organic compounds

Structural comparison of three N-(4-halogenophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine hydrochlorides

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2-{1-[(4-Chloroanilino)methylidene]ethyl}pyridinium chloride methanol solvate, $C_{13}H_{13}ClN_3^+ \cdot Cl^- \cdot CH_3OH$, (I), crystallizes as discrete cations and anions, with one molecule of methanol as solvent in the asymmetric unit. The N—C—C—N torsion angle in the cation indicates a *cis* conformation. The cations are located parallel to the ($\bar{2}$02) plane and are connected through hydrogen bonds by a methanol solvent molecule and a chloride anion, forming zigzag chains in the direction of the *b* axis. The crystal structure of 2-{1-[(4-fluoroanilino)methylidene]ethyl}pyridinium chloride, $C_{13}H_{13}FN_3^+ \cdot Cl^-$, (II), contains just one anion and one cation in the asymmetric unit but no solvent. In contrast with (I), the N—C—C—N torsion angle in the cation corresponds with a *trans* conformation. The cations are located parallel to the (100) plane and are connected by hydrogen bonds to the chloride anions, forming zigzag chains in the direction of the *b* axis. In addition, the crystal packing is stabilized by weak π–π interactions between the pyridinium and benzene rings. The crystal of (II) is a nonmerohedral monoclinic twin which emulates an orthorhombic diffraction pattern. Twinning occurs *via* a twofold rotation about the *c* axis and the fractional contribution of the minor twin component refined to 0.324 (3). 2-{1-[(4-Fluoroanilino)methylidene]ethyl}pyridinium chloride methanol disolvate, $C_{13}H_{13}FN_3^+ \cdot Cl^- \cdot 2CH_3OH$, (III), is a pseudopolymorph of (II). It crystallizes with two anions, two cations and four molecules of methanol in the asymmetric unit. Two symmetry-equivalent cations are connected by hydrogen bonds to a chloride anion and a methanol solvent molecule, forming a centrosymmetric dimer. A further methanol molecule is hydrogen bonded to each chloride anion. These aggregates are connected by C—H···O contacts to form infinite chains. It is remarkable that the geometric structures of two compounds having two different formula units in their asymmetric units are essentially the same.

Comment

Luminescent organometallic compounds such as boron nitrogen addition compounds have attracted much attention recently due to their potential applications. Therefore, nitrogen addition compounds are also candidates for photodynamic therapy (PDT), which is a non-invasive technique for the treatment of a variety of solid tumour types by the combined use of visible or near-visible light with photosensitizing drugs. Recently, Liu *et al.* (2002) synthesized luminescent boron complexes based on 5-fluoro-2-(2-pyridyl)-indole- and 5-chloro-2-(2-pyridyl)indole-substituted ligands. Since our group has experience in the preparation of aromatic systems with multiple boron substituents (Haberecht *et al.*, 2004), we decided to examine the properties of the addition compounds of 5-chloro-2-(2-pyridyl)indole and 5-fluoro-2-(2-pyridyl)indole with multiple boron-substituted arenes. The starting materials for the syntheses of these indole derivatives, N-(4-chlorophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine and N-(4-fluorophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine, were prepared according to a slightly altered literature procedure (Liu *et al.*, 2002), as shown in the scheme below.

(I) X = Cl; Sol = MeOH
(II) X = F; Sol = nul
(III) X = F; Sol = 2MeOH
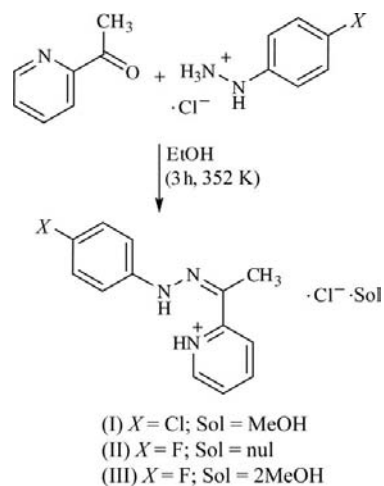
In this paper, we describe the solid-state structures of the hydrochlorides of N-(4-chlorophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine and N-(4-fluorophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine. In this context, it should be noted that we could isolate two pseudopolymorphs of the N-(4-fluorophenyl)-N′-[1-(2-pyridyl)ethylidene]hydrazine cation with chloride counter-ions.

