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

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Abstract

The title compounds, $C_{13}H_{10}N_2O_3$ and $C_{14}H_{11}FN_2O_3$, 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).
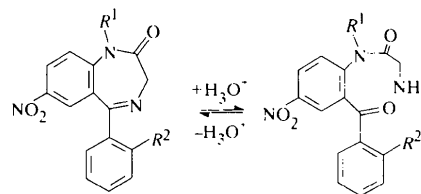
(I) R^1 = H, R^2 = H
(III) R^1 = CH$_3$, R^2 = F
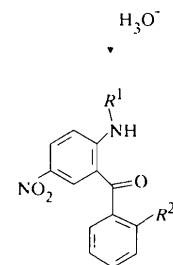
(II) R^1 = H, R^2 = H
(IV) R^1 = CH$_3$, R^2 = F

Benzophenones almost always crystallize in the propeller conformation, with the torsion angles $\varphi 1$ and $\varphi 2$ (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)°] and (IV) [$\varphi 1$ = −8.5 (4) and $\varphi 2$ = −57.7 (4)°]. The previously reported polymorph of (II) has $\varphi 1$ = 24.6 and $\varphi 2$ = 49.1°. By way of comparison, the corresponding angles observed in energy-optimized structures of benzophenone are $\varphi 1$ = $\varphi 2$ = 26.2° (Kendrick, 1990) and $\varphi 1$ = $\varphi 2$ =

30° (Rappoport *et al.*, 1990), while in the crystal structure of benzophenone $\varphi1 = 29.4$ and $\varphi2 = 30.9°$ (Fleischer *et al.*, 1968).
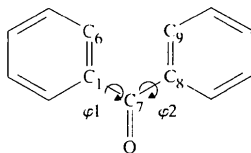
In both compounds, an amino H atom forms an intramolecular hydrogen bond with the carbonyl O atom, O1 [in compound (II), H1B···O1 = 2.03 Å, and in compound (IV), H1···O1 = 1.98 Å]. Another feature common to both structures is the presence of a single intermolecular hydrogen bond between an amino H atom and an O atom [H1A···O3($-1 + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) = 2.14 Å in (II) and H1···O1($-x$, $-y$, $-z$) = 2.42 Å in (IV)]. These features are shown in Figs. 1 and 2.

Fig. 1. The atomic arrangement and hydrogen bonding in molecules of (II). Displacement ellipsoids are shown at the 50% probability level. H atoms have been set artificially small for clarity. O3' is related to O3 by the symmetry operation $-1 + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$.
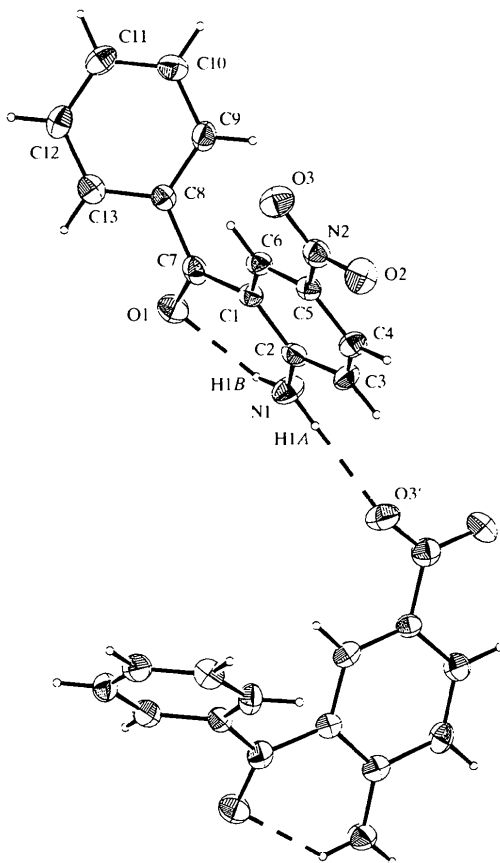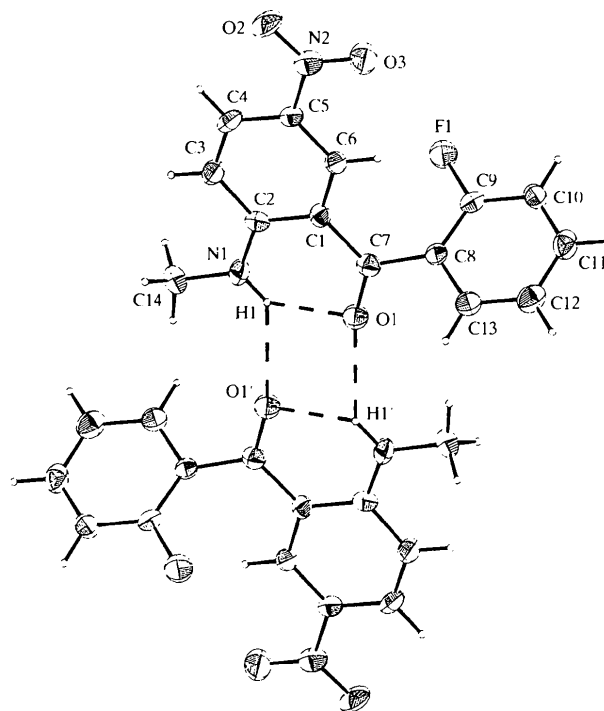

