

Crystal Structure of (*S*)-1-Phenylethylammonium (*R*)-Mandelate and a Comparison of Diastereomeric Mandelate Salts of 1-Phenylethylamine

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The crystal structure of (*S*)-1-phenylethylammonium (*R*)-mandelate has been investigated, $C_8H_{12}N^+C_8H_7O_3^-$, $M_r = 273.33$, triclinic, $P1$, $T = 122.0(5)$ K, $a = 6.398(1)$, $b = 14.807(3)$, $c = 16.109(2)$ Å, $\alpha = 75.33(1)$, $\beta = 82.974(2)$, $\gamma = 81.03(2)^\circ$, $V = 1452.9(5)$ Å³, $Z = 4$, $D_x = 1.250$ g cm⁻³, $\lambda(\text{CuK}\alpha) = 1.54184$ Å, $\mu = 6.98$ cm⁻¹, $F(000) = 584$. The structure was refined against $|F|^2$ including all 6518 unique reflections to a final residual of $R_w = 0.1178$. The corresponding final residual based on F for 5663 observed reflections with $|F_o|^2 > 2\sigma(|F_o|^2)$ was $R = 0.0449$. Each of the four cations are hydrogen-bonded to two crystallographically equivalent anions related by translation symmetry in the direction of the crystallographic a -axis forming hydrogen-bonded chains. These chains are connected by hydrogen bonds forming sheets defined by the a -axis and the diagonal of the bc -plane. Similar hydrogen bonded layers are found in the diastereomeric salt (*R*)-1-phenylethylammonium (*R*)-mandelate, but the conformations of the ions differ in the two diastereomeric salts.

Racemic 1-phenylethylamine can be resolved with optically active mandelic acid through the formation of diastereomeric salts. When equimolar amounts of racemic 1-phenylethylamine and (*S*)-mandelic acid are mixed in water (*S*)-1-phenylethylammonium (*S*)-mandelate, (*S*-PEA)(*S*-MA), will precipitate as the less soluble salt.¹ Mixing the racemic base and the acid in the molar ratio 1:3 gives (*R*)-1-phenylethylammonium (*S*)-mandelate · dimandelic acid, (*R*-PEA)3(*S*-MA), as the less soluble compound.¹ The results from the resolution of racemic 1-phenylethylamine with (*S*)-mandelic acid can be transferred to the resolution with (*R*)-mandelic acid, as two salts of opposite absolute configuration have identical structural and physical behavior except that they show opposite optical rotation.

The crystal structures of (*R*-PEA)3(*S*-MA) and (*S*-PEA)(*S*-MA) have been reported.^{1–3} (*S*-PEA)(*S*-MA) exists in two polymorphic modifications, orthorhombic monoclinic. These are very similar both in the conformation of their ions and in their hydrogen-bond patterns. The structures of (*S*-PEA)3(*R*-MA) and (*R*-PEA)(*R*-MA) are obtained by inversion of the reported structures.

(*S*)-1-Phenylethylammonium (*R*)-mandelate, (*S*-PEA)(*R*-MA), is very soluble in water. If equimolar amounts of (*S*)-1-phenylethylamine and (*R*)-mandelic acid are mixed in water and the solution allowed to evaporate without any external intervention, a sticky

mass is obtained. Very slowly some of the (*S*)-1-phenylethylamine evaporates and crystals of (*S*-PEA)3(*R*-MA) appear.¹ If the solution contains some dust or crystal seeds or if it is stirred, (*S*-PEA)(*R*-MA) precipitates as a white microcrystalline residue, but it has not yet been possible to obtain crystals from water of a quality that makes them suitable for single-crystal diffraction measurements. However, by recrystallization from toluene it was possible to obtain a suitable crystal that was used in the present structure determination of (*S*-PEA)(*R*-MA). Here the crystal structure of the salt is presented and compared with the structure of (*R*-PEA)(*R*-MA).

