S = 1.090	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
2916 reflections	Extinction coefficient: 0.017 (4)
213 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.3195P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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

C2—O2	1.193 (4)	C4—C5	1.438 (5)
C2—O1	1.332 (4)	C5—O3	1.203 (4)
C2—C3	1.502 (5)	C5—O4	1.349 (4)
C3—C4	1.352 (4)	C11—N1	1.357 (4)
C3—C12	1.424 (4)	C11—C12	1.365 (5)
O2—C2—C3—C4	91.1 (4)	N1—C11—C12—C3	178.4 (3)
C12—C3—C4—C5	178.3 (3)	C21—C11—C12—C13	−179.0 (3)
C3—C4—C5—O3	2.8 (6)	C12—C11—C21—C22	−89.6 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···O2^{i}	0.930	2.528	3.404 (5)	157.1
C6—H6*B*···O3^{ii}	0.960	2.680	3.477 (5)	140.8
C14—H14*A*···O3^{iii}	0.970	2.589	3.468 (5)	150.8
C14—H14*A*···O4^{iv}	0.970	2.603	3.393 (4)	138.7

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

The structure was solved by direct methods (Sheldrick, 1985) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (Sheldrick, 1997). All H atoms were found in difference Fourier syntheses, but the final refinement was carried out using a riding model, with displacement parameters for the H atoms constrained to 1.5 times (CH_3 groups) or 1.2 times (secondary CH_2 groups and conjugated CH groups) the displacement parameters of the respective C atoms.

Data collection: *CAD-4-PC* (Enraf–Nonius 1994). Cell refinement: *CAD-4-PC*. Data reduction: *CAD-4-PC*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Brandenburg, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1327). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. (1998). *DIAMOND*. Version 2.0*f*. Crystal Impact, GbR, Bonn, Germany.

Chinchilla, R. & Bäckvall, J.-E. (1994). *The Chemistry of Functional Groups*, edited by S. Patai & Z. Rappoport, *The Chemistry of Enamines (Part 2)*, pp. 995–999. New York: Wiley Interscience.

Enraf–Nonius (1994). *CAD-4-PC*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Hickmott, P. W. (1994). *The Chemistry of Functional Groups*, edited by S. Patai & Z. Rappoport, *The Chemistry of Enamines (Part 1)*, pp. 798–801. New York: Wiley Interscience.

Jung, M. E. (1991). *Comprehensive Organic Synthesis*, Vol 4, *Additions to and Substitutions of C—C π-Bonds*, edited by B. M. Trost & I. Fleming, p. 45. Oxford: Pergamon Press.

Livingstone, R. (1973). *Rodd's Chemistry of Carbon Compounds*, edited by S. Coffey, 2nd ed., Vol. 4, Part A, *Heterocyclic Compounds: 1-Pyrrolines*, pp. 368–371; *2-Pyrrolines*, pp. 373–374. New York: Elsevier.

Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Zellmer, D., Niewa, R., Preut, H. & Kreher, R. P. (1997). *Acta Cryst.* C**53**, 251–253.

Acta Cryst. (1999). C**55**, 825–827

4-Chloro-*N*-(*p*-fluorobenzyl)-2-nitroaniline

M. Murat Candan,[a] Engin Kendi[a] and Hakan Göker[b]

[a]*Department of Physics Engineering, Hacettepe University, Beytepe 06532, Ankara, Turkey, and* [b]*Department of Pharmaceutical Chemistry, Ankara University, Tandoğan 06100, Ankara, Turkey. E-mail: kendi@eti.cc.hun.edu.tr*

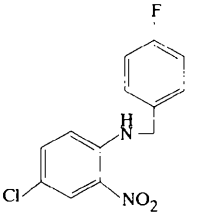
(*Received 4 August 1998; accepted 26 January 1999*)

Abstract

The title molecule, $C_{13}H_{10}ClFN_2O_2$, is bent almost orthogonally at the methylene, with a dihedral angle of 91.60 (6)° between the two benzene rings. The *o*-nitro and amino groups are almost coplanar with the benzene ring due to intramolecular hydrogen bonds.

