Supplementary Information

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Abstract

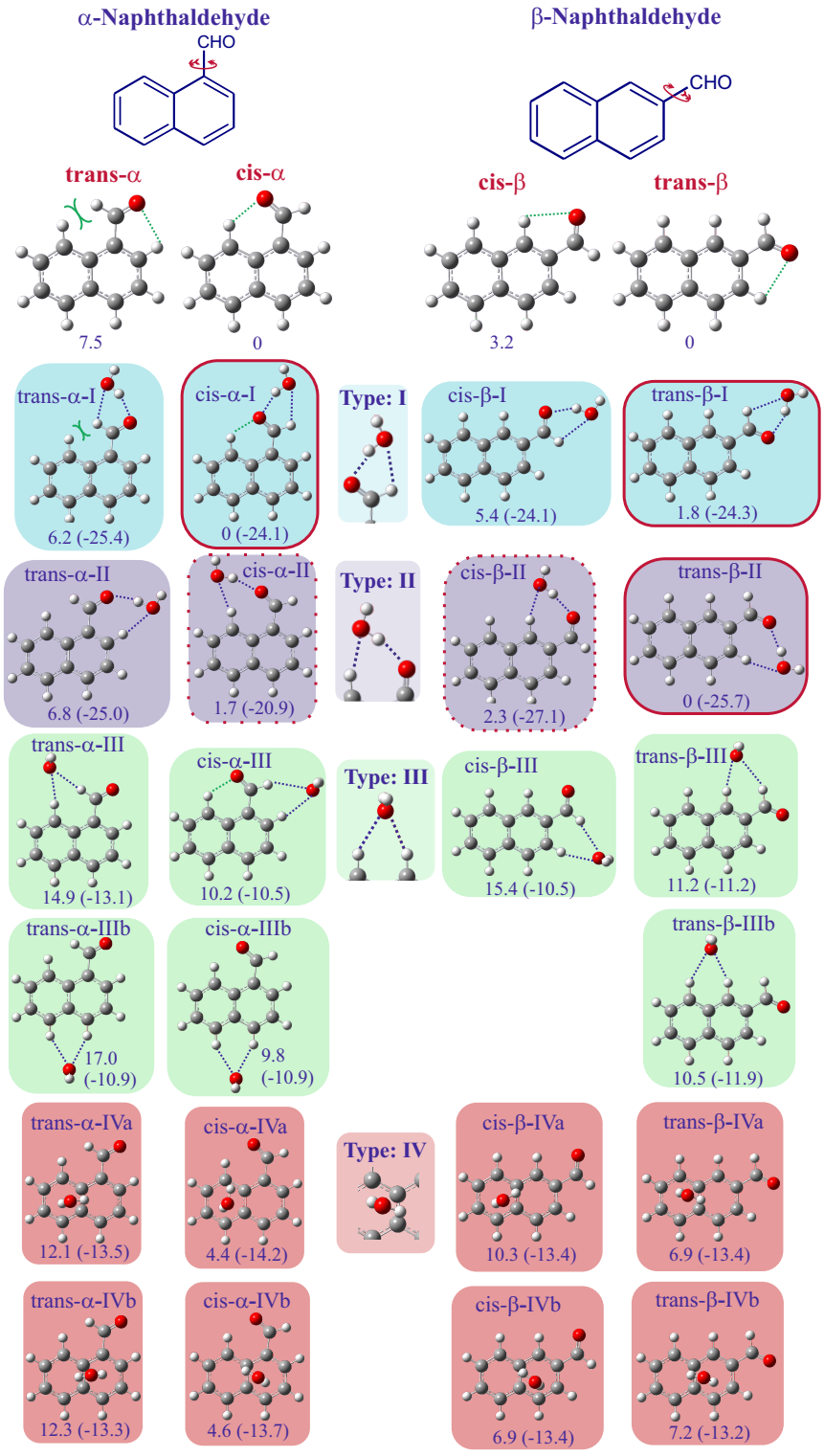

Figure 1: Enlarged version of figure 1.

Table 1: Full set of calculated relative energies (in kJ/mol), rotational constants (in MHz) and dipole moment components (in D).

