

## 9-Oxo-4,5-diazoniafluorene sulfate

D. Paul Rillema,\* Robert Kirgan and Curtis Moore

1854 N. Fairmount, Box 51, Wichita, KS 67260, USA

Correspondence e-mail: paul.rillema@wichita.edu

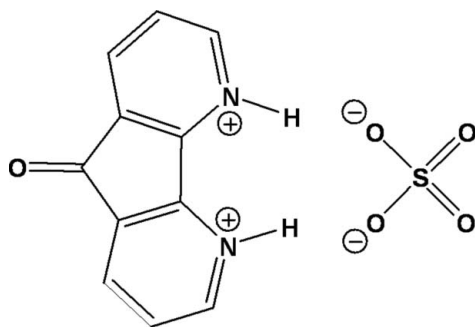
Received 25 July 2007; accepted 5 August 2007

 Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.057;  $wR$  factor = 0.138; data-to-parameter ratio = 12.1.

The diimine ligand 4,5-diazafluoren-9-one crystallized from an acid solution as the diprotonated sulfate salt,  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}^{2+} \cdot \text{SO}_4^{2-}$ . Both H atoms reside on the N atoms of the diazafluorenone ring and the sulfate anion hydrogen bonds to them. Both ions lie on a mirror plane.

### Related literature

For related literature, see: Balagopalakrishna *et al.* (1996); Menon *et al.* (1994); Ravikumar *et al.* (1995); Siemeling & Schepplmann (2004); Zhang *et al.* (2003).



### Experimental

#### Crystal data

 $\text{C}_{11}\text{H}_8\text{N}_2\text{O}^{2+} \cdot \text{SO}_4^{2-}$ 
 $M_r = 280.25$ 

 Orthorhombic,  $Pnma$ 
 $a = 11.9016$  (12) Å

 $b = 11.9344$  (12) Å

 $c = 7.8351$  (7) Å

 $V = 1112.89$  (19) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 0.31$  mm<sup>-1</sup>
 $T = 150$  (2) K

 $0.15 \times 0.13 \times 0.12$  mm

#### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer

Absorption correction: numerical (SADABS; Bruker, 2006)

 $T_{\min} = 0.956$ ,  $T_{\max} = 0.965$ 

9704 measured reflections

1140 independent reflections

 794 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.134$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.057$ 
 $wR(F^2) = 0.138$ 
 $S = 1.07$ 

1140 reflections

94 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.35$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>
**Table 1**

Selected bond distances and angles (Å, °).

The angles are obtained from the angle formed by the first three atoms listed in the table.

Atoms	Distances (Å)	Angle (°)
S—O···H—N(ring)	1.820	115.90
S—O···N(ring)	2.665 (8)	122.3 (4)
(Ring)C=O···H—N(ring)	2.777	121.14
(Ring)C=O···N(ring)	3.059 (9)	133.8 (4)

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXTL* (Bruker, 2006); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge funding from the National Science Foundation and the Department of Education for Graduate Assistance in Areas of National Need.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2152).

### References

- Balagopalakrishna, C., Kimbrough, J. T. & Westmoreland, T. D. (1996). *Inorg. Chem.* **35**, 7758–7768.
- Bruker (2006). *APEX2*, *SAINT*, *SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Menon, S., Balagopalakrishna, C., Rajasekharan, M. V. & Ramakrishna, B. L. (1994). *Inorg. Chem.* **33**, 950–954.
- Ravikumar, K., Venkata Lakshmi, N., Swamy, G. Y. S. K. & Chandra Mohan, K. (1995). *Acta Cryst.* **C51**, 1556–1558.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemeling, U. & Schepplmann, I. (2004). *Organometallics*, **23**, 626–628.
- Zhang, R.-L., Liu, H.-M., Zhao, J.-S., Gu, A.-P., He, S.-Y., Liu, J.-N. & Shi, Q.-Z. (2003). *Wuji Huaxue Xuebao (Chin. J. Inorg. Chem.)*, **19**, 722–726.

