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# Diaqua[2,6-bis(2,6-diethyl-4-sulfonatophenyl)-3,5-dimethyl-2,6-diazoniaheptan-4-ido]sodium(I)

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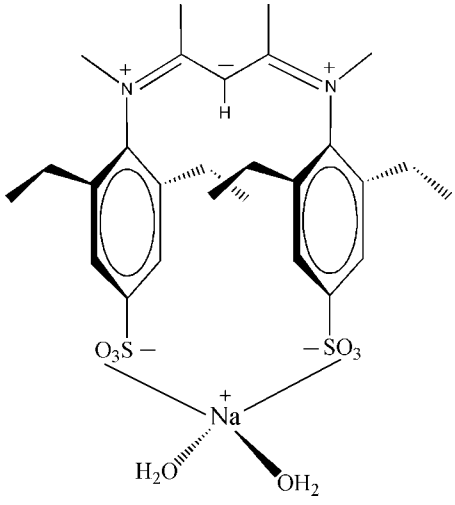
Key indicators: single-crystal X-ray study; $T$ = 193 K; mean $\sigma$(C–C) = 0.005 Å; H-atom completeness 90%; disorder in main residue; $R$ factor = 0.064; $wR$ factor = 0.186; data-to-parameter ratio = 12.3.

The title compound, $[Na(C_{25}H_{33}N_2O_6S_2)(H_2O)_2]$, was obtained as a product of the reaction of sodium 4-amino-3,5-diethylbenzenesulfonate with acetylacetone in the presence of hydrochloric acid in methanol. The molecule lies on a crystallographic twofold rotation axis and is a 'triple' internal salt which has three positive charge centers and three negative charge centers. The Na atom has a tetrahedral coordination geometry. The O atoms of the sulfonate groups are disordered over two positions with site occupancy factors of 0.87 and 0.13; the methyl groups of the ethyl substituents are disordered equally over two positions.

## Related literature

Related crystal structures of $\beta$-diimine Schiff base compounds have been reported (Brownstein *et al.*, 1983; Lesikar & Richards, 2006).




## Experimental

### Crystal data

$[Na(C_{25}H_{33}N_2O_6S_2)(H_2O)_2]$
$M_r$ = 580.64
Tetragonal, $I4_1/a$
$a$ = 12.1767 (3) Å
$c$ = 41.055 (3) Å
$V$ = 6087.2 (4) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.24 mm$^{-1}$
$T$ = 193 (2) K
0.22 × 0.18 × 0.11 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.950, $T_{max}$ = 0.975
20660 measured reflections
2699 independent reflections
1517 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.108

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.186
$S$ = 1.01
2699 reflections
220 parameters
81 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.85 (4) | 2.01 (4) | 2.854 (6) | 175 (4) |
| N1—H1···O2$A^{i}$ | 0.85 (4) | 2.08 (5) | 2.83 (3) | 148 (4) |

Symmetry code: (i) $-y+\frac{1}{4}, x-\frac{3}{4}, -z+\frac{5}{4}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2437).

## References

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# supplementary materials

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# Diaqua[2,6-bis(2,6-diethyl-4-sulfonatophenyl)-3,5-dimethyl-2,6-diazoniaheptan-4-ido]sodium(I)

**X. Guo, Q. Wang, K. Harms and H. Sun**

## Comment

In the title compound both N atoms are protonated, rather than the sulfonate groups. In the title molecule (Fig. 1) the sodium atom is coordinated in a distorted tetrahedral geometry by two O atoms of two sulfonate groups and two water molecules. There is an intermolecular hydrogen bond between the N—H group and an O atom of a sulfonate group. The O atoms of the $–SO_3$ groups are disordered over two sites as are the terminal $–CH_3$ groups of the ethyl substituents.

Similar crystal structures have been reported in the literature *e.g.* 2-*N*-phenylamino-4-*N*-phenylimino-2-pentene hydrochloride and 4-(2,4,6-trimethylphenyliminio)-2-(2,4,6-trimethylphenylamino) pent-2-ene)iodide tetrachloro-arsenate (Brownstein *et al.*, 1983; Lesikar & Richards, 2006). The bond lengths and angles of these compounds are similar to those in the title compound. There is also intermolecular hydrogen bonding in 2-*N*-phenylamino-4-*N*-phenylimino-2-pentene hydrochloride.

