Table S1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves calculated using different methods in combination with the basis set 6-311++G(d,p) given in Figure 2. The potential is expanded as $V(\varphi) = \sum_{i=0}^{6} a_i f_i$.

		MP2		**B3LYP-D3BJ**		**M06-2X**	
i	**f_i**	**a_i / Hartree**	**a_i / cm^{-1}**	**a_i / Hartree**	**a_i / cm^{-1}**	**a_i / Hartree**	**a_i / cm^{-1}**
0	1	–743.5311916		–745.1229207		–744.9051433	
1	cos α	0.0028798	632.1	0.0029098	638.6	0.0031160	683.9
2	cos 2α	0.0019198	421.3	0.0014663	321.8	0.0013606	298.6
3	cos 3α	0.0013365	293.3	0.0009516	208.8	0.0012842	281.9
4	cos 4α	–0.0000195	–4.3	–0.0002997	–65.8	–0.0003624	–79.5
5	cos 5α	–0.0001154	–25.3	–0.0002322	–51.0	–0.0002568	–56.4
6	cos 6α	–0.0000843	–18.5	–0.0001263	–27.7	–0.0001612	–35.4

Table S2a: Nuclear coordinates in the principal axis system of *syn*-2PT and *syn*-C_1-2PT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 1).

	syn			***syn*-C_1**		
	***a* / Å**	***b* / Å**	***c* / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	1.456117	–1.068910	–0.001120	–1.425833	–0.996238	0.254844
C2	0.238294	0.148986	–0.026017	–0.117773	0.040897	–0.169793
C3	0.799023	1.424550	–0.018429	–0.558553	1.346264	–0.383623
C4	2.212207	1.395798	–0.001248	–1.949355	1.490184	–0.179608
C5	2.702798	0.099129	0.010986	–2.547706	0.289409	0.170759
C6	–1.185448	–0.244282	0.007579	1.240941	–0.522254	–0.308733
O7	–1.511642	–1.426265	0.005583	1.433700	–1.731191	–0.218555
C8	–2.210229	0.878001	0.051818	2.385416	0.456373	–0.480162
C9	–3.643985	0.365936	–0.032649	2.767487	1.065373	0.878463
H10	3.738959	–0.215527	0.018085	–3.592871	0.111123	0.391075
H11	2.847947	2.274112	0.001793	–2.496545	2.419991	–0.287911
H12	0.207180	2.333266	–0.025575	0.102771	2.158244	–0.665391
H13	–2.046611	1.439292	0.980700	3.226298	-0.105303	–0.895256
H14	–1.990902	1.571496	–0.768932	2.110935	1.245735	–1.187078
H15	–3.859336	–0.318246	0.790567	3.040577	0.273916	1.582180
H16	–4.347855	1.201449	0.010884	3.622152	1.738740	0.770310
H17	–3.805358	–0.178476	–0.965846	1.933921	1.630514	1.304393

Table S2b: Nuclear coordinates in the principal axis system of *anti*-2PT and *anti*-C_1-2PT calculated at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 1).

	anti			***anti*-C_1**		
	***a* / Å**	***b* / Å**	***c* / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	1.099446	–1.204830	0.078603	0.950111	–1.140002	–0.345710
C2	0.288352	0.316970	0.037589	0.184278	0.387191	–0.108543
C3	1.199980	1.363632	–0.062459	1.103078	1.343126	0.314990
C4	2.539798	0.918524	–0.087529	2.411701	0.826757	0.431822
C5	2.636546	–0.463186	–0.020129	2.477640	–0.519817	0.105100
C6	–1.188412	0.459930	0.014194	–1.269272	0.614848	–0.297548
O7	–1.701405	1.566525	0.118265	–1.722777	1.753125	–0.277448
C8	–2.014906	–0.800719	–0.177295	–2.170530	–0.597062	–0.419678
C9	–3.510253	–0.560055	–0.003688	–2.534641	–1.118626	0.979733
H10	3.532510	–1.070837	–0.007143	3.348220	–1.163379	0.095270
H11	3.405298	1.568197	–0.155130	3.276633	1.400721	0.745249
H12	0.875141	2.396935	–0.112830	0.804975	2.365382	0.519900
H13	–1.793798	–1.186669	–1.181312	–3.071398	–0.281771	–0.952686
H14	–1.654866	–1.562684	0.525883	–1.681298	–1.386698	–1.000875
H15	–3.863945	0.191879	–0.711809	–3.035041	–0.334200	1.554160
H16	–4.065697	–1.487335	–0.167249	–3.208707	–1.976139	0.905548
H17	–3.728552	–0.195626	1.002962	–1.641039	–1.431822	1.527205

Table S3a: Rotational constants and dihedral angles of *syn*-2PT calculated at various levels of theory. The deviations between the calculated and the experimental values are given as ΔA, ΔB and ΔC.

Method/Basis Set	***A* / MHz**	**Δ*A* / MHz**	***B* / MHz**	**Δ*B* / MHz**	***C* / MHz**	**Δ*C* / MHz**	***α* / °**	***β* / °**
MP2/6-31G(d,p)	3410.4	–17.0	879.3	2.1	705.1	0.2	0.0	180.0
MP2/6-31+G(d,p)	3393.4	–34.0	877.5	0.3	703.6	–1.3	–3.2	174.2
MP2/6-31++G(d,p)	3391.1	–36.3	877.8	0.6	703.8	–1.1	–3.7	172.5
MP2/6-311G(d,p)	3404.6	–22.8	877.6	0.4	703.8	–1.1	0.0	180.0
MP2/6-311+G(d,p)	3396.0	–31.4	876.8	–0.4	703.1	–1.8	–2.4	175.9
MP2/6-311++G(d,p)	3394.9	–32.5	877.0	–0.2	703.1	–1.8	–2.6	175.2
MP2/6-311G(df,pd)	3429.5	2.1	883.0	5.8	708.3	3.4	0.0	180.0
MP2/6-311+G(df,pd)	3418.4	–9.0	882.1	4.9	707.5	2.6	–3.5	174.5
MP2/6-311++G(df,pd)	3418.3	–9.1	882.2	5.0	707.6	2.7	–3.5	174.1
MP2/6-311G(3df,3pd)	3442.3	14.9	885.9	8.7	710.7	5.8	0.0	180.0
MP2/6-311+G(3df,3pd)	3432.6	5.2	885.4	8.2	709.9	5.0	0.0	180.0
MP2/6-311++G(3df,3pd)	3432.7	5.3	885.4	8.2	709.9	5.0	0.0	–180.0
MP2/cc-pVDZ	3370.3	–57.1	870.7	–6.5	698.0	–6.9	0.0	180.0
MP2/cc-pVTZ	3423.4	–4.0	883.9	6.7	708.6	3.7	0.0	180.0
MP2/aug-cc-pVDZ	3351.6	–75.8	869.8	–7.4	696.6	–8.3	0.0	180.0
MP2/aug-cc-pVTZ	3419.5	–7.9	883.9	6.7	708.4	3.5	0.0	180.0

