

and probably on the H atoms bonded to the nitrogens as already shown by CNDO/2 calculations on imidazolines (Carpy, Léger, Leclerc, Decker, Rouot & Wermuth, 1982).

Among the centres, those which have commonly been implicated in the interaction of α -ligands with their receptor are the quaternary N and the hydroxyphenyl ring (Pullman, Coubeils, Courrière & Gervois, 1972). We have calculated the distances D between the two nitrogens of the guanidine function and the centre π of the hydroxyphenyl ring: $N(16)-\pi = 4.40$ (1) and $N(19)-\pi = 5.12$ (1) Å and the distances H between the two nitrogens and the plane containing the ring: -1.575 (3) and 0.191 (3) Å respectively. The distance D related to N(19) is in good agreement with those found in imidazoline agonists (≈ 5 Å) but H is much smaller (~ 0.2 Å instead of ~ 1 Å). In contrast this H distance seems consistent with those found in various α -antagonists such as WB-4101 (Carpy, Colleter & Léger, 1981) and raubasine (Dubost, Léger, Goursole, Carpy & Colleter, 1983).

The crystalline cohesion is ensured by two hydrogen bonds involving the two nitrogens of the imidazoline ring and the Cl⁻ ions: $N(16)\cdots Cl(22)(2-x, 1-y, 1-z) = 3.141$ (3) Å, $H(160)\cdots Cl(22) = 2.35$ (4) Å, $N-H\cdots Cl = 139$ (3)°, $Cl(22)\cdots N(19)(x, \frac{1}{2}-y, \frac{1}{2}+z) = 3.224$ (3) Å, $Cl(22)\cdots H(190) = 2.27$ (4) Å, $Cl\cdots H-N = 167$ (3)°, by C-H \cdots O bonds and by van der Waals contacts.

The sample was kindly provided by CIBA-GEIGY Limited (Basle, Switzerland).

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Structure of (+)-2,2-Dimethoxy-2-(6-methoxy-2-naphthyl)-1-methylethyl 2-Oxo-10-bornanesulfonate, C₂₆H₃₄O₇S

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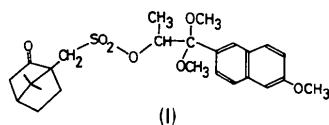
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Abstract. $M_r = 490.6$, orthorhombic, $P2_12_12_1$, $a = 10.703$ (1), $b = 29.091$ (5), $c = 8.435$ (1) Å, $V = 2626.4$ (5) Å³, $Z = 4$, $D_x = 1.24$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.41$ mm⁻¹, $F(000) = 1048$, $T = 298$ (2) K. Final $R = 0.047$ for 1916 unique observed reflections. The absolute configuration around the asymmetric C atom has been established as R .

Introduction. New methods for the synthesis of α -arylalkanoic acids by the use of 1,2-rearrangement of the aryl group have been designed to obtain biologically important substances (Tsuchihashi, Kitajima & Mitamura, 1981). Crystals of the title compound (I), a starting material of the 1,2-rearrangement reaction, have been subjected to X-ray crystal-structure analysis

in order to establish the absolute configuration around the asymmetric C atom and to elucidate the reaction mechanism, especially the stereochemical course of the reaction.



