Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structural Study of 1- and 2-Naphthol: New Insights into the Non-covalent H-H Interaction in *cis*-1-Naphthol

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Electronic Supplementary Information

Contents:

Spectroscopic Parameters, Spectra, and Conversion Pathway for 1- and 2-naphthol

Table S1. Spectroscopic parameters for the naphthol isomers from theory and from fits of experimental data.

	cis-1-naphthol (B3LYP-D3(BJ)/def2-TZVP)	*cis*-1-naphthol[a] (experiment)	*trans*-1-naphthol (B3LYP-D3(BJ)/def2-TZVP)	*trans*-1-naphthol[a,c] (experiment)
A /MHz	1959.8594	1947.51340(61)	1955.1739	1942.10135(21)
B	1130.8399	1124.307930(90)	1139.0560	1133.623460(88)
C	717.1278	713.096200(63)	719.7438	716.017810(49)
Δ_J /kHz	0.05262	[0.0136][b]	0.05331	0.01810(70)
Δ_{JK}	-0.08807	[0.0409][b]	-0.09152	0.0240(35)
Δ_K	0.04032	0.30(12)	0.04306	0.059(20)
δ_J	0.01201	0.00382(21)	0.01177	0.00630(34)
δ_K	-0.01278	0.0440(98)	-0.01482	0.0355(19)
N	-	60	-	117
σ /kHz	-	2.1	-	2.2
ΔE_0 / kJ mol^{-1}	3.3	-	0.0	-
Δ / amu Å^2	-0.0443	-0.2925(2)	0.0001	-0.2124(2)
|μ|/ D	μ_a=1.4, μ_b=0.3, μ_c=0.1	$\mu_a > \mu_b$	μ_a=1.2, μ_b=0.1, μ_c=0.0	$\mu_a > \mu_b$

	cis-2-naphthol (B3LYP-D3(BJ)/def2-TZVP)	*cis*-2-naphthol[c] (experiment)	*trans*-2-naphthol (B3LYP-D3(BJ)/def2-TZVP)	*trans*-2-naphthol (experiment)
A /MHz	2870.7044	2849.15700(28)	2868.6589	2845.35720(37)
B	828.9859	824.63285(12)	829.6421	825.5363521(13)
C	643.2358	639.72412(11)	643.5280	640.087128(16)
Δ_J /kHz	0.00797	0.0130(27)	0.00793	0.00706(17)
Δ_{JK}	0.01426	[0.014844][d]	0.01508	[0.015080][e]
Δ_K	0.18312	0.170(29)	0.18328	0.2615(17)
δ_J	0.00200	0.00260(60)	0.00197	0.00180(92)
δ_K	0.02966	[0.030525][d]	0.02969	[0.02969][e]
N	-	41	-	49
σ /kHz	-	1.4	-	2.7
ΔE_0 / kJ mol^{-1}	0.0	-	2.1	-
Δ / amu Å^2	0.0001	-0.2366(2)	0.0000	-0.251(1)
|μ|/ D	μ_a=0.2, μ_b=1.0, μ_c=0.1	$\mu_b > \mu_a$	μ_a=0.6, μ_b=1.4, μ_c=0.0	$\mu_b > \mu_a$

[a] assigned rotational transitions from Whitham et al.[20] are included in fit.

[b] fixed at the values from Whitham et al. [20]

[c] note that the spectroscopic constants derived by Goubet et al.[21] for *trans*-1-naphthol and *cis*-2-naphthol have significantly higher accuracy than the values reported here because of the much larger number of transitions in the fits. Unfortunately, their transition frequencies are not published, so that they were not included in our fits.

[c] fixed at the values from Goubet et al.[21]

[d] fixed at the values from theory.

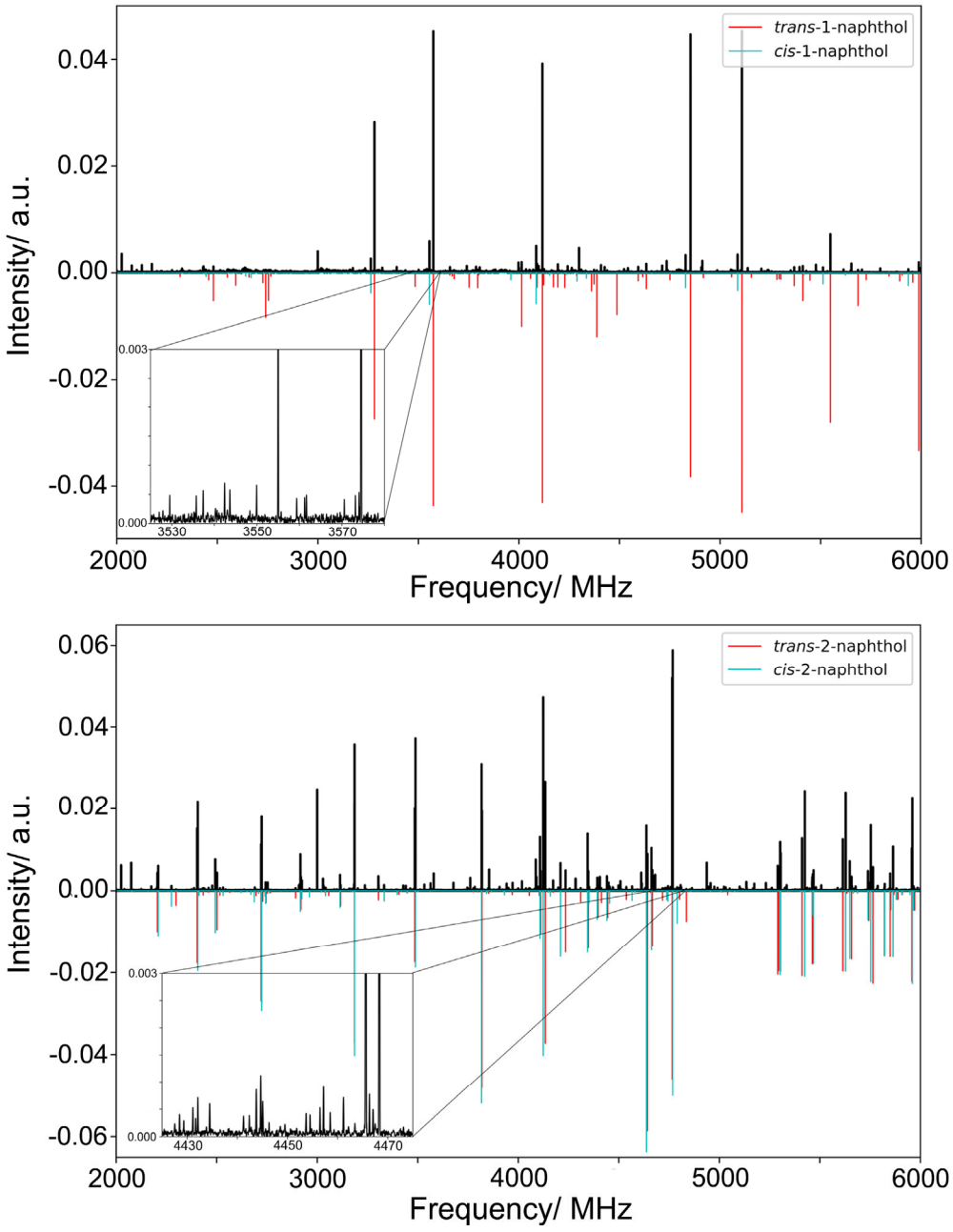


Figure S1. Broadband rotational spectra of 1-naphthol (top) and 2-naphthol (bottom). The experimental spectra are in black, while the red and blue spectra represent the simulated spectra for the *trans*- and *cis*-conformer, respectively.

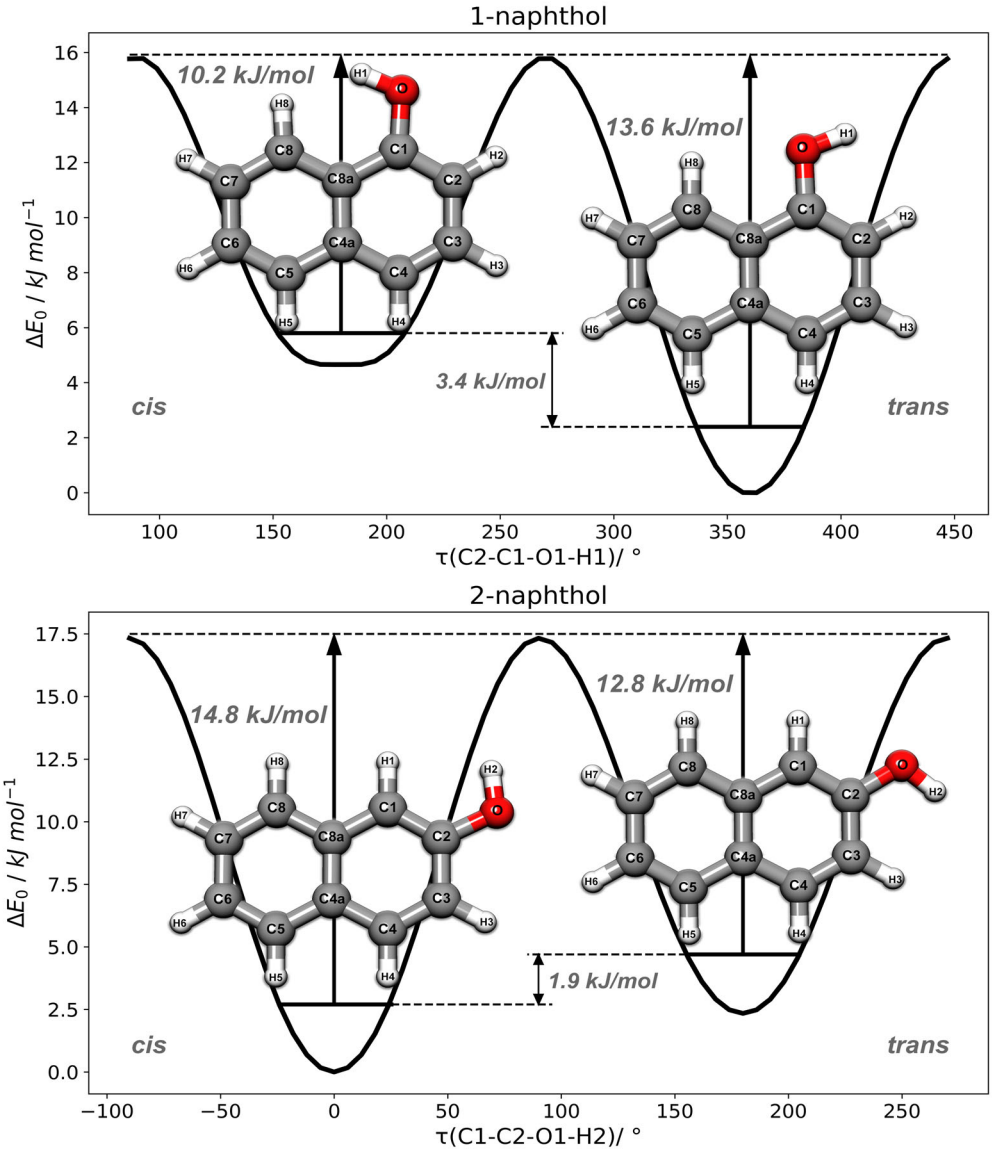


Figure S2. Potential energy curves and zero-pointed corrected *cis-trans* barriers for 1-naphthol (top) and 2-naphthol (bottom), calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Rotational Transition Frequencies

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
1	0	1	0	0	0	1837.398	-0.007
5	2	3	5	2	4	2668.247	-0.001
2	1	2	1	1	1	3263.597	-0.002
2	0	2	1	0	1	3555.025	-0.002
4	1	3	4	1	4	3960.015	0.007
2	1	1	1	1	0	4086.020	0.001
2	1	2	1	0	1	4086.800	-0.004
2	2	1	2	0	2	4235.020	-0.005
6	2	4	6	2	5	4289.167	-0.007
3	2	2	3	0	3	4659.584	0.001
3	1	3	2	1	2	4828.862	-0.002
3	0	3	2	0	2	5087.650	-0.003
4	2	3	4	0	4	5417.279	0.002
3	2	2	2	2	1	5512.212	-0.000
5	1	4	5	1	5	5623.450	0.005
3	2	1	2	2	0	5936.774	0.001
3	1	2	2	1	1	6039.545	-0.001
4	1	4	3	1	3	6341.026	-0.003
4	0	4	3	0	3	6496.777	-0.001
4	2	3	3	2	2	7254.472	0.001
5	1	5	4	1	4	7812.217	0.005
4	1	3	3	1	2	7856.723	-0.001
5	0	5	4	0	4	7884.514	0.006
6	1	6	5	1	5	9258.636	0.004
5	1	4	4	1	3	9475.640	-0.008
5	3	2	4	3	1	9809.353	0.001

Table S2. Measured frequencies of assigned rotational transitions of *cis*-1-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

Table S3. Measured frequencies of assigned rotational transitions of *trans*-1-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
1	0	1	0	0	0	1849.640	-0.001
3	2	1	3	1	2	2457.272	-0.002
3	1	2	3	1	3	2481.055	-0.000
2	2	0	2	1	1	2550.181	-0.001
1	1	1	0	0	0	2658.118	-0.001
4	2	2	4	1	3	2726.881	0.003
5	2	3	5	2	4	2740.972	0.002
7	3	4	7	3	5	2754.832	-0.001
2	0	2	1	1	1	2766.057	0.002
2	1	2	1	1	1	3281.677	-0.000

5	2	3	5	1	4	3484.039	-0.003
2	0	2	1	0	1	3574.533	-0.001
3	1	2	2	2	1	3656.192	-0.000
2	2	1	2	1	2	3678.248	-0.001
4	1	3	4	1	4	4013.698	-0.001
2	1	2	1	0	1	4090.154	-0.001
2	1	1	1	1	0	4116.887	-0.001
4	1	3	4	0	4	4123.074	0.000
4	3	1	4	2	2	4171.805	-0.002
2	2	1	2	0	2	4193.869	-0.001
3	2	2	3	1	3	4373.798	0.013
6	2	4	6	2	5	4387.622	-0.001
8	3	5	8	3	6	4487.575	-0.004
3	0	3	2	1	2	4593.506	-0.000
3	3	0	3	2	1	4615.560	0.001
3	2	2	3	0	3	4633.665	-0.001
6	2	4	6	1	5	4751.213	-0.000
3	1	3	2	1	2	4853.387	0.001
3	0	3	2	0	2	5109.127	-0.001
3	3	1	3	2	2	5155.527	-0.001
4	2	3	4	1	4	5302.553	-0.003
3	1	3	2	0	2	5369.008	0.000
4	2	3	4	0	4	5411.929	-0.002
4	3	2	4	2	3	5447.473	-0.006
3	2	2	2	2	1	5548.922	-0.000
5	1	4	5	1	5	5686.213	-0.002
5	1	4	5	0	5	5727.304	-0.003
5	3	3	5	2	4	5958.694	0.001
3	2	1	2	2	0	5988.718	0.001
4	1	3	3	2	2	6010.509	-0.001
3	1	2	2	1	1	6081.625	-0.001
7	2	5	7	2	6	6223.969	0.002
4	0	4	3	1	3	6261.220	-0.001
4	1	4	3	1	3	6370.596	-0.000
7	2	5	7	1	6	6380.619	0.009
5	2	4	5	1	5	6429.283	-0.003
5	2	4	5	0	5	6470.377	-0.001
4	0	4	3	0	3	6521.101	-0.001
2	2	1	1	1	0	6542.319	-0.002
4	1	4	3	0	3	6630.474	-0.002
5	3	3	5	1	4	6701.765	-0.001
4	3	2	4	1	3	6736.338	0.002
2	2	0	1	1	1	7084.677	0.002

