Supporting Information for

The rich conformational landscape of perillyl alcohol revealed by broadband rotational spectroscopy and theoretical modelling

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Table S1. The theoretical raw ΔD_e and *ZPE* corrected ΔD_0 relative dissociation energies (in kJ mol^{-1}), rotational constants (in MHz) and electric dipole moment components (in Debye) of the 54 half-chair conformers calculated at B3LYP-B3DJ/def2-TZVP and LMP2/Aug-cc-pVQZ levels of theory

	B3LYP-B3DJ/Def2-TZVP									LMP2/Aug-cc-pVQZ								
Conformer[a]	ΔD_e	ΔD_0	ΔG[b]	A	B	C	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	Conformer[a]	ΔD_e	ΔD_0[c]	A	B	C	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$
Eq-TG-G+	0.0	0.0	0.0	2790	520	502	1.1	0.7	0.8	**Eq-TG-G+**	0.0	0.0	2800	524	505	1.2	0.8	0.7
Eq-TG-T	1.1	1.0	1.0	2829	531	481	1.2	1.2	0.3	**Ax-G+G+G-**	0.1	0.6	2039	669	643	1.3	0.8	1.0
Eq-G+G+G+	1.2	1.1	0.5	2722	519	507	1.2	1.0	0.3	**Eq-TG-T**	0.7	0.7	2836	535	484	1.3	1.2	0.2
Eq-TG-G-	2.2	2.0	1.0	2794	529	483	1.2	0.6	0.3	**Eq-G+G+G+**	1.2	1.1	2716	523	512	1.3	1.0	0.4
Eq-TTG+	2.7	2.2	2.3	2774	519	491	1.0	0.6	0.6	**Ax-TG-G-**	0.7	1.4	1687	758	714	1.5	1.2	0.3
Eq-G+G+T	2.4	2.3	1.8	2702	531	490	1.2	1.3	0.1	**Eq-G+G+T**	2.0	1.9	2696	535	494	1.3	1.2	0.2
Ax-G+G+G-	1.9	2.4	3.1	2122	644	620	1.3	0.6	1.2	Eq-TG-G-	2.2	2.1	2803	534	485	1.2	0.7	0.3
Eq-G+G+G-	3.3	3.2	2.3	2642	539	489	1.1	0.6	0.5	**Eq-TTG+**	3.3	2.8	2777	523	494	1.1	0.7	0.7
Eq-TTT	3.8	3.2	3.5	2729	534	474	1.1	0.0	1.3	Eq-G+G+G-	3.3	3.2	2631	545	492	1.2	0.3	0.7
Ax-TG-G-	2.6	3.2	3.8	1741	725	687	1.5	1.2	0.3	**Ax-G+TG-**	3.4	3.4	1961	680	658	1.9	0.5	0.4
Eq-G+TG+	3.8	3.3	3.4	2784	518	490	0.9	0.8	1.3	**Eq-TTT**	4.0	3.5	2731	538	477	1.1	0.1	1.2
Eq-G+TT	4.7	4.1	4.1	2744	531	473	0.9	0.6	0.5	Eq-G-G-G+	4.5	3.5	2822	525	504	0.8	0.6	0.7
Eq-TTG-	5.1	4.5	4.1	2794	528	475	1.2	1.1	1.0	Eq-G+TG+	4.4	3.9	2788	522	494	1.0	0.9	1.3
Ax-G+TG-	4.6	4.6	5.3	2037	655	632	1.9	0.5	0.3	Ax-G-G+G-	4.6	4.2	2011	676	648	0.0	0.1	1.0
Eq-G-G-G+	5.6	4.6	3.8	2814	521	500	1.0	0.4	0.7	Eq-G-G+G+	5.3	4.3	2738	525	511	0.9	0.4	1.5
Eq-G+TG-	6.0	5.4	4.7	2822	527	472	1.0	0.8	0.9	Ax-TTG-	4.3	4.3	2023	668	649	1.1	1.5	1.0
Ax-TTG-	5.4	5.5	6.4	2109	643	624	1.1	1.5	1.2	Eq-G-G-T	5.4	4.4	2862	536	483	0.7	1.1	1.2
Eq-G-G+G+	6.6	5.6	4.7	2747	520	506	0.9	0.3	1.6	Eq-G+TT	4.9	4.4	2746	536	477	1.0	0.7	0.6
Eq-G-G-T	6.9	5.9	5.2	2856	531	480	0.8	1.0	1.3	Eq-G-TG+	6.5	5.0	2786	525	496	1.0	1.5	0.2
Eq-G+G-G+	7.1	6.0	4.2	2817	516	496	0.8	0.7	0.9	Eq-G-G+T	5.9	5.0	2724	537	494	0.9	0.3	1.0
Eq-TG+G+	6.8	6.1	5.1	2746	518	502	1.0	0.8	1.5	Eq-TTG-	5.6	5.0	2791	533	477	1.3	1.1	0.9
Eq-G-TG+	7.8	6.2	5.1	2785	521	492	1.1	1.5	0.4	Eq-G-TT	7.1	5.6	2740	541	479	1.0	1.1	0.5
Eq-G-G+T	7.5	6.6	5.9	2732	531	489	1.0	0.2	0.9	Ax-G-TG-	6.5	5.6	2004	676	655	0.2	1.5	0.9
Eq-G-G-G-	8.0	6.9	5.3	2808	530	482	0.8	0.4	1.5	Eq-G-G-G-	6.8	5.4	2815	535	485	0.7	0.2	1.5
Eq-TG+T	7.7	7.0	6.3	2730	528	486	0.9	0.8	0.5	Ax-G-G-G-	6.3	5.7	1733	744	701	0.9	0.8	0.9
Ax-G-G+G-	7.6	7.1	6.9	2093	649	625	0.0	0.0	0.9	Eq-G+G-G+	7.1	5.9	2825	520	500	1.0	0.6	1.0
Eq-G+G-T	8.2	7.1	5.6	2856	527	476	1.0	0.1	1.5	Eq-TG+G+	6.8	6.1	2737	521	507	1.1	0.8	1.5
Eq-G-TT	8.6	7.2	6.4	2741	536	475	1.2	1.0	0.5	Eq-G-G+G-	7.3	6.3	2655	547	491	0.9	0.8	0.3
Eq-G-G+G-	8.5	7.6	6.3	2667	540	488	1.0	0.1	0.8	Ax-TG+G-	7.1	6.4	2014	668	642	1.8	0.9	0.3
Eq-G+G-G-	9.3	8.2	5.9	2811	526	479	1.0	1.4	1.1	Ax-G+G-G-	7.0	6.8	1740	736	694	1.3	1.7	1.0
Eq-TG+G-	9.0	8.2	6.9	2667	537	484	0.9	0.8	1.2	Eq-G+G-T	7.9	6.8	2862	531	479	1.1	0.1	1.5
Ax-G+G-G-	8.6	8.3	8.1	1815	702	666	1.3	0.9	1.8	Eq-TG+T	7.4	6.8	2722	533	491	1.0	0.8	0.7
Ax-TG+G-	8.9	8.3	7.1	2093	643	620	1.7	1.0	0.2	Eq-G-TG-	8.9	7.3	2808	536	477	0.8	1.8	0.0
Eq-G-TG-	10.1	8.5	6.8	2813	530	475	1.0	1.7	0.1	Eq-G+G-G-	9.4	8.2	2820	530	481	1.2	1.3	1.1
Ax-G-TG-	9.5	8.6	8.5	2083	651	630	0.4	1.5	0.7	Eq-TG+G-	9.0	8.3	2655	542	488	1.1	1.2	0.7
Ax-G-G-G-	9.2	8.6	8.2	1815	706	670	0.8	0.9	0.9	Eq-G+TG-	9.4	8.8	2820	530	481	1.2	1.3	1.1
Ax-G+G+G+	8.4	9.2	10.1	2225	630	622	0.7	0.1	1.4	Ax-TG-T	8.3	9.0	1561	791	750	1.6	0.7	1.3
Ax-TG-G+	8.8	9.9	11.1	1843	724	670	0.8	0.8	1.1	**Ax-G+G+G+**	8.3	9.1	2160	650	641	0.9	0.4	1.4
Ax-TG-T	10.0	11.2	12.0	1608	752	716	1.6	1.3	0.6	Ax-G+G+T	8.4	9.7	1933	683	650	1.4	1.3	0.8
Ax-G+G+T	10.0	11.3	12.5	2000	660	623	1.3	1.4	0.9	**Ax-TG-G+**	9.1	10.2	1815	742	685	0.9	1.1	1.0
Ax-G+TG+	11.1	11.6	13.1	2053	661	632	1.1	0.0	0.5	Ax-G+TT	11.0	11.9	1675	733	687	1.7	0.3	0.1
Ax-TTG+	11.6	12.1	13.3	2108	649	628	0.3	1.5	0.4	Ax-G+TG+	11.5	12.0	2021	680	650	1.3	0.0	0.5
Ax-G+TT	12.1	13.0	14.6	1720	703	659	1.6	0.2	0.0	Ax-G-G-G+	11.9	12.1	1805	750	695	1.5	0.1	1.1