## Experimental

1.7 ml concentrated hydrochloric acid was added to a anhydrous methanol solution of 5.02 g (20 mmol) 3, 5-diethyl-4-amido-benzenesulfonate sodium and 1.05 g (10.5 mmol) acetyl acetone and refluxed for 6 days. A white precipitate was observed and filtered off and then washed with anhydrous methanol and a white product was obtained. This product was dissolved in methanol, and recrystallized at 258 K for 5 days, the title compound was obtained as colorless crystals (Yield 53%).

## Refinement

The H atoms on the hydrate ligands were not visible in the difference Fourier maps and have not been included in the refinement although they are included in the molecular formula. All the other H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and with $U_{iso}$(H) = 1.2 (1.5 for methyl groups) times $U_{eq}$(C). The O atoms of the unique $–SO_3$ group are disordered over two sites with refined occupancies 0.869 (11) and 0.131 (11). In addition the methyl groups of the ethyl substituents are also disordered with equall occupancies for both components.

## Figures

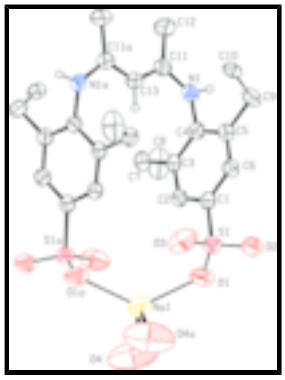


Fig. 1. The molecular structure with atom labels and 30% probability displacement ellipsoids for non-H atoms. Only selected H atoms are shown. The disorder is not shown.

## Diaqua[2,6-bis(2,6-diethyl-4-sulfonatophenyl)-3,5-dimethyl-2,6-\ diazoniaheptan-4-*ido*]sodium(I)

*Crystal data*

| | |
|---|---|
| $[Na(C_{25}H_{33}N_2O_6S_2)(H_2O)_2]$ | $Z = 8$ |
| $M_r = 580.64$ | $F_{000} = 2432$ |
| Tetragonal, $I4_1/a$ | $D_x = 1.258$ Mg m$^{-3}$ |
| Hall symbol: -I 4ad | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 12.1767$ (3) Å | Cell parameters from 3063 reflections |
| $b = 12.1767$ (3) Å | $\theta = 3.1$–$20.4$º |
| $c = 41.055$ (3) Å | $\mu = 0.24$ mm$^{-1}$ |
| $\alpha = 90$º | $T = 193$ (2) K |
| $\beta = 90$º | Block, colourless |
| $\gamma = 90$º | 0.22 × 0.18 × 0.11 mm |
| $V = 6087.2$ (4) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 2699 independent reflections |
| Radiation source: fine-focus sealed tube | 1517 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.108$ |
| $T = 193(2)$ K | $\theta_{max} = 25.0$º |
| ω scans | $\theta_{min} = 2.2$º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -14 \rightarrow 14$ |
| $T_{min} = 0.950$, $T_{max} = 0.975$ | $k = -10 \rightarrow 13$ |
| 20660 measured reflections | $l = -48 \rightarrow 48$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.064$

$wR(F^2) = 0.186$

$S = 1.01$

2699 reflections

220 parameters

81 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.102P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.38$ e Å$^{-3}$

$\Delta\rho_{min} = -0.31$ e Å$^{-3}$

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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.5271 (3) | 0.0576 (3) | 0.66152 (8) | 0.0504 (9) | |
| C2 | 0.4370 (3) | 0.1229 (3) | 0.65483 (9) | 0.0515 (9) | |
| H2 | 0.4037 | 0.1634 | 0.6720 | 0.062* | |
| C3 | 0.3946 (3) | 0.1304 (3) | 0.62371 (9) | 0.0502 (9) | |
| C4 | 0.4459 (3) | 0.0701 (3) | 0.59912 (8) | 0.0503 (9) | |
| C5 | 0.5358 (3) | 0.0018 (3) | 0.60522 (8) | 0.0534 (9) | |
| C6 | 0.5743 (3) | −0.0025 (3) | 0.63688 (8) | 0.0555 (10) | |
| H6 | 0.6353 | −0.0483 | 0.6418 | 0.067* | |
| C7 | 0.2966 (3) | 0.2026 (3) | 0.61710 (10) | 0.0623 (10) | |
| H7A | 0.2892 | 0.2559 | 0.6352 | 0.075* | |
| H7B | 0.3103 | 0.2448 | 0.5969 | 0.075* | |
| C8 | 0.1899 (4) | 0.1414 (5) | 0.61348 (17) | 0.118 (2) | |
| H8A | 0.2000 | 0.0796 | 0.5985 | 0.178* | |
| H8B | 0.1337 | 0.1910 | 0.6048 | 0.178* | |
| H8C | 0.1664 | 0.1138 | 0.6348 | 0.178* | |
| C9 | 0.5914 (3) | −0.0633 (3) | 0.57863 (9) | 0.0679 (11) | |
| H9A | 0.6275 | −0.1282 | 0.5885 | 0.082* | 0.50 |
| H9B | 0.5349 | −0.0902 | 0.5632 | 0.082* | 0.50 |
| H9C | 0.5855 | −0.0251 | 0.5580 | 0.082* | 0.50 |
| H9D | 0.6687 | −0.0729 | 0.5837 | 0.082* | 0.50 |