species	c-α-I	c-α-II	c-α-III	c-α-IIIb	c-α-IVa	c-α-IVb	t-α-I	t-α-II	t-α-III	t-α-IIIb	t-α-IVa	t-α-IVb
	MP2/aug-cc-pVTZ											
ΔE_{ZPE}	0.00	1.74	10.18	9.80	4.38	4.64	6.23	6.85	14.90	16.97	12.09	12.31
A	1317.5	1024.2	1343.5	1187.2	980.2	942.2	1211.6	1618.4	890.4	1159.0	1114.2	1089.1
B	501.9	678.8	512.6	556.9	721.7	771.2	521.3	481.3	706.9	537.0	630.3	654.9
C	363.4	408.6	371.7	379.8	549.6	568.9	364.5	372.0	394.8	367.6	532.2	546.6
μ_a	3.2	3.0	2.1	5.5	0.1	1.6	-2.9	-3.2	4.2	5.7	2.3	3.4
μ_b	-0.7	-1.4	2.6	-1.8	2.4	1.7	0.6	-0.4	-0.9	0.0	1.1	-0.2
μ_c	0.0	-0.5	0.0	0.0	-1.9	2.5	0.0	-0.5	-0.7	0.0	-2.5	-2.4
	B98/aug-cc-pVTZ											
ΔE_{ZPE}	0.0	1.40	8.53	7.72			4.80	5.38	14.49	15.34		
A	1296.0	1026.0	1339.6	1179.0			1248.1	1630.3	887.0	1141.4		
B	489.7	650.7	498.5	541.8			490.3	471.7	684.4	525.7		
C	355.4	398.6	363.9	371.8			352.0	366.1	387.0	360.5		
μ_a	-4.2	-3.7	1.8	5.8			-3.9	-3.8	-0.6	6.0		
μ_b	-0.8	-1.3	2.7	-1.7			1.0	-0.1	2.2	-0.1		
μ_c	0.0	0.9	0.0	0.0			0.0	-0.7	0.0	0.0		
	B3LYP/6-311g++(d,p)											
ΔE_{ZPE}	0.0	3.29	10.84	10.94			6.48	6.88	16.79	18.12		
A	1285.1	1024.1	1337.2	1180.0			1251.4	1626.5	887.1	1148.6		
B	489.4	656.1	508.6	552.7			487.1	474.6	699.4	534.0		
C	354.4	400.2	369.1	377.1			350.6	367.5	391.8	365.1		
μ_a	-4.4	-3.7	2.2	6.1			-3.9	-3.7	-0.4	6.4		
μ_b	-0.6	-1.5	3.0	-1.9			1.2	-0.2	2.7	0.0		
μ_c	0.0	0.9	0.0	0.0			0.0	-0.7	0.0	0.0		
	B3LYP-D3/6-311g++(d,p)											
ΔE_{ZPE}	0.0	2.24										
A	1301.4	1021.2										
B	497.2	677.9										
C	359.8	407.8										
μ_a	4.0	3.6										
μ_b	-0.7	-2.3										
μ_c	0.0	-0.9										
species	t-β-I	t-β-II	t-β-III	t-β-IIIb	t-β-IVa	t-β-IVb	c-β-I	c-β-II	c-β-III	c-β-IVa	c-β-IVb	
	MP2/aug-cc-pVTZ											
ΔE_{ZPE}	1.78	0.00	11.20	10.52	6.91	7.15	5.37	2.28	15.40	10.33	10.66	
A	2250.2	1946.1	1126.0	981.5	1511.2	1488.9	2383.6	1310.1	1492.6	1386.5	1316.5	
B	349.3	408.9	523.6	582.1	476.0	495.2	348.1	525.2	429.2	498.7	530.4	
C	302.4	337.9	358.0	366.0	461.6	478.3	303.8	374.9	333.9	471.4	483.2	
μ_a	-3.7	3.1	1.6	3.2	-2.7	-3.9	-3.6	-2.0	-0.6	-1.6	-3.3	
μ_b	-0.4	-1.4	3.8	3.5	-0.5	1.7	-0.3	-1.8	3.7	-1.7	0.1	
μ_c	0.0	0.0	0.0	0.0	-2.5	-1.7	0.0	0.0	0.0	-2.4	-2.3	
	B98/aug-cc-pVTZ											
ΔE_{ZPE}	0.21	0.0		9.80			3.57	1.81	14.09			
A	2369.6	1950.9		944.7			2364.6	1301.9	1459.3			
B	334.7	402.3		580.0			338.9	517.1	422.2			
C	293.3	333.6		360.0			296.4	370.2	328.0			
μ_a	-4.6	-3.8		3.3			-4.6	-2.5	-0.3			
μ_b	-0.5	-1.4		-3.5			-0.2	-1.9	3.6			
μ_c	0.0	-0.7		0.0			0.0	-0.5	0.0			
	B3LYP/6-311g++(d,p)											
ΔE_{ZPE}	0.51	0.0		11.94			3.71	1.42	14.78			
A	2416.0	1945.7		970.7			2341.8	1305.9	1478.7			
B	330.3	404.4		579.4			336.8	519.5	427.3			
C	290.6	334.9		363.4			294.5	371.7	332.0			
μ_a	-4.9	-3.7		-3.5			-4.9	-2.5	-0.4			
μ_b	-0.7	-1.4		3.7			-0.1	-1.9	4.0			
μ_c	0.0	-0.7		0.0			0.0	-0.7	0.0			

c and t stand for *cis* and *trans*, respectively. Group IV structures have been calculated at the MP2 level only. The *trans*-β-III structure is not converging using DFT methods. Tests calculations including London dispersion were only performed on the two lowest energy conformers of the α-naphthaldehyde monohydrate.

Table 2: Cartesian coordinates for the optimized geometry for the α-naphthaldehyde water complex (*cis*-α-I) observed at the MP2/aug-cc-pVTZ level of theory

Number	Atom	x	y	z
		α-cis-I		
1	C	−0.627 172	−0.632 555	0.000 003
2	C	−0.530 245	−2.016 898	0.000 006
3	C	0.715 585	−2.664 579	−0.000 001
4	C	1.869 514	−1.913 161	−0.000 006
5	C	3.011 728	0.262 375	−0.000 001
6	C	2.964 172	1.638 726	0.000 005
7	C	1.720 732	2.299 458	0.000 011
8	C	0.537 959	1.587 542	0.000 007
9	C	0.553 103	0.172 303	0.000 000
10	C	1.819 637	−0.498 427	−0.000 003
11	H	−0.410 635	2.101 677	0.000 009
12	H	1.689 179	3.381 509	0.000 018
13	H	3.881 631	2.213 041	0.000 008
14	H	3.962 564	−0.257 664	−0.000 004
15	H	2.839 451	−2.397 766	−0.000 011
16	H	0.765 762	−3.745 321	−0.000 002
17	H	−1.443 701	−2.601 566	0.000 012
18	H	−2.774 856	−0.902 879	0.000 036
19	O	−2.346 626	1.063 605	−0.000 039
20	C	−2.002 892	−0.113 416	0.000 001
21	H	−4.253 256	0.867 913	−0.000 013
22	O	−5.084 197	0.365 227	0.000 025
23	H	−5.774 338	1.032 993	−0.000 090

Table 3: Cartesian coordinates for the optimized geometry for the α-naphthaldehyde water complex (*cis*-α-I) observed at the B98/aug-cc-pVQZ level of theory