Fig. 2. The atomic arrangement and hydrogen bonding in molecules of (IV). Displacement ellipsoids are shown at the 50% probability level. H atoms have been set artificially small for clarity. Primed (') atoms are generated from their unprimed counterparts by inversion through the origin.

Atom H1 in compound (IV) therefore acts as a donor for two hydrogen bonds in a bifurcated system. The previously published polymorph of 2-amino-5-nitro-benzophenone, (IIP) (Dvorkin *et al.*, 1985), is also monoclinic ($P2_1/b$, $a = 7.851$, $b = 12.686$, $c = 11.121$ Å and $\gamma = 95.58°$) and possesses a similar hydrogen-bonding network to that of the structure reported here. The amino H-atom bond geometries for these three compounds are given in Table 3, where the O-atom coordinates of (IIP) are transposed by $-x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$.

A scan of the close contacts in the crystal structure of (IV) also reveals a short C—H···O contact: H14C···O2($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) = 2.38 Å.

Experimental

Nitrazepam was hydrolysed with aqueous HCl to give (II), and flunitrazepam was hydrolysed with aqueous HCl to give (IV). Crystals of (II) were obtained from aqueous HCl solution, while (IV) was recrystallized by slow evaporation of an ethanol solution.

Compound (II)

Crystal data

$C_{13}H_{10}N_2O_3$	Mo $K\alpha$ radiation
$M_r = 242.23$	$\lambda = 0.7107$ Å

Monoclinic
$P2_1/c$
$a = 5.7358 (15)$ Å
$b = 14.693 (2)$ Å
$c = 13.1120 (12)$ Å
$\beta = 98.87 (4)°$
$V = 1091.8 (3)$ Å^3
$Z = 4$
$D_x = 1.474$ Mg m^{-3}
D_m not measured

Cell parameters from 250
  reflections
$\theta = 2.10-25.09°$
$\mu = 0.107$ mm^{-1}
$T = 150 (2)$ K
Needle
$0.20 \times 0.15 \times 0.15$ mm
Yellow

Data collection

Delft Instruments FAST
  diffractometer
Area-detector scans
Absorption correction: none
4705 measured reflections
1705 independent reflections

1004 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.082$
$\theta_{max} = 25.09°$
$h = -6 \rightarrow 6$
$k = -17 \rightarrow 17$
$l = -15 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.077$
$S = 0.757$
1705 reflections
164 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0128P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.037$
$\Delta\rho_{max} = 0.192$ e Å^{-3}
$\Delta\rho_{min} = -0.143$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

O3—N2	1.243 (2)	N1—C2	1.336 (3)
O2—N2	1.225 (2)	N2—C5	1.443 (3)
O1—C7	1.236 (2)		
C6—C1—C7—C8	21.7 (3)	C1—C7—C8—C9	45.9 (3)

Compound (IV)

Crystal data

$C_{14}H_{11}FN_2O_3$
$M_r = 274.25$
Monoclinic
$P2_1/n$
$a = 4.2150 (17)$ Å
$b = 13.6020 (18)$ Å
$c = 21.547 (7)$ Å
$\beta = 94.7480 (11)°$
$V = 1231.1 (7)$ Å^3
$Z = 4$
$D_x = 1.480$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 250
  reflections
$\theta = 2.42-24.98°$
$\mu = 0.116$ mm^{-1}
$T = 150 (2)$ K
Needle
$0.22 \times 0.18 \times 0.12$ mm
Yellow

Data collection

Delft Instruments FAST
  diffractometer
Area-detector scans
Absorption correction: none
5315 measured reflections
1946 independent reflections

736 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.094$
$\theta_{max} = 24.98°$
$h = -4 \rightarrow 3$
$k = -15 \rightarrow 14$
$l = -25 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.068$
$S = 0.496$
1946 reflections
184 parameters
H atoms: see below
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.156$ e Å^{-3}
$\Delta\rho_{min} = -0.139$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