| | | | | | |
|---|---|---|---|---|---|
| C10 | 0.6760 (6) | 0.0018 (6) | 0.55996 (17) | 0.0545 (19) | 0.50 |
| H10A | 0.7139 | −0.0466 | 0.5445 | 0.082* | 0.50 |
| H10B | 0.7295 | 0.0330 | 0.5752 | 0.082* | 0.50 |
| H10C | 0.6396 | 0.0612 | 0.5480 | 0.082* | 0.50 |
| C10A | 0.5352 (10) | −0.1738 (10) | 0.5755 (3) | 0.125 (4) | 0.50 |
| H10D | 0.4582 | −0.1629 | 0.5693 | 0.188* | 0.50 |
| H10E | 0.5386 | −0.2124 | 0.5965 | 0.188* | 0.50 |
| H10F | 0.5723 | −0.2176 | 0.5588 | 0.188* | 0.50 |
| C11 | 0.4461 (3) | 0.1622 (3) | 0.54605 (9) | 0.0606 (10) | |
| C12 | 0.4170 (4) | 0.1490 (4) | 0.51115 (9) | 0.0894 (15) | |
| H12A | 0.4840 | 0.1366 | 0.4984 | 0.134* | |
| H12B | 0.3803 | 0.2156 | 0.5034 | 0.134* | |
| H12C | 0.3676 | 0.0860 | 0.5086 | 0.134* | |
| C13 | 0.5000 | 0.2500 | 0.55988 (14) | 0.0584 (14) | |
| N1 | 0.4111 (3) | 0.0809 (3) | 0.56575 (8) | 0.0583 (9) | |
| O4 | 0.3487 (4) | 0.2510 (8) | 0.78203 (14) | 0.262 (4) | |
| Na1 | 0.5000 | 0.2500 | 0.74867 (6) | 0.0922 (8) | |
| S1 | 0.58590 (9) | 0.05700 (8) | 0.70120 (2) | 0.0612 (4) | |
| O1 | 0.4967 (4) | 0.0733 (5) | 0.72347 (10) | 0.0889 (18) | 0.869 (11) |
| O2 | 0.6390 (5) | −0.0470 (4) | 0.70533 (9) | 0.0819 (16) | 0.869 (11) |
| O3 | 0.6590 (6) | 0.1505 (5) | 0.70159 (15) | 0.119 (2) | 0.869 (11) |
| O2A | 0.6973 (18) | 0.023 (4) | 0.6994 (7) | 0.099 (14) | 0.131 (11) |
| O1A | 0.506 (2) | 0.001 (4) | 0.7204 (9) | 0.117 (15) | 0.131 (11) |
| O3A | 0.590 (3) | 0.1683 (14) | 0.7130 (8) | 0.095 (9) | 0.131 (11) |
| H1 | 0.377 (3) | 0.022 (3) | 0.5607 (9) | 0.067 (13)* | |
| H13 | 0.5000 | 0.2500 | 0.5828 (12) | 0.048 (13)* | |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.045 (2) | 0.045 (2) | 0.061 (2) | −0.0081 (16) | −0.0005 (17) | 0.0017 (17) |
| C2 | 0.050 (2) | 0.047 (2) | 0.057 (2) | −0.0037 (17) | 0.0048 (18) | −0.0015 (17) |
| C3 | 0.045 (2) | 0.041 (2) | 0.065 (2) | −0.0067 (15) | −0.0019 (18) | 0.0014 (17) |
| C4 | 0.052 (2) | 0.044 (2) | 0.055 (2) | −0.0092 (17) | −0.0070 (18) | −0.0011 (17) |
| C5 | 0.052 (2) | 0.048 (2) | 0.060 (2) | 0.0011 (18) | −0.0046 (18) | −0.0016 (18) |
| C6 | 0.051 (2) | 0.056 (2) | 0.060 (2) | 0.0065 (18) | −0.0029 (18) | −0.0007 (18) |
| C7 | 0.057 (2) | 0.058 (2) | 0.073 (2) | 0.0061 (19) | −0.006 (2) | −0.002 (2) |
| C8 | 0.061 (3) | 0.095 (4) | 0.200 (6) | 0.003 (3) | −0.011 (4) | 0.006 (4) |
| C9 | 0.075 (3) | 0.069 (3) | 0.060 (2) | 0.011 (2) | −0.010 (2) | −0.017 (2) |
| C10 | 0.042 (4) | 0.072 (5) | 0.049 (4) | 0.016 (4) | 0.002 (3) | −0.012 (4) |
| C10A | 0.124 (10) | 0.146 (11) | 0.106 (8) | 0.018 (8) | −0.003 (7) | −0.039 (8) |
| C11 | 0.067 (3) | 0.058 (3) | 0.057 (2) | 0.002 (2) | −0.007 (2) | −0.003 (2) |
