Supporting information

Table S1: Complete list of experimental lines measured for the 15c5 rotamer assigned to the MP2 conformer IV. For each line, the table indicates the assigned rotational transition, the experimental line position, ν_{exp}, and the difference with respect to the best–fit position of the line, ν_{fit}, provided by the rotational constants given in Table II. Note that the similar data for conformers I, II and II can be found in ref.[19].

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{exp} (MHz)	$\nu_{fit} - \nu_{exp}$ (MHz)
4	4	0	3	3	1	5120.1989	-0.0026
5	5	1	4	4	0	6459.7137	-0.0039
5	5	0	4	4	1	6463.8746	-0.0035
5	3	2	4	2	3	5846.3385	-0.0076
5	4	2	4	3	1	5803.0265	-0.0052
5	4	1	4	3	2	5935.3048	0.0158
6	5	1	5	4	2	7240.8168	0.0055
6	5	2	5	4	2	7233.7848	0.0009
7	4	3	6	3	3	7233.4849	-0.0004
8	0	8	7	1	7	4888.8009	-0.0037
8	1	8	7	0	7	4889.283	-0.0008
8	2	7	7	1	6	5405.5537	0.0027
9	0	9	8	0	8	5468.7377	-0.0007
9	1	9	8	0	8	5468.7609	-0.0025
9	1	9	8	1	8	5468.6686	0.0040
9	0	9	8	1	8	5468.6362	-0.0033
9	1	8	8	1	7	5974.9019	0.0028
9	2	8	8	2	7	5971.2628	0.0053
9	2	7	8	2	6	6520.8234	-0.0042
9	2	7	8	3	6	6424.377	0.0053
10	0	10	9	0	9	6048.3831	-0.0120
10	1	10	9	1	9	6048.3831	0.0068
10	0	10	9	1	9	6048.3831	0.0131
10	1	10	9	0	9	6048.3831	-0.0183
10	1	9	9	2	8	6551.0146	0.0050
10	2	9	9	1	8	6552.993	0.0035
10	3	8	9	2	7	7088.4745	-0.0078
10	2	8	9	3	7	7040.3941	-0.0001
10	3	8	9	2	7	7088.4817	-0.0006
11	0	11	10	1	10	6628.0824	0.0013
11	1	11	10	0	10	6628.0824	-0.0065
11	1	10	10	2	9	7130.9368	0.0020
11	2	10	10	1	9	7131.4969	0.0013
12	1	12	11	0	11	7207.7892	-0.0049
12	0	12	11	1	11	7207.7892	-0.0030
12	1	11	11	2	10	7710.5171	-0.0025
12	2	11	11	1	10	7710.6737	0.0001
13	1	12	12	2	11	8290.0702	0.0126
13	2	12	12	1	11	8290.0864	-0.0125
13	2	11	12	3	10	8795.2702	0.0001
13	3	11	12	2	10	8796.8322	-0.0001
13	0	13	12	0	12	7787.5087	0.0021
13	1	13	12	1	12	7787.5087	0.0024
14	0	14	13	1	13	8367.2237	0.0011
14	1	14	13	0	13	8367.2238	0.0011
14	2	12	13	3	11	9374.4827	-0.0007
14	3	12	13	2	11	9374.9415	-0.0008
14	0	14	13	1	13	8367.2232	0.0006
14	1	14	13	0	13	8367.2232	0.0005

