# organic compounds

# 10-Methyl-9-phenoxycarbonylacridinium trifluoromethanesulfonate monohydrate

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In the crystal structure of the title compound, $C_{21}H_{16}NO_2{}^+ \cdot CF_3SO_3{}^- \cdot H_2O$, the anions and the water molecules are linked by O—H···O interactions, while the cations form inversion dimers through $\pi$–$\pi$ interactions between acridine ring systems. These dimers are linked by C—H···O and C—F···$\pi$ interactions to adjacent anions, and by C—H···$\pi$ interactions to neighboring cations. The water molecule links two H atoms of the cation by C—H···O interactions and two adjacent anions by O—H···O interactions. The acridine and benzene ring systems are oriented at 15.6 (1)°. The carboxyl group is twisted at an angle of 77.0 (1)° relative to the acridine skeleton. The mean planes of the adjacent acridine units are either parallel or inclined at an angle of 18.4 (1)°.

## Related literature

For background to the chemiluminogenic properties of 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulf-onates, see: Brown *et al.* (2009); Rak *et al.* (1999); Roda *et al.* (2003); Zomer & Jacquemijns (2001). For related structures, see: Sikorski *et al.* (2007); Trzybiński *et al.* (2009). For inter-molecular interactions, see: Bianchi *et al.* (2004); Dorn *et al.* (2005); Hunter *et al.* (2001); Novoa *et al.* (2006); Takahashi *et al.* (2001). For the synthesis, see: Sato (1996); Trzybiński *et al.* (2009).
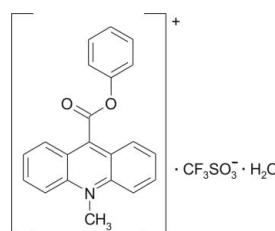


## Experimental

### Crystal data

| | |
|---|---|
| $C_{21}H_{16}NO_2{}^+ \cdot CF_3SO_3{}^- \cdot H_2O$ | $V$ = 2127.14 (11) Å$^3$ |
| $M_r$ = 481.44 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a$ = 11.3807 (4) Å | $\mu$ = 0.22 mm$^{-1}$ |
| $b$ = 9.5785 (2) Å | $T$ = 295 K |
| $c$ = 19.7134 (6) Å | $0.78 \times 0.16 \times 0.10$ mm |
| $\beta$ = 98.172 (3)° | |

### Data collection

| | |
|---|---|
| Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer | 46462 measured reflections |
| Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008). | 3792 independent reflections |
| | 2422 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.741, $T_{max}$ = 1.000 | $R_{int}$ = 0.060 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.064 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.211 | |
| $S$ = 1.03 | |
| 3792 reflections | $\Delta\rho_{max}$ = 0.59 e Å$^{-3}$ |
| 305 parameters | $\Delta\rho_{min}$ = −0.39 e Å$^{-3}$ |
| 3 restraints | |

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

$Cg4$ is the centroid of the C18–C23 ring.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2···O28[i] | 0.93 | 2.59 | 3.424 (4) | 149 |
| C8—H8···O25 | 0.93 | 2.52 | 3.360 (6) | 150 |
| C19—H19···O25 | 0.93 | 2.57 | 3.232 (5) | 129 |
| C24—H24$A$···$Cg4$[ii] | 0.96 | 2.69 | 3.484 (4) | 140 |
| C24—H24$C$···O29[ii] | 0.96 | 2.60 | 3.544 (5) | 168 |
| O25—H25$A$···O27 | 0.85 (4) | 1.98 (3) | 2.816 (5) | 170 (8) |
| O25—H25$B$···O28[iii] | 0.86 (4) | 2.14 (6) | 2.948 (6) | 156 (7) |

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

**Table 2**
C—F···$\pi$ interactions (Å, °).

$Cg1$ and $Cg2$ are the centroids of the C9/N10/C11–C14 and C1–C4/C11/C12 rings, respectively.

| $X$—$I$···$J$ | $I$···$J$ | $X$···$J$ | $X$—$I$···$J$ |
|---|---|---|---|
| C30—F31···$Cg2$[iv] | 3.269 (3) | 4.075 (4) | 117.8 (2) |
| C30—F32···$Cg1$[iv] | 3.744 (3) | 4.463 (4) | 116.1 (3) |

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

**Table 3**
$\pi$–$\pi$ interactions (Å, °).

$Cg1$ and $Cg2$ are the centroids of the C9/N10/C11–C14 and C1–C4/C11/C12 rings, respectively. $CgI$···$CgJ$ is the distance between ring centroids. The dihedral angle is that between the planes of the rings $I$ and $J$. $CgI$_Perp is the perpendicular distance of $CgI$ from ring $J$. $CgI$_Offset is the distance between $CgI$ and the perpendicular projection of $CgJ$ on ring $I$.

| $I$ | $J$ | $CgI$···$CgJ$ | Dihedral angle | $CgI$_Perp | $CgI$_Offset |
|---|---|---|---|---|---|
| 1 | 2[v] | 3.682 (2) | 1.92 (1) | 3.568 (1) | 0.909 (1) |
| 2 | 1[v] | 3.682 (2) | 1.92 (1) | 3.591 (1) | 0.814 (1) |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2742).