| C12 | 0.125 (4) | 0.085 (3) | 0.058 (3) | −0.008 (3) | −0.023 (3) | −0.003 (2) |
| C13 | 0.074 (4) | 0.053 (4) | 0.048 (3) | −0.003 (3) | 0.000 | 0.000 |
| N1 | 0.066 (2) | 0.048 (2) | 0.061 (2) | −0.0042 (17) | −0.0150 (16) | −0.0086 (17) |
| O4 | 0.124 (4) | 0.491 (12) | 0.171 (5) | −0.108 (6) | 0.038 (3) | 0.070 (6) |
| Na1 | 0.1482 (18) | 0.099 (2) | 0.0908 (17) | −0.0076 (14) | 0.000 | 0.000 |
| S1 | 0.0625 (7) | 0.0653 (8) | 0.0559 (6) | −0.0015 (5) | −0.0058 (5) | −0.0010 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.087 (3) | 0.120 (4) | 0.059 (2) | 0.034 (3) | 0.005 (2) | −0.008 (3) |
| O2 | 0.087 (4) | 0.096 (3) | 0.063 (2) | 0.038 (3) | −0.009 (2) | 0.001 (2) |
| O3 | 0.125 (5) | 0.136 (4) | 0.096 (4) | −0.079 (4) | −0.045 (3) | 0.026 (3) |
| O2A | 0.040 (16) | 0.18 (4) | 0.078 (16) | 0.064 (18) | −0.010 (13) | −0.05 (2) |
| O1A | 0.045 (17) | 0.17 (3) | 0.14 (3) | −0.05 (2) | −0.006 (15) | 0.09 (3) |
| O3A | 0.14 (2) | 0.065 (15) | 0.081 (17) | −0.075 (15) | −0.050 (16) | 0.017 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C6 | 1.374 (5) | C10A—H10E | 0.9800 |
| C1—C2 | 1.382 (5) | C10A—H10F | 0.9800 |
| C1—S1 | 1.779 (4) | C11—N1 | 1.347 (5) |
| C2—C3 | 1.381 (5) | C11—C13 | 1.377 (4) |
| C2—H2 | 0.9500 | C11—C12 | 1.484 (5) |
| C3—C4 | 1.396 (5) | C12—H12A | 0.9800 |
| C3—C7 | 1.507 (5) | C12—H12B | 0.9800 |
| C4—C5 | 1.397 (5) | C12—H12C | 0.9800 |
| C4—N1 | 1.440 (4) | C13—C11$^{i}$ | 1.377 (4) |
| C5—C6 | 1.383 (5) | C13—H13 | 0.94 (4) |
| C5—C9 | 1.509 (5) | N1—H1 | 0.85 (4) |
| C6—H6 | 0.9500 | O4—Na1 | 2.295 (5) |
| C7—C8 | 1.505 (6) | Na1—O3A$^{i}$ | 2.08 (4) |
| C7—H7A | 0.9900 | Na1—O3A | 2.08 (4) |
| C7—H7B | 0.9900 | Na1—O4$^{i}$ | 2.295 (5) |
| C8—H8A | 0.9800 | Na1—O1 | 2.387 (6) |
| C8—H8B | 0.9800 | Na1—O1$^{i}$ | 2.387 (6) |
| C8—H8C | 0.9800 | Na1—O3$^{i}$ | 2.992 (9) |
| C9—C10 | 1.509 (8) | Na1—O3 | 2.992 (9) |
| C9—C10A | 1.516 (13) | Na1—S1 | 3.2274 (19) |
| C9—H9A | 0.9900 | Na1—S1$^{i}$ | 3.2274 (19) |
| C9—H9B | 0.9900 | S1—O2A | 1.422 (13) |
| C9—H9C | 0.9700 | S1—O1A | 1.430 (14) |
| C9—H9D | 0.9700 | S1—O2 | 1.431 (4) |
| C10—H10A | 0.9800 | S1—O1 | 1.433 (4) |
| C10—H10B | 0.9800 | S1—O3A | 1.439 (15) |
| C10—H10C | 0.9800 | S1—O3 | 1.445 (4) |
| C10A—H10D | 0.9800 | | |
| C6—C1—C2 | 119.5 (3) | C11$^{i}$—C13—H13 | 114.4 (3) |
| C6—C1—S1 | 120.2 (3) | C11—N1—C4 | 123.1 (3) |
| C2—C1—S1 | 120.2 (3) | C11—N1—H1 | 129 (3) |
| C3—C2—C1 | 121.2 (3) | C4—N1—H1 | 107 (3) |
| C3—C2—H2 | 119.4 | O3A$^{i}$—Na1—O3A | 90.6 (16) |
| C1—C2—H2 | 119.4 | O3A$^{i}$—Na1—O4 | 89.7 (9) |
| C2—C3—C4 | 117.8 (3) | O3A—Na1—O4 | 147.7 (9) |
| C2—C3—C7 | 120.1 (3) | O3A$^{i}$—Na1—O4$^{i}$ | 147.7 (9) |
| C4—C3—C7 | 122.1 (3) | O3A—Na1—O4$^{i}$ | 89.7 (9) |