B3LYP-D3/6-31G(d,p)	3395.6	–31.8	870.4	–6.8	698.7	–6.2	0.0	–180.0
B3LYP-D3/6-31+G(d,p)	3385.0	–42.4	868.2	–9.0	696.9	–8.0	0.0	–180.0
B3LYP-D3/6-31++G(d,p)	3385.0	–42.4	868.2	–9.0	696.9	–8.0	0.0	–180.0
B3LYP-D3/6-311G(d,p)	3406.5	–20.9	871.5	–5.7	699.9	–5.0	0.0	180.0
B3LYP-D3/6-311+G(d,p)	3400.3	–27.1	870.5	–6.7	699.0	–5.9	0.0	180.0
B3LYP-D3/6-311++G(d,p)	3400.1	–27.3	870.5	–6.7	699.0	–5.9	0.0	–180.0
B3LYP-D3/6-311G(df,pd)	3416.5	–10.9	873.8	–3.4	701.8	–3.1	0.0	180.0
B3LYP-D3/6-311+G(df,pd)	3410.6	–16.8	872.8	–4.4	700.9	–4.0	0.0	180.0
B3LYP-D3/6-311++G(df,pd)	3410.6	–16.8	872.8	–4.4	700.9	–4.0	0.0	180.0
B3LYP-D3/6-311G(3df,3pd)	3437.9	10.5	876.3	–0.9	704.3	–0.6	0.0	–180.0
B3LYP-D3/6-311+G(3df,3pd)	3429.9	2.5	875.8	–1.4	703.6	–1.3	0.0	–180.0
B3LYP-D3/6-311++G(3df,3pd)	3429.7	2.3	875.8	–1.4	703.6	–1.3	0.0	180.0
B3LYP-D3/cc-pVDZ	3385.4	–42.0	868.5	–8.7	697.2	–7.7	0.0	180.0
B3LYP-D3/cc-pVTZ	3423.8	–3.6	874.6	–2.6	702.6	–2.3	0.0	180.0
B3LYP-D3/aug-cc-pVDZ	3377.9	–49.5	867.3	–9.9	696.0	–8.9	0.0	–180.0
B3LYP-D3/aug-cc-pVTZ	3421.1	–6.3	874.5	–2.7	702.4	–2.5	0.0	180.0
B3LYP-D3BJ/6-31G(d,p)	3400.4	–27.0	872.9	–4.3	700.6	–4.3	0.0	180.0
B3LYP-D3BJ/6-31+G(d,p)	3389.2	–38.2	870.7	–6.5	698.7	–6.2	0.0	–180.0
B3LYP-D3BJ/6-31++G(d,p)	3389.2	–38.2	870.7	–6.5	698.7	–6.2	0.0	180.0
B3LYP-D3BJ/6-311G(d,p)	3410.7	–16.7	874.0	–3.2	701.7	–3.2	0.0	180.0
B3LYP-D3BJ/6-311+G(d,p)	3404.1	–23.3	873.1	–4.1	700.8	–4.1	0.0	–180.0
B3LYP-D3BJ/6-311++G(d,p)	3404.0	–23.4	873.1	–4.1	700.8	–4.1	0.0	–180.0
B3LYP-D3BJ/6-311G(df,pd)	3420.5	–6.9	876.3	–0.9	703.6	–1.3	0.0	–180.0
B3LYP-D3BJ/6-311+G(df,pd)	3414.1	–13.3	875.4	–1.8	702.7	–2.2	0.0	–180.0
B3LYP-D3BJ/6-311++G(df,pd)	3414.0	–13.4	875.4	–1.8	702.7	–2.2	0.0	–180.0
B3LYP-D3BJ/6-311G(3df,3pd)	3441.7	14.3	878.8	1.6	706.0	1.1	0.0	–180.0
B3LYP-D3BJ/6-311+G(3df,3pd)	3433.2	5.8	878.3	1.1	705.4	0.5	0.0	–180.0
B3LYP-D3BJ/6-311++G(3df,3pd)	3433.1	5.7	878.4	1.2	705.4	0.5	0.0	–180.0
B3LYP-D3BJ/cc-pVDZ	3390.4	–37.0	871.0	–6.2	699.0	–5.9	0.0	180.0
B3LYP-D3BJ/cc-pVTZ	**3427.5**	**0.1**	**877.2**	**0.0**	**704.4**	**–0.5**	**0.0**	**–180.0**
B3LYP-D3BJ/aug-cc-pVDZ	3382.3	–45.1	869.8	–7.4	697.9	–7.0	0.0	–180.0
B3LYP-D3BJ/aug-cc-pVTZ	3424.7	-2.7	877.1	–0.1	704.2	–0.7	0.0	–180.0
M06-2X/6-31G(d,p)	3436.0	8.6	878.6	1.4	705.7	0.8	0.0	–180.0
M06-2X/6-31+G(d,p)	3427.5	0.1	876.7	–0.5	704.2	–0.7	0.0	180.0
M06-2X/6-31++G(d,p)	3427.5	0.1	876.7	–0.5	704.2	–0.7	0.0	180.0
M06-2X/6-311G(d,p)	3441.7	14.3	879.5	2.3	706.5	1.6	0.0	180.0
M06-2X/6-311+G(d,p)	3437.2	9.8	878.6	1.4	705.8	0.9	0.0	180.0
M06-2X/6-311++G(d,p)	3437.1	9.7	878.6	1.4	705.8	0.9	0.0	180.0
M06-2X/6-311G(df,pd)	3449.4	22.0	881.2	4.0	708.0	3.1	0.0	180.0
M06-2X/6-311+G(df,pd)	3445.3	17.9	880.3	3.1	707.2	2.3	0.0	180.0
M06-2X/6-311++G(df,pd)	3445.2	17.8	880.3	3.1	707.2	2.3	0.0	180.0
M06-2X/6-311G(3df,3pd)	3469.5	42.1	883.3	6.1	710.1	5.2	0.0	180.0
M06-2X/6-311+G(3df,3pd)	3463.1	35.7	882.9	5.7	709.7	4.8	0.0	180.0
M06-2X/6-311++G(3df,3pd)	3463.0	35.6	882.9	5.7	709.6	4.7	0.0	180.0
M06-2X/cc-pVDZ	**3427.0**	**–0.4**	**877.4**	**0.2**	**704.6**	**–0.3**	**0.0**	**180.0**
M06-2X/cc-pVTZ	3456.1	28.7	882.6	5.4	709.1	4.2	0.0	180.0
M06-2X/aug-cc-pVDZ	3420.5	–6.9	876.1	–1.1	703.6	–1.3	0.0	–180.0

M06-2X/aug-cc-pVTZ	3454.9	27.5	882.5	5.3	709.0	4.1	0.0	180.0
CCSD/cc-pVDZ	3372.0	–55.4	863.9	–13.3	693.7	–11.2	0.0	180.0
Experiment	**3427.4**		**877.2**		**704.9**			

Table S3b: Rotational constants and dihedral angles of *anti*-2PT calculated at various levels of theory. The deviations between the calculated and the experimental values are given as Δ*A*, Δ*B* and Δ*C*.