2-{1-[(4-Chloroanilino)methylidene]ethyl}pyridinium chloride methanol solvate, (I), crystallizes as discrete cations and anions with one molecule of methanol as solvent in the asymmetric unit (Fig. 1). The cation features a planar molecule (r.m.s. deviation for all non-H atoms = 0.0873 Å). The C═N double bond is *trans* configured, whereas the N2—C2—C21—N22 torsion angle [8.60 (15)°] corresponds with a *cis* conformation. The cations are located parallel to the ($\bar{2}$02) plane. Two cations are connected through hydrogen bonds by a methanol solvent molecule and a chloride anion to form zigzag chains in the direction of the *b* axis (Fig. 2). The chloride anion acts as an acceptor for two hydrogen bonds,

Figure 1
A perspective view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
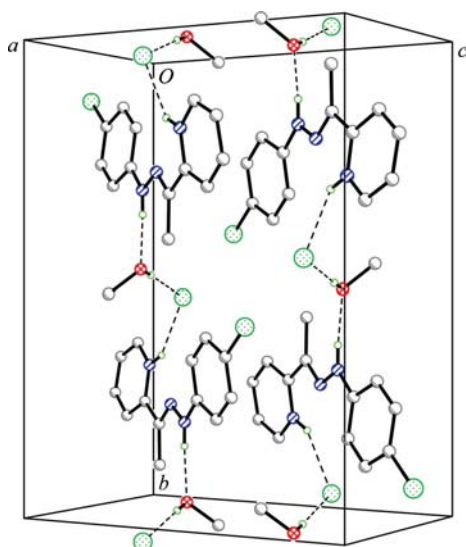

Figure 2
A packing diagram for (I). H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are drawn as dashed lines. (Colour code for the spheres in the electronic version of the paper: C grey, H small green, Cl large green, N blue and O red.)
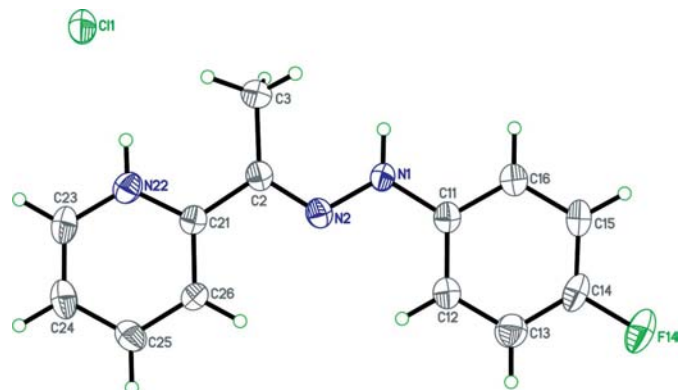

Figure 3
A perspective view of the asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
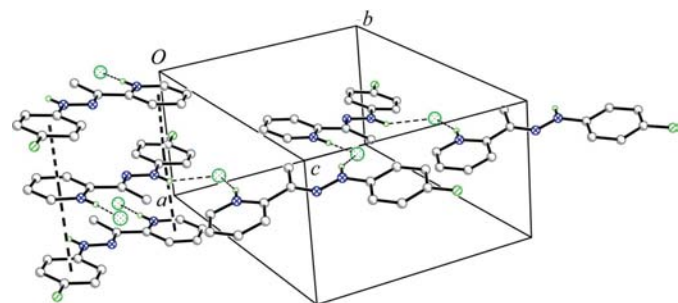

Figure 4
A packing diagram for (II). H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are drawn as narrow dashed lines and π–π stacking interactions as heavy dashed lines. (Colour code for the spheres in the electronic version of the paper: C grey, H small green, F medium green, Cl large green and N blue.)

one from the pyridinium N atom and the other one from the methanolic O atom. The methanol molecule, on the other hand, accepts a hydrogen bond from the amino N atom.

