non-elect.} + \Delta\Delta G_{solv;elect}$

Thus the energy change of reaction [$A(sol) + e \rightarrow A^{\cdot -}(sol)$] can be computed including the electrostatic terms as ($-EA + \Delta\Delta G_{solv;elec.}$). In order to have the same sign as the electron affinity, ΔE can be written:

(S5) $\Delta E = EA - \Delta\Delta G_{solv;elect}$

Within the framework of continuum solvation models here used, it is clear that since the neutral and a valence anion are closely related [the latter having occupied the LUMO of the of the former, similar orbitals, identical (or slightly different) structure and so forth the same solute cavity and practically the same non-electrostatic terms], the main variation in going from one solvent to another will be in the electrostatic screening accounted by the different dielectric constants of the media (ε). Although the solvation models here used are quantum self consistent reaction field (SCRF) based on the apparent surface charges models from Tomasi's group, which are by far more accurate than a multipolar solution of the Poisson-Boltzman equation for a solute in a spherical cavity immersed in a dielectric, this oversimplification can be useful for understanding the variation of the ΔE vs $1/\varepsilon$, thus the electrostatic contribution to the solvation energy is given by the expansion:[28]

(S6) $$\Delta G_{solv;elect} = -\frac{1}{2}\frac{q}{a}\frac{\varepsilon - 1}{\varepsilon} - \frac{|\mu|^2}{a^3}\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{|\Theta|^2}{a^5}\frac{\varepsilon - 1}{3\varepsilon + 2} + \ldots$$

Where a is the radius of the cavity and q, μ,Θ, ... correspond to the charge (monopole), dipole, quadrupole, etc. The first two terms correspond to the simple Born and Onsager models respectively; all terms vanish as ε trends to 1, so $\Delta\Delta G_{solv;elec}$ also vanishes.

The whole set of calculations in solvents of decreasing ε used for obtaining the ΔE value at ε=1 is shown in detail in the following tables S2 and S3 for the "work" and the "blank" subsets, respectively. The ΔE *vs* $1/\varepsilon$ profiles obtained for all compounds informed on main text Tables 1 and 2 are shown on figs. S1, S2 and S3 (except for ethylene, trimethylethylene and furan, which are already shown on main text)

TABLE S2. $\Delta E(1/\varepsilon)$ scanning. Extrapolation details for the EA informed on main text table 1.

Species	Media	ε [a]	Anion type	*E*(neutral) /Hartree[b]	*E*(anion) /Hartree[b]	ΔE /eV
Adenine	Argon	1.43	*V*	-467.4833	-467.4773	-0.1647
	Krypton	1.52	*V*	-467.4842	-467.4811	-0.0846
	Heptane	1.92	*V*	-467.4873	-467.4941	0.1865
	Ciclohexane	2.02	*V*	-467.4880	-467.4968	0.2398
	Benzene	2.25	*V*	-467.4894	-467.5018	0.3393
	Ethyl ether	4.34	*V*	-467.4960	-467.5247	0.7807
	Chloroform	4.90	*V*	-467.4971	-467.5279	0.8373
	Chlorobenzene	5.62	*V*	-467.4980	-467.5308	0.8928
	Tetrahydrofuran	7.58	*V*	-467.4999	-467.5364	0.9927
	Dichloroethane	10.36	*V*	-467.5014	-467.5408	1.0700
	Acetone	20.70	*V*	-467.5036	-467.5469	1.1766
	Ethanol	24.55	*V*	-467.5040	-467.5479	1.1944
	Acetonitrile	36.64	*V*	-467.5049	-467.5497	1.2187
	Dimethylsulfoxide	46.70	*V*	-467.5055	-467.5504	1.2204
	Water	78.39	*V*	-467.5055	-467.5518	1.2593
Chloroethylene	Argon	1.43	*V*	-538.2488	-538.2244	-0.6625
	Krypton	1.52	*V*	-538.2489	-538.2279	-0.5718
	Heptane	1.92	*V*	-538.2494	-538.2396	-0.2653
	Ciclohexane	2.02	*V*	-538.2494	-538.2419	-0.2057
	Benzene	2.25	*V*	-538.2496	-538.2462	-0.0946
	Ethyl ether	4.34	*V*	-538.2506	-538.2650	0.3935
	Chloroform	4.90	*V*	-538.2507	-538.2674	0.4549
	Chlorobenzene	5.62	*V*	-538.2508	-538.2698	0.5151
	Tetrahydrofuran	7.58	*V*	-538.2511	-538.2740	0.6219
	Dichloroethane	10.36	*V*	-538.2513	-538.2772	0.7044
	Acetone	20.70	*V*	-538.2516	-538.2817	0.8173
	Ethanol	24.55	*V*	-538.2517	-538.2824	0.8353
	Acetonitrile	36.64	*V*	-538.2518	-538.2836	0.8669
	Dimethylsulfoxide	46.70	*V*	-538.2518	-538.2842	0.8805
	Water	78.39	*V*	-538.2519	-538.2850	0.9024
Cytosine	Argon	1.43	*V*	-395.0822	-395.0833	0.0306
Vertical EA	Krypton	1.52	*V*	-395.0833	-395.0873	0.1097
	Heptane	1.92	*V*	-395.0874	-395.1012	0.3765
	Ciclohexane	2.02	*V*	-395.0883	-395.1040	0.4282
	Benzene	2.25	*V*	-395.0900	-395.1093	0.5246
	Ethyl ether	4.34	*V*	-395.0988	-395.1335	0.9464
	Chloroform	4.90	*V*	-395.1001	-395.1368	0.9997
	Chlorobenzene	5.62	*V*	-395.1013	-395.1400	1.0515
	Tetrahydrofuran	7.58	*V*	-395.1038	-395.1458	1.1440
	Dichloroethane	10.36	*V*	-395.1058	-395.1505	1.2155
	Acetone	20.70	*V*	-395.1087	-395.1570	1.3140
	Ethanol	24.55	*V*	-395.1092	-395.1581	1.3298
	Dimethylsulfoxide	46.70	*V*	-395.1104	-395.1607	1.3689
Cytosine	Argon	1.43	*V*	-395.0822	-395.0970	0.5114
Adiabatic EA	Krypton	1.52	*V*	-395.0833	-395.1010	0.5901
	Heptane	1.92	*V*	-395.0874	-395.1148	0.8544
	Ciclohexane	2.02	*V*	-395.0883	-395.1176	0.9058
	Benzene	2.25	*V*	-395.0900	-395.1228	1.0009
	Ethyl ether	4.34	*V*	-395.0988	-395.1468	1.4157
	Chloroform	4.90	*V*	-395.1001	-395.1500	1.4675
	Chlorobenzene	5.62	*V*	-395.1013	-395.1532	1.5185
	Tetrahydrofuran	7.58	*V*	-395.1038	-395.1589	1.6084
	Dichloroethane	10.36	*V*	-395.1058	-395.1635	1.6778
	Acetone	20.70	*V*	-395.1087	-395.1699	1.7735
	Ethanol	24.55	*V*	-395.1092	-395.1710	1.7893
	Dimethylsulfoxide	46.70	*V*	-395.1104	-395.1736	1.8263

