Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.232 (3)	N2—C3	1.343 (3)
O2—C3	1.206 (3)	N2—C2	1.468 (3)
O3—C3	1.353 (3)	C1—C2	1.544 (3)
O3—C4	1.464 (3)	C2—C8	1.543 (4)
N1—C1	1.333 (3)	C2—C11	1.567 (4)
C3—O3—C4	121.8 (2)	C8—C2—C1	111.6 (2)
C3—N2—C2	127.2 (2)	N2—C2—C11	108.9 (2)
O1—C1—N1	121.1 (2)	C8—C2—C11	112.6 (2)
O1—C1—C2	120.3 (2)	C1—C2—C11	109.8 (2)
N1—C1—C2	118.6 (2)	O2—C3—N2	127.0 (2)
N2—C2—C8	110.4 (2)	O2—C3—O3	125.3 (2)
N2—C2—C1	103.15 (19)	N2—C3—O3	107.8 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.86	1.98	2.551 (3)	122.7
N1—H1*A*···O1^{i}	0.94	1.97	2.905 (3)	173.8
N1—H1*B*···O2^{ii}	0.85	2.21	2.930 (3)	142.1

Symmetry codes: (i) $2-x,-y,-z$; (ii) $\frac{5}{2}-x,y-\frac{1}{2},\frac{1}{2}-z$.

The structure was refined anisotropically by full-matrix least-squares methods. The H atoms at C5, C6 and C7 were fixed at ideal positions, and the other H atoms were located from a difference Fourier map. During the refinement, H atoms were allowed to ride on their parent atoms. Two 'free variables' were assigned, one to refine common isotropic displacement parameters for all methyl H atoms, and one for the rest of the H atoms. The high U_{eq} values of the *tert*-butyl group may indicate some rotational disorder. Software used for molecular geometry calculations: *PARST* (Nardelli, 1983).

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1318). Services for accessing these data are described at the back of the journal.

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2,5-Dichloro-1-(*p*-chlorobenzyl)-1*H*-benzimidazole

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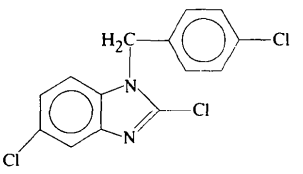
Abstract

The crystal structure of the title compound, $C_{14}H_9Cl_3N_2$, is stabilized by C—H···Cl hydrogen bonds. All of the Cl atoms are involved in hydrogen bonding as acceptors.

Comment

Benzimidazole derivatives have provided a large number of biologically active compounds, and changing the substitution pattern on the benzimidazole moiety greatly alters the biological activity. For instance, amides and carbonates of 2-aminobenzimidazole have proved of considerable value as anthelmintic and antineoplastic agents, particularly in veterinary practice (Ram *et al.*, 1992). A series of benzimidazolone derivatives are useful for central nervous system disorders (Preston, 1974). Incorporation of a 4-aminopiperidine moiety onto the benzimidazole leads to a potent antihistamine, astemizole (Awouters *et al.*, 1983). Antibacterial and antifungal activities of the benzimidazoles have also attracted research interest (Kuş *et al.*, 1996). Gastric secretion inhibitors such as omeprazole and lansoprazole are extremely potent anti-ulcer drugs (Nishina *et al.*,

1996). The title compound, (I), is a benzimidazole which serves as a precursor for the 2-substituted benzimidazole derivatives. Its structure was assigned by NMR, mass spectroscopy and elemental analysis results, as well as by X-ray crystallography.



(I)

X-ray structure analysis of (I) revealed that the molecule is bent almost orthogonally at the methylene which connects the phenyl ring and the benzimidazole ring system. The dihedral angle between the benzimidazole moiety and the benzyl at N1 is 108.43 (6)°. In 6-chloro-1-(phenylmethyl)-2-[*N*-(phenylmethyl)-*N*-(2,6-dichlorophenyl)]aminomethyl-1*H*-benzimidazole, this dihedral angle is 105.1 (1)° (Tunçbilek *et al.*, 1997).

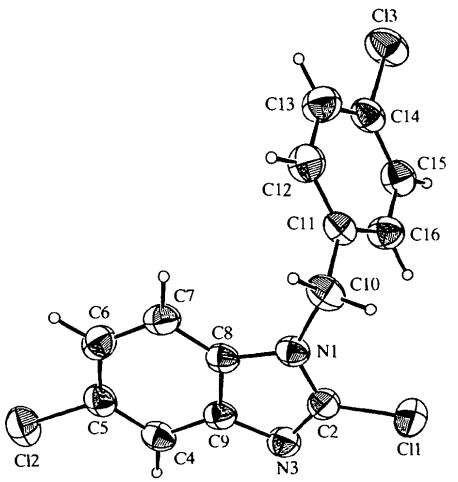


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of an arbitrary radius.

