research communications

Crystallographic and spectroscopic characterization of 4-nitro-2-(trifluoromethyl)benzoic acid and 4-nitro-3-(trifluoromethyl)benzoic acid

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The title compounds, both $C_8H_4F_3NO_4$, represent two isomers of nitro trifluoromethyl benzoic acid. The compounds each contain a nitro functionality *para* to the carboxylic acid group, with the trifluoromethyl substituent *ortho* to the acid group in the 2-isomer and *ortho* to the nitro group in the 3-isomer. The regiochemistry with respect to the trifluoromethyl group results in steric interactions that rotate the carboxylic acid group or the nitro group out of the aromatic plane in the 2- and 3-isomer, respectively. Each molecule engages in intermolecular hydrogen bonding, forming head-to-tail dimers with graph-set notation $R_2^2(8)$ and donor–acceptor hydrogen-bonding distances of 2.7042 (14) Å in the 2-isomer and 2.6337 (16) in the 3-isomer. Recrystallization attempts did not yield untwinned crystals.

1. Chemical context

The title compounds, 4-nitro-2-(trifluoromethyl)benzoic acid (I) and 4-nitro-3-(trifluoromethyl)benzoic acid (II), are trisubstituted aromatic compounds featuring a carboxylic acid, a nitro group and a trifluoromethyl group. Although all ten isomers of nitro trifluoromethyl benzoic acid are available commercially, none of their crystal structures have been reported. 4-Nitro-2-(trifluoromethyl)benzoic acid (I) may be synthesized from 2-(trifluoromethyl)benzoic acid by treating it with concentrated sulfuric acid, stirring, and adding fuming nitric acid dropwise (Kompella *et al.*, 2017). 4-Nitro-2-(trifluoromethyl)benzoic acid (I) has been used in the syntheses of potential pharmaceuticals, for example in anti-tumor pyridinone (Cheung *et al.*, 2017) and urea derivatives (Nishio *et al.*, 2017). 4-Nitro-3-(trifluoromethyl)benzoic acid (II) was first reported in 1951 after being prepared from the corresponding nitrile (Caldwell & Sayin, 1951). The compound has recently been used for the synthesis of glutamate receptor antagonists (Selvam *et al.*, 2018) that have potential as therapies for diseases such as Parkinson's.
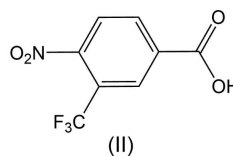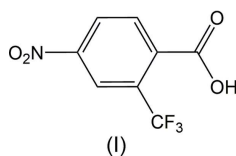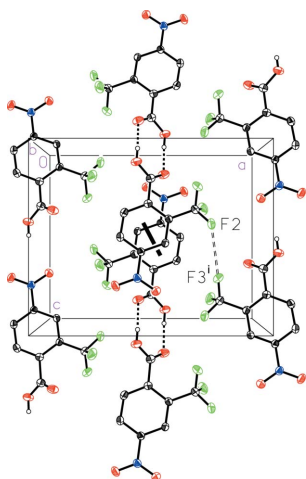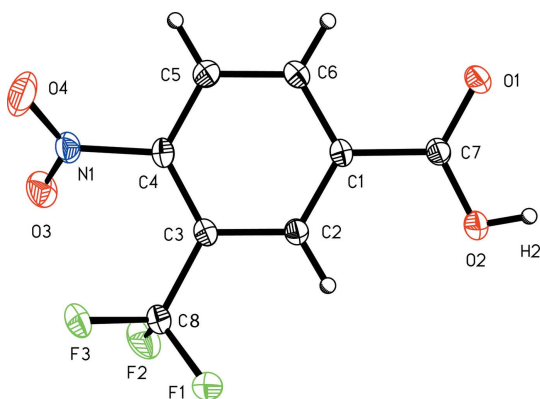

2. Structural commentary

4-Nitro-2-(trifluoromethyl)benzoic acid, (I) (Fig. 1), and 4-nitro-3-(trifluoromethyl)benzoic acid, (II) (Fig. 2), exhibit similar metrical parameters. The aromatic nitro bond length
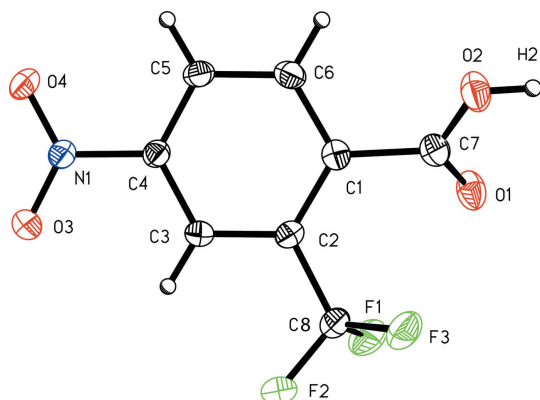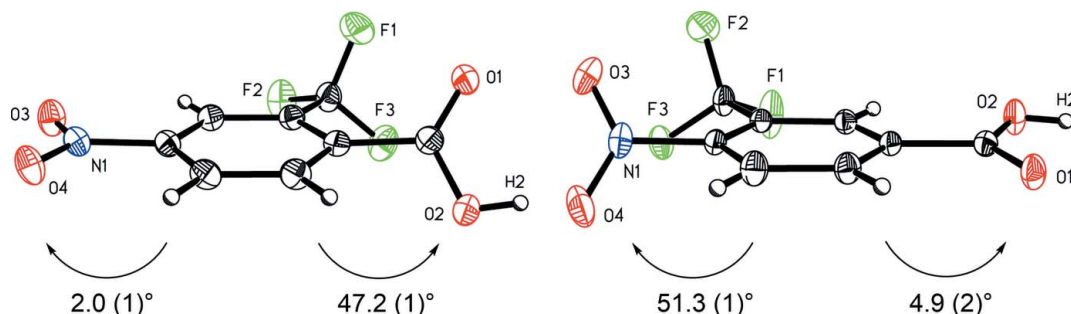
Figure 1
A view of 4-nitro-2-(trifluoromethyl)benzoic acid (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Figure 2
A view of 4-nitro-3-(trifluoromethyl)benzoic acid (II) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

