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9-(2,6-Dichlorophenoxycarbonyl)-10-methylacridinium trifluoromethanesulfonate and its precursor 2,6-dichlorophenyl acridine-9-carboxylate

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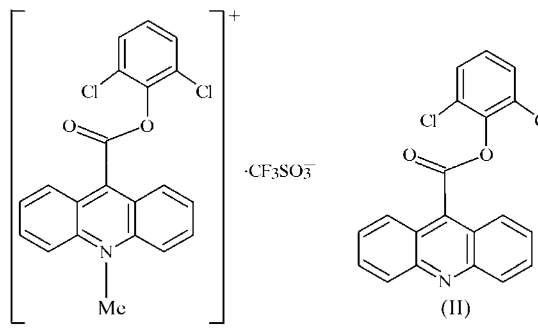
The title compounds, $C_{21}H_{14}Cl_2NO_2^+\cdot CF_3O_3S^-$, (I), and $C_{20}H_{11}Cl_2NO_2$, (II), form triclinic crystals. Adjacent cations of (I) are oriented either parallel or antiparallel; in the latter case, they are related by a centre of symmetry. Together with the $CF_3SO_3^-$ anions, the antiparallel-oriented cations of (I) form layers in which the molecules are linked *via* a network of C—H···O and π–π interactions (between the benzene rings). These layers, in turn, are linked *via* a network of multidirectional π–π interactions between the acridine rings, and the whole lattice is stabilized by electrostatic interactions between ions. Adjacent molecules of (II) are oriented either parallel or antiparallel; in the latter case, they are related by a centre of symmetry. Parallel-oriented molecules are arranged in chains stabilized *via* C—H···Cl interactions. These chains are oriented either parallel or antiparallel and are stabilized, in the latter case, *via* multidirectional π–π interactions and more generally *via* dispersive interactions. Acridine and independent benzene moieties lie parallel in the lattices of (I) and (II), and are mutually oriented at an angle of 33.4 (2)° in (I) and 9.3 (2)° in (II).

Comment

Numerous acridine-based derivatives are important owing to their chemiluminogenic ability and their utility as chemiluminescent indicators or fragments of chemiluminescent labels, with applications in immunoassays, nucleic acid diagnostics and quantitative assays of biomolecules, such as antigens, antibodies, hormones and enzymes, as well as DNA–RNA structural analyses (Becker *et al.*, 1999; Dodeigne *et al.*, 2000; Zomer & Jacquemijns, 2001). Among acridine-based chemiluminogens, phenyl acridine-9-carboxylates are the most promising analytical agents, since they exhibit relatively high quantum yields of light emission and stability (Adamczyk *et al.*, 1999; Dodeigne *et al.*, 2000; Razawi & McCapra, 2000; Renotte *et al.*, 2000; Smith *et al.*, 2000; Zomer & Jacquemijns, 2001). Continuing the search for new analytically interesting acridine-based chemiluminogens, we synthesized phenyl acridine-9-carboxylate substituted with two Cl atoms, (II), and its trifluoromethanesulfonate salt, (I), methylated at the endocyclic N atom, in order to determine how the presence of heavy Cl atoms in the phenyl fragment affects the stability and chemiluminogenic ability of this group of compounds. Presenting as it does the crystal structure of chemiluminogen (I) and its precursor (II), this paper extends, together with our earlier publications on the crystallography of phenyl acridine-9-carboxylates (Meszko *et al.*, 2002; Sikorski *et al.*, 2005), the range of chemiluminogens with potentially interesting applications.



(I) (II)

With respective average deviations from planarity of 0.0077 and 0.0094 Å, the acridine and benzene moieties in (I) are oriented at an angle of 33.4 (2)° (defined as δ, the angle between the mean planes delineated by all the non-H atoms of the acridine and benzene moieties; Fig. 1 and Table 1). The carboxyl group is twisted at an angle of 62.0 (2)° relative to the acridine skeleton (defined as ε, the angle between the mean

