Supplementary Information

Melting pseudosymmetry and thermal expansion in 3-benzoylpropionic acid

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1. Conformational isomerism in BPA

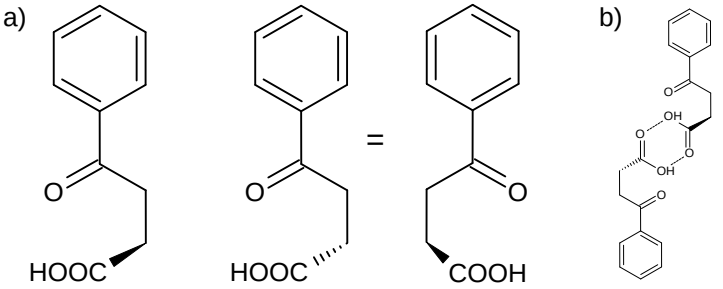

Figure S1. Conformational isomerism in BPA, depending on a position of the carboxylic group in respect to benzoylpropionic part (a). Two molecules in a dimer related by the inversion symmetry form a pair of the conformational enantiomers

2. Cumulative intensity distribution in BPA structure at 200 K

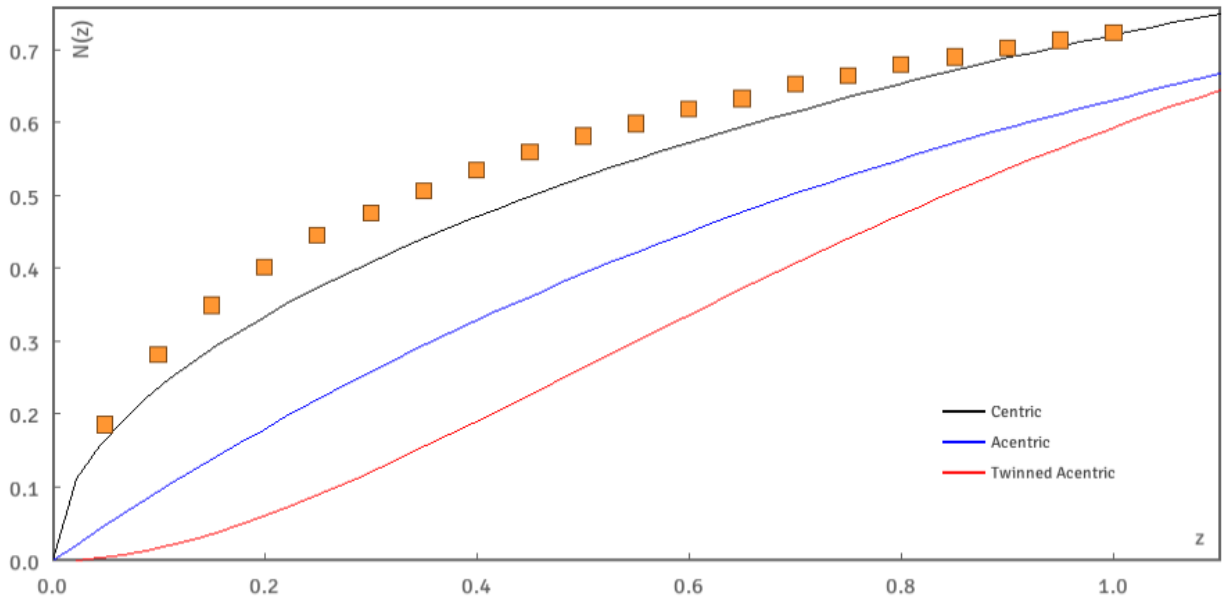

Figure S2. Cumulative intensity distribution in BPA dataset collected at 200K. Z is the normalized intensity and N(Z) is its cumulative distribution.

