Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*R*)-(+)-2-Phenylpropyl *p*-Toluenesulfonate, $C_{16}H_{18}O_3S$

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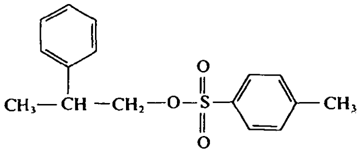
Abstract

The structure of an important precursor of a ferroelectric liquid crystal is reported. The two phenyl rings are nearly coplanar, having a dihedral angle of 5.0°, and are at a distance of 3.79 (2) Å from each other.

Comment

In connection with a project on the design and synthesis of ferroelectric liquid crystals (FLC), we required an efficient route to obtain several chiral precursors (Merlo, Gallardo, Taylor & Kroin, 1993). (*S*)-(−)-Ethyl lactate is particularly attractive as a chiral synthon as it is readily available in both enantiomeric forms with very high optical purity and, therefore, has been used in numerous applications (Seuring & Seebach, 1977). Recently, we described an efficient method for the preparation of (*R*)-(−)-*p*-(2-methylhexyl)aniline, (1), from (*S*)-(−)-ethyl lactate (Merlo & Gallardo, 1993), which is of considerable interest as a building block for liquid-crystalline materials having ferroelectric properties.

We have also found that the optical purity [illegible] the aniline enantiomeric to (1) can be ensured by using (*R*)-(+)-2-phenylpropyl *p*-toluenesulfonate (2) as a crystalline intermediate (Merlo & Gallardo, 1993). The molecular structure determination of the title compound (2) was undertaken by X-ray diffraction. The stereochemistry of



(2)

the title compound and its atomic numbering scheme are illustrated in Fig. 1, which shows the *cis* relationship between the two aromatic rings. The absolute configuration was assigned to agree with the known chirality at C(2) arising from its precursor (*R*)-(−)-*p*-(2-methylhexyl)aniline.

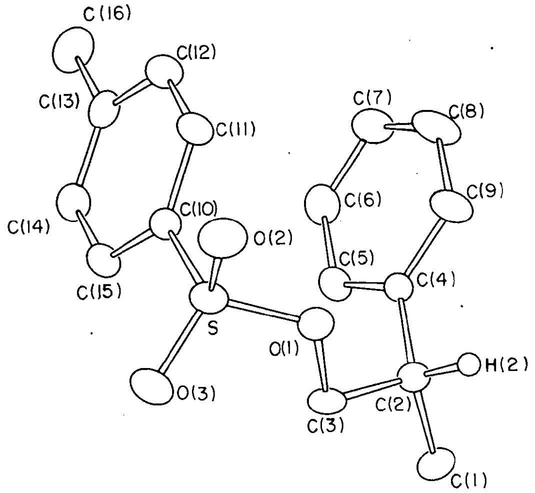


Fig. 1. Perspective view of the molecule with atomic numbering. The atom H(2) is represented by a sphere of arbitrary radius.

Experimental

(*R*)-(−)-2-Phenylpropanol (55 mmol, 7.5 g) was dissolved in dry pyridine (50 ml) and *p*-toluenesulfonyl chloride (60 mmol, 11.40 g) was added in small portions at 273 K. After 2 h at 273 K the mixture was poured onto ice and water, then extracted with chloroform. The organic solution was washed once with hydrochloric acid 10% (100 ml), twice with water (100 ml) and once with brine. After drying (sodium sulfate) and evaporation of the solvent, the product was recrystallized three times from hexane to yield (64%) (*R*)-(+)-2-phenylpropyl *p*-toluenesulfonate; $[\alpha]_D^{25} = +9.0$ (*c* 0.2, $CHCl_3$), m.p. 335 K. ^1H NMR (60 MHz, TMS, $CDCl_3$): $\delta = 1.2$ (*d*, 3H, $J = 7$ Hz, CH_3); 3.0 (*m*, 1H, CH); 4.1 (*d*, 2H, $J = 7$ Hz, CH_2); 7.3 (*s*, 5H, Ar); 7.4 (*d*, 2H, $J = 8$ Hz, Ar); 7.8 (*d*, 2H, $J = 8$ Hz, Ar). Analysis: calculated for $C_{16}H_{18}SO_3$, C 66.20, H 6.20, S 11.03%; found, C 66.23, H 6.23, S 11.07%.

