ELECTRONIC SUPPLEMENTARY INFORMATION

Rotational Spectra of Tetracyclic Quinolizidine Alkaloids: Does a Water Molecule Flip Sparteine?†

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Figure S1. Conformational energies of sparteine using different ab initio and DFT methods. The trans-lone pair conformation (chair-chair-boat-chair or CCBC) is the most stable in all cases, as observed in the jet spectrum.

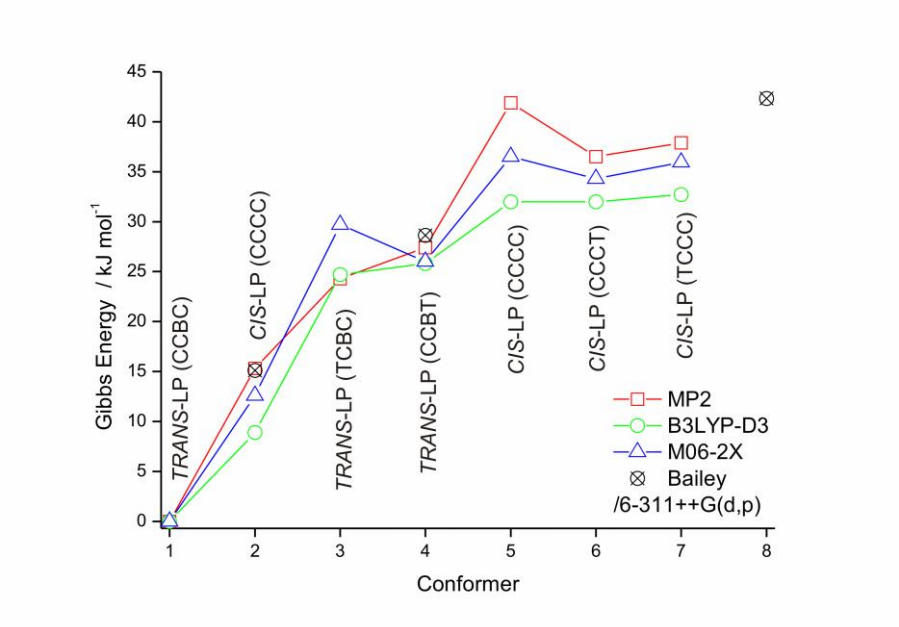

Figure S2. A section of the rotational spectrum of sparteine comparing the spectra of the dimers with $H_2{}^{16}O$ and $H_2{}^{18}O$. Transitions of the heavier dimer with $H_2{}^{18}O$ exhibit larger moments of inertia, so they are shifted to lower frequencies. Nuclear quadrupole coupling effects are not resolvable for these quantum numbers.

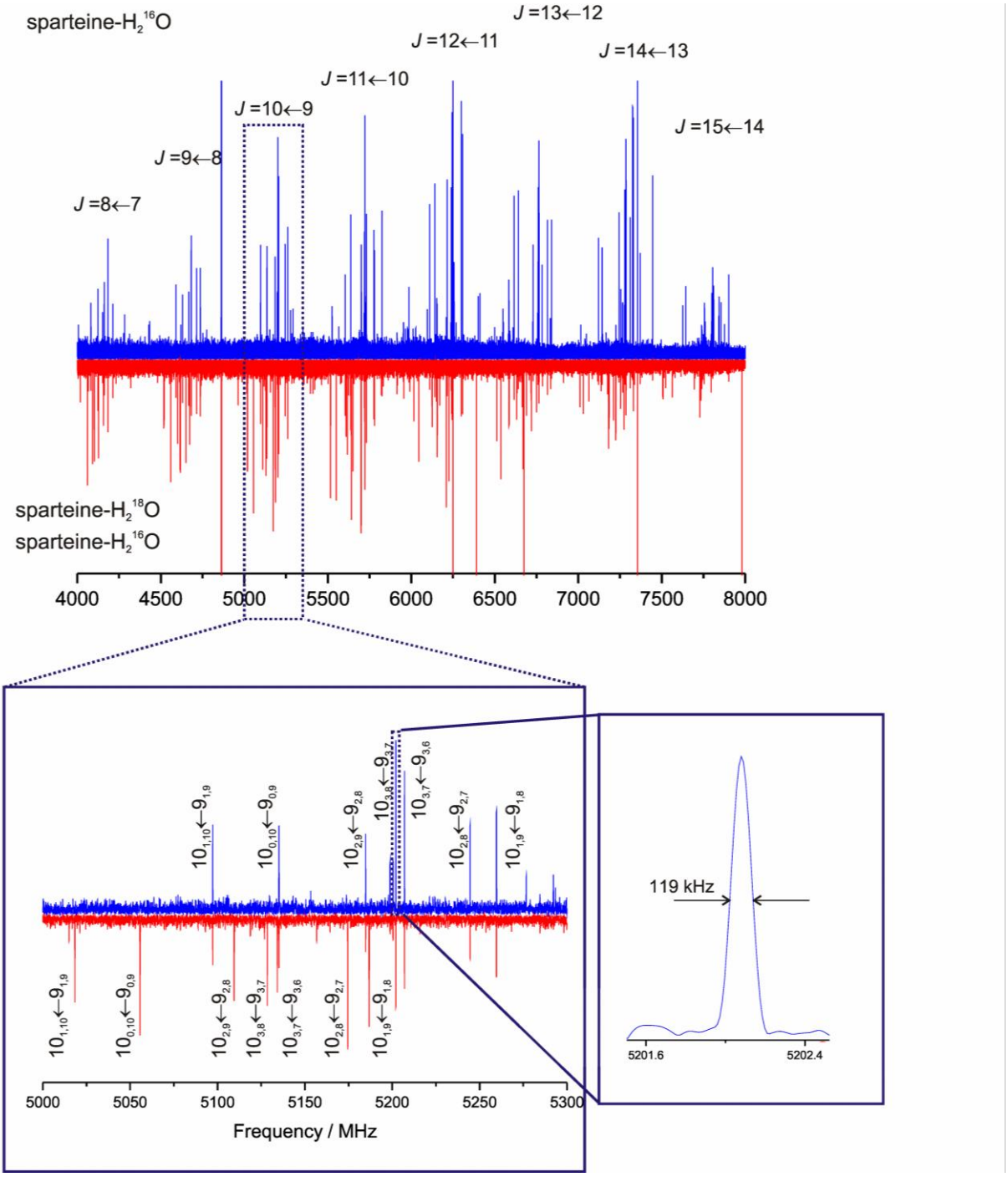

Figure S3. Geometry of the observed conformer of the sparteine-water dimer, showing the three structural parameters fitted in the determination of the effective structure of Table S14 (distance *r*(O···N), angle ∠(O···N-C11) and dihedral τ(O···N-C11-C12)).