C4—N1 of 1.4718 (16) Å in (I) and 1.4751 (19) in (II) are similar, as are the aromatic trifluoromethyl bond lengths C2—C8 of 1.5114 (17) Å in (I) and C3—C8 of 1.508 (2) Å in (II). The nitro N—O distances lie between 1.2154 (19) and 1.2271 (14) Å; average 1.224 (6) Å. Whereas the carboxylic acid group in (I) is not significantly disordered, with an O1—C7 carbonyl bond length of 1.219 (2) Å and an O2—C7 acid bond length of 1.3139 (16) Å, the carboxylic acid group in (II) exhibits some twofold disorder, with an O1—C7 bond length of 1.2528 (18) Å and O2—C7 acid bond length of 1.281 (2) Å.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^i	0.85 (1)	1.86 (2)	2.7042 (14)	175 (2)

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

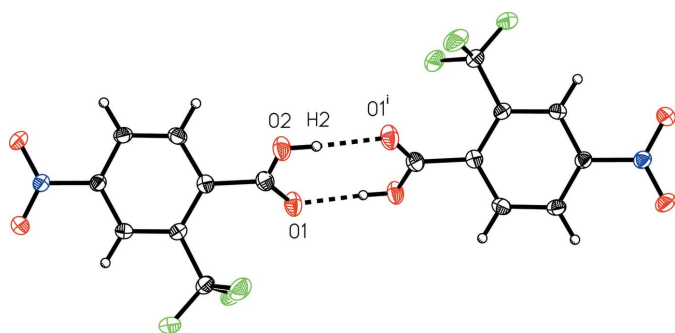| D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^i	0.83 (2)	1.82 (2)	2.6337 (16)	168 (2)

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

A notable difference in the molecular structures of the title compounds is the influence of the trifluoromethyl substituent on the co-planarity of the carboxylic acid and nitro groups with the aromatic ring plane (Fig. 3). In 4-nitro-2-(trifluoromethyl)benzoic acid (I), the trifluoromethyl group *ortho* to the carboxylic acid moiety rotates it out of the plane of the aromatic ring, with a plane-to-plane angle of 47.2 (1)°, whereas the nitro group is almost co-planar with the aromatic ring, with an angle of 2.0 (1)°. Conversely, in 4-nitro-3-(trifluoromethyl)benzoic acid (II), the trifluoromethyl group *ortho* to the nitro moiety rotates it out of the plane of the aromatic ring, with a plane-to-plane angle of 51.3 (1)°, whereas the carboxylic acid group is closer to co-planar with the aromatic ring, with an angle of 4.9 (2)°.

3. Supramolecular features

The molecules of the title compounds pack together in the solid state with hydrogen bonding between the carboxylic acid hydrogen atom and the carbonyl oxygen atom of the symmetry-related carboxyl group in a neighboring molecule, forming a dimer with graph-set notation $R_2^2(8)$. This centrosymmetric pairwise hydrogen-bonding dimer formation results in short hydrogen-bonding distances of 2.7042 (14) Å in (I) (Fig. 4, Table 1) and 2.6337 (16) in (II) (Fig. 5, Table 2).

The molecular packing in the unit cell of 4-nitro-2-(trifluoromethyl)benzoic acid (I) (Fig. 6) reveals a dimerized face-to-face geometrical arrangement of the aromatic rings related by inversion, with a ring centroid-to-centroid distance of

Figure 3
Side-by-side views of 4-nitro-2-(trifluoromethyl)benzoic acid (I) (left) and 4-nitro-3-(trifluoromethyl)benzoic acid (II) indicating the rotation of the carboxyl and nitro groups out of the mean plane of the aromatic ring.

