




Please cite the Published Version

Mewis, Ryan E , Hulme, Matthew C, Marron, Jack, Langley, Stuart K , Sutcliffe, Oliver B 
and Benjamin, Sophie L (2025) Synthesis and crystal structures of five fluorinated diphenidine derivatives. Acta Crystallographica Section E Crystallographic Communications, 81 (3). pp. 229-234. ISSN 2056-9890

DOI: <https://doi.org/10.1107/s2056989025001288>

Publisher: International Union of Crystallography (IUCr)

Version: Published Version

Downloaded from: <https://e-space.mmu.ac.uk/638625/>

Usage rights:  [Creative Commons: Attribution 4.0](https://creativecommons.org/licenses/by/4.0/)

Additional Information: This is an open access article which first appeared in Acta Crystallographica Section E Crystallographic Communications

Enquiries:

If you have questions about this document, contact openresearch@mmu.ac.uk. Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)



Synthesis and crystal structures of five fluorinated diphenidine derivatives

Ryan E. Mewis,^{a*} Matthew C. Hulme,^a Jack Marron,^a Stuart K. Langley,^a Oliver B. Sutcliffe^{a*} and Sophie L. Benjamin^b

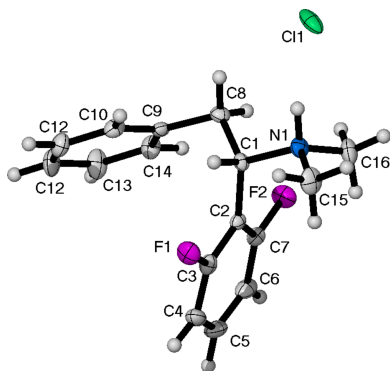
^aDepartment of Natural Sciences, Manchester Metropolitan University, John Dalton Building, Chester St., Manchester, M1 5GD, United Kingdom, and ^bSchool of Science and Technology, Nottingham Trent University, Nottingham NG11, 8NS, United Kingdom. *Correspondence e-mail: r.mewis@mmu.ac.uk, o.sutcliffe@mmu.ac.uk

Diphenidine (**1a**), a dissociative anaesthetic, was first reported in 2013. Since then, a number of derivatives *e.g.* 2-methoxyphenidine (**1b**) have been produced by clandestine laboratories and sold as *research chemicals*. Fluorinated diphenidines, namely, [1-(2,6-difluorophenyl)-2-phenylethyl]dimethylazanium chloride, C₁₆H₁₈F₂N⁺·Cl⁻, (**I**), [1-(2,6-difluorophenyl)-2-phenylethyl](ethyl)azanium chloride dichloromethane hemisolvate, 2C₁₆H₁₈F₂N⁺·2Cl⁻·CH₂Cl₂, (**II**), *tert*-butyl[1-(2,6-difluorophenyl)-2-phenylethyl]azanium chloride, C₁₈H₂₂F₂N⁺·Cl⁻, (**III**), 1-[1-(2,6-difluorophenyl)-2-phenylethyl]pyrrolidin-1-ium chloride, C₁₈H₂₀F₂N⁺·Cl⁻, (**IV**), and 1-[1-(2,3,4,5,6-pentafluorophenyl)-2-phenylethyl]piperidin-1-ium chloride, C₁₉H₁₉F₅N⁺·Cl⁻, (**V**), were synthesized and structurally characterized by ¹H, ¹³C and ¹⁹F NMR spectroscopy, and single-crystal X-ray diffraction. All five structures exhibit hydrogen bonding between the quaternary amine hydrogen atoms and the chlorine. The N—H···Cl distances for (**II**) and (**III**) range from 2.21 to 2.31 Å, whereas (**I**), (**IV**) and (**V**) exhibit shorter N—H···Cl distances (2.07–2.20 Å). Compounds (**IV**) and (**V**) include pyrrolidine and piperidine rings, respectively; the pyrrolidine ring adopts an envelope conformation whereas the piperidine ring adopts a chair conformation. The crystal packing in compounds (**I**)–(**V**) is characterized by C—H···π interactions; no π–π interactions are observed.

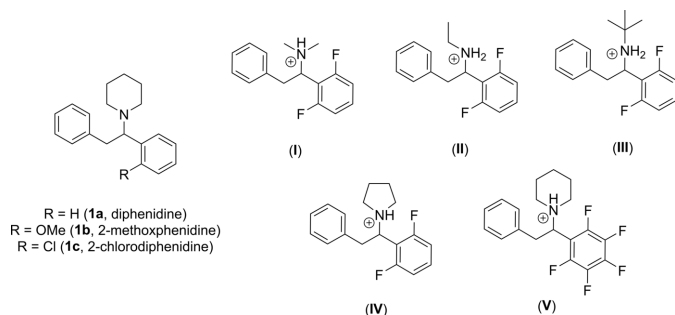
1. Chemical context

Over the past two decades, there has been a significant increase in the number of new psychoactive substances (NPS) seized by law enforcement agencies globally (King, 2013; UNODC, 2024). Current convention uses a functional ‘effect group’ categorization to define NPS within six broad overlapping groups: (i) synthetic cannabinoid receptor agonists; (ii) classic hallucinogens; (iii) stimulants; (iv) opioid receptor agonists; (v) sedatives/hypnotics and (vi) dissociatives (UNODC, 2024; Tettey *et al.*, 2018; Shafi *et al.*, 2020). NPS are assigned to a specific ‘effect group’ based on their chemical structure and psychopharmacological effects (UNODC, 2024; Tettey *et al.*, 2018). 1,2-Diarylethamines are dissociative, psychoactive substances, which distort perceptions, produce feelings of detachment, and induce a state of anaesthesia by antagonizing ionotropic *N*-methyl-D-aspartate receptors (NMDAR) in the central nervous system (UNODC, 2024; Morris & Wallach, 2014).

The first of these dissociative anaesthetics was 1-(1,2-diphenylethyl)piperidine (diphenidine, **1a**) (Wallach *et al.*, 2015) reported in 2013 (Morris & Wallach, 2014), followed by 1-[1-(2-methoxyphenyl)-2-phenylethyl]piperidine (2-methoxyphenidine, **1b**) (McLaughlin *et al.*, 2016), which have both been marketed as ‘*research chemicals*’ and encountered in tablet or



powder forms (UNODC, 2024; Wallach *et al.*, 2015; McLaughlin *et al.*, 2016; Odoardi *et al.*, 2016; Strano Rossi *et al.*, 2014) or in combination with synthetic cannabinoids such as AB-CHMINACA, 5F-AMB (Hasegawa *et al.*, 2015) and 5F-AB-PINACA (Wurita *et al.*, 2014). Though both the supply and production of **1a**, **1b** and the recently disclosed 1-[1-(2-chlorophenyl)-2-phenylethyl]piperidine (2-chlorodiphenidine, **1c**) (Wallach *et al.*, 2016; Sahai *et al.*, 2018), are now controlled in the United Kingdom by the 2016 Psychoactive Substances Act (Reuter & Pardo, 2017), the emergence of novel 1,2-diarylethylamine derivatives, such as the fluorinated compounds, (**I**)–(**V**), still raises considerable legal and analytical challenges in both the forensic identification and discrimination of these materials. This is due to the inference of diphenidine-based NPS in several fatalities in Europe (Morris & Wallach, 2014; Wallach *et al.*, 2015, 2016; McLaughlin *et al.*, 2016; Strano Rossi *et al.*, 2014; Hasegawa *et al.*, 2015; Wurita *et al.*, 2014; Sahai *et al.*, 2018; Reuter & Pardo, 2017; Elliott *et al.*, 2015; Helander *et al.*, 2015; Hofer *et al.*, 2014), Asia (Hasegawa *et al.*, 2015; Minakata *et al.*, 2016; Kudo *et al.*, 2015) and **1a** being placed under international control, within schedule II of the United Nations Convention on Psychotropic Substances (1971), on 14th April 2021 (UNODC, 2021).



2. Structural commentary

Compound (**I**) (Fig. 1) crystallizes in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit. The torsion angle between the two quaternary carbons of the phenyl rings and the bridging ethyl chain is $53.4(2)^\circ$.

Compound (**II**) (Fig. 2) crystallizes in the $I2/a$ space group. It consists of one molecule in the asymmetric unit, as well as half of a single molecule of dichloromethane (DCM). The terminal carbon of the ethyl group (C15, C15A) is disordered over two positions [0.707(5):0.293(5) occupancy]. The closest contact between one of the fluorine atoms of the 2,6-difluorophenyl ring and a hydrogen atom of DCM is 2.335 \AA . The torsion angle for (**II**), as defined previously for (**I**), is $-55.9(2)^\circ$. The final non-cyclic aliphatic analogue, (**III**) (Fig. 3), crystallizes in the monoclinic space group $P2_1/c$ with a single formula unit in the asymmetric unit cell. The torsion angle is the largest of all the structures presented herein at $63.8(2)^\circ$.

Compound (**IV**) (Fig. 4) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. Torsion

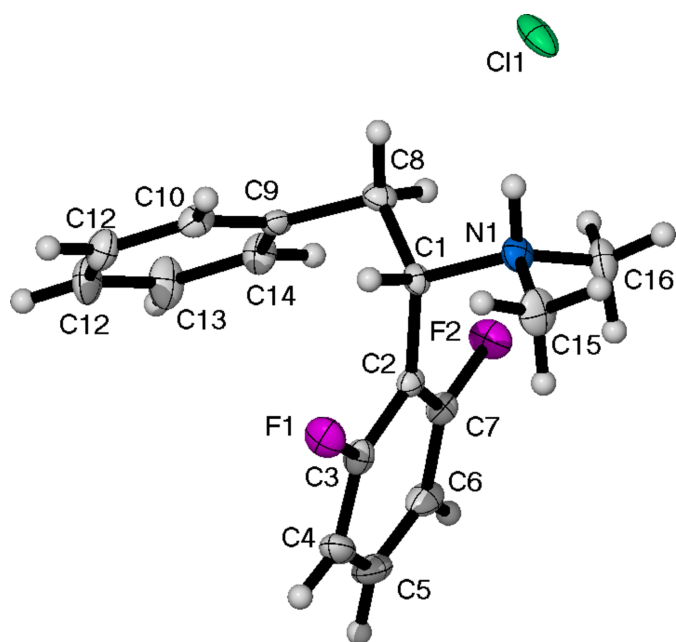


Figure 1
 The molecular structure of (**I**), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

angles of $-54.6(3)$ and $58.9(3)^\circ$ are very similar to (**I**) and (**III**). The pyrrolidine ring present in the structure adopts an envelope conformation.

Compound (**V**) (Fig. 5) crystallizes in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit. The torsion angle defined is the smallest of the crystal structures presented at $47.3(2)^\circ$. The piperidine ring is in the chair conformation. All five structures exhibit hydrogen bonding between the quaternary amine and the chlorine (Tables 1–5). The five structures can be split in to two groups; (**II**) and (**III**) both have two *R* groups attached to the amine whereas the

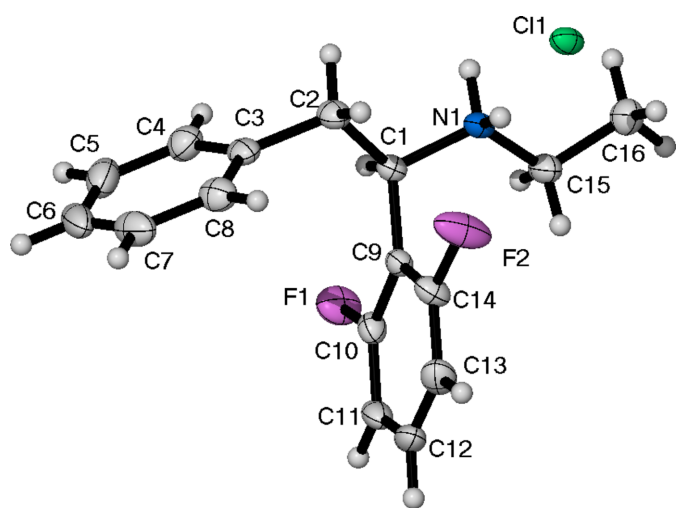


Figure 2
 The molecular structure of (**II**), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. The half molecule of DCM present has been omitted.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1M1···Cl1	0.93 (2)	2.08 (2)	3.0006 (17)	167.3 (19)

remainder all possess three. The N–H···Cl distance for the former grouping range from 2.21 to 2.31 Å, with N–H–Cl angles of 151–168° (Tables 2 and 3). Interestingly, in (II), a shorter N–H1A···Cl distance of 2.11 Å (compared to 2.30 Å for N–H1B···Cl) is observed to a symmetry-related [symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$] Cl atom. The latter group, consisting of (I), (IV) and (V) exhibit shorter