Table S2: Same as Table S1 for the 15c5 rotamer assigned to the MP2 conformer V.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{exp} (MHz)	$\nu_{fit} - \nu_{exp}$ (MHz)
8	0	8	7	1	7	4972.9013	0.0002
8	1	8	7	0	7	4972.9013	-0.0085
8	3	5	7	3	4	6591.4177	0.0001
9	1	9	8	1	8	5562.9493	-0.0022
9	0	9	8	0	8	5562.9493	-0.0031
9	2	8	8	2	7	6068.1234	0.0056
9	1	8	8	1	7	6068.1924	-0.0177
10	1	10	9	1	9	6153.0145	0.0099
10	0	10	9	0	9	6153.0145	0.0098
10	2	9	9	2	8	6658.0169	0.0038
10	1	9	9	1	8	6658.0329	0.0041
11	1	11	10	1	10	6743.0569	-0.0032
11	0	11	10	0	10	6743.0569	-0.0032
12	0	12	11	0	11	7333.1138	-0.0026
12	1	12	11	1	11	7333.1138	-0.0026
12	2	11	11	2	10	7837.9294	0.00778
12	1	11	11	1	10	7837.9294	0.00737
13	0	13	12	0	12	7923.1694	-0.0030
13	1	13	12	1	12	7923.1694	-0.0030
13	1	12	12	1	11	8427.9236	0.0044
13	2	12	12	2	11	8427.9236	0.0045
12	3	10	11	3	9	8343.8344	0.0030
12	2	10	11	2	9	8343.8521	-0.0038
14	0	14	13	0	13	8513.2251	-0.0020
14	1	14	13	1	13	8513.2251	-0.0020
14	1	13	13	1	12	9017.935	0.0022
14	2	13	13	2	12	9017.935	0.0022
15	0	15	14	0	14	9103.2816	0.0017
15	1	15	14	1	14	9103.2816	0.0017
15	1	14	14	1	13	9607.9535	-0.0035
15	2	14	14	2	13	9607.9535	-0.0035
16	0	16	15	0	15	9693.3334	0.0030
16	1	16	15	1	15	9693.3334	0.0030
16	1	15	15	1	14	10197.9834	-0.0043
16	2	15	15	2	14	10197.9834	-0.0043

Table S3: Same as Table S1 for the 15c5 rotamer assigned to the MP2 conformer VI.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{exp} (MHz)	$\nu_{fit} - \nu_{exp}$ (MHz)
8	0	8	7	1	7	4827.2339	0.0028
8	1	8	7	0	7	4827.2339	-0.0001
9	0	9	8	1	8	5398.6527	0.0010
9	1	9	8	0	8	5398.6527	0.00065
10	0	10	9	1	9	5970.0766	0.00065
10	1	10	9	0	9	5970.0766	0.0006
11	0	11	10	1	10	6541.5014	-0.001
11	1	11	10	0	10	6541.5014	-0.001
11	1	10	10	2	9	7053.1369	0.0001
11	2	10	10	1	9	7053.1369	-0.0007
12	0	12	11	1	11	7112.9292	-0.0009
12	1	12	11	0	11	7112.9292	-0.0009
13	0	13	12	1	12	7684.3569	-0.0011
13	1	13	12	0	12	7684.3569	-0.0011
13	1	12	12	2	11	8195.8793	0.0001
14	0	14	13	0	13	8255.7854	-0.0002
14	1	14	13	1	13	8255.7854	-0.0002
15	0	15	14	0	14	8827.2131	0.0006
15	1	15	14	1	14	8827.2131	0.0006
16	0	16	15	0	15	9398.6391	0.0006
16	1	16	15	1	15	9398.6391	0.0006

Table S4: Same as Table S1 for the 15c5 rotamer assigned to the MP2 conformer VIII.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{exp} (MHz)	$\nu_{fit} - \nu_{exp}$ (MHz)
6	6	0	5	5	0	8876.4626	-0.0043
6	6	1	5	5	1	8876.5151	0.0044
9	0	9	8	1	8	5413.5383	0.0062
9	1	9	8	0	8	5417.502	0.0014
10	0	10	9	1	9	5988.6335	0.0055
10	1	10	9	0	9	5990.1733	0.0045
11	0	11	10	1	10	6563.0417	0.0018
11	1	11	10	0	10	6563.6285	0.0016
11	1	10	10	2	9	7052.6752	-0.0009
11	2	10	10	1	9	7077.2823	-0.0027
12	0	12	11	1	11	7137.1919	0.0016
12	1	12	11	0	11	7137.4128	0.0022
13	1	13	12	0	12	7711.3279	-0.0011
13	0	13	12	1	12	7711.2446	-0.0028
14	1	14	13	0	13	8285.2987	-0.0061
14	0	14	13	1	13	8285.2696	-0.0053