Method/Basis Set	***A* / MHz**	**Δ*A* / MHz**	***B* / MHz**	**Δ*B* / MHz**	***C* / MHz**	**Δ*C* / MHz**	***α* / °**	***β* / °**
MP2/6-31G(d,p)	3268.9	–5.1	903.6	–2.1	714.1	–2.1	–180.0	180.0
MP2/6-31+G(d,p)	3242.8	–31.2	904.3	–1.5	715.3	–1.0	172.8	171.7
MP2/6-31++G(d,p)	3241.1	–32.9	904.5	–1.2	715.5	–0.8	172.8	171.4
MP2/6-311G(d,p)	3267.4	–6.6	902.9	–2.8	713.7	–2.6	–180.0	–180.0
MP2/6-311+G(d,p)	3247.0	–27.0	904.6	–1.1	715.7	–0.5	173.3	172.7
MP2/6-311++G(d,p)	3245.4	–28.6	904.8	–1.0	716.0	–0.2	172.8	172.5
MP2/6-311G(df,pd)	3290.8	16.8	909.1	3.4	718.7	2.4	178.8	178.1
MP2/6-311+G(df,pd)	3266.8	–7.2	910.7	5.0	720.9	4.7	172.5	172.1
MP2/6-311++G(df,pd)	3265.7	–8.3	910.8	5.0	721.1	4.9	172.1	172.0
MP2/6-311G(3df,3pd)	3302.2	28.2	913.2	7.5	721.7	5.4	–180.0	180.0
MP2/6-311+G(3df,3pd)	3293.8	19.8	913.7	7.9	721.6	5.3	–180.0	180.0
MP2/6-311++G(3df,3pd)	3293.9	19.9	913.7	7.9	721.6	5.3	–180.0	180.0
MP2/cc-pVDZ	3231.7	–42.3	895.7	–10.1	707.5	–8.7	–180.0	180.0
MP2/cc-pVTZ	3284.1	10.1	911.2	5.4	719.5	3.3	–180.0	180.0
MP2/aug-cc-pVDZ	3215.3	–58.7	897.6	–8.2	707.9	–8.3	–180.0	180.0
B3LYP-D3/6-31G(d,p)	3249.9	–24.1	894.7	–11.1	707.6	–8.6	–180.0	–180.0
B3LYP-D3/6-31+G(d,p)	3240.8	–33.2	893.9	–11.9	706.7	–9.5	–180.0	180.0
B3LYP-D3/6-31++G(d,p)	3240.7	–33.3	893.9	–11.8	706.7	–9.5	–180.0	–180.0
B3LYP-D3/6-311G(d,p)	3260.1	–13.9	895.9	–9.8	708.9	–7.3	–180.0	–180.0
B3LYP-D3/6-311+G(d,p)	3253.6	–20.4	896.4	–9.4	708.9	–7.4	–180.0	180.0
B3LYP-D3/6-311++G(d,p)	3253.4	–20.6	896.4	–9.3	708.9	–7.3	–180.0	180.0
B3LYP-D3/6-311G(df,pd)	3269.7	–4.3	898.7	–7.1	711.1	–5.2	–180.0	–180.0
B3LYP-D3/6-311+G(df,pd)	3263.5	–10.5	899.1	–6.6	711.0	–5.2	–180.0	180.0
B3LYP-D3/6-311++G(df,pd)	3263.3	–10.7	899.1	–6.6	711.0	–5.2	–180.0	180.0
B3LYP-D3/6-311G(3df,3pd)	3291.7	17.7	901.6	–4.1	713.9	–2.3	–179.9	180.0
B3LYP-D3/6-311+G(3df,3pd)	3284.1	10.1	902.3	–3.5	714.0	–2.3	–180.0	180.0
B3LYP-D3/6-311++G(3df,3pd)	3284.0	10.0	902.3	–3.5	714.0	–2.3	–180.0	180.0
B3LYP-D3/cc-pVDZ	3239.1	–34.9	892.9	–12.8	706.1	–10.1	180.0	–180.0
B3LYP-D3/cc-pVTZ	3276.8	2.8	900.6	–5.1	712.6	–3.7	–180.0	180.0
B3LYP-D3/aug-cc-pVDZ	3233.5	–40.5	893.6	–12.1	706.3	–10.0	–180.0	180.0
B3LYP-D3/aug-cc-pVTZ	3274.2	0.2	901.0	–4.7	712.7	–3.5	–180.0	180.0
B3LYP-D3BJ/6-31G(d,p)	3247.0	–27.0	899.1	–6.7	710.2	–6.0	180.0	–180.0
B3LYP-D3BJ/6-31+G(d,p)	3237.7	–36.3	898.4	–7.4	709.4	–6.9	–180.0	–180.0
B3LYP-D3BJ/6-31++G(d,p)	3237.7	–36.3	898.4	–7.4	709.4	–6.9	–180.0	180.0
B3LYP-D3BJ/6-311G(d,p)	3256.8	–17.2	900.4	–5.4	711.5	–4.7	180.0	180.0
B3LYP-D3BJ/6-311+G(d,p)	3250.0	–24.0	901.0	–4.8	711.6	–4.7	–180.0	180.0

