

C6aA—C10aA—C10bA	118.9 (4)	C10B—C10aB—C10bB	122.9 (4)
N1A—C10bA—C4aA	121.3 (4)	N1B—C10bB—C4aB	120.7 (4)
N1A—C10bA—C10aA	118.2 (4)	N1B—C10bB—C10aB	118.7 (4)
C4aA—C10bA—C10aA	120.5 (4)	C4aB—C10bB—C10aB	120.5 (4)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O10A—H10A...N1A	1.36 (6)	1.45 (5)	2.573 (5)	132 (4)
O10B—H10B...N1B	1.34 (4)	1.41 (4)	2.562 (5)	138 (3)

The background and integrated intensity for each reflection were obtained by the profile-analysis method of Lehmann & Larsen (1974).

Data collection: $P2_1$ diffractometer software. Cell refinement: $P2_1$ diffractometer software. Data reduction: PRADIR (Jaskólski, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: Stereochemical Workstation Operation Manual (Siemens, 1989). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Effect of Substituents on the Crystal Structure of β -Amino Alcohols. 2-[(3,4-Dimethoxybenzyl)(methyl)amino]-2-phenylethanol

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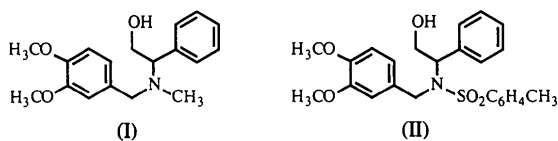
Abstract

The crystal structure of 2-[(3,4-dimethoxybenzyl)-(methyl)amino]-2-phenylethanol, $C_{18}H_{23}NO_3$, (I), has been determined. The influence of the type and size of the groups bonded to the N atom in the crystal structure of (I) was studied and compared with the influence of such groups on the crystal structure of 2-[(3,4-dimethoxybenzyl)(*p*-toluenesulfonyl)amino]-2-phenylethanol, (II). The N atom of compound (I) shows sp^3 character and is synclinal to the OH group, while the N atom of compound (II) shows sp^2 character and is antiperiplanar to the OH group.

Comment

β -Amino alcohols constitute an interesting class of substances with pharmaceutical and other biological activities (Reetz, 1991). They can also be used as intermediates in the synthesis of nitrogen heterocycles with potential pharmacological activity, such as 3-arylisquinoline derivatives (Venkov & Vodenicharov, 1990). These facts have prompted us to begin crystallographic studies of β -amino alcohols (Arriortua *et al.*, 1995). We have also found it interesting to determine the effects of the substituents on these crystal structures. In this context, we decided to study the arrangement of

the substituents bonded to the N atom as a function of their type and size. Thus, we have compared the crystal structure of the title compound, (I), with that of 2-[(3,4-dimethoxybenzyl)(*p*-toluenesulfonyl)amino]-2-phenylethanol, (II) (Arriortua *et al.*, 1995).



The change of substituents bonded to the N atom affects the N—CH—CH₂OH fragment in the studied β -amino alcohols. The sum of valence angles around the N atom is 338.1 (6) $^\circ$ for compound (I), indicating typical sp^3 character. This value is different from the value of 356.6 (3) $^\circ$ found for the sum around the N atom of compound (II), now indicating sp^2 , which probably emanates from an overlap of the remaining filled N-atom *p* orbital with an empty S-atom *d* orbital of the *p*-toluenesulfonyl group (Cook, Glick, Rigau & Johnson, 1971). The pyramidal character of the N atom in (I) is also evidenced by the value of its deviation from the valence-atom plane [0.402 (3) Å] compared with the rather planar environment [0.164 (2) Å] around the N atom in derivative (II).

The N atom and the hydroxyl group in the β -amino alcohol (I) are in a synclinal conformation [N—C1—C16—O17 -44.5 (5) $^\circ$; O17 deviation from the N—C1—C16 plane -0.930 (4) Å]. Thus, two short intramolecular non-bonding contacts between the hydroxyl group and the N and C1 atoms can be seen [O17...N 2.679 (5) Å, O17—H17...N 117 (3) $^\circ$; C1...O17 2.383 (5) Å, C1—H1...O17 94 (4) $^\circ$], which stabilize the aforementioned synclinal conformation. However, both these intramolecular contacts are not possible in the β -amino alcohol (II) structure resulting from the fact that the conformation between the N atom and the hydroxyl group is antiperiplanar [N—C10—C17—O3 179.0 (2) $^\circ$]. In addition, the hydroxyl group maintains a *gauche* conformation about the H atom of the asymmetric C atom in both β -amino alcohols [H1—C1—C16—O17 69 (1) $^\circ$ in (I) and H10—C10—C17—O3 -63 (2) $^\circ$ in (II)].

