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9-(Methylsulfanyl)acridinium trifluoromethanesulfonate

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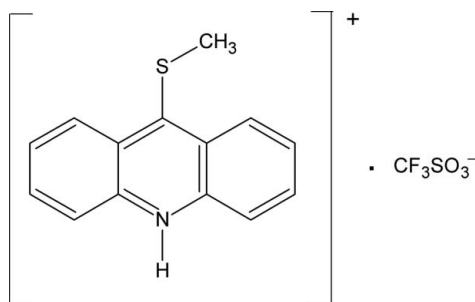
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.050; wR factor = 0.161; data-to-parameter ratio = 12.6.

In the crystal structure of the title compound, $\text{C}_{14}\text{H}_{12}\text{NS}^+\text{CF}_3\text{SO}_3^-$, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds link cations and anions into ion pairs. Inversely oriented ion pairs form stacks through multidirectional $\pi-\pi$ interactions among the acridine units. The crystal structure features a network of $\text{C}-\text{H}\cdots\text{O}$ interactions among stacks and also long-range electrostatic interactions among ions. In the packing of the molecules, the acridine units are nearly parallel in stacks or inclined at an angle of $33.07(2)^\circ$ in the four adjacent stacks with which they interact *via* weak $\text{C}-\text{H}\cdots\text{O}$ interactions. The methylsulfanyl group is twisted through an angle of $60.53(2)^\circ$ with respect to the acridine ring.

Related literature

For general background, see: Wróblewska *et al.* (2004); Zomer & Jacquemijns (2001). For related structures, see: Meszko *et al.* (2002); Mrozek *et al.* (2002); Storoniak *et al.* (2000). For molecular interactions, see: Aakeröy *et al.* (1992); Bianchi *et al.* (2004); Hunter *et al.* (2001); Spek (2009); Steiner (1991). For the synthesis, see: Berny *et al.* (1992); Sato (1996).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{NS}^+\cdot\text{CF}_3\text{SO}_3^-$
 $M_r = 375.40$
 Monoclinic, $P2_1/c$
 $a = 7.2992(2)$ Å
 $b = 17.3090(6)$ Å
 $c = 13.0582(4)$ Å
 $\beta = 103.910(3)^\circ$

$V = 1601.42(9)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.38$ mm⁻¹
 $T = 295$ K
 $0.45 \times 0.40 \times 0.20$ mm

Data collection

Oxford Diffraction Gemini R Ultra
 Ruby CCD diffractometer
 Absorption correction: none
 13308 measured reflections

2841 independent reflections
 1944 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.161$
 $S = 1.06$
 2841 reflections
 226 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}7-\text{H}7\cdots\text{O}18^{\text{i}}$	0.99 (4)	2.38 (4)	3.315 (5)	158 (3)
$\text{N}10-\text{H}10\cdots\text{O}19$	0.86 (2)	1.86 (2)	2.712 (4)	172 (3)

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

Table 2

 $\pi-\pi$ Interactions (Å, °).

$\text{C}g_i$	$\text{C}g_j$	$\text{C}g_i\cdots\text{C}g_j$	Dihedral angle	Interplanar distance	Offset
$\text{C}g1$	$\text{C}g1^{\text{ii}}$	3.827 (2)	0.0	3.468 (2)	1.618 (2)
$\text{C}g1$	$\text{C}g3^{\text{ii}}$	3.634 (2)	1.4	3.474 (2)	1.066 (2)
$\text{C}g1$	$\text{C}g3^{\text{iii}}$	3.810 (2)	1.4	3.412 (2)	1.695 (2)
$\text{C}g2$	$\text{C}g3^{\text{ii}}$	3.830 (2)	4.0	3.492 (2)	1.573 (2)
$\text{C}g3$	$\text{C}g1^{\text{ii}}$	3.634 (2)	1.4	3.483 (2)	1.037 (2)
$\text{C}g3$	$\text{C}g1^{\text{iii}}$	3.810 (2)	1.4	3.386 (2)	1.747 (2)
$\text{C}g3$	$\text{C}g2^{\text{ii}}$	3.830 (2)	4.0	3.449 (2)	1.665 (2)