3. DSC measurements of BPA crystals

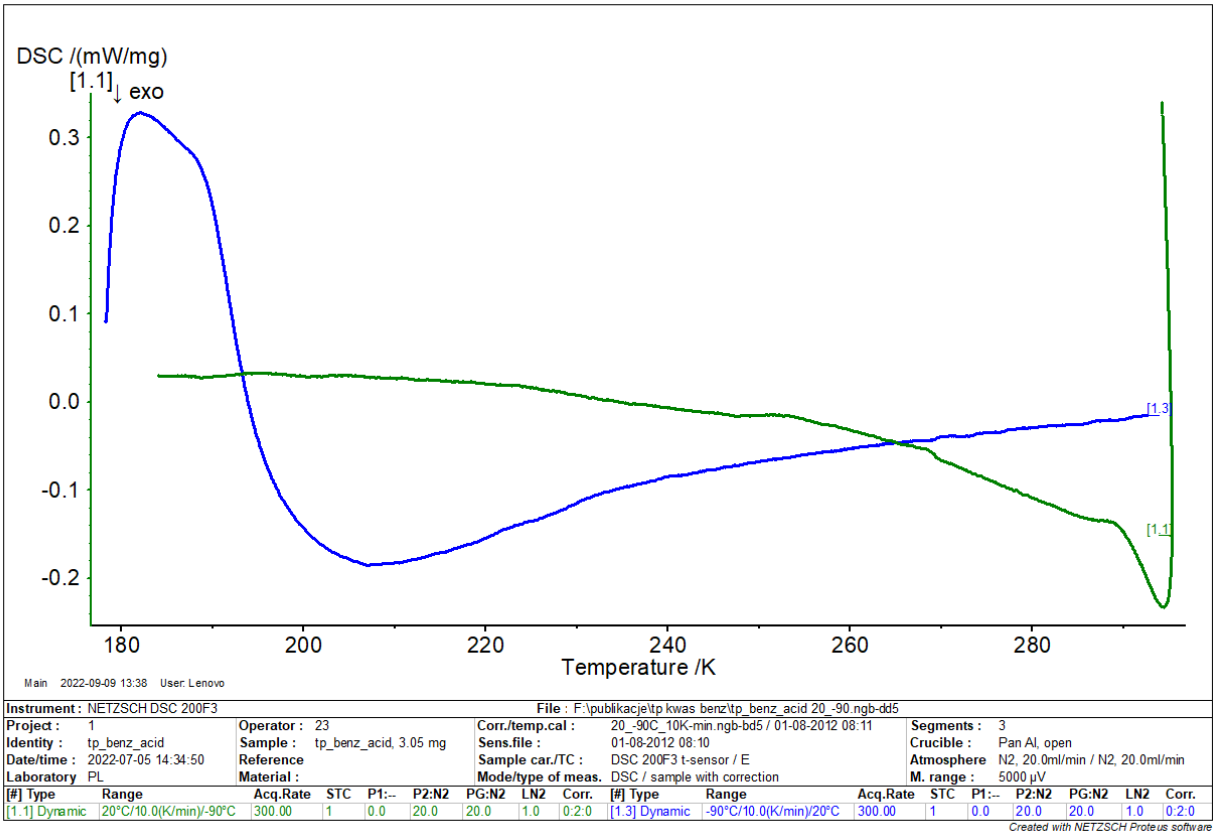

Figure S3. DSC measurement of BPA crystals in 180-295 K range. The lack of the significant thermal events is seen during the heating (blue curve) and cooling (green curve) cycles.

