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10-Methyl-9-(2-nitrophenoxycarbonyl)-acridinium trifluoromethanesulfonate

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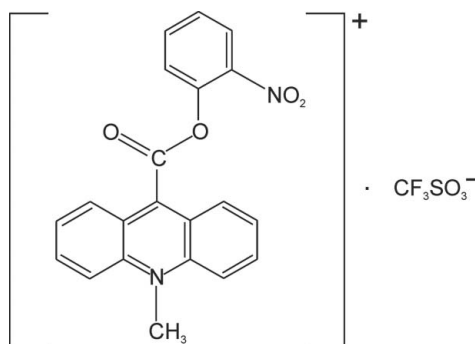
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.064; wR factor = 0.130; data-to-parameter ratio = 10.0.

The crystal structure of the title compound, $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_4^+\cdot\text{CF}_3\text{O}_3\text{S}^-$, is stabilized by $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds, by $\text{C}-\text{F}\cdots\pi$, $\text{N}-\text{O}\cdots\pi$ and $\text{S}-\text{O}\cdots\pi$ interactions, and by $\text{O}\cdots\text{O}$ [2.70 (4) Å] and $\text{O}\cdots\text{F}$ [2.85 (1) or 2.92 (1) Å] contacts; $\pi-\pi$ interactions are also present. In the packing of the molecules, acridine units are either parallel or inclined at an angle of 12.5 (1)°. The nitrophenoxycarbonyl unit is disordered over two position; the site occupancy factors are 0.89 and 0.11.

Related literature

For general background, see: Adamczyk *et al.* (2004); Becker *et al.* (1999); Rak *et al.* (1999); Razavi & McCapra (2000*a,b*); Roda *et al.* (2003); Zomer & Jacquemijns (2001). For related structures, see: Bianchi *et al.* (2004); Butcher *et al.* (2004); Dorn *et al.* (2005); Hunter & Sanders (1990); Kaafarani *et al.* (2003); Lyssenko & Antipin (2004); Sato (1996); Sikorski *et al.* (2007); Sridhar *et al.* (2006); Steiner (1999). For analysis of intermolecular interactions, see: Spek (2003).



Experimental

Crystal data

$\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_4^+\cdot\text{CF}_3\text{O}_3\text{S}^-$
 $M_r = 508.42$
 Monoclinic, $P2_1/c$
 $a = 12.459$ (4) Å
 $b = 21.361$ (6) Å
 $c = 8.123$ (3) Å
 $\beta = 108.42$ (3)°

$V = 2051.1$ (12) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 100$ (2) K
 $0.40 \times 0.10 \times 0.02$ mm

Data collection

Kuma KM-4 CCD κ -geometry diffractometer
 Absorption correction: none
 22835 measured reflections

3671 independent reflections
 2959 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.079$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.130$
 $S = 1.20$
 3671 reflections
 366 parameters

21 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2}\cdots\text{O30}^{\text{i}}$	0.95	2.39	3.111 (4)	132
$\text{C3}-\text{H3}\cdots\text{O25}^{\text{i}}$	0.95	2.59	3.268 (10)	129
$\text{C5}-\text{H5}\cdots\text{F34}^{\text{ii}}$	0.95	2.55	3.339 (4)	141
$\text{C6}-\text{H6}\cdots\text{O31}$	0.95	2.44	3.196 (4)	136
$\text{C20}-\text{H20}\cdots\text{O29}^{\text{j}}$	0.95	2.59	3.273 (9)	129
$\text{C27}-\text{H27A}\cdots\text{O29}^{\text{iii}}$	0.98	2.57	3.246 (4)	126
$\text{C27}-\text{H27C}\cdots\text{O30}^{\text{ii}}$	0.98	2.56	3.508 (4)	162

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

Table 2

$\text{C}-\text{F}\cdots\pi$, $\text{N}-\text{O}\cdots\pi$ and $\text{S}-\text{O}\cdots\pi$ interactions (Å, °).

X	I	J	$I\cdots J$	$X\cdots J$	$X-I\cdots J$
C32	F33	Cg4^{iv}	3.690 (4)	4.002 (5)	93.6 (2)
C32	F33	Cg4A^{iv}	3.949 (18)	4.31 (2)	96.6 (3)
C32	F34	Cg4^{iv}	3.356 (4)	4.002 (5)	109.3 (2)
C32	F34	Cg4A^{iv}	3.663 (18)	4.31 (2)	110.3 (3)
N24	O25	Cg4^{ii}	3.443 (9)	3.710 (5)	92.7 (5)
N24	O25	Cg4A^{ii}	3.13 (2)	3.45 (2)	94.8 (6)
N24A	O25A	Cg4^{ii}	3.41 (4)	4.19 (3)	126 (3)
N24A	O25A	Cg4A^{ii}	3.10 (4)	3.91 (3)	128 (3)
S28	O30	Cg1^{ii}	3.810 (3)	3.707 (2)	74.9 (1)
S28	O31	Cg1^{ii}	3.529 (3)	3.707 (2)	85.6 (1)
S28	O31	Cg3^{ii}	3.205 (3)	4.221 (2)	126.7 (1)

Symmetry codes: (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$. Notes: Cg represents the centroid of each ring, as follows: Cg1 ring C9/C11/C12/N10/C14/C13, Cg3 ring C5-C8/C13/C14, Cg4 ring C18-C23 and Cg4A ring C18A-C23A.

Table 3

 π - π interactions (\AA , $^\circ$).

CgI	CgJ	$Cg \cdots Cg$	Dihedral angle	Interplanar distance	Offset
1	2 ^v	3.547 (2)	3.4	3.504 (3)	0.556 (3)
2	2 ^v	3.981 (2)	0.0	3.504 (3)	1.891 (3)

Symmetry codes: (v) $-x + 1, -y + 1, -z + 1$. Notes: Cg represents the centroid of each ring, as follows: $Cg1$ ring C9/C11/C12/N10/C14/C13 and $Cg2$ ring C1-C4/C12/C11. $Cg \cdots Cg$ is the distance between ring centroids. The dihedral angle is that between the planes of the rings CgI and CgJ . The interplanar distance is the perpendicular distance of CgI from ring J . The offset is the perpendicular distance of ring I from ring J .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2382).