Ax-G-G-G+	13.6	13.7	14.4	1849	722	672	1.6	1.1	0.0	**Ax-TTG+**	12.0	12.5	2065	670	646	0.5	1.5	0.4
Ax-G-G+G+	13.9	13.8	14.1	2202	634	627	0.7	1.2	0.4	Ax-G-G+G+	12.7	12.6	2137	654	647	0.5	1.2	0.5
Ax-G+G-G+	13.8	14.1	14.8	1835	718	671	0.3	1.3	1.0	Ax-G-G+T	12.6	12.9	1909	690	659	0.1	0.5	1.1
Ax-TTT	13.3	14.2	15.7	1767	694	650	0.7	0.7	1.6	Ax-TTT	12.1	13.0	1714	723	679	0.7	1.0	1.4
Ax-G-TG+	15.6	15.2	15.4	2079	660	634	1.3	0.7	1.1	Ax-G-TG+	14.1	13.7	2040	681	653	1.0	0.7	1.1
Ax-TG+G+	15.3	15.3	15.1	2193	630	623	1.0	0.0	0.8	Ax-G+G-G+	13.6	13.9	1795	743	691	0.4	1.0	1.4
Ax-G-G+T	15.5	15.8	16.3	1976	665	630	0.1	0.4	1.1	Ax-G-G-T	14.5	13.9	1605	767	731	1.0	0.0	1.2
Ax-TG+T	16.3	16.7	16.7	1952	664	630	1.5	0.6	0.0	Ax-G-TT	14.4	14.3	1696	734	687	0.6	1.0	0.5
Ax-G-TT	17.5	17.4	17.7	1746	703	656	0.8	0.9	0.3	Ax-TG+T	14.6	15.0	1892	687	657	1.6	0.6	0.1
Ax-G+G-T	17.0	17.5	17.7	1638	728	697	0.8	0.8	1.6	Ax-TG+G+	15.1	15.1	2134	649	642	1.2	0.1	0.7
Ax-G-G-T	17.3	17.6	18.1	1657	730	696	1.0	1.2	0.3	Ax-G+G-T	15.4	16.0	1584	765	732	0.9	1.3	1.3

[a] The bolded conformers are the ones which survive the conformational conversion in a jet expansion. Those in red are the ones observed experimentally. See the main text for discussions.

[b] Calculated at the 298 K.

[c] The *ZPE* corrections were obtained at the B3LYP-D3(BJ)/def2-TZVP level.

