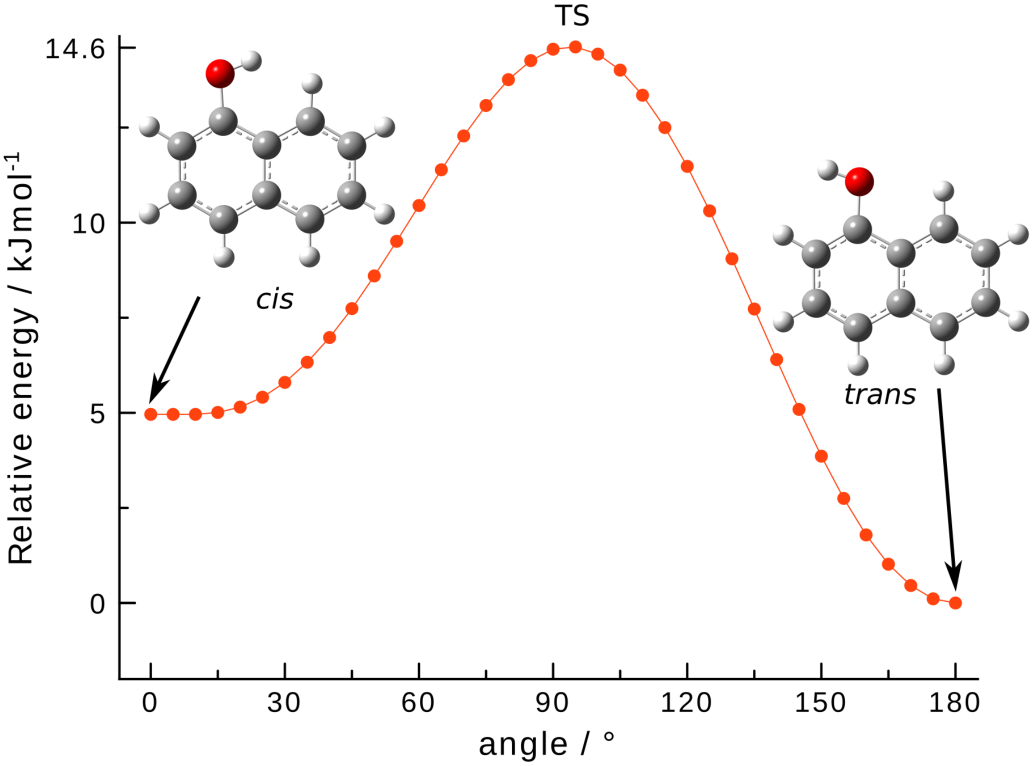

Figure S1: Conformational landscape of 1-hydroxynaphthalene: Potential energy curve resulting from the MP2/cc-pVTZ calculation (values at equilibrium). Energies are indicated relative to *trans*-1-hydroxynaphthalene. Angle values are corresponding to the C−C−O−H dihedral angle.

Table S1: Results from the energy calculations on the hydroxynaphthalene molecules. Δ_{E} values are relative to the lower energy conformer of each species.

			1-hydroxynaphthalene			2-hydroxynaphthalene		
			cis	TS	*trans*	*cis*	TS	*trans*
B97-1[a]	E_{eq}	/ E_h	-461.1344478	-461.1302821	-461.1364003	-461.1368716	-461.1301344	-461.1359809
	E_{ZPE}	/ E_h	-460.9839570	-460.9802350	-460.9854290	-460.9860680	-460.9803100	-460.9853160
	ω	/ cm^{-1}	87.70	330.20	140.10	122.10	350.90	122.30
	ΔE_{eq}	/ kJ/mol	5.1	16.1	0	0	17.69	2.34
		/ cm^{-1}	429	1,343	0	0	1,478.64	195.49
	ΔE_{ZPE}	/ kJ/mol	3.9	11.7[d]	0	0	13.0[d]	1.97
		/ cm^{-1}	323	975[d]	0	0	1,088[d]	165.04
MP2[b]	E_{eq}	/ E_h	-460.1680434	-460.1643641	-460.1699345	-460.1698188	-460.1636588	-460.1688217
	E_{ZPE}	/ E_h	-460.0171110	-460.0135300	-460.0183590	-460.0184030	-460.0130740	-460.0175580
	ω	/ cm^{-1}	-57.20	332.10	138.40	120.90	340.90	120.90
	ΔE_{eq}	/ kJ/mol	5.0	14.6	0	0	16.2	2.6
		/ cm^{-1}	415	1,223	0	0	1,352	219
	ΔE_{ZPE}	/ kJ/mol	3.3	10.7[d]	0	0	11.9[d]	2.2
		/ cm^{-1}	274	895[d]	0	0	994[d]	185
hybrid[c]	E_{ZPE}	/ E_h	-460.0175526	-460.0143170	-460.0189632	-460.0190152	-460.0138344	-460.0181568
	ΔE_{ZPE}	/ kJ/mol	3.7	10.2[d]	0	0	11.5[d]	2.3
		/ cm^{-1}	310	855[d]	0	0	962[d]	188
	Pop.[e]	/ %	18		82	71		29
	ΔE_{12} [f]	/ kJ/mol	–	–	0.1	0	–	–
		/ cm^{-1}	–	–	11	0	–	–

