How Does Excited-State Antiaromaticity Affect the Acidity Strengths of Photoacids?

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1. Ground state NICS(1)$_{zz}$ values for aromatic acids and their conjugate bases

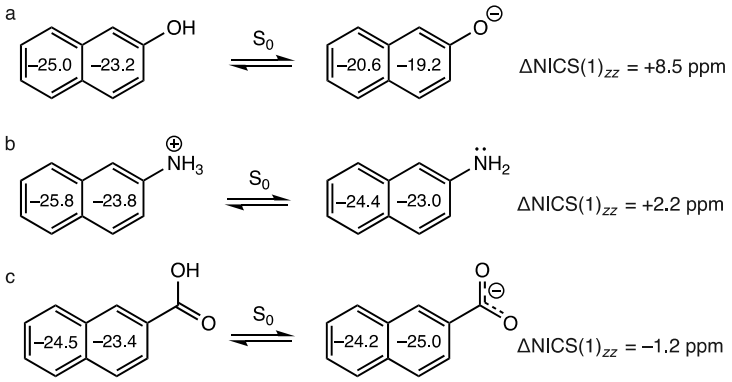


Figure S1. Computed NICS(1)$_{zz}$ and ΔNICS(1)$_{zz}$ (sum of NICS(1)$_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_0 states of the acid and conjugated base at CASSCF(12,12)/6-311+G(d,p), for a) 2-naphthol, b) 2-naphthylammonium, and c) 2-naphthoic acid. Negative ΔNICS(1)$_{zz}$ values indicate aromaticity gain, and positive values indicate aromaticity loss, upon formation of the conjugate base.

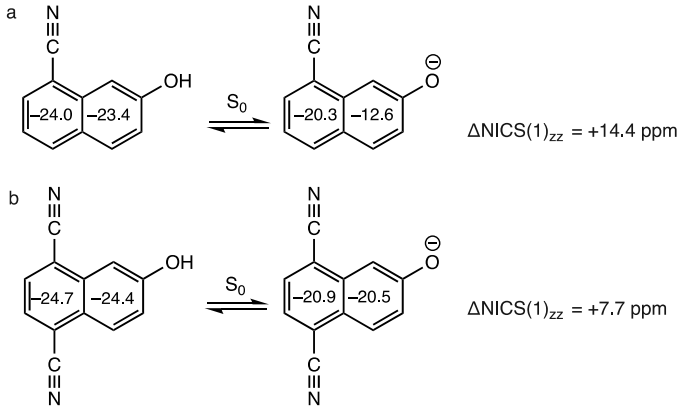
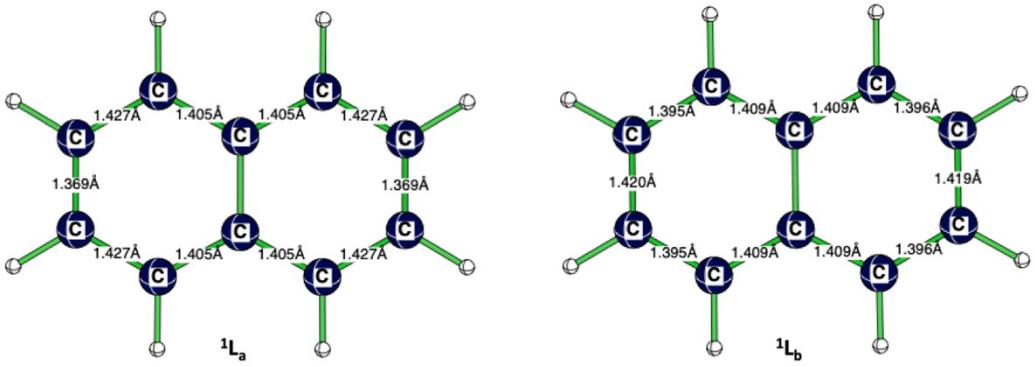


Figure S2. Computed NICS(1)$_{zz}$ and ΔNICS(1)$_{zz}$ (sum of NICS(1)$_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_0 states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 8-cyano-2-naphthol and b) 5,8-dicyano-2-naphthol. Positive ΔNICS(1)$_{zz}$ values indicate aromaticity loss upon formation of the conjugate base.

2. Harmonic Oscillator Model of Electron Delocalization (HOMED) analyses for the ^1L_a and ^1L_b states of naphthalene



HOMED = 0.936 **HOMED = 0.973**

Figure S3. Optimized geometries and computed HOMED values for naphthalene (constrained C_{2v} symmetry) in the ^1L_a (B_{2u}) and ^1L_b (B_{3u}) states, at TD-ωB97X-D/6-311+G(d,p). The smaller HOMED value for the ^1L_a state suggests greater excited-state antiaromatic character compared to the ^1L_b state.

HOMED is a geometric criterion for quantifying the aromaticity of cyclic compounds. The HOMED values are calculated according to the equation bellow.

$$HOMED = 1 - \frac{\alpha}{n}\sum\left[R_o - R_i\right]^2$$

Where n is the number of bonds and $\alpha = 2\left\{\left(R_o - R_s\right)^2 + \left(R_o - R_d\right)^2\right\}^{-1}$.

