

9-(4-Chlorophenoxy-carbonyl)-10-methyl-acridinium trifluoromethanesulfonate

Damian Trzybiński, Karol Krzyminiński and Jerzy Błażejowski*‡

Faculty of Chemistry, University of Gdańsk, J. Sobieskiego 18, 80-952 Gdańsk, Poland

Correspondence e-mail: bla@chem.univ.gda.pl

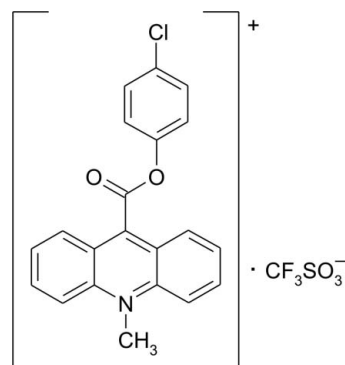
Received 28 September 2010; accepted 4 October 2010

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.050; wR factor = 0.112; data-to-parameter ratio = 12.6.

In the crystal of the title compound, $\text{C}_{21}\text{H}_{15}\text{ClNO}_2^+ \cdot \text{CF}_3\text{SO}_3^-$, adjacent cations are linked through $\text{C}-\text{H} \cdots \pi$ and $\pi-\pi$ interactions [centroid-centroid distance = $3.987(2)$ Å], and neighboring cations and anions *via* $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{F} \cdots \pi$ interactions. The acridine ring system and benzene ring are oriented at a dihedral angle of $1.0(1)^\circ$ while the carboxyl group is twisted at an angle of $85.0(1)^\circ$ relative to the acridine skeleton. The mean planes of adjacent acridine units are either parallel or inclined at an angle of $78.2(1)^\circ$ in the crystal structure.

Related literature

For background to the chemiluminogenic properties of 9-phenoxy-carbonyl-10-methylacridinium trifluoromethanesulfonates, see: Brown *et al.* (2009); King *et al.* (2007); Rak *et al.* (1999); Roda *et al.* (2003); Zomer & Jacquemijns (2001). For related structures, see: Sikorski *et al.* (2005); Trzybiński *et al.* (2010). For intermolecular interactions, see: 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.* (2010).



Experimental

Crystal data

$\text{C}_{21}\text{H}_{15}\text{ClNO}_2^+ \cdot \text{CF}_3\text{SO}_3^-$
 $M_r = 497.87$
 Monoclinic, $P2_1/n$
 $a = 13.3025(11)$ Å
 $b = 8.6750(9)$ Å
 $c = 19.6191(18)$ Å
 $\beta = 106.577(10)^\circ$

$V = 2169.9(4)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹
 $T = 295$ K
 $0.35 \times 0.28 \times 0.06$ mm

Data collection

Oxford Diffraction Gemini R Ultra
 Ruby CCD diffractometer
 11162 measured reflections

3777 independent reflections
 2679 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.112$
 $S = 1.08$
 3777 reflections

299 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg4 is the centroid of the C18–C23 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3–H3 \cdots O28 ⁱ	0.93	2.59	3.328 (5)	136
C4–H4 \cdots O28	0.93	2.45	3.370 (4)	171
C5–H5 \cdots O27 ⁱⁱ	0.93	2.39	3.258 (4)	154
C6–H6 \cdots O29 ⁱⁱ	0.93	2.54	3.304 (5)	140
C8–H8 \cdots O29 ⁱⁱⁱ	0.93	2.59	3.332 (4)	137
C19–H19 \cdots O29 ⁱⁱⁱ	0.93	2.44	3.349 (4)	165
C25–H25C \cdots O27	0.96	2.51	3.387 (4)	152
C25–H25B \cdots Cg4 ^{iv}	0.96	2.65	3.519 (4)	151

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

Table 2

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

Cg1 and Cg3 are the centroids of the C9/N10/C11–C14 and C5–C8/C13/C14 rings, respectively.

X	I	J	$I \cdots J$	$X \cdots J$	$X-I \cdots J$
C30	F31	Cg1 ⁱⁱ	3.570 (3)	3.916 (4)	94.4 (2)
C30	F32	Cg1 ⁱⁱ	3.337 (3)	3.916 (4)	105.8 (2)
C30	F33	Cg3 ⁱⁱ	3.387 (3)	4.073 (4)	111.9 (2)

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

‡ to whom correspondence should be addressed

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).

This study was financed by the State Funds for Scientific Research (grant DS/8220-4-0087-0).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5039).