Number	Atom	x	y	z
		α-cis-I		
1	C	−0.578 747	−0.712 461	0.008 885
2	C	−0.392 716	−2.084 200	0.006 300
3	C	0.890 226	−2.657 222	−0.000 788
4	C	1.991 519	−1.839 571	−0.005 423
5	C	3.007 220	0.405 208	−0.009 187
6	C	2.881 242	1.770 881	−0.008 229
7	C	1.599 119	2.356 335	−0.001 845
8	C	0.464 193	1.579 478	0.003 886
9	C	0.558 390	0.165 537	0.003 402
10	C	1.860 936	−0.427 288	−0.003 642
11	H	−0.511 828	2.038 299	0.008 296
12	H	1.505 640	3.435 162	−0.001 757
13	H	3.762 033	2.400 325	−0.012 691
14	H	3.986 713	−0.058 142	−0.014 479
15	H	2.988 122	−2.265 826	−0.010 879
16	H	1.002 561	−3.733 336	−0.002 633
17	H	−1.264 765	−2.728 460	0.009 823
18	H	−2.705 427	−1.116 783	0.018 908
19	O	−2.402 839	0.865 679	0.024 205
20	C	−1.985 734	−0.275 591	0.017 761
21	H	−4.331 223	0.776 417	−0.016 066
22	O	−5.236 528	0.433 292	−0.054 156
23	H	−5.778 038	1.103 328	0.364 420

Table 4: Cartesian coordinates for the optimized geometry for the β-naphthaldehyde water complex (*trans*-β-I) observed at the MP2/aug-cc-pVTZ level of theory

Number	Atom	x	y	z
		β-trans-I		
1	C	0.199 729	0.833 163	0.000 046
2	C	1.082 577	−0.230 091	0.000 039
3	C	0.609 044	−1.563 602	0.000 002
4	C	−0.742 964	−1.804 608	−0.000 027
5	C	−3.070 525	−0.961 984	−0.000 048
6	C	−3.955 005	0.095 922	−0.000 038
7	C	−3.478 742	1.423 823	0.000 000
8	C	−2.124 588	1.678 364	0.000 027
9	C	−1.195 025	0.611 974	0.000 019
10	C	−1.675 908	−0.735 681	−0.000 019
11	H	−1.755 175	2.697 252	0.000 056
12	H	−4.182 789	2.245 836	0.000 008
13	H	−5.021 007	−0.091 489	−0.000 059
14	H	−3.436 401	−1.982 206	−0.000 077
15	H	−1.117 747	−2.821 806	−0.000 057
16	H	1.329 267	−2.371 450	−0.000 004
17	H	0.580 607	1.850 264	0.000 074
18	H	2.800 163	1.123 054	0.000 096
19	O	3.394 637	−0.806 288	0.000 067
20	C	2.523 628	0.054 901	0.000 069
21	H	4.969 556	0.292 136	−0.000 055
22	O	5.444 932	1.138 895	−0.000 132
23	H	6.374 484	0.897 825	0.000 217

Table 5: Cartesian coordinates for the optimized geometry for the β-naphthaldehyde water complex (*trans*-β-I) observed at the B98/aug-cc-pVQZ level of theory

Number	Atom	x	y	z
		β-trans-I		
1	C	0.149 870	0.864 806	0.007 410
2	C	1.057 695	−0.172 742	0.006 111
3	C	0.604 929	−1.519 462	0.000 175
4	C	−0.734 191	−1.789 480	−0.004 099
5	C	−3.087 260	−0.991 951	−0.007 191
6	C	−3.988 042	0.045 145	−0.005 910
7	C	−3.540 548	1.384 993	−0.000 173
8	C	−2.197 127	1.663 884	0.004 204
9	C	−1.242 344	0.615 999	0.003 055
10	C	−1.694 777	−0.739 708	−0.002 780
11	H	−1.848 553	2.689 844	0.008 519
12	H	−4.263 298	2.190 804	0.000 686
13	H	−5.050 772	−0.161 999	−0.009 369
14	H	−3.433 883	−2.018 461	−0.011 666
15	H	−1.085 852	−2.814 438	−0.008 743
16	H	1.341 215	−2.312 272	−0.001 077
17	H	0.504 466	1.890 520	0.011 681
18	H	2.742 423	1.219 775	0.015 036
19	O	3.381 598	−0.688 503	0.010 476
20	C	2.495 756	0.140 902	0.010 814
21	H	5.067 757	0.251 782	−0.011 669
22	O	5.720 256	0.967 674	−0.032 090
23	H	6.551 468	0.558 816	0.211 322

Table 6: Cartesian coordinates for the optimized geometry for the β-naphthaldehyde water complex (*trans*-β-II) observed at the MP2/aug-cc-pVTZ level of theory

Number	Atom	x	y	z
		β-trans-II		
1	C	−0.095 061	−1.366 702	0.000 003
2	C	1.120 578	−0.706 472	0.000 015
3	C	1.175 945	0.709 118	0.000 025
4	C	0.005 276	1.428 377	0.000 020
5	C	−2.469 208	1.508 292	−0.000 001
6	C	−3.682 383	0.852 760	−0.000 011
7	C	−3.731 400	−0.557 222	−0.000 012
8	C	−2.567 591	−1.294 805	−0.000 007
9	C	−1.309 627	−0.647 519	0.000 001
10	C	−1.257 201	0.782 091	0.000 007
11	H	−2.601 683	−2.378 129	−0.000 008
12	H	−4.689 720	−1.060 304	−0.000 017
13	H	−4.603 423	1.421 276	−0.000 018
14	H	−2.431 339	2.591 448	−0.000 001
15	H	0.035 399	2.511 985	0.000 027
16	H	2.133 547	1.212 922	0.000 027
17	H	−0.118 601	−2.452 723	0.000 002
18	H	2.162 709	−2.616 409	−0.000 016
19	O	3.485 532	−1.097 396	−0.000 002
20	C	2.340 228	−1.526 138	−0.000 001
21	H	4.245 788	0.653 557	−0.000 022
22	O	4.401 908	1.611 067	−0.000 038
23	H	5.357 722	1.706 465	0.000 181

Table 7: Cartesian coordinates for the optimized geometry for the β-naphthaldehyde water complex (*trans*-β-II) observed at the B98/aug-cc-pVQZ level of theory