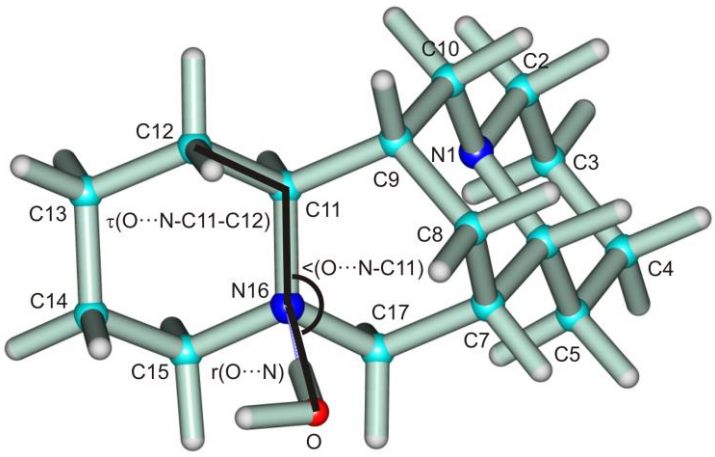

Table S1. Conformational energies of sparteine (6-311++G(d,p) basis set). Isomers are labelled according to the relative orientation of the two nitrogen lone pairs (*cis*/*trans* lp) and the conformation of the four A-B-C-D rings (C=*Chair*, B=*Boat*, T=*Twist*), as shown in Figure 1.

M06-2X

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE_{ZPE} / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
Trans-lp (CCBC)	990.0	304.8	290.4	0.0	0.0
Cis-lp (CCCC)	958.3	333.4	310.7	13.1	12.6
Trans-lp (TCBC)	920.7	322.2	306.6	27.7	29.7
Trans-lp (CCBT)	1013.8	304.1	291.9	28.0	26.0
Cis-lp (CCCC)	821.1	408.4	361.3	35.6	36.5
Cis-lp (CCCT)	924.9	328.1	314.6	35.8	34.3
Cis-lp (TCCC)	881.9	370.0	335.6	36.7	36.0

B3LYP-D3

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE_{ZPE} / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
Trans-lp (CCBC)	978.7	302.0	287.6	0.0	0.0
Cis-lp (CCCC)	955.7	327.3	306.1	8.9	8.9
Trans-lp (TCBC)	890.2	324.0	310.3	26.6	24.7
Trans-lp (CCBT)	1000.7	301.3	289.0	27.8	25.9
Cis-lp (CCCC)	829.3	395.5	351.5	31.0	32.0
Cis-lp (CCCT)	922.0	322.9	309.9	33.2	32.0
Cis-lp (TCCC)	875.0	364.1	331.0	33.6	32.7

MP2

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
Trans-lp (CCBC)	978.1	307.2	293.	0.0	0.0
Cis-lp (CCCC)	958.8	334.6	311.7	15.4	15.3
Trans-lp (TCBC)	892.8	329.4	316.3	26.1	24.3
Trans-lp (CCBT)	1008.6	305.9	294.1	28.5	27.4
Cis-lp (CCCC)	820.7	410.0	362.2	40.9	41.9
Cis-lp (CCCT)	917.5	331.4	317.7	37.5	36.5
Cis-lp (TCCC)	882.3	371.2	336.5	38.7	37.9

Table S2. Conformational search for monohydrated sparteine (M06-2X/6-31+G(d,p)). Isomers are labelled according to the relative orientation of the two nitrogen lone pairs (*cis*/*trans* lp) and the water binding site (either rings AB, CD or both, or the aliphatic skeleton), as shown in Figure 3.

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	*ΔE* / *kJ mol*$^{-1}$	*ΔG* / *kJ mol*$^{-1}$
Trans-1p – W(CD)	757.1	274.1	254.9	0.0	0.0
Trans-1p – W(AB)	782.2	285.7	278.3	-1.3	0.9
Cis-1p – W(AB-CD)	793.5	303.6	286.8	5.0	8.8
Cis-1p – W(AB-CD)	745.5	319.8	296.2	20.1	21.5
Trans-lp – W (skeleton)	853.6	240.0	229.3	29.4	22.6
Trans-lp – W (skeleton)	609.1	296.5	242.2	27.4	22.7
Trans-lp – W (skeleton)	679.1	272.4	243.9	28.9	22.8
Trans-lp – W (skeleton)	912.8	220.9	209.8	29.8	23.6
Trans-lp – W (skeleton)	603.0	298.7	241.6	28.6	23.8
Trans-lp – W (skeleton)	565.8	297.8	241.9	29.3	24.1
Trans-lp – W (skeleton)	690.2	265.4	243.4	28.2	24.6
Trans-lp – W (skeleton)	750.7	260.5	239.1	31.4	26.6
Trans-lp – W (skeleton)	633.1	276.0	233.1	31.1	27.4
Trans-lp – W (skeleton)	596.4	287.0	232.9	30.8	27.5

Table S3. Conformational energies for the three most stable isomers of sparteine-water.