Symmetry codes: (ii) $-x, -y + 2, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$. Notes: $\text{C}g1$, $\text{C}g2$ and $\text{C}g3$ are the centroids of the $\text{C}9/\text{N}10/\text{C}11-\text{C}14$, $\text{C}1-\text{C}4/\text{C}11/\text{C}12$ and $\text{C}5-\text{C}8/\text{C}13/\text{C}14$ rings, respectively. $\text{C}g_i\cdots\text{C}g_j$ is the distance between ring centroids. The dihedral angle is that between the planes of rings $\text{C}g_i$ and $\text{C}g_j$. The interplanar distance is the perpendicular distance of $\text{C}g_j$ from ring i . The offset is the perpendicular distance of ring i from ring j .

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: *ORTEPII* (Johnson, 1976); 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: NG2540).

References

- Aakeröy, C. B., Seddon, K. R. & Leslie, M. (1992). *Struct. Chem.* **3**, 63–65.
- Berny, H., Bsiri, N., Charbit, J. J., Galy, A. M., Soyfer, J. C., Galy, J. P., Barbe, J., Sharples, D., Mesa Valle, C. M., Mascaro, C. & Osuna, A. (1992). *Arzneim. Forsch. Drug Res.* **42**, 674–679.
- Bianchi, R., Forni, A. & Pilati, T. (2004). *Acta Cryst.* **B60**, 559–568.
- Hunter, C. A., Lawson, K. R., Perkins, J. & Urch, C. J. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 651–669.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Meszko, J., Sikorski, A., Huta, O. M., Konitz, A. & Błażejowski, J. (2002). *Acta Cryst.* **C58**, o669–o671.
- Mrozek, A., Karolak-Wojciechowska, J., Amiel, P. & Barbe, J. (2002). *Acta Cryst.* **E58**, o1065–o1067.
- Oxford Diffraction. (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
- Sato, N. (1996). *Tetrahedron Lett.* **37**, 8519–8522.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Steiner, T. (1991). *Chem. Commun.* pp. 313–314.
- Storoniak, P., Krzymiński, K., Dokurno, P., Konitz, A. & Błażejowski, J. (2000). *Aust. J. Chem.* **53**, 627–633.
- Wróblewska, A., Huta, O. M., Midyanyj, S. V., Patsay, I. O. & Błażejowski, J. (2004). *J. Org. Chem.* **69**, 1607–1614.
- Zomer, G. & Jacquemijns, M. (2001). *Chemiluminescence in Analytical Chemistry*, edited by A. M. Garcia-Campana & W. R. G. Baeyens, pp. 529–549. New York: Marcel Dekker.

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9-(Methylsulfanyl)acridinium trifluoromethanesulfonate

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Comment

Acridinium cations containing various substituents at position 9 and alkyl substituents at the endocyclic N atom (position 10) are susceptible to oxidation by H₂O₂ or other oxidants in alkaline media, leading to the formation of electronically excited 10-alkyl-9-acridinones capable of emitting light with a quantum yield of several percent (Zomer & Jacquemijns, 2001; Wróblewska *et al.*, 2004). The chemiluminescence phenomenon described above is governed by the features of the substituent at position 9. In the search for derivatives that could exhibit enhanced chemiluminescence, we turned our attention to compounds in which the C atom at position 9 is bound to the S atom. The simplest compound that we were able to synthesize was 9-(methylthio)acridinium trifluoromethanesulfonate. It was obtained by the reaction of 9-thioacridinone (Berny *et al.*, 1992) with methyl trifluoromethanesulfonate, which usually leads to quaternarization of the endocyclic N atom (Sato, 1996). The cation of the reaction product has a protonated endocyclic N atom, enabling it to react with oxidants, thereby facilitating the investigation of chemiluminescence phenomena. This paper presents the crystal structure of the title compound. This is, to our knowledge, only the second report on the crystal structure of an acridine derivatives S-substituted at position 9 (for the first one, see Mrozek *et al.*, 2002).

