Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Quantifying soft degrees of freedom in volatile organic compounds: Insight from quantum chemistry and focused single molecule experiments

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1 Spectroscopic Data

Table S1. Observed frequencies of the most abundant conformer of EMPE used in the XIAM fit (see Table 1 in the ms.). This observed conformer corresponds to the lowest energy (conformer 1) optimized at the B3LYP/6-311++G(d,p) level of theory (see Table S9).

Upper level			*Lower Level*				
J	K_a	K_c	*J*	K_a	K_c	*Obs.*[a]	*Obs.–calc.*[b]
3	3	1	2	2	1	10.646411	0.8
4	2	2	3	1	2	8.870125	-5.6
4	2	3	3	1	3	9.335080	-4.6
4	3	1	3	2	1	11.855379	3.5
5	1	4	4	0	4	8.187785	-0.4
5	2	3	4	1	3	9.994629	0.9
5	2	3	4	1	3	9.994628	-0.1
5	2	4	4	1	4	10.729815	-2.1
5	3	2	4	2	2	13.054154	1.5
5	3	3	4	2	3	13.112100	2.8
6	2	5	5	1	5	12.167869	3.1
6	3	4	5	2	4	14.361509	2.3
7	0	7	6	0	6	8.336376	-0.1
7	1	6	6	0	6	11.314828	0.9
7	1	6	6	1	5	8.787249	0.1
7	2	5	6	1	5	12.299488	-2.1
7	1	7	6	1	6	8.188736	-0.3
7	2	5	6	2	4	8.716419	0.1
7	2	6	6	2	5	8.510813	0.4
7	3	4	6	3	3	8.585475	0.0
7	3	5	6	3	4	8.570460	1.4
8	0	8	7	0	7	9.473386	0.3
8	1	7	7	0	7	12.993400	-1.6
8	1	7	7	1	6	10.014950	-0.4
8	2	6	7	1	6	13.512973	-0.1
8	1	8	7	1	7	9.343605	0.7
8	2	6	7	2	5	10.000733	0.2
8	2	7	7	2	6	9.712774	0.3
8	3	5	7	3	4	9.828405	-0.5
8	3	6	7	3	5	9.798831	0.8
8	4	4	7	4	3	9.794053	-1.5
8	4	5	7	4	4	9.793085	1.5
8	5	3	7	5	2	9.786038	-6.6
8	6	2	7	6	1	9.783045	1.1
8	6	3	7	6	2	9.783045	1.3
9	0	9	8	0	8	10.602139	-0.2
9	1	8	8	1	7	11.229526	-0.7
9	2	7	8	1	7	14.785145	0.2
9	1	9	8	1	8	10.494338	-0.4
9	2	7	8	2	6	11.287122	0.1
9	2	8	8	2	7	10.909421	-0.2
9	3	6	8	3	5	11.079990	0.0
9	3	7	8	3	6	11.026983	-0.2
9	4	5	8	4	4	11.025506	0.5
9	4	6	8	4	5	11.023195	0.7
9	6	3	8	6	2	11.008424	0.7

9	6	4	8	6	3	11.008424	1.2
10	0	10	9	0	9	11.726674	-0.4
10	1	9	9	1	8	12.428621	-0.2
10	1	10	9	1	9	11.641297	0.1
10	2	8	9	2	7	12.570503	-0.6
10	2	9	9	2	8	12.100306	-0.4
10	3	7	9	3	6	12.342019	-0.3
9	4	5	9	3	7	9.745091	-0.9
10	3	8	9	3	7	12.254035	0.1
10	4	6	9	4	5	12.259994	-0.6
10	4	7	9	4	6	12.255037	-0.1
10	5	5	9	5	4	12.241764	0.6
10	5	6	9	5	5	12.241635	1.3
10	6	4	9	6	3	12.234684	-1.0
10	6	5	9	6	4	12.234684	0.9
11	0	11	10	0	10	12.849991	-0.2
11	1	10	10	1	9	13.610391	-0.5
11	1	11	10	1	10	12.784941	0.0
11	2	9	10	2	8	13.846658	0.0
11	2	10	10	2	9	13.285100	-0.1
10	4	7	10	3	7	9.546601	-2.2
11	3	8	10	3	7	13.615751	-0.5
11	3	9	10	3	8	13.479008	0.0
11	4	7	10	4	6	13.498283	-0.2
11	4	8	10	4	7	13.488502	0.2
11	5	6	10	5	5	13.471922	1.1
11	5	7	10	5	6	13.471599	0.0
11	6	5	10	6	4	13.461926	-2.9
11	6	6	10	6	5	13.461926	3.1
11	7	4	10	7	3	13.457479	-0.5
11	7	5	10	7	4	13.457479	-0.5
11	8	3	10	8	2	13.456013	0.7
11	8	4	10	8	3	13.456013	0.7
12	0	12	11	0	11	13.973844	-0.7
12	1	11	11	1	10	14.774109	-0.3
12	1	12	11	1	11	13.925783	0.8
12	2	11	11	2	10	14.463624	0.2
12	2	11	11	2	10	14.463623	-0.3
12	3	9	11	3	8	14.901301	-0.3
12	3	9	11	3	8	14.901301	-0.1
12	3	10	11	3	9	14.700895	0.3
12	3	10	11	3	9	14.700896	0.7
12	4	8	11	4	7	14.741351	-0.2
12	4	9	11	4	8	14.723336	0.5
12	5	7	11	5	6	14.703898	0.0
12	5	8	11	5	7	14.703169	1.6
12	6	6	11	6	5	14.690250	-8.6
12	6	7	11	6	6	14.690250	8.0
12	7	5	11	7	4	14.683915	-0.4
12	7	6	11	7	5	14.683915	-0.1
12	8	4	11	8	3	14.681366	-0.4
12	8	5	11	8	4	14.681366	-0.4

[a] Observed frequencies in GHz

[b] Observed – calculated frequencies in kHz

2 Quantum Chemical Calculations

Conformational Sampling

All calculations were performed using the Gaussian16[1] program package. The Cartesian coordinates of the five lowest energy conformers in the principal axis of inertia system given in Tables S9-S13 were optimized at the B3LYP level of theory, and in Tables S14-S18 at the MP2 level of theory. The Cartesian coordinates of the lowest energy conformer observed under experimental conditions provided in Tables S19-S22 were optimized at the B3LYP-D3, PBE0-D3, MN15, and wB97X-D levels of theory, respectively. Harmonic frequency calculations were carried out to verify the nature of the stationary points and identify any negative vibrational frequencies around the dihedral angle Θ (see Fig. 1 of the ms.).