Experimental. The mixture of diastereoisomers of (I) synthesized by reacting 2-hydroxy-1-(6-methoxy-2-naphthyl)-1-propanone dimethyl acetal in pyridine with 2-oxo-10-bornanesulfonyl chloride. One of the diastereoisomers having $[\alpha]_D^{25}$ of $+32.5^\circ$ [CHCl_3 , 10.00 g dm^{-3}] was isolated by recrystallization from methanol solution (m.p. 375–378 K). Thin tabular (001) crystals, approximate dimensions $0.5 \times 0.2 \times 0.05 \text{ mm}$. Preliminary determination of lattice parameters and space group ($P2_12_12_1$ from systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd) made with a Weissenberg camera. Philips automated four-circle diffractometer, graphite monochromator, $\text{Cu K}\alpha$ radiation. Cell dimensions obtained by least-squares methods from 2θ values of 15 reflections ($38 < 2\theta < 80^\circ$). θ - 2θ scan technique, $2\theta \leq 120^\circ$ (h 0–12, k 0–32, l 0–9), scan speed 2° min^{-1} (θ). No significant variation in 3 standard reflections during data collection. 2267 independent reflections measured, 1916 intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination. Corrections for Lorentz, polarization, not for absorption. Position of S atom deduced from a Patterson map, attempts to solve structure by heavy-atom method failed; structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms using *UNICSIII* computation program system (Sakurai & Kobayashi, 1979). All H atoms located from a difference synthesis and introduced in refinement. $\sum w(|F_o| - |F_c|)^2$ minimized; weights assigned as $w = 0.25$ for $|F_o| \geq 15$ and $w = 1.0$ for $|F_o| < 15$; final $R = 0.047$, $wR = 0.037$, $S = 1.0$, 477 parameters refined. Maximum shift for x coordinate of H(C21) = 2σ . $\Delta\rho = -0.24$ – $0.24 \text{ e } \text{Å}^{-3}$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

The absolute structure was determined with reference to the known absolute configuration of (+)-camphor (2-bornanone) (Wunderlich, 1967). In order to confirm the absolute configuration, a refinement was made separately with the enantiomeric structure. It converged to $R = 0.050$ and $wR = 0.039$ and could be rejected at the 0.005 significance level by the Hamilton (1965) test.

Table 1. Positional parameters ($\times 10^4$; for S $\times 10^5$) and equivalent isotropic temperature factors (Hamilton, 1959)

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
S	84851 (14)	23895 (5)	−6461 (16)	4.0
O(1)	7272 (4)	2571 (1)	−988 (4)	5.0
O(2)	9323 (4)	2288 (1)	−1921 (4)	5.3
O(3)	8208 (3)	1932 (1)	309 (4)	3.4
O(4)	9723 (3)	994 (1)	2466 (4)	3.9
O(5)	8828 (3)	1692 (1)	3288 (4)	3.3
O(6)	7702 (4)	3552 (1)	100 (5)	6.1
O(7)	2930 (4)	−218 (1)	449 (7)	8.2
C(1)	9326 (5)	2753 (2)	702 (6)	3.6
C(2)	8574 (5)	3002 (2)	1974 (6)	3.3
C(3)	7919 (5)	3440 (2)	1440 (7)	4.6
C(4)	7650 (6)	3719 (2)	2934 (8)	5.7
C(5)	8234 (5)	3412 (2)	4245 (8)	4.8
C(6)	7395 (6)	2997 (2)	4479 (8)	4.9
C(7)	7566 (5)	2721 (2)	2887 (6)	3.8
C(8)	9384 (5)	3208 (2)	3350 (7)	3.7
C(9)	10071 (6)	2849 (2)	4290 (8)	4.7
C(10)	10334 (6)	3566 (2)	2754 (8)	5.4
C(11)	9274 (7)	1264 (2)	−833 (7)	5.8
C(12)	9198 (5)	1589 (2)	570 (6)	3.8
C(13)	8826 (5)	1339 (2)	2129 (6)	3.4
C(14)	10965 (5)	1150 (2)	2790 (8)	5.1
C(15)	8534 (6)	1535 (2)	4867 (6)	4.5
C(16)	5326 (5)	1152 (2)	1910 (6)	3.6
C(17)	6461 (5)	1359 (2)	2119 (6)	3.4
C(18)	7561 (5)	1097 (2)	1998 (6)	3.4
C(19)	7490 (5)	638 (2)	1686 (8)	5.0
C(20)	6324 (6)	427 (2)	1433 (8)	5.1
C(21)	6235 (7)	−48 (2)	1037 (13)	9.3
C(22)	5093 (7)	−237 (2)	749 (13)	9.7
C(23)	3998 (6)	23 (2)	807 (10)	6.7
C(24)	4050 (6)	476 (2)	1202 (8)	4.4
C(25)	5226 (5)	682 (2)	1519 (7)	3.8
C(26)	1798 (6)	23 (2)	439 (11)	8.4