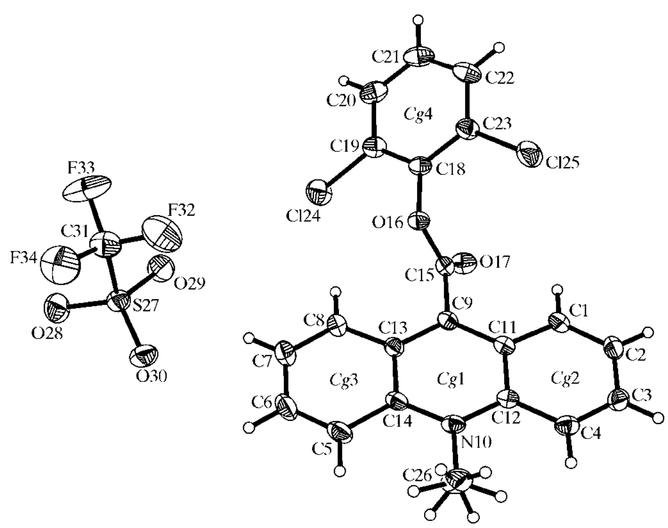


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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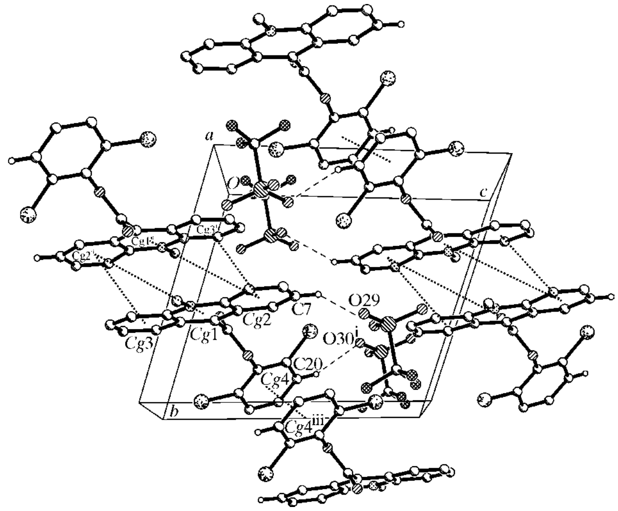

Figure 2
The arrangement of the ions of (I) in the unit cell, viewed along the *a* axis. The C—H···O interactions are represented by dashed lines [symmetry code: (i) $x - 1, y, z$] and the π–π interactions by dotted lines [symmetry codes: (ii) $-x, 1 - y, -z$; (iii) $-x, 2 - y, 1 - z$]. H atoms not involved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

planes delineated by all the non-H atoms of the acridine moiety 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 crystalline phase, adjacent cations of (I) are oriented either parallel or antiparallel. In the latter case, they are related by a centre of symmetry (Fig. 2). Antiparallel-oriented cations of (I), together with $CF_3SO_3^-$ anions, form layers in which the molecules are linked *via* a network of C—H···O interactions involving H atoms from the acridine moiety (at C7) or H atoms from the benzene moiety (at C20), and two of the O atoms of the $CF_3SO_3^-$ anion (Fig. 2, Table 2), as well as

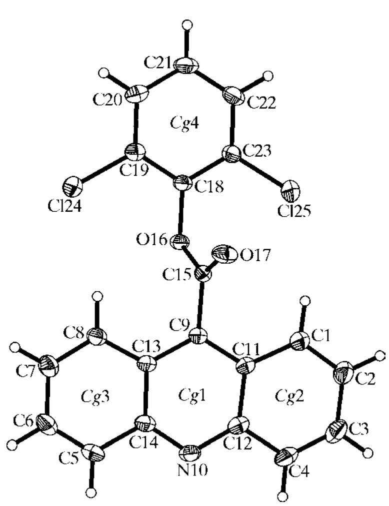

Figure 3
The molecular structure of (II), showing the atom-labelling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

π–π interactions between benzene rings (Fig. 2, Table 3). These layers are linked *via* a network of multidirectional π–π interactions between acridine rings (Fig. 2, Table 3). The whole lattice is stabilized by electrostatic interactions between the ions.

With respective average deviations from planarity of 0.0107 and 0.0036 Å, the δ angle between the acridine and benzene moieties in (II) is 9.3 (2)° (Fig. 3, Table 4). The carboxyl group is twisted at an ε angle of 77.2 (2)° relative to the acridine skeleton.

Adjacent molecules of (II) are oriented either parallel or antiparallel. In the latter case, they are related by a centre of symmetry. Parallel-oriented molecules are arranged in chains stabilized *via* C—H···Cl interactions involving one of the H atoms of the acridine moiety (at C7) and one of the Cl atoms (Cl25) (Fig. 4 and Table 5). Oriented either parallel or antiparallel (Fig. 4), these chains are stabilized in the latter case *via* multidirectional π–π interactions involving the acridine and benzene moieties (Fig. 4 and Table 6), and more generally *via* dispersive interactions.