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# supporting information

# 10-Methyl-9-phenoxycarbonylacridinium trifluoromethanesulfonate monohydrate

**Damian Trzybiński, Karol Krzymiński, Artur Sikorski and Jerzy Błażejowski**

### S1. Comment

The crystal structures of six 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulfonates can be found in the Cambridge Structural Database. All of them were determined in our laboratory and concern derivatives substituted in the phenyl fragment. For a long time we were unable to obtain crystals of the parent compound, i.e. unsubstituted 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulfonate, suitable for X-Ray investigations. Eventually we succeeded, and we present here the crystal structure of the monohydrate of this compound. The reason for our interest in this group of compounds is their chemiluminogenic properties, which means they can be used as chemiluminescent indicators or the chemiluminogenic fragments of chemiluminescent labels (Zomer & Jacquemijns, 2001). These compounds are rouitenely applied in assays of biologically and environmentally important entities such as antigens, antibodies, enzymes or DNA fragments (Roda *et al.*, 2003; Brown *et al.*, 2009). The cations of the above mentioned salts undergo oxidation with hydrogen peroxide in alkaline media; at the same time the phenoxycarbonyl fragment is removed and the remainder of the molecule is converted to electronically excited, light-emitting 10-methyl-9-acridinone (Rak *et al.*, 1999). This forms the basis for analytical applications (Zomer & Jacquemijns, 2001).

In the cation of the title compound (Fig. 1), the bond lengths and angles characterizing the geometry of the acridinium moiety are typical of acridine-based derivatives (Sikorski *et al.*, 2007; Trzybiński *et al.*, 2009). With respective average deviations from planarity of 0.0292 (3) Å and 0.0016 (3) Å, the acridine and benzene ring systems are oriented at 15.6 (1)°. The carboxyl group is twisted at an angle of 77.0 (1)° relative to the acridine skeleton. The mean planes of the adjacent acridine moieties are parallel (at an angle of 0.0 (1)°) or inclined at an angle of 18.4 (1)° in the lattice.

In the crystal structure, the anions form hydrates with water molecules through O–H⋯O interactions, while the inversely oriented cations form dimers through π–π interactions involving acridine moieties (Tables 1 and 3, Figs. 1 and 2). These dimers are linked by C–H⋯O (Table 1, Fig. 2) and C–F⋯π (Table 2, Fig. 2) interactions to adjacent anions, and by C–H⋯π (Table 1, Fig. 2) interactions to neighboring cations. The water molecule links two sites of the cation by C–H⋯O interactions and two adjacent anions by O–H⋯O interactions (Table 1, Figs. 1 and 2). The O–H⋯O and C–H⋯O interactions are of the hydrogen bond type (Bianchi *et al.*, 2004; Novoa *et al.*, 2006). The C–H⋯π interactions should be of an attractive nature (Takahashi *et al.*, 2001), like the C–F⋯π (Dorn *et al.*, 2005) and the π–π (Hunter *et al.*, 2001) interactions. The crystal structure is stabilized by a network of these short-range specific interactions and by long-range electrostatic interactions between ions.

### S2. Experimental

The compound was synthesized following a procedure described elsewhere (Trzybiński *et al.*, 2009). 9-(Chlorocarbonyl)-acridine was prepared by treating acridine-9-carboxylic acid with a tenfold molar excess of thionyl chloride. The compound obtained was esterified with phenol in anhydrous dichloromethane in the presence of *N,N*-diethylethanamine

and a catalytic amount of *N,N*-dimethyl-4-pyridinamine (room temperature, 15h). The product – phenyl acridine-9-carboxylate – was purified chromatographically (SiO$_2$, cyclohexane/ethyl acetate, 3/2 v/v) and quaternarized with a five-fold molar excess of methyl trifluoromethanesulfonate dissolved in anhydrous dichloromethane (under an Ar atmosphere at room temperature for 3h) (Sato, 1996). The crude 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulfonate was dissolved in a small amount of ethanol, filtered and precipitated with a 25 v/v excess of diethyl ether. Yellow crystals suitable for X-ray investigations were grown from ethanol/H$_2$O, 4/1 v/v, solution (m.p. 263-265K).