F1—C9	1.365 (3)	O3—N2	1.236 (3)
O1—C7	1.230 (3)	N1—C2	1.343 (3)
O2—N2	1.236 (3)	N2—C5	1.447 (4)
C6—C1—C7—C8	−8.5 (4)	C1—C7—C8—C9	−57.7 (4)

Table 3. *Hydrogen-bond geometry (Å, °)*

	N—H	O···H	N···O	N—H···O
(II) (intra)	0.86	2.03	2.664 (3)	123
(II) (inter)	0.86	2.14	2.972 (3)	164
(IV) (intra)	0.88	1.97	2.658 (4)	134
(IV) (inter)	0.88	2.41	3.112 (4)	137
(IIP) (intra)	1.00	2.01	2.698	124
(IIP) (inter)	0.92	2.18	3.083	175

The unit-cell and intensity data were obtained using the routines *ENDEX, REFINE* and *MADONL* in the *MADNES* suite of software (Pflugrath & Messerschmidt, 1989) and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr *et al.* (1993). All non-H atoms were refined with anisotropic displacement parameters. The H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached atoms with a common isotropic displacement parameter, which converged to 0.027 (2) Å^2 for (II), and to 0.026 (3) (non-methyl) and 0.070 (6) Å^2 (methyl) for (IV). We attribute the poor value of S for structure (IV) to the effects of uncertainties on F^2 in a very weak data set.

For both compounds, program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (II); *SHELXL97* (Sheldrick, 1997) for (IV). For both compounds, molecular graphics: *ZORTEP* (Zsolnai, 1997).

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3-tert-Butyl-2-hydroxy-5-methoxyazobenzene†

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Abstract

The structure of the title compound, $C_{17}H_{20}N_2O_2$, shows features characteristic of azobenzene derivatives and is perfectly planar in the solid state with a *trans* configuration. The molecule has an intramolecular O1—H1···N1 hydrogen bond.

† IUPAC name: 2-*tert*-butyl-4-methoxy-6-(phenyldiazenyl)phenol.

Comment

Azo compounds are widely used in the textile industry as synthetic colouring materials. The structure of the title compound, (I), is very similar to the structures of azo compounds studied previously (Işik *et al.*, 1997; Glowka & Olubek, 1994; Rodrigues *et al.*, 1996). The two phenyl rings are in a *trans* configuration. The lengths of the two C—N bonds are almost identical and have an average value of 1.410(3) Å. The average value of the C—N—N angles is 115.7(2)°. The N=N bond length is 1.274(3) Å, in accordance with the expected value for aromatic azo compounds. The whole molecule, except for two methyls of the *tert*-butyl group, lies on a crystallographic mirror plane, so that the molecule is perfectly planar.

(I)
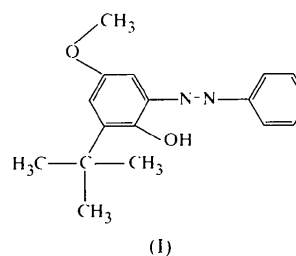
The planarity of the molecule facilitates an O1—H1···N1 intramolecular hydrogen bond, in which the O1 hydroxyl group adjacent to the N=N bond serves as the donor to the N1 atom. The O1—H1···N1 angle is 149.6(2)° and the length of the hydrogen bond (H1···N1) is 1.598(2) Å. The length of the O1···N1 bond is 2.534(2) Å, which is shorter than a typical hydrogen bond of this type [N···O = 2.78(10) Å; Vinogradov & Linnell, 1971]. This shows the presence of a very strong intramolecular interaction in the molecule. There are no intermolecular interactions other
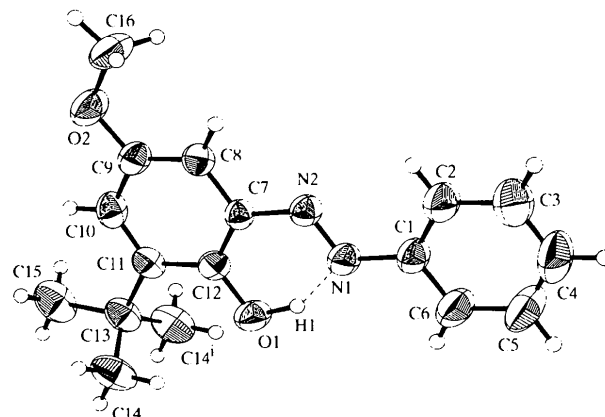

Fig. 1. *ORTEP*II (Johnson, 1976) view of the title molecule and the atomic numbering. The displacement ellipsoids are at the 50% probability level. H atoms are shown as spheres of arbitrary size. [Symmetry code: (i) x, $\frac{1}{2} - y$, z.]