Quininium mandelates – Systematic study of chiral discrimination in crystals of diastereomeric salts

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Supporting Information

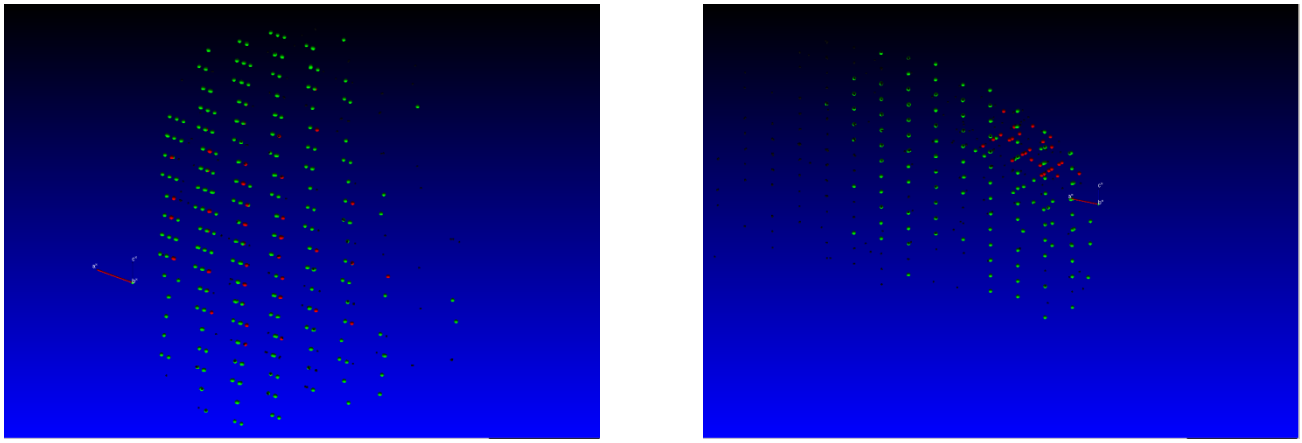
Experimental details, crystallographic information (Table 1S),

hydrogen bond metrics (Table 2S) and torsion angles (Table 3S) of compounds **1-5**.

Experimental details of data collection and refinement:

Intensity data were collected on a Bruker DUO APEX II diffractometer[1] with graphite-monochromated Mo-Kα_1 radiation (λ = 0.71073 Å) at 173 K using an Oxford Cryostream 700. Data reduction and cell refinement were performed using *DENZO*[2] or *SAINT-Plus.*[3] The space groups were determined from systematic absences by *XPREP*[4] and further justified by the refinement results. The structures were solved using *SHELXS-97*[5] and refined using full-matrix least squares methods in *SHELXL-97*[5] with the aid of the program *X-Seed*.[6] The hydrogen atoms bound to carbon atoms were placed at idealized positions and refined as riding atoms with U_{iso} (H) = 1.2 U_{eq} (Ar-H, CH_2) or 1.5 U_{eq}(CH_3). The refinement of the hydroxyl hydrogen and hydrogens of the nitrogen atoms was carried out by first locating them on a difference electron density map and subsequently imposing an appropriate bond length constraint. Diagrams and publication material were generated using *PLATON*[7] and *X-Seed.*

Several crystallisation yielded crystals which judging from their diffraction (Figure 1S a) were inter-grown. Attempts were made with the twin indexing program CELL_NOW[8] to index individual domains. This program assigned 50% of the reflections (maximum deviation from integer values set to 0.1) to the main domain and 28% to the second domain (rotated less than 179.6° around the *b*-axis). Twin integration was not successful and instead the data were treated in a default manner, i.e. indexing and data reduction as if the data were from a single crystal. However R-factors for several data collections treated in this manner could not be optimized to below 14 %. Diffraction from a smaller crystal afforded by a subsequent crystallisation yielded a 'cleaner' diffraction pattern (Figure 1S b). Even though there seems evidence of a second domain (CELL_NOW indicated the first domain to consist of 80% of the reflections to a maximum integer deviation of 0.1) rotated 141° about the real axis (0 -0.33 1), treating the data as a twin yielded higher R-factors than treating it as a single crystal.