B3LYP-D3BJ/6-311++G(d,p)	3249.8	–24.2	901.0	–4.7	711.6	–4.6	–180.0	180.0
B3LYP-D3BJ/6-311G(df,pd)	3265.9	–8.1	903.2	–2.5	713.7	–2.5	180.0	180.0
B3LYP-D3BJ/6-311+G(df,pd)	3259.4	–14.6	903.8	–1.9	713.8	–2.5	–180.0	180.0
B3LYP-D3BJ/6-311++G(df,pd)	3259.2	–14.8	903.9	–1.9	713.8	–2.4	–180.0	180.0
B3LYP-D3BJ/6-311G(3df,3pd)	3287.2	13.2	906.4	0.6	716.7	0.4	–180.0	–180.0
B3LYP-D3BJ/6-311+G(3df,3pd)	3279.4	5.4	907.1	1.3	716.7	0.5	–180.0	180.0
B3LYP-D3BJ/6-311++G(3df,3pd)	3279.3	5.3	907.1	1.3	716.7	0.5	–180.0	180.0
B3LYP-D3BJ/cc-pVDZ	3236.5	–37.5	897.3	–8.4	708.7	–7.5	–180.0	180.0
B3LYP-D3BJ/cc-pVTZ	**3272.7**	**–1.3**	**905.3**	**–0.4**	**715.3**	**–0.9**	**–179.9**	**–180.0**
B3LYP-D3BJ/aug-cc-pVDZ	3230.3	–43.7	898.2	–7.5	709.0	–7.3	–180.0	–180.0
B3LYP-D3BJ/aug-cc-pVTZ	3269.8	–4.2	905.8	0.1	715.5	–0.7	–180.0	180.0
M06-2X/6-31G(d,p)	3286.7	12.7	904.7	–1.0	715.7	–0.6	–180.0	–180.0
M06-2X/6-31+G(d,p)	3279.5	5.5	904.0	–1.8	714.9	–1.4	–180.0	180.0
M06-2X/6-31++G(d,p)	3279.3	5.3	904.0	–1.7	714.9	–1.4	–180.0	180.0
M06-2X/6-311G(d,p)	3293.4	19.4	906.0	0.3	716.8	0.6	–180.0	–180.0
M06-2X/6-311+G(d,p)	3288.3	14.3	906.4	0.7	716.8	0.6	–180.0	180.0
M06-2X/6-311++G(d,p)	3288.0	14.0	906.5	0.8	716.8	0.6	–180.0	–180.0
M06-2X/6-311G(df,pd)	3301.1	27.1	908.2	2.4	718.5	2.2	–180.0	–180.0
M06-2X/6-311+G(df,pd)	3296.3	22.3	908.6	2.8	718.5	2.3	–179.9	180.0
M06-2X/6-311++G(df,pd)	3296.2	22.2	908.6	2.8	718.5	2.3	–179.9	180.0
M06-2X/6-311G(3df,3pd)	3321.5	47.5	911.0	5.2	721.2	4.9	–180.0	180.0
M06-2X/6-311+G(3df,3pd)	3315.4	41.4	911.5	5.7	721.2	5.0	–180.0	180.0
M06-2X/6-311++G(3df,3pd)	3315.4	41.4	911.5	5.7	721.2	5.0	–180.0	180.0
M06-2X/cc-pVDZ	**3278.7**	**4.7**	**903.5**	**–2.2**	**714.6**	**–1.6**	**–180.0**	**180.0**
M06-2X/cc-pVTZ	3307.7	33.7	910.8	5.0	720.4	4.2	–180.0	180.0
M06-2X/aug-cc-pVDZ	3274.7	0.7	903.9	–1.8	714.7	–1.6	–180.0	180.0
M06-2X/aug-cc-pVTZ	3306.6	32.6	911.1	5.4	720.6	4.4	–180.0	180.0
CCSD/6-311++G(d,p)	3244.2	–29.8	897.9	–7.8	711.0	–5.3	173.6	174.6
CCSD/cc-pVDZ	3223.0	–51.0	889.8	–15.9	703.5	–12.8	–180.0	180.0
Experiment	**3274.0**		**905.7**		**716.2**			

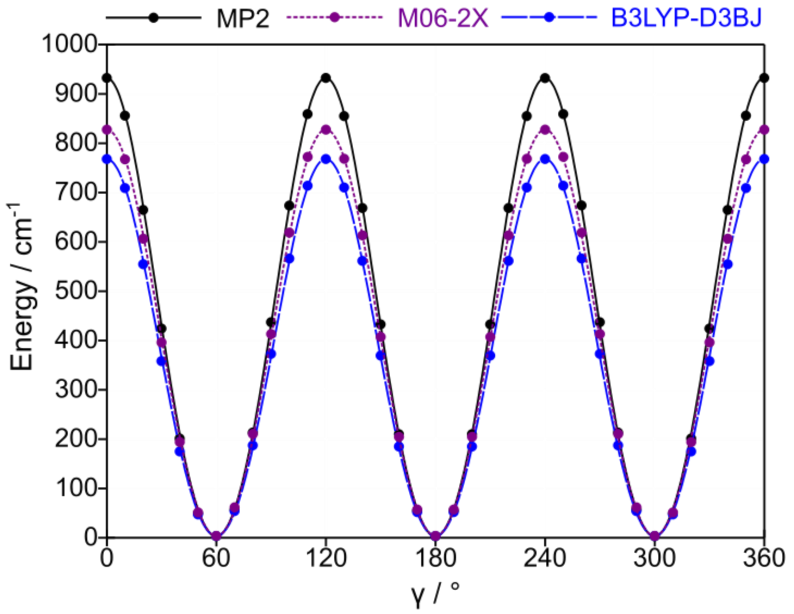

Figure S1: The potential energy curves of *syn*-2PT obtained by rotating the methyl group around the C8–C9 bond in 10° steps calculated at the different levels of theory with the 6-311++G(d,p) basis set. The predicted rotational barriers are 929.3 cm^{-1} (MP2), 823.8 cm^{-1} (M06-2X) and 764.5 cm^{-1} (B3LYP-D3BJ). The Fourier coefficients of the parameterized potential are given in Table S4.

Table S4: Coefficients of the one-dimensional Fourier expansion for the potential energy curve of *syn*-2PT given in Figure S1 calculated using different methods in combination with the basis set 6-311++G(d,p). The potential is expanded as $V(\varphi) = \sum_{i=0}^{2} a_i f_i$.

		MP2		**B3LYP-D3BJ**		**M06-2X**	
i	**f$_i$**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**
0	1	–743.591750		–745.1212221		–744.9032898	
1	cos 3α	0.0021111	463.3	0.0017355	380.9	0.0018733	411.1
2	cos 6α	0.0000805	17.7	0.0000429	9.4	0.0000232	5.1

Table S5: Observed frequencies ν_{obs} of 201 rotational transitions of *syn*-2PT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	**Species**	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**				**MHz**	**kHz**
1	2	0	2	1	0	1	A	3155.7033	–0.3
2	3	0	3	2	0	2	A	4712.5964	–0.2
3	4	0	4	3	0	3	A	6245.1040	–0.2
4	5	0	5	4	0	4	A	7747.4055	–0.1
5	6	0	6	5	0	5	A	9217.1304	–0.3
6	7	0	7	6	0	6	A	10656.5614	–0.7
7	8	0	8	7	0	7	A	12072.2521	–0.5
8	9	0	9	8	0	8	A	13472.8402	–0.3
9	10	0	10	9	0	9	A	14866.3298	0.2
10	11	0	11	10	0	10	A	16258.3959	–0.1
11	12	0	12	11	0	11	A	17652.1589	–0.2
12	13	0	13	12	0	12	A	19048.8281	0.7
13	14	0	14	13	0	13	A	20448.5041	–0.1
14	16	0	16	15	0	15	A	23255.1592	0.6
15	4	0	4	3	1	3	A	4088.6400	2.1
16	5	0	5	4	1	4	A	5868.4507	1.2
17	6	0	6	5	1	5	A	7640.2300	1.5
18	7	0	7	6	1	6	A	9381.8094	3.4
19	8	0	8	7	1	7	A	11078.0117	1.9
20	9	0	9	8	1	8	A	12722.2717	0.8
21	10	0	10	9	1	9	A	14315.5702	1.0
22	11	0	11	10	1	10	A	15863.7818	–0.5
23	12	0	12	11	1	11	A	17374.9293	0.8
24	13	0	13	12	1	12	A	18857.1752	–0.4
25	14	0	14	13	1	13	A	20317.7589	0.3
26	15	0	15	14	1	14	A	21762.5782	1.3
27	2	1	1	2	0	2	A	2903.2592	–2.4
28	3	1	2	3	0	3	A	3189.8822	–2.4
29	4	1	3	4	0	4	A	3599.9412	–0.8
30	5	1	4	5	0	5	A	4153.8831	4.6
31	7	1	6	7	0	7	A	5764.5981	3.9
32	9	1	8	9	0	9	A	8074.3749	3.8
33	12	1	11	12	0	12	A	12500.6450	3.1
34	13	1	12	13	0	13	A	14093.0648	1.2
35	14	1	13	14	0	14	A	15689.6540	2.6
36	2	1	2	1	0	1	A	5542.1227	–3.7
37	3	1	3	2	0	2	A	6869.0581	–4.8
38	4	1	4	3	0	3	A	8124.0624	2.1
39	4	1	4	3	0	3	E	8124.0531	–3.0
40	5	1	5	4	0	4	A	9324.3027	–5.1
41	6	1	6	5	0	5	A	10491.8819	–4.9
42	7	1	7	6	0	6	A	11650.8002	–4.7