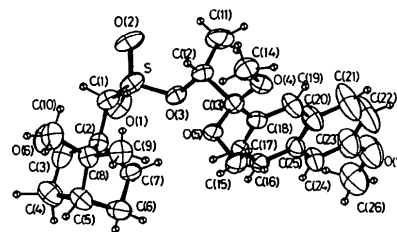


Fig. 1. An ORTEP drawing of the molecule with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0.08 Å.

Discussion. Final atomic parameters are listed in Table 1.* An ORTEP drawing (Johnson, 1965) of the molecule is shown in Fig. 1, and bond lengths and angles are given in Table 2. The absolute configuration around the asymmetric C atom C(12) is *R*. Methyl (−)- α -(6-methoxy-2-naphthyl)propionate (II) was obtained by hydrolysis of (I) under reflux with an equimolar amount of calcium carbonate in a mixture of

* Lists of structure factors, anisotropic thermal parameters, mean-square displacement tensors, H-atom coordinates, bond lengths and bond angles in the naphthyl ring and a projection of the crystal structure along c have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38674 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

S—O(1)	1.431 (4)	C(2)—C(3)	1.522 (8)
S—O(2)	1.431 (4)	C(2)—C(7)	1.557 (8)
S—O(3)	1.584 (3)	C(2)—C(8)	1.568 (8)
S—C(1)	1.795 (6)	C(3)—C(4)	1.526 (9)
O(3)—C(12)	1.472 (6)	C(4)—C(5)	1.553 (9)
O(4)—C(13)	1.418 (6)	C(5)—C(6)	1.518 (8)
O(4)—C(14)	1.431 (6)	C(5)—C(8)	1.561 (8)
O(5)—C(13)	1.418 (6)	C(6)—C(7)	1.575 (8)
O(5)—C(15)	1.443 (6)	C(8)—C(9)	1.503 (8)
O(6)—C(3)	1.199 (7)	C(8)—C(10)	1.540 (8)
O(7)—C(23)	1.375 (8)	C(11)—C(12)	1.517 (8)
O(7)—C(26)	1.400 (7)	C(12)—C(13)	1.555 (7)
C(1)—C(2)	1.524 (8)	C(13)—C(18)	1.530 (8)
O(1)—S—O(2)	119.6 (2)	C(4)—C(5)—C(8)	101.0 (5)
O(1)—S—O(3)	104.0 (2)	C(6)—C(5)—C(8)	103.1 (5)
O(1)—S—C(1)	111.4 (3)	C(5)—C(6)—C(7)	103.1 (5)
O(2)—S—O(3)	109.0 (2)	C(2)—C(7)—C(6)	103.6 (4)
O(2)—S—C(1)	106.5 (2)	C(2)—C(8)—C(5)	93.9 (4)
O(3)—S—C(1)	105.5 (2)	C(2)—C(8)—C(9)	113.3 (5)
S—O(3)—C(12)	120.7 (3)	C(2)—C(8)—C(10)	112.5 (5)
C(13)—O(4)—C(14)	116.3 (4)	C(5)—C(8)—C(9)	113.2 (5)
C(13)—O(5)—C(15)	114.0 (4)	C(5)—C(8)—C(10)	114.9 (5)
C(23)—O(7)—C(26)	117.8 (4)	C(9)—C(8)—C(10)	108.6 (5)
S—C(1)—C(2)	117.5 (4)	O(3)—C(12)—C(11)	110.1 (4)
C(1)—C(2)—C(3)	115.6 (4)	O(3)—C(12)—C(13)	105.0 (4)
C(1)—C(2)—C(7)	117.7 (5)	C(11)—C(12)—C(13)	112.5 (5)
C(1)—C(2)—C(8)	114.3 (4)	O(4)—C(13)—O(5)	111.9 (4)
C(3)—C(2)—C(7)	105.5 (4)	O(4)—C(13)—C(12)	109.1 (4)
C(3)—C(2)—C(8)	98.8 (4)	O(4)—C(13)—C(18)	106.7 (4)
C(7)—C(2)—C(8)	102.6 (4)	O(5)—C(13)—C(12)	104.1 (4)
O(6)—C(3)—C(2)	126.5 (5)	O(5)—C(13)—C(18)	112.6 (4)
O(6)—C(3)—C(4)	126.7 (5)	C(12)—C(13)—C(18)	112.4 (4)
C(2)—C(3)—C(4)	106.7 (5)	O(7)—C(23)—C(22)	114.5 (5)
C(3)—C(4)—C(5)	101.9 (5)	O(7)—C(23)—C(24)	125.6 (6)
C(4)—C(5)—C(6)	108.2 (5)		

