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

Supplementary Information

Wavelength Resolved Specific Optical Rotations and Homochiral Equilibria

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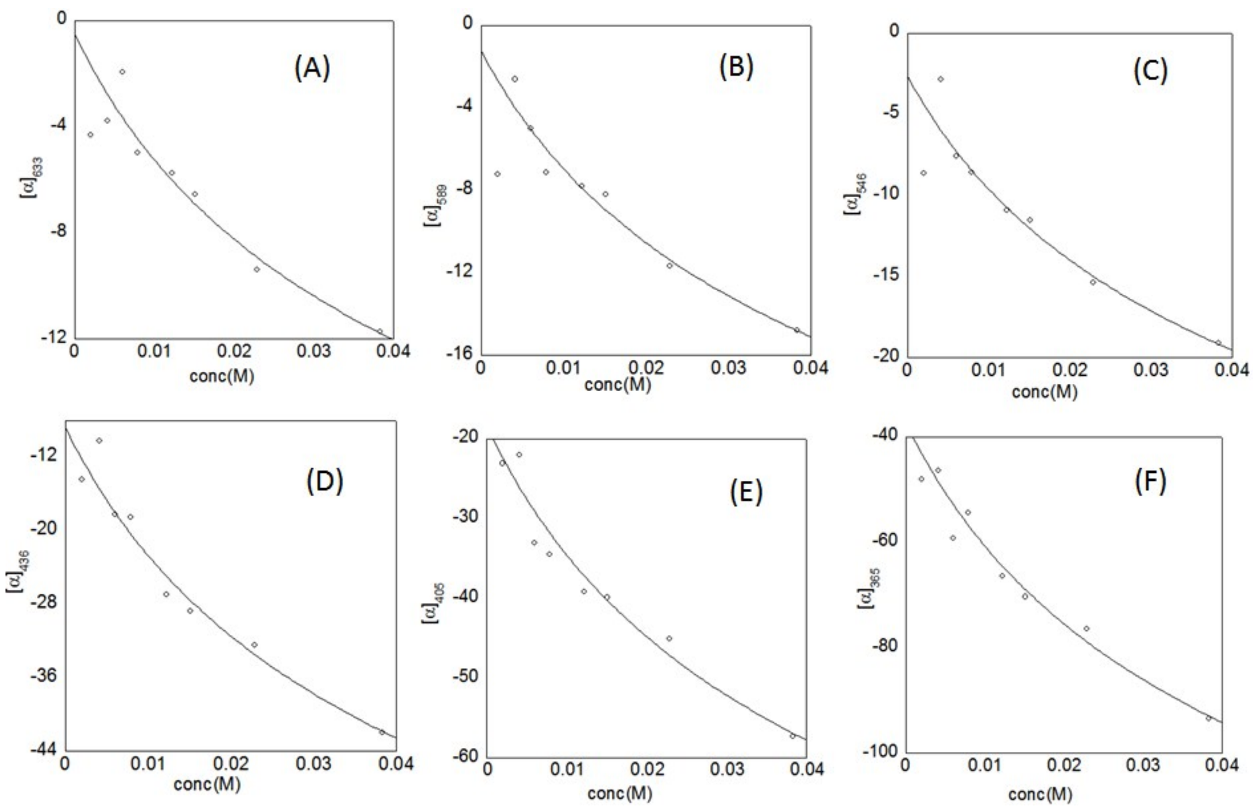

Figure S1.Weighted non-linear least squares (WLNS) fit of experimental [α] to Eq. (15). Open circles are experimental data points and solid line is the WLNS fit. The panels (A)-(F) are wavelength resolved [α] at 633, 589, 546, 436, 405 and 365 nm, respectively. The relative uncertainty is lower at shorter wavelengths and higher concentrations.

Conformational analysis was undertaken with MacroModel program[1] using Mixed Torsional/Low-mode sampling procedure. Two low energy conformations of monomer and four low energy conformations of dimer were identified. These conformations are same as those found previously by Goldsmith et al[2]. The populations of conformations optimized using B3LYP, B3LYP-GD2[3], and M06-2X[4] functionals are summarized in Table S1.

Table S1: Populations of geometry optimized conformers at various levels of theory using 6-311++G(2d,2p) basis set					
	with PCM			Vacuum	
conformer[a]	B3LYP	B3LYP-GD2[b]	M06-2X[c]	B3LYP-GD2	M06-2X
M-1	0.96	0.96	0.98	0.98	0.99
M-2	0.04	0.04	0.02	0.02	0.01
D-1	0.89	0.97	0.98	0.97	0.98
D-2	0.03	0.01	0.00	0.01	0.00
D-3	0.06	NA[d]	NA[d]	NA[d]	NA[d]
D-4	0.02	0.02	0.02	0.02	0.02

[a]M-1 and M-2 are monomer conformers; D1-D4 are dimer conformers; [b]GD2 is Grimm's long range dispersion correction(J. Comp. Chem., 27 (2006) 1787-99); [c]M06-2X is a functional dveloped by Truhlar and coworkers (Theor. Chem. Acc., 120 (2008) 215-41); [d]this conformer converged to one of the other conformers

B3LYP-GD2 and M06-2X level calculations clearly indicate that the dimer form of pantolactone has only one conformer as the predominant one.

The geometries optimized at B3LYP/6-311++G(2d,2p)/PCM level of theory were used for all further calculations. For calculations in CCl_4 solvent, SOR calculations were undertaken at B3LYP/6-311++G(2d,2p) and CAM-B3LYP/aug-cc-pVTZ levels of theory using PCM. For calculations of SOR in $CHCl_3$ solvent, the dominant dimer conformer was used at various levels of theory using PCM. These results are summarized in Tables S2 and S3. The solvent influence is limited, as can be seen when the results obtained in CCl_4 and $CHCl_3$ are compared at CAM-B3LYP/aug-cc-PVTZ level. The calculated SORs at this level of theory are also closest to the experimental values.