Species	Media	ε [a]	Anion type	*E*(neutral) /Hartree	*E*(anion) /Hartree	ΔE /eV
Ethylene	Argon	1.43	*V*	-78.6195	-78.5823	-1.0123
	Krypton	1.52	*V*	-78.6196	-78.5859	-0.9162
	Heptane	1.92	*V*	-78.6198	-78.5980	-0.5913
	Ciclohexane	2.02	*V*	-78.6198	-78.6004	-0.5281
	Benzene	2.25	*V*	-78.6199	-78.6048	-0.4103
	Ethyl ether	4.34	*V*	-78.6204	-78.6244	0.1088
	Chloroform	4.90	*V*	-78.6204	-78.6268	0.1740
	Chlorobenzene	5.62	*V*	-78.6205	-78.6293	0.2384
	Tetrahydrofuran	7.58	*V*	-78.6206	-78.6335	0.3520
	Dichloroethane	10.36	*V*	-78.6207	-78.6369	0.4398
	Acetone	20.70	*V*	-78.6209	-78.6414	0.5600
	Ethanol	24.55	*V*	-78.6209	-78.6422	0.5790
	Acetonitrile	36.64	*V*	-78.6209	-78.6434	0.6127
	Dimethylsulfoxide	46.70	*V*	-78.6209	-78.6440	0.6274
	Water	78.39	*V*	-78.6210	-78.6448	0.6494
Ethyl Radical	Argon	1.43	*V*	-79.1882	-79.2054	0.5081
Adiabatic EA	Krypton	1.52	*V*	-79.1882	-79.2093	0.6147
	Heptane	1.92	*V*	-79.1883	-79.2227	0.9767
	Benzene	2.25	*V*	-79.1884	-79.2303	1.1795
	Ethyl ether	4.34	*V*	-79.1886	-79.2521	1.7681
	Chloroform	4.90	*V*	-79.1886	-79.2549	1.8431
	Chlorobenzene	5.62	*V*	-79.1887	-79.2576	1.9172
	Tetrahydrofuran	7.58	*V*	-79.1887	-79.2625	2.0489
	Dichloroethane	10.36	*V*	-79.1888	-79.2663	2.1514
	Acetone	20.70	*V*	-79.1888	-79.2716	2.2932
	Ethanol	24.55	*V*	-79.1888	-79.2725	2.3159
	Acetonitrile	36.64	*V*	-79.1889	-79.2740	2.3558
	Dimethylsulfoxide	46.70	*V*	-79.1889	-79.2746	2.3731
	Water	78.39	*V*	-79.1889	-79.2756	2.4002
Thiophene	Argon	1.43	*V*	-553.0906	-553.0686	-0.5995
	Krypton	1.52	*V*	-553.0908	-553.0720	-0.5107
	Heptane	1.92	*V*	-553.0915	-553.0838	-0.2100
	Ciclohexane	2.02	*V*	-553.0916	-553.0861	-0.1514
	Benzene	2.25	*V*	-553.0919	-553.0904	-0.0420
	Ethyl ether	4.34	*V*	-553.0934	-553.1097	0.4415
	Chloroform	4.90	*V*	-553.0937	-553.1121	0.5030
	Chlorobenzene	5.62	*V*	-553.0939	-553.1146	0.5631
	Tetrahydrofuran	7.58	*V*	-553.0943	-553.1190	0.6705
	Dichloroethane	10.36	*V*	-553.0947	-553.1224	0.7536
	Acetone	20.70	*V*	-553.0952	-553.1271	0.8681
	Ethanol	24.55	*V*	-553.0953	-553.1279	0.8867
	Acetonitrile	36.64	*V*	-553.0954	-553.1292	0.9190
	Dimethylsulfoxide	46.70	*V*	-553.0955	-553.1298	0.9325
	Water	78.39	*V*	-553.0956	-553.1308	0.9559
Thymine	Argon	1.43	*V*	-454.3060	-454.3148	0.2390
	Krypton	1.52	*V*	-454.3069	-454.3184	0.3128
	Heptane	1.92	*V*	-454.3102	-454.3308	0.5621
	Ciclohexane	2.02	*V*	-454.3109	-454.3334	0.6105
	Benzene	2.25	*V*	-454.3124	-454.3381	0.6998
	Ethyl ether	4.34	*V*	-454.3194	-454.3596	1.0931
	Chloroform	4.90	*V*	-454.3206	-454.3626	1.1425
	Chlorobenzene	5.62	*V*	-454.3215	-454.3653	1.1907
	Tetrahydrofuran	7.58	*V*	-454.3235	-454.3704	1.2762
	Dichloroethane	10.36	*V*	-454.3251	-454.3745	1.3427
	Acetone	20.70	*V*	-454.3275	-454.3802	1.4335
	Ethanol	24.55	*V*	-454.3279	-454.3812	1.4488
	Dimethylsulfoxide	46.70	*V*	-454.3288	-454.3833	1.4845
	Water	78.39	*V*	-454.3295	-454.3849	1.4658