Number	Atom	x	y	z
		β-trans-II		
1	C	−0.105 327	1.359 358	−0.004 035
2	C	1.110 670	0.707 163	0.015 213
3	C	1.160 016	−0.714 137	0.035 777
4	C	−0.002 752	−1.432 517	0.035 402
5	C	−2.486 242	−1.511 901	0.012 997
6	C	−3.693 187	−0.856 528	−0.007 262
7	C	−3.744 019	0.555 350	−0.026 934
8	C	−2.583 723	1.287 341	−0.026 037
9	C	−1.322 198	0.640 378	−0.005 442
10	C	−1.270 208	−0.787 559	0.014 524
11	H	−2.616 866	2.370 382	−0.041 259
12	H	−4.703 433	1.056 380	−0.042 853
13	H	−4.615 900	−1.423 084	−0.008 347
14	H	−2.450 798	−2.594 644	0.027 892
15	H	0.028 750	−2.515 494	0.050 779
16	H	2.119 071	−1.215 156	0.053 091
17	H	−0.133 400	2.444 334	−0.019 103
18	H	2.152 317	2.618 831	0.005 612
19	O	3.472 245	1.107 532	0.020 294
20	C	2.334 541	1.525 839	0.013 594
21	H	4.298 516	−0.646 235	−0.040 519
22	O	4.515 602	−1.588 369	−0.081 718
23	H	5.390 092	−1.665 558	0.301 397

Table 8: List of assigned rotational transitions for the most stable conformer of α-naphthaldehyde (*cis*-α-I) and their simulations out of the best fit using SPFIT program

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc.MHz	Diff./MHz	Est. error/MHz
8	0	8	7	1	7	6032.8139	6032.8130	0.0009	0.002
9	0	9	8	1	8	6781.8029	6781.8022	0.0007	0.004
10	0	10	9	1	9	7517.2609	7517.2622	−0.0013	0.004
11	0	11	10	1	10	8244.7380	8244.7366	0.0014	0.002
12	0	12	11	1	11	8967.6917	8967.6876	0.0042	0.002
13	0	13	12	1	12	9688.1550	9688.1566	−0.0016	0.004
14	0	14	13	1	13	10 407.3002	10 407.2988	0.0014	0.004
15	0	15	14	1	14	11 125.7480	11 125.7475	0.0006	0.002
16	0	16	15	1	15	11 843.8436	11 843.8406	0.0030	0.004
5	0	5	4	0	4	4002.6664	4002.6622	0.0042	0.002
6	0	6	5	0	5	4714.6928	4714.6915	0.0013	0.002
7	0	7	6	0	6	5419.1318	5419.1334	−0.0016	0.002
8	0	8	7	0	7	6124.4673	6124.4676	−0.0003	0.002
9	0	9	8	0	8	6833.2902	6833.2905	−0.0003	0.002
10	0	10	9	0	9	7545.3689	7545.3677	0.0012	0.002
11	0	11	10	0	10	8259.7446	8259.7454	−0.0008	0.002
12	0	12	11	0	11	8975.5669	8975.5651	0.0018	0.002
13	0	13	12	0	12	9692.2337	9692.2338	−0.0001	0.002
14	0	14	13	0	13	10 409.3808	10 409.3849	−0.0041	0.002
15	0	15	14	0	14	11 126.8035	11 126.8044	−0.0009	0.002
16	0	16	15	0	15	11 844.3675	11 844.3717	−0.0042	0.002
17	0	17	16	0	16	12 562.0192	12 562.0200	−0.0008	0.002
18	0	18	17	0	17	13 279.7132	13 279.7126	0.0006	0.002
19	0	19	18	0	18	13 997.4316	13 997.4291	0.0025	0.002
7	1	6	6	1	5	6176.4221	6176.4247	−0.0026	0.002
8	1	7	7	1	6	6939.8376	6939.8366	0.0010	0.002
9	1	8	8	1	7	7664.6763	7664.6754	0.0009	0.002
10	1	9	9	1	8	8364.6362	8364.6357	0.0005	0.002
11	1	10	10	1	9	9055.5713	9055.5733	−0.0020	0.002
12	1	11	11	1	10	9748.2425	9748.2415	0.0010	0.002
13	1	12	12	1	11	10 446.8107	10 446.8100	0.0007	0.002
14	1	13	13	1	12	11 151.3775	11 151.3766	0.0009	0.002
15	1	14	14	1	13	11 860.5725	11 860.5730	−0.0005	0.002
16	1	15	15	1	14	12 572.9216	12 572.9237	−0.0021	0.002
17	1	16	16	1	15	13 287.2893	13 287.2871	0.0022	0.002
7	2	5	6	2	4	6400.3341	6400.3330	0.0011	0.002
8	2	6	7	2	5	7324.3668	7324.3662	0.0006	0.002
9	2	7	8	2	6	8215.6377	8215.6370	0.0007	0.002
10	2	8	9	2	7	9066.6741	9066.6737	0.0004	0.002
11	2	9	10	2	8	9871.2784	9871.2798	−0.0014	0.002
12	2	10	11	2	9	10 627.5119	10 627.5119	0.0000	0.002
13	2	11	12	2	10	11 341.7148	11 341.7147	0.0001	0.002
14	2	12	13	2	11	12 028.6718	12 028.6733	−0.0015	0.002
15	2	13	14	2	12	12 705.5829	12 705.5838	−0.0009	0.002
16	2	14	15	2	13	13 384.9316	13 384.9315	0.0001	0.002
8	3	5	7	3	4	7128.1039	7128.1036	0.0003	0.002
9	3	6	8	3	5	8110.6799	8110.6816	−0.0017	0.002
10	3	7	9	3	6	9098.6993	9098.6993	0.0001	0.002

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Table 8 – Continued from previous page

