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Optical Resolution of 2-(2′-Hydroxyethylamino)-1-phenylethanol, and the Crystal Structures of Two Polymorphic Modifications of the (2*R*,3*R*)-*O*,*O*′-Dibenzoyl Hydrogen Tartrate Salt of the (*S*)-(+)-Enantiomer

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Successful separation of the enantiomers of 2-(2′-hydroxyethylamino)-1-phenylethanol was achieved using (2*R*,3*R*)-*O*,*O*′-dibenzoyltartaric acid as a resolving agent. The less soluble salt, (*S*)-*N*-(2′-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium (2*R*,3*R*)-*O*,*O*′-dibenzoyl hydrogen tartrate, was found to crystallize in two polymorphic modifications. The more stable modification is orthorhombic, space group $P2_12_12_1$ with cell dimensions $a=8.0096(8)$, $b=12.0536(13)$, $c=28.063(4)$ Å, $V=2709.3(6)$ Å^3, $Z=4$, $D_x=1.323$ g cm^{-3}. X-Ray diffraction data measured at 295.7(5) K with Cu$K\alpha$ ($\lambda=1.541\,84$ Å) radiation were used for the crystal structure determination, $R=0.0501$ for 4951 reflections with $I>2\sigma(I)$. The less stable modification is monoclinic, space group $P2_1$. X-Ray diffraction data measured at 122.0(5) K conform to a cell of $a=8.0047(8)$, $b=11.865(2)$, $c=28.065(5)$ Å, $\beta=91.410(11)°$, $V=2664.7(7)$ Å^3, $Z=4$, $D_x=1.345$ g cm^{-3}, for Cu$K\alpha$ ($\lambda=1.541\,84$ Å) radiation. This monoclinic crystal structure was refined to $R=0.0503$ for 3233 reflections with $I>2\sigma(I)$; the two independent ion pairs are almost related by the pseudotranslational symmetry of $c/2$. Both crystal structures established that the $(+)_D$ rotation of the 2-(2′-hydroxyethylamino)-1-phenylethanol corresponds to the *S* enantiomer.

The hydrogen bonding scheme is identical in the two modifications, leading to hydrogen bonded sheets. In the monoclinic modification each crystallographically independent ion pair forms separate sheets related by the pseudotranslational symmetry of $c/2$. A two-fold screw axis parallel to c relates the sheets in the orthorhombic modification.

Levamisole, the *S*-enantiomer of 6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole, is one of the most effective anthelmintic drugs. As the *S*-isomer has a much higher biological activity than the *R*-isomer, it is important to devise preparative routes that efficiently can give the optically pure *S*-enantiomer.[1]

2-(2′-Hydroxyethylamino)-1-phenylethanol (**1**) is a reaction intermediate in some of the synthetic pathways leading to Levamisole. Aiming at a stereoselective synthesis, optically pure 2-(2′-hydroxyethylamino)-1-phenylethanol seemed to be a good starting material, since its pure enantiomers can be prepared from optically active styreneoxide or by resolution.

Previously Bettoni *et al.*[2] had described the preparation of an isomer of 2-(2′-hydroxyethylamino)-1-phenylethanol. Through three supposedly stereoselective reaction steps (*S*)-mandelic acid was transformed to (*S*)-styreneoxide which was reacted with ethanolamine. The reported optical rotation ($[\alpha]_D=2.6°$) and melting point (361–363 K) of the product obtained this way are almost identical to the values of the racemate (364–366 K), which could suggest that the compound prepared this way was not optically pure.

During the optical resolution of 2-(2′-hydroxyethylamino)-1-phenylethanol with (2*R*,3*R*)-*O*,*O*′-dibenzoyltartaric acid we found that the less soluble diastereomeric

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salt had been isolated in two different polymorphic forms as described in the following. Initially a platelike single crystal was selected from the crystalline mass that was obtained by the optical resolution performed in an ethanol–water mixture. The X-ray diffraction data recorded at 122 K showed that the compound belongs to the monoclinic crystal system with two crystallographically independent ion pairs in the asymmetric unit. A later inspection of the Weissenberg photographs recorded at room temperature at the same time on another crystal showed orthorhombic symmetry, and the systematically absent reflections were consistent with space group $P2_12_12_1$. This lead us to believe that a phase transition had taken place by cooling the crystal to 122 K, and we undertook a data collection at room temperature (295.7 K) for the orthorhombic crystal. In order to investigate the temperature for this assumed phase transition, DSC measurements were performed on the original sample. However, the DSC traces recorded during the heating and cooling did not reveal any signs of phase transitions.

Re-examination of the original batch under the microscope ca. one year after its preparation did not reveal any platelike crystals in the sample: it only contained needle-shaped crystals. One of the needle-shaped crystals was examined more closely. It had the same orthorhombic cell at room temperature and at 122 K.

The powder diffraction patterns are not suited to distinguish between the orthorhombic and monoclinic modification as they have virtually identical cell dimensions, but were used to check that the single crystals are representative of the bulk.

We conclude that we have encountered another example of disappearing polymorphs, which according to Dunitz and Bernstein[3] are not such a rare phenomenon.

In this paper we describe the optical resolution of 2-(2′-hydroxyethylamino)-1-phenylethanol with (2*R*,3*R*)-*O*,*O*′-dibenzoyltartaric acid and the crystal structures of two polymorphic modifications of the less soluble diastereomeric salt.

Experimental

Preparations.

Optical resolution. 14.20 g (37.73 mmol) of (2*R*,3*R*)-*O*,*O*′-dibenzoyltartaric acid (DBTA) monohydrate dissolved in 35 ml ethanol were slowly added to the solution of 13.60 g (75.04 mmol) of 2-(2′-hydroxyethylamino)-1-phenylethanol and 3.2 ml (38.31 mmol) of conc. hydrochloric acid in 75 ml of water. After the mixture had been stirred for 2 h at 293–295 K, the precipitate was removed by filtering and washed twice with 10 ml portions of water and dried under infrared light. 19.24 g (35.65 mmol, 95.04%) m.p. 436–439 K, $[\alpha]_D = -62.6$ (c = 1, methanol) of the product were obtained.

After the ethanol had been removed by vacuum distillation, the mother liquor, kept at 278 K overnight, yielded another crop, 0.62 g (1.15 mmol, 3.06%) of the diastereomeric salt.

Crystals suitable for the single crystal diffraction study were obtained from the precipitate isolated during the resolution process.

