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# 9-(2,5-Dimethylphenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate

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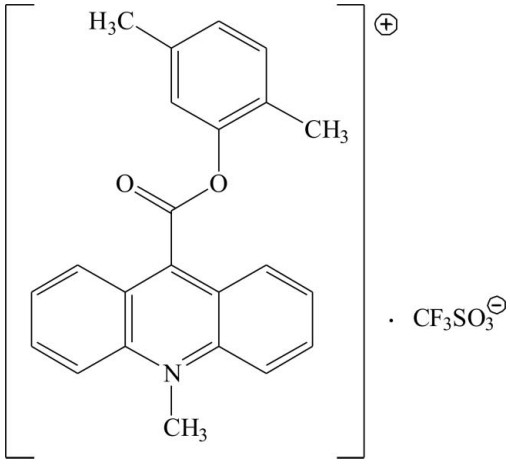
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.061; $wR$ factor = 0.185; data-to-parameter ratio = 12.9.

In the title compound, $C_{23}H_{20}NO_2^+\cdot CF_3SO_3^-$, the acridine ring system is oriented at a dihedral angle of 23.1 (1)° with respect to the benzene ring and the carboxyl group is twisted at an angle of 74.1 (1)° relative to the acridine skeleton. In the crystal, adjacent cations are linked through C—H···$\pi$ interactions and neighboring cations and anions *via* weak C—H···O hydrogen bonds. The mean planes of adjacent acridine units are either parallel or inclined at angles of 15.0 (1), 26.9 (1) and 48.1 (1)° in the crystal structure.

## Related literature

For general background to the chemiluminogenic properties of 9-phenoxycarbonyl-10-methylacridinium trifluoromethanesulfonates, see: Brown *et al.* (2009); King *et al.* (2007); Krzymiński *et al.* (2011); Roda *et al.* (2003). For related structures, see: Krzymiński *et al.* (2009). For intermolecular interactions, see: Novoa *et al.* (2006); Takahashi *et al.* (2001). For the synthesis, see: Sato (1996); Krzymiński *et al.* (2011).




## Experimental

### Crystal data

$C_{23}H_{20}NO_2^+\cdot CF_3SO_3^-$
$M_r$ = 491.48
Orthorhombic, *Pbca*
$a$ = 12.3604 (17) Å
$b$ = 17.341 (3) Å
$c$ = 21.101 (3) Å
$V$ = 4522.8 (12) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.21 mm$^{-1}$
$T$ = 295 K
0.60 × 0.15 × 0.10 mm

### Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
$T_{min}$ = 0.960, $T_{max}$ = 0.985
32535 measured reflections
4000 independent reflections
2050 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.106

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.185
$S$ = 1.01
4000 reflections
310 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

*Cg*2 is the centroid of the C1–C4/C11/C12 benzene ring.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C4—H4···O29$^{i}$ | 0.93 | 2.59 | 3.257 (5) | 129 |
| C5—H5···O30 | 0.93 | 2.58 | 3.466 (5) | 160 |
| C6—H6···O28 | 0.93 | 2.52 | 3.303 (5) | 142 |
| C7—H7···O29$^{ii}$ | 0.93 | 2.39 | 3.188 (5) | 144 |
| C20—H20···*Cg*2$^{iii}$ | 0.93 | 2.81 | 3.439 (4) | 126 |
| C25—H25*B*···O28$^{ii}$ | 0.96 | 2.49 | 3.289 (5) | 141 |
| C26—H26*A*···O30$^{i}$ | 0.96 | 2.47 | 3.314 (5) | 146 |

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5358).

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# supplementary materials

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# 9-(2,5-Dimethylphenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate

**D. Trzybinski, K. Krzyminski and J. Blazejowski**

## Comment

Chemiluminescing 9-(phenoxycarbonyl)-10-methylacridinium cations are widely applied as indicators or fragments of labels in assays of biologically and environmentally important entities such as antigens, antibodies, enzymes or DNA fragments (Roda *et al.*, 2003; King *et al.*, 2007; Brown *et al.*, 2009). The cations of these salts are oxidized by $H_2O_2$ in alkaline media, a reaction that is accompanied by the removal of the phenoxycarbonyl fragment and the conversion of the remaining part of the molecules to electronically excited, light-emitting 10-methyl-9-acridinone (Krzymiński *et al.*, 2011). The efficiency of chemiluminescence – crucial to analytical applications – is affected by the constitution of the phenyl fragment. Here we present the crystal structure of 9-(2,5-dimethylphenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate, whose chemiluminogenic features we have thoroughly investigated (Krzymiński *et al.*, 2011).