Calculation of the torsional states

As some of the potential energy curves suggest the existence of a double well minimum potential and the torsion of the aliphatic carbon chain (C_5H_{12}) against the ethyl carboxyl group (COO-C_2H_5), we made a simple model of two rigid tops rotating against each other to see if the lowest torsional energy states lies above the double minimum potential shown in Figure 4 of the manuscript. We used an effective moment of inertia $I = \frac{I_a I_c}{I_a + I_c} = 127.51\ \mathrm{u\AA}^2$ calculated from the moments of inertia of the aliphatic group $I_c = 396.36\ \mathrm{u\AA}^2$ and the ethyl carboxyl group with $I_e = 187.98\ \mathrm{u\AA}^2$ to describe the kinetic part of the Hamiltonian. For the potential terms in the potential energy operator, we use the values derived from the parameterized potential curve at the MN15/6-311++G(d,p) level of theory, given in Figure S1. The corresponding coefficients are given in Table S2 below. The energy eigenvalues were obtained by a direct diagonalization of the Hamilton matrix set up in the plane wave basis $\psi_m = \frac{1}{\sqrt{2\pi}} e^{imx}$ with m = 0, ±1, ±2, … ±∞. The matrix was truncated at $|m|$ = 40, corresponding to a size of 41 x 41, where convergence for the lowest energy levels was achieved. Table S3 provides the torsional energy levels up to v = 5. The lowest energy eigenvalue is depicted in Figure 4 of the manuscript.

[1] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

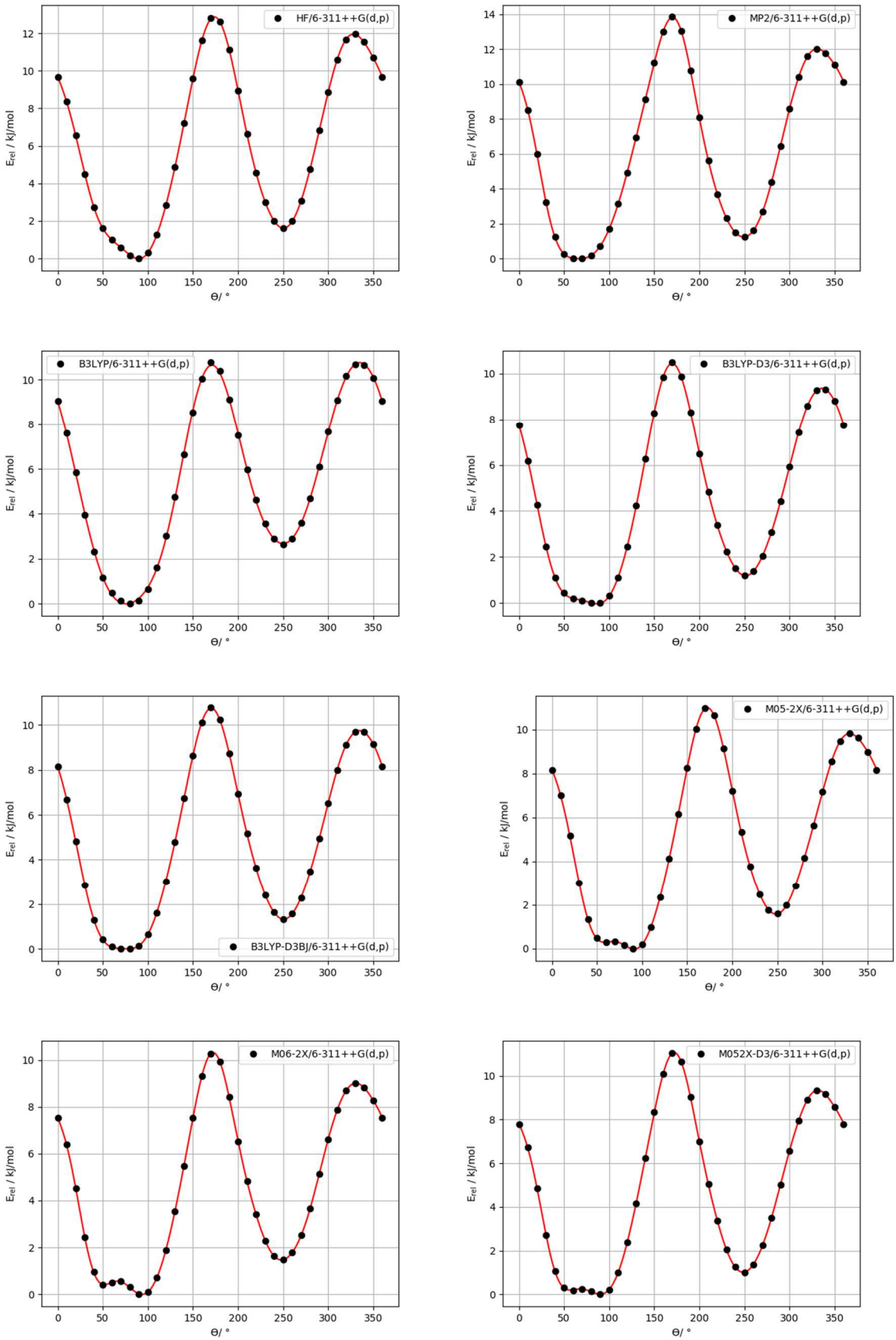

Figure S1. Potential energy curves for the rotation around the dihedral angle Θ (see Figure 2 of the ms.) optimized at different levels of theory. The electronic energies for the data are given in Table S3.