Isolation of **1** *from the diastereomeric salt.* The two crops of the diastereomeric salt (19.86 g, 36.80 mmol) were combined and stirred with 75 ml of water, 15 g of NaCl, 6.4 ml (76.62 mmol) of conc. hydrochloric acid and 50 ml of ethylacetate for 10 min. The phases were separated, and 4.6 g (114.97 mmol) of sodium hydroxide were dissolved in the aqueous phase, which was then extracted four times with 15 ml portions of dichloromethane. The combined dichloromethane phases were dried over Na_2SO_4 and evaporated *in vacuo*. Yield: 6.23 g (34.38 mmol, 91.62%) of yellowish oil, which turned opaque. $[\alpha]_D = 48.2$ (c = 1, chloroform); 31.3 (c = 1, methanol).

Isolation of **1** *from the mother liquor.* To the mother liquor from the resolution 20 g of NaCl and 2.3 g (57.48 mmol) of NaOH were added. This solution was extracted four times with 15 ml portions of dichloromethane. The combined dichloromethane phases were dried over Na_2SO_4 and evaporated under vacuum. Yield: 6.75 g (37.24 mmol, 99.23%) of a yellowish oil, which turned opaque. $[\alpha]_D = -45.5$ (c = 1, chloroform); −29.8 (c = 1, methanol).

Purification: Preparation of optically pure compound. 5.5 g (30.35 mmol) of 2-(2′-hydroxyethylamino)-1-phenylethanol $[\alpha]_D = 44.3$ (c = 1, chloroform); 28.9 (c = 1, methanol) and 11.42 g (30.34 mmol) of DBTA monohydrate were refluxed in 80 ml of ethanol for 15 min, then cooled to 283 K. After filtration and drying 12.56 g (23.28 mmol, 76.73%) {m.p.: 441–443 K, $[\alpha]_D = -60.5$ (c = 1, methanol)} of diasteromeric salt were obtained. Following the procedure described above, 4.02 g $[\alpha]_D = 55.5$ (c = 1, chloroform); 36.5 (c = 1, methanol) of 2-(2′-hydroxyethylamino)-1-phenylethanol were obtained.

Spectroscopic measurements. Optical rotations were measured at ambient temperature at 589 nm (Na_D) with a Perkin Elmer 241 polarimeter.

^1H *NMR spectra* were recorded at 298 K using a Varian Unity 400 spectrometer. Solutions of 3 mg of 2-(2′-hydroxyethylamino)-1-phenylethanol in 600 µl of $CDCl_3$ were used for the purity determination. 20 mg of (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol were applied as chiral shift reagent. The optically active **1** used for purity determination {$[\alpha]_D = 55.5$ (c = 1, chloroform); 36.5 (c = 1, methanol)} was prepared as described above.

Thermodynamic measurements. Melting points were measured on samples in capillary tubes with a Gallenkampf capillary-melting-point aparatus.

A PL-DSC differential scanning calorimeter calibrated with mercury and gallium was used to check for the transformation of polymorphic modifications in the range 130–320 K using a heating rate of 10 K min^{-1}. The DSC instrument was then calibrated with tin and

indium and used for the examination of the phase transition between 300 and 460 K using a heating rate of 5 K min^{-1}.

X-Ray crystallography. A Guinier–Hägg camera was used to record the powder diffraction pattern for the (2*R*,3*R*)-DBTA salt of (*S*)-**1** prepared from optically pure samples. Graphite monochromated Cu*K*α was used and Si employed as an internal standard.

The program LAZY-PULVERIX[4] was used to compute the powder diffraction diagram based on the results obtained from the single crystal X-ray diffraction studies.

The data collections were performed with a CAD4 diffractometer for crystals kept at 295.7(5) and 122.0(5) K; the latter temperature was achieved by an Enraf-Nonius gas-flow temperature device. The temperature was monitored with a thermocouple placed in the exhaust pipe. Cu*K*α (λ = 1.541 84 Å) radiation obtained from a graphite monochromator was used for both data collections. The different experimental conditions with a summary of the information of the results from data reduction and structure refinement are presented in Table 1. An analysis of the profiles of selected reflections provided the basis for the choice of scan mode and scan interval for the data collections. The 96 steps of the reflection profiles were stored and used in the data reduction performed with the DREADD data reduction package.[5] The orientation of the crystals was checked after every 300 reflections. The intensities of three standard reflections measured after every 10 000 s showed systematic decay during the data collection for both modifications. Corrections were made for these variations, as well as Lorentz, polarization and background effects. The data set of the orthorhombic modification was also corrected for the effect of absorption using numerical integration. The reflections measured only in

Table 1. Crystal data and summary of the data collection and structure refinement results.

	Orthorhombic modification	Monoclinic modification
Formula	$C_{28}H_{29}NO_{10}$	$C_{28}H_{29}NO_{10}$
Formula weight	539.52	539.52
Radiation/Å	1.541 84	1.541 84
Temperature/K	295.7(5)	112.0(5)
Space group	$P2_12_12_1$	$P2_1$
a/Å	8.0096(8)	8.0047(8)
b/Å	12.0536(13)	11.865(2)
c/Å	28.063(4)	28.065(5)
β/°	90	91.410(11)
V/Å^3	2709.3(6)	2664.7(7)
Z	4	4
D_x/g cm^{-3}	1.323	1.345
Absorption coefficient/mm^{-1}	0.808	0.863
F(000)	1136	1136
Crystal size/mm	0.08 × 0.11 × 0.74	0.03 × 0.15 × 0.50
Refl. used in determ. of cell parameters	22	13
θ range/°	30.75–41.21	31.28–42.86
Scan type	ω–2θ	ω–2θ
Standard reflections	(1,1,4)(1,2,2)(2,1,0)	(0,1,2)(1,1,−4)(2,1,2)
Max. variation of intensity control refl. (%)	8.1	16.2
θ range for data collection/°	3.15–74.91	3.15–74.87
Range of *h*	0 to 10	−3 to −10
Range of *k*	−15 to 15	−6 to −14
Range of *l*	−35 to 35	−35 to 31
R_{int}	0.0244	0.0272
Transmission factor range	0.750–0.939	—
No. of measured reflections, incl. standard reflections	8975	4426
No. of independent reflections (total/used in refinement)	5569/5568	4071/4055
No. of observed reflections [$I > 2\sigma(I)$]	4951	3233
w^{-1} P=[max. (F_o^2, 0)+2F_c^2]/3	$\sigma^2(F_o^2)+(0.0896P)^2+0.1600P$	$\sigma^2(F_o^2)+(0.0617P)^2+3.4171P$
No. of variables	367	703
No. of restraints	0	1
R for $F > 4\sigma(F)$	0.0501	0.0503
wR_2 for all F^2 data	0.1399	0.1608
S for all F^2 data	1.059	1.218
Max. shift/e.s.d.	−0.002	−0.102
Max. and min. Δρ/e Å^{-3}	0.216 and −0.235	0.254 and −0.363
Absolute structure parameter	0.2(2)	0.1(3)

the prescan, i.e. with the highest possible scan-speed and having intensities less than ten times the e.s.d., were omitted, as they have been shown to suffer from systematic errors.[6] Finally reflections related by the symmetry of the crystal class were averaged.