**supplementary materials**

*Acta Cryst.* (2007). E63, o3740 [ doi:10.1107/S1600536807038457 ]

## 9-Oxo-4,5-diazoniafluorene sulfate

D. P. Rillema, R. Kirgan and C. Moore

### Comment

The structure of the title compound, (I), is shown below. The molecule is of interest because the non-protonated form is used to make metal complexes in our laboratory. Some synthetic reactions need to be executed in acidic solutions, so a better understanding of the protonation behavior is useful for designing synthetic routes. Some monoprotonated forms have been reported (Balagopalakrishna *et al.*, 1996), (Menon *et al.*, 1994), (Ravikumar *et al.*, 1995), (Zhang *et al.*, 2003). The compound sits on a mirror plane in the orthorhombic space group *Pnma*. Each diazafluorenone ring has a 2+ charge which is balanced by the 2- charge of the sulfate group that is hydrogen bonded. Table 1 gives the bond distances for selected atoms and Figure 2 shows the placement of the bonds. The ketone group on the ring structure forms hydrogen bonds with the protons, but this could also be electrostatic attraction between the oxygen and nitrogen. The sulfate group forms two hydrogen bonds with the ring structure at a distance of 1.82 Å from the hydrogen atoms and 2.665 Å from the nitrogen atoms. The sulfate anion also forms hydrogen bonds with the hydrogen atoms on the ring. These distances are long and not included in the table but can be viewed in the cif file. The angles listed in Table 1 are obtained from the angle formed by the first three atoms listed in table. The angles formed by the S—O—H(N) and C=O—H(N) are slightly larger than the H—O—H angle of 109.5 found for water.

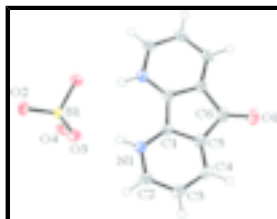
### Experimental

1,8-diazafluoren-9-one was synthesized as previously reported (Siemeling & Scheppelmann, 2004). The title compound was crystallized by allowing slow evaporation of a dilute sulfuric acid solution (1 M) containing the compound. The crystals formed on the bottom of the beaker and were collected for analysis.

### Refinement

All H atoms were initially located in a difference Fourier map but were eventually placed in their geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.88 Å and C—H = 0.95 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2_{\text{eq}}(\text{C}, \text{N})$ .

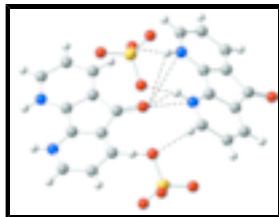
### Figures



Scheme 1. Schematic drawing of the title molecule.

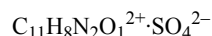
Figure 1. ORTEP drawing with 50% ellipsoids.

Figure 2. Drawing showing hydrogen bonds



## 9-Oxo-4,5-diazoniafluorene sulfate

### Crystal data



$M_r = 280.25$

Orthorhombic, *Pnma*

Hall symbol: -P2ac2n

$a = 11.9016 (12) \text{ \AA}$

$b = 11.9344 (12) \text{ \AA}$

$c = 7.8351 (7) \text{ \AA}$

$V = 1112.89 (19) \text{ \AA}^3$

$Z = 4$

$F_{000} = 576$

$D_x = 1.673 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

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

Cell parameters from 2024 reflections

$\theta = 3.1\text{--}25.5^\circ$

$\mu = 0.31 \text{ mm}^{-1}$

$T = 150 (2) \text{ K}$

Block, colorless

$0.15 \times 0.13 \times 0.12 \text{ mm}$

### Data collection

Bruker Kappa APEX II CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 150(2) \text{ K}$

$\varphi$  and  $\omega$  scans

Absorption correction: numerical (SADABS; Sheldrick, 1997)

$T_{\min} = 0.956$ ,  $T_{\max} = 0.965$

9704 measured reflections

1140 independent reflections

794 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.134$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 3.1^\circ$

$h = -14 \rightarrow 10$

$k = -14 \rightarrow 14$

$l = -9 \rightarrow 9$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.138$

$S = 1.07$

1140 reflections

94 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.4328P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$