the dihedral angle between the C(13)—O(5)—C(15) and C(13)—O(4)—C(14) planes being 87(1)°. Four intramolecular distances less than 2.9 Å are observed for the O atoms of these methoxy groups. The values of O(4)...C(15), O(4)...C(19), O(5)...O(3) and O(5)...C(14) are 2.863 (6), 2.687 (6), 2.691 (5) and 2.810 (6) Å, respectively. The naphthyl moiety is essentially planar with deviations less than 0.05 Å for each atom in the least-squares plane. The torsion angle C(24)—C(23)—O(7)—C(26) is 2(1)°. The bond angle C(24)—C(23)—O(7) of 125.6(6)° is greater than C(22)—C(23)—O(7) of 114.5(5)° because of the steric interaction between C(24) and C(26) [2.821(9) Å].

The crystal structure consists of discrete molecules separated by normal van der Waals distances.* The shortest intermolecular distance is 3.185(8) Å for O(6)...C(14)(-½+x, ½-y, -z).

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* See deposition footnote.

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water and *N,N*-dimethylformamide. 1,2-rearrangement of the 6-methoxy-2-naphthyl group took place during the course of the hydrolysis. The absolute configuration around the asymmetric C atom of (II) could be deduced as *R* based on the known absolute configuration of (+)-(*R*)-α-(6-methoxy-2-naphthyl)propionic acid (Kitajima, Mitamura, Kobayashi, Tsuchihashi, Ohba & Saito, 1982). Thus it was revealed that the inversion of the absolute configuration around the asymmetric C atom occurs with the aryl-group rearrangement.

The torsion angle O(3)—C(12)—C(13)—C(18) is 60.9(5)°. The two bulky groups of 6-methoxy-2-naphthyl [C(18)] and 2-oxo-10-bornanesulfonate [O(3)] are in a *gauche* position with respect to the C(12)—C(13) bond axis. However, there is no short contact between these groups. The two methoxy groups bonded to the C(13) atom are bent into a spiral shape,

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The Structure of *N,N'*-Hexamethylenedibenzamide, C₂₀H₂₄N₂O₂

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Abstract. $M_r = 324.43$, monoclinic, $P2_1/c$, $a = 1.247 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178 \text{ \AA}$, $\mu(\text{Cu } K\alpha) = 5.136 (2)$, $b = 5.346 (1)$, $c = 31.497 (12)$, $\beta = 0.61 \text{ mm}^{-1}$, $F(000) = 348$, $T = 295 \text{ K}$, $R = 0.044$ for 92.81 (3)°, $V = 863.8 \text{ \AA}^3$, $Z = 2$, $D_m = 1.23$, $D_x = 1219$ observed reflections. The structure of *N,N'*-

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