Table S2: Comparison of Predicted SORs of monomer and dimer species of (R)-(−)-α-Hydroxy-β,β-dimethyl-γ-butyrolactone in CCl_4 at CAM-B3LYP/aug-cc-pVTZ and B3LYP/6-311++G(2d,2p) levels of theory				
	CAM-B3LYP/aug-cc-pVTZ		B3LYP/6-311++G(2d,2p)	
nm	$[\alpha]_m$	$[\alpha]_d$	$[\alpha]_m$	$[\alpha]_d$
633	-7.7	-109.6	-15.3	-122.1
589	-9.6	-128.4	-18.8	-143.4
546	-12.3	-152.1	-23.5	-170.5
436	-27.7	-257.8	-48.9	-293.9
405	-37.3	-310.2	-64.4	-356.9
365	-58.8	-409.5	-98.3	-479.4

Table S3: SORs predicted for dimeric aggregate of (*R*)-(-)-α-hydroxy-β,β-dimethyl-γ-butyrolactone in $CHCl_3$ at different levels of theory						
Optimization level -->	B3lyp/6-311++G(2d,2p)/PCM				M06-2x/6-311++G(2d,2p)/PCM	
SOR Functional -->	B3LYP	B3LYP	CAM-B3LYP	M06-2X	B3LYP	M06-2X
Basis set -->	aug-cc-pVTZ	6-311++G(2,2p	aug-cc-pVTZ	aug-cc-pVTZ	6-311++G(2,2p)	6-311++G(2,2p)
λ (nm)						
633	-133.2	-130.0	-115.5	-123.8	-126.2	-128.5
589	-156.3	-152.6	-135.2	-145.3	-148.0	-150.7
546	-185.5	-181.3	-160.1	-172.4	-175.5	-178.8
436	-317.7	-311.6	-270.8	-294.6	-299.1	-305.4
405	-384.4	-377.6	-325.5	-355.9	-361.1	-369.0
365	-513.2	-505.6	-428.8	-473.3	-480.2	-490.8

The optimized Cartesian coordinates for the lowest energy conformer at B3LYP/6-311++G(2d,2p) /PCM(CCl_4) level are given for monomer and dimer forms of pantolactone in Tables S4 and S5 respectively.

Table S4: B3LYP/6-311++G(2d,2p) /PCM(CCl_4) optimized structure (x,y,z coordinates) of the Lowest energy conformer of monomer (SCF Energy= -460.4975 Hartrees):

C	-0.495112	-1.531711	-0.199223
C	-0.985153	-0.084041	0.015752
C	0.248715	0.658729	-0.534736
H	-0.911943	-2.242761	0.508214
H	-0.673492	-1.881833	-1.215911
H	0.211545	0.630994	-1.633256
C	1.396925	-0.248016	-0.118397
O	2.535436	0.085184	0.079782
O	0.415363	1.981126	-0.088000
H	1.361869	2.127738	0.040053
O	0.947794	-1.507893	0.018053
C	-1.181350	0.201546	1.511392
H	-1.407902	1.252978	1.673700
H	-2.008851	-0.394362	1.897312
H	-0.291559	-0.040406	2.093755
C	-2.265258	0.207822	-0.767231
H	-2.564097	1.247515	-0.634996
H	-2.130311	0.026970	-1.834457
H	-3.086601	-0.420150	-0.418443

Table S5: B3LYP/6-311++G(2d,2p)/PCM(CCl_4) optimized structure (x,y,z coordinates) of the Lowest energy conformer of dimer (SCF Energy= -921.0093 Hartrees):

C	4.16756	0.767626	-0.862621
C	3.76002	-0.35561	0.106942
C	2.23635	-0.353942	-0.135843
H	5.05712	1.31169	-0.558064
H	4.29173	0.409411	-1.88464
H	2.0336	-0.875145	-1.08216
C	1.94952	1.12441	-0.411112
O	0.90815	1.72394	-0.281592
O	1.49142	-0.899341	0.909617
H	0.614965	-1.15971	0.571828
O	3.06271	1.72254	-0.859843
C	4.08068	0.041229	1.55605
H	3.6762	-0.691927	2.25012
H	5.161	0.09265	1.69536
H	3.65955	1.01303	1.81631
C	4.41583	-1.69002	-0.245941
H	4.0522	-2.47509	0.416512
H	4.19674	-1.98495	-1.27312
H	5.49962	-1.63378	-0.132546
C	-4.16749	-0.767299	-0.863234
C	-3.76002	0.355592	0.106759
C	-2.23632	0.353971	-0.135873
H	-5.05709	-1.31145	-0.558955
H	-4.29155	-0.408726	-1.88514
H	-2.03347	0.875501	-1.08199
C	-1.9495	-1.12429	-0.41163
O	-0.908155	-1.72389	-0.282224
O	-1.49148	0.898989	0.90985
H	-0.615004	1.15948	0.572225
O	-3.06266	-1.72224	-0.860676
C	-4.08084	-0.041743	1.5557
H	-3.67642	0.691167	2.25007
H	-5.16118	-0.093195	1.69487
H	-3.65975	-1.01364	1.81567
C	-4.41576	1.69015	-0.245726
H	-4.05216	2.47497	0.417032
H	-4.19656	1.98541	-1.27278
H	-5.49956	1.6339	-0.132453

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References

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