Figure 4
A view of the intermolecular hydrogen bonding in 4-nitro-2-(trifluoromethyl)benzoic acid (I). [Symmetry code: (i) −x + 1, −y + 1, −z.]
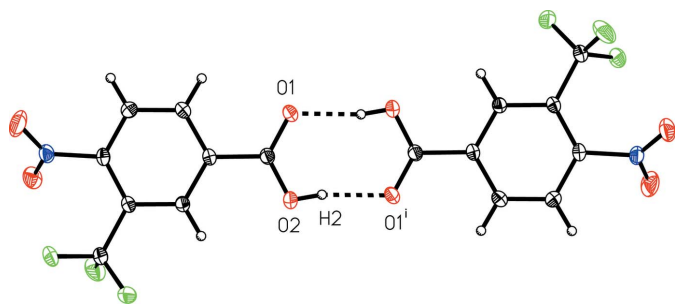
3.907 (1) Å, a centroid-to-plane distance of 3.820 (1) Å, and a ring-offset slippage of 0.822 (2) Å. An intermolecular fluorine–fluorine interaction is also observed with a length of 2.927 (1) Å that is similar to the sum of the van der Waals radii (2.94 Å; Bondi, 1964). The hydrogen bonded dimers of 4-nitro-3-(trifluoromethyl)benzoic acid (II) pack together in a similar way, but with a longer fluorine–fluorine contact [2.975 (2) Å] and a highly offset face-to-face geometric arrangement of the aromatic rings characterized by a large ring-offset slippage of 1.733 (2) Å such that the aromatic rings are barely overlapped (Fig. 7).
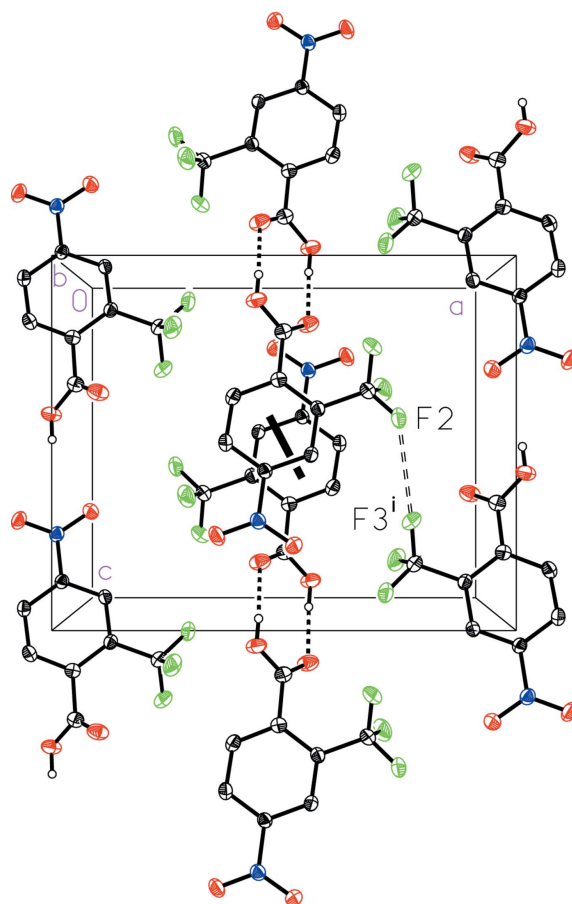
4. Database survey

The Cambridge Structural Database (Groom *et al.*, 2016) contains no isomers of nitro trifluoromethyl benzoic acid. A related derivative of 4-nitro-3-(trifluoromethyl)benzoic acid (II) is 3-methyl-4-nitrobenzoic acid (TOYGIZ), which exhibits a similar hydrogen-bonding motif and hydrogen-bonding distance of 2.617 Å (Saha *et al.*, 2015). As with (II), the methyl group *ortho* to the nitro moiety in TOYGIZ rotates it out of the plane of the aromatic ring whereas the carboxylic acid group is closer to co-planar with the aromatic ring.

5. Synthesis and crystallization

4-Nitro-2-(trifluoromethyl)benzoic acid (I) (97%) was purchased from Alfa Aesar and 4-nitro-3-(trifluoromethyl)-

Figure 6
A view of the packing in 4-nitro-2-(trifluoromethyl)benzoic acid (I) with a double-dashed line indicating the F···F interaction and a thick solid line indicating a centroid-to-centroid interaction. [Symmetry code: (i) −x + $\frac{3}{2}$, y, z + $\frac{1}{2}$.]

Figure 5
A view of the intermolecular hydrogen bonding in 4-nitro-3-(trifluoromethyl)benzoic acid (II). [Symmetry code: (i) −x, −y + 1, −z.]
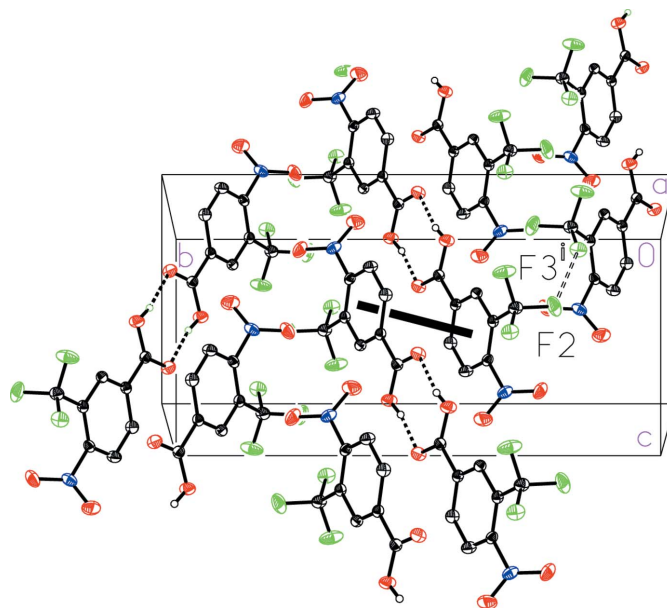
Figure 7
A view of the packing in 4-nitro-3-(trifluoromethyl)benzoic acid (II) with a double-dashed line indicating the F···F interaction and a thick solid line indicating a centroid-to-centroid interaction. [Symmetry code: (i) −$\frac{1}{2}$ + x, $\frac{1}{2}$ − y, −$\frac{1}{2}$ + z.]