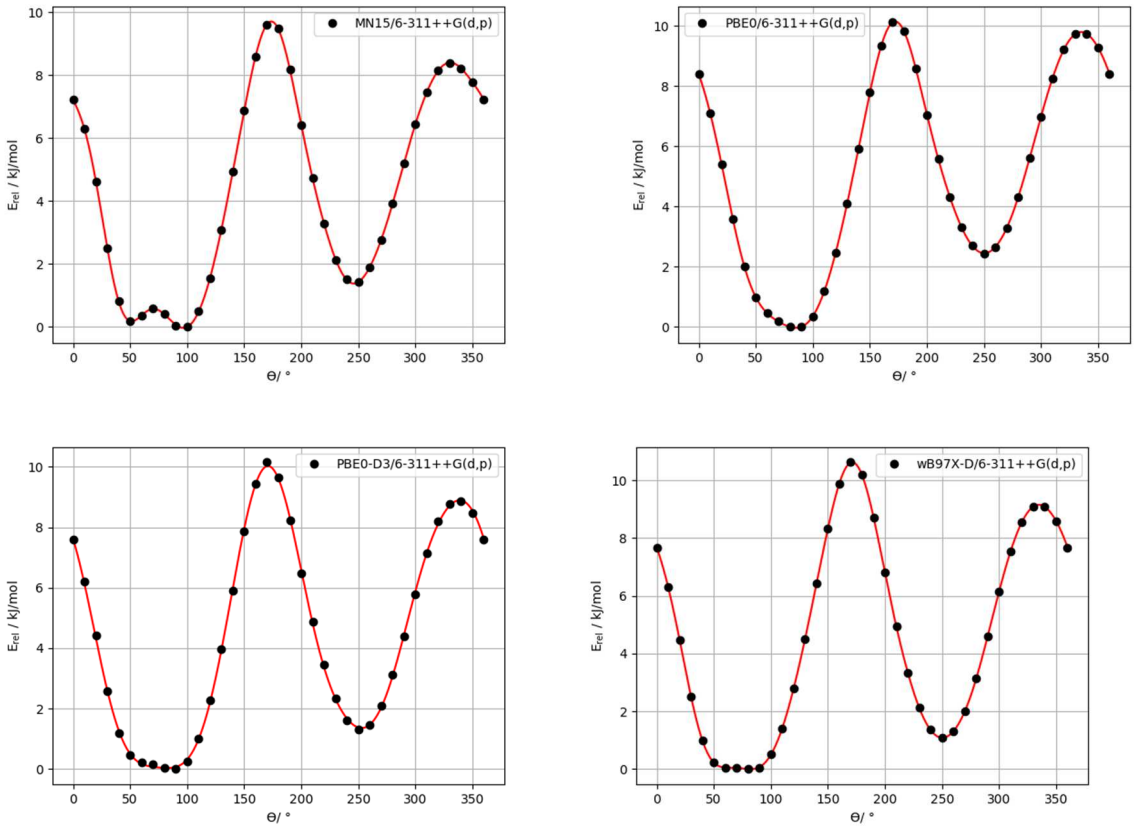

Figure S1 (continued). See caption of Figure S1.

Table S2. Fourier coefficients of the potential energy curve at the MN15/6-311++G(d,p) level of theory shown in Figure 4 of the manuscript, which was obtained by varying the dihedral angle Θ in a grid of 10° at a starting value of 0°, while all other parameters were left to optimize. The potential is expanded as $V(\Theta) = a_0 \sum_{k=1}^{9} \mathrm{a}_k \cdot \cos\left(k\Theta \cdot \frac{2\pi}{360}\right) + \mathrm{b}_k \cdot \sin\left(k\Theta \cdot \frac{2\pi}{360}\right)$.

a_k	Hartree	b_k	Hartree
0	-464.5189211		
1	-0.0000597	1	-0.0006205
2	0.0012796	2	-0.0007794
3	-0.0003668	3	-0.0000611
4	0.0002208	4	-0.0001021
5	0.0000495	5	0.0000972
6	0.0000380	6	0.0000586
7	-0.0000352	7	0.0000562
8	-0.0000093	8	0.0000032
9	-0.0000143	9	0.0000044

Table S3. Torsional energy levels of EMPE calculated[a] using the potential term at the MN15/6-311++G(d,p) level of theory.

v[b]	$v_{abs.}$/ Hartree	v_{rel}/ kJ/mol
0	-464.520939	0.00
1	-464.520850	0.23
2	-464.520763	0.46
3	-464.520678	0.69
4	-464.520596	0.90
5	-464.520517	1.11

[a] Calculations converged within 0.0000001 Hartree at m_{max} = 40. Sample calculation at m = 100 yielded the same energies.

[b] Main torsional quantum number v, absolute energy levels $v_{abs.}$, relative energy levels v_{rel} with respect to the lowest torsional state.

Table S4. Electronic energies corresponding to the data points shown in the potential energy curves in Figure S1.

Θ (°)	HF	MP2	B3LYP	B3LYP-D3	B3LYP-D3-BJ	wB97X-D
0	-462.134736	-463.729346	-465.097824	-465.119130	-465.134631	-464.948195
10	-462.135220	-463.729961	-465.098371	-465.119727	-465.135185	-464.948718
20	-462.135913	-463.730921	-465.099049	-465.120455	-465.135895	-464.949414
30	-462.136702	-463.731974	-465.099766	-465.121151	-465.136638	-464.950160
40	-462.137365	-463.732725	-465.100396	-465.121659	-465.137232	-464.950740
50	-462.137791	-463.733097	-465.100835	-465.121920	-465.137569	-464.951036
60	-462.138027	-463.733197	-465.101086	-465.122010	-465.137692	-464.951100
70	-462.138193	-463.733190	-465.101218	-465.122047	-465.137724	-464.951101
80	-462.138344	-463.733125	-465.101272	-465.122082	-465.137729	-464.951120
90	-462.138411	-463.732932	-465.101224	-465.122083	-465.137670	-464.951099
100	-462.138289	-463.732552	-465.101027	-465.121967	-465.137477	-464.950928
110	-462.137928	-463.731999	-465.100657	-465.121664	-465.137110	-464.950580
120	-462.137335	-463.731319	-465.100123	-465.121154	-465.136572	-464.950060
130	-462.136558	-463.730548	-465.099465	-465.120472	-465.135903	-464.949404
140	-462.135668	-463.729726	-465.098739	-465.119695	-465.135166	-464.948674
150	-462.134765	-463.728921	-465.098025	-465.118929	-465.134445	-464.947950
160	-462.133989	-463.728249	-465.097449	-465.118333	-465.133877	-464.947358
170	-462.133538	-463.727920	-465.097169	-465.118090	-465.133631	-464.947074
180	-462.133602	-463.728227	-465.097310	-465.118323	-465.133834	-464.947243
190	-462.134169	-463.729088	-465.097798	-465.118915	-465.134402	-464.947803
200	-462.135007	-463.730110	-465.098412	-465.119608	-465.135093	-464.948528
210	-462.135888	-463.731055	-465.099000	-465.120250	-465.135760	-464.949237
220	-462.136664	-463.731798	-465.099516	-465.120794	-465.136348	-464.949846
230	-462.137266	-463.732310	-465.099916	-465.121230	-465.136814	-464.950313
240	-462.137653	-463.732623	-465.100166	-465.121512	-465.137104	-464.950602
250	-462.137790	-463.732727	-465.100263	-465.121631	-465.137219	-464.950706
260	-462.137651	-463.732584	-465.100175	-465.121556	-465.137130	-464.950624
270	-462.137240	-463.732176	-465.099907	-465.121306	-465.136852	-464.950358
280	-462.136597	-463.731530	-465.099483	-465.120909	-465.136410	-464.949926
290	-462.135816	-463.730735	-465.098944	-465.120398	-465.135850	-464.949370
300	-462.135029	-463.729925	-465.098355	-465.119821	-465.135242	-464.948784
310	-462.134376	-463.729236	-465.097811	-465.119258	-465.134682	-464.948253
320	-462.133969	-463.728784	-465.097402	-465.118808	-465.134259	-464.947861
330	-462.133860	-463.728622	-465.097197	-465.118556	-465.134039	-464.947659
340	-462.134017	-463.728710	-465.097217	-465.118537	-465.134043	-464.947663
350	-462.134340	-463.728964	-465.097437	-465.118735	-465.134250	-464.947847
360	-462.134736	-463.729346	-465.097824	-465.119130	-465.134631	-464.948195

Table S4 (continued). See header of Table S3.