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc./MHz	Diff./MHz	Est. error/MHz
11	3	8	10	3	7	10 072.5012	10 072.5030	−0.0018	0.002
12	3	9	11	3	8	11 016.3562	11 016.3545	0.0017	0.002
14	3	11	13	3	10	12 775.1907	12 775.1871	0.0036	0.002
15	3	12	14	3	11	13 577.7229	13 577.7251	−0.0022	0.002
8	4	4	7	4	3	6947.7715	6947.7736	−0.0021	0.002
9	4	5	8	4	4	7857.2378	7857.2371	0.0007	0.002
10	4	6	9	4	5	8789.4010	8789.4034	−0.0024	0.002
11	4	7	10	4	6	9749.6307	9749.6300	0.0007	0.002
15	4	11	14	4	10	13 757.3733	13 757.3741	−0.0008	0.002
9	5	4	8	5	3	7783.6282	7783.6261	0.0021	0.002
10	5	5	9	5	4	8671.9507	8671.9492	0.0015	0.002
11	5	6	10	5	5	9570.3807	9570.3825	−0.0018	0.002
5	1	5	4	1	4	3870.4139	3870.4143	−0.0004	0.002
6	1	6	5	1	5	4616.4855	4616.4865	−0.0010	0.002
7	1	7	6	1	6	5353.8078	5353.8086	−0.0008	0.002
8	1	8	7	1	7	6084.3004	6084.3013	−0.0009	0.002
9	1	9	8	1	8	6809.9070	6809.9077	−0.0007	0.002
10	1	10	9	1	9	7532.2696	7532.2709	−0.0013	0.002
11	1	11	10	1	10	8252.6152	8252.6142	0.0010	0.002
12	1	12	11	1	11	8971.7667	8971.7648	0.0019	0.002
13	1	13	12	1	12	9690.2416	9690.2426	−0.0010	0.002
14	1	14	13	1	13	10 408.3548	10 408.3558	−0.0010	0.002
15	1	15	14	1	14	11 126.2763	11 126.2785	−0.0022	0.002
16	1	16	15	1	15	11 844.1029	11 844.1056	−0.0027	0.002
17	1	17	16	1	16	12 561.8837	12 561.8864	−0.0027	0.002
18	1	18	17	1	17	13 279.6480	13 279.6460	0.0020	0.002
19	1	19	18	1	18	13 997.3991	13 997.3961	0.0030	0.002
20	1	20	19	1	19	14 715.1409	14 715.1421	−0.0012	0.002
8	2	7	7	2	6	6643.7730	6643.7725	0.0005	0.002
9	2	8	8	2	7	7417.9830	7417.9820	0.0010	0.002
10	2	9	9	2	8	8178.1643	8178.1645	−0.0002	0.002
11	2	10	10	2	9	8926.1775	8926.1758	0.0017	0.002
12	2	11	11	2	10	9664.3651	9664.3661	−0.0010	0.002
13	2	12	12	2	11	10 395.1749	10 395.1741	0.0008	0.002
14	2	13	13	2	12	11 120.7937	11 120.7935	0.0002	0.002
16	2	15	15	2	14	12 563.0405	12 563.0430	−0.0025	0.002
17	2	16	16	2	15	13 281.8389	13 281.8393	−0.0004	0.002
18	2	17	17	2	16	13 999.9336	13 999.9330	0.0006	0.002
7	3	5	6	3	4	6042.5255	6042.5249	0.0006	0.002
8	3	6	7	3	5	6901.0930	6901.0951	−0.0021	0.002
9	3	7	8	3	6	7749.2226	7749.2216	0.0010	0.002
10	3	8	9	3	7	8583.7901	8583.7922	−0.0021	0.002
11	3	9	10	3	8	9402.5698	9402.5700	−0.0002	0.002
12	3	10	11	3	9	10 204.3742	10 204.3734	0.0008	0.002
13	3	11	12	3	10	10 989.1485	10 989.1494	−0.0009	0.002
16	3	14	15	3	13	13 255.6848	13 255.6830	0.0018	0.002
17	3	15	16	3	14	13 989.7689	13 989.7688	0.0001	0.002
7	4	4	6	4	3	6047.1615	6047.1620	−0.0005	0.002
8	4	5	7	4	4	6926.8346	6926.8343	0.0003	0.002
9	4	6	8	4	5	7808.9943	7808.9957	−0.0014	0.002
10	4	7	9	4	6	8691.0423	8691.0396	0.0027	0.002
11	4	8	10	4	7	9569.5403	9569.5398	0.0005	0.002
15	4	12	14	4	11	12 974.5406	12 974.5401	0.0006	0.002

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Table 8 – Continued from previous page

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc./MHz	Diff./MHz	Est. error/MHz
16	4	13	15	4	12	13 784.9113	13 784.9111	0.0002	0.002
9	5	5	8	5	4	7781.1181	7781.1168	0.0013	0.002
10	5	6	9	5	5	8665.0801	8665.0813	−0.0012	0.002
9	1	9	8	0	8	6861.3915	6861.3959	−0.0044	0.004
10	1	10	9	0	9	7560.3794	7560.3764	0.0030	0.004
11	1	11	10	0	10	8267.6249	8267.6229	0.0020	0.002
12	1	12	11	0	11	8979.6432	8979.6423	0.0009	0.002
13	1	13	12	0	12	9694.3198	9694.3199	−0.0001	0.004
14	1	14	13	0	13	10 410.4441	10 410.4418	0.0023	0.004
15	1	15	14	0	14	11 127.3368	11 127.3355	0.0013	0.002
16	1	16	15	0	15	11 844.6362	11 844.6367	−0.0005	0.004

Table 9: List of assigned rotational transitions for the second most stable conformer of β-naphthaldehyde (*trans*-β-I) and their simulations out of the best fit using SPFIT program