4	2	3	3	2	2	7299.366	-0.000
6	1	5	6	1	6	7336.284	-0.001
4	3	2	3	3	1	7591.315	-0.002
6	2	5	6	0	6	7714.264	-0.001
4	3	1	3	3	0	7729.093	0.001
5	1	5	4	1	4	7846.416	-0.001
2	2	0	1	0	1	7893.159	0.006
4	1	3	3	1	2	7903.243	0.004
5	0	5	4	0	4	7914.702	0.002
5	1	5	4	0	4	7955.792	0.000

Table S4. Measured frequencies of assigned rotational transitions of *cis*-2-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
1	1	0	1	0	1	2209.433	0.001
2	1	1	2	0	2	2406.436	-0.001
3	0	3	2	1	2	2493.315	-0.001
3	1	2	3	0	3	2724.020	0.001
2	1	2	1	1	1	2743.806	0.002
2	0	2	1	0	1	2916.615	-0.002
2	1	1	1	1	0	3113.621	-0.001
4	1	3	4	0	4	3186.057	-0.001
4	3	1	5	2	4	3332.956	0.003
1	1	1	0	0	0	3488.881	0.001
5	1	4	5	0	5	3817.735	-0.002
3	1	3	2	1	2	4108.378	-0.001
4	0	4	3	1	3	4124.399	-0.001
6	1	5	5	2	4	4210.154	0.000
3	0	3	2	0	2	4345.026	-0.000
3	2	2	2	2	1	4393.069	-0.000
3	2	1	2	2	0	4441.112	-0.000
3	3	1	4	2	2	4566.116	-0.003
6	1	5	6	0	6	4637.525	0.002
3	1	2	2	1	1	4662.609	0.000
3	3	0	4	2	3	4744.698	0.001
2	1	2	1	0	1	4768.330	0.002
6	2	4	6	1	5	5302.829	-0.002
7	2	5	7	1	6	5305.223	-0.004
5	2	3	5	1	4	5425.342	-0.000
4	1	4	3	1	3	5464.836	0.001
8	2	6	8	1	7	5468.910	-0.003
4	2	2	4	1	3	5628.617	-0.000
7	1	6	7	0	7	5648.833	0.000
4	0	4	3	0	3	5739.464	0.001
5	0	5	4	1	4	5753.640	0.001
9	2	7	9	1	8	5822.737	-0.001
4	2	3	3	2	2	5848.006	-0.000
3	2	1	3	1	2	5864.169	0.001
4	3	2	3	3	1	5880.199	0.002
4	3	1	3	3	0	5883.163	-0.001
3	1	3	2	0	2	5960.089	-0.001
4	2	2	3	2	1	5965.948	-0.003

2	2	0	2	1	1	6085.668	0.004
4	1	3	3	1	2	6201.504	0.003
2	2	1	2	1	2	6628.296	0.001

Table S5. Measured frequencies of assigned rotational transitions of *trans*-2-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
1	1	0	1	0	1	2205.270	0.000
5	1	4	4	2	3	2298.211	-0.010
2	1	1	2	0	2	2402.909	-0.002
3	0	3	2	1	2	2501.886	0.001
2	2	0	3	1	3	2516.691	0.004
3	1	2	3	0	3	2721.618	-0.002
8	2	6	7	3	5	2728.994	0.005
2	1	2	1	1	1	2745.798	0.001
4	3	2	5	2	3	2892.790	0.004
2	0	2	1	0	1	2919.051	-0.003
7	4	3	8	3	6	2919.739	-0.003
2	1	1	1	1	0	3116.697	0.002
4	1	3	4	0	4	3185.433	-0.004
4	3	1	5	2	4	3305.007	-0.005
1	1	1	0	0	0	3485.444	0.001
5	1	4	5	0	5	3819.652	-0.009
3	1	3	2	1	2	4111.311	0.001
4	0	4	3	1	3	4134.196	0.000
6	1	5	5	2	4	4235.301	-0.008
6	4	3	7	3	4	4310.392	-0.002
3	0	3	2	0	2	4348.448	0.001
3	2	2	2	2	1	4396.869	0.000
6	4	2	7	3	5	4413.621	0.006
3	2	1	2	2	0	4445.291	0.000
3	3	1	4	2	2	4537.629	0.001
6	1	5	6	0	6	4642.702	-0.010
3	1	2	2	1	1	4667.156	0.000
3	3	0	4	2	3	4717.604	0.007
2	1	2	1	0	1	4765.619	0.003
9	2	7	8	3	6	4836.036	-0.031
6	2	4	6	1	5	5290.499	-0.006
7	2	5	7	1	6	5295.399	-0.010
5	2	3	5	1	4	5411.525	-0.003
8	2	6	8	1	7	5462.669	-0.016
4	1	4	3	1	3	5468.650	0.004
4	2	2	4	1	3	5614.197	-0.001
7	1	6	7	0	7	5657.738	-0.021
4	0	4	3	0	3	5743.622	0.001

5	0	5	4	1	4	5764.281	0.002
9	2	7	9	1	8	5821.179	-0.021
3	2	1	3	1	2	5849.785	0.001
4	2	3	3	2	2	5852.999	0.000
4	3	2	3	3	1	5885.443	0.003
4	3	1	3	3	0	5888.447	0.002
5	4	1	6	3	4	5909.708	-0.006
3	1	3	2	0	2	5957.873	0.001
4	2	2	3	2	1	5971.849	-0.004
2	2	0	2	1	1	6071.652	0.003
4	1	3	3	1	2	6207.438	0.000
7	1	6	6	2	5	6212.612	-0.008

Rotational Transition Frequencies for ^{13}C Isotopologues

Table S6. Frequencies of rotational transitions of ^{13}C isotopologues of *cis*-1-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
C1							
2	1	1	1	1	0	4069.750	0.000
3	0	3	2	0	2	5070.468	0.007
3	1	2	2	1	1	6016.128	-0.020
4	1	4	3	1	3	6318.845	-0.003
C2							
2	0	2	1	0	1	3523.205	-0.010
2	1	1	1	1	0	4041.101	-0.010
2	1	2	1	1	1	3234.272	0.001
3	1	3	2	1	2	4787.668	0.001
3	0	3	2	0	2	5048.596	-0.002
3	2	1	2	2	0	5864.477	0.000
3	1	2	2	1	1	5976.626	0.080
C3							
2	1	2	1	1	1	3235.800	-0.001
2	0	2	1	0	1	3524.722	0.000
2	1	1	1	1	0	4052.38	-0.002
3	1	3	2	1	2	4787.421	0.002
3	0	3	2	0	2	5043.366	0.000
3	2	1	2	2	0	5888.905	-0.002
3	1	2	2	1	1	5989.328	-0.000
4	0	4	3	0	3	6439.765	-0.007
C4							
2	1	2	1	1	1	3250.353	-0.010
2	0	2	1	0	1	3540.305	0.005
2	1	1	1	1	0	4079.394	-0.004
3	1	3	2	1	2	4806.556	0.009
3	0	3	2	0	2	5058.696	-0.003
3	2	2	2	2	1	5497.317	-0.002
3	1	2	2	1	1	6025.395	0.003
4	0	4	3	0	3	6456.079	-0.002
C4a							
2	1	2	1	1	1	3260.108	-0.001
2	0	2	1	0	1	3551.162	-0.002
2	1	1	1	1	0	4083.796	-0.002
3	1	3	2	1	2	4823.105	-0.007

3	2	2	2	2	1	5507.934	0.005
3	1	2	2	1	1	6035.329	-0.000
4	1	4	3	1	3	6332.783	0.005
C5							
2	1	2	1	1	1	3241.183	-0.007
2	0	2	1	0	1	3530.640	0.002
2	1	1	1	1	0	4057.083	-0.002
3	1	3	2	1	2	4795.947	0.000
3	0	3	2	0	2	5053.449	0.003
3	2	2	2	2	1	5473.714	0.008
3	1	2	2	1	1	5997.152	-0.004
4	0	4	3	0	3	6453.439	-0.002
C6							
2	0	2	1	0	1	3510.074	-0.000
2	1	1	1	1	0	4022.589	-0.001
3	1	3	2	1	2	4770.681	0.000
3	0	3	2	0	2	5032.463	-0.000
3	1	2	2	1	1	5950.630	0.001
C7							
2	1	2	1	1	1	3229.464	-0.005
2	0	2	1	0	1	3517.951	-0.003
2	1	1	1	1	0	4037.621	0.005
3	1	3	2	1	2	4779.894	0.002
3	0	3	2	0	2	5039.086	0.002
3	1	2	2	1	1	5970.399	-0.005
3	2	2	2	2	1	5450.315	0.006
C8							
2	1	2	1	1	1	3251.607	0.001
2	0	2	1	0	1	3541.851	0.003
2	1	1	1	1	0	4074.887	0.001
3	1	3	2	1	2	4810.055	0.002
3	0	3	2	0	2	5065.703	-0.001
3	2	2	2	2	1	5494.866	-0.002
3	1	2	2	1	1	6021.397	-0.000
C8a							
2	1	2	1	1	1	3263.166	0.011
2	0	2	1	0	1	3554.530	0.005
3	1	3	2	1	2	4828.066	0.006
3	0	3	2	0	2	5086.512	0.004
3	1	2	2	1	1	6039.271	-0.004
4	1	4	3	1	3	6339.789	-0.012

Table S7. Frequencies of rotational transitions of ^{13}C isotopologues of *trans*-1-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
C1							
2	1	2	1	1	1	3269.839	0.001
2	0	2	1	0	1	3561.694	0.001
2	1	1	1	1	0	4100.547	0.001
3	1	3	2	1	2	4836.292	0.001
3	0	3	2	0	2	5091.958	0.000
3	2	2	2	2	1	5527.785	-0.002
3	1	2	2	1	1	6058.148	0.000
4	1	4	3	1	3	6348.641	0.000
4	0	4	3	0	3	6499.734	0.000
C2							
2	1	2	1	1	1	3251.972	0.000
2	0	2	1	0	1	3542.433	0.000
2	1	1	1	1	0	4071.202	-0.001
3	1	3	2	1	2	4811.766	0.001
3	0	3	2	0	2	5069.925	-0.001
3	2	2	2	2	1	5492.377	-0.002
3	1	2	2	1	1	6017.818	0.002
4	1	4	3	1	3	6318.697	0.000
4	0	4	3	0	3	6474.256	0.000
C3							
2	1	2	1	1	1	3253.375	0.000
2	0	2	1	0	1	3543.672	0.001
2	1	1	1	1	0	4082.334	-0.002
3	1	3	2	1	2	4811.267	0.001
3	0	3	2	0	2	5064.260	0.000
3	2	2	2	2	1	5501.783	0.001
3	2	1	2	2	0	5939.306	0.001
3	1	2	2	1	1	6030.160	0.000
4	1	4	3	1	3	6314.995	-0.002
4	0	4	3	0	3	6463.488	0.001
C4							
2	1	2	1	1	1	3268.209	0.001
2	0	2	1	0	1	3559.391	0.000
2	1	1	1	1	0	4110.011	0.000
3	1	3	2	1	2	4830.640	0.001
3	0	3	2	0	2	5079.509	0.000
3	2	2	2	2	1	5533.661	-0.002
3	2	1	2	2	0	5987.817	0.001

3	1	2	2	1	1	6066.888	0.000
4	1	4	3	1	3	6337.451	-0.001
4	0	4	3	0	3	6479.799	0.001
C4a							
2	1	2	1	1	1	3278.135	-0.002
2	0	2	1	0	1	3570.586	-0.001
2	1	1	1	1	0	4114.671	-0.001
3	1	3	2	1	2	4847.529	0.001
3	0	3	2	0	2	5101.715	-0.001
3	2	2	2	2	1	5544.604	-0.001
3	2	1	2	2	0	5987.496	0.002
3	1	2	2	1	1	6077.354	0.000
4	1	4	3	1	3	6362.178	-0.001
4	0	4	3	0	3	6510.838	0.002
C5							
2	1	2	1	1	1	3259.082	0.001
2	0	2	1	0	1	3549.952	-0.001
2	1	1	1	1	0	4087.707	-0.001
3	1	3	2	1	2	4820.199	0.000
3	0	3	2	0	2	5074.657	0.000
3	2	2	2	2	1	5510.088	-0.002
3	2	1	2	2	0	5945.525	0.001
3	1	2	2	1	1	6038.892	0.000
4	1	4	3	1	3	6327.305	-0.001
4	0	4	3	0	3	6477.411	0.002
C6							
2	1	2	1	1	1	3240.063	0.000
2	0	2	1	0	1	3529.528	0.000
2	1	1	1	1	0	4052.926	-0.001
3	1	3	2	1	2	4795.052	0.000
3	0	3	2	0	2	5054.120	-0.001
3	2	2	2	2	1	5469.741	-0.001
3	2	1	2	2	0	5885.364	0.001
3	1	2	2	1	1	5992.234	0.000
4	1	4	3	1	3	6297.835	-0.001
4	0	4	3	0	3	6455.410	0.002
C7							
2	1	2	1	1	1	3247.407	-0.002
2	0	2	1	0	1	3537.398	0.000
2	1	1	1	1	0	4068.086	0.000
3	1	3	2	1	2	4804.307	0.000
3	0	3	2	0	2	5060.666	0.000
3	2	2	2	2	1	5486.620	0.000

3	2	1	2	2	0	5912.574	0.000
3	1	2	2	1	1	6012.090	0.000
4	1	4	3	1	3	6308.065	0.001
4	0	4	3	0	3	6461.422	-0.001
C8							
2	1	2	1	1	1	3269.650	0.000
2	0	2	1	0	1	3561.270	0.000
2	1	1	1	1	0	4105.737	0.000
3	1	3	2	1	2	4834.498	0.000
3	0	3	2	0	2	5087.039	-0.001
3	2	2	2	2	1	5531.539	0.000
3	2	1	2	2	0	5976.037	-0.001
3	1	2	2	1	1	6063.382	0.001
4	1	4	3	1	3	6344.518	0.001
4	0	4	3	0	3	6491.496	0.000
C8a							
2	1	2	1	1	1	3281.250	-0.002
2	0	2	1	0	1	3574.049	-0.001
3	1	3	2	1	2	4852.614	0.000
3	0	3	2	0	2	5108.030	0.000
3	2	2	2	2	1	5548.588	0.001
3	2	1	2	2	0	5989.143	-0.001
3	1	2	2	1	1	6081.364	0.000
4	1	4	3	1	3	6369.417	0.002
4	0	4	3	0	3	6519.511	-0.001