In contrast with (I), in which the cation bears a chloro substituent in the *para* position of the benzene ring, the cation of 2-{1-[(4-fluoroanilino)methylidene]ethyl}pyridinium chloride, (II), bears a fluoro substituent in the *para* position of the benzene ring (Fig. 3). As in (I), this cation features a planar molecule (r.m.s. deviation for all non-H atoms = 0.0245 Å), with the C=N double bond again in a *trans* configuration. The main difference from the cation in (I) is that the N2—C2—C21—N22 torsion angle [−178.1 (4)°] now has a *trans* conformation. The cations are located in the (100)

plane. Cations and anions are connected by N—H⋯Cl hydrogen bonds to form zigzag chains running along the *b* axis (Fig. 4). The chloride anion acts as an acceptor for two hydrogen bonds from the N—H functions of two different cations. In addition, the crystal structure of (II) is also stabilized by weak π–π stacking interactions. Two molecules related by a centre of inversion are stacked one above the other, so that the pyridinium ring is stacked between two benzene rings, one at ($-x$, $1 - y$, $1 - z$) (centroid–centroid distance = 3.635 Å and offset angle = 21.8°) and one at ($1 - x$, $1 - y$, $1 - z$) (centroid–centroid distance = 3.690 Å and offset angle = 25.7°).

2-{1-[(4-Fluoroanilino)methylidene]ethyl}pyridinium chloride methanol disolvate, (III), is a pseudopolymorph of (II). In contrast with (II), which crystallizes with just one cation and one anion in the asymmetric unit, (III) crystallizes with two cations, two anions and four methanol molecules in the asymmetric unit (Figs. 5a and 5b). Both cations are essentially planar (r.m.s. deviations for all non-H atoms = 0.0326 and 0.0463 Å). The C=N double bond is *trans* configured and the N—C—C—N torsion angle [N2—C2—C21—N22 = −4.6 (2)° and N2A—C2A—C21A—N22A = 3.5 (2)°] corresponds with a *cis* conformation. This is the main
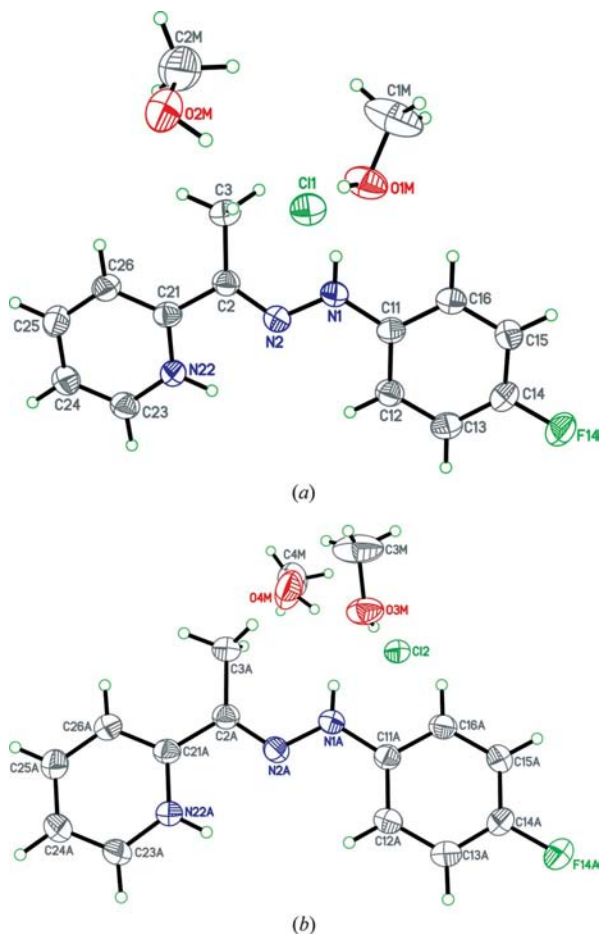
Figure 5
Perspective views of (*a*) the first formula unit and (*b*) the second formula unit in the asymmetric unit of (III), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
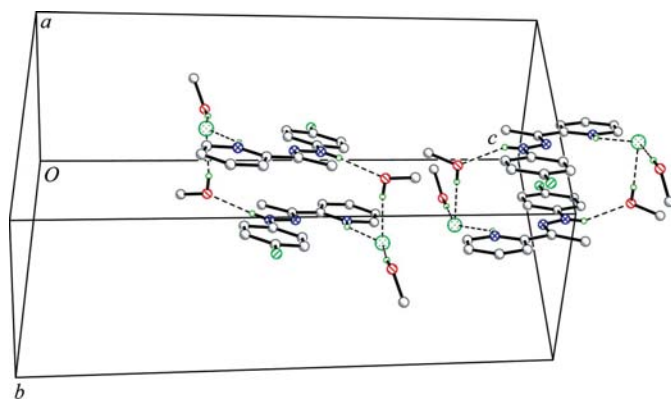