Species	Media	ε [a]	Anion type	*E*(neutral) /Hartree	*E*(anion) /Hartree	ΔE /eV
Uracil	Argon	1.43	*V*	-414.9754	-414.9863	0.2986
	Krypton	1.52	*V*	-414.9764	-414.9902	0.3765
	Heptane	1.92	*V*	-414.9800	-415.0034	0.6386
	Ciclohexane	2.02	*V*	-414.9808	-415.0061	0.6885
	Benzene	2.25	*V*	-414.9823	-415.0111	0.7820
	Ethyl ether	4.34	*V*	-414.9900	-415.0337	1.1878
	Chloroform	4.90	*V*	-414.9911	-415.0366	1.2383
	Chlorobenzene	5.62	*V*	-414.9922	-415.0395	1.2877
	Tetrahydrofuran	7.58	*V*	-414.9943	-415.0448	1.3749
	Dichloroethane	10.36	*V*	-414.9960	-415.0490	1.4420
	Acetone	20.70	*V*	-414.9984	-415.0548	1.5336
	Ethanol	24.55	*V*	-414.9988	-415.0557	1.5480
	Dimethylsulfoxide	46.70	*V*	-414.9998	-415.0581	1.5847
	Water	78.39	*V*	-415.0004	-415.0594	1.5685

a) Dielectric constant of the solvent. b) Total energy in solution including all electrostatic terms.

TABLE S3. $\Delta E(1/\varepsilon)$ scanning. Extrapolation details for the EAs informed on main text table 2.