Comment

The nitro-aromatic amines crystallize as planar molecules joined by intermolecular hydrogen bonds between the amine group and the O atoms of the nitro group (Dhaneshwar *et al.*, 1978; Prasad *et al.*, 1982). However, in the absence of any specific electrostatic interaction, the *o*-nitro group is twisted out of the plane of the aryl ring (Punte *et al.*, 1989; Punte & Rivero, 1991; Low *et al.*, 1996). In order to investigate the effect of the *p*-fluorobenzyl group on the planarity of the *o*-nitro group and its attached aryl ring, the structure determination of the title compound, (I), was undertaken.



(I)

The present compound is a precursor which is used for the selective synthesis for *N'*-(*p*-fluorobenzyl)-5-chloro-1*H*-benzimidazole derivatives (Göker *et al.*, 1995). Its structure was also assigned by NMR.

The X-ray structure analysis of (I) revealed that the molecule (Fig. 1) is bent almost orthogonally at the methylene which connects the aniline and phenyl rings. The dihedral angle between the aniline and benzyl groups is 91.60 (6)°. There are small rotations of the amino and *o*-nitro groups with respect to the mean ring plane, with torsion angles of −3.4 (3) and 3.9 (3)°, respectively. These values are similar to those in 2,4 dinitroaniline [2.7 (5) and 4.3 (4)°; Prasad *et al.*, 1982] and smaller than the corresponding values reported for *N,N*-diisopropyl-2,4-dinitroaniline [28.5 (5) and 40.5 (4)°; Punte *et al.*, 1989].

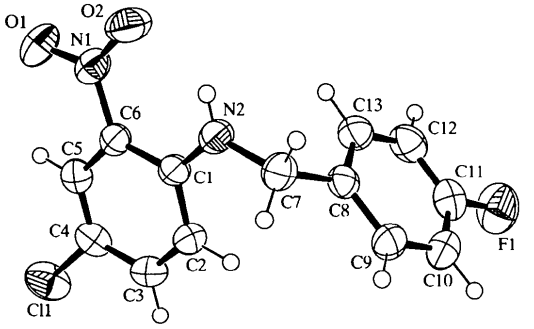


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound, showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

The C1—N2 bond length [1.350 (3) Å] suggests some double-bond character. This length is analogous to that found in 2,4-dinitroaniline [1.352 (6) Å; Prasad *et al.*, 1982], *N,N*-diethyl-4-nitroaniline [1.351 (4) and 1.354 (4) Å; Maurin & Krygowsky, 1988] and *N*-cyclohexyl-*N*-isopropyl-2,4-dinitroaniline [1.370 (3) Å; Punte *et al.*, 1991]. The *para*-Cl atom shows a slight deviation from the phenyl-ring plane [C2—C3—C4—Cl1 −178.2 (2)°].

The C1—C2 and C1—C6 bond lengths [1.413 (3) and 1.417 (3) Å, respectively] show that C—C bonds involving the C atom bonded to the amino substituent are longer than the accepted value for benzene [1.397 Å] and the mean value for the remaining C—C bonds in the benzene ring is 1.392 Å. The value of the endocyclic angle at C1 [115.3 (2)°] is considerably less than 120° and similar to that observed in some polynitro-aromatic compounds such as 2,3,4,6-tetranitroaniline [114 (4)°; Dickinson *et al.*, 1966] and *N,N*-dimethyl-2,4-dinitroaniline [115.2 (3)°; Low *et al.*, 1996]. This feature, as expected for a substituent that causes a decrease in the *ipso* angle (Domenicano *et al.*, 1975), together with an enlargement of the endocyclic angles at C2 and C6 [122.3 (2) and 122.0 (2)°, respectively], may be explained as being produced by a combination of the electron-releasing property of the amino group and electron withdrawal by the *ortho*-NO_2 group.