Figure 6
A partial packing diagram for (III). H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are drawn as dashed lines. (Colour code for the spheres in the electronic version of the paper: C grey, H small green, F medium green, Cl large green, N blue and O red.)

difference from the cation in (II), where the N—C—C—N linkage adopts a *trans* conformation. Both independent cations in the asymmetric unit of (III), which have essentially the same geometric parameters (r.m.s. deviation for all non-H
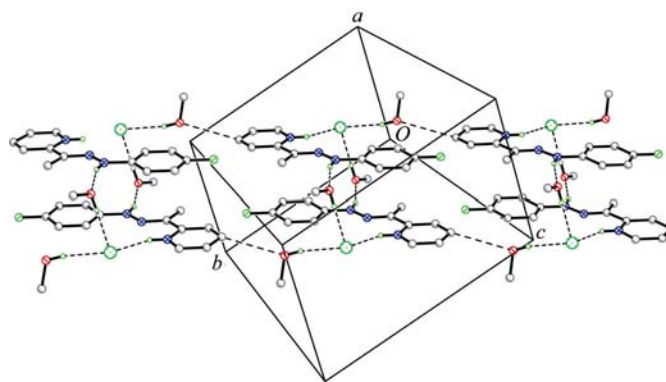

Figure 7
A partial packing diagram for (III), indicating how two hydrogen-bonded formula units are connected into an infinite chain *via* C—H···O contacts. H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonds are drawn as dashed lines. (Colour code for the spheres in the electronic version of the paper: C grey, H small green, F medium green, Cl large green, N blue and O red.)
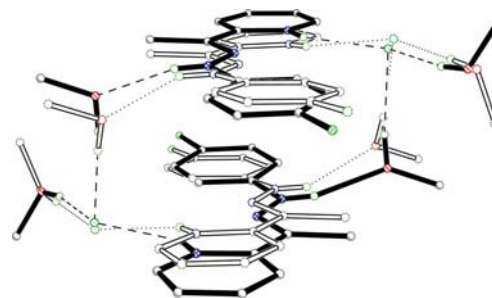

Figure 8
Least-squares fit of the two hydrogen-bonded dimers of (III). All non-H atoms of the cations are fitted; r.m.s. deviation = 0.849 Å. Atoms [and their symmetry equivalents, operator $(1 - x, 1 - y, 2 - z)$] of the first formula unit in the asymmetric unit are drawn with open bonds and their hydrogen bonds with dotted lines. Atoms [and their symmetry equivalents, operator $(1 - x, 1 - y, 1 - z)$] of the second formula unit in the asymmetric unit are drawn with solid bonds and their hydrogen bonds are drawn with dashed lines.

atoms = 0.074 Å), form with their symmetry equivalents a centrosymmetric dimer connected by hydrogen bonds to two chloride anions and two methanol molecules. A further methanol molecule is hydrogen bonded to each chloride anion (Fig. 6). The O atom of this methanol molecule does not act as an acceptor for a classical hydrogen bond but for a C—H···O contact (Table 3); the centrosymmetric aggregates are connected *via* this contact to form an infinite chain (Fig. 7) running along the diagonal between the *a* and *b* axes. π–π stacking interactions between aromatic rings cannot be observed in this structure, because the rings are not positioned directly over one another. The two hydrogen-bonded complexes formed by the different formula units in the asymmetric unit of (III) are rather similar (Fig. 8). The major difference between these two aggregates is the orientation of the outer methanol molecule. In one complex, the methanolic methyl group points away from the centre of the complex (solid bonds in Fig. 8), whereas in the other complex this methyl group points in the opposite direction (open bonds in Fig. 8).