### S3. Refinement

The H-atoms of the water molecule were located on a Fourier-difference map, restrained by DFIX command 0.85 for O–H distances and by DFIX 1.39 for H···H distance and refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$. All other H atoms were positioned geometrically, with C—H = 0.93 Å and 0.96 Å for the aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for the aromatic H atoms and $x = 1.5$ for the methyl H atoms.
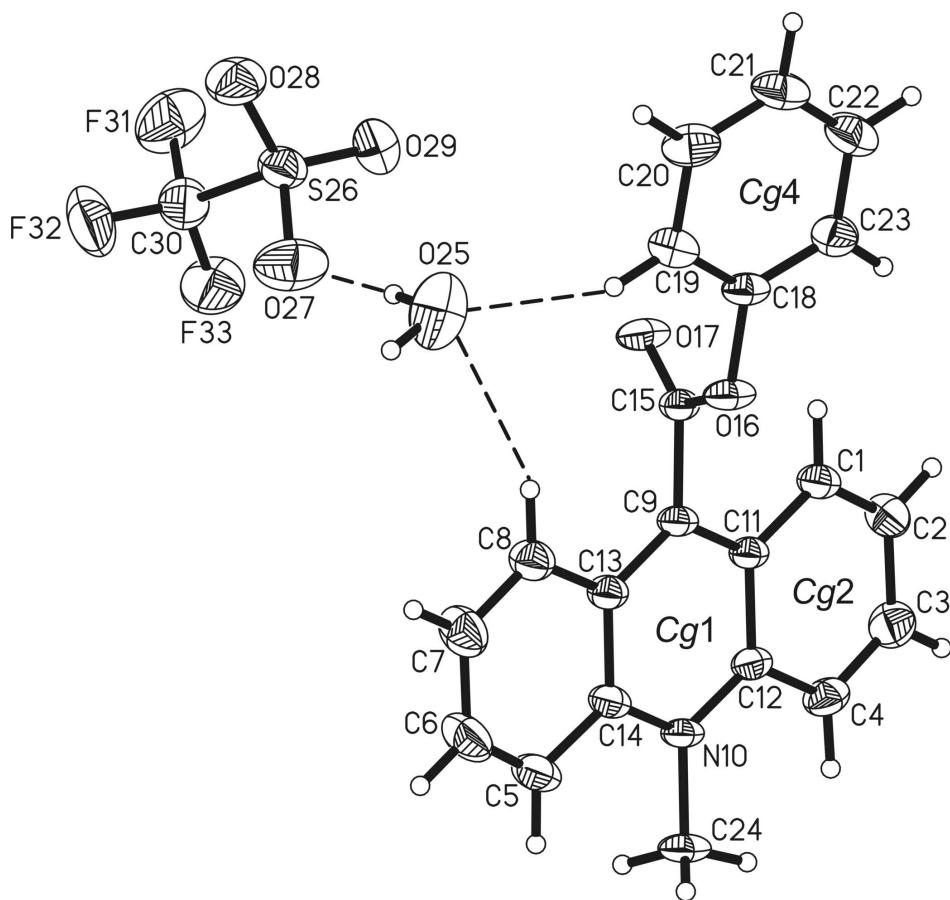


**Figure 1**

The molecular structure of the title compound showing the atom labeling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radius. *Cg*1, *Cg*2 and *Cg*4 denote the ring centroids. The O–H···O and C–H···O hydrogen bonds are represented by dashed lines.
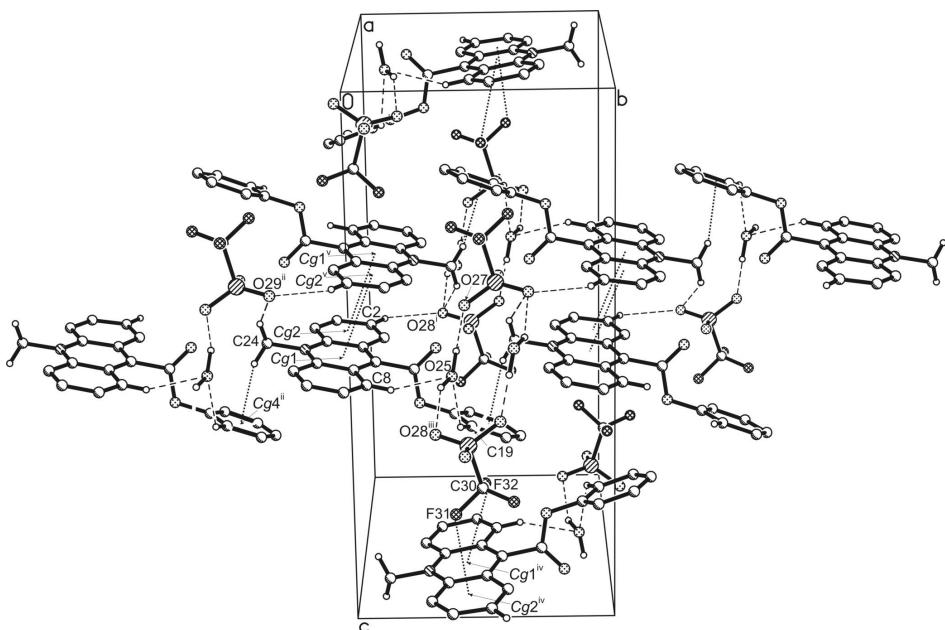
**Figure 2**