References

- Brown, R. C., Li, Z., Rutter, A. J., Mu, X., Weeks, O. H., Smith, K. & Weeks, I. (2009). *Org. Biomol. Chem.* **7**, 386–394.
- Dorn, T., Janiak, C. & Abu-Shandi, K. (2005). *CrystEngComm*, **7**, 633–641.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hunter, C. A., Lawson, K. R., Perkins, J. & Urch, C. J. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 651–669.
- King, D. W., Cooper, W. J., Rusak, S. A., Peake, B. M., Kiddle, J. J., O'Sullivan, D. W., Melamed, M. L., Morgan, C. R. & Theberge, S. M. (2007). *Anal. Chem.* **79**, 4169–4176.
- Novoa, J. J., Mota, F. & D'Oria, E. (2006). *Hydrogen Bonding – New Insights*, edited by S. Grabowski, pp. 193–244. The Netherlands: Springer.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
- Rak, J., Skurski, P. & Błażejowski, J. (1999). *J. Org. Chem.* **64**, 3002–3008.
- Roda, A., Guardigli, M., Michelini, E., Mirasoli, M. & Pasini, P. (2003). *Anal. Chem.* **75**, 462–470.
- Sato, N. (1996). *Tetrahedron Lett.* **37**, 8519–8522.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sikorski, A., Krzymiński, K., Konitz, A. & Błażejowski, J. (2005). *Acta Cryst.* **C61**, o227–o230.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Takahashi, O., Kohno, Y., Iwasaki, S., Saito, K., Iwaoka, M., Tomada, S., Umezawa, Y., Tsuboyama, S. & Nishio, M. (2001). *Bull. Chem. Soc. Jpn.* **74**, 2421–2430.
- Trzybiński, D., Krzymiński, K., Sikorski, A. & Błażejowski, J. (2010). *Acta Cryst.* **E66**, o1313–o1314.
- Zomer, G. & Jacquemijns, M. (2001). *Chemiluminescence in Analytical Chemistry*, edited by A. M. Garcia-Campana & W. R. G. Baeyens, pp. 529–549. New York: Marcel Dekker.

supplementary materials

Acta Cryst. (2010). E66, o2771-o2772 [doi:10.1107/S1600536810039541]

9-(4-Chlorophenoxy-carbonyl)-10-methylacridinium trifluoromethanesulfonate

D. Trzybinski, K. Krzyminski and J. Blazejowski

Comment

The long-known chemiluminescence of 9-(phenoxy-carbonyl)-10-methylacridinium salts has been used as chemiluminescent indicators and labels that are widely applied in assays of biologically and environmentally important entities such as antigens, antibodies, enzymes or DNA fragments (Zomer & Jacquemijns, 2001; Roda *et al.*, 2003; King *et al.*, 2007; Brown *et al.*, 2009). The cations of these salts are oxidized by H₂O₂ in alkaline media, a reaction that is accompanied by the removal of the phenoxy-carbonyl fragment and the conversion of the remaining part of the molecules to electronically excited, light-emitting 10-methyl-9-acridinone (Rak *et al.*, 1999). The efficiency of chemiluminescence – crucial for analytical applications – is affected by the constitution of the phenyl fragment (Zomer & Jacquemijns, 2001). In continuing our investigations on the latter aspect, we synthesized 9-(4-chlorophenoxy-carbonyl)-10-methylacridinium trifluoromethanesulfonate, whose crystal structure is presented here.

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.*, 2005; Trzybiński *et al.*, 2010). With respective average deviations from planarity of 0.0412 (3) Å and 0.0034 (3) Å, the acridine and benzene ring systems are almost parallel (are oriented at a dihedral angle of 1.0 (1)°). The carboxyl group is twisted at an angle of 85.0 (1)° relative to the acridine skeleton. The mean planes of the adjacent acridine moieties are parallel (remain at an angle 0.0 (1)°) or inclined at an angle of 78.2 (1)° in the crystal lattice.

In the crystal structure, the adjacent cations are linked by C–H⋯π (Table 1, Fig. 2) and π–π (Table 3, Fig. 2) contacts, and the cations and neighboring anions via C–H⋯O (Table 1, Figs. 1 and 2) and C–F⋯π (Table 2, Fig. 2) interactions. The C–H⋯O interactions are of the hydrogen bond type (Novoa *et al.* 2006). The C–H⋯π (Takahashi *et al.*, 2001), C–F⋯π (Dorn *et al.*, 2005) and π–π (Hunter *et al.*, 2001) interactions should be of an attractive nature. The crystal structure is stabilized by a network of these short-range specific interactions and by long-range electrostatic interactions between ions.