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supporting information

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10-Methyl-9-(2-nitrophenoxycarbonyl)acridinium trifluoromethanesulfonate

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S1. Comment

Phenyl 10-alkylacridinium-9-carboxylates are known to be chemiluminescent indicators or chemiluminogenic fragments of chemiluminescent labels, which have found numerous applications in assays of biologically and environmentally important entities (Becker *et al.*, 1999; Adamczyk *et al.*, 2004). The reaction of the above-mentioned cations with hydrogen peroxide in alkaline media produces light, and the determination of its intensity enables labeled entities or entities present in the medium to be assayed quantitatively, even at the attomole level (Roda *et al.*, 2003). Investigations have revealed that oxidation of these cations is accompanied by the removal of the phenoxycarbonyl fragment and conversion of the rest of the molecule to electronically excited, light-emitting 10-alkyl-9-acridinones (Rak *et al.*, 1999; Razavi & McCapra, 2000a,b; Zomer & Jacquemijns, 2001). It may thus be expected that the efficiency of chemiluminescence is affected by changes in the structure of the phenyl fragment. In order to find out whether this actually takes place, investigations were undertaken on phenyl 10-methylacridinium-9-carboxylates differently substituted in the phenyl fragment. Here, the crystal structure of the NO₂-phenyl-substituted derivative is presented. The compound was synthesized and investigated since the strongly electron attracting NO₂ group present in the phenyl fragment may be expected to substantially influence its stability and chemiluminogenic ability.

Parameters characterizing the geometry of the acridine ring are typical of acridine-based derivatives (Sikorski *et al.*, 2007).

Cations are disordered within the nitrophenoxycarbonyl fragment and occupy two positions, with occupancy factors of 0.886 (4) and 0.114 (4) for C15/O16/O17/C18/C19/H19/C20/H20/C21/H21/C22/H22/C23/N24/O25/O26 and C15A/O16A/O17A/C18A/C19A/H19A/C20A/H20A/C21A/H21A/C22A/H22A/C23A/N24A/O25A/O26A, respectively. The dihedral angles between the mean planes delineated by atoms C9/C15/O16/O17 and C9/C15A/O16A/O17A, C23/N24/O25/O26 and C23A/N24A/O25A/O26A, and C18—C23 and C18A—C23A are 47.4 (3)°, 42.2 (3)° and 12.8 (3)°, respectively. They reflect the mutual arrangement of the disordered structures. This is the first case of disorder to be reported in 9-(phenoxycarbonyl)-acridines or 9-(phenoxycarbonyl)-10-methylacridinium salts.

With respective average deviations from planarity of 0.027 and 0.009 Å or 0.033 Å, the acridine and benzene (C18—C23 or C18A—C23A) ring systems in the cation are oriented at 3.0 (1)° or 11.1 (4)° to each other (Fig. 1). The carboxyl group (C15/O16/O17 or C15A/O16A/O17A) is twisted at an angle of 65.8 (1)° or 113.0 (4)° relative to the acridine skeleton. The mean planes of the acridine moieties lie either parallel or are inclined at an angle of 12.5 (1)° in the lattice. The benzene rings are either parallel or inclined at an angle of 15.7 (1)° or 23.0 (4)°.

All the O and F atoms of the trifluoromethanesulfonate anions are involved in weak multidirectional C—H···O and C—H···F hydrogen bonds (Table 1 and Figs. 2 and 3), and C—F··· π (phenyl), S—O··· π (acridine) interactions (Table 2 and Figs. 2 and 3), as well as O···F contacts [O25···F35 = 2.85 (1) Å or O25A···F35A = 2.92 (4) Å (symmetry code: (vi) $x + 1$, $y, z + 1$); Figs. 2 and 4] with cations. The cations are involved in weak C—H···O (nitro) (Table 1 and Fig. 2), N—O (nitro)··· π (phenyl) (Table 2 and Figs. 2, 3 and 4) and π - π (acridine) (Table 3 and Fig. 4) interactions, as well as O

(carbonyl)⋯O (nitro) contacts [O17A⋯O25A = 2.70 (4) Å (symmetry code: (ii) $x, -y + 3/2, z - 1/2$); Fig. 2].

All the interactions demonstrated were found by *PLATON* (Spek, 2003). The C–H⋯O (Bianchi *et al.*, 2004; Steiner, 1999) and C–H⋯F (Bianchi *et al.*, 2004; Lyssenko & Antipin, 2004) interactions exhibit a hydrogen-bond-type nature. The C–F⋯ π (phenyl) and S–O⋯ π (acridine) interactions (Dorn *et al.*, 2005), and also N–O (nitro)⋯F interactions, the latter identified as O⋯F contacts (Lyssenko & Antipin, 2004), should be of an attractive nature. Such an attractive nature is also exhibited by π - π interactions (Hunter & Sanders, 1990), N–O (nitro)⋯ π (phenyl) (Kaafarani *et al.*, 2003) interactions and O (carbonyl)⋯O (nitro) (Butcher *et al.*, 2004) contacts have been disclosed in crystals of other compounds.

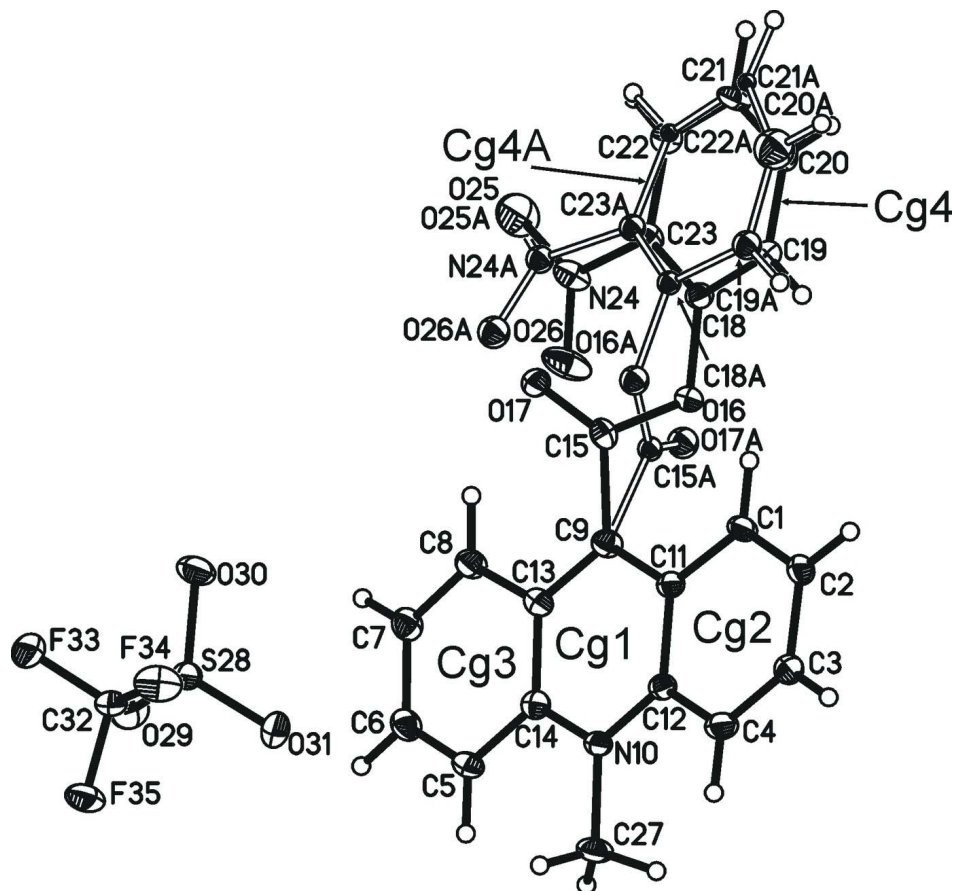
The crystal structure is stabilized by a network of the aforementioned short-range interactions, as well as by long-range electrostatic interactions between ions.

