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## Ethyl *trans*-7-Benzoyloxy-4-hydroxy-6-methoxy-1-(3,4,5-trimethoxyphenethyl)-1,2,3,4-tetrahydro-2-isoquinolinecarboxylate

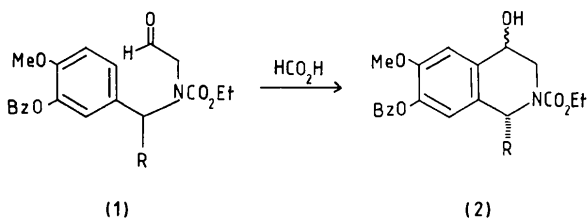
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**Abstract.**  $C_{31}H_{37}NO_8$ , triclinic,  $P\bar{1}$ ,  $a = 12.700$  (2),  $b = 12.045$  (2),  $c = 10.699$  (2) Å,  $\alpha = 107.47$  (1),  $\beta = 112.79$  (1),  $\gamma = 83.25$  (1)°,  $U = 1439.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.27$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 6.67$  mm<sup>-1</sup>. Final  $R = 0.048$  for 4027 unique diffractometer data. The structural data confirm the earlier configurational assignments and show that the solid-state conformation has the 1 and 4 substituents in pseudo-axial positions.

**Introduction.** An efficient synthesis of diastereoisomeric 4-hydroxy-1-benzyl- and 1-phenethyltetrahydroisoquinolines (2) *via* acid-catalyzed cyclization of aldehydes (1) under mild conditions has recently been reported (Elliott, Hewgill, McDonald & McKenna, 1980). Stereochemical assignments for isomers (2) were made on the basis of chemical transformations and <sup>1</sup>H NMR data. The assignments suggested that the bulky substituent at C(1) must adopt a pseudo-axial conformation. Although this can be rationalized on the basis of the steric requirements of the  $-\text{NCO}_2\text{Et}$  group, we sought a conclusive result by carrying out an X-ray diffraction analysis on the major diastereoisomer formed when  $R = 3,4,5$ -trimethoxyphenethyl.



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Intensities were measured on a Syntex  $P2_1$  four-circle diffractometer with graphite-monochromated Cu  $K\alpha$  radiation using a  $\theta$ - $2\theta$  scan technique. 5552 reflections were measured ( $3.0 \leq 2\theta \leq 130^\circ$ ) for a crystal  $0.19 \times 0.38 \times 0.11$  mm and corrected for the  $L_p$  factor, but no correction was made for absorption. The data were averaged to give 4027 unique reflections [ $F > 3\sigma(F)$ ]. Cell dimensions were derived from the angular measurements of 15 strong reflections in the range  $40 \leq 2\theta \leq 55^\circ$ .

All non-hydrogen atoms were located by multi-solution  $\sum_2$  sign expansion. H atoms were located from a difference synthesis. The structure was refined by blocked-full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for the H atoms. H atoms in geometrically similar environments were constrained to have identical temperature factors. Com-

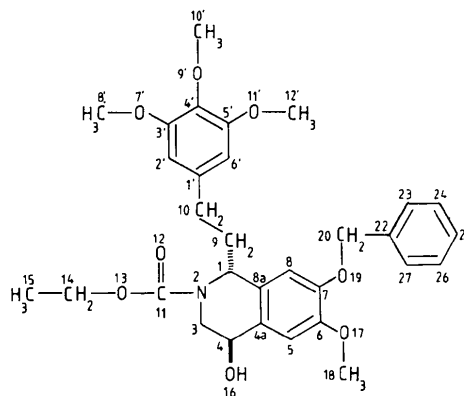


Fig. 1. A schematic diagram of the molecule with the atom labelling indicated.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic  $U$  values ( $\text{\AA}^2 \times 10^3$ )