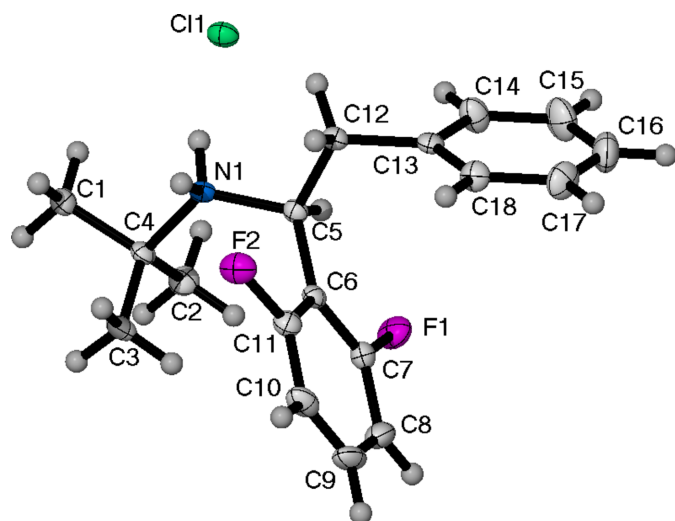
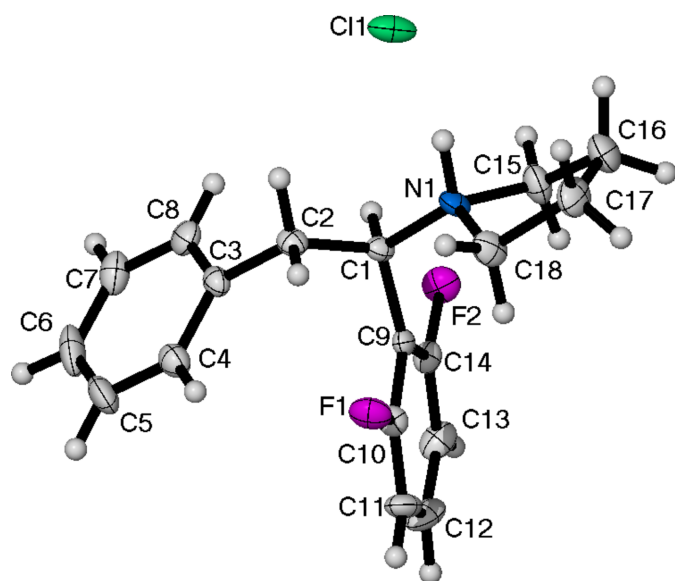

Figure 3
 The molecular structure of (III), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

Figure 4
 The molecular structure of (IV), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. Only one molecule present in the asymmetric unit is shown.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1B···Cl1	0.89 (2)	2.30 (2)	3.1417 (14)	156.0 (16)

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···Cl1	0.92 (2)	2.21 (3)	3.115 (2)	167.7 (19)
N1–H1B···Cl1 ⁱ	0.95 (2)	2.31 (2)	3.1684 (19)	151 (2)

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

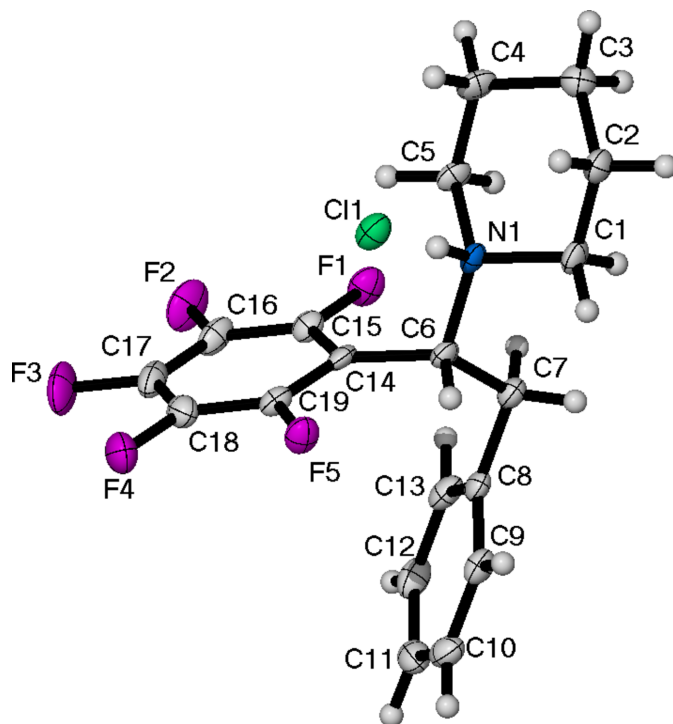
Table 4
 Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1'···Cl1	0.99 (1)	2.07 (2)	3.021 (5)	163 (6)
N2–H2···Cl2	0.98 (1)	2.08 (2)	3.052 (5)	169 (6)

Table 5
 Hydrogen-bond geometry (Å, °) for (V).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···Cl1	0.85 (3)	2.20 (3)	3.051 (3)	178 (3)

N–H···Cl distances (2.07–2.20 Å, Tables 1, 4 and 5) as well as N–H–Cl angles that are all greater than 163°.


Figure 5
 The molecular structure of (V), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

3. Supramolecular features

Molecules of **(I)** exhibit no π - π interactions, as despite the unsubstituted phenyl rings being aligned when viewed along the *c*-axis direction, the shortest centroid-centroid distance is 7.947 Å [symmetry operation 1 + *x*, *y*, *z*]. Molecules are linked together by C—H... π interactions; the distance of the centroid of the unsubstituted phenyl ring to the nearest aromatic protons of a substituted aromatic ring are 3.274 and 3.951 Å [$Cg1 \cdots H4^i = 3.274$ Å and $Cg1 \cdots H5^i = 3.951$ Å; *Cg1* is the centroid of C9-C14 ring; symmetry code: (i) 1 + *x*, *y*, *z*]. Another C—H... π interaction exists between the centroid of the difluorinated ring and a phenyl ring proton of a neighbouring molecule [$Cg2 \cdots H11^{ii} = 2.982$ Å; *Cg2* is the centroid of the C2-C7 ring; symmetry code: (ii) 1 - *x*, *y* - $\frac{1}{2}$, $\frac{1}{2}$ - *z*].

Analysis of **(II)**–**(V)** reveals that these also exhibit no π - π interactions. Similarly to **(I)**, they do exhibit weak C—H... π interactions with distances of 3.244–3.425, 3.427–3.744 and 2.929–3.459 Å for **(II)**, **(III)** and **(IV)**, respectively, between the nearest ring hydrogen of the difluorinated ring and that of the centroid of the nearest neighbouring phenyl ring. **(II)** also exhibits a C—H... π interaction between the non-fluorinated phenyl rings of neighbouring molecules [$Cg3 \cdots H4^{iii} = 2.969$ Å; *Cg3* is the centroid of ring C3–C8; symmetry code: (iii) -*x*, *y* - $\frac{1}{2}$, $\frac{1}{2}$ - *z*]. Similarly, **(III)** has the same interaction [$Cg4 \cdots H17^{iv} = 3.785$ Å and $Cg4 \cdots H18^{iv} = 4.105$ Å; *Cg4* is the centroid of ring C13–C18; symmetry code: (iv) -*x*, *y* - $\frac{1}{2}$, *z* - $\frac{1}{2}$]. For **(IV)**, the pyrrolidine ring exhibits two sets of C—H... π interactions to the phenyl [$Cg5 \cdots H17A^v = 3.349$ Å and $Cg5 \cdots H18A^v = 3.417$ Å; *Cg5* is the centroid of ring C27–C32; symmetry code: (v) 1 - *x*, 2 - *y*, 1 - *z*] and difluorinated rings [$Cg6 \cdots H33A^{vi} = 4.179$ Å and $Cg6 \cdots H33B^{vi} = 4.068$ Å; *Cg6* is the centroid of ring C27–C32; symmetry code: (vi) 1 - *x*, 1 - *y*, 1 - *z*]. For **(V)**, there is a C—H... π interaction between a hydrogen atom of the piperidine ring and the pentafluorophenyl ring [$Cg7 \cdots H4A^{vii} = 2.865$ Å; *Cg7* is the centroid of ring C14–C19; symmetry code: (vii) (*x*) -*x*, 1 - *y*, 1 - *z*]. This C—H... π interaction is the shortest identified of the crystal structures presented. C—H... π interactions also exist between the two non-fluorinated phenyl rings of neighbouring molecules [$Cg8 \cdots H12^{viii} = 3.550$ Å and $Cg8 \cdots H11^{viii} = 3.748$ Å; *Cg8* is the centroid of ring C8–C13; symmetry code: (viii) -*x*, *y*, *z*] and between piperidine ring hydrogen atoms and non-fluorinated phenyl rings [$Cg9 \cdots H1B^{ix} = 3.220$ Å and $Cg9 \cdots H3B^{ix} = 3.426$ Å; *Cg9* is the centroid of ring C8–C13; symmetry code: (ix) 1 - *x*, 1 - *y*, -*z*].

4. Database survey

A search of the Cambridge Structural Database (version 5.45, update in June 2024; Groom *et al.*; 2016) for phenidine derivatives resulted in four hits. All four hits are 2-methoxyphenidine (**1b**) with a variety of solvates, some unknown (REBKOC; Jurásek *et al.*, 2022), and bromo- and chlorozincate ions (REBLOD and REBLIX; Jurásek *et al.*, 2022). Entry FIDHIN (Jurásek *et al.*, 2023) is the hydrochloride salt of the *R*-isomer of **1b** and as such is comparable to **(V)** due to

the presence of a piperidine ring. Similar to **(V)**, it has N—H...Cl distances of 2.120 and 2.123 Å (two molecules in the asymmetric unit). The piperidine ring is the chair conformation, which is again directly comparable to **(V)**. Entry REBKOC, mirrors that of FIDHIN except a chloroform solvent molecule is present in the asymmetric unit. It has an N—H—Cl distance of 2.209 Å and a Cl₃C—H...A distance of 2.387 Å; the presence of this solvent molecule has elongated the distance. The remaining two entries REBLOD and REBLIX (Jurásek *et al.*, 2022) both possess ZnCl₂Br₄²⁻ and ZnCl₂Br₄²⁻ ions in the asymmetric unit cell. Again, the piperidine ring is in the chair conformation for both REBLOD and REBLIX.

5. Synthesis and crystallization

General method for diarylethylamine synthesis

All diphenidine derivatives and analogues were synthesized using an adaptation of the published method (Le Gall *et al.*, 2009). The following modifications were applied to the published method: To zinc dust (2.0 g, 30 mmol) suspended in acetonitrile (40 mL), was added benzyl bromide (0.4 mL, 3.4 mmol) and trifluoroacetic acid (0.2 mL). The resulting solution was stirred for 5 minutes and then benzyl bromide (3.0 mL, 25 mmol), the required amine (0.99 mL, 10 mmol) followed by the pre-requisite benzaldehyde (11 mmol), were introduced to the mixture, and the solution was stirred at room temperature for an additional 1 h. The resulting solution was poured into a saturated aqueous NH₄Cl solution (150 mL) and extracted with dichloromethane (2 × 100 mL). The combined organic layers were dried (MgSO₄) and concentrated *in vacuo* to give a crude yellowish oil. The oil was then dissolved in diethyl ether (150 mL) and concentrated sulfuric acid (0.75 mL) was added dropwise to the vigorously stirred solution. After five minutes, the precipitated ammonium salt was filtered, washed with diethyl ether (2 × 50 mL) and air dried for 5–10 minutes. The ammonium salt was re-dissolved in aqueous sodium hydroxide (5% *w/v*, 150 mL) and then extracted with dichloromethane (2 × 100 mL). The combined organic fractions were again dried (MgSO₄) and concentrated *in vacuo* to give a yellow oil. The oil was dissolved in diethyl ether (200 mL), treated with hydrogen chloride (4 *M* in dioxane, 3.0 mL, 12 mmol) and left to stand for 5 minutes. The crystallized products were filtered and washed sequentially with the minimum amount of ice-cold acetone and if necessary an ice-cold mixture of ethyl acetate–diethyl ether (1:5) to afford the corresponding hydrochloride salts as colourless to off-white powders.

(I) afforded 0.40 g (15%) of a white powder. Colourless crystals suitable for X-ray diffraction were grown from EtOAc/diethyl ether. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.4–7.5 (*m*, 1 H), 7.1–7.2 (*m*, 5 H), 7.0 (*br. s.*, 1 H), 6.9 (*br. s.*, 1 H), 4.9 (*dd*, *J* = 12.36, 2.75 Hz, 1 H), 4.0 (*dd*, *J* = 12.82, 3.66 Hz, 1 H), 3.6–3.7 (*m*, 1 H), 2.8 (*br. s.*, 3 H), 2.7 (*br. s.*, 3 H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 162.5 (*dd*, *J* = 251.12, 7.67 Hz, C-F), 135.8, 133.6, 133.5, 133.4, 129.3, 129.1, 127.7, 113.5, 112.7, 107.0, 61.8, 43.0, 38.4, 34.7. ¹⁹F NMR (56 MHz, CD₂Cl₂): δ -111.21

Table 6
Experimental details.