Experimental

Preparation. (*S*-PEA)(*R*-MA) was prepared by dissolving equimolar amounts of (*S*)-1-phenylethylamine and (*R*)-mandelic acid in ethanol. After the solvent had evaporated, a white microcrystalline residue remained, which was recrystallized three times from toluene. The resulting crystals were colorless, very thin plates elongated in the direction of the a -axis. One of these was selected for the diffraction measurements. After several crystallizations from toluene it was noticed that some crystals appeared with a different crystal habit. They were not thin plates but more like rods. Weissenberg photographs of one of

these were identical to those obtained for (S-PEA)3(R-MA).

Crystal structure determination. The crystal selected for the diffraction measurements had dimensions $0.015 \times 0.1 \times 0.45$ mm³. The data collection was performed using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized CuK α radiation, $\lambda = 1.54184$ Å. The crystal was cooled during the data collection by an Enraf-Nonius gas-flow low-temperature device. The temperature $T = 122.0$ K was monitored with a thermocouple in the exhaust pipe; it was constant within 0.5 K. Intensities were measured using the $\omega - 2\theta$ scan mode, $\Delta\omega = 1.0 + (0.15 \tan \theta)^\circ$, the maximum scan time was 60 s. The unit-cell parameters were determined by least-squares refinement based on angles of 18 reflections with $25 < \theta < 33^\circ$. The orientation of the crystal was checked after every 600 reflections. The intensities of the reflections (113), (120) and (011) were remeasured after every

10⁴ s. These measurements showed no systematic variations. Reflections were measured in the range $0 < h < 8$, $-18 < k < 18$, $-19 < l < 19$, the maximum $\sin \theta / \lambda$ was 0.626 Å⁻¹. Data reduction was performed using the DREADD programs⁴ and included corrections for Lorentz polarization and background effects, as no correction of absorption (absorption coefficient 0.698 mm⁻¹) or decay was necessary. 6518 unique reflections were measured. The measurements of the three standard reflections were averaged to $R_{\text{int}} = 0.0198$.

The structure was solved by direct methods using the program SHELXS-86⁵ and refined using the full-matrix least-squares method minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$, $w^{-1} = \sigma_{cs}^2(F_o^2) + (0.0778P)^2$, $P = (F_o^2 + 2F_c^2)/3$. The program SHELXL-92⁶ was used in the refinement. Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogens bonded to tertiary and aromatic carbon atoms were fixed in ideal positions. The remaining hydrogens were refined with the restraint of a

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$).