Θ (°)	MN15	M05-2X	M05-2X-D3	M06-2X	PBE0	PBE0-D3
0	-464.517820	-465.016991	-465.019231	-464.874762	-464.538726	-464.551866
10	-464.518163	-465.017423	-465.019642	-464.875193	-464.539225	-464.552392
20	-464.518812	-465.018126	-465.020347	-464.875909	-464.539866	-464.553073
30	-464.519611	-465.018949	-465.021169	-464.876703	-464.540563	-464.553772
40	-464.520249	-465.019588	-465.021788	-464.877261	-464.541163	-464.554304
50	-464.520501	-465.019912	-465.022084	-464.877470	-464.541552	-464.554579
60	-464.520432	-465.019981	-465.022127	-464.877441	-464.541749	-464.554666
70	-464.520342	-465.019974	-465.022101	-464.877419	-464.541857	-464.554700
80	-464.520413	-465.020034	-465.022146	-464.877513	-464.541926	-464.554742
90	-464.520547	-465.020094	-465.022199	-464.877626	-464.541926	-464.554757
100	-464.520565	-465.020013	-465.022115	-464.877591	-464.541788	-464.554655
110	-464.520380	-465.019714	-465.021813	-464.877353	-464.541475	-464.554371
120	-464.519978	-465.019201	-465.021294	-464.876908	-464.540990	-464.553887
130	-464.519390	-465.018525	-465.020612	-464.876281	-464.540369	-464.553243
140	-464.518688	-465.017745	-465.019825	-464.875541	-464.539668	-464.552504
150	-464.517944	-465.016952	-465.019027	-464.874751	-464.538962	-464.551764
160	-464.517296	-465.016280	-465.018356	-464.874076	-464.538372	-464.551163
170	-464.516905	-465.015909	-465.017996	-464.873711	-464.538069	-464.550891
180	-464.516959	-465.016037	-465.018147	-464.873844	-464.538186	-464.551079
190	-464.517448	-465.016611	-465.018754	-464.874414	-464.538652	-464.551626
200	-464.518129	-465.017352	-465.019531	-464.875138	-464.539239	-464.552286
210	-464.518767	-465.018063	-465.020280	-464.875789	-464.539797	-464.552905
220	-464.519313	-465.018665	-465.020914	-464.876327	-464.540283	-464.553439
230	-464.519756	-465.019143	-465.021420	-464.876756	-464.540659	-464.553863
240	-464.519994	-465.019417	-465.021722	-464.877001	-464.540896	-464.554139
250	-464.520021	-465.019484	-465.021812	-464.877067	-464.540995	-464.554262
260	-464.519846	-465.019333	-465.021675	-464.876951	-464.540917	-464.554195
270	-464.519515	-465.018997	-465.021345	-464.876670	-464.540671	-464.553954
280	-464.519074	-465.018513	-465.020862	-464.876231	-464.540281	-464.553569
290	-464.518584	-465.017945	-465.020288	-464.875676	-464.539791	-464.553083
300	-464.518116	-465.017358	-465.019693	-464.875105	-464.539264	-464.552549
310	-464.517727	-465.016844	-465.019170	-464.874628	-464.538781	-464.552041
320	-464.517466	-465.016491	-465.018803	-464.874314	-464.538415	-464.551640
330	-464.517370	-465.016351	-465.018648	-464.874195	-464.538221	-464.551410
340	-464.517435	-465.016432	-465.018710	-464.874269	-464.538219	-464.551379
350	-464.517606	-465.016674	-465.018934	-464.874471	-464.538393	-464.551534
360	-464.517820	-465.016991	-465.019231	-464.874762	-464.538726	-464.551866

Table S5. Quantum chemical data obtained for the optimization and harmonic frequency calculations of the observed conformer of EMPE (conformer 1) at different levels of theory using different Pople basis sets.

	A [a]	B	C	μ	ν	E	ZPE	θ
HF								
6-31G(d,p)	2.258	0.621	0.550	1.95	25.11	-462.040384	-461.792425	96.3
6-31++G(d,p)	2.122	0.633	0.558	2.04	21.17	-462.047897	-461.800565	88.7
6-311G(d,p)	2.255	0.621	0.550	1.93	24.64	-462.132839	-461.886423	95.9
6-311++G(d,p)	2.134	0.632	0.557	2.00	22.2	-462.138411	-461.892137	89.3
MP2								
6-31G(d,p)	2.122	0.640	0.561	1.89	15.38	-462.036282	-463.300865	89.4
6-31++G(d,p)	1.611	0.759	0.599	2.03	17.17	-462.042990	-463.327946	58.2
6-311G(d,p)	1.552	0.794	0.608	1.89	23.23	-462.128122	-463.483205	53.0
6-311++G(d,p)	1.680	0.734	0.594	1.94	10.57	-462.133830	-463.498525	63.2
B3LYP								
6-31G(d,p)	2.201	0.617	0.545	1.78	19.97	-464.985418	-464.752911	95.3
6-31++G(d,p)	1.877	0.657	0.564	1.91	14.87	-465.001635	-464.769993	76.4
6-311G(d,p)	2.196	0.617	0.545	1.78	19.84	-465.094448	-464.863377	94.8
6-311++G(d,p)	1.956	0.645	0.560	1.87	14.49	-465.101272	-464.870405	80.8
B3LYP-D3								
6-31G(d,p)	2.299	0.615	0.542	1.81	24.34	-465.006417	-464.773352	100.7
6-31++G(d,p)	1.829	0.674	0.571	1.90	7.52	-465.022424	-464.790285	73.8
6-311G(d,p)	2.300	0.614	0.542	1.80	24.05	-465.115421	-464.883790	100.6
6-311++G(d,p)	2.040	0.639	0.558	1.87	11.91	-465.122091	-464.890720	85.6
B3LYP-D3BJ								
6-31G(d,p)	2.219	0.622	0.548	1.79	19.49	-465.021904	-464.789092	95.8
6-31++G(d,p)	1.744	0.698	0.579	1.91	9.58	-465.038058	-464.806098	68.5
6-311G(d,p)	2.216	0.622	0.549	1.78	19.53	-465.130939	-464.899561	95.5
6-311++G(d,p)	1.866	0.671	0.572	1.86	8.85	-465.137732	-464.906549	75.8
wB97X-D								
6-31G(d,p)	2.237	0.624	0.550	1.82	19.45	-464.844912	-464.610104	96.0
6-31++G(d,p)	1.649	0.738	0.592	1.95	12.03	-464.856887	-464.622733	61.3
6-311G(d,p)	2.231	0.625	0.551	1.81	18.92	-464.944891	-464.711502	95.3
6-311++G(d,p)	2.011	0.650	0.566	1.88	13.70	-464.951124	-464.717857	83.1
M05-2X								
6-31G(d,p)	2.341	0.621	0.547	1.80	22.21	-464.906134	-464.669369	100.9
6-31++G(d,p)	2.125	0.639	0.560	1.89	15.58	-464.918055	-464.682067	87.5
6-311G(d,p)	2.328	0.622	0.549	1.80	23.96	-465.014286	-464.778576	99.5
6-311++G(d,p)	2.185	0.635	0.558	1.87	21.35	-465.020094	-464.784454	90.8
M05-2X-D3								
6-31G(d,p)	2.337	0.622	0.548	1.80	22.10	-464.908238	-464.671480	101.0
6-31++G(d,p)	2.109	0.641	0.561	1.89	13.45	-464.920159	-464.684207	88.2
6-311G(d,p)	2.325	0.623	0.550	1.80	23.45	-465.016389	-464.780693	99.6
6-311++G(d,p)	2.179	0.636	0.559	1.87	20.74	-465.022199	-464.786572	91.1
M06-2X								
6-31G(d,p)	2.377	0.619	0.544	1.76	28.81	-464.755813	-464.520919	104.1
6-31++G(d,p)	2.187	0.632	0.555	1.85	18.25	-464.767694	-464.533614	92.7
6-311G(d,p)	2.373	0.619	0.545	1.76	29.09	-464.871832	-464.637867	103.3