4. Calculation of the potential energy of BPA molecule

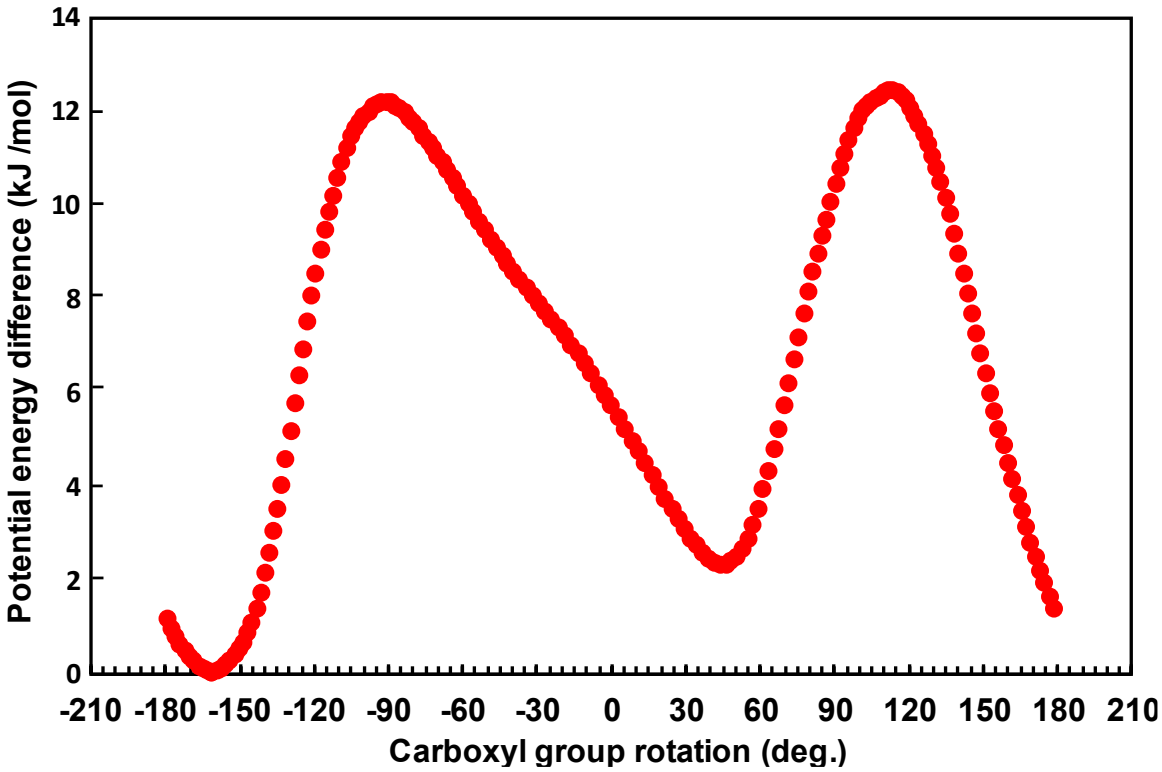

Figure S4. Potential energy of BPA molecule as a function of the rotation of the carboxyl group (see Figure 6).

4. Comparison of the selected crystallographic parameters with the reported structures

Table S1 Crystal data and structure refinement for the reported structures of BPA

Identification code	VERMAG[1]	VERMAG01[2]	This study
Empirical formula	$C_{10}H_{10}O_3$	$C_{10}H_{10}O_3$	$C_{10}H_{10}O_3$
Formula weight	178.18	178.18	178.18
Temperature/K	295	235(1)	290.00(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	15.071(10)	12.728(6)	12.8223(5)
b/Å	5.435(9)	5.200(3)	5.2450(2)
c/Å	16.058(10)	14.426(6)	14.5064(5)
α/°	90	90	90
β/°	129.57(10)	111.33(3)	111.569(4)
γ/°	90	90	90
Volume/Å^3	1013.91	889.391	907.28(6)
Z	4	4	4
ρ_{calc}g/cm^3	1.167	1.331	1.304
μ/mm^{-1}	0.68	0.106	0.801
F(000)	376	376	376
Crystal size/mm^3	0.30 × 0.40 × 0.45	0.175 × 0.175 × 0.075	0.29 × 0.29 × 0.03
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71069)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	N/A	3.00 to 50.00	7.886 to 160.064
Index ranges	N/A	$-11 \le h \le 11$, $0 \le k \le 14$, $0 \le l \le 27$	$-16 \le h \le 14$, $-5 \le k \le 6$, $-16 \le l \le 18$
Reflections collected	828	1559	9404
Independent reflections	637	859	1893 [R_{int} = 0.0275, R_{sigma} = 0.0231]
Data/restraints/parameters	637/0/N/A	859/0/158	1893/0/158
Goodness-of-fit on F^2	N/A	1.05	1.08
Final R indexes [I>=2σ (I)]	R_1 = 0.1, wR_2 = 0.1	R_1 = 0.058, wR_2 = 0.066	R_1 = 0.0433, wR_2 = 0.1203
Final R indexes [all data]	R_1 = 0.1, wR_2 = 0.1	R_1 = 0.058, wR_2 = 0.066	R_1 = 0.0519, wR_2 = 0.1268
Largest diff. peak/hole / e Å^{-3}	0.13/-0.13	0.23/-0.06	0.14/-0.15

5. PXRD data

Table S2 Unit cell parameters for BPA polymorphs and NaCl from temperature PXRD experiments

