Fig. 1. A *PLUTO* diagram of the title molecule with atom-numbering scheme.

diagram of the title compound with the atomic numbering scheme is shown in Fig. 1. The *A*, *B* and *C* rings adopt normal chair conformations with average endocyclic absolute torsion angles of 55.2, 54.7 and 55.4°, respectively. The *D* ring adopts a 14α-envelope conformation with the asymmetry parameters $\Delta C_s(13) = 23.8$ (32.5), $\Delta C_s(14) = 4.2$ (1.4), $\Delta C_2(13–14) = 13.4$ (22.7), the values in parentheses being the ideal values for a 14α-envelope conformation (Duax & Norton, 1975). The X-ray structure of the title molecule shows that all the ring junctions adopt a *trans* configuration [H(5)—C(5)—C(10)—C(19) = 178.3 (4), H(8)—C(8)—C(9)—H(9) = 173.8 (4), C(18)—C(13)—C(14)—O(14) = −176.1 (4)°]. The progesterone side-chain orientation is normally restricted to a region over the *D* ring; the torsion angle C(16)—C(17)—C(20)—O(20) in 84 structures having a ketone group at C(20) is observed to be between 0 and −41°, *i.e.* (−)synperiplanar to the C(16)—C(17) bond (Duax, Griffin,

Rohrer & Weeks, 1980). In this structure, the carbonyl at C(20) is antiperiplanar to the unsaturated C(16)—C(17) bond [C(16)—C(17)—C(20)—O(20) = 164.6 (6)°] as has been observed in four other 16-en-20-one structures (Khazheeva, Simonov, Kamernitskii, Pavlova-Grishina & Skorova, 1982; Duax, Langs, Strong & Osawa, 1979; Surcouf, 1979; Duax, Weeks & Strong, 1979). The molecules are stabilized in the crystal lattice by hydrogen bonding [O(3)⋯O(20) = 2.879, O(3)—H(O3) = 0.813, H(O3)⋯O(20) = 2.110 Å, O(3)—H(O3)⋯O(20) = 161.01°; O(7)⋯O(14) = 2.612 Å].

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Structures of Sobrerol Enantiomers and Racemates. III. (±)-*cis*-5-Hydroxy-α,α,4-trimethyl-3-cyclohexene-1-methanol (Racemic *cis*-Sobrerol)

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Abstract. $C_{10}H_{18}O_2$, $M_r = 170.25$, monoclinic, $P2_1/c$, $a = 16.955$ (1), $b = 9.313$ (1), $c = 13.380$ (1) Å, $\beta = 111.44$ (1)°, $V = 1966.5$ (3) Å^3, $Z = 8$, $D_m = 1.148$, $D_x = 1.150$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.73$ cm^{-1}, $F(000) = 752$, $T = 296$ K, $R = 0.026$ for 1318 unique reflections with $I > 3\sigma(I)$. The asymmetric unit of the crystal contains two molecules joined by O—H⋯O [2.839 (2) Å] hydrogen bonds and C—H⋯O [3.432 (3) Å] weak contacts. Enantiomorphic molecules connected by O—H⋯O [2.810 (2)

and 2.843 (2) Å] hydrogen bonds are arranged in stacked pairs. Interlinking between pairs via O—H···O [2.894 (2) Å] hydrogen bonds and C—H···O [3.454 (3) Å] weak contacts produces a waved network throughout the crystal lattice. The difference in stability of the cis- and trans-sobrerol racemic compounds is accounted for in terms of their crystal structures.

Introduction. In previous articles the crystal structures of trans-sobrerol as both laevo enantiomer (Giuseppetti, Tadini & Bettinetti, 1992a) and racemic compound (Giuseppetti, Tadini & Bettinetti, 1992b) were solved. We thought it of interest to extend the study to sobrerol crystals of cis configuration, with the aim of gaining information on both the geometry and molecular packing of diastereoisomeric molecules and of explaining the differences in their physical–chemical properties in terms of their crystal structures. The present paper deals with the structure of the polymorph of the cis-sobrerol racemic compound available as a single crystal (Bettinetti, Giordano, Fronza, Italia, Pellegata, Villa & Ventura, 1990).