[a] B97-1/cc-pVTZ anharmonic calculation [b] MP2/cc-pVTZ anharmonic calculation [c] hybrid B97-1/MP2/cc-pVTZ calculation, see text [d] For the transition states, ΔE_{ZPE} is calculated according to the formula $\Delta E_{\mathrm{ZPE}} = E(\mathrm{TS}) - E(\mathrm{GS}) - \omega(\mathrm{TS})/2$ [e] Population at 300 K [f] Energy difference between the lower state conformers of 1- and 2-hydroxynaphthalene

Table S2: Results from the energy calculations on the naphthaldehyde molecules. Δ_{E} values are relative to the lower energy conformer of each species.

			1-naphthaldehyde			**2-naphthaldehyde**		
			cis	TS	*trans*	*cis*	TS	*trans*
B97-1[a]	E_{eq}	/ E_h	-499.2369962	-499.2233235	-499.2339542	-499.2386084	-499.2243882	-499.2398478
	E_{ZPE}	/ E_h	-499.080972	-499.06842	-499.078206	-499.082942	-499.069577	-499.084122
	ω	/ cm^{-1}	85.6	158.6	84.4	86.3	173.9	78.8
	ΔE_{eq}	/ kJ/mol	0	35.9	8.0	3.3	40.6	0
		/ cm^{-1}	0	3001	668	272	3393	0
	ΔE_{ZPE}	/ kJ/mol	0	32.0	7.3	3.1	37.1	0
		/ cm^{-1}	0	2676	607	259	3105	0
MP2[b]	E_{eq}	/ E_h	-498.1872922	-498.1752513	-498.1841598	-498.1880392	-498.1751578	-498.1893045
	E_{ZPE}	/ E_h	-498.030536	-498.01949	-498.027667	-498.031632	-498.019528	-498.032875
	ω	/ cm^{-1}	79.3	145.3	65.7	83.7	162.9	77
	ΔE_{eq}	/ kJ/mol	0	31.6	8.2	3.3	37.1	0
		/ cm^{-1}	0	2643	687	278	3105	0
	ΔE_{ZPE}	/ kJ/mol	0	28.1	7.5	3.3	34.1	0
		/ cm^{-1}	0	2352	630	273	2848	0
hybrid[c]	E_{ZPE}	/ E_h	-498.031268	-498.0203478	-498.0284116	-498.0323728	-498.0203466	-498.0335787
	ΔE_{ZPE}	/ kJ/mol	0	27.7	7.5	3.2	33.7	0
		/ cm^{-1}	0	2317	627	265	2817	0
	Pop.[e]	/ %	95		5	22		78
	ΔE_{12} [f]	/ kJ/mol	6.1	–	–	–	–	0
		/ cm^{-1}	507	–	–	–	–	0

[a] B97-1/cc-pVTZ anharmonic calculation [b] MP2/cc-pVTZ anharmonic calculation [c] hybrid B97-1/MP2/cc-pVTZ calculation, see text [d] For the transition states, ΔE_{ZPE} is calculated according to the formula $\Delta E_{\mathrm{ZPE}} = E(\mathrm{TS}) - E(\mathrm{GS}) - \omega(\mathrm{TS})/2$ [e] Population at 300 K [f] Energy difference between the lower state conformers of 1- and 2-naphthaldehyde

Table S3: Energies in kJ mol^{-1} of the four conformers of naphthaldehyde relative to the most stable isomer *trans* 2-naphthaldehyde computed at various levels of theory. CBS values are extrapolated from aug-cc-pVTZ and aug-cc-pVQZ basis set calculations.