$$U_{\text{eq}} = \frac{1}{3} \{ \sin \alpha \sin \beta \sin \gamma [U_{11} \sin \alpha / (\sin \beta \sin \gamma) + \dots + U_{12} \times (\sin 2\gamma / \sin^2 \gamma)] \}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C(1)	4426 (2)	586 (2)	1931 (2)	37 (1)
N(2)	4149 (1)	-124 (1)	2660 (2)	36 (1)
C(3)	3847 (2)	526 (2)	3866 (2)	39 (1)
C(4)	2770 (2)	1217 (2)	3398 (2)	39 (1)
C(4a)	2822 (2)	1884 (2)	2433 (2)	37 (1)
C(5)	2059 (2)	2814 (2)	2210 (2)	43 (1)
C(6)	2055 (2)	3433 (2)	1316 (2)	44 (1)
C(7)	2838 (2)	3143 (2)	633 (2)	44 (1)
C(8)	3586 (2)	2232 (2)	852 (2)	43 (1)
C(8a)	3582 (2)	1589 (2)	1750 (2)	37 (1)
C(9)	5660 (2)	1030 (2)	2699 (2)	43 (1)
C(10)	6568 (2)	71 (2)	2828 (2)	42 (1)
C(11)	3991 (2)	-1282 (2)	2051 (2)	40 (1)
O(12)	4102 (2)	-1807 (1)	951 (2)	56 (1)
O(13)	3715 (1)	-1803 (1)	2843 (2)	52 (1)
C(14)	3407 (2)	-3019 (2)	2221 (3)	60 (1)
C(15)	3407 (3)	-3481 (2)	3367 (3)	76 (2)
O(16)	1836 (1)	411 (1)	2704 (2)	49 (1)
O(17)	1327 (1)	4337 (1)	1024 (2)	60 (1)
C(18)	544 (3)	4666 (3)	1728 (3)	81 (2)
O(19)	2784 (2)	3808 (1)	-225 (2)	57 (1)
C(20)	3500 (3)	3470 (2)	-1016 (3)	81 (2)
C(22)	3347 (2)	4288 (2)	-1891 (3)	59 (1)
C(23)	3644 (3)	3904 (3)	-3071 (3)	69 (1)
C(24)	3573 (3)	4655 (3)	-3860 (3)	85 (2)
C(25)	3188 (3)	5769 (3)	-3494 (4)	92 (2)
C(26)	2857 (4)	6139 (3)	-2372 (4)	107 (2)
C(27)	2927 (4)	5394 (2)	-1568 (3)	92 (2)
C(1')	7742 (2)	588 (2)	3351 (2)	39 (1)
C(2')	8390 (2)	969 (2)	4780 (2)	43 (1)
C(3')	9409 (2)	1567 (2)	5236 (2)	44 (1)
C(4')	9772 (2)	1768 (2)	4258 (2)	41 (1)
C(5')	9135 (2)	1344 (2)	2822 (2)	41 (1)
C(6')	8121 (2)	756 (2)	2367 (2)	42 (1)
O(7')	10102 (1)	2013 (2)	6614 (2)	67 (1)
C(8')	9849 (2)	1784 (2)	7678 (2)	66 (1)
O(9')	10763 (1)	2378 (1)	4679 (2)	51 (1)
C(10')	10595 (2)	3607 (2)	5101 (3)	77 (2)
O(11')	9594 (1)	1560 (2)	1946 (2)	57 (1)
C(12')	8959 (2)	1179 (3)	469 (3)	82 (2)

plex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed. The weighting scheme used in the final stages of refinement was  $w = 2.488/[\sigma^2(F) + 0.0004F^2]$ . The final residuals were  $R = 0.048$  and  $R' = \sum w^{\frac{1}{2}}\Delta / \sum w^{\frac{1}{2}}|F_o| = 0.052$ . Final positional parameters for the non-hydrogen atoms are given in Table 1; bond lengths and angles are given in Tables 2 and 3 respectively.\* Fig. 1 is a schematic diagram of the molecule in which the atomic numbering has been indicated and Fig. 2 is an ORTEP plot.

\* Lists of structure factors, anisotropic thermal parameters for the non-hydrogen atoms, positional and thermal parameters for the H atoms, and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36347 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths ( $\text{\AA}$ )

N(2)—C(1)	1.466 (4)	C(18)—O(17)	1.422 (5)
C(8a)—C(1)	1.524 (5)	C(20)—O(19)	1.418 (6)
C(9)—C(1)	1.533 (5)	C(22)—C(20)	1.502 (7)
C(3)—N(2)	1.460 (4)	C(23)—C(22)	1.388 (6)
C(11)—N(2)	1.352 (3)	C(27)—C(22)	1.370 (5)
C(4)—C(3)	1.505 (5)	C(24)—C(23)	1.385 (7)
C(4a)—C(4)	1.510 (6)	C(25)—C(24)	1.368 (6)
O(16)—C(4)	1.433 (3)	C(26)—C(25)	1.357 (7)
C(5)—C(4a)	1.406 (4)	C(27)—C(26)	1.392 (6)
C(8a)—C(4a)	1.379 (4)	C(2')—C(1')	1.385 (3)
C(6)—C(5)	1.375 (5)	C(6')—C(1')	1.387 (5)
C(7)—C(6)	1.405 (5)	C(3')—C(2')	1.396 (4)
O(17)—C(6)	1.372 (4)	C(4')—C(3')	1.385 (5)
C(8)—C(7)	1.377 (4)	O(7')—C(3')	1.366 (3)
O(19)—C(7)	1.367 (4)	C(5')—C(4')	1.393 (3)
C(8a)—C(8)	1.405 (5)	O(9')—C(4')	1.381 (4)
C(10)—C(9)	1.531 (5)	C(6')—C(5')	1.384 (4)
C(1')—C(10)	1.512 (5)	O(11')—C(5')	1.375 (4)
O(12)—C(11)	1.210 (4)	C(8')—O(7')	1.403 (5)
O(13)—C(11)	1.356 (4)	C(10')—O(9')	1.428 (4)
C(14)—O(13)	1.445 (4)	C(12')—O(11')	1.422 (4)
C(15)—C(14)	1.491 (6)		