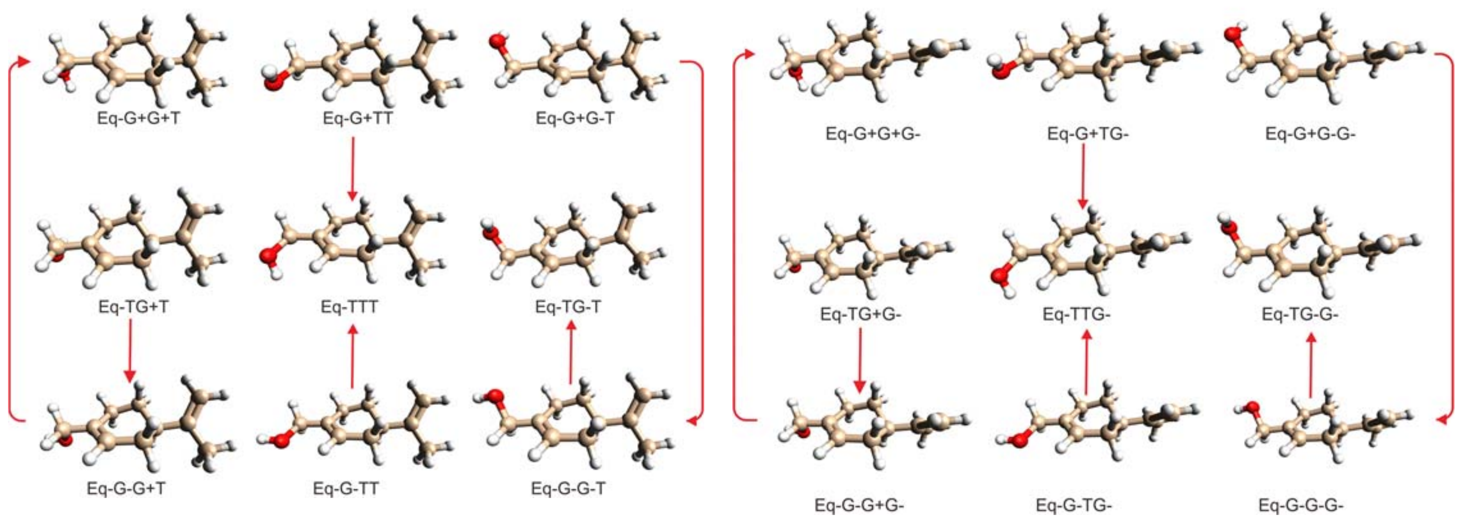

Figure S1. Optimized geometries of the nine Eq-XXT (left) and nine Eq-XXG- (right) conformers where X can take on G+, T, and G-. The red arrows indicate that the corresponding conformational barriers are low enough to facilitate a nearly complete conformational cooling of the higher energy conformers in a jet expansion. See the main text for discussion.

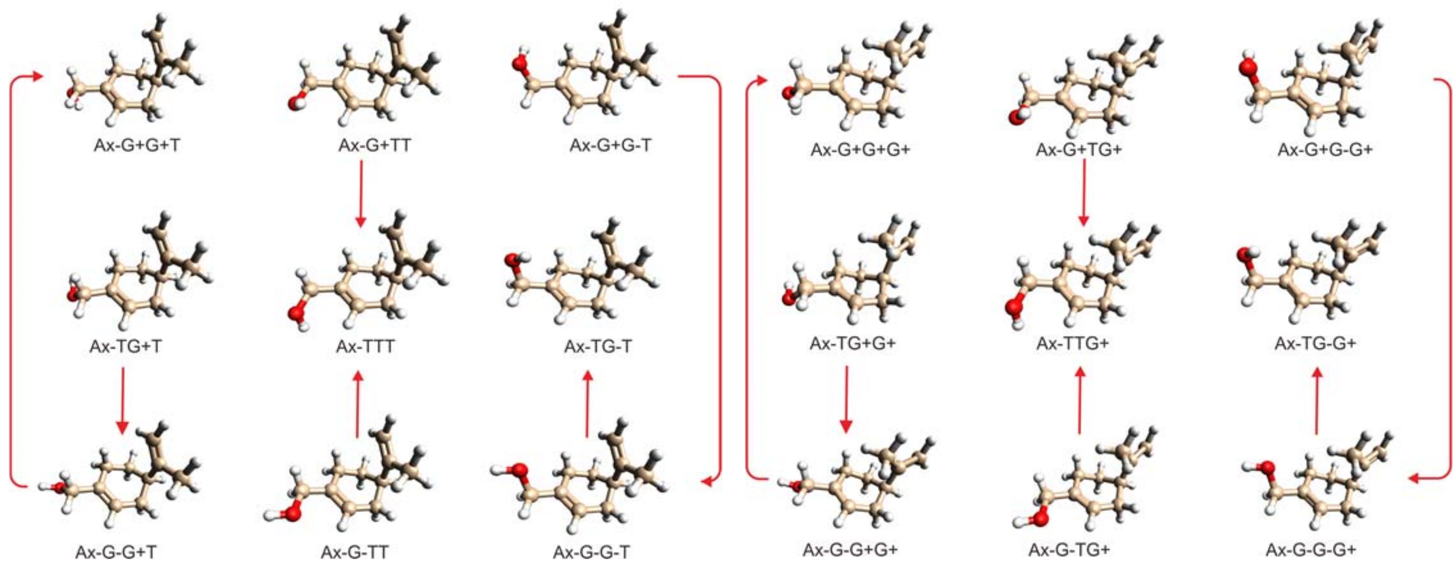

Figure S2. Optimized geometries of the nine Ax-XXT (left) and nine Ax-XXG- (right) conformers where X can take on G+, T, and G-. The red arrows indicate that the corresponding conformational barriers are low enough to facilitate a nearly complete conformational cooling of the higher energy conformers in a jet expansion. See the main text for discussion.