Table S5: Same as Table S1 for the 15c5 rotamer assigned to the MP2 conformer IX.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{exp} (MHz)	$\nu_{fit} - \nu_{exp}$ (MHz)
7	0	7	6	1	6	4160.421	0.0016
7	1	7	6	0	6	4177.9751	0.0025
8	0	8	7	1	7	4725.0798	-0.0020
8	1	8	7	0	7	4731.9004	0.00032
9	0	9	8	1	8	5286.6342	-0.0026
9	1	9	8	0	8	5289.2043	0.0018
10	0	10	9	1	9	5846.9525	-0.0020
10	1	10	9	0	9	5847.8965	-0.0005
10	1	9	9	2	8	6335.4152	-0.0008
10	2	9	9	1	8	6372.5247	0.0035
11	0	11	10	1	10	6406.8078	0.0013
11	1	11	10	0	10	6407.1473	0.0010
11	3	8	10	4	7	7075.7899	0.0002
12	0	12	11	1	11	6966.4922	-0.0014
12	1	12	11	0	11	6966.6148	0.0005
12	1	11	11	2	10	7467.6384	-0.0011
12	2	11	11	1	10	7473.8215	-0.0008
13	0	13	12	1	12	7526.1279	0.0005
13	1	13	12	0	12	7526.1701	0.0004
13	1	12	12	2	11	8028.4676	-0.0017
14	0	14	13	1	13	8085.7459	-0.0012
14	1	14	13	0	13	8085.7603	-0.0015
15	0	15	14	1	14	8645.3646	-0.0009
15	1	15	14	0	14	8645.3734	0.0029
16	0	16	15	1	15	9204.9878	0.0018
16	1	16	15	0	15	9204.9878	0.0001

Table S6: Atomic cartesian coordinates (x, y, z, in Å) for the nine lowest energy conformers of 15–crown–5 predicted by the MP2/6-311++G(d,p) computation.