Experimental

4-Chlorophenylacridine-9-carboxylate was synthesized by esterification of 9-(chloro-carbonyl)acridine (obtained by treating acridine-9-carboxylic acid with a tenfold molar excess of thionyl chloride) with 4-chlorophenol in anhydrous dichloromethane in the presence of *N,N*-diethylethanamine and a catalytic amount of *N,N*-dimethyl-4-pyridinamine (room temperature, 15h) (Sato, 1996). The product was purified chromatographically (SiO₂, cyclohexane/ethyl acetate, 1/1 v/v) and subsequently quaternarized with a fivefold molar excess of methyl trifluoromethanesulfonate dissolved in anhydrous dichloromethane. The crude 9-(4-chlorophenoxy-carbonyl)-10-methylacridinium trifluoromethanesulfonate was dissolved in a small amount of ethanol, filtered and precipitated with a 20 v/v excess of diethyl ether. Yellow crystals suitable for X-ray investigations were grown from absolute ethanol solution (m.p. 488–489 K).

Refinement

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 $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.2$ for the aromatic and $x = 1.5$ for the methyl H atoms.

Figures

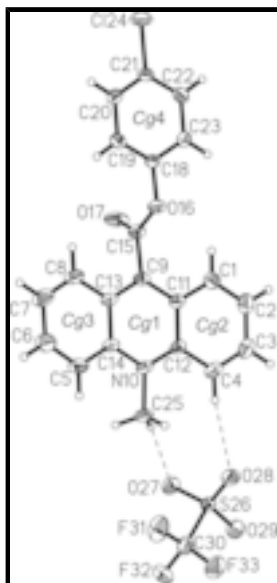


Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radius. Cg1, Cg2, Cg3 and Cg4 denote the ring centroids. The C—H \cdots O interactions are represented by dashed lines.

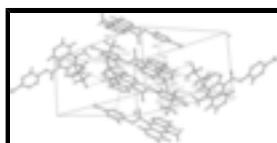


Fig. 2. The arrangement of the ions in the crystal structure. The C—H \cdots O interactions are represented by dashed lines, the C—H \cdots π , C—F \cdots π , and π — π contacts by dotted lines. H atoms not involved in interactions have been omitted. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 3/2, y - 1/2, -z + 1/2$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + 1, -y + 2, -z + 1$.]

9-(4-Chlorophenoxy carbonyl)-10-methylacridinium trifluoromethanesulfonate

Crystal data

$\text{C}_{21}\text{H}_{15}\text{ClNO}_2^+ \cdot \text{CF}_3\text{SO}_3^-$

$M_r = 497.87$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 13.3025$ (11) Å

$b = 8.6750$ (9) Å

$c = 19.6191$ (18) Å

$\beta = 106.577$ (10)°

$V = 2169.9$ (4) Å³

$Z = 4$

$F(000) = 1016$

$D_x = 1.524$ Mg m⁻³

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

Cell parameters from 1665 reflections

$\theta = 3.0$ – 29.1 °

$\mu = 0.33$ mm⁻¹

$T = 295$ K

Plate, yellow

$0.35 \times 0.28 \times 0.06$ mm

Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer	2679 reflections with $I > 2\sigma(I)$
Radiation source: Enhanced (Mo) X-ray Source graphite	$R_{\text{int}} = 0.031$
Detector resolution: 10.4002 pixels mm^{-1}	$\theta_{\text{max}} = 25.1^\circ$, $\theta_{\text{min}} = 3.2^\circ$
ω scans	$h = -15 \rightarrow 15$
11162 measured reflections	$k = -10 \rightarrow 8$
3777 independent reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.4339P]$
3777 reflections	where $P = (F_o^2 + 2F_c^2)/3$
299 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6412 (3)	0.7757 (4)	0.51159 (16)	0.0551 (8)
H1	0.5968	0.8280	0.5327	0.066*
C2	0.7459 (3)	0.7893 (4)	0.53941 (18)	0.0655 (9)
H2	0.7736	0.8503	0.5794	0.079*
C3	0.8127 (3)	0.7105 (4)	0.50748 (19)	0.0642 (9)
H3	0.8848	0.7193	0.5274	0.077*
C4	0.7761 (2)	0.6220 (4)	0.44874 (17)	0.0545 (8)
H4	0.8226	0.5731	0.4284	0.065*
C5	0.4792 (3)	0.3888 (4)	0.27537 (17)	0.0610 (9)
H5	0.5241	0.3355	0.2551	0.073*
C6	0.3742 (3)	0.3699 (5)	0.2497 (2)	0.0827 (12)
H6	0.3480	0.3034	0.2116	0.099*