Table S8. Frequencies of rotational transitions of ^{13}C isotopologues of *cis*-2-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
C1							
	2	1	1	2	0	2	2389.725	0.017
	4	1	3	4	0	4	3172.361	-0.006
	1	1	1	0	0	0	3467.968	-0.005
	4	0	4	3	1	3	4128.181	0.016
	2	1	2	1	0	1	4743.803	0.000
	5	0	5	4	1	4	5752.625	-0.012
	3	1	3	2	0	2	5931.802	0.000
C2							
	4	1	3	4	0	4	3175.116	-0.010
	1	1	1	0	0	0	3484.749	-0.001
	5	1	4	5	0	5	3797.195	0.007
	4	0	4	3	1	3	4080.998	-0.009
	2	1	2	1	0	1	4757.210	0.006
	5	0	5	4	1	4	5701.479	0.007
	3	1	3	2	0	2	5942.966	-0.003
C3							
	4	1	3	4	0	4	3164.651	0.010
	1	1	1	0	0	0	3462.809	0.000
	5	1	4	5	0	5	3794.545	-0.006
	4	0	4	3	1	3	4106.272	0.000
	3	0	3	2	0	2	4319.604	0.001
	2	1	2	1	0	1	4734.495	-0.007
	3	1	3	2	0	2	5918.868	0.003
C4							
	2	1	1	2	0	2	2367.779	0.012
	4	1	3	4	0	4	3160.057	0.012
	1	1	1	0	0	0	3442.654	-0.011
	5	1	4	5	0	5	3803.144	-0.009
	4	0	4	3	1	3	4154.077	-0.003
	3	0	3	2	0	2	4334.256	-0.008
	2	1	2	1	0	1	4717.144	-0.004
	5	0	5	4	1	4	5776.494	0.008
	3	1	3	2	0	2	5903.128	0.005
C4a							
	2	1	1	2	0	2	2397.935	0.013
	3	1	2	3	0	3	2716.329	0.007
	4	1	3	4	0	4	3179.710	-0.010

	1	1	1	0	0	0	3478.498	-0.001
	4	0	4	3	1	3	4128.773	-0.006
	2	1	2	1	0	1	4756.507	-0.002
	5	0	5	4	1	4	5756.096	0.009
	3	1	3	2	0	2	5946.697	-0.005
C5								
	3	0	3	2	1	2	2486.093	-0.009
	3	1	2	3	0	3	2701.819	-0.005
	4	1	3	4	0	4	3162.801	-0.012
	1	1	1	0	0	0	3459.924	0.007
	5	1	4	5	0	5	3793.203	0.009
	4	0	4	3	1	3	4107.109	0.006
	2	1	2	1	0	1	4731.159	0.006
	5	0	5	4	1	4	5725.785	0.000
	4	0	4	3	0	3	5703.776	0.001
	3	1	3	2	0	2	5915.025	-0.007
C6								
	1	1	0	1	0	1	2214.260	0.008
	2	1	1	2	0	2	2406.207	-0.009
	3	1	2	3	0	3	2715.161	0.011
	4	1	3	4	0	4	3163.862	-0.006
	1	1	1	0	0	0	3479.655	-0.007
	5	1	4	5	0	5	3776.733	0.000
	4	0	4	3	1	3	4038.624	-0.014
	3	0	3	2	0	2	4292.009	-0.011
	2	1	2	1	0	1	4745.078	0.010
	5	0	5	4	1	4	5650.256	0.018
	3	1	3	2	0	2	5924.750	-0.005
C7								
	3	1	2	3	0	3	2705.361	-0.008
	4	1	3	4	0	4	3158.752	0.010
	1	1	1	0	0	0	3466.034	0.006
	5	1	4	5	0	5	3778.291	-0.004
	4	0	4	3	1	3	4062.688	0.001
	2	1	2	1	0	1	4732.159	0.001
	3	1	3	2	0	2	5911.975	-0.004
C8								
	3	1	2	3	0	3	2694.877	0.016
	4	1	3	4	0	4	3160.402	-0.014
	1	1	1	0	0	0	3449.820	0.001
	5	1	4	5	0	5	3797.328	0.000
	4	0	4	3	1	3	4130.874	0.008
	6	1	5	6	0	6	4623.745	0.002

	2	1	2	1	0	1	4722.426	0.001
	5	0	5	4	1	4	5751.089	-0.005
	3	1	3	2	0	2	5907.089	-0.003
C8a								
	2	1	1	2	0	2	2401.077	-0.002
	3	1	2	3	0	3	2719.289	0.008
	4	1	3	4	0	4	3182.335	-0.004
	1	1	1	0	0	0	3482.455	0.000
	4	0	4	3	1	3	4128.181	0.003
	2	1	2	1	0	1	4761.165	-0.001
	3	1	3	2	0	2	5952.084	0.000

Table S9. Frequencies of rotational transitions of ^{13}C isotopologues of *trans*-2-naphthol. $\Delta\nu^a$ is the difference between observed and calculated frequencies.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{Exp}/ MHz	$\Delta\nu^a$/ MHz
C1							
4	1	3	4	0	4	3171.826	-0.001
1	1	1	0	0	0	3464.708	0.005
2	1	2	1	0	1	4741.258	0.002
5	2	3	5	1	4	5362.168	-0.001
3	1	3	2	0	2	5929.754	-0.003
C2							
4	1	3	4	0	4	3174.484	0.002
4	0	4	3	1	3	4090.654	-0.001
2	1	2	1	0	1	4754.524	-0.011
3	1	3	2	0	2	5940.797	0.008
C3							
2	1	1	2	0	2	2383.807	-0.012
4	1	3	4	0	4	3163.991	0.003
1	1	1	0	0	0	3459.285	0.000
2	1	2	1	0	1	4731.714	0.010
5	2	3	5	1	4	5362.957	0.002
3	1	3	2	0	2	5916.555	-0.007
C4							
3	1	2	3	0	3	2687.666	0.003
1	1	1	0	0	0	3439.034	-0.010
4	0	4	3	1	3	4164.006	0.011
2	1	2	1	0	1	4714.223	-0.008
5	2	3	5	1	4	5287.898	0.003
5	0	5	4	1	4	5787.189	-0.008
3	1	3	2	0	2	5900.683	0.008
C4a							
1	1	1	0	0	0	3475.018	-0.002
5	1	4	5	0	5	3814.894	0.000
2	1	2	1	0	1	4753.735	0.004
3	1	3	2	0	2	5944.413	-0.002
C5							
3	1	2	3	0	3	2699.485	0.002
1	1	1	0	0	0	3456.552	-0.012
4	0	4	3	1	3	4116.584	-0.001
2	1	2	1	0	1	4728.508	0.009
C6							
4	1	3	4	0	4	3163.142	-0.010

1	1	1	0	0	0	3476.291	0.004
5	1	4	5	0	5	3778.448	0.007
4	0	4	3	1	3	4048.277	-0.003
2	1	2	1	0	1	4742.411	-0.003
4	2	2	4	1	3	5647.609	-0.002
3	1	3	2	0	2	5922.605	0.004
C7							
3	1	2	3	0	3	2702.907	0.006
1	1	1	0	0	0	3462.492	-0.015
5	1	4	5	0	5	3780.186	0.001
2	1	2	1	0	1	4729.345	-0.022
3	2	1	3	1	2	5832.618	0.004
3	1	3	2	0	2	5909.708	0.020
C8							
4	1	3	4	0	4	3160.054	0.000
1	1	1	0	0	0	3446.433	-0.002
2	1	2	1	0	1	4719.799	0.004
3	1	3	2	0	2	5904.970	-0.002
C8a							
3	1	2	3	0	3	2716.954	0.004
4	1	3	4	0	4	3181.767	-0.002
1	1	1	0	0	0	3479.101	-0.001
2	1	2	1	0	1	4758.540	-0.004
3	1	3	2	0	2	5949.967	0.003

Rotational and Centrifugal Distortion Constants for ^{13}C Isotopologues

Table S10. Experimental rotational constants and centrifugal distortion constants for ^{13}C Isotopologues of *cis*-1-naphthol.

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	1944.27(16)	1947.050(26)	1928.5610(90)	1919.490(25)	1940.959(41)
B / MHz	1119.6924(67)	1111.1331(17)	1115.16790(63)	1123.4788(15)	1123.9108(10)
C / MHz	710.6501(69)	707.7129(17)	706.87770(60)	708.9618(15)	712.06640(92)
Δ_J / kHz	[0.0136]	[0.0136]	[0.0136]	[0.0136]	[0.0135]
Δ_{JK} / kHz	[0.0409]	[0.0409]	[0.0409]	[0.0409]	[0.0408]
δ_J	[-0.006]	[-0.006]	[-0.006]	[-0.006]	[-0.006]
δ_K	[-0.0018]	[-0.0018]	[-0.0018]	[-0.0018]	[-0.0018]
N	4	7	8	8	7
σ / kHz	14.4	6.5	2.4	5.7	3.9
Δ / amu Å^2	-0.14(2)	-0.2920(9)	-0.2908(9)	-0.2784(9)	-0.299(7)

	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	1935.954(21)	1947.0190(65)	1938.910(22)	1932.3160(78)	1946.112(49)
B / MHz	1116.2582(12)	1105.69790(27)	1110.4222(11)	1121.63140(41)	1124.3530(31)
C / MHz	708.3112(12)	705.49660(32)	706.3493(10)	709.99190(39)	712.9342(18)
Δ_J / kHz	[0.0135]	[0.0136]	[0.0134]	[0.0134]	[0.0136]
Δ_{JK} / kHz	[0.0408]	[0.0409]	[0.0406]	[0.0404]	[0.0409]
δ_J	[-0.006]	[-0.006]	[-0.006]	[-0.006]	[-0.006]
δ_K	[-0.0019]	[-0.0018]	[-0.0019]	[-0.0018]	[-0.0018]
N	8	5	7	7	6
σ / kHz	4.1	0.7	3.8	1.4	7.8
Δ / amu Å^2	-0.294(3)	-0.1369(9)	-0.294(3)	-0.306(1)	-0.299(7)

Table S11. Experimental rotational constants and centrifugal distortion constants for ^{13}C isotopologues of *trans*-1-naphthol.

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	1938.1110(43)	1941.7080(49)	1923.4450(36)	1914.1280(21)	1935.5150(38)
B / MHz	1128.97530(26)	1120.20480(30)	1124.20450(25)	1132.72820(15)	1133.23540(27)
C / MHz	713.62120(21)	710.58920(24)	709.72380(21)	711.82680(13)	714.967100(22)
Δ_J / kHz	[0.0170]	[0.0170]	[0.0170]	[0.0170]	[0.0170]
Δ_{JK} / kHz	[0.021]	[0.021]	[0.021]	[0.021]	[0.021]
Δ_K / kHz	[0.070]	[0.070]	[0.070]	[0.070]	[0.070]
δ_J / kHz	[0.0059]	[0.0059]	[0.0059]	[0.0059]	[0.0059]
δ_K / kHz	[0.023]	[0.023]	[0.023]	[0.023]	[0.023]
N	9	9	10	10	10
σ / kHz	1.1	1.2	1.2	0.7	1.3
Δ / amu Å^2	-0.2131(6)	-0.2130(7)	-0.2118(5)	-0.2119(3)	-0.2134(6)

	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	1930.4220(34)	1941.5720(27)	1933.6590(21)	1927.0710(20)	1940.8140(36)
B / MHz	1125.50560(24)	1114.84010(18)	1119.60650(15)	1130.94520(14)	1133.66830(27)
C / MHz	711.19190(19)	708.40780(15)	709.26740(12)	712.90180(12)	715.86120(21)
Δ_J / kHz	[0.0170]	[0.0170]	[0.0170]	[0.0170]	[0.0170]
Δ_{JK} / kHz	[0.021]	[0.021]	[0.021]	[0.021]	[0.021]
Δ_K / kHz	[0.070]	[0.070]	[0.070]	[0.070]	[0.070]
δ_J / kHz	[0.0059]	[0.0059]	[0.0059]	[0.0059]	[0.0059]
δ_K / kHz	[0.023]	[0.023]	[0.023]	[0.023]	[0.023]
N	10	10	10	10	9
σ / kHz	1.1	0.9	0.7	0.7	1.1
Δ / amu Å ^{2}	-0.2127(5)	-0.2122(4)	-0.2121(3)	-0.2126(3)	-0.2128(5)

Table S12. Experimental rotational constants and centrifugal distortion constants for ^{13}C isotopologues of *cis*-2-naphthol.

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	2830.202(11)	2848.666(11)	2827.105(11)	2805.5672(74)	2839.6381(61)
B	823.2344(26)	818.8827(19)	820.0495(24)	824.2133(13)	824.2505(14)
C	637.9165(25)	636.2285(19)	635.8482(21)	637.2430(13)	639.0066(13)
Δ_J / kHz	[0.0130]	[0.0130]	[0.0130]	[0.0130]	[0.0130]
Δ_K	[0.140]	[0.140]	[0.140]	[0.140]	[0.140]
δ_J	[0.00410]	[0.00410]	[0.00410]	[0.00410]	[0.00410]
N	7	7	7	9	8
σ / kHz	10.3	6.8	5.4	8.5	7.7
Δ / amu Å^2	-0.229(3)	-0.230(3)	-0.230(3)	-0.229(2)	-0.228(2)

	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	2824.4429(43)	2847.1016(55)	2833.107(10)	2813.658(10)	2843.242(11)
B	819.89499(74)	813.1838(10)	814.9305(27)	821.9521(18)	824.5297(53)
C	635.61953(76)	632.7051(11)	633.0662(24)	636.3053(18)	639.3568(14)
Δ_J / kHz	[0.0130]	[0.0130]	[0.0130]	[0.0130]	[0.0130]
Δ_{JK}	[0.140]	[0.140]	[0.140]	[0.140]	[0.140]
δ_J	[0.00410]	[0.00410]	[0.00410]	[0.00410]	[0.00410]
N	10	11	7	9	7
σ / kHz	7.1	9.9	5.6	7.7	3.6
Δ / amu Å^2	-0.129(1)	-0.220(1)	-0.230(4)	-0.229(2)	-0.228(4)

Table S13. Experimental rotational constants and centrifugal distortion constants for ^{13}C isotopologues of *trans*-2-naphthol.