R_s (single bond length), R_d (double bond length), and R_0 (optimal bond length) are the CC bond lengths of the reference compounds based on the optimized geometries at ωB97XD/6-311+G(d,p). The reference compounds for R_s, R_d, and R_0 are ethane, ethene, and benzene, respectively. Larger HOMED values indicate more bond length equalization (cf. HOMED of benzene at the S_0 state is 1.000).

Raczyńska, E. D., Hallman, M., Kolczyńska, K., Stępniewski, T. M. *Symmetry*, 2010, **2**, 1485–1509.

3. Relevant bond lengths for acids and conjugate bases in the S_1 state

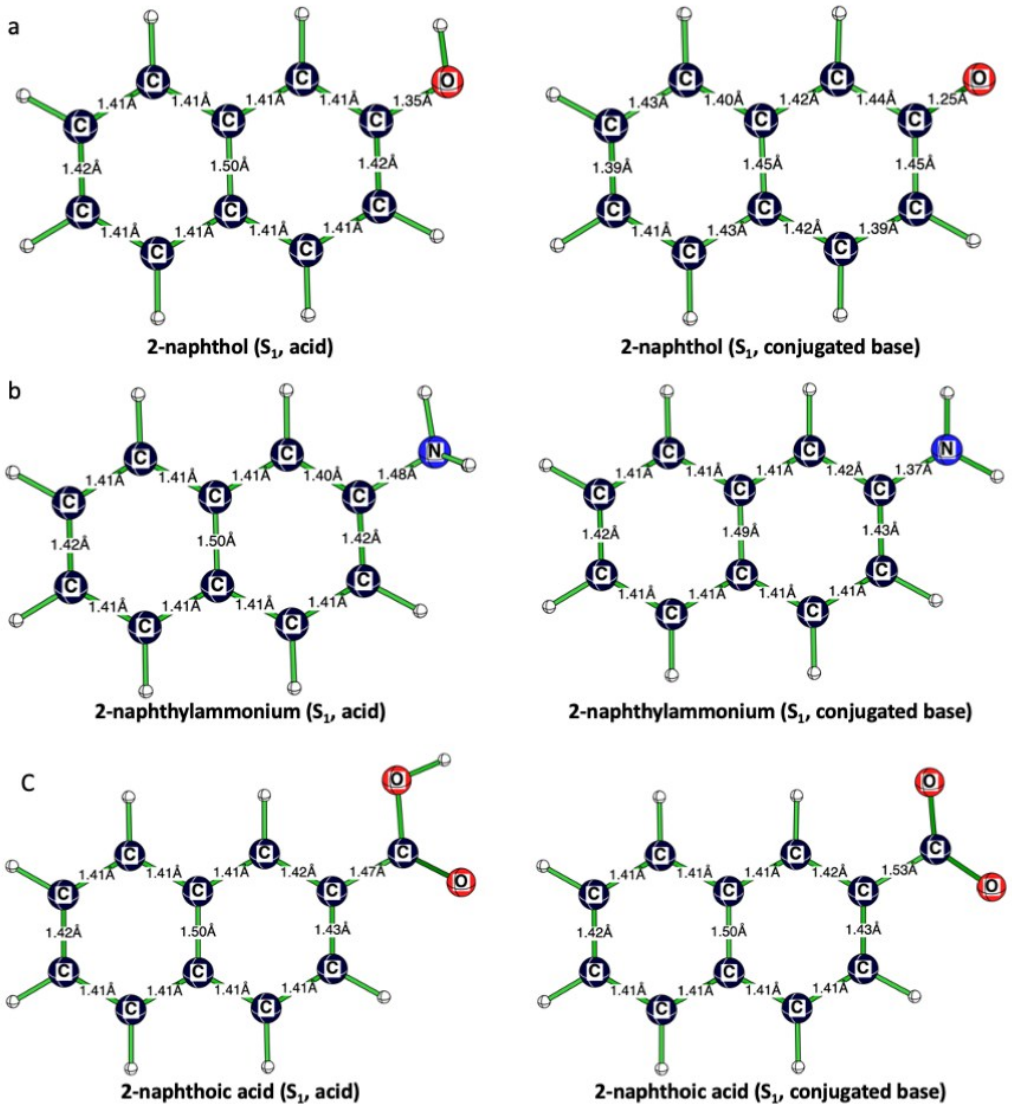


Figure S4. Optimized geometries of the acids and conjugate bases of a) 2-naphthol, b) 2-naphthylammonium, and c) 2-naphthoic acid at CASSCF/6-311+G(d,p) in the S_1 state.

