Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

10-Methyl- and 9,10-dimethylacridinium methyl sulfate

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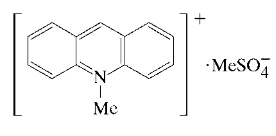
Received 2 September 2002
Accepted 20 September 2002
Online 22 October 2002

The title compounds, $C_{14}H_{12}N^+\cdot CH_3O_4S^-$, (I), and $C_{15}H_{14}N^+\cdot CH_3O_4S^-$, (II), respectively, crystallize with the planar 10-methylacridinium or 9,10-dimethylacridinium cations arranged in layers, parallel to the twofold axis in (I) and perpendicular to the 2_1 axis in (II). Adjacent cations in both compounds are packed in a 'head-to-tail' manner. The methyl sulfate anion only exhibits planar symmetry in (II). The cations and anions are linked through C—H···O interactions involving three O atoms of the anion, six acridine H atoms and the CH_3 group on the N atom in (I), and the four O atoms of the anion, three acridine H atoms and the carbon-bound CH_3 group in (II). The methyl sulfate anions are oriented differently in the two compounds relative to the cations, being nearly perpendicular in (I) but parallel in (II). Electrostatic interaction between the ions and the network of C—H···O interactions leads to relatively compact crystal lattices in both structures.

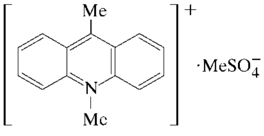
Comment

Methylation of acridines is the simplest way of converting them into stable cationic forms (Storoniak *et al.*, 2000) which are fairly readily soluble in water. Unlike their protonated forms, methylated acridines are resistant to changes in pH and are thus convenient derivatives for numerous applications. In undertaking these investigations, we also wished to consider the susceptibility to oxidation of acridinium cations methylated at the N atom. This process requires the presence of oxidizing agents (*e.g.* peroxides) and may be accompanied by chemiluminescence (Dodeigne *et al.*, 2000). In this context, we recently investigated 9-carboxy-10-methylacridinium phenyl ester (Rak *et al.*, 1999) and 9-cyano-10-methylacridinium hydrogen dinitrate (Huta *et al.*, 2002), and determined the structure of the latter.

It is also interesting that the 9,10-dimethylacridinium cation exhibits relatively high acidity, due to the ability of the 9-methyl group to lose an H atom, and can therefore serve as a model for investigating this feature of organic compounds (Suzuki & Tanaka, 2001). The present work is a continuation of our search for 10-methylacridinium derivatives capable of undergoing oxidation leading to the formation of electronically excited 9-acridinones. Both compounds under study here, *viz*. 10-methylacridinium methyl sulfate, (I), and 9,10-dimethylacridinium methyl sulfate, (II), contain the simplest possible 10-methylacridinium cations. They can thus be regarded as convenient models for the study of the susceptibility to oxidation of this group of compounds.



(I)



(II)

The methyl sulfate anion in (I) (Fig. 1) does not exhibit planar symmetry, unlike that in (II), as demonstrated by the O2—S1—O1—C16 torsion angle (Table 1). Atoms C9 and N10, as well as the methyl group in the cation, are arranged in an almost linear fashion [C9···N10—C15 = 178.0 (2)°]. The methyl group in the cation is fixed in a certain position, as in 10-methylacridinium halides (Storoniak *et al.*, 2000). The methyl group of the anion is similarly fixed; this is not the case in (II).

In (I), the anions are arranged almost perpendicular to the nearly planar acridine moieties [the angle between the O1/S1/O2 plane and the *ac* plane is 85.7 (1)°], which form layers parallel to the *b* axis [the angle between the mean plane formed by the non-H atoms of the cation and the *ac* plane is 89.8 (1)°] (Fig. 2). The cations and anions are fixed, as a result of multidirectional C—H···O interactions involving three O atoms of the anion and the six H atoms attached to the acridine C atoms in ring positions 1–5 and 9, as well as those belonging to the methyl group at N10 (Table 2).

The methyl sulfate anion in (II) lies in the crystallographic symmetry plane (Fig. 3). As a consequence, 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 (Table 3). Atoms C9 and N10, together with the methyl groups attached to them, are arranged in a linear fashion [C15—C9···N10—C16 = 179.5 (2)°]. However, the H atoms of both