There is an intramolecular hydrogen bond between the N2 and O2 atoms, as expected. Details of the intra- and intermolecular hydrogen bonds are given in Table 2.

Experimental

The title compound was obtained by the nucleophilic substitution of 2,5-dichloronitrobenzene with *p*-fluorobenzylamine. A mixture of 2,5-dichloronitrobenzene (5.2 mmol, 1 g) and *p*-fluorobenzylamine (8.84 mmol, 1.1 g) in toluene (15 ml) was refluxed for 7 h. Toluene was evaporated and the residue crystallized from EtOH/water, then from toluene/*n*-hexane, as an orange product [yield 0.67 g (46%), m.p. 361 K]. ^{1}H NMR (DMSO-d_6): 4.55 (*d*, *J* = 5.5 Hz, 2H, CH_2), 6.8–7.5 (6H aromatic), 8.05 (*d*, 1H, 3-H), 8.7 (*t*, *J* = 5.5 Hz, 1H, NH).

Crystal data

$C_{13}H_{10}ClFN_2O_2$
M_r = 280.69
Monoclinic
$P2_1/c$
a = 9.063 (1) Å
b = 16.543 (2) Å
c = 8.460 (1) Å
β = 83.11 (1)°
V = 1259.1 (2) Å^3
Z = 4
D_x = 1.481 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9–18°
μ = 0.311 mm^{-1}
T = 295 K
Prismatic
0.30 × 0.30 × 0.30 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.855, T_{max} = 0.911
2724 measured reflections
2396 independent reflections
1941 reflections with $I > \sigma(I)$
R_{int} = 0.019
θ_{max} = 26.3°
h = 0 → 10
k = 0 → 20
l = −10 → 10
3 standard reflections
frequency: 120 min
intensity decay: −2.1%

Refinement

Refinement on F
R = 0.039
wR = 0.046
S = 0.97
1941 reflections
176 parameters
H atoms: see below
$w = 1/[\sigma F^2 + (0.02F)^2 + 0.5]$ except $w = 0$ if $F^2 <$ cutoff × σF^2, cutoff = 1.0
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cl1—C4	1.738 (3)	N2—C7	1.453 (3)
F1—C11	1.357 (3)	N2—HN	0.79 (2)
O1—N1	1.225 (3)	C1—C2	1.413 (3)
O2—N1	1.239 (3)	C1—C6	1.417 (3)

N1—C6	1.441 (3)	C7—C8	1.514 (3)
N2—C1	1.350 (3)		
O1—N1—O2	121.5 (2)	N2—C7—C8	113.8 (2)
C1—N2—C7	123.9 (2)	F1—C11—C10	118.7 (3)
C2—C1—C6	115.3 (2)	C10—C11—C12	122.6 (2)
C1—C2—C3	122.3 (2)	C11—C12—C13	118.4 (2)
C1—C6—C5	122.0 (2)		
O1—N1—C6—C5	3.9 (3)	C2—C3—C4—C11	−178.2 (2)
C7—N2—C1—C2	−3.4 (3)	N2—C7—C8—C9	−146.7 (2)
C1—N2—C7—C8	73.9 (2)	F1—C11—C12—C13	178.9 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—HN···O2	0.79 (2)	2.03 (2)	2.624 (2)	132 (2)
N2—HN···O2^{i}	0.79 (2)	2.49 (2)	3.048 (3)	129 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$.

H atoms, except for the amino H atom, were placed geometrically 0.95 Å from their parent atoms and a riding model was used with $U(H) = 1.3U_{eq}(C)$. The amino H atom was taken from a difference Fourier map and was refined isotropically.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1990). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*. Hydrogen bonds were calculated with *PARST* (Nardelli, 1995).

The authors acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1168). Services for accessing these data are described at the back of the journal.

References

Dhaneshwar, N. N., Tavale, S. S. & Pant, L. M. (1978). *Acta Cryst.* B**34**, 2507–2509.