atom	Conformer I			Conformer II			Conformer III			Conformer IV			Conformer V		
C	0.707	0.143	-0.384	0.089	0.004	-0.007	-0.002	-0.004	-0.008	-0.427	-1.815	-0.718	-0.069	0.079	0.107
C	0.567	0.238	1.118	0.031	0.047	1.508	-0.006	0.096	1.506	-0.386	-1.547	0.773	0.666	-0.611	1.248
O	0.980	-0.989	1.690	1.291	0.016	2.155	1.338	0.010	1.980	0.350	-0.386	1.106	1.755	0.159	1.738
C	0.986	-0.936	3.100	1.936	-1.255	2.145	1.825	1.160	2.642	1.750	-0.606	1.282	1.393	1.224	2.606
C	1.605	-2.216	3.614	3.074	-1.309	1.149	2.265	2.266	1.702	2.313	0.676	1.862	1.820	2.554	2.022
O	2.949	-2.246	3.181	4.144	-0.519	1.659	1.122	2.865	1.118	3.680	0.444	2.206	0.988	2.819	0.913
C	3.626	-3.433	3.552	5.179	-0.301	0.720	1.473	3.910	0.233	4.577	1.452	1.779	1.436	3.900	0.121
C	4.918	-3.515	2.757	4.890	0.826	-0.254	0.209	4.499	-0.344	5.106	1.196	0.381	0.509	4.014	-1.064
O	4.742	-3.920	1.411	4.027	0.370	-1.288	-0.307	3.623	-1.329	4.033	1.289	-0.536	-0.734	4.528	-0.606
C	4.138	-2.954	0.547	3.599	1.436	-2.114	-1.602	4.030	-1.740	4.439	1.017	-1.864	-1.788	4.361	-1.538
C	2.743	-3.425	0.177	2.712	0.886	-3.213	-2.085	3.145	-2.871	3.204	0.753	-2.692	-2.604	3.111	-1.272
O	2.198	-2.510	-0.757	1.506	0.345	-2.693	-2.335	1.818	-2.449	2.729	-0.538	-2.367	-1.825	1.959	-1.544
C	0.883	-2.884	-1.132	1.530	-1.073	-2.577	-1.231	0.944	-2.647	1.476	-0.808	-2.960	-2.596	0.776	-1.403
C	0.195	-1.715	-1.811	0.293	-1.529	-1.824	-1.473	-0.306	-1.824	1.042	-2.198	-2.529	-1.703	-0.447	-1.532
O	-0.282	-0.743	-0.895	0.362	-1.331	-0.421	-1.353	-0.101	-0.428	0.839	-2.299	-1.131	-1.068	-0.837	-0.330
H	0.556	1.141	-0.820	-0.885	0.320	-0.412	0.556	-0.904	-0.307	-1.209	-2.559	-0.944	-0.509	1.025	0.430
H	1.713	-0.210	-0.622	0.857	0.694	-0.371	0.489	0.881	-0.426	-0.681	-0.875	-1.226	0.634	0.298	-0.707
H	1.203	1.059	1.486	-0.419	1.000	1.803	-0.571	-0.742	1.925	-1.410	-1.372	1.121	-0.039	-0.849	2.056
H	-0.478	0.456	1.383	-0.611	-0.769	1.868	-0.474	1.036	1.814	0.016	-2.427	1.294	1.096	-1.548	0.884
H	1.584	-0.081	3.452	2.337	-1.419	3.151	2.699	0.829	3.213	1.915	-1.432	1.990	1.898	1.074	3.570
H	-0.036	-0.836	3.497	1.216	-2.047	1.908	1.079	1.555	3.346	2.241	-0.840	0.333	0.310	1.240	2.779
H	1.544	-2.239	4.714	2.740	-0.933	0.182	2.838	3.017	2.272	1.754	0.954	2.765	1.723	3.346	2.782
H	1.054	-3.081	3.215	3.409	-2.354	1.029	2.917	1.843	0.923	2.225	1.476	1.123	2.873	2.488	1.711
H	3.009	-4.316	3.328	6.062	-0.026	1.306	2.024	4.696	0.775	4.108	2.444	1.828	-1.405	4.345	-2.568
H	3.852	-3.425	4.632	5.406	-1.221	0.159	2.111	3.534	-0.580	5.423	1.436	2.475	-2.450	5.228	-1.431
H	5.561	-4.277	3.207	5.835	1.183	-0.695	0.431	5.481	-0.792	5.547	0.189	0.342	0.379	3.022	-1.510
H	5.432	-2.545	2.811	4.419	1.655	0.294	-0.519	4.640	0.466	5.888	1.937	0.144	0.946	4.696	-1.810
H	4.082	-1.973	1.026	4.465	1.945	-2.569	-1.578	5.076	-2.091	5.084	0.128	-1.896	2.461	3.711	-0.235
H	4.754	-2.886	-0.355	3.034	2.171	-1.521	-2.304	3.955	-0.897	4.995	1.873	-2.278	1.428	4.838	0.696
H	2.110	-3.460	1.073	2.439	1.707	-3.886	-3.036	3.550	-3.235	2.444	1.514	-2.461	-3.499	3.126	-1.918
H	2.803	-4.434	-0.258	3.258	0.130	-3.792	-1.363	3.167	-3.700	3.452	0.814	-3.764	-2.929	3.108	-0.221
H	0.300	-3.159	-0.242	1.523	-1.528	-3.581	-1.160	0.665	-3.711	0.740	-0.051	-2.648	-3.372	0.748	-2.185
H	0.918	-3.746	-1.819	2.429	-1.403	-2.043	-0.297	1.431	-2.348	1.549	-0.782	-4.060	-3.092	0.754	-0.421
H	0.871	-1.265	-2.552	-0.593	-1.030	-2.242	-0.775	-1.093	-2.152	0.131	-2.482	-3.078	-0.961	-0.266	-2.325
H	-0.692	-2.086	-2.333	0.185	-2.610	-1.964	-2.497	-0.648	-1.997	1.835	-2.908	-2.777	-2.323	-1.302	-1.820

Table S6: Continues.