Species	Media	ε	Anion type	*E*(neutral) /Hartree	*E*(anion) /Hartree	ΔE /eV
Acetone	Argon	1.43	*V*	-193.2283	-193.2027	-0.6960
	Krypton	1.52	*V*	-193.2285	-193.2062	-0.6075
	Heptane	1.92	*V*	-193.2294	-193.2182	-0.3039
	Ciclohexane	2.02	*V*	-193.2296	-193.2207	-0.2427
	Benzene	2.25	*V*	-193.2300	-193.2252	-0.1288
	Ethyl ether	4.34	*V*	-193.2318	-193.2461	0.3871
	Chloroform	4.90	*V*	-193.2321	-193.2489	0.4556
	Chlorobenzene	5.62	*V*	-193.2324	-193.2515	0.5206
	Tetrahydrofuran	7.58	*V*	-193.2329	-193.2565	0.6408
	Dichloroethane	10.36	*V*	-193.2333	-193.2603	0.7344
	Acetone	20.70	*V*	-193.2340	-193.2658	0.8653
	Ethanol	24.55	*V*	-193.2341	-193.2667	0.8890
	Acetonitrile	36.64	*V*	-193.2343	-193.2683	0.9263
	Dimethylsulfoxide	46.70	*V*	-193.2343	-193.2688	0.9383
	Water	78.39	*V*	-193.2345	-193.2704	0.9754
cis-butene	Argon	1.43	*N*	-157.2782	-157.2521	-0.7108
	Krypton	1.52	*N*	-157.2783	-157.2546	-0.6445
	Heptane	1.92	*N*	-157.2785	-157.2631	-0.4194
	Ciclohexane	2.02	*N*	-157.2786	-157.2648	-0.3756
	Benzene	2.25	*N*	-157.2787	-157.2679	-0.2937
	Ethyl ether	4.34	*V*	-157.2792	-157.2610	-0.4940
	Chloroform	4.90	*V*	-157.2793	-157.2634	-0.4307
	Chlorobenzene	5.62	*V*	-157.2793	-157.2658	-0.3692
	Tetrahydrofuran	7.58	*V*	-157.2795	-157.2700	-0.2581
	Dichloroethane	10.36	*V*	-157.2796	-157.2733	-0.1717
	Acetone	20.70	*V*	-157.2798	-157.2779	-0.0518
	Ethanol	24.55	*V*	-157.2798	-157.2787	-0.0322
	Acetonitrile	36.64	*V*	-157.2799	-157.2800	0.0018
	Dimethylsulfoxide	46.70	*V*	-157.2799	-157.2815	0.0438
	Water	78.39	*V*	-157.2800	-157.2815	0.0422
Furan	Argon	1.43	*V*	-230.1023	-230.0630	-1.0699
	Krypton	1.52	*V*	-230.1026	-230.0664	-0.9829
	Heptane	1.92	*V*	-230.1033	-230.0781	-0.6869
	Ciclohexane	2.02	*V*	-230.1035	-230.0804	-0.6290
	Benzene	2.25	*V*	-230.1038	-230.0847	-0.5208
	Ethyl ether	4.34	*V*	-230.1055	-230.1041	-0.0386
	Chloroform	4.90	*V*	-230.1058	-230.1066	0.0229
	Chlorobenzene	5.62	*V*	-230.1060	-230.1091	0.0834
	Tetrahydrofuran	7.58	*V*	-230.1065	-230.1135	0.1911
	Dichloroethane	10.36	*V*	-230.1069	-230.1170	0.2749
	Acetone	20.70	*V*	-230.1074	-230.1218	0.3903
	Ethanol	24.55	*V*	-230.1075	-230.1225	0.4087
	Acetonitrile	36.64	*V*	-230.1077	-230.1239	0.4412
	Dimethylsulfoxide	46.70	*V*	-230.1078	-230.1245	0.4553
	Water	78.39	*V*	-230.1079	-230.1255	0.4785
Propene	Argon	1.43	*V*	-117.9512	-117.9076	-1.1877
	Krypton	1.52	*V*	-117.9513	-117.9109	-1.0997
	Heptane	1.92	*V*	-117.9515	-117.9222	-0.7994
	Ciclohexane	2.02	*V*	-117.9516	-117.9244	-0.7405
	Benzene	2.25	*V*	-117.9517	-117.9285	-0.6302
	Ethyl ether	4.34	*V*	-117.9522	-117.9472	-0.1365
	Chloroform	4.90	*V*	-117.9523	-117.9496	-0.0733
	Chlorobenzene	5.62	*V*	-117.9523	-117.9519	-0.0112
	Tetrahydrofuran	7.58	*V*	-117.9525	-117.9561	0.0996
	Dichloroethane	10.36	*V*	-117.9526	-117.9594	0.1858
	Acetone	20.70	*V*	-117.9528	-117.9640	0.3049
	Ethanol	24.55	*V*	-117.9528	-117.9647	0.3241