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	C ₁₆ H ₁₈ F ₂ N ⁺ ·Cl ⁻	2C ₁₆ H ₁₈ F ₂ N ⁺ ·2Cl ⁻ ·CH ₂ Cl ₂	C ₁₈ H ₂₂ F ₂ N ⁺ ·Cl ⁻	C ₁₈ H ₂₀ F ₂ N ⁺ ·Cl ⁻	C ₁₉ H ₁₉ F ₅ N ⁺ ·Cl ⁻
<i>M_r</i>	297.76	680.45	325.81	323.80	391.80
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>I</i> 2/ <i>a</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, $\bar{P}1$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	123	123	123	123	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.9474 (3), 12.7652 (5), 15.3998 (7)	22.9963 (14), 7.8729 (5), 19.033 (1)	11.3115 (6), 10.5400 (5), 14.8039 (7)	8.1365 (4), 12.7421 (10), 16.0451 (8)	9.3155 (5), 22.2529 (13), 8.2699 (3)
α , β , γ (°)	90, 99.368 (4), 90	90, 92.130 (5), 90	90, 105.044 (5), 90	88.059 (5), 82.349 (4), 86.140 (5)	90, 90.165 (5), 90
<i>V</i> (Å ³)	1541.48 (11)	3443.5 (4)	1704.48 (15)	1644.42 (17)	1714.32 (15)
<i>Z</i>	4	4	4	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.26	0.39	0.24	0.25	0.28
Crystal size (mm)	0.5 × 0.4 × 0.2	0.3 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.5 × 0.4 × 0.3	0.2 × 0.1 × 0.05
Data collection					
Diffractometer	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Agilent 2014)	Analytical (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Analytical (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Analytical (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Analytical (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.884, 0.950	0.911, 0.962	0.944, 0.976	0.888, 0.928	0.967, 0.986
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6424, 2715, 2305	12738, 3034, 2813	7223, 3008, 2343	13277, 5775, 4892	5523, 2896, 2117
<i>R</i> _{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.027 0.595	0.021 0.595	0.036 0.595	0.032 0.595	0.049 0.595
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.040, 0.088, 1.06	0.031, 0.077, 1.07	0.049, 0.095, 1.06	0.090, 0.206, 1.19	0.056, 0.123, 1.01
No. of reflections	2715	3034	3008	5775	2896
No. of parameters	186	224	210	403	239
No. of restraints	1	0	0	2	0
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	H atoms treated by a mixture of independent and constrained refinement	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)	0.20, -0.26	0.25, -0.22	0.22, -0.25	0.59, -0.34	0.30, -0.25

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *X-SEED* (Barbour, 2020).

(*br. s.*, 2F). FT-IR (ATR, cm⁻¹) 2306[RM1], 1624 (C=O), 1457 (C=C). M.p. = 385–387 K.

(II) afforded 2.24 g (64%) of a white powder. Colourless crystals suitable for X-ray diffraction were grown from DCM/diethyl ether. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.26 (*br. s.*, 1H, NH), 9.18 (*br. s.*, 1H, NH), 7.02–7.20 (*m*, 7H, Ar-H), 7.50 (*dd*, 1H, *J* = 11.2, 4.2 Hz, Ar-H), 4.75 (*m*, 1H, NHCHCH₂), 3.65 (*dd*, 1H, *J* = 12.8, 4.8 Hz, NHCHCH₂), 3.18 (*m*, 1H, NHCHCH₂), 2.95 (*m*, 2H, NHCH₂CH₃), 1.28 (*t*, 3H, *J* = 7.0 Hz, NHCH₂CH₃). ¹⁹F{¹H} NMR (400 MHz, DMSO-*d*₆) δ -113.68 (*s*, 2F); IR (ATR, cm⁻¹): 2944 (C–H), 2670 (C–H), 1475 (C=C), 1202 (C–F). M.p. = 478 K.

(III) afforded 1.93 g (67%) of a white powder. Colourless crystals suitable for X-ray diffraction were grown from CHCl₃/diethyl ether. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.3 (*d*, *J* = 9.16 Hz, 1H), 8.9 (*dd*, *J* = 11.91, 5.04 Hz, 1H), 7.4–7.5 (*m*, 1H), 7.1–7.3 (*m*, 4H), 7.0 (*dd*, *J* = 7.56, 2.06 Hz, 2H), 6.9 (*s*, 1H), 4.7 (*dd*, *J* = 11.68, 4.35 Hz, 1H), 3.7 (*dd*, *J* = 12.82, 4.12 Hz, 1H), 3.3–3.4 (*m*, 1H), 1.4 (*s*, 9H). ¹³C{¹H} NMR

(101 MHz, (CD₃)₂SO) δ 135.4, 132.2, 132.1, 132.0, 128.7, 128.2, 126.9, 112.5, 112.3, 111.8, 111.6, 111.4, 58.8, 49.4, 38.1, 25.3. ¹⁹F NMR (56 MHz, (CD₃)₂SO) δ -109.94 (*br. s.*, 1F), -116.79 (*br. s.*, 1F). FT-IR (ATR, cm⁻¹) 2612, 1625, 1565, 1467; M.p. = 535–538 K.

(IV) afforded 2.22 g (77%) of a white powder. Colourless crystals suitable for X-ray diffraction were grown from DCM/diethyl ether. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.4 (*tt*, *J* = 8.47, 6.41 Hz, 1H), 7.1–7.2 (*m*, 5H), 7.0 (*br. s.*, 1H), 6.8 (*br. s.*, 1H), 4.9 (*dd*, *J* = 12.14, 3.89 Hz, 1H), 3.9 (*dd*, *J* = 13.28, 4.58 Hz, 2H), 3.6 (*t*, *J* = 12.59 Hz, 2H), 2.9 (*br. s.*, 1H), 2.8 (*br. s.*, 1H), 2.2 (*br. s.*, 5H), 1.9 (*br. s.*, 2H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 161.6 (*dd*, *J* = 250.16, 7.67 Hz) C–F, 136.0, 133.3, 133.2, 133.1, 129.2, 129.1, 127.6, 113.4, 112.5, 109.0, 108.8, 108.7, 59.9, 50.6, 35.9, 23.4, 23.2. ¹⁹F NMR (56 MHz, CD₂Cl₂) δ -108.10 (*br. s.*, 1F), -114.18 (*br. s.*, 1F). FT-IR (ATR, cm⁻¹) 2352, 1623, 1460. M.p. = 486–488 K.

(V) afforded 1.55 g (52%) of a white powder. Colourless crystals suitable for X-ray diffraction were grown from CHCl₃/

diethyl ether. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.11–7.28 (*m*, 5 H), 4.90 (*d*, $J = 12.36$ Hz, 1 H), 4.23 (*dd*, $J = 12.82$, 3.66 Hz, 1 H), 3.80 (*d*, $J = 11.45$ Hz, 1 H), 3.44–3.55 (*m*, 2 H), 2.57–2.70 (*m*, 1 H), 2.48 (*d*, $J = 9.62$ Hz, 1 H), 2.24–2.38 (*m*, 1 H), 1.91 (*t*, $J = 14.88$ Hz, 2 H), 1.80 (*d*, $J = 13.74$ Hz, 1 H), 1.22–1.37 (*m*, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 120.9, 115.0, 114.6, 113.5, 91.0, 48.2, 34.5, 19.2, 9.0, 8.9, 8.1. ^{19}F NMR (56 MHz, CD_2Cl_2) δ –134.86, –139.28, –152.81 (*t*, $J = 22.4$ Hz), –162.69. FT-IR (ATR, cm^{-1}) 2309, 1503, 1459. $M_p = 502$ –504 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as riding contributions in idealized positions with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl groups). All structures were solved by direct methods. For (**II**) the terminal carbon of the ethyl group (C15, C15A), is disordered over two positions [0.707 (5):0.293 (5) occupancy]. All non-H atoms were refined anisotropically. The H atoms were placed in calculated positions, except for H1N1 (**I**), H1A and H1B (**II**), H1' and H2 (**IV**) and H2 (**V**), which were all found. For (**V**), a DFIX instruction was applied to N1–H1' and N2–H2 (fixed at 0.98 Å).

Acknowledgements

We thank Manchester knowledge and drug exchange (MANDRAKE) for the preparation of the reference compounds, which were produced under Home Office licence (in accordance with Manchester Metropolitan University's Home Office license, Ref. No. 423023) requirements and agreed procedures.

References

Agilent (2014). *CrysAlis PRO*, Agilent Technologies, Yarnton, England.
 Barbour, L. J. (2020). *J. Appl. Cryst.* **53**, 1141–1146.
 Elliott, S. P., Brandt, S. D., Wallach, J., Morris, H. & Kavanagh, P. V. (2015). *J. Anal. Toxicol.* **39**, 287–293.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Hasegawa, K., Wurita, A., Minakata, K., Gonmori, K., Nozawa, H., Yamagishi, I., Watanabe, K. & Suzuki, O. (2015). *Forensic Toxicol.* **33**, 380–387, doi: 10.1007/s11419-015-0272-y.
 Helander, A., Beck, O. & Bäckberg, M. (2015). *Clin. Toxicol.* **53**, 446–453.
 Hofer, K. E., Degrandi, C., Müller, D. M., Zürrer-Härdi, U., Wahl, S., Rauber-Lüthy, C. & Ceschi, A. (2014). *Clin. Toxicol.* **52**, 1288–1291.

Jurásek, B., Fagan, P., Dolenský, B., Paškanová, N., Dobšíková, K., Raich, I., Jurok, R., Setnička, V., Kohout, M., Čejka, J. & Kuchař, M. (2023). *New J. Chem.* **47**, 4543–4551.
 Jurásek, B., Rimpelová, S., Babor, M., Čejka, J., Bartůněk, V. & Kuchař, M. (2022). *Int. J. Mol. Sci.* **23**, 2083.
 King, L. A. (2013). *Novel Psychoactive Substances*, edited by P. I. Dargan and D. M. Wood, pp. 3–27. Academic Press, Boston: Academic Press. doi: 10.1016/B978-0-12-415816-0.00001-8.
 Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
 Kudo, K., Usumoto, Y., Kikura-Hanajiri, R., Sameshima, N., Tsuji, A. & Ikeda, N. (2015). *Leg. Med.* **17**, 421–426.
 Le Gall, E., Haurena, C., Sengmany, S., Martens, T. & Troupel, M. (2009). *J. Org. Chem.* **74**, 7970–7973.
 McLaughlin, G., Morris, N., Kavanagh, P. V., Power, J. D., O'Brien, J., Talbot, B., Elliott, S. P., Wallach, J., Hoang, K., Morris, H. & Brandt, S. D. (2016). *Drug Test. Anal.* **8**, 98–109.
 Minakata, K., Yamagishi, I., Nozawa, H., Hasegawa, K., Gonmori, K., Suzuki, M., Wurita, A., Suzuki, O. & Watanabe, K. (2016). *Forensic Toxicol.* **34**, 151–157.
 Morris, H. & Wallach, J. (2014). *Drug Test. Anal.* **6**, 614–632.
 Odoardi, S., Romolo, F. S. & Strano-Rossi, S. (2016). *Forensic Sci. Int.* **265**, 116–120.
 Reuter, P. & Pardo, B. (2017). *Addiction*, **112**, 25–31.
 Sahai, M. A., Davidson, C. N., Dutta, C. & Opacka-Juffry, J. (2018). *Brain Sci.* pp. 8.
 Shafi A., Berry, A. J., Sumnall, H., Wood, D. M. & Tracy, D. K. (2020). *Ther. Adv. Psychopharmacol.*, **10**, 2045125320967197. <https://doi.org/10.1177/2045125320967197>.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Strano Rossi, S., Odoardi, S., Gregori, A., Peluso, G., Ripani, L., Ortar, G., Serpelloni, G. & Romolo, F. S. (2014). *Rapid Commun. Mass Spectrom.* **28**, 1904–1916.
 Tettey, J. N. A., Crean, C., Ifeagwu, S. C. & Raitelhuber, M. (2018). *New Psychoactive Substances: Pharmacology, Clinical, Forensic and Analytical Toxicology*, edited by H. H. Maurer & S. D. Brandt. pp. 51–67. Cham: Springer International Publishing. https://doi.org/10.1007/164_2018_127
 UNODC (2021). Resolution adopted by the Commission on 14th April 2021 – Inclusion of diphenidine in Schedule II of the Convention on Psychotropic Substances of 1971. Decision 64/6., 2021, https://www.unodc.org/documents/commissions/CND/Drug_Resolutions/2020-2029/2021/decision_64_6.pdf
 UNODC (2024). The Challenge of New Psychoactive Substances – A Technical Update. A Report from the Global SMART programme (Laboratory and Scientific Section), <https://www.unodc.org/unodc/en/scientists/the-challenge-of-new-psychoactive-substances.html>
 Wallach, J., Kang, H., Colestock, T., Morris, H., Bortolotto, Z. A., Collingridge, G. L., Lodge, D., Halberstadt, A. L., Brandt, S. D. & Adejare, A. (2016). *PLoS One*, **11**, e0157021.
 Wallach, J., Kavanagh, P. V., McLaughlin, G., Morris, N., Power, J. D., Elliott, S. P., Mercier, M. S., Lodge, D., Morris, H., Dempster, N. M. & Brandt, S. D. (2015). *Drug Test. Anal.* **7**, 358–367.
 Wurita, A., Hasegawa, K., Minakata, K., Watanabe, K. & Suzuki, O. (2014). *Forensic Toxicol.* **32**, 331–337.

supporting information

Acta Cryst. (2025). E81 [https://doi.org/10.1107/S2056989025001288]

