Electronic Supplementary Information

for

When two symmetrically independent molecules must be different: "Crystallization-induced diastereomerization" of chiral β-hydroxy sulfone on the basis of natural (−)-β-pinene

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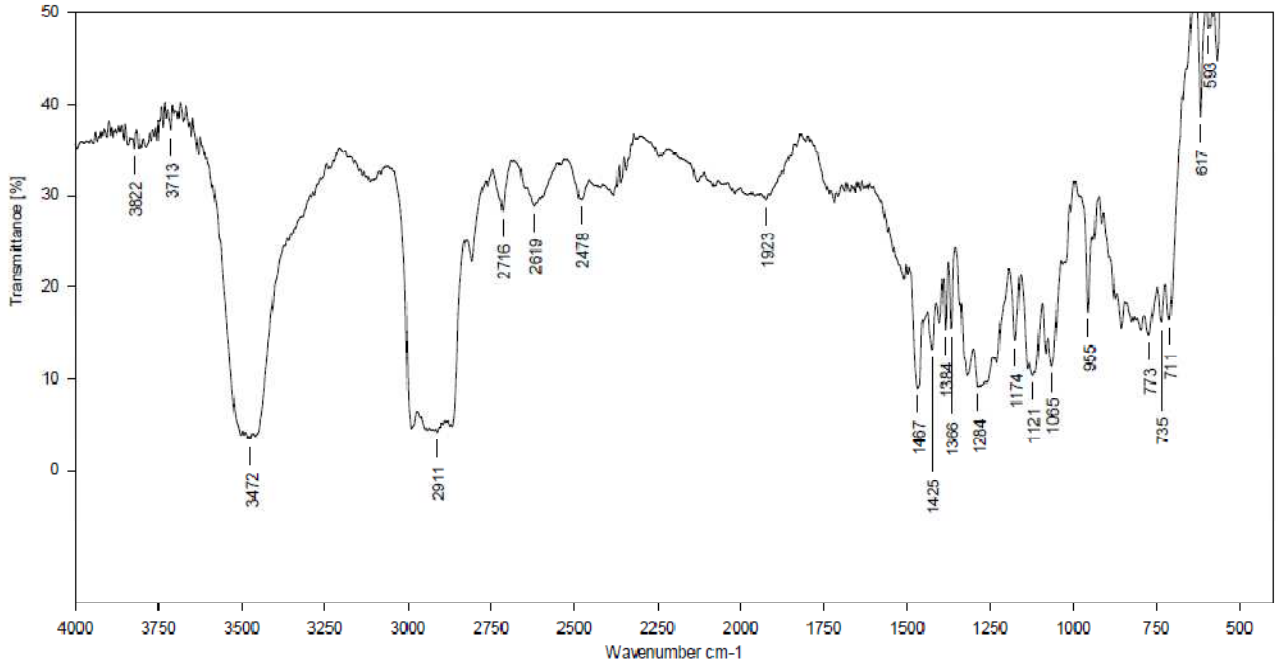

Fig. S1 IR crystalline phase spectrum of sulfone **3**.

Table S1 Selected geometrical parameters of molecules **2a**, **2b** and **3** in crystals by X-ray data

