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## Structures of Sobrerol Enantiomers and Racemates. II. (±)-*trans*-5-Hydroxy- $\alpha,\alpha,4$ -trimethyl-3-cyclohexene-1-methanol (Racemic *trans*-Sobrerol)

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**Abstract.** C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>,  $M_r = 170.25$ , orthorhombic, *Pna*2<sub>1</sub>,  $a = 6.570$  (2),  $b = 19.031$  (4),  $c = 7.949$  (2) Å,  $V = 993.9$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.131$ ,  $D_x = 1.138$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.720$  cm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 296$  K,  $R = 0.021$  for 444 unique reflections with  $I > 3\sigma(I)$ . The molecular geometry and conformation are substantially the same as for the *trans*-sobrerol enantiomer. Homochiral molecules are linked head-to-tail via O—H···O bonds [2.755 (5) Å] forming polymer-like chains joined by O—H···O bonds [2.840 (5) Å] and C—H(*sp*<sup>3</sup>)···O contacts as in *trans*-sobrerol. Paired chains alternate in the crystal with chains of molecules of opposite chiralities, the distance being rather longer than that between paired homochiral chains in the enantiomer. The weaker interchain forces in the racemic structure explain why the crystal is more soluble in water and has a lower melting point than the enantiomer. The same intrachain interactions and hydrogen-bonding pattern account for the analogous spectroscopic properties of the enantiomer and racemic crystals.

**Introduction.** High structural analogies between the enantiomer and racemic compound of *trans*-sobrerol have been supposed to account for the similarities of their spectroscopic properties and unit-cell parameters (Bettinetti, Giordano, Fronza, Italia, Pellegata, Villa & Ventura, 1990). On the other hand, different intermolecular forces must be responsible for the different physical properties (melting point, solubility) of the two crystalline forms. In the previous study (Giuseppetti, Tadini & Bettinetti, 1992) the

crystal structure of the *laevo* enantiomer of *trans*-sobrerol was determined. In this paper we report the crystal structure determination of the racemic compound.

**Experimental.** Single crystals of the title compound obtained by recrystallization from ethanol, m.p. 404.8 K (Bettinetti *et al.*, 1990). Density measured with a helium pycnometer (Micrometric Instrument Corporation 1302/1303) 1.131 g cm<sup>-3</sup>. Prismatic crystal (0.58 × 0.18 × 0.18 mm). Philips 1100 four-circle diffractometer, graphite monochromator; 48 reflections ( $2 < \theta < 25^\circ$ ) used for measuring lattice parameters with Philips *LAT* routine.  $\omega$ - $2\theta$  scan mode, scan speed 0.05° s<sup>-1</sup>, scan width 2.0°,  $\theta$  range 2–25° (intensities negligible at  $\theta > 25^\circ$ ). Three standard reflections every 180 min, mean intensity variation 2.1%, maximum intensity variation 2.7%. 3516 reflections measured [ $-7 \leq h \leq 7$ ,  $-22 \leq k \leq 22$ ,  $l \leq 9$ ; maximum  $(\sin\theta)/\lambda = 0.59$  Å<sup>-1</sup>], 720 unique, 444 with  $I > 3\sigma(I)$ . Corrections for Lorentz-polarization and experimental absorption, between 1.001 and 1.057, following North, Phillips & Mathews (1968). Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least-squares refinement on *F*. Coordinates of H atoms calculated by geometrical considerations (*XANADU*; Roberts & Sheldrick, 1975).  $\Delta\rho$  maps showed random fluctuations between +0.14 and -0.15 e Å<sup>-3</sup>; parameters refined: anisotropic thermal parameters for non-H atoms, isotropic for H atoms; scale factor and secondary-extinction parameter [ $g = 1.4(1) \times 10^{-4}$ ] calculated

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = (1/3)\sum_i B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}$
C(1)	8829 (5)	1000 (2)	10322 (2)	3.14 (11)
C(2)	10632 (6)	1486 (2)	10635 (8)	4.83 (15)
C(3)	11677 (6)	1673 (2)	9029 (9)	4.45 (15)
C(4)	10945 (6)	1588 (1)	7513 (8)	3.99 (14)
C(5)	8840 (6)	1294 (1)	7264 (5)	3.37 (12)
C(6)	7605 (5)	1289 (2)	8877 (6)	3.28 (9)
C(7)	7583 (5)	830 (2)	11913 (6)	4.00 (10)
C(8)	5982 (7)	283 (2)	11560 (8)	5.94 (17)
C(9)	6619 (7)	1474 (2)	12728 (9)	5.34 (14)
O(10)	8974 (5)	558 (1)	13168 (5)	5.08 (10)
C(11)	12098 (9)	1762 (2)	5950 (9)	6.21 (18)
O(12)	8964 (4)	586 (1)	6633 (6)	4.41 (9)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