The two structures were solved by direct methods using SHELXS-86[7] and refined by the full matrix least-squares method, SHELXL-93[8] minimizing $\Sigma w(F_o^2 - F_c^2)^2$. Scattering factors were taken from Ref. 9 and used as contained in the program. After anisotropic displacement parameters were introduced for the non-hydrogen atoms, the difference Fourier map showed the positions for most of the hydrogen atoms. The positional parameters of the hydrogen atoms bonded to N or O atoms were included in the refinement of the orthorhombic modification. In the monoclinic modification it was not possible to locate the hydrogen atom bonded to O11A from the difference electron density. The remaining hydrogen atoms bonded to N or O were located from the difference Fourier maps, and were refined as 'riding' on the non-hydrogen atom to which they are bonded. In both modifications the isotropic displacement parameters for these hydrogen atoms were made equal to U_{eq} of the parent N and O atom multiplied by 1.2 and 1.5, respectively. The hydrogen atoms bonded to C atoms were generated in idealized positions and refined as 'riding' on the C atom to which they are bonded with restraints on their positional and isotropic displacement parameters.

The absolute structures of the compound were chosen to match the known configuration of (2*R*,3*R*)-*O*,*O*'-dibenzoyltartaric acid. The refinements resulted in absolute structure parameters[10] of 0.2(2) and 0.1(3), thus establishing the absolute configuration of the cation as *S*. For the monoclinic form the polar axis restraint was applied according to the method of Flack and Schwarzenbach.[11]

During the refinement of the monoclinic modification a severe correlation was detected of the anisotropic parameters of atoms related by non-crystallographic symmetry. Since the data to parameter ratio was rather low due to the omission of weak reflections measured only in pre-scan mode, a damping coefficient of 100 was introduced to achieve convergency. Therefore the standard deviations of the monoclinic form are artificially reduced. An attempt was later made to use the weak reflections during the refinement, but the correlation between the independent ion-pairs was not reduced, and the refinement did not provide a more realistic model. Therefore the weak reflections were omitted in the final refinements.

The final fractional coordinates for non-H atoms are listed in Tables 2 and 3 for the orthorhombic and monoclinic modifications, respectively. The anisotropic displacement parameters, parameters for the hydrogen atoms and lists of the observed and calculated structure factors for both modifications can be obtained from one of the authors (S.L.).

Results and discussion

The resolution process and optical purity determination. The optical resolution was successful using half of an equivalent of (2*R*,3*R*)-*O*,*O*'-dibenzoyltartaric acid in the presence of half of an equivalent achiral auxilary agent (HCl). The (+)-isomer is isolated in the less soluble diastereomeric salt. Decomposition of the salt affords an opaque oily product which can be further purified by precipitation with DBTA monohydrate and subsequent recovering the base. Optically pure **1** has an optical rotation $[\alpha]_D = 55.5$ ($c = 1$, chloroform); 36.5 ($c = 1$, methanol) and is a clear oil; this is in contrast to the apparence of partially optically pure **1**, which is opaque. The base was observed to solidify only when its enantiomeric composition was close to the racemate. It should be mentioned that an increase in the ionic strength by addition of NaCl enhances the yield of the base.

The optical purity of **1** was determined by ^{1}H NMR spectroscopy. The (N)H and (O)H signals shifted upfield from 4.80 ppm in CD_3OD for a partially optically active compound to 2.67 and 2.57 ppm in the $CDCl_3$ solutions of racemic and optically pure base. Apart from this the spectrum of **1** recorded in $CDCl_3$ is identical to that previously reported by Bettoni *et al.* in CD_3OD.[2]

The quartet signal with ppm 4.80–4.83 of the hydrogen atom bonded to the chiral carbon atom becomes an octet after addition of the chiral shift reagent to the solution of the racemate. The spectrum of the optically pure compound measured under the same condition showed only a quartet. Since the minor component needs to be present in ca. 5% to be detectable, the enantiomeric excess was estimated to be higher than 0.96 because addition of 1% of racemic **1** made the other quartet appear.

Description of the crystal structures. Both crystalline modifications contain discrete (*S*)-*N*-(2'-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium cations and (2*R*,3*R*)-*O*,*O*'-dibenzoyl hydrogen tartrate anions linked by an extensive system of hydrogen bonds. The molecular geometries of the three independent cations and anions are illustrated in Figs. 1 and 2. The drawings, the bond lengths and angles listed in Tables 4 and 5 show that the three ions are virtually identical.

The pseudosymmetry of the monoclinic modification has lead to a less reliable structure determination. Therefore one should refer to the molecular geometry observed in the orthorhombic modification.

The diethylammonium chain adopts an extended conformation with antiperiplanar arrangements around both C–N bonds and the C12–C13 bond. The plane of the phenyl group is almost perpendicular to the C12–C13 bond, the torsion angle C12–C13–C14–C19 being ca. 75°.

The bond lengths in the monoclinic modification display significant differences which we attribute to the correlation between the parameters of the corresponding

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (in Å^2) in the orthorhombic modification.