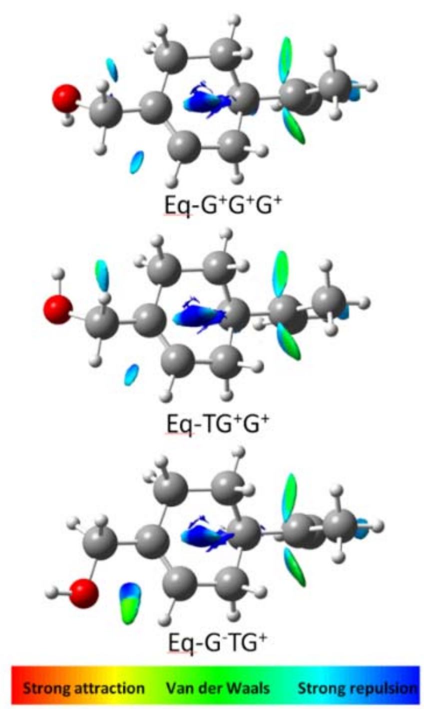

Figure S3. The NCI analysis of Eq-G+G+G+, Eq-TG+G+, and Eq-G-TG+. The Eq-TG+G+ and Eq-G-TG+ conformers are less stable than Eq-G+G+G+ primarily because of the more severe steric repulsion, represented by the larger blue areas associated with the OH group.

Table S2. Measured transition frequencies of Ax-G+G+G-

zJ'	K_a'	K_c'	J"	K_a"	K_c"	ν_{EXP} / MHz	$\Delta\nu^a$/ MHz
2	1	2	1	1	1	2539.0260	0.0002
2	0	2	1	0	1	2563.6280	0.0003
2	1	1	1	1	0	2588.8765	0.0002
3	1	3	2	1	2	3808.3308	0.0006
3	0	3	2	0	2	3844.6020	0.0007
3	1	2	2	1	1	3883.1100	0.0006
4	1	4	3	1	3	5077.3940	0.0009
4	0	4	3	0	3	5124.6011	0.0010
4	2	2	3	2	1	5130.9498	0.0006
4	2	3	3	2	2	5127.6503	0.0006
4	1	3	3	1	2	5177.0789	0.0009
3	1	3	2	0	2	5185.3261	0.0006
5	0	5	4	1	4	5109.8335	0.0004
4	0	4	3	1	3	3783.8946	0.0003
2	1	2	1	0	1	3940.6163	0.0004
1	1	0	0	0	0	2708.4915	0.0037
4	0	4	3	1	2	3634.3163	0.0015
2	1	1	1	0	1	4015.4012	0.0062
3	1	2	2	0	2	5334.9001	0.0066
5	0	5	4	1	3	4860.5237	0.0010
6	2	4	6	1	6	4529.2912	0.0001
3	2	2	3	1	3	4317.1483	0.0014
3	2	1	3	1	3	4318.8018	0.0017
3	2	1	3	1	2	4169.2372	0.0014
3	2	2	3	1	2	4167.5766	0.0017

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S3. Measured transition frequencies of Ax-TG-G-

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{EXP} / MHz	$\Delta\nu^a$/ MHz
2	1	2	1	1	1	2819.8980	0.0003
2	0	2	1	0	1	2859.2250	0.0004
2	1	1	1	1	0	2901.0650	0.0003
3	1	3	2	1	2	4229.0510	0.0007
3	0	3	2	0	2	4285.7030	0.0008
3	1	2	2	1	1	4350.8010	0.0007
4	1	4	3	1	3	5637.3107	0.0010
4	0	4	3	0	3	5708.4827	0.0011
4	1	3	3	1	2	5799.5247	0.0010
2	1	2	1	0	1	3788.2200	0.0004
4	0	4	3	1	3	4836.1500	0.0004
3	1	3	2	0	2	5158.0280	0.0006
4	2	3	3	2	2	5719.9520	0.0007
4	2	2	3	2	1	5732.3820	0.0007
3	0	3	2	1	2	3356.7060	0.0042
2	2	1	1	1	0	5806.0470	0.0130

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S4. Measured transition frequencies of Eq-TTT

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
5	1	5	4	1	4	4875.4010	0.0009
5	0	5	4	0	4	5006.0020	0.0010
4	1	4	3	1	3	3902.0756	0.0007
4	0	4	3	0	3	4012.0250	0.0008
4	1	3	3	1	2	4141.4000	0.0007
3	1	3	2	1	2	2927.5890	0.0004
3	0	3	2	0	2	3013.2514	0.0005
3	1	2	2	1	1	3107.1366	0.0004
2	1	1	1	0	1	4308.2950	0.0004
1	1	0	0	0	0	3242.3990	0.0002
6	0	6	5	1	4	3305.1500	0.0002
8	0	8	7	1	6	4790.4480	0.0001
3	1	2	2	0	2	5404.5735	0.0006
1	1	1	1	0	1	2176.4980	0.0002
7	0	7	6	1	5	4075.2006	0.0002
3	1	3	3	0	3	2032.2030	0.0018
2	1	2	2	0	2	2117.8710	0.0021

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S5. Measured transition frequencies of Eq-TTG+

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
3	1	3	2	1	2	2981.9680	0.0004
3	0	3	2	0	2	3023.2270	0.0005
3	1	2	2	1	1	3066.2530	0.0004
4	1	4	3	1	3	3975.6495	0.0007
4	0	4	3	0	3	4029.7270	0.0008
4	1	3	3	1	2	4088.0260	0.0007
5	1	5	4	1	4	4969.0750	0.0009
5	0	5	4	0	4	5035.2015	0.0010
5	2	4	4	2	3	5039.8760	0.0005
5	1	4	4	1	3	5109.5260	0.0009
6	1	6	5	1	5	5962.1750	0.0010
2	1	1	1	0	1	4309.0001	0.0030
2	1	2	1	0	1	4224.7080	0.0030
3	1	3	2	0	2	5190.7500	0.0033
3	1	2	2	0	2	5359.3490	0.0034
1	1	1	0	0	0	3244.7180	0.0019
1	1	0	0	0	0	3272.8250	0.0019
2	0	2	1	0	1	2015.8932	0.0066