Table 3. Bond angles ( $^\circ$ )

C(8a)—C(1)—N(2)	110.5 (3)	C(15) C(14) O(13)	107.2 (3)
C(9)—C(1)—N(2)	111.5 (3)	C(18)—O(17)—C(6)	117.0 (3)
C(9)—C(1)—C(8a)	111.2 (3)	C(20) O(19) C(7)	116.7 (3)
C(3)—N(2)—C(1)	115.4 (3)	C(22) C(20)—O(19)	110.1 (3)
C(11)—N(2)—C(1)	119.1 (3)	C(23)—C(22)—C(20)	118.4 (3)
C(11)—N(2)—C(3)	124.4 (3)	C(27) C(22)—C(20)	122.5 (4)
C(4)—C(3)—N(2)	110.5 (3)	C(27)—C(22)—C(23)	119.1 (4)
C(4a)—C(4)—C(3)	111.1 (3)	C(24)—C(23)—C(22)	120.0 (4)
O(16)—C(4)—C(3)	107.3 (3)	C(25)—C(24)—C(23)	120.1 (5)
O(16)—C(4)—C(4a)	111.3 (2)	C(26)—C(25)—C(24)	120.3 (5)
C(5)—C(4a)—C(4)	118.9 (3)	C(27)—C(26)—C(25)	120.2 (4)
C(8a)—C(4a)—C(4)	121.6 (3)	C(26)—C(27)—C(22)	120.2 (5)
C(8a)—C(4a)—C(5)	119.5 (3)	C(2')—C(1')—C(10)	121.2 (3)
C(6)—C(5)—C(4a)	121.1 (3)	C(6')—C(1')—C(10)	118.2 (3)
C(7)—C(6)—C(5)	119.4 (3)	C(6')—C(1')—C(2')	120.4 (3)
O(17)—C(6)—C(5)	124.7 (3)	C(3')—C(2')—C(1')	119.8 (3)
O(17)—C(6)—C(7)	115.9 (3)	C(4')—C(3')—C(2')	119.9 (3)
C(8)—C(7)—C(6)	119.5 (3)	O(7')—C(3')—C(2')	125.2 (3)
O(19)—C(7)—C(6)	115.7 (3)	O(7')—C(3')—C(4')	114.9 (3)
O(19)—C(7)—C(8)	124.8 (3)	C(5')—C(4')—C(3')	119.8 (3)
C(8a)—C(8)—C(7)	121.2 (3)	O(9')—C(4')—C(3')	121.2 (3)
C(4a)—C(8a)—C(1)	122.5 (3)	O(9')—C(4')—C(5')	119.1 (3)
C(8)—C(8a)—C(1)	118.3 (3)	C(6')—C(5')—C(4')	120.4 (3)
C(8)—C(8a)—C(4a)	119.3 (3)	O(11')—C(5')—C(4')	114.8 (3)
C(10)—C(9)—C(1)	114.6 (3)	O(11')—C(5')—C(6')	124.7 (3)
C(1')—C(10)—C(9)	110.2 (3)	C(5')—C(6')—C(1')	119.6 (3)
O(12)—C(11)—N(2)	125.1 (3)	C(8')—O(7')—C(3')	119.1 (3)
O(13)—C(11)—N(2)	111.6 (3)	C(10')—O(9')—C(4')	112.1 (3)
O(13)—C(11)—O(12)	123.2 (3)	C(12')—O(11')—C(5')	117.2 (3)
C(14)—O(13)—C(11)	116.3 (3)		