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc.MHz	Diff./MHz	Est. error/MHz
8	0	8	7	0	7	5068.8528	5068.8522	0.0006	0.002
9	0	9	8	0	8	5684.5666	5684.5663	0.0003	0.002
10	0	10	9	0	9	6295.2149	6295.2152	−0.0003	0.002
11	0	11	10	0	10	6901.0905	6901.0909	−0.0004	0.002
12	0	12	11	0	11	7502.7357	7502.7370	−0.0013	0.002
13	0	13	12	0	12	8100.8832	8100.8833	−0.0001	0.001
14	0	14	13	0	13	8696.3517	8696.3514	0.0003	0.001
15	0	15	14	0	14	9289.9571	9289.9554	0.0017	0.002
16	0	16	15	0	15	9882.4280	9882.4220	0.0060	0.004
8	1	7	7	1	6	5296.2419	5296.2373	0.0046	0.002
9	1	8	8	1	7	5952.4827	5952.4822	0.0005	0.002
10	1	9	9	1	8	6606.4412	6606.4379	0.0033	0.002
11	1	10	10	1	9	7257.7190	7257.7172	0.0019	0.002
12	1	11	11	1	10	7905.8992	7905.8985	0.0007	0.002
13	1	12	12	1	11	8550.5301	8550.5316	−0.0015	0.002
14	1	13	13	1	12	9191.1433	9191.1485	−0.0052	0.002
10	2	8	9	2	7	6516.7601	6516.7573	0.0028	0.002
11	2	9	10	2	8	7186.9456	7186.9434	0.0022	0.004
12	2	10	11	2	9	7859.8570	7859.8549	0.0021	0.004
13	2	11	12	2	10	8534.5996	8534.5993	0.0003	0.002
14	2	12	13	2	11	9210.1777	9210.1803	−0.0026	0.002
10	3	7	9	3	6	6437.0456	6437.0457	−0.0001	0.002
12	3	9	11	3	8	7737.5534	7737.5547	−0.0013	0.002
9	1	9	8	1	8	5550.8602	5550.8637	−0.0035	0.002
10	1	10	9	1	9	6162.5302	6162.5315	−0.0013	0.002
11	1	11	10	1	10	6772.8708	6772.8729	−0.0021	0.002
12	1	12	11	1	11	7381.8808	7381.8808	0.0000	0.002
13	1	13	12	1	12	7989.5738	7989.5730	0.0008	0.002
14	1	14	13	1	13	8595.9893	8595.9902	−0.0009	0.002
15	1	15	14	1	14	9201.1949	9201.1918	0.0031	0.002
10	2	9	9	2	8	6396.1939	6396.1982	−0.0043	0.002
11	2	10	10	2	9	7030.8218	7030.8211	0.0007	0.002
12	2	11	11	2	10	7664.0418	7664.0433	−0.0015	0.002
13	2	12	12	2	11	8295.7551	8295.7559	−0.0008	0.002
10	3	8	9	3	7	6430.3797	6430.3783	0.0014	0.002
12	3	10	11	3	9	7720.9093	7720.9073	0.0020	0.002

Table 10: List of assigned rotational transitions for the most stable conformer of β-naphthaldehyde (*trans*-β-II) and their simulations out of the best fit using SPFIT program

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc.MHz	Diff./MHz	Est. error/MHz
10	0	10	9	1	9	6520.8689	6520.8701	−0.0012	0.0020
11	0	11	10	1	10	7297.1015	7297.1007	0.0008	0.0020
12	0	12	11	1	11	8053.3278	8053.3297	−0.0019	0.0020
13	0	13	12	1	12	8791.3750	8791.3746	0.0004	0.0020
14	0	14	13	1	13	9513.7464	9513.7459	0.0005	0.0020
15	0	15	14	1	14	10 223.1460	10 223.1442	0.0018	0.0020
16	0	16	15	1	15	10 922.1352	10 922.1347	0.0005	0.0020
17	0	17	16	1	16	11 612.9773	11 612.9767	0.0006	0.0020
18	0	18	17	1	17	12 297.5613	12 297.5618	−0.0005	0.0020
19	0	19	18	1	18	12 977.4175	12 977.4174	0.0001	0.0020
20	0	20	19	1	19	13 653.7451	13 653.7442	0.0009	0.0020
9	0	9	8	0	8	6390.0765	6390.0765	0.0000	0.0020
10	0	10	9	0	9	7056.9981	7056.9980	0.0002	0.0020
11	0	11	10	0	10	7719.6608	7719.6620	−0.0012	0.0020
12	0	12	11	0	11	8380.1894	8380.1908	−0.0014	0.0020
13	0	13	12	0	12	9040.1414	9040.1424	−0.0010	0.0020
14	0	14	13	0	13	9700.4781	9700.4781	0.0001	0.0020
15	0	15	14	0	14	10 361.6761	10 361.6758	0.0003	0.0020
16	0	16	15	0	15	11 023.8881	11 023.8888	−0.0007	0.0020
17	0	17	16	0	16	11 687.0847	11 687.0841	0.0006	0.0020
18	0	18	17	0	17	12 351.1403	12 351.1406	−0.0003	0.0020
19	0	19	18	0	18	13 015.9076	13 015.9091	−0.0015	0.0020
20	0	20	19	0	19	13 681.2433	13 681.2436	−0.0003	0.0020
8	1	7	7	1	6	6117.7333	6117.7338	−0.0005	0.0020
9	1	8	8	1	7	6863.3154	6863.3153	0.0002	0.0020
10	1	9	9	1	8	7600.8875	7600.8874	0.0001	0.0020
11	1	10	10	1	9	8329.0663	8329.0670	−0.0007	0.0020
12	1	11	11	1	10	9046.5714	9046.5714	0.0000	0.0020
13	1	12	12	1	11	9752.4291	9752.4287	0.0004	0.0020
14	1	13	13	1	12	10 446.2317	10 446.2314	0.0003	0.0020
15	1	14	14	1	13	11 128.3653	11 128.3648	0.0005	0.0020
16	1	15	15	1	14	11 800.1034	11 800.1030	0.0004	0.0020
17	1	16	16	1	15	12 463.4883	12 463.4885	−0.0002	0.0020
18	1	17	17	1	16	13 120.9990	13 120.9982	0.0008	0.0020
19	1	18	18	1	17	13 775.1109	13 775.1116	−0.0007	0.0020
20	1	19	19	1	18	14 427.9382	14 427.9387	−0.0005	0.0020
8	2	6	7	2	5	6040.2265	6040.2274	−0.0009	0.0020
9	2	7	8	2	6	6826.1484	6826.1484	0.0000	0.0020
10	2	8	9	2	7	7615.0391	7615.0405	−0.0014	0.0020
11	2	9	10	2	8	8403.9461	8403.9448	0.0013	0.0020
12	2	10	11	2	9	9190.1248	9190.1239	0.0009	0.0020
13	2	11	12	2	10	9971.3123	9971.3122	0.0001	0.0020
14	2	12	13	2	11	10 745.7303	10 745.7304	−0.0001	0.0020
15	2	13	14	2	12	11 511.9590	11 511.9593	−0.0003	0.0020
16	2	14	15	2	13	12 268.7830	12 268.7831	−0.0001	0.0020
17	2	15	16	2	14	13 015.0755	13 015.0752	0.0003	0.0020
18	2	16	17	2	15	13 749.7624	13 749.7629	−0.0005	0.0020
11	3	8	10	3	7	8201.4590	8201.4592	−0.0002	0.0020