6-311++G(d,p)	2.212	0.631	0.555	1.82	20.96	-464.877635	-464.643812	93.6
MN15								
6-31G(d,p)	2.417	0.615	0.540	1.80	28.61	-464.411864	-464.178376	107.1
6-31++G(d,p)	2.232	0.626	0.551	1.92	21.37	-464.426995	-464.194547	95.1
6-311G(d,p)	2.417	0.616	0.542	1.79	28.63	-464.514423	-464.282182	106.0
6-311++G(d,p)	2.277	0.625	0.551	1.87	24.26	-464.520577	-464.288466	96.7
PBE0								
6-31G(d,p)	2.288	0.621	0.548	1.79	22.04	-464.436901	-464.202836	101.3
6-31++G(d,p)	1.982	0.653	0.567	1.89	12.24	-464.4495291	-464.216222	81.3
6-311G(d,p)	2.280	0.622	0.550	1.78	21.77	-464.535353	-464.302766	100.5
6-311++G(d,p)	2.060	0.644	0.563	1.85	15.0	-464.541938	-464.309561	87.7
PBE0-D3								
6-31G(d,p)	2.329	0.6214	0.547	1.81	24.28	-464.449799	-464.215420	99.0
6-31++G(d,p)	1.979	0.658	0.569	1.88	6.69	-464.462330	-464.228760	81.2
6-311G(d,p)	2.323	0.622	0.549	1.80	24.06	-464.548242	-464.315341	98.1
6-311++G(d,p)	2.099	0.643	0.563	1.86	14.25	-464.554760	-464.322098	85.4

[a] Rotational constants A, B, C in GHz; dipole moment μ in Debye; lowest vibrational frequency ν in cm^{-1}; electronic energies E in Hartree; sum of electronic and zero-point energies ZPE in Hartree; relative energies E_{rel} and ZPE_{rel} in kJ/mol, dihedral angle Θ in degree (see Figure 2 in the ms.).

Table S6. Quantum chemical data obtained through optimization of the conformers of EMPE at the B3LYP/6-311++G(d,p) level of theory.

Conf.	A [a]	B	C	μ	ν	E	E_{rel}	ZPE	ZPE_{rel}
1	1.956	0.645	0.560	1.87	14.5	-465.101272	0.00	-464.870405	0.00
2	2.236	0.653	0.569	1.69	18.6	-465.100634	1.68	-464.869582	2.16
3	1.726	0.752	0.591	1.69	20.9	-465.100541	1.92	-464.869493	2.39
4	1.474	0.784	0.651	2.10	25.1	-465.100263	2.65	-464.869357	2.75
5	1.920	0.622	0.516	2.00	18.5	-465.100137	2.98	-464.869290	2.93
6	1.620	0.764	0.604	1.92	20.8	-465.099537	4.56	-464.868626	4.67
7	1.447	0.886	0.661	1.92	29.2	-465.099513	4.62	-464.868442	5.15
8	1.940	0.671	0.551	2.00	18.0	-465.099042	5.85	-464.868013	6.28
9	2.812	0.590	0.529	1.95	14.4	-465.098426	7.47	-464.867427	7.82
10	1.729	0.801	0.652	1.81	25.9	-465.098490	7.30	-464.867389	7.92
11	2.061	0.684	0.587	1.85	23.7	-465.098392	7.56	-464.867173	8.49
12	2.613	0.625	0.553	1.77	16.9	-465.097797	9.28	-464.866645	9.88
13	2.301	0.653	0.589	1.77	17.1	-465.097737	9.28	-464.866555	10.11
14	1.500	0.887	0.738	2.14	32.8	-465.097393	10.18	-464.866277	10.84
15	2.550	0.581	0.516	2.04	20.0	-465.095993	13.86	-464.864991	14.21
16	1.498	0.996	0.737	1.95	34.8	-465.096279	13.11	-464.864976	14.25
17	2.832	0.602	0.553	1.86	18.3	-465.094413	18.01	-464.863345	18.54
18	2.421	0.648	0.624	1.68	20.3	-465.093728	19.81	-464.862481	20.80
19	2.421	0.648	0.624	1.68	20.3	-465.093728	19.81	-464.862480	20.81

[a] Rotational constants A, B, C in GHz; dipole moment μ in Debye; lowest vibrational frequency ν in cm^{-1}; electronic energies E in Hartree; sum of electronic and zero-point energies ZPE in Hartree; relative energies E_{rel} and ZPE_{rel} in kJ/mol.

Table S7. Quantum chemical data obtained through optimization of the conformers of EMPE at the MP2/6-311++G(d,p) level of theory.

Conf.	A [a]	B	C	μ	ν	E	$E_{rel.}$	ZPE	$ZPE_{rel.}$
1	1.681	0.734	0.594	1.94	10.7	-463.733200	0.00	-463.498524	0.00
2	2.177	0.685	0.591	1.74	15.8	-463.732962	0.62	-463.498098	1.12
3	1.500	0.907	0.648	1.79	20.8	-463.733101	0.26	-463.498218	0.80
4	1.443	0.832	0.676	2.25	28.0	-463.732727	1.24	-463.498109	1.09
5	1.973	0.625	0.521	2.09	22.7	-463.731431	4.64	-463.496782	4.57
6	1.561	0.830	0.631	2.05	26.1	-463.732087	2.92	-463.497403	2.94
7	1.429	0.957	0.695	2.07	36.0	-463.732668	1.40	-463.497808	1.88
8	2.066	0.665	0.558	2.10	26.5	-463.731457	4.58	-463.496477	5.37
9	2.610	0.617	0.556	2.00	14.2	-463.730442	7.24	-463.495542	7.83
10	1.738	0.841	0.677	1.87	31.0	-463.731992	3.17	-463.496986	4.04
11	2.180	0.690	0.605	1.96	31.9	-463.731414	4.69	-463.496232	6.02
12	2.525	0.655	0.577	1.82	18.1	-463.730139	8.04	-463.495056	9.11
13	2.050	0.721	0.636	1.82	10.7	-463.730256	7.73	-463.495171	8.80
14	1.490	0.950	0.775	2.28	36.7	-463.731162	5.35	-463.496320	5.79
15	3.407	0.522	0.515	1.95	13.1	-463.727498	14.97	-463.492554	15.67
16	1.536	1.040	0.766	2.08	43.1	-463.730482	7.14	-463.495381	8.25
17	2.731	0.622	0.575	1.93	18.6	-463.726832	16.72	-463.491846	17.53
18	1.769	0.843	0.748	1.95	30.8	-463.726907	16.52	-463.491632	18.09
19	2.302	0.687	0.662	1.74	19.0	-463.726646	17.21	-463.491472	18.52

[a] Rotational constants A, B, C in GHz; dipole moment μ in Debye; lowest vibrational frequency ν in cm^{-1}; electronic energies E in Hartree; sum of electronic and zero-point energies ZPE in Hartree; relative energies E_{rel} and ZPE_{rel} in kJ/mol.