Method	1-naphthaldehyde		2-naphthaldehyde	
	cis	*trans*	*cis*	***trans***
MP2/cc-pVTZ[a]	5.3	13.5	3.3	0.0
MP2/CBS	5.8	13.9	3.6	0.0
CCSD(T)/CBS	6.6	14.0	3.6	0.0
PNO-LCCSD(T)-F12/aug-cc-pVTZ	6.7	13.8	3.5	0.0

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[a] See values reported in Table S2.

Table S4: Calculated IR fundamental vibrational modes of *cis*-1-naphthaldehyde and *trans*-2-naphthaldehyde and comparison with proposed experimental assignments. Energies are given in cm^{-1} and intensities in km.mol^{-1}.

		cis-1-naphthaldehyde						*trans*-2-naphthaldehyde					
		B97-1		MP2		Hybrid	Exp.	B97-1		MP2		Hybrid	Exp.
ν	sym.	E_h	E_a	E_h	I_h	E	E	E_h	E_a	E_h	I_h	E	E
1	A’	3224	3070	3268	7.5	3114	3064	3189	3062	3234	3.5	3107	
2	A’	3184	3062	3232	8.5	3109	3064	3185	3061	3233	11.6	3109	3070
3	A’	3182	3077	3230	14.0	3125	3064	3173	3052	3220	13.4	3099	2980
4	A’	3167	3032	3215	10.5	3080	3064	3161	3045	3205	0.7	3089	
5	A’	3158	3055	3202	6.4	3099	3064	3159	3009	3203	5.3	3053	
6	A’	3154	3009	3200	0.4	3055	3064	3155	3013	3200	2.3	3058	
7	A’	3150	3018	3195	2.7	3064	3064	3143	2998	3184	6.1	3039	
8	A’	2861	2684	2936	118.0	2759	2721	2870	2680	2949	108.4	2760	2717
9	A’	1772	1743	1740	161.0	1712	1715	1781	1752	1745	231.6	1717	1720
10	A’	1653	1611	1669	3.7	1628		1660	1620	1678	6.0	1638	1637
11	A’	1626	1592	1625	7.0	1591	1601	1635	1599	1635	4.5	1600	1603
12	A’	1605	1566	1619	11.1	1580	1583	1606	1572	1617	5.2	1582	
13	A’	1542	1504	1561	29.8	1523	1516	1539	1504	1556	2.2	1521	
14	A’	1488	1456	1495	0.9	1462		1495	1467	1506	10.7	1478	1468
15	A’	1474	1437	1491	7.3	1454	1457	1471	1439	1491	12.7	1459	1447
16	A’	1438	1405	1481	5.2	1448	1457	1424	1408	1472	2.5	1456	
17	A’	1418	1378	1443	2.9	1404		1401	1363	1456	0.1	1418	
18	A’	1388	1351	1435	2.8	1399		1388	1357	1416	1.6	1385	
19	A’	1368	1335	1414	2.6	1381		1369	1338	1374	25.2	1343	1347
20	A’	1292	1249	1290	2.1	1248		1285	1271	1294	37.5	1279	1262
21	A’	1237	1211	1266	18.6	1240	1220?	1278	1255	1284	4.5	1261	
22	A’	1232	1204	1240	16.5	1212	1214?	1236	1212	1259	0.0	1235	
23	A’	1189	1165	1192	12.7	1168	1171	1184	1163	1195	41.5	1174	1154
24	A’	1184	1155	1181	2.1	1152		1172	1154	1178	0.1	1160	
25	A’	1165	1142	1166	3.4	1143		1165	1166	1161	0.1	1163	
26	A’	1097	1077	1103	2.3	1084		1137	1124	1136	21.6	1123	1121
27	A’	1069	1041	1074	35.4	1046	1056	1039	1022	1047	2.3	1030	
28	A’	1042	1012	1050	3.9	1020		969	956	970	1.0	956	
29	A’	895	881	893	15.3	878	887	891	879	893	6.2	881	882
30	A’	805	795	807	0.7	797		785	774	789	21.2	778	785
31	A’	718	704	718	15.1	704	712	766	755	767	23.7	757	763
32	A’	659	649	656	18.3	646	647	640	633	632	1.9	626	
33	A’	553	547	551	2.5	544	548	612	606	609	3.6	603	603
34	A’	502	495	498	1.6	492	497	520	514	516	0.1	511	
35	A’	437	433	434	1.5	431	430	390	389	386	5.5	384	388
36	A’	366	362	360	0.1	356		349	350	348	2.8	349	
37	A’	218	166	219	6.5	166	225 ?	177	184	175	6.0	183	177
38	A”	1022	1003	1015	0.4	995		1028	1011	1018	1.1	1001	
39	A”	1016	1011	977	0.7	973		1002	994	968	0.1	961	
40	A”	995	994	962	0.8	962		998	995	960	0.1	957	
41	A”	979	975	951	0.1	947		972	968	948	1.5	943	
42	A”	937	930	909	0.0	902		918	909	878	9.7	869	?
43	A”	893	880	870	0.0	856		880	864	859	20.1	843	857
44	A”	823	818	806	91.7	801	802	843	831	835	35.4	822	820
45	A”	792	777	755	8.0	740		788	778	754	27.7	745	742
46	A”	753	740	725	0.3	711		760	751	726	0.2	717	
47	A”	639	637	614	0.0	612		645	640	620	0.9	614	
48	A”	539	529	529	6.0	520	525	512	508	502	0.3	497	
49	A”	479	472	469	0.4	462		485	479	477	15.9	471	472
50	A”	414	408	407	3.6	402	400	401	395	393	0.0	387	
51	A”	273	266	265	5.7	258	255	297	289	293	3.3	285	
52	A”	181	178	178	0.9	175		192	188	187	4.7	184	181
53	A”	152	146	147	3.7	141	143	160	156	157	4.8	152	152
54	A”	86	76	79	3.5	70	76	79	78	77	1.6	76	