In the cations of the title compound (Fig. 1), the bond lengths and angles characterizing the geometry of the acridine skeleton are typical of acridine-based derivatives (Storoniak *et al.*, 2000; Meszko *et al.*, 2002; Mrozek *et al.*, 2002). The C9–S15 and S15–C16 bond lengths (1.754 (3) Å and 1.807 (4) Å, respectively) correlate well with those reported for 9-(thio-2'-methyl-4'-nitrophenyl)acridine (Mrozek *et al.*, 2002). The C9–S15–C16 fragment and the acridine ring system, with an average deviation from planarity of 0.037 (4) Å, are oriented at 60.53 (2)° to each other. The acridine units in the lattice are either parallel (within stacks) or inclined at an angle of 33.07 (2)° (in four adjacent stacks with which they interact *via* C–H···O hydrogen bonds).

In the crystal structure, N–H···O hydrogen bonds (Aakeröy *et al.*, 1992) link cations and anions in ion pairs (Table 1, Fig. 1). Inversely oriented ion pairs form stacks in which the central ring (Cg1) and the aromatic rings (Cg2 and Cg3) are involved in multidirectional π - π interactions (Table 2, Fig. 2) of an attractive nature (Hunter *et al.*, 2001). The crystal structure is stabilized by a network of C–H···O hydrogen type bonding interactions (Steiner, 1991; Bianchi *et al.*, 2004) between neighbouring stacks (Figs 2 and 3) as well as by long-range electrostatic interactions between ions.

Experimental

9-(Methylthio)acridinium trifluoromethanesulfonate was synthesized in two steps. First, 9-thioacridinone was synthesized by heating with stirring a mixture of 9(10*H*)-acridinone, tetraphosphorus decasulfide and freshly distilled pyridine at 100°C for 1 h (Berny *et al.*, 1992). The reactant mixture was subsequently poured into 30% aq ammonia and the resulting precipitate of 9-thioacridinone filtered off. This compound was then treated with a fivefold molar excess of methyl trifluoromethanesulfonate dissolved in dichloromethane for 3 h (Ar atmosphere, room temperature) (Sato, 1996). The crude 9-(methylthio)acridinium trifluoromethanesulfonate thus formed was dissolved in a small amount of ethanol, filtered, and

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again precipitated with a 25 v/v excess of diethyl ether (yield: 87%). Yellow crystals suitable for X-ray investigations were grown from absolute ethanol solution (m.p. 421–423 K).

Refinement

H atoms involved in C–H \cdots O interactions were located in a difference map and refined without constrains. H atoms involved in N–H \cdots O interaction were located in a difference map and refined using the N–H distance restraint of 0.86 (2) Å. Other H atoms were positioned geometrically, with C–H = 0.93 Å (aromatic) and 0.96 Å (methyl), and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (aromatic) or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ (methyl).

Figures

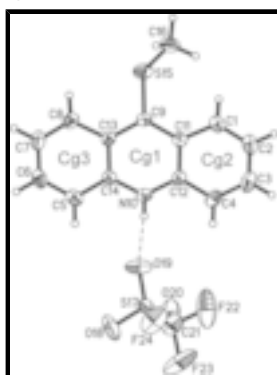


Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radius. The N10–H10 \cdots O19 hydrogen bond is represented by a dashed line. Cg1, Cg2 and Cg3 denote the ring centroids.



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

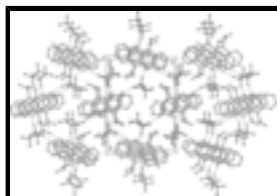


Fig. 3. Stacks of the ion pairs in the crystal structure viewed along the a axis. The N–H \cdots O and C–H \cdots O interactions are represented by dashed lines. H atoms not involved in interactions have been omitted.