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 (Krzymiński *et al.*, 2009). With respective average deviations from planarity of 0.022 (3) Å and 0.006 (3) Å, the acridine and benzene ring systems are oriented at a dihedral angle of 23.1 (1)°. The carboxyl group is twisted at an angle of 74.1 (1)° relative to the acridine skeleton. The mean planes of the adjacent acridine moieties are parallel (at an angle 0.0 (1)°) or inclined at angles of 15.0 (1), 26.9 (1) and 48.1 (1)° in the crystal lattice.

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

## Experimental

2,5-Dimethylphenylacridine-9-carboxylate was synthesized by esterification of 9-(chlorocarbonyl)acridine (obtained in the reaction of acridine-9-carboxylic acid with a tenfold molar excess of thionyl chloride) with 2,5-dimethylphenol in anhydrous dichloromethane in the presence of N,N-diethylethanamine and a catalytic amount of N,N-dimethyl-4-pyridinamine (room temperature, 15 h) (Sato, 1996; Krzymiński *et al.*, 2011). The product was purified chromatographically ($SiO_2$, 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-(2,5-dimethylphenoxycarbonyl)-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 ethanol/water solution (1:1 v/v) (m.p. 509–511 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 $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for the aromatic and $x = 1.5$ for the methyl H atoms.

**Figures**

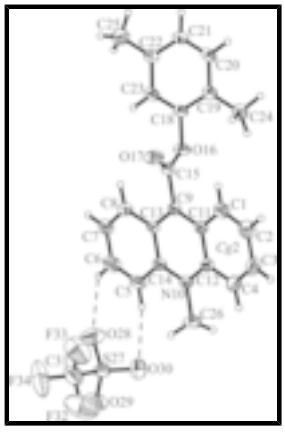


Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radius. *Cg*2 denotes the ring centroid. The C–H···O interactions are represented by dashed lines.

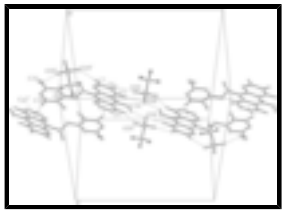


Fig. 2. The arrangement of the ions in the crystal structure. The C–H···O interactions are represented by dashed lines, the C–H···π contacts by dotted lines. H atoms not involved in interactions have been omitted. [Symmetry codes: (i) –*x* + 1, –*y* + 1, –*z* + 1; (ii) –*x* + 1, *y* – 1/2, –*z* + 1/2;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

**9-(2,5-Dimethylphenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate**

*Crystal data*

| | |
|---|---|
| $C_{23}H_{20}NO_2^+ \cdot CF_3SO_3^-$ | $F(000) = 2032$ |
| $M_r = 491.48$ | $D_x = 1.444$ Mg m$^{-3}$ |
| Orthorhombic, *Pbca* | Mo *K*α radiation, λ = 0.71073 Å |
| Hall symbol: -P 2ac 2ab | Cell parameters from 4734 reflections |
| *a* = 12.3604 (17) Å | θ = 3.4–26.0° |
| *b* = 17.341 (3) Å | μ = 0.21 mm$^{-1}$ |
| *c* = 21.101 (3) Å | *T* = 295 K |
| *V* = 4522.8 (12) Å$^3$ | Needle, yellow |
| *Z* = 8 | 0.60 × 0.15 × 0.10 mm |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer | 4000 independent reflections |
| Radiation source: enhanced (Mo) X-ray source | 2050 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.106$ |
| Detector resolution: 10.4002 pixels mm$^{-1}$ | $\theta_{max} = 25.1°$, $\theta_{min} = 3.5°$ |
| ω scans | $h = -14 \rightarrow 12$ |
| Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008) | $k = -20 \rightarrow 20$ |
| $T_{min} = 0.960$, $T_{max} = 0.985$ | $l = -23 \rightarrow 25$ |
| 32535 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.185$ | H-atom parameters constrained |
| $S = 1.01$ | $w = 1/[\sigma^2(F_o^2) + (0.0901P)^2 + 0.2728P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 4000 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 310 parameters | $\Delta\rho_{max} = 0.36$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.23$ 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 | 0.7203 (3) | 0.1485 (2) | 0.5953 (2) | 0.0692 (11) |
| H1 | 0.7452 | 0.0981 | 0.5906 | 0.083* |
| C2 | 0.7290 (4) | 0.1843 (3) | 0.6520 (2) | 0.0872 (14) |
| H2 | 0.7599 | 0.1587 | 0.6863 | 0.105* |
| C3 | 0.6911 (4) | 0.2608 (3) | 0.6593 (2) | 0.0858 (14) |
| H3 | 0.6977 | 0.2849 | 0.6984 | 0.103* |
| C4 | 0.6455 (3) | 0.2995 (2) | 0.6105 (2) | 0.0713 (12) |
| H4 | 0.6197 | 0.3493 | 0.6167 | 0.086* |
| C5 | 0.5462 (3) | 0.3125 (2) | 0.3893 (2) | 0.0667 (11) |
| H5 | 0.5235 | 0.3633 | 0.3943 | 0.080* |
| C6 | 0.5383 (4) | 0.2782 (2) | 0.3321 (2) | 0.0815 (13) |
| H6 | 0.5102 | 0.3061 | 0.2981 | 0.098* |
| C7 | 0.5711 (4) | 0.2021 (2) | 0.3224 (2) | 0.0720 (12) |
| H7 | 0.5637 | 0.1796 | 0.2826 | 0.086* |
| C8 | 0.6132 (3) | 0.1613 (2) | 0.3704 (2) | 0.0600 (10) |
| H8 | 0.6365 | 0.1111 | 0.3633 | 0.072* |
| C9 | 0.6641 (3) | 0.15331 (18) | 0.48358 (18) | 0.0474 (9) |
| N10 | 0.5964 (2) | 0.30431 (15) | 0.50005 (16) | 0.0503 (7) |
| C11 | 0.6738 (3) | 0.18708 (19) | 0.54298 (17) | 0.0502 (9) |
| C12 | 0.6370 (3) | 0.26519 (19) | 0.55098 (19) | 0.0503 (9) |
| C13 | 0.6231 (2) | 0.19343 (17) | 0.43212 (17) | 0.0452 (9) |
| C14 | 0.5886 (3) | 0.27166 (18) | 0.44149 (19) | 0.0493 (9) |
| C15 | 0.7004 (3) | 0.07054 (19) | 0.47513 (17) | 0.0504 (9) |