	Acetonitrile	36.64	*V*	-117.9528	-117.9660	0.3576
	Dimethylsulfoxide	46.70	*V*	-117.9529	-117.9665	0.3715
	Water	78.39	*V*	-117.9529	-117.9674	0.3953

Species	Media	ε [a]	Anion type	*E*(neutral) /Hartree	*E*(anion) /Hartree	ΔE /eV
Pyrrole	Argon	1.43	*N*	-210.2441	-210.22	-0.57790
	Kripton	1.52	*N*	-210.2445	-210.23	-0.52347
	Ciclohexane	2.02	*N*	-210.2462	-210.24	-0.30399
	Benzene	2.25	*N*	-210.2468	-210.24	-0.23776
	Ether	4.34	*V*	-210.2500	-210.23	-0.58594
	Chloroform	4.90	*V*	-210.2505	-210.23	-0.52880
	Chlorobenzene	5.62	*V*	-210.2509	-210.23	-0.47169
	Tetrahydrofuran	7.58	*V*	-210.2518	-210.24	-0.37051
	Dichloroethane	10.36	*V*	-210.2526	-210.24	-0.29132
	Acetone	20.70	*V*	-210.2537	-210.25	-0.15927
	Dimethylsulfoxide	46.70	*V*	-210.2543	-210.25	-0.11914
	Water	78.39	*V*	-210.2546	-210.25	-0.09799
Trans-butene	Argon	1.43	*N*	-157.2818	-157.2477	-0.9298
	Krypton	1.52	*N*	-157.2819	-157.2501	-0.8650
	Heptane	1.92	*V*	-157.2821	-157.2410	-1.1195
	Ciclohexane	2.02	*V*	-157.2822	-157.2430	-1.0645
	Benzene	2.25	*V*	-157.2823	-157.2469	-0.9616
	Ethyl ether	4.34	*V*	-157.2828	-157.2644	-0.4983
	Chloroform	4.90	*V*	-157.2828	-157.2667	-0.4379
	Chlorobenzene	5.62	*V*	-157.2829	-157.2690	-0.3793
	Tetrahydrofuran	7.58	*V*	-157.2831	-157.2730	-0.2730
	Dichloroethane	10.36	*V*	-157.2832	-157.2762	-0.1900
	Acetone	20.70	*V*	-157.2834	-157.2806	-0.0747
	Ethanol	24.55	*V*	-157.2834	-157.2813	-0.0557
	Acetonitrile	36.64	*V*	-157.2834	-157.2826	-0.0226
	Dimethylsulfoxide	46.70	*V*	-157.2835	-157.2831	-0.0097
	Water	78.39	*V*	-157.2835	-157.2841	0.0163
Trimethylethylene	Argon	1.43	*N*	-196.6070	-196.5827	-0.6620
	Krypton	1.52	*N*	-196.6071	-196.5851	-0.5989
	Heptane	1.92	*N*	-196.6072	-196.5931	-0.3846
	Ciclohexane	2.02	*N*	-196.6073	-196.5947	-0.3429
	Benzene	2.25	*N*	-196.6073	-196.5976	-0.2649
	Ethyl ether	4.34	*N*	-196.6077	-196.6112	0.0956
	Chloroform	4.90	*N*	-196.6078	-196.6131	0.1451
	Chlorobenzene	5.62	*V*	-196.6078	-196.5984	-0.2558
	Tetrahydrofuran	7.58	*V*	-196.6079	-196.6022	-0.1574
	Dichloroethane	10.36	*V*	-196.6080	-196.6051	-0.0796
	Acetone	20.70	*V*	-196.6082	-196.6093	0.0297
	Ethanol	24.55	*V*	-196.6082	-196.6100	0.0482
	Acetonitrile	36.64	*V*	-196.6082	-196.6112	0.0797
	Dimethylsulfoxide	46.70	*V*	-196.6083	-196.6117	0.0927
	Water	78.39	*V*	-196.6083	-196.6126	0.1166
Guanine	Ciclohexane	2.02	*N*	-542.7610	-542.7620	0.0281
	Benzene	2.25	*V*	-542.7634	-542.7620	-0.0373
	Ethyl ether	4.34	*V*	-542.7752	-542.7925	0.4718
	Chloroform	4.90	*V*	-542.7772	-542.7968	0.5324
	Chlorobenzene	5.62	*V*	-542.7787	-542.8009	0.6040
	Tetrahydrofuran	7.58	*V*	-542.7823	-542.8086	0.7161
	Dichloroethane	10.36	*V*	-542.7851	-542.8148	0.8079
	Acetone	20.70	*V*	-542.7891	-542.8235	0.9354
	Ethanol	24.55	*V*	-542.7898	-542.8250	0.9576
	Acetonitrile	36.64	*V*	-542.7910	-542.8275	0.9948
	Dimethylsulfoxide	46.70	*V*	-542.7915	-542.8286	1.0093
	Water	78.39	*V*	-542.7934	-542.8308	1.0165