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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7931 (3)	0.3118 (2)	0.0791 (4)	0.0184 (7)
C2	0.7283 (3)	0.4924 (3)	0.0531 (4)	0.0239 (8)
H2	0.6695	0.5427	0.0239	0.029*
C3	0.8294 (3)	0.5351 (3)	0.1087 (4)	0.0254 (8)
H3	0.8394	0.6138	0.1182	0.031*
C4	0.9162 (3)	0.4635 (3)	0.1509 (4)	0.0239 (8)
H4	0.9863	0.4914	0.1903	0.029*
C5	0.8977 (3)	0.3494 (3)	0.1336 (4)	0.0204 (7)
C6	0.9715 (4)	0.2500	0.1631 (5)	0.0218 (10)
N1	0.7103 (2)	0.3809 (2)	0.0387 (3)	0.0209 (6)
H1	0.6451	0.3549	0.0033	0.025*
O1	1.0703 (3)	0.2500	0.2015 (4)	0.0292 (8)
O2	0.6620 (3)	0.7500	0.1629 (4)	0.0324 (9)
O3	0.50345 (19)	0.64879 (17)	0.0518 (3)	0.0260 (6)
O4	0.4856 (3)	0.7500	0.3159 (4)	0.0326 (9)
S1	0.54194 (10)	0.7500	0.15386 (13)	0.0199 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0169 (18)	0.0198 (15)	0.0186 (15)	0.0004 (14)	0.0038 (14)	0.0017 (12)
C2	0.025 (2)	0.0187 (16)	0.0277 (17)	-0.0010 (15)	0.0020 (15)	-0.0002 (13)
C3	0.029 (2)	0.0190 (16)	0.0287 (17)	-0.0034 (15)	0.0040 (15)	-0.0045 (13)
C4	0.022 (2)	0.0264 (17)	0.0236 (16)	-0.0079 (15)	0.0034 (14)	-0.0059 (13)
C5	0.0170 (19)	0.0253 (16)	0.0191 (15)	-0.0016 (15)	0.0033 (13)	-0.0008 (12)
C6	0.017 (3)	0.032 (3)	0.017 (2)	0.000	0.0011 (19)	0.000
N1	0.0183 (16)	0.0207 (14)	0.0238 (14)	-0.0024 (12)	-0.0011 (11)	-0.0010 (10)
O1	0.021 (2)	0.0406 (19)	0.0264 (16)	0.000	-0.0040 (15)	0.000
O2	0.016 (2)	0.0286 (18)	0.053 (2)	0.000	-0.0058 (15)	0.000
O3	0.0276 (14)	0.0200 (12)	0.0304 (12)	-0.0006 (11)	-0.0048 (11)	-0.0035 (9)
O4	0.034 (2)	0.042 (2)	0.0221 (16)	0.000	0.0025 (15)	0.000

# supplementary materials

S1                    0.0160 (7)            0.0192 (6)            0.0246 (6)            0.000                    -0.0022 (5)            0.000

## Geometric parameters (Å, °)

C1—N1	1.323 (4)	C4—H4	0.9500
C1—C5	1.390 (4)	C5—C6	1.494 (4)
C1—C1 <sup>i</sup>	1.476 (6)	C6—O1	1.214 (5)
C2—N1	1.352 (4)	C6—C5 <sup>i</sup>	1.494 (4)
C2—C3	1.377 (5)	N1—H1	0.8800
C2—H2	0.9500	O2—S1	1.430 (3)
C3—C4	1.381 (5)	O3—S1	1.519 (2)
C3—H3	0.9500	O4—S1	1.436 (3)
C4—C5	1.386 (4)	S1—O3 <sup>ii</sup>	1.519 (2)
N1—C1—C5	122.7 (3)	C1—C5—C6	108.6 (3)
N1—C1—C1 <sup>i</sup>	128.54 (17)	O1—C6—C5 <sup>i</sup>	127.45 (18)
C5—C1—C1 <sup>i</sup>	108.80 (17)	O1—C6—C5	127.45 (18)
N1—C2—C3	121.9 (3)	C5 <sup>i</sup> —C6—C5	105.1 (4)
N1—C2—H2	119.0	C1—N1—C2	118.4 (3)
C3—C2—H2	119.0	C1—N1—H1	120.8
C2—C3—C4	120.0 (3)	C2—N1—H1	120.8
C2—C3—H3	120.0	O2—S1—O4	115.0 (2)
C4—C3—H3	120.0	O2—S1—O3	109.11 (12)
C3—C4—C5	117.7 (3)	O4—S1—O3	108.96 (12)
C3—C4—H4	121.1	O2—S1—O3 <sup>ii</sup>	109.11 (12)
C5—C4—H4	121.1	O4—S1—O3 <sup>ii</sup>	108.96 (12)
C4—C5—C1	119.3 (3)	O3—S1—O3 <sup>ii</sup>	105.29 (17)
C4—C5—C6	132.2 (3)		