| | | | | |
|---|---|---|---|---|
| O16 | 0.61431 (18) | 0.02474 (12) | 0.47079 (13) | 0.0576 (7) |
| O17 | 0.7921 (2) | 0.05008 (14) | 0.47341 (14) | 0.0755 (9) |
| C18 | 0.6283 (3) | −0.05622 (18) | 0.46459 (19) | 0.0483 (9) |
| C19 | 0.6315 (3) | −0.09995 (19) | 0.51964 (19) | 0.0518 (9) |
| C20 | 0.6311 (2) | −0.1796 (2) | 0.5100 (2) | 0.0563 (10) |
| H20 | 0.6318 | −0.2121 | 0.5451 | 0.068* |
| C21 | 0.6297 (3) | −0.2116 (2) | 0.4508 (2) | 0.0552 (10) |
| H21 | 0.6294 | −0.2650 | 0.4468 | 0.066* |
| C22 | 0.6289 (3) | −0.16674 (19) | 0.39689 (19) | 0.0542 (10) |
| C23 | 0.6272 (3) | −0.08684 (19) | 0.4050 (2) | 0.0553 (10) |
| H23 | 0.6252 | −0.0545 | 0.3699 | 0.066* |
| C24 | 0.6348 (3) | −0.0649 (2) | 0.5843 (2) | 0.0699 (11) |
| H24A | 0.5841 | −0.0231 | 0.5865 | 0.105* |
| H24B | 0.7063 | −0.0459 | 0.5927 | 0.105* |
| H24C | 0.6161 | −0.1032 | 0.6153 | 0.105* |
| C25 | 0.6290 (4) | −0.2022 (2) | 0.3319 (2) | 0.0846 (13) |
| H25A | 0.7006 | −0.1995 | 0.3143 | 0.127* |
| H25B | 0.5796 | −0.1746 | 0.3051 | 0.127* |
| H25C | 0.6070 | −0.2552 | 0.3348 | 0.127* |
| C26 | 0.5592 (3) | 0.38590 (18) | 0.5077 (2) | 0.0727 (12) |
| H26A | 0.5623 | 0.4000 | 0.5517 | 0.109* |
| H26B | 0.4862 | 0.3906 | 0.4927 | 0.109* |
| H26C | 0.6054 | 0.4194 | 0.4836 | 0.109* |
| S27 | 0.44245 (10) | 0.50390 (5) | 0.30301 (6) | 0.0740 (4) |
| O28 | 0.4254 (3) | 0.43431 (19) | 0.2715 (2) | 0.1310 (14) |
| O29 | 0.3900 (3) | 0.57019 (19) | 0.2803 (2) | 0.1239 (13) |
| O30 | 0.4320 (3) | 0.4936 (2) | 0.37051 (17) | 0.1162 (12) |
| C31 | 0.5832 (5) | 0.5223 (4) | 0.2920 (3) | 0.1130 (19) |
| F32 | 0.6101 (4) | 0.5876 (3) | 0.3223 (3) | 0.218 (3) |
| F33 | 0.6458 (3) | 0.4707 (3) | 0.3148 (2) | 0.1741 (18) |
| F34 | 0.6094 (4) | 0.5364 (4) | 0.2353 (3) | 0.221 (3) |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.084 (3) | 0.060 (2) | 0.064 (3) | 0.000 (2) | −0.005 (2) | 0.006 (2) |
| C2 | 0.113 (4) | 0.092 (4) | 0.056 (3) | 0.000 (3) | −0.015 (3) | 0.008 (3) |
| C3 | 0.103 (3) | 0.097 (4) | 0.058 (3) | −0.004 (3) | 0.010 (3) | −0.017 (3) |
| C4 | 0.074 (3) | 0.072 (3) | 0.068 (3) | 0.001 (2) | 0.009 (2) | −0.011 (3) |
| C5 | 0.085 (3) | 0.039 (2) | 0.076 (3) | 0.0017 (18) | −0.002 (2) | 0.014 (2) |
| C6 | 0.115 (4) | 0.061 (3) | 0.069 (3) | 0.000 (2) | −0.019 (3) | 0.016 (3) |
| C7 | 0.107 (3) | 0.059 (3) | 0.050 (3) | −0.010 (2) | −0.005 (2) | 0.002 (2) |
| C8 | 0.076 (3) | 0.044 (2) | 0.061 (3) | −0.0047 (17) | 0.006 (2) | −0.002 (2) |
| C9 | 0.0457 (18) | 0.0386 (18) | 0.058 (3) | −0.0028 (14) | 0.0055 (17) | 0.0033 (18) |
| N10 | 0.0522 (16) | 0.0377 (15) | 0.061 (2) | −0.0010 (12) | 0.0015 (15) | −0.0024 (16) |
| C11 | 0.057 (2) | 0.045 (2) | 0.049 (2) | −0.0060 (16) | 0.0012 (18) | 0.0022 (19) |
| C12 | 0.0508 (19) | 0.049 (2) | 0.051 (3) | −0.0053 (16) | 0.0118 (17) | −0.005 (2) |
