

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.317 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.058$	$\Delta\rho_{\min} = -0.295 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.149$	Extinction correction:
$S = 0.919$	<i>SHELXL96</i> (Sheldrick, 1996)
6096 reflections	Extinction coefficient:
380 parameters	0.018 (2)
H atoms: see below	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2]$	<i>International Tables for</i>
where $P = (F_o^2 + 2F_c^2)/3$	<i>Crystallography</i> (Vol. C)
$(\Delta/\sigma)_{\max} < 0.001$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

C1—O1	1.222 (3)	C1A—O1A	1.225 (2)
C23—N23	1.140 (3)	C23A—N23A	1.136 (3)
C26—N26	1.143 (3)	C26A—N26A	1.145 (3)
C29—N29	1.146 (3)	C29A—N29A	1.138 (3)
C2—C1—C11	122.9 (2)	C2A—C1A—C11A	123.6 (2)
C2—C1—O1	119.1 (2)	C2A—C1A—O1A	119.6 (2)

The data collection nominally covered over a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least 26° in θ . Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H(aromatic) = 0.95 and C—H(secondary) = 0.99 \AA .

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1313). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 854–856

1-Benzyl-2-(2,6-dichloroanilinomethyl)-1*H*-benzimidazole

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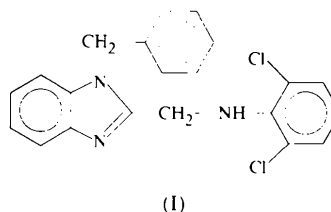
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Abstract

The benzimidazole ring of the title compound, C₂₁H₁₇Cl₂N₃, is planar and makes an angle of 98.38 (6) $^\circ$ with the phenyl ring of the benzyl substituent at N1. The molecules are joined together by C—H \cdots N intermolecular hydrogen bonds.

Comment

Benzimidazole is a heterocyclic ring system present in naturally occurring cyanocobalamin. Substituted benzimidazoles, such as omeprazole (Brandstrom *et al.*, 1985), astemizole (Awouters *et al.*, 1983) and emedastine difumarate (Sakai *et al.*, 1989; Saito *et al.*, 1993), have attracted considerable attention as therapeutics for the treatment of some diseases, such as peptic ulcers and severe hypersecretion in Zollinger–Ellison syndrome. To examine their chemical properties and antimicrobial activity, a series of 1-(*p*-substituted-benzyl)benzimidazole compounds were synthesized, one of which is the title compound, (I). Its structure was assigned on the basis of NMR, mass spectrometric and elemental analysis. The X-ray structure was investigated in order to determine the conformation and packing of (I).



The bond lengths and angles are as expected. Bond lengths N1—C2 [1.364 (3) \AA] and C2—N3 [1.308 (3) \AA] are in good agreement with the values reported for benzimidazole [1.361 (7) and 1.315 (8) \AA ; Escande & Galigne, 1974] and 2-(*o*-methoxyphenoxy)-1-methylbenzimidazole [1.360 (2) and 1.295 (2) \AA ; Vasudevan *et al.*, 1994]. The N1—C10 [1.458 (3) \AA] and N2—

C20 [1.464 (3) Å] bond lengths have expected $C_{sp^3}-N$ values (Allen *et al.*, 1987).

The benzimidazole ring system is planar. The displacements of all atoms contained in the ring are less than 0.011 (2) Å from the least-squares plane. The benzimidazole plane and the plane through the phenyl ring of the benzyl group at N1 form a dihedral angle of 98.38 (6)°. In 1-(phenylmethyl)-2-(4-methoxyphenylmethyl)-1*H*-benzimidazole-5-carboxylic acid and 1,2-di(phenylmethyl)-1*H*-benzimidazole-5-carboxylic acid, the corresponding angles are 88.5 (1) and 95.0 (2)°, respectively (Özbey *et al.*, 1998). The orientation of the anilino substituent at C2 is defined by the torsion angles C2—C20—N2—C21 139.3 (2) and C20—N2—C21—C22 -124.3 (2)°, and is governed by a C20—H202...Cl2 intramolecular interaction; C20...Cl2 3.125 (2), H202...Cl2 2.778 (1) Å and C20—H202...Cl2 102.27 (11)°. The molecules are joined together by C—H...N intermolecular hydrogen bonds. Atom N2 forms an intermolecular hydrogen bond with H15 [C15...N2ⁱ 3.655 (2), H15...N2ⁱ 2.818 (2) Å and C15—H15...N2ⁱ 147.9 (2)°; symmetry code: (i) -x + 1, -y + 1, -z].

