$C_{23}H_{22}N_2O_7$

C(9)	0.0253 (2)	0.2670 (1)	0.7045 (1)	0.033 (1)
C(10)	0.1371 (2)	0.2238 (1)	0.6841 (1)	0.028 (1)
C(11)	0.1282 (2)	0.0700 (1)	0.3327 (1)	0.023 (1)
C(12)	0.1805 (2)	−0.0160 (1)	0.2978 (1)	0.030 (1)
C(13)	0.1857 (2)	−0.0268 (2)	0.2065 (1)	0.035 (1)
C(14)	0.1347 (2)	0.0515 (1)	0.1527 (1)	0.026 (1)
C(15)	0.0821 (2)	0.1378 (1)	0.1867 (1)	0.024 (1)
C(16)	0.0776 (2)	0.1506 (1)	0.2764 (1)	0.025 (1)
O(17)	0.1281 (1)	0.0601 (1)	0.0612 (1)	0.039 (1)
C(18)	0.0583 (2)	0.1517 (2)	0.0375 (1)	0.036 (1)
O(19)	0.0387 (1)	0.2046 (1)	0.1178 (1)	0.039 (1)
N(20)	0.2887 (1)	0.2226 (1)	0.4369 (1)	0.023 (1)
O(21)	0.2401 (1)	0.3000 (1)	0.4635 (1)	0.036 (1)
O(22)	0.3549 (1)	0.2226 (1)	0.3769 (1)	0.038 (1)
C(23)	0.2857 (2)	0.0221 (1)	0.6246 (1)	0.022 (1)
C(24)	0.3092 (2)	0.0234 (1)	0.7255 (1)	0.022 (1)
C(25)	0.2192 (2)	−0.0175 (1)	0.7697 (1)	0.030 (1)
C(26)	0.2264 (2)	−0.0166 (2)	0.8688 (1)	0.045 (1)
C(27)	0.3579 (2)	0.0104 (2)	0.9168 (1)	0.036 (1)
C(28)	0.4155 (2)	0.0981 (2)	0.8696 (1)	0.043 (1)
C(29)	0.4279 (2)	0.0712 (2)	0.7734 (1)	0.030 (1)
N(30)	0.3970 (2)	−0.0322 (1)	0.5911 (1)	0.027 (1)
O(31)	0.4992 (1)	0.0138 (1)	0.5967 (1)	0.035 (1)
O(32)	0.3791 (1)	−0.1190 (1)	0.5605 (1)	0.047 (1)

The structure was solved by direct methods and the non-H atoms were refined anisotropically using full-matrix least-squares methods. All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, to which each was bonded for the final cycles of refinement.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Software used to prepare material for publication: *NRCVAX*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: VJ1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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X-ray Structure Investigations of Potential β-Blockers. II. 6,7-Dimethoxy-1-phenyl-1,2,3,4-tetrahydroisoquinoline

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Abstract

The saturated part of the isoquinoline moiety in the title compound, $C_{17}H_{19}NO_2$, has a twist conformation and the phenyl ring substituent is in an equatorial position. The absolute configuration of the molecule is R and molecules form infinite chains by means of weak hydrogen bonds.

Comment

Tetrahydroisoquinolines represent a class of biologically active phenylethylamines (Brzezińska, 1994). The title compound, (I), seems to be a weak competitive antagonist for β-adrenoreceptors. A series of substituted 1,2,3,4-tetrahydroisoquinolines have been synthesized because of their expected activity. The title compound was obtained by the simple Pictet–Spengler reaction of 2-(3,4-dimethoxyphenyl)ethylamine with benzaldehyde (Sarges, 1974).
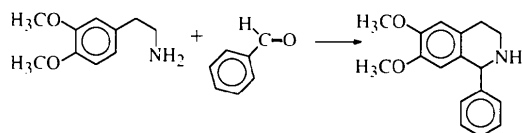
(I)

