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Hydrogen bonding in C-substituted nitroanilines: molecular ladders in 2-trifluoromethyl-4-nitroaniline and sheets of $R_4^4(12)$ and $R_4^4(32)$ rings in 3-trifluoromethyl-4-nitroaniline

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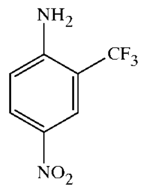
In 2-trifluoromethyl-4-nitroaniline, $C_7H_5F_3N_2O_2$, (I), the molecules lie across a mirror plane in space group *Pnma*. The molecules are linked by paired N—H···O hydrogen bonds to form a $C(8)[R_2^2(6)]$ chain of rings, pairs of which are linked into a molecular ladder by a single C—H···O hydrogen bond. The isomeric 3-trifluoromethyl-4-nitroaniline, (II), has $Z' = 2$ in space group $P2_1/c$. Each molecule is linked to four others by N—H···O hydrogen bonds to form sheets built from alternating $R_4^4(12)$ and $R_4^4(32)$ rings.

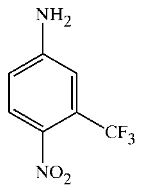
Comment

In the structure of 4-nitroaniline (Tonogaki *et al.*, 1993), each molecule is linked to four others by means of N—H···O hydrogen bonds, and the molecules are thereby linked into (4,4)-nets (Batten & Robson, 1998). The resulting sheets, which contain a single type of $R_4^4(22)$ ring, are weakly linked by aromatic π–π-stacking interactions. The introduction of a single methyl group in 2-methyl-4-nitroaniline gives rise to a different structure in the form of a three-dimensional framework, even though each molecule is still linked to four others by N—H···O hydrogen bonds (Ferguson *et al.*, 2001). The structure now consists of two intersecting sets of sheets built from a single type of $R_8^8(54)$ ring. However, entirely different patterns of N—H···O hydrogen bonds are observed in the two polymorphs of 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001). In the triclinic polymorph, the molecules are linked into chains *via* a rather unusual supramolecular synthon comprising pairs of N—H···O hydrogen bonds forming an $R_2^2(6)$ ring, while in the orthorhombic polymorph, each molecule acts as just a single donor and single acceptor of N—H···O hydrogen bonds, with the formation of simple $C(8)$ chains. In both polymorphs, the chains are further linked into sheets by means of I···NO_2 interactions.

Continuing our study of C-substituted nitroanilines (Cannon *et al.*, 2001; Ferguson *et al.*, 2001; Glidewell *et al.*, 2001; McWilliam *et al.*, 2001; Zakaria *et al.*, 2001; Garden *et al.*, 2001), we have now investigated the isomeric pair 2-trifluoromethyl-4-nitroaniline, (I), and 3-trifluoromethyl-4-nitroaniline, (II), which exhibit yet further modes of supramolecular aggregation.



(I)



(II)

Compound (I) (Fig. 1) crystallizes in space group *Pnma* with $Z' = \frac{1}{2}$, so that all the atoms, apart from two of the F atoms, lie on a mirror plane, selected as that at $y = \frac{1}{4}$. The molecules are linked into chains by N—H···O hydrogen bonds (Table 1) and these chains are linked in pairs by a single C—H···O

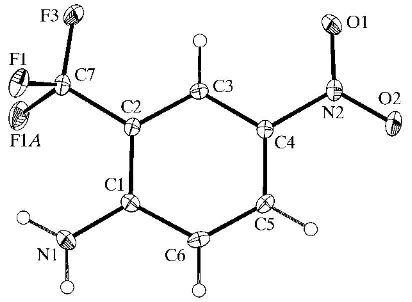


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

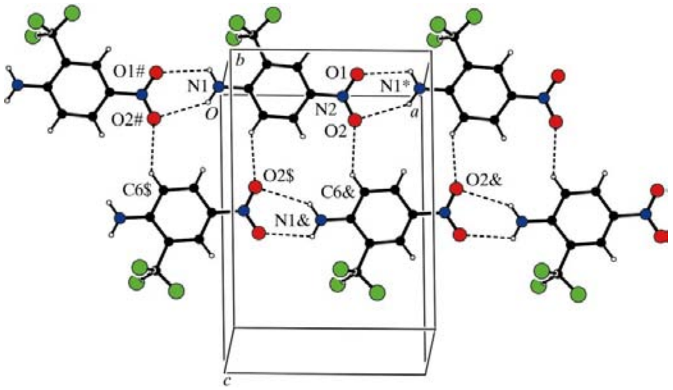


Figure 2
Part of the crystal structure of (I) showing the linking of pairs of $C(8)[R_2^2(6)]$ chains of rings into a molecular ladder. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(1 + x, \frac{1}{4}, z)$, $(x - 1, \frac{1}{4}, z)$, $(x - \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$, respectively.