The bond distances and angles of the imidazole ring are in agreement with those in 2-chlorobenzimidazole (Panneerselvam & Soriano-García, 1996) and in 2-(*o*-methoxyphenoxy)-1-methylbenzimidazole (Vasudevan *et al.*, 1994). The exocyclic angles around atom N1 show considerable asymmetry, although the sum of the valence angles around N1 is 360°, indicating no significant pyramidalization of this atom. The benzimidazole ring system has a π-conjugated system. The observed bond lengths for C10—C11 [1.518 (3) Å] and C10—N1 [1.464 (2) Å] are normal for Csp^3—Csp^2 and Csp^3—N bonds. Similar distances [1.506 (3) and 1.460 (3) Å, respectively] have been reported for 1-benzyl-2-(2,6-dichloroanilinomethyl)-1*H*-benzimidazole (Kendi *et al.*, 1998). Although the theoretical length of a Csp^2—Cl bond is given as 1.734 Å by Allen *et al.* (1987), the C2—Cl1 distance in this class of compounds is found to be rather shorter, as is shown by the value of 1.715 (4) Å in 2-chlorobenzimidazole. It is interesting to note the difference in bond lengths between C2—Cl1 [1.711 (2) Å], C5—Cl2 [1.748 (2) Å] and C14—Cl3 [1.746 (2) Å], due to the fact that Cl1 is linked to the imidazole moiety and Cl2 and Cl3 are linked to the benzo and phenyl moieties: the shorter Cl1—C2 bond corresponds to the smaller N1—C2—N3 angle.

The crystal structure of the title compound is stabilized by C—H···Cl hydrogen bonds. All the Cl atoms are involved in hydrogen bonding as acceptors. The details of the hydrogen bonds are given in Table 2.

Experimental

The title compound was synthesised by converting the tautomeric alcohol function of 1-(*p*-chlorophenylmethyl)-5-chloro-2(1*H*)-benzimidazolone to chlorine, using phosphorus oxychloride and dry hydrogen chloride gas.

Crystal data

$C_{14}H_9Cl_3N_2$
M_r = 311.598
Triclinic
$P\bar{1}$
a = 6.5118 (4) Å
b = 8.1702 (6) Å
c = 13.9142 (8) Å
α = 72.501 (5)°
β = 75.962 (5)°
γ = 71.093 (6)°
V = 659.22 (8) Å^3
Z = 2
D_x = 1.5698 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–18°
μ = 0.680 mm^{-1}
T = 295 K
Prismatic
0.60 × 0.56 × 0.32 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
T_{min} = 0.768, T_{max} = 0.804
2877 measured reflections
2679 independent reflections

2303 reflections with $I > 3\sigma(I)$
R_{int} = 0.006
θ_{max} = 27.6°
$h = -7 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = -16 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 0.3%

Refinement

Refinement on F
R = 0.030
wR = 0.031

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

$S = 1.37$
2303 reflections
172 parameters
H atoms: see below
Weighting scheme: see below
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C2	1.711 (2)	N3—C2	1.296 (2)
Cl2—C5	1.748 (2)	N3—C9	1.391 (2)
Cl3—C14	1.746 (2)	C8—C9	1.400 (3)
N1—C2	1.361 (3)	C10—C11	1.518 (3)
N1—C8	1.383 (2)	C14—C15	1.367 (3)
N1—C10	1.464 (2)		
C2—N1—C8	104.9 (1)	C4—C5—C6	123.5 (2)
C2—N1—C10	129.0 (1)	N1—C8—C9	105.4 (1)
C8—N1—C10	126.1 (1)	N3—C9—C8	110.6 (1)
C2—N3—C9	103.0 (2)	N1—C10—C11	113.0 (2)
Cl1—C2—N1	121.0 (1)	Cl3—C14—C13	119.2 (2)
N1—C2—N3	116.2 (2)	Cl3—C14—C15	119.1 (2)
Cl2—C5—C4	117.9 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C10—H101···Cl1	2.79	3.184 (3)	106
C13—H13···Cl2^{i}	2.92	3.639 (3)	133
C10—H101···Cl3^{ii}	2.86	3.668 (2)	143

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1-x, -y, 1-z$.

The weighting scheme used was as follows: $w = 1.0$ if $F >$ threshold; $w = [\text{threshold}/F]^2$ if $F \geq$ threshold; $w = 0$ if $F^2 <$ cutoff $\times \sigma F^2$; where threshold = 332.77 and cutoff = 3.0. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically 0.95 Å from the corresponding C atoms. For all H atoms a riding model was used with $U_{iso}(H) = 1.3U_{eq}(C)$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP* in *MolEN*. Software used to prepare material for publication: *MolEN* and *PARST*95 (Nardelli, 1995).

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4-Chloro-2-[2-(dimethylamino)ethylaminomethyl]phenol and 2-[2-(dimethylamino)ethylaminomethyl]-6-methoxyphenol

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Abstract

The structures of the title compounds, $C_{11}H_{17}ClN_2O$, (1*a*), and $C_{12}H_{20}N_2O_2$, (1*b*), show that unlike the related 4-nitro compound, the phenolic H atoms do not migrate to the amino groups. In both compounds, there are intermolecular hydrogen bonds between the phenolic O atoms and the amino group of neighbouring molecules [N···O 2.656 (3) for (1*a*) and 2.696 (2) Å for (1*b*)] and weak bifurcated hydrogen bonds involving the imino H atoms [N1···O1 3.005 (2) and N1···N2 2.910 (3) Å for (1*a*), and 3.111 (2) and 2.894 (3) Å for (1*b*)]. The differences in structure are attributed to the acidities of the phenolic groups.

Comment

Brzezinski *et al.* (1990) reported IR continuum studies which showed that the phenolic proton of disubstituted *ortho* Mannich bases of the formula $HOC_6H_3(CH_2NR_2)_2$ exhibit an intra/intermolecular proton transfer equilibrium, O—H···N ⇌ O···H—N, between the phenolic O atom and the amino N atom. It was further reported that the differences between the intra- and intermolecular hydrogen-bonded systems of 2-$HOC_6H_3XCH_2NR_2$