Table S8. Quantum chemical data obtained through optimization of the conformers of EMPE at the wB97X-D/6-311++G(d,p) level of theory.

Conf.	A [a]	B	C	μ	ν	E	E_{rel}	ZPE	$ZPE_{rel.}$
1	2.011	0.650	0.566	1.88	13.7	-464.951124	0.68	-464.717857	0.00
2	2.323	0.660	0.578	1.71	24.9	-464.951156	0.60	-464.717627	0.60
3	1.458	0.937	0.653	1.78	28.2	-464.951384	0.00	-464.717832	0.07
4	1.450	0.822	0.670	2.13	25.6	-464.950706	1.78	-464.717425	1.13
5	1.882	0.648	0.522	2.04	23.6	-464.950054	3.49	-464.716731	2.96
6	1.563	0.822	0.624	1.97	22.9	-464.950479	2.38	-464.717220	1.67
7	1.418	0.961	0.693	1.95	35.2	-464.950970	1.09	-464.717425	1.13
8	2.018	0.678	0.558	2.06	24	-464.950180	3.16	-464.716662	3.14
9	2.747	0.605	0.544	1.96	14.4	-464.949260	5.58	-464.715864	5.23
10	1.726	0.839	0.674	1.82	26.6	-464.950149	3.24	-464.716535	3.47
11	2.176	0.690	0.600	1.90	31.4	-464.950245	2.99	-464.716502	3.56
12	2.592	0.642	0.567	1.77	21.7	-464.949074	6.06	-464.715377	6.51
13	2.245	0.679	0.609	1.77	16	-464.949172	5.81	-464.715422	6.39
14	1.480	0.957	0.774	2.17	38.9	-464.949646	4.56	-464.715983	4.92
15	3.469	0.530	0.506	1.91	18.9	-464.946579	12.62	-464.713061	12.59
16	1.520	1.059	0.770	1.97	47.3	-464.949667	4.51	-464.715514	6.15
17	2.796	0.615	0.567	1.88	20	-464.946194	13.63	-464.712531	13.98
18	1.757	0.843	0.747	1.84	27.4	-464.946215	13.57	-464.712295	14.60
19	2.391	0.669	0.647	1.68	23.4	-464.946132	13.79	-464.712179	14.91

[a] Rotational constants A, B, C in GHz; dipole moment μ in Debye; lowest vibrational frequency ν in cm^{-1}; electronic energies E in Hartree; sum of electronic and zero-point energies ZPE in Hartree; relative energies E_{rel} and ZPE_{rel} in kJ/mol.

Table S9. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the B3LYP/6-311G++(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.682894	-1.476298	-0.053037
C	-2.266508	-1.020948	-0.416260
C	-2.011191	0.452583	-0.078758
C	-0.609166	0.954785	-0.458036
C	0.463558	0.264670	0.371723
O	1.548010	-0.043718	-0.372685
C	2.664193	-0.649384	0.327156
C	3.756392	-0.910464	-0.689693
H	-2.746388	1.075265	-0.602511
H	4.617250	-1.368959	-0.195587
H	-4.437343	-0.890234	-0.587702
H	-3.871161	-1.359856	1.018604
H	-1.540100	-1.647410	0.113231
H	-2.164215	0.616377	0.993224
C	-0.476187	2.477670	-0.255367
O	0.390527	0.042798	1.557526
H	4.085961	0.019168	-1.159184
H	3.409297	-1.588650	-1.472488
H	2.991623	0.031462	1.116366
H	2.318419	-1.569312	0.803962
H	0.517544	2.833704	-0.538615
H	-1.211241	3.002208	-0.871130
H	-0.652500	2.744224	0.789915
H	-3.840041	-2.528535	-0.305467
H	-2.093759	-1.182888	-1.487406
H	-0.409125	0.725283	-1.508894

Table S10. Cartesian coordinates of conformer 2 of EMPE in the principal axis of inertia system as optimized at the B3LYP/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.838935	-1.149933	0.102362
C	-2.434236	-0.797713	-0.395930
C	-1.951478	0.568499	0.104592
C	-0.556230	0.970033	-0.400025
C	0.514820	0.045164	0.159259
O	1.433864	-0.273198	-0.780201
C	2.552560	-1.099751	-0.365309
C	3.690207	-0.257843	0.187947
H	-2.661278	1.341118	-0.214477
H	4.541919	-0.901964	0.425499
H	-4.574471	-0.409700	-0.228667
H	-3.871993	-1.183775	1.195627
H	-1.732123	-1.573918	-0.071844
H	-1.944517	0.577950	1.199699
C	-0.203680	2.418133	-0.005135
O	0.568214	-0.340609	1.303473
H	3.387164	0.254843	1.102629
H	4.017578	0.484457	-0.544004
H	2.199499	-1.822866	0.370689
H	2.849498	-1.622558	-1.274967
H	0.783569	2.705125	-0.375949
H	-0.937134	3.109591	-0.427649
H	-0.210455	2.533826	1.081744
H	-4.160400	-2.126456	-0.270016
H	-2.422190	-0.807037	-1.492777
H	-0.522919	0.888748	-1.490420

Table S11. Cartesian coordinates of conformer 3 of EMPE in the principal axis of inertia system as optimized at the B3LYP/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.455697	-1.653116	0.051104
C	-2.121895	-1.050781	-0.400171
C	-1.947599	0.406334	0.043328
C	-0.634132	1.055803	-0.418415
C	0.569452	0.403883	0.246500
O	1.614124	0.313285	-0.607387
C	2.858352	-0.222554	-0.086280
C	2.904247	-1.736827	-0.205202
H	-2.777386	1.004797	-0.351488
H	3.881479	-2.101388	0.124818
H	-4.302553	-1.091043	-0.355633
H	-3.543875	-1.641856	1.141771
H	-1.300177	-1.654383	0.000505
H	-2.004894	0.467812	1.135233
C	-0.602955	2.565122	-0.101740
O	0.617423	0.047618	1.400409
H	2.754681	-2.050844	-1.240980
H	2.139738	-2.200719	0.420378
H	3.628682	0.248048	-0.698139
H	2.971242	0.097672	0.950108
H	0.327680	3.025631	-0.442224
H	-1.433228	3.069037	-0.603019
H	-0.698932	2.735649	0.973740
H	-3.556571	-2.690467	-0.279602
H	-2.045878	-1.108715	-1.493017
H	-0.519975	0.926983	-1.498932