A perspective view of (I) showing the atomic numbering scheme is given in Fig. 1. The saturated part of the isoquinoline moiety has a twist conformation, with a twofold pseudo-axis passing through the midpoints of the C9—C10 and N1—C8 bonds [asymmetry parameter $\Delta_2(N1-C8) = 0.004\,(1)$]. The aromatic rings are planar within experimental error. The phenyl ring in position 1 is equatorial and makes an angle of 92.16 (8)° with the aromatic part of the isoquinoline moiety. The presence of the benzene ring does not cause any significant disturbance within the remainder of the molecule. The skeleton of the molecule, discounting the phenyl ring, displays pseudosymmetry around the twofold axis bi-
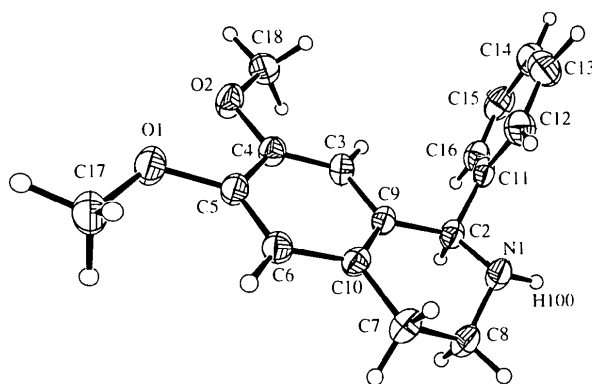
Fig. 1. A perspective view of the title compound showing the atomic numbering scheme and ellipsoids plotted at the 40% probability level.

secting the N1—C8, C9—C10 and C4—C5 bonds. The absolute configuration at C2 is *R*.

Molecules are linked by intermolecular hydrogen bonds [H100···O2^i 2.67 (3), N1···O2^i 3.379 (3) Å, N1—H100···O2^i 136 (3)°; symmetry code: (i) $-x+\frac{1}{2}$, $-y+1$, $z-\frac{1}{2}$]. Thus, the crystal structure is built up of chains of molecules linked by hydrogen bonds around the 2_1 screw axis, the chains running in the [001] direction.

Experimental

Crystals of the title compound were obtained from an ethanol solution at room temperature. The density D_m was measured by flotation in bromoform/xylene.

Crystal data

$C_{17}H_{19}NO_2$	Cu $K\alpha$ radiation
$M_r = 269.33$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 6.110 (1)$ Å	$\theta = 20–40°$
$b = 14.106 (1)$ Å	$\mu = 0.649$ mm^{-1}
$c = 16.6090 (9)$ Å	$T = 293 (2)$ K
$V = 1431.5 (3)$ Å^3	Prism
$Z = 4$	$0.4 \times 0.2 \times 0.2$ mm
$D_x = 1.2498$ Mg m^{-3}	Colourless
$D_m = 1.244$ Mg m^{-3}	

Data collection

KM-4 diffractometer	$\theta_{max} = 79.81°$
$\omega–2\theta$ scans	$h = 0 \rightarrow 7$
Absorption correction:	$k = 0 \rightarrow 18$
none	$l = -21 \rightarrow 21$
3339 measured reflections	3 standard reflections
2955 independent reflections	monitored every 100
2427 observed reflections	reflections
$[I > 2\sigma(I)]$	intensity decay: $<1\%$
$R_{int} = 0.0197$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.022$
$R(F) = 0.0429$	$\Delta\rho_{max} = 0.16$ e Å^{-3}

$wR(F^2) = 0.1221$
$S = 1.276$
2950 reflections
257 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0240P)^2 + 0.6343P]$
where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{min} = -0.17$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter $= 0.00 (39)$