Dickinson, C., Stewart, J. M. & Holden, J. R. (1966). *Acta Cryst.* **21**, 663–670.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.

Enraf–Nonius (1990). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Göker, H., Kuş, C. & Abbasoğlu, U. (1995). *Arch. Pharm.* **328**, 425–430.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Low, J. N., Doidge-Harrison, M. S. V. & Cobo, J. (1996). *Acta Cryst.* C**52**, 964–966.

Maurin, J. & Krygowsky, T. M. (1988). *J. Mol. Struct.* **172**, 413–421.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–354.

Prasad, L., Gabe, E. J. & Le Page, Y. (1982). *Acta Cryst.* B**38**, 674–675.

Punte, G. & Rivero, B. E. (1991). *Acta Cryst.* C**47**, 2118–2122.

Punte, G., Rivero, B. E., Socolovsky, S. E. & Nudelman, N. S. (1989). *Acta Cryst.* C**45**, 1952–1957.

Punte, G., Rivero, B. E., Socolovsky, S. E. & Nudelman, N. S. (1991). *Acta Cryst.* C**47**, 1222–1227.

Acta Cryst. (1999). C**55**, 827–829

A new 14:15-seco-15-norpregnane derivative from *Mandevilla illustris* Woodson (Apocynaceae)

IVO VENCATO,[a] RIVALDO NIERO,[a] JOÃO L. MONTANARI,[a] JOÃO B. CALIXTO,[b] ANTONIO E. G. SANT'ANA[c] AND ROSENDO A. YUNES[a]

[a]*Departamento Química, UFSC, 88040-900 Florianópolis SC, Brazil,* [b]*Departamento Farmacologia, UFSC, 88040-900 Florianópolis SC, Brazil, and* [c]*Departamento Química, UFAL, 57072-970 Maceió AL, Brazil. E-mail: vencato@qmc.ufsc.br*

(*Received 29 June 1998; accepted 11 January 1999*)

Abstract

The structure of a new 14:15-seco-15-norpregnane derivative, 3′-14-epoxy-4′,15-dioxaandrost-5-en-3β-yl acetate, $C_{22}H_{30}O_5$, isolated from the ethyl acetate extract of *Mandevilla illustris* (Apocynaceae), is described. Its chemical substructure contains an unusual 1-methyl-2,5,9-trioxatricyclo[4.2.1.$0^{3,7}$]nonane moiety. Features of the packing include an intermolecular C—H···O contact (C19—H···O5) of 3.230 (7) Å.

Comment

Mandevilla velutina and *M. illustris* (Apocynaceae) are native Brazilian plants, and infusions or alcoholic extracts of their rhizomes are used in popular medicines as anti-inflammatory agents and in the treatment of snakebites. Extracts and different compounds from these plants have been shown to antagonize bradykinin-induced muscle contraction and to have potent inflammatory activity (Calixto *et al.*, 1985; 1987; Calixto, Nicolau, Pizzolatti & Yunes, 1988; Calixto, Nicolau & Yunes, 1988; Calixto *et al.*, 1991). We have previously isolated from *M. velutina*, a compound with a novel pregnane structure, which was named velutinol A and which showed bradykinin antagonist activity (Yunes, Pizzolatti *et al.*, 1993); the structure of velutinol A was confirmed in a previous report (Bento *et al.*, 1996). The isolation from *M. illustris* of a compound named illustrol, (I), with a closely related 14:15-seco-15-norpregnane structure, was subsequently reported (Yunes, Brum *et al.*, 1993). Although alcoholic extracts of *M. illustris* antagonize bradykinin, illustrol was shown to be inactive in isolated rat uterus and isolated guinea pig ileum bradykinin-induced muscle contraction assays (Yunes, Brum *et al.*, 1993).

In this study, we report the crystal structure of the acetylated derivative of illustrol, (II), a new natural compound isolated from *M. illustris*, to define clearly