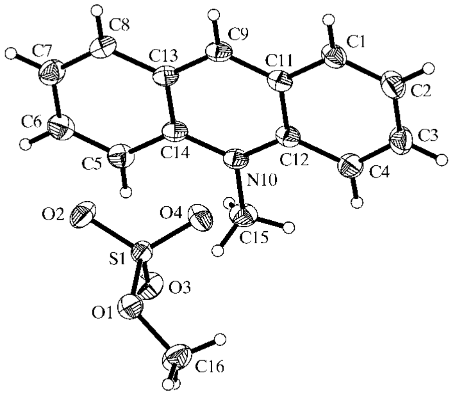


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

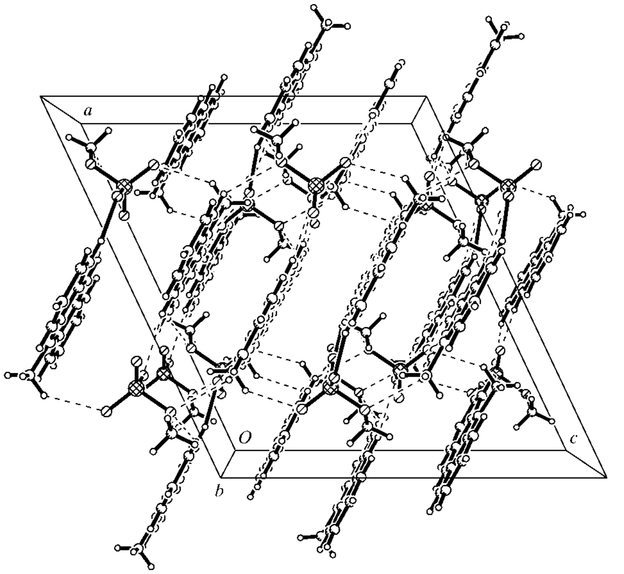


Figure 2
The arrangement of molecules of (I) in the unit cell, viewed along the *b* axis. Short C—H···O contacts are represented by dashed lines.

methyl groups occupy two orientations, twisted through 39 and 60° for CH_3 attached to atoms C9 and N10, respectively, each with an occupancy of 0.5.

In the crystal of (II), the cations and anions are arranged in layers perpendicular to the 2_1 axis (parallel to the *ac* plane; Fig. 4), with adjacent ions arranged 'head-to-tail'. These layers are linked *via* C—H···O interactions involving all four O atoms of the anion and the three H atoms attached to the acridine C atoms at ring positions 1, 2 and 4, and those belonging to the carbon-bound methyl group at C9 (Table 4). The cations and anions form columns along the [010] direction and are held in place by the network of these multidirectional interactions.

The methyl group at N10 in (II) occupies two orientations, as in 9-cyano-10-methylacridinium hydrogen dinitrate (Huta *et al.*, 2002), while in (I) it is fixed, as in the 10-methylacridinium halides (Storoniak *et al.*, 2000). It is also of interest to note that the methyl sulfate anion in (II) is symmetrical. This is a unique feature among salts containing this anion for which crystal structures have so far been established (Blake *et al.*, 2000; Brand & Vahrenkamp, 2000; Handrosch *et al.*, 1999; Senge & Kalisch, 1999); none of these contains symmetrical methyl sulfate anions. It is perhaps also worth mentioning that (II) is the first ionic substance containing the 9,10-dimethylacridinium cation for which the structure has been determined by X-ray methods. Therefore, 9,10-dimethylacridinium methyl sulfate appears to be a crystalline substance combining the symmetries of both cation and anion.

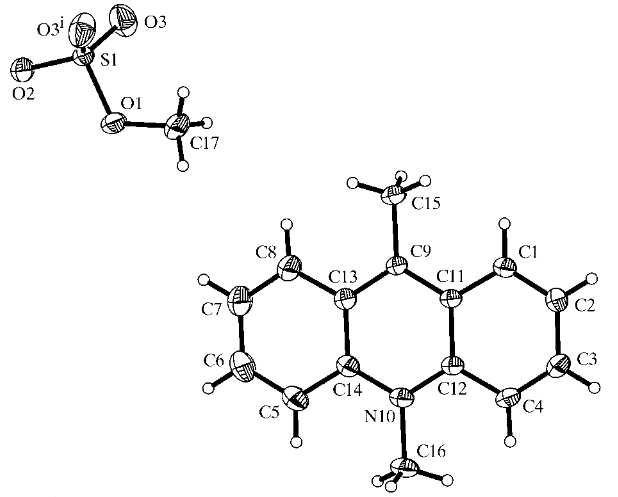


Figure 3
The molecular structure of (II), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $x, \frac{1}{2} - y, z$].

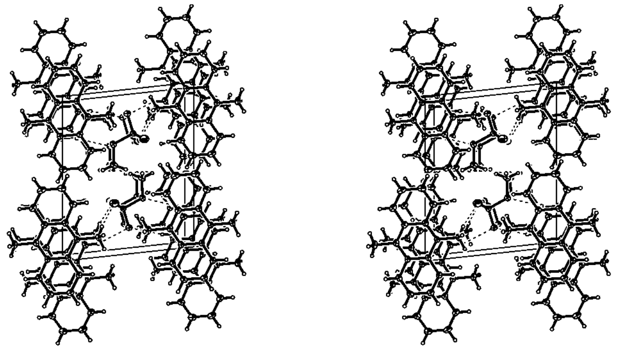


Figure 4
A stereoview of the packing diagram of (II), viewed along the *b* axis, with the *a* axis vertical and the *c* axis horizontal. Short C—H···O contacts (Table 4) are represented by dashed lines.