43	8	1	8	7	0	7	A	12822.8173	–4.9
44	9	1	9	8	0	8	A	14023.6003	–0.6
45	10	1	10	9	0	9	A	15260.9402	–3.1
46	11	1	11	10	0	10	A	16535.6252	–1.4
47	12	1	12	11	0	11	A	17843.8116	0.6
48	13	1	13	12	0	12	A	19179.5728	–0.3
49	14	1	14	13	0	13	A	20536.7220	0.2
50	16	1	16	15	0	15	A	23294.2702	–0.6
51	2	1	1	1	1	0	A	3336.4190	–0.4
52	3	1	2	2	1	1	A	4999.2197	0.1
53	4	1	3	3	1	2	A	6655.1615	–0.2
54	5	1	4	4	1	3	A	8301.3421	0.1
55	6	1	5	5	1	4	A	9934.3305	0.7
56	7	1	6	6	1	5	A	11550.0786	–0.1
57	8	1	7	7	1	6	A	13143.9449	–0.2
58	9	1	8	8	1	7	A	14710.9244	–0.5
59	10	1	9	9	1	8	A	16246.2460	–1.4
60	11	1	10	10	1	9	A	17746.4094	–0.6
61	12	1	11	11	1	10	A	19210.4969	–1.2
62	3	1	3	2	1	2	A	4482.6395	–0.5
63	4	1	4	3	1	3	A	5967.5940	0.0
64	5	1	5	4	1	4	A	7445.3513	–0.4
65	6	1	6	5	1	5	A	8914.9840	–0.6
66	7	1	7	6	1	6	A	10376.0476	–1.3
67	8	1	8	7	1	7	A	11828.5789	–0.4
68	9	1	9	8	1	8	A	13273.0309	–0.4
69	10	1	10	9	1	9	A	14710.1827	–0.2
70	11	1	11	10	1	10	A	16141.0128	–0.1
71	12	1	12	11	1	11	A	17566.5806	0.2
72	13	1	13	12	1	12	A	18987.9215	0.3
73	14	1	14	13	1	13	A	20405.9769	0.8
74	15	1	15	14	1	14	A	21821.5508	1.0
75	8	1	7	7	2	6	A	7510.1492	–3.1
76	8	1	7	7	2	6	E	7510.1669	3.1
77	9	1	8	8	2	7	A	9666.8532	–2.1
78	9	1	8	8	2	7	E	9666.8696	3.4
79	10	1	9	9	2	8	A	11824.3636	–2.7
80	10	1	9	9	2	8	E	11824.3775	1.0
81	11	1	10	10	2	9	A	13958.9940	–1.9
82	11	1	10	10	2	9	E	13959.0059	0.7
83	12	1	11	11	2	10	A	16046.7625	–2.1
84	12	1	11	11	2	10	E	16046.7749	2.0
85	13	1	12	12	2	11	A	18066.7423	–2.3
86	13	1	12	12	2	11	E	18066.7515	–0.2
87	2	2	0	1	1	1	A	11167.9304	2.7
88	2	2	0	2	1	1	A	7659.2230	–5.6
89	3	2	1	3	1	2	A	7439.8230	–6.0

90	3	2	1	3	1	2	E	7439.8154	–2.3
91	4	2	2	4	1	3	E	7189.5319	1.7
92	5	2	3	5	1	4	A	6942.6837	3.2
93	5	2	3	5	1	4	E	6942.6665	–2.0
94	8	2	6	8	1	7	A	6606.4561	1.5
95	8	2	6	8	1	7	E	6606.4430	–1.3
96	2	2	1	2	1	2	A	8167.6285	–2.2
97	2	2	1	2	1	2	E	8167.6122	0.9
98	3	2	2	3	1	3	A	8431.1924	–5.8
99	3	2	2	3	1	3	E	8431.1837	–0.2
100	4	2	3	4	1	4	A	8785.3091	–3.9
101	4	2	3	4	1	4	E	8785.2966	–3.0
102	5	2	4	5	1	5	E	9231.5466	2.8
103	6	2	5	6	1	6	A	9771.0678	–7.4
104	6	2	5	6	1	6	E	9771.0595	–2.4
105	7	2	6	7	1	7	A	10404.1395	–4.6
106	7	2	6	7	1	7	E	10404.1360	5.2
107	9	2	8	9	1	9	A	11945.4863	–5.6
108	9	2	8	9	1	9	E	11945.4711	–7.2
109	10	2	9	10	1	10	A	12847.0857	–3.7
110	10	2	9	10	1	10	E	12847.0801	4.6
111	12	2	11	12	1	12	A	14883.4917	–2.9
112	12	2	11	12	1	12	E	14883.4766	–3.6
113	4	2	2	3	1	3	A	14878.1253	3.1
114	4	2	2	3	1	3	E	14878.1124	2.7
115	5	2	3	4	1	4	E	16964.9971	1.3
116	6	2	4	5	1	5	E	19249.1869	0.7
117	3	2	2	2	1	1	A	12397.0044	5.0
118	4	2	3	3	1	2	A	13719.4901	1.4
119	4	2	3	3	1	2	E	13719.4726	–2.8
120	5	2	4	4	1	3	A	14955.9286	5.7
121	5	2	4	4	1	3	E	14955.9068	–3.1
122	6	2	5	5	1	4	A	16109.0887	5.2
123	7	2	6	6	1	5	A	17183.8739	2.4
124	7	2	6	6	1	5	E	17183.8549	–3.9
125	8	2	7	7	1	6	A	18188.0177	2.9
126	9	2	8	8	1	7	A	19132.8082	2.1
127	9	2	8	8	1	7	E	19132.7901	–3.6
128	10	2	9	9	1	8	A	20033.6647	3.2
129	10	2	9	9	1	8	E	20033.6479	–1.6
130	11	2	10	10	1	9	A	20910.1484	4.9
131	11	2	10	10	1	9	E	20910.1318	–0.2
132	2	2	0	3	1	3	A	3693.4207	–6.7
133	3	2	1	2	2	0	A	4779.8172	–2.8
134	4	2	2	3	2	1	A	6404.8735	–1.4
135	5	2	3	4	2	2	A	8054.4797	–0.6
136	6	2	4	5	2	3	A	9729.5416	–0.5