Atom	x	y	z	U_{eq}^a	Atom	x	y	z	U_{eq}^a
C(1A)	913(5)	-687(2)	2892(2)	23(1)	C(1C)	1068(4)	3134(2)	8778(2)	20(1)
O(1A)	1630(3)	85(1)	2733(1)	26(1)	O(1C)	1723(3)	3926(1)	8551(1)	24(1)
O(2A)	-948(3)	-791(2)	2790(2)	29(1)	O(2C)	-875(3)	3012(2)	8872(1)	25(1)
C(2A)	2426(5)	-1593(2)	3206(2)	24(1)	C(2C)	2735(4)	2256(2)	8918(2)	20(1)
O(3A)	4073(4)	-1356(2)	3586(2)	29(1)	O(3C)	4368(3)	2377(2)	9387(1)	23(1)
C(3A)	3214(5)	-2033(2)	2454(2)	24(1)	C(3C)	3656(4)	2091(2)	8056(2)	19(1)
C(4A)	1840(5)	-2425(2)	2082(2)	29(2)	C(4C)	2353(5)	1832(2)	7545(2)	25(1)
C(5A)	2544(6)	-2810(2)	1385(2)	35(2)	C(5C)	3098(5)	1695(2)	6741(2)	29(2)
C(6A)	4649(6)	-2801(2)	1037(2)	38(2)	C(6C)	5194(5)	1805(2)	6429(2)	30(2)
C(7A)	6016(6)	-2400(2)	1397(2)	36(2)	C(7C)	6504(5)	2049(2)	6935(2)	29(2)
C(8A)	5331(5)	-2019(2)	2101(2)	29(2)	C(8C)	5756(5)	2200(2)	7745(2)	24(1)
C(9A)	7494(6)	250(3)	4405(2)	38(2)	C(9C)	4543(7)	4400(3)	10098(2)	41(2)
C(10A)	5298(5)	414(2)	4083(2)	23(1)	C(10C)	4959(5)	5031(2)	9216(2)	27(2)
N(A)	5518(4)	447(2)	3135(2)	23(1)	N(C)	5704(4)	4444(2)	8582(2)	22(1)
C(11A)	3982(5)	1301(2)	4242(2)	25(2)	C(11C)	6450(6)	5745(2)	9170(2)	32(2)
C(12A)	1933(5)	1270(3)	4629(2)	31(2)	C(12C)	6047(9)	6641(3)	8652(3)	53(3)
C(13A)	650(7)	2096(3)	4730(2)	46(2)	C(13C)	7333(12)	7328(4)	8622(3)	76(6)
C(14A)	1423(9)	2937(3)	4460(3)	55(4)	C(14C)	9053(10)	7106(4)	9123(4)	71(4)
C(15A)	3503(9)	2978(3)	4085(3)	49(3)	C(15C)	9472(7)	6214(4)	9643(4)	60(2)
C(16A)	4759(7)	2165(2)	3973(2)	35(2)	C(16C)	8183(6)	5528(3)	9669(3)	41(2)
C(1B)	2462(4)	2217(2)	1536(2)	19(1)	C(1D)	6009(5)	6305(2)	6357(2)	25(2)
O(1B)	1836(3)	2191(2)	833(1)	24(1)	O(1D)	7974(4)	6371(2)	6254(2)	33(1)
O(2B)	4370(3)	2215(2)	1666(1)	24(1)	O(2D)	5079(3)	5764(2)	6962(1)	27(1)
C(2B)	781(4)	2288(2)	2293(2)	18(1)	C(2D)	4693(5)	6985(2)	5659(2)	26(2)
O(3B)	-855(3)	1733(1)	2318(1)	21(1)	O(3D)	6033(4)	7270(2)	4899(1)	33(1)
C(3B)	-111(4)	3302(2)	2218(2)	20(1)	C(3D)	3605(5)	7818(2)	6000(2)	25(2)
C(4B)	1260(5)	3943(2)	2258(2)	25(1)	C(4D)	1429(6)	7929(3)	6235(3)	39(2)
C(5B)	523(5)	4870(2)	2225(2)	28(2)	C(5D)	485(6)	8706(3)	6542(3)	45(2)
C(6B)	-1627(5)	5193(2)	2144(2)	30(2)	C(6D)	1683(7)	9370(3)	6615(2)	39(2)
C(7B)	-2981(5)	4575(2)	2089(2)	31(2)	C(7D)	3854(7)	9267(3)	6385(3)	39(2)
C(8B)	-2257(5)	3635(2)	2127(2)	24(1)	C(8D)	4796(6)	8495(2)	6080(2)	36(2)
C(9B)	-4137(5)	343(2)	928(2)	28(2)	C(9D)	-318(5)	3936(2)	6509(2)	30(2)
C(10B)	-1924(5)	637(2)	791(2)	22(1)	C(10D)	1706(5)	4377(2)	6443(2)	26(2)
N(B)	-2091(4)	1697(2)	577(2)	20(1)	N(D)	1294(4)	5102(2)	6964(2)	26(1)
C(11B)	-580(5)	241(2)	99(2)	22(1)	C(11D)	2495(5)	4819(2)	5525(2)	27(2)
C(12B)	1427(5)	-256(2)	252(2)	30(2)	C(12D)	4646(5)	4653(2)	5249(2)	31(2)
C(13B)	2623(6)	-650(3)	-380(3)	40(2)	C(13D)	5405(6)	5068(3)	4419(2)	36(2)
C(14B)	1833(6)	-574(3)	-1153(2)	40(2)	C(14D)	4056(6)	5646(2)	3848(2)	36(2)
C(15B)	-177(6)	-89(3)	-1312(2)	39(2)	C(15D)	1899(6)	5809(2)	4111(2)	33(2)
C(16B)	-1369(6)	327(2)	-692(2)	31(2)	C(16D)	1133(5)	5397(2)	4939(2)	30(2)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} -tensor.