S2. Experimental

9-(2-Nitrophenoxy carbonyl)-10-methylacridinium trifluoromethanesulfonate was synthesized by treating 2-nitrophenyl acridine-9-carboxylate [obtained in the same way as described elsewhere (Sato, 1996; Sikorski *et al.*, 2007)], dissolved in anhydrous dichloromethane, with a fivefold molar excess of methyl trifluoromethanesulfonate, dissolved in the same solvent, under an Ar atmosphere at room temperature for 4 h. The crude salt was dissolved in small amount of ethanol, filtered and precipitated with 25 *v/v* excess of diethyl ether (yield 63%). Yellow crystals suitable for X-ray investigations were grown from absolute ethanol solution.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C–H distances of 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl group. The geometries of the disordered nitrophenoxy carbonyl fragment were refined anisotropically assuming C–C distances in the C18A–C23A benzene ring equal to 1.39 Å (Sridhar *et al.*, 2006).

**Figure 1**

The molecular structure of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Cg1, Cg2, Cg3, Cg4 and Cg4 A denote the ring centroids.

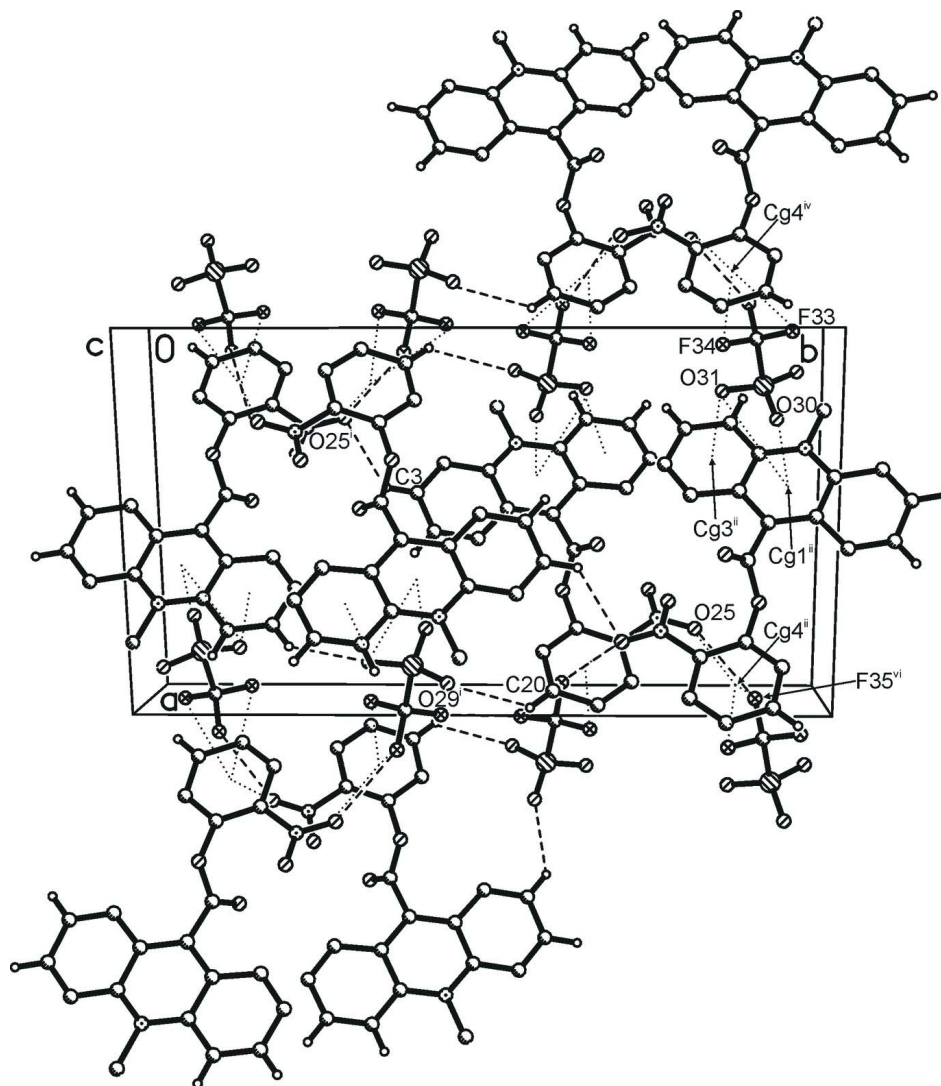


Figure 2

The arrangement of the ions in the unit cell, viewed along the *c* axis. The O \cdots F contacts, and C—H \cdots O interactions are represented by dashed lines, and C—F \cdots π , N—O \cdots π and S—O \cdots π interactions by dotted lines. Disordered C15A/O16A/O17A/C18A/C19A/H19A/C20A/H20A/C21A/H21A/C22A/H22A/C23A/ N24A/O25A/O26A atoms and H atoms not involved in interactions have been omitted. [Symmetry codes: (i) $-x + 1, y - 1/2, -z + 3/2$; (ii) $x, -y + 3/2, z - 1/2$; (iv) $x - 1, -y + 3/2, z - 1/2$; (vi) $x + 1, y, z + 1$.]