Crystal data

$C_{16}H_{18}O_3S$
$M_r = 290.4$
Monoclinic
$P2_1$
$a = 5.923$ (1) Å
$b = 15.708$ (2) Å
$c = 8.421$ (2) Å
$\beta = 105.70$ (2)°
$V = 754.2$ (3) Å^3
$Z = 2$
$D_x = 1.28$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5.7\text{–}15.5°$
$\mu = 0.176$ mm^{-1}
$T = 296$ K
Irregular
0.25 × 0.18 × 0.35 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4400 measured reflections
3279 independent reflections
1977 observed reflections [$F > 6.0\sigma(F)$]

$R_{\text{int}} = 0.022$
$\theta_{\text{max}} = 29.15°$
$h = -9 \rightarrow 11$
$k = -1 \rightarrow 25$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 30 min
intensity variation: 1.5%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.065$
$S = 3.84$
1977 reflections
181 parameters
H-atom parameters not refined
$w = 3.012/[\sigma^2(F) + 0.0051F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.30$
$\Delta\rho_{\text{max}} = 0.34$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\text{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.2960 (2)	0.2625	0.4280 (1)	4.20 (4)
O(1)	0.3536 (6)	0.1652 (3)	0.4506 (4)	4.4 (1)
O(2)	0.0543 (5)	0.2676 (4)	0.4233 (5)	5.7 (2)
O(3)	0.3743 (7)	0.2946 (3)	0.2937 (4)	5.6 (2)
C(1)	0.855 (1)	0.0153 (4)	0.4783 (8)	5.5 (2)
C(2)	0.6534 (9)	0.0584 (3)	0.5320 (6)	4.1 (2)
C(3)	0.573 (1)	0.1349 (4)	0.4220 (5)	4.4 (2)
C(4)	0.7197 (9)	0.0830 (3)	0.7111 (5)	3.8 (2)
C(5)	0.911 (1)	0.1332 (4)	0.7786 (7)	4.9 (2)
C(6)	0.973 (1)	0.1560 (4)	0.9436 (7)	5.7 (2)
C(7)	0.836 (1)	0.1278 (5)	1.0425 (7)	6.2 (3)
C(8)	0.651 (1)	0.0773 (6)	0.9778 (7)	7.3 (4)
C(9)	0.587 (1)	0.0543 (5)	0.8136 (7)	5.4 (2)
C(10)	0.4639 (7)	0.3076 (3)	0.6123 (5)	3.5 (1)
C(11)	0.386 (1)	0.2997 (4)	0.7514 (7)	4.9 (2)
C(12)	0.517 (1)	0.3329 (4)	0.8994 (7)	5.2 (2)
C(13)	0.724 (1)	0.3750 (3)	0.9076 (7)	4.6 (2)
C(14)	0.7974 (9)	0.3842 (4)	0.7656 (7)	4.7 (2)
C(15)	0.6685 (8)	0.3503 (4)	0.6180 (7)	4.4 (2)
C(16)	0.872 (1)	0.4102 (5)	1.0708 (9)	6.4 (3)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—S	1.566 (4)	C(3)—O(1)	1.464 (6)
O(2)—S	1.423 (3)	C(2)—C(1)	1.543 (8)
O(3)—S	1.426 (4)	C(3)—C(2)	1.514 (8)
C(10)—S	1.751 (4)	C(4)—C(2)	1.503 (6)
O(2)—S—O(1)	104.0 (3)	C(3)—O(1)—S	118.1 (3)
O(3)—S—O(1)	109.6 (2)	C(3)—C(2)—C(1)	108.0 (4)
O(3)—S—O(2)	119.9 (3)	C(4)—C(2)—C(1)	113.2 (5)
C(10)—S—O(1)	103.5 (2)	C(4)—C(2)—C(3)	111.3 (4)
C(10)—S—O(2)	109.1 (2)	C(2)—C(3)—O(1)	107.7 (4)
C(10)—S—O(3)	109.4 (2)		

