Electronic supplementary information for:

Accessing Centnerszwer's Quasiracemate – Molecular Shape Controlled Molecular Recognition

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Supporting Information

S1. Crystal growth attempts of Centnerszwer's Quasiracemate (+)-1/(-)-2

Crystal growth attempts of Centnerszwer's Quasiracemate (+)-**1**/(-)-**2** were conducted using the slow evaporation method at room temperature and -5°C using a variety of single solvent (acetone, 2-butanone, dichloromethane, ethanol, methanol, and THF) and mixed solvent systems (1:1 dichloromethane:hexanes). Crystal growth experiments also explored the use of the vapor diffusion method (dichloromethane/pentane). In each case, materials retrieved from these studies consisted of either the starting homochiral Cl- or Br-succinic acids or amorphous conglomerate solids as determined by melting point or X-ray diffraction data.

This study also investigated the crystal growth behavior of components (+)-**1** and (-)-**2** from the melt. Samples of (+)-**1** and (-)-**2** were deposited under a cover slip on a glass slide to give an interface of contact between the two components. Heating the sample using an Instec HCS302 hot stage, a single eutectic point could be observed indicating the lack of a quasiracemic phase of (+)-**1**/(-)-**2**. These results were complicated by the possible decomposition of component (-)-**2**.

S2. X-ray Crystallography

Table S2. Crystallographic data for 2-chloro and 2-bromosuccinic acid structures.

	(-)-**1**	(+)-**2**	(+)-**1**·Im	(-)-**2**·Im
Crystal data				
CCDC deposit no.	1470675	1470676	1470679	1470678
Empirical formula	$C_4H_5ClO_4$	$C_4H_5BrO_4$	$C_{17}H_9ClN_2O_4$	$C_{17}H_9BrN_2O_4$
Crystal System, space group	Orthorhombic $P2_12_12_1$	Orthorhombic $P2_12_12_1$	triclinic $P1$	Monoclinic $P2_1$
M_r	152.5	196.99	220.61	265.07.41
a, Å	7.5593(3)	7.5647(5)	5.0265(3)	7.2825(2)
b, Å	8.5020(3)	8.6337(7)	6.1840(3)	8.8079(3)
c, Å	9.0604(4)	9.2380(7)	8.1859(4)	8.0544(2)
α, deg	90	90	93.095(3)	90
β, deg	90	90	102.264(3)	108.936(2)
γ, deg	90	90	106.883(3)	90
V, (Å^3)	582.30(4)	603.35(8)	236.10(2)	488.68(3)
Z, Z'	4, 1	4, 1	1, 1	2, 1
D_{calc} (g cm^{-3})	1.740	2.169	1.552	1.801
μ (mm^{-1}), rad. type	5.371, Cu $K\alpha$	8.870, Cu $K\alpha$	3.574, Cu $K\alpha$	5.729, Cu $K\alpha$
F_{000}	312	384	114	264
temp (K)	100(2)	100(2)	100(2)	100(2)
Crystal form, color	plate, colorless	plate, colorless	plate, colorless	plate, colorless
Crystal size, mm	0.10 x 0.24 x 0.26	0.03 x 0.08 x 0.09	0.31 x 0.29 x 0.08	0.03 x 0.10 x 0.13
Data collection				
Diffractometer	Bruker Apex II	Bruker Apex II	Bruker Apex II	Bruker Apex II
T_{min}/ T_{max}	0.487/0.753	0.475/0.753	0.609/0.753	0.609/0.753
No. of refls. (meas., uniq., and obs.)	8317/1068/1060	4637/1060/1010	5075/1486/1465	10932/1761/1740
R_{int}	0.0380	0.0401	0.0276	0.0305
θ_{max} (°)	68.22	68.24	68.04	68.17
Refinement				
$R/R^2\omega$ (obs data)	0.0400/0.1028	0.0264/0.0562	0.0234/0.0575	0.0184/0.0473
$R/R^2\omega$ (all data)	0.0401/0.1029	0.0284/0.0568	0.0238/0.0577	0.0187/0.0473
S	1.12	1.06	0.97	0.97
No. of refls.	5223	1060	1486	1740
No. of parameters	88	88	134	136
$\Delta\rho_{max/min}$ (e·Å^{-3})	0.613/-0.242	0.607/-0.350	0.233/-0.158	0.303/-0.210
Flack-x	0.08(4)	0.02(2)	0.052(19)	0.019(9)

Table S2. Crystallographic data for 2-chloro and 2-bromosuccinic acid structures. (continued)