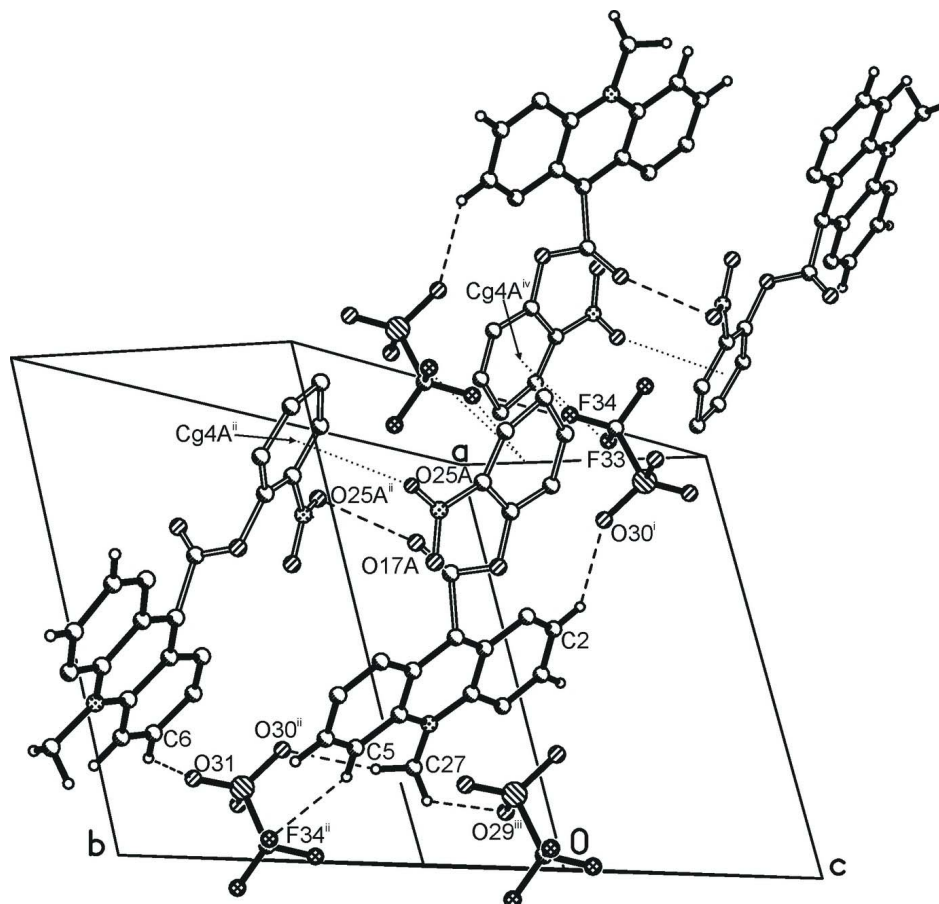


Figure 3

The arrangement of the ions in the unit cell. The O...O contacts, and C—H...O and C—H...F interactions are represented by dashed lines and C—F... π and N—O... π interactions by dotted lines. Disordered C15/O16/O17/C18/C19/H19/C20/H20/C21/H21/C22/H22/C23/N24/O25/O26 atoms and H atoms not involved in interactions have been omitted. [Symmetry codes: (i) $-x + 1, y - 1/2, -z + 3/2$; (ii) $x, -y + 3/2, z - 1/2$; (iii) $x, -y + 3/2, z + 1/2$; (iv) $x - 1, -y + 3/2, z - 1/2$.]

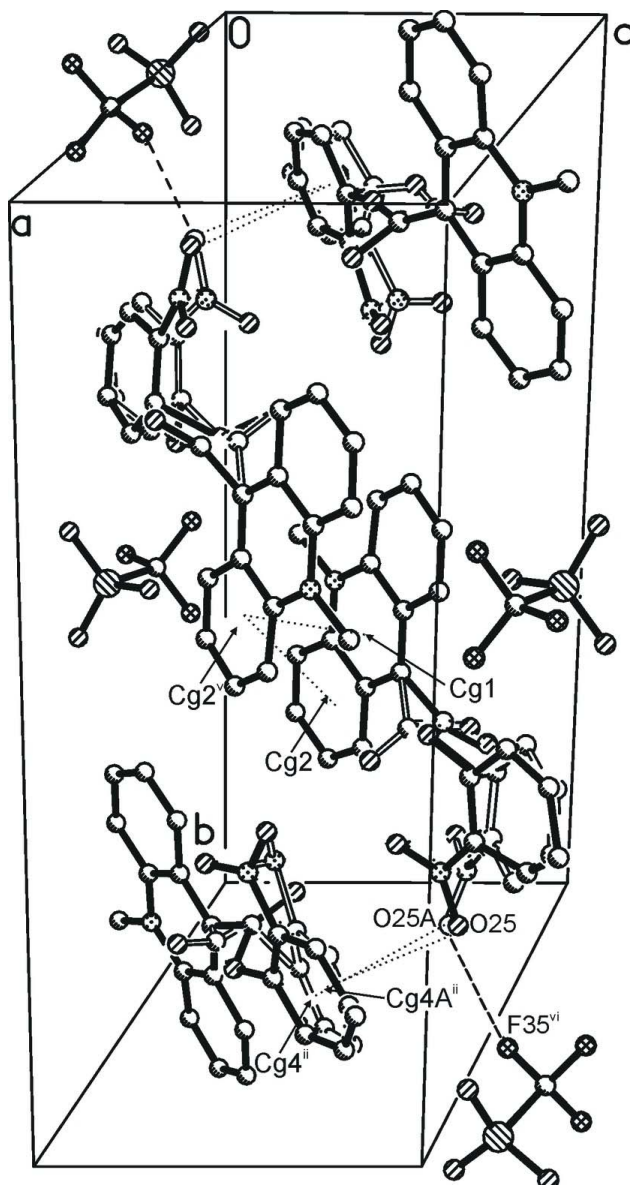


Figure 4

The arrangement of the ions in the unit cell, viewed approximately along the *a* axis. The O...F contacts are represented by dashed lines, and N-O... π and π - π interactions by dotted lines. H atoms have been omitted. [Symmetry codes: (ii) $x, -y + 3/2, z - 1/2$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $x + 1, y, z + 1$.]