M06-2X/6-311++G(d,p)

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE_{ZPE} / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
trans-lp – W(CD)	754.7	274.5	254.4	0.0	0.0
trans-lp – W(AB)	780.2	286.2	278.4	0.0	2.8
cis-lp – W(AB-CD)	759.8	314.1	298.2	-2.2	1.5

B3LYP-D3/6-311++G(d,p)

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE_{ZPE} / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
trans-lp – W(CD)	758.0	269.8	253.2	2.4	0.0
trans-lp – W(AB)	782.0	282.0	275.5	1.9	0.7
cis-lp – W(AB-CD)	768.1	306.4	288.5	0.0	-0.1

MP2/6-311++G(d,p)

	A / *MHz*	*B* / *MHz*	*C* / *MHz*	ΔE / *kJ mol*$^{-1}$	ΔG / *kJ mol*$^{-1}$
trans-lp – W(CD)	745.7	276.4	256.3	0.0	0.0
trans-lp – W(AB)	772.7	286.1	276.8	1.6	2.4
cis-lp – W(AB-CD)	763.3	311.5	295.2	2.0	4.4

Table S4. Experimental rotational transitions for sparteine (obs), along with residuals (res) and transition uncertainties (w). All frequencies in MHz.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	res	w
6	0	6	5	0	5	3561.9302	0.0021	0.025
6	2	5	5	2	4	3568.6381	-0.0120	0.010
6	2	4	5	2	3	3576.3787	0.0069	0.010
7	0	7	6	0	6	4152.3105	-0.0054	0.025
7	2	6	6	2	5	4162.8561	-0.0075	0.010
7	3	5	6	3	4	4166.3258	0.0201	0.010
7	3	4	6	3	3	4166.5814	0.0026	0.010
7	2	5	6	2	4	4175.1548	0.0170	0.010
8	1	8	7	1	7	4698.4598	0.0137	0.010
8	0	8	7	0	7	4741.2888	-0.0087	0.025
8	2	7	7	2	6	4756.8123	-0.0063	0.010
8	4	5	7	4	4	4761.0639	-0.0289	0.010
8	3	5	7	3	4	4762.4640	-0.0153	0.010
8	2	6	7	2	5	4775.0654	0.0161	0.010
8	1	7	7	1	6	4811.7120	-0.0062	0.010
9	1	9	8	1	8	5284.5215	0.0005	0.010
9	0	9	8	0	8	5328.7598	-0.0196	0.025
9	2	8	8	2	7	5350.4817	0.0026	0.010
9	6	3	8	6	2	5355.5608	-0.0203	0.010
9	5	5	8	5	4	5355.9397	0.0047	0.010
9	4	6	8	4	5	5356.5976	-0.0066	0.010
9	3	7	8	3	6	5357.7138	0.0159	0.010
9	3	6	8	3	5	5358.7224	0.0269	0.010
9	2	7	8	2	6	5376.1717	0.0103	0.010
9	1	8	8	1	7	5411.5692	0.0011	0.010
10	1	10	9	1	9	5870.2216	0.0042	0.010
10	0	10	9	0	9	5914.7271	-0.0058	0.010
10	2	9	9	2	8	5943.8201	0.0106	0.010
10	6	4	9	6	3	5950.8332	-0.0137	0.010
10	5	6	9	5	5	5951.3196	-0.0128	0.010
10	4	7	9	4	6	5952.2636	0.0178	0.010
10	4	6	9	4	5	5952.2671	-0.0087	0.010
10	3	8	9	3	7	5953.5976	0.0078	0.010
10	3	7	9	3	6	5955.2926	-0.0021	0.010
10	2	8	9	2	7	5978.4634	-0.0004	0.010
10	1	9	9	1	8	6010.7903	0.0060	0.010
11	0	11	10	0	10	6499.1969	-0.0054	0.010
11	2	10	10	2	9	6536.7627	-0.0122	0.010
11	6	6	10	6	5	6546.1632	-0.0130	0.010
11	4	7	10	4	6	6548.0947	0.0050	0.010
11	3	9	10	3	8	6549.6158	0.0204	0.010
11	3	8	10	3	7	6552.3515	-0.0026	0.010
11	2	9	10	2	8	6581.8553	-0.0162	0.010

11	1	10	10	1	9	6609.2730	0.0110	0.010
12	6	7	11	6	6	7141.5782	0.0025	0.010
12	5	8	11	5	7	7142.4118	-0.0029	0.010
12	4	9	11	4	8	7143.9703	0.0034	0.010
12	4	8	11	4	7	7144.0961	0.0165	0.010
12	3	10	11	3	9	7145.6980	0.0054	0.010
12	3	9	11	3	8	7149.9586	-0.0015	0.010
13	7	6	12	7	5	7736.4410	0.0201	0.010
13	6	8	12	6	7	7737.0644	0.0129	0.010
13	5	9	12	5	8	7738.1196	0.0014	0.010
13	4	10	12	4	9	7740.0615	-0.0060	0.010
13	4	9	12	4	8	7740.2582	-0.0090	0.010
13	3	11	12	3	10	7741.8327	-0.0199	0.010
13	3	10	12	3	9	7748.1759	-0.0316	0.010

Table S5. Experimental rotational transitions for sparteine···$H_2{}^{16}O$ (obs), along with residuals (res) and transition uncertainties (w). All frequencies in MHz.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	res	w
8	1	8	7	1	7	4081.6819	-0.0276	0.010
8	0	8	7	0	7	4123.2918	-0.0370	0.025
8	2	7	7	2	6	4151.0667	-0.0164	0.010
8	4	5	7	4	4	4159.0520	0.0150	0.010
8	4	4	7	4	3	4159.0520	-0.0119	0.010
8	3	6	7	3	5	4160.3286	0.0099	0.010
8	3	5	7	3	4	4161.9184	0.0043	0.010
8	2	6	7	2	5	4183.8647	0.0174	0.010
8	1	7	7	1	6	4213.9423	-0.0086	0.010
9	1	9	8	1	8	4589.7891	-0.0231	0.010
9	0	9	8	0	8	4630.1834	-0.0447	0.025
9	2	8	8	2	7	4668.2081	-0.0093	0.010
9	3	7	8	3	6	4681.1453	0.0105	0.010
9	3	6	8	3	5	4684.0496	0.0064	0.010
9	2	7	8	2	6	4713.5593	0.0077	0.010
9	1	8	8	1	7	4737.4683	-0.0015	0.010
10	1	10	9	1	9	5097.2958	-0.0263	0.010
10	0	10	9	0	9	5135.1444	-0.0358	0.025
10	2	9	9	2	8	5184.7386	-0.0057	0.010
10	6	4	9	6	3	5197.8503	-0.0085	0.010
10	5	6	9	5	5	5198.7459	0.0051	0.010
10	4	7	9	4	6	5200.3979	0.0119	0.010
10	4	6	9	4	5	5200.5334	0.0078	0.010
10	3	8	9	3	7	5202.0788	0.0062	0.010
10	3	7	9	3	6	5207.0261	0.0073	0.010
10	2	8	9	2	7	5244.5666	0.0113	0.010
10	1	9	9	1	8	5259.6673	-0.0030	0.010
11	1	11	10	1	10	5604.2313	-0.0149	0.010
11	0	11	10	0	10	5638.5272	-0.0262	0.025
11	2	10	10	2	9	5700.5923	-0.0129	0.010
11	7	5	10	7	3	5717.3848	-0.0200	0.010
11	7	5	10	7	4	5717.3848	-0.0200	0.010
11	6	5	10	6	4	5718.1045	0.0166	0.010
11	5	7	10	5	6	5719.2729	0.0065	0.010
11	4	8	10	4	7	5721.4237	0.0029	0.010
11	4	7	10	4	6	5721.6976	-0.0014	0.010
11	3	9	10	3	8	5723.0834	0.0108	0.010
11	3	8	10	3	7	5731.0301	0.0074	0.010
11	2	9	10	2	8	5776.4167	0.0114	0.010
11	1	10	10	1	9	5780.3098	-0.0074	0.010
12	1	12	11	1	11	6110.5861	-0.0198	0.010
12	0	12	11	0	11	6140.7535	-0.0250	0.025
12	2	11	11	2	10	6215.7385	-0.0088	0.010