supplementary materials

C7	0.3035 (3)	0.4472 (5)	0.2787 (2)	0.0811 (12)
H7	0.2316	0.4327	0.2597	0.097*
C8	0.3403 (2)	0.5423 (4)	0.33414 (19)	0.0610 (9)
H8	0.2933	0.5927	0.3536	0.073*
C9	0.4901 (2)	0.6658 (3)	0.42070 (14)	0.0407 (7)
N10	0.62580 (17)	0.5155 (3)	0.35967 (12)	0.0408 (5)
C11	0.5976 (2)	0.6831 (3)	0.45086 (14)	0.0408 (7)
C12	0.6666 (2)	0.6045 (3)	0.41855 (15)	0.0416 (7)
C13	0.4494 (2)	0.5676 (3)	0.36378 (15)	0.0426 (7)
C14	0.5202 (2)	0.4893 (3)	0.33286 (14)	0.0421 (7)
C15	0.4160 (2)	0.7658 (3)	0.44662 (15)	0.0451 (7)
O16	0.39162 (15)	0.7040 (2)	0.50208 (10)	0.0497 (5)
O17	0.3831 (2)	0.8846 (3)	0.41934 (13)	0.0785 (8)
C18	0.3180 (2)	0.7867 (3)	0.52827 (14)	0.0410 (7)
C19	0.2135 (2)	0.7596 (4)	0.49788 (15)	0.0503 (8)
H19	0.1910	0.6928	0.4594	0.060*
C20	0.1421 (2)	0.8339 (4)	0.52579 (16)	0.0566 (8)
H20	0.0706	0.8176	0.5063	0.068*
C21	0.1776 (3)	0.9314 (4)	0.58220 (15)	0.0535 (8)
C22	0.2823 (3)	0.9565 (4)	0.61275 (15)	0.0558 (8)
H22	0.3049	1.0220	0.6516	0.067*
C23	0.3544 (2)	0.8829 (3)	0.58496 (15)	0.0484 (7)
H23	0.4259	0.8987	0.6045	0.058*
Cl24	0.08737 (9)	1.02661 (14)	0.61618 (5)	0.0951 (4)
C25	0.6984 (2)	0.4487 (4)	0.32249 (17)	0.0568 (8)
H25A	0.6590	0.4126	0.2763	0.085*
H25B	0.7360	0.3641	0.3497	0.085*
H25C	0.7473	0.5262	0.3173	0.085*
S26	0.99146 (6)	0.51449 (9)	0.33370 (4)	0.0456 (2)
O27	0.91136 (17)	0.6102 (2)	0.28913 (11)	0.0578 (6)
O28	0.96649 (17)	0.4501 (3)	0.39381 (11)	0.0709 (7)
O29	1.09667 (17)	0.5708 (3)	0.34719 (12)	0.0704 (7)
C30	0.9908 (3)	0.3493 (4)	0.27794 (18)	0.0641 (9)
F31	0.89748 (18)	0.2801 (2)	0.25860 (13)	0.0971 (7)
F32	1.01300 (19)	0.3885 (3)	0.21805 (11)	0.0974 (8)
F33	1.06074 (19)	0.2433 (3)	0.30961 (12)	0.0989 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.056 (2)	0.0547 (19)	0.0543 (19)	0.0055 (16)	0.0160 (16)	0.0022 (16)
C2	0.064 (2)	0.065 (2)	0.059 (2)	-0.0006 (19)	0.0042 (18)	-0.0015 (17)
C3	0.0434 (19)	0.072 (2)	0.071 (2)	0.0002 (18)	0.0048 (17)	0.0125 (19)
C4	0.0419 (19)	0.0549 (19)	0.069 (2)	0.0081 (15)	0.0189 (16)	0.0107 (17)
C5	0.057 (2)	0.058 (2)	0.076 (2)	-0.0016 (17)	0.0320 (18)	-0.0180 (18)
C6	0.063 (3)	0.088 (3)	0.098 (3)	-0.015 (2)	0.024 (2)	-0.044 (2)
C7	0.043 (2)	0.094 (3)	0.108 (3)	-0.013 (2)	0.024 (2)	-0.034 (2)
C8	0.0386 (18)	0.065 (2)	0.086 (2)	0.0017 (16)	0.0285 (17)	-0.0115 (19)