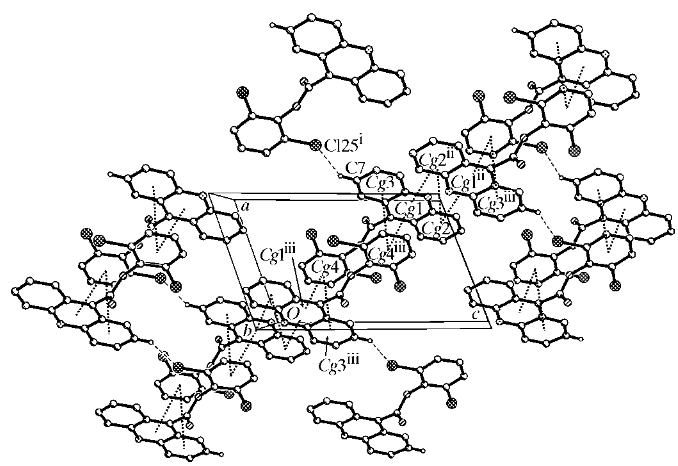

Figure 4
The arrangement of the molecules of (II) in the unit cell, viewed along the *b* axis. The C—H···Cl interactions are represented by dashed lines [symmetry code: (i) $x + 1, y + 1, z$] and the π–π interactions by dotted lines [symmetry codes: (ii) $2 - x, 1 - y, 2 - z$; (iii) $1 - x, 1 - y, 1 - z$]. H atoms not involved in C—H···Cl interactions have been omitted.

Experimental

Compound (II) was synthesized by the conversion of commercially available acridine-9-carboxylic acid to the acid chloride (heating the former compound with excess thionyl chloride), followed by the reaction of the latter with 2,6-dichlorophenol (Sato, 1996). The crude product was purified chromatographically [SiO_2, cyclohexane–ethyl acetate (1:1 *v*/*v*)]. Elemental analysis (% found/calculated): C 81.1/80.7, H 5.1/5.2, N 4.3/4.3. Yellow crystals suitable for X-ray investigations were grown from cyclohexane (m.p. 515–517 K). Compound (I) was obtained upon treating compound (II) with a tenfold molar excess of methyl trifluoromethanesulfonate dissolved in dichloromethane. The product was purified by repeated recrystallization from absolute ethanol. Yellow crystals suitable for X-ray investigations were grown from absolute ethanol (m.p. 404–405 K).

Compound (I)

Crystal data

$C_{21}H_{14}Cl_2NO_2^+\cdot CF_3O_3S^-$
$M_r = 532.31$
Triclinic, $P\bar{1}$
$a = 9.434$ (2) Å
$b = 10.905$ (2) Å
$c = 12.260$ (2) Å
$\alpha = 103.14$ (3)°
$\beta = 103.40$ (3)°
$\gamma = 109.51$ (3)°
$V = 1090.8$ (6) Å^3
$Z = 2$
$D_x = 1.621$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 2.1$–25.5°
$\mu = 0.46$ mm^{-1}
$T = 290$ (2) K
Prism, yellow
0.5 × 0.4 × 0.3 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
4264 measured reflections
4064 independent reflections
2056 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 25.5°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 1.7%

Table 1
Selected geometric parameters (Å, °) for (I).

C9—C11	1.403 (4)	C15—O17	1.187 (4)
C9—C15	1.499 (4)	O16—C18	1.396 (3)
N10—C12	1.372 (4)	C18—C19	1.369 (4)
N10—C26	1.480 (4)	C19—Cl24	1.725 (4)
C15—O16	1.344 (4)		
C9—C15—O16	110.1 (3)	C15—O16—C18	118.8 (2)
C9—C15—O17	125.6 (3)	O16—C15—O17	124.2 (3)
C9—C15—O16—C18	171.0 (2)	C15—O16—C18—C19	98.6 (4)
C11—C9—C15—O17	59.5 (4)	O16—C18—C19—Cl24	−8.7 (5)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7⋯O29	0.93	2.52	3.316 (5)	144
C20—H20⋯O30^{i}	0.93	2.52	3.404 (5)	160

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

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

Cg represents the centre of gravity of the rings, as follows: $Cg1$ ring N10/C12/C11/C9/C13/C14, $Cg2$ ring C1/C2/C3/C4/C12/C11, $Cg3$ ring C5/C6/C7/C8/C13/C14 and $Cg4$ ring C18/C19/C20/C21/C22/C23.