12	9	3	11	9	2	6236.6076	-0.0239	0.010
12	8	4	11	8	3	6236.9873	-0.0068	0.010
12	7	5	11	7	4	6237.5418	-0.0089	0.010
12	6	7	11	6	6	6238.4516	0.0080	0.010
12	5	8	11	5	7	6239.9882	0.0103	0.010
12	5	7	11	5	6	6239.9882	-0.0004	0.010
12	4	9	11	4	8	6242.7241	0.0119	0.010
12	4	8	11	4	7	6243.2366	0.0049	0.010
12	3	10	11	3	9	6244.0710	0.0098	0.010
12	3	9	11	3	8	6256.2772	0.0289	0.010
12	1	11	11	1	10	6299.1722	0.0084	0.010
12	2	10	11	2	9	6308.5774	-0.0004	0.010
13	1	13	12	1	12	6616.4282	-0.0063	0.010
13	0	13	12	0	12	6642.2776	0.0007	0.010
13	2	12	12	2	11	6730.1143	-0.0094	0.010
13	8	6	12	8	5	6757.0668	-0.0153	0.010
13	7	6	12	7	5	6757.8116	0.0151	0.010
13	6	8	12	6	7	6758.9516	0.0137	0.010
13	5	9	12	5	8	6760.9091	0.0172	0.010
13	4	10	12	4	9	6764.2715	0.0068	0.010
13	3	11	12	3	10	6764.9617	0.0082	0.010
13	4	9	12	4	8	6765.1829	-0.0002	0.010
13	3	10	12	3	9	6782.8992	0.0142	0.010
13	1	12	12	1	11	6815.9704	0.0051	0.010
13	2	11	12	2	10	6840.5536	0.0033	0.010
14	0	14	13	0	13	7143.4263	0.0221	0.010
14	1	14	13	1	13	7121.7775	0.0034	0.010
14	2	13	13	2	12	7243.6942	-0.0017	0.010
14	9	6	13	9	5	7276.6509	-0.0078	0.010
14	8	6	13	8	5	7277.2668	0.0154	0.010
14	7	8	13	7	7	7278.1593	0.0089	0.010
14	6	9	13	6	8	7279.5905	0.0079	0.010
14	6	8	13	6	7	7279.5905	0.0071	0.010
14	5	10	13	5	9	7282.0482	0.0241	0.010
14	5	9	13	5	8	7282.0482	-0.0214	0.010
14	3	12	13	3	11	7285.6607	0.0053	0.010
14	4	11	13	4	10	7286.0744	0.0001	0.010
14	4	10	13	4	9	7287.6229	-0.0021	0.010
14	3	11	13	3	10	7311.0940	-0.0025	0.010
14	1	13	13	1	12	7330.5015	-0.0005	0.010
14	2	12	13	2	11	7371.8431	-0.0087	0.010
15	1	15	14	1	14	7626.6947	0.0218	0.010
15	0	15	14	0	14	7644.4509	0.0263	0.010
15	2	14	14	2	13	7756.4329	-0.0016	0.010
15	8	7	14	8	6	7797.5183	0.0100	0.010
15	7	8	14	7	7	7798.6286	0.0076	0.010
15	6	10	14	6	9	7800.3887	-0.0008	0.010
15	5	11	14	5	10	7803.3848	-0.0049	0.010
15	5	10	14	5	9	7803.4410	-0.0351	0.010

15	3	13	14	3	12	7806.0654	-0.0028	0.010
15	4	12	14	4	11	7808.1211	-0.0070	0.010
15	4	11	14	4	10	7810.6286	-0.0151	0.010
15	3	12	14	3	11	7840.9722	-0.0177	0.010
15	1	14	14	1	13	7842.6138	0.0046	0.010
15	2	13	14	2	12	7902.0432	-0.0458	0.010