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	2826.4266(13)	2844.7845(71)	2823.0746(29)	2801.4505(33)	2835.6648(58)
B	824.12060(87)	819.7675(17)	820.9595(20)	825.1224(12)	825.0998(23)
C	638.27650(66)	636.5836(14)	636.2098(14)	637.5932(11)	639.3556(17)
Δ_J / kHz	[0.0130]	[0.0130]	[0.0130]	[0.0130]	[0.0130]
Δ_K	[0.140]	[0.140]	[0.140]	[0.140]	[0.140]
δ_K	[0.00410]	[0.00410]	[0.00410]	[0.00410]	[0.00410]
N	5	4	6	7	4
σ / kHz	2.7	6.8	7.2	7.6	2.4
Δ / amu Å^2	-0.252(1)	-0.249(2)	-0.254(2)	-0.253(2)	-0.278(3)

	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	2824.4429(63)	2843.2229(20)	2829.0763(53)	2809.7545(59)	2839.3825(11)
B	819.89499(21)	814.06279(75)	815.8434(34)	822.9028(30)	825.4301(27)
C	635.61953(16)	633.06372(69)	633.4304(28)	636.6802(17)	639.7204(15)
Δ_J / kHz	[0.0130]	[0.0130]	[0.0130]	[0.0130]	[0.0130]
Δ_{JK}	[0.140]	[0.140]	[0.140]	[0.140]	[0.140]
δ_K	[0.00410]	[0.00410]	[0.00410]	[0.00410]	[0.00410]
N	5	7	6	4	5
σ / kHz	8.4	5.5	13.8	2.4	3.0
Δ / amu Å^2	-0.2286(4)	-0.253(1)	-0.249(4)	-0.236(3)	-0.251(3)

Structural Parameters

Table S14. Substitution (r_s), semi-experimental (r_{se}), and theoretical structural parameters for *cis*-1-naphthol

Bond length	r_s	r_{se}	**MP2**	**B3LYP-D3**	***Bond angle***	r_s	r_{se}	**MP2**	**B3LYP-D3**
r(1-2)	1.340(8)	1.40(3)	1.379	1.373	**∠(2-1-8a)**	121.7(6)	121.0(24)	120.83	120.41
r(1-8a)	1.421(5)	1.38(3)	1.421	1.424	**∠(1-2-3)**	120.1(3)	119.2(22)	120.27	120.44
r(2-3)	1.421(7)	1.38(4)	1.406	1.406	**∠(2-3-4)**	120.7(1)	121.4(22)	120.62	120.15
r(4a-8a)	1.426(7)	1.41(2)	1.433	1.429	**∠(3-4-4a)**	119.3(2)	120.9(21)	120.15	121.11
r(3-4)	1.375(3)	1.35(5)	1.377	1.370	**∠(4-4a-8a)**	119.9(5)	118.2(22)	119.75	118.44
r(4-4a)	1.407(5)	1.43(6)	1.413	1.414	**∠(5-4a-8a)**	118.7(5)	120.0(19)	118.40	119.22
r(4a-5)	1.440(5)	1.53(3)	1.415	1.415	**∠(7-8-8a)**	121.3(2)	120.5(23)	120.13	120.87
r(5-6)	1.380(4)	1.21(4)	1.377	1.370	**∠(1-8a-8)**	123.9(5)	122.4(22)	121.87	122.08
r(6-7)	1.411(6)	1.50(40	1.409	1.409	**∠(4a-5-6)**	121.2(2)	120.1(21)	120.99	120.86
r(7-8)	1.383(3)	1.40(4)	1.379	1.371	**∠(5-6-7)**	120.0(1)	120.1(22)	120.18	120.01
r(8-8a)	1.437(4)	1.39(3)	1.415	1.415	**∠(6-7-8)**	120.4(1)	120.9(22)	120.55	120.58

Table S15. Substitution (r_s), semi-experimental (r_{se}), and theoretical structural parameters for *trans*-1-naphthol

Bond length	r_s	r_{se}	**MP2**	**B3LYP-D3**	***Bond angle***	r_s	r_{se}	**MP2**	**B3LYP-D3**
r(1-2)	1.364(5)	1.39(2)	1.378	1.371	**∠(2-1-8a)**	121.4(3)	120.6(6)	120.83	120.41
r(1-8a)	1.392(1)	1.46(4)	1.419	1.412	**∠(1-2-3)**	119.4(2)	120.5(5)	120.27	120.44
r(2-3)	1.423(6)	1.39(2)	1.410	1.413	**∠(2-3-4)**	120.5(1)	120.9(4)	120.62	120.15
r(4a-8a)	1.414(4)	1.39(2)	1.429	1.428	**∠(3-4-4a)**	119.4(1)	120.9(4)	120.15	121.11
r(3-4)	1.379(3)	1.36(1)	1.376	1.369	**∠(4-4a-8a)**	119.9(3)	120.7(6)	119.75	118.44
r(4-4a)	1.408(4)	1.42(2)	1.415	1.414	**∠(5-4a-8a)**	119.1(2)	117.3(6)	118.40	119.22
r(4a-5)	1.436(4)	1.41(2)	1.415	1.414	**∠(7-8-8a)**	120.7(1)	118.8(6)	120.13	120.45
r(5-6)	1.381(4)	1.37(2)	1.378	1.370	**∠(1-8a-8)**	121.9(3)	120.6(6)	121.87	122.08
r(6-7)	1.410(6)	1.42(2)	1.410	1.412	**∠(4a-5-6)**	120.8(2)	120.8(9)	120.99	120.86
r(7-8)	1.380(2)	1.37(1)	1.379	1.370	**∠(5-6-7)**	120.3(1)	120.3(4)	120.18	120.01
r(8-8a)	1.392(1)	1.38(2)	1.414	1.417	**∠(6-7-8)**	120.5(1)	120.3(5)	120.55	120.58

Table S16. Substitution (r_s), semi-experimental (r_{se}), and theoretical structural parameters for *cis*-2-naphthol

Bond length	r_s	r_{se}	**MP2**	**B3LYP-D3**	***Bond angle***	r_s	r_{se}	**MP2**	**B3LYP-D3**
r(1-2)	1.398(6)	1.368(4)	1.377	1.371	**∠(2-1-8a)**	118.8(3)	120.3(4)	120.353	120.52
r(1-8a)	1.403(9)	1.45(1)	1.414	1.415	**∠(1-2-3)**	121.6(1)	121.2(4)	120.623	120.59
r(2-3)	1.378(9)	1.409(6)	1.411	1.413	**∠(2-3-4)**	119.9(1)	119.7(3)	120.031	119.88
r(3-4)	1.375(3)	1.356(7)	1.374	1.366	**∠(3-4-4a)**	120.7(1)	121.8(5)	121.034	121.36
r(4-4a)	1.420(4)	1.421(7)	1.416	1.416	**∠(4-4a-8a)**	118.6(4)	118.5(4)	118.646	118.49
r(4a-5)	1.426(3)	1.414(7)	1.414	1.413	**∠(5-4a-8a)**	119.9(4)	118.8(4)	119.230	119.14
r(4a-8a)	1.404(4)	1.422(4)	1.429	1.426	**∠(1-8a-8)**	121.3(2)	121.9(4)	121.912	122.25
r(5-6)	1.384(3)	1.370(4)	1.378	1.371	**∠(4a-5-6)**	120.2(2)	120.9(6)	120.670	120.91
r(6-7)	1.378(4)	1.411(5)	1.411	1.410	**∠(5-6-7)**	120.2(1)	119.9(3)	120.19	119.98
r(7-8)	1.378(2)	1.366(5)	1.379	1.371	**∠(6-7-8)**	120.7(1)	120.3(3)	120.366	120.53
r(8-8a)	1.436(7)	1.398(5)	1.415	1.415	**∠(7-8-8a)**	120.5(3)	120.4(4)	120.775	120.85

Table S17. Substitution (r_s), semi-experimental (r_{se}), and theoretical structural parameters for *trans*-2-naphthol

Bond length	r_s	r_{se}	**MP2**	**B3LYP-D3**	***Bond angle***	r_s	r_{se}	**MP2**	**B3LYP-D3**
r(1-2)	1.386(5)	1.40(4)	1.376	1.371	**∠(2-1-8a)**	119.2(3)	117(3)	120.269	119.267
r(1-8a)	1.393(6)	1.22(7)	1.412	1.415	**∠(1-2-3)**	120.0(2)	121(2)	120.471	120.999
r(2-3)	1.402(8)	1.42(2)	1.411	1.413	**∠(2-3-4)**	119.9(1)	120(2)	120.286	119.919
r(3-4)	1.382(3)	1.32(3)	1.377	1.366	**∠(3-4-4a)**	120.5(1)	122(2)	120.817	120.574
r(4-4a)	1.429(4)	1.50(3)	1.414	1.416	**∠(4-4a-8a)**	118.4(4)	112(7)	118.578	117.748
r(4a-5)	1.414(3)	1.49(3)	1.414	1.413	**∠(5-4a-8a)**	120.2(3)	124(8)	119.323	121.297
r(4a-8a)	1.411(3)	1.48(4)	1.430	1.426	**∠(1-8a-8)**	121.3(2)	119(3)	121.763	121.125
r(5-6)	1.380(3)	1.20(2)	1.378	1.371	**∠(4a-5-6)**	119.5(2)	123(3)	120.611	119.930
r(6-7)	1.411(4)	1.50(1)	1.411	1.410	**∠(5-6-7)**	120.1(1)	120(2)	120.204	120.128
r(7-8)	1.386(2)	1.37(2)	1.378	1.371	**∠(6-7-8)**	120.4(1)	121(2)	120.406	120.504
r(8-8a)	1.435(5)	1.47(4)	1.416	1.415	**∠(7-8-8a)**	120.9(2)	121(3)	120.796	120.757

Data from AIMA11 QTAIM Calculations

Table S18. Compilation of results from QTAIM calculations with the AIMA11 program for *cis*- and *trans*-1-naphthol. All energies are in kcal/mol.

	***trans*-1-naphthol**	***cis*-1-naphthol**	**Δ (*trans* – *cis*)**
***ab initio* energy**	-2.8948295089E+05	-2.8948181925E+05	-1.1316397750
C-skeleton[a]	-2.3893145383E+05	-2.3892238752E+05	-9.0663095050
C-skeleton + O-atom	-2.8655709929E+05	-2.8654901952E+05	-8.0797621625
Ring H-atoms	-2.6895304201E+03	-2.6952714802E+03	5.7410600680
All H-atoms	-2.9258579782E+03	-2.9328113415E+03	6.9533632738
Total AIM energy	-2.8948295726E+05	-2.8948183087E+05	-1.1263938750
av H-atoms (not OH, H-H contact)	-3.8498116888E+02	-3.8338342209E+02	-1.5977467875
(av H-atoms) – (H-H contact)	-5.3377620175	11.587525563	
H12 (C-H … H)	-3.7964340686E+02	-3.9497094765E+02	15.327540793
H19 (O-H … H)	-2.3632755809E+02	-2.3753986129E+02	1.2123032057
O18	-4.7625645456E+04	-4.7626632003E+04	0.98654734250
q(H12)[b] **/ e**	0.056720892460	-0.0046104091000	
q(H19) / e	0.57607206328	0.57506762675	
C4-C11-O18 angle / °	116.469	121.826	
H … H distance / Å	2.27396	1.87624	
Bond Path Length / Å		2.098360697	
C4-C11-O18-H19 / °	-180	6.462	

[a]The energies are the scaled electronic kinetic energies of the atoms ("K_scaled" in AIMAll), an approximation to the virial-based total energies. [b]Net charge of the atom in units of the electron charge.

Table S19. Electron density derived properties related to the H12-H19 close contact in *cis*-1-naphthol at different levels of theory.

	B3LYP	**wB97XD**	**MP2**
BCP ρ [e/bohr^3] [a]	0.01496	0.01534	0.01581
BCP $\Delta^2\rho$ [e/bohr^5] [b]	0.05825	0.05530	0.05783
BCP H [hartree/bohr^3] [c]	-0.002514	-0.001843	-0.001549
BCP ε [d]	1.0898	0.9651	1.0868
RCP ρ [e/bohr^3]	0.01456	0.01581	0.01539
RCP $\Delta^2\rho$ [e/bohr^5]	0.06948	0.07003	0.07061
q(H12) [e] [e]	-0.004610	-0.014655	0.006553
q(H19) [e]	0.5751	0.5996	0.6135
IBSI [f]	0.031	0.036	0.045

[a] Electron density; [b] Laplacian of electron density; [c] Total energy density; [d] Bond ellipticity $\varepsilon=(\lambda_1/\lambda_2)-1$; [e] Net charge of atom; Intrinsic Bond Strength Index.

Semi-Experimental Rotational Constants for ^{12}C and ^{13}C Isotopologues

Table S20. Experimental, semi-experimental, and ab initio rotational constants and inertial defects for all four conformers of naphthol

***cis*-1-naphthol**	**Experiment**	**Semi-Experiment**	**B3LYP-D3**
A / MHz	1947.51310	1962.355	1959.859
B / MHz	1124.30739	1130.679	1130.8340
C / MHz	713.09734	717.334	717.128
Δ_I / amu Å^2	-0.2925	0.0175	-0.0468
***trans*-1-naphthol**			
A / MHz	1942.10150	1955.784	1955.174
B / MHz	1133.62357	1141.283	1139.056
C / MHz	716.01804	720.758	719.744
Δ_I / amu Å^2	-0.2124	-0.0417	-0.0003
***cis*-2-naphthol**			
A / MHz	2849.15630	2870.909	2870.704
B / MHz	824.63286	829.670	828.986
C / MHz	639.7240	643.692	643.236
Δ_I / amu Å^2	-0.2364	-0.0415	-0.0001
***trans*-2-naphthol**			
A / MHz	2845.35700	2867.769	2868.659
B / MHz	825.53621	830.467	829.642
C / MHz	640.08728	644.012	643.528
Δ_I / amu Å^2	-0.2510	-0.0398	-0.0000

Table S21. Semi-experimental rotational constants and inertial defects for ^{13}C isotopologues of *cis*-1-naphthol

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	1959.089	1961.892	1943.403	1934.332	1955.801
B	1126.065	1117.505	1121.539	1129.851	1130.283
C	714.889	711.951	711.116	713.200	716.304
Δ / amu Å^2	0.167	0.014	0.024	0.042	0.010
	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	1950.796	1961.861	1953.752	1947.158	1960.954
B	1122.630	1112.070	1116.794	128.003	1130.725
C	712.549	709.734	710.587	714.230	717.172
Δ / amu Å^2	0.018	0.017	0.016	0.009	0.011

Table S22. Semi-experimental rotational constants and inertial defects for ^{13}C isotopologues of *trans*-1-naphthol

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	1951.794	1955.391	1937.120	1927.810	1949.200
B	1120.205	1127.864	1131.860	1140.390	1140.890
C	710.5892	715.392	714.464	716.567	719.707
Δ / amu Å^2	-0.042	-0.041	-0.038	-0.038	-0.042
	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	1944.105	1955.260	1947.340	1940.750	1954.500
B	1133.165	1122.500	1127.270	1138.600	1141.330
C	715.932	713.148	714.007	717.642	720.601
Δ / amu Å^2	-0.040	-0.039	-0.039	-0.040	-0.042

Table S23. Semi-experimental rotational constants and inertial defects for ^{13}C isotopologues of *cis*-2-naphthol

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	2851.955	2870.419	2848.858	2827.320	2861.391
B	828.271	823.919	825.086	829.250	829.287
C	641.884	640.196	639.816	641.211	642.974
Δ / amu Å^2	-0.029	-0.036	-0.032	-0.025	-0.032
	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	2846.196	2868.854	2854.860	2835.411	2864.995
B	824.931	818.221	819.967	826.989	829.566
C	639.587	636.672	637.034	640.273	643.324
Δ / amu Å^2	-0.030	-0.035	-0.033	-0.028	-0.032

Table S24. Semi-experimental rotational constants and inertial defects for ^{13}C isotopologues of *trans*-2-naphthol

	^{13}C-1	**^{13}C-2**	**^{13}C-3**	**^{13}C-4**	**^{13}C-4a**
A / MHz	2848.8383	2867.1962	2845.486	2823.8622	2858.0765
B	829.05174	824.69864	825.8906	830.05354	830.03094
C	642.20149	640.50859	640.1348	641.51819	643.28059
Δ / amu Å^2	-0.037	-0.040	-0.034	-0.032	-0.065
	^{13}C-5	**^{13}C-6**	**^{13}C-7**	**^{13}C-8**	**^{13}C-8a**
A / MHz	2846.8546	2865.6346	2851.488	2832.166	2861.7942
B	824.82613	818.99393	820.77454	827.8339	830.36124
C	639.54452	636.98871	637.35539	640.6052	643.64539
Δ / amu Å^2	-0.014	-0.043	-0.036	-0.017	-0.038