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S6. Measured transition frequencies of Eq-G+G+G+

J'	K_a'	K_c'	J"	K_a''	K_c''	A/E	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
4	2	3	3	2	2	A	4098.8030	-0.0024
4	2	3	3	2	2	E	4098.9503	-0.0023
4	2	2	3	2	1	A	4099.3240	-0.0024
4	2	2	3	2	1	E	4099.1761	0.0015
5	2	4	4	2	3	A	5123.4390	-0.0026
5	2	4	4	2	3	E	5123.5751	0.0084
5	2	3	4	2	2	A	5124.4800	-0.0032
5	2	3	4	2	2	E	5124.3514	-0.0010
2	K	2	1	K	1	E	8615.4049	-0.0084
2	K	2	1	K	-1	E	8603.0752	0.0032
2	K	-2	1	K	-1	E	8604.1629	0.0092
3	2	2	2	1	1	A	9615.9813	-0.0051
3	2	2	2	1	1	E	9615.5557	0.0080
3	K	-2	2	K	-1	E	9616.6517	-0.0073
2	1	2	1	1	1	A	2037.0970	0.0026
2	1	2	1	1	1	E	2037.0970	-0.0002
2	0	2	1	0	1	A	2049.3690	-0.0018
2	0	2	1	0	1	E	2049.3690	-0.0007
2	1	1	1	1	0	A	2061.7460	-0.0055
2	1	1	1	1	0	E	2061.7460	-0.0005
2	1	1	2	0	2	A	2205.3250	-0.0021
2	1	1	2	0	2	E	2205.3250	-0.0010
3	1	2	3	0	3	A	2224.0000	0.0063
3	1	2	3	0	3	E	2224.0000	0.0084
3	0	3	2	0	2	A	3073.9240	-0.0020
3	0	3	2	0	2	E	3073.9240	-0.0002
3	1	3	2	1	2	A	3055.6130	0.0018
3	1	3	2	1	2	E	3055.6130	0.0026
3	1	2	2	1	1	A	3092.5990	0.0065
3	1	2	2	1	1	E	3092.5990	0.0091
4	0	4	3	0	3	A	4098.3230	-0.0019
4	0	4	3	0	3	E	4098.3230	0.0005
4	1	4	3	1	3	A	4074.0910	-0.0007
4	1	4	3	1	3	E	4074.0910	0.0012
4	1	3	3	1	2	A	4123.3880	-0.0037
4	1	3	3	1	2	E	4123.3880	-0.0010

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S7. Measured transition frequencies of Eq-G+G+T

J'	K_a'	K_c'	J''	K_a''	K_c''	A/E	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
3	2	2	2	2	1	A	3058.6410	-0.0018
3	2	2	2	2	1	E	3058.9010	0.0076
3	2	1	2	2	0	A	3060.8830	-0.0015
3	2	1	2	2	0	E	3060.6283	-0.0032
2	2	1	1	1	0	A	8529.9847	-0.0073
2	2	1	1	1	0	E	8529.6037	-0.0018
2	2	0	1	1	1	A	8570.8341	0.0027
2	2	0	1	1	1	E	8571.1847	-0.0034
3	2	2	2	1	1	A	9509.2616	0.0014
3	2	2	2	1	1	E	9509.1339	0.0074
3	2	1	2	1	2	A	9632.9018	0.0030
3	2	1	2	1	2	E	9632.9993	-0.0028
2	0	2	1	0	1	A	2038.5330	-0.0022
2	0	2	1	0	1	E	2038.5330	-0.0014
2	1	1	1	1	0	A	2079.3740	-0.0006
2	1	1	1	1	0	E	2079.3740	0.0016
2	1	1	2	0	2	A	2231.3240	0.0000
2	1	1	2	0	2	E	2231.3240	0.0039
3	1	2	3	0	3	A	2293.6280	-0.0030
3	1	2	3	0	3	E	2293.6280	0.0011
3	0	3	2	0	2	A	3056.3990	-0.0021
3	0	3	2	0	2	E	3056.3990	-0.0009
3	1	3	2	1	2	A	2997.8760	-0.0007
3	1	3	2	1	2	E	2997.8760	0.0003
3	1	2	2	1	1	A	3118.7110	0.0029
3	1	2	2	1	1	E	3118.7110	0.0043
4	1	4	3	1	3	A	3996.5230	-0.0015
4	1	4	3	1	3	E	3996.5230	0.0002
4	1	3	3	1	2	A	4157.6080	-0.0023
4	1	3	3	1	2	E	4157.6080	-0.0008

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S8. Measured transition frequencies of Eq-TG-G+

J'	K_a'	K_c'	J''	K_a''	K_c''	A/E	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
2	2	1	1	1	0	A	8840.1597	-0.0024
2	2	1	1	1	0	E	8839.8642	-0.0048
2	2	0	1	1	0	A	8840.2724	-0.0008
2	2	0	1	1	0	E	8840.5595	0.0039
2	2	1	1	1	1	A	8858.5021	-0.0033
2	2	1	1	1	1	E	8858.2218	0.0065
2	2	0	1	1	1	A	8858.6104	-0.0061
2	2	0	1	1	1	E	8858.9019	0.0000
3	2	2	2	1	1	A	9840.2581	-0.0009
3	2	2	2	1	1	E	9840.1025	0.0088
3	2	1	2	1	1	A	9840.8163	0.0016
3	2	1	2	1	1	E	9840.9728	0.0028
3	2	2	2	1	2	A	9895.2963	0.0061
3	2	2	2	1	2	E	9895.1193	-0.0062
3	2	1	2	1	2	A	9895.8433	-0.0025
3	2	1	2	1	2	E	9895.9990	-0.0028
2	1	2	1	1	1	A	2018.5260	-0.0086
2	1	2	1	1	1	E	2018.5260	-0.0082
7	1	7	7	0	7	A	2024.9890	0.0006
7	1	7	7	0	7	E	2024.9890	-0.0006
2	0	2	1	0	1	A	2036.7680	0.0007
2	0	2	1	0	1	E	2036.7680	0.0022
2	1	1	1	1	0	A	2055.2240	0.0016
2	1	1	1	1	0	E	2055.2240	0.0043
3	0	3	2	0	2	A	3054.8750	0.0002
3	0	3	2	0	2	E	3054.8750	0.0026
3	1	3	2	1	2	A	3027.7320	-0.0006
3	1	3	2	1	2	E	3027.7320	0.0012
3	1	2	2	1	1	A	3082.7690	0.0020
3	1	2	2	1	1	E	3082.7690	0.0047
4	0	4	3	0	3	A	4072.6480	-0.0028
4	0	4	3	0	3	E	4072.6480	0.0004
4	1	3	3	1	2	A	4110.2280	-0.0032
4	1	3	3	1	2	E	4110.2280	0.0003