C9	0.0458 (18)	0.0348 (15)	0.0479 (16)	0.0071 (13)	0.0235 (14)	0.0073 (13)
N10	0.0377 (13)	0.0403 (13)	0.0514 (13)	0.0090 (11)	0.0240 (11)	0.0084 (11)
C11	0.0454 (18)	0.0338 (15)	0.0455 (16)	0.0060 (13)	0.0167 (14)	0.0081 (12)
C12	0.0377 (17)	0.0388 (16)	0.0512 (17)	0.0065 (13)	0.0172 (13)	0.0121 (14)
C13	0.0396 (17)	0.0387 (15)	0.0554 (17)	0.0060 (13)	0.0227 (14)	0.0039 (13)
C14	0.0396 (17)	0.0370 (15)	0.0560 (17)	0.0045 (13)	0.0237 (14)	0.0027 (13)
C15	0.0490 (18)	0.0407 (17)	0.0517 (17)	0.0095 (14)	0.0239 (15)	0.0049 (14)
O16	0.0550 (13)	0.0479 (12)	0.0560 (12)	0.0168 (10)	0.0316 (10)	0.0107 (9)
O17	0.110 (2)	0.0622 (15)	0.0876 (17)	0.0457 (15)	0.0674 (15)	0.0311 (13)
C18	0.0443 (18)	0.0428 (16)	0.0401 (15)	0.0089 (13)	0.0188 (14)	0.0044 (13)
C19	0.053 (2)	0.0585 (19)	0.0414 (16)	-0.0012 (15)	0.0157 (15)	-0.0035 (14)
C20	0.0387 (18)	0.081 (2)	0.0514 (18)	0.0058 (16)	0.0144 (15)	0.0060 (17)
C21	0.057 (2)	0.068 (2)	0.0418 (16)	0.0242 (17)	0.0241 (15)	0.0113 (15)
C22	0.068 (2)	0.057 (2)	0.0411 (16)	0.0115 (17)	0.0140 (16)	-0.0056 (14)
C23	0.0401 (17)	0.0562 (19)	0.0464 (16)	0.0050 (15)	0.0081 (14)	0.0026 (15)
Cl24	0.0976 (8)	0.1281 (9)	0.0771 (6)	0.0595 (7)	0.0531 (6)	0.0170 (6)
C25	0.0459 (19)	0.069 (2)	0.066 (2)	0.0127 (16)	0.0333 (16)	0.0015 (16)
S26	0.0369 (4)	0.0554 (5)	0.0466 (4)	-0.0024 (4)	0.0151 (3)	-0.0039 (4)
O27	0.0521 (13)	0.0545 (13)	0.0673 (14)	0.0069 (11)	0.0176 (11)	0.0104 (11)
O28	0.0590 (15)	0.1053 (19)	0.0566 (13)	0.0177 (13)	0.0296 (11)	0.0210 (13)
O29	0.0442 (13)	0.0904 (17)	0.0758 (15)	-0.0218 (12)	0.0157 (11)	-0.0182 (13)
C30	0.053 (2)	0.069 (2)	0.063 (2)	0.0070 (19)	0.0048 (17)	-0.0033 (18)
F31	0.0796 (16)	0.0704 (14)	0.1195 (18)	-0.0186 (12)	-0.0069 (14)	-0.0203 (13)
F32	0.1092 (19)	0.130 (2)	0.0568 (12)	0.0208 (15)	0.0297 (12)	-0.0186 (13)
F33	0.0931 (17)	0.0805 (15)	0.1065 (17)	0.0384 (13)	0.0016 (14)	-0.0116 (13)

Geometric parameters (Å, °)

C1—C2	1.349 (4)	C13—C14	1.428 (4)
C1—C11	1.417 (4)	C15—O17	1.186 (3)
C1—H1	0.9300	C15—O16	1.334 (3)
C2—C3	1.402 (5)	O16—C18	1.423 (3)
C2—H2	0.9300	C18—C23	1.364 (4)
C3—C4	1.354 (5)	C18—C19	1.367 (4)
C3—H3	0.9300	C19—C20	1.384 (4)
C4—C12	1.415 (4)	C19—H19	0.9300
C4—H4	0.9300	C20—C21	1.366 (4)
C5—C6	1.353 (5)	C20—H20	0.9300
C5—C14	1.407 (4)	C21—C22	1.368 (4)
C5—H5	0.9300	C21—Cl24	1.739 (3)
C6—C7	1.401 (5)	C22—C23	1.386 (4)
C6—H6	0.9300	C22—H22	0.9300
C7—C8	1.341 (5)	C23—H23	0.9300
C7—H7	0.9300	C25—H25A	0.9600
C8—C13	1.418 (4)	C25—H25B	0.9600
C8—H8	0.9300	C25—H25C	0.9600
C9—C13	1.386 (4)	S26—O28	1.427 (2)
C9—C11	1.391 (4)	S26—O29	1.434 (2)
C9—C15	1.506 (4)	S26—O27	1.434 (2)