Non-Covalent Interaction (NCI) Plots

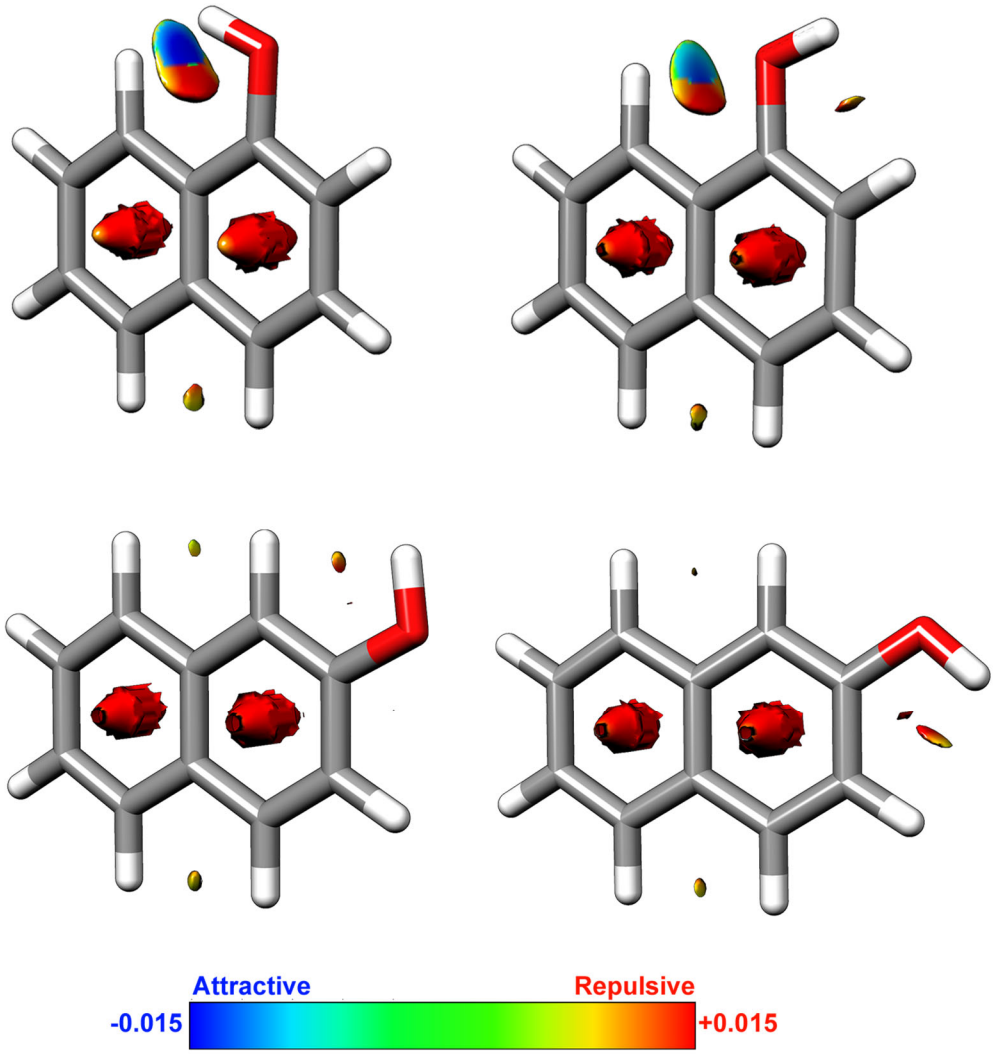


Figure S3. Results from non-covalent interactions (NCI) analyses of the four experimentally assigned naphthol conformers (s=0.75). The 3D isosurfaces presented contain attractive (blue) and repulsive (red) regions. See, however, the text for the close-contact H-atoms in *cis*-1-naphthol.

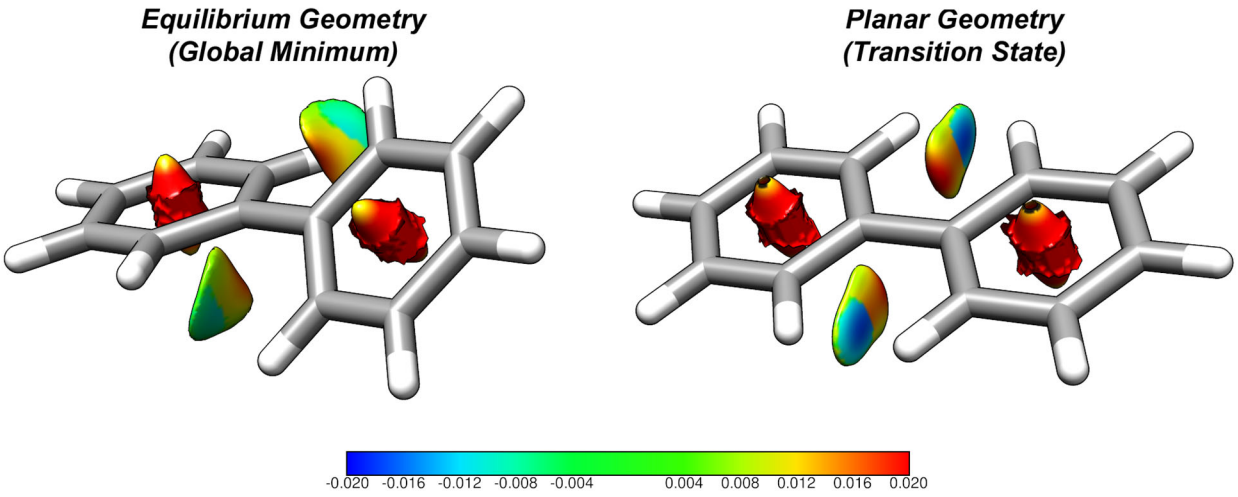


Figure S4. Results from non-covalent interactions (NCI) analyses of biphenyl. The 3D isosurfaces presented contain attractive (blue) and repulsive (red) regions.

Local Mode Analyses

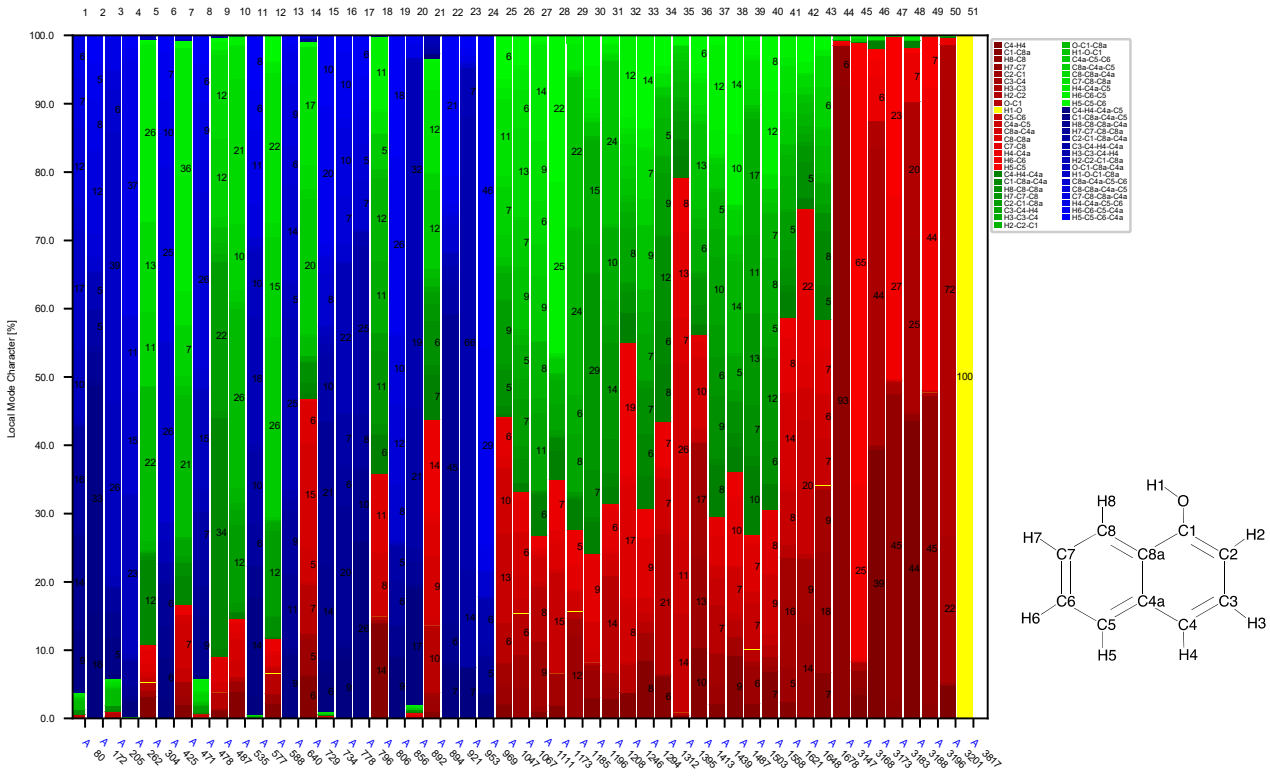


Figure S5. Decomposition of normal vibrational modes into %LVM contributions for *cis*-1-naphthol (B3LYP-D3(BJ)). % Contribution from O-H local stretching mode to O-H normal mode (3817 cm^{-1}) is shown in yellow. Numbering of local modes are as in the scheme.

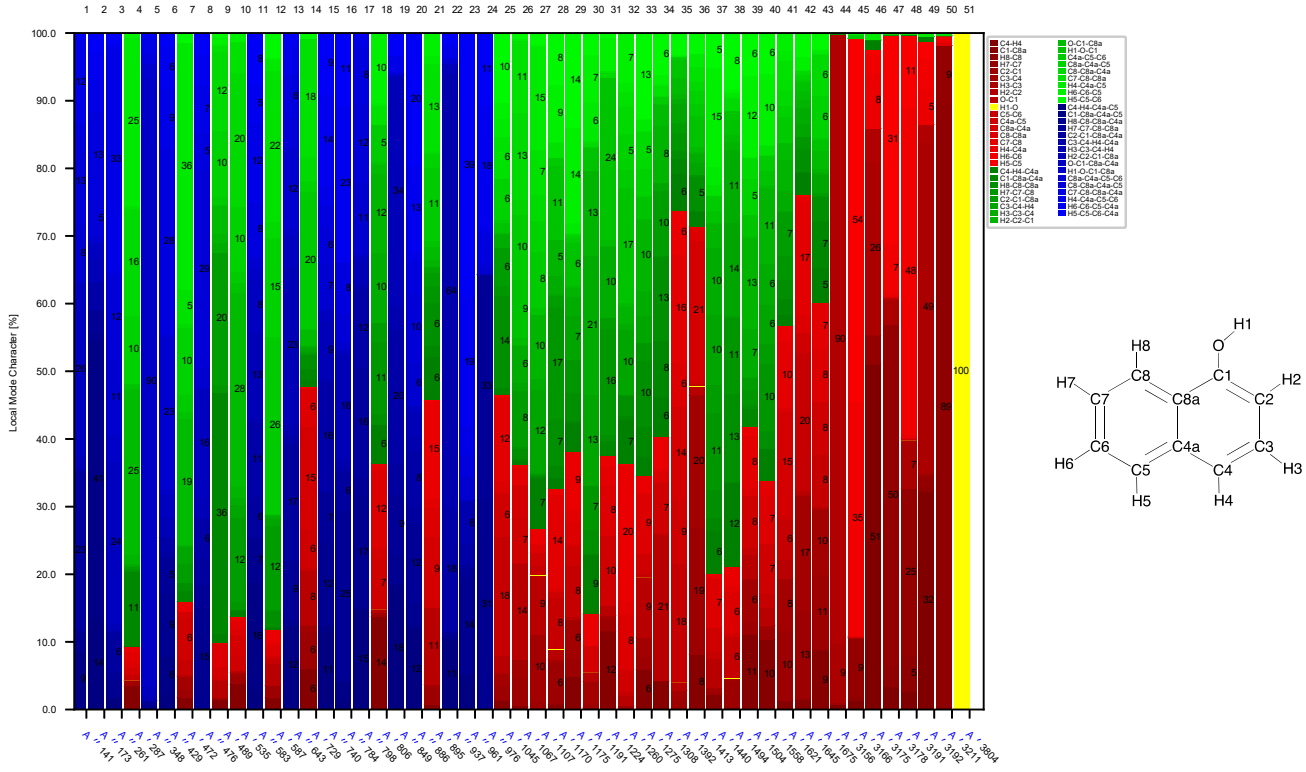


Figure S6. Decomposition of normal vibrational modes into %LVM contributions for *trans*-1-naphthol (B3LYP-D3(BJ)). % Contribution from O-H local stretching mode to O-H normal mode (3804 cm^{-1}) is shown in yellow. Numbering of local modes are as in the scheme.

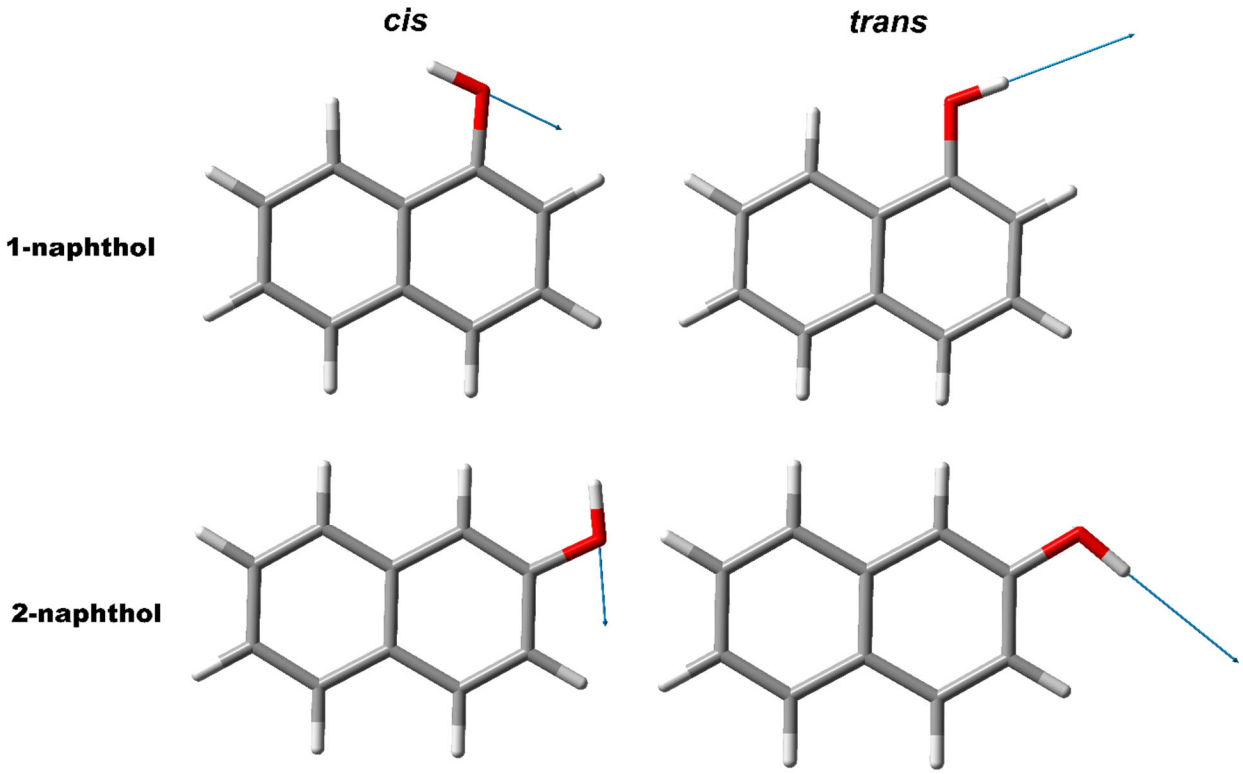


Figure S7. Vibrational displacement vectors for the O-H stretching vibration

Table S25. [b] For each local mode, the local mode force constant k[a] (mDyn/Å for stretching and mDyn.Å/Rad^2 for bending vibrations) and local mode frequency ω[a] (cm^{-1}) are given. Reported values are for MP2/aug-cc-pVTZ calculations followed by values for B3LYP-D3(BJ)/def2-TZVP calculations in parentheses.