The arrangement of the ions in the crystal structure. The O–H···O and C–H···O interactions are represented by dashed lines, the C–H···$\pi$, C–F···$\pi$ and $\pi$–$\pi$ contacts by dotted lines. H atoms not involved in interactions have been omitted. [Symmetry codes: (i) –$x$ + 1, –$y$ + 1, –$z$ + 1; (ii) $x$, $y$ – 1, $z$; (iii) –$x$, –$y$ + 1, –$z$ + 1; (iv) $x$ – 1/2, –$y$ + 1/2, $z$ – 1/2; (v) –$x$ + 1, –$y$, –$z$ + 1.]

## 10-Methyl-9-phenoxycarbonylacridinium trifluoromethanesulfonate monohydrate

*Crystal data*
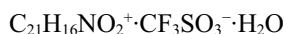
| | |
|---|---|
| $C_{21}H_{16}NO_2{}^+\cdot CF_3SO_3{}^-\cdot H_2O$ | $F(000) = 992$ |
| $M_r = 481.44$ | $D_x = 1.503$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 15973 reflections |
| $a = 11.3807$ (4) Å | $\theta = 3.0–29.3°$ |
| $b = 9.5785$ (2) Å | $\mu = 0.22$ mm$^{-1}$ |
| $c = 19.7134$ (6) Å | $T = 295$ K |
| $\beta = 98.172$ (3)° | Needle, yellow |
| $V = 2127.14$ (11) Å$^3$ | $0.78 \times 0.16 \times 0.10$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer | 46462 measured reflections |
| | 3792 independent reflections |
| Radiation source: Enhanced (Mo) X-ray Source | 2422 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.060$ |
| Detector resolution: 10.4002 pixels mm$^{-1}$ | $\theta_{max} = 25.1°$, $\theta_{min} = 3.0°$ |
| $\omega$ scans | $h = -13\rightarrow13$ |
| Absorption correction: multi-scan | $k = -11\rightarrow11$ |
| (*CrysAlis RED*; Oxford Diffraction, 2008). | $l = -23\rightarrow23$ |
| $T_{min} = 0.741$, $T_{max} = 1.000$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.064$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.211$ | |
| $S = 1.03$ | H atoms treated by a mixture of independent and constrained refinement |
| 3792 reflections | |
| 305 parameters | $w = 1/[\sigma^2(F_o^2) + (0.146P)^2]$ |
| 3 restraints | where $P = (F_o^2 + 2F_c^2)/3$ |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} < 0.001$ |
| | $\Delta\rho_{max} = 0.59$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.39$ e Å$^{-3}$ |

*Special details*

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

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.6362 (3) | 0.0857 (3) | 0.60005 (15) | 0.0534 (7) |
| H1 | 0.6328 | 0.1816 | 0.6067 | 0.064* |
| C2 | 0.7417 (3) | 0.0248 (3) | 0.59672 (17) | 0.0647 (8) |
| H2 | 0.8103 | 0.0788 | 0.5999 | 0.078* |
| C3 | 0.7481 (3) | −0.1205 (4) | 0.58836 (19) | 0.0703 (9) |
| H3 | 0.8218 | −0.1620 | 0.5877 | 0.084* |
| C4 | 0.6494 (3) | −0.2020 (3) | 0.58122 (16) | 0.0613 (8) |
| H4 | 0.6561 | −0.2979 | 0.5753 | 0.074* |
| C5 | 0.2201 (3) | −0.2410 (3) | 0.56540 (18) | 0.0700 (10) |
| H5 | 0.2234 | −0.3363 | 0.5567 | 0.084* |
| C6 | 0.1149 (4) | −0.1788 (4) | 0.5680 (2) | 0.0859 (12) |
| H6 | 0.0464 | −0.2332 | 0.5615 | 0.103* |
| C7 | 0.1041 (3) | −0.0366 (4) | 0.5799 (2) | 0.0822 (11) |
| H7 | 0.0296 | 0.0029 | 0.5805 | 0.099* |
| C8 | 0.2025 (3) | 0.0440 (3) | 0.59056 (17) | 0.0637 (9) |
| H8 | 0.1954 | 0.1389 | 0.5991 | 0.076* |
| C9 | 0.4195 (3) | 0.0648 (2) | 0.59775 (13) | 0.0450 (7) |
| N10 | 0.4351 (2) | −0.2193 (2) | 0.57446 (11) | 0.0476 (6) |
| C11 | 0.5304 (3) | 0.0064 (3) | 0.59353 (12) | 0.0439 (7) |
| C12 | 0.5374 (3) | −0.1418 (3) | 0.58269 (13) | 0.0468 (7) |
| C13 | 0.3168 (3) | −0.0151 (3) | 0.58886 (14) | 0.0493 (7) |
| C14 | 0.3255 (3) | −0.1614 (3) | 0.57599 (14) | 0.0506 (7) |
| C15 | 0.4143 (2) | 0.2199 (3) | 0.61254 (14) | 0.0454 (7) |
| O16 | 0.4005 (2) | 0.24024 (17) | 0.67778 (10) | 0.0597 (6) |
| O17 | 0.4242 (2) | 0.30844 (19) | 0.57195 (10) | 0.0647 (6) |
| C18 | 0.4040 (3) | 0.3808 (3) | 0.70187 (14) | 0.0523 (8) |
| C19 | 0.3003 (3) | 0.4502 (3) | 0.70065 (17) | 0.0635 (9) |
| H19 | 0.2286 | 0.4080 | 0.6836 | 0.076* |