supplementary materials

N10—C12	1.367 (4)	S26—C30	1.801 (4)
N10—C14	1.372 (3)	C30—F33	1.330 (4)
N10—C25	1.485 (3)	C30—F31	1.333 (4)
C11—C12	1.429 (4)	C30—F32	1.335 (4)
C2—C1—C11	121.2 (3)	C5—C14—C13	118.9 (3)
C2—C1—H1	119.4	O17—C15—O16	125.0 (3)
C11—C1—H1	119.4	O17—C15—C9	122.7 (3)
C1—C2—C3	119.3 (3)	O16—C15—C9	112.2 (2)
C1—C2—H2	120.4	C15—O16—C18	116.4 (2)
C3—C2—H2	120.4	C23—C18—C19	122.7 (3)
C4—C3—C2	122.5 (3)	C23—C18—O16	118.8 (3)
C4—C3—H3	118.8	C19—C18—O16	118.3 (2)
C2—C3—H3	118.8	C18—C19—C20	118.3 (3)
C3—C4—C12	119.6 (3)	C18—C19—H19	120.8
C3—C4—H4	120.2	C20—C19—H19	120.8
C12—C4—H4	120.2	C21—C20—C19	119.5 (3)
C6—C5—C14	119.7 (3)	C21—C20—H20	120.3
C6—C5—H5	120.1	C19—C20—H20	120.3
C14—C5—H5	120.1	C20—C21—C22	121.8 (3)
C5—C6—C7	122.2 (3)	C20—C21—C124	119.2 (3)
C5—C6—H6	118.9	C22—C21—C124	119.0 (2)
C7—C6—H6	118.9	C21—C22—C23	119.1 (3)
C8—C7—C6	119.4 (3)	C21—C22—H22	120.4
C8—C7—H7	120.3	C23—C22—H22	120.4
C6—C7—H7	120.3	C18—C23—C22	118.6 (3)
C7—C8—C13	121.5 (3)	C18—C23—H23	120.7
C7—C8—H8	119.3	C22—C23—H23	120.7
C13—C8—H8	119.3	N10—C25—H25A	109.5
C13—C9—C11	121.7 (2)	N10—C25—H25B	109.5
C13—C9—C15	118.9 (3)	H25A—C25—H25B	109.5
C11—C9—C15	119.1 (3)	N10—C25—H25C	109.5
C12—N10—C14	122.3 (2)	H25A—C25—H25C	109.5
C12—N10—C25	118.6 (2)	H25B—C25—H25C	109.5
C14—N10—C25	119.1 (2)	O28—S26—O29	115.20 (14)
C9—C11—C1	122.9 (3)	O28—S26—O27	115.00 (13)
C9—C11—C12	118.2 (3)	O29—S26—O27	115.57 (14)
C1—C11—C12	118.9 (3)	O28—S26—C30	103.23 (17)
N10—C12—C4	121.8 (3)	O29—S26—C30	102.62 (16)
N10—C12—C11	119.6 (3)	O27—S26—C30	102.48 (14)
C4—C12—C11	118.6 (3)	F33—C30—F31	107.0 (3)
C9—C13—C8	122.9 (3)	F33—C30—F32	106.6 (3)
C9—C13—C14	118.8 (3)	F31—C30—F32	106.6 (3)
C8—C13—C14	118.3 (3)	F33—C30—S26	112.6 (2)
N10—C14—C5	122.0 (2)	F31—C30—S26	112.0 (2)
N10—C14—C13	119.1 (2)	F32—C30—S26	111.6 (3)
C11—C1—C2—C3	0.1 (5)	C6—C5—C14—C13	1.1 (5)
C1—C2—C3—C4	0.9 (5)	C9—C13—C14—N10	-1.0 (4)
C2—C3—C4—C12	-1.3 (5)	C8—C13—C14—N10	178.3 (3)