	Sulfoxides **2a**+**2b**				Sulfone **3**	
	Monoclinic modification		Triclinic modification			
Parameter	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B
Bond length	***d***, Å					
S^1-O^2	1.516(4)	1.516(4)	1.507(3)	1.505(3)	1.431(3)	1.409(4)
S^1-O^3	-	-	-	-	1.447(3)	1.454(3)
S^1-C^{10}	1.789(8)	1.807(8)	1.801(5)	1.801(5)	1.773(5)	1.744(6)
S^1-C^{11}	1.792(9)	1.767(9)	1.779(4)	1.800(4)	1.773(6)	1.779(5)
O^1-C^{12}	1.41(1)	1.40(1)	1.394(7)	1.424(7)	1.448(7)	1.379(7)
C^2-C^{10}	1.51(1)	1.52(1)	1.504(7)	1.531(6)	1.535(6)	1.591(9)
C^{11}-C^{12}	1.52(1)	1.48(1)	1.515(7)	1.491(7)	1.477(8)	1.518(7)
Valence angle	***ω***, °					
O^2-S^1-C^{10}	104.3(3)	105.6(3)	105.0(2)	105.7(2)	109.0(2)	109.2(3)
O^2-S^1-C^{11}	105.1(3)	105.6(3)	106.0(2)	106.3(2)	109.0(2)	107.7(2)
C^{10}-S^1-C^{11}	98.7(4)	97.7(4)	98.5(2)	97.7(2)	104.6(2)	105.8(3)
C^1-C^2-C^{10}	114.1(8)	112.1(7)	114.7(4)	111.2(4)	110.4(4)	109.1(6)
C^3-C^2-C^{10}	113.8(9)	114.2(7)	112.3(4)	113.1(4)	115.1(4)	111.0(6)
S^1-C^{10}-C^2	111.7(6)	111.6(5)	111.1(3)	111.1(3)	114.2(3)	110.3(4)
S^1-C^{11}-C^{12}	110.6(5)	112.4(6)	110.3(3)	110.1(3)	116.0(4)	114.5(3)
O^1-C^{12}-C^{11}	108.6(7)	110.7(7)	109.6(4)	110.4(4)	109.5(4)	109.8(4)
Torsion angle	***τ***, °					
$O^2S^1C^{10}C^2$	63.5(6)	-56.4(6)	61.4(3)	-55.0(3)	-46.9(4)	-72.4(5)
$C^{11}S^1C^{10}C^2$	171.5(6)	-165.0(5)	170.6(3)	-164.3(3)	-163.3(3)	171.9(4)
$O^2S^1C^{11}C^{12}$	-59.2(6)	64.9(6)	-58.5(4)	63.8(4)	-32.2(4)	162.2(4)
$C^{10}S^1C^{11}C^{12}$	-166.7(5)	173.4(5)	-166.9(3)	172.7(3)	84.2(4)	-81.1(4)
$C^3C^2C^{10}S^1$	-161.1(6)	-47.6(8)	-163.0(4)	-49.0(4)	-60.5(5)	-127.0(5)
$C^{10}C^2C^3C^4$	-141.2(9)	-143.4(7)	-141.4(5)	-144.0(4)	-138.4(5)	-131.6(7)
$C^1C^2C^{10}S^1$	70.1(9)	-177.1(5)	68.5(5)	-175.4(3)	170.8(3)	109.1(6)
$C^3C^4C^5C^6$	44(1)	42.8(9)	43.8(7)	41.3(6)	45.8(8)	53.2(9)
$C^4C^5C^6C^9$	40(1)	41(1)	42.0(7)	40.9(6)	39.5(8)	38.8(10)
$S^1C^{11}C^{12}O^1$	-59.7(7)	58.2(7)	-60.4(4)	58.9(5)	-66.6(5)	65.6(5)

Table S2 C-H…O interactions in various types associates according to DFT calculations

	Interaction	Type of associates	Distance H…A, Å	Distance D…A, Å	Angle ∠D-H…A, °
1	C^{3A}-H^{3A}...O^{3A}	**cyclic dimer**	2.69	3.29	114
		mon1	2.72	3.29	112
		mon1_Hbond	2.68	3.24	111
2	C^{10A}-H^{10C}...O^{1A}	**cyclic dimer**	2.31	3.19	135
		mon1	2.36	3.22	134
3	C^{10B}-H^{10B}...O^{1B}	**cyclic dimer**	2.32	3.19	135
		mon2	2.36	3.22	135
		mon2_Hbond	2.58	3.35	127
4	C^{1B}-H^{1D}...O^{2B}	**cyclic dimer**	2.56	3.35	129
		mon2	2.57	3.35	127
		mon2_Hbond	2.55	3.33	127

Table S3 Experimental frequencies (ν(OH), cm^{-1}), FHWM ($\nu_{1/2}$, cm^{-1}), intensities (I) of the ν(OH) IR bands of monomeric and dimeric forms of sulfone **3** and B3LYP/6-31G (d,p) calculated ν(OH) frequencies

Types of molecule forms / associates	Experimental data ν, cm^{-1} / $\nu_{1/2}$ / I			Computed frequency, cm^{-1}
	Crystal	Solution in CCl_4		
		10^{-2} mol/L	10^{-3} mol/L	
Cyclic dimer	3472	3496 / 152 / 103.6	3487 / 91 / 3.2	3506, 3515
Linear dimer (intermolecular hydrogen bond)	-	3550 / 60 / 47.3	3552 / 62 / 11.9	3561
Monomers with intramolecular hydrogen bonds: **mon1_Hbond**, **mon2_Hbond**	-	-	-	3586, 3614
Monomers without intramolecular hydrogen bonds: **mon1**, **mon2** (free OH vibration)	-	3631 / 14 / 15.6	3631 / 16 / 3.43	3689