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_8H_4F_3NO_4$	$C_8H_4F_3NO_4$
M_r	235.12	235.12
Crystal system, space group	Orthorhombic, $Pccn$	Monoclinic, $P2_1/n$
Temperature (K)	125	125
a, b, c (Å)	12.1612 (17), 14.847 (2), 9.8265 (14)	6.8986 (8), 17.240 (2), 7.6912 (9)
α, β, γ (°)	90, 90, 90	90, 107.685 (2), 90
V (Å^3)	1774.2 (4)	871.50 (18)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.18	0.18
Crystal size (mm)	$0.24 \times 0.24 \times 0.15$	$0.30 \times 0.20 \times 0.10$
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)	Multi-scan (*TWINABS*; Sheldrick, 2008a)
T_{min}, T_{max}	0.86, 0.97	0.89, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40170, 2727, 2064	4385, 2665, 2116
R_{int}	0.050	0.071
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.716	0.715
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.109, 1.04	0.048, 0.150, 1.05
No. of reflections	2727	2873
No. of parameters	148	150
No. of restraints	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.46, −0.24	0.50, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *SHELXTL* (Sheldrick, 2008b), *OLEX2* (Dolomanov et al., 2009) and *Mercury* (Macrae et al., 2008).

benzoic acid (II) (97%) were purchased from Aldrich Chemical Company. (I) was recrystallized from tetrahydrofuran and (II) was used as received.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model with C—H = 0.95 and U_{iso}(H) = $1.2U_{eq}$(C) of the aryl C-atoms the hydrogens are riding on. The positions of the carboxylic acid hydrogen atoms were found in the difference map and the atoms refined semi-freely using a distance restraint d(O—H) = 0.84 Å, and U_{iso}(H) = $1.2U_{eq}$(O). 4-Nitro-3-(trifluoromethyl)benzoic acid (II) was found to be multiply non-merohedrally twinned. Recrystallization attempts did not yield untwinned crystals. Three components were integrated with *SAINT* using the multiple-component orientation matrix produced by *CELL_NOW* (Sheldrick, 2003), and the data were absorption corrected and scaled with *TWINABS* (Sheldrick, 2008a). The initial solution was found and refined with merged and roughly detwinned HKLF 4 format data before final refinement against HKLF5 format data constructed from all observations involving domain 1 only. The twin ratio (*SHELXL* BASF parameters) refined to 0.0961 (3) and 0.0326 (2).

7. Analytical data

(I) ^{1}H NMR (Bruker Avance III HD 400 MHz, DMSO d_6): δ 8.07 (d, 1 H, $C_{aryl}H$, J_{ortho} = 8.4 Hz), 8.50 (d, 1 H, $C_{aryl}H$, J_{meta} = 2.2 Hz), 8.56 (dd, 1 H, $C_{aryl}H$, J_{ortho} = 8.4 Hz, J_{meta} = 2.2 Hz), 14.28 (br s, 1 H, OH). ^{13}C NMR (^{13}C{^{1}H}, 100.6 MHz, DMSO d_6): δ 121.76 (q, $C_{aryl}H$, J_{C-F} = 5.4 Hz), 122.31 (q, CF_3, J_{C-F} = 274 Hz), 127.20 (q, $C_{aryl}CF_3$, J_{C-F} = 33.5 Hz), 127.64 (s, $C_{aryl}H$), 131.35 (s, $C_{aryl}H$), 137.86 (s, $C_{aryl}COOH$), 148.27 (s, $C_{aryl}NO_2$), 166.44 (s, COOH). IR (Thermo Nicolet iS50, ATR, cm^{-1}): 3133 (s br, O—H str), 3096 (s, C_{aryl}-H str), 2922 (s), 2660 (m), 2531 (m), 1723 (s, C=O str), 1618 (s), 1540 (s), 1498 (m), 1407 (s), 1357 (s), 1317 (s), 1294 (s), 1268 (s), 1177 (m), 1153 (s), 1115 (s), 1048 (s), 920 (s), 899 (m), 861 (m), 803 (s), 769 (w), 742 (m), 700 (m), 656 (m), 563 (m), 503 (m). GC–MS (Agilent Technologies 7890A GC/5975C MS): M^+ = 249 amu, corresponding to the methyl ester of (I), prepared from the parent carboxylic acid using a literature procedure (Di Raddo, 1993).