| | | | |
|---|---|---|---|
| C20 | 0.3034 (4) | 0.5869 (4) | 0.7257 (2) | 0.0763 (11) |
| H20 | 0.2335 | 0.6375 | 0.7252 | 0.092* |
| C21 | 0.4108 (4) | 0.6459 (4) | 0.7509 (2) | 0.0797 (11) |
| H21 | 0.4134 | 0.7366 | 0.7679 | 0.096* |
| C22 | 0.5133 (4) | 0.5729 (4) | 0.7514 (2) | 0.0815 (11) |
| H22 | 0.5855 | 0.6142 | 0.7683 | 0.098* |
| C23 | 0.5108 (3) | 0.4375 (3) | 0.72675 (17) | 0.0669 (9) |
| H23 | 0.5805 | 0.3866 | 0.7272 | 0.080* |
| C24 | 0.4419 (3) | −0.3729 (3) | 0.56256 (17) | 0.0637 (9) |
| H24A | 0.3966 | −0.4213 | 0.5928 | 0.095* |
| H24B | 0.5232 | −0.4026 | 0.5714 | 0.095* |
| H24C | 0.4102 | −0.3937 | 0.5159 | 0.095* |
| O25 | 0.1330 (4) | 0.3806 (6) | 0.5581 (2) | 0.1480 (15) |
| H25A | 0.136 (7) | 0.397 (9) | 0.5162 (16) | 0.222* |
| H25B | 0.064 (4) | 0.350 (10) | 0.563 (4) | 0.222* |
| S26 | 0.15677 (9) | 0.55386 (9) | 0.38344 (5) | 0.0715 (4) |
| O27 | 0.1121 (4) | 0.4342 (3) | 0.41645 (19) | 0.1242 (12) |
| O28 | 0.0899 (3) | 0.6777 (3) | 0.38719 (15) | 0.0997 (9) |
| O29 | 0.2829 (3) | 0.5641 (3) | 0.39743 (18) | 0.1067 (10) |
| C30 | 0.1269 (4) | 0.5037 (5) | 0.2942 (2) | 0.0903 (12) |
| F31 | 0.1687 (3) | 0.6041 (3) | 0.25626 (16) | 0.1375 (12) |
| F32 | 0.0152 (3) | 0.4950 (4) | 0.27144 (17) | 0.1380 (12) |
| F33 | 0.1787 (3) | 0.3873 (3) | 0.28194 (15) | 0.1227 (10) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.065 (2) | 0.0385 (14) | 0.0567 (17) | −0.0056 (13) | 0.0088 (14) | −0.0035 (12) |
| C2 | 0.061 (2) | 0.0628 (19) | 0.071 (2) | −0.0063 (16) | 0.0092 (16) | −0.0077 (15) |
| C3 | 0.067 (2) | 0.068 (2) | 0.076 (2) | 0.0102 (18) | 0.0113 (17) | −0.0048 (17) |
| C4 | 0.078 (2) | 0.0434 (16) | 0.063 (2) | 0.0136 (15) | 0.0108 (16) | −0.0023 (13) |
| C5 | 0.082 (3) | 0.0491 (17) | 0.078 (2) | −0.0199 (17) | 0.0084 (18) | −0.0067 (15) |
| C6 | 0.063 (3) | 0.082 (3) | 0.111 (3) | −0.027 (2) | 0.008 (2) | −0.018 (2) |
| C7 | 0.056 (2) | 0.086 (3) | 0.104 (3) | −0.0065 (19) | 0.011 (2) | −0.019 (2) |
| C8 | 0.064 (2) | 0.0529 (17) | 0.074 (2) | −0.0019 (15) | 0.0097 (17) | −0.0084 (14) |
| C9 | 0.0643 (19) | 0.0295 (13) | 0.0413 (14) | −0.0039 (12) | 0.0074 (13) | −0.0014 (10) |
| N10 | 0.0708 (17) | 0.0262 (10) | 0.0461 (13) | −0.0039 (10) | 0.0091 (11) | −0.0018 (8) |
| C11 | 0.0603 (18) | 0.0320 (13) | 0.0392 (14) | −0.0017 (12) | 0.0065 (12) | −0.0017 (10) |
| C12 | 0.0670 (19) | 0.0334 (13) | 0.0398 (14) | 0.0012 (13) | 0.0072 (13) | 0.0018 (10) |
| C13 | 0.0632 (19) | 0.0371 (14) | 0.0469 (15) | −0.0020 (13) | 0.0058 (13) | −0.0028 (11) |
| C14 | 0.066 (2) | 0.0377 (14) | 0.0481 (16) | −0.0117 (13) | 0.0071 (13) | −0.0022 (11) |
| C15 | 0.0543 (18) | 0.0311 (13) | 0.0505 (17) | −0.0011 (11) | 0.0071 (13) | −0.0024 (12) |
| O16 | 0.0985 (17) | 0.0294 (9) | 0.0546 (13) | −0.0024 (9) | 0.0226 (11) | −0.0024 (8) |
| O17 | 0.1108 (19) | 0.0318 (10) | 0.0544 (12) | −0.0024 (10) | 0.0214 (12) | 0.0035 (9) |
| C18 | 0.082 (2) | 0.0329 (14) | 0.0457 (15) | −0.0025 (14) | 0.0201 (15) | −0.0031 (11) |
| C19 | 0.072 (2) | 0.0525 (18) | 0.069 (2) | −0.0098 (16) | 0.0234 (17) | −0.0085 (14) |
| C20 | 0.090 (3) | 0.0555 (19) | 0.091 (3) | 0.0138 (18) | 0.039 (2) | −0.0100 (17) |
| C21 | 0.111 (3) | 0.0485 (18) | 0.083 (3) | −0.011 (2) | 0.026 (2) | −0.0207 (17) |