On the other hand, the observed conformation around the C1—N bond for compound (I) shows *gauche* interactions between the methyl and benzyl groups bonded to the N atom and the remaining groups at C1, as indicated by the torsion angles C2—C1—N—C9 -72.3 (5) $^\circ$ and C2—C1—N—C8 55.9 (5) $^\circ$. The small size of the methyl group bonded to the N atom in derivative (I) allows a *gauche* conformation relative to the phenyl group, but this conformation is not possible for compound (II) as a result of the large *p*-toluenesulfonyl group being bonded to the same heteroatom [S—N—C10—C11 -128.8 (2) $^\circ$].

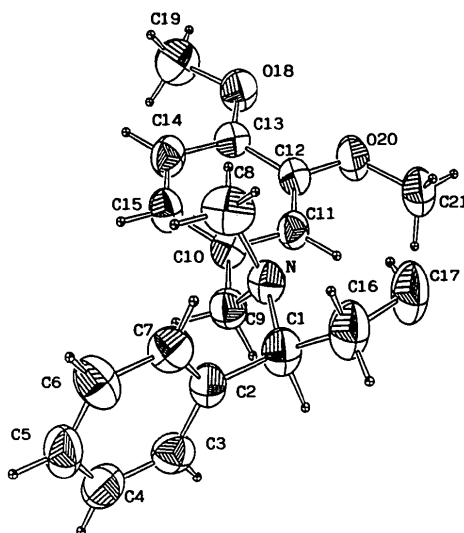


Fig. 1. View of C₁₈H₂₃NO₃ showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The β -amino alcohol was prepared by a classical reductive amination reaction between 3,4-dimethoxybenzaldehyde and 2-amino-2-phenylethanol yielding, after reduction with NaBH₄, the intermediate 2-[(3,4-dimethoxybenzyl)amino]-2-phenylethanol, which reacted with formaldehyde under reductive conditions (NaBH₃CN) affording the 2-[(3,4-dimethoxybenzyl)(methylamino)-2-phenylethanol]. The compound was recrystallized from methanol and fully characterized by NMR, IR and MS spectroscopy, and elemental analysis.

Crystal data

C₁₈H₂₃NO₃
M_r = 301.4
 Orthorhombic
 P2₁2₁2₁
a = 10.731 (6) Å
b = 18.016 (6) Å
c = 8.347 (5) Å
V = 1613.7 (14) Å³
Z = 4
D_x = 1.24 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 1–25 $^\circ$
 μ = 0.078 mm⁻¹
T = 295 K
 Tabular
 0.10 × 0.07 × 0.04 mm
 Colourless

Data collection

Philips PW1100 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1742 measured reflections
 1313 independent reflections
 1307 observed reflections
 [*I* > 2 σ (*I*)]

*R*_{int} = 0.03
 θ_{\max} = 25 $^\circ$
h = -11 → 11
k = 0 → 19
l = 0 → 9
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.0%

Refinement

Refinement on *F*
R = 0.052
wR = 0.15

(Δ/σ)_{max} = 0.23
 $\Delta\rho_{\max}$ = 0.29 e Å⁻³
 $\Delta\rho_{\min}$ = -0.17 e Å⁻³

$S = 0.998$
1307 reflections
201 parameters
Only H-atom U 's refined
Unit weights applied

Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

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

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C1	0.4618 (4)	0.1973 (2)	1.5611 (5)	0.054 (1)
C2	0.5099 (4)	0.1279 (2)	1.6449 (5)	0.046 (1)
C3	0.6126 (4)	0.0931 (2)	1.5804 (5)	0.051 (1)
C4	0.6583 (4)	0.0287 (3)	1.6433 (7)	0.063 (1)
C5	0.6019 (5)	-0.0031 (2)	1.7728 (6)	0.065 (1)
C6	0.5010 (5)	0.0307 (2)	1.8405 (6)	0.061 (1)
C7	0.4547 (4)	0.0959 (2)	1.7786 (5)	0.054 (1)
N	0.3541 (3)	0.1840 (2)	1.4526 (4)	0.046 (1)
C8	0.2461 (4)	0.1488 (3)	1.5250 (5)	0.065 (1)
C9	0.3922 (4)	0.1454 (2)	1.3084 (5)	0.048 (1)
C10	0.2937 (4)	0.1461 (2)	1.1809 (5)	0.044 (1)
C11	0.2653 (4)	0.2117 (2)	1.1024 (5)	0.042 (1)
C12	0.1750 (3)	0.2141 (2)	0.9861 (5)	0.040 (1)
C13	0.1099 (3)	0.1496 (2)	0.9447 (4)	0.041 (1)
C14	0.1388 (4)	0.0842 (2)	1.0229 (5)	0.050 (1)
C15	0.2300 (4)	0.0830 (2)	1.1402 (5)	0.048 (1)
C16	0.4322 (6)	0.2603 (2)	1.6706 (7)	0.072 (1)
O17	0.3770 (4)	0.3190 (2)	1.5838 (5)	0.078 (1)
O18	0.0218 (3)	0.1567 (2)	0.8278 (3)	0.055 (1)
C19	-0.0323 (5)	0.0909 (3)	0.7687 (7)	0.070 (1)
O20	0.1422 (3)	0.2757 (2)	0.9015 (4)	0.057 (1)
C21	0.2022 (5)	0.3433 (2)	0.9412 (6)	0.062 (1)

Table 2. *Selected geometric parameters (\AA , $^\circ$)*

C1—N	1.488 (6)	C10—C15	1.370 (6)
C1—C16	1.492 (6)	C10—C11	1.385 (5)
C1—C2	1.523 (6)	C11—C12	1.372 (5)
C2—C3	1.377 (6)	C12—O20	1.362 (5)
C2—C7	1.389 (6)	C12—C13	1.398 (5)
C3—C4	1.364 (6)	C13—O18	1.365 (5)
C4—C5	1.365 (7)	C13—C14	1.382 (5)
C5—C6	1.365 (7)	C14—C15	1.385 (6)
C6—C7	1.375 (6)	C16—O17	1.413 (6)
N—C9	1.449 (5)	O18—C19	1.409 (6)
N—C8	1.453 (6)	O20—C21	1.417 (5)
C9—C10	1.500 (6)		
N—C1—C16	109.2 (4)	C15—C10—C11	118.8 (4)
N—C1—C2	114.3 (3)	C15—C10—C9	121.3 (4)
C16—C1—C2	114.5 (4)	C11—C10—C9	119.9 (4)
C3—C2—C7	117.8 (4)	C12—C11—C10	121.1 (4)
C3—C2—C1	117.7 (4)	O20—C12—C11	125.1 (3)
C7—C2—C1	124.5 (4)	O20—C12—C13	114.8 (3)
C4—C3—C2	121.6 (4)	C11—C12—C13	120.1 (4)
C3—C4—C5	120.1 (4)	O18—C13—C14	124.9 (4)
C6—C5—C4	119.5 (4)	O18—C13—C12	116.4 (3)
C5—C6—C7	120.8 (5)	C14—C13—C12	118.6 (4)
C6—C7—C2	120.1 (4)	C13—C14—C15	120.4 (4)
C9—N—C8	111.1 (3)	C10—C15—C14	121.0 (4)
C9—N—C1	111.3 (3)	O17—C16—C1	110.2 (4)
C8—N—C1	115.9 (3)	C13—O18—C19	117.2 (3)
N—C9—C10	112.7 (3)	C12—O20—C21	117.5 (3)

Structure solution: *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Structure refinement: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965). Geometric calculations: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[4,4',6,6'-Tetramethyl-(2,2'-isobutylidene-di-*o*-phenylene)] (2,6,7-Trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl) Phosphite, $C_{25}H_{32}P_2O_6$ †

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Abstract

The eight-membered ring in the diphosphite exists in a boat-chair conformation in which the electron lone pair on the P atom and the bridged methine have an *anti* relationship. The sterically more demanding isopropyl

† Dedicated to Professor Edward J. Grubbs on the occasion of his 60th birthday.