10-Methyl-9-(2-nitrophenoxycarbonyl)acridinium trifluoromethanesulfonate

Crystal data

$C_{21}H_{15}N_2O_4^+ \cdot CF_3O_3S^-$

$M_r = 508.42$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 12.459 (4) \text{ \AA}$

$b = 21.361 (6) \text{ \AA}$

$c = 8.123 (3) \text{ \AA}$

$\beta = 108.42 (3)^\circ$

$V = 2051.1 (12) \text{ \AA}^3$

$Z = 4$

$F(000) = 1040$

$D_x = 1.646 \text{ Mg m}^{-3}$

Melting point: 500-502 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 22931 reflections
 $\theta = 4.6\text{--}32.0^\circ$
 $\mu = 0.24\text{ mm}^{-1}$

$T = 100\text{ K}$
 Plate, yellow
 $0.40 \times 0.10 \times 0.02\text{ mm}$

Data collection

Kuma KM4 CCD κ -geometry
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 22835 measured reflections
 3671 independent reflections

2959 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.079$
 $\theta_{\text{max}} = 25.3^\circ$, $\theta_{\text{min}} = 4.6^\circ$
 $h = -14 \rightarrow 14$
 $k = -25 \rightarrow 25$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.130$
 $S = 1.20$
 3671 reflections
 366 parameters
 21 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.37\text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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)
C1	0.5397 (2)	0.49641 (14)	0.8189 (4)	0.0232 (7)	
H1	0.6035	0.5134	0.9052	0.028*	
C2	0.5215 (2)	0.43405 (14)	0.8152 (4)	0.0244 (7)	
H2	0.5736	0.4074	0.8954	0.029*	
C3	0.4250 (2)	0.40863 (14)	0.6920 (4)	0.0256 (7)	
H3	0.4112	0.3649	0.6926	0.031*	
C4	0.3514 (3)	0.44534 (14)	0.5727 (4)	0.0270 (7)	
H4	0.2861	0.4272	0.4923	0.032*	
C5	0.2406 (3)	0.64981 (14)	0.3137 (4)	0.0259 (7)	
H5	0.1804	0.6312	0.2244	0.031*	
C6	0.2548 (3)	0.71290 (15)	0.3180 (4)	0.0270 (7)	
H6	0.2043	0.7379	0.2307	0.032*	
C7	0.3419 (3)	0.74185 (14)	0.4480 (4)	0.0276 (7)	
H7	0.3494	0.7861	0.4485	0.033*	
C8	0.4158 (3)	0.70724 (14)	0.5734 (4)	0.0259 (7)	
H8	0.4750	0.7274	0.6608	0.031*	
C9	0.4804 (2)	0.60253 (14)	0.6994 (4)	0.0228 (7)	

N10	0.30150 (19)	0.54800 (11)	0.4416 (3)	0.0202 (6)	
C11	0.4655 (2)	0.53731 (14)	0.6964 (3)	0.0198 (7)	
C12	0.3708 (2)	0.51042 (13)	0.5666 (3)	0.0197 (7)	
C13	0.4053 (2)	0.64062 (14)	0.5748 (3)	0.0217 (7)	
C14	0.3153 (2)	0.61197 (14)	0.4420 (4)	0.0214 (7)	
C15	0.5682 (3)	0.63250 (16)	0.8509 (5)	0.0203 (8)	0.886 (4)
O16	0.6746 (2)	0.61632 (10)	0.8552 (3)	0.0228 (6)	0.886 (4)
O17	0.54773 (18)	0.66490 (10)	0.9577 (3)	0.0233 (6)	0.886 (4)
C18	0.7648 (3)	0.63594 (16)	1.0013 (5)	0.0214 (8)	0.886 (4)
C19	0.8199 (4)	0.5892 (2)	1.1130 (6)	0.0238 (11)	0.886 (4)
H19	0.7951	0.5471	1.0913	0.029*	0.886 (4)
C20	0.9110 (6)	0.6034 (4)	1.2562 (16)	0.024 (3)	0.886 (4)
H20	0.9488	0.5717	1.3352	0.028*	0.886 (4)
C21	0.9461 (6)	0.6656 (4)	1.2820 (10)	0.0287 (19)	0.886 (4)
H21	1.0091	0.6757	1.3801	0.034*	0.886 (4)
C22	0.8935 (5)	0.7129 (3)	1.1712 (8)	0.0236 (16)	0.886 (4)
H22	0.9202	0.7548	1.1900	0.028*	0.886 (4)
C23	0.8005 (4)	0.69750 (19)	1.0318 (7)	0.0237 (13)	0.886 (4)
N24	0.7429 (3)	0.74990 (16)	0.9243 (5)	0.0288 (8)	0.886 (4)
O25	0.7664 (7)	0.8028 (5)	0.9836 (11)	0.054 (3)	0.886 (4)
O26	0.6766 (2)	0.73880 (12)	0.7809 (3)	0.0415 (8)	0.886 (4)
C15A	0.612 (2)	0.6275 (10)	0.776 (3)	0.016 (5)*	0.114 (4)
O16A	0.6247 (17)	0.6231 (8)	0.943 (3)	0.022 (5)*	0.114 (4)
O17A	0.6748 (15)	0.6451 (8)	0.706 (2)	0.026 (5)*	0.114 (4)
C18A	0.737 (2)	0.6387 (8)	1.058 (4)	0.015 (7)*	0.114 (4)
C19A	0.801 (2)	0.5901 (16)	1.155 (4)	0.022 (12)*	0.114 (4)
H19A	0.7753	0.5480	1.1409	0.027*	0.114 (4)
C20A	0.905 (4)	0.607 (3)	1.273 (13)	0.04 (4)*	0.114 (4)
H20A	0.9403	0.5732	1.3464	0.053*	0.114 (4)
C21A	0.968 (3)	0.662 (2)	1.307 (6)	0.000 (10)*	0.114 (4)
H21A	1.0423	0.6690	1.3819	0.000*	0.114 (4)
C22A	0.890 (3)	0.703 (2)	1.202 (5)	0.000 (10)*	0.114 (4)
H22A	0.9125	0.7456	1.2248	0.000*	0.114 (4)
C23A	0.786 (3)	0.6977 (13)	1.071 (5)	0.018 (13)*	0.114 (4)
N24A	0.718 (2)	0.7556 (14)	0.982 (4)	0.020 (8)*	0.114 (4)
O25A	0.762 (3)	0.802 (2)	0.974 (5)	0.000 (8)*	0.114 (4)
O26A	0.6136 (15)	0.7479 (8)	0.911 (2)	0.027 (5)*	0.114 (4)
C27	0.2090 (3)	0.51967 (15)	0.3011 (4)	0.0317 (8)	
H27A	0.1377	0.5242	0.3271	0.047*	
H27B	0.2249	0.4751	0.2912	0.047*	
H27C	0.2027	0.5408	0.1914	0.047*	
S28	0.15313 (6)	0.90846 (3)	0.25166 (9)	0.0233 (2)	
O29	0.11820 (19)	0.95900 (10)	0.1300 (3)	0.0358 (6)	
O30	0.23911 (17)	0.92471 (11)	0.4117 (3)	0.0357 (6)	
O31	0.16858 (18)	0.84963 (10)	0.1774 (3)	0.0330 (6)	
C32	0.0297 (3)	0.89497 (15)	0.3214 (4)	0.0277 (7)	
F33	0.00993 (15)	0.94384 (9)	0.4102 (2)	0.0424 (5)	
F34	0.04372 (16)	0.84469 (9)	0.4239 (2)	0.0420 (5)	