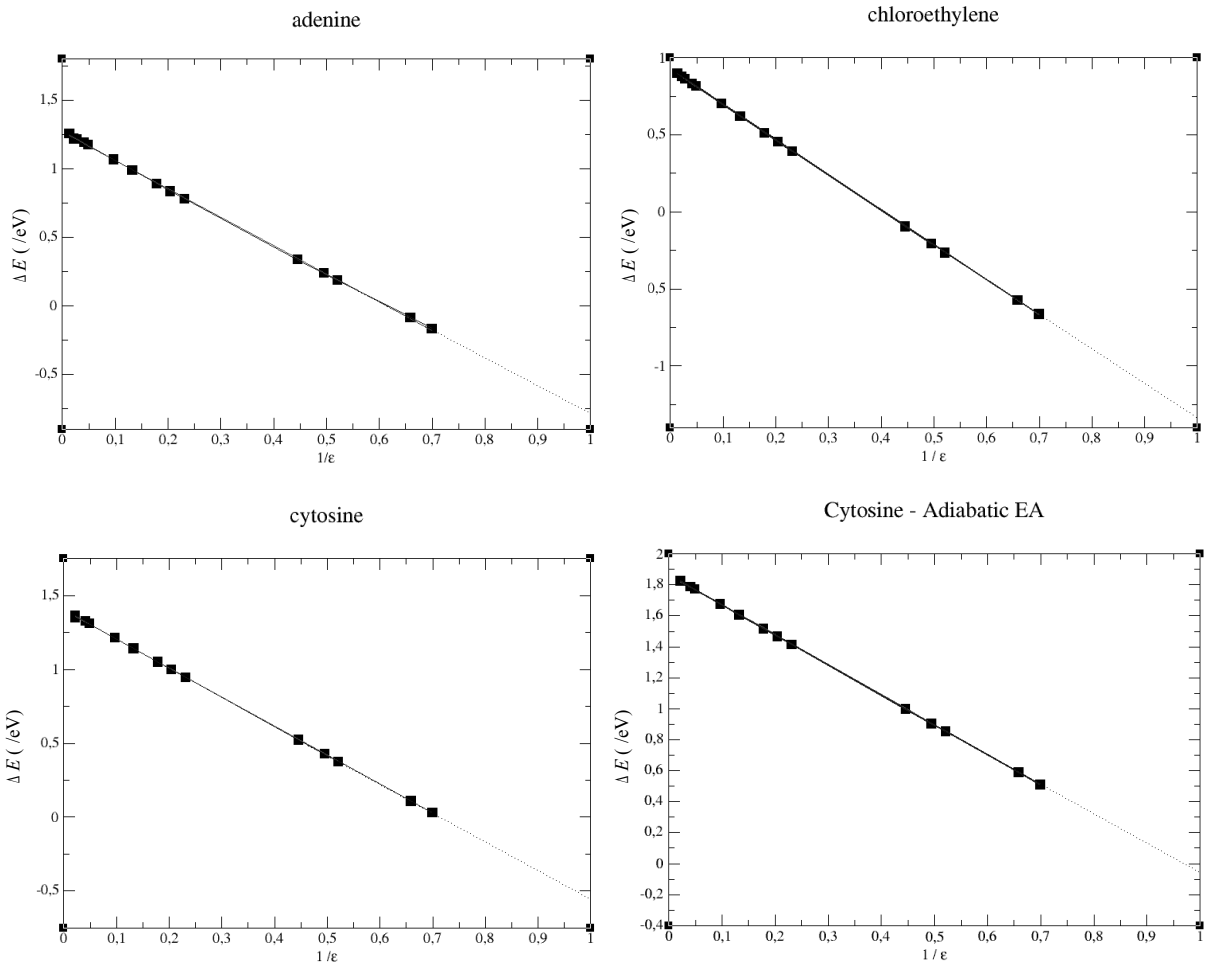

Figure S1: $\Delta E(1/\varepsilon)$ profiles obtained for adenine, chloroethylene and cytosine

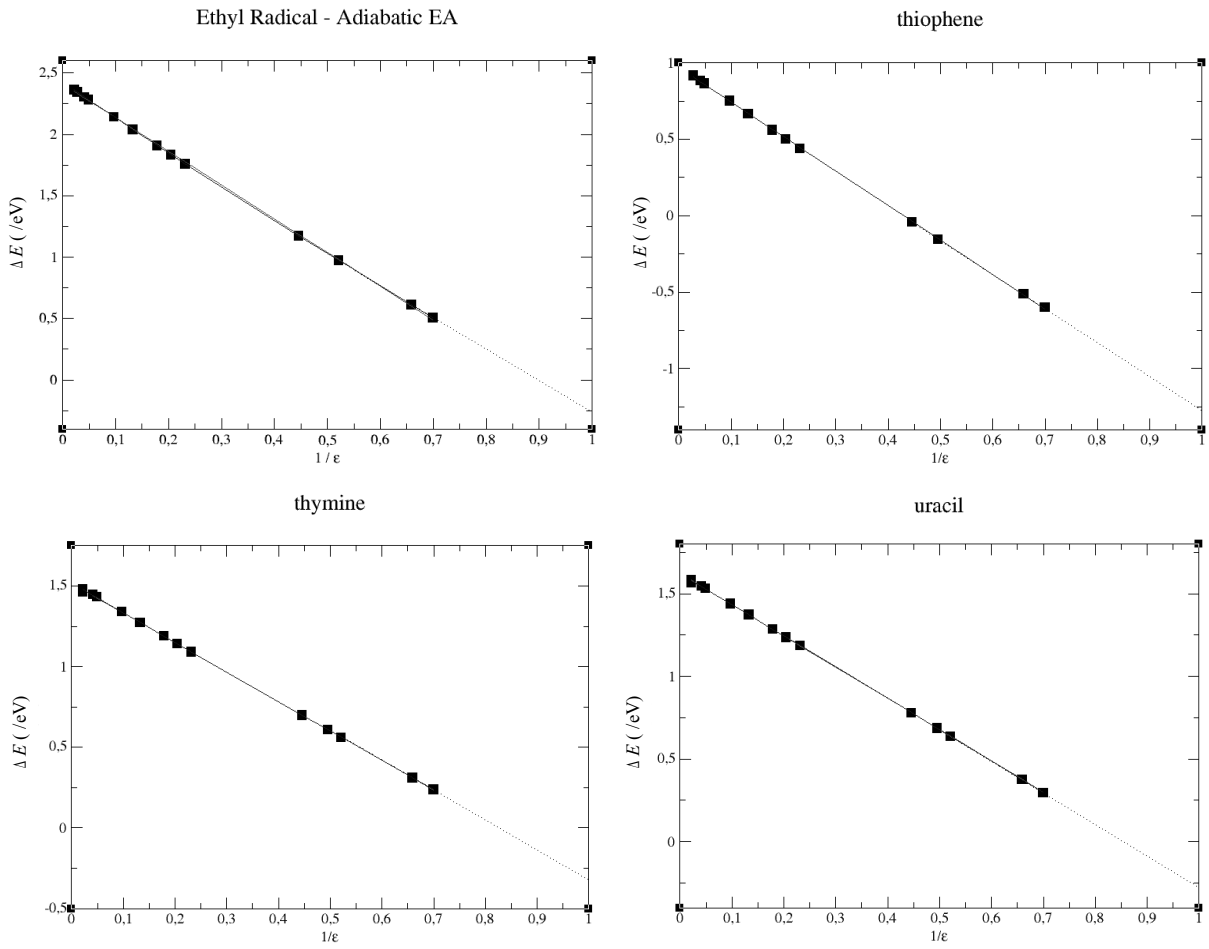

Figure S2: $\Delta E(1/\varepsilon)$ profiles obtained for ethyl radical, thiophene, thymine and uracil