137	7	2	5	6	2	4	A	11426.2378	–0.8
138	8	2	6	7	2	5	A	13136.3442	–2.9
139	3	2	2	2	2	1	A	4746.2100	2.6
140	3	2	2	2	2	1	E	4746.2157	3.1
141	4	2	3	3	2	2	A	6321.7094	0.5
142	5	2	4	4	2	3	A	7891.5962	0.4
143	6	2	5	5	2	4	A	9454.5026	0.0
144	7	2	6	6	2	5	A	11009.1174	–0.4
145	8	2	7	7	2	6	A	12554.2219	–0.1
146	9	2	8	8	2	7	A	14088.7367	0.2
147	10	2	9	9	2	8	A	15611.7805	0.1
148	3	3	1	2	2	0	A	17924.9233	4.1
149	4	3	2	3	2	1	A	19489.4971	2.4
150	4	3	2	3	2	1	E	19489.4067	1.0
151	5	3	3	4	2	2	A	21021.3322	1.0
152	5	3	3	4	2	2	E	21021.2940	2.0
153	6	3	4	5	2	3	A	22498.7213	1.0
154	6	3	4	5	2	3	E	22498.6948	2.2
155	3	3	0	2	2	1	A	17933.6158	1.4
156	3	3	0	2	2	1	E	17933.8408	–4.6
157	4	3	1	3	2	2	A	19533.3540	2.5
158	4	3	1	3	2	2	E	19533.4011	3.6
159	5	3	2	4	2	3	A	21153.7564	–1.8
160	3	3	0	3	2	1	E	13145.5850	4.0
161	5	3	2	5	2	3	A	12974.0602	–2.5
162	6	3	3	6	2	4	A	12790.7184	3.6
163	6	3	3	6	2	4	E	12790.6994	0.7
164	8	3	5	8	2	6	A	12179.8988	1.9
165	8	3	5	8	2	6	E	12179.8775	1.6
166	4	3	2	4	2	3	A	13209.8354	0.4
167	4	3	2	4	2	3	E	13209.7486	0.7
168	5	3	3	5	2	4	A	13254.9473	–3.3
169	5	3	3	5	2	4	E	13254.9167	4.4
170	6	3	4	6	2	5	A	13332.3161	–1.2
171	6	3	4	6	2	5	E	13332.2930	2.5
172	7	3	5	7	2	6	A	13452.4578	2.4
173	7	3	5	7	2	6	E	13452.4332	1.1
174	8	3	6	8	2	7	A	13626.0119	–0.8
175	8	3	6	8	2	7	E	13625.9924	1.6
176	9	3	7	9	2	8	A	13863.2060	–0.6
177	9	3	7	9	2	8	E	13863.1852	–0.2
178	4	3	1	4	2	2	A	13086.4264	–1.1
179	4	3	1	4	2	2	E	13086.4740	2.3
180	6	3	3	5	2	4	A	22808.3610	4.4
181	6	3	3	5	2	4	E	22808.3413	0.2
182	5	3	2	4	3	1	A	7942.1169	1.4
183	5	3	2	4	3	1	E	7942.0647	–1.7

184	6	3	3	5	3	2	A	9546.1950	0.8
185	6	3	3	5	3	2	E	9546.1807	–2.0
186	7	3	4	6	3	3	A	11161.1629	–2.3
187	5	3	3	4	3	2	A	7936.7101	–1.3
188	5	3	3	4	3	2	E	7936.7597	–0.6
189	6	3	4	5	3	3	A	9531.8671	–2.3
190	6	3	4	5	3	3	E	9531.8811	0.5
191	7	3	5	6	3	4	A	11129.2568	0.9
192	8	3	6	7	3	5	A	12727.7789	–0.4
193	4	4	0	4	3	1	A	18438.2480	0.5
194	5	4	1	5	3	2	A	18425.2556	–3.9
195	6	4	2	6	3	3	A	18400.3063	2.4
196	7	4	3	7	3	4	A	18356.0687	–3.0
197	4	4	1	4	3	2	A	18440.0479	–0.7
198	5	4	2	5	3	3	A	18432.4090	–3.3
199	6	4	3	6	3	4	A	18421.5439	–1.6
200	7	4	4	7	3	5	A	18408.4348	–3.5
201	4	4	1	5	3	2	A	10496.1272	1.8

Table S6: Observed frequencies ν_{obs} of 135 rotational transitions of *anti*-2PT, with $\nu_{obs}–\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K*** K_a	K_c	***J***	K_a	K_c	**Species**	ν_{obs}	$\nu_{obs}–\nu_{calc}$
	upper level			**lower level**				**MHz**	**kHz**
1	2	0	2	1	0	1	A	3233.0313	–0.9
2	3	0	3	2	0	2	A	4822.4766	–0.3
3	4	0	4	3	0	3	A	6380.7904	–0.7
4	5	0	5	4	0	4	A	7901.5837	0.0
5	6	0	6	5	0	5	A	9384.0023	0.5
6	7	0	7	6	0	6	A	10833.7562	0.5
7	8	0	8	7	0	7	A	12261.1817	0.2
8	9	0	9	8	0	8	A	13677.2371	0.0
9	10	0	10	9	0	9	A	15090.2141	0.6
10	12	0	12	11	0	11	A	17922.7399	0.3
11	13	0	13	12	0	12	A	19344.2815	0.8
12	14	0	14	13	0	13	A	20768.8765	0.1
13	15	0	15	14	0	14	A	22195.8273	0.0
14	16	0	16	15	0	15	A	23624.4912	1.1
15	3	0	3	2	1	2	A	2632.7742	–0.4
16	3	0	3	2	1	2	E	2632.7765	–0.6
17	4	0	4	3	1	3	A	4438.5437	3.1
18	4	0	4	3	1	3	E	4438.5395	–3.5
19	5	0	5	4	1	4	A	6251.9501	–0.3
20	6	0	6	5	1	5	A	8043.6780	0.2
21	7	0	7	6	1	6	A	9791.0736	–1.1
22	8	0	8	7	1	7	A	11482.1107	–0.3