Synthesis and crystal structures of five fluorinated diphenidine derivatives

Ryan E. Mewis, Matthew C. Hulme, Jack Marron, Stuart K. Langley, Oliver B. Sutcliffe and Sophie L. Benjamin

Computing details

1-[1-(2,3,4,5,6-Pentafluorophenyl)-2-phenylethyl]piperidin-1-ium chloride (V)

Crystal data

$C_{19}H_{19}F_5N^+Cl^-$

$M_r = 391.80$

Monoclinic, $P2_1/c$

$a = 9.3155$ (5) Å

$b = 22.2529$ (13) Å

$c = 8.2699$ (3) Å

$\beta = 90.165$ (5)°

$V = 1714.32$ (15) Å³

$Z = 4$

$F(000) = 808$

$D_x = 1.518$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9843 reflections

$\theta = 3.0$ – 26.5 °

$\mu = 0.28$ mm⁻¹

$T = 123$ K

Block, colourless

$0.2 \times 0.1 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur
diffractometer

Radiation source: fine-focus sealed tube
scans in ϕ and ω

Absorption correction: analytical
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.967$, $T_{\max} = 0.986$

5523 measured reflections

2896 independent reflections

2117 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.1$ °

$h = -10$ → 11

$k = -18$ → 26

$l = -8$ → 9

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.123$

$S = 1.01$

2896 reflections

239 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.3121P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.24269 (9)	0.51019 (4)	0.68922 (9)	0.0315 (2)
F1	0.07331 (19)	0.42667 (8)	0.0555 (2)	0.0327 (5)
F5	0.31205 (19)	0.36912 (8)	0.53597 (19)	0.0307 (5)
F4	0.1190 (2)	0.28212 (8)	0.5801 (2)	0.0404 (5)
F2	-0.1166 (2)	0.33964 (10)	0.1010 (2)	0.0474 (6)
F3	-0.0977 (2)	0.26613 (9)	0.3625 (2)	0.0492 (6)
C14	0.1989 (3)	0.40279 (14)	0.2969 (3)	0.0218 (7)
C18	0.1081 (4)	0.31807 (14)	0.4497 (4)	0.0281 (8)
C6	0.3167 (3)	0.44932 (13)	0.2723 (3)	0.0215 (7)
H6	0.395538	0.438117	0.348882	0.026*
C5	0.1334 (3)	0.53469 (14)	0.2445 (4)	0.0256 (8)
H5A	0.055024	0.505280	0.260780	0.031*
H5B	0.148162	0.539641	0.126760	0.031*
C4	0.0922 (3)	0.59416 (15)	0.3182 (4)	0.0308 (8)
H4A	0.070518	0.588238	0.434277	0.037*
H4B	0.003969	0.609188	0.264765	0.037*
C8	0.4205 (3)	0.38395 (14)	0.0529 (3)	0.0246 (8)
C1	0.3883 (3)	0.55697 (14)	0.3002 (4)	0.0267 (8)
H1A	0.477032	0.541589	0.351631	0.032*
H1B	0.407412	0.562601	0.183476	0.032*
C19	0.2066 (3)	0.36364 (14)	0.4273 (3)	0.0229 (7)
C10	0.5654 (4)	0.29493 (15)	0.0849 (4)	0.0320 (8)
H10	0.641115	0.274303	0.138504	0.038*
C16	-0.0118 (4)	0.34743 (16)	0.2098 (4)	0.0310 (8)
C2	0.3486 (3)	0.61639 (15)	0.3748 (4)	0.0286 (8)
H2A	0.427250	0.645549	0.357103	0.034*
H2B	0.336184	0.611273	0.492819	0.034*
N1	0.2689 (3)	0.51174 (11)	0.3216 (3)	0.0208 (6)
C7	0.3833 (3)	0.44745 (14)	0.1024 (3)	0.0258 (8)
H7A	0.314639	0.464662	0.023408	0.031*
H7B	0.471239	0.472407	0.101079	0.031*
C15	0.0873 (3)	0.39271 (14)	0.1886 (3)	0.0242 (8)
C17	-0.0007 (4)	0.30990 (15)	0.3412 (4)	0.0323 (9)
C12	0.3791 (4)	0.29713 (16)	-0.1148 (4)	0.0327 (9)
H12	0.327115	0.277949	-0.199197	0.039*
C3	0.2103 (4)	0.64091 (15)	0.3016 (4)	0.0317 (8)
H3A	0.182086	0.678299	0.358033	0.038*
H3B	0.225342	0.650474	0.185948	0.038*
C11	0.4883 (4)	0.26676 (15)	-0.0364 (4)	0.0315 (9)
H11	0.510387	0.226548	-0.065800	0.038*
C9	0.5318 (3)	0.35331 (15)	0.1277 (4)	0.0279 (8)
H9	0.586002	0.372763	0.209846	0.033*
C13	0.3452 (4)	0.35548 (15)	-0.0706 (4)	0.0303 (8)
H13	0.270025	0.376141	-0.125034	0.036*
H1	0.261 (4)	0.5105 (14)	0.425 (4)	0.038 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0238 (5)	0.0421 (5)	0.0286 (4)	0.0016 (4)	0.0007 (4)	0.0024 (4)
F1	0.0234 (11)	0.0457 (12)	0.0289 (9)	-0.0008 (10)	-0.0060 (8)	0.0025 (8)
F5	0.0222 (11)	0.0387 (12)	0.0313 (9)	-0.0010 (9)	-0.0049 (8)	0.0063 (8)
F4	0.0404 (13)	0.0362 (12)	0.0446 (11)	-0.0041 (10)	0.0081 (10)	0.0109 (9)
F2	0.0290 (12)	0.0668 (15)	0.0464 (11)	-0.0172 (11)	-0.0084 (10)	-0.0126 (10)
F3	0.0418 (14)	0.0461 (13)	0.0596 (13)	-0.0280 (12)	0.0088 (11)	-0.0072 (10)
C14	0.0128 (17)	0.0257 (17)	0.0271 (16)	0.0031 (15)	0.0054 (14)	-0.0046 (13)
C18	0.030 (2)	0.0277 (19)	0.0271 (17)	0.0013 (17)	0.0061 (16)	0.0021 (14)
C6	0.0123 (17)	0.0248 (18)	0.0273 (16)	0.0005 (15)	0.0013 (14)	-0.0005 (13)
C5	0.0143 (18)	0.034 (2)	0.0285 (16)	0.0029 (16)	-0.0038 (14)	-0.0015 (14)
C4	0.0173 (19)	0.039 (2)	0.0362 (18)	0.0073 (17)	-0.0046 (16)	-0.0018 (15)
C8	0.0188 (18)	0.0282 (18)	0.0268 (16)	-0.0001 (16)	0.0079 (15)	0.0034 (14)
C1	0.0140 (18)	0.033 (2)	0.0329 (18)	-0.0044 (16)	0.0020 (15)	0.0030 (14)
C19	0.0171 (18)	0.0295 (19)	0.0222 (16)	0.0020 (16)	0.0003 (14)	-0.0027 (14)
C10	0.027 (2)	0.037 (2)	0.0325 (18)	0.0074 (18)	0.0072 (16)	0.0058 (16)
C16	0.0186 (19)	0.044 (2)	0.0302 (18)	-0.0056 (18)	0.0010 (16)	-0.0122 (16)
C2	0.0187 (19)	0.0299 (19)	0.0373 (18)	-0.0037 (16)	0.0022 (15)	0.0005 (15)
N1	0.0128 (15)	0.0278 (15)	0.0220 (14)	-0.0014 (13)	-0.0002 (12)	0.0023 (12)
C7	0.0196 (19)	0.0291 (19)	0.0288 (17)	0.0010 (16)	0.0056 (15)	0.0031 (14)
C15	0.0213 (19)	0.0306 (19)	0.0207 (16)	0.0004 (16)	0.0025 (14)	-0.0021 (14)
C17	0.025 (2)	0.0299 (19)	0.042 (2)	-0.0084 (17)	0.0106 (17)	-0.0100 (16)
C12	0.025 (2)	0.043 (2)	0.0299 (18)	-0.0082 (19)	0.0031 (16)	-0.0075 (16)
C3	0.030 (2)	0.0292 (19)	0.0355 (18)	0.0026 (17)	0.0013 (17)	0.0020 (15)
C11	0.035 (2)	0.0279 (19)	0.0321 (19)	0.0015 (18)	0.0110 (17)	-0.0003 (15)
C9	0.0194 (19)	0.035 (2)	0.0289 (17)	-0.0028 (16)	0.0026 (15)	-0.0007 (14)
C13	0.0197 (19)	0.043 (2)	0.0284 (17)	0.0030 (17)	0.0048 (15)	0.0011 (15)

Geometric parameters (Å, °)

F1—C15	1.342 (3)	C1—C2	1.506 (4)
F5—C19	1.335 (3)	C1—N1	1.511 (4)
F4—C18	1.347 (3)	C1—H1A	0.9900
F2—C16	1.338 (4)	C1—H1B	0.9900
F3—C17	1.340 (4)	C10—C9	1.383 (5)
C14—C15	1.388 (4)	C10—C11	1.382 (5)
C14—C19	1.388 (4)	C10—H10	0.9500
C14—C6	1.523 (4)	C16—C17	1.374 (5)
C18—C17	1.364 (5)	C16—C15	1.378 (4)
C18—C19	1.380 (4)	C2—C3	1.523 (4)
C6—N1	1.515 (4)	C2—H2A	0.9900
C6—C7	1.538 (4)	C2—H2B	0.9900
C6—H6	1.0000	N1—H1	0.85 (3)
C5—N1	1.502 (4)	C7—H7A	0.9900
C5—C4	1.507 (4)	C7—H7B	0.9900
C5—H5A	0.9900	C12—C11	1.381 (5)

C5—H5B	0.9900	C12—C13	1.386 (5)
C4—C3	1.521 (4)	C12—H12	0.9500
C4—H4A	0.9900	C3—H3A	0.9900
C4—H4B	0.9900	C3—H3B	0.9900
C8—C9	1.385 (4)	C11—H11	0.9500
C8—C13	1.390 (4)	C9—H9	0.9500
C8—C7	1.512 (4)	C13—H13	0.9500
C15—C14—C19	115.9 (3)	C1—C2—C3	111.1 (3)
C15—C14—C6	124.2 (3)	C1—C2—H2A	109.4
C19—C14—C6	119.6 (3)	C3—C2—H2A	109.4
F4—C18—C17	120.1 (3)	C1—C2—H2B	109.4
F4—C18—C19	119.7 (3)	C3—C2—H2B	109.4
C17—C18—C19	120.2 (3)	H2A—C2—H2B	108.0
N1—C6—C14	112.0 (2)	C5—N1—C1	110.0 (2)
N1—C6—C7	113.0 (2)	C5—N1—C6	116.4 (2)
C14—C6—C7	113.3 (3)	C1—N1—C6	111.2 (2)
N1—C6—H6	105.9	C5—N1—H1	111 (2)
C14—C6—H6	105.9	C1—N1—H1	102 (2)
C7—C6—H6	105.9	C6—N1—H1	105 (2)
N1—C5—C4	110.0 (3)	C8—C7—C6	111.5 (2)
N1—C5—H5A	109.7	C8—C7—H7A	109.3
C4—C5—H5A	109.7	C6—C7—H7A	109.3
N1—C5—H5B	109.7	C8—C7—H7B	109.3
C4—C5—H5B	109.7	C6—C7—H7B	109.3
H5A—C5—H5B	108.2	H7A—C7—H7B	108.0
C5—C4—C3	112.2 (3)	F1—C15—C16	116.9 (3)
C5—C4—H4A	109.2	F1—C15—C14	120.6 (3)
C3—C4—H4A	109.2	C16—C15—C14	122.5 (3)
C5—C4—H4B	109.2	F3—C17—C18	120.7 (3)
C3—C4—H4B	109.2	F3—C17—C16	119.8 (3)
H4A—C4—H4B	107.9	C18—C17—C16	119.5 (3)
C9—C8—C13	118.6 (3)	C11—C12—C13	120.2 (3)
C9—C8—C7	120.7 (3)	C11—C12—H12	119.9
C13—C8—C7	120.6 (3)	C13—C12—H12	119.9
C2—C1—N1	110.8 (2)	C4—C3—C2	109.3 (3)
C2—C1—H1A	109.5	C4—C3—H3A	109.8
N1—C1—H1A	109.5	C2—C3—H3A	109.8
C2—C1—H1B	109.5	C4—C3—H3B	109.8
N1—C1—H1B	109.5	C2—C3—H3B	109.8
H1A—C1—H1B	108.1	H3A—C3—H3B	108.3
F5—C19—C18	117.7 (3)	C12—C11—C10	119.9 (3)
F5—C19—C14	120.2 (3)	C12—C11—H11	120.0
C18—C19—C14	122.1 (3)	C10—C11—H11	120.0
C9—C10—C11	119.6 (3)	C10—C9—C8	121.2 (3)
C9—C10—H10	120.2	C10—C9—H9	119.4
C11—C10—H10	120.2	C8—C9—H9	119.4
F2—C16—C17	120.4 (3)	C12—C13—C8	120.4 (3)