F35 -0.06374 (14) 0.88552 (9) 0.1871 (2) 0.0383 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0183 (16)	0.0225 (17)	0.0237 (16)	-0.0010 (12)	-0.0004 (13)	-0.0002 (14)
C2	0.0232 (17)	0.0199 (17)	0.0269 (17)	0.0035 (13)	0.0037 (14)	0.0013 (14)
C3	0.0242 (18)	0.0209 (17)	0.0296 (17)	-0.0006 (13)	0.0055 (15)	-0.0024 (14)
C4	0.0269 (18)	0.0261 (18)	0.0244 (17)	-0.0034 (14)	0.0028 (14)	-0.0041 (14)
C5	0.0242 (18)	0.0297 (19)	0.0185 (16)	0.0031 (14)	-0.0006 (13)	0.0014 (14)
C6	0.0268 (18)	0.0278 (18)	0.0245 (17)	0.0045 (14)	0.0054 (14)	0.0054 (15)
C7	0.0272 (18)	0.0215 (17)	0.0321 (18)	0.0013 (14)	0.0067 (15)	0.0041 (15)
C8	0.0236 (17)	0.0201 (17)	0.0292 (17)	-0.0014 (13)	0.0014 (14)	0.0014 (14)
C9	0.0226 (17)	0.0209 (17)	0.0229 (16)	-0.0027 (13)	0.0043 (13)	0.0015 (14)
N10	0.0196 (13)	0.0203 (13)	0.0180 (13)	0.0000 (10)	0.0018 (11)	-0.0008 (11)
C11	0.0180 (16)	0.0235 (17)	0.0188 (15)	-0.0017 (12)	0.0071 (13)	-0.0028 (13)
C12	0.0185 (16)	0.0221 (16)	0.0189 (15)	-0.0017 (12)	0.0065 (13)	-0.0024 (13)
C13	0.0191 (16)	0.0253 (17)	0.0204 (15)	0.0002 (13)	0.0057 (13)	0.0024 (14)
C14	0.0215 (17)	0.0241 (17)	0.0201 (16)	-0.0010 (13)	0.0087 (13)	0.0002 (14)
C15	0.022 (2)	0.0167 (19)	0.022 (2)	0.0029 (15)	0.0066 (19)	0.0084 (17)
O16	0.0190 (14)	0.0237 (13)	0.0220 (14)	0.0007 (10)	0.0013 (12)	-0.0028 (11)
O17	0.0247 (14)	0.0191 (13)	0.0240 (13)	0.0000 (10)	0.0048 (11)	-0.0015 (11)
C18	0.017 (2)	0.027 (2)	0.021 (2)	-0.0016 (15)	0.0064 (18)	-0.0052 (17)
C19	0.024 (2)	0.022 (2)	0.024 (2)	0.0007 (16)	0.006 (2)	-0.0038 (18)
C20	0.023 (4)	0.024 (4)	0.024 (3)	0.0065 (17)	0.007 (3)	0.002 (2)
C21	0.018 (3)	0.040 (4)	0.021 (3)	0.003 (3)	-0.005 (3)	-0.002 (2)
C22	0.025 (3)	0.021 (3)	0.026 (3)	-0.0035 (18)	0.009 (2)	0.002 (2)
C23	0.023 (2)	0.021 (3)	0.026 (3)	0.0007 (15)	0.006 (2)	0.0054 (18)
N24	0.0216 (19)	0.031 (2)	0.029 (2)	-0.0035 (15)	0.0013 (18)	0.0065 (17)
O25	0.052 (3)	0.022 (2)	0.074 (4)	-0.0030 (15)	0.001 (2)	0.0051 (18)
O26	0.0337 (16)	0.0399 (16)	0.0378 (17)	-0.0129 (12)	-0.0075 (14)	0.0188 (13)
C27	0.0317 (19)	0.0291 (18)	0.0226 (16)	0.0004 (15)	-0.0078 (14)	0.0004 (15)
S28	0.0229 (4)	0.0225 (4)	0.0223 (4)	-0.0002 (3)	0.0039 (3)	-0.0007 (3)
O29	0.0486 (15)	0.0244 (12)	0.0308 (12)	-0.0008 (10)	0.0075 (11)	0.0056 (10)
O30	0.0236 (12)	0.0456 (14)	0.0315 (12)	-0.0035 (10)	-0.0004 (10)	-0.0030 (11)
O31	0.0359 (14)	0.0275 (12)	0.0359 (13)	0.0074 (10)	0.0118 (11)	-0.0043 (11)
C32	0.0272 (19)	0.0307 (19)	0.0198 (16)	0.0020 (14)	-0.0003 (14)	-0.0047 (15)
F33	0.0330 (11)	0.0523 (13)	0.0413 (11)	0.0043 (9)	0.0112 (9)	-0.0191 (10)
F34	0.0447 (12)	0.0468 (13)	0.0325 (11)	-0.0133 (9)	0.0095 (9)	0.0070 (10)
F35	0.0232 (10)	0.0496 (12)	0.0348 (11)	-0.0054 (8)	-0.0012 (9)	-0.0076 (9)

Geometric parameters (Å, °)

