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9-(2,6-Dibromophenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.123
Data-to-parameter ratio = 12.5

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

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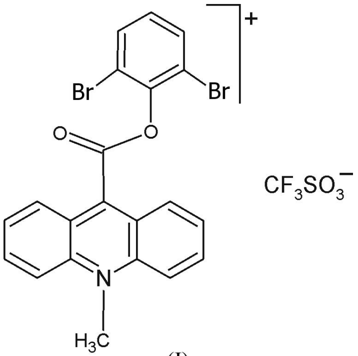
In the title compound, $C_{21}H_{14}Br_2NO_2^+\cdot CF_3O_3S^-$, adjacent cations are oriented either parallel or antiparallel. Together with the $CF_3O_3S^-$ anions, the antiparallel-oriented cations form layers in which the ions are linked *via* a network of C—H···O (O from the anions) and π–π interactions (between the benzene rings). These layers, in turn, are linked *via* a network of five multidirectional π–π interactions between the acridine rings, and the crystal structure is stabilized by electrostatic interactions between the ions. The acridine and independent benzene rings are mutually oriented at an angle of 35.9 (3)°.

Comment

In the last 25 years or so, acridine-based derivatives have attracted interest as chemiluminescent agents, since they can be oxidized by H_2O_2, persulfates or peroxides to form light-emitting products (Zomer & Jacquemijns, 2001; Rak *et al.*, 1999). Phenyl acridine-9-carboxylates are particularly interesting compounds of this type, since they can be oxidized quite efficiently to electronically excited 9-acridinones (Dodeigne *et al.*, 2000; Razawi & McCapra, 2000; Smith *et al.*, 2000; Zomer & Jacquemijns, 2001), which are known to be efficient light emitters (Boużyk *et al.*, 2003). This is the reason why these compounds are widely applied as chemiluminescent indicators or fragments of chemiluminescent labels in immunological, medical, environmental and biochemical analyses (Becker *et al.*, 1999; Dodeigne *et al.*, 2000; Zomer & Jacquemijns, 2001).



(I)

Continuing the search for new analytically useful chemiluminogens, we synthesized the title trifluoromethanesulfonate salt, (I), of dibromophenyl acridine-9-carboxylate, methylated at the endocyclic N atom, in order to study how the presence of heavy Br atoms affects the stability and chemiluminogenic properties of this group of derivatives. This paper, together with our earlier publications (Meszko *et al.*, 2002; Sikorski *et al.*, 2005*a*,*b*), thus extends the prospects of finding further interesting chemiluminogens.

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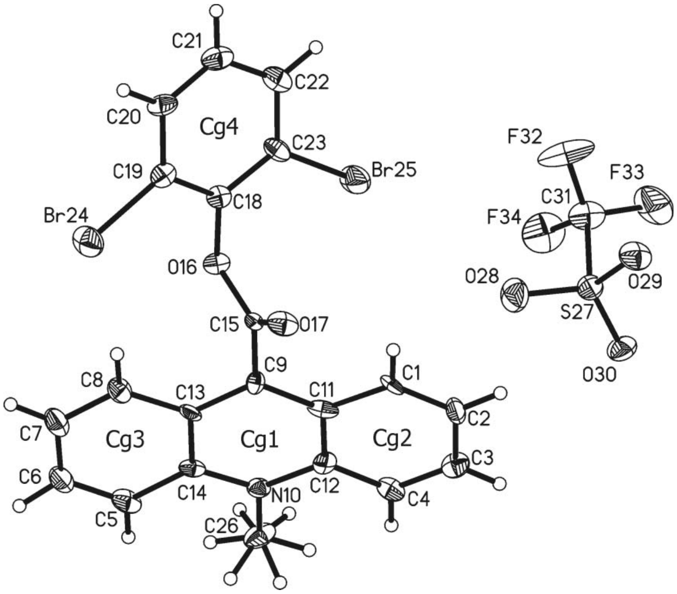

Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Both disorder components are shown.

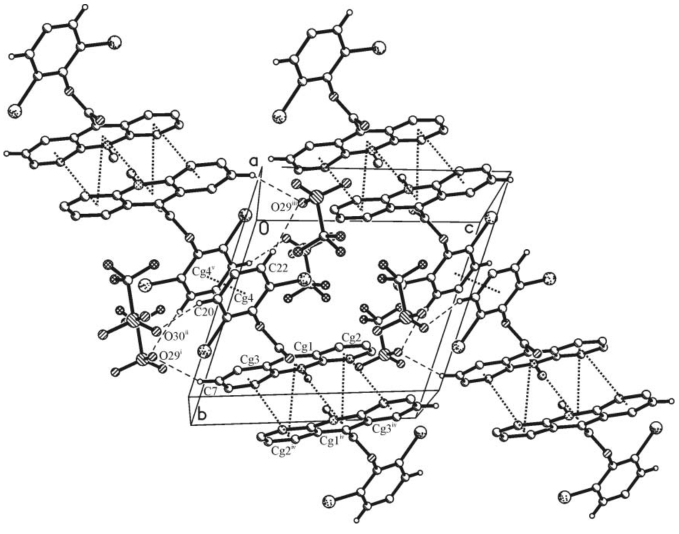

Figure 2
The arrangement of the ions in the unit cell of (I), viewed along the *a* axis. The C—H⋯O interactions are represented by dashed lines and the π–π interactions by dotted lines. H atoms not involved in C—H⋯O interactions have been omitted. [Symmetry codes: (i) $x-1, y, z-1$; (ii) $x, y, z-1$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 2-y, 1-z$; (v) $-x, 1-y, -z$.]