Table S6. Experimental rotational transitions for sparteine···$H_2{}^{18}O$ (obs), along with residuals (res) and transition uncertainties (w). All frequencies in MHz.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	res	w
8	1	8	7	1	7	4018.8283	-0.0428	0.010
8	0	8	7	0	7	4060.7854	-0.0335	0.025
8	2	7	7	2	6	4091.1965	-0.0129	0.010
8	3	6	7	3	5	4101.3637	0.0117	0.010
8	3	5	7	3	4	4103.2249	0.0093	0.010
8	2	6	7	2	5	4127.1481	0.0266	0.010
8	1	7	7	1	6	4156.3630	0.0049	0.010
9	1	9	8	1	8	4518.9132	-0.0199	0.010
9	0	9	8	0	8	4559.2098	-0.0364	0.025
9	2	8	8	2	7	4600.6697	-0.0109	0.010
9	5	4	8	5	3	4611.8736	-0.0321	0.010
9	3	7	8	3	6	4614.8585	0.0126	0.010
9	3	6	8	3	5	4618.2502	0.0093	0.010
9	2	7	8	2	6	4650.2242	0.0183	0.010
9	1	8	8	1	7	4672.3105	0.0035	0.010
10	1	10	9	1	9	5018.3360	-0.0241	0.010
10	0	10	9	0	9	5055.6491	-0.0314	0.025
10	2	9	9	2	8	5109.4760	-0.0078	0.010
10	4	7	9	4	6	5126.7414	0.0075	0.010
10	4	6	9	4	5	5126.9084	0.0016	0.010
10	3	8	9	3	7	5128.4694	0.0141	0.010
10	3	7	9	3	6	5134.2289	0.0057	0.010
10	2	8	9	2	7	5174.5799	0.0140	0.010
10	1	9	9	1	8	5186.7788	0.0005	0.010
11	1	11	10	1	10	5517.1494	-0.0149	0.010
11	0	11	10	0	10	5550.5331	-0.0218	0.025
11	2	10	10	2	9	5617.5501	-0.0059	0.010
11	6	6	10	6	5	5636.8302	-0.0184	0.010
11	5	6	10	5	5	5638.1560	0.0064	0.010
11	4	8	10	4	7	5640.5051	0.0048	0.010
11	4	7	10	4	6	5640.8496	0.0050	0.010
11	3	9	10	3	8	5642.1188	0.0087	0.010
11	3	8	10	3	7	5651.3773	0.0094	0.010
11	1	10	10	1	9	5699.5006	-0.0071	0.010
11	2	9	10	2	8	5699.6893	0.0166	0.010
12	1	12	11	1	11	6015.3503	-0.0236	0.010
12	0	12	11	0	11	6044.3296	-0.0195	0.025
12	2	11	11	2	10	6124.8279	-0.0129	0.010
12	5	8	11	5	7	6151.5673	0.0061	0.010
12	5	8	11	5	7	6151.5673	0.0061	0.010
12	5	7	11	5	6	6151.5673	-0.0080	0.010
12	4	9	11	4	8	6154.5508	0.0065	0.010
12	4	8	11	4	7	6155.1982	0.0111	0.010
12	3	10	11	3	9	6155.7353	0.0105	0.010
12	3	9	11	3	8	6169.9120	0.0232	0.010
12	1	11	11	1	10	6210.2322	0.0101	0.010
12	2	10	11	2	9	6224.9419	0.0002	0.010

13	1	13	12	1	12	6513.0262	-0.0029	0.010
13	0	13	12	0	12	6537.5148	0.0062	0.010
13	2	12	12	2	11	6631.2761	-0.0130	0.010
13	6	8	12	6	7	6663.0662	0.0122	0.010
13	5	9	12	5	8	6665.2228	0.0203	0.010
13	4	10	12	4	9	6668.8750	0.0069	0.010
13	3	11	12	3	10	6669.2050	0.0031	0.010
13	4	9	12	4	8	6669.9943	-0.0094	0.010
13	3	10	12	3	9	6689.9995	0.0109	0.010
13	1	12	12	1	11	6718.6574	-0.0001	0.010
13	2	11	12	2	10	6749.8150	0.0046	0.010
14	1	14	13	1	13	7010.1921	0.0125	0.010
14	0	14	13	0	13	7030.4163	0.0260	0.010
14	2	13	13	2	12	7136.8611	-0.0011	0.010
14	7	8	13	7	7	7174.8215	-0.0057	0.010
14	6	9	13	6	8	7176.3946	-0.0049	0.010
14	5	10	13	5	9	7179.0890	0.0048	0.010
14	5	10	13	5	9	7179.0890	0.0048	0.010
14	3	12	13	3	11	7182.4288	-0.0066	0.010
14	4	11	13	4	10	7183.4555	-0.0085	0.010
14	4	10	13	4	9	7185.3673	-0.0123	0.010
14	3	11	13	3	10	7211.8156	-0.0135	0.010
14	1	13	13	1	12	7224.5855	-0.0043	0.010
14	2	12	13	2	11	7273.7600	-0.0300	0.010
15	1	15	14	1	14	7506.9051	0.0252	0.010
15	0	15	14	0	14	7523.2720	0.0278	0.010
15	3	13	14	3	12	7695.3093	-0.0058	0.010
15	1	14	14	1	13	7727.8636	-0.0080	0.010
15	3	12	14	3	11	7735.4559	-0.0368	0.010

Table S7. Rotational parameters for the dimer sparteine···$H_2{}^{18}O$.

	Experiment	*Theory*[b]
		Trans-lp – W_{CD}
A / MHz[a]	754.733(44)	730.6/739.4/743.9
B / MHz	264.75898(39)	273.6/271.8/267.0
C / MHz	247.34013(41)	252.4/250.6/249.4
Δ_J / Hz	13.94(87)	5.2/6.0/4.7
Δ_{JK} / Hz	-129.5(78)	-13./-16./-14.
Δ_K / kHz		0.11/0.15/0.10
δ_J / Hz		0.47/0.87/0.31
δ_K / Hz		15./35./24.
$\lvert\mu_a\rvert$ / D		0.55/0.55/0.66
$\lvert\mu_b\rvert$ / D		2.43/2.53/2.43
$\lvert\mu_c\rvert$ / D		0.96/0.56/1.03
μ_{TOT} / D		2.67/2.64/2.73
N	76	
σ / kHz	16.4	

[a]Rotational constants (A, B, C), centrifugal distortion constants (Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K), Electric dipole moments (μ_α, α=a, b, c), number of fitted transitions (N) and rms deviation of the fit (σ). [b]MP2/ M06-2X/ B3LYP-D3 calculations, respectively.