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S9. Measured transition frequencies of Eq-TG-T

J'	K_a'	K_c'	J"	K_a"	K_c"	A/E	ν_{EXP} / MHz	$\Delta\nu^a$ / MHz
3	2	2	2	2	1	A	3026.1240	-0.0032
3	2	2	2	2	1	E	3026.4264	-0.0037
3	2	1	2	2	0	A	3029.2830	-0.0033
3	2	1	2	2	0	E	3028.9751	-0.0048
3	2	1	4	1	4	A	3153.5810	0.0007
3	2	1	4	1	4	E	3153.7030	0.0017
2	2	1	1	1	0	A	8928.4036	0.0005
2	2	1	1	1	0	E	8927.9519	0.0032
2	2	0	1	1	1	A	8978.5433	-0.0032
2	2	0	1	1	1	E	8978.9696	0.0010
3	2	2	2	1	1	A	9887.7607	0.0007
3	2	2	2	1	1	E	9887.6077	-0.0032
3	2	1	2	1	1	A	9891.7095	0.0003
3	2	1	2	1	1	E	9891.8194	-0.0021
3	0	3	2	0	2	A	3022.9750	0.0068
3	0	3	2	0	2	E	3022.9750	0.0086
3	1	3	2	1	2	A	2951.6150	0.0061
3	1	3	2	1	2	E	2951.6150	0.0082
3	1	2	2	1	1	A	3099.6506	-0.0072
3	1	2	2	1	1	E	3099.6506	-0.0058
4	0	4	3	0	3	A	4026.9510	0.0010
4	0	4	3	0	3	E	4026.9510	0.0036
5	0	5	4	0	4	A	5027.8100	-0.0019
5	0	5	4	0	4	E	5027.8100	0.0015
1	1	0	1	0	1	A	2336.5540	-0.0052
1	1	0	1	0	1	E	2336.5540	-0.0032
3	1	2	3	0	3	A	2463.3940	0.0021
3	1	2	3	0	3	E	2463.3940	0.0050
4	1	3	4	0	4	A	2568.3780	-0.0010
4	1	3	4	0	4	E	2568.3780	0.0008
5	1	4	5	0	5	A	2703.9540	-0.0001
5	1	4	5	0	5	E	2703.9540	0.0001

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S10. The percantage diffrerences between the experimental and theoretical rotational constants of the eight observed conformers

B3LYP	|ΔA|%[a]	|ΔB|%[a]	|ΔC|%[a]	ave%[b]	LMP2	|ΔA|%[a]	|ΔB|%[a]	|ΔC|%[a]	ave%[b]
Eq-G+G+G+	0.8	0.1	0.2	0.4	Eq-G+G+G+	0.6	0.9	1.1	0.9
Eq-G+G+T	0.8	0.2	0.1	0.4	Eq-G+G+T	0.6	1.0	0.9	0.8
Eq-TG-G+	0.4	0.3	0.4	0.4	Eq-TG-G+	0.7	1.1	1.0	0.9
Eq-TG-T	0.5	0.4	0.3	0.4	Eq-TG-T	0.7	1.1	0.9	0.9
Eq-TTG+	0.7	0.2	0.2	0.4	Eq-TTG+	0.8	0.9	0.8	0.9
Eq-TTT	0.7	0.2	0.2	0.4	Eq-TTT	0.8	0.9	0.8	0.9
ave for Eq[c]	0.6	0.2	0.2	0.4	ave for Eq[c]	0.7	1.0	0.9	0.9
Ax-G+G+G-	3.3	1.4	1.4	2.0	Ax-G+G+G-	0.8	2.4	2.3	1.8
Ax-TG-G-	2.2	1.4	1.1	1.6	Ax-TG-G-	1.0	3.1	2.8	2.3
ave for Ax[d]	2.7	1.4	1.2	1.8	ave for Ax[d]	0.9	2.7	2.5	2.0

[a] Percentage error in the A, B and C constants between the experimental and theoretical values.
[b] Average percentage error is A, B and C for each conformer.
[c] Average error for the six equatorial conformers observed.
[d] Average error for the two axial equatorial conformers observed.