	***cis*-1-naphthol**		***trans*-1-naphthol**	
Parameter[b]	**k[a]**	**ω[a]**	**k[a]**	**ω[a]**
O1-H1	8.169 (8.085)	3824.2 (3804.5)	8.097 (8.057)	3807.2 (3797.8)
C1-O1	5.825 (5.609)	1200.8 (1178.3)	5.790 (5.673)	1197.3 (1185.0)
H1-O1-C1	0.743 (0.735)	1254.1 (1248.9)	0.745 (0.749)	1253.1 (1258.6)
O1-C1-C2	1.716 (1.694)	774.6 (772.9)	1.756 (1.804)	798.1 (810.7)
O1-C1-C3	1.771 (1.728)	787.2 (777.0)	1.727 (1.777)	762.8 (774.6)
	***cis*-2-naphthol**		***trans*-2-naphthol**	
	k[a]	**ω[a]**	**k[a]**	**ω[a]**
O1-H1	8.091 (8.035)	3805.8 (3792.6)	8.143 (8.070)	3818.0 (3800.9)
C1-O1	5.851 (5.735)	1203.6 (1191.5)	5.824 (5.709)	1200.7(1188.8)
H1-O1-C1	0.749 (0.754)	1256.4 (1262.6)	0.754 (0.759)	1261.4 (1267.0)
O1-C1-C2	1.599 (1.647)	763.1(776.3)	1.540 (1.593)	735.9 (751.6)
O1-C1-C3	1.548 (1.600)	723.3 (736.4)	1.597 (1.646)	748.1 (759.2)

	References					
	water		**methanol**		**2-propanol**	
	k[a]	**ω[a]**	**k[a]**	**ω[a]**	**k[a]**	**ω[a]**
O1-H1	8.348 (8.151)	3865.9 (3819.9)	8.288 (8.091)	3851.9 (3805.9)	8.158 (8.045)	3821.5 (3795.0)
C1-O1			4.775 (4.628)	1087.3 (1070.4)	4.417 (4.220)	1045.6 (1022.1)
H1-O1-C1	-	-	0.731 (0.736)	1241.6 (1245.2)	0.718 (0.723)	1227.0 (1232.1)
O1-C1-C2	-	-	-	-	1.280 (1.301)	609.3 (613.6)
O1-C1-C3	-	-	-	-	1.323 (1.340)	608.8 (613.0)
	propen-2-ol				**phenol**	
	k[a]	**ω[a]**			**k[a]**	**ω[a]**
O1-H1	8.221 (8.120)	3836.4 (3812.7)			8.132 (8.054)	3815.5 (3797.1)
C1-O1	5.572 (5.426)	1174.5 (1159.0)			5.838 (5.729)	1202.2 (1190.9)
H1-O1-C1	0.762 (0.768)	1269.9 (1275.3)			0.751 (0.755)	1258.4 (1264.0)
O1-C1-C2	1.408 (1.461)	668.6 (680.3)			1.599 (1.642)	756.0 (767.0)
O1-C1-C3	1.375 (1.428)	708.4 (724.7)			1.543 (1.590)	729.8 (743.0)

Inertial Defect Differences

Table S26. Inertial defects and defect differences between calculated and experimental defect values for all four naphthol conformers. [a]The experimental inertial defect values. [b]The calculated inertial defect values obtained from summing Oka's equation over the lowest out-of-plane vibrational modes. [c]Moment of inertia values from the fit of Jahn et al..

	[a]Δ_e / amu Å^2	[b]$\Delta_{I=2}$/ amu Å^2	$\Delta_e - \Delta_{I=2}$ / amu Å^2	[c]$(I_{cc})^{1/2}$ / amu$^{0.5}$ Å	$(I_{cc})^{1/2}$ / amu$^{0.5}$ Å
***cis*-1-naphthol**	-0.2925	-0.62	0.33	30.8	26.6
***trans*-1-naphthol**	-0.2124	-0.43	0.22	20.6	26.6
***cis-2*-naphthol**	-0.2365	-0.46	0.23	21.5	28.1
***trans-2*-naphthol**	-0.251	-0.46	0.21	19.6	28.1

Table S27. The calculated inertial defect values obtained from summing Oka's equation over the lowest out-of-plane vibrational modes.

	[a]$\Delta_{I=1}$/ amu Å^2	[b]$\Delta_{1=2}$/ amu Å^2	[c]$\Delta_{I=3}$/ amu Å^2	[d]$\Delta_{I=4}$/ amu Å^2	[e]$\Delta_{I=5}$/ amu Å^2
***cis* 1-naphthol**	-0.42	-0.62	-0.78	-0.91	-0.99
***trans* 1-naphthol**	-0.24	-0.43	-0.56	-0.68	-0.78
***cis 2*-naphthol**	-0.28	-0.46	-0.57	-0.67	-0.74
***trans 2*-naphthol**	-0.28	-0.46	-0.57	-0.68	-0.76

[a]Summed over the lowest out-of-plane modes, [b]two lowest out-of-plane modes, [c]three lowest out-of-plane modes, [d]four lowest out-of-plane modes, [e]five lowest out-of-plane modes.

Table S28. Inertial defect differences between the experiment and calculated inertial defect values summed over Oka's equation.

	$\Delta_e - \Delta_{I=1}$ / amu Å^2	$\Delta_e - \Delta_{I=2}$ / amu Å^2	$\Delta_e - \Delta_{I=3}$ / amu Å^2	$\Delta_e - \Delta_{I=4}$ / amu Å^2	$\Delta_e - \Delta_{I=5}$ / amu Å^2
***cis* 1-naphthol**	0.13	0.33	0.49	0.62	0.70
***trans* 1-naphthol**	0.03	0.22	0.35	0.47	0.57
***cis 2*-naphthol**	0.04	0.23	0.34	0.43	0.51
***trans 2*-naphthol**	0.03	0.21	0.32	0.43	0.52

Table S29. Lowest out-of-plane modes and the theoretical and experimental inertial defects from previous work and for the four isomers of naphthol.

	Δ_{exp} / amu Å^2	Lowest out-of-plane (l=1) / cm^{-1}	(l=2)	(l=3)	(l=4)	(l=5)	$(I_{cc})^{1/2}$	Rings
Quinoline[a]	-0.13405	173[g]	182[g]	-	-	-	23.6	2
Isoquinoline[a]	-0.13485	171[g]	185[g]	-	-	-	23.8	2
Phthalazine[b]	-0.154	170[g]	177[g]	-	-	-	23.7	2
Quinazoline[b]	-0.136	172[g]	180[g]	-	-	-	23.5	2
Quinoxaline[b]	-0.119	173[g]	184[g]	-	-	-	23.3	2
Acridine[c]	-0.4363	93[g]	114[g]	238[g]	-	-	36.3	3
Phenanthroline[c]	-0.4423	98[g]	104[g]	238[g]	-	-	34.4	3
Phenanthridine[c]	-0.4576	99[g]	104[g]	233[g]	-	-	34.9	3
5,6-Benzoquinoline[d]	-0.471	93[g]	100[g]	222[g]	-	-	34.9	3
7,8-Benzoquinoline[d]	-0.413	98[g]	115[g]	228[g]	-	-	34.6	3
Benzanthrone[e]	-1.054	45[g]	94[g]	135[g]	165[g]	-	43.9	4
Naphthalene[f]	-0.137	172	186	395	480	487	23.9	2
cis-1-naphthol	-0.2925	80	172	205	262	425	26.6	2
trans-1-naphthol	-0.2124	141	173	261	287	348	26.6	2
cis-2-naphthol	-0.2365	122	182	300	366	411	28.1	2
trans-2-naphthol	-0.251	122	181	299	307	411	28.1	2

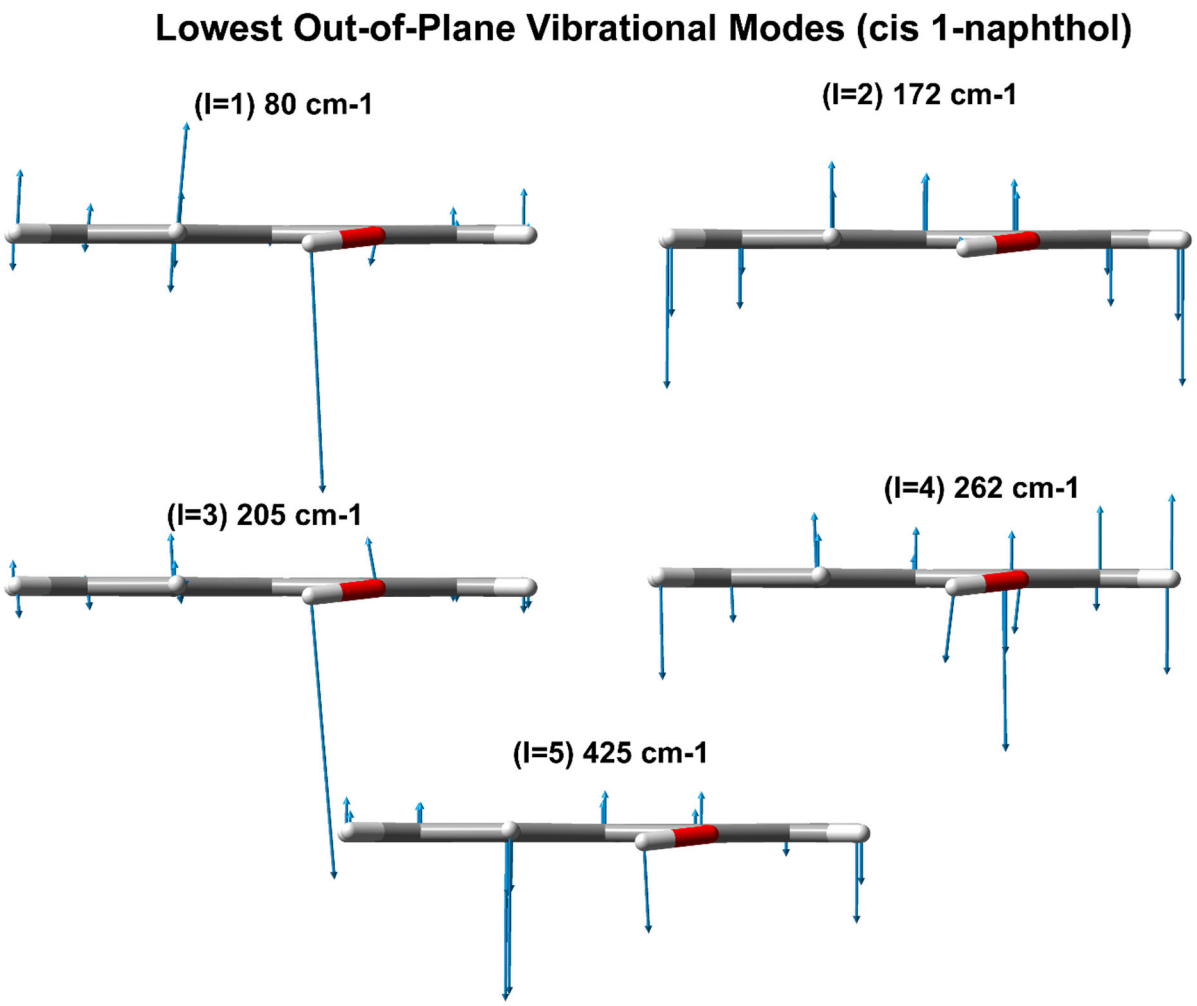
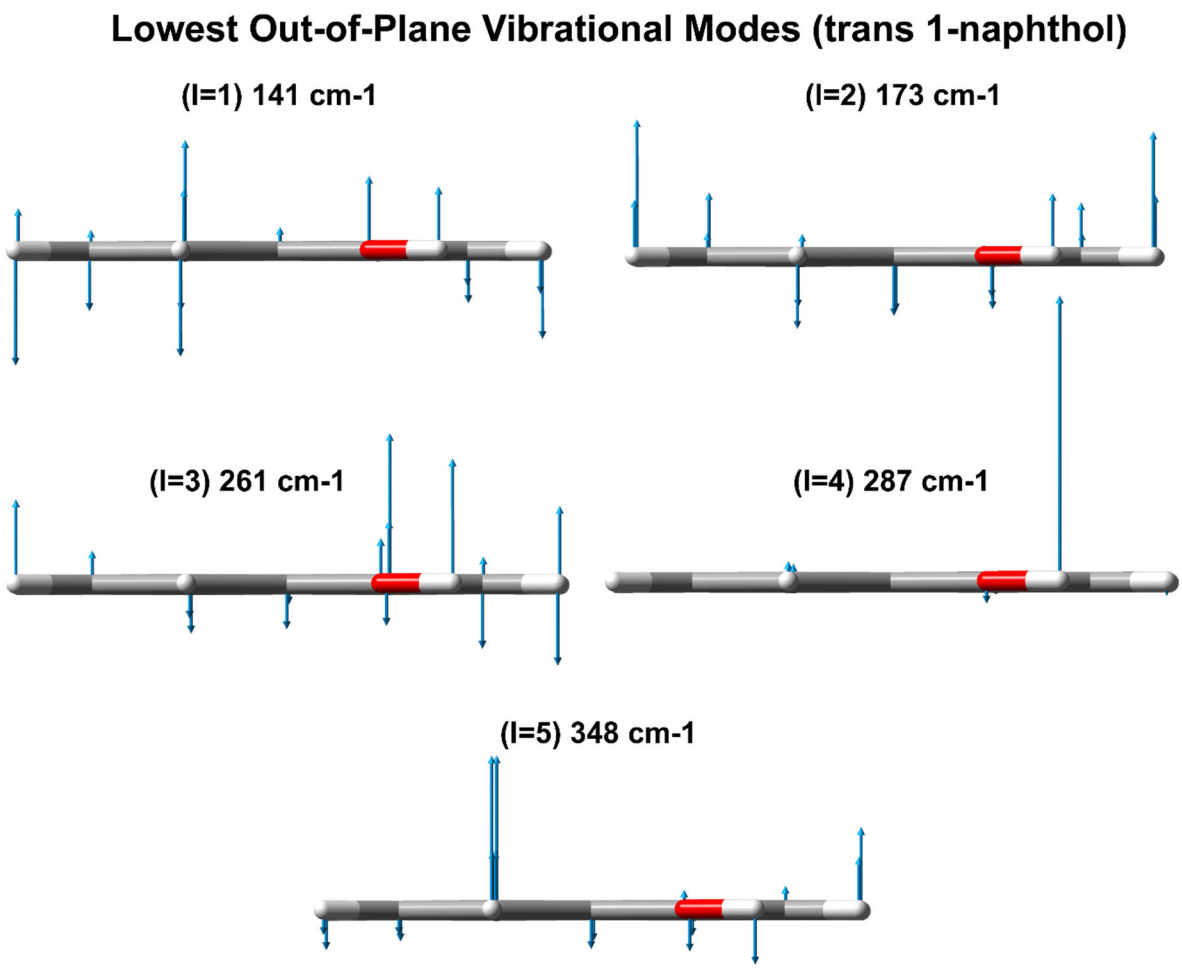
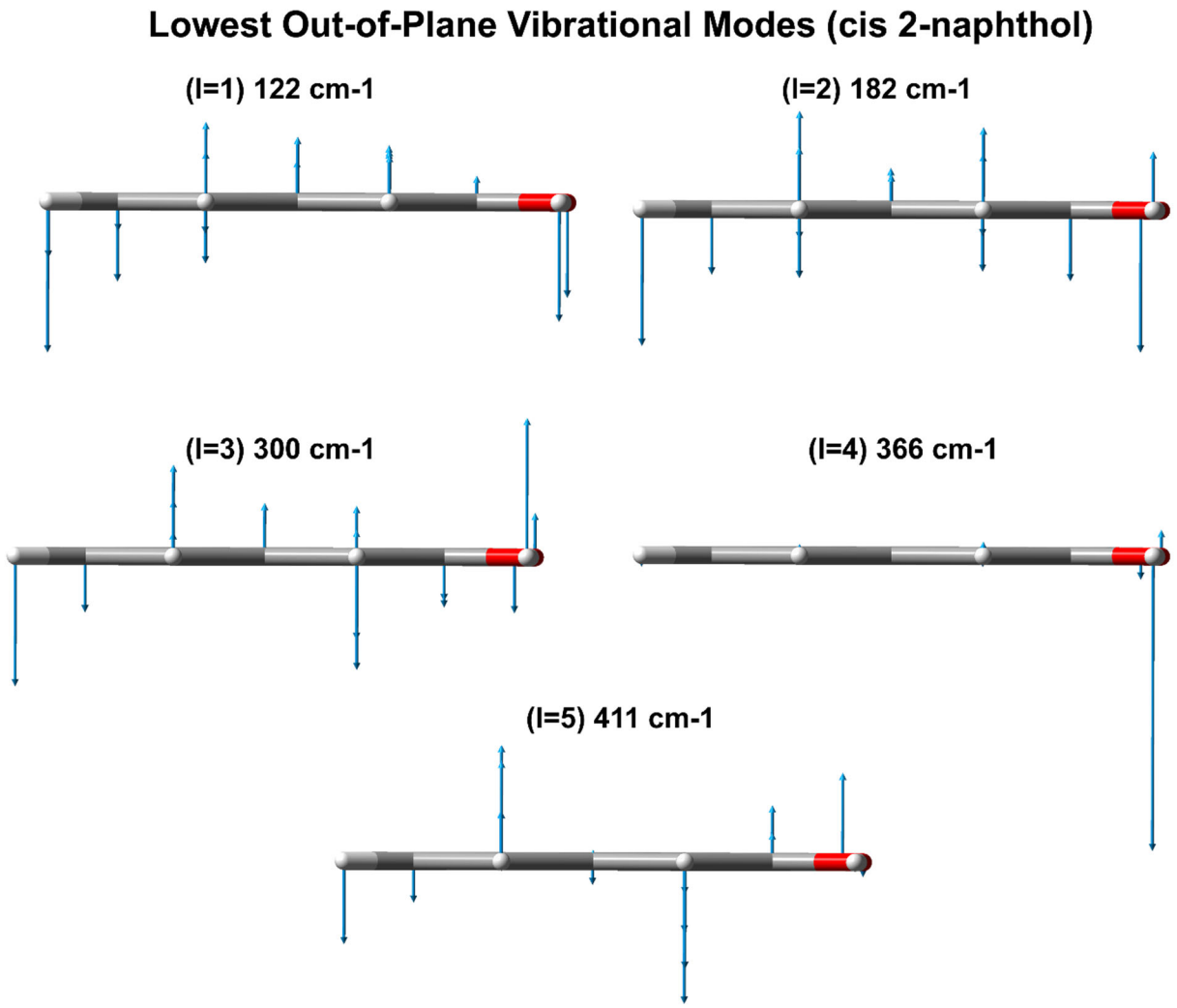