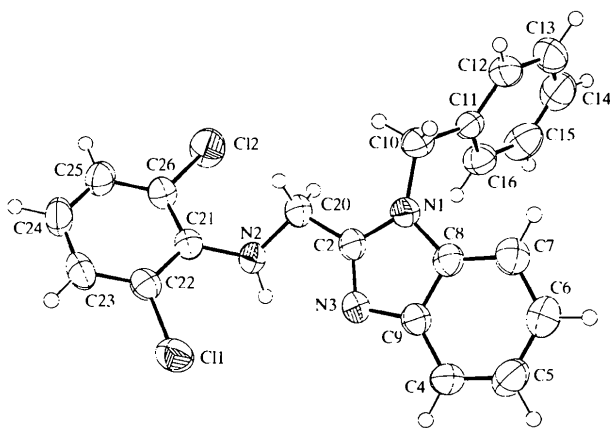


Fig. 1. The molecular structure of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

Experimental

2-Chloromethyl-1*H*-benzimidazole was prepared by the condensation of *o*-phenylenediamine and monochloroacetic acid. Substitution of this precursor with 2,6-dichloroaniline gave 2-(2,6-dichloro-1-anilino)-1*H*-benzimidazole. To a solution of this compound (0.856 mmol, 0.25 g) in 0.5 ml of DMF, NaH (2 mmol, 50% dispersion in oil) was added, followed by a solution of benzyl bromide (1 mmol) in 1 ml of DMF added dropwise. The resulting mixture was stirred for 2.5 h at 333 K. Water was added and the compound extracted with $CHCl_3$. The organic layer was washed with water and dried over Na_2SO_4 . The residue was chromatographed with *n*-hexane- $CHCl_3$ (1:2) to give 0.14 g (43.6%) of product; m.p. 415 K.

Analysis calculated for $C_{21}H_{17}Cl_2N_3 \cdot 0.5H_2O$: C 64.45, H 4.60, N 10.74%; found: C 64.65, H 4.30, N 10.66%. 1H NMR ($CDCl_3$, 400 MHz): 4.7 (*d*, 2H, CH_2NH), 4.94 (*t*, 1H, NH), 5.47 (*s*, 2H, CH_2), 6.8–7.9 p.p.m. (aromatic, 11H). Mass (70 eV) EI: 381 (M^+ , 2.99), 346 (5.32), 290 (8.3), 254 (16.25), 256 (5.96), 219 (23.4), 91 (100), 65 (27.3). Elemental analysis of the compound suggested 0.5 H_2O in the formula unit. Since the compound is highly hygroscopic, it is possible that the water was included during the elemental analysis. The crystal structure of the compound does not contain water of crystallization.

Crystal data

$C_{21}H_{17}Cl_2N_3$
 $M_r = 382.291$
 Monoclinic
 $P2_1/n$
 $a = 11.2662$ (13) Å
 $b = 9.8162$ (10) Å
 $c = 17.2773$ (18) Å
 $\beta = 102.47$ (1)°
 $V = 1865.6$ (4) Å³
 $Z = 4$
 $D_x = 1.361$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10-18^\circ$
 $\mu = 0.357$ mm⁻¹
 $T = 295$ K
 Prism
 $0.80 \times 0.60 \times 0.20$ mm
 Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scans (MolEN; Fair, 1990)
 $T_{min} = 0.838$, $T_{max} = 0.931$
 4146 measured reflections
 3782 independent reflections

2456 reflections with $I > 3\sigma(I)$
 $R_{int} = 0.008$
 $\theta_{max} = 26.3^\circ$
 $h = -14 \rightarrow 13$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 21$
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.3%