| | | | |
|---|---|---|---|
| C3—C4—C5 | 122.3 (3) | O4—Na1—O4$^{i}$ | 106.7 (3) |
| C3—C4—N1 | 120.5 (3) | O3A$^{i}$—Na1—O1 | 96.7 (8) |
| C5—C4—N1 | 117.1 (3) | O3A—Na1—O1 | 43.4 (8) |
| C6—C5—C4 | 117.1 (3) | O4—Na1—O1 | 104.5 (3) |
| C6—C5—C9 | 120.5 (3) | O4$^{i}$—Na1—O1 | 105.5 (3) |
| C4—C5—C9 | 122.3 (3) | O3A$^{i}$—Na1—O1$^{i}$ | 43.4 (8) |
| C1—C6—C5 | 122.0 (3) | O3A—Na1—O1$^{i}$ | 96.7 (8) |
| C1—C6—H6 | 119.0 | O4—Na1—O1$^{i}$ | 105.5 (3) |
| C5—C6—H6 | 119.0 | O4$^{i}$—Na1—O1$^{i}$ | 104.5 (3) |
| C8—C7—C3 | 114.4 (3) | O1—Na1—O1$^{i}$ | 128.6 (3) |
| C8—C7—H7A | 108.7 | O3A$^{i}$—Na1—O3$^{i}$ | 8.7 (9) |
| C3—C7—H7A | 108.7 | O3A—Na1—O3$^{i}$ | 94.6 (8) |
| C8—C7—H7B | 108.7 | O4—Na1—O3$^{i}$ | 82.2 (2) |
| C3—C7—H7B | 108.7 | O4$^{i}$—Na1—O3$^{i}$ | 155.1 (3) |
| H7A—C7—H7B | 107.6 | O1—Na1—O3$^{i}$ | 94.26 (17) |
| C7—C8—H8A | 109.5 | O1$^{i}$—Na1—O3$^{i}$ | 50.64 (15) |
| C7—C8—H8B | 109.5 | O3A$^{i}$—Na1—O3 | 94.6 (8) |
| H8A—C8—H8B | 109.5 | O3A—Na1—O3 | 8.7 (9) |
| C7—C8—H8C | 109.5 | O4—Na1—O3 | 155.1 (3) |
| H8A—C8—H8C | 109.5 | O4$^{i}$—Na1—O3 | 82.2 (2) |
| H8B—C8—H8C | 109.5 | O1—Na1—O3 | 50.64 (15) |
| C10—C9—C5 | 113.4 (4) | O1$^{i}$—Na1—O3 | 94.26 (17) |
| C10—C9—C10A | 137.1 (6) | O3$^{i}$—Na1—O3 | 99.5 (2) |
| C5—C9—C10A | 108.9 (5) | O3A$^{i}$—Na1—S1 | 95.4 (8) |
| C10—C9—H9A | 108.9 | O3A—Na1—S1 | 19.4 (8) |
| C5—C9—H9A | 108.9 | O4—Na1—S1 | 128.6 (2) |
| C10A—C9—H9A | 61.7 | O4$^{i}$—Na1—S1 | 95.5 (2) |
| C10—C9—H9B | 108.9 | O1—Na1—S1 | 24.15 (13) |
| C5—C9—H9B | 108.9 | O1$^{i}$—Na1—S1 | 112.89 (15) |
| C10A—C9—H9B | 48.6 | O3$^{i}$—Na1—S1 | 96.57 (13) |
| H9A—C9—H9B | 107.7 | O3—Na1—S1 | 26.52 (8) |
| C10—C9—H9C | 49.8 | O3A$^{i}$—Na1—S1$^{i}$ | 19.4 (8) |
| C5—C9—H9C | 110.3 | O3A—Na1—S1$^{i}$ | 95.4 (8) |
| C10A—C9—H9C | 108.6 | O4—Na1—S1$^{i}$ | 95.5 (2) |
| H9A—C9—H9C | 140.5 | O4$^{i}$—Na1—S1$^{i}$ | 128.6 (2) |
| H9B—C9—H9C | 63.2 | O1—Na1—S1$^{i}$ | 112.89 (15) |
| C10—C9—H9D | 60.7 | O1$^{i}$—Na1—S1$^{i}$ | 24.15 (13) |
| C5—C9—H9D | 110.1 | O3$^{i}$—Na1—S1$^{i}$ | 26.52 (8) |
| C10A—C9—H9D | 110.4 | O3—Na1—S1$^{i}$ | 96.57 (13) |
| H9A—C9—H9D | 52.2 | S1—Na1—S1$^{i}$ | 105.70 (8) |
| H9B—C9—H9D | 140.4 | O2A—S1—O1A | 123 (2) |
| H9C—C9—H9D | 108.5 | O2A—S1—O2 | 47 (2) |
| C9—C10—H9C | 40.0 | O1A—S1—O2 | 80 (2) |

