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Four trifluoromethylnitrobenzene analogues

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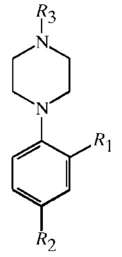
The crystal structures of four trifluoromethylnitrobenzene analogues $(CF_3)C_6H_3(NO_2)[C_4H_8N_2]R$ (where $C_4H_8N_2$ is piperazinyl and R is ethyl carboxylate, $CO_2C_2H_5$, or phenyl, C_6H_5), have been determined, and their conformations and packing arrangements are compared. The four compounds are ethyl 4-[4-nitro-2-(trifluoromethyl)phenyl]piperazine-1-carboxylate, (I), and ethyl 4-[2-nitro-4-(trifluoromethyl)phenyl]piperazine-1-carboxylate, (II), both $C_{14}H_{16}F_3N_3O_4$, and 1-[4-nitro-2-(trifluoromethyl)phenyl]-4-phenylpiperazine, (III), and 1-[2-nitro-4-(trifluoromethyl)phenyl]-4-phenylpiperazine, (IV), both $C_{17}H_{16}F_3N_3O_2$. All molecules adopt a rod-like conformation, while the asymmetric units of (II) and (IV) contain two unique molecules that pack as monodirectional pairs. All molecules pack with C—H···O/F close contacts to all but one of the O atoms and to five of the 18 F atoms.

Comment

As part of a continuing series of studies into the conformational and solid-state packing modes of similar compounds, we have been investigating chemical isomers based on 3-nitrobenzotrifluoride (CAS No. 98-46-4, trifluoromethylnitrobenzene) where the nitro and trifluoromethyl (CF_3) groups are interchanged in relation to a third substituent on the benzene ring. These studies have the purpose not only of comparing structural behaviour in the individual components but also of attempting to prepare cocrystalline adducts with such compounds without the use of strong hydrogen-bonding associations, as achieved by Wheeler and co-workers (Hendi *et al.*, 2001; Fomulu *et al.*, 2002*a*,*b*). NO_2 and CF_3 groups are known to be weak hydrogen-bond acceptors from strong hydrogen-bond donors (Allen *et al.*, 1997; Brammer *et al.*, 2001), and in the absence of such donors, solid-state packing can only, if at all, be influenced by weaker C—H interactions. Furthermore, the choice of the third substituent is based on the use of a group that is flexible, not too bulky and lacking in strong hydrogen-bond donors. With this in mind, we prepared a series of analogues of 3-nitrobenzotrifluoride containing 4-substituted piperazines. Previous efforts concentrated on the use of thiophenol derivatives and led to the structural characterization of 1-(4-chlorophenylsulfanyl)-2-nitro-4-(trifluoromethyl)benzene and 1-(4-chlorophenylsulfanyl)-4-nitro-2-(trifluoromethyl)benzene (Lynch & McClenaghan, 2003), whose similar conformations did not aid cocrystal formation. Instead, it was suggested that the role of the C—H···O interactions in both individual structures promoted phase separation when attempts were made to cocrystallize the two. We report here the single-crystal structures of ethyl 4-[4-nitro-2-(trifluoromethyl)phenyl]piperazine-1-carboxylate, (I), ethyl 4-[2-nitro-4-(trifluoromethyl)phenyl]piperazine-1-carboxylate, (II), 1-[4-nitro-2-(trifluoromethyl)phenyl]-4-phenylpiperazine, (III), and 1-[2-nitro-4-(trifluoromethyl)phenyl]-4-phenylpiperazine, (IV), and comment on their structural similarities/differences.



(I) R_1=CF_3, R_2=NO_2, R_3=$COOCH_2Me$
(II) R_1=NO_2, R_2=CF_3, R_3=$COOCH_2Me$
(III) R_1=CF_3, R_2=NO_2, R_3=C_6H_5
(IV) R_1=NO_2, R_2=CF_3, R_3=C_6H_5

The difficulty in making structural comparisons between chemical isomers is that the structures of both are required. For the phenylsulfanyl-containing 3-nitrobenzotrifluorides (trifluoromethylnitrobenzenes), only one matching pair was characterized. Fortunately, for the 4-substituted piperazines, full structural analyses of two pairs were completed, thus allowing comparisons not only between (I) and (II), and (III) and (IV), but also between (I) and (III), and (II) and (IV), which share similar nitro (NO_2) and trifluoromethyl (CF_3)

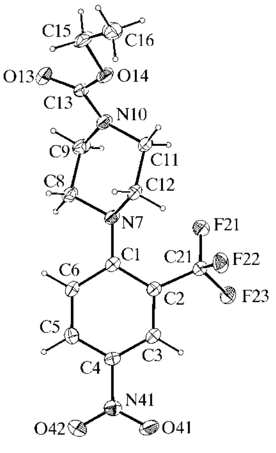


Figure 1
The molecular configuration and atom-numbering scheme for (I), showing 50% probability displacement ellipsoids.