9-(Methylsulfanyl)acridinium trifluoromethanesulfonate

Crystal data

$\text{C}_{14}\text{H}_{12}\text{NS}^+\cdot\text{CF}_3\text{S}_1\text{O}_3^-$

$M_r = 375.40$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 7.2992(2)\ \text{\AA}$

$b = 17.3090(6)\ \text{\AA}$

$c = 13.0582(4)\ \text{\AA}$

$\beta = 103.910(3)^\circ$

$F_{000} = 768$

$D_x = 1.557\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5491 reflections

$\theta = 3.1\text{--}29.2^\circ$

$\mu = 0.38\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, yellow

$V = 1601.42 (9) \text{ \AA}^3$
 $Z = 4$ $0.45 \times 0.4 \times 0.2 \text{ mm}$

Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer	2841 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1944 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.028$
Detector resolution: $10.4002 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 25.1^\circ$
$T = 295 \text{ K}$	$\theta_{\text{min}} = 3.1^\circ$
ω scans	$h = -8 \rightarrow 8$
Absorption correction: none	$k = -20 \rightarrow 20$
13308 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.161$	$w = 1/[\sigma^2(F_o^2) + (0.1054P)^2]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2841 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
226 parameters	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.0169 (4)	1.03470 (19)	0.2103 (2)	0.0567 (7)
H1	-0.0740	1.0824	0.1916	0.068*
C2	-0.0343 (4)	0.9785 (2)	0.1374 (2)	0.0702 (9)
H2	-0.1039	0.9879	0.0690	0.084*
C3	0.0508 (5)	0.9058 (2)	0.1626 (3)	0.0751 (10)
H3	0.0404	0.8684	0.1103	0.090*
C4	0.1478 (4)	0.8897 (2)	0.2624 (3)	0.0630 (8)

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H4	0.2023	0.8414	0.2791	0.076*
C5	0.3767 (3)	0.9596 (2)	0.6240 (2)	0.0577 (8)
H5	0.4190	0.9092	0.6380	0.069*
C6	0.4067 (4)	1.0138 (2)	0.7023 (2)	0.0657 (9)
H6	0.4717	0.9998	0.7700	0.079*
C7	0.3425 (4)	1.0895 (2)	0.6832 (3)	0.0670 (9)
H7	0.380 (4)	1.127 (2)	0.742 (3)	0.079 (10)*
C8	0.2485 (4)	1.11202 (18)	0.5862 (2)	0.0573 (7)
H8	0.2070	1.1628	0.5750	0.069*
C9	0.1176 (3)	1.07880 (15)	0.3956 (2)	0.0442 (6)
N10	0.2546 (3)	0.93052 (14)	0.44086 (19)	0.0478 (6)
H10	0.300 (4)	0.8858 (12)	0.462 (2)	0.071 (10)*
C11	0.0877 (3)	1.02193 (16)	0.3156 (2)	0.0453 (6)
C12	0.1652 (3)	0.94706 (16)	0.3405 (2)	0.0455 (6)
C13	0.2116 (3)	1.05863 (16)	0.49974 (19)	0.0438 (6)
C14	0.2796 (3)	0.98202 (16)	0.5208 (2)	0.0441 (6)
S15	0.03215 (12)	1.17329 (5)	0.36941 (8)	0.0731 (3)
C16	0.1546 (5)	1.2067 (2)	0.2729 (3)	0.0770 (10)
H16A	0.1099	1.2572	0.2488	0.116*
H16B	0.1314	1.1716	0.2142	0.116*
H16C	0.2877	1.2089	0.3044	0.116*
S17	0.36383 (10)	0.71528 (5)	0.50824 (6)	0.0577 (3)
O18	0.4183 (4)	0.6911 (2)	0.6130 (2)	0.1215 (12)
O19	0.4246 (4)	0.79237 (14)	0.4965 (3)	0.1040 (10)
O20	0.1780 (3)	0.6955 (2)	0.4545 (2)	0.1045 (10)
C21	0.5109 (6)	0.6611 (3)	0.4413 (4)	0.0960 (13)
F22	0.4700 (5)	0.6751 (3)	0.3414 (3)	0.193 (2)
F23	0.4819 (6)	0.5867 (2)	0.4487 (4)	0.2000 (19)
F24	0.6911 (3)	0.67460 (17)	0.4790 (3)	0.1366 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0519 (15)	0.068 (2)	0.0489 (15)	0.0013 (14)	0.0100 (12)	0.0050 (15)
C2	0.0620 (18)	0.096 (3)	0.0504 (17)	-0.0082 (18)	0.0092 (14)	-0.0036 (18)
C3	0.0695 (19)	0.092 (3)	0.067 (2)	-0.0095 (19)	0.0227 (17)	-0.031 (2)
C4	0.0542 (16)	0.059 (2)	0.077 (2)	0.0015 (14)	0.0176 (15)	-0.0158 (16)
C5	0.0438 (14)	0.070 (2)	0.0586 (18)	-0.0061 (13)	0.0101 (13)	0.0162 (16)
C6	0.0537 (16)	0.095 (3)	0.0466 (17)	-0.0186 (17)	0.0077 (13)	0.0052 (17)
C7	0.0646 (18)	0.086 (3)	0.0510 (18)	-0.0206 (18)	0.0156 (15)	-0.0155 (18)
C8	0.0582 (16)	0.0533 (19)	0.0639 (19)	-0.0093 (13)	0.0218 (14)	-0.0097 (14)
C9	0.0383 (12)	0.0407 (16)	0.0555 (16)	0.0005 (11)	0.0151 (11)	0.0019 (12)
N10	0.0417 (11)	0.0395 (14)	0.0618 (15)	0.0004 (10)	0.0118 (10)	0.0048 (12)
C11	0.0379 (12)	0.0494 (17)	0.0499 (15)	0.0018 (11)	0.0129 (11)	0.0016 (12)
C12	0.0375 (12)	0.0475 (17)	0.0534 (16)	-0.0055 (11)	0.0144 (11)	-0.0059 (13)
C13	0.0400 (12)	0.0448 (16)	0.0496 (15)	-0.0082 (11)	0.0166 (11)	-0.0039 (12)
C14	0.0353 (12)	0.0488 (17)	0.0489 (15)	-0.0069 (11)	0.0113 (11)	0.0023 (12)
S15	0.0800 (6)	0.0507 (6)	0.0909 (7)	0.0178 (4)	0.0248 (5)	0.0059 (4)