C(1)—C(2)	1.524 (4)	C(5)—C(6)	1.517 (5)
C(1)—C(6)	1.507 (4)	C(5)—O(12)	1.441 (3)
C(2)—C(3)	1.492 (6)	C(7)—C(1)	1.541 (4)
C(3)—C(4)	1.307 (6)	C(7)—C(8)	1.506 (4)
C(4)—C(5)	1.505 (4)	C(7)—C(9)	1.524 (5)
C(4)—C(11)	1.493 (6)	C(7)—O(10)	1.448 (4)
C(2)—C(1)—C(6)	108.6 (2)	C(4)—C(5)—O(12)	110.0 (2)
C(2)—C(1)—C(7)	114.0 (2)	C(6)—C(5)—O(12)	108.5 (2)
C(6)—C(1)—C(7)	114.8 (2)	C(5)—C(6)—C(1)	111.2 (2)
C(1)—C(2)—C(3)	111.2 (3)	C(1)—C(7)—C(8)	111.3 (2)
C(2)—C(3)—C(4)	126.1 (3)	C(1)—C(7)—C(9)	113.6 (2)
C(3)—C(4)—C(5)	120.4 (3)	C(1)—C(7)—O(10)	107.8 (2)
C(3)—C(4)—C(11)	123.6 (3)	C(8)—C(7)—C(9)	110.2 (3)
C(5)—C(4)—C(11)	116.1 (3)	C(8)—C(7)—O(10)	108.8 (2)
C(4)—C(5)—C(6)	112.5 (3)	C(9)—C(7)—O(10)	104.9 (3)

Table 3. Hydrogen-bonding and intermolecular-contact geometry ( $\text{\AA}$ ,  $^\circ$ )

Donor	Acceptor	R—H	R...R'	H...R'	R—H...R'
O(10)—H(26)...	O(12)	0.81 (3)	2.840 (5)	2.04 (3)	172 (2)
		[0.86 (3)]	2.843 (4)	2.01 (3)	165 (2)]*
O(12)—H(30)...	O(10 <sup>ii</sup> )	0.81 (3)	2.755 (5)	1.97 (3)	165 (3)
		[0.77 (2)]	2.758 (4)	1.99 (2)	171 (2)]*
C(1)—H(13)...	O(12)	0.93 (3)	3.507 (4)	2.77 (3)	137 (2)
		[0.99 (2)]	3.480 (4)	2.76 (2)	130 (2)]*
C(1)—H(13)...	O(10 <sup>ii</sup> )	0.93 (3)	3.716 (4)	2.82 (3)	163 (2)
		[0.99 (2)]	3.676 (4)	2.70 (2)	166 (2)]*

Symmetry code: (i)  $-x+2, -y, z+\frac{1}{2}$ ; (ii)  $x, y, z-1$  [(i)  $-x+\frac{1}{2}, y-\frac{1}{2}, -z+1$ ; (ii)  $x, y+1, z$ ].\*

\* Corresponding values found in the structure of the *trans*-sobrerol enantiomer (Giuseppetti *et al.*, 1992).

from the anisotropic coefficients following Coppens & Hamilton (1970). Final value of  $R_{\text{obs}} = 0.021$ ,  $R_{\text{all}} = 0.049$ , unit weights,  $S = 0.279$ . Maximum  $\Delta/\sigma = 0.058$  in the last cycle of refinement. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). A locally modified version of *ORFLS* (Busing, Martin & Levy, 1962) and the program *PARST* (Nardelli, 1983) were used. Fig. 1 was drawn with *ORTEPII* (Johnson, 1976).

**Discussion.** Final atomic coordinates\* are listed in Table 1. The interatomic bond distances and angles (Table 2 and Fig. 1), and the geometry of the cyclohexene ring are very close to those found for the enantiomer (Giuseppetti *et al.*, 1992). Another common feature is the very short C(2)—C(9) [3.118 (5)  $\text{\AA}$ ] and C(6)—C(8) [3.058 (5)  $\text{\AA}$ ] distances, indicating a considerable crowding around the 2-hydroxyisopropyl group, which probably allows O(10) to participate more effectively in hydrogen bonding.