fixed angle and distance to the non-hydrogen atoms. All 6518 independent reflections were included in the refinement, which gave final residual $R_w = 0.1178$ based on F^2 for 733 parameters; the residual based on F for 5663 reflections with $|F_o|^2 > 2\sigma(|F_o|^2)$ was $R = 0.0449$. $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2} = 1.075$ and $(\Delta/\sigma)_{\max} = 0.003$. The final difference Fourier had $(\Delta\rho)_{\max} = 0.201 e \text{ \AA}^{-3}$ and $(\Delta\rho)_{\min} = -0.321 e \text{ \AA}^{-3}$. The final fractional coordinates for non-hydrogen atoms are listed in Table 1. Scattering-factors including the contribution from anomalous dispersion were used as contained in the program. Lists of observed and calculated structure factors, anisotropic thermal parameters for non-hydrogen atoms and positional parameters for the hydrogen atoms are available from the author.

Powder diffraction. Powder diffraction measurements were used to examine if the same modification was obtained whether (S-PEA)(R-MA) was recrystallized from toluene, prepared in water or precipitated in the mother liquor of the resolution.

The program LAZY PULVERIX⁷ was used to construct a powder diffraction pattern of the structure determined by single-crystal X-ray diffraction.

A Guinier-Hägg camera with $\text{CuK}\alpha$ radiation using silicon as internal standard was used for the powder diffraction measurements. The resulting line patterns were identical for the three preparations and in agreement with the pattern calculated from the structure.

Discussion

Crystal structure. The structure contains four crystallographically independent cations labelled A, B, C and D and four anions labelled A, B, C and D. The atomic numbering scheme is illustrated in the ORTEP drawings (Fig. 1). In order to facilitate the comparison of the mandelate ions, O(1) is selected as the carboxylate oxygen with the smaller torsion angle O-C(1)-C(2)-O(3) to the hydroxylic O(3), and the phenyl ring is numbered with C(4) in a position *anti* to the hydroxy group. In the 1-phenylethylammonium ion C(12) is the carbon in position *anti* to the amine group.

The mandelate ion. The mandelate ion contains two planar groups, the phenyl ring and the carboxylate group. This makes it possible to describe the conformation of the ion by the two torsion angles O(1)-C(1)-C(2)-O(3) and O(3)-C(2)-C(3)-C(4). From Tables 2 and 3 it is apparent that the geometries of the four mandelate ions are very similar, but they show differences in the conformations. The torsion angle O(1)-C(1)-C(2)-O(3) is found in the range 22–44°. The orientation of the phenyl ring is very similar in the A, B and C ions [O(3)-C(2)-C(3)-C(4) = 171–175°]; in the D ion it is 131.7°. The torsion angles of the mandelate ion found in the diastereomeric (R)-1-phenylethylammonium (R)-mandelate

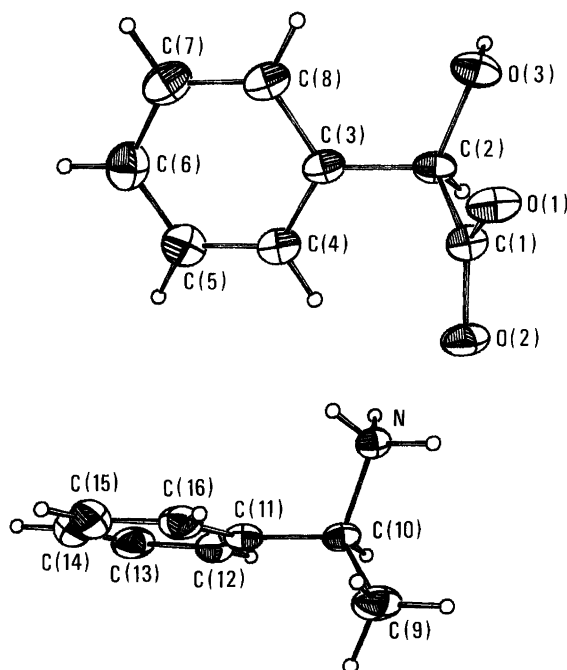


Fig. 1. ORTEP drawings of the ions labelled A illustrating the atomic numbering scheme in the mandelate anions (above) and the ammonium cations (below). The thermal ellipsoids enclose 50% probability, and the H atoms are drawn as spheres with a fixed radius.