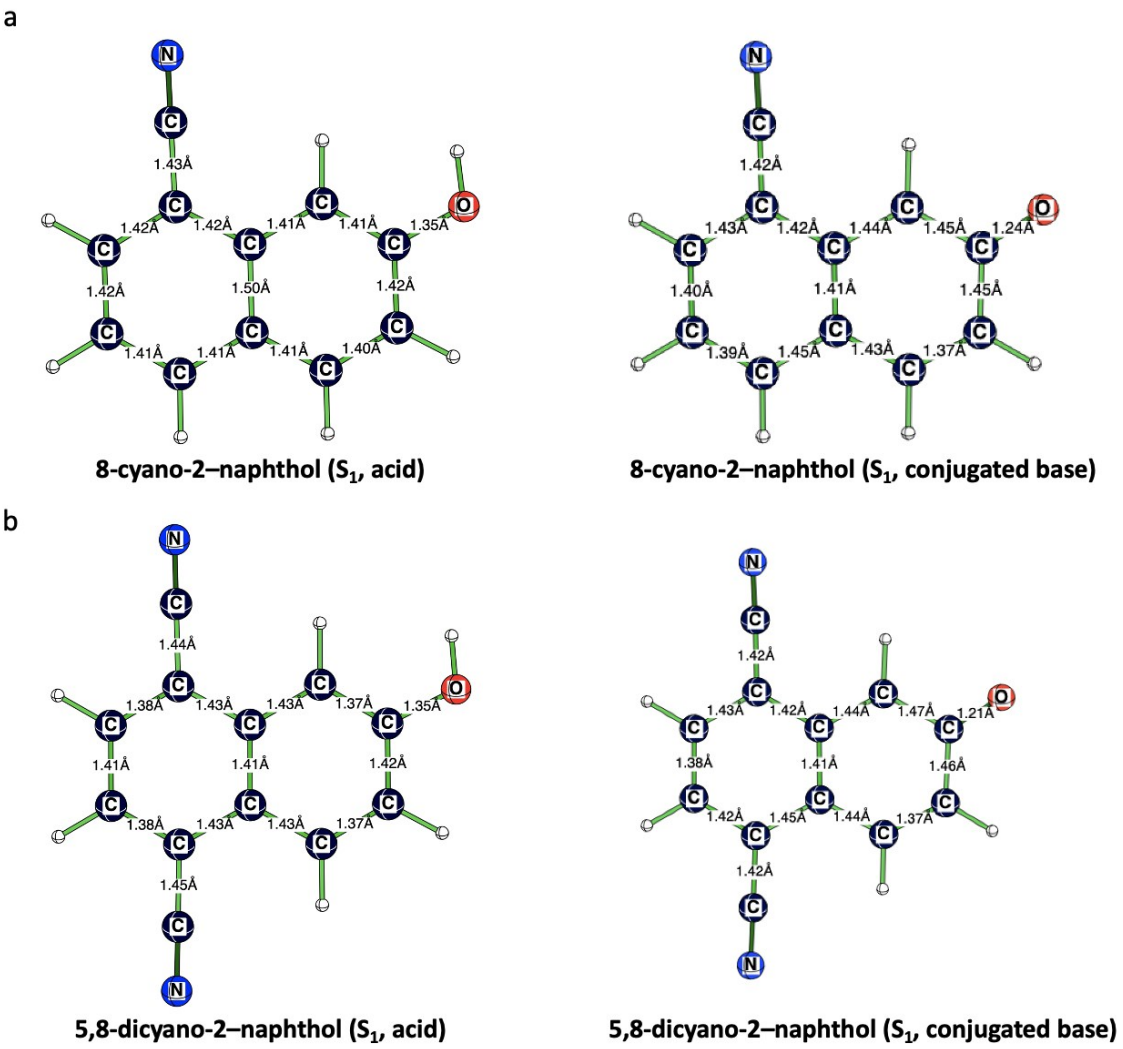


Figure S5. Optimized geometries of the acids and conjugate bases of a) 8-cyano-2-naphthol and b) 5,8-dicyano-2-naphthol at CASSCF/6-311+G(d,p) in the S_1 state.

4. Reaction energies of deprotonation reactions

Table S1. Computed deprotonation energies (ΔE, in kcal/mol) the reaction: ArOH + H_2O → ArO^- + H_3O^+. Energies were computed at CASSCF(12,12)/6-311+G(d,p), with all active orbitals and electrons of the acid (ArOH) and conjugated base (ArO^-). The geometries and energies of H_2O and H_3O^+ were computed at RHF/6-311+G(d,p). Since symmetry constraint was enforced in the CASSCF computations, no zero-point energy corrections are included to the ΔE values. $\Delta\Delta E = \Delta E(S_1) - \Delta E(S_0)$. Negative $\Delta\Delta E$ values indicate decreased endothermicity. Positive $\Delta\Delta E$ values indicate increased endothermicity.

ArOH	$\Delta E(S_0)$	$\Delta E(S_1)$	$\Delta\Delta E$
2-naphthol	181.25	163.26	–17.99
2-naphthylammonium	57.19	54.42	–2.77
2-naphthoic acid	181.94	183.33	+1.39
8-cyano-2-naphthol	182.87	154.02	–28.85
5,8-cyano-2-naphthol	173.87	144.59	–29.28

5. Full reference for the Dalton2016 program

K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansik, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawlowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski, and H. Ågren, *WIREs Comput. Mol. Sci.*, 2014, **4**, 269–284.