			BPA $P2_1/c$			**NaCl**	
Temperature (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	a (Å)	V (Å^3)
200	15.368(1)	5.2139(2)	22.408(1)	97.781(2)	1779.0(1)	5.6206(2)	177.56(2)
210	15.381(1)	5.2165(2)	22.419(1)	97.759(2)	1782.5(2)	5.6228(2)	177.77(2)
220	15.3910(9)	5.2193(2)	22.436(1)	97.730(2)	1786.0(1)	5.6247(2)	177.95(2)
230	15.403(1)	5.2219(2)	22.451(1)	97.705(2)	1789.5(2)	5.6268(2)	178.15(2)
			BPA $P2_1/n$			**NaCl**	
	a (Å)	a (Å)	c (Å)	β (°)	V (Å^3)	a (Å)	V (Å^3)
240	12.7448(6)	5.2234(2)	14.447(7)	111.299(3)	895.93(7)	5.6280(2)	178.27(2)
250	12.7606(6)	5.2273(2)	14.4553(6)	111.337(2)	898.13(6)	5.6301(2)	178.47(2)
260	12.7747(5)	5.2307(2)	14.4655(6)	111.391(2)	900.01(6)	5.6322(2)	178.67(2)
270	12.7881(6)	5.2340(2)	14.4754(6)	111.440(3)	901.83(7)	5.6342(2)	178.86(2)
280	12.8018(6)	5.2372(2)	14.4859(7)	111.493(2)	903.67(7)	5.6362(2)	179.04(2)
290	12.8159(5)	5.2447(2)	14.4984(6)	111.599(2)	906.29(6)	5.6389(2)	179.30(2)
300	12.8306(5)	5.2506(2)	14.5098(6)	111.640(2)	908.62(6)	5.6411(2)	179.51(2)
310	12.8478(5)	5.2546(2)	14.5225(6)	111.704(2)	910.90(6)	5.6438(2)	179.77(2)