CgI	CgJ	$Cg\cdots Cg$†	Dihedral angle‡	Interplanar distance§	Offset¶
$Cg1$	$Cg2^{ii}$	3.532 (2)	1.9	3.488 (3)	0.556 (2)
$Cg2$	$Cg1^{ii}$	3.532 (2)	1.9	3.482 (3)	0.556 (2)
$Cg2$	$Cg3^{ii}$	3.956 (2)	5.5	3.510 (3)	1.825 (2)
$Cg3$	$Cg2^{ii}$	3.956 (2)	5.5	3.334 (3)	2.130 (2)
$Cg4$	$Cg4^{iii}$	3.788 (2)	0.0	3.473 (3)	1.512 (2)

† $Cg\cdots Cg$ 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. ¶ The offset is the perpendicular distance of ring I from ring J. Symmetry codes: (ii) $-x, 1 - y, -z$; (iii) $-x, 2 - y, 1 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.121$
$S = 1.00$
4064 reflections
309 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.5298P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0037 (1)

Compound (II)

Crystal data

$C_{20}H_{11}Cl_2NO_2$
$M_r = 368.20$
Triclinic, $P\bar{1}$
$a = 8.004$ (2) Å
$b = 9.423$ (2) Å
$c = 12.428$ (2) Å
$\alpha = 101.92$ (3)°
$\beta = 107.04$ (3)°
$\gamma = 105.37$ (3)°
$V = 822.0$ (4) Å^3
$Z = 2$
$D_x = 1.488$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 2.4$–25.5°
$\mu = 0.41$ mm^{-1}
$T = 290$ (2) K
Prism, yellow
0.4 × 0.3 × 0.3 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
3188 measured reflections
3040 independent reflections
2004 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.5°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -9 \rightarrow 15$
3 standard reflections every 200 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.098$
$S = 1.01$
3040 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.1815P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.017 (2)

Table 4
Selected geometric parameters (Å, °) for (II).

C9—C11	1.396 (3)	C15—O17	1.187 (2)
C9—C15	1.500 (3)	O16—C18	1.395 (2)
N10—C12	1.337 (3)	C18—C19	1.381 (3)
C15—O16	1.351 (2)	C19—Cl24	1.725 (2)
C9—C15—O16	110.75 (16)	C15—O16—C18	118.14 (15)
C9—C15—O17	125.26 (18)	O16—C15—O17	123.99 (17)
C9—C15—O16—C18	−177.47 (14)	C15—O16—C18—C19	−105.7 (2)
C11—C9—C15—O17	−75.1 (3)	O16—C18—C19—Cl24	2.8 (3)

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7⋯Cl25^{i}	0.93	2.83	3.570 (3)	137

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

Table 6
π–π interactions (Å, °) in (II).

Cg represents the centre of gravity of the rings, as follows: *Cg*1 ring N10/C12/C11/C9/C13/C14, *Cg*2 ring C1/C2/C3/C4/C12/C11, *Cg*3 ring C5/C6/C7/C8/C13/C14 and *Cg*4 ring C18/C19/C20/C21/C22/C23.

CgI	*CgJ*	*Cg*···*Cg*†	Dihedral angle‡	Interplanar distance§	Offset¶
*Cg*1	$Cg2^{ii}$	3.986 (2)	0.8	3.466 (3)	1.969 (2)
*Cg*1	$Cg4^{iii}$	3.754 (2)	8.6	3.449 (3)	1.482 (2)
*Cg*2	$Cg1^{ii}$	3.986 (2)	0.8	3.461 (3)	1.977 (2)
*Cg*2	$Cg2^{ii}$	3.593 (2)	0.0	3.470 (3)	0.932 (2)
*Cg*3	$Cg4^{iii}$	3.762 (2)	8.7	3.418 (3)	1.572 (2)
*Cg*4	$Cg1^{iii}$	3.754 (2)	8.6	3.536 (3)	1.260 (2)
*Cg*4	$Cg3^{iii}$	3.762 (2)	8.7	3.537 (3)	1.282 (2)

† *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*. ¶ The offset is the perpendicular distance of ring *I* from ring *J*. Symmetry codes: (ii) $2-x, 1-y, 2-z$; (iii) $1-x, 1-y, 1-z$.

The methyl H atoms in (I) were located from difference Fourier syntheses and refined as a rigid rotating group, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$; the location of these atoms was assumed in three unique positions with an occupancy factor of 0.5. All other H atoms were placed geometrically and refined using a riding model, with C—H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *KM-4 Software* (Kuma, 1989); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); publication software: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1365). Services for accessing these data are described at the back of the journal.

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