(II) ^{1}H NMR (Bruker Avance III HD 400 MHz, DMSO d_6): δ 8.28 (d, 1H, $C_{aryl}H$, J_{ortho} = 8.4 Hz), 8.36 (d, 1H, $C_{aryl}H$, J_{meta} = 1.6 Hz), 8.43 (dd, 1 H, $C_{aryl}H$, J_{ortho} = 8.0 Hz, J_{meta} = 1.8 Hz), 14.06 (br s, 1H, OH). ^{13}C NMR (^{13}C{^{1}H}, 100.6 MHz, DMSO d_6): δ 121.53 (q, $C_{aryl}CF_3$, J_{C-F} = 33.9 Hz), 121.64 (q, CF_3, J_{C-F} = 273 Hz), 126.0 (s, $C_{aryl}H$), 128.30 (q, $C_{aryl}H$, J_{C-F} = 5.2 Hz), 135.02 (s, $C_{aryl}H$), 135.13 (s, $C_{aryl}COOH$), 149.38 (s, C_{aryl} NO_2), 164.48 (s, COOH). ^{19}F NMR (^{19}F{^{1}H}, 376.5 MHz, DMSO d_6): −59.24 (s, 3F, CF_3). IR (Thermo Scientific iS50, ATR, cm^{-1}): 3104 (m br, O-H str), 3067 (m, C_{aryl}-H str), 2848 (m), 2646 (m),

2575 (*m*), 1700 (*s*, C=O *str*), 1618 (*m*), 1598 (*m*), 1548 (*s*), 1438 (*m*), 1409 (*m*), 1363 (*m*), 1313 (*m*), 1267 (*s*) 1176 (*m*), 1163 (*s*), 1140 (*s*), 1125 (*s*), 1049 (*m*), 912 (*m*), 889 (*m*), 827 (*m*), 779 (*m*), 766 (*m*), 747 (*m*), 721 (*w*), 702 (*m*), 654 (*m*), 616 (*w*), 545 (*m*), 506 (*m*), 419 (*m*). GC–MS (Agilent Technologies 7890A GC/5975C MS): M^+ = 249 amu, corresponding to the methyl ester of (II), prepared from the parent carboxylic acid using a literature procedure (Raddo, 1993).

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supporting information

Crystallographic and spectroscopic characterization of 4-nitro-2-(trifluoromethyl)benzoic acid and 4-nitro-3-(trifluoromethyl)benzoic acid

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008b); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008b), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

4-Nitro-2-(trifluoromethyl)benzoic acid (I)

Crystal data

$C_8H_4F_3NO_4$	$D_x = 1.760$ Mg m^{-3}
$M_r = 235.12$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pccn*	Cell parameters from 7558 reflections
$a = 12.1612$ (17) Å	$\theta = 2.2–30.2°$
$b = 14.847$ (2) Å	$\mu = 0.18$ mm^{-1}
$c = 9.8265$ (14) Å	$T = 125$ K
$V = 1774.2$ (4) Å^3	Block, colourless
$Z = 8$	$0.24 \times 0.24 \times 0.15$ mm
$F(000) = 944$	