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positions. The structures of (I)–(IV) are shown, perpendicular to the 3-nitrobenzotrifluoride ring, in Figs. 1–4, respectively, with interactions and contacts listed in Tables 1–4. Compounds (II) and (IV), where the CF_3 group is *para* to the piperazine ring, each have two unique molecules in their asymmetric units. For ease of comparison, these molecules are both shown as described above (Figs. 2 and 4) and not as they would appear in the lattice. The numbering of both the *N*-phenyl and piperazine rings has also been standardized to aid evaluation. An initial inspection of the molecules of (I)–(IV) shows that each adopts a linear rod-like conformation, as expected. Similarities arise in the rotation of the piperazine rings in (I), (II*A*) and (IV*B*), and (II*B*) and (IV*A*), which can be quantified *via* the C2—C1—N7—C8 torsion angles, listed in Table 5.

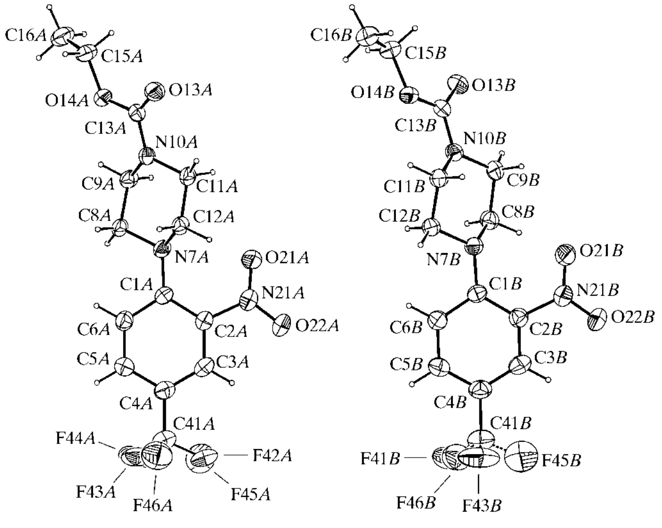

Figure 2
The molecular configuration and atom-numbering scheme for (II), showing 50% probability displacement ellipsoids. For clarity, both molecules have been shown perpendicular to their benzene rings, and their positions, or orientations, cannot be compared directly to one another.

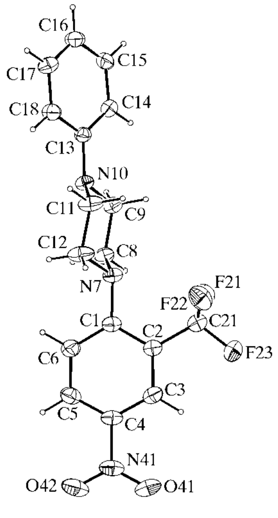

Figure 3
The molecular configuration and atom-numbering scheme for (III), showing 50% probability displacement ellipsoids.

The twists in the *N*-phenyl rings can be represented by their dihedral angles with the 3-nitrobenzotrifluoride ring, *viz*. 46.4 (1)° (III), and 59.6 (1) and 66.9 (1)° (IV). Both CF_3 groups in (II) are unequally disordered over two rotational occupancies, the major occupancies for both molecules being 85%. The minor-occupancy sites are rotated 30 (3) (molecule *A*) and 23 (6)° (molecule *B*) with respect to the major-occu-

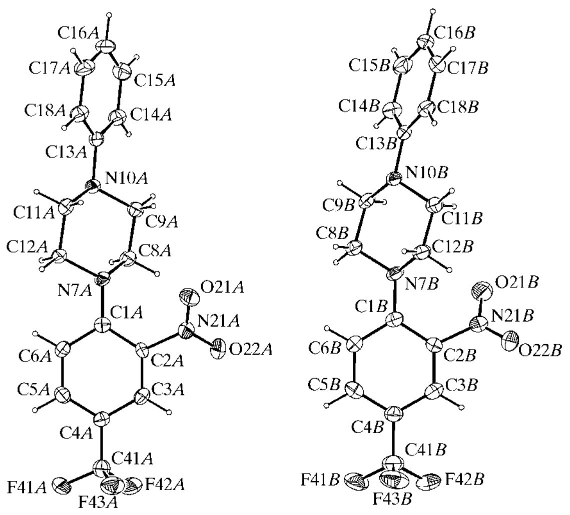

Figure 4
The molecular configuration and atom-numbering scheme for (IV), showing 50% probability displacement ellipsoids. For clarity, both molecules have been shown perpendicular to their benzene rings, and their positions, or orientations, cannot be compared directly to one another.