6. Optimized Cartesian coordinates for all structures in C_s symmetry at CASSCF/6-311+G(d,p)

2-naphthol (S_0, acid)

	X	Y	Z
O	3.64539	0.59330	0.00000
C	2.42669	0.00000	0.00000
C	2.42860	–1.42152	0.00000
C	1.24344	–2.10428	0.00000
C	–0.00661	–1.41329	0.00000
C	–1.25087	–2.10268	0.00000
C	–2.43786	–1.41105	0.00000
C	–2.43176	0.00672	0.00000
C	–1.24221	0.69441	0.00000
C	0.00000	0.00000	0.00000
C	1.24818	0.69440	0.00000
H	1.24478	–3.18004	0.00000
H	–3.37360	–1.94077	0.00000
H	–1.24977	–3.17882	0.00000
H	–1.23935	1.77058	0.00000
H	–3.36381	0.54327	0.00000
H	3.37308	–1.93338	0.00000
H	1.24878	1.77197	0.00000
H	3.56466	1.53043	0.00000

CASSCF Energy = –458.44533594 a.u.

2-naphthol (S_0, conjugate base)

	X	Y	Z
O	3.60529	0.56048	0.00000
C	2.48445	0.00000	0.00000
C	2.38580	–1.45854	0.00000
C	1.19366	–2.12481	0.00000
C	–0.05255	–1.42458	0.00000
C	–1.30362	–2.08782	0.00000
C	–2.49208	–1.38935	0.00000
C	–2.45351	0.03007	0.00000
C	–1.25189	0.69733	0.00000
C	0.00000	0.00000	0.00000
C	1.23830	0.67509	0.00000
H	1.18017	–3.20475	0.00000
H	–3.43621	–1.90741	0.00000
H	–1.31537	–3.16679	0.00000
H	–1.23860	1.77506	0.00000
H	–3.37615	0.58797	0.00000
H	3.31567	–2.00415	0.00000
H	1.25003	1.75338	0.00000

CASSCF Energy = –457.87734304 a.u.

2-naphthol (S_1, acid)

	X	Y	Z
O	3.63548	0.64908	0.00000
C	2.45230	0.00000	0.00000
C	2.50336	–1.41670	0.00000
C	1.29551	–2.14374	0.00000
C	0.04138	–1.49894	0.00000
C	–1.18590	–2.19574	0.00000
C	–2.41919	–1.51068	0.00000
C	–2.45704	–0.08909	0.00000
C	–1.25367	0.64603	0.00000
C	0.00000	0.00000	0.00000
C	1.22651	0.69391	0.00000
H	1.32689	–3.21847	0.00000
H	–3.33683	–2.06925	0.00000
H	–1.17628	–3.27115	0.00000
H	–1.28608	1.72117	0.00000
H	–3.40069	0.42315	0.00000
H	3.45697	–1.90722	0.00000
H	1.22538	1.77128	0.00000
H	3.51185	1.58166	0.00000
O	3.63548	0.64908	0.00000

CASSCF Energy = –458.29623707 a.u.

2-naphthol (S_1, conjugate base)

	X	Y	Z
O	3.57870	0.67076	0.00000
C	2.52742	0.00000	0.00000
C	2.53831	–1.44846	0.00000
C	1.31345	–2.10341	0.00000
C	0.05508	–1.44708	0.00000
C	–1.18137	–2.16803	0.00000
C	–2.41386	–1.47837	0.00000
C	–2.45759	–0.08799	0.00000
C	–1.23434	0.65897	0.00000
C	0.00000	0.00000	0.00000
C	1.25229	0.67357	0.00000
H	1.30142	–3.18364	0.00000
H	–3.33259	–2.04389	0.00000
H	–1.16768	–3.24527	0.00000
H	–1.26115	1.73573	0.00000
H	–3.40502	0.42406	0.00000
H	3.47739	–1.96916	0.00000
H	1.28522	1.75011	0.00000

CASSCF Energy = –457.75708491 a.u.

2-naphthylammonium (S_0, acid)

	X	Y	Z
N	3.68934	0.73391	0.00000
C	2.40251	0.00000	0.00000
C	2.45652	–1.41312	0.00000
C	1.27061	–2.10026	0.00000
C	0.01967	–1.41573	0.00000
C	–1.21601	–2.12312	0.00000
C	–2.40658	–1.44130	0.00000
C	–2.42267	–0.02121	0.00000
C	–1.24724	0.68595	0.00000
C	0.00000	0.00000	0.00000
C	1.23663	0.70771	0.00000
H	1.28047	–3.17454	0.00000
H	–3.33543	–1.98097	0.00000
H	–1.20297	–3.19791	0.00000
H	–1.25827	1.76122	0.00000
H	–3.36277	0.49862	0.00000
H	1.22966	1.78447	0.00000
H	3.39847	–1.93313	0.00000
H	4.25276	0.50587	0.81398
H	4.25276	0.50587	–0.81398
H	3.54354	1.73220	0.00000

CASSCF Energy = –438.97752621 a.u.