Data collection

Bruker APEXII CCD diffractometer	40170 measured reflections
Radiation source: fine-focus sealed tube	2727 independent reflections
Graphite monochromator	2064 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{int} = 0.050$
φ and ω scans	$\theta_{max} = 30.6°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2013)	$h = -17 \rightarrow 17$
	$k = -21 \rightarrow 21$
$T_{min} = 0.86$, $T_{max} = 0.97$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.039$	
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.5851P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2727 reflections	$(\Delta/\sigma)_{max} = 0.001$
148 parameters	$\Delta\rho_{max} = 0.46$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.73315 (7)	0.52183 (6)	0.34266 (10)	0.0370 (2)
F2	0.76500 (7)	0.65169 (7)	0.42859 (9)	0.0367 (2)
F3	0.70454 (7)	0.64131 (6)	0.22366 (9)	0.0347 (2)
O1	0.55716 (9)	0.49377 (7)	0.14946 (10)	0.0306 (2)
O2	0.43545 (9)	0.59970 (7)	0.08655 (10)	0.0289 (2)
H2	0.4403 (15)	0.5727 (12)	0.0103 (16)	0.035*
O3	0.52250 (8)	0.69576 (7)	0.79079 (10)	0.0285 (2)
O4	0.34577 (8)	0.69044 (7)	0.76367 (10)	0.0284 (2)
N1	0.44022 (9)	0.68191 (7)	0.72167 (11)	0.0211 (2)
C1	0.48757 (10)	0.59507 (8)	0.31669 (12)	0.0198 (2)
C2	0.57846 (10)	0.61229 (8)	0.40071 (12)	0.0192 (2)
C3	0.56260 (10)	0.64170 (8)	0.53324 (13)	0.0193 (2)
H3A	0.623518	0.65393	0.590881	0.023*
C4	0.45566 (10)	0.65286 (8)	0.57974 (12)	0.0187 (2)
C5	0.36455 (10)	0.63879 (8)	0.49877 (13)	0.0213 (2)
H5A	0.29241	0.648629	0.53275	0.026*
C6	0.38158 (10)	0.60982 (9)	0.36620 (13)	0.0222 (3)
H6A	0.320197	0.599895	0.308322	0.027*
C7	0.49830 (11)	0.55800 (9)	0.17519 (13)	0.0225 (3)
C8	0.69530 (11)	0.60658 (9)	0.34899 (13)	0.0247 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0285 (5)	0.0381 (5)	0.0443 (5)	0.0138 (4)	0.0073 (4)	−0.0025 (4)
F2	0.0182 (4)	0.0570 (6)	0.0350 (5)	−0.0067 (4)	0.0034 (3)	−0.0103 (4)
F3	0.0296 (4)	0.0487 (6)	0.0259 (4)	−0.0011 (4)	0.0093 (3)	0.0043 (4)
O1	0.0402 (6)	0.0281 (5)	0.0235 (5)	0.0113 (4)	−0.0049 (4)	−0.0053 (4)
O2	0.0364 (5)	0.0316 (5)	0.0188 (4)	0.0093 (4)	−0.0041 (4)	−0.0024 (4)
O3	0.0230 (5)	0.0384 (6)	0.0241 (5)	−0.0012 (4)	−0.0023 (4)	−0.0077 (4)
O4	0.0206 (4)	0.0340 (5)	0.0307 (5)	0.0012 (4)	0.0075 (4)	−0.0080 (4)
N1	0.0194 (5)	0.0214 (5)	0.0225 (5)	0.0008 (4)	0.0020 (4)	−0.0030 (4)
C1	0.0220 (6)	0.0180 (5)	0.0195 (5)	0.0006 (4)	−0.0006 (4)	0.0002 (4)
C2	0.0170 (5)	0.0202 (6)	0.0203 (6)	0.0015 (4)	0.0021 (4)	0.0011 (4)
C3	0.0160 (5)	0.0213 (6)	0.0206 (5)	0.0003 (4)	−0.0014 (4)	−0.0002 (4)
C4	0.0178 (5)	0.0185 (5)	0.0197 (5)	0.0008 (4)	0.0013 (4)	−0.0011 (4)
C5	0.0158 (5)	0.0223 (6)	0.0259 (6)	0.0008 (4)	0.0002 (4)	−0.0013 (5)
C6	0.0191 (5)	0.0230 (6)	0.0247 (6)	−0.0006 (4)	−0.0042 (5)	−0.0019 (5)
C7	0.0254 (6)	0.0204 (6)	0.0218 (6)	−0.0007 (5)	−0.0014 (5)	−0.0001 (4)

C8	0.0203 (6)	0.0312 (7)	0.0224 (6)	0.0017 (5)	0.0031 (5)	−0.0012 (5)

Geometric parameters (Å, º)

F1—C8	1.3413 (16)	C1—C2	1.4031 (17)
F2—C8	1.3337 (16)	C1—C7	1.5011 (17)
F3—C8	1.3399 (16)	C2—C3	1.3871 (17)
O1—C7	1.2188 (16)	C2—C8	1.5114 (17)
O2—C7	1.3139 (16)	C3—C4	1.3884 (16)
O2—H2	0.851 (14)	C3—H3A	0.95
O3—N1	1.2267 (14)	C4—C5	1.3800 (17)
O4—N1	1.2271 (14)	C5—C6	1.3874 (18)
N1—C4	1.4718 (16)	C5—H5A	0.95
C1—C6	1.3950 (18)	C6—H6A	0.95
C7—O2—H2	108.7 (12)	C4—C5—C6	117.93 (11)
O3—N1—O4	124.05 (11)	C4—C5—H5A	121.0
O3—N1—C4	118.02 (10)	C6—C5—H5A	121.0
O4—N1—C4	117.93 (10)	C5—C6—C1	120.94 (11)
C6—C1—C2	119.61 (11)	C5—C6—H6A	119.5
C6—C1—C7	117.45 (11)	C1—C6—H6A	119.5
C2—C1—C7	122.91 (11)	O1—C7—O2	124.95 (12)
C3—C2—C1	120.02 (11)	O1—C7—C1	122.01 (12)
C3—C2—C8	117.65 (11)	O2—C7—C1	113.00 (11)
C1—C2—C8	122.18 (11)	F2—C8—F3	107.01 (11)
C2—C3—C4	118.48 (11)	F2—C8—F1	106.28 (11)
C2—C3—H3A	120.8	F3—C8—F1	106.84 (11)
C4—C3—H3A	120.8	F2—C8—C2	111.84 (11)
C5—C4—C3	122.98 (11)	F3—C8—C2	111.48 (11)
C5—C4—N1	119.23 (11)	F1—C8—C2	113.01 (11)
C3—C4—N1	117.79 (10)		
C6—C1—C2—C3	1.57 (18)	C4—C5—C6—C1	0.26 (19)
C7—C1—C2—C3	−176.30 (12)	C2—C1—C6—C5	−1.91 (19)
C6—C1—C2—C8	−173.81 (12)	C7—C1—C6—C5	176.08 (12)
C7—C1—C2—C8	8.32 (19)	C6—C1—C7—O1	−130.98 (14)
C1—C2—C3—C4	0.39 (18)	C2—C1—C7—O1	46.94 (19)
C8—C2—C3—C4	175.97 (11)	C6—C1—C7—O2	46.69 (16)
C2—C3—C4—C5	−2.13 (19)	C2—C1—C7—O2	−135.40 (13)
C2—C3—C4—N1	178.49 (11)	C3—C2—C8—F2	−15.31 (17)
O3—N1—C4—C5	−178.53 (12)	C1—C2—C8—F2	160.17 (12)
O4—N1—C4—C5	1.73 (17)	C3—C2—C8—F3	−135.07 (12)
O3—N1—C4—C3	0.87 (17)	C1—C2—C8—F3	40.41 (17)
O4—N1—C4—C3	−178.87 (11)	C3—C2—C8—F1	104.58 (14)
C3—C4—C5—C6	1.80 (19)	C1—C2—C8—F1	−79.94 (15)
N1—C4—C5—C6	−178.82 (11)		