F2—C16—C15	119.8 (3)	C12—C13—H13	119.8
C17—C16—C15	119.7 (3)	C8—C13—H13	119.8

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots C11	0.85 (3)	2.20 (3)	3.051 (3)	178 (3)

[1-(2,6-Difluorophenyl)-2-phenylethyl]dimethylazanium chloride (I)*Crystal data*

$C_{16}H_{18}F_2N^+Cl^-$	$F(000) = 624$
$M_r = 297.76$	$D_x = 1.283 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.9474 (3) \text{ \AA}$	Cell parameters from 8632 reflections
$b = 12.7652 (5) \text{ \AA}$	$\theta = 3.0\text{--}26.6^\circ$
$c = 15.3998 (7) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$\beta = 99.368 (4)^\circ$	$T = 123 \text{ K}$
$V = 1541.48 (11) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.5 \times 0.4 \times 0.2 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur diffractometer	2715 independent reflections
Radiation source: fine-focus sealed tube	2305 reflections with $I > 2\sigma(I)$
scans in ϕ and ω	$R_{\text{int}} = 0.027$
Absorption correction: analytical (CrysAlisPro; Agilent 2014)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.1^\circ$
$T_{\text{min}} = 0.884$, $T_{\text{max}} = 0.950$	$h = -9 \rightarrow 9$
6424 measured reflections	$k = -14 \rightarrow 15$
	$l = -18 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.7459P]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2715 reflections	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
186 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
1 restraint	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C8	0.8942 (2)	0.41635 (15)	0.29692 (12)	0.0230 (4)
H8A	0.997147	0.441707	0.336303	0.028*
H8B	0.918077	0.345200	0.276392	0.028*

C3	0.4368 (2)	0.45234 (14)	0.28669 (13)	0.0235 (4)
C7	0.5501 (2)	0.30531 (14)	0.22760 (13)	0.0234 (4)
C2	0.5752 (2)	0.38564 (13)	0.28907 (12)	0.0188 (4)
C14	0.8167 (2)	0.45121 (15)	0.13360 (13)	0.0286 (5)
H14	0.825573	0.378177	0.123370	0.034*
C6	0.4032 (2)	0.29047 (16)	0.16854 (13)	0.0295 (5)
H6	0.392555	0.233545	0.128282	0.035*
C10	0.8393 (2)	0.59657 (15)	0.23204 (13)	0.0251 (4)
H10	0.863656	0.624451	0.289921	0.030*
C5	0.2715 (2)	0.36051 (17)	0.16928 (14)	0.0346 (5)
H5	0.168621	0.351866	0.128876	0.042*
C12	0.7556 (3)	0.62399 (16)	0.07667 (14)	0.0357 (5)
H12	0.722285	0.669788	0.028305	0.043*
C11	0.7913 (3)	0.66314 (15)	0.16121 (14)	0.0303 (5)
H11	0.782997	0.736312	0.170946	0.036*
C4	0.2871 (2)	0.44303 (17)	0.22793 (14)	0.0318 (5)
H4	0.197122	0.492047	0.227789	0.038*
C13	0.7688 (3)	0.51778 (16)	0.06310 (14)	0.0384 (5)
H13	0.744851	0.490217	0.005099	0.046*
F1	0.45166 (14)	0.53325 (8)	0.34416 (8)	0.0334 (3)
F2	0.68097 (14)	0.23779 (8)	0.22353 (8)	0.0329 (3)
C1	0.7428 (2)	0.41269 (14)	0.34703 (11)	0.0186 (4)
H1	0.729073	0.485786	0.368148	0.022*
C9	0.8521 (2)	0.48917 (14)	0.21896 (12)	0.0204 (4)
Cl1	1.14563 (7)	0.36912 (4)	0.51711 (4)	0.03725 (17)
N1	0.7819 (2)	0.34594 (12)	0.42918 (10)	0.0248 (4)
C15	0.6669 (3)	0.37192 (17)	0.49322 (14)	0.0363 (5)
H15A	0.703925	0.333884	0.548299	0.055*
H15B	0.549887	0.351557	0.468782	0.055*
H15C	0.671182	0.447444	0.504801	0.055*
C16	0.7872 (3)	0.23087 (15)	0.41449 (14)	0.0336 (5)
H16A	0.672229	0.205541	0.391314	0.050*
H16B	0.829292	0.195665	0.470357	0.050*
H16C	0.863511	0.215610	0.372127	0.050*
H1N1	0.893 (3)	0.3638 (16)	0.4538 (15)	0.039 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C8	0.0196 (9)	0.0288 (10)	0.0196 (10)	-0.0001 (8)	-0.0003 (8)	-0.0001 (8)
C3	0.0274 (10)	0.0239 (10)	0.0210 (10)	-0.0010 (8)	0.0090 (8)	0.0012 (8)
C7	0.0241 (10)	0.0230 (9)	0.0234 (10)	-0.0028 (8)	0.0048 (8)	-0.0003 (8)
C2	0.0198 (9)	0.0210 (9)	0.0156 (9)	-0.0032 (7)	0.0033 (7)	0.0019 (8)
C14	0.0388 (12)	0.0233 (10)	0.0241 (11)	-0.0015 (9)	0.0064 (9)	-0.0025 (9)
C6	0.0299 (11)	0.0352 (11)	0.0219 (11)	-0.0117 (9)	-0.0004 (9)	-0.0028 (9)
C10	0.0257 (10)	0.0296 (10)	0.0205 (11)	-0.0053 (8)	0.0049 (8)	-0.0032 (9)
C5	0.0228 (10)	0.0516 (14)	0.0274 (12)	-0.0124 (10)	-0.0020 (9)	0.0082 (11)
C12	0.0502 (13)	0.0307 (11)	0.0262 (12)	-0.0007 (10)	0.0061 (10)	0.0109 (10)

C11	0.0386 (12)	0.0222 (10)	0.0317 (12)	-0.0025 (9)	0.0105 (9)	-0.0004 (9)
C4	0.0192 (10)	0.0413 (12)	0.0353 (13)	0.0027 (9)	0.0052 (9)	0.0120 (10)
C13	0.0638 (15)	0.0343 (12)	0.0167 (11)	-0.0026 (11)	0.0051 (10)	0.0008 (9)
F1	0.0348 (6)	0.0300 (6)	0.0367 (7)	0.0077 (5)	0.0094 (5)	-0.0057 (5)
F2	0.0351 (6)	0.0283 (6)	0.0339 (7)	0.0039 (5)	0.0018 (5)	-0.0116 (5)
C1	0.0219 (9)	0.0192 (9)	0.0141 (9)	0.0008 (7)	0.0010 (7)	0.0006 (8)
C9	0.0145 (9)	0.0260 (10)	0.0210 (10)	-0.0017 (7)	0.0042 (7)	0.0026 (8)
C11	0.0431 (3)	0.0269 (3)	0.0332 (3)	0.0104 (2)	-0.0191 (2)	-0.0082 (2)
N1	0.0298 (9)	0.0277 (9)	0.0159 (8)	-0.0003 (7)	0.0008 (7)	0.0024 (7)
C15	0.0497 (13)	0.0419 (12)	0.0202 (11)	0.0030 (10)	0.0141 (10)	0.0049 (10)
C16	0.0461 (13)	0.0251 (10)	0.0282 (12)	0.0029 (9)	0.0019 (10)	0.0076 (9)

Geometric parameters (Å, °)

C8—C9	1.512 (3)	C5—C4	1.380 (3)
C8—C1	1.532 (3)	C5—H5	0.9500
C8—H8A	0.9900	C12—C13	1.378 (3)
C8—H8B	0.9900	C12—C11	1.380 (3)
C3—F1	1.353 (2)	C12—H12	0.9500
C3—C4	1.378 (3)	C11—H11	0.9500
C3—C2	1.386 (3)	C4—H4	0.9500
C7—F2	1.360 (2)	C13—H13	0.9500
C7—C6	1.371 (3)	C1—N1	1.515 (2)
C7—C2	1.388 (3)	C1—H1	1.0000
C2—C1	1.518 (2)	N1—C15	1.487 (3)
C14—C13	1.382 (3)	N1—C16	1.488 (2)
C14—C9	1.386 (3)	N1—H1N1	0.93 (2)
C14—H14	0.9500	C15—H15A	0.9800
C6—C5	1.378 (3)	C15—H15B	0.9800
C6—H6	0.9500	C15—H15C	0.9800
C10—C11	1.386 (3)	C16—H16A	0.9800
C10—C9	1.392 (3)	C16—H16B	0.9800
C10—H10	0.9500	C16—H16C	0.9800
C9—C8—C1	109.13 (14)	C3—C4—C5	118.14 (19)
C9—C8—H8A	109.9	C3—C4—H4	120.9
C1—C8—H8A	109.9	C5—C4—H4	120.9
C9—C8—H8B	109.9	C12—C13—C14	120.2 (2)
C1—C8—H8B	109.9	C12—C13—H13	119.9
H8A—C8—H8B	108.3	C14—C13—H13	119.9
F1—C3—C4	118.01 (17)	N1—C1—C2	113.84 (14)
F1—C3—C2	117.86 (16)	N1—C1—C8	111.51 (14)
C4—C3—C2	124.11 (18)	C2—C1—C8	113.39 (15)
F2—C7—C6	117.17 (17)	N1—C1—H1	105.8
F2—C7—C2	118.28 (16)	C2—C1—H1	105.8
C6—C7—C2	124.53 (18)	C8—C1—H1	105.8
C3—C2—C7	114.24 (16)	C14—C9—C10	118.25 (17)
C3—C2—C1	119.49 (16)	C14—C9—C8	121.50 (17)

C7—C2—C1	125.73 (16)	C10—C9—C8	120.17 (17)
C13—C14—C9	121.15 (18)	C15—N1—C16	110.90 (16)
C13—C14—H14	119.4	C15—N1—C1	111.34 (14)
C9—C14—H14	119.4	C16—N1—C1	115.81 (15)
C7—C6—C5	118.07 (19)	C15—N1—H1N1	108.8 (14)
C7—C6—H6	121.0	C16—N1—H1N1	104.7 (13)
C5—C6—H6	121.0	C1—N1—H1N1	104.7 (14)
C11—C10—C9	120.47 (18)	N1—C15—H15A	109.5
C11—C10—H10	119.8	N1—C15—H15B	109.5
C9—C10—H10	119.8	H15A—C15—H15B	109.5
C6—C5—C4	120.89 (18)	N1—C15—H15C	109.5
C6—C5—H5	119.6	H15A—C15—H15C	109.5
C4—C5—H5	119.6	H15B—C15—H15C	109.5
C13—C12—C11	119.35 (19)	N1—C16—H16A	109.5
C13—C12—H12	120.3	N1—C16—H16B	109.5
C11—C12—H12	120.3	H16A—C16—H16B	109.5
C12—C11—C10	120.54 (18)	N1—C16—H16C	109.5
C12—C11—H11	119.7	H16A—C16—H16C	109.5
C10—C11—H11	119.7	H16B—C16—H16C	109.5

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N1...Cl1	0.93 (2)	2.08 (2)	3.0006 (17)	167.3 (19)

1-[1-(2,6-Difluorophenyl)-2-phenylethyl]pyrrolidin-1-ium chloride (IV)*Crystal data*

C₁₈H₂₀F₂N⁺·Cl⁻
M_r = 323.80
 Triclinic, *P*1
a = 8.1365 (4) Å
b = 12.7421 (10) Å
c = 16.0451 (8) Å
 α = 88.059 (5)°
 β = 82.349 (4)°
 γ = 86.140 (5)°
V = 1644.42 (17) Å³

Z = 4
F(000) = 680
D_x = 1.308 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 9872 reflections
 θ = 3.0–25.4°
 μ = 0.25 mm⁻¹
T = 123 K
 Block, colourless
 0.5 × 0.4 × 0.3 mm

Data collection

Oxford Diffraction Xcalibur
 diffractometer
 Radiation source: fine-focus sealed tube
 scans in ϕ and ω
 Absorption correction: analytical
 (SADABS; Krause *et al.*, 2015)
T_{min} = 0.888, *T_{max}* = 0.928
 13277 measured reflections

5775 independent reflections
 4892 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{\max} = 25.0°, θ_{\min} = 3.0°
h = -9→8
k = -15→15
l = -19→19

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.090$ $wR(F^2) = 0.206$ $S = 1.19$