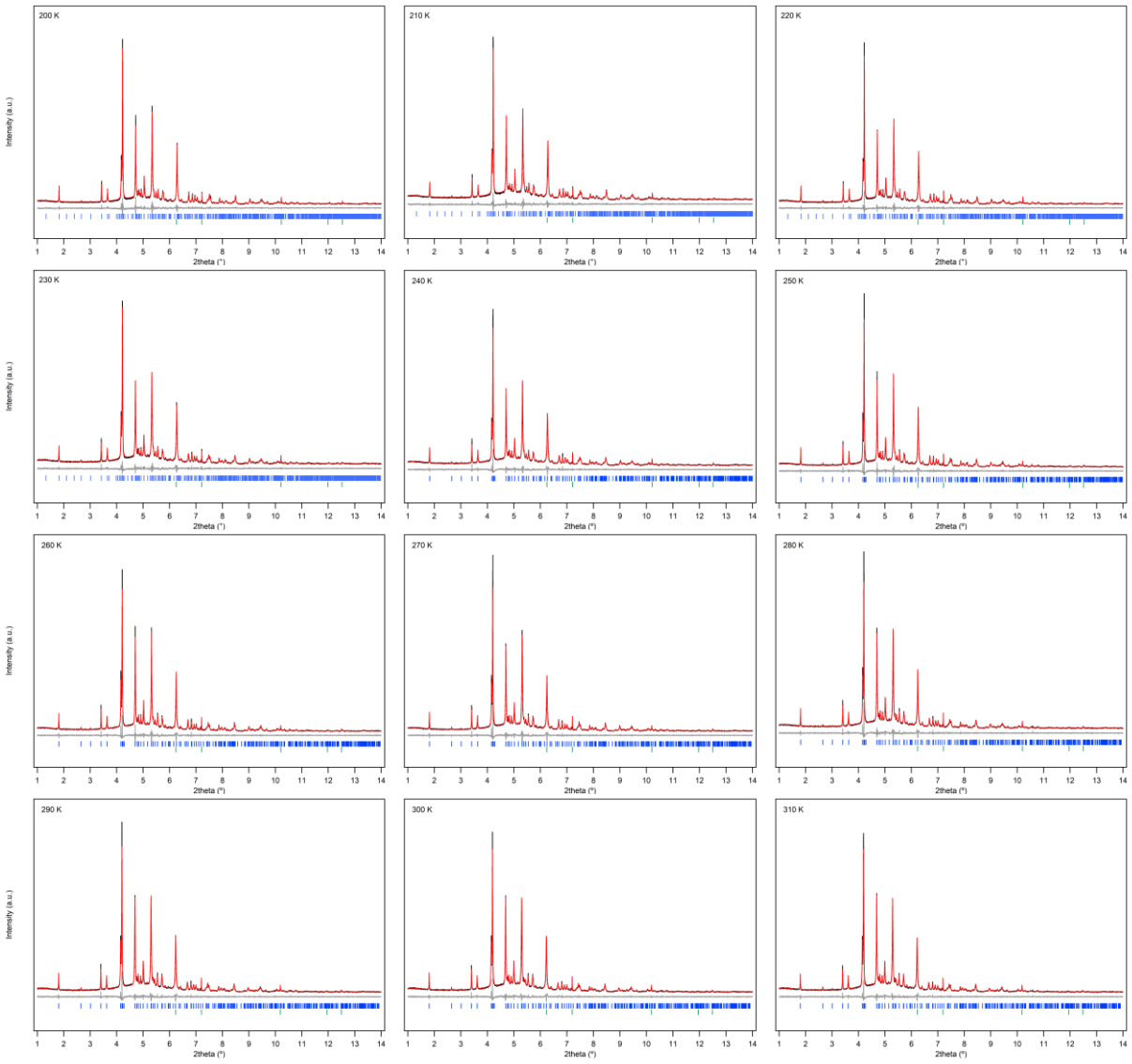

Figure S5. PXRD patterns collected for a mixture of BPA and NaCl. Data was fitted by Pawley refinement: black and red curve represents data and fit, respectively. Blue and green ticks signify the calculated Bragg peak positions for BPA and NaCl, respectively.

6. Lattice parameters from SC XRD

Table S3 Unit cell parameters (in Å) for BPA from single-crystal XRD experiments upon cooling, indexed in both LT and RT unit-cell settings. The values have been rounded up to the last significant figures.

	RT $P2_1/n$ setting					**LT $P2_1/c$ setting**				
T (K)	*a*	*b*	*c*	*β*	Volume	*a*	*b*	*c*	*β (deg.)*	Volume
290	12.8218	5.2386	14.5099	111.553	906.46	15.4328	5.2383	22.6124	97.586	1812.02
280	12.8092	5.2346	14.4945	111.475	904.40	15.4368	5.2371	22.5766	97.596	1809.17
270	12.7932	5.2346	14.4811	111.422	902.76	15.4304	5.2346	22.5559	97.625	1805.77
260	12.7767	5.2308	14.4697	111.356	900.64	15.4303	5.2322	22.514	97.63	1801.56
250	12.7623	5.2283	14.4575	111.291	898.84	15.4287	5.2281	22.4864	97.653	1797.66
245	12.7555	5.2279	14.4532	111.293	898.01	15.4201	5.2278	22.4818	97.661	1796.15
240	12.7467	5.2281	14.449	111.272	897.29	15.419	5.2263	22.4693	97.676	1794.45
235	12.741	5.2262	14.4442	111.275	896.25	15.411	5.2248	22.4605	97.693	1792.23
230	12.7355	5.2252	14.4426	111.271	895.62	15.4045	5.2234	22.4518	97.711	1790.22
220	12.7175	5.222	14.4328	111.23	893.44	15.3922	5.2222	22.4341	97.736	1786.87
210	12.67	5.2184	14.419	110.89	890.68	15.381	5.2199	22.4181	97.775	1783.34
200	12.6944	5.2185	14.4113	111.283	889.58	15.3685	5.2184	22.4015	97.796	1779.97

Table S4 Unit cell parameters (in Å) for BPA from single-crystal XRD experiments upon heating, indexed in standard setting for RT phase. The values have been rounded up to the last significant figures.

Standard $P2_1/c$ setting (RT phase)				
T (K)	*a*	*b*	*c*	*β (deg.)*
240	14.4507	5.2289	15.4102	129.586
250	14.4635	5.2320	15.4141	129.545
260	14.4736	5.2352	15.4181	129.514
270	14.4811	5.2347	15.4284	129.474
280	14.4951	5.2425	15.4265	129.433
290	14.5064	5.2450	15.4301	129.394

References

1 S. Selladurai, M. S. Kumar and K. Subramanian, *Proc. / Indian Acad. Sci.*, 1990, **102**, 39–43.

2 H. W. Thompson, P. A. Vanderhoff and R. A. Lalancette, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 1991, **47**, 1443–1445.