| | | | | | |
|---|---|---|---|---|---|
| C22 | 0.099 (3) | 0.064 (2) | 0.080 (3) | −0.017 (2) | 0.010 (2) | −0.0235 (18) |
| C23 | 0.077 (2) | 0.0539 (18) | 0.069 (2) | 0.0022 (16) | 0.0076 (17) | −0.0084 (15) |
| C24 | 0.096 (2) | 0.0253 (13) | 0.072 (2) | −0.0041 (14) | 0.0191 (17) | −0.0056 (12) |
| O25 | 0.121 (3) | 0.191 (4) | 0.130 (3) | 0.034 (3) | 0.009 (2) | 0.014 (3) |
| S26 | 0.0867 (8) | 0.0584 (5) | 0.0688 (6) | −0.0088 (4) | 0.0084 (5) | −0.0088 (4) |
| O27 | 0.174 (3) | 0.092 (2) | 0.118 (3) | −0.020 (2) | 0.058 (2) | 0.0251 (17) |
| O28 | 0.133 (3) | 0.0679 (16) | 0.098 (2) | 0.0144 (16) | 0.0154 (17) | −0.0183 (14) |
| O29 | 0.090 (2) | 0.100 (2) | 0.119 (2) | −0.0072 (16) | −0.0236 (17) | −0.0098 (17) |
| C30 | 0.094 (3) | 0.081 (3) | 0.092 (3) | 0.014 (2) | 0.001 (2) | −0.019 (2) |
| F31 | 0.192 (3) | 0.131 (2) | 0.0935 (19) | 0.021 (2) | 0.034 (2) | 0.0265 (16) |
| F32 | 0.105 (2) | 0.155 (3) | 0.138 (2) | 0.0063 (18) | −0.0372 (18) | −0.058 (2) |
| F33 | 0.161 (3) | 0.0951 (18) | 0.110 (2) | 0.0314 (17) | 0.0119 (17) | −0.0364 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.345 (4) | C15—O17 | 1.182 (3) |
| C1—C11 | 1.414 (4) | C15—O16 | 1.332 (3) |
| C1—H1 | 0.9300 | O16—C18 | 1.426 (3) |
| C2—C3 | 1.405 (5) | C18—C19 | 1.352 (5) |
| C2—H2 | 0.9300 | C18—C23 | 1.357 (5) |
| C3—C4 | 1.358 (5) | C19—C20 | 1.398 (5) |
| C3—H3 | 0.9300 | C19—H19 | 0.9300 |
| C4—C12 | 1.404 (4) | C20—C21 | 1.374 (6) |
| C4—H4 | 0.9300 | C20—H20 | 0.9300 |
| C5—C6 | 1.345 (5) | C21—C22 | 1.358 (6) |
| C5—C14 | 1.412 (4) | C21—H21 | 0.9300 |
| C5—H5 | 0.9300 | C22—C23 | 1.384 (5) |
| C6—C7 | 1.391 (5) | C22—H22 | 0.9300 |
| C6—H6 | 0.9300 | C23—H23 | 0.9300 |
| C7—C8 | 1.351 (5) | C24—H24A | 0.9600 |
| C7—H7 | 0.9300 | C24—H24B | 0.9600 |
| C8—C13 | 1.424 (4) | C24—H24C | 0.9600 |
| C8—H8 | 0.9300 | O25—H25A | 0.85 (2) |
| C9—C13 | 1.387 (4) | O25—H25B | 0.85 (2) |
| C9—C11 | 1.393 (4) | S26—O28 | 1.417 (3) |
| C9—C15 | 1.517 (3) | S26—O29 | 1.426 (3) |
| N10—C14 | 1.369 (4) | S26—O27 | 1.445 (3) |
| N10—C12 | 1.371 (4) | S26—C30 | 1.809 (5) |
| N10—C24 | 1.494 (3) | C30—F32 | 1.290 (5) |
| C11—C12 | 1.439 (4) | C30—F33 | 1.299 (5) |
| C13—C14 | 1.430 (4) | C30—F31 | 1.346 (5) |
| | | | |
| C2—C1—C11 | 121.2 (3) | O17—C15—O16 | 125.8 (2) |
| C2—C1—H1 | 119.4 | O17—C15—C9 | 124.2 (2) |
| C11—C1—H1 | 119.4 | O16—C15—C9 | 110.0 (2) |
| C1—C2—C3 | 119.8 (3) | C15—O16—C18 | 117.2 (2) |
| C1—C2—H2 | 120.1 | C19—C18—C23 | 123.0 (3) |
| C3—C2—H2 | 120.1 | C19—C18—O16 | 118.4 (3) |