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hydrogen bond. The amino atom N1 in the molecule at $(x, \frac{1}{4}, z)$ acts as a hydrogen-bond donor *via* H11 and H12 to O1 and O2, respectively, in the molecule at $(x - 1, \frac{1}{4}, z)$, so generating by translation a $C(8)[R_2^2(6)]$ chain of rings parallel to [100] (Fig. 2), where the $R_2^2(6)$ ring is necessarily planar. Four such chains run through each unit cell. A pair of chains related by the 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{4})$ are weakly linked by a soft hydrogen bond; atom C6 in the molecule at $(x, \frac{1}{4}, z)$ acts as a hydrogen-bond donor to O2 in the molecule at $(x - \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z)$, while atom C6 at $(x - \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z)$ in turn acts as a donor to O2 at $(x - 1, \frac{1}{4}, z)$. This combination of hard and soft hydrogen bonds thus generates a molecular ladder, in which a pair of [100] chains plays the role of the uprights, while the C—H···O hydrogen bonds provide the rungs. Between the rungs, there are $R_3^2(12)$ rings (Fig. 2). The $C(8)[R_2^2(6)]$ chain of rings in (I) is thus analogous to that in triclinic 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001). In this latter compound, the linking of the chains into sheets again involves chains of like polarity, related to one another by translation. Two molecular ladders pass through each unit cell in (I), at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, but there are no direction-specific interactions between neighbouring ladders.

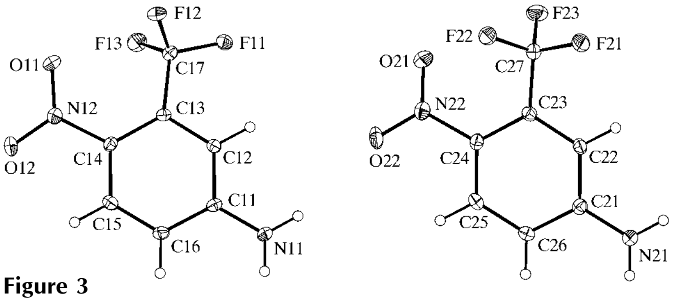

Figure 3
A view of the two independent molecules of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

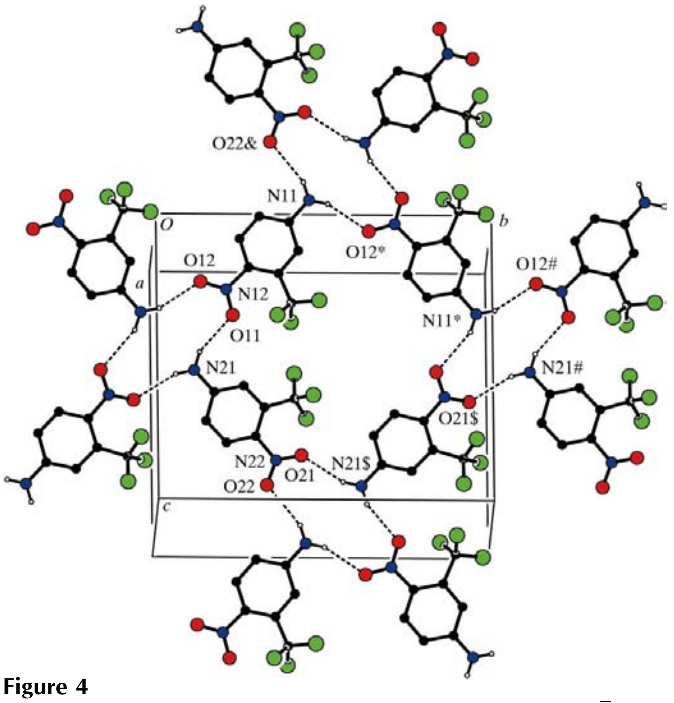

Figure 4
Part of the crystal structure of (II) showing the formation of a $(10\overline{1})$ sheet built from $R_4^4(12)$ and $R_4^4(32)$ rings. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(-x - 1, \frac{1}{2} + y, \frac{1}{2} - z)$, $(x, 1 + y, z)$, $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x - 1, y, z - 1)$, respectively.

Compound (II) crystallizes in space group $P2_1/c$ with $Z' = 2$, and each molecule (Fig. 3) is linked to four others, *via* N—H···O hydrogen bonds (Table 3), into sheets parallel to $(10\overline{1})$. The formation of these sheets can readily be analysed in terms of three distinct one-dimensional motifs. There are two spiral chains parallel to [010], each comprising one type of molecule only, and a translational chain parallel to [101] containing both types of molecule.