Table S11. Comparison of the experimental and theoretical conformational abundances treating the axial and equatorial conformers *separately* and without/with conformational conversion

Levels of theory		B3LYP-D3BJ					LMP2				
Conformer[a]	Exp %	350K %	C_350K %	150K %	C_150K %	ΔD_0 kJ mol^{-1}	350K %	C_350K %	150K %	C_150K %	ΔD_0[b] kJ mol^{-1}
Eq-TG-G+	**30**	**14**	**19**	**36**	**37**	**0.0**	**14**	**19**	**34**	**36**	**0.0**
Eq-TG-T	**25**	**10**	**23**	**16**	**24**	**1.0**	**11**	**24**	**19**	**27**	**0.7**
Eq-G+G+G+	**22**	**10**	**14**	**15**	**16**	**1.1**	**9**	**14**	**14**	**15**	**1.1**
Eq-G+G+T	**10**	7	**16**	**6**	**9**	**2.3**	**7**	**18**	**7**	**11**	**1.9**
Eq-TG-G-	0	7	0	7	0	2.0	7	0	6	0	2.1
Eq-TTG+	**7**	**7**	**13**	**6**	**9**	**2.2**	**5**	**11**	**4**	**6**	**2.8**
Eq-G+G+G-	0	5	0	3	0	3.2	4	0	3	0	3.2
Eq-G-G-G+	0	3	0	1	0	4.6	4	0	2	0	3.5
Eq-TTT	**7**	**5**	**16**	**3**	**6**	**3.2**	**4**	**13**	**2**	**4**	**3.5**
Eq-G+TG+	0	5	0	3	0	3.3	3	0	1	0	3.9
Eq-G-G+G+	0	2	0	0	0	5.6	3	0	1	0	4.3
Eq-G+TT	0	4	0	1	0	4.1	3	0	1	0	4.4
Eq-G-G-T	0	2	0	0	0	5.9	3	0	1	0	4.4
Eq-G-G+T	0	2	0	0	0	6.6	2	0	1	0	5.0
Eq-G-TG+	0	2	0	0	0	6.2	2	0	1	0	5.0
Eq-TTG-	0	3	0	1	0	4.5	2	0	1	0	5.0
Eq-G-G-G-	0	1	0	0	0	6.9	2	0	0	0	5.4
Eq-G-TT	0	1	0	0	0	7.2	2	0	0	0	5.6
Eq-G+G-G+	0	2	0	0	0	6.0	2	0	0	0	5.9
Eq-TG+G+	0	2	0	0	0	6.1	2	0	0	0	6.1
Eq-G-G+G-	0	1	0	0	0	7.6	2	0	0	0	6.3
Eq-G+G-T	0	1	0	0	0	7.1	1	0	0	0	6.8
Eq-TG+T	0	1	0	0	0	7.0	1	0	0	0	6.8
Eq-G-TG-	0	1	0	0	0	8.5	1	0	0	0	7.3

Eq-G+G-G-	0	1	0	0	0	8.2	1	0	0	0	8.2
Eq-TG+G-	0	1	0	0	0	8.2	1	0	0	0	8.3
Eq-G+TG-	0	2	0	0	0	5.4	1	0	0	0	8.8
Sum	100	100	100	100	100	N/A	100	100	100	100	N/A
Ax-G+G+G-	**63**	**26**	**35**	**54**	**56**	**2.4**	**27**	**38**	**56**	**59**	**0.6**
Ax-TG-G-	**37**	**20**	**27**	**29**	**29**	**3.2**	**20**	**28**	**29**	**31**	**1.4**
Ax-G+TG-	**0**	**12**	**25**	**9**	**14**	**4.6**	**10**	**23**	**6**	**10**	**3.4**
Ax-G-G+G-	0	5	0	1.2	0	7.1	8	0	3	0	4.2
Ax-TTG-	0	9	0	4.5	0	5.5	8	0	3	0	4.3
Ax-G-TG-	0	3	0	0.4	0	8.6	5	0	1	0	5.6
Ax-G-G-G-	0	3	0	0.4	0	8.6	5	0	1	0	5.7
Ax-TG+G-	0	4	0	0.5	0	8.3	4	0	0	0	6.4
Ax-G+G-G-	0	4	0	0.5	0	8.3	3	0	0	0	6.8
Ax-TG-T	0	1	0	0	0	11.2	2	0	0	0	9.0
Ax-G+G+G+	**0**	**3**	**5**	**0**	**0**	**9.2**	**2**	**4**	**0**	**0**	**9.1**
Ax-G+G+T	0	1	0	0	0	11.3	1	0	0	0	9.7
Ax-TG-G+	**0**	**2**	**5**	**0**	**0**	**9.9**	**1**	**4**	**0**	**0**	**10.2**
Ax-G+TT	0	1	0	0	0	13	1	0	0	0	11.9
Ax-G+TG+	0	1	0	0	0	11.6	1	0	0	0	12.0
Ax-G-G-G+	0	0	0	0	0	13.7	1	0	0	0	12.1
Ax-TTG+	**0**	**1**	**3**	**0**	**0**	**12.1**	**1**	**3**	**0**	**0**	**12.5**
Ax-G-G+G+	0	0	0	0	0	13.8	0	0	0	0	12.6
Ax-G-G+T	0	0	0	0	0	15.8	0	0	0	0	12.9
Ax-TTT	0	0	0	0	0	14.2	0	0	0	0	13.0
Ax-G-TG+	0	0	0	0	0	15.2	0	0	0	0	13.7
Ax-G+G-G+	0	0	0	0	0	14.1	0	0	0	0	13.9
Ax-G-G-T	0	0	0	0	0	17.6	0	0	0	0	13.9
Ax-G-TT	0	0	0	0	0	17.4	0	0	0	0	14.3
Ax-TG+T	0	0	0	0	0	16.7	0	0	0	0	15.0
Ax-TG+G+	0	0	0	0	0	15.3	0	0	0	0	15.1
Sum	100	100	100	100	100	N/A	100	100	100	100	N/A

[a] The ordering is based on ΔD_0. The bolded conformers are the ones which survive the conformational conversion in a jet expansion. Those in red are the ones observed experimentally. See the main text for discussions.

[b] The *ZPE* corrections were taken from the B3LYP-D3(BJ) calculations.