The bond lengths and angles within the cation of (I) may be regarded as typical (Table 1). With respective average deviations from planarity of 0.0280 and 0.0086 Å, the acridine and benzene ring systems are oriented at an angle of 35.9 (3)° (the angle between the mean planes defined by all the non-H atoms of these systems; Fig. 1). The carboxyl group is twisted at an angle of 60.6 (3)° relative to the acridine skeleton (the angle between the mean planes defined by all the non-H atoms of the acridine system and atoms C15, O16 and O17). The H atoms of the methyl group occupy two orientations, rotated by 60° with respect to one another, each with an occupancy of 0.5.

In the crystal structure, adjacent cations are oriented either parallel or antiparallel. Together with the $CF_3O_3S^-$ anions, the antiparallel-oriented cations form layers in which the molecules are linked *via* a network of C—H⋯O interactions involving an H atom from the benzene ring (at C20) and atom O30 of the $CF_3O_3S^-$ anion, bifurcated C—H⋯O interactions involving an H atom from the acridine ring system (at C7), an H atom from the benzene ring (at C22) and atom O29 of the $CF_3O_3S^-$ anion (Fig. 2 and Table 2), and π–π interactions between the benzene rings (Fig. 2 and Table 3). These layers are linked *via* a network of five multidirectional π–π interactions between acridine groups (Fig. 2 and Table 3). The crystal structure is stabilized by electrostatic interactions between the ions (Storoniak *et al.*, 2000).

Experimental

The title compound was obtained by treating 2,6-dibromophenyl acridine-9-carboxylate (0.27 mmol, synthesized by heating acridine-9-carboxylic acid (0.5 mmol) with a tenfold molar excess of thionyl chloride and reacting the product thus obtained with an equimolar amount of 2,6-dibromophenol; Sato, 1996) with a fivefold molar excess of methyl trifluoromethanesulfonate dissolved in dichloromethane (4 ml). The crude salt was dissolved in ethanol (3 ml), filtered and precipitated in the presence of excess diethyl ether (150 ml). Elemental analysis: (% found/calculated): C 43.4/42.5, H 2.2/2.3, N 2.1/2.2. Dark-yellow crystals of (I) suitable for X-ray investigations were grown from anhydrous ethanol (m.p. 481–483 K).

Crystal data

$C_{21}H_{14}Br_2NO_2^+\cdot CF_3O_3S^-$
$M_r = 621.21$
Triclinic, $P\overline{1}$
$a = 9.414\ (2)$ Å
$b = 11.041\ (2)$ Å
$c = 12.347\ (2)$ Å
$\alpha = 105.83\ (3)°$
$\beta = 103.87\ (3)°$
$\gamma = 107.40\ (3)°$
$V = 1103.7\ (6)$ Å^3
$Z = 2$
$D_x = 1.869$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 2.1$–$25.0°$
$\mu = 3.83$ mm^{-1}
$T = 290\ (2)$ K
Prism, yellow
0.4 × 0.3 × 0.2 mm

Data collection

Kuma KM4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.280$, $T_{\max} = 0.465$
4059 measured reflections
3860 independent reflections
1691 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 3.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.123$
$S = 0.94$
3860 reflections
309 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0042 (11)

Table 1
Selected geometric parameters (Å, °).

C9—C11	1.417 (7)	C15—O17	1.196 (6)
C9—C15	1.505 (8)	O16—C18	1.413 (6)
N10—C12	1.371 (7)	C18—C19	1.371 (8)
N10—C26	1.488 (7)	C19—Br24	1.879 (6)
C15—O16	1.336 (7)		
C9—C15—O16	110.1 (5)	C15—O16—C18	118.7 (4)
C9—C15—O17	124.5 (5)	O16—C15—O17	125.4 (5)
C9—C15—O16—C18	−169.6 (5)	C15—O16—C18—C19	−98.7 (6)
C11—C9—C15—O17	−56.7 (8)	O16—C18—C19—Br24	10.2 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O29^{i}	0.93	2.52	3.362 (8)	150
C20—H20···O30^{ii}	0.93	2.52	3.413 (8)	161
C22—H22···O29^{iii}	0.93	2.59	3.523 (9)	176

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

Table 3
Geometry of the π–π interactions (Å,°).

CgI	*CgJ*	*Cg*···*Cg*	Dihedral angle	Interplanar distance	Offset
1	1^{iv}	3.968 (3)	0.0	3.515 (4)	1.841 (4)
1	2^{iv}	3.610 (4)	2.1	3.468 (4)	1.003 (4)
2	1^{iv}	3.610 (4)	2.1	3.458 (4)	1.037 (4)
2	3^{iv}	3.836 (4)	7.1	3.500 (4)	1.570 (4)
3	2^{iv}	3.835 (4)	7.1	3.281 (4)	1.986 (4)
4	4^{v}	3.719 (4)	0.0	3.462 (4)	1.358 (4)

Symmetry codes: (iv) $-x, 2-y, 1-z$; (v) $-x, 1-y, -z$. Notes: *Cg*1 is the centroid of the ring C9/C11/C12/N10/C14/C13, *Cg*2 is the centroid of the ring C1–C4/C12/C11, *Cg*3 is the centroid of the ring C5–C8/C13/C14 and *Cg*4 is the centroid of the ring C18–C23. *Cg*···*Cg* is the distance between ring centroids. The dihedral angle is that between the planes of *CgI* and *CgJ*. The interplanar distance is the perpendicular distance of *CgI* from ring *J*. Offset is the perpendicular distance of ring *I* from ring *J*.

Methyl H atoms were located in difference Fourier syntheses and refined as a rigid rotating group, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C); this group was refined as disordered over two orientations, each with an occupancy factor of 0.5. All other H atoms were placed geometrically and refined using a riding model, with C—H = 0.93 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *KM-4 Software* (Kuma Diffraction, 1989); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; 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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