Atom	x	y	z	U_{eq}[a]
Cation				
N1	0.7611(2)	0.19335(14)	0.75427(6)	0.0484(4)
O10	0.7301(2)	−0.04328(14)	0.74494(6)	0.0622(4)
O13	0.9663(2)	0.3680(2)	0.75232(6)	0.0652(4)
C10	0.6583(3)	0.0292(2)	0.71119(9)	0.0624(5)
C11	0.6123(3)	0.1387(2)	0.73266(9)	0.0570(5)
C12	0.7169(3)	0.2965(2)	0.78058(8)	0.0521(5)
C13	0.8739(3)	0.3584(2)	0.79500(8)	0.0532(5)
C14	0.8254(3)	0.4691(2)	0.81652(8)	0.0540(5)
C15	0.8391(3)	0.5672(2)	0.79134(9)	0.0603(5)
C16	0.7888(4)	0.6663(2)	0.81096(11)	0.0701(7)
C17	0.7202(4)	0.6690(2)	0.85575(11)	0.0773(7)
C18	0.7015(5)	0.5723(2)	0.88074(11)	0.0886(9)
C19	0.7557(4)	0.4729(2)	0.86152(10)	0.0753(7)
Anion				
O11	−0.1233(2)	−0.04636(14)	0.86806(6)	0.0588(4)
O12	−0.0330(2)	0.09523(13)	0.82378(6)	0.0577(4)
O2	0.1802(2)	−0.10721(11)	0.89135(5)	0.0462(3)
O21	0.1598(3)	−0.26091(13)	0.84669(6)	0.0659(4)
O3	0.2934(2)	0.10854(11)	0.89342(5)	0.0476(3)
O31	0.3959(3)	0.2571(2)	0.85552(8)	0.0886(6)
O41	0.4877(2)	−0.07183(14)	0.80942(6)	0.0614(4)
O42	0.5889(2)	0.0290(2)	0.86919(7)	0.0727(5)
C1	−0.0094(2)	0.0110(2)	0.84683(7)	0.0432(4)
C2	0.1653(2)	−0.0387(2)	0.84976(7)	0.0421(4)
C21	0.1620(2)	−0.2172(2)	0.88517(7)	0.0482(4)
C22	0.1434(3)	−0.2767(2)	0.93092(8)	0.0599(5)
C23	0.1001(5)	−0.3874(2)	0.92990(11)	0.0829(9)
C24	0.0763(7)	−0.4442(3)	0.9718(2)	0.1085(13)
C25	0.0970(9)	−0.3942(4)	1.0138(2)	0.137(2)
C26	0.1465(12)	−0.2878(4)	1.01516(13)	0.178(4)
C27	0.1667(8)	−0.2268(3)	0.97358(11)	0.127(2)
C3	0.3016(2)	0.0476(2)	0.84980(7)	0.0435(4)
C31	0.3569(3)	0.2119(2)	0.89194(9)	0.0582(5)
C32	0.3703(3)	0.2620(2)	0.93992(10)	0.0681(6)
C33	0.4184(5)	0.3729(3)	0.9426(2)	0.1011(11)
C34	0.4346(7)	0.4219(4)	0.9858(2)	0.137(2)
C35	0.4047(7)	0.3638(5)	1.0265(2)	0.136(2)
C36	0.3553(7)	0.2568(5)	1.0243(2)	0.134(2)
C37	0.3379(5)	0.2043(3)	0.98043(11)	0.0927(10)
C4	0.4746(2)	−0.0041(2)	0.84241(7)	0.0469(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atoms. We notice that the average of the two molecules within its standard deviation gives the geometry of the cation in the orthorhombic form.

The molecular dimensions of the three anions listed in Table 5 show the same systematic variations as the cations, the geometry of the anion in the orthorhombic form representing the average of the two anions in the monoclinic modification. The only deviation from this picture is in orientation of the phenyl group C32–C37, which differs ca. 10° between the two modifications. The large displacement parameters of the carbon atoms of the phenyl rings indicate significant thermal disorder that can explain the deviations of the C–C bond lengths from the idealized value.

The carbon chain C1–C2–C3–C4 of the anion adopts the antiperiplanar conformation usually observed for this anion. O2 is significantly displaced from the plane defined by O11, O12, C1 and C2, being synperiplanar with O11. Similar differences are not observed for the other half of the molecule. The angle between the least squares planes of the carboxylate and the carboxylic acid groups is ca. 84°.

Crystal packing. The orthorhombic modification contains one cation and one anion per asymmetric unit, whereas the monoclinic modification has two cations and two anions in the asymmetric unit almost related by pseudo-translational symmetry of $c/2$, an arrangement apparent from the stereo pairs in Figs. 3 and 4.

In accordance with the pseudosymmetry the two ion pairs in the monoclinic modification show identical hydrogen bond patterns linking cation B to anion A,

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (in Å^2) in the monoclinic modification.

Atom	*x*	*y*	*z*	U_{eq}[a]
Cations				
N1B	0.7600(6)	0.2344(4)	0.5017(2)	0.0205(11)
O10B	0.7232(5)	−0.0036(4)	0.4951(2)	0.0276(10)
O13B	0.9729(5)	0.4132(4)	0.49987(14)	0.0258(9)
C10B	0.6498(8)	0.0709(6)	0.4598(2)	0.0285(14)
C11B	0.6082(8)	0.1841(5)	0.4807(2)	0.029(2)
C12B	0.7224(8)	0.3421(5)	0.5298(2)	0.0262(14)
C13B	0.8842(7)	0.4035(5)	0.5436(2)	0.0220(13)
C14B	0.8393(7)	0.5145(5)	0.5664(2)	0.0249(13)
C15B	0.8451(8)	0.6132(5)	0.5388(2)	0.0241(13)
C16B	0.7952(8)	0.7166(6)	0.5601(2)	0.031(2)
C17B	0.7362(9)	0.7166(6)	0.6039(3)	0.033(2)
C18B	0.7284(10)	0.6196(6)	0.6306(2)	0.036(2)
C19B	0.7778(10)	0.5184(5)	0.6108(2)	0.032(2)
N1D	0.7611(6)	0.2425(4)	0.0022(2)	0.0240(12)
O10D	0.7205(5)	0.0007(4)	−0.0059(2)	0.0298(10)
O13D	0.9710(5)	0.4134(4)	0.0006(2)	0.0304(10)
C10D	0.6473(8)	0.0711(6)	−0.0404(2)	0.030(2)
C11D	0.6076(7)	0.1852(6)	−0.0197(2)	0.0266(14)
C12D	0.7234(7)	0.3422(5)	0.0287(2)	0.0237(13)
C13D	0.8844(8)	0.4037(6)	0.0431(2)	0.0273(14)
C14D	0.8379(8)	0.5173(5)	0.0644(2)	0.0238(13)
C15D	0.8444(8)	0.6168(6)	0.0394(2)	0.029(2)
C16D	0.7946(8)	0.7154(6)	0.0577(2)	0.0278(14)
C17D	0.7303(9)	0.7201(6)	0.1053(2)	0.031(2)
C18D	0.7251(10)	0.6211(6)	0.1310(2)	0.038(2)
C19D	0.7792(9)	0.5204(7)	0.1120(2)	0.032(2)
Anions				
O11A	−0.1185(5)	−0.0005(4)	0.6190(2)	0.0278(10)
O12A	−0.0312(5)	0.1409(4)	0.5725(2)	0.0260(10)
O2A	0.1880(5)	−0.0594(4)	0.64222(13)	0.0226(9)
O21A	0.1651(6)	−0.2191(4)	0.5989(2)	0.0291(10)
O3A	0.2987(5)	0.1615(4)	0.64179(14)	0.0237(9)
O31A	0.4057(6)	0.3082(4)	0.6023(2)	0.0366(12)
O41A	0.4884(5)	−0.0271(4)	0.5603(2)	0.0286(10)
O42A	0.5937(5)	0.0823(4)	0.6181(2)	0.0332(11)
C1A	−0.0057(7)	0.0592(6)	0.5965(2)	0.0233(13)
C2A	0.1678(7)	0.0065(5)	0.5999(2)	0.0205(12)
C21A	0.1695(7)	−0.1728(5)	0.6370(2)	0.0183(12)
C22A	0.1547(8)	−0.2316(6)	0.6834(2)	0.032(2)
C23A	0.1033(10)	−0.3422(7)	0.6824(3)	0.042(2)
C24A	0.0859(10)	−0.4034(7)	0.7243(3)	0.046(2)
C25A	0.0995(13)	−0.3493(9)	0.7670(3)	0.065(3)
C26A	0.1470(14)	−0.2319(9)	0.7683(3)	0.064(3)
C27A	0.1762(11)	−0.1775(7)	0.7259(3)	0.042(2)
C3A	0.3063(7)	0.0955(5)	0.5996(2)	0.0212(12)
C31A	0.3626(7)	0.2679(5)	0.6392(2)	0.0238(13)
C32A	0.3722(8)	0.3253(6)	0.6853(2)	0.030(2)
C33A	0.4407(9)	0.4324(7)	0.6877(3)	0.041(2)
C34A	0.4584(10)	0.4920(6)	0.7294(3)	0.044(2)
C35A	0.4029(11)	0.4367(7)	0.7748(3)	0.050(2)
C36A	0.325(2)	0.3306(8)	0.7699(3)	0.062(3)
C37A	0.3146(11)	0.2766(7)	0.7277(3)	0.046(2)
C4A	0.4800(7)	0.0438(5)	0.5927(2)	0.0213(12)
O11C	−0.1199(5)	0.0012(4)	0.1187(2)	0.0272(10)
O12C	−0.0322(5)	0.1412(4)	0.0719(2)	0.0266(10)
O2C	0.1868(5)	−0.0597(4)	0.14314(13)	0.0222(9)
O21C	0.1682(6)	−0.2191(4)	0.0995(2)	0.0328(11)
O3C	0.2977(5)	0.1615(3)	0.14203(14)	0.0223(9)
O31C	0.4026(7)	0.3072(4)	0.1008(2)	0.0380(12)
O41C	0.4879(5)	−0.0276(4)	0.0596(2)	0.0287(10)
O42C	0.5969(5)	0.0781(4)	0.1191(2)	0.0292(10)
C1C	−0.0080(7)	0.0558(5)	0.0968(2)	0.0178(11)
C2C	0.1694(7)	0.0075(5)	0.1008(2)	0.0190(12)
C21C	0.1694(8)	−0.1704(5)	0.1376(2)	0.0278(14)
C22C	0.1493(8)	−0.2298(5)	0.1841(2)	0.0260(14)
C23C	0.1092(9)	−0.3438(6)	0.1830(2)	0.034(2)

