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trans-(2*R*,5*R*)-2,5-Dimethylpyrrolidinium (*S*)-Mandelate at 238 K

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Abstract. $C_6H_{14}N^+.C_8H_7O_3^-$, $M_r = 251{\cdot}33$, triclinic, $P\bar{1}$, $Z = 1$, $F(000) = 272$, at 238 K, $a = 7{\cdot}610\ (4)$, $b = 8{\cdot}325\ (4)$, $c = 5{\cdot}863\ (4)$ Å, $\alpha = 96{\cdot}58\ (5)$, $\beta = 102{\cdot}58\ (5)$, $\gamma = 78{\cdot}90\ (5)°$, $V = 354{\cdot}7\ (8)$ Å^3, $D_x = 1{\cdot}18$, $D_m = 1{\cdot}15$ Mg m^{-3} (measured at 296 K, by flotation in a carbon tetrachloride/cyclohexane mixture). Full-matrix least-squares refinement of 795 reflections resulted in a final conventional R index of 0·038. The absolute configuration of the (−)-*trans*-2,5-dimethylpyrrolidine moiety is 2*R*,5*R*.

Introduction. Single crystals of $C_{14}H_{21}NO_3$ formed as clear tablets from a dichloromethane solution upon standing at room temperature. The specimen crystal used to collect the intensity data was of dimensions 0·3 × 0·1 × 0·1 mm. Intensity data were collected using a Syntex $P2_1$ automated four-circle diffractometer and graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å. The data crystal was kept at 238 K with a Syntex LT-1 low-temperature inert-gas flow system (N_2). Intensity data were measured by the ω-scan technique, with ω-scan rate variable from 1·5 to 5·0° min^{-1}. Each reflection was scanned symmetrically over 1·0° in ω about the $K\bar{\alpha}$ maximum and background offset ±1·0° in ω from the $K\bar{\alpha}$ maximum. Four check reflections were remeasured after every 96 reflections. An analysis of check reflections (Henslee & Davis, 1975) indicated no significant change from the initial intensities during the 22·5 h data-collection period. Usual corrections and standard-deviation assignments to the data were as detailed elsewhere (Riley & Davis, 1975); absorption corrections ($\mu = 0{\cdot}088$ mm^{-1}) were not applied; the p factor was set at 0·05. Of 925 reflections measured in the range $4° \le 2\theta \le 45°$, only 795 with $I_o \ge 1{\cdot}5\sigma(I_o)$ were used in the ensuing solution and refinement of the structure.

The structure was solved by direct phasing methods, using the *MULTAN* program package (Main, Woolfson, Declercq & Germain, 1974). Full-matrix least-squares refinement of all non-hydrogen atoms, initially isotropic and then anisotropic, resulted in convergence. A difference map at this stage yielded the locations of all H atoms, which were included isotropically in later cycles of refinement. At full convergence, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0{\cdot}038$ and $R_w = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2} = 0{\cdot}039$. The function minimized was $(\sum w||F_o| - |F_c||^2)$, where the weights w are $1/\sigma(|F_o|)^2$, the reciprocal square of the standard deviation of each observation $|F_o|$. Neutral-atom scattering factors for O, N, C (*International Tables for X-ray Crystallography*, 1974) and H (Stewart, Davidson & Simpson, 1965) were used. In the final cycle of least-squares refinement, no non-hydrogen parameter shifted by more than 0·12 of its e.s.d., and no H parameter by more than 0·25 of its e.s.d. The largest peaks on a final difference map were about 0·15 e Å^{-3}.

Final atomic fractional coordinates, with estimated standard deviations as obtained from the inverse matrix, are presented in Table 1.†

Discussion. *trans*-2,5-Dimethylpyrrolidine, prepared by catalytic reduction (Overberger, Palmer, Marks & Byrd, 1955) of the *N*-aminopyrrolidine (Dervan & Uyehara, 1976) and resolved *via* the salts of mandelic acid, has been studied extensively. The present work has been undertaken to determine the absolute configuration of (−)-*trans*-2,5-dimethylpyrrolidine, which

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† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34746 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic fractional coordinates for trans-(2R,5R)-dimethylpyrrolidinium (S)-mandelate*

The atomic-numbering scheme is indicated in Fig. 1; the number of a H corresponds to that of the C, N, or O atom to which it is bound. Numbers in parentheses are estimated standard deviations in the units of the least significant digits for the corresponding parameters. Atomic fractional coordinates of C(1) were held constant in order to define the origin of the space group, *P*1.