C16	0.083 (2)	0.056 (2)	0.087 (2)	-0.0126 (17)	0.0096 (19)	0.0185 (17)
S17	0.0620 (5)	0.0550 (5)	0.0527 (5)	-0.0016 (3)	0.0070 (3)	0.0084 (3)
O18	0.124 (2)	0.173 (3)	0.0551 (15)	-0.023 (2)	-0.0018 (15)	0.0306 (16)
O19	0.1003 (18)	0.0507 (16)	0.172 (3)	0.0158 (13)	0.0536 (18)	0.0300 (16)
O20	0.0605 (14)	0.159 (3)	0.0864 (18)	-0.0124 (15)	0.0026 (13)	-0.0175 (17)
C21	0.077 (3)	0.081 (3)	0.122 (4)	0.005 (2)	0.007 (2)	-0.023 (3)
F22	0.144 (3)	0.345 (6)	0.097 (2)	0.028 (3)	0.044 (2)	-0.063 (3)
F23	0.177 (3)	0.085 (2)	0.331 (6)	-0.001 (2)	0.047 (3)	-0.088 (3)
F24	0.0666 (14)	0.132 (2)	0.199 (3)	0.0187 (13)	0.0096 (15)	-0.057 (2)

Geometric parameters (Å, °)

C1—C2	1.346 (4)	C9—C11	1.414 (4)
C1—C11	1.421 (4)	C9—S15	1.754 (3)
C1—H1	0.9300	N10—C12	1.347 (3)
C2—C3	1.407 (5)	N10—C14	1.351 (3)
C2—H2	0.9300	N10—H10	0.860 (18)
C3—C4	1.354 (4)	C11—C12	1.420 (4)
C3—H3	0.9300	C13—C14	1.419 (4)
C4—C12	1.407 (4)	S15—C16	1.807 (4)
C4—H4	0.9300	C16—H16A	0.9600
C5—C6	1.365 (5)	C16—H16B	0.9600
C5—C14	1.417 (4)	C16—H16C	0.9600
C5—H5	0.9300	S17—O18	1.393 (3)
C6—C7	1.394 (5)	S17—O20	1.411 (2)
C6—H6	0.9300	S17—O19	1.426 (3)
C7—C8	1.346 (4)	S17—C21	1.803 (5)
C7—H7	1.00 (4)	C21—F22	1.289 (6)
C8—C13	1.433 (4)	C21—F23	1.312 (5)
C8—H8	0.9300	C21—F24	1.310 (5)
C9—C13	1.412 (4)		
C2—C1—C11	120.6 (3)	C9—C11—C1	124.0 (3)
C2—C1—H1	119.7	C12—C11—C1	117.1 (2)
C11—C1—H1	119.7	N10—C12—C4	119.6 (3)
C1—C2—C3	121.4 (3)	N10—C12—C11	119.4 (2)
C1—C2—H2	119.3	C4—C12—C11	121.1 (3)
C3—C2—H2	119.3	C9—C13—C14	119.0 (2)
C4—C3—C2	120.5 (3)	C9—C13—C8	123.7 (3)
C4—C3—H3	119.7	C14—C13—C8	117.3 (2)
C2—C3—H3	119.7	N10—C14—C13	119.4 (2)
C3—C4—C12	119.2 (3)	N10—C14—C5	119.9 (3)
C3—C4—H4	120.4	C13—C14—C5	120.8 (3)
C12—C4—H4	120.4	C9—S15—C16	102.83 (15)
C6—C5—C14	118.5 (3)	S15—C16—H16A	109.5
C6—C5—H5	120.7	S15—C16—H16B	109.5
C14—C5—H5	120.7	H16A—C16—H16B	109.5
C5—C6—C7	121.7 (3)	S15—C16—H16C	109.5