| | | | |
|---|---|---|---|
| C9—C10—H9D | 39.3 | O2A—S1—O1 | 142.8 (14) |
| H9C—C10—H9D | 78.1 | O1A—S1—O1 | 36 (2) |
| C9—C10—H10A | 109.5 | O2—S1—O1 | 112.9 (3) |
| H9C—C10—H10A | 103.5 | O2A—S1—O3A | 105.1 (19) |
| H9D—C10—H10A | 95.4 | O1A—S1—O3A | 107 (2) |
| C9—C10—H10B | 109.5 | O2—S1—O3A | 141.0 (13) |
| H9C—C10—H10B | 142.3 | O1—S1—O3A | 71.5 (17) |
| H9D—C10—H10B | 81.0 | O2A—S1—O3 | 69 (2) |
| C9—C10—H10C | 109.5 | O1A—S1—O3 | 142 (2) |
| H9C—C10—H10C | 75.1 | O2—S1—O3 | 114.7 (3) |
| H9D—C10—H10C | 146.8 | O1—S1—O3 | 110.5 (4) |
| C9—C10A—H10D | 109.5 | O3A—S1—O3 | 39.9 (15) |
| C9—C10A—H10E | 109.5 | O2A—S1—C1 | 109.8 (11) |
| H10D—C10A—H10E | 109.5 | O1A—S1—C1 | 103.4 (15) |
| C9—C10A—H10F | 109.5 | O2—S1—C1 | 107.1 (2) |
| H10D—C10A—H10F | 109.5 | O1—S1—C1 | 106.2 (2) |
| H10E—C10A—H10F | 109.5 | O3A—S1—C1 | 108.5 (12) |
| N1—C11—C13 | 118.2 (4) | O3—S1—C1 | 104.8 (2) |
| N1—C11—C12 | 115.1 (4) | O2A—S1—Na1 | 123.7 (14) |
| C13—C11—C12 | 126.6 (4) | O1A—S1—Na1 | 78 (3) |
| C11—C12—H12A | 109.5 | O2—S1—Na1 | 135.95 (16) |
| C11—C12—H12B | 109.5 | O1—S1—Na1 | 43.0 (3) |
| H12A—C12—H12B | 109.5 | O3A—S1—Na1 | 28.8 (17) |
| C11—C12—H12C | 109.5 | O3—S1—Na1 | 67.6 (4) |
| H12A—C12—H12C | 109.5 | C1—S1—Na1 | 114.80 (13) |
| H12B—C12—H12C | 109.5 | S1—O1—Na1 | 112.9 (4) |
| C11—C13—C11$^{i}$ | 131.3 (5) | S1—O3—Na1 | 85.9 (4) |
| C11—C13—H13 | 114.4 (3) | S1—O3A—Na1 | 132 (2) |
| C6—C1—C2—C3 | −1.1 (5) | O4$^{i}$—Na1—S1—O1 | 116.1 (4) |
| S1—C1—C2—C3 | 175.5 (3) | O1$^{i}$—Na1—S1—O1 | −135.6 (3) |
| C1—C2—C3—C4 | −0.2 (5) | O3$^{i}$—Na1—S1—O1 | −85.7 (3) |
| C1—C2—C3—C7 | −179.8 (3) | O3—Na1—S1—O1 | 176.1 (4) |
| C2—C3—C4—C5 | 1.4 (5) | S1$^{i}$—Na1—S1—O1 | −111.1 (3) |
| C7—C3—C4—C5 | −179.0 (3) | O3A$^{i}$—Na1—S1—O3A | 76 (3) |
| C2—C3—C4—N1 | −175.1 (3) | O4—Na1—S1—O3A | 170 (3) |
| C7—C3—C4—N1 | 4.4 (5) | O4$^{i}$—Na1—S1—O3A | −73 (3) |
| C3—C4—C5—C6 | −1.2 (5) | O1—Na1—S1—O3A | 171 (3) |
| N1—C4—C5—C6 | 175.4 (3) | O1$^{i}$—Na1—S1—O3A | 35 (3) |
| C3—C4—C5—C9 | −179.9 (3) | O3$^{i}$—Na1—S1—O3A | 85 (3) |
| N1—C4—C5—C9 | −3.2 (5) | O3—Na1—S1—O3A | −13 (3) |
| C2—C1—C6—C5 | 1.2 (5) | S1$^{i}$—Na1—S1—O3A | 60 (3) |
| S1—C1—C6—C5 | −175.4 (3) | O3A$^{i}$—Na1—S1—O3 | 89.5 (9) |
| C4—C5—C6—C1 | −0.1 (5) | O3A—Na1—S1—O3 | 13 (3) |
| C9—C5—C6—C1 | 178.6 (4) | O4—Na1—S1—O3 | −176.6 (3) |
| C2—C3—C7—C8 | −102.8 (5) | O4$^{i}$—Na1—S1—O3 | −60.0 (3) |
| C4—C3—C7—C8 | 77.7 (5) | O1—Na1—S1—O3 | −176.1 (4) |