| | | | |
|---|---|---|---|
| C4—C3—C2 | 121.8 (3) | C23—C18—O16 | 118.6 (3) |
| C4—C3—H3 | 119.1 | C18—C19—C20 | 118.4 (3) |
| C2—C3—H3 | 119.1 | C18—C19—H19 | 120.8 |
| C3—C4—C12 | 120.1 (3) | C20—C19—H19 | 120.8 |
| C3—C4—H4 | 120.0 | C21—C20—C19 | 119.3 (3) |
| C12—C4—H4 | 120.0 | C21—C20—H20 | 120.3 |
| C6—C5—C14 | 119.8 (3) | C19—C20—H20 | 120.3 |
| C6—C5—H5 | 120.1 | C22—C21—C20 | 120.6 (3) |
| C14—C5—H5 | 120.1 | C22—C21—H21 | 119.7 |
| C5—C6—C7 | 122.7 (3) | C20—C21—H21 | 119.7 |
| C5—C6—H6 | 118.6 | C21—C22—C23 | 120.3 (4) |
| C7—C6—H6 | 118.6 | C21—C22—H22 | 119.8 |
| C8—C7—C6 | 119.7 (4) | C23—C22—H22 | 119.8 |
| C8—C7—H7 | 120.2 | C18—C23—C22 | 118.3 (4) |
| C6—C7—H7 | 120.2 | C18—C23—H23 | 120.8 |
| C7—C8—C13 | 120.6 (3) | C22—C23—H23 | 120.8 |
| C7—C8—H8 | 119.7 | N10—C24—H24A | 109.5 |
| C13—C8—H8 | 119.7 | N10—C24—H24B | 109.5 |
| C13—C9—C11 | 121.7 (2) | H24A—C24—H24B | 109.5 |
| C13—C9—C15 | 120.6 (3) | N10—C24—H24C | 109.5 |
| C11—C9—C15 | 117.7 (2) | H24A—C24—H24C | 109.5 |
| C14—N10—C12 | 122.6 (2) | H24B—C24—H24C | 109.5 |
| C14—N10—C24 | 118.1 (2) | H25A—O25—H25B | 110 (3) |
| C12—N10—C24 | 119.3 (2) | O28—S26—O29 | 117.75 (19) |
| C9—C11—C1 | 123.1 (2) | O28—S26—O27 | 114.5 (2) |
| C9—C11—C12 | 118.3 (2) | O29—S26—O27 | 112.1 (2) |
| C1—C11—C12 | 118.6 (3) | O28—S26—C30 | 104.19 (19) |
| N10—C12—C4 | 122.2 (2) | O29—S26—C30 | 104.5 (2) |
| N10—C12—C11 | 119.2 (3) | O27—S26—C30 | 101.4 (2) |
| C4—C12—C11 | 118.6 (3) | F32—C30—F33 | 109.3 (4) |
| C9—C13—C8 | 122.3 (2) | F32—C30—F31 | 105.2 (4) |
| C9—C13—C14 | 119.0 (3) | F33—C30—F31 | 107.7 (4) |
| C8—C13—C14 | 118.7 (3) | F32—C30—S26 | 113.3 (3) |
| N10—C14—C5 | 122.4 (3) | F33—C30—S26 | 112.4 (3) |
| N10—C14—C13 | 119.2 (2) | F31—C30—S26 | 108.6 (3) |
| C5—C14—C13 | 118.5 (3) | | |
| | | | |
| C11—C1—C2—C3 | −1.6 (5) | C6—C5—C14—N10 | 179.5 (3) |
| C1—C2—C3—C4 | 2.2 (5) | C6—C5—C14—C13 | −0.4 (5) |
| C2—C3—C4—C12 | −0.6 (5) | C9—C13—C14—N10 | 1.6 (4) |
| C14—C5—C6—C7 | 0.9 (6) | C8—C13—C14—N10 | −179.8 (3) |
| C5—C6—C7—C8 | −1.1 (7) | C9—C13—C14—C5 | −178.5 (3) |
| C6—C7—C8—C13 | 0.8 (6) | C8—C13—C14—C5 | 0.1 (4) |
| C13—C9—C11—C1 | 177.8 (3) | C13—C9—C15—O17 | −104.9 (4) |
| C15—C9—C11—C1 | −2.2 (4) | C11—C9—C15—O17 | 75.1 (4) |
| C13—C9—C11—C12 | −2.8 (4) | C13—C9—C15—O16 | 76.8 (3) |
| C15—C9—C11—C12 | 177.2 (2) | C11—C9—C15—O16 | −103.2 (3) |
| C2—C1—C11—C9 | 178.9 (3) | O17—C15—O16—C18 | −3.4 (4) |