2-naphthylammonium (S_0, conjugated base)

	X	Y	Z
N	3.66118	0.64675	0.00000
C	2.43917	0.00000	0.00000
C	2.41429	–1.42745	0.00000
C	1.22674	–2.10653	0.00000
C	–0.01971	–1.41367	0.00000
C	–1.26770	–2.09632	0.00000
C	–2.45071	–1.39836	0.00000
C	–2.43409	0.02021	0.00000
C	–1.24074	0.70046	0.00000
C	0.00000	0.00000	0.00000
C	1.24803	0.68726	0.00000
H	–1.23190	1.77666	0.00000
H	–1.27253	–3.17270	0.00000
H	1.22715	–3.18262	0.00000
H	1.24786	1.76425	0.00000
H	–3.36276	0.56299	0.00000
H	–3.39003	–1.92185	0.00000
H	3.34503	–1.96846	0.00000
H	3.71561	1.63476	0.00000

H	4.50826	0.13617	0.00000

CASSCF Energy = –438.60730518 a.u.

2-naphthylammonium (S_1, acid)

	X	Y	Z
N	3.69056	0.75523	0.00000
C	2.42205	0.00000	0.00000
C	2.49705	–1.41469	0.00000
C	1.29497	–2.14565	0.00000
C	0.04072	–1.49921	0.00000
C	–1.18299	–2.20091	0.00000
C	–2.42134	–1.52144	0.00000
C	–2.45596	–0.09970	0.00000
C	–1.25465	0.64302	0.00000
C	0.00000	0.00000	0.00000
C	1.21575	0.71110	0.00000
H	1.33872	–3.21835	0.00000
H	–3.33684	–2.08039	0.00000
H	–1.16595	–3.27535	0.00000
H	–1.29496	1.71732	0.00000
H	–3.39720	0.41523	0.00000
H	1.20555	1.78732	0.00000
H	3.44588	–1.92009	0.00000
H	4.26048	0.53893	0.81381
H	4.26048	0.53893	–0.81381
H	3.52605	1.75078	0.00000

CASSCF Energy = –438.82715545 a.u.

2-naphthylammonium (S_1, conjugated base)

	X	Y	Z
N	3.64162	0.70762	0.00000
C	2.46510	0.00000	0.00000
C	2.50012	–1.42567	0.00000
C	1.28676	–2.14476	0.00000
C	0.03755	–1.49382	0.00000
C	–1.19487	–2.18640	0.00000
C	–2.41965	–1.49569	0.00000
C	–2.45573	–0.07594	0.00000
C	–1.24883	0.65103	0.00000
C	0.00000	0.00000	0.00000
C	1.22810	0.68726	0.00000
H	–1.27399	1.72663	0.00000
H	–1.19074	–3.26206	0.00000
H	1.31120	–3.21996	0.00000
H	1.22800	1.76384	0.00000
H	–3.39819	0.43869	0.00000
H	–3.33961	–2.05157	0.00000
H	3.44224	–1.94137	0.00000
H	3.64476	1.69775	0.00000
H	4.51579	0.24302	0.00000

CASSCF Energy = –438.46161497 a.u.

2-naphthoic acid (S_0, acid)

	X	Y	Z
C	–2.43513	–1.40626	0.00000
C	–1.25167	–2.10144	0.00000
C	–0.00411	–1.41330	0.00000
C	0.00000	0.00000	0.00000
C	–1.24221	0.69959	0.00000
C	–2.43091	0.01438	0.00000
H	1.24002	–3.18326	0.00000
H	–3.37158	–1.93473	0.00000
H	–1.25351	–3.17730	0.00000
C	1.24273	–2.10758	0.00000
C	1.24530	0.69210	0.00000
H	–1.23436	1.77542	0.00000
H	–3.36366	0.54917	0.00000
C	2.43263	0.00000	0.00000
C	2.42922	–1.42531	0.00000

H	1.24781	1.76534	0.00000
H	3.36667	–1.94741	0.00000
C	3.74459	0.69895	0.00000
O	4.80082	0.14447	0.00000
O	3.64941	2.03201	0.00000
H	4.52107	2.39648	0.00000

CASSCF Energy = –571.26391566 a.u.

2-naphthoic acid (S_0, conjugated base)

	X	Y	Z
C	0.10928	3.65053	0.00000
C	1.11033	2.70967	0.00000
C	0.80960	1.31670	0.00000
C	–0.54435	0.90371	0.00000
C	–1.56388	1.90141	0.00000
C	–1.25058	3.23887	0.00000
H	2.85828	0.62347	0.00000
H	0.35037	4.69992	0.00000
H	2.14248	3.01852	0.00000
C	1.82521	0.31509	0.00000
C	–0.85092	–0.48896	0.00000
H	–2.59306	1.58556	0.00000
H	–2.03211	3.97942	0.00000
C	0.13706	–1.44487	0.00000
C	1.49795	–1.01737	0.00000
H	–1.87461	–0.81497	0.00000
H	2.25816	–1.77519	0.00000
C	–0.21270	–2.94774	0.00000
O	0.75871	–3.70601	0.00000
O	–1.41714	–3.21695	0.00000

CASSCF Energy = –570.69515610 a.u.

