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2-Methylamino-5-chlorobenzophenone

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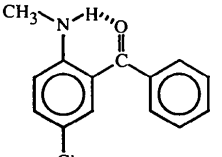
Abstract

Intramolecular hydrogen bonding is present in 2-methylamino-5-chlorophenyl phenyl ketone, $C_{14}H_{12}ClNO$, and the phenyl rings are inclined by 54.39 (8)° with respect to one another. The Cl···Cl intermolecular separation of 3.355 (2) Å is considerably less than the sum of the van der Waals radii.

Comment

Diazepam is a well known benzodiazepine drug prescribed for the short-term relief of severe anxiety: its crystal structure has been determined previously (Camerman & Camerman, 1972). The drug is hydrolyzed to the title compound, 2-methylamino-5-chlorobenzophenone (MACB), and the hydrolysis kinetics have been investigated by a number of workers (Han, Yakatan & Maness, 1977; Nakano, Inotsume, Kohri & Arita, 1979; Anisuzzaman, 1995). The two phenyl rings of MACB are inclined by 54.39 (8)° with respect to one another such that the H6···H9 distance is 2.455 (3) Å. In benzophenone (Fleischer, Sung & Hawkinson, 1968), this angle is 56°, which is in reasonable agreement with the energy minimum conformation predicted using *ab initio* molecular-orbital calculations (Kendrick, 1990).



MACB

The N···O separation is 2.674 (3) Å and the geometry of the intramolecular hydrogen bonding is N—H1 0.880 (3), H1···O 1.994 (3) Å and N—H1···O 133.13 (6)°. The Cl···Cl($2-x$, $1-y$, $1-z$) separation is 3.355 (2) Å, which is less than the sum of the van der Waals radii (3.50 Å; Bondi, 1964). Recent surveys (Gavezzotti & Filippini, 1993; Rowland & Taylor, 1996) of halogen-containing crystal structures in the Cambridge Structural Database (Allen & Kennard, 1993) show a significant number of Cl···Cl non-bonded contacts of <3.5 Å. It has been suggested (Pedireddi *et al.*, 1994) that polarization and anisotropic electron distribution are important factors in the formation of these short contacts. A short intermolecular distance C10···O($\frac{1}{2}+x$, $\frac{1}{2}-y$, z) of 3.172 (3) Å may involve a weak hydrogen-bonded contact; the C—H···O angle is 124.30 (6)° and the H10···O distance is 2.538 (3)°. Interactions of this type may influence the packing of molecules in the crystal. Reference to the Cambridge Structural Database for 3762 aromatic-C—H···O=C contacts less than the sum of the C···O van der Waals radii (3.22 Å) shows a mean C···O distance of 2.800 (4) Å, with an angular range of 74–179° [mean 134.3 (3)°].

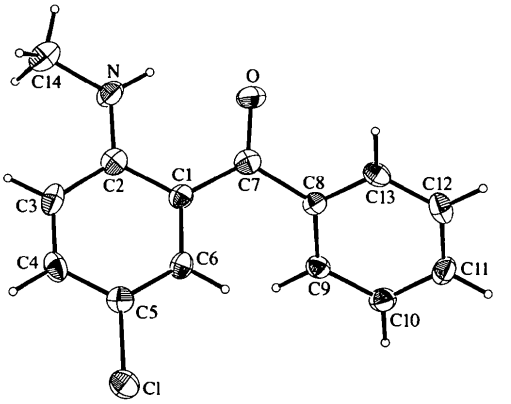


Fig. 1. The atomic arrangement in the title molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

Diazepam was hydrolyzed with aqueous HCl to give the title compound, which was then recrystallized from aqueous ethanol.

Crystal data

$C_{14}H_{12}ClNO$
$M_r = 245.70$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$P2_1/a$
a = 12.928 (5) Å
b = 5.546 (5) Å
c = 16.445 (5) Å
β = 92.392 (5)°
V = 1178.1 (12) Å^3
Z = 4
D_x = 1.385 Mg m^{-3}
D_m not measured

Cell parameters from 250 reflections
θ = 2.48–24.91°
μ = 0.305 mm^{-1}
T = 150 (2) K
Lozenge
0.22 × 0.16 × 0.10 mm
Yellow

Data collection

Delft Instruments FAST diffractometer
Area detector scans
Absorption correction: none
4719 measured reflections
1783 independent reflections

1152 reflections with $I > 2\sigma(I)$
R_{int} = 0.0628
θ_{max} = 24.91°
$h = -14 \rightarrow 11$
$k = -5 \rightarrow 6$
$l = -16 \rightarrow 18$

Refinement

Refinement on F^2
$R(F)$ = 0.033
$wR(F^2)$ = 0.0708
S = 0.736
1780 reflections
156 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl—C5	1.745 (2)	C1—C2	1.437 (3)
O—C7	1.237 (2)	C1—C7	1.466 (3)
N—C2	1.362 (3)	C7—C8	1.501 (3)
N—C14	1.441 (3)		
C2—N—C14	124.1 (2)	O—C7—C8	116.9 (2)
O—C7—C1	122.0 (2)	C1—C7—C8	121.2 (2)
C6—C1—C7—O	−163.8 (2)	O—C7—C8—C13	41.3 (3)
C2—C1—C7—O	13.6 (3)	C1—C7—C8—C13	−138.8 (2)
C6—C1—C7—C8	16.3 (3)	O—C7—C8—C9	−133.3 (2)
C2—C1—C7—C8	−166.3 (2)	C1—C7—C8—C9	46.6 (3)

The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989), and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached C atoms, with common isotropic displacement parameters of 0.024 (9) (for non-methyl H atoms) and 0.044 (1) Å^2 (for methyl H atoms).

Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996).

The use of the EPSRC X-ray Crystallographic Service at the University of Wales, Cardiff, and the assistance of Neil S. Stewart of the Cambridge Crystallographic Data Centre are gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Dipeptide pGlu–Pro-NH_2

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Abstract

The crystal structure of the pGlu–Pro-NH_2 dipeptide, *cis*-1-(5-oxo-L-prolyl)-L-prolinamide hydrate [*cis*-1-(5-oxo-L-prolyl)pyrrolidine-2-carboxamide hydrate], $C_{10}H_{15}N_3O_3.H_2O$, has been determined in order to establish