Table 3. (Continued.)

Atom	x	y	z	U_{eq}[a]
C24C	0.0779(11)	−0.3986(7)	0.2258(3)	0.052(2)
C25C	0.1085(12)	−0.3452(7)	0.2685(3)	0.048(2)
C26C	0.1567(12)	−0.2370(8)	0.2697(3)	0.051(2)
C27C	0.1743(11)	−0.1739(6)	0.2279(2)	0.041(2)
C3C	0.3033(7)	0.0953(5)	0.0988(2)	0.0210(12)
C31C	0.3606(8)	0.2656(6)	0.1376(2)	0.0281(14)
C32C	0.3702(8)	0.3229(6)	0.1860(2)	0.029(2)
C33C	0.4393(10)	0.4320(6)	0.1864(3)	0.042(2)
C34C	0.4537(11)	0.4832(8)	0.2313(3)	0.054(2)
C35C	0.3972(12)	0.4387(8)	0.2678(3)	0.053(2)
C36C	0.3244(14)	0.3358(7)	0.2690(3)	0.052(2)
C37C	0.3114(10)	0.2740(6)	0.2261(2)	0.037(2)
C4C	0.4786(8)	0.0437(5)	0.0921(2)	0.0222(12)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

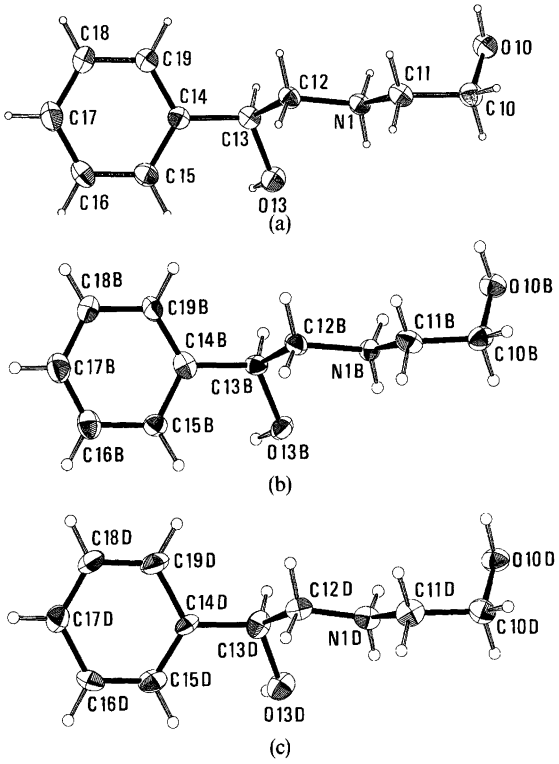

Fig. 1. ORTEPII[12] drawings showing the molecular geometry of the *N*-(2'-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium cations in the two modifications of **1**. DBTA (a) orthorhombic, (b) monoclinic molecule B and (c) monoclinic molecule D. The thermal ellipsoids are scaled to include 20% probability (a) and 50% (b,c). The hydrogen atoms are drawn as spheres with fixed radius.