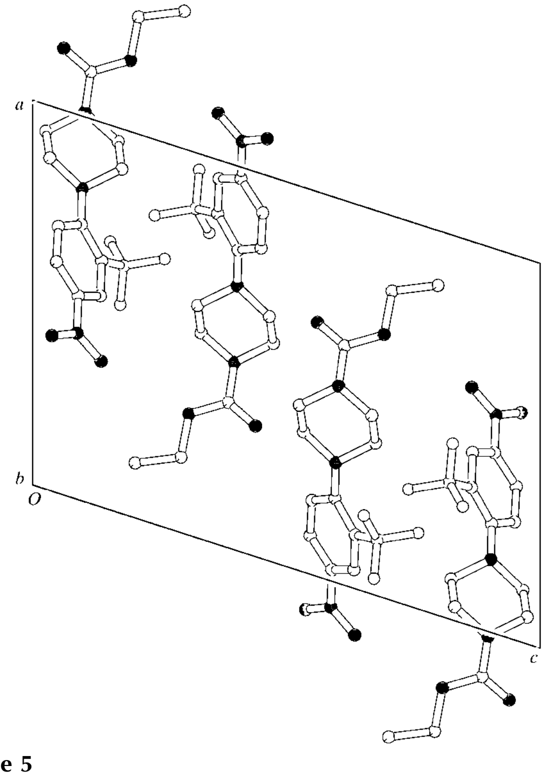

Figure 5
A packing diagram of (I), viewed along the *b* axis.

pancy sites. The rotational positions of the comparative CF_3 groups in (II) and (IV) are similar; the C3—C4—C41—F43 torsion angles are listed in Table 5. Comparative CF_3 rotational positions in (I) and (III) can be defined by the C1—C2—C21—F22 torsion angle (Table 5). Two torsion angles can be used to define the conformation of the carboxylate groups in (I) and (II), *viz*. C9—N10—C13—O14 and C13—O14—C15—C16 (Table 5), and these angles indicate very different rotational positions with respect to atom C9.

Packing diagrams for (I)–(IV) are shown in Figs. 5–8, respectively, while C—H···O/F close contacts are listed in Tables 1–4, respectively. The number of these contacts, per molecule, increases for the two ethyl carboxylate-containing analogues as a result of the addition of the two ethyl carboxylate O atoms. All O atoms, except for atom O22*B* in (II), across all molecules have at least one listed close contact, whereas only five out of a possible 18 F atoms have a C—H···F association, and there are none for either molecule in (II). However, in (III), atom F22 lies 3.010 (2) Å from atom N41($x, \frac{1}{2} - y, -\frac{1}{2} + z$). The packing diagrams are typical for rod-shaped molecules, with three of the four being either monoclinic $P2_1/c$ or $P2_1/n$. It is interesting to note the manner in which the molecules of (II) and (IV) associate as monodirectional pairs in close proximity to one another. The interplanar distance between the two benzene ring centroids in (II) is 3.95 (1) Å and the dihedral angle is 30.9 (4)°. Another feature is the 90° triclinic cell angle in (II). No additional symmetry could be found in this structure and the two molecules display no pseudosymmetry relationship; thus the cell angle is real. It may eventuate that at 150 K the structure of (II) is near a phase change to a higher crystal system and that one angle had already moved to fit the higher cell, but this remains to be proved. Attempts to cocrystallize all possible combinations of (I)–(IV) by dissolving equimolar amounts of two components in various solvents, with warming, and then allowing evaporation to dryness led to the recrystallization in each case of the individual compounds. This result was confirmed by distinct differences in crystal morphology as well as IR analysis of each crystal type. In addition to differing C—H···O/F associations, the role of the paired formation in (II) and (IV) may be responsible for the inability of these compounds to form cocrystalline adducts without the presence of strong complimentary hydrogen-bonding groups. Unfortunately, the existence of pairing in (II) and (IV) adds a new consideration to our use of the 2-nitro-4-(trifluoromethyl)benzene analogue.

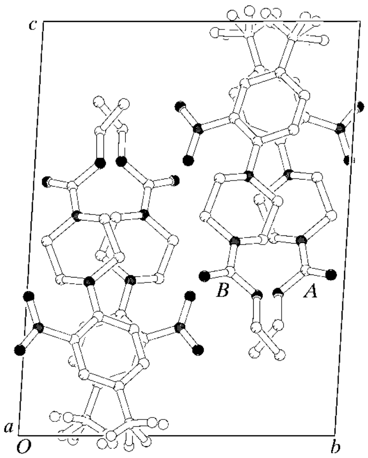

Figure 6
A packing diagram of (II), viewed along the *a* axis. The positions of molecules *A* and *B* throughout the unit cell are indicated.