Note. *h* in E_h stands for harmonic, and *a* in E_a for anharmonic

Table S5: Rotational constants of the four studied species at various stages of the calculations and comparison with the experimental values.

	MP2 B_e	Δ^a	hybrid^b B_0	exp. B_0	δ_{hybrid} ^{c} / %
***trans*-1-hydroxynaphthalene**					
A / MHz	1947	-14	1934	1942.100623 (53)	0.42
B / MHz	1140	-8	1132	1133.623211 (21)	0.14
C / MHz	719	-5	714	716.017762 (14)	0.28
***cis*-2-hydroxynaphthalene**					
A / MHz	2862	-25	2837	2849.155543 (64)	0.43
B / MHz	828	-4	823	824.632161 (25)	0.20
C / MHz	642	-4	638	639.723697 (15)	0.27
***cis*-1-naphthaldehyde**					
A / MHz	1389	-8	1380	1384.40872 (21)	0.32
B / MHz	1004	-8	995	999.015243 (71)	0.40
C / MHz	583	-4	579	580.551953 (19)	0.27
***trans*-2-naphthaldehyde**					
A / MHz	2824	-22	2802	2810.43194 (15)	0.30
B / MHz	583	-3	580	581.095981 (24)	0.19
C / MHz	483	-3	480	481.700564 (18)	0.35

$^a\Delta = B_0 - B_e$ $\quad$ $^b B_0^{hybrid} = B_e^{MP2} - (B_e^{B97-1} - B_0^{B97-1})$

$^c\delta_{\text{hybrid}} = (B_{\text{exp.}} - B_{\text{hybrid}})/B_{\text{hybrid}} \times 100$

Table S6: Rotational constants of *trans*-1-hydroxynaphthalene in the ground and excited vibrational states. Error (1σ) on experimental parameters are given between parenthesis in units of the last digit.

