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N-(5-Nitro-2-pyrrolidinylphenyl)trifluoroacetamide

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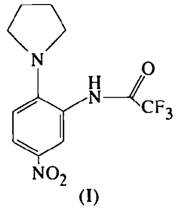
Abstract

The reaction of 2-fluoro-5-nitroaniline with pyrrolidine and triethylamine in DMF gives 2-pyrrolidinyl-5-nitroaniline, and subsequent treatment with trifluoroacetic acid and thionyl chloride in DMF results in the title compound, $C_{12}H_{12}F_3N_3O_3$, the molecular structure of which, determined by X-ray crystallography, is described. In recent years, the interest in using organic crystals with a charge-transfer interaction *via* highly delocalized π-electron states (*e.g.* nitroanilines with donor and acceptor substituents in *para* positions) has increased considerably, since many of them have shown non-linear optical properties [Chemla & Zyss (1986). In *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols. 1 and 2. Orlando: Academic Press]. *N*-(5-Nitro-2-pyrrolidinylphenyl)trifluoroacetamide (TPNB) is a donor–acceptor substituted benzene derivative and belongs to a family of compounds which produce high molecular non-linearity. TPNB shows a charge transfer (CT) between the *para*-disposed pyrrolidino donor and nitro acceptor groups.



(I)

Comment

The title compound, (I), consists of discrete monomeric molecules. An *ORTEP*II plot (Johnson, 1976) together with the atomic numbering scheme is shown in Fig. 1. The crystal structure can be described in terms of discrete molecules with two independent molecules in the asymmetric unit. An analysis of semi-normal probability (Abrahams & Keve, 1971) indicates that differences in the bond lengths and angles of these molecules are statistically insignificant. The average values will therefore be discussed. The sum of the angles around the N1 atom [358.7 (2)°] reflects a planar sp^2 geometry. The N2 atom also shows planar sp^2 geometry. As expected, the *para*-nitro groups are rotated slightly out of their respective aromatic planes [N3—O2—O3 14.6 (2) and N3*B*—O2*B*—O3*B* 8.6 (2)°]. The mean N—O bond lengths are in the usual range (1.228–1.238 Å) for aromatic NO_2 groups and compare well with data available for such systems (MacNicol & Mallinson, 1995; Hsu, Nordman & Kenny, 1993). The nitro group is almost planar, with the N atom 0.062 (2) Å out of the O2, O3, C9 plane.

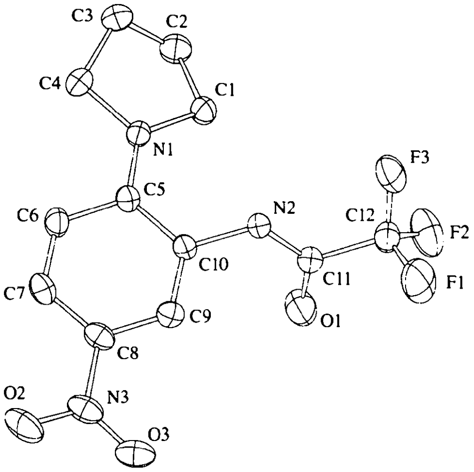


Fig. 1 The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

In order to check the possible tautomerization in the studied molecule, *i.e.* $R\mathrm{NHC({=}O)CF_3}$ or $R\mathrm{N{=}C(OH)CF_3}$, we have located the H1 and H1*B* atoms (bound to the N2 and N2*B* atoms, respectively) from a difference Fourier map. These bonds confirm the structure proposed for both molecules, *i.e.* the keto form.

It is interesting to note that the π-system deformation results from steric interactions between the lateral chain and the phenyl ring. This π-system deformation can be measured by the torsion angle [C5—C10—N2—C11 128.3 (3)°] at the function bond level or by the dihedral angle between the phenyl ring and the mean plane of atoms N2, C11, O1 and C12 [52.0 (2)°].

The dihedral angle between the least-squares planes of the phenyl and pyrrolidino rings is 20.3 (3)°. In the latter, the N atom has a planar conformation. The puckering parameters for the pyrrolidine ring are q_2 = 0.393 (4) Å and φ_2 = 94.0 (8)° (Cremer & Pople, 1975), which indicates a distorted envelope conformation.

The differences between the C—F bonds are probably due to librational effects. One large anisotropic displacement parameter for the F atoms suggests either a large component of vibration amplitude or slight disorder. There is presumably a slight disorder.

The average distance values are C_{sp^3}—C_{sp^3} 1.512 (3), C_{sp^2}—C_{sp^2} 1.388 (3), N—O 1.231 (3), C═O 1.214 (3) and C—F 1.317 (3) Å. The valence angles involving tetrahedral and trigonal C atoms have mean values of 105.0 (3) and 120.7 (3)°, respectively.