2-naphthoic acid (S_1, acid)

	X	Y	Z
O	3.64018	2.04169	0.00000
O	4.81878	0.16749	0.00000
C	3.75158	0.70726	0.00000
C	2.46131	0.00000	0.00000
C	2.46618	–1.42834	0.00000
C	1.25482	–2.14988	0.00000
C	0.00785	–1.49686	0.00000
C	–1.22752	–2.18135	0.00000
C	–2.45094	–1.48498	0.00000
C	–2.45900	–0.06433	0.00000
C	–1.24754	0.65835	0.00000
C	0.00000	0.00000	0.00000
C	1.22418	0.69334	0.00000
H	1.28563	–3.22465	0.00000
H	–3.37789	–2.02693	0.00000
H	–1.22559	–3.25683	0.00000
H	–1.27072	1.73349	0.00000
H	–3.39330	0.46555	0.00000
H	1.22108	1.76596	0.00000
H	3.40560	–1.94489	0.00000
H	4.50787	2.41501	0.00000

CASSCF Energy = –571.11762536 a.u.

2-naphthoic acid (S_1, conjugated base)

	X	Y	Z
O	3.69308	2.00163	0.00000
O	4.82565	0.07918	0.00000
C	3.80293	0.77322	0.00000
C	2.47861	0.00000	0.00000
C	2.47355	–1.42818	0.00000
C	1.26083	–2.15048	0.00000
C	0.01020	–1.49943	0.00000
C	–1.22610	–2.18361	0.00000
C	–2.45068	–1.48580	0.00000
C	–2.46327	–0.06244	0.00000

C	–1.24886	0.65750	0.00000
C	0.00000	0.00000	0.00000
C	1.23457	0.68036	0.00000
H	1.28199	–3.22803	0.00000
H	–3.37828	–2.03003	0.00000
H	–1.22750	–3.26029	0.00000
H	–1.26788	1.73330	0.00000
H	–3.40067	0.46427	0.00000
H	1.25351	1.75400	0.00000
H	3.41888	–1.93341	0.00000

CASSCF Energy = –570.54661602 a.u.

8-cyano-2-naphthol (S_0, acid)

	X	Y	Z
O	3.63798	0.59387	0.00000
N	–1.32491	3.26187	0.00000
C	–1.29758	2.12112	0.00000
C	–1.25988	0.67913	0.00000
C	0.00000	0.00000	0.00000
C	1.24486	0.69718	0.00000
C	2.42224	0.00000	0.00000
C	2.42660	–1.42070	0.00000
C	1.24234	–2.10337	0.00000
C	–0.00748	–1.41297	0.00000
C	–1.24594	–2.11192	0.00000
C	–2.44005	–1.43399	0.00000
C	–2.44813	–0.02043	0.00000
H	1.25055	1.77279	0.00000
H	3.37135	–1.93148	0.00000
H	1.24145	–3.17874	0.00000
H	–1.23434	–3.18744	0.00000
H	–3.37214	–1.96824	0.00000
H	–3.37974	0.51420	0.00000
H	3.55991	1.53168	0.00000

CASSCF Energy = –550.22353452 a.u.

8-cyano-2-naphthol (S_0, conjugated base)

	X	Y	Z
C	–1.34517	2.11109	0.00000
C	–1.25509	0.67319	0.00000
C	0.02188	0.02411	0.00000
C	1.24566	0.70964	0.00000
C	2.49582	0.04031	0.00000
C	2.42300	–1.43597	0.00000
C	1.24662	–2.10645	0.00000
C	–0.01784	–1.41131	0.00000
C	–1.23319	–2.10097	0.00000
C	–2.45524	–1.43525	0.00000
C	–2.45244	–0.03887	0.00000
N	–1.46337	3.24850	0.00000
O	3.60487	0.58842	0.00000
H	1.25790	1.78485	0.00000
H	3.36247	–1.96321	0.00000
H	1.23519	–3.18560	0.00000
H	–1.21339	–3.17919	0.00000
H	–3.38315	–1.97906	0.00000
H	–3.38146	0.50425	0.00000

CASSCF Energy = –549.65328789 a.u.

8-cyano-2-naphthol (S_1, acid)

	X	Y	Z
O	3.62858	0.64606	0.00000
N	–1.39839	3.21482	0.00000
C	–1.34080	2.07357	0.00000
C	–1.26708	0.64240	0.00000
C	0.00000	0.00000	0.00000
C	1.22225	0.69331	0.00000
C	2.44498	0.00000	0.00000
C	2.49402	–1.41853	0.00000

C	1.28963	–2.14153	0.00000
C	0.03562	–1.49796	0.00000
C	–1.18926	–2.20134	0.00000
C	–2.42463	–1.52181	0.00000
C	–2.47505	–0.10466	0.00000
H	1.22438	1.76906	0.00000
H	3.44729	–1.90930	0.00000
H	1.31800	–3.21605	0.00000
H	–1.17419	–3.27592	0.00000
H	–3.34140	–2.08055	0.00000
H	–3.41600	0.40970	0.00000
H	3.51236	1.57995	0.00000

CASSCF Energy = –550.07578679 a.u.

8-cyano-2-naphthol (S_1, conjugated base)

	X	Y	Z
O	3.60487	0.58842	0.00000
N	–1.46337	3.24850	0.00000
C	–1.34517	2.11109	0.00000
C	–1.25509	0.67319	0.00000
C	0.02188	0.02411	0.00000
C	1.24566	0.70964	0.00000
C	2.49582	0.04031	0.00000
C	2.42300	–1.43597	0.00000
C	1.24662	–2.10645	0.00000
C	–0.01784	–1.41131	0.00000
C	–1.23319	–2.10097	0.00000
C	–2.45524	–1.43525	0.00000
C	–2.45244	–0.03887	0.00000
H	1.25790	1.78485	0.00000
H	3.36247	–1.96321	0.00000
H	1.23519	–3.18560	0.00000
H	–1.21339	–3.17919	0.00000
H	–3.38315	–1.97906	0.00000
H	–3.38146	0.50425	0.00000

CASSCF Energy = –549.55057558 a.u.