Table S12. Cartesian coordinates of conformer 4 of EMPE in the principal axis of inertia system as optimized at the B3LYP/6-311G++(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	3.199935	-1.816632	-0.018755
C	2.212474	-0.773998	0.513442
C	1.696748	0.168150	-0.580284
C	0.733100	1.260260	-0.078342
C	-0.515808	0.681924	0.571043
O	-1.174530	-0.156474	-0.259738
C	-2.399839	-0.742655	0.245313
C	-2.964870	-1.634687	-0.841030
H	2.549569	0.669794	-1.053750
H	-3.893526	-2.095000	-0.492944
H	4.076890	-1.339082	-0.467317
H	2.736920	-2.444506	-0.786497
H	1.367396	-1.285669	0.988420
H	1.201180	-0.412206	-1.365859
C	0.340387	2.231905	-1.206668
O	-0.901970	0.943170	1.686074
H	-2.263754	-2.431643	-1.099085
H	-3.184738	-1.061695	-1.744702
H	-2.170362	-1.300175	1.156328
H	-3.087010	0.063113	0.513589
H	-0.333214	3.012635	-0.843815
H	1.233754	2.718492	-1.607026
H	-0.155709	1.702335	-2.023308
H	3.552967	-2.474512	0.779984
H	2.691938	-0.184025	1.303446
H	1.222237	1.827202	0.718914

Table S13 Cartesian coordinates of conformer 5 of EMPE in the principal axis of inertia system as optimized at the B3LYP/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.703260	-1.623466	0.443815
C	-2.883852	-0.603609	-0.353341
C	-1.529480	-0.300366	0.299164
C	-0.633334	0.669854	-0.511772
C	0.743351	0.699096	0.133646
O	1.521283	-0.309182	-0.321010
C	2.840269	-0.427115	0.268011
C	3.532669	-1.604128	-0.388054
H	-1.687280	0.119999	1.299783
H	4.534765	-1.723028	0.032814
H	-3.909693	-1.260821	1.455587
H	-3.170690	-2.575166	0.535877
H	-2.716763	-0.982505	-1.369003
H	-0.988842	-1.243441	0.436277
C	-1.208870	2.086956	-0.608893
O	1.109810	1.490380	0.969929
H	3.629508	-1.451213	-1.465305
H	2.978185	-2.530026	-0.219065
H	3.379443	0.508924	0.105684
H	2.730233	-0.564559	1.346354
H	-0.542764	2.743368	-1.174085
H	-2.176888	2.078906	-1.113304
H	-1.335800	2.521248	0.385084
H	-4.663528	-1.825125	-0.038625
H	-3.464425	0.318149	-0.459709
H	-0.507591	0.249416	-1.514925

Table S14. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the MP2/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.267185	-1.863244	0.137175
C	-1.939809	-1.214643	-0.257557
C	-1.982176	0.308407	-0.130954
C	-0.683659	0.996798	-0.569110
C	0.448882	0.511640	0.309005
O	1.437404	-0.064296	-0.411986
C	2.550623	-0.550471	0.369539
C	3.537674	-1.166101	-0.599022
H	-2.804668	0.702812	-0.742934
H	4.401912	-1.549009	-0.048388
H	-4.079620	-1.503726	-0.503003
H	-3.521920	-1.618775	1.173495
H	-1.138204	-1.610585	0.378664
H	-2.189314	0.586158	0.910732
C	-0.793273	2.521494	-0.449896
O	0.477511	0.621830	1.518366
H	3.886685	-0.422408	-1.319209
H	3.077955	-1.994123	-1.143609
H	2.985311	0.286531	0.922876
H	2.179608	-1.279450	1.095386
H	0.125958	3.014943	-0.781317
H	-1.621006	2.885696	-1.066291
H	-0.981145	2.801222	0.590980
H	-3.222819	-2.952730	0.047318
H	-1.686270	-1.483920	-1.290976
H	-0.454813	0.719827	-1.603892

Table S15. Cartesian coordinates of conformer 2 of EMPE in the principal axis of inertia system as optimized at the MP2/6-311G++(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.743085	-1.195629	0.143782
C	-2.346548	-0.825269	-0.357182
C	-1.928358	0.577560	0.083928
C	-0.549986	0.993456	-0.435438
C	0.510688	0.076423	0.133163
O	1.380762	-0.328427	-0.820983
C	2.483117	-1.137448	-0.351239
C	3.584443	-0.270220	0.231769
H	-2.666793	1.307488	-0.274479
H	4.437037	-0.896486	0.512421
H	-4.491061	-0.493180	-0.238758
H	-3.780041	-1.164275	1.237499
H	-1.619059	-1.554944	0.019100
H	-1.920846	0.631640	1.179894
C	-0.206067	2.433868	-0.029368
O	0.594506	-0.238302	1.303330
H	3.231491	0.251930	1.123098
H	3.920997	0.462313	-0.506512
H	2.110291	-1.854474	0.383485
H	2.822181	-1.668780	-1.241759
H	0.780409	2.727707	-0.402181
H	-0.949111	3.125016	-0.439099
H	-0.208834	2.525274	1.061399
H	-4.029464	-2.201963	-0.176075
H	-2.318098	-0.881644	-1.453089
H	-0.523075	0.906714	-1.527209

Table S16. Cartesian coordinates of conformer 3 of EMPE in the principal axis of inertia system as optimized at the MP2/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-2.948524	-2.012512	0.152389
C	-1.748293	-1.193867	-0.324717
C	-1.871825	0.282790	0.052252
C	-0.711681	1.148556	-0.457852
C	0.577547	0.637312	0.146772
O	1.431608	0.184751	-0.799927
C	2.675988	-0.359614	-0.303817
C	2.494287	-1.790692	0.170119
H	-2.807818	0.686857	-0.356758
H	3.463518	-2.208160	0.460478
H	-3.875771	-1.636546	-0.292611
H	-3.048757	-1.950903	1.240932
H	-0.829933	-1.606661	0.111035
H	-1.925325	0.382316	1.144446
C	-0.904293	2.618977	-0.071369
O	0.819819	0.628180	1.337202
H	2.078555	-2.405332	-0.632618
H	1.829449	-1.828874	1.034991
H	3.349932	-0.305834	-1.160135
H	3.050221	0.280797	0.497964
H	-0.089229	3.241933	-0.453157
H	-1.846337	2.992965	-0.484175
H	-0.933804	2.717087	1.017709
H	-2.846797	-3.067524	-0.119069
H	-1.646397	-1.281042	-1.414092
H	-0.638803	1.053379	-1.546495

Table S17. Cartesian coordinates of conformer 4 of EMPE in the principal axis of inertia system as optimized at the MP2/6-311G++(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	3.061665	-1.871186	-0.002572
C	2.083274	-0.816695	0.515973
C	1.684404	0.183419	-0.569303
C	0.748997	1.290564	-0.068389
C	-0.493404	0.706645	0.568374
O	-1.124803	-0.134418	-0.285507
C	-2.330455	-0.734432	0.232300
C	-2.863989	-1.655754	-0.843775
H	2.587938	0.659582	-0.974456
H	-3.784047	-2.134058	-0.495219
H	3.980990	-1.401079	-0.367195
H	2.619651	-2.432712	-0.832277
H	1.184160	-1.312443	0.903214
H	1.198507	-0.345718	-1.398494
C	0.358591	2.250366	-1.200061
O	-0.899569	0.950910	1.686163
H	-2.135420	-2.435080	-1.079784
H	-3.087553	-1.095928	-1.755023
H	-2.088834	-1.274688	1.152055
H	-3.040385	0.058640	0.483662
H	-0.299806	3.046135	-0.837395
H	1.257284	2.713757	-1.619339
H	-0.156601	1.706853	-1.997387
H	3.334588	-2.583929	0.781328
H	2.530612	-0.275061	1.359227
H	1.247707	1.852005	0.729684