| C13 | 0.0497 (19) | 0.0353 (18) | 0.051 (2) | −0.0035 (14) | 0.0058 (16) | 0.0035 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C14 | 0.052 (2) | 0.0384 (18) | 0.057 (3) | −0.0064 (15) | 0.0017 (18) | 0.0023 (19) |
| C15 | 0.054 (2) | 0.0421 (19) | 0.056 (3) | 0.0008 (17) | 0.0040 (18) | 0.0039 (17) |
| O16 | 0.0504 (14) | 0.0342 (12) | 0.088 (2) | 0.0021 (10) | 0.0011 (13) | 0.0011 (13) |
| O17 | 0.0518 (16) | 0.0522 (15) | 0.123 (3) | 0.0057 (12) | 0.0045 (16) | −0.0069 (16) |
| C18 | 0.0467 (19) | 0.0346 (18) | 0.064 (3) | 0.0009 (14) | −0.0008 (18) | 0.0045 (19) |
| C19 | 0.0448 (19) | 0.048 (2) | 0.062 (3) | −0.0001 (15) | −0.0006 (18) | 0.005 (2) |
| C20 | 0.050 (2) | 0.047 (2) | 0.072 (3) | −0.0021 (16) | −0.0019 (19) | 0.023 (2) |
| C21 | 0.051 (2) | 0.0379 (19) | 0.076 (3) | −0.0014 (15) | −0.0022 (19) | 0.005 (2) |
| C22 | 0.058 (2) | 0.044 (2) | 0.061 (3) | 0.0023 (16) | −0.0029 (19) | 0.003 (2) |
| C23 | 0.061 (2) | 0.042 (2) | 0.062 (3) | 0.0027 (16) | −0.0010 (19) | 0.014 (2) |
| C24 | 0.075 (3) | 0.071 (3) | 0.064 (3) | −0.001 (2) | 0.001 (2) | 0.003 (2) |
| C25 | 0.117 (4) | 0.064 (3) | 0.073 (3) | 0.004 (2) | −0.008 (3) | −0.004 (2) |
| C26 | 0.087 (3) | 0.040 (2) | 0.092 (3) | 0.0105 (19) | 0.001 (2) | −0.013 (2) |
| S27 | 0.1049 (9) | 0.0443 (6) | 0.0728 (9) | 0.0084 (5) | −0.0034 (6) | −0.0028 (6) |
| O28 | 0.172 (4) | 0.080 (2) | 0.141 (4) | 0.003 (2) | −0.026 (3) | −0.040 (2) |
| O29 | 0.140 (3) | 0.080 (2) | 0.152 (4) | 0.027 (2) | −0.003 (3) | 0.034 (2) |
| O30 | 0.166 (4) | 0.112 (3) | 0.071 (2) | 0.007 (2) | 0.020 (2) | 0.007 (2) |
| C31 | 0.130 (5) | 0.102 (4) | 0.108 (5) | −0.007 (4) | 0.007 (4) | 0.029 (4) |
| F32 | 0.187 (4) | 0.143 (4) | 0.323 (8) | −0.075 (3) | −0.048 (4) | 0.026 (4) |
| F33 | 0.110 (3) | 0.186 (4) | 0.227 (5) | 0.038 (2) | 0.005 (2) | 0.091 (3) |
| F34 | 0.167 (4) | 0.357 (7) | 0.139 (4) | 0.025 (4) | 0.059 (3) | 0.111 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.354 (6) | O16—C18 | 1.421 (4) |
| C1—C11 | 1.413 (5) | C18—C23 | 1.364 (5) |
| C1—H1 | 0.9300 | C18—C19 | 1.388 (5) |
| C2—C3 | 1.415 (6) | C19—C20 | 1.397 (5) |
| C2—H2 | 0.9300 | C19—C24 | 1.495 (5) |
| C3—C4 | 1.352 (6) | C20—C21 | 1.367 (5) |
| C3—H3 | 0.9300 | C20—H20 | 0.9300 |
| C4—C12 | 1.394 (5) | C21—C22 | 1.378 (5) |
| C4—H4 | 0.9300 | C21—H21 | 0.9300 |
| C5—C6 | 1.349 (6) | C22—C23 | 1.396 (5) |
| C5—C14 | 1.411 (5) | C22—C25 | 1.503 (6) |
| C5—H5 | 0.9300 | C23—H23 | 0.9300 |
| C6—C7 | 1.397 (6) | C24—H24A | 0.9600 |
| C6—H6 | 0.9300 | C24—H24B | 0.9600 |
| C7—C8 | 1.340 (5) | C24—H24C | 0.9600 |
| C7—H7 | 0.9300 | C25—H25A | 0.9600 |
| C8—C13 | 1.421 (5) | C25—H25B | 0.9600 |
| C8—H8 | 0.9300 | C25—H25C | 0.9600 |
| C9—C13 | 1.386 (5) | C26—H26A | 0.9600 |
| C9—C11 | 1.389 (5) | C26—H26B | 0.9600 |
| C9—C15 | 1.514 (5) | C26—H26C | 0.9600 |
| N10—C14 | 1.363 (4) | S27—O28 | 1.394 (3) |
| N10—C12 | 1.366 (4) | S27—O29 | 1.404 (3) |
| N10—C26 | 1.496 (4) | S27—O30 | 1.441 (4) |
| C11—C12 | 1.439 (5) | S27—C31 | 1.784 (7) |

