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

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Key indicators

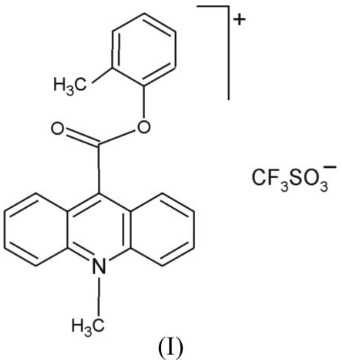
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.067
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the triclinic crystalline phase of the title compound, $C_{22}H_{18}NO_2^+\cdot CF_3O_3S^-$, the mean planes of the acridine ring systems lie parallel to each other. The benzene rings are also parallel. However, the acridine system and benzene ring in each cation are inclined at an angle of 28.5 (1)°, and the acridine system and carboxyl group are at an angle of 87.8 (2)° to each other. The structure is stabilized by C—H$\cdots$O and C—H$\cdots\pi$ hydrogen bonds and π–π interactions.

Comment

Phenyl 10-alkylacridinium-9-carboxylates have been successfully applied as chemiluminescent indicators or as the chemiluminogenic fragments of chemiluminescent labels, which are widely used in assays of biologically and environmentally important entities such as antigens, antibodies, enzymes or DNA fragments (Goto *et al.*, 1991; Yang *et al.*, 2002; Adamczyk *et al.*, 2004). The reactions of these cations with hydrogen peroxide in alkaline media produce light, and the determination of its intensity enables labelled entities to be assayed quantitatively at the attomole level (Roda *et al.*, 2003). Our own investigations (Rak *et al.*, 1999) and those of others (Dodeigne *et al.*, 2000; Zomer & Jacquemijns, 2001) have revealed that oxidation of these compounds removes the phenyl fragment and converts the rest of the molecule to electronically excited light-emitting 10-methyl-9-acridinones. The efficiency of the chemiluminescence should thus be affected by changes in the constitution of the phenyl ester fragment. In order to investigate this possibility, comprehensive studies were undertaken to establish how different substituents in the phenyl fragment influence the structure and properties of this group of compounds (Sikorski *et al.*, 2005). Here, we present the crystal structure of the title compound, (I).



(I)

Table 1 gives parameters characterizing the geometries of the central acridine ring and the ester fragment. They are

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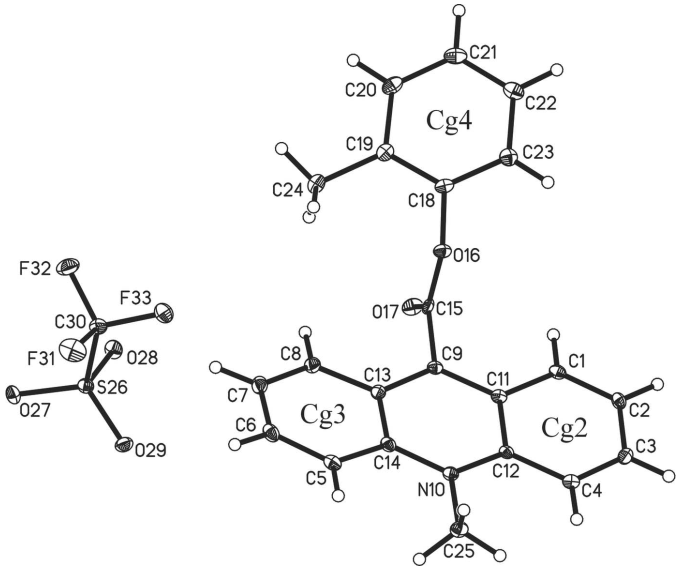

Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

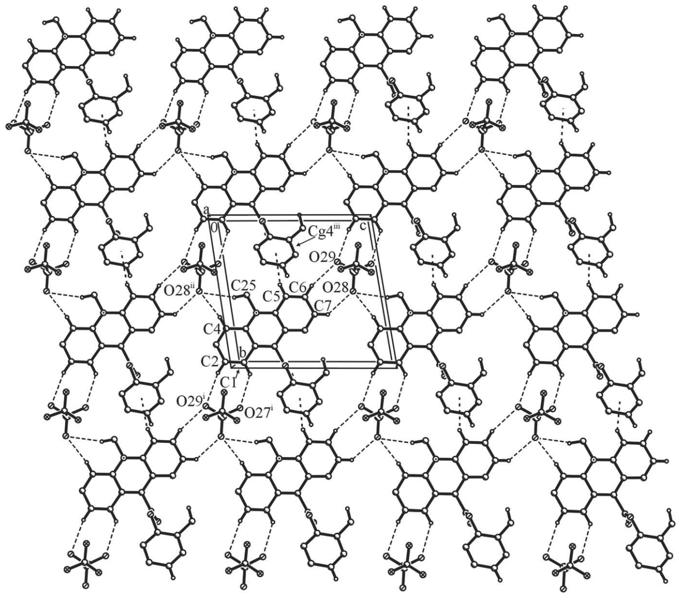

Figure 2
The arrangement of the ions of (I) in the (100) plane of the crystal. The C—H···O and C—H···π interactions are represented by dashed lines. H atoms not involved in these interactions have been omitted [symmetry codes: (i) $x, y + 1, z - 1$; (ii) $x, y, z - 1$; (iii) $x, y - 1, z$].

typical of acridine-based derivatives (Hempel *et al.*, 1979; Meszko *et al.*, 2002; Mrozek *et al.*, 2002; Sikorski *et al.*, 2005).