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

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

	x	y	z	U_{eq}
N1	0.2602 (4)	0.5626 (2)	0.6282 (1)	0.0468 (8)
C8	0.1718 (6)	0.6507 (2)	0.6607 (2)	0.050 (1)
C7	−0.0174 (5)	0.6263 (2)	0.7158 (2)	0.044 (9)
C10	0.0471 (5)	0.5507 (2)	0.7758 (1)	0.037 (7)
C9	0.2284 (4)	0.4938 (2)	0.7625 (1)	0.035 (7)
C2	0.3765 (5)	0.5080 (2)	0.6895 (1)	0.039 (8)
C6	−0.0814 (5)	0.5364 (2)	0.8452 (2)	0.038 (8)
C5	−0.0314 (5)	0.4660 (2)	0.8996 (1)	0.037 (7)
C4	0.1525 (4)	0.4083 (2)	0.8861 (1)	0.037 (8)
C3	0.2791 (5)	0.4233 (2)	0.8188 (2)	0.039 (9)
O1	−0.1461 (4)	0.4454 (1)	0.9682 (1)	0.048 (6)
C17	−0.3258 (6)	0.5058 (2)	0.9876 (2)	0.050 (1)
O2	0.1910 (4)	0.3399 (1)	0.9432 (1)	0.048 (7)
C18	0.3702 (6)	0.2773 (2)	0.9290 (2)	0.049 (1)
C11	0.4523 (5)	0.4143 (2)	0.6560 (1)	0.040 (8)
C12	0.3130 (6)	0.3587 (2)	0.6104 (2)	0.054 (1)
C13	0.3749 (8)	0.2696 (3)	0.5842 (2)	0.068 (1)
C14	0.5807 (7)	0.2348 (3)	0.6027 (2)	0.066 (1)
C15	0.7226 (7)	0.2902 (3)	0.6467 (2)	0.063 (1)
C16	0.6602 (5)	0.3792 (2)	0.6732 (2)	0.050 (1)

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

N1—C8	1.459 (3)	C5—O1	1.369 (3)
N1—C2	1.461 (3)	C4—C3	1.376 (3)
C8—C7	1.515 (4)	C4—O2	1.373 (3)
C7—C10	1.511 (3)	O1—C17	1.427 (4)
C10—C9	1.386 (3)	O2—C18	1.427 (4)
C10—C6	1.409 (3)	C11—C12	1.383 (4)
C9—C2	1.526 (3)	C11—C16	1.394 (4)
C9—C3	1.400 (3)	C12—C13	1.383 (5)
C2—C11	1.506 (3)	C13—C14	1.385 (6)
C6—C5	1.377 (3)	C14—C15	1.377 (5)
C5—C4	1.406 (3)	C15—C16	1.385 (5)
C8—N1—C2	111.9 (2)	C4—C5—O1	114.8 (2)
N1—C8—C7	108.2 (2)	C5—C4—O2	115.7 (2)
C8—C7—C10	111.1 (3)	C5—C4—C3	119.3 (2)
C7—C10—C6	119.7 (2)	C3—C4—O2	125.0 (2)
C7—C10—C9	120.8 (2)	C9—C3—C4	121.9 (3)
C9—C10—C6	119.6 (2)	C5—O1—C17	117.0 (2)
C10—C9—C3	118.8 (2)	C4—O2—C18	116.8 (2)
C10—C9—C2	121.7 (2)	C2—C11—C16	121.1 (2)
C2—C9—C3	119.5 (2)	C2—C11—C12	120.7 (3)
N1—C2—C9	109.5 (2)	C12—C11—C16	118.2 (3)
C9—C2—C11	111.2 (2)	C11—C12—C13	121.3 (3)
N1—C2—C11	110.8 (2)	C12—C13—C14	120.1 (3)
C10—C6—C5	121.1 (3)	C13—C14—C15	119.2 (4)
C6—C5—O1	125.9 (2)	C14—C15—C16	120.7 (3)
C6—C5—C4	119.4 (2)	C11—C16—C15	120.5 (3)

Data collection: *Kuma KM-4 Software* (Kuma, 1992). Cell refinement: *Kuma KM-4 Software*. Data reduction: *Kuma KM-4 Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *OR-TEX*3.1a (McArdle, 1995). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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2-Amino-4-nitrobenzothiazole