are 12 and 144°, respectively, and the torsion angles corresponding to a conformation of minimum energy are 40 and 130°, respectively.²

Table 2. Bond lengths in (S-PEA)(R-MA) (in Å).

	A	B	C	D
Mandelate ion				
O(1)–C(1)	1.253(4)	1.257(3)	1.258(3)	1.264(4)
O(2)–C(1)	1.260(4)	1.263(3)	1.269(3)	1.247(4)
C(1)–C(2)	1.537(4)	1.538(4)	1.535(4)	1.544(4)
C(2)–O(3)	1.410(4)	1.419(3)	1.419(3)	1.416(4)
C(2)–C(3)	1.515(4)	1.501(4)	1.504(4)	1.513(4)
C(3)–C(4)	1.390(4)	1.407(4)	1.396(4)	1.393(5)
C(3)–C(8)	1.405(4)	1.397(4)	1.394(4)	1.390(4)
C(4)–C(5)	1.383(5)	1.371(4)	1.378(4)	1.390(5)
C(5)–C(6)	1.394(5)	1.395(5)	1.393(5)	1.372(6)
C(6)–C(7)	1.384(5)	1.380(4)	1.382(5)	1.388(6)
C(7)–C(8)	1.386(5)	1.384(4)	1.394(4)	1.382(5)
1-Phenylethylammonium ion				
N–C(10)	1.504(4)	1.508(4)	1.494(4)	1.497(4)
C(9)–C(10)	1.520(4)	1.521(4)	1.508(5)	1.520(4)
C(10)–C(11)	1.508(4)	1.505(4)	1.513(4)	1.515(4)
C(11)–C(12)	1.383(5)	1.394(4)	1.382(5)	1.397(5)
C(11)–C(16)	1.391(5)	1.397(4)	1.398(5)	1.395(4)
C(12)–C(13)	1.397(5)	1.390(5)	1.393(7)	1.386(5)
C(13)–C(14)	1.361(7)	1.372(6)	1.393(9)	1.374(5)
C(14)–C(15)	1.396(7)	1.391(6)	1.379(8)	1.395(5)
C(15)–C(16)	1.379(6)	1.392(5)	1.395(5)	1.383(4)

Table 3. Bond angles and selected torsion angles in (S-PEA)(R-MA) (in Å).