Experimental

The title material was prepared from commercially available 2-fluoro-5-nitroaniline (Sigma) by a two-stage synthetic procedure. In the first step, 2-fluoro-5-nitroaniline was treated with a mixture of pyrrolidine and triethylamine in a dipolar aprotic solvent such as DMF in a round-bottomed flask fitted with a reflux condenser and a nitrogen bubbler. A mixture of trifluoroacetic acid, thionyl chloride and dry DMF (a drop), which had been refluxed for 1 h, was added to the 2-pyrrolidino-5-nitroaniline intermediate in pyridine at 273 K under a nitrogen atmosphere.

Crystal data

$C_{12}H_{12}F_3N_3O_3$
M_r = 303.24
Monoclinic
$P2_1/n$
a = 8.192 (3) Å
b = 19.278 (5) Å
c = 16.952 (2) Å
β = 100.2 (2)°
V = 2635 (2) Å^3
Z = 8
D_x = 1.529 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 8–17°
μ = 1.218 mm^{-1}
T = 293 K
Prism
0.32 × 0.16 × 0.10 mm
Red

Data collection

Siemens AED diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4238 measured reflections
3928 independent reflections
3258 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0422

$\theta_{\rm max}$ = 60.04°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = -19 \rightarrow 18$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0446
$wR(F^2)$ = 0.1370
S = 0.635
3928 reflections
389 parameters
H atoms not refined, except for H1 and H1*B*
$w = 1/[\sigma^2(F_o^2) + (0.158P)^2 + 3.0996P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.006
$\Delta\rho_{\rm max}$ = 0.461 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.316 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0047 (4)
Scattering factors from *SHELXL*93

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

N1—C5	1.348 (3)	N1*B*—C5*B*	1.351 (3)
N1—C4	1.464 (3)	N1*B*—C1*B*	1.469 (3)
N1—C1	1.472 (3)	N1*B*—C4*B*	1.473 (3)
C8—N3	1.433 (3)	C8*B*—N3*B*	1.438 (4)
C10—N2	1.433 (3)	C10*B*—N2*B*	1.426 (3)
N2—C11	1.324 (3)	N2*B*—C11*B*	1.332 (3)
C11—O1	1.215 (3)	C11*B*—O1*B*	1.213 (3)
C11—C12	1.521 (4)	C11*B*—C12*B*	1.525 (4)
C12—F1	1.298 (3)	C12*B*—F2*B*	1.308 (3)
C12—F2	1.312 (3)	C12*B*—F3*B*	1.329 (3)
C12—F3	1.327 (3)	C12*B*—F1*B*	1.331 (3)
N3—O3	1.238 (3)	N3*B*—O3*B*	1.228 (4)
N3—O2	1.228 (3)	N3*B*—O2*B*	1.228 (3)
C5—N1—C4	122.1 (2)	C5*B*—N1*B*—C1*B*	126.9 (2)
C5—N1—C1	125.9 (2)	C5*B*—N1*B*—C4*B*	121.5 (2)
C4—N1—C1	110.7 (2)	C1*B*—N1*B*—C4*B*	110.2 (2)
N1—C1—C2	103.3 (2)	N1*B*—C1*B*—C2*B*	103.7 (2)
C11—N2—C10	123.0 (2)	C11*B*—N2*B*—C10*B*	124.6 (2)
O3—N3—O2	122.9 (2)	O3*B*—N3*B*—O2*B*	122.4 (3)
O3—N3—C8	118.5 (2)	O3*B*—N3*B*—C8*B*	118.4 (3)
O2—N3—C8	118.6 (3)	O2*B*—N3*B*—C8*B*	119.2 (3)

Data collection and cell refinement used *DIF*4 (Stoe & Cie, 1992*a*). Data reduction used *REDU*4 (Stoe & Cie, 1992*b*). The collected $\theta_{\rm max}$ angle was only 60° due to instrumental problems. The structure was solved by direct methods and Fourier methods using *SHELXS*86 (Sheldrick, 1985). Refinement was performed with *SHELXL*93 (Sheldrick, 1993) using full-matrix least squares, with anisotropic displacement parameters for all non-H atoms. H atoms were included at calculated positions and refined using a riding model, with an overall isotropic displacement parameter, except for the H2 and H2*B* atoms, which were found and refined with an overall isotropic displacement parameter. Molecular graphics were produced using *ORTEP*II (Johnson, 1976) and material for publication was prepared using *SHELXL*93 and *PARST*96 (Nardelli, 1983, 1995).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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