| | | | |
|---|---|---|---|
| C13—C14 | 1.436 (4) | C31—F34 | 1.264 (6) |
| C15—O17 | 1.188 (4) | C31—F33 | 1.276 (6) |
| C15—O16 | 1.331 (4) | C31—F32 | 1.343 (7) |
| C2—C1—C11 | 120.4 (4) | C23—C18—O16 | 117.9 (3) |
| C2—C1—H1 | 119.8 | C19—C18—O16 | 117.8 (3) |
| C11—C1—H1 | 119.8 | C18—C19—C20 | 114.7 (4) |
| C1—C2—C3 | 120.0 (4) | C18—C19—C24 | 122.9 (3) |
| C1—C2—H2 | 120.0 | C20—C19—C24 | 122.4 (4) |
| C3—C2—H2 | 120.0 | C21—C20—C19 | 122.3 (4) |
| C4—C3—C2 | 121.4 (4) | C21—C20—H20 | 118.8 |
| C4—C3—H3 | 119.3 | C19—C20—H20 | 118.8 |
| C2—C3—H3 | 119.3 | C20—C21—C22 | 121.7 (3) |
| C3—C4—C12 | 120.4 (4) | C20—C21—H21 | 119.2 |
| C3—C4—H4 | 119.8 | C22—C21—H21 | 119.2 |
| C12—C4—H4 | 119.8 | C21—C22—C23 | 117.3 (4) |
| C6—C5—C14 | 120.3 (4) | C21—C22—C25 | 121.4 (3) |
| C6—C5—H5 | 119.8 | C23—C22—C25 | 121.2 (4) |
| C14—C5—H5 | 119.8 | C18—C23—C22 | 120.0 (3) |
| C5—C6—C7 | 121.7 (4) | C18—C23—H23 | 120.0 |
| C5—C6—H6 | 119.1 | C22—C23—H23 | 120.0 |
| C7—C6—H6 | 119.1 | C19—C24—H24A | 109.5 |
| C8—C7—C6 | 120.1 (4) | C19—C24—H24B | 109.5 |
| C8—C7—H7 | 120.0 | H24A—C24—H24B | 109.5 |
| C6—C7—H7 | 120.0 | C19—C24—H24C | 109.5 |
| C7—C8—C13 | 121.3 (3) | H24A—C24—H24C | 109.5 |
| C7—C8—H8 | 119.3 | H24B—C24—H24C | 109.5 |
| C13—C8—H8 | 119.3 | C22—C25—H25A | 109.5 |
| C13—C9—C11 | 121.8 (3) | C22—C25—H25B | 109.5 |
| C13—C9—C15 | 119.5 (3) | H25A—C25—H25B | 109.5 |
| C11—C9—C15 | 118.7 (3) | C22—C25—H25C | 109.5 |
| C14—N10—C12 | 122.2 (3) | H25A—C25—H25C | 109.5 |
| C14—N10—C26 | 118.0 (3) | H25B—C25—H25C | 109.5 |
| C12—N10—C26 | 119.8 (3) | N10—C26—H26A | 109.5 |
| C9—C11—C1 | 122.7 (3) | N10—C26—H26B | 109.5 |
| C9—C11—C12 | 118.4 (3) | H26A—C26—H26B | 109.5 |
| C1—C11—C12 | 118.9 (3) | N10—C26—H26C | 109.5 |
| N10—C12—C4 | 121.6 (3) | H26A—C26—H26C | 109.5 |
| N10—C12—C11 | 119.4 (3) | H26B—C26—H26C | 109.5 |
| C4—C12—C11 | 118.9 (4) | O28—S27—O29 | 118.4 (3) |
| C9—C13—C8 | 123.5 (3) | O28—S27—O30 | 110.5 (2) |
| C9—C13—C14 | 118.4 (3) | O29—S27—O30 | 113.4 (2) |
| C8—C13—C14 | 118.1 (3) | O28—S27—C31 | 103.9 (3) |
| N10—C14—C5 | 121.7 (3) | O29—S27—C31 | 105.1 (3) |
| N10—C14—C13 | 119.8 (3) | O30—S27—C31 | 103.8 (3) |
| C5—C14—C13 | 118.5 (3) | F34—C31—F33 | 109.8 (6) |
| O17—C15—O16 | 125.6 (3) | F34—C31—F32 | 102.9 (6) |
| O17—C15—C9 | 124.7 (3) | F33—C31—F32 | 105.2 (6) |
| O16—C15—C9 | 109.7 (3) | F34—C31—S27 | 114.0 (5) |
| C15—O16—C18 | 119.9 (2) | F33—C31—S27 | 114.6 (5) |