Table S18. Cartesian coordinates of conformer 5 of EMPE in the principal axis of inertia system as optimized at the MP2/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	2.969409	-1.843943	-0.140063
C	1.903107	-0.928047	0.461830
C	1.704426	0.344349	-0.362098
C	0.681962	1.314403	0.243515
C	-0.651941	0.630980	0.452378
O	-1.119778	0.125615	-0.714898
C	-2.380276	-0.574802	-0.630863
C	-2.180349	-1.998338	-0.141902
H	2.663278	0.873555	-0.450404
H	-3.135477	-2.532636	-0.161708
H	3.936097	-1.332060	-0.191873
H	2.692662	-2.142192	-1.156750
H	0.952288	-1.471189	0.529615
H	1.385707	0.080690	-1.378261
C	0.508815	2.563661	-0.629829
O	-1.245044	0.545657	1.508497
H	-1.803076	-2.003957	0.882441
H	-1.475351	-2.526288	-0.789705
H	-3.053201	-0.019950	0.026728
H	-2.766645	-0.554246	-1.651188
H	-0.217051	3.256853	-0.192959
H	1.466686	3.085040	-0.724096
H	0.165020	2.282946	-1.629393
H	3.099592	-2.752351	0.455664
H	2.181693	-0.654235	1.487484
H	1.015442	1.611474	1.244192

Table S19. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the B3LYP-D3/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.726052	-1.393394	-0.109171
C	-2.300732	-0.960062	-0.462346
C	-2.011069	0.491017	-0.064446
C	-0.596515	0.964127	-0.423460
C	0.450318	0.192707	0.363620
O	1.566323	-0.015322	-0.367246
C	2.664130	-0.681541	0.306220
C	3.796969	-0.806252	-0.691419
H	-2.729869	1.154445	-0.559978
H	4.649559	-1.305571	-0.223424
H	-4.466486	-0.764762	-0.614475
H	-3.902843	-1.313445	0.967839
H	-1.585693	-1.621126	0.039246
H	-2.157026	0.611363	1.014208
C	-0.402853	2.465309	-0.131740
O	0.334532	-0.163501	1.512643
H	4.120795	0.178049	-1.037130
H	3.487428	-1.392679	-1.559421
H	2.947300	-0.091285	1.181435
H	2.316988	-1.655149	0.660873
H	0.604657	2.795722	-0.396081
H	-1.117918	3.054527	-0.711456
H	-0.568460	2.672918	0.928799
H	-3.913407	-2.430103	-0.402012
H	-2.135223	-1.080091	-1.540215
H	-0.406176	0.787661	-1.486557

Table S20. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the PBE0-D3/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.727638	-1.348411	-0.126638
C	-2.308613	-0.926612	-0.480240
C	-1.997889	0.500844	-0.047755
C	-0.589022	0.960913	-0.405836
C	0.447221	0.162582	0.353145
O	1.565817	-0.002845	-0.368028
C	2.643404	-0.685899	0.290759
C	3.793356	-0.763048	-0.680629
H	-2.713597	1.189048	-0.515164
H	4.637990	-1.278671	-0.215723
H	-4.465464	-0.696343	-0.606274
H	-3.893256	-1.295956	0.954250
H	-1.595847	-1.610055	-0.003937
H	-2.130075	0.592984	1.036745
C	-0.372925	2.442880	-0.082463
O	0.320975	-0.246768	1.479728
H	4.121526	0.236278	-0.977031
H	3.507464	-1.313307	-1.580392
H	2.906937	-0.135203	1.198774
H	2.296280	-1.676801	0.598099
H	0.637943	2.766197	-0.344656
H	-1.083261	3.056672	-0.643154
H	-0.529930	2.628264	0.984276
H	-3.933504	-2.374184	-0.445303
H	-2.153788	-1.019189	-1.563157
H	-0.405694	0.804797	-1.474852

Table S21. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the MN15/6-311G++(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.834750	-1.181745	-0.181455
C	-2.401391	-0.813842	-0.549216
C	-1.995992	0.542417	0.019985
C	-0.574960	0.958298	-0.344276
C	0.438897	0.045391	0.309932
O	1.607960	0.048830	-0.349270
C	2.662164	-0.729329	0.237795
C	3.878739	-0.586145	-0.646458
H	-2.686430	1.313742	-0.343482
H	4.708886	-1.164982	-0.237063
H	-4.539257	-0.434820	-0.559598
H	-3.954259	-1.229536	0.904489
H	-1.715232	-1.579438	-0.172544
H	-2.084139	0.522992	1.112683
C	-0.271516	2.392479	0.108650
O	0.262217	-0.582642	1.327367
H	4.186477	0.458779	-0.713296
H	3.668232	-0.949219	-1.653806
H	2.843523	-0.365675	1.252194
H	2.328976	-1.766919	0.316913
H	0.749480	2.683475	-0.145771
H	-0.960446	3.090724	-0.371811
H	-0.399978	2.479200	1.191387
H	-4.122868	-2.151569	-0.592559
H	-2.288629	-0.795377	-1.640159
H	-0.425249	0.888786	-1.427515

Table S22. Cartesian coordinates of conformer 1 of EMPE in the principal axis of inertia system as optimized at the wB97X-D/6-311++G(d,p) level of theory.

Atom	a / Å	b / Å	c / Å
C	-3.678630	-1.433978	-0.085323
C	-2.260787	-0.989474	-0.432341
C	-2.003016	0.473119	-0.076193
C	-0.600493	0.960816	-0.441227
C	0.454156	0.226952	0.363398
O	1.547740	-0.028614	-0.368945
C	2.640154	-0.664163	0.314342
C	3.757613	-0.851420	-0.685737
H	-2.730550	1.107657	-0.596276
H	4.608540	-1.334999	-0.199850
H	-4.421417	-0.834146	-0.620530
H	-3.870635	-1.322572	0.985935
H	-1.542506	-1.623554	0.098731
H	-2.159808	0.623312	0.997556
C	-0.437364	2.465802	-0.184946
O	0.357265	-0.065930	1.528127
H	4.089260	0.109678	-1.084314
H	3.433979	-1.479336	-1.518478
H	2.944594	-0.034650	1.154266
H	2.293313	-1.616771	0.722278
H	0.563664	2.810659	-0.455180
H	-1.162614	3.026481	-0.779641
H	-0.609695	2.693984	0.870286
H	-3.843937	-2.482016	-0.347345
H	-2.079302	-1.138899	-1.503541
H	-0.404598	0.761309	-1.499056