C1—C2	1.350 (4)	C20—H20	0.9500
C1—C11	1.423 (4)	C21—C22	1.374 (7)
C1—H1	0.9500	C21—H21	0.9500
C2—C3	1.408 (4)	C22—C23	1.380 (5)
C2—H2	0.9500	C22—H22	0.9500

C3—C4	1.354 (4)	C23—N24	1.461 (6)
C3—H3	0.9500	N24—O26	1.219 (4)
C4—C12	1.415 (4)	N24—O25	1.227 (10)
C4—H4	0.9500	C15A—O17A	1.17 (3)
C5—C6	1.358 (4)	C15A—O16A	1.31 (3)
C5—C14	1.411 (4)	O16A—C18A	1.46 (3)
C5—H5	0.9500	C18A—C19A	1.390 (8)
C6—C7	1.396 (4)	C18A—C23A	1.390 (8)
C6—H6	0.9500	C19A—C20A	1.390 (8)
C7—C8	1.356 (4)	C19A—H19A	0.9500
C7—H7	0.9500	C20A—C21A	1.390 (8)
C8—C13	1.430 (4)	C20A—H20A	0.9500
C8—H8	0.9500	C21A—C22A	1.390 (8)
C9—C13	1.401 (4)	C21A—H21A	0.9500
C9—C11	1.405 (4)	C22A—C23A	1.390 (8)
C9—C15	1.506 (5)	C22A—H22A	0.9500
C9—C15A	1.65 (3)	C23A—N24A	1.54 (5)
N10—C12	1.366 (4)	N24A—O25A	1.13 (6)
N10—C14	1.377 (4)	N24A—O26A	1.26 (3)
N10—C27	1.472 (4)	C27—H27A	0.9800
C11—C12	1.431 (4)	C27—H27B	0.9800
C13—C14	1.426 (4)	C27—H27C	0.9800
C15—O17	1.199 (4)	S28—O31	1.433 (2)
C15—O16	1.361 (5)	S28—O29	1.435 (2)
O16—C18	1.415 (4)	S28—O30	1.441 (2)
C18—C19	1.378 (5)	S28—C32	1.821 (3)
C18—C23	1.385 (5)	C32—F35	1.335 (3)
C19—C20	1.378 (6)	C32—F33	1.336 (3)
C19—H19	0.9500	C32—F34	1.336 (4)
C20—C21	1.393 (6)		
C2—C1—C11	121.5 (3)	C21—C20—H20	120.9
C2—C1—H1	119.2	C22—C21—C20	122.7 (7)
C11—C1—H1	119.2	C22—C21—H21	118.7
C1—C2—C3	119.8 (3)	C20—C21—H21	118.7
C1—C2—H2	120.1	C21—C22—C23	117.8 (6)
C3—C2—H2	120.1	C21—C22—H22	121.1
C4—C3—C2	121.2 (3)	C23—C22—H22	121.1
C4—C3—H3	119.4	C22—C23—C18	120.8 (5)
C2—C3—H3	119.4	C22—C23—N24	115.8 (4)
C3—C4—C12	120.6 (3)	C18—C23—N24	123.4 (4)
C3—C4—H4	119.7	O26—N24—O25	124.0 (5)
C12—C4—H4	119.7	O26—N24—C23	118.6 (3)
C6—C5—C14	119.9 (3)	O25—N24—C23	117.3 (5)
C6—C5—H5	120.0	O17A—C15A—O16A	130 (3)
C14—C5—H5	120.0	O17A—C15A—C9	131 (2)
C5—C6—C7	121.5 (3)	O16A—C15A—C9	98.7 (19)
C5—C6—H6	119.2	C15A—O16A—C18A	115 (2)

C7—C6—H6	119.2	C19A—C18A—C23A	118 (3)
C8—C7—C6	120.5 (3)	C19A—C18A—O16A	117 (2)
C8—C7—H7	119.7	C23A—C18A—O16A	125 (2)
C6—C7—H7	119.7	C18A—C19A—C20A	116 (4)
C7—C8—C13	120.4 (3)	C18A—C19A—H19A	122.0
C7—C8—H8	119.8	C20A—C19A—H19A	122.0
C13—C8—H8	119.8	C19A—C20A—C21A	134 (6)
C13—C9—C11	120.6 (3)	C19A—C20A—H20A	112.9
C13—C9—C15	119.3 (3)	C21A—C20A—H20A	112.9
C11—C9—C15	119.6 (3)	C22A—C21A—C20A	100 (5)
C13—C9—C15A	116.3 (9)	C22A—C21A—H21A	130.0
C11—C9—C15A	116.0 (9)	C20A—C21A—H21A	130.0
C12—N10—C14	122.2 (2)	C23A—C22A—C21A	136 (4)
C12—N10—C27	119.4 (2)	C23A—C22A—H22A	112.2
C14—N10—C27	118.4 (2)	C21A—C22A—H22A	112.2
C9—C11—C1	122.9 (3)	C22A—C23A—C18A	114 (3)
C9—C11—C12	119.0 (3)	C22A—C23A—N24A	122 (3)
C1—C11—C12	118.1 (3)	C18A—C23A—N24A	122 (3)
N10—C12—C4	121.9 (3)	O25A—N24A—O26A	122 (3)
N10—C12—C11	119.5 (3)	O25A—N24A—C23A	121 (3)
C4—C12—C11	118.6 (3)	O26A—N24A—C23A	117 (2)
C9—C13—C14	118.9 (3)	N10—C27—H27A	109.5
C9—C13—C8	122.8 (3)	N10—C27—H27B	109.5
C14—C13—C8	118.2 (3)	H27A—C27—H27B	109.5
N10—C14—C5	120.9 (3)	N10—C27—H27C	109.5
N10—C14—C13	119.7 (3)	H27A—C27—H27C	109.5
C5—C14—C13	119.4 (3)	H27B—C27—H27C	109.5
O17—C15—O16	123.8 (3)	O31—S28—O29	114.95 (13)
O17—C15—C9	124.8 (3)	O31—S28—O30	115.49 (13)
O16—C15—C9	111.3 (3)	O29—S28—O30	114.64 (14)
C15—O16—C18	117.1 (3)	O31—S28—C32	103.36 (14)
C19—C18—C23	120.4 (4)	O29—S28—C32	103.35 (14)
C19—C18—O16	115.8 (3)	O30—S28—C32	102.57 (13)
C23—C18—O16	123.8 (3)	F35—C32—F33	107.3 (2)
C20—C19—C18	120.1 (5)	F35—C32—F34	107.2 (3)
C20—C19—H19	119.9	F33—C32—F34	107.5 (2)
C18—C19—H19	119.9	F35—C32—S28	112.0 (2)
C19—C20—C21	118.2 (6)	F33—C32—S28	111.3 (2)
C19—C20—H20	120.9	F34—C32—S28	111.4 (2)
C11—C1—C2—C3	-2.3 (4)	C15—O16—C18—C23	-71.5 (5)
C1—C2—C3—C4	2.2 (4)	C23—C18—C19—C20	0.1 (10)
C2—C3—C4—C12	1.2 (4)	O16—C18—C19—C20	178.1 (8)
C14—C5—C6—C7	-0.4 (4)	C18—C19—C20—C21	-1.1 (15)
C5—C6—C7—C8	0.6 (4)	C19—C20—C21—C22	0.3 (17)
C6—C7—C8—C13	-0.3 (4)	C20—C21—C22—C23	1.6 (13)
C13—C9—C11—C1	179.5 (3)	C21—C22—C23—C18	-2.6 (10)
C15—C9—C11—C1	-8.7 (4)	C21—C22—C23—N24	176.1 (6)