Experimental. Single crystals of the title compound obtained by recrystallization from water (low-melting polymorph, m.p. 370.5 K) (Bettinetti et al., 1990). Density obtained from direct volume and mass measurements. Prismatic crystal (0.35 × 0.32 × 0.21 mm). Philips PW1100 four-circle diffractometer, graphite monochromator; 48 reflections ($2 < \theta < 20°$) used for measuring lattice parameters with Philips LAT routine. ω–2θ scan mode, scan speed 0.05° s^{-1}, scan width 2.0°, θ range 2–20° (intensities negligible at $\theta > 20°$). Three standard reflections every 180 min, mean intensity variation 1.4%, max. intensity variation 2.6%. 3665 reflections measured [$-15 \le h \le 15$, $-8 \le k \le 8$, $0 \le l \le 12$; max. $(\sin\theta)/\lambda = 0.48$ Å^{-1}], 1386 unique, 1318 with $I > 3\sigma(I)$. Corrections for Lorentz–polarization and experimental absorption, range of transmission factors from 1.002 to 1.036, following North, Phillips & Mathews (1968). Structure solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least-squares refinement on F. Coordinates of H atoms calculated by geometrical considerations (XANADU; Roberts & Sheldrick, 1979), confirmed by a final ΔF synthesis, and included in the last refinement. $\Delta\rho$ maps showed random fluctuations between +0.15 and −0.16 e Å^{-3}. Parameters refined: anisotropic non-H atoms, isotropic H atoms; scale factor and secondary-extinction parameter [$g = 1.04\ (2) \times 10^{-4}$] calculated from the anisotropic coefficients following Coppens & Hamilton (1970). Final value of $R_{obs} = 0.026$, $R_{all} = 0.046$, unit weights, $S = 0.565$. Max.

$(\Delta/\sigma) = 0.148$ in 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, 1963) 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.* Two molecules in the asymmetric unit are linked by an O(10)—H(38)···O(24) hydrogen bond [2.839 (2) Å]. A C(8)—H(34)···O(24) [3.432 (3) Å] weak contact (Berkovitch-Yellin & Leiserowitz, 1984) also participates in the interaction between the molecules (Fig. 1). The cyclohexene ring takes on the most stable half-chair conformation, with an equatorial 1-hydroxy-1-methylethyl group and a pseudo-equatorial hydroxy substituent. The interatomic bond distances and angles (Table 2) and the geometry of the cyclohexene rings are very close to those found for the trans-sobrerol racemic compound (Giuseppetti et al., 1992). Intermolecular interactions (Table 3) in the two racemic compounds are also similar. The molecular packing in the crystal of the title compound is more complex (Fig. 2). The enantiomorphic molecules, connected by O(24)—H(60)···O(20) [2.810 (2) Å] and O(12)—H(42)···O(10) [2.843 (2) Å] hydrogen bonds, are arranged in stacked pairs. Interlinking between pairs occurs via
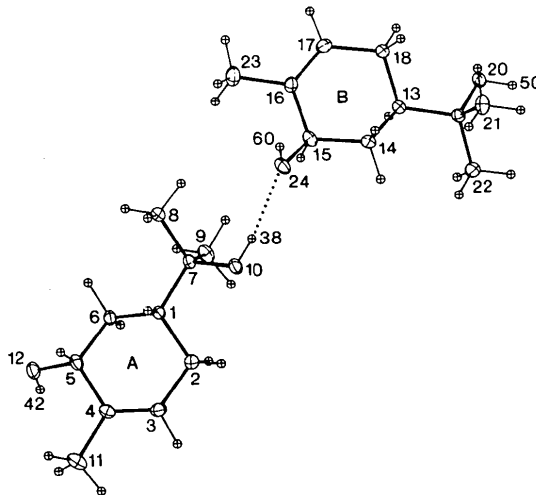

Fig. 1. ORTEPII drawing of the racemic cis-sobrerol molecule with 30% probability ellipsoids.

