Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(4-Nitrophenyl)-4-piperidinol

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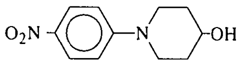
Abstract

The title compound, $C_{11}H_{14}N_2O_3$, is a non-linear optical chromophore. The piperidinol ring is in a chair conformation. The C—N—C fragment of the piperidinol moiety is nearly coplanar with the nitrophenyl ring system. The molecular stacking allows hydrogen bonding between the piperidinol hydroxy group and the nitro group.

Comment

The present study is part of a program designed to investigate the structure–property relationships among non-linear optical (NLO) materials. Organic NLO materials have potential for use in optical limiting devices for applications in sensor protection, optical storage devices and waveguides (Prasad & Williams, 1991). Owing to their versatility of chemical synthesis, organic materials are increasingly being investigated for their NLO properties (Prasad & Williams, 1991; Hann & Bloor, 1991; Chemla & Zyss, 1987; Miyata, 1992). Organic structures are versatile because they may be grown as single crystals, as Langmuir–Blodgett films or incorporated as chromophoric mesogens in polymer systems (Prasad & Williams, 1991).

Second-order NLO effects are highly dependent on the geometrical arrangement of the molecules in the crystal phase. For a crystalline material to exhibit second-order optical non-linearity, the crystal must be non-centrosymmetric (Prasad & Williams, 1991; Hann & Bloor, 1989). The present crystals, (I), are centrosymmetric and therefore do not exhibit NLO behavior. The production of a non-centrosymmetric material by using the compound as a chromophoric mesogen on a polymer backbone is being investigated. Molecular substitution on the piperidinol moiety is also being investigated, but the substituent must not interfere with the molecular features responsible for the optical non-linearity (Zyss & Oudar, 1982).



(I)

Bond lengths and angles in the nitrophenyl group are consistent with those of both nitrobenzene itself (Trotter, 1959) and the nitrophenyl moiety found in related compounds (Fkyerat *et al.*, 1995; Ishihara *et al.*, 1992; Hall *et al.*, 1986; Twieg & Dirk, 1986). Bond lengths and angles in the piperidinol ring are consistent with those of piperidine (Suwinska, Palenik & Gerdil, 1986). The piperidinol moiety adopts a chair conformation

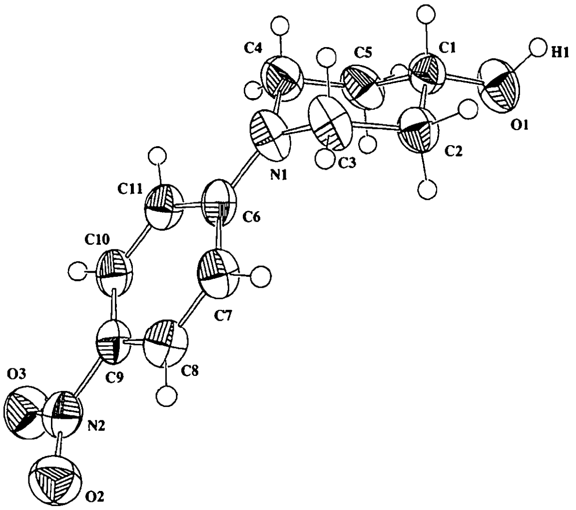


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(Fig. 1), with C3—N1—C4 nearly coplanar with the nitrophenyl ring. The O1 hydroxy group is oriented equatorially at C1. The molecules stack along the *a* axis, with the charge-transfer axis of the molecule (N2···N1) inclined by 48.2 (8)° to the *c* axis.

Molecules are linked by O1—H···O2($\frac{3}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$) hydrogen bonds of length 2.865 (5) Å, similar to those found in *N*-(4-nitrophenyl)-L-prolinol (2.84 Å; Fkyerat *et al.*, 1995).

Experimental

Crystals of the title compound were prepared according to the method of Taylor & Skotnicki (1981) and recrystallized from 2-propanol. The density D_m was measured by flotation in a 78% solution of sucrose.

Crystal data

$C_{11}H_{14}N_2O_3$
$M_r = 222.24$
Monoclinic
$P2_1/n$
$a = 4.863\,(2)$ Å
$b = 10.804\,(1)$ Å
$c = 20.139\,(5)$ Å
$\beta = 96.19\,(3)°$
$V = 1051.8\,(5)$ Å^3
$Z = 4$
$D_x = 1.403$ Mg m^{-3}
$D_m = 1.398$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5–12°$
$\mu = 0.097$ mm^{-1}
$T = 296$ K
Hexagonal needle
0.60 × 0.30 × 0.20 mm
Bright yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3782 measured reflections
1843 independent reflections
1094 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.045$
$\theta_{\text{max}} = 24.98°$
$h = -5 \rightarrow 5$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 0$
3 standard reflections frequency: 240 min intensity decay: 1%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.041$
$S = 1.376$
1094 reflections
201 parameters
H atoms refined isotropically
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.023$
$\Delta\rho_{\text{max}} = 0.431$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.5740 (8)	0.6355 (4)	0.7604 (2)	0.046 (2)
C2	0.4387 (9)	0.7593 (4)	0.7454 (2)	0.049 (2)
C3	0.5098 (13)	0.8103 (4)	0.6791 (2)	0.056 (3)
C4	0.5835 (13)	0.6045 (5)	0.6379 (2)	0.061 (3)
C5	0.5068 (11)	0.5480 (4)	0.7027 (2)	0.058 (2)
C6	0.2350 (9)	0.7410 (4)	0.5744 (2)	0.043 (2)
C7	0.0644 (9)	0.8465 (3)	0.5715 (2)	0.046 (2)
C8	−0.1423 (10)	0.8638 (4)	0.5212 (2)	0.048 (2)
C9	−0.1885 (9)	0.7766 (4)	0.4707 (2)	0.042 (2)
C10	−0.0195 (10)	0.6736 (4)	0.4702 (2)	0.048 (2)
C11	0.1876 (10)	0.6552 (4)	0.5211 (2)	0.048 (2)
N1	0.4387 (9)	0.7220 (3)	0.6254 (2)	0.055 (2)
N2	−0.4137 (8)	0.7929 (3)	0.4194 (2)	0.050 (2)
O1	0.4887 (8)	0.5816 (3)	0.8192 (2)	0.068 (2)
O2	−0.5450 (7)	0.8903 (3)	0.4177 (2)	0.064 (2)
O3	−0.4692 (8)	0.7101 (3)	0.3786 (1)	0.065 (2)