| | | | |
|---|---|---|---|
| C23—C18—C19 | 124.0 (3) | F32—C31—S27 | 109.3 (5) |
| C11—C1—C2—C3 | 0.1 (6) | C9—C13—C14—N10 | −0.3 (4) |
| C1—C2—C3—C4 | 0.2 (7) | C8—C13—C14—N10 | 179.7 (3) |
| C2—C3—C4—C12 | −1.5 (7) | C9—C13—C14—C5 | −179.6 (3) |
| C14—C5—C6—C7 | 0.1 (6) | C8—C13—C14—C5 | 0.4 (5) |
| C5—C6—C7—C8 | −1.0 (7) | C13—C9—C15—O17 | 105.8 (4) |
| C6—C7—C8—C13 | 1.6 (6) | C11—C9—C15—O17 | −73.8 (5) |
| C13—C9—C11—C1 | −176.8 (3) | C13—C9—C15—O16 | −74.9 (4) |
| C15—C9—C11—C1 | 2.8 (5) | C11—C9—C15—O16 | 105.5 (3) |
| C13—C9—C11—C12 | 1.7 (5) | O17—C15—O16—C18 | 1.2 (6) |
| C15—C9—C11—C12 | −178.7 (3) | C9—C15—O16—C18 | −178.1 (3) |
| C2—C1—C11—C9 | 179.2 (4) | C15—O16—C18—C23 | −95.3 (4) |
| C2—C1—C11—C12 | 0.7 (5) | C15—O16—C18—C19 | 91.0 (4) |
| C14—N10—C12—C4 | 179.4 (3) | C23—C18—C19—C20 | −1.3 (5) |
| C26—N10—C12—C4 | −0.3 (5) | O16—C18—C19—C20 | 172.0 (3) |
| C14—N10—C12—C11 | 0.4 (5) | C23—C18—C19—C24 | 178.8 (3) |
| C26—N10—C12—C11 | −179.2 (3) | O16—C18—C19—C24 | −7.9 (5) |
| C3—C4—C12—N10 | −176.6 (4) | C18—C19—C20—C21 | 1.1 (5) |
| C3—C4—C12—C11 | 2.3 (5) | C24—C19—C20—C21 | −178.9 (3) |
| C9—C11—C12—N10 | −1.5 (5) | C19—C20—C21—C22 | 0.2 (5) |
| C1—C11—C12—N10 | 177.0 (3) | C20—C21—C22—C23 | −1.4 (5) |
| C9—C11—C12—C4 | 179.5 (3) | C20—C21—C22—C25 | 179.1 (3) |
| C1—C11—C12—C4 | −1.9 (5) | C19—C18—C23—C22 | 0.1 (5) |
| C11—C9—C13—C8 | 179.1 (3) | O16—C18—C23—C22 | −173.1 (3) |
| C15—C9—C13—C8 | −0.4 (5) | C21—C22—C23—C18 | 1.2 (5) |
| C11—C9—C13—C14 | −0.8 (5) | C25—C22—C23—C18 | −179.3 (3) |
| C15—C9—C13—C14 | 179.6 (3) | O28—S27—C31—F34 | 67.3 (6) |
| C7—C8—C13—C9 | 178.7 (3) | O29—S27—C31—F34 | −57.8 (6) |
| C7—C8—C13—C14 | −1.3 (5) | O30—S27—C31—F34 | −177.1 (6) |
| C12—N10—C14—C5 | 179.8 (3) | O28—S27—C31—F33 | −60.5 (6) |
| C26—N10—C14—C5 | −0.5 (5) | O29—S27—C31—F33 | 174.5 (5) |
| C12—N10—C14—C13 | 0.5 (4) | O30—S27—C31—F33 | 55.1 (6) |
| C26—N10—C14—C13 | −179.8 (3) | O28—S27—C31—F32 | −178.2 (5) |
| C6—C5—C14—N10 | −179.2 (4) | O29—S27—C31—F32 | 56.7 (5) |
| C6—C5—C14—C13 | 0.2 (5) | O30—S27—C31—F32 | −62.6 (5) |