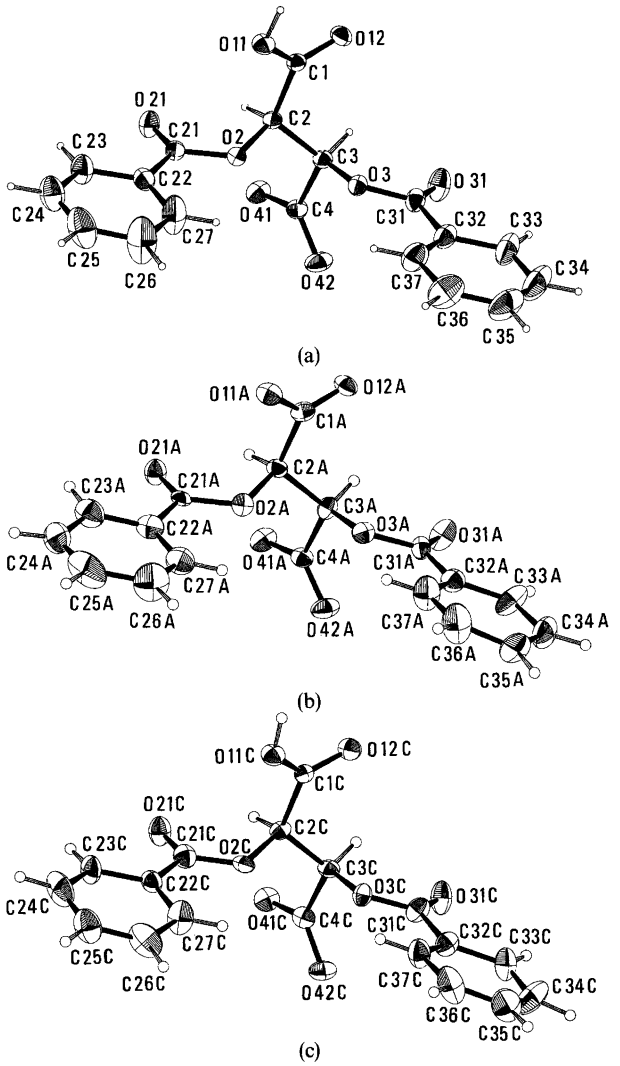

Fig. 2. ORTEPII[12] drawings showing the molecular geometry of the (2*R*,3*R*)-*O*,*O*'-dibenzoyl hydrogen tartrate anions in the two modifications of **1**. DBTA (a) orthorhombic, (b) monoclinic molecule A and (c) monoclinic molecule C. The thermal ellipsoids are scaled to include 20% probability (a) and 50% (b,c). The hydrogen atoms are drawn as spheres with fixed radius.

and cation D to anion C. The orthorhombic modification which has one independent ion pair displays an identical pattern of hydrogen bonds. Table 6 contains information on the hydrogen bonding motifs in the two structures.

The two protons of the ammonium group take part in intra- and intermolecular interactions. In both cations the intramolecular H1N–O10 and H2N–O13 distances are smaller than the sum of the atoms' van der Waals

Table 4. Bond distances (in Å), bond and selected torsion angles (in °) in the (*S*)-*N*-(2′-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium cation.

Atom	Orthorhombic	Monoclinic molecule B	Monoclinic molecule D
N1–C12	1.489(3)	1.536(7)	1.435(8)
N1–C11	1.491(3)	1.465(8)	1.521(7)
O10–C10	1.411(3)	1.441(7)	1.398(8)
O13–C13	1.412(3)	1.437(7)	1.397(7)
C10–C11	1.497(3)	1.506(9)	1.511(9)
C12–C13	1.517(3)	1.527(8)	1.526(8)
C13–C14	1.515(3)	1.512(8)	1.525(9)
C14–C19	1.382(4)	1.352(9)	1.426(8)
C14–C15	1.382(3)	1.404(8)	1.376(9)
C15–C16	1.376(4)	1.426(9)	1.342(9)
C16–C17	1.372(4)	1.329(9)	1.444(9)
C17–C18	1.369(4)	1.375(10)	1.380(10)
C18–C19	1.384(4)	1.386(9)	1.382(10)
C12–N1–C11	112.4(2)	112.1(5)	113.6(5)
O10–C10–C11	112.1(2)	111.8(5)	110.8(5)
N1–C11–C10	110.9(2)	109.4(5)	112.4(5)
N1–C12–C13	110.3(2)	110.6(5)	110.1(5)
O13–C13–C14	113.6(2)	114.8(5)	113.1(5)
O13–C13–C12	104.4(2)	104.9(4)	104.4(5)
C14–C13–C12	109.1(2)	108.3(5)	108.3(5)
C19–C14–C15	118.1(2)	119.8(6)	118.3(6)
C19–C14–C13	119.8(2)	121.0(6)	118.7(6)
C15–C14–C13	121.9(2)	118.9(5)	123.0(5)
C16–C15–C14	121.0(2)	118.3(6)	122.4(6)
C17–C16–C15	120.3(2)	119.8(6)	120.3(6)
C18–C17–C16	119.5(3)	121.8(7)	117.8(6)
C17–C18–C19	120.2(3)	119.3(6)	121.3(6)
C14–C19–C18	120.8(3)	120.9(6)	119.9(6)
O10–C10–C11–N1	57.9(3)	57.5(7)	57.1(7)
C10–C11–N1–C12	−173.7(2)	−171.9(5)	−170.7(5)
C11–N1–C12–C13	−170.9(2)	−169.8(5)	−171.6(5)
N1–C12–C13–C14	173.5(2)	174.0(5)	171.6(5)
C12–C13–C14–C15	−102.8(2)	−100.2(6)	−100.7(7)
C12–C13–C14–C19	73.2(3)	73.0(7)	77.0(7)
O13–C13–C14–C15	13.2(3)	16.6(8)	14.5(8)
O13–C13–C14–C19	−170.9(2)	−170.3(6)	−167.8(5)
O13–C13–C12–N1	51.7(2)	51.0(6)	50.8(6)

radii. In addition the same protons have shorter hydrogen-bond interactions to the carbonyl groups O12 and O21 of two anions related by a translational symmetry and by a two-fold screw axis, respectively. The carboxylic acid group of the anion is connected by a short hydrogen bond to the oxygen atom O42 from the carboxylate group. The hydrogen bond between the hydroxy groups of the cation connect cations related by the two-fold screw axis. In contrast to another related salt,[13] the ions do not interact via hydrogen bonding between oppositely charged groups.

The acid salts of dicarboxylic acids are frequently characterized by very short hydrogen bonds connecting the carboxylic acid and carboxylate groups, which has been shown to have covalent character.[14] In salts of tartaric acids[15] and substituted tartaric acids[13] this type of hydrogen bond is formed between molecules related by translational symmetry along a 7–8 Å axis as observed in the present structures.

The donor–acceptor distances in the orthorhombic modification are, as expected, almost identical to the arithmetic mean of the two equivalent donor–acceptor distances in the monoclinic modification. The only exception to this observation is the N–O12 distance, which is significantly longer in the orthorhombic modification than in the two monoclinic ion pairs (Table 6).

Comparison of the monoclinic and orthorhombic modifications. The hydrogen bond interactions are identical in the orthorhombic and in the monoclinic modification, so one may wonder about the origin of the differences between the two structures. Within the experimental accuracy the three cations and anions adopt geometries that make them almost superimposable. The cell

Table 5. Bond distances (in Å), bond and selected torsion angles (in °) in the (2*R*,3*R*)-*O*,*O*'-dibenzoyl hydrogen tartrate anion.

