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

Supporting information for

Matrix-Isolation Vibrational Circular Dichroism (VCD) Spectroscopy of Chiral 1-Phenyl-1-Propanol

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Experimental and computational details.

Both enantiomers of **1PP** were directly purchased from TCI solution and have been used without further purification.

All experiments were carried out on a matrix system equipped with a Sumitomo F-70H closed-cycle helium compressor and connected to Sumitomo RDK-408D2 cold head.

IR and VCD spectra were taken with a Bruker Invenio-R FT-IR spectrometer equipped with a PMA 50 module for VCD measurements. The spectral resolution of the spectra was 2 cm^{-1}. For MI-IR and MI-VCD spectra, 50 and 20 000 scans were accumulated.

Geometry optimizations, the calculation of the vibrational spectra, PES and transition states were carried out using the Gaussian 09 Rev. E software package[1] in the gas phase with tight conversion and ultrafine integration grids. Other consideration such as the integral equation formalism of the polarizable continuum model (IEFPCM) for Argon or explicit solvation on the alcohol group with N_2 were compared but did not lead to any changes compared to the gas phase. The calculations were carried out at the B3PW91/6-311++G(2d,p) level of theory. Vibrational line broadening was simulated by assigning a Lorentzian band shape with half-width at half height (HWHH) of 2 cm^{-1} to the calculated dipole and rotational strength. A scale factor of $\sigma = 0.98$ was used for the calculated frequencies. The PES was determined by varying either the α or β angle with a step of 5° while relaxing the other coordinates.

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[1] Gaussian 09, Rev E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Wallingford CT, USA, 2013

Table S1. Monomeric structures of (*S*)-**1PP**: Torsional angles (in degree), relative zero-point corrected electronic energies, Gibbs free energies (ΔE_{ZPC} and ΔG_{298K}, in kcal/mol), the corresponding Boltzmann weights χ (in percentage) and the connecting transition states as obtained at the B3PW91/6-311++G(2d,p) level of theory.

	α (C_{Ar}-C*-O-H)	**β (C_{Ar}-C*-CH_2-CH_3)**	**γ (C_{Ar}-C_{Ar}-C*-CH_2)**	**ΔE_{ZPC}**	**$\chi(E_{ZPC})$**
c1	-55.7	175.1	80.4	0.0[a)]	50.5
c2	-50.9	64.4	72.3	0.35	26.4
c3	-55.8	-62.9	94.7	1.11	6.6
c4	176.5	176.6	93.8	1.27	4.9
c5	170.6	64.2	77.5	1.67	2.3
c6	178.3	-61.2	106.5	1.94	1.4
c7	74.5	172.4	116.5	1.80	1.8
c8	45.5	63.2	51.0	1.85	1.7
c9	74.5	-63.7	122.0	2.4	0.6
c10	42.5	174.0	52.4	1.68	2.3
c11	49.3	173.7	15.0	1.92	1.5
TS(1→7)	27.2	175.0		1.51	
TS(1→4)	-132.8 (=227.2)	175.1		1.57	
TS(2→8)	28.5	63.9		1.67	
TS(4→7)	119.0	173.3		1.93	
TS(7→11)	61.5	177.1		2.21	
TS(5→8)	111.8	62.2		2.28	
TS(3→6)	-127.3 (=232.7)	-63.6		2.37	
TS(2→5)	-130.0 (=230.0)	62.5		2.43	
TS(6→9)	121.3	-62.5		2.58	
TS(3→9)	30.6	-64.6		3.37	
TS(1→2)	-54.0	119.4		3.38	
TS(4→5)	176.5	119.1		5.00	
TS(7→8)	67.3	117.7		5.18	
TS(2→3)	-55.0	-2.0		5.23	
TS(1→3)	-54.3	-121.3 (=238.7)		5.47	
TS(4→6)	178.6	-119.8 (=240.2)		6.55	
TS(5→6)	177.2	-1.1		6.73	
TS(7→9)	70.8	-124.6 (=235.4)		6.81	
TS(8→9)	81.5	-2.1		7.47	

[a)] referenced to E_{ZPC}(**c1**) = -425.182305 hartree.