Atom N11 in the type 1 molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H12, to O12 in the type 1 molecule at $(-x - 1, \frac{1}{2} + y, \frac{1}{2} - z)$, so producing a $C(8)$ chain parallel to [010] generated by the 2_1 screw axis along $(-\frac{1}{2}, y, \frac{1}{4})$ (Fig. 4). Similarly, atom N21 in the type 2 molecule at (x, y, z) acts as a donor, *via* H22, to O21 in the type 2 molecule at $(-x, y - \frac{1}{2}, \frac{3}{2} - z)$, producing another $C(8)$ spiral, this time generated by the 2_1 axis along $(0, y, \frac{3}{4})$. Within the asymmetric unit, atom N21 acts as a donor, *via* H21, to O11, while atom N11 at (x, y, z) acts as a donor, *via* H11, to O22 at $(x - 1, y, z - 1)$. The combination of the [101] chain with the two independent [010] chains generates a $(10\overline{1})$ sheet built of $R_4^4(12)$ and $R_4^4(32)$ rings, alternating in a checkerboard fashion (Fig. 4). The interior of the large rings is occupied by the CF_3 groups, the conformations of which are such that the two sets of F atoms are meshed together.

The $(10\overline{1})$ sheets in (II) are weakly linked by aromatic π–π-stacking interactions. For the aromatic rings of molecules in adjacent sheets, the minimum distance between the ring centroids of a type 1 molecule at (x, y, z) and a type 2 molecule at $(x - 1, \frac{1}{2} - y, z - \frac{1}{2})$ is 3.552 (2) Å, with the planes separated by 3.385 (3) Å.

The bond lengths in (I) and (II) present no unexpected features. In compound (II), there is evidence from the exocyclic bond angles (Table 2) for significant repulsion between the adjacent nitro and trifluoromethyl groups.

Experimental

Samples of compounds (I) and (II) were purchased from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol.

Compound (I)

Crystal data

$C_7H_5F_3N_2O_2$
$M_r = 206.13$
Orthorhombic, *Pnma*
$a = 9.0274$ (4) Å
$b = 6.5933$ (4) Å
$c = 13.1170$ (8) Å
$V = 780.73$ (8) Å^3
$Z = 4$
$D_x = 1.754$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 961 reflections
$\theta = 2.7$–$27.6°$
$\mu = 0.18$ mm^{-1}
$T = 150$ (2) K
Block, red
0.20 × 0.15 × 0.01 mm

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O1^{i}	0.88	2.41	2.870 (2)	113
N1—H12$\cdots$O2^{i}	0.88	2.57	3.299 (2)	141
C6—H6$\cdots$O2^{ii}	0.95	2.59	3.398 (3)	143

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$.

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.987$, $T_{\max} = 0.998$
3944 measured reflections
961 independent reflections
725 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 27.6°$
$h = -9 \rightarrow 11$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.118$
$S = 1.06$
961 reflections
82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.0530P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Compound (II)

Crystal data

$C_7H_5F_3N_2O_2$
$M_r = 206.13$
Monoclinic, $P2_1/c$
$a = 7.1048$ (2) Å
$b = 15.3832$ (5) Å
$c = 14.3091$ (6) Å
$\beta = 91.9102$ (12)°
$V = 1563.04$ (9) Å^3
$Z = 8$
$D_x = 1.752$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3541 reflections
$\theta = 3.0$–27.5°
$\mu = 0.18$ mm^{-1}
$T = 150$ (2) K
Plate, yellow
0.40 × 0.16 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.812$, $T_{\max} = 0.983$
12 016 measured reflections
3541 independent reflections
2369 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 19$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.114$
$S = 0.98$
3541 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0153 (19)

Compound (I) crystallized in the orthorhombic system. The systematic absences permitted space groups $Pna2_1$ and $Pnma$; $Pnma$ was selected and confirmed by the analysis. For compound (II), space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms were treated as riding, with C—H = 0.95 Å and N—H = 0.88 Å.

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

C12—C13—C17	116.11 (16)	C22—C23—C27	116.85 (16)
C14—C13—C17	125.73 (15)	C24—C23—C27	124.24 (16)
C13—C14—N12	123.44 (15)	C23—C24—N22	123.06 (16)
C15—C14—N12	116.53 (16)	C25—C24—N22	116.73 (16)
O11—N12—C14—C13	−16.7 (2)	O21—N22—C24—C23	28.1 (2)

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$\cdots$O22^{i}	0.88	2.42	3.221 (2)	152
N11—H12$\cdots$O12^{ii}	0.88	2.26	3.088 (2)	157
N21—H21$\cdots$O11	0.88	2.31	3.088 (2)	148
N21—H22$\cdots$O21^{iii}	0.88	2.28	3.101 (2)	155

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. The authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided the computing facilities for this work, and JLW thanks CNPq, Brazil, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1528). Services for accessing these data are described at the back of the journal.

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