Atom	Orthorhombic	Monoclinic molecule A	Monoclinic molecule C
O11–C1	1.290(2)	1.321(7)	1.275(7)
O12–C1	1.219(2)	1.195(7)	1.244(7)
O2–C21	1.344(2)	1.361(7)	1.329(8)
O2–C2	1.435(2)	1.427(7)	1.435(7)
O21–C21	1.202(3)	1.202(7)	1.216(8)
O3–C31	1.346(3)	1.365(7)	1.341(8)
O3–C3	1.429(2)	1.423(6)	1.447(7)
O31–C31	1.200(3)	1.199(8)	1.199(8)
O41–C4	1.239(2)	1.242(7)	1.246(7)
O42–C4	1.250(3)	1.231(7)	1.267(7)
C1–C2	1.524(2)	1.524(8)	1.533(8)
C2–C3	1.509(3)	1.532(8)	1.497(8)
C21–C22	1.479(3)	1.484(8)	1.497(9)
C22–C27	1.353(4)	1.363(10)	1.405(9)
C22–C23	1.379(4)	1.375(11)	1.391(9)
C23–C24	1.372(4)	1.391(10)	1.395(9)
C24–C25	1.335(6)	1.362(13)	1.370(12)
C25–C26	1.343(7)	1.443(14)	1.341(12)
C26–C27	1.389(5)	1.379(11)	1.401(9)
C3–C4	1.534(3)	1.536(8)	1.547(8)
C31–C32	1.480(3)	1.463(9)	1.520(8)
C32–C37	1.358(4)	1.411(10)	1.361(10)
C32–C33	1.393(4)	1.385(10)	1.408(9)
C33–C34	1.355(6)	1.371(9)	1.403(10)
C34–C35	1.361(7)	1.510(11)	1.246(12)
C35–C36	1.350(8)	1.410(13)	1.353(13)
C36–C37	1.391(4)	1.348(10)	1.412(10)
C21–O2–C2	117.0(2)	116.2(5)	116.4(5)
C31–O3–C3	115.6(2)	116.2(5)	113.7(4)
O12–C1–O11	125.6(2)	126.5(6)	125.7(5)
O12–C1–C2	119.9(2)	120.8(5)	118.5(5)
O11–C1–C2	114.4(2)	112.5(5)	115.8(5)
O2–C2–C3	109.63(14)	108.4(4)	111.3(5)
O2–C2–C1	110.28(14)	111.2(5)	109.8(4)
C3–C2–C1	113.2(2)	112.1(5)	113.6(5)
O21–C21–O2	123.4(2)	123.3(5)	124.8(6)
O21–C21–C22	124.4(2)	124.3(5)	123.1(6)
O2–C21–C22	112.2(2)	112.4(5)	112.1(6)
C27–C22–C23	118.9(3)	119.8(7)	120.5(6)
C27–C22–C21	122.6(2)	122.4(7)	121.6(6)
C23–C22–C21	118.5(2)	117.5(6)	117.9(6)
C24–C23–C22	120.0(3)	121.2(7)	118.7(7)
C25–C24–C23	120.9(4)	119.3(8)	120.3(8)
C24–C25–C26	119.5(3)	119.5(8)	120.6(8)
C25–C26–C27	121.0(4)	118.7(8)	121.7(8)
C22–C27–C26	119.5(3)	121.0(8)	117.7(7)
O3–C3–C2	108.75(14)	109.2(4)	108.0(4)
O3–C3–C4	111.5(2)	112.5(5)	111.4(4)
C2–C3–C4	111.9(2)	112.5(5)	112.5(5)
O31–C31–O3	123.0(2)	122.1(6)	124.9(6)
O31–C31–C32	124.8(2)	124.7(6)	125.2(6)
O3–C31–C32	112.1(2)	113.2(5)	109.8(5)
C37–C32–C33	120.0(3)	118.2(6)	122.0(6)
C37–C32–C31	122.6(2)	123.0(6)	122.6(6)
C33–C32–C31	117.4(3)	118.8(6)	115.4(6)
C34–C33–C32	119.5(4)	123.1(7)	115.3(7)
C33–C34–C35	120.7(4)	118.0(7)	122.2(8)
C36–C35–C34	120.2(4)	116.4(6)	124.6(8)
C35–C36–C37	120.3(5)	121.8(9)	118.0(8)
C32–C37–C36	119.2(4)	122.1(8)	117.7(7)
O41–C4–O42	126.7(2)	128.5(6)	126.9(6)
O41–C4–C3	116.4(2)	115.4(5)	115.4(5)
O42–C4–C3	116.8(2)	116.0(5)	117.7(5)

Table 5. (Continued.)

Atom	Orthorhombic	Monoclinic molecule A	Monoclinic molecule C
O11–C1–C2–O2	−25.9(2)	−27.3(7)	−24.0(7)
O12–C1–C2–O2	157.5(2)	157.8(5)	158.1(5)
C2–O2–C21–O21	11.7(3)	12.5(8)	12.9(10)
O2–C21–C22–C23	170.9(2)	167.6(6)	172.1(6)
O2–C21–C22–C27	−8.9(4)	−6.7(9)	−9.5(9)
C1–C2–C3–C4	−168.3(2)	−168.2(5)	−167.8(5)
O41–C4–C3–O3	169.6(2)	170.3(5)	169.9(5)
O42–C4–C3–O3	−12.6(3)	−13.4(8)	−10.8(7)
C3–O3–C31–O31	10.5(3)	8.0(8)	7.4(9)
O3–C31–C32–C33	−173.6(3)	177.6(6)	178.1(6)
O3–C31–C32–C37	6.4(4)	−2.4(9)	−3.9(9)

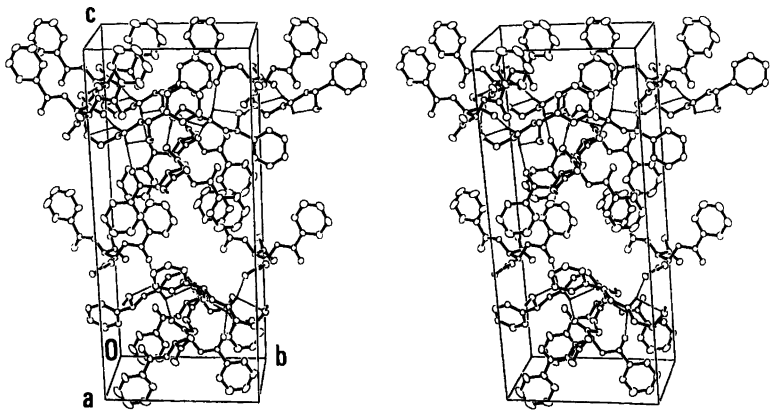

Fig. 3. Stereo pair[12] illustrating the packing of the orthorhombic modification of (*S*)-*N*-(2′-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium (2*R*,3*R*)-*O*,*O*′-dibenzoyl hydrogen tartrate viewed along the ***a***-axis. The hydrogen bonds are shown as thin lines. The hydrogen atoms not involved in the hydrogen bonding system are omitted for clarity.