The cations in the three structures presented in this paper differ only in the halogen substituent in the *para* position of the benzene ring. In (I) there is a Cl residue, whereas in (II) and (III) there is an F atom at this position. Bond lengths and angles in all these (essentially planar) cations are almost the same. There is just one conformational difference between the three cations which is the N—C—C—N torsion angle. This shows a *cis* conformation in (I) and (III), and a *trans* conformation in (II). It is remarkable that in all three cases the pyridinium N atom donates a hydrogen bond to the Cl atom, irrespective of the orientation of the pyridinium ring with respect to the rest of the cation. When methanol molecules are present in the crystal structures, these solvent molecules act as an acceptor for the hydrogen bond from the amino unit. It may be suspected that the additional methanol solvent which is included in the crystal structures of (I) and (III) causes the cation to adopt the *trans* conformation, because a different hydrogen-bond pattern is formed.

Experimental

Reagents and solvents were obtained from Aldrich Chemicals. NMR spectra were run at ambient temperature using Bruker AMX 250, Bruker DPX 250 and Bruker Avance 400 spectrometers. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet.

For the preparation of 2-{1-[(4-chloroanilino)methylidene]ethyl}-pyridinium chloride methanol solvate, (I), 2-acetylpyridine (2.84 g, 23.44 mmol), 4-chlorophenylhydrazine hydrochloride (5.00 g, 28.09 mmol) and ten drops of acetic acid in ethanol (150 ml) were heated under reflux for 3 h. After cooling the reaction mixture to room temperature, a yellow–orange precipitate was formed. After dissolving this precipitate in a minimum amount of methanol, single crystals of (I) were grown at 278 K by slow evaporation of the solvent (yield 3.75 g, 49%; m.p. 516–519 K). ^{1}H NMR (250.1 MHz, DMSO): δ 10.67 (s, 1H, NH), 8.80 (dd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H5), 8.49 (pseudo-t, 1H, H6), 8.32 (d, $^3J_{HH}$ = 8.1 Hz, H7), 7.84 (pseudo-t, 1H, H8), 7.74–7.70 (m, 2H, H3, H3′), 7.39–7.35 (m, 2H, H2, H2′), 2.49 (s, 3H, CH$_3$); ^{13}C NMR (100.6 MHz, DMSO): δ 149.9 (C11), 144.9 (C24), 143.4 (C21), 143.0 (C23), 128.9 (C13/15), 124.8 (C14), 124.1 (C25), 123.1 (C26), 116.1 (C12/16), 12.7 (CH$_3$).

For the preparation of 2-{1-[(4-fluoroanilino)methylidene]ethyl}-pyridinium chloride, (II), 2-acetylpyridine (3.10 g, 25.59 mmol), 4-fluorophenylhydrazine hydrochloride (5.00 g, 30.75 mmol) and ten drops of acetic acid in ethanol (100 ml) were heated under reflux for 3 h. A yellow precipitate was formed during the reaction. After recrystallization of this precipitate from ethanol, X-ray quality crystals of compound (II) were obtained by slow evaporation of the solvent (yield 4.94 g, 73%; m.p. 525–527 K). After dissolving (II) in a minimum amount of methanol, single crystals of (III) were grown at 278 K by slow evaporation of the solvent. ^{1}H NMR (250.1 MHz, DMSO): δ 10.64 (s, 1H, NH), 8.80 (d, $^3J_{HH}$ = 5.7 Hz, 1H, H5), 8.50

(pseudo-t, 1H, H6), 8.32 (pseudo-d, H7), 7.84 (pseudo-t, 1H, H8), 7.77–7.71 (m, 2H, H3, H3′), 7.22–7.14 (m, 2H, H2, H2′), 2.45 (s, 3H, CH$_3$); ^{13}C NMR (100.6 MHz, DMSO): δ 157.8 (d, $^1J_{CF}$ = 237.0 Hz, C14), 150.1 (C11), 145.3 (C24), 142.9 (C23), 141.2 (C21), 124.2 (C26), 123.3 (C25), 115.9 (d, $^3J_{CF}$ = 7.5 Hz, C12/16), 115.6 (d, $^2J_{CF}$ = 22.4 Hz, C13/15), 12.6 (CH$_3$).