Table S12. Comparison of the experimental and theoretical conformational abundances treating the axial and equatorial conformers *together* and without/with conformational conversion

Levels of theory		B3LYP-D3BJ					LMP2				
Conformer[a]	Exp %	350K %	C_350K %	150K %	C_150K %	ΔD_0 kJ mol^{-1}	350K %	C_350K %	150K %	C_150K %	ΔD_0[b] kJ mol^{-1}
Eq-TG-G+	**27**	**12**	**15**	**33**	**34**	**0.0**	**10**	**14**	**25**	**26**	**0.0**
Eq-TG-T	**23**	**8**	**18**	**15**	**22**	**1.0**	**8**	**17**	**14**	**20**	**0.7**
Eq-G+G+G+	**20**	**8**	**11**	**14**	**14**	**1.1**	**7**	**10**	**10**	**11**	**1.1**
Eq-TG-G-	0	6	0	7	0	2.0	5	0	5	0	2.1
Eq-TTG+	**6**	**5**	**11**	**6**	**8**	**2.2**	**4**	**8**	**3**	**4**	**2.8**
Eq-G+G+T	**9**	**5**	**13**	**5**	**8**	**2.3**	**5**	**13**	**5**	**8**	**1.9**
Ax-G+G+G-	**6**	**5**	**7**	**5**	**5**	**2.4**	**8**	**11**	**15**	**16**	**0.6**
Ax-TG-G-	**3**	**4**	**5**	**3**	**3**	**3.2**	**6**	**8**	**8**	**8**	**1.4**
Eq-G+G+G-	0	4	0	3	0	3.2	3	0	2	0	3.2
Eq-TTT	**6**	**4**	**13**	**3**	**5**	**3.2**	**3**	**9**	**1**	**3**	**3.5**
Eq-G+TG+	0	4	0	2	0	3.3	3	0	1	0	3.9
Eq-G+TT	0	3	0	1	0	4.1	2	0	1	0	4.4

Eq-TTG-	0	2	0	1	0	4.5	2	0	0	0	5.0
Ax-G+TG-	**0**	**2**	**5**	**1**	**1**	**4.6**	**3**	**7**	**2**	**3**	**3.4**
Eq-G-G-G+	0	2	0	1	0	4.6	3	0	1	0	3.5
Eq-G+TG-	0	2	0	0	0	5.4	0	0	0	0	8.8
Ax-TTG-	0	2	0	0	0	5.5	0	0	1	0	4.3
Eq-G-G+G+	0	2	0	0	0	5.6	2	0	1	0	4.3
Eq-G-G-T	0	2	0	0	0	5.9	2	0	1	0	4.4
Eq-G+G-G+	0	1	0	0	0	6.0	1	0	0	0	5.9
Eq-TG+G+	0	1	0	0	0	6.1	1	0	0	0	6.1
Eq-G-TG+	0	1	0	0	0	6.2	2	0	0	0	5.0
Eq-G-G+T	0	1	0	0	0	6.6	2	0	0	0	5.0
Eq-G-G-G-	0	1	0	0	0	6.9	2	0	0	0	5.4
Eq-TG+T	0	1	0	0	0	7.0	1	0	0	0	6.8
Ax-G-G+G-	0	1	0	0	0	7.1	2	0	0	0	4.2
Eq-G+G-T	0	1	0	0	0	7.1	1	0	0	0	6.8
Eq-G-TT	0	1	0	0	0	7.2	1	0	0	0	5.6
Eq-G-G+G-	0	1	0	0	0	7.6	1	0	0	0	6.3
Eq-G+G-G-	0	1	0	0	0	8.2	1	0	0	0	8.2
Eq-TG+G-	0	1	0	0	0	8.2	1	0	0	0	8.3
Ax-TG+G-	0	1	0	0	0	8.3	1	0	0	0	6.4
Ax-G+G-G-	0	1	0	0	0	8.3	1	0	0	0	6.8
Eq-G-TG-	0	1	0	0	0	8.5	1	0	0	0	7.3
Ax-G-TG-	0	1	0	0	0	8.6	1	0	0	0	5.6
Ax-G-G-G-	0	1	0	0	0	8.6	1	0	0	0	5.7
Ax-G+G+G+	**0**	**0**	**1**	**0**	**0**	**9.2**	**0**	**1**	**0**	**0**	**9.1**
Ax-TG-G+	**0**	**0**	**1**	**0**	**0**	**9.9**	**0**	**1**	**0**	**0**	**10.2**
Ax-TG-T	0	0	0	0	0	11.2	0	0	0	0	9.0
Ax-G+G+T	0	0	0	0	0	11.3	0	0	0	0	9.7
Ax-G+TG+	0	0	0	0	0	11.6	0	0	0	0	12.0
Ax-TTG+	**0**	**0**	**1**	**0**	**0**	**12.1**	**0**	**1**	**0**	**0**	**12.5**
Ax-G+TT	0	0	0	0	0	13.0	0	0	0	0	11.9
Ax-G-G-G+	0	0	0	0	0	13.7	0	0	0	0	12.1
Ax-G-G+G+	0	0	0	0	0	13.8	0	0	0	0	12.6
Ax-G+G-G+	0	0	0	0	0	14.1	0	0	0	0	13.9
Ax-TTT	0	0	0	0	0	14.2	0	0	0	0	13
Ax-G-TG+	0	0	0	0	0	15.2	0	0	0	0	13.7
Ax-TG+G+	0	0	0	0	0	15.3	0	0	0	0	15.1
Ax-G-G+T	0	0	0	0	0	15.8	0	0	0	0	12.9
Ax-TG+T	0	0	0	0	0	16.7	0	0	0	0	15.0
Ax-G-TT	0	0	0	0	0	17.4	0	0	0	0	14.3
Ax-G+G-T	0	0	0	0	0	17.5	0	0	0	0	16.0
Ax-G-G-T	0	0	0	0	0	17.6	0	0	0	0	13.9
Sum	100	100	100	100	100	N/A	100	100	100	100	N/A

[a] The ordering is based on ΔD_0. The bolded conformers are the ones which survive the conformational conversion in a jet expansion. Those in red are the ones observed experimentally. See the main text for discussions.

[b] The *ZPE* corrections were taken from the B3LYP-D3(BJ) calculations.