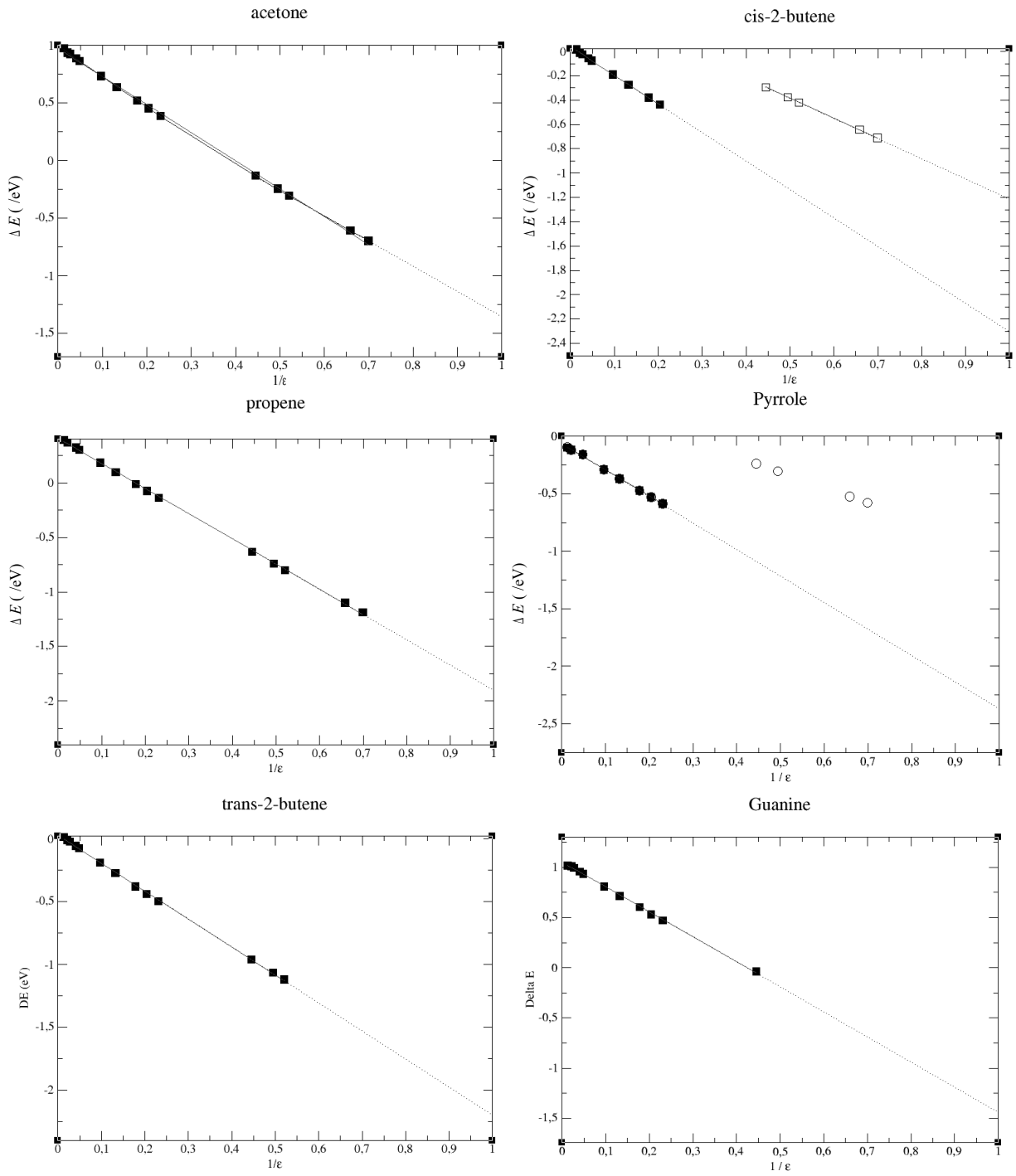

Figure S3: $\Delta E(1/\varepsilon)$ profiles obtained for acetone, *cis*-2-butene, propene, pyrrole, *trans*-2-butene and guanine.

Part 2. Alternative extrapolations and basis sets

According to the comparison with the EA values obtained directly by using eq. 1 and extrapolated values obtained by means of the linear and quadratic fit, it was concluded that the simple linear fit used in this communication only introduces an slight offset. Work is in progress in order to enhance the extrapolation technique, using a more complete set of experimental values and solvation models. Alternative extrapolations on the "blank" subset are given in the next table

TABLE S4 Experimental and calculated EA for compounds which has gas phase valence anion states ("blank" subset). [a] Different Extrapolations of ΔE vs $1/\varepsilon$

species	EA Experimental [b]	anion type	EA eq. 1 [b]	EA corrected eq. 3 Linear regression	EA corrected eq.3 Quadratic regression
Adenine	-0.64	*V*	-0.74	-0.80	-0.74
Chloroethylene	-1.29	*V*	-1.32	-1.36	-1.31
Cytosine	-0.36	*V*	-0.55	-0.56	-0.55
	-0.06[c]	*V*	-0.068[c]	-0.074[c]	-0.058[c]
Ethylene	-1.78	*V*	-1.71	-1.75	-1.70
Ethyl Radical[c]	-0.26[c]	*V*	-0.25[c]	-0.33[c]	-0.23[c]
Thiophene	-1.17	*V*	-1.24	-1.29	-1.23
Thymine	-0.31	*V*	-0.30	-0.31	-0.30
Uracil	-0.21	*V*	-0.27	-0.27	-0.21

a) B3LYP/6-311+G(2df,p), all EAs in eV. b) Experimental values and calculated EAs using eq 1 from ref. 1. c) Adiabatic EA.