Compound (I)

Crystal data

C$_{13}$H$_{13}$ClN$_3$$^+$·Cl$^-$·CH$_4$O	V = 1486.18 (17) Å^3
M_r = 314.21	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.6715 (5) Å	μ = 0.44 mm^{-1}
b = 16.0963 (10) Å	T = 173 K
c = 12.0406 (8) Å	0.38 × 0.24 × 0.08 mm
β = 91.666 (5)°	

Data collection

Stoe IPDS II two-circle diffractometer	24993 measured reflections
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)	4284 independent reflections
	3625 reflections with $I > 2\sigma(I)$
	R_{int} = 0.055
T_{min} = 0.852, T_{max} = 0.966	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.096	
S = 1.05	
4284 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
195 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Compound (II)

Crystal data

C$_{13}$H$_{13}$FN$_3$$^+$·Cl$^-$	V = 1250.9 (3) Å^3
M_r = 265.71	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 6.8522 (12) Å	μ = 0.30 mm^{-1}
b = 11.5134 (16) Å	T = 173 K
c = 15.856 (2) Å	0.38 × 0.09 × 0.05 mm
β = 90.048 (16)°	

Data collection

Stoe IPDS II two-circle diffractometer	6993 measured reflections
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)	2161 independent reflections
	1662 reflections with $I > 2\sigma(I)$
	R_{int} = 0.116
T_{min} = 0.894, T_{max} = 0.985	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062	165 parameters
$wR(F^2)$ = 0.163	H-atom parameters constrained
S = 0.99	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
2161 reflections	$\Delta\rho_{min}$ = −0.63 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1M	0.84 (2)	2.04 (2)	2.8656 (14)	165.9 (19)
O1M—H1$M\cdots$Cl1	0.79 (2)	2.35 (2)	3.1425 (12)	174 (2)
N22—H22$\cdots$Cl1^i	0.89 (2)	2.39 (2)	3.1356 (11)	141.8 (17)

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N22—H22$\cdots$Cl1	0.88	2.33	3.168 (4)	159
N1—H1$\cdots$Cl1^i	0.88	2.48	3.289 (4)	153

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

Compound (III)

Crystal data

$C_{13}H_{13}FN_3{}^+\cdot Cl^-\cdot 2CH_4O$
$M_r = 329.80$
Triclinic, $P\bar{1}$
$a = 7.0088\ (8)$ Å
$b = 11.7258\ (14)$ Å
$c = 21.843\ (2)$ Å
$\alpha = 96.321\ (9)°$
$\beta = 92.066\ (9)°$

$\gamma = 107.247\ (9)°$
$V = 1699.6\ (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 173$ K
$0.42 \times 0.26 \times 0.14$ mm

Data collection

Stoe IPDS II two-circle
 diffractometer
Absorption correction: multi-scan
 (*MULABS*; Spek, 2009;
 Blessing, 1995)
 $T_{min} = 0.904$, $T_{max} = 0.967$

21250 measured reflections
7158 independent reflections
4239 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.058$
$S = 0.85$
7158 reflections
435 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

The H atoms could be located in a difference Fourier map. H atoms bonded to N and O atoms in (I) and (III) were freely refined. The amino H atom of (II) was refined using a riding model, with N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. H atoms bonded to C atoms were refined using a riding model, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, or with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The methyl groups were allowed to rotate but not to tip. The crystal of (II) turned out to be a nonmerohedral twin with β close to 90°, emulating an orthorhombic structure. The twin law ($\bar{1}$00/0$\bar{1}$0/001) is a twofold rotation about the c axis and the fractional contribution of the minor twin component refined to 0.324 (3).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1M	0.826 (16)	2.158 (16)	2.9136 (17)	152.1 (14)
N22—H22$\cdots$Cl1^{i}	0.907 (17)	2.401 (16)	3.1633 (15)	141.8 (13)
N1A—H1$A\cdots$O3M	0.834 (16)	2.081 (17)	2.8806 (18)	160.4 (16)
N22A—H22$A\cdots$Cl2^{ii}	0.883 (18)	2.382 (18)	3.1292 (15)	142.5 (15)
O1M—H1$M\cdots$Cl1	0.92 (3)	2.18 (3)	3.0807 (16)	168 (2)
O2M—H2$M\cdots$Cl1	0.91 (3)	2.19 (3)	3.1029 (17)	178 (3)
O3M—H3$M\cdots$Cl2	0.86 (2)	2.21 (2)	3.0678 (16)	172 (2)
O4M—H4$M\cdots$Cl2	0.85 (3)	2.30 (3)	3.1329 (18)	167 (2)
C25—H25$\cdots$O2M^{iii}	0.95	2.42	3.315 (2)	157
C25A—H25$A\cdots$O4M^{iv}	0.95	2.44	3.318 (3)	153

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

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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