5,8-cyano-2-naphthol (S_0, acid)

	X	Y	Z
O	3.62290	0.63107	0.00000
N	–1.33349	3.25942	0.00000
N	–1.29645	–4.67269	0.00000
C	–1.30567	2.12954	0.00000
C	–1.26734	0.68526	0.00000
C	–0.00662	0.00828	0.00000
C	1.23072	0.71603	0.00000
C	2.41460	0.02994	0.00000
C	2.42828	–1.38986	0.00000
C	1.25267	–2.08718	0.00000
C	–0.00133	–1.40517	0.00000
C	–1.25184	–2.09781	0.00000
C	–2.45017	–1.41961	0.00000
C	–2.45650	–0.00892	0.00000
C	–1.27362	–3.54286	0.00000
H	1.26797	–3.16080	0.00000
H	1.22435	1.79119	0.00000
H	3.37608	–1.89441	0.00000
H	–3.37691	–1.96082	0.00000
H	–3.38897	0.52276	0.00000
H	3.54265	1.56892	0.00000

CASSCF Energy = –641.94596636 a.u.

5,8–dicyano–2–naphthol (S_0, conjugated base)

	X	Y	Z
O	3.57761	0.57247	0.00000
N	–1.43539	3.23784	0.00000
N	–1.40508	–4.68874	0.00000
C	–1.33237	–3.55884	0.00000
C	–1.28084	–2.11223	0.00000

C	–2.49162	–1.42933	0.00000
C	–2.47177	–0.02949	0.00000
C	–1.26969	0.65908	0.00000
C	–1.33591	2.09965	0.00000
C	–0.00034	–0.01037	0.00000
C	1.22327	0.67389	0.00000
C	2.47666	0.00682	0.00000
C	2.39518	–1.45585	0.00000
C	1.21685	–2.13737	0.00000
C	–0.03689	–1.44660	0.00000
H	1.21801	–3.21366	0.00000
H	1.23474	1.74896	0.00000
H	3.33149	–1.98738	0.00000
H	–3.42105	–1.96642	0.00000
H	–3.39593	0.51938	0.00000

CASSCF Energy = –641.38971094 a.u.

5,8-cyano-2-naphthol (S_1, acid)

	X	Y	Z
C	-1.30545	2.15245	0.00000
C	-1.26163	0.71606	0.00000
C	-0.00904	0.04979	0.00000
C	1.22174	0.72459	0.00000
C	2.43464	0.01736	0.00000
C	2.46108	-1.40242	0.00000
C	1.25116	-2.11077	0.00000
C	0.00794	-1.44788	0.00000
C	-1.24230	-2.12691	0.00000
C	-2.46871	-1.41782	0.00000
C	-2.48316	-0.00443	0.00000
C	-1.28185	-3.56398	0.00000
N	-1.33729	3.28322	0.00000
N	-1.31973	-4.69426	0.00000
O	3.62519	0.64212	0.00000
H	1.27044	-3.18413	0.00000
H	1.23521	1.79988	0.00000
H	3.40597	-1.90870	0.00000
H	-3.39215	-1.96331	0.00000
H	-3.41485	0.52572	0.00000
H	3.52922	1.57862	0.00000

CASSCF Energy = –641.79957391a.u.

5,8-cyano-2-naphthol (S_1, conjugated base)

	X	Y	Z
O	3.58990	0.61986	0.00000
N	–1.31397	3.28746	0.00000
N	–1.35446	–4.67566	0.00000
C	–1.30398	–3.52818	0.00000
C	–1.25241	–2.11103	0.00000
C	–2.46773	–1.37318	0.00000
C	–2.46521	0.00349	0.00000
C	–1.22907	0.73200	0.00000
C	–1.26297	2.14840	0.00000
C	–0.00401	0.01546	0.00000
C	1.25991	0.69063	0.00000
C	2.55342	–0.00770	0.00000
C	2.48674	–1.46112	0.00000
C	1.27069	–2.08418	0.00000
C	0.01117	–1.39720	0.00000
H	1.24650	–3.16066	0.00000
H	1.30324	1.76350	0.00000
H	3.40939	–2.01092	0.00000
H	–3.40041	–1.90864	0.00000
H	–3.39448	0.54283	0.00000

CASSCF Energy = –641.29016982 a.u.