As well as in ref. 1, a smaller basis set, 6-31+G* has been found to be similar results, with an small offset of about 0.2 eV respect to the triple zeta one. The results with the smaller basis are given in Tables S5 and S6 for the blank and work subsets respectively (same as tables 1 and 2 on the main text)

TABLE S5. Experimental and calculated EA for compounds which has gas phase valence anion states ("blank" subset). 6-31+G* basis set. [a]

species	Gas phase anion type	EA calc (eq. 1)[b]	EA corrected Linear regression (eq. 3)	EA Experimental[b]
Adenine	V	-0.85	-0.89	-0.64
Chloroethylene	V	-1.42	-1.45	-1.29
Cytosine	V	-0.63	-0.65	-0.36
		-0.032[c]	-0.057 [c]	-0.06 [c]
Ethylene	V	-1.78	-1.82	-1.78
Ethyl Radical [c]	V	-0.32 [c]	-0.41[c]	-0.26 [c]
Thiophene	V	-1.32	-1.37	-1.17
Thymine	V	-0.37	-0.38	-0.31
Uracil	V	-0.35	-0.35	-0.21

a) All energies in eV. b) Calculated in referenced 1, experimental values taken from bibliography in ref. 1. c) Adiabatic Electron Affinities.

TABLE S3. Experimental and calculated EA for compounds which has gas phase non valence states ("work" subset). 6-31+G* basis set. [a]

species	Gas phase anion type	EA calc (eq. 1)[b]	EA corrected (eq. 3) Linear regression	EA Experimental[b]
Acetone	*N*	-1.26	-1.56	-1.51
cis-Butene	*N*	-1.45	-2.39	-2.22
Furan	*N*	-1.41	-1.82	-1.76
Propene	*N*	-1.61	-1.99	-1.99
Pyrrole	*N*	-1.10	-2.42	-2.38
trans-Butene	*N*	-1.48	-2.28	-2.10
Trimethylethylene	*N*	-1.12	-2.11	-2.24
Guanine[c]	*N*	-0.40	-1.63	

a) All energies in eV. b) Calculated in ref. 1, experimental values taken from bibliography in ref. 1.

Part 3. Additional molecular graphics plots

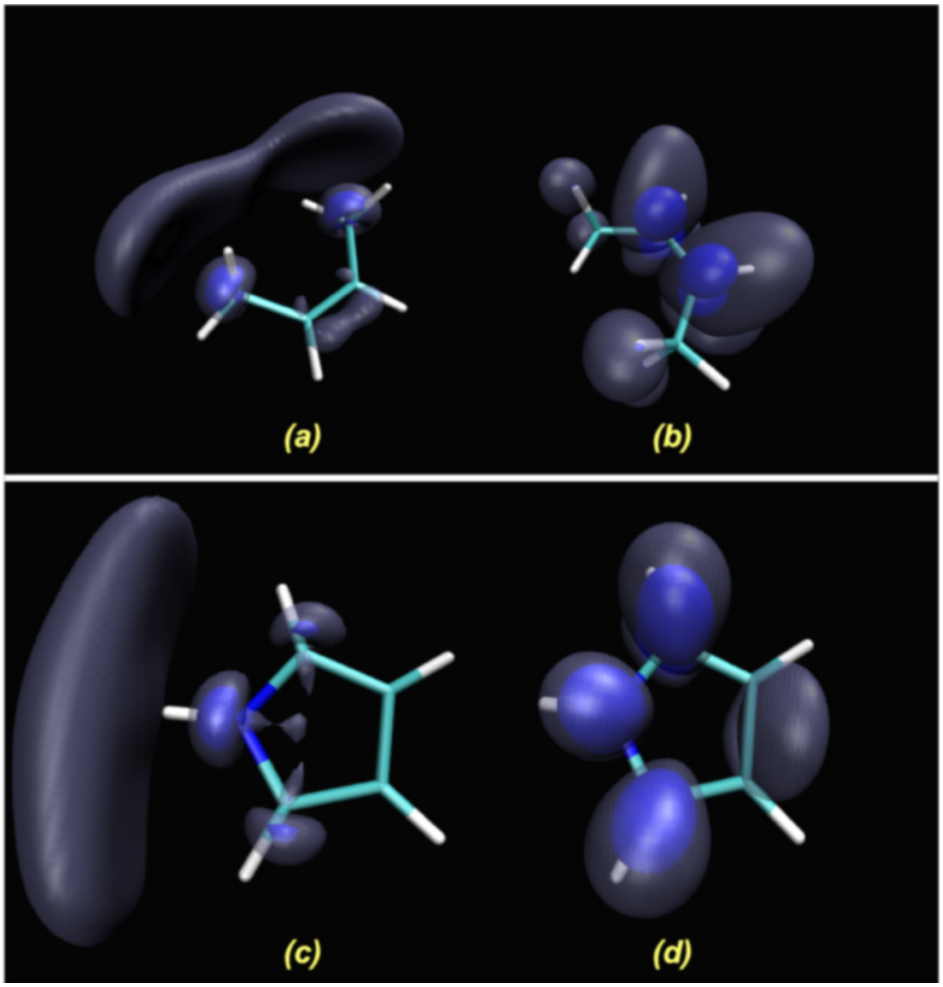

Figure S4: Spin density plots (as in main text Figure 1) obtained for the cis-butene RA in gas phase (a) and in acetonitrile (b) and for the pyrrole RA in gas phase (c) and in chlorobenzene (d).