| | | | |
|---|---|---|---|
| C2—C1—C11—C12 | −0.4 (4) | C9—C15—O16—C18 | 174.8 (2) |
| C14—N10—C12—C4 | 179.8 (3) | C15—O16—C18—C19 | 94.4 (3) |
| C24—N10—C12—C4 | −0.8 (4) | C15—O16—C18—C23 | −87.5 (3) |
| C14—N10—C12—C11 | 0.1 (4) | C23—C18—C19—C20 | 0.5 (5) |
| C24—N10—C12—C11 | 179.5 (2) | O16—C18—C19—C20 | 178.6 (3) |
| C3—C4—C12—N10 | 178.8 (3) | C18—C19—C20—C21 | −0.4 (5) |
| C3—C4—C12—C11 | −1.5 (4) | C19—C20—C21—C22 | 0.4 (6) |
| C9—C11—C12—N10 | 2.3 (3) | C20—C21—C22—C23 | −0.4 (6) |
| C1—C11—C12—N10 | −178.3 (2) | C19—C18—C23—C22 | −0.6 (5) |
| C9—C11—C12—C4 | −177.4 (2) | O16—C18—C23—C22 | −178.7 (3) |
| C1—C11—C12—C4 | 2.0 (4) | C21—C22—C23—C18 | 0.5 (6) |
| C11—C9—C13—C8 | −177.7 (3) | O28—S26—C30—F32 | −53.1 (4) |
| C15—C9—C13—C8 | 2.3 (4) | O29—S26—C30—F32 | −177.2 (3) |
| C11—C9—C13—C14 | 0.9 (4) | O27—S26—C30—F32 | 66.1 (4) |
| C15—C9—C13—C14 | −179.1 (2) | O28—S26—C30—F33 | −177.6 (3) |
| C7—C8—C13—C9 | 178.3 (3) | O29—S26—C30—F33 | 58.2 (4) |
| C7—C8—C13—C14 | −0.3 (5) | O27—S26—C30—F33 | −58.5 (4) |
| C12—N10—C14—C5 | 178.0 (3) | O28—S26—C30—F31 | 63.3 (4) |
| C24—N10—C14—C5 | −1.3 (4) | O29—S26—C30—F31 | −60.8 (3) |
| C12—N10—C14—C13 | −2.1 (4) | O27—S26—C30—F31 | −177.5 (3) |
| C24—N10—C14—C13 | 178.6 (2) | | |

*Hydrogen-bond geometry (Å, º)*

Cg4 is the centroid of the C18–C23 ring.

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| C2—H2⋯O28[i] | 0.93 | 2.59 | 3.424 (4) | 149 |
| C8—H8⋯O25 | 0.93 | 2.52 | 3.360 (6) | 150 |
| C19—H19⋯O25 | 0.93 | 2.57 | 3.232 (5) | 129 |
| C24—H24*A*⋯Cg4[ii] | 0.96 | 2.69 | 3.484 (4) | 140 |
| C24—H24*C*⋯O29[ii] | 0.96 | 2.60 | 3.544 (5) | 168 |
| O25—H25*A*⋯O27 | 0.85 (4) | 1.98 (3) | 2.816 (5) | 170 (8) |
| O25—H25*B*⋯O28[iii] | 0.86 (4) | 2.14 (6) | 2.948 (6) | 156 (7) |

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