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

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	480 (1)	1076 (2)	3224 (2)	2.41 (7)
C(2)	649 (1)	1347 (3)	2199 (2)	3.48 (8)
C(3)	−159 (1)	1386 (2)	1230 (2)	3.47 (8)
C(4)	−928 (1)	1539 (2)	1251 (2)	3.07 (8)
C(5)	−1052 (1)	1700 (2)	2307 (2)	2.99 (7)
C(6)	−236 (1)	2069 (3)	3225 (2)	2.75 (7)
C(7)	1269 (1)	1145 (2)	4255 (2)	2.60 (7)
C(8)	1091 (2)	547 (3)	5206 (2)	3.71 (8)
C(9)	1640 (2)	2645 (3)	4502 (2)	4.03 (8)
O(10)	1881 (1)	214 (2)	4063 (1)	3.25 (5)
C(11)	−1712 (2)	1490 (3)	252 (2)	4.45 (9)
O(12)	−1701 (1)	2736 (2)	2243 (1)	3.81 (5)
C(13)	5424 (1)	1462 (2)	7313 (2)	2.49 (7)
C(14)	4704 (1)	566 (3)	6554 (2)	2.89 (7)
C(15)	3869 (1)	896 (2)	6686 (2)	3.01 (8)
C(16)	3948 (1)	962 (2)	7839 (2)	2.96 (8)
C(17)	4703 (1)	1045 (3)	8614 (2)	3.50 (8)
C(18)	5532 (1)	1078 (3)	8458 (2)	3.48 (8)
C(19)	6246 (1)	1380 (2)	7086 (2)	2.57 (7)
O(20)	6842 (1)	2298 (1)	7883 (1)	3.12 (5)
C(21)	6608 (2)	−123 (3)	7197 (3)	4.14 (9)
C(22)	6126 (1)	2002 (3)	5986 (2)	3.76 (8)
C(23)	3140 (2)	994 (4)	8064 (3)	4.46 (9)
O(24)	3228 (1)	−112 (2)	6075 (1)	3.53 (5)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Molecule A		Molecule B	
C(1)—C(2)	1.521 (3)	C(13)—C(18)	1.516 (3)
C(1)—C(6)	1.526 (3)	C(13)—C(14)	1.521 (3)
C(1)—C(7)	1.533 (3)	C(13)—C(19)	1.533 (3)
C(2)—C(3)	1.503 (3)	C(17)—C(18)	1.496 (3)
C(3)—C(4)	1.321 (3)	C(16)—C(17)	1.322 (3)
C(4)—C(5)	1.510 (3)	C(15)—C(16)	1.500 (3)
C(4)—C(11)	1.503 (3)	C(16)—C(23)	1.506 (3)
C(5)—C(6)	1.516 (3)	C(14)—C(15)	1.520 (3)
C(5)—O(12)	1.443 (2)	C(15)—O(24)	1.443 (2)
C(7)—C(8)	1.517 (3)	C(19)—C(22)	1.524 (3)
C(7)—C(9)	1.518 (3)	C(19)—C(21)	1.514 (3)
C(7)—O(10)	1.446 (2)	C(19)—O(20)	1.450 (2)
C(2)—C(1)—C(6)	108.2 (2)	C(14)—C(13)—C(18)	108.4 (2)
C(2)—C(1)—C(7)	114.5 (2)	C(18)—C(13)—C(19)	113.9 (2)
C(6)—C(1)—C(7)	113.9 (2)	C(14)—C(13)—C(19)	114.0 (2)
C(1)—C(2)—C(3)	111.6 (2)	C(13)—C(18)—C(17)	112.0 (2)
C(2)—C(3)—C(4)	125.4 (2)	C(16)—C(17)—C(18)	125.5 (2)
C(3)—C(4)—C(5)	120.4 (2)	C(15)—C(16)—C(17)	120.4 (2)
C(3)—C(4)—C(11)	122.4 (2)	C(17)—C(16)—C(23)	122.2 (2)
C(5)—C(4)—C(11)	117.1 (2)	C(15)—C(16)—C(23)	117.4 (2)
C(4)—C(5)—C(6)	112.5 (2)	C(14)—C(15)—C(16)	113.0 (2)
C(4)—C(5)—O(12)	112.1 (2)	C(16)—C(15)—O(24)	112.0 (2)
C(6)—C(5)—O(12)	110.3 (2)	C(14)—C(15)—O(24)	110.1 (2)
C(1)—C(6)—C(5)	110.6 (2)	C(13)—C(14)—C(15)	111.5 (2)
C(1)—C(7)—C(8)	111.4 (2)	C(13)—C(19)—C(22)	111.2 (2)
C(1)—C(7)—C(9)	113.0 (2)	C(13)—C(19)—C(21)	113.1 (2)
C(1)—C(7)—O(10)	105.2 (2)	C(13)—C(19)—O(20)	105.3 (2)
C(8)—C(7)—C(9)	110.4 (2)	C(21)—C(19)—C(22)	110.6 (2)
C(8)—C(7)—O(10)	107.8 (2)	C(22)—C(19)—O(20)	107.3 (2)
C(9)—C(7)—O(10)	108.8 (2)	C(21)—C(19)—O(20)	108.9 (2)

O(20)—H(50)···O(12) [2.894 (2) Å] hydrogen bonds complemented by C(22)—H(56)···O(12) [3.454 (3) Å] weak contacts, and produces a waved network throughout the crystal lattice. The intermolecular network of forces in crystals of *cis*-sobrerol exceeds,

Table 3. *Hydrogen bonding and intermolecular contact geometry* (Å, °)

D—H···A	D—H	D···A	H···A	D—H···A
O(10)—H(38)···O(24)	0.82 (2)	2.839 (2)	2.02 (1)	172 (2)
C(8)—H(34)···O(24)	0.99 (2)	3.432 (3)	2.67 (2)	134 (3)
O(24)—H(60)···O(20^{iii})	0.84 (2)	2.810 (2)	1.98 (2)	169 (2)
O(12)—H(42)···O(10^i)	0.82 (3)	2.843 (2)	2.03 (2)	171 (2)
O(20)—H(50)···O(12^{ii})	0.88 (2)	2.894 (2)	2.02 (2)	173 (2)
C(22)—H(56)···O(12^{ii})	1.00 (2)	3.454 (3)	2.71 (2)	131 (3)