	x	*y*	*z*
C(1)	0·4186	0·3132	0·1057
C(2)	0·3309 (11)	0·3676 (8)	−0·1161 (11)
C(3)	0·1525 (12)	0·3543 (9)	−0·2042 (12)
C(4)	0·0543 (11)	0·2879 (8)	−0·0789 (12)
C(5)	0·1391 (11)	0·2351 (10)	0·1407 (12)
C(6)	0·3173 (11)	0·2471 (9)	0·2284 (11)
C(7)	0·6148 (10)	0·3309 (8)	0·2084 (12)
C(8)	0·6212 (10)	0·4786 (9)	0·3854 (10)
C(9)	0·5381 (11)	0·8702 (9)	0·8758 (12)
C(10)	0·6351 (12)	0·9553 (9)	0·7370 (13)
C(11)	0·8295 (13)	0·9182 (10)	0·8540 (14)
C(12)	0·8583 (10)	0·7491 (9)	0·9400 (13)
C(13)	0·3521 (14)	0·8390 (14)	0·7586 (20)
C(14)	0·9705 (16)	0·7334 (15)	1·1862 (16)
N	0·6693 (9)	0·7142 (7)	0·9224 (11)
O(1)	0·7134 (9)	0·1873 (7)	0·3165 (10)
O(2)	0·5911 (9)	0·6191 (7)	0·3150 (10)
O(3)	0·6514 (9)	0·4483 (7)	0·5974 (9)
H(2)	0·395 (8)	0·408 (7)	−0·193 (10)
H(3)	0·087 (10)	0·386 (9)	−0·362 (14)
H(4)	−0·078 (8)	0·272 (6)	−0·148 (9)
H(5)	0·067 (9)	0·182 (8)	0·210 (11)
H(6)	0·386 (8)	0·212 (6)	0·368 (10)
H(7)	0·670 (6)	0·354 (5)	0·095 (8)
H(9)	0·541 (8)	0·916 (7)	1·014 (12)
H(10*a*)	0·610 (8)	0·901 (7)	0·581 (11)
H(10*b*)	0·590 (7)	1·066 (8)	0·721 (10)
H(11*a*)	0·886 (12)	0·995 (10)	0·991 (15)
H(11*b*)	0·932 (12)	0·922 (11)	0·772 (15)
H(12)	0·914 (6)	0·669 (6)	0·843 (9)
H(13*a*)	0·285 (9)	0·782 (7)	0·840 (10)
H(13*b*)	0·265 (11)	0·951 (10)	0·727 (12)
H(13*c*)	0·361 (12)	0·770 (12)	0·604 (18)
H(14*a*)	0·981 (10)	0·620 (9)	1·214 (12)
H(14*b*)	1·117 (12)	0·765 (9)	1·187 (13)
H(14*c*)	0·909 (7)	0·822 (7)	1·278 (9)
H(N1)	0·646 (12)	0·653 (10)	1·012 (16)
H(N2)	0·638 (10)	0·631 (9)	0·815 (15)
H(O)	0·711 (11)	0·216 (9)	0·467 (15)

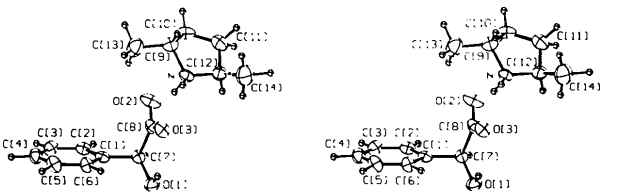

Fig. 1. A stereoview of *trans*-(2*R*,5*R*)-dimethylpyrrolidinium (*S*)-mandelate, illustrating the atomic-numbering scheme and molecular chirality. For non-hydrogen atoms, thermal ellipsoids are of 40% probability; for H atoms, spheres are of radius 0·1 Å.

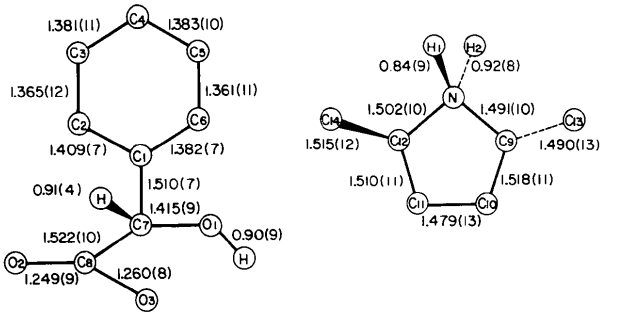

Fig. 2. Bond lengths (Å). Numbers in parentheses are the estimated standard deviations in the last digits shown. For clarity, the H atoms attached to C atoms are omitted, except for H(7) on C(7), the mandelate chiral center.

was assumed to be 2*R*,5*R* in an asymmetric induction study (Whitesell & Felman, 1977). A single-crystal X-ray diffraction study of the salt of (−)-*trans*-2,5-dimethylpyrrolidine and (+)-mandelic acid allows such an assignment in a relative way. The salt contains both the chiral amine and the chiral acid groups. The configuration of one chiral center is determined provided that the other is known. The structure refinement results in coordinates which would describe the salt as either 2*R*,5*R* amine/*S* acid or 2*S*,5*S* amine/*R* acid.