	MP2	Δ^a	hybrid^b	scaled^c	exp.	δ_{hybrid} ^{d} / %	δ_{scaled} ^{e} / %
Equilibrium							
A_e / MHz	1947						
B_e / MHz	1140						
C_e / MHz	719						
Ground state							
A_0 / MHz			1934		1942.100623 (53)	0.42	
B_0 / MHz			1132		1133.623211 (21)	0.16	
C_0 / MHz			714		716.017762 (14)	0.26	
$\mathbf{v_{51} = 1}$							
E / cm^{-1}			136				
A_v / MHz		-14	1933	1941	1941.73727 (53)	0.44	0.015
B_v / MHz		-8	1132	1134	1132.951050 (68)	0.11	-0.051
C_v / MHz		-4	715	717	716.402565 (43)	0.23	-0.030
$\mathbf{v_{50} = 1}$							
E / cm^{-1}			166.4				
A_v / MHz		-16	1931	1939	1939.60653 (22)	0.44	0.016
B_v / MHz		-6	1133	1135	1134.394385 (36)	0.11	-0.053
C_v / MHz		-4	715	717	716.571336 (25)	0.23	-0.032
$\mathbf{v_{51} = 2}$							
E / cm^{-1}			272.2				
A_v / MHz		-15	1933	1941	1941.1817 (43)	0.43	0.003
B_v / MHz		-9	1131	1133	1132.3400 (16)	0.12	-0.042
C_v / MHz		-4	715	717	716.785770 (55)	0.23	-0.027
$\mathbf{v_{50} = 2}$							
E / cm^{-1}			332.8				
A_v / MHz		-19	1929	1937	1937.1523 (11)	0.44	0.019
B_v / MHz		-6	1134	1136	1135.16069 (49)	0.11	-0.052
C_v / MHz		-3	715	717	717.121942 (55)	0.23	-0.030

[a] $\Delta = B_0 - B_e$ [b] $B_0^{hybrid} = B_e^{MP2} - (B_e^{B97-1} - B_0^{B97-1})$

[c] $B_{\text{scaled}} = B_{v\ \text{hybrid}} \times B_{0\ \text{exp}} / B_{0\ \text{hybrid}}$

[d] $\delta_{\text{hybrid}} = (B_{\text{exp.}} - B_{\text{hybrid}})/B_{\text{hybrid}} \times 100$

[e] $\delta_{\text{scaled}} = (B_{\text{exp.}} - B_{\text{scaled}})/B_{\text{scaled}} \times 100$

Table S7: Full set of rotational parameters (in MHz) for *trans*-1-hydroxynaphthalene in excited vibrational states. Error (1σ) on parameters are given between parenthesis in units of the last digit. Parameters in brackets are fixed to the ground state value.

	$v_{51} = 1$	$v_{50} = 1$	$v_{51} = 2$	$v_{50} = 2$
A_v	1941.73727 (53)	1939.60653 (22)	1941.1817 (43)	1937.1523 (11)
B_v	1132.951050 (68)	1134.394385 (36)	1132.3400 (16)	1135.16069 (49)
C_v	716.402565 (43)	716.571336 (25)	716.785770 (55)	717.121942 (55)
$\Delta_J \times 10^6$	17.9061 (20)	18.0313 (10)	17.9912 (16)	18.0842 (16)
$\Delta_{JK} \times 10^3$	0.0185871 (92)	0.0134017 (43)	0.016961 (48)	0.014049 (34)
$\Delta_K \times 10^3$	0.04257 (14)	0.045458 (62)	0.04502 (35)	0.03692 (23)
$\delta_J \times 10^6$	6.41897 (11)	6.47433 (58)	[6.43578]	[6.43578]
$\delta_K \times 10^3$	0.0360674 (88)	0.0338925 (51)	[0.0351740]	[0.0351740]
# lines	2 567	2 547	1 093	1 035
RMS / kHz	34	34	72	44

[a] Hybrid rotational constants and MP2 centrifugal distorsion terms, see text

[b] $\delta = (B_{\text{Exp.}} - B_{\text{Calc}})/B_{\text{Calc.}} \times 100$

Table S8: Calculated charges on atoms in naphthalene, benzaldehyde and the two isomers of naphthaldehyde at the MP2/aug-cc-pVQZ level using NBO6 software. Values are given in atomic units. See Fig. 5 for atomic numbering.