	A	B	C	D
Mandelate ion				
O(1)–C(1)–O(2)	125.3(3)	125.1(3)	124.4(3)	126.4(3)
O(1)–C(1)–C(2)	118.2(3)	118.0(2)	117.7(2)	114.7(3)
O(2)–C(1)–C(2)	116.4(3)	116.8(2)	117.9(2)	118.9(3)
C(1)–C(2)–O(3)	107.9(2)	111.4(2)	110.4(2)	109.6(3)
C(1)–C(2)–C(3)	109.1(2)	109.0(2)	109.0(2)	109.1(3)
O(3)–C(2)–C(3)	113.3(3)	110.8(2)	110.1(2)	111.7(3)
C(2)–C(3)–C(4)	120.7(3)	118.7(2)	118.8(3)	121.8(3)
C(2)–C(3)–C(8)	120.3(3)	122.9(2)	122.3(3)	119.5(3)
C(4)–C(3)–C(8)	119.0(3)	118.4(3)	118.9(3)	118.7(3)
C(3)–C(4)–C(5)	120.8(3)	121.4(3)	121.3(3)	120.2(3)
C(4)–C(5)–C(6)	120.2(3)	119.7(3)	119.9(3)	120.4(4)
C(5)–C(6)–C(7)	119.2(3)	119.4(3)	119.3(3)	120.1(3)
C(6)–C(7)–C(8)	121.1(3)	121.4(3)	121.2(3)	119.6(3)
C(3)–C(8)–C(7)	119.7(3)	119.7(3)	119.5(3)	121.1(3)
O(1)–C(1)–C(2)–O(3)	24.0(4)	38.6(3)	44.2(3)	22.4(4)
O(3)–C(2)–C(3)–C(4)	171.1(3)	174.7(2)	171.6(2)	131.7(3)
1-Phenylethylammonium ion				
N–C(10)–C(9)	109.2(3)	109.5(2)	109.6(3)	108.1(3)
N–C(10)–C(11)	109.7(2)	111.3(2)	111.2(3)	110.1(2)
C(9)–C(10)–C(11)	113.1(3)	111.3(2)	115.0(3)	113.5(3)
C(10)–C(11)–C(12)	119.9(3)	120.6(3)	119.5(4)	119.9(3)
C(10)–C(11)–C(16)	121.1(3)	120.4(3)	121.3(3)	121.9(3)
C(12)–C(11)–C(16)	118.9(3)	118.9(3)	119.1(4)	118.2(3)
C(11)–C(12)–C(13)	120.5(4)	120.1(3)	121.1(5)	120.7(3)
C(12)–C(13)–C(14)	120.0(4)	120.8(3)	119.3(5)	120.7(3)
C(13)–C(14)–C(15)	120.2(4)	119.8(4)	120.2(4)	119.3(3)
C(14)–C(15)–C(16)	119.8(4)	119.9(4)	120.3(5)	120.3(3)
C(11)–C(16)–C(15)	120.6(4)	120.4(3)	120.0(4)	120.8(3)
N–C(10)–C(11)–C(12)	107.8(3)	109.3(3)	93.4(4)	104.3(3)
C(9)–C(10)–C(11)–C(12)	–130.0(3)	–128.3(3)	–141.3(4)	–134.4(3)

The 1-phenylethylammonium ion. The conformation of the (S)-1-phenylethylammonium ion is described by the torsion angle N–C(10)–C(11)–C(12) given in Table 3. The conformations of the cations are quite similar, with the torsion angle in the range 93–109°. In the diastereomeric salt (S-PEA)(S-MA) this torsion angle is 144°.

The conformation corresponding to minimum energy is 120°. ⁸

Crystal packing. The molecular packing is illustrated by a stereo drawing in Fig. 2. The independent ions are distinguished by different atom and bonding symbols, and

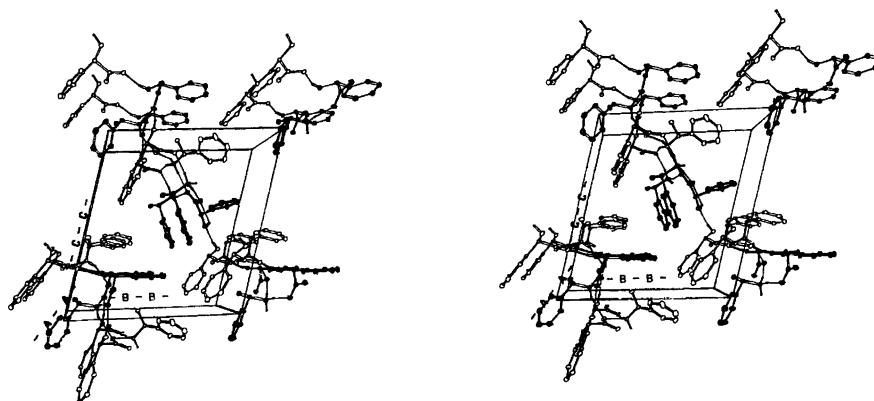


Fig. 2. Stereo drawing of the packing in (S-PEA)(R-MA) seen in the direction of the *a*-axis. The ions are identified by (A) open bonds, white atoms, (B) open bonds, black atoms, (C) full bonds, white atoms and (D) full bonds, black atoms. The hydrogen bonds are indicated by the thin lines.