C5—C6—H6	119.2	H16A—C16—H16C	109.5
C7—C6—H6	119.2	H16B—C16—H16C	109.5

supplementary materials

C8—C7—C6	120.9 (3)	O18—S17—O20	115.38 (19)
C8—C7—H7	121 (2)	O18—S17—O19	111.4 (2)
C6—C7—H7	117 (2)	O20—S17—O19	117.40 (19)
C7—C8—C13	120.8 (3)	O18—S17—C21	104.9 (2)
C7—C8—H8	119.6	O20—S17—C21	104.20 (19)
C13—C8—H8	119.6	O19—S17—C21	101.4 (2)
C13—C9—C11	119.5 (2)	F22—C21—F23	105.0 (5)
C13—C9—S15	119.1 (2)	F22—C21—F24	108.3 (4)
C11—C9—S15	121.4 (2)	F23—C21—F24	108.2 (4)
C12—N10—C14	123.7 (2)	F22—C21—S17	111.9 (3)
C12—N10—H10	124 (2)	F23—C21—S17	110.5 (4)
C14—N10—H10	112 (2)	F24—C21—S17	112.7 (3)
C9—C11—C12	118.9 (2)		
C11—C1—C2—C3	-0.4 (5)	S15—C9—C13—C8	-2.4 (3)
C1—C2—C3—C4	2.2 (5)	C7—C8—C13—C9	-178.6 (2)
C2—C3—C4—C12	-1.0 (5)	C7—C8—C13—C14	-0.6 (4)
C14—C5—C6—C7	0.8 (4)	C12—N10—C14—C13	-1.0 (4)
C5—C6—C7—C8	-0.2 (5)	C12—N10—C14—C5	-179.6 (2)
C6—C7—C8—C13	0.1 (4)	C9—C13—C14—N10	0.7 (3)
C13—C9—C11—C12	-4.4 (3)	C8—C13—C14—N10	-177.4 (2)
S15—C9—C11—C12	178.03 (18)	C9—C13—C14—C5	179.3 (2)
C13—C9—C11—C1	175.3 (2)	C8—C13—C14—C5	1.2 (3)
S15—C9—C11—C1	-2.3 (3)	C6—C5—C14—N10	177.3 (2)
C2—C1—C11—C9	177.8 (3)	C6—C5—C14—C13	-1.3 (4)
C2—C1—C11—C12	-2.5 (4)	C13—C9—S15—C16	120.7 (2)
C14—N10—C12—C4	179.4 (2)	C11—C9—S15—C16	-61.7 (2)
C14—N10—C12—C11	-1.4 (4)	O18—S17—C21—F22	177.1 (4)
C3—C4—C12—N10	177.3 (3)	O20—S17—C21—F22	55.5 (4)
C3—C4—C12—C11	-1.9 (4)	O19—S17—C21—F22	-66.9 (4)
C9—C11—C12—N10	4.2 (4)	O18—S17—C21—F23	60.6 (4)
C1—C11—C12—N10	-175.6 (2)	O20—S17—C21—F23	-61.0 (4)
C9—C11—C12—C4	-176.7 (2)	O19—S17—C21—F23	176.6 (4)
C1—C11—C12—C4	3.6 (4)	O18—S17—C21—F24	-60.6 (4)
C11—C9—C13—C14	2.0 (3)	O20—S17—C21—F24	177.8 (4)
S15—C9—C13—C14	179.63 (17)	O19—S17—C21—F24	55.4 (4)
C11—C9—C13—C8	-180.0 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 \cdots O18 ⁱ	0.99 (4)	2.38 (4)	3.315 (5)	158 (3)
N10—H10 \cdots O19	0.86 (2)	1.86 (2)	2.712 (4)	172 (3)