| | | | |
|---|---|---|---|
| C6—C5—C9—C10 | −94.6 (5) | O1$^{i}$—Na1—S1—O3 | 48.3 (3) |
| C4—C5—C9—C10 | 84.0 (5) | O3$^{i}$—Na1—S1—O3 | 98.1 (3) |
| C6—C5—C9—C10A | 92.4 (6) | S1$^{i}$—Na1—S1—O3 | 72.7 (2) |
| C4—C5—C9—C10A | −89.0 (6) | O3A$^{i}$—Na1—S1—C1 | −7.0 (9) |
| N1—C11—C13—C11$^{i}$ | 172.5 (4) | O3A—Na1—S1—C1 | −83 (3) |
| C12—C11—C13—C11$^{i}$ | −10.5 (3) | O4—Na1—S1—C1 | 86.9 (3) |
| C13—C11—N1—C4 | −12.9 (5) | O4$^{i}$—Na1—S1—C1 | −156.5 (2) |
| C12—C11—N1—C4 | 169.8 (4) | O1—Na1—S1—C1 | 87.4 (3) |
| C3—C4—N1—C11 | 83.0 (5) | O1$^{i}$—Na1—S1—C1 | −48.26 (18) |
| C5—C4—N1—C11 | −93.7 (4) | O3$^{i}$—Na1—S1—C1 | 1.62 (15) |
| C6—C1—S1—O2A | 20 (3) | O3—Na1—S1—C1 | −96.5 (3) |
| C2—C1—S1—O2A | −157 (3) | S1$^{i}$—Na1—S1—C1 | −23.80 (12) |
| C6—C1—S1—O1A | −113 (2) | O2A—S1—O1—Na1 | 86 (3) |
| C2—C1—S1—O1A | 71 (2) | O1A—S1—O1—Na1 | 160 (3) |
| C6—C1—S1—O2 | −29.4 (4) | O2—S1—O1—Na1 | 133.7 (3) |
| C2—C1—S1—O2 | 154.1 (4) | O3A—S1—O1—Na1 | −4.7 (13) |
| C6—C1—S1—O1 | −150.2 (4) | O3—S1—O1—Na1 | 3.8 (4) |
| C2—C1—S1—O1 | 33.2 (4) | C1—S1—O1—Na1 | −109.2 (2) |
| C6—C1—S1—O3A | 134.3 (19) | O3A$^{i}$—Na1—O1—S1 | 88.2 (10) |
| C2—C1—S1—O3A | −42.2 (19) | O3A—Na1—O1—S1 | 4.4 (12) |
| C6—C1—S1—O3 | 92.8 (5) | O4—Na1—O1—S1 | 179.6 (3) |
| C2—C1—S1—O3 | −83.7 (5) | O4$^{i}$—Na1—O1—S1 | −68.1 (3) |
| C6—C1—S1—Na1 | 164.6 (3) | O1$^{i}$—Na1—O1—S1 | 55.6 (2) |
| C2—C1—S1—Na1 | −11.9 (3) | O3$^{i}$—Na1—O1—S1 | 96.6 (3) |
| O3A$^{i}$—Na1—S1—O2A | 132 (3) | O3—Na1—O1—S1 | −2.2 (2) |
| O3A—Na1—S1—O2A | 56 (3) | S1$^{i}$—Na1—O1—S1 | 77.1 (3) |
| O4—Na1—S1—O2A | −134 (3) | O2A—S1—O3—Na1 | −143.0 (13) |
| O4$^{i}$—Na1—S1—O2A | −17 (3) | O1A—S1—O3—Na1 | −26 (3) |
| O1—Na1—S1—O2A | −134 (3) | O2—S1—O3—Na1 | −131.8 (2) |
| O1$^{i}$—Na1—S1—O2A | 91 (3) | O1—S1—O3—Na1 | −2.8 (3) |
| O3$^{i}$—Na1—S1—O2A | 141 (3) | O3A—S1—O3—Na1 | 9.8 (19) |
| O3—Na1—S1—O2A | 43 (3) | C1—S1—O3—Na1 | 111.13 (16) |
| S1$^{i}$—Na1—S1—O2A | 115 (3) | O3A$^{i}$—Na1—O3—S1 | −92.9 (9) |
| O3A$^{i}$—Na1—S1—O1A | −106.4 (16) | O3A—Na1—O3—S1 | −30 (5) |
| O3A—Na1—S1—O1A | 177 (3) | O4—Na1—O3—S1 | 6.3 (6) |
| O4—Na1—S1—O1A | −12.5 (14) | O4$^{i}$—Na1—O3—S1 | 119.5 (3) |
| O4$^{i}$—Na1—S1—O1A | 104.1 (14) | O1—Na1—O3—S1 | 2.0 (2) |
| O1—Na1—S1—O1A | −12.0 (15) | O1$^{i}$—Na1—O3—S1 | −136.4 (3) |
| O1$^{i}$—Na1—S1—O1A | −147.6 (14) | O3$^{i}$—Na1—O3—S1 | −85.7 (2) |
| O3$^{i}$—Na1—S1—O1A | −97.7 (13) | S1$^{i}$—Na1—O3—S1 | −112.3 (2) |
| O3—Na1—S1—O1A | 164.1 (13) | O2A—S1—O3A—Na1 | −135 (2) |
| S1$^{i}$—Na1—S1—O1A | −123.1 (13) | O1A—S1—O3A—Na1 | −3(3) |
| O3A$^{i}$—Na1—S1—O2 | −167.6 (11) | O2—S1—O3A—Na1 | −97 (3) |