The y coordinate of S was held to fix the origin during refinement. H atoms were included at geometrically idealized positions (C—H 0.98 Å, $U = 0.0800$ Å^2); their parameters were not refined, but their coordinates were recalculated after each cycle. Most of the calculations were performed on an IBM 3090 computer at the Universidade Federal de Santa Catarina. Data collection, cell refinement and data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELX*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl *N*,*N*-Diallyl-*O*-*tert*-butyltyrosyl-α-aminoisobutyrl-α-aminoisobutyrate, $C_{28}H_{43}N_3O_5$

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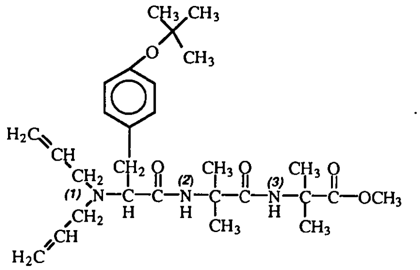
Abstract

In this N- and C-protected tripeptide the nine backbone atoms are essentially planar and fully extended except for N1 and C3′ which lie below the plane and are folded in towards it. The tyrosine side chain extends away from the opposite side of the plane. There is one $(N—H)_i\cdots(O{=}C)_i$ intramolecular hydrogen bond and a weak $(N—H)_{i+2}\cdots(O{=}C)_i$ intermolecular hydrogen bond [where (i) = 2].

Comment

N,*N*-Diallylenkephalin analogs have been shown to have activity as δ-selective opiate antagonists (Thornber *et al.*, 1986). The title compound, (I), was synthesized at the Research Triangle Institute, North Carolina, as part of a program designed to study the relative antagonist activity within this family of compounds.



(I)

The shape of the peptide backbone is defined by the following torsion angles: ψ_1 = 20.6 (6), ω_2 = −172.2 (5), φ_2 = 179.2 (5), ψ_2 = 172.2 (5), ω_3 = 176.2 (4) and φ_3 = −54.7 (6)°. The tyrosyl side chain extends away from the main peptide backbone, χ_1 = −144.1°, and is rotated about the C1β—C1γ bond such that the aromatic ring is approximately *gauche* to the plane formed by backbone atoms C1α-C3α with the angle between the two planes being 41.5°. The hydrogen-bond parameters, N···O, H···O and N—H···O are 2.566, 2.091 Å and 113.6°, respectively, for the intramolecular N2···O2 hydrogen bond, and 3.242, 2.531 Å and 139.5°, respectively, for the weak intermolecular N3···O1 hydrogen bond. There are no other intermolecular approaches less than van der Waals separations. The *tert*-butyl group on O1ζ is disordered with a ratio of 4:1 for the high to low occupancy.

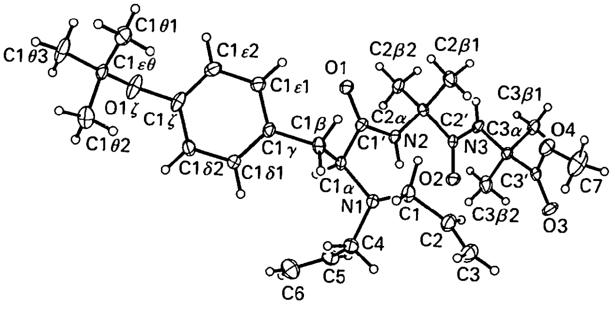


Fig. 1. Structure of the tripeptide showing 20% probability displacement ellipsoids. The disordered *tert*-butyl group on C1εθ is not shown.

Experimental

Crystal data

$C_{28}H_{43}N_3O_5$
M_r = 501.65

Cu *K*α radiation
λ = 1.54178 Å