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

Table 1. Selected bond distances; the angles are obtained from the angle formed by the first three atoms listed in the table

Atoms	Distances (Å)	Angle (°)
S—O <sup>⋯</sup> H—N(Ring)	1.820	115.90
S—O <sup>⋯</sup> N(Ring)	2.665	122.25
(Ring)C=O <sup>⋯</sup> H—N(Ring)	2.777	121.14
(Ring)C=O <sup>⋯</sup> N(Ring)	3.059	133.83

Fig. 1

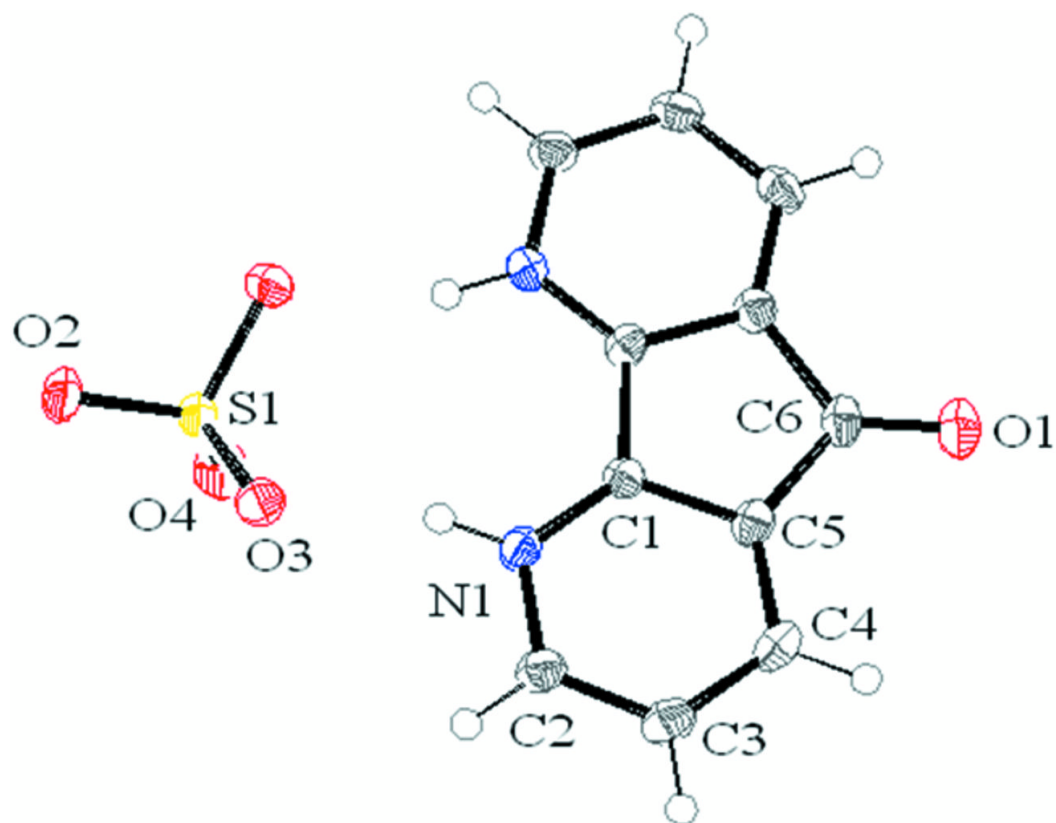


Fig. 2