C14—C5—C6—C7	-0.3 (6)	C9—C13—C14—C5	179.6 (3)
C5—C6—C7—C8	-0.6 (7)	C8—C13—C14—C5	-1.1 (4)
C6—C7—C8—C13	0.6 (6)	C13—C9—C15—O17	-82.2 (4)
C13—C9—C11—C1	-176.2 (3)	C11—C9—C15—O17	92.9 (4)
C15—C9—C11—C1	8.8 (4)	C13—C9—C15—O16	96.9 (3)
C13—C9—C11—C12	4.3 (4)	C11—C9—C15—O16	-88.0 (3)
C15—C9—C11—C12	-170.7 (2)	O17—C15—O16—C18	1.9 (4)
C2—C1—C11—C9	179.9 (3)	C9—C15—O16—C18	-177.1 (2)
C2—C1—C11—C12	-0.6 (4)	C15—O16—C18—C23	-96.8 (3)
C14—N10—C12—C4	175.5 (2)	C15—O16—C18—C19	86.8 (3)
C25—N10—C12—C4	-6.3 (4)	C23—C18—C19—C20	0.4 (4)
C14—N10—C12—C11	-4.7 (4)	O16—C18—C19—C20	176.7 (3)
C25—N10—C12—C11	173.5 (2)	C18—C19—C20—C21	0.1 (5)
C3—C4—C12—N10	-179.4 (3)	C19—C20—C21—C22	-0.9 (5)
C3—C4—C12—C11	0.8 (4)	C19—C20—C21—C124	179.1 (2)
C9—C11—C12—N10	-0.1 (4)	C20—C21—C22—C23	1.1 (5)
C1—C11—C12—N10	-179.6 (2)	C124—C21—C22—C23	-178.9 (2)
C9—C11—C12—C4	179.7 (2)	C19—C18—C23—C22	-0.2 (4)
C1—C11—C12—C4	0.2 (4)	O16—C18—C23—C22	-176.4 (2)
C11—C9—C13—C8	177.0 (3)	C21—C22—C23—C18	-0.6 (4)
C15—C9—C13—C8	-8.0 (4)	O28—S26—C30—F33	-60.1 (3)
C11—C9—C13—C14	-3.8 (4)	O29—S26—C30—F33	60.0 (3)
C15—C9—C13—C14	171.2 (2)	O27—S26—C30—F33	-179.9 (3)
C7—C8—C13—C9	179.5 (3)	O28—S26—C30—F31	60.5 (3)
C7—C8—C13—C14	0.3 (5)	O29—S26—C30—F31	-179.4 (2)
C12—N10—C14—C5	-175.4 (3)	O27—S26—C30—F31	-59.2 (3)
C25—N10—C14—C5	6.4 (4)	O28—S26—C30—F32	180.0 (2)
C12—N10—C14—C13	5.2 (4)	O29—S26—C30—F32	-60.0 (3)
C25—N10—C14—C13	-173.0 (2)	O27—S26—C30—F32	60.2 (3)
C6—C5—C14—N10	-178.3 (3)		

Hydrogen-bond geometry (Å, °)

Cg4 is the centroid of the C18—C23 ring.

<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>
C3—H3...O28 ⁱ	0.93	2.59	3.328 (5)	136
C4—H4...O28	0.93	2.45	3.370 (4)	171
C5—H5...O27 ⁱⁱ	0.93	2.39	3.258 (4)	154
C6—H6...O29 ⁱⁱ	0.93	2.54	3.304 (5)	140
C8—H8...O29 ⁱⁱⁱ	0.93	2.59	3.332 (4)	137
C19—H19...O29 ⁱⁱⁱ	0.93	2.44	3.349 (4)	165
C25—H25C...O27	0.96	2.51	3.387 (4)	152
C25—H25B...Cg4 ^{iv}	0.96	2.65	3.519 (4)	151

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

Table 2

supplementary materials

C–F... π interactions (\AA , $^\circ$).

Cg1 and *Cg3* are the centroids of the C9/N10/C11–C14 and C5–C8/C13/C14 rings, respectively.

<i>X</i>	<i>I</i>	<i>J</i>	<i>I...J</i>	<i>X...J</i>	<i>X–I...J</i>
C30	F31	<i>Cg1</i> ⁱⁱ	3.570 (3)	3.916 (4)	94.4 (2)
C30	F32	<i>Cg1</i> ⁱⁱ	3.337 (3)	3.916 (4)	105.8 (2)
C30	F33	<i>Cg3</i> ⁱⁱ	3.387 (3)	4.073 (4)	111.9 (2)

Symmetry code: (ii) $-x + 3/2, y - 1/2, -z + 1/2$.