23	9	0	9	8	1	8	A	13115.3559	–0.1
24	9	0	9	8	1	8	E	13115.3605	3.6
25	10	0	10	9	1	9	A	14696.7963	–1.1
26	10	0	10	9	1	9	E	14696.7991	1.1
27	11	0	11	10	1	10	A	16235.8761	0.3
28	12	0	12	11	1	11	A	17742.4807	0.2
29	13	0	13	12	1	12	A	19225.3272	0.6
30	14	0	14	13	1	13	A	20691.3810	0.2
31	15	0	15	14	1	14	A	22145.8753	–2.0
32	5	1	4	5	0	5	A	4172.0012	0.8
33	5	1	4	5	0	5	E	4171.9960	–2.1
34	6	1	5	6	0	6	A	4989.6610	1.7
35	6	1	5	6	0	6	E	4989.6548	–2.3
36	11	1	10	11	0	11	A	11653.7128	–1.0
37	11	1	10	11	0	11	E	11653.7101	–1.0
38	2	1	2	1	0	1	A	5422.7354	0.9
39	2	1	2	1	0	1	E	5422.7290	–3.0
40	3	1	3	2	0	2	A	6764.7284	1.1
41	3	1	3	2	0	2	E	6764.7230	–1.8
42	4	1	4	3	0	3	A	8030.4244	0.0
43	4	1	4	3	0	3	E	8030.4186	–3.2
44	5	1	5	4	0	4	A	9241.9082	0.5
45	5	1	5	4	0	4	E	9241.9051	–0.2
46	6	1	6	5	0	5	A	10426.6839	1.1
47	6	1	6	5	0	5	E	10426.6790	–1.4
48	7	1	7	6	0	6	A	11612.8290	2.7
49	7	1	7	6	0	6	E	11612.8241	0.0
50	8	1	8	7	0	7	A	12823.0596	–3.0
51	9	1	9	8	0	8	A	14070.6551	1.9
52	9	1	9	8	0	8	E	14070.6431	–8.5
53	10	1	10	9	0	9	A	15359.1143	0.0
54	11	1	11	10	0	10	A	16685.0363	0.7
55	11	1	11	10	0	10	E	16685.0289	–5.6
56	13	1	13	12	0	12	A	19421.7763	–0.1
57	14	1	14	13	0	13	A	20818.8259	–0.5
58	15	1	15	14	0	14	A	22227.7322	–1.5
59	16	1	16	15	0	15	A	23644.7147	0.4
60	2	1	1	1	1	0	A	3433.4649	–2.0
61	2	1	1	1	1	0	E	3433.4680	1.1
62	3	1	2	2	1	1	A	5143.1642	1.1
63	3	1	2	2	1	1	E	5143.1586	–4.5
64	4	1	3	3	1	2	A	6843.8542	–0.6
65	5	1	4	4	1	3	A	8531.5979	–0.7
66	6	1	5	5	1	4	A	10201.6615	0.9
67	7	1	6	6	1	5	A	11848.4320	0.1
68	8	1	7	7	1	6	A	13465.5925	0.9
69	9	1	8	8	1	7	A	15046.7483	0.9

70	11	1	10	10	1	9	A	18083.6850	1.1
71	12	1	11	11	1	10	A	19540.4734	1.1
72	2	1	2	1	1	1	A	3054.4417	–3.1
73	2	1	2	1	1	1	E	3054.4448	–0.1
74	3	1	3	2	1	2	A	4575.0247	–0.4
75	4	1	4	3	1	3	A	6088.1737	–0.2
76	5	1	5	4	1	4	A	7592.2751	0.7
77	6	1	6	5	1	5	A	9086.3594	0.7
78	7	1	7	6	1	6	A	10570.1456	0.3
79	8	1	8	7	1	7	A	12043.9926	0.6
80	9	1	9	8	1	8	A	13508.7730	0.9
81	10	1	10	9	1	9	A	14965.6979	–0.3
82	11	1	11	10	1	10	A	16416.1349	0.0
83	13	1	13	12	1	12	A	19302.8228	0.6
84	14	1	14	13	1	13	A	20741.3308	0.1
85	2	2	0	1	1	1	A	10738.7473	–1.0
86	2	2	0	1	1	1	E	10738.7402	–2.3
87	3	2	1	2	1	2	A	12593.6948	4.2
88	3	2	1	2	1	2	E	12593.6757	–7.7
89	4	2	2	3	1	3	A	14605.1746	2.0
90	4	2	2	3	1	3	E	14605.1721	6.9
91	5	2	3	4	1	4	A	16810.8115	1.3
92	7	2	5	6	1	6	A	21950.3955	–1.1
93	3	2	1	3	1	2	A	6881.9978	3.6
94	3	2	1	3	1	2	E	6881.9837	–3.3
95	4	2	2	4	1	3	A	6624.6432	–3.3
96	5	2	3	5	1	4	A	6386.8651	5.7
97	5	2	3	5	1	4	E	6386.8521	–0.1
98	2	2	1	1	1	0	A	10538.3083	–5.0
99	3	2	2	2	1	1	A	11970.7775	–0.3
100	3	2	2	2	1	1	E	11970.7733	3.5
101	4	2	3	3	1	2	A	13307.0155	–1.9
102	4	2	3	3	1	2	E	13307.0101	0.5
103	5	2	4	4	1	3	A	14548.7730	0.1
104	5	2	4	4	1	3	E	14548.7617	–3.5
105	6	2	5	5	1	4	A	15699.9803	0.1
106	6	2	5	5	1	4	E	15699.9710	–1.6
107	7	2	6	6	1	5	A	16767.6598	2.0
108	7	2	6	6	1	5	E	16767.6477	–2.5
109	8	2	7	7	1	6	A	17762.9468	3.4
110	2	2	1	2	1	2	A	7673.3808	1.2
111	2	2	1	2	1	2	E	7673.3732	3.0
112	3	2	2	3	1	3	A	7964.2862	0.2
113	4	2	3	4	1	4	A	8355.5172	2.3
114	5	2	4	5	1	5	A	8848.8538	3.1
115	6	2	5	6	1	6	A	9445.3031	5.2
116	6	2	5	6	1	6	E	9445.2860	–4.3

117	8	2	7	8	1	8	A	10944.2207	4.4
118	8	2	7	8	1	8	E	10944.2015	–7.2
119	4	2	2	3	2	1	A	6586.5063	–0.7
120	5	2	3	4	2	2	A	8293.8110	–0.5
121	6	2	4	5	2	3	A	10030.2289	–0.1
122	7	2	5	6	2	4	A	11787.9939	3.3
123	8	2	6	7	2	5	A	13554.4712	1.2
124	4	2	3	3	2	2	A	6479.4045	1.8
125	5	2	4	4	2	3	A	8085.6106	0.3
126	6	2	5	5	2	4	A	9682.8069	1.0
127	7	2	6	6	2	5	A	11269.3384	0.3
128	8	2	7	7	2	6	A	12843.7204	2.8
129	4	3	2	4	2	3	A	12350.9653	–1.6
130	5	3	2	4	3	1	A	8151.6731	–1.4
131	6	3	3	5	3	2	A	9803.2117	4.8
132	8	3	5	7	3	4	A	13156.3934	–1.0
133	5	3	3	4	3	2	A	8143.4489	–0.2
134	5	3	3	4	3	2	E	8143.4539	–7.0
135	6	3	4	5	3	3	A	9781.4585	3.0

Table S7: Molecular parameters of *syn*-2PT and *anti*-2PT obtained with the program *XIAM* where the angles between the internal rotor axis and the principal axes of inertia are fixed to values predicted at the B3LYP-D3BJ/6-311++G(d,p) level of theory.