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$.

Table 2

π - π Interactions (\AA , $^\circ$).

Cg_I	Cg_J	$Cg\cdots Cg$	Dihedral angle	Interplanar distance	Offset
$Cg1$	$Cg1^{ii}$	3.827 (2)	0.0	3.468 (2)	1.618 (2)

Cg1	Cg3 ⁱⁱ	3.634 (2)	1.44	3.474 (2)	1.066 (2)
Cg1	Cg3 ⁱⁱⁱ	3.810 (2)	1.44	3.412 (2)	1.695 (2)
Cg2	Cg3 ⁱⁱ	3.830 (2)	3.96	3.492 (2)	1.573 (2)
Cg3	Cg1 ⁱⁱ	3.634 (2)	1.44	3.483 (2)	1.037 (2)
Cg3	Cg1 ⁱⁱⁱ	3.810 (2)	1.44	3.386 (2)	1.747 (2)
Cg3	Cg2 ⁱⁱ	3.830 (2)	3.96	3.449 (2)	1.665 (2)

Symmetry codes: (ii) $-x, -y+2, -z+1$; (iii) $-x+1, -y+2, -z+1$. Notes: Cg1, Cg2 and Cg3 are the centroids of the C9/N10/C11–C14, C1–C4/C11/C12 and C5–C8/C13/C14 rings, respectively. Cg \cdots Cg is the distance between ring centroids. The dihedral angle is that between the planes of the rings Cg $_I$ and Cg $_J$. The interplanar distance is the perpendicular distance of Cg $_I$ from ring J . The offset is the perpendicular distance of ring I from ring J .