C15A—C9—C11—C1	30.1 (10)	C19—C18—C23—C22	1.9 (9)
C13—C9—C11—C12	-1.5 (4)	O16—C18—C23—C22	-175.9 (5)
C15—C9—C11—C12	170.4 (3)	C19—C18—C23—N24	-176.8 (5)
C15A—C9—C11—C12	-150.9 (10)	O16—C18—C23—N24	5.4 (8)
C2—C1—C11—C9	178.3 (3)	C22—C23—N24—O26	164.5 (5)
C2—C1—C11—C12	-0.7 (4)	C18—C23—N24—O26	-16.8 (8)
C14—N10—C12—C4	175.3 (3)	C22—C23—N24—O25	-14.1 (9)
C27—N10—C12—C4	-4.8 (4)	C18—C23—N24—O25	164.6 (6)
C14—N10—C12—C11	-4.1 (4)	C13—C9—C15A—O17A	-50 (3)
C27—N10—C12—C11	175.7 (2)	C11—C9—C15A—O17A	101 (3)
C3—C4—C12—N10	176.2 (3)	C15—C9—C15A—O17A	-154 (4)
C3—C4—C12—C11	-4.3 (4)	C13—C9—C15A—O16A	128.8 (13)
C9—C11—C12—N10	4.4 (4)	C11—C9—C15A—O16A	-80.5 (16)
C1—C11—C12—N10	-176.5 (2)	C15—C9—C15A—O16A	24.6 (10)
C9—C11—C12—C4	-175.1 (3)	O17A—C15A—O16A—C18A	-4 (4)
C1—C11—C12—C4	4.0 (4)	C9—C15A—O16A—C18A	176.8 (14)
C11—C9—C13—C14	-1.7 (4)	C15A—O16A—C18A—C19A	-112 (3)
C15—C9—C13—C14	-173.6 (3)	C15A—O16A—C18A—C23A	65 (4)
C15A—C9—C13—C14	147.6 (10)	C23A—C18A—C19A—C20A	7 (7)
C11—C9—C13—C8	179.1 (3)	O16A—C18A—C19A—C20A	-175 (6)
C15—C9—C13—C8	7.3 (4)	C18A—C19A—C20A—C21A	-8 (14)
C15A—C9—C13—C8	-31.5 (10)	C19A—C20A—C21A—C22A	8 (13)
C7—C8—C13—C9	178.9 (3)	C20A—C21A—C22A—C23A	-11 (9)
C7—C8—C13—C14	-0.3 (4)	C21A—C22A—C23A—C18A	13 (8)
C12—N10—C14—C5	-178.3 (2)	C21A—C22A—C23A—N24A	178 (5)
C27—N10—C14—C5	1.8 (4)	C19A—C18A—C23A—C22A	-9 (5)
C12—N10—C14—C13	0.9 (4)	O16A—C18A—C23A—C22A	174 (3)
C27—N10—C14—C13	-178.9 (2)	C19A—C18A—C23A—N24A	-174 (3)
C6—C5—C14—N10	179.1 (3)	O16A—C18A—C23A—N24A	9 (5)
C6—C5—C14—C13	-0.2 (4)	C22A—C23A—N24A—O25A	27 (6)
C9—C13—C14—N10	2.0 (4)	C18A—C23A—N24A—O25A	-169 (4)
C8—C13—C14—N10	-178.7 (2)	C22A—C23A—N24A—O26A	-157 (4)
C9—C13—C14—C5	-178.7 (3)	C18A—C23A—N24A—O26A	7 (5)
C8—C13—C14—C5	0.5 (4)	O31—S28—C32—F35	-66.2 (2)
C13—C9—C15—O17	61.8 (4)	O29—S28—C32—F35	53.9 (2)
C11—C9—C15—O17	-110.2 (4)	O30—S28—C32—F35	173.4 (2)
C15A—C9—C15—O17	156.3 (16)	O31—S28—C32—F33	173.78 (19)
C13—C9—C15—O16	-120.4 (3)	O29—S28—C32—F33	-66.1 (2)
C11—C9—C15—O16	67.6 (4)	O30—S28—C32—F33	53.4 (2)
C15A—C9—C15—O16	-25.9 (15)	O31—S28—C32—F34	53.8 (2)
O17—C15—O16—C18	4.3 (5)	O29—S28—C32—F34	173.94 (19)
C9—C15—O16—C18	-173.5 (3)	O30—S28—C32—F34	-66.6 (2)
C15—O16—C18—C19	110.6 (4)		

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>
C2—H2...O30 ⁱ	0.95	2.39	3.111 (4)	132

C3—H3···O25 ⁱ	0.95	2.59	3.268 (10)	129
C5—H5···F34 ⁱⁱ	0.95	2.55	3.339 (4)	141
C6—H6···O31	0.95	2.44	3.196 (4)	136
C20—H20···O29 ⁱ	0.95	2.59	3.273 (9)	129
C27—H27A···O29 ⁱⁱⁱ	0.98	2.57	3.246 (4)	126
C27—H27C···O30 ⁱⁱ	0.98	2.56	3.508 (4)	162

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