		1-naphthaldehyde		2-naphthaldehyde		naphthalene	benzaldehyde		
atom	#	*cis*	*trans*	*cis*	*trans*		atom	#	
C	1	-0.0738	-0.0937	-0.1125	-0.0997	-0.1726	C	1	-0.0954
C	2	-0.2295	-0.2246	-0.1247	-0.1105	-0.2177	C	2	-0.2109
C	3	-0.1628	-0.1388	-0.2209	-0.2056	-0.2177	C	3	-0.2029
C	4	-0.1641	-0.2116	-0.1730	-0.1916	-0.1726	C	4	-0.1497
C	5	-0.1352	-0.1279	-0.2285	-0.1341	-0.1726	C	5	-0.2112
C	6	-0.2326	-0.2358	-0.1421	-0.2395	-0.2177	C	6	-0.2130
C	7	-0.1812	-0.2067	-0.2324	-0.2096	-0.2177	H	7	0.2354
C	8	-0.2247	-0.2101	-0.1789	-0.1277	-0.1726	H	8	0.2142
C	9	0.0053	0.0015	-0.0601	-0.1527	-0.0192	H	9	0.2068
C	10	-0.0863	-0.0360	-0.0154	0.0086	-0.0192	H	10	0.2141
H	11	0.2483	0.2108	0.2132	0.2020	0.1928	H	11	0.2134
H	12	0.2132	0.2165	0.2168	0.2167	0.2072	H	12	0.1093
H	13	0.2158	0.2151	0.2031	0.2152	0.2072	O	13	-0.4800
H	14	0.2002	0.1969	0.2132	0.1996	0.1928	C	14	0.3698
H	15	0.2087	0.2088	0.2128	0.2105	0.1928			
H	16	0.2074	0.2050	0.2160	0.2335	0.2072			
H	17	0.2145	0.2366	0.2166	0.1975	0.2072			
H	18	0.1087	0.1136	0.1095	0.1082	0.1928			
O	19	-0.4903	-0.4805	-0.4806	-0.4817				
C	20	0.3583	0.3607	0.3677	0.3607				

Table S9: Calculated charges on atoms in naphthalene, hydroxybenzene, and the two isomers of hydroxynaphthalene at the MP2/aug-cc-pVQZ level using NBO6 software. Values are given in atomic units. See Fig. 5 for atomic numbering.

		1-hydroxynaphthalene		2-hydroxynaphthalene		naphthalene	hydroxybenzene		
atom	#	*cis*	*trans*	*cis*	*trans*		atom	#	
	1	0.2765	0.2716	-0.3345	-0.2098	-0.1726	C	1	0.3414
	2	-0.2756	-0.2554	0.3487	0.2520	-0.2177	C	2	-0.2838
	3	-0.2136	-0.2243	-0.2971	-0.2815	-0.2177	C	3	-0.1891
	4	-0.1675	-0.1637	-0.1172	-0.1845	-0.1726	C	4	-0.2452
	5	-0.1778	-0.1583	-0.2127	-0.1457	-0.1726	C	5	-0.1900
	6	-0.2466	-0.2540	-0.2294	-0.2481	-0.2177	C	6	-0.3103
	7	-0.1938	-0.1356	-0.2295	-0.2186	-0.2177	H	7	0.2241
	8	-0.1811	-0.2261	-0.1486	-0.1936	-0.1726	H	8	0.2142
	9	-0.0945	-0.0539	0.0058	-0.0029	-0.0192	H	9	0.2142
	10	-0.0007	-0.0876	-0.0411	-0.0441	-0.0192	H	10	0.2140
	11	0.1795	0.2282	0.1936	0.2048	0.1928	H	11	0.2077
	12	0.2105	0.2033	0.2099	0.2134	0.2072	H	12	0.4729
	13	0.2161	0.2118	0.2144	0.2119	0.2072	O	13	-0.6700
	14	0.2070	0.2075	0.2065	0.1990	0.1928			
	15	0.1963	0.2026	0.1960	0.2069	0.1928			
	16	0.2254	0.2026	0.2267	0.2104	0.2072			
	17	0.2146	0.2101	0.2046	0.2099	0.2072			
	18	0.4751	0.4785	0.4742	0.4749	0.1928			
	19	-0.6498	-0.6573	-0.6702	-0.6542				