Par.[a]	**Unit**	***syn***	***Calc.***[b]	***anti***	***Calc.***[b]
A_0	MHz	3427.43880(19)	3383.114	3274.03476(39)	3222.920
B_0	MHz	877.177067(48)	866.872	905.747027(78)	895.759
C_0	MHz	704.893296(31)	696.450	716231414 (37)	707.766
D_J	kHz	0.01812(15)	0.0175	0.02330(31)	0.0228
D_{JK}	kHz	0.0749(27)	0.0820	0.0621(69)	0.0419
D_K	kHz	0.4474(93)	0.4541	1.842(58)	0.4957
d_1	kHz	–0.00370(10)	–0.0039	–0.00639(30)	–0.0056
d_2	kHz	–0.000275(69)	–0.0004	–0.00138(25)	–0.0004
V_3	cm^{-1}	807.00(54)	764.5	865.4(88)	753.0
$\angle(i,a)$	deg	19.9[c]	19.9	9.9[c]	9.9
$\angle(i,b)$	deg	70.2[c]	70.2	80.1[c]	80.1
$\angle(i,c)$	deg	90.0[c]	90.0	90.0[c]	90.0
N_A/N_E[d]	-	150/51		103/32	
σ[e]	kHz	2.6		2.5	

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. [b] Ground state rotational constants and centrifugal distortion constants from anharmonic frequency calculations, all other parameters from optimisations at the B3LYP-D3BJ/6-311++G(d,p) level of theory. [c] Fixed to the values calculated at the B3LYP-D3BJ/6-311++G(d,p) level predicting a planar geometry. [d] Number of A and E species transitions. [e] Standard deviation of the fit.

Table S8a: Observed frequencies ν_{obs} of 23 rotational transitions of the ^{34}S isotopologue of *syn*-2PT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	*J*	K_a	K_c	*J*	K_a	K_c	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**			**MHz**	**kHz**
1	2	0	2	1	0	1	3130.6784	–0.1
2	3	0	3	2	0	2	4674.7172	–1.0
3	4	0	4	3	0	3	6194.0013	–0.3
4	5	0	5	4	0	4	7682.6943	0.5
5	6	0	6	5	0	5	9138.5519	1.6
6	2	1	2	1	0	1	5472.7622	–3.2
7	5	1	5	4	0	4	9219.1284	–1.8
8	6	1	6	5	0	5	10376.0502	–0.8
9	7	1	7	6	0	6	11525.3196	–0.2
10	3	1	3	2	1	2	4445.3162	–0.2
11	4	1	4	3	1	3	5917.6849	–1.1
12	5	1	5	4	1	4	7382.7606	–0.2
13	3	1	2	2	1	1	4961.7111	1.0
14	4	1	3	3	1	2	6604.9657	0.2
15	5	1	4	4	1	3	8238.2752	0.1
16	2	2	0	1	1	1	11009.4573	–3.3
17	3	2	1	2	1	2	12785.4664	–0.5
18	4	2	2	3	1	3	14696.4655	–7.9
19	4	2	3	3	1	2	13536.1898	4.1
20	3	2	1	3	1	2	7307.0851	–10.1
21	6	2	5	5	2	4	9379.2202	0.7
22	3	3	0	2	2	1	17673.5653	6.1
23	3	3	1	2	2	0	17664.7218	5.5

Table S8b: Observed frequencies ν_{obs} of 15 rotational transitions of the ^{13}C(6) isotopologue (for atom numbering see Figure 1) of *syn*-2PT with $\nu_{obs}–\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K_a***	***K_c***	***J***	***K_a***	***K_c***	ν_{obs}	$\nu_{obs}–\nu_{calc}$
	upper level			**lower level**			**MHz**	**kHz**
1	2	0	2	1	0	1	3148.8581	–0.6
2	3	0	3	2	0	2	4702.4997	0.9
3	4	0	4	3	0	3	6231.9455	1.1
4	5	0	5	4	0	4	7731.4034	1.0
5	2	1	2	1	0	1	5536.8014	0.1
6	3	1	3	2	0	2	6861.2767	–4.0
7	4	1	4	3	0	3	8114.0453	–1.3
8	5	1	5	4	0	4	9312.1487	–1.9
9	3	1	3	2	1	2	4473.3385	0.3
10	5	1	5	4	1	4	7430.0502	1.9
11	2	2	0	1	1	1	11162.2901	3.0
12	3	2	1	2	1	2	12945.8286	–4.3
13	4	2	2	3	1	3	14862.9280	–1.0
14	3	2	2	2	1	1	12389.3421	2.0
15	4	2	3	3	1	2	13709.4111	2.5

Table S8c: Observed frequencies ν_{obs} of 14 rotational transitions of the ^{13}C(8) isotopologue (for atom numbering see Figure 1) of *syn*-2PT, with $\nu_{obs}–\nu_{calc}$ obtained from a fit with the program *XIAM*.

No.	***J***	***K_a***	***K_c***	***J***	***K_a***	***K_c***	ν_{obs}	$\nu_{obs}–\nu_{calc}$
	upper level			**lower level**			**MHz**	**kHz**
1	3	0	3	2	0	2	4674.5215	0.2
2	4	0	4	3	0	3	6194.9983	–0.9
3	5	0	5	4	0	4	7685.7609	1.6
4	2	1	2	1	0	1	5508.1655	–3.6
5	3	1	3	2	0	2	6824.9792	–0.4
6	4	1	4	3	0	3	8070.5414	2.3
7	5	1	5	4	0	4	9261.7360	–2.2
8	3	1	3	2	1	2	4446.8861	0.4
9	5	1	5	4	1	4	7386.1996	1.2
10	5	1	4	4	1	3	8232.9167	0.8
11	2	2	0	1	1	1	11108.0603	2.8
12	3	2	1	2	1	2	12880.6632	5.2
13	4	2	2	3	1	3	14785.7556	–5.1
14	4	2	3	3	1	2	13640.5904	–1.7

Table S8d: Observed frequencies ν_{obs} of 12 rotational transitions of the ^{13}C(9) isotopologue (for atom numbering see Figure 1) of *syn*-2PT, with $\nu_{obs}-\nu_{calc}$ obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level			MHz	kHz
1	2	0	2	1	0	1	3091.1949	0.5
2	3	0	3	2	0	2	4617.5420	–1.3
3	4	0	4	3	0	3	6121.4372	–0.3
4	2	1	2	1	0	1	5500.6074	–2.6
5	4	1	4	3	0	3	8039.4466	–0.7
6	5	1	5	4	0	4	9220.0956	0.3
7	5	1	5	4	1	4	7302.0868	1.3
8	2	2	0	1	1	1	11139.0376	–1.7
9	3	2	1	2	1	2	12884.8388	0.7
10	4	2	2	3	1	3	14757.6418	–0.1
11	3	2	2	2	1	1	12349.8256	2.6
12	4	2	3	3	1	2	13650.0156	–0.4

Table S8e: Observed frequencies ν_{obs} of 4 rotational transitions of the ^{34}S isotopologue of *anti*-2PT, with $\nu_{obs}-\nu_{calc}$ obtained from a tentative fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level			MHz	kHz
1	2	2	0	1	1	1	10558.2584	–0.2
2	5	1	5	4	0	4	9134.7002	2.1
3	6	0	6	5	0	5	9318.5508	0.0
4	6	1	6	5	0	5	10310.7978	–1.7