(a) (b)

Figure 1S Reciprocal lattice view down the b* axis in structure 5. The green reflections indicate the main domain.

[1] Bruker 2005. APEX2. Version 1.0-27. Bruker AXS Inc., Madison,Wisconsin, USA
[2] Otwinowski, Z. and Minor W. in International Tables for Crystallography, Vol. F, ed. Rossman M. G. and Arnold, E. Kluwer, Dordrecht, 2000.
[3] Bruker 2004. SAINT-Plus (including XPREP). Version 7.12. Bruker AXS Inc., Madison, Wisconsin, USA.
[4] Bruker 2003, XPREP2. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA
[5] Sheldrick, G. M. SHELXS-97 and SHELXL-97 Programs for crystal structure determination and refinement. University of Göttingen, 1997.
[6] Barbour, L. J. J. Supramol. Chem., 2001, 1, 189-191.
[7] Spek, A. L. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2008.
[8] Sheldrick, G. M. CELL_NOW Version 2008-2, Index Twins and Other Problem Crystals, University of Göttingen, 2008.

Table 1S Crystallographic data for structures 1-5.

	1	**2**	**3**	**4**	**5**
CCDC No.					
Chemical formula	$C_{28}H_{32}N_2O_5$	$C_{28}H_{32}N_2O_5$	$C_{28}H_{32}N_2O_5$	$C_{28}H_{32}N_2O_5$	$C_{28}H_{32}N_2O_5$
Formula weight	476.56	476.56	476.56	476.56	476.56
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_12_12_1$ (No.19)	$P2_1$ (No.4)	$P2_1$ (No.4)	$P2_1$ (No.4)	$P2_1$ (No.4)
a/Å	6.5538(19)	10.4121(14)	10.381(3)	10.4377(14)	10.415(2)
b/Å	12.554(3)	18.574(3)	18.456(5)	18.501(2)	18.416(4)
c/Å	31.974(9)	19.070(3)	19.036(5)	19.116(2)	18.845(4)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	90.00	102.635(3)	102.557(5)	102.318(2)	101.431(7)
γ/°	90.00	90.00	90.00	90.00	90.00
V/Å^3	2630.7(13)	3598.6(8)	3559.7(18)	3606.5(8)	3542.8(14)
Z'/*Z*	1/4	3/6	3/6	3/6	3/6
D_{calc}/Mg m^{-3}	1.203	1.319	1.334	1.317	1.340
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
Crystal size /mm	0.45 x 0.45 x 0.40	0.10 x 0.10 x 0.10	0.35 x 0.21 x 0.17	0.10 x 0.10 x 0.10	0.38 x 0.26 x 0.13
Colour, crystal form	colourless, chunk	colourless, chunk	colourless, chunk	colourless, chunk	colourless, plate
No. of total reflections	9097	19770	42152	47197	28583
No. of unique reflections	2853	7610	12252	6629	9161
$\Theta_{min-max}$/°	2.06 / 25.70	2.00 / 26.43	2.01 / 26.58	2.00 / 25.10	1.56 / 28.51
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$ *S*	0.0493/ 0.1261 1.124	0.0468/ 0.1304 1.027	0.0519/ 0.1240 1.035	0.0329/ 0.0815 1.118	0.0528/ 0.1394 1.040
no. of parameters	324	988	1049	1038	970
max. and av. shift /esd	0.000 / 0.000	1.466 / 0.002	1.118 / 0.001	0.000 /0.000	0.000 /0.000
res. peak max./min. (e/Å^3)	0.871 / -0.213	0.909 / -0.383	0.512 / -0.291	0.282 / -0.173	0.364 / -0.270

Table 2S Hydrogen bond parameters in structures 1-5.