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Table 10 – Continued from previous page

J'	K'_a	K'_c	J	K_a	K_c	Obs./MHz	Calc./MHz	Diff./MHz	Est. error/MHz
12	3	9	11	3	8	8973.2888	8973.2890	−0.0002	0.0020
13	3	10	12	3	9	9753.2101	9753.2097	0.0004	0.0020
14	3	11	13	3	10	10 541.2912	10 541.2913	−0.0001	0.0020
15	3	12	14	3	11	11 336.7868	11 336.7873	−0.0005	0.0020
11	4	7	10	4	6	8142.4406	8142.4401	0.0005	0.0020
12	4	8	11	4	7	8891.0095	8891.0101	−0.0006	0.0020
13	4	9	12	4	8	9642.3441	9642.3438	0.0003	0.0020
14	4	10	13	4	9	10 397.0214	10 397.0209	0.0006	0.0020
15	4	11	14	4	10	11 155.7415	11 155.7408	0.0007	0.0020
9	1	9	8	1	8	6260.2807	6260.2814	−0.0007	0.0020
10	1	10	9	1	9	6943.4313	6943.4314	−0.0001	0.0020
11	1	11	10	1	10	7623.9624	7623.9617	0.0007	0.0020
12	1	12	11	1	11	8302.0973	8302.0975	−0.0002	0.0020
13	1	13	12	1	12	8978.1065	8978.1067	−0.0002	0.0020
14	1	14	13	1	13	9652.2789	9652.2775	0.0014	0.0020
15	1	15	14	1	14	10 324.8975	10 324.8984	−0.0009	0.0020
16	1	16	15	1	15	10 996.2420	10 996.2421	−0.0001	0.0020
17	1	17	16	1	16	11 666.5547	11 666.5555	−0.0008	0.0020
18	1	18	17	1	17	12 336.0538	12 336.0534	0.0004	0.0020
19	1	19	18	1	18	13 004.9163	13 004.9168	−0.0005	0.0020
20	1	20	19	1	19	13 673.2951	13 673.2942	0.0009	0.0020
10	2	9	9	2	8	7307.7402	7307.7398	0.0004	0.0020
11	2	10	10	2	9	8024.1543	8024.1549	−0.0006	0.0020
12	2	11	11	2	10	8736.7410	8736.7401	0.0009	0.0020
13	2	12	12	2	11	9445.3252	9445.3249	0.0003	0.0020
14	2	13	13	2	12	10 149.8082	10 149.8077	0.0005	0.0020
15	2	14	14	2	13	10 850.1643	10 850.1641	0.0002	0.0020
16	2	15	15	2	14	11 546.4507	11 546.4501	0.0006	0.0020
17	2	16	16	2	15	12 238.8017	12 238.8011	0.0007	0.0020
18	2	17	17	2	16	12 927.4267	12 927.4260	0.0008	0.0020
19	2	18	18	2	17	13 612.5943	13 612.5959	−0.0016	0.0020
11	3	9	10	3	8	8143.0194	8143.0190	0.0004	0.0020
12	3	10	11	3	9	8884.8903	8884.8898	0.0005	0.0020
13	3	11	12	3	10	9625.4159	9625.4154	0.0005	0.0020
14	3	12	13	3	11	10 364.0326	10 364.0332	−0.0006	0.0020
15	3	13	14	3	12	11 100.1916	11 100.1922	−0.0006	0.0020
11	4	8	10	4	7	8139.6191	8139.6191	0.0000	0.0020
12	4	9	11	4	8	8885.7609	8885.7620	−0.0011	0.0020
13	4	10	12	4	9	9633.1079	9633.1082	−0.0003	0.0020
14	4	11	13	4	10	10 381.5237	10 381.5235	0.0002	0.0020
15	4	12	14	4	11	11 130.7959	11 130.7961	−0.0002	0.0020
9	1	9	8	0	8	6926.2037	6926.2043	−0.0006	0.0020
10	1	10	9	0	9	7479.5585	7479.5592	−0.0007	0.0020
11	1	11	10	0	10	8046.5225	8046.5230	−0.0005	0.0020
12	1	12	11	0	11	8628.9592	8628.9586	0.0006	0.0020
13	1	13	12	0	12	9226.8747	9226.8745	0.0002	0.0020
14	1	14	13	0	13	9839.0118	9839.0096	0.0022	0.0020
15	1	15	14	0	14	10 463.4306	10 463.4299	0.0007	0.0020
16	1	16	15	0	15	11 097.9970	11 097.9963	0.0007	0.0020
17	1	17	16	0	16	11 740.6607	11 740.6630	−0.0023	0.0020
18	1	18	17	0	17	12 389.6336	12 389.6323	0.0013	0.0020
19	1	19	18	0	18	13 043.4080	13 043.4085	−0.0005	0.0020