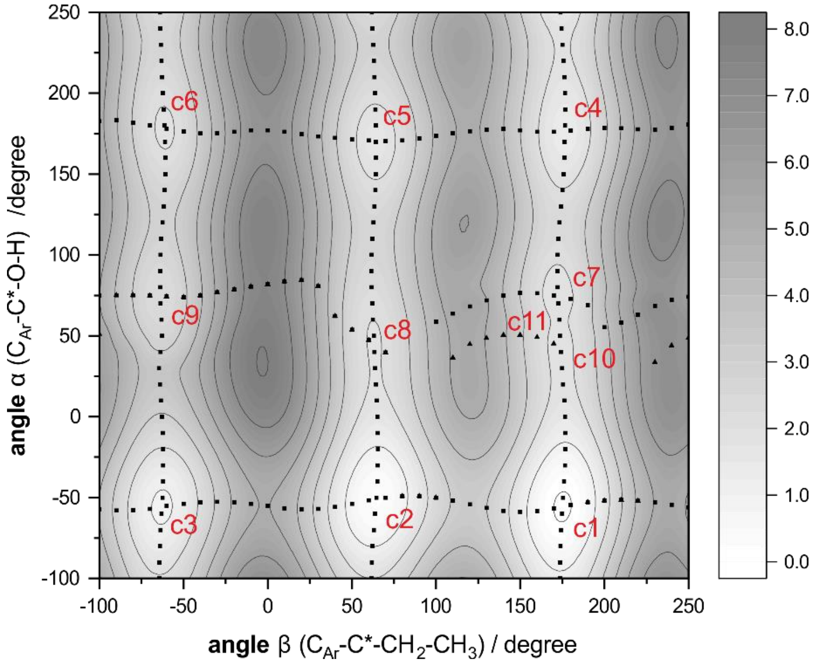

Figure S1. Potential energy surface of (*S*)-1PP obtained by constraint geometry optimization holding the angles α and β fixed. The energy scale refers to relative zero-point corrected energies in kcal/mol. The conformers c10/c11 differ from c7 only in the phenyl ring orientation and a few points on the pathways to c8 and c9 could be computed before the phenyl ring relaxed to the main traces c7→c8 and c7→c9.

Table S2. Conformers of dimeric (*S*)-**1PP**, their relative zero-point corrected electronic energies (ΔE_{ZPC} in kcal/mol) and the corresponding Boltzmann weights χ (in percentage). The bis structures correspond to the second H-bonding interaction in a dimeric pair. Only structures with Boltzmann weights >1% are listed.

	ΔE_{ZPC}	**$\chi(E_{ZPC})$ @ 298 K**	**$\chi(E_{ZPC})$ @ 25 K**
c1c2	0.00[a)]	15.0	76.2
c1c1	0.06	14.4	23.8
c2c2	0.43	7.7	
c2c1	0.51	6.7	
c1c1bis	0.60	5.8	
c2c1bis	0.68	5.1	
c1c2bis	0.69	5.0	
c1c3	0.84	3.9	
c1c4	0.93	3.3	
c3c2	1.13	2.3	
c1c5	1.14	2.3	
c3c1	1.18	2.2	
c2c2bis	1.20	2.1	
c2c3	1.28	1.8	
c1c10	1.34	1.7	
c1c10bis	1.44	1.34	
c2c4	1.49	1.3	
c1c8	1.56	1.1	
c1c6	1.59	1.1	
c1c3bis	1.60	1.1	

[a)] referenced to E_{ZPC}(**c1c2**) = -850.370185 hartree

Table S3. Conformers of trimeric (*S*)-**1PP** build based on monomers c1 and c2, their relative zero-point corrected electronic energies (ΔE_{ZPC} in kcal/mol) and the corresponding Boltzmann weights χ (in percentage).

	ΔE_{ZPC}	$\chi(E_{ZPC})$ @ 35 K
c1c1c2	0.00[a)]	88.5
c1c2c2	0.18	7.1
c1c1c1	0.21	4.2
c2c1c2	0.42	0.2
c2c2c2	0.58	0.0

[a)] referenced to E_{ZPC}(**c1c2**) = -1275.558801 hartree.