Table S8. Predicted atomic coordinates (angstrom) for *trans*-lp sparteine (B3LYP-D3/6-311++G(d,p), principal axes of inertia labelled as *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å
N	1.5353	0.7273	-0.2594
C	2.7229	1.2782	-0.9120
C	3.5843	0.1954	-1.5572
C	3.9884	-0.8482	-0.5126
C	2.7337	-1.4035	0.1660
C	1.8540	-0.2909	0.7532
C	0.5479	-0.8423	1.3700
C	-0.2021	0.3044	2.0550
C	-0.5782	1.2918	0.9462
C	0.7058	1.8042	0.2821
C	-1.5435	0.6162	-0.0732
C	-2.9260	1.2804	-0.0526
C	-3.8997	0.6064	-1.0228
C	-3.9592	-0.8982	-0.7423
C	-2.5527	-1.4956	-0.7407
N	-1.6822	-0.8213	0.2194
C	-0.3837	-1.4959	0.3093
H	-1.0921	-0.0615	2.5693
H	0.4419	0.7911	2.7955
H	-1.0828	2.1611	1.3804
H	1.2732	2.4001	1.0253
H	0.4524	2.4814	-0.5410
H	2.4295	0.1799	1.5790
H	0.8365	-1.5937	2.1113
H	4.4661	0.6570	-2.0131
H	3.0139	-0.2861	-2.3596
H	2.1575	-1.9753	-0.5683
H	3.0012	-2.0935	0.9734
H	3.3411	1.8426	-0.1835
H	2.3895	1.9973	-1.6669
H	4.5673	-1.6566	-0.9698
H	4.6363	-0.3778	0.2384
H	-1.1175	0.7388	-1.0879
H	-0.5773	-2.5390	0.5743
H	0.1108	-1.4960	-0.6754
H	-4.5736	-1.4107	-1.4897
H	-4.4189	-1.0728	0.2367
H	-4.8945	1.0567	-0.9468
H	-3.5551	0.7695	-2.0523
H	-2.8111	2.3423	-0.2967
H	-3.3217	1.2223	0.9689
H	-2.5944	-2.5568	-0.4758
H	-2.1295	-1.4372	-1.7649

Table S9. Predicted atomic coordinates (angstrom) for *cis*-lp sparteine (B3LYP-D3/6-311++G(d,p), principal axes of inertia labelled as *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å
N	1.5333	0.5570	-0.5539
C	2.8143	0.6722	-1.2433
C	3.5746	-0.6533	-1.2551
C	3.7604	-1.1749	0.1725
C	2.4039	-1.2349	0.8814
C	1.6902	0.1229	0.8408
C	0.3516	0.1185	1.6177
C	-0.2962	1.5026	1.5196
C	-0.5947	1.7376	0.0341
C	0.7422	1.7719	-0.7176
C	-1.5795	0.6797	-0.5096
C	-3.0323	0.9492	-0.0502
C	-3.9936	-0.1056	-0.6162
C	-3.5083	-1.5186	-0.2660
C	-2.0500	-1.6958	-0.7250
N	-1.1355	-0.6874	-0.2015
C	-0.6862	-0.9216	1.1640
H	-1.2046	1.5478	2.1272
H	0.3814	2.2781	1.8931
H	-1.0638	2.7182	-0.1039
H	1.3047	2.6625	-0.3645
H	0.5657	1.9154	-1.7893
H	2.3403	0.8512	1.3776
H	0.6000	-0.1051	2.6616
H	4.5416	-0.5163	-1.7500
H	3.0042	-1.3820	-1.8413
H	1.7728	-1.9780	0.3842
H	2.5247	-1.5452	1.9252
H	3.4484	1.4527	-0.7700
H	2.6203	1.0025	-2.2685
H	4.2364	-2.1606	0.1681
H	4.4302	-0.5009	0.7222
H	-1.5719	0.7567	-1.6074
H	-1.5091	-0.9005	1.9056
H	-0.2659	-1.9307	1.2070
H	-3.3358	1.9530	-0.3682
H	-3.0852	0.9328	1.0441
H	-5.0096	0.0616	-0.2446
H	-4.0374	-0.0026	-1.7090
H	-1.6712	-2.6845	-0.4476
H	-2.0178	-1.6403	-1.8221
H	-4.1431	-2.2771	-0.7371
H	-3.5771	-1.6733	0.8174

Table S10. Predicted atomic coordinates (angstrom) for monohydrated sparteine *trans*-lp – W(CD) (B3LYP-D3/6-311++G(d,p), principal axes of inertia labelled *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å	Atom	*a* / Å	*b* / Å	*c* / Å
N	-1.8130	-0.7069	0.2969	O	3.0544	2.4457	0.7109
C	-3.0869	-1.4232	0.2047	H	3.9909	2.2555	0.6111
C	-3.9271	-0.9601	-0.9828	H	2.5828	1.6659	0.3326
C	-4.1720	0.5481	-0.8986				
C	-2.8299	1.2772	-0.7986				
C	-1.9768	0.7549	0.3656				
C	-0.5887	1.4342	0.4266				
C	0.1360	0.9613	1.6916				
C	0.3525	-0.5456	1.5253				
C	-1.0174	-1.2269	1.4112				
C	1.2460	-0.8455	0.2862				
C	2.5746	-1.4953	0.6873				
C	3.4448	-1.8076	-0.5339				
C	3.6326	-0.5467	-1.3838				
C	2.2840	0.0978	-1.7055				
N	1.5183	0.3888	-0.4853				
C	0.2798	1.1157	-0.8223				
H	1.0763	1.4918	1.8393				
H	-0.4883	1.1517	2.5712				
H	0.8443	-0.9491	2.4161				
H	-1.5553	-1.0998	2.3715				
H	-0.8883	-2.3043	1.2587				
H	-2.5079	1.0210	1.3039				
H	-0.7574	2.5133	0.4791				
H	-4.8724	-1.5118	-0.9944				
H	-3.3974	-1.1971	-1.9124				
H	-2.2863	1.1469	-1.7397				
H	-2.9797	2.3529	-0.6596				
H	-3.6761	-1.2888	1.1349				
H	-2.8670	-2.4920	0.1209				
H	-4.7380	0.9024	-1.7657				
H	-4.7783	0.7686	-0.0106				
H	0.7005	-1.5474	-0.3692				
H	0.5802	2.0424	-1.3170				
H	-0.3019	0.5243	-1.5432				
H	4.1554	-0.7776	-2.3171				
H	4.2533	0.1740	-0.8395				
H	4.4129	-2.2146	-0.2262				
H	2.9528	-2.5808	-1.1376				
H	2.3636	-2.4095	1.2519				
H	3.1049	-0.8128	1.3628				
H	2.4336	1.0398	-2.2413				
H	1.7046	-0.5678	-2.3718				

Table S11. Principal axes system coordinates (angstrom) of the oxygen atom in sparteine-water obtained from the Kraitchman equations, and comparison with the predicted atomic coordinates for the dimer *trans*-lp – W(CD) in Table S10.