atom	Conformer VI			Conformer VII			Conformer VIII			Conformer IX		
C	-0.746	-1.109	1.301	0.035	0.032	-0.013	-0.113	-0.949	-0.316	-0.006	-0.015	-0.022
C	-0.053	-0.572	2.531	0.043	0.050	1.497	0.208	-0.351	1.032	0.002	0.060	1.498
O	1.281	-0.259	2.188	1.392	0.009	1.911	1.569	-0.586	1.341	1.354	0.023	1.957
C	2.081	0.039	3.314	1.532	-0.203	3.299	1.901	-0.028	2.601	1.762	1.137	2.726
C	3.527	-0.134	2.912	2.986	0.020	3.644	3.368	-0.267	2.880	2.199	2.319	1.884
O	3.744	-1.517	2.721	3.224	1.424	3.662	4.159	0.619	2.107	1.069	2.913	1.265
C	5.020	-1.814	2.183	4.551	1.793	3.332	5.232	-0.006	1.421	1.452	4.038	0.496
C	5.001	-3.246	1.675	4.718	2.076	1.852	4.773	-0.768	0.193	0.226	4.711	-0.069
O	4.440	-3.389	0.384	4.611	0.869	1.123	4.304	0.163	-0.756	-0.293	3.941	-1.136
C	3.050	-3.076	0.300	4.759	1.084	-0.267	3.567	-0.464	-1.787	-1.390	4.603	-1.745
C	2.592	-3.635	-1.041	4.343	-0.167	-1.004	2.997	0.634	-2.666	-1.912	3.775	-2.902
O	1.279	-3.212	-1.375	2.934	-0.173	-1.140	2.253	0.057	-3.741	-2.594	2.607	-2.492
C	0.242	-3.936	-0.730	2.457	-1.433	-1.570	0.851	0.231	-3.658	-1.762	1.483	-2.202
C	-0.755	-2.950	-0.165	0.947	-1.388	-1.698	0.174	-0.644	-2.621	-1.996	1.051	-0.761
O	-0.173	-2.360	0.982	0.303	-1.299	-0.440	0.437	-0.129	-1.328	-1.335	-0.181	-0.501
H	-1.823	-1.212	1.512	0.809	0.718	-0.370	0.298	-1.968	-0.375	0.564	-0.891	-0.342
H	-0.616	-0.405	0.466	-0.947	0.351	-0.391	-1.207	-1.007	-0.432	0.462	0.883	-0.441
H	-0.587	0.321	2.893	-0.513	-0.820	1.874	-0.002	0.727	1.010	-0.529	-0.808	1.902
H	-0.074	-1.339	3.319	-0.443	0.968	1.865	-0.438	-0.819	1.793	-0.498	0.974	1.834
H	1.904	1.070	3.660	1.236	-1.231	3.562	1.705	1.053	2.606	2.625	0.802	3.312
H	1.859	-0.652	4.139	0.910	0.500	3.872	1.297	-0.501	3.393	0.971	1.450	3.421
H	3.717	0.418	1.980	3.211	-0.406	4.633	3.601	-1.316	2.657	2.702	3.056	2.533
H	4.186	0.262	3.701	3.600	-0.468	2.882	3.565	-0.091	3.947	2.915	1.976	1.122
H	5.798	-1.697	2.955	4.769	2.715	3.883	5.902	0.800	1.112	1.987	4.761	1.133
H	5.253	-1.140	1.345	5.268	1.024	3.650	5.782	-0.683	2.091	2.119	3.737	-0.325
H	4.464	-3.871	2.405	5.705	2.542	1.684	3.968	-1.468	0.460	0.512	5.711	-0.435
H	6.029	-3.609	1.584	3.936	2.781	1.532	5.619	-1.349	-0.213	-0.525	4.833	0.724
H	2.503	-3.524	1.140	5.809	1.327	-0.501	2.749	-1.056	-1.357	-1.070	5.589	-2.124
H	2.870	-1.997	0.332	4.124	1.918	-0.600	4.212	-1.125	-2.387	-2.199	4.753	-1.014
H	2.667	-4.731	-1.043	4.817	-0.193	-1.999	2.368	1.290	-2.057	-2.645	4.379	-3.447
H	3.249	-3.247	-1.823	4.681	-1.043	-0.432	3.813	1.219	-3.101	-1.087	3.533	-3.585
H	0.634	-4.551	0.088	2.894	-1.696	-2.550	0.598	1.283	-3.463	-2.039	0.660	-2.871
H	-0.252	-4.594	-1.458	2.731	-2.210	-0.841	0.464	-0.043	-4.645	-0.707	1.730	-2.356
H	-0.963	-2.188	-0.929	0.614	-2.326	-2.157	-0.912	-0.654	-2.809	-3.065	0.884	-0.604
H	-1.697	-3.459	0.096	0.650	-0.559	-2.355	0.554	-1.673	-2.710	-1.658	1.840	-0.077