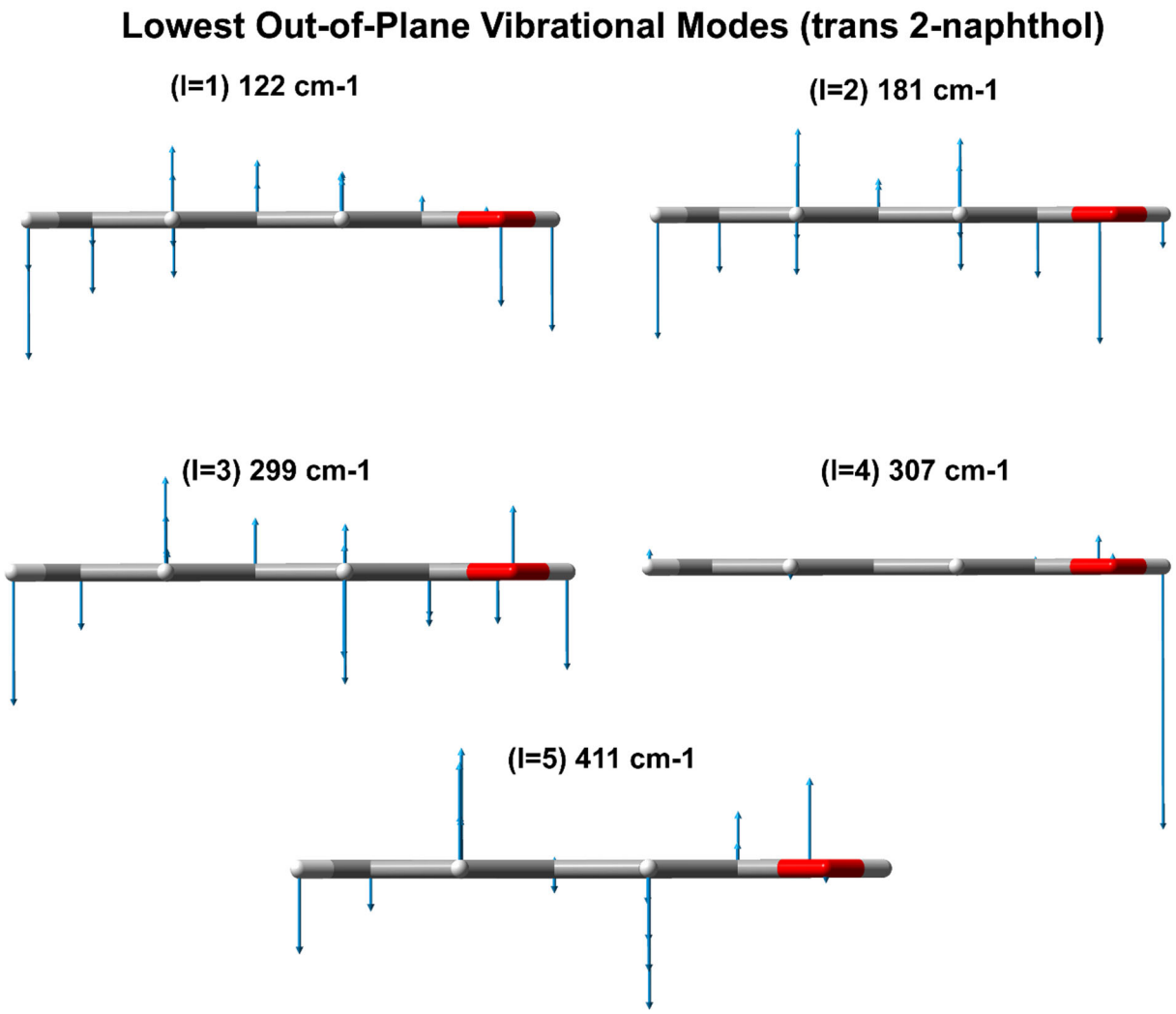
Figure S8. Lowest out-of-plane vibrational modes, with their respective displacement vectors, for *cis*-1-naphthol calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.



Figures S9. Lowest out-of-plane vibrational modes, with their respective displacement vectors, for *trans*-1-naphthol calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.



Figures S10. Lowest out-of-plane vibrational modes, with their respective displacement vectors, for *cis*-2-naphthol calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.



Figures S11. Lowest out-of-plane vibrational modes, with their respective displacement vectors, for *trans*-2-naphthol calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

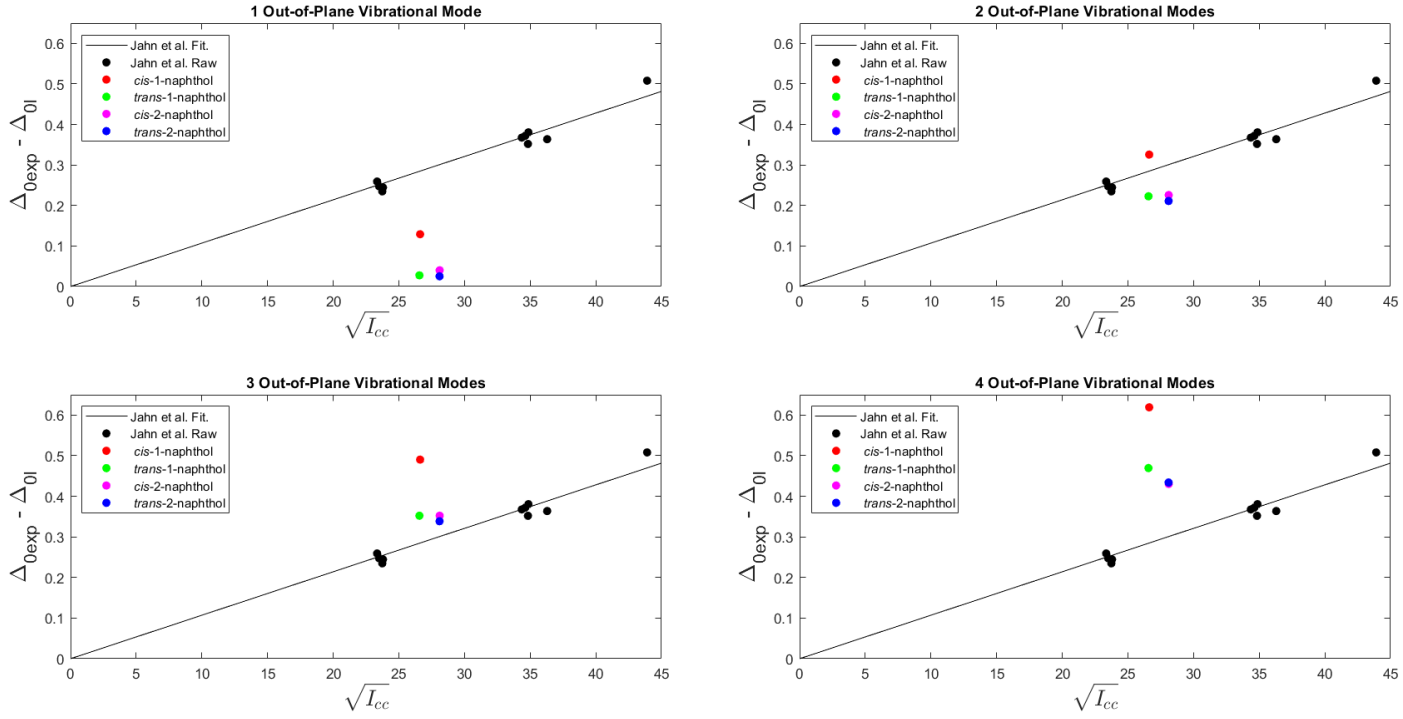


Figure S12. Inertial defect differences for the four isomers of naphthol compared to the results of Jahn et al. The four plots contain different numbers of out-of-plane vibrations used to sum over Oka's equation.