D-H...A	*D-H/Å*	*H...A/Å*	*D...A/Å*	*D-H...A/°*	*configuration of the anion*
1					
N11-H11...O33	1.04	1.64	2.632(4)	157.6	S
2					
N11A-H11A...O31A	0.91(5)	1.76(5)	2.634(4)	158(4)	R
N11B-H11B...O31B	0.83(4)	1.81(4)	2.626(4)	170(4)	R
N11C-H11C...O31C	0.81(5)	1.86(5)	2.610(4)	155(4)	S
3					
N11A-H11A...O31A	0.87(3)	1.83(3)	2.617(3)	151(3)	R
N11B-H11B...O31B	0.75(3)	1.89(3)	2.626(3)	168(3)	R
N11C-H11C...O31C	0.86(4)	1.82(4)	2.609(6)	152(3)	S
N11D-H11D...O31D	0.86(4)	1.82(5)	2.56(3)	142(3)	R
4					
N11A-H11A...O31A	0.85(3)	1.84(3)	2.631(3)	154(2)	R
N11B-H11B...O31B	0.84(3)	1.81(3)	2.632(3)	166(3)	R
N11C-H11C...O31C	0.87(4)	1.83(3)	2.616(5)	150(3)	S
N11D-H11D...O31D	0.87(4)	1.84(4)	2.60(2)	145(3)	R
5					
N11A-H11A...O31A	0.83(4)	1.92(4)	2.712(3)	160(4)	R
N11B-H11B...O31B	0.81(3)	1.83(3)	2.576(3)	153(3)	R
N11C-H11C...O31C	0.92(4)	2.00(4)	2.791(3)	143(3)	R

Table 3S Torsion angles in structures 1-5.

		1	**2**	**3**	**4**	**5**
τ_1	*pair A*	-4.1(5)	-8.4(5)	-7.4(4)	-7.1(4)	-6.5(4)
	pair B	-	-5.9(5)	-6.2(4)	-7.0(4)	-9.4(4)
	pair C	-	-2.2(5)	-2.1(4)	-3.3(4)	-7.6(4)
τ_2	*pair A*	-23.6(4)	-17.1(4)	-16.8(3)	-16.5(3)	-21.1(3)
	pair B	-	-22.7(4)	-22.7(3)	-22.6(3)	-17.3(3)
	pair C	-	-13.4(4)	-13.0(3)	-12.9(3)	-11.4(4)
τ_3	*pair A*	-84.0(3)	-77.3(3)	-77.4(3)	-76.8(3)	-79.8(2)
	pair B	-	-80.5(3)	-79.8(3)	-80.7(2)	-78.7(2)
	pair C	-	-75.2(3)	-75.3(3)	-74.5(3)	-70.5(3)
τ_4	*pair A*	-124.2(5)	111.1(6)	115.7(5)	117.0(4)	120.8(4)
	pair B	-	-103.2(4)	-104.6(4)	-105.9(3)	-111.4(4)
	pair C	-	-117.6(4)	-117.8(3)	-117.3(3)	-111.1(4)
τ_5	*pair A*	-108.5(4)	101.8(4)	102.3(3)	103.7(3)	120.2(3)
	pair B	-	91.2(4)	91.3(3)	91.0(3)	123.4(3)
	pair C	-	-106.4(4)	-107.8(4)	-113.8(7)	126.0(3)
	anion D	-	-	111(3)	109.9(17)	-
τ_6	*pair A*	-5.5(4)	28.6(4)	28.2(3)	27.6(3)	13.5(3)
	pair B	-	34.2(4)	34.0(3)	33.3(3)	19.4(3)
	pair C	-	6.4(4)	7.9(7)	4.0(13)	29.6(3)
	anion D	-	-	23(7)	26.1(18)	-
τ_7	*pair A*	-122.2(2)	-162.2	-165.2	-167.9	-165.0
	pair B	-	+82.2	+83.6	+78.5	-55.2
	pair C	-	-124.9	-129.1	-131.9	-53.5
	anion D	-	-	-163.8	-173.6	-