Many studies have been carried out on the chirality of mandelic acid. A comprehensive summary (Klyne & Buckingham, 1974) of the stereochemistry related to mandelic acid indicates an *S* configuration of (+)-mandelic acid. The *S* acid thereby determines the absolute configuration of (−)-*trans*-2,5-dimethylpyrrolidine to be 2*R*,5*R*.

Fig. 1 represents the determined stereochemistry and the atomic-numbering scheme. Figs. 2 and 3 give bond distances and bond angles for the non-hydrogen atoms. Although not crystallographically required to do so, the amine portion of the structure exhibits virtual C_2 symmetry: *e.g.* chemically equivalent non-hydrogen bond lengths agree within two e.s.d.'s, while chemically equivalent non-hydrogen bond angles differ by no more than 3°. The C—C and C—N bond lengths of the amine portion are normal, with the possible exception of C(10)—C(11), which appears somewhat short. The N atom has tetrahedral geometry as revealed by the bond angles in Fig. 3, consistent with sp^3 hybridization. The acid moiety exhibits no abnormalities in the bond distances and angles. The carboxyl group forms a dihedral angle of 105·2° with the phenyl ring. This angle is 100·0° in the structure of (±)-mandelic acid (Wei & Ward, 1977).

The crystal structure is comprised of (−)-*trans*-2,5-dimethylpyrrolidinium cations and (+)-mandelate anions, linked by hydrogen bonds between carboxyl O atoms and pyrrolidinium H atoms to form an infinite chain of ions which extends along the *c* axis. Hydrogen-bonding parameters for the N—H(N1)···O(2) system are N···O(2) = 2·73 (1), N—H(N1) = 0·84 (10), H(N1)···O(2) = 1·97 (10) Å, and the angle

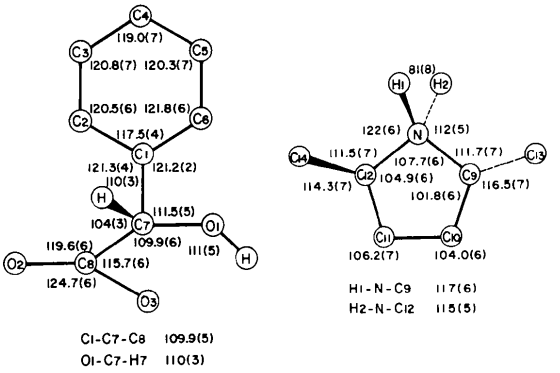

Fig. 3. Bond angles (°). Numbers in parentheses are the estimated standard deviations in the last digits shown. For clarity, the H atoms attached to C atoms are omitted, except for H(7) on C(7), the mandelate chiral center.

N–H(N1)···O(2) = 150 (3)°; those for N–H(N2)···O(3) are 2·75 (1), 0·92 (10), 1·87 (10) Å, and 163 (3)°, correspondingly. Since both observed N···O distances are smaller than the sum of the van der Waals radii (Bondi, 1964), and since both observed N–H···O angles are very favorable, the N–H···O interactions are strong. A third possible hydrogen bond is in the O(1)–H(O)···O(3) system, whose geometrical descriptions are O(1)···O(3) = 2·60 (1), O(1)–H(O) = 0·90 (9), H(O)···O(3) = 1·91 (10) Å, and the angle O(1)–H(O)···O(3) = 123 (3)°. Atom O(3) is therefore involved in two hydrogen bonds, an interionic one to N–H(2) as part of the infinite hydrogen-bonding chain, and an intraionic one to O(1)–H(O), thereby forming the five membered ring $\overline{\text{C(7)–O(1)–H(O)···O(3)–C(8)}}$. This ring formation may be regarded as a weak interaction which restricts the hydroxyl H position in the crystalline state.

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trans-(2*R*,5*R*)-1-(*p*-Bromophenylsulfonyl)-2,5-dimethylpyrrolidine at 238 K

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Abstract. $C_{12}H_{16}BrNO_2S$, M_r = 318·24, orthorhombic, $P2_12_12_1$, Z = 4, $F(000)$ = 648, at 238 K, a = 11·558 (4), b = 15·390 (3), c = 7·634 (3) Å, D_x = 1·56, D_m = 1·53 Mg m^{-3} (296 K, measured by flotation in an aqueous $AgNO_3$ solution). Full-matrix least-squares refinement of 1270 reflections resulted in a final R value of 0·029. Utilization of the anomalous-dispersion effects of Br and S has allowed the direct determination of the absolute configuration of (–)-*trans*-2,5-dimethylpyrrolidine as 2*R*,5*R*.

Introduction. Single crystals of $C_{12}H_{16}BrNO_2S$ were grown by slow evaporation from a methanol solution. With an air tumbler, several large, clear prisms were ground to spheroids of diameter *ca* 0·4 mm. X-ray diffraction work was carried out with a Syntex $P2_1$

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