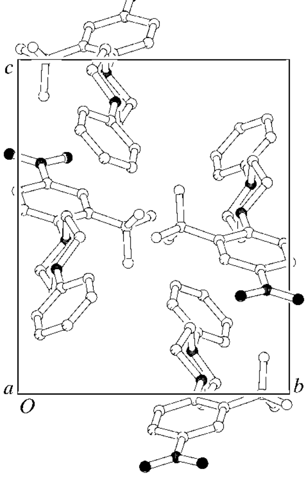

Figure 7
A packing diagram of (III), viewed along the *a* axis.

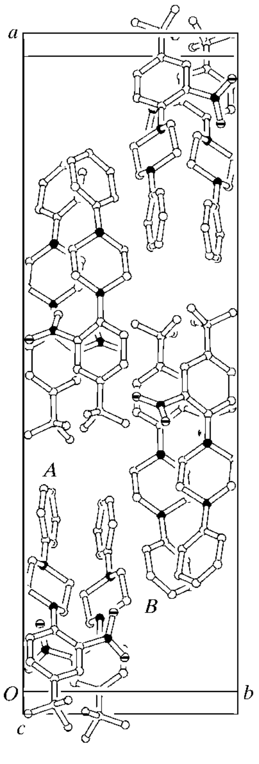

Figure 8
A packing diagram of (IV), viewed along the *c* axis. The positions of molecules *A* and *B* throughout the unit cell are indicated.

Experimental

All compounds were obtained from Key Organics Ltd. Crystals of (I) were obtained by recrystallization from 40–60 petroleum ether, crystals of (II) were grown from absolute ethanol solution, while crystals of (III) and (IV) were grown from 5% aqueous ethanol solutions.

Compound (I)

Crystal data

$C_{14}H_{16}F_3N_3O_4$
$M_r = 347.30$
Monoclinic, $P2_1/n$
$a = 12.555\ (3)$ Å
$b = 7.2688\ (15)$ Å
$c = 17.366\ (4)$ Å
$\beta = 107.85\ (3)°$
$V = 1508.5\ (6)$ Å^3
$Z = 4$

$D_x = 1.529$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5964 reflections
$\theta = 2.9–27.5°$
$\mu = 0.14$ mm^{-1}
$T = 120\ (2)$ K
Plate, yellow
0.20 × 0.14 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.993$, $T_{max} = 0.993$
10 705 measured reflections

3438 independent reflections
2583 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.135$
$S = 1.04$
3438 reflections
218 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.252P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5⋯O42^{i}	0.95	2.42	3.346 (2)	164
C6—H6⋯O13^{ii}	0.95	2.34	3.278 (2)	171
C9—H92⋯O13	0.99	2.38	2.786 (2)	104
C11—H111⋯O14	0.99	2.26	2.697 (2)	105
C11—H111⋯O41^{iii}	0.99	2.58	3.456 (2)	147
C12—H121⋯F21	0.99	2.48	2.917 (2)	106
C12—H121⋯F22	0.99	2.38	3.295 (2)	154

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

Compound (II)

Crystal data

$C_{14}H_{16}F_3N_3O_4$
$M_r = 347.30$
Triclinic, $P\overline{1}$
$a = 8.8211\ (18)$ Å
$b = 11.717\ (2)$ Å
$c = 15.528\ (3)$ Å
$\alpha = 86.55\ (3)°$
$\beta = 81.97\ (3)°$
$\gamma = 90.00\ (3)°$
$V = 1586.3\ (5)$ Å^3

$Z = 4$
$D_x = 1.454$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3808 reflections
$\theta = 1.0–27.5°$
$\mu = 0.13$ mm^{-1}
$T = 150\ (2)$ K
Prism, yellow
0.42 × 0.24 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.987$, $T_{max} = 0.987$
17 250 measured reflections