Salicylamide (S_0, acid)

	X	Y	Z
O	–1.10798	3.51519	0.00000

O	2.38880	1.38026	0.00000
N	1.15244	3.70479	0.00000
C	–0.11898	2.87323	0.00000
C	0.00661	1.40474	0.00000
C	1.21336	0.69012	0.00000
C	1.20472	–0.70153	0.00000
C	–0.00223	–1.38968	0.00000
C	–1.21442	–0.69377	0.00000
C	–1.20804	0.69012	0.00000
H	3.14076	0.80996	0.00000
H	–2.13033	1.23821	0.00000
H	–2.14640	–1.22597	0.00000
H	0.00436	–2.46369	0.00000
H	2.13689	–1.23867	0.00000
H	1.14489	4.30445	–0.81324
H	1.14489	4.30445	0.81324
H	1.99191	3.13366	0.00000

CASSCF Energy = –473.92075756 a.u.

Salicylamide (S_0, conjugated base)

	X	Y	Z
O	1.09489	3.51878	0.00000
O	2.43138	1.25627	0.00000
N	–1.12599	3.58991	0.00000
C	0.04637	2.91045	0.00000
C	0.01261	1.41566	0.00000
C	1.21811	0.69193	0.00000
C	1.19233	–0.71064	0.00000
C	–0.00860	–1.39662	0.00000
C	–1.21807	–0.69226	0.00000
C	–1.19637	0.69193	0.00000
H	2.35036	2.20220	0.00000
H	–2.15639	–1.21573	0.00000
H	–0.00934	–2.47182	0.00000
H	2.13334	–1.22862	0.00000
H	–2.13802	1.20752	0.00000
H	–2.01368	3.15734	0.00000
H	–1.07847	4.58156	0.00000

CASSCF Energy = –473.59315143 a.u.

Salicylamide (S_1, acid)

	X	Y	Z
O	–1.18477	3.52206	0.00000
O	2.35248	1.38714	0.00000
N	1.07475	3.77192	0.00000
C	–0.15605	2.89316	0.00000
C	–0.01316	1.47921	0.00000
C	1.20157	0.70927	0.00000
C	1.21066	–0.71688	0.00000
C	0.00810	–1.45218	0.00000
C	–1.19876	–0.72869	0.00000
C	–1.20842	0.70927	0.00000
H	3.11507	0.82782	0.00000
H	–2.14646	1.22784	0.00000
H	–2.14211	–1.23972	0.00000
H	0.02101	–2.52301	0.00000
H	2.16239	–1.21753	0.00000
H	1.03243	4.38476	–0.80885
H	1.03243	4.38476	0.80885
H	1.94798	3.26649	0.00000

CASSCF Energy = –473.77615455 a.u.

Salicylamide (S_1, conjugated base)

	X	Y	Z
O	–1.14871	3.57668	0.00000
O	2.31823	1.37540	0.00000
N	1.13807	3.67083	0.00000
C	–0.13924	2.88046	0.00000
C	–0.03679	1.44571	0.00000

C	1.23751	0.70939	0.00000
C	1.21964	–0.69470	0.00000
C	–0.01277	–1.42861	0.00000
C	–1.20030	–0.74117	0.00000
C	–1.20730	0.70939	0.00000
H	–2.14547	1.23090	0.00000
H	–2.14133	–1.25948	0.00000
H	0.00483	–2.50249	0.00000
H	2.16656	–1.20120	0.00000
H	1.15347	4.26864	–0.81081
H	1.15347	4.26864	0.81081
H	1.93059	3.02095	0.00000

CASSCF Energy = –473.43530750 a.u.

7. Optimized Cartesian coordinates for ^1L_a and ^1L_b naphthalene at TD-ωB97X-D/6-311+G(d,p)

Naphthalene ^1L_a – B_{2u} (C_{2v})

	X	Y	Z
C	–0.03249	1.39250	0.00000
C	1.20004	0.71758	0.00000
C	2.43539	1.38734	0.00000
C	3.67317	0.67675	0.00000
C	3.67031	–0.69209	0.00000
C	2.42957	–1.39751	0.00000
C	1.19703	–0.72258	0.00000
C	–0.03831	–1.39235	0.00000
C	–1.27610	–0.68176	0.00000
C	–1.27324	0.68708	0.00000
H	–2.20712	–1.23574	0.00000
H	–0.04813	–2.47738	0.00000
H	–0.03778	2.47756	0.00000
H	–2.20194	1.24495	0.00000
H	2.44520	2.47237	0.00000
H	2.43485	–2.48256	0.00000
H	4.60420	1.23073	0.00000
H	4.59902	–1.24996	0.00000

Total Electronic Energy = –385.651420328 a.u.

Naphthalene ^1L_b – B_{3u} (C_{2v})

	X	Y	Z
C	–1.25136	0.65780	0.00000
C	–0.05206	1.39678	0.00000
C	–0.01295	2.80504	0.00000
C	1.19822	3.49870	0.00000
C	2.42766	2.78983	0.00000
C	2.43413	1.39410	0.00000
C	1.23495	0.65472	0.00000
C	1.19623	–0.75343	0.00000
C	–0.01482	–1.44677	0.00000
C	–1.24468	–0.73766	0.00000
H	–2.18044	–1.28293	0.00000
H	–0.01791	–2.52981	0.00000
H	2.13249	–1.30176	0.00000
H	–2.19496	1.19339	0.00000
H	3.37789	0.85879	0.00000
H	–0.94906	3.35363	0.00000
H	1.20140	4.58165	0.00000
H	3.36331	3.33514	0.00000

Total Electronic Energy = –385.656804006 a.u.