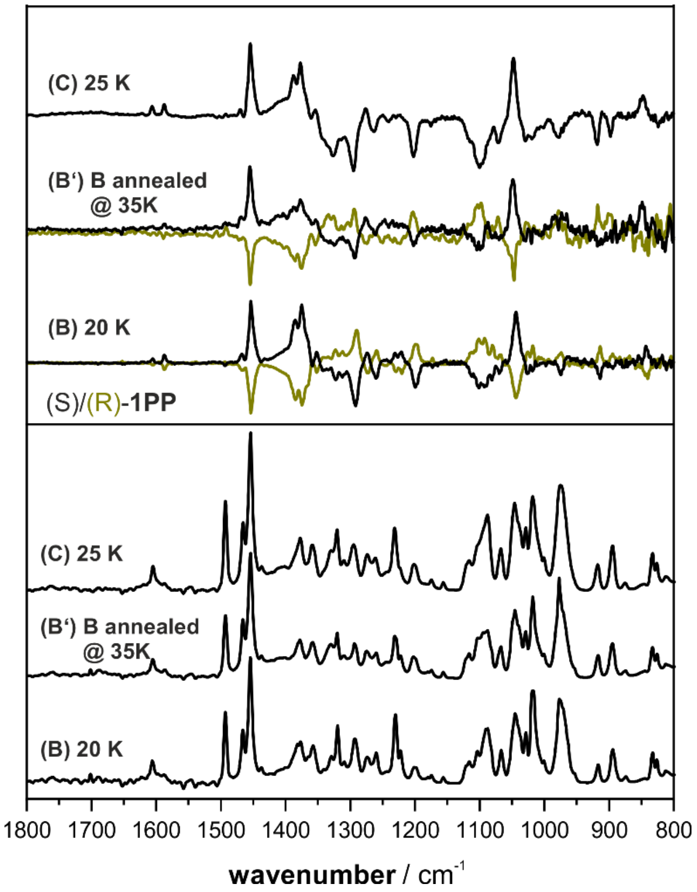

Figure S2. Comparison of the experimental IR and VCD spectra of **1PP**.

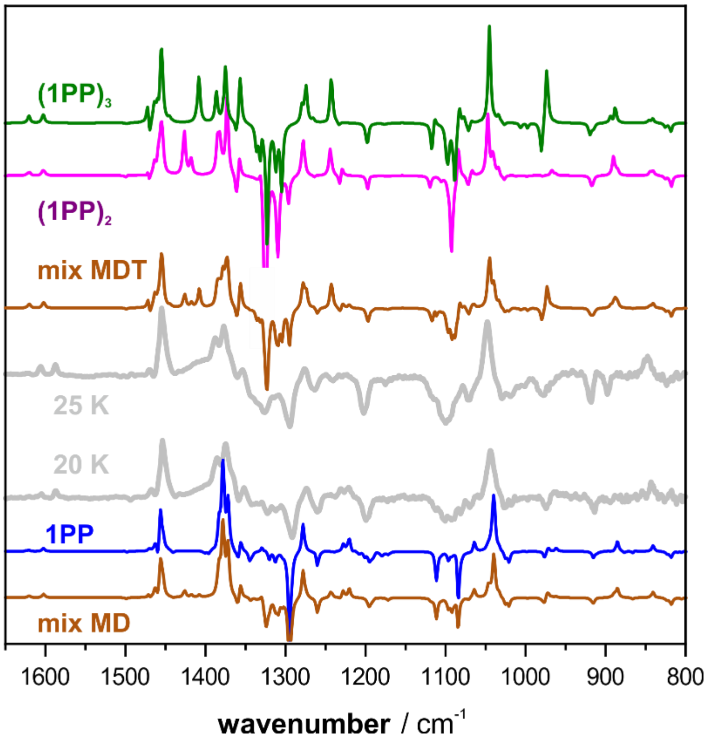

Figure S3. Simulated mixture spectra of **1PP**, **(1PP)$_2$** and **(1PP)$_3$** explaining the experimental VCD spectra recorded at 20 K and 25 K. MixMD = 80:15:5 / mixMDT = 30:30:40 of monomer/dimer/trimer.