Refinement

Refinement on F
 $R = 0.034$
 $wR = 0.039$
 $S = 0.71$
 2456 reflections
 235 parameters
 H atoms riding (see below)
 $w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.166$ e Å⁻³
 $\Delta\rho_{min} = -0.080$ e Å⁻³
 Extinction correction: none
 Scattering factors from International Tables for X-ray Crystallography (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

C11—C22	1.739 (2)	N1—C10	1.458 (3)
C12—C26	1.737 (2)	N2—C20	1.464 (3)
N1—C2	1.364 (3)	N3—C2	1.308 (3)
C2—N1—C8	106.1 (2)	N2—C20—C2	108.8 (2)
C20—N2—C21	119.4 (2)	C12—C26—C21	119.9 (1)
C2—N3—C9	104.5 (2)	C12—C26—C25	117.7 (2)
N1—C2—N3	114.0 (2)		

All H atoms, except the amino H atom, were geometrically located 0.95 Å from their parent atoms and included as riding; each H-atom displacement parameter was fixed at 1.3 U_{eq} of the attached atom. The amino H atom was found from the difference map and refined as riding on N2.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *MolEN*. Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1518). Services for accessing these data are described at the back of the journal.

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2-Amino-5-nitrobenzophenone and 2'-Fluoro-2-methylamino-5-nitrobenzophenone

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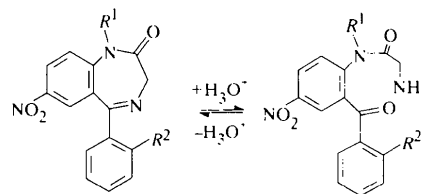
Abstract

The title compounds, C₁₃H₁₀N₂O₃ and C₁₄H₁₁FN₂O₃, were prepared by acid degradation of the 1,4-benzodiazepine drugs nitrazepam and flunitrazepam, respec-

tively. The structure of 2-amino-5-nitrobenzophenone reported here is a polymorphic form of a known structure.

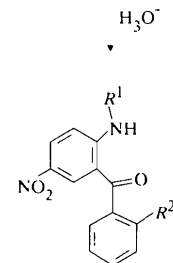
Comment

The 1,4-benzodiazepine drugs nitrazepam and flunitrazepam are prescribed for the short-term treatment of insomnia. Both drugs are hydrolysed in aqueous acid solution to produce substituted benzophenone products *via* a ring-opened intermediate. Thus nitrazepam, (I) (see scheme below), hydrolyses to 2-amino-5-nitrobenzophenone, (II) (Han *et al.*, 1977; Broxton & Morrison, 1985; Davidson & Smail, 1991; Anisuzzaman, 1995), and flunitrazepam, (III), to 2-methylamino-2'-fluoro-5-nitrobenzophenone, (IV) (Debruyne *et al.*, 1984; Moro *et al.*, 1991; Anisuzzaman, 1995). Crystal structures have been reported for (I) (Gilli *et al.*, 1977), (II) (Dvorkin *et al.*, 1985) and (III) (Butcher *et al.*, 1983), but not for (IV). We report here two new structures, namely, that of (IV) and that of a polymorph of the previously reported compound (II).



(I) $R^1 = \text{H}, R^2 = \text{H}$

(III) $R^1 = \text{CH}_3, R^2 = \text{F}$



(II) $R^1 = \text{H}, R^2 = \text{H}$

(IV) $R^1 = \text{CH}_3, R^2 = \text{F}$

Benzophenones almost always crystallize in the propeller conformation, with the torsion angles φ_1 and φ_2 (see scheme below) taking the same sign (Rappoport *et al.*, 1990). This is indeed the case for compounds (II) [$\varphi_1 = 21.7(3)$ and $\varphi_2 = 45.9(3)^\circ$] and (IV) [$\varphi_1 = -8.5(4)$ and $\varphi_2 = -57.7(4)^\circ$]. The previously reported polymorph of (II) has $\varphi_1 = 24.6$ and $\varphi_2 = 49.1^\circ$. By way of comparison, the corresponding angles observed in energy-optimized structures of benzophenone are $\varphi_1 = \varphi_2 = 26.2^\circ$ (Kendrick, 1990) and $\varphi_1 = \varphi_2 =$