hydrogen bonds are illustrated as thin lines. All possible donor atoms are involved in hydrogen bonds. The hydrogen-bond geometry is given in Table 4. An inspection of the table shows that the nitrogen in the cation labelled A is involved in two hydrogen bonds to the carboxylic oxygens O(1) and O(2) of the A-mandelate ion. These two acceptors belong to two anions connected with translational symmetry in the direction of the crystallographic a -axis, which means that the ions labelled A form hydrogen-bonded chains in this direction. Similar hydrogen-bonded chains of cations and anions labelled B, C and D are formed in the direction of the a -axis. The third hydrogen of the protonated nitrogens is donated to a carboxylic oxygen in a neighbouring chain in all four entities. The distances in N(A)–H(NA3)–O(2B) and N(B)–H(NB3)–O(2C) are much larger than the equivalent distances of the C and D cations, indicating rather weak bonds. In this way each of the pairs of ions with the same label show a very similar hydrogen-bond pattern. The only difference in hydrogen-bond patterns is found in the hydrogen bonds involving the hydroxy groups. H(O3) of the mandelate ion A forms a hydrogen bond to O(3) of the mandelate ion D. The hydroxy groups of the B and C anions are donors in hydrogen bonds to carboxylate groups of the mandelate ions A and B, respectively. In D an intramolecular hydrogen bond is formed. This means that the parallel hydrogen-bonded chains in the direction of the crystallographic a -axis are connected by hydrogen bonds forming a plane defined by the a -axis and the diagonal of the bc -plane. The hydrogen-bond pattern is shown schematically in Fig. 3.

Comparison of the diastereomeric salts. In the resolution of racemic 1-phenylethylamine with (*R*)-mandelic acid in the molar ratio 1:1 the monoclinic modification of (*R*-PEA)(*R*-MA) is obtained, and therefore this modification is used in the comparison of the diastereomeric salts.

Table 4. Hydrogen-bond geometry (in Å and °).

D–H···A	D–A	H–A	∠ DHA
N(A)–H(NA1)–O(1A)	2.808(3)	1.903(4)	172(2)
N(A)–H(NA2)–O(2A) ^a	2.774(3)	1.865(3)	178(1)
N(A)–H(NA3)–O(2B)	3.112(3)	2.35(1)	141(2)
O(3A)–H(O3A)–O(3D) ^b	2.804(3)	1.979(3)	167.4(3)
N(B)–H(NB1)–O(1B)	2.828(3)	1.928(5)	170(2)
N(B)–H(NB2)–O(2B) ^c	2.821(3)	1.921(4)	170(1)
N(B)–H(NB3)–O(2C) ^d	3.031(3)	2.28(1)	140(1)
O(3B)–H(O3B)–O(1A)	2.675(3)	1.875(3)	158.7(3)
N(C)–H(NC1)–O(1C)	2.782(3)	1.97(1)	147(2)
N(C)–H(NC2)–O(2C) ^a	2.794(3)	1.931(7)	158(1)
N(C)–H(NC3)–O(2D)	2.867(3)	1.999(8)	159(2)
O(3C)–H(O3C)–O(1B) ^a	2.648(3)	1.865(3)	154.7(2)
N(D)–H(ND1)–O(1D) ^c	2.759(3)	1.857(5)	170(2)
N(D)–H(ND2)–O(2D)	2.750(3)	1.865(8)	164(2)
N(D)–H(ND3)–O(1C)	2.722(3)	1.873(9)	154(2)
O(3D)–H(O3D)–O(1D)	2.599(3)	2.17(2)	112(2)

^a($x+1, y, z$). ^b($x, y-1, z$). ^c($x-1, y, z$). ^d($x, y, z-1$).

^e($x, y, z+1$).