Experimental

Commercially available acridine was purified by sublimation (Storoniak *et al.*, 2000). 9-Methylacridine was synthesized according to the procedure described by Tsuge *et al.* (1963). 10-Methylacridinium and 9,10-dimethylacridinium methyl sulfate were prepared by the reaction of acridine and 9-methylacridine, respectively, with dimethyl sulfate (Bahr *et al.*, 1996; Mooser *et al.*, 1972). Yellow crystals of (I) and red crystals of (II), suitable for X-ray analyses, were grown from solutions in 96% ethyl alcohol.

Compound (I)

Crystal data

$C_{14}H_{12}N^+\cdot CH_3O_4S^-$
$M_r = 305.34$
Monoclinic, $C2/c$
$a = 16.199$ (5) Å
$b = 12.661$ (4) Å
$c = 14.785$ (4) Å
$\beta = 115.23$ (3)°
$V = 2743.1$ (16) Å^3
$Z = 8$
$D_x = 1.479$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 6.0$–$24.0°$
$\mu = 2.25$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.4 × 0.3 × 0.3 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
2774 measured reflections
2663 independent reflections
2150 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\max} = 72°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections
every 200 reflections
intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.168$
$S = 1.11$
2663 reflections
193 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1082P)^2 + 1.7878P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0019 (3)

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

S1—O1	1.599 (2)	S1—O4	1.436 (2)
S1—O2	1.438 (2)	O1—C16	1.422 (4)
S1—O3	1.430 (2)	N10—C15	1.473 (3)
O1—S1—O2	100.83 (12)	C12—N10—C15	120.4 (2)
O2—S1—O3	114.68 (13)	C16—O1—S1	116.73 (18)
O2—S1—O4	114.46 (14)		
O2—S1—O1—C16	173.4 (2)	C11—C9—C13—C14	−1.0 (4)
C15—N10—C12—C11	177.8 (2)	C12—N10—C14—C13	2.8 (4)

Table 2
Short-contact geometry (Å, °) for (I).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C1—H1*A*$\cdots$O2^{i}	0.93	2.60	3.424 (4)	149
C2—H2*A*$\cdots$O1^{ii}	0.93	2.50	3.261 (4)	139
C3—H3*A*$\cdots$O3^{iii}	0.93	2.57	3.276 (4)	133
C4—H4*A*$\cdots$O2^{iii}	0.93	2.54	3.449 (4)	164
C5—H5*A*$\cdots$O1^{iv}	0.93	2.52	3.300 (4)	141
C9—H9*A*$\cdots$O2^{i}	0.93	2.57	3.412 (4)	151
C15—H15*A*$\cdots$O3	0.96	2.53	3.344 (4)	141

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

Compound (II)

Crystal data

$C_{15}H_{14}N^+ \cdot CH_3O_4S^-$
$M_r = 319.37$
Monoclinic, $P2_1/m$
$a = 9.271$ (2) Å
$b = 6.822$ (1) Å
$c = 11.591$ (2) Å
$\beta = 96.24$ (3)°
$V = 728.7$ (2) Å^3
$Z = 2$

$D_x = 1.455$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 6$–24°
$\mu = 2.14$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.40 × 0.40 × 0.35 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
1620 measured reflections
1565 independent reflections
1454 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 72°$

$h = -8 \rightarrow 11$
$k = -8 \rightarrow 0$
$l = -14 \rightarrow 8$
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.137$
$S = 1.13$
1565 reflections
131 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0839P)^2 + 0.1827P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.070 (5)

Table 3
Selected geometric parameters (Å, °) for (II).

S1—O1	1.571 (2)	O1—C17	1.438 (4)
S1—O2	1.433 (2)	N10—C16	1.493 (3)
S1—O3	1.4221 (18)		
O1—S1—O2	102.19 (11)	C11—C9—C15	120.9 (2)
O2—S1—O3	114.44 (8)	C12—N10—C16	119.3 (2)
C17—O1—S1	116.82 (19)		

Table 4
Short-contact geometry (Å, °) for (II).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C1—H1*A*$\cdots$O2	0.93	2.43	3.341 (3)	166
C2—H2*A*$\cdots$O1	0.93	2.49	3.239 (4)	137
C4—H4*A*$\cdots$O2^{i}	0.93	2.48	3.363 (4)	158
C15—H15*A*$\cdots$O3^{ii}	0.96	2.47	3.423 (3)	171
C15—H15*A*$^{iii}\cdots$O3^{iv}	0.96	2.47	3.423 (3)	171

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

All H atoms were placed geometrically and refined using a riding model, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C) for methyl H atoms, and C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) for all others.

For both compounds, data collection: *KM*-4 *Software* (Kuma Diffraction, 1989); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

This research was partially funded by the Polish State Committee for Scientific Research through the Polish–Ukrainian Executive Programme of Research and Technical Co-operation (grant No. PRO: III.28/1998; contract No. 157), and grant BW/8000-5-0281-2.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1138). Services for accessing these data are described at the back of the journal.

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