Hydrogen bonds and contacts are shown in Table 3. The analogies in the nature and strength of the intermolecular interactions in the two crystals are evident. This agrees with the very close unit-cell

\* Lists of structure factors, anisotropic temperature factors for non-H atoms, refined H-atom coordinates, interatomic bond distances and angles involving H atoms, and parameters describing the geometry of the cyclohexene ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54670 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0281]

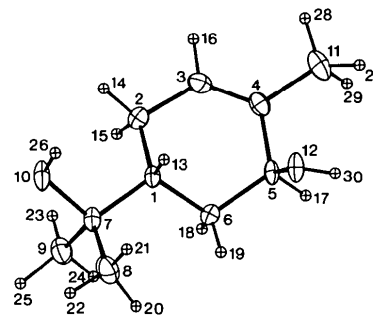


Fig. 1. ORTEPII (Johnson, 1976) drawing of the racemic *trans*-sobrerol molecule with 30% probability ellipsoids.

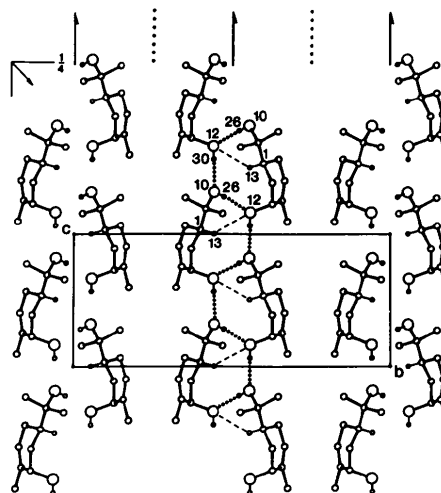


Fig. 2. Molecular packing along the *a* axis in the crystal of racemic *trans*-sobrerol.

parameters, and accounts for the similar spectroscopic properties (Bettinetti *et al.*, 1990). The molecular packing in the crystal of the title compound is illustrated in Fig. 2. Homochiral molecules are linked head-to-tail *via* O(12)—H(30)⋯O(10) bonds [2.755 (5) Å] forming polymer-like chains normal to **b**. Parallel chains of homochiral molecules are joined by hydrogen bonds O(10)—H(26)⋯O(12) [2.840 (5) Å], complemented by C(1)—H(13)⋯O(12) [3.507 (4) Å] contacts (Berkovitch-Yellin & Leisero-witz, 1984), while C(1)—H(13)⋯O(10) interactions [3.716 (4) Å] lie within the limits of the van der Waals radii. A similar situation is found in the molecular packing of the enantiomer. Paired chains alternate in the crystal lattice with analogous chains of molecules of the opposite chirality, with distances between equivalent atoms in the 4.4–7.4 Å range. This is considerably longer than the 4–5 Å range found in the enantiomer; the distance between the centres of cyclohexene rings of the title compound is 5.60 Å (4.32 Å in the enantiomer crystal). These weaker interchain forces are consistent with the lower melting point (404.8 *versus* 423.8 K) and the higher solubility (16.8 *versus* 11.3 g L<sup>-1</sup> in water at 398 K).

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## Structures of Partially Deuterated Sodium Trihydrogen Dimalonate and Sodium Hydrogen Malonate (a Reinvestigation) at 120 K

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**Abstract.** (1) Na<sup>+</sup>.C<sub>3</sub>(H,D)H<sub>2</sub>O<sub>4</sub><sup>-</sup>.C<sub>3</sub>(H,D)<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, *M<sub>r</sub>* = 230.11 (undeuterated), orthorhombic, *Pnma*, *a* = 8.484 (2), *b* = 6.859 (2), *c* = 14.950 (5) Å, *V* = 870.0 (7) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.757 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 1.951 cm<sup>-1</sup>, *F*(000) = 472, *T* = 120 K, *R* = 0.031 for 1064 observed reflections. (2) Na<sup>+</sup>.C<sub>3</sub>H<sub>3</sub>O<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 126.04, monoclinic, *P2<sub>1</sub>/c*, *a* = 6.671 (2), *b* = 7.390 (3), *c* = 9.359 (4) Å, β = 100.49 (3)°, *V* = 453.7 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.845 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 2.363 cm<sup>-1</sup>, *F*(000) = 256, *T* = 120 K, *R* = 0.025 for 1439 observed reflections. Partially deuterated sodium trihydrogen dimalonate is a superacid salt containing one malonic acid molecule and one

hydrogen malonate ion. Three different asymmetric hydrogen bonds occur in this compound. The malonic acid molecule contains a short intramolecular hydrogen bond of length 2.532 (2) Å. One short [2.548 (2) Å] and one long [2.738 (2) Å] intermolecular hydrogen bond connect the malonic acid molecule and the hydrogen malonate ion forming infinite chains in the structure. A comparison is made with the crystal structure of sodium hydrogen malonate where the hydrogen malonate ions are connected by short asymmetric hydrogen bonds of length 2.5546 (9) Å forming infinite chains in the structure. In both compounds the Na ions are octahedrally coordinated by O atoms.