*Hydrogen-bond geometry (Å, °)*

*Cg*2 is the centroid of the C1–C4/C11/C12 benzene ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4···O29$^{i}$ | 0.93 | 2.59 | 3.257 (5) | 129 |
| C5—H5···O30 | 0.93 | 2.58 | 3.466 (5) | 160 |
| C6—H6···O28 | 0.93 | 2.52 | 3.303 (5) | 142 |
| C7—H7···O29$^{ii}$ | 0.93 | 2.39 | 3.188 (5) | 144 |
| C20—H20···Cg2$^{iii}$ | 0.93 | 2.81 | 3.439 (4) | 126 |
| C25—H25B···O28$^{ii}$ | 0.96 | 2.49 | 3.289 (5) | 141 |
| C26—H26A···O30$^{i}$ | 0.96 | 2.47 | 3.314 (5) | 146 |

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

**Fig. 1**

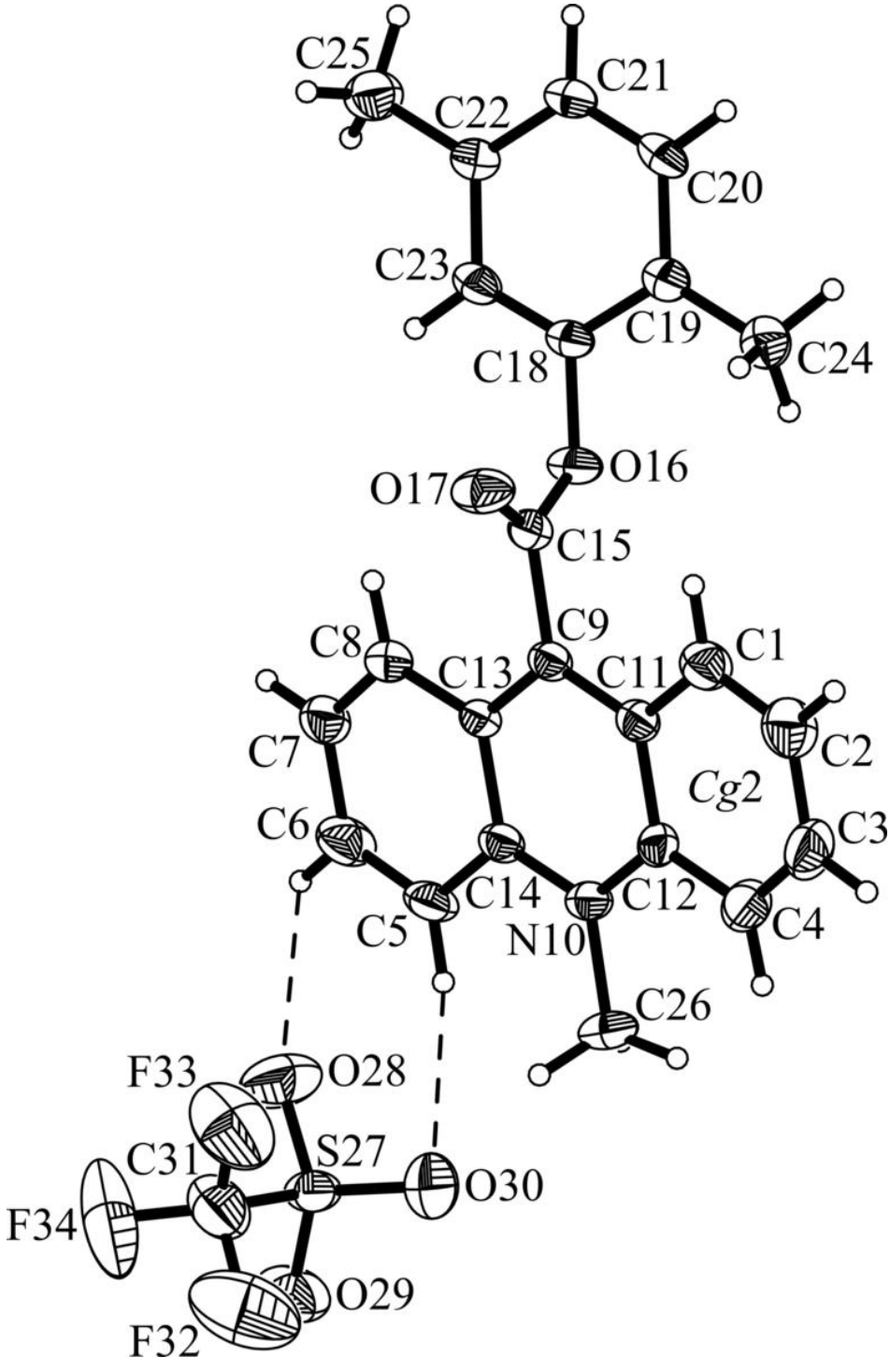
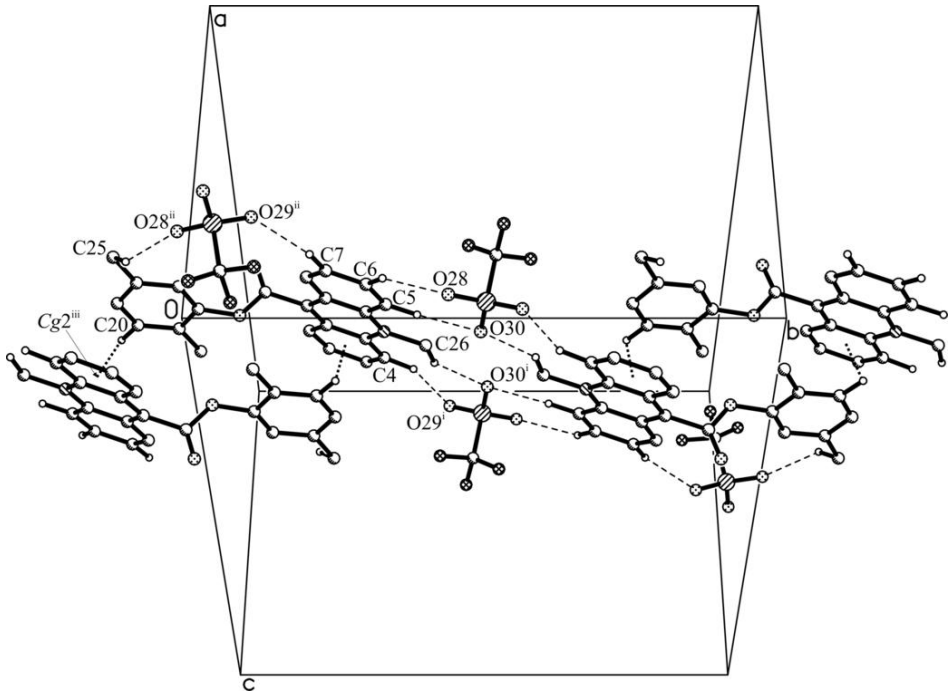

C25
C21
C22
C20
C23
C19
C24
C18
O16
O17
C15
C9
C8
C13
C11
C1
C7
C2
Cg2
C6
C3
C14
C12
C5
N10
C4
C26
F33
O28
C31
S27
O30
F34
O29
F32

**Fig. 2**


a
b
c
O28ii
O29ii
C25
C7
C6
C5
O28
O30
C26
C4
O30i
O29i
Cg2iii
C20