5775 reflections

403 parameters

2 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 10.4102P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$ *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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl2	1.11424 (18)	0.86611 (11)	0.52129 (8)	0.0292 (3)
Cl1	0.6097 (2)	0.63420 (11)	1.00579 (9)	0.0366 (4)
F1	0.3393 (4)	0.7014 (3)	0.6933 (2)	0.0340 (8)
F2	0.0752 (4)	0.4329 (3)	0.8568 (2)	0.0335 (8)
F3	0.9182 (4)	0.7720 (3)	0.2168 (2)	0.0339 (8)
F4	0.5878 (4)	1.0740 (3)	0.3087 (2)	0.0396 (9)
N2	0.8306 (6)	0.8731 (4)	0.4140 (3)	0.0242 (10)
N1	0.3190 (6)	0.6384 (4)	0.9063 (3)	0.0244 (10)
C27	0.7599 (6)	0.9234 (4)	0.2683 (3)	0.0201 (11)
C9	0.2164 (6)	0.5657 (4)	0.7790 (3)	0.0205 (11)
C28	0.6271 (7)	0.9934 (4)	0.2546 (3)	0.0251 (12)
C1	0.3471 (6)	0.5569 (4)	0.8386 (3)	0.0212 (11)
H1	0.335348	0.487106	0.868486	0.025*
C21	1.0944 (6)	1.0169 (4)	0.2351 (3)	0.0227 (11)
C19	0.8667 (6)	0.9430 (4)	0.3359 (3)	0.0218 (11)
H19	0.836336	1.016817	0.354039	0.026*
C3	0.5585 (6)	0.4696 (4)	0.7320 (3)	0.0244 (12)
C20	1.0529 (7)	0.9374 (4)	0.3056 (3)	0.0252 (12)
H20A	1.113949	0.951212	0.353117	0.030*
H20B	1.088997	0.865768	0.285632	0.030*
C14	0.0907 (7)	0.4965 (4)	0.7874 (3)	0.0252 (12)
C32	0.7907 (7)	0.8440 (4)	0.2094 (3)	0.0258 (12)
C11	0.1145 (8)	0.6272 (5)	0.6475 (4)	0.0325 (14)
H11	0.122464	0.673672	0.599757	0.039*
C22	1.1007 (7)	1.1225 (5)	0.2533 (4)	0.0309 (13)
H22	1.075832	1.144702	0.309803	0.037*
C2	0.5263 (7)	0.5557 (4)	0.7956 (3)	0.0242 (12)
H2A	0.546795	0.624627	0.767039	0.029*
H2B	0.603436	0.544026	0.838268	0.029*
C25	1.1662 (7)	1.0602 (5)	0.0882 (4)	0.0327 (14)

H25	1.187292	1.039035	0.031390	0.039*
C10	0.2208 (7)	0.6305 (4)	0.7066 (3)	0.0239 (12)
C8	0.5647 (7)	0.3644 (5)	0.7585 (4)	0.0321 (13)
H8	0.546327	0.346785	0.816886	0.038*
C36	0.6658 (7)	0.8977 (5)	0.4644 (4)	0.0348 (14)
H36A	0.575698	0.900454	0.428380	0.042*
H36B	0.663620	0.965988	0.492346	0.042*
C15	0.1649 (8)	0.6286 (5)	0.9678 (4)	0.0351 (14)
H15A	0.174375	0.564876	1.004224	0.042*
H15B	0.065945	0.625638	0.938275	0.042*
C33	0.8366 (8)	0.7563 (5)	0.4037 (4)	0.0346 (14)
H33A	0.952397	0.726924	0.389866	0.042*
H33B	0.771135	0.738088	0.359065	0.042*
C26	1.1262 (7)	0.9866 (4)	0.1518 (3)	0.0256 (12)
H26	1.120489	0.914988	0.138423	0.031*
C31	0.6991 (8)	0.8323 (5)	0.1447 (4)	0.0346 (14)
H31	0.722886	0.774732	0.107981	0.042*
C13	-0.0197 (7)	0.4882 (5)	0.7300 (4)	0.0338 (14)
H13	-0.103175	0.438879	0.738846	0.041*
C5	0.6205 (8)	0.4144 (6)	0.5880 (4)	0.0428 (16)
H5	0.638539	0.431937	0.529606	0.051*
C29	0.5330 (8)	0.9887 (5)	0.1896 (4)	0.0359 (15)
H29	0.445057	1.039810	0.182690	0.043*
C17	0.2484 (8)	0.8097 (5)	0.9603 (4)	0.0394 (15)
H17A	0.172625	0.871072	0.948940	0.047*
H17B	0.342017	0.834403	0.986302	0.047*
C30	0.5719 (8)	0.9062 (6)	0.1348 (4)	0.0392 (16)
H30	0.509337	0.900738	0.089399	0.047*
C7	0.5979 (7)	0.2849 (5)	0.7000 (4)	0.0380 (15)
H7	0.599135	0.213208	0.718453	0.046*
C24	1.1755 (8)	1.1644 (5)	0.1071 (4)	0.0386 (15)
H24	1.204076	1.214593	0.063287	0.046*
C23	1.1434 (8)	1.1956 (5)	0.1892 (4)	0.0361 (14)
H23	1.150355	1.267240	0.202027	0.043*
C18	0.3116 (8)	0.7526 (4)	0.8797 (4)	0.0329 (14)
H18A	0.234606	0.766623	0.837207	0.040*
H18B	0.423028	0.774539	0.855950	0.040*
C12	-0.0056 (8)	0.5533 (5)	0.6597 (4)	0.0390 (15)
H12	-0.078813	0.547876	0.618826	0.047*
C4	0.5858 (7)	0.4928 (5)	0.6459 (4)	0.0312 (13)
H4	0.580421	0.564153	0.626864	0.037*
C6	0.6290 (8)	0.3101 (6)	0.6148 (5)	0.0487 (19)
H6	0.656059	0.256025	0.575020	0.058*
C35	0.6475 (9)	0.8081 (6)	0.5286 (4)	0.0473 (18)
H35A	0.530490	0.788934	0.539572	0.057*
H35B	0.683247	0.827842	0.582205	0.057*
C16	0.1547 (9)	0.7276 (5)	1.0185 (4)	0.0420 (16)
H16A	0.207772	0.713990	1.070222	0.050*

H16B	0.037391	0.752837	1.034725	0.050*
C34	0.7597 (9)	0.7161 (6)	0.4895 (4)	0.0449 (17)
H34A	0.847256	0.694674	0.525112	0.054*
H34B	0.693919	0.654893	0.483513	0.054*
H1'	0.397 (7)	0.632 (5)	0.948 (3)	0.054*
H2	0.911 (6)	0.875 (5)	0.454 (3)	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0390 (8)	0.0279 (7)	0.0220 (7)	0.0035 (6)	-0.0099 (6)	-0.0062 (5)
Cl1	0.0553 (10)	0.0307 (8)	0.0290 (8)	-0.0163 (7)	-0.0203 (7)	0.0075 (6)
F1	0.041 (2)	0.0338 (19)	0.0285 (18)	-0.0134 (15)	-0.0076 (15)	0.0094 (14)
F2	0.0333 (19)	0.0309 (18)	0.0360 (19)	-0.0100 (14)	-0.0017 (15)	0.0077 (15)
F3	0.038 (2)	0.0304 (18)	0.0321 (19)	0.0034 (15)	-0.0013 (15)	-0.0111 (14)
F4	0.034 (2)	0.0281 (18)	0.057 (2)	0.0064 (15)	-0.0083 (17)	-0.0129 (16)
N2	0.028 (3)	0.027 (2)	0.016 (2)	-0.003 (2)	-0.0015 (19)	0.0012 (19)
N1	0.031 (3)	0.027 (2)	0.016 (2)	-0.003 (2)	-0.0052 (19)	-0.0038 (19)
C27	0.023 (3)	0.021 (3)	0.017 (3)	-0.004 (2)	-0.002 (2)	0.000 (2)
C9	0.022 (3)	0.021 (3)	0.018 (3)	0.005 (2)	-0.002 (2)	-0.005 (2)
C28	0.023 (3)	0.025 (3)	0.027 (3)	-0.006 (2)	-0.002 (2)	-0.001 (2)
C1	0.026 (3)	0.020 (3)	0.018 (3)	-0.001 (2)	-0.006 (2)	-0.002 (2)
C21	0.015 (3)	0.029 (3)	0.024 (3)	-0.001 (2)	-0.001 (2)	-0.001 (2)
C19	0.026 (3)	0.021 (3)	0.018 (3)	-0.005 (2)	-0.003 (2)	0.002 (2)
C3	0.020 (3)	0.031 (3)	0.023 (3)	-0.003 (2)	-0.001 (2)	-0.005 (2)
C20	0.026 (3)	0.029 (3)	0.022 (3)	-0.004 (2)	-0.006 (2)	-0.001 (2)
C14	0.023 (3)	0.023 (3)	0.030 (3)	0.000 (2)	-0.003 (2)	-0.002 (2)
C32	0.027 (3)	0.027 (3)	0.022 (3)	-0.006 (2)	0.002 (2)	-0.001 (2)
C11	0.043 (4)	0.033 (3)	0.024 (3)	0.005 (3)	-0.015 (3)	0.001 (2)
C22	0.031 (3)	0.034 (3)	0.028 (3)	-0.006 (3)	-0.002 (3)	-0.006 (3)
C2	0.023 (3)	0.028 (3)	0.022 (3)	-0.006 (2)	-0.005 (2)	-0.003 (2)
C25	0.032 (3)	0.044 (4)	0.021 (3)	-0.005 (3)	0.002 (2)	0.001 (3)
C10	0.024 (3)	0.023 (3)	0.025 (3)	-0.004 (2)	-0.002 (2)	-0.001 (2)
C8	0.020 (3)	0.039 (3)	0.037 (3)	0.002 (2)	-0.003 (2)	-0.002 (3)
C36	0.027 (3)	0.053 (4)	0.024 (3)	-0.008 (3)	0.004 (2)	-0.004 (3)
C15	0.038 (4)	0.035 (3)	0.029 (3)	0.001 (3)	0.008 (3)	-0.004 (3)
C33	0.045 (4)	0.032 (3)	0.028 (3)	-0.007 (3)	-0.007 (3)	0.005 (3)
C26	0.023 (3)	0.031 (3)	0.024 (3)	-0.005 (2)	-0.003 (2)	-0.001 (2)
C31	0.036 (3)	0.044 (4)	0.025 (3)	-0.020 (3)	0.003 (3)	-0.011 (3)
C13	0.025 (3)	0.029 (3)	0.049 (4)	-0.007 (2)	-0.010 (3)	0.000 (3)
C5	0.038 (4)	0.063 (5)	0.026 (3)	0.002 (3)	0.004 (3)	-0.015 (3)
C29	0.030 (3)	0.038 (4)	0.042 (4)	-0.008 (3)	-0.016 (3)	0.011 (3)
C17	0.044 (4)	0.032 (3)	0.043 (4)	0.005 (3)	-0.007 (3)	-0.016 (3)
C30	0.035 (4)	0.062 (4)	0.026 (3)	-0.022 (3)	-0.013 (3)	0.003 (3)
C7	0.027 (3)	0.035 (3)	0.050 (4)	0.000 (3)	0.002 (3)	-0.011 (3)
C24	0.037 (4)	0.047 (4)	0.031 (3)	-0.007 (3)	-0.002 (3)	0.015 (3)
C23	0.034 (3)	0.026 (3)	0.048 (4)	-0.003 (3)	-0.002 (3)	-0.001 (3)
C18	0.046 (4)	0.022 (3)	0.031 (3)	-0.001 (3)	-0.005 (3)	-0.005 (2)

C12	0.033 (3)	0.041 (4)	0.049 (4)	0.000 (3)	-0.024 (3)	-0.005 (3)
C4	0.029 (3)	0.038 (3)	0.026 (3)	-0.004 (3)	0.000 (2)	-0.003 (3)
C6	0.031 (4)	0.057 (5)	0.056 (5)	0.000 (3)	0.008 (3)	-0.034 (4)
C35	0.045 (4)	0.075 (5)	0.023 (3)	-0.020 (4)	0.001 (3)	0.003 (3)
C16	0.046 (4)	0.047 (4)	0.031 (3)	0.004 (3)	0.001 (3)	-0.012 (3)
C34	0.047 (4)	0.056 (4)	0.034 (4)	-0.015 (3)	-0.009 (3)	0.018 (3)

Geometric parameters (Å, °)

F1—C10	1.357 (6)	C3—C4	1.393 (8)
F2—C14	1.352 (6)	C3—C2	1.510 (7)
F3—C32	1.353 (6)	C14—C13	1.381 (8)
F4—C28	1.361 (6)	C32—C31	1.373 (8)
N2—C36	1.491 (7)	C11—C10	1.369 (8)
N2—C33	1.500 (7)	C11—C12	1.393 (9)
N2—C19	1.520 (6)	C22—C23	1.389 (8)
N1—C15	1.498 (7)	C25—C24	1.381 (9)
N1—C18	1.502 (7)	C25—C26	1.383 (8)
N1—C1	1.513 (6)	C8—C7	1.394 (8)
C27—C28	1.390 (7)	C36—C35	1.513 (9)
C27—C32	1.396 (7)	C15—C16	1.515 (8)
C27—C19	1.513 (7)	C33—C34	1.521 (8)
C9—C14	1.385 (7)	C31—C30	1.373 (9)
C9—C10	1.400 (7)	C13—C12	1.374 (9)
C9—C1	1.518 (7)	C5—C4	1.378 (9)
C28—C29	1.378 (8)	C5—C6	1.382 (10)
C1—C2	1.528 (7)	C29—C30	1.386 (9)
C21—C26	1.391 (7)	C17—C18	1.516 (8)
C21—C22	1.392 (8)	C17—C16	1.550 (9)
C21—C20	1.513 (7)	C7—C6	1.388 (10)
C19—C20	1.526 (7)	C24—C23	1.375 (9)
C3—C8	1.392 (8)	C35—C34	1.534 (10)
C36—N2—C33	103.9 (4)	F3—C32—C31	117.2 (5)
C36—N2—C19	114.4 (4)	F3—C32—C27	118.1 (5)
C33—N2—C19	118.5 (4)	C31—C32—C27	124.8 (5)
C15—N1—C18	103.7 (4)	C10—C11—C12	117.7 (5)
C15—N1—C1	115.1 (4)	C23—C22—C21	120.2 (5)
C18—N1—C1	118.3 (4)	C3—C2—C1	110.2 (4)
C28—C27—C32	113.3 (5)	C24—C25—C26	120.2 (6)
C28—C27—C19	120.6 (5)	F1—C10—C11	117.3 (5)
C32—C27—C19	125.7 (5)	F1—C10—C9	118.0 (5)
C14—C9—C10	113.8 (5)	C11—C10—C9	124.7 (5)
C14—C9—C1	120.1 (5)	C3—C8—C7	120.4 (6)
C10—C9—C1	125.5 (5)	N2—C36—C35	104.2 (5)
F4—C28—C29	117.1 (5)	N1—C15—C16	103.7 (5)
F4—C28—C27	117.7 (5)	N2—C33—C34	103.2 (5)
C29—C28—C27	125.2 (5)	C25—C26—C21	120.3 (5)