With respective average deviations from planarity of 0.007 and 0.015 Å, the acridine and benzene ring systems in the cation are oriented at 28.5 (1)° to each other (Fig. 1). The carboxyl group is twisted at an angle of 87.8 (2)° relative to the acridine skeleton. The mean planes of the acridine ring systems lie parallel to each other in the crystalline phase. The benzene rings are also parallel.

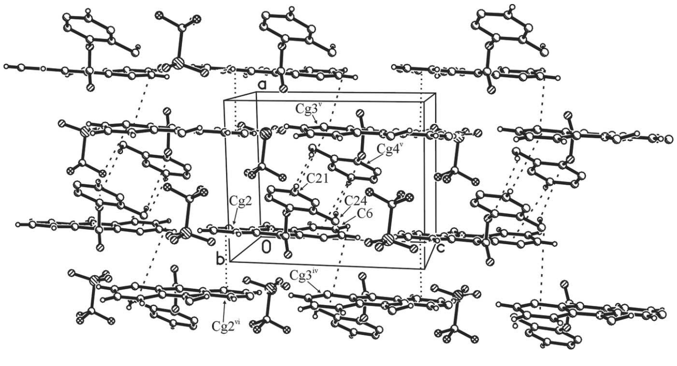

Figure 3
The arrangement of the ions of (I), viewed approximately along the [010] axis. C—H···π interactions are represented by dashed lines and π–π interactions by dotted lines. H atoms not involved in C—H···π interactions have been omitted [symmetry codes: (iv) $-x$, minus;$y + 1$, $-z + 1$; (v) $-x + 1, -y + 2, -z + 1$; (vi) $-x, -y + 2, -z$].

All of the O atoms of the trifluoromethanesulfonate anions are involved in weak C—H···O hydrogen bonds, resulting in layers parallel to the (100) plane (Table 2 and Fig. 2). Cations in the layer are additionally linked by C—H···π interactions (Table 2 and Fig. 2). Consecutive layers are linked by C—H···π hydrogen bonds, resulting in bilayer sheets (Table 2 and Fig. 3). Finally, as shown in Fig. 3, consecutive bilayer sheets are connected by C—H···π hydrogen bonds and π–π interactions (Table 3) between acridine rings of the cations.

Experimental

9-(2-Methylphenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate was synthesized by treating 2-methylphenyl acridine-9-carboxylate, obtained as described by Sikorski *et al.* (2006), 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 3 h). The crude salt was purified by repeated precipitation from ethanol–diethyl ether (1:20 *v*/*v*) solution (yield 82%). Elemental analysis (found/calculated): C 58.40/57.86, H 3.79/3.80, N 2.91/2.93%. Pale-yellow crystals of (I) suitable for X-ray investigations were grown from absolute ethanol [m.p. 489–491 K (decomposition)].

Crystal data

$C_{22}H_{18}NO_2^{+}\cdot CF_3O_3S^{-}$
$M_r = 477.45$
Triclinic, $P\overline{1}$
$a = 9.160$ (2) Å
$b = 10.558$ (2) Å
$c = 11.060$ (2) Å
$\alpha = 80.35$ (3)°
$\beta = 87.87$ (3)°
$\gamma = 80.03$ (3)°
$V = 1038.5$ (4) Å^3

$Z = 2$
$D_x = 1.527$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5975 reflections
$\theta = 3.1$–25.0°
$\mu = 0.22$ mm^{-1}
$T = 100$ (2) K
Needle, pale yellow
0.30 × 0.15 × 0.10 mm

Data collection

Kuma KM-4-CCD κ-geometry diffractometer
ω scans
Absorption correction: none
6626 measured reflections
3564 independent reflections

2437 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 25.0$°
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.067$
$S = 1.00$
3564 reflections
300 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C9—C11	1.392 (3)	C15—O17	1.196 (2)
C9—C15	1.511 (3)	O16—C18	1.427 (2)
N10—C12	1.380 (2)	C18—C19	1.378 (3)
N10—C25	1.484 (2)	C19—C24	1.504 (3)
C15—O16	1.348 (2)		
C9—C15—O16	107.48 (17)	C9—C15—O17	126.14 (18)
C11—C9—C15—O17	95.4 (2)	C15—O16—C18—C19	77.0 (2)

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

*Cg*3 is the centroid of the ring C5–C8/C13/C14 and *Cg*4 is the centroid of the ring C18–C23.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O27^{i}	0.95	2.50	3.247 (2)	136
C2—H2···O29^{i}	0.95	2.50	3.435 (2)	166
C4—H4···O28^{ii}	0.95	2.39	3.322 (2)	165
C6—H6···O29	0.95	2.53	3.450 (3)	163
C7—H7···O28	0.95	2.53	3.253 (3)	133
C25—H25*C*···O28^{ii}	0.98	2.58	3.423 (3)	144
C5—H5···*Cg*4^{iii}	0.95	3.08	3.773 (2)	132
C6—H6···*Cg*3^{iv}	0.95	3.36	3.822 (2)	112
C21—H21···*Cg*3^{v}	0.95	3.38	3.954 (2)	121
C24—H24*B*···*Cg*4^{v}	0.98	2.87	3.649 (2)	137

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

Table 3
π–π interactions (Å, °) in (I).

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

CgI	*CgJ*	*Cg*···*Cg*	Dihedral angle	Interplanar distance	Offset
2	2^{vi}	3.789 (2)	0.0	3.361 (2)	1.634 (2)

Notes: *Cg*···*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*. Symmetry code: (vi) $-x, -y+2, -z$.

All H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.95 Å and with U_{iso}(H) = $1.2U_{eq}$(C), or C—H = 0.98 Å and U_{iso}(H) = $1.5U_{eq}$(C) for the methyl group.

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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