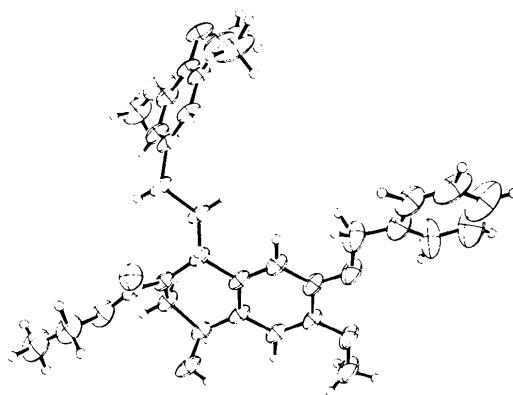


Fig. 2. An ORTEP plot (Johnson, 1965) with 50% probability thermal ellipsoids for the anisotropic atoms.

**Discussion.** The structure confirms a *trans* configuration of the 1 and 4 substituents and shows that both are pseudo-axial. The only significant intermolecular contact is a hydrogen bond between H(16) and O(11'), the latter in the molecule at  $x - 1, y, z$ . The H(16)···O(11') distance is 2.17 (3) Å; the O(16)–H(16)–O(11') angle is 168 (1)°.

The geometry of the 3,4,5-trimethoxyphenethyl substituent was compared to those found in this same fragment in other molecules by use of the Cambridge Crystallographic Database search and geometry calculation systems (Allen *et al.*, 1979). The arrangement of the three adjacent methoxy groups in this substituent is typical. The 3' and 5' groups are nearly coplanar with the benzene ring: the plane of the former [C(3'), O(7'), C(8')] makes an angle of 5.2 (8)° with the mean plane of the benzene ring [C(1')–C(6')]; that of the latter [C(5'), O(11'), C(12')] makes an angle of 1.8 (8)° (see also Table 4). The plane of the 4' group [C(4'), O(9'), C(10')] makes an angle of 99.4 (8)° with the benzene mean plane. The C–O–CH<sub>3</sub> bond angles in the 3' and 5' groups, 119.1 (3) and 117.2 (3)°,

respectively, are significantly larger than the corresponding angle in the 4' group, 112.1 (3)°. This is the result of steric interaction with the ring protons at positions 2' and 6' respectively. The geometry of the methoxy group at the 6 position of the isoquinoline is similar to those of the 3' and 5' groups: the group is nearly coplanar with the aromatic ring C(4a)–C(8a) [the angle is 5.1 (8)°; see also Table 4] and the C–O–CH<sub>3</sub> angle is 117.0 (3)°.

The plane of atoms C(7), O(19), C(20) and C(22) is perpendicular to that of the aromatic ring C(4a)–C(8a). The phenyl ring C(22)–C(27) makes an angle of 27.0 (8)° with this aromatic ring. The pattern of thermal parameters for the atoms in this phenyl ring is unusual and not readily interpretable in terms of any imagined thermal motion of the ring. Refinement of the ring as a rigid body did not improve the thermal parameters.

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Table 4. Deviations (Å) of atoms from mean planes

Average e.s.d. is 0.005 Å.			
(a) Mean plane through atoms C(1')–C(6')			
C(1')	0.014	O(7')	0.007
C(2')	–0.008	C(8')	–0.096
C(3')	–0.006	O(9')	0.042
C(4')	0.014	O(11')	–0.034
C(5')	–0.008	C(12')	–0.014
C(6')	–0.006		
(b) Mean plane through atoms C(4a)–C(8a)			
C(4a)	–0.007	C(8)	0.005
C(5)	0.006	C(8a)	0.002
C(6)	0.001	O(17)	–0.026
C(7)	–0.006	C(18)	0.008

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## Structure of *p*-Nitroaniline Hydrochloride

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**Abstract.** C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>.Cl<sup>–</sup>, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 4.9794 (5), *b* = 16.331 (2), *c* = 10.282 (1) Å, β = 115.01 (1)°, *Z* = 4, *D*<sub>m</sub> = 1.519, *D*<sub>x</sub> = 1.530 Mg m<sup>–3</sup>, λ(Cu *K*α<sub>1</sub>) = 1.54051 Å, λ(Mo *K*α) = 0.7107 Å, μ(Mo *K*α) = 46 mm<sup>–1</sup>, *F*(000) = 360. The structure of *p*-nitroaniline hydrochloride was determined from

diffractometer data; final *R* = 0.073 for 1477 reflexions. The molecular structures of *p*-nitroaniline and *p*-nitroaniline hydrochloride are compared.

**Introduction.** Crystals of *p*-nitroaniline hydrochloride were obtained by the addition of gaseous hydrogen