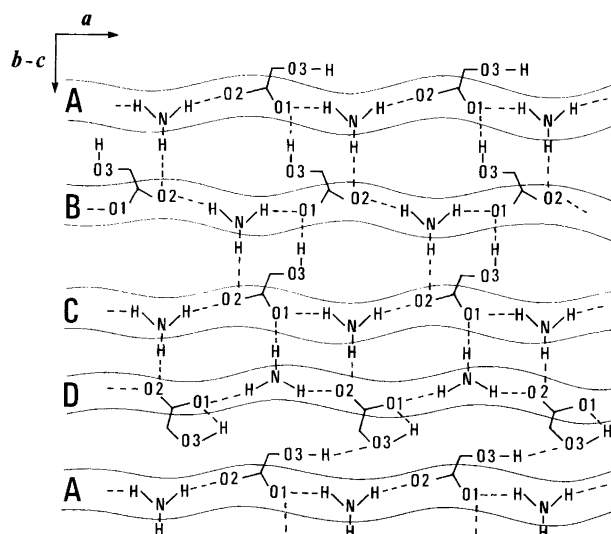


Fig. 3. Schematic illustration of a hydrogen bonded layer in (*S*-PEA)(*R*-MA). Only the donor and acceptor groups of the molecules are illustrated. The hydrogen-bonded chains of each pair of ions with the same label are highlighted by the wavy lines with the label given at the left side. The orientation with respect to the crystallographic axis is given by arrows.

The monoclinic modification of (*R*-PEA)(*R*-MA) crystallizes in the space group $P2_1$ with $a = 8.322(4)$, $b = 6.801(2)$, $c = 12.885(3)$ Å, $\beta = 91.74(3)^\circ$, $Z = 2$. The hydrogen-bond geometry in this salt is given in Table 5, and the hydrogen-bond pattern of the (*R*-PEA)(*R*-MA) is illustrated in Fig. 4.

The two diastereomeric salts have almost identical densities, 1.250 g cm^{-3} for (*S*-PEA)(*R*-MA) and 1.245 g cm^{-3} for (*R*-PEA)(*R*-MA), and there are great similarities in their hydrogen-bond patterns. In both structures hydrogen-bonded chains are formed in the direction of a translational period (crystallographic axis) of 6.5 Å. These chains are connected by hydrogen bonds forming

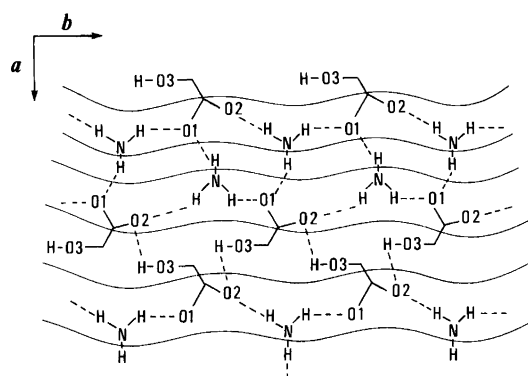


Fig. 4. Schematic illustration of a hydrogen bonded layer in (*R*-PEA)(*R*-MA). Only the donor and acceptor groups of the ions are illustrated. The hydrogen-bonded chains are highlighted by the wavy lines, and the orientation with respect to the crystallographic axis is given by arrows.

Table 5. Hydrogen-bond geometry in (R-PEA)(R-MA) (in Å and °).

D—H···A	D—A	H—A	∠DHA
N—H(N1)—O(1)	2.844(2)	1.96(2)	160(2)
N—H(N2)—O(2) ^a	2.828(2)	1.96(2)	164(2)
N—H(N3)—O(1) ^b	2.825(2)	1.94(2)	158(2)
O(3)—H(O3)—O(2) ^c	2.779(1)	2.00(2)	160(2)

^a(*x*, -1 + *y*, *z*). ^b(1 - *x*, - $\frac{1}{2}$ + *y*, 1 - *z*). ^c(2 - *x*, - $\frac{1}{2}$ + *y*, 1 - *z*).

layers. These similarities in the two structures were very surprising considering the large difference in solubility for the salts. Further investigations are needed to explain this behaviour.

There are no similarities in the structures of (S-PEA)(R-MA) and (S-PEA)₃(R-MA). The presence of carboxylic acid groups in (S-PEA)₃(R-MA) causes a hydrogen-bond pattern that is completely different from those found in the other two salts.

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