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Abstract

The crystal structure of the title compound, $C_7H_5N_3O_2S$, consists of centrosymmetric dimers, the principal intradimer interaction being two pairs of three-centre hydrogen bonds involving the amino group, the ring N atom and one O atom of the nitro group. The structure is compared with those of three unsubstituted 2-aminobenzothiazoles reported earlier. The molecule exists as a resonance hybrid of two tautomers, one neutral and the other dipolar. There is some indication that π density localized in the N_{amino}—C—N_{ring} portion of the molecule is in part transferred to the nitro group, but this should be confirmed by other techniques.

Comment

As part of our study of the relationship between molecular and electronic structures and absorption properties of benzothiazole derivatives, we prepared a series of 2-aminobenzothiazoles having a nitro group in various positions on the benzene ring. These compounds can be described as polarized molecules having electron-releasing (amino) and electron-accepting (nitro) groups bonded to the unsaturated framework, with an absorption in the near-ultraviolet and visible region due to delocalization

of π electrons. Indeed, these derivatives were found to exhibit pronounced colour changes depending on the position of the nitro group, which makes their utilization as organic dyes a possibility. Thus, it is of interest to examine the extent of conjugation in these molecules by combined use of theoretical and experimental methods. We report here on the crystal structure of the 4-nitro isomer, (I).

(I)
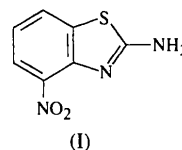
As shown in Fig. 1 the molecule is nearly planar. The six C atoms [C(4)–C(9)] of the benzene ring are essentially exactly coplanar (r.m.s. deviation 0.0017 Å); atoms C(2) and N(3) lie in the benzene plane [deviations 0.002 (1) and 0.000 (1) Å, respectively], while atom S(1) deviates by 0.008 (1) Å from this plane. As for the ring substituents, atom N(2) is displaced by 0.014 (1) Å on the same side as atom S(1) and the N(4) atom of the nitro group is displaced by 0.014 (1) Å in the opposite direction. The N(2) atom is sp^2 hybridized, as evidenced by the sum of the valence angles around this atom [359 (1)°], with the lone-pair electrons available for π bonding [torsion angle N(3)—C(2)—N(2)—H(1) 6 (1)°]. The nitro group at C(4) is rotated by 10.6 (2)° from the mean plane of the benzene ring.
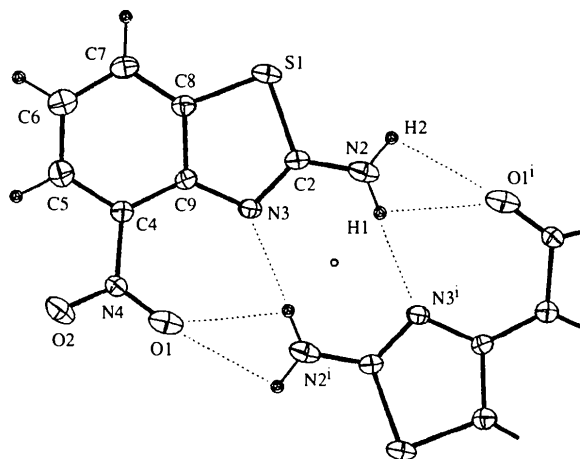

Fig. 1. *ORTEP*II (Johnson, 1971) drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are shown at 50% probability levels. Part of the symmetry-related molecule is shown to illustrate the hydrogen bonding. [Symmetry code: (i) $-x$, $1 - y$, $1 - z$.]

The two C—S distances [1.754 (1) and 1.726 (1) Å] in the thiazole ring have values intermediate between those reported for a C_{sp^3}—S single (1.81 Å) and a double bond (1.61 Å) (Khan, Taylor, Lehn & Dietrich, 1988), but are longer than the C—S bond in thio-