Charge Model 5 Analysis

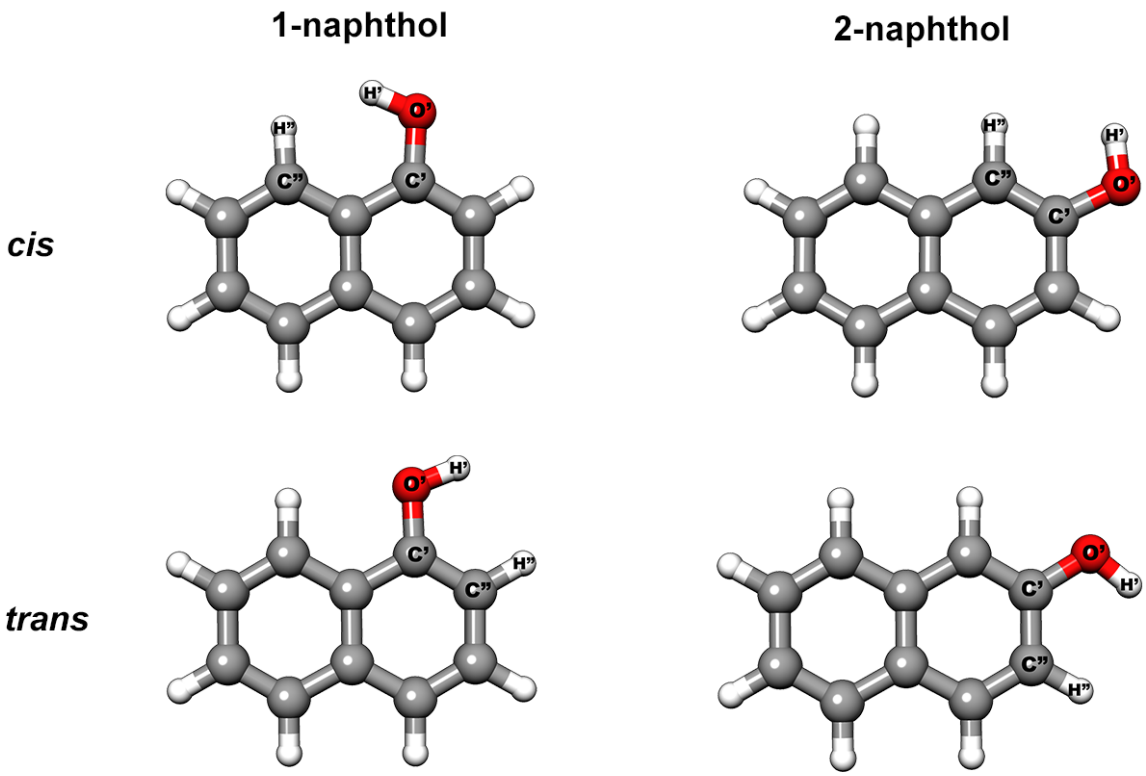


Figure S13. Atom labelling used in the descriptions of the H-H interactions

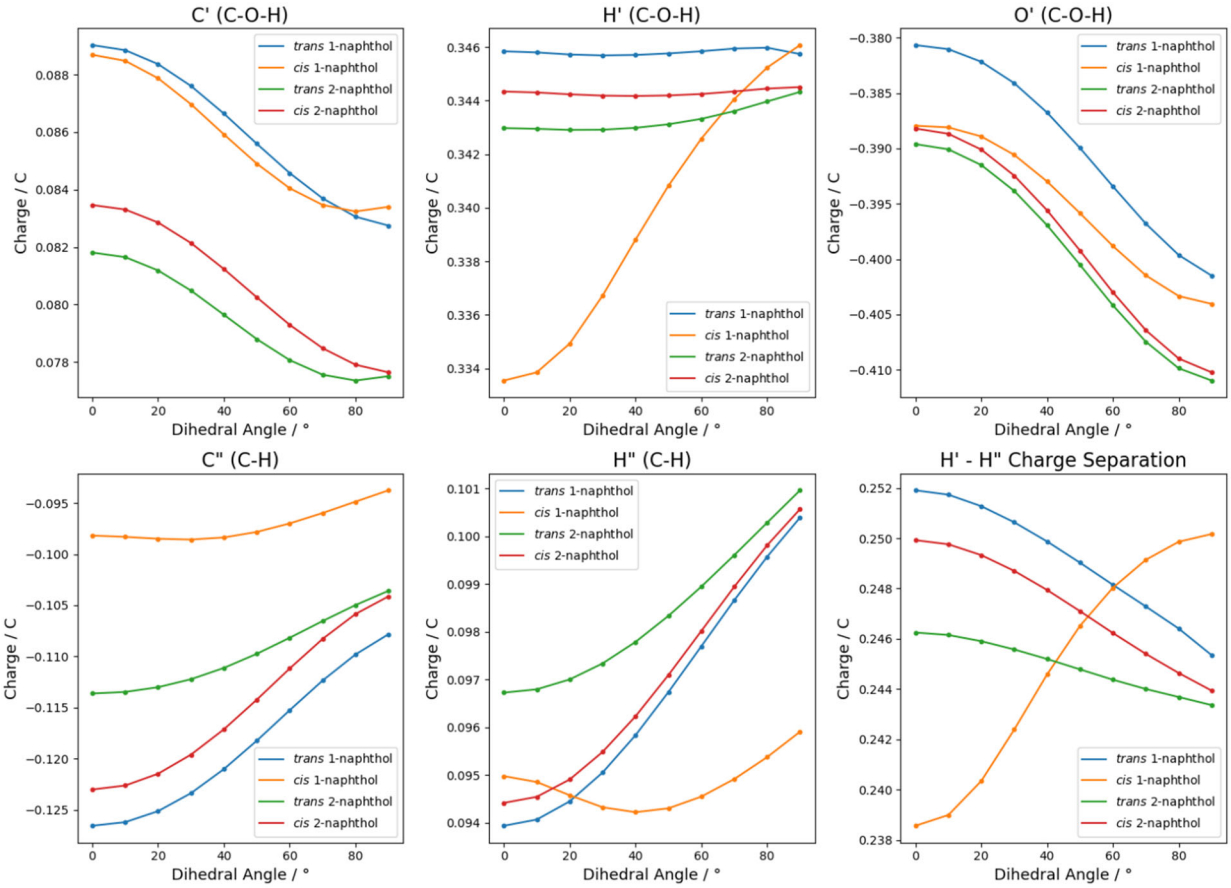


Figure S14. Charge Model 5 (CM5) charges for atoms involved in the H-H interaction for all four naphthol isomers. The H'-H" charge separation was calculated by subtracting the H" charge from the H' charge.

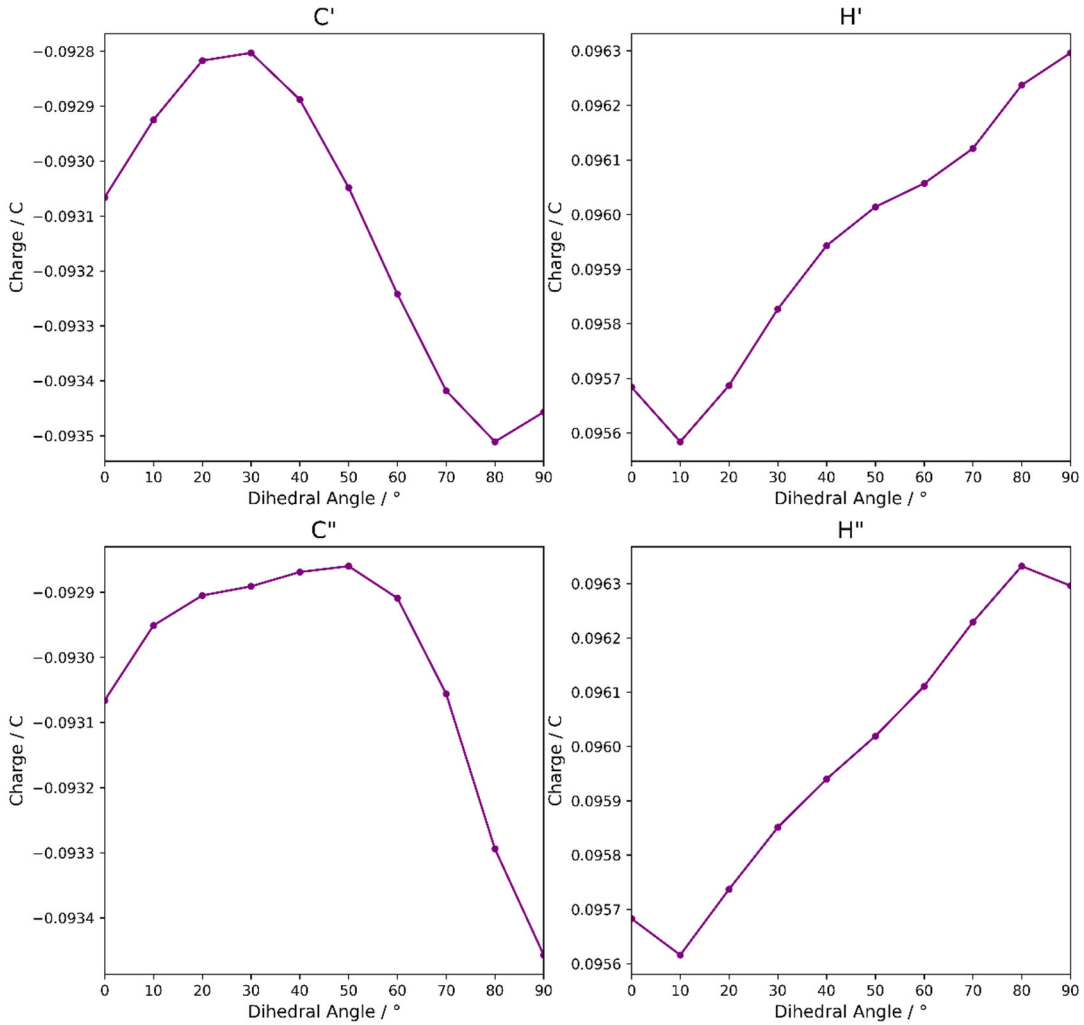


Figure S15. Charge Model 5 (CM5) charges for atoms involved in the H-H interaction for biphenyl. The H'-H" charge separation was calculated by subtracting the H" charge from the H' charge.

Table S30. Net CM5 charge change from 90° to 0° for five atom types. Positive charge difference indicates electron density decreases as the dihedral angle approaches zero. Negative charge difference indicates electron density increases as the dihedral angle approaches zero.

	C'	O'	H'	H"	C"
***trans*-1-naphthol**	0.006276	0.020825	0.000103	-0.006450	-0.018738
***cis*-1-naphthol**	0.005287	0.016097	-0.012526	-0.000930	-0.004424
***trans*-2-naphthol**	0.004300	0.021359	-0.001350	-0.004230	-0.010043
***cis*-2-naphthol**	0.005819	0.022029	-0.000165	-0.006150	-0.018889
Biphenyl	0.000391	-	-0.000610	-0.000613	-0.093294

NBO Analysis

Table S31. Occupancy for each bonding[b] and anti-bonding[c] orbital for all four isomers of naphthol. [a]Average occupancy for *trans* 1-naphthol, *cis* 2-naphthol, and *trans* 2-naphthol.

	***trans*-1-naphthol**	***Cis-2*-naphthol**	***trans-2*-naphthol**	**Average[a]**	***cis*-1-naphthol**
O'-H' BD[b]	1.98737	1.98764	1.98781	1.98761	1.98690
O'-H' BD*[c]	0.00690	0.00681	0.00648	0.00673	0.00911
C"-H" BD	1.97857	1.97741	1.97873	1.97824	1.97677
C"-H" BD*	0.01287	0.01422	0.01334	0.01348	0.01561

Table S32. Interaction energies between bonding and antibonding orbitals obtained from second order perturbative treatment of the Fock matrix for *trans*-1-naphthol

***trans*-1-naphthol**	**C-H BD --- O-H BD* / kJ mol^{-1}**	**O-H BD --- C-H BD* / kJ mol^{-1}**	**Sum of Interactions / kJ mol^{-1}**
0	0.46	0.21	0.67
10	0.42	0.21	0.63
20	0.29	0.21	0.50
30	0.17	0.21	0.38
40	0.00	0.21	0.21
50	0.00	0.17	0.17
60	0.00	0.17	0.17
70	0.00	0.17	0.17
80	0.00	0.21	0.21
90	0.00	0.00	0.00

Table S33. Interaction energies between bonding and antibonding orbitals obtained from second order perturbative treatment of the Fock matrix for c*is*-1-naphthol

***cis*-1-naphthol**	**C-H BD --- O-H BD* / kJ mol^{-1}**	**O-H BD --- C-H BD* / kJ mol^{-1}**	**Sum of Interactions / kJ mol^{-1}**
0	3.85	0.38	4.23
10	3.35	0.38	3.72
20	2.26	0.29	2.55
30	1.13	0.21	1.34
40	0.42	0.17	0.59
50	0.13	0.08	0.21
60	0.08	0.00	0.08
70	0.00	0.00	0.00
80	0.00	0.00	0.00

90	0.00	0.00	0.00

Table S34. Interaction energies between bonding and antibonding orbitals obtained from second order perturbative treatment of the Fock matrix for *trans*-2-naphthol

***trans*-2-naphthol**	**C-H BD --- O-H BD* / kJ mol^{-1}**	**O-H BD --- C-H BD* / kJ mol^{-1}**	**Sum of Interactions / kJ mol^{-1}**
0	0.42	0.17	0.59
10	0.38	0.17	0.54
20	0.25	0.17	0.42
30	0.13	0.13	0.25
40	0.00	0.13	0.13
50	0.00	0.13	0.13
60	0.00	0.13	0.13
70	0.00	0.13	0.13
80	0.00	0.13	0.13
90	0.00	0.13	0.13

Table S35. Interaction energies between bonding and antibonding orbitals obtained from second order perturbative treatment of the Fock matrix for c*is*-2-naphthol

***cis*-2-naphthol**	**C-H BD --- O-H BD* / kJ mol^{-1}**	**O-H BD --- C-H BD* / kJ mol^{-1}**	**Sum of Interactions / kJ mol^{-1}**
0	0.42	0.25	0.67
10	0.38	0.25	0.63
20	0.25	0.21	0.46
30	0.13	0.21	0.33
40	0.04	0.21	0.25
50	0.00	0.21	0.21
60	0.00	0.21	0.21
70	0.00	0.21	0.21
80	0.00	0.21	0.21
90	0.00	0.21	0.21

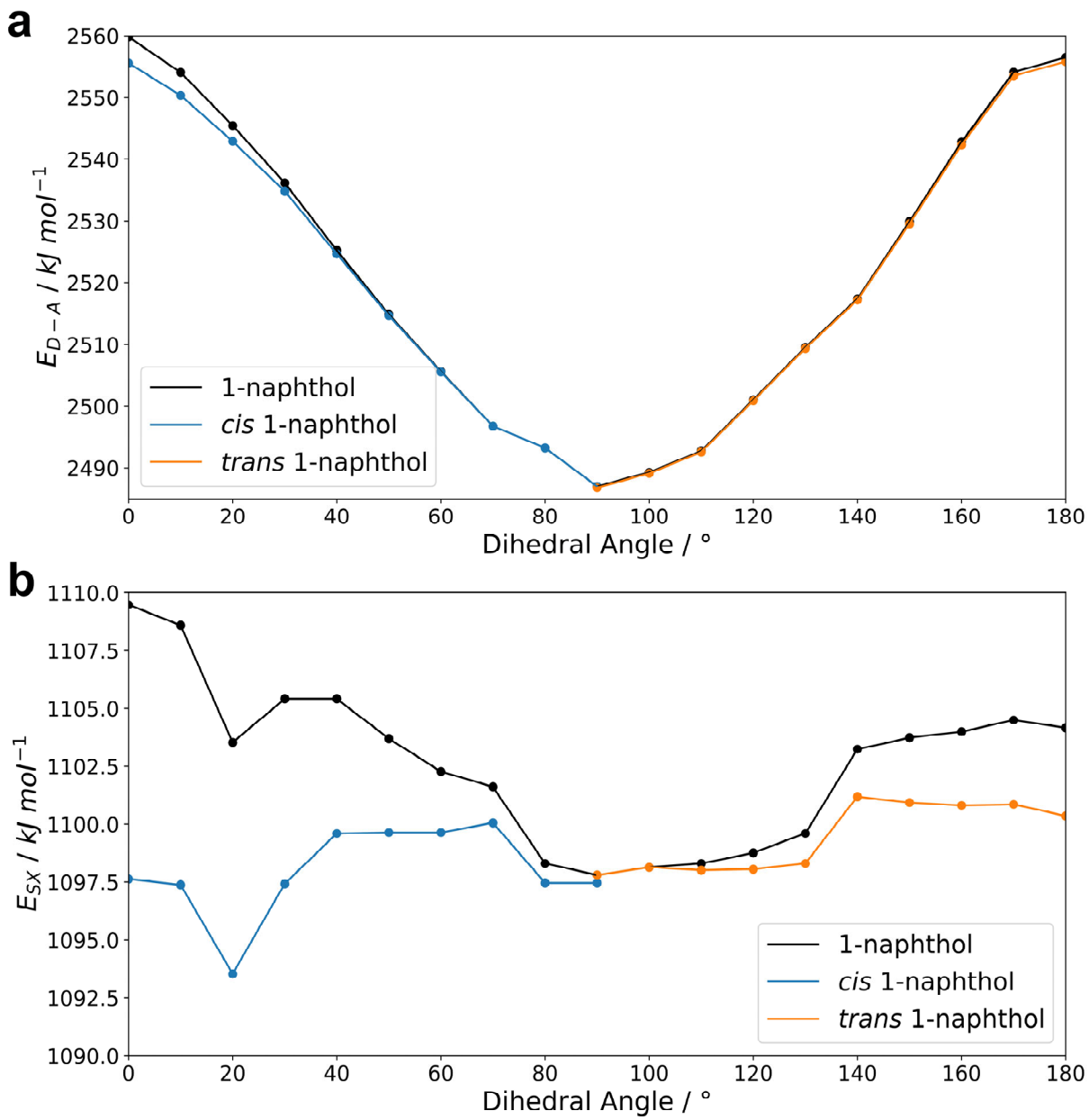


Figure S16. [a]Summed donor-acceptor (attraction) energies for 1-naphthol with the close contact H-H interactions subtracted. [b]Pairwise steric exchange (repulsion) energies for 1-naphhtol with close contact H-H interactions subtracted.

Table 36. Attraction and repulsion energy comparison for *cis*-1-naphthol at the B3LYP-D3(BJ)/def-TZVP and ωB97XD/Jun-cc-pVTZ level of theory

	Attraction /kJ mol^{-1}		Repulsion /kJ mol^{-1}	
Dihedral Angle	**B3LYP-D3(BJ)**	**ωB97XD**	**B3LYP-D3(BJ)**	**ωB97XD**
0	4.2	4.8	11.8	13.5
30	1.3	1.7	8.0	8.7
60	0.1	0.1	2.6	2.7
90	0.0	0.0	0.3	0.3