N1—C1—C9	113.3 (4)	C30—C31—C32	118.0 (6)
N1—C1—C2	110.0 (4)	C12—C13—C14	118.2 (5)
C9—C1—C2	114.7 (4)	C4—C5—C6	120.0 (6)
C26—C21—C22	119.0 (5)	C28—C29—C30	117.2 (6)
C26—C21—C20	121.1 (5)	C18—C17—C16	105.3 (5)
C22—C21—C20	119.9 (5)	C31—C30—C29	121.4 (5)
C27—C19—N2	113.2 (4)	C6—C7—C8	120.1 (6)
C27—C19—C20	114.3 (4)	C23—C24—C25	120.0 (6)
N2—C19—C20	110.0 (4)	C24—C23—C22	120.2 (6)
C8—C3—C4	118.4 (5)	N1—C18—C17	104.2 (5)
C8—C3—C2	120.3 (5)	C13—C12—C11	121.0 (5)
C4—C3—C2	121.3 (5)	C5—C4—C3	121.4 (6)
C21—C20—C19	111.0 (4)	C5—C6—C7	119.7 (6)
F2—C14—C13	117.9 (5)	C36—C35—C34	105.5 (5)
F2—C14—C9	117.6 (5)	C15—C16—C17	105.7 (5)
C13—C14—C9	124.6 (5)	C33—C34—C35	105.9 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1' \cdots C11	0.99 (1)	2.07 (2)	3.021 (5)	163 (6)
N2—H2' \cdots C12	0.98 (1)	2.08 (2)	3.052 (5)	169 (6)

[1-(2,6-Difluorophenyl)-2-phenylethyl](ethyl)azanium chloride dichloromethane hemisolvate (II)*Crystal data*2C₁₆H₁₈F₂N⁺·2Cl⁻·CH₂Cl₂*M_r* = 680.45Monoclinic, *I*2/*a**a* = 22.9963 (14) Å*b* = 7.8729 (5) Å*c* = 19.033 (1) Å β = 92.130 (5)°*V* = 3443.5 (4) Å³*Z* = 4*F*(000) = 1416*D_x* = 1.313 Mg m⁻³Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 8967 reflections

 θ = 3.0–26.4° μ = 0.39 mm⁻¹*T* = 123 K

Block, colourless

0.3 × 0.2 × 0.1 mm

*Data collection*Oxford Diffraction Xcalibur
diffractometer

Radiation source: fine-focus sealed tube

scans in ϕ and ω Absorption correction: analytical
(SADABS; Krause *et al.*, 2015)*T_{min}* = 0.911, *T_{max}* = 0.962

12738 measured reflections

3034 independent reflections

2813 reflections with *I* > 2 σ (*I*)*R_{int}* = 0.021 θ_{\max} = 25.0°, θ_{\min} = 3.3°*h* = -27→26*k* = -9→9*l* = -21→22*Refinement*Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.031*wR*(*F*²) = 0.077*S* = 1.07

3034 reflections

224 parameters

0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 2.8401P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.28641 (2)	0.60990 (5)	0.16223 (2)	0.02972 (12)	
Cl1S	0.31326 (2)	0.28821 (7)	0.00859 (3)	0.05486 (16)	
F1	0.05520 (5)	1.14129 (13)	0.11535 (6)	0.0466 (3)	
F2	0.17656 (5)	0.69870 (15)	0.04908 (5)	0.0570 (3)	
N1	0.19574 (5)	0.90437 (17)	0.17878 (7)	0.0248 (3)	
C1	0.13169 (6)	0.88167 (19)	0.16264 (7)	0.0251 (3)	
H1	0.110554	0.967062	0.191048	0.030*	
C9	0.11629 (6)	0.91562 (18)	0.08602 (7)	0.0242 (3)	
C3	0.05036 (7)	0.6689 (2)	0.17558 (8)	0.0308 (3)	
C13	0.12414 (8)	0.8489 (2)	-0.03848 (9)	0.0391 (4)	
H13	0.140233	0.779839	-0.073793	0.047*	
C12	0.08611 (7)	0.9784 (2)	-0.05562 (9)	0.0392 (4)	
H12	0.075593	0.999429	-0.103567	0.047*	
C11	0.06315 (7)	1.0777 (2)	-0.00420 (9)	0.0369 (4)	
H11	0.037235	1.168104	-0.016069	0.044*	
C14	0.13806 (7)	0.8227 (2)	0.03156 (8)	0.0326 (4)	
C10	0.07854 (6)	1.04341 (19)	0.06485 (8)	0.0288 (3)	
C4	0.00903 (8)	0.7455 (2)	0.21652 (9)	0.0399 (4)	
H4	0.021169	0.820557	0.253303	0.048*	
C15	0.2196 (4)	1.0751 (12)	0.1558 (4)	0.0316 (19)	0.707 (5)
H15A	0.195508	1.167814	0.174557	0.038*	0.707 (5)
H15B	0.217609	1.082569	0.103855	0.038*	0.707 (5)
C8	0.03174 (8)	0.5597 (2)	0.12252 (9)	0.0388 (4)	
H8	0.059436	0.506416	0.093985	0.047*	
C2	0.11439 (7)	0.7045 (2)	0.18834 (9)	0.0326 (4)	
H2A	0.137251	0.617767	0.163763	0.039*	
H2B	0.124134	0.695173	0.239296	0.039*	
C7	-0.02704 (9)	0.5276 (3)	0.11066 (10)	0.0501 (5)	
H7	-0.039328	0.451887	0.074176	0.060*	
C5	-0.04964 (8)	0.7136 (3)	0.20423 (11)	0.0490 (5)	
H5	-0.077544	0.767277	0.232379	0.059*	
C6	-0.06771 (8)	0.6042 (3)	0.15123 (11)	0.0524 (5)	
H6	-0.107970	0.581969	0.142816	0.063*	
C16	0.28347 (10)	1.0963 (3)	0.18310 (13)	0.0360 (7)	0.707 (5)

H16A	0.285642	1.081935	0.234280	0.054*	0.707 (5)
H16B	0.297386	1.209892	0.171032	0.054*	0.707 (5)
H16C	0.307818	1.010445	0.161259	0.054*	0.707 (5)
C1S	0.250000	0.4136 (3)	0.000000	0.0302 (5)	
H1S1	0.252617	0.487565	-0.041826	0.036*	0.5
H1S2	0.247383	0.487565	0.041827	0.036*	0.5
C16A	0.1932 (3)	1.2115 (7)	0.1843 (3)	0.0383 (18)	0.293 (5)
H16D	0.155523	1.220984	0.158750	0.057*	0.293 (5)
H16E	0.216492	1.313058	0.175641	0.057*	0.293 (5)
H16F	0.186879	1.201409	0.234797	0.057*	0.293 (5)
H1B	0.2162 (8)	0.819 (2)	0.1612 (9)	0.036 (5)*	
H1A	0.2010 (7)	0.893 (2)	0.2273 (10)	0.034 (5)*	
C15A	0.2248 (10)	1.057 (3)	0.1594 (10)	0.037 (6)	0.293 (5)
H15C	0.227354	1.060956	0.107617	0.044*	0.293 (5)
H15D	0.264950	1.056010	0.180153	0.044*	0.293 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0298 (2)	0.0380 (2)	0.02123 (18)	0.00784 (16)	0.00001 (14)	-0.00054 (15)
Cl1S	0.0491 (3)	0.0558 (3)	0.0581 (3)	0.0262 (2)	-0.0191 (2)	-0.0251 (2)
F1	0.0486 (6)	0.0405 (6)	0.0507 (6)	0.0214 (5)	0.0023 (5)	-0.0013 (5)
F2	0.0669 (7)	0.0629 (7)	0.0402 (6)	0.0416 (6)	-0.0113 (5)	-0.0158 (5)
N1	0.0261 (7)	0.0268 (7)	0.0211 (7)	0.0025 (6)	-0.0028 (5)	0.0011 (6)
C1	0.0246 (7)	0.0264 (8)	0.0239 (7)	0.0019 (6)	-0.0022 (6)	0.0004 (6)
C9	0.0217 (7)	0.0253 (8)	0.0254 (7)	-0.0011 (6)	-0.0027 (6)	0.0023 (6)
C3	0.0340 (8)	0.0268 (8)	0.0313 (8)	-0.0038 (7)	-0.0044 (7)	0.0103 (7)
C13	0.0366 (9)	0.0524 (11)	0.0280 (8)	-0.0036 (8)	-0.0014 (7)	-0.0061 (8)
C12	0.0325 (9)	0.0556 (11)	0.0287 (8)	-0.0121 (8)	-0.0080 (7)	0.0119 (8)
C11	0.0271 (8)	0.0381 (9)	0.0448 (10)	-0.0028 (7)	-0.0082 (7)	0.0179 (8)
C14	0.0301 (8)	0.0358 (9)	0.0314 (8)	0.0074 (7)	-0.0057 (6)	-0.0028 (7)
C10	0.0242 (7)	0.0266 (8)	0.0356 (8)	0.0002 (6)	0.0009 (6)	0.0031 (7)
C4	0.0433 (10)	0.0393 (10)	0.0372 (9)	-0.0060 (8)	0.0029 (8)	0.0050 (8)
C15	0.023 (2)	0.030 (3)	0.041 (3)	-0.011 (3)	-0.0100 (19)	0.014 (2)
C8	0.0451 (10)	0.0303 (9)	0.0405 (10)	-0.0053 (8)	-0.0048 (8)	0.0039 (7)
C2	0.0331 (9)	0.0294 (8)	0.0349 (9)	-0.0014 (7)	-0.0056 (7)	0.0078 (7)
C7	0.0563 (12)	0.0426 (11)	0.0499 (11)	-0.0201 (9)	-0.0178 (9)	0.0104 (9)
C5	0.0373 (10)	0.0504 (11)	0.0599 (12)	0.0000 (9)	0.0101 (9)	0.0196 (10)
C6	0.0349 (10)	0.0546 (12)	0.0665 (13)	-0.0143 (9)	-0.0130 (9)	0.0315 (11)
C16	0.0326 (14)	0.0355 (14)	0.0397 (14)	-0.0085 (10)	-0.0007 (10)	0.0018 (10)
C1S	0.0286 (11)	0.0273 (11)	0.0340 (12)	0.000	-0.0070 (9)	0.000
C16A	0.040 (3)	0.031 (3)	0.043 (3)	-0.010 (3)	-0.010 (3)	-0.002 (3)
C15A	0.053 (9)	0.042 (8)	0.015 (5)	0.024 (5)	-0.009 (4)	0.006 (5)

Geometric parameters (Å, °)

Cl1S—C1S	1.7606 (13)	C3—C2	1.510 (2)
F1—C10	1.3580 (18)	C13—C12	1.375 (3)

F2—C14	1.3516 (18)	C13—C14	1.375 (2)
N1—C15A	1.43 (2)	C12—C11	1.374 (3)
N1—C1	1.5040 (19)	C11—C10	1.375 (2)
N1—C15	1.522 (8)	C4—C5	1.384 (3)
C1—C9	1.512 (2)	C15—C16	1.550 (8)
C1—C2	1.535 (2)	C8—C7	1.385 (3)
C9—C14	1.378 (2)	C7—C6	1.374 (3)
C9—C10	1.379 (2)	C5—C6	1.379 (3)
C3—C8	1.382 (2)	C16A—C15A	1.51 (2)
C3—C4	1.389 (2)		
C15A—N1—C1	120.8 (11)	F2—C14—C9	116.80 (14)
C1—N1—C15	114.0 (4)	C13—C14—C9	124.89 (15)
N1—C1—C9	111.62 (12)	F1—C10—C11	118.07 (14)
N1—C1—C2	107.84 (12)	F1—C10—C9	117.92 (14)
C9—C1—C2	114.45 (13)	C11—C10—C9	124.01 (15)
C14—C9—C10	114.19 (14)	C5—C4—C3	120.64 (17)
C14—C9—C1	123.60 (13)	N1—C15—C16	110.2 (7)
C10—C9—C1	122.21 (13)	C3—C8—C7	120.44 (18)
C8—C3—C4	118.70 (16)	C3—C2—C1	112.35 (13)
C8—C3—C2	120.46 (15)	C6—C7—C8	120.56 (18)
C4—C3—C2	120.84 (15)	C6—C5—C4	120.15 (19)
C12—C13—C14	117.66 (16)	C7—C6—C5	119.51 (18)
C11—C12—C13	120.75 (15)	C11S—C1S—C11S ⁱ	111.79 (12)
C12—C11—C10	118.49 (15)	N1—C15A—C16A	111.2 (13)
F2—C14—C13	118.30 (14)		