	(±)-**1**·Im[1]	(±)-**2**·Im	(+)-**1**/(-)-**2**·Im	(+)-**1**/(-)-**2**·BPDO
Crystal data				
CCDC deposit no.	1211267	1470677	1470680	1470681
Empirical formula	$C_7H_9ClN_2O_4$	$C_7H_9BrN_2O_4$	$C_{14}H_{18}BrClN_4O_8$	$C_{29}H_{36}N_2O_{12}S_3$
Crystal System, space group	triclinic $P\bar{1}$	triclinic $P\bar{1}$	triclinic $P1$	triclinic $P1$
M_r	220.61	265.07	485.68	725.89
a, Å	8.084(3)	8.0994(4)	8.1185(8)	7.7692(3)
b, Å	8.253(5)	8.3605(4)	8.2996(8)	10.7311(4)
c, Å	8.990(5)	8.8967(7)	8.8998(9)	14.5005(13)
α, deg	101.10(5)	101.264(3)	100.911(5)	102.275(3)
β, deg	107.72(4)	102.378(3)	106.931(5)	93.038(2)
γ, deg	117.47(4)	106.468(3)	117.952(4)	107.620(3)
V, (Å^3)	465.93	467.59(5)	467.58(8)	746.66(6)
Z, Z'	1, 1	2, 1	1, 1	1, 1
D_{calc} (g cm^{-3})	1.572	1.883	1.725	1.614
μ (mm^{-1}), rad. type		5.987, Cu $K\alpha$	4.798, Cu $K\alpha$	3.337, Cu $K\alpha$
F_{000}		264	246	370
temp (K)	297(2)	100(2)	100(2)	100(2)
Crystal form, color		prism, colorless	prism, colorless	plate, colorless
Crystal size, mm		0.07 x 0.08 x 0.21	0.09 x 0.11 x 0.19	0.04 x 0.09 x 0.16
Data collection				
Diffractometer		Bruker Apex II	Bruker Apex II	Bruker Apex II
T_{min}/ T_{max}		0.553/0.911	0.661/0.753	0.626/0.753
No. of refls. (meas., uniq., and obs.)		10122/1670/1605	10562/2949/2936	24878/2680/2263
R_{int}		0.0420	0.0240	0.0456
θ_{max} (°)		68.23	68.23	68.22
Refinement				
R/R^2_ω (obs data)		0.0425/0.1140	0.0331/0.0831	0.0345/0.0794
R/R^2_ω (all data)		0.0436/0.1158	0.0333/0.0832	0.0361/0.0803
S		1.10	0.98	1.06
No. of refls.		1670	2949	2680
No. of parameters		136	272	458
$\Delta\rho_{max/min}$ (e·Å^{-3})		1.786/-0.752	0.387/-0.298	0.310/-0.277
Flack-x		-	0.03(3)	0.018(18)

1. J. C. MacDonald, P. C. Dorrestein and M. M. Pilley, *Cryst.Growth Des.*, **2001**, 1, 29.

S3. Hydrogen-Bond Tables

Table S3. Hydrogen bond parameters for 2-chloro and 2-bromosuccinic acid structures.

compound	*D*–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
(-)-**1**	O1–H···O4^{i}	0.84(3)	1.81(3)	2.649(4)	173(6)
	O3–H···O2^{ii}	0.85(3)	1.82(3)	2.663(4)	174(6)
(+)-**2**	O1–H···O4^{ii}	0.84(3)	1.80(3)	2.647(4)	175(5)
	O3–H···O2^{i}	0.85(3)	1.81(3)	2.653(4)	172(5)
(+)-**1**·Im	N1–H···O1^{iii}	0.83(2)	1.92(2)	2.735(3)	166(4)
	O3–H···O2^{iv}	0.83(2)	1.77(2)	2.595(2)	176(4)
	N2–H···O2^{v}	0.88(2)	1.87(2)	2.752(3)	177(4)
(-)-**2**·Im	N1–H···O1^{iii}	0.83(3)	1.89(3)	2.670(4)	155(4)
	O3–H···O2^{iv}	0.82(3)	1.77(3)	2.591(4)	175(5)
	N2–H···O2^{vi}	0.84(3)	1.91(3)	2.743(4)	169(5)
(±)-**2**·Im	N1–H···O1^{iii}	0.84(3)	1.91(2)	2.719(4)	162(5)
	O3–H···O2^{ii}	0.85(3)	1.69(2)	2.538(3)	174(5)
	N2–H···O2^{vii}	0.85(3)	1.90(2)	2.734(4)	171(5)
(+)-**1**/(-)-**2**·Im	N1–H···O1^{iii}	0.85(3)	1.88(3)	2.728(7)	175(9)
	O4–H···O1^{iv}	0.84(3)	1.73(2)	2.568(7)	171(8)
	N2–H···O2^{viii}	0.83(3)	1.97(4)	2.741(7)	154(6)
	N3–H···O5^{iii}	0.82(3)	1.94(3)	2.744(7)	165(8)
	O8–H···O5^{i}	0.84(3)	1.70(3)	2.535(7)	170(8)
	N4–H···O6^{vii}	0.83(3)	1.88(3)	2.715(7)	177(7)
(+)-**1**/(-)-**2**·BPDO	O1–H···O9^{iii}	0.86(3)	1.73(3)	2.561(7)	160(6)
	O3–H···O10^{ix}	0.85(3)	1.75(3)	2.574(7)	163(7)
	O5–H···O11^{iii}	0.86(3)	1.72(3)	2.561(7)	166(6)
	O7–H···O12^{x}	0.86(3)	1.71(3)	2.562(7)	175(7)

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*, *y*, *z*; (iv) *x*, *y*, *z*+1; (v) *x*+1, *x*-1, *z*; (vi) *x*, *y*+1, *z*; (vii) *x*-1, *y*-1, *z*-1; (viii) *x*+1, *y*+1, *z*+1; (ix) *x*+1, *y*+2, *z*+1; (x) *x*-1, *y*-2, *z*-1.