Table 11: Calculated natural charges of *cis*-α-naphthaldehyde and its hydrate *cis*-α-I, and the electronic charge variation

n°	Atom	*cis*-α Charge	*cis*-α-I Charge	Variation / %
1	C	−0.097	−0.103	−6
2	C	−0.189	−0.181	4
3	C	−0.243	−0.240	1
4	C	−0.105	−0.101	4
5	C	−0.146	−0.222	−52
6	C	−0.218	−0.135	38
7	C	−0.201	−0.233	−16
8	C	−0.164	−0.165	−1
9	C	0.001	0.021	2000
10	C	−0.103	−0.090	12
11	H	0.230	0.229	0
12	H	0.211	0.212	0
13	H	0.215	0.206	−4
14	H	0.199	0.211	6
15	H	0.201	0.202	1
16	H	0.217	0.219	1
17	H	0.214	0.218	2
18	H	0.108	0.137	26
19	O	−0.491	−0.523	−7
20	C	0.361	0.359	0
21	H	-	0.476	-
22	O	-	−0.959	-
23	H	-	0.463	-

Variation stands for $\left(\frac{\text{charge in monomer}-\text{charge in hydrate}}{\text{charge in monomer}} \times 100\right)$

Table 12: Calculated natural charges of *trans*-β-naphthaldehyde and its hydrate *trans*-β-I, and the electronic charge variation

n°	Atom	*trans*-β Charge	*trans*-β-I Charge	Variation / %
1	C	−0.100	−0.128	−29
2	C	−0.122	−0.117	4
3	C	−0.167	−0.222	−33
4	C	−0.189	−0.185	2
5	C	−0.131	−0.221	−69
6	C	−0.236	−0.145	38
7	C	−0.229	−0.252	−10
8	C	−0.116	−0.149	−28
9	C	−0.145	−0.012	92
10	C	0.000	−0.005	−1141
11	H	0.200	0.198	−1
12	H	0.217	0.215	−1
13	H	0.215	0.207	−4
14	H	0.198	0.209	6
15	H	0.207	0.214	4
16	H	0.221	0.233	6
17	H	0.195	0.195	0
18	H	0.109	0.135	24
19	O	−0.483	−0.513	−6
20	C	0.356	0.361	1
21	H	-	0.477	-
22	O	-	−0.960	-
23	H	-	0.463	-

Variation stands for $\left(\frac{\text{charge in monomer} - \text{charge in hydrate}}{\text{charge in monomer}} \times 100\right)$

Table 13: Calculated natural charges of *trans*-β-naphthaldehyde and its hydrate *trans*-β-II, and the electronic charge variation

n°	Atom	*trans*-β Charge	*trans*-β-II Charge	Variation / %
1	C	−0.100	−0.138	−38
2	C	−0.122	−0.118	3
3	C	−0.167	−0.225	−35
4	C	−0.189	−0.124	35
5	C	−0.131	−0.221	−68
6	C	−0.236	−0.150	36
7	C	−0.229	−0.229	0
8	C	−0.116	−0.208	−79
9	C	−0.145	−0.029	80
10	C	0.000	−0.013	−2936
11	H	0.200	0.214	7
12	H	0.217	0.216	−1
13	H	0.215	0.203	−6
14	H	0.198	0.215	8
15	H	0.207	0.201	−3
16	H	0.221	0.249	13
17	H	0.195	0.198	2
18	H	0.109	0.117	7
19	O	−0.483	−0.520	−8
20	C	0.356	0.377	6
21	H	-	0.484	-
22	O	-	−0.962	-
23	H	-	0.465	-

Variation stands for $\left(\frac{\text{charge in monomer} - \text{charge in hydrate}}{\text{charge in monomer}} \times 100\right)$

Table 14: Structures, relative energies, rotational constants and dipole moment components of the most stables dihydrates for α-naphthaldehyde at MP2/aug-cc-pVTZ level of theory.

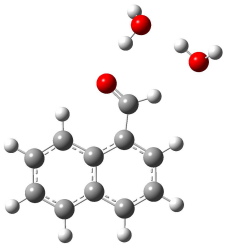
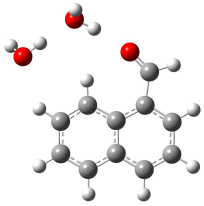
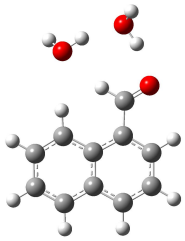
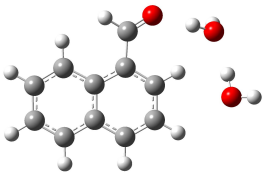
species	*cis*-α-I-II	*cis*-α-II-III	*trans*-α-I-II	*trans*-α-II-III
ΔE / kJ.mol^{-1}	0.0	2.8	1.5	7.7
A / MHz	1136.2	869.4	935.0	1174.2
B / MHz	357.2	473.3	432.7	380.6
C / MHz	272.0	308.1	296.2	293.8
μ_a / D	-2.3	-3.2	-1.8	-2.7
μ_b / D	0.7	1.2	-0.1	-0.4
μ_c / D	0.3	-0.4	-0.2	0.6
				

Table 15: Structures, relative energies, rotational constants and dipole moment components of the most stables dihydrates for β-naphthaldehyde at MP2/aug-cc-pVTZ level of theory.

species	*cis*-β-I-II	*cis*-β-II-III	*trans*-β-I-II	*trans*-β-II-III
ΔE / kJ.mol^{-1}	3.6	0.9	0.0	2.3
A / MHz	1763.1	835.0	1516.2	1208.4
B / MHz	256.6	456.7	269.2	327.3
C / MHz	224.2	296.1	228.8	257.9
μ_a / D	-3.5	-2.0	-3.6	3.4
μ_b / D	-0.3	-1.8	0.1	-1.5
μ_c / D	0.2	-0.2	0.2	0.0