5256 independent reflections
3744 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.194$
$S = 1.08$
5256 reflections
489 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1213P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3A—H3A⋯O22A	0.95	2.29	2.634 (4)	100
C6A—H6A⋯O13B^{iv}	0.95	2.46	3.286 (3)	145
C8A—H81A⋯O13B^{iv}	0.99	2.54	3.300 (3)	133
C9A—H91A⋯O14A	0.99	2.23	2.649 (3)	104
C11A—H12A⋯O13A	0.99	2.42	2.789 (3)	101
C11A—H12A⋯O13A^{v}	0.99	2.59	3.411 (3)	140
C12A—H14A⋯O21A	0.99	2.30	2.830 (4)	113
C6B—H6B⋯O13A^{v}	0.95	2.44	3.241 (4)	142
C8B—H81B⋯O21B	0.99	2.30	2.839 (4)	113
C9B—H91B⋯O13B	0.99	2.43	2.800 (4)	101
C9B—H91B⋯O13B^{vi}	0.99	2.59	3.401 (3)	139
C11B—H12B⋯O14B	0.99	2.24	2.651 (3)	104
C12B—H14B⋯O13A^{v}	0.99	2.57	3.332 (3)	134

Symmetry codes: (iv) $1 - x, 1 - y, 1 - z$; (v) $1 - x, 2 - y, 1 - z$; (vi) $2 - x, 1 - y, 1 - z$.

Compound (III)

Crystal data

$C_{17}H_{16}F_3N_3O_2$
$M_r = 351.33$
Monoclinic, $P2_1/c$
$a = 13.390\ (3)$ Å
$b = 9.853\ (2)$ Å
$c = 12.503\ (3)$ Å
$\beta = 102.97\ (3)°$
$V = 1607.5\ (7)$ Å^3
$Z = 4$

$D_x = 1.452$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 140 reflections
$\theta = 2.9–30.5°$
$\mu = 0.12$ mm^{-1}
$T = 150\ (2)$ K
Prism, colourless
0.24 × 0.16 × 0.14 mm

Data collection

Nonius KappaCCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.952$, $T_{max} = 0.981$
12 114 measured reflections

3659 independent reflections
2565 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.131$
$S = 1.06$
3659 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2 + 0.026P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···F23	0.95	2.34	2.679 (2)	100
C16—H16···O41^{vii}	0.95	2.54	3.255 (2)	133
C12—H121···O42^{viii}	0.99	2.56	3.475 (2)	154

Symmetry codes: (vii) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$; (viii) $-x, -y, 1-z$.

Compound (IV)

Crystal data

$C_{17}H_{16}F_3N_3O_2$	D_x = 1.467 Mg m^{-3}
M_r = 351.33	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 16 227 reflections
a = 30.6687 (12) Å	θ = 2.9–33.3°
b = 9.9731 (3) Å	μ = 0.12 mm^{-1}
c = 10.4592 (3) Å	T = 150 (2) K
β = 95.8496 (10)°	Plate, yellow
V = 3182.41 (18) Å^3	0.20 × 0.15 × 0.04 mm
Z = 8	

Data collection

Nonius KappaCCD area-detector diffractometer	5553 independent reflections
φ and ω scans	2917 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	R_{int} = 0.084
T_{min} = 0.995, T_{max} = 0.995	θ_{max} = 25.0°
14 139 measured reflections	$h = -36 \rightarrow 36$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.053	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.119	$(\Delta/\sigma)_{max} < 0.001$
S = 0.95	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
5553 reflections	$\Delta\rho_{min}$ = −0.41 e Å^{-3}
451 parameters	

Table 4
Hydrogen-bonding geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
C5A—H5A···F43A^{ix}	0.95	2.46	3.303 (3)	148
C3B—H3B···O22B^{v}	0.95	2.51	3.455 (3)	176
C16B—H16B···F42A^{x}	0.95	2.52	3.453 (3)	167
C15B—H15B···O21A	0.95	2.46	3.358 (4)	158

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

All H atoms were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.95 (aromatic H atoms), 0.98 (CH_3 H atoms) and 0.99 Å (CH_2 H atoms). The isotropic displacement parameters were set equal to $1.25U_{eq}$ of the carrier atom. A high R_{int} value for (II) was the result of weak high-angle data.

Table 5
Selected torsion angles (°) for (I)–(IV).

Torsion angle	(I)	(II)	(III)	(IV)
C2—C1—N7—C8	159.36 (15)	−161.3 (3) −63.9 (4)	102.29 (2)	51.5 (4) 165.1 (3)
C1—C2—C21—F22	96.21 (18)		61.05 (18)	
C3—C4—C41—F43		109.1 (4) 143.5 (4)		76.2 (3) −31.3 (4)
C9—N10—C13—O14	170.69 (14)	−10.6 (3) 168.0 (2)		
C13—O14—C15—C16	174.27 (15)	−159.1 (2) 160.3 (2)		

For all four compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*, *SCALEPACK* (Otwinowski & Minor, 1997) and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1189). Services for accessing these data are described at the back of the journal.

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