Table 3

π – π interactions (\AA , $^\circ$).

<i>I</i>	<i>J</i>	<i>CgI...CgJ</i>	Dihedral angle	<i>CgI</i> _Perp	<i>CgI</i> _Offset
2	4 ^v	3.987 (2)	2.96 (15)	3.477 (2)	1.951 (2)

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

Notes: *Cg2* and *Cg4* are the centroids of the C1–C4/C11/C12 and C18–C23 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 perpendicular projection of *CgJ* on ring *I*.

Fig. 1

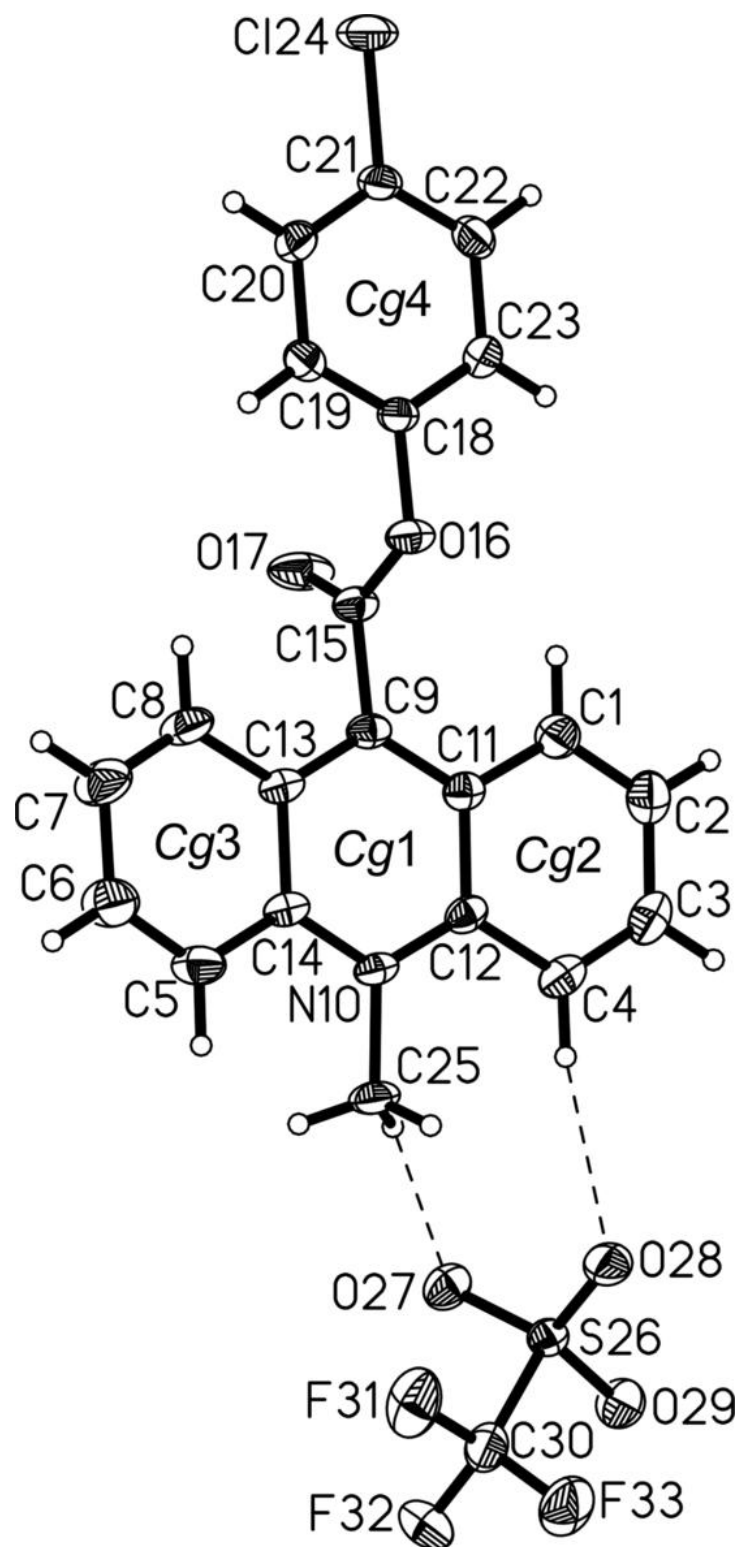


Fig. 2