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O1^{i}	0.85 (1)	1.86 (2)	2.7042 (14)	175 (2)
C3—H3$A\cdots$F3^{ii}	0.95	2.47	3.3942 (15)	164

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+3/2, y, z+1/2$.

4-Nitro-3-(trifluoromethyl)benzoic acid (II)

Crystal data

$C_8H_4F_3NO_4$	$F(000) = 472$
$M_r = 235.12$	$D_x = 1.792$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.8986$ (8) Å	Cell parameters from 9889 reflections
$b = 17.240$ (2) Å	$\theta = 2.4$–30.5°
$c = 7.6912$ (9) Å	$\mu = 0.18$ mm^{-1}
$\beta = 107.685$ (2)°	$T = 125$ K
$V = 871.50$ (18) Å^3	Plate, colourless
$Z = 4$	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	4385 measured reflections
Radiation source: fine-focus sealed tube	2665 independent reflections
Graphite monochromator	2116 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{int} = 0.071$
φ and ω scans	$\theta_{max} = 30.5°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2008a)	$h = -9 \rightarrow 9$
	$k = 0 \rightarrow 24$
$T_{min} = 0.89$, $T_{max} = 0.98$	$l = 0 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.048$	
$wR(F^2) = 0.150$	$w = 1/[\sigma^2(F_o^2) + (0.0909P)^2 + 0.092P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2873 reflections	$(\Delta/\sigma)_{max} < 0.001$
150 parameters	$\Delta\rho_{max} = 0.50$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 3-component twin. BASF 0.0961 (3) 0.0326 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
F1	0.86853 (17)	0.33150 (8)	0.38868 (15)	0.0394 (3)
F2	0.78710 (18)	0.23188 (6)	0.51840 (16)	0.0356 (3)

F3	0.97458 (14)	0.32129 (6)	0.68002 (13)	0.0258 (3)
O1	0.03937 (17)	0.49961 (7)	0.22770 (15)	0.0228 (3)
O2	0.22198 (18)	0.44236 (8)	0.06814 (16)	0.0242 (3)
H2	0.136 (3)	0.4651 (13)	−0.015 (3)	0.029*
O3	0.7408 (2)	0.25918 (8)	0.88052 (18)	0.0303 (3)
O4	0.7540 (2)	0.37201 (10)	1.00889 (17)	0.0386 (4)
N1	0.7034 (2)	0.32815 (9)	0.87729 (19)	0.0220 (3)
C1	0.3254 (2)	0.42454 (9)	0.3879 (2)	0.0152 (3)
C2	0.4976 (2)	0.38357 (9)	0.3829 (2)	0.0158 (3)
H2A	0.527015	0.377515	0.27074	0.019*
C3	0.6270 (2)	0.35142 (9)	0.5426 (2)	0.0157 (3)
C4	0.5782 (2)	0.36199 (9)	0.7032 (2)	0.0164 (3)
C5	0.4107 (2)	0.40416 (10)	0.7112 (2)	0.0210 (3)
H5A	0.384027	0.411841	0.824123	0.025*
C6	0.2823 (2)	0.43502 (10)	0.5510 (2)	0.0192 (3)
H6A	0.16486	0.463335	0.552985	0.023*
C7	0.1847 (2)	0.45815 (9)	0.2175 (2)	0.0168 (3)
C8	0.8138 (2)	0.30861 (10)	0.5324 (2)	0.0216 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0313 (6)	0.0661 (9)	0.0253 (6)	0.0241 (6)	0.0153 (5)	0.0160 (5)
F2	0.0352 (6)	0.0242 (6)	0.0408 (7)	0.0118 (4)	0.0016 (5)	−0.0074 (5)
F3	0.0144 (4)	0.0356 (6)	0.0241 (5)	0.0043 (4)	0.0008 (4)	0.0032 (4)
O1	0.0203 (6)	0.0266 (6)	0.0190 (6)	0.0099 (5)	0.0023 (4)	−0.0002 (4)
O2	0.0243 (6)	0.0307 (7)	0.0155 (5)	0.0114 (5)	0.0027 (5)	0.0023 (5)
O3	0.0330 (7)	0.0253 (7)	0.0316 (7)	0.0080 (5)	0.0083 (6)	0.0120 (5)
O4	0.0482 (9)	0.0425 (9)	0.0169 (6)	0.0057 (7)	−0.0024 (6)	−0.0009 (6)
N1	0.0189 (6)	0.0279 (8)	0.0186 (7)	0.0042 (5)	0.0050 (5)	0.0076 (5)
C1	0.0138 (6)	0.0145 (7)	0.0156 (7)	0.0004 (5)	0.0018 (5)	0.0012 (5)
C2	0.0151 (6)	0.0165 (7)	0.0151 (7)	0.0011 (5)	0.0034 (5)	0.0005 (5)
C3	0.0141 (6)	0.0148 (7)	0.0167 (7)	0.0011 (5)	0.0022 (5)	0.0005 (5)
C4	0.0160 (7)	0.0154 (7)	0.0155 (7)	0.0002 (5)	0.0016 (5)	0.0029 (5)
C5	0.0208 (7)	0.0262 (9)	0.0173 (7)	0.0035 (6)	0.0076 (6)	0.0028 (6)
C6	0.0154 (7)	0.0217 (8)	0.0198 (7)	0.0037 (6)	0.0044 (6)	0.0012 (6)
C7	0.0168 (6)	0.0159 (7)	0.0161 (7)	0.0018 (5)	0.0028 (5)	−0.0002 (5)
C8	0.0197 (7)	0.0255 (8)	0.0180 (7)	0.0073 (6)	0.0035 (6)	0.0033 (6)