Symmetry code: (i) $-x+1/2, y, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B \cdots C11	0.89 (2)	2.30 (2)	3.1417 (14)	156.0 (16)

tert-Butyl[1-(2,6-difluorophenyl)-2-phenylethyl]azanium chloride (III)

Crystal data

$C_{18}H_{22}F_2N^+Cl^-$
 $M_r = 325.81$
 Monoclinic, $P2_1/c$
 $a = 11.3115$ (6) \AA
 $b = 10.5400$ (5) \AA
 $c = 14.8039$ (7) \AA
 $\beta = 105.044$ (5) $^\circ$
 $V = 1704.48$ (15) \AA^3
 $Z = 4$

$F(000) = 688$
 $D_x = 1.270$ Mg m^{-3}
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 8922 reflections
 $\theta = 3.0\text{--}26.2^\circ$
 $\mu = 0.24$ mm^{-1}
 $T = 123$ K
 Block, colourless
 $0.4 \times 0.2 \times 0.1$ mm

Data collection

Oxford Diffraction Xcalibur
diffractometer
Radiation source: fine-focus sealed tube
scans in ϕ and ω
Absorption correction: analytical
(SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.944$, $T_{\max} = 0.976$
7223 measured reflections

3008 independent reflections
2343 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -13 \rightarrow 13$
 $k = -8 \rightarrow 12$
 $l = -17 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.095$
 $S = 1.06$
3008 reflections
210 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.5824P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.39037 (5)	1.13981 (5)	0.05585 (4)	0.02430 (17)
F1	0.09857 (12)	0.74034 (14)	0.10106 (9)	0.0339 (4)
F2	0.39994 (13)	0.60187 (13)	-0.04167 (9)	0.0323 (4)
N1	0.41820 (17)	0.84575 (19)	0.06664 (12)	0.0173 (4)
C1	0.5951 (2)	0.8889 (2)	0.19595 (15)	0.0253 (6)
H1C	0.648652	0.862937	0.156776	0.038*
H1D	0.636607	0.873592	0.261856	0.038*
H1E	0.576024	0.979356	0.186458	0.038*
C2	0.3904 (2)	0.8518 (2)	0.22761 (15)	0.0266 (6)
H2A	0.367671	0.941068	0.215264	0.040*
H2B	0.431267	0.840815	0.294127	0.040*
H2C	0.316581	0.799009	0.211062	0.040*
C3	0.5069 (2)	0.6716 (2)	0.18050 (15)	0.0264 (6)
H3A	0.430789	0.622529	0.168216	0.040*
H3B	0.555718	0.655092	0.244475	0.040*
H3C	0.553596	0.646429	0.136139	0.040*
C4	0.4769 (2)	0.8122 (2)	0.16915 (14)	0.0193 (5)
C5	0.2864 (2)	0.8140 (2)	0.02029 (14)	0.0186 (5)
H5	0.234618	0.867019	0.050999	0.022*
C6	0.2527 (2)	0.6777 (2)	0.03035 (14)	0.0185 (5)
C7	0.1596 (2)	0.6448 (2)	0.07147 (15)	0.0233 (5)
C8	0.1273 (2)	0.5219 (3)	0.08481 (17)	0.0325 (6)

H8	0.064723	0.504267	0.115178	0.039*
C9	0.1874 (2)	0.4250 (3)	0.05328 (17)	0.0352 (7)
H9	0.166274	0.339447	0.061977	0.042*
C10	0.2784 (2)	0.4506 (2)	0.00904 (17)	0.0313 (6)
H10	0.319903	0.384076	-0.013306	0.038*
C11	0.3068 (2)	0.5751 (2)	-0.00151 (15)	0.0234 (6)
C12	0.2600 (2)	0.8573 (2)	-0.08193 (14)	0.0213 (5)
H12A	0.290438	0.944996	-0.084222	0.026*
H12B	0.304422	0.801691	-0.115937	0.026*
C13	0.1247 (2)	0.8529 (2)	-0.12948 (14)	0.0207 (5)
C14	0.0489 (2)	0.9493 (3)	-0.11500 (17)	0.0332 (6)
H14	0.082380	1.018435	-0.075390	0.040*
C15	-0.0752 (3)	0.9463 (3)	-0.15751 (19)	0.0444 (8)
H15	-0.126360	1.013158	-0.147073	0.053*
C16	-0.1250 (2)	0.8465 (3)	-0.21498 (19)	0.0415 (7)
H16	-0.210343	0.844521	-0.244199	0.050*
C17	-0.0509 (2)	0.7503 (3)	-0.22978 (17)	0.0368 (7)
H17	-0.084782	0.681460	-0.269479	0.044*
C18	0.0738 (2)	0.7533 (2)	-0.18684 (15)	0.0274 (6)
H18	0.124631	0.685936	-0.197099	0.033*
H1A	0.423 (2)	0.933 (2)	0.0648 (15)	0.020 (6)*
H1B	0.471 (2)	0.818 (2)	0.0302 (16)	0.033 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0305 (3)	0.0186 (3)	0.0261 (3)	0.0042 (3)	0.0115 (2)	0.0024 (3)
F1	0.0296 (8)	0.0364 (9)	0.0419 (8)	0.0001 (7)	0.0202 (7)	0.0009 (7)
F2	0.0383 (9)	0.0276 (8)	0.0363 (8)	0.0065 (7)	0.0190 (7)	0.0004 (7)
N1	0.0222 (11)	0.0132 (11)	0.0172 (10)	0.0009 (10)	0.0063 (8)	0.0011 (9)
C1	0.0248 (14)	0.0286 (15)	0.0205 (12)	-0.0010 (12)	0.0021 (10)	0.0037 (11)
C2	0.0302 (14)	0.0320 (15)	0.0186 (12)	-0.0025 (13)	0.0081 (10)	-0.0008 (11)
C3	0.0329 (15)	0.0232 (14)	0.0205 (12)	0.0024 (12)	0.0021 (10)	0.0061 (11)
C4	0.0213 (13)	0.0210 (12)	0.0142 (11)	0.0003 (11)	0.0021 (9)	0.0035 (10)
C5	0.0198 (13)	0.0168 (12)	0.0196 (12)	0.0025 (11)	0.0056 (9)	0.0006 (10)
C6	0.0197 (13)	0.0191 (12)	0.0151 (11)	0.0001 (11)	0.0019 (9)	0.0020 (10)
C7	0.0207 (13)	0.0252 (14)	0.0225 (12)	0.0007 (12)	0.0029 (10)	0.0010 (11)
C8	0.0302 (15)	0.0340 (16)	0.0317 (14)	-0.0100 (13)	0.0051 (11)	0.0075 (13)
C9	0.0429 (17)	0.0215 (15)	0.0338 (15)	-0.0113 (14)	-0.0031 (12)	0.0069 (12)
C10	0.0389 (16)	0.0182 (13)	0.0315 (14)	0.0024 (13)	-0.0003 (12)	-0.0005 (12)
C11	0.0264 (14)	0.0242 (14)	0.0198 (12)	0.0009 (12)	0.0061 (10)	0.0019 (11)
C12	0.0228 (13)	0.0209 (13)	0.0197 (11)	0.0004 (11)	0.0047 (9)	0.0041 (11)
C13	0.0241 (13)	0.0213 (13)	0.0171 (11)	-0.0003 (12)	0.0059 (9)	0.0054 (11)
C14	0.0326 (16)	0.0272 (15)	0.0347 (14)	0.0043 (13)	-0.0005 (12)	-0.0044 (12)
C15	0.0326 (17)	0.0459 (19)	0.0513 (18)	0.0166 (15)	0.0047 (13)	-0.0013 (16)
C16	0.0226 (15)	0.052 (2)	0.0457 (16)	0.0001 (15)	0.0015 (12)	0.0001 (16)
C17	0.0356 (17)	0.0408 (17)	0.0305 (14)	-0.0099 (15)	0.0024 (12)	-0.0106 (13)
C18	0.0272 (15)	0.0280 (15)	0.0278 (13)	0.0015 (12)	0.0086 (11)	-0.0018 (12)

Geometric parameters (Å, °)

F1—C7	1.356 (3)	C6—C7	1.390 (3)
F2—C11	1.367 (2)	C7—C8	1.374 (3)
N1—C5	1.508 (3)	C8—C9	1.374 (4)
N1—C4	1.532 (3)	C8—H8	0.9500
N1—H1A	0.92 (2)	C9—C10	1.382 (4)
N1—H1B	0.95 (2)	C9—H9	0.9500
C1—C4	1.524 (3)	C10—C11	1.369 (3)
C1—H1C	0.9800	C10—H10	0.9500
C1—H1D	0.9800	C12—C13	1.510 (3)
C1—H1E	0.9800	C12—H12A	0.9900
C2—C4	1.523 (3)	C12—H12B	0.9900
C2—H2A	0.9800	C13—C18	1.379 (3)
C2—H2B	0.9800	C13—C14	1.382 (3)
C2—H2C	0.9800	C14—C15	1.381 (4)
C3—C4	1.520 (3)	C14—H14	0.9500
C3—H3A	0.9800	C15—C16	1.377 (4)
C3—H3B	0.9800	C15—H15	0.9500
C3—H3C	0.9800	C16—C17	1.369 (4)
C5—C6	1.504 (3)	C16—H16	0.9500
C5—C12	1.534 (3)	C17—C18	1.389 (3)
C5—H5	1.0000	C17—H17	0.9500
C6—C11	1.384 (3)	C18—H18	0.9500
C5—N1—C4	121.50 (16)	F1—C7—C8	118.5 (2)
C5—N1—H1A	105.3 (14)	F1—C7—C6	117.6 (2)
C4—N1—H1A	104.3 (14)	C8—C7—C6	123.9 (2)
C5—N1—H1B	111.4 (14)	C9—C8—C7	118.6 (2)
C4—N1—H1B	108.5 (15)	C9—C8—H8	120.7
H1A—N1—H1B	104.2 (19)	C7—C8—H8	120.7
C4—C1—H1C	109.5	C8—C9—C10	120.7 (2)
C4—C1—H1D	109.5	C8—C9—H9	119.6
H1C—C1—H1D	109.5	C10—C9—H9	119.6
C4—C1—H1E	109.5	C11—C10—C9	117.8 (2)
H1C—C1—H1E	109.5	C11—C10—H10	121.1
H1D—C1—H1E	109.5	C9—C10—H10	121.1
C4—C2—H2A	109.5	F2—C11—C10	118.5 (2)
C4—C2—H2B	109.5	F2—C11—C6	116.5 (2)
H2A—C2—H2B	109.5	C10—C11—C6	124.9 (2)
C4—C2—H2C	109.5	C13—C12—C5	111.39 (17)
H2A—C2—H2C	109.5	C13—C12—H12A	109.4
H2B—C2—H2C	109.5	C5—C12—H12A	109.4
C4—C3—H3A	109.5	C13—C12—H12B	109.4
C4—C3—H3B	109.5	C5—C12—H12B	109.4
H3A—C3—H3B	109.5	H12A—C12—H12B	108.0
C4—C3—H3C	109.5	C18—C13—C14	118.6 (2)
H3A—C3—H3C	109.5	C18—C13—C12	121.4 (2)

H3B—C3—H3C	109.5	C14—C13—C12	120.0 (2)
C3—C4—C2	111.26 (19)	C15—C14—C13	120.7 (3)
C3—C4—C1	109.42 (19)	C15—C14—H14	119.7
C2—C4—C1	110.85 (19)	C13—C14—H14	119.7
C3—C4—N1	111.22 (18)	C16—C15—C14	120.2 (3)
C2—C4—N1	108.81 (18)	C16—C15—H15	119.9
C1—C4—N1	105.11 (17)	C14—C15—H15	119.9
C6—C5—N1	114.40 (18)	C17—C16—C15	119.6 (3)
C6—C5—C12	113.12 (18)	C17—C16—H16	120.2
N1—C5—C12	107.39 (16)	C15—C16—H16	120.2
C6—C5—H5	107.2	C16—C17—C18	120.1 (3)
N1—C5—H5	107.2	C16—C17—H17	119.9
C12—C5—H5	107.2	C18—C17—H17	119.9
C11—C6—C7	114.0 (2)	C13—C18—C17	120.7 (2)
C11—C6—C5	124.53 (19)	C13—C18—H18	119.6
C7—C6—C5	121.5 (2)	C17—C18—H18	119.6

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots C11	0.92 (2)	2.21 (3)	3.115 (2)	167.7 (19)
N1—H1B \cdots C11 ⁱ	0.95 (2)	2.31 (2)	3.1684 (19)	151 (2)

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