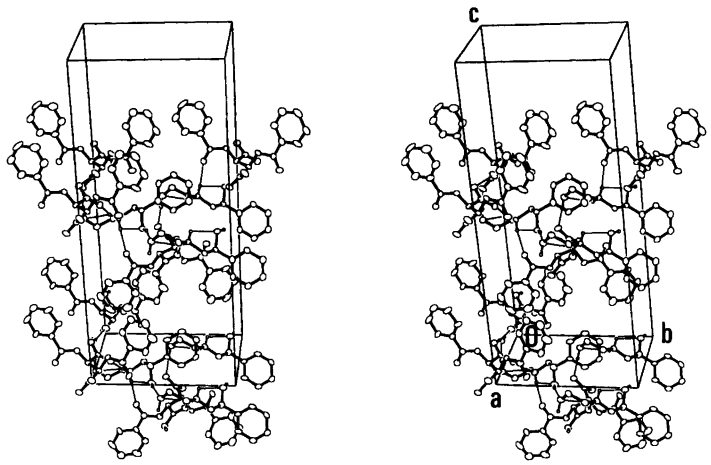

Fig. 4. Stereo pair[12] illustrating the packing of the monoclinic modification of (*S*)-*N*-(2′-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium (2*R*,3*R*)-*O*,*O*′-dibenzoyl hydrogen tartrate viewed along the ***a***-axis. The hydrogen bonds are shown as thin lines. The hydrogen atoms not involved in the hydrogen bonding system are omitted for clarity.

parameters are virtually identical; the variations are as expected for structures measured at 122 and 296 K. With the similarity in the hydrogen bonds the difference between the two modifications must have its origin in weaker interactions. An inspection of the packing diagrams in Figs. 3 and 4 shows that, besides the hydrogen bonds that connect the ion pairs to form a sheet parallel to the ***a*** and ***b*** directions, there are interactions between the aromatic groups from different sheets. In the orthorhombic modification these interactions are between ion

Table 6. Hydrogen bonds for (*S*)-*N*-(2'-hydroxyethyl)-2-phenyl-2-hydroxyethylammonium (2*R*,3*R*)-*O*,*O*'-dibenzoyl hydrogen tartrate.

D–H · · · A	D · · · A/Å	D–H · · · A/°	H · · · A/Å
Orthorhombic modification			
N1–H1N · · · O10	2.875(2)	103(2)	2.52(2)
N1–H1N · · · O12[a]	2.815(2)	159(2)	1.91(3)
N1–H2N · · · O13	2.671(2)	107(2)	2.27(3)
N1–H2N · · · O21[b]	2.955(2)	143(2)	2.19(3)
O10–H010 · · · O41	2.676(2)	162(3)	1.87(4)
O13–H013 · · · O10[c]	2.658(2)	155(3)	1.79(4)
O11–H11 · · · O42[d]	2.478(2)	170(3)	1.56(4)
Monoclinic modification			
N1B–H1NB · · · O10B	2.845(7)	112	2.4
N1B–H1NB · · · O12A[a]	2.794(6)	148	2.0
N1B–H2NB · · · O13B	2.722(7)	109	2.3
N1B–H2NB · · · O21A[e]	2.953(6)	138	2.2
O10B–H01B · · · O41A	2.670(6)	171	1.8
O13B–H03B · · · O10B[f]	2.626(6)	156	1.6
O11A–H11A · · · O42A[d]	2.504(6)		
N1D–H1ND · · · O10D	2.895(7)	104	2.6
N1D–H1ND · · · O12C[a]	2.802(6)	162	2.0
N1D–H2ND · · · O13D	2.635(7)	108	2.2
N1D–H2ND · · · O21C[g]	2.958(7)	140	2.2
O10D–H01D · · · O41C	2.670(6)	168	1.7
O13D–H03D · · · O10D[h]	2.679(6)	154	1.8
O11C–H11C · · · O42C[d]	2.444(6)	153	1.6

[a] $1+x, y, z$. [b] $1-x, 0.5+y, 1.5-z$. [c] $2-x, 0.5+y, 1.5-z$. [d] $x-1, y, z$. [e] $1-x, 0.5+y, 1-z$. [f] $2-x, 0.5+y, 1-z$. [g] $1-x, 0.5+y, -z$. [h] $2-x, 0.5+y, -z$.

pairs related by the two-fold screw axis parallel to the *c* axis.

The pseudo-translational symmetry of *c*/2 also gives rise to the intersheet interactions in the monoclinic modification. The dibenzoyl hydrogen tartrate ions almost possess the symmetry of a two-fold axis parallel to the *c*-axis. This explains that the anions occupy the almost identical positions in both modifications, leading to identical interactions between the phenyl groups of the anions in the two modifications as shown in Fig. 5. The significant difference between the crystal packings is associated with the cations, which are found in a different orientation in every other layer.

These structural differences must correspond to very small differences in the free energy of the two modifications, and could explain why a metastable monoclinic modification was precipitated during the initial preparation. The relation between these two polymorphic

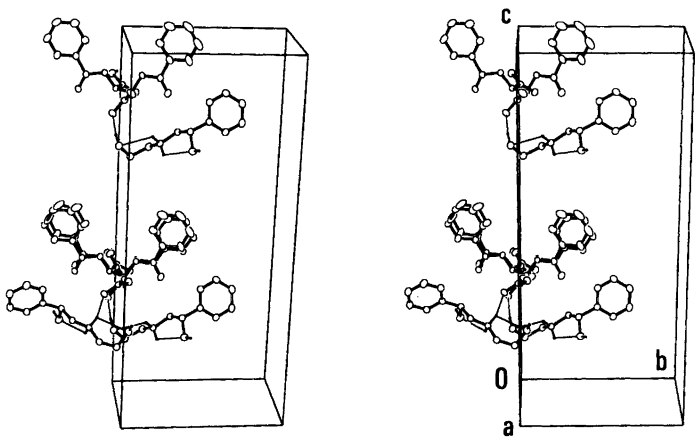

Fig. 5. Stereo pair[12] illustrating the similarity of the packing in the orthorhombic and monoclinic modification. The molecules drawn with solid bonds are related by a two-fold screw axes parallel to the *c*-axis. The molecules drawn with open bonds are generated by translation of ca. 0.5 along the *c*-axis. The two anions are superimposable except for the carboxylic acid/carboxylate groups.

modifications resembles those described for the orthorhombic and monoclinic modifications of (*S*)-1-phenylethylammonium (*S*)-mandelate.[16]

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