Geometric parameters (Å, º)

F1—C8	1.332 (2)	C1—C2	1.393 (2)
F2—C8	1.335 (2)	C1—C7	1.491 (2)
F3—C8	1.3424 (18)	C2—C3	1.395 (2)
O1—C7	1.2528 (18)	C2—H2A	0.95
O2—C7	1.281 (2)	C3—C4	1.387 (2)
O2—H2	0.826 (16)	C3—C8	1.508 (2)
O3—N1	1.2154 (19)	C4—C5	1.383 (2)

O4—N1	1.226 (2)	C5—C6	1.387 (2)
N1—C4	1.4751 (19)	C5—H5A	0.95
C1—C6	1.386 (2)	C6—H6A	0.95

C7—O2—H2	107.5 (16)	C4—C5—C6	118.62 (15)
O3—N1—O4	125.51 (15)	C4—C5—H5A	120.7
O3—N1—C4	117.88 (14)	C6—C5—H5A	120.7
O4—N1—C4	116.54 (15)	C1—C6—C5	119.98 (15)
C6—C1—C2	120.69 (13)	C1—C6—H6A	120.0
C6—C1—C7	118.92 (14)	C5—C6—H6A	120.0
C2—C1—C7	120.39 (14)	O1—C7—O2	124.04 (14)
C1—C2—C3	120.00 (14)	O1—C7—C1	119.12 (14)
C1—C2—H2A	120.0	O2—C7—C1	116.84 (13)
C3—C2—H2A	120.0	F1—C8—F2	107.05 (14)
C4—C3—C2	117.95 (14)	F1—C8—F3	106.48 (14)
C4—C3—C8	123.56 (13)	F2—C8—F3	106.73 (13)
C2—C3—C8	118.48 (14)	F1—C8—C3	111.13 (13)
C5—C4—C3	122.73 (14)	F2—C8—C3	112.97 (14)
C5—C4—N1	115.73 (14)	F3—C8—C3	112.10 (14)
C3—C4—N1	121.53 (14)		

C6—C1—C2—C3	1.1 (2)	C2—C1—C6—C5	−0.4 (2)
C7—C1—C2—C3	−179.15 (14)	C7—C1—C6—C5	179.87 (15)
C1—C2—C3—C4	−0.2 (2)	C4—C5—C6—C1	−1.2 (2)
C1—C2—C3—C8	−179.01 (14)	C6—C1—C7—O1	5.0 (2)
C2—C3—C4—C5	−1.5 (2)	C2—C1—C7—O1	−174.71 (15)
C8—C3—C4—C5	177.26 (15)	C6—C1—C7—O2	−175.09 (15)
C2—C3—C4—N1	178.27 (14)	C2—C1—C7—O2	5.2 (2)
C8—C3—C4—N1	−3.0 (2)	C4—C3—C8—F1	−155.52 (15)
O3—N1—C4—C5	127.62 (17)	C2—C3—C8—F1	23.2 (2)
O4—N1—C4—C5	−49.6 (2)	C4—C3—C8—F2	84.14 (19)
O3—N1—C4—C3	−52.1 (2)	C2—C3—C8—F2	−97.15 (17)
O4—N1—C4—C3	130.66 (17)	C4—C3—C8—F3	−36.5 (2)
C3—C4—C5—C6	2.2 (2)	C2—C3—C8—F3	142.23 (14)
N1—C4—C5—C6	−177.56 (14)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1[i]	0.83 (2)	1.82 (2)	2.6337 (16)	168 (2)
C5—H5A···O2[ii]	0.95	2.51	3.440 (2)	165

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) *x*, *y*, *z*+1.