Symmetry code: (i) $-x, \frac{1}{2}+y, -z+\frac{1}{2}$; (ii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.
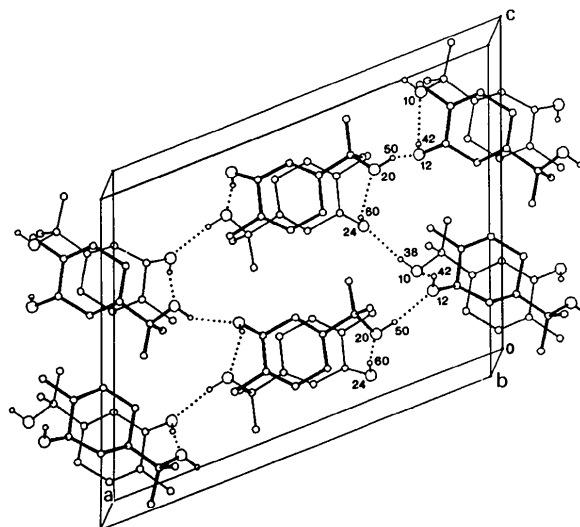
Fig. 2. Molecular packing in the crystal of racemic *cis*-sobrerol.

both qualitatively and quantitatively, that existing in the *trans*-sobrerol racemic compound (Giuseppetti *et al.*, 1992b) and can reasonably account for the higher stability of the *cis* diastereoisomer resulting from the phase diagrams (Bettinetti *et al.*, 1990).

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Structure and Conformation of 3-(Dibenzylamino)phenylacetonitrile

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Abstract. $C_{22}H_{20}N_2$, $M_r = 312.41$, orthorhombic, $P2_12_12_1$, $Z = 4$, $F(000) = 664$. For Mo $K\alpha_1$, $\lambda = 0.070930$ Å, $a = 6.021$ (1), $b = 15.989$ (4), $c = 17.906$ (5) Å, $V = 1723.8$ (7) Å^3, $D_x = 1.204$ Mg m^{-3}, $\mu = 0.0659$ mm^{-1} for 1774 measured reflections. For Cu $K\alpha_1$, $\lambda = 1.540562$ Å, $a = 6.025$ (1), $b = 15.990$ (5), $c = 17.921$ (2) Å, $V = 1726.5$ (6) Å^3, $D_x = 1.202$ Mg m^{-3}, $\mu = 0.5088$ mm^{-1} for 1942 measured reflections. The crystal structure analysis of the title compound confirms the prevailing *meta*-directing effect of nitrogen in arynic condensation reactions. The results of two analyses, carried out on data collected with Mo $K\alpha$ and Cu $K\alpha$ radiations, are in quite good agreement showing that, when the crystal sample is good, acceptable results can be obtained even with an unfavourable ratio between the number of observations and the number of refined parameters.

Introduction. As part of our study on the arynic condensation of nitrile enolates, in order to obtain starting materials for further synthesis, the condensation reaction below has been carried out (DME = 1,2-dimethoxyethane). Compound (3) is of particular interest since the benzyl groups can be removed to give the corresponding aniline which can be easily functionalized.
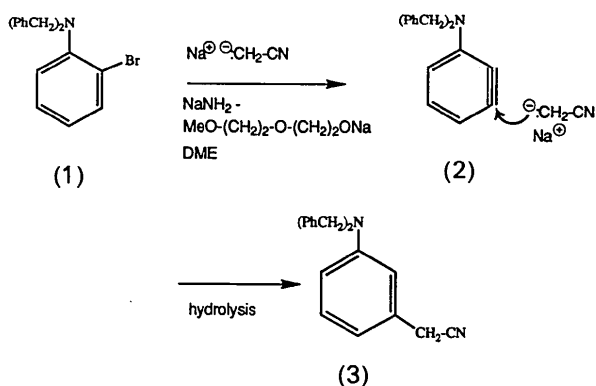
Although the prevailing *meta*-directing effect of nitrogen in arynic condensations is well established, some exceptions are known (Pansegrau, Rieker & Meyers, 1988). Moreover, it was not possible to assign the correct structure to compound (3), as even the ^{1}H and ^{13}C NMR data were not enough for this purpose. For these reasons the X-ray crystal structure analysis of this compound was carried out, by collecting the intensity data with molybdenum radiation initially, and then with copper radiation,

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