	Experiment				Theory (B3LYP-D3)		
Atom	$\|a\|$ / Å	$\|b\|$ / Å	$\|c\|$ / Å	Atom	a / Å	b / Å	c / Å
O	3.382(2)	2.255(2)	0.748(10)	O	3.0544	2.4457	0.7109

Table S12. Predicted atomic coordinates (angstrom) for monohydrated sparteine *trans*-lp – W(AB) (B3LYP-D3/6-311++G(d,p), principal axes of inertia labelled *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å	Atom	*a* / Å	*b* / Å	*c* / Å
N	1.4996	-0.0590	0.7300	O	0.7141	2.6611	0.2652
C	2.7465	0.3946	1.3773	H	-0.1931	2.7729	-0.0310
C	3.6604	1.1478	0.4122	H	0.8456	1.6905	0.3471
C	3.9706	0.2854	-0.8140				
C	2.6636	-0.1912	-1.4539				
C	1.7713	-0.9208	-0.4419				
C	0.4500	-1.4265	-1.0611				
C	-0.3059	-2.2528	-0.0151				
C	-0.6526	-1.2900	1.1241				
C	0.6451	-0.7325	1.7215				
C	-1.6071	-0.1711	0.6126				
C	-2.9918	-0.2812	1.2652				
C	-3.9499	0.7971	0.7525				
C	-4.0121	0.7601	-0.7773				
C	-2.6054	0.8275	-1.3702				
N	-1.7504	-0.2350	-0.8512				
C	-0.4708	-0.2806	-1.5661				
H	-1.2090	-2.6928	-0.4413				
H	0.3251	-3.0678	0.3548				
H	-1.1593	-1.8342	1.9274				
H	1.1988	-1.5632	2.1966				
H	0.4148	-0.0070	2.5087				
H	2.3270	-1.8169	-0.0990				
H	0.7260	-2.0623	-1.9075				
H	4.5796	1.4238	0.9384				
H	3.1692	2.0746	0.1027				
H	2.1270	0.6724	-1.8585				
H	2.8647	-0.8699	-2.2895				
H	3.2871	-0.4746	1.7960				
H	2.4684	1.0399	2.2151				
H	4.5693	0.8447	-1.5390				
H	4.5678	-0.5847	-0.5115				
H	-1.1834	0.8081	0.9042				
H	-0.7022	-0.4332	-2.6240				
H	0.0507	0.6867	-1.4975				
H	-4.6126	1.5897	-1.1640				
H	-4.4876	-0.1708	-1.1051				
H	-4.9462	0.6661	1.1858				
H	-3.5905	1.7823	1.0772				
H	-2.8760	-0.2074	2.3519				
H	-3.3985	-1.2758	1.0456				
H	-2.6487	0.7307	-2.4592				
H	-2.1699	1.8278	-1.1596				

Table S13. Predicted atomic coordinates (angstrom) for monohydrated sparteine *cis*-lp – W(AB-CD) (B3LYP-D3/6-311++G(d,p), principal axes of inertia labelled *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å	Atom	*a* / Å	*b* / Å	*c* / Å
N	-1.4912	-0.2871	-0.6707	O	-0.8005	2.4222	-1.1854
C	-2.8209	-0.0510	-1.2565	H	-0.0094	2.7952	-0.7897
C	-3.6457	0.9303	-0.4228	H	-0.8217	1.4982	-0.8502
C	-3.7467	0.4600	1.0315				
C	-2.3467	0.1735	1.5847				
C	-1.5989	-0.8284	0.6983				
C	-0.2336	-1.2579	1.2798				
C	0.4225	-2.2673	0.3334				
C	0.6779	-1.5256	-0.9841				
C	-0.6792	-1.1126	-1.5724				
C	1.6516	-0.3458	-0.7709				
C	3.1085	-0.8264	-0.5769				
C	4.0621	0.3571	-0.3604				
C	3.5664	1.2440	0.7886				
C	2.1093	1.6592	0.5276				
N	1.1944	0.5391	0.3158				
C	0.7719	-0.1259	1.5462				
H	1.3485	-2.6576	0.7643				
H	-0.2383	-3.1237	0.1611				
H	1.1437	-2.2000	-1.7109				
H	-1.2244	-2.0381	-1.8418				
H	-0.5336	-0.5445	-2.4967				
H	-2.2086	-1.7563	0.6637				
H	-0.4460	-1.7328	2.2443				
H	-4.6404	1.0290	-0.8692				
H	-3.1654	1.9115	-0.4648				
H	-1.7767	1.1069	1.6257				
H	-2.4053	-0.2245	2.6036				
H	-3.3655	-1.0101	-1.3570				
H	-2.6748	0.3485	-2.2636				
H	-4.2556	1.2105	1.6443				
H	-4.3500	-0.4557	1.0841				
H	1.6324	0.2698	-1.6819				
H	1.6150	-0.5675	2.1101				
H	0.3318	0.6347	2.1979				
H	4.1934	2.1360	0.8915				
H	3.6336	0.6972	1.7362				
H	5.0782	-0.0002	-0.1666				
H	4.1093	0.9558	-1.2799				
H	3.4162	-1.4102	-1.4514				
H	3.1684	-1.4964	0.2876				
H	1.7224	2.2728	1.3475				
H	2.0920	2.2820	-0.3787				

Table S14. Effective structure (angstrom) for monohydrated sparteine *trans*-lp – W(CD) following a fit of six moments of inertia (principal inertial axes labelled *a*, *b*, *c*).