Fig. 1

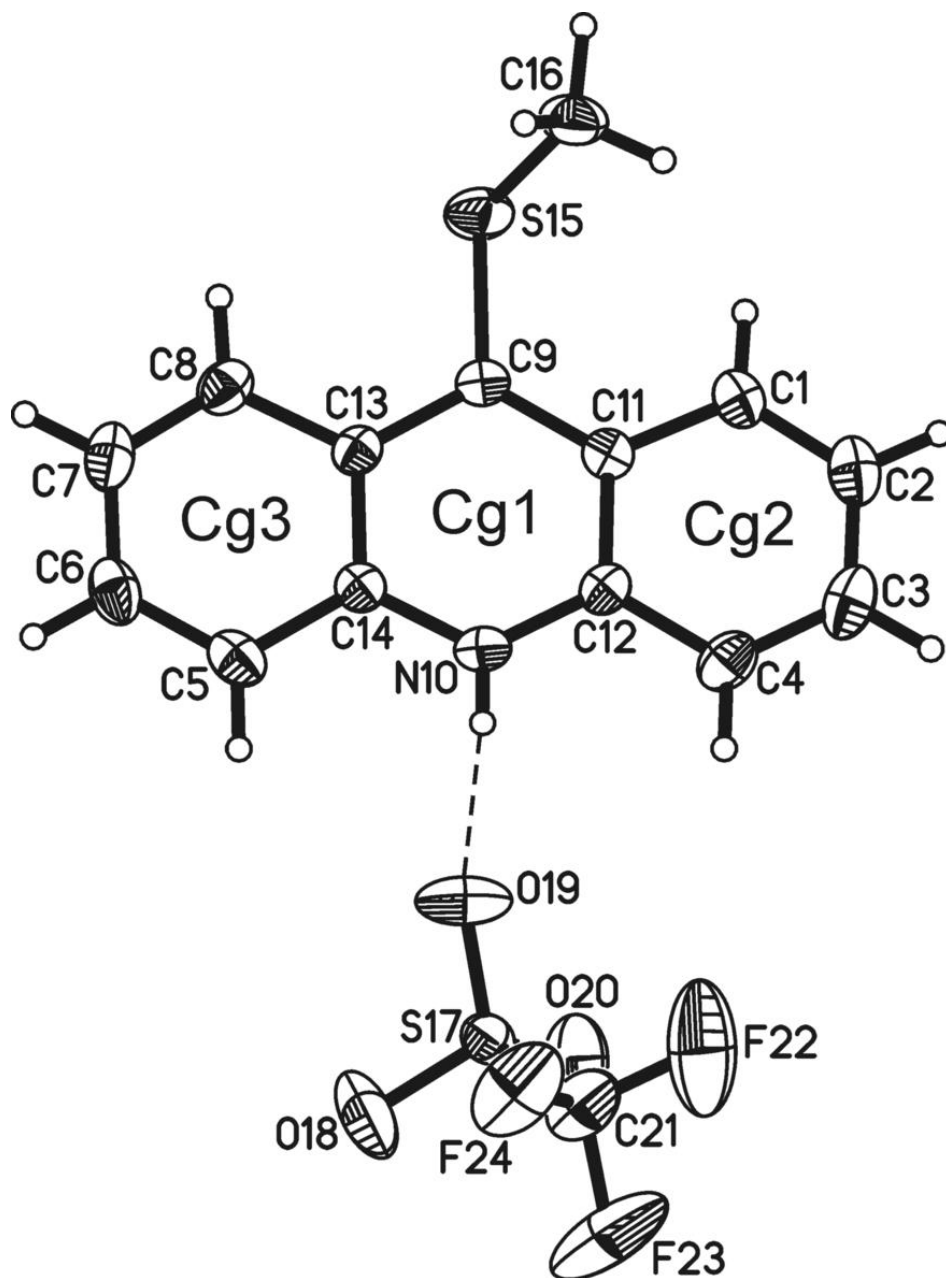


Fig. 2

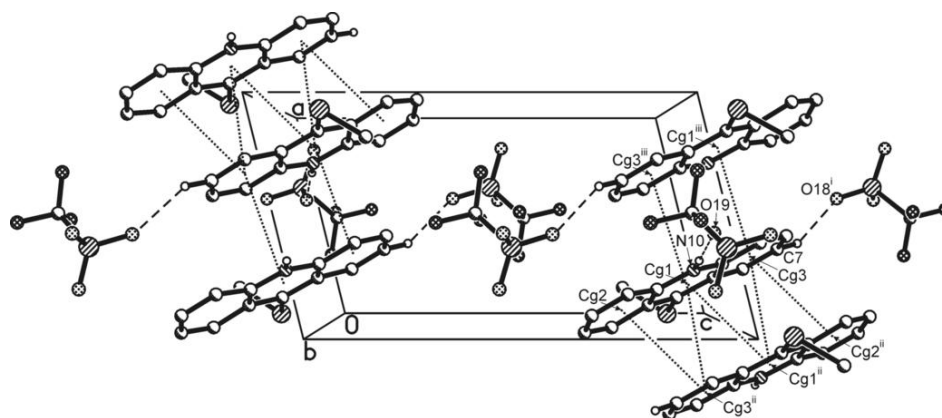


Fig. 3