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

C1—O1	1.421 (5)	N2—O3	1.225 (5)
C6—N1	1.363 (5)	N2—O2	1.229 (5)
C9—N2	1.433 (5)		
C1—C2—C3	111.3 (4)	O3—N2—O2	122.0 (4)
C3—N1—C4	111.7 (4)		
C7—C6—N1—C3	−3.5 (7)	C10—C9—N2—O3	6.2 (6)

All non-H atoms were refined anisotropically by full-matrix least squares. H atoms were located from difference Fourier synthesis and their positions and isotropic displacement parameters refined using full-matrix least squares.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 *DIFDAT ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*3.2 *GENTAN*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ REGWT*. Molecular graphics: *Xtal*3.2 *ORTEP*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

The authors would like to thank Steve Pollack (Howard University, Washington, DC, USA) for providing the title compound and Michael Chabinyc, now at Stanford University, for help with *Xtal*3.2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Identification of the *N*-Alkylation Product of 3-(2-Pyrrolyl)pyridazine

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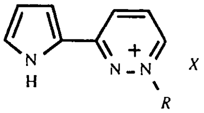
Abstract

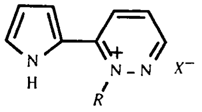
The title compound has been unequivocally identified as 1-ethyl-3-(2-pyrrolyl)pyridazinium tetrafluoroborate, $C_{10}H_{12}N_3^+.BF_4^-$.

Comment

3-(2-Pyrrolyl)pyridazine may be *N*-alkylated to yield either the 1- or the 2-alkylpyridazinium salt, (1) or (2), respectively. Molecular-orbital calculations (Domingo, 1993) indicate that conjugation of the pyridazine ring with the π-electron excessive pyrrole should enhance the nucleophilicity of N2, but the observed rates of alkylation of 2-(2-pyrrolyl)pyridine and 3-(2-pyrrolyl)-pyridine (Karatza, 1992) show that the 3-pyridyl system is considerably more reactive than the 2-pyridyl system. *N*-Alkylation of 3-(2-pyrrolyl)pyridazine with triethyloxonium tetrafluoroborate yields a single product, as confirmed by TLC analysis and by NMR spectroscopy, the structure of which could not be identified unambiguously from the ^1H or ^{13}C NMR spectroscopic data (Whitmore, 1994).



(1)



(2)

A projection of the crystal structure of the *N*-ethylated product (Fig. 1) shows unequivocally that it is the N1 atom of the pyridazine ring which is alkylated [(1), *R* = Et, *X* = BF_4]. The two rings are almost coplanar with an angle of only 5.4 (1)° between their mean planes. The C(1)—C(5) bond length [1.435 (3) Å] between the two rings indicates a high degree of conjugation between the π-electron excessive pyrrole ring and the π-electron deficient pyridazinium ring. The BF_4^- anions are linked to the cations by hydrogen-bonding interactions, the shortest of which are C9—H9*A*···F1 $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ [H···F = 2.39 (4) Å] and N3—H3*A*···F3 $(x - 1, \frac{1}{2} - y, \frac{1}{2} + z)$ [H···F = 2.16 (6) Å].

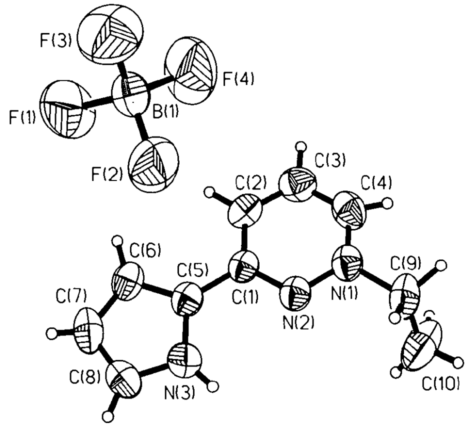


Fig. 1. *ORTEP*II (Johnson, 1976) view of the 1-ethyl-3-(2-pyrrolyl)-pyridazinium cation and the BF_4^- anion showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The *N*-alkylated product was obtained by the reaction of triethyloxonium tetrafluoroborate with 3-(2-pyrrolyl)-pyridazine in CH_2Cl_2 at room temperature. Recrystallization was from EtOH.

Crystal data

$C_{10}H_{12}N_3^+.BF_4^-$
$M_r = 261.0$
Monoclinic
$P2_1/c$
$a = 8.232\ (2)$ Å
$b = 11.599\ (3)$ Å
$c = 12.996\ (4)$ Å
$\beta = 105.85\ (2)°$
$V = 1193.8$ Å^3
$Z = 4$
$D_x = 1.452$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 5$–$15°$
$\mu = 0.126$ mm^{-1}
$T = 295$ K
Prism
0.70 × 0.50 × 0.30 mm
Yellow

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans
Absorption correction: none

$R_{\text{int}} = 0.023$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 14$