Atom	*a* / Å	*b* / Å	*c* / Å	Atom	*a* / Å	*b* / Å	*c* / Å
N	-1.8310	-0.7275	0.2102	O	3.2235	2.2935	0.7260
C	- 3.1051	-1.4219	0.0154	H	4.1310	2.0879	0.4859
C	- 3.9287	-0.8143	-1.1177	H	2.6770	1.5625	0.3505
C	- 4.1709	0.6731	-0.8536				
C	- 2.8280	1.3791	-0.6484				
C	- 1.9920	0.7160	0.4543				
C	- 0.6037	1.3772	0.6152				
C	0.1034	0.7509	1.8225				
C	0.3187	-0.7259	1.4766				
C	-1.0510	-1.3826	1.2632				
C	1.2277	-0.8763	0.2214				
C	2.5490	-1.5751	0.5573				
C	3.4347	-1.7400	-0.6817				
C	3.6366	-0.3860	-1.3694				
C	2.2942	0.2984	-1.6275				
N	1.5131	0.4417	-0.3905				
C	0.2800	1.2098	-0.6518				
H	4.2518	0.2608	-0.7334				
H	4.1711	-0.5040	-2.3169				
H	2.9491	-2.4319	-1.3809				
H	4.3974	-2.1850	-0.4134				
H	3.0719	-0.9818	1.3176				
H	2.3285	-2.5503	1.0038				
H	0.6890	-1.4915	-0.5217				
H	0.7981	-1.2369	2.3180				
H	-0.9226	-2.4342	0.9822				
H	-1.6011	-1.3711	2.2249				
H	-2.8868	-2.4730	-0.1951				
H	-3.7059	-1.3994	0.9472				
H	-4.8755	-1.3568	-1.2084				
H	-3.3875	-0.9384	-2.0626				
H	-4.7883	0.7863	0.0471				
H	-4.7245	1.1324	-1.6779				
H	-2.9767	2.4306	-0.3815				
H	-2.2722	1.3622	-1.5918				
H	-2.6148	0.8249	1.3679				
H	-0.5317	0.8352	2.7105				
H	1.0432	1.2558	2.0457				
H	-0.7706	2.4420	0.7967				
H	-0.2936	0.7130	-1.4467				
H	0.5892	2.1890	-1.0263				
H	1.7219	-0.2788	-2.3774				
H	2.4530	1.2981	-2.0425				

Table S15. Atomic coordinates of sparteine-(water)$_2$ (B3LYP-D3/6-311++G(d,p)). The predicted rotation constants are *A*=638.8 MHz, *B*=257.2 MHz, *C*=238.6 MHz.

Atom	*a* / Å	*b* / Å	*c* / Å	Atom	*a* / Å	*b* / Å	*c* / Å
N	-1.7747	0.3166	-0.6559	O	3.1710	-2.5761	0.3530
C	-3.1041	0.8756	-0.9634	H	4.1030	-2.3535	0.4227
C	-4.0053	0.9419	0.2692	H	2.6892	-1.7131	0.3728
C	-4.1388	-0.4404	0.9131	O	-0.8345	2.3748	1.1179
C	-2.7473	-1.0116	1.1986	H	-1.5397	3.0263	1.1607
C	-1.8795	-1.0396	-0.0645	H	-1.1682	1.6554	0.5330
C	-0.4776	-1.6397	0.1778				
C	0.2510	-1.7454	-1.1660				
C	0.4383	-0.3113	-1.6695				
C	-0.9426	0.3252	-1.8740				
C	1.3233	0.5119	-0.6902				
C	2.6615	0.9088	-1.3248				
C	3.5023	1.7561	-0.3642				
C	3.6757	1.0286	0.9730				
C	2.3236	0.5821	1.5307				
N	1.5928	-0.2473	0.5552				
C	0.3802	-0.8153	1.1775				
H	1.2038	-2.2640	-1.0653				
H	-0.3569	-2.3155	-1.8771				
H	0.9260	-0.3253	-2.6493				
H	-1.4617	-0.2130	-2.6875				
H	-0.8342	1.3673	-2.1928				
H	-2.9571	1.8751	-1.3848				
H	-3.5990	0.2673	-1.7425				
H	-3.5799	1.6412	0.9971				
H	-4.9833	1.3361	-0.0238				
H	-4.6763	-1.1096	0.2292				
H	-4.7292	-0.3841	1.8324				
H	-2.8200	-2.0310	1.5904				
H	-2.2578	-0.4040	1.9661				
H	-2.3850	-1.7004	-0.7963				
H	-0.6335	-2.6408	0.5893				
H	-0.2133	-0.0177	1.6393				
H	0.7253	-1.4666	1.9846				
H	1.7190	1.4605	1.8086				
H	2.4700	-0.0171	2.4343				
H	4.1732	1.6728	1.7048				
H	4.3161	0.1501	0.8326				
H	4.4758	1.9909	-0.8059				
H	2.9911	2.7110	-0.1905				
H	3.2042	-0.0030	-1.6029				
H	2.4631	1.4635	-2.2483				
H	0.7947	1.4407	-0.4310				

Table S16. Structural data and predicted binding energy for O-H···N hydrogen bonds in amines.

	Experiment		Theory[a]		
	r(H···N) / Å	∠(O-H···N) /deg	r(H···N) / Å	∠(O-H···N) /deg	E_B / kJ mol^{-1}
Tertiary amines					
Trimethyl amine-water[b]	1.818	[180.0]	1.868	171.5	-37.40
Cyclic tertiary amines					
Sparteine-Water[c] (*trans*-lp – $W_{AB\text{-}CD}$)			1.915	156.3	-54.1
Sparteine-Water[c] (*cis*-lp – W_{CD})	1.778	171.2	1.853	171.3	-43.4
Tropinone-Water[d] (*equat* – W)			1.845	167.4	-42.3
Cyclic secondary amines					
Pyrrolidine-Water[e] (*equat* – W_E)	1.89	163.5	1.877	163.9	-41.3
Piperidine-water[f] (*equat* – W_{II})			1.875	167.3	-41.6
Morpholine-water[g]	1.954	[180]	1.881	165.1	-39.2
Primary amines					
Aniline-water[h]	2.125	[180]	1.995	174.7	-27.3

[a]All theoretical parameters recalculated here with B3LYP-D3/6-311++G(d,p). [b]M. J. Tubergen, R. L. Kuczkowski, *J. Am. Chem. Soc*. **1993**, *115*, 9263. [c]This work, [d]P. Écija, M. Vallejo-López, L. Evangelisti, J. A. Fernández, A. Lesarri, W. Caminati, E. J. Cocinero, *ChemPhysChem* **2014**, *15*, 918. [e]W. Caminati, A. Dell'Erba, G. Maccaferri, P. G. Favero, *J. Am. Chem. Soc*. **1998**, *120*, 2616. [f]M. J. Tubergen, R. L. Kuczkowski, *Chem. Phys.* **1998**, *239*, 97. [g]O. Indris, W. Stahl, U. Kretschmer, *J. Mol. Spectrosc*. **1998**, *190*, 372. [h]U. Spoerel, W. Stahl, *J. Mol. Spectrosc*. **1998**, *190*, 278.