| | | | |
|---|---|---|---|
| O3A—Na1—S1—O2 | 116 (3) | O1—S1—O3A—Na1 | 6.6 (19) |
| O4—Na1—S1—O2 | −73.7 (5) | O3—S1—O3A—Na1 | −161 (4) |
| O4$^{i}$—Na1—S1—O2 | 42.9 (4) | C1—S1—O3A—Na1 | 108 (2) |
| O1—Na1—S1—O2 | −73.2 (4) | O3A$^{i}$—Na1—O3A—S1 | −105 (3) |
| O1$^{i}$—Na1—S1—O2 | 151.2 (4) | O4—Na1—O3A—S1 | −14 (4) |
| O3$^{i}$—Na1—S1—O2 | −159.0 (4) | O4$^{i}$—Na1—O3A—S1 | 108 (2) |
| O3—Na1—S1—O2 | 102.9 (4) | O1—Na1—O3A—S1 | −5.5 (16) |
| S1$^{i}$—Na1—S1—O2 | 175.6 (4) | O1$^{i}$—Na1—O3A—S1 | −148 (2) |
| O3A$^{i}$—Na1—S1—O1 | −94.4 (10) | O3$^{i}$—Na1—O3A—S1 | −97 (2) |
| O3A—Na1—S1—O1 | −171 (3) | O3—Na1—O3A—S1 | 138 (7) |
| O4—Na1—S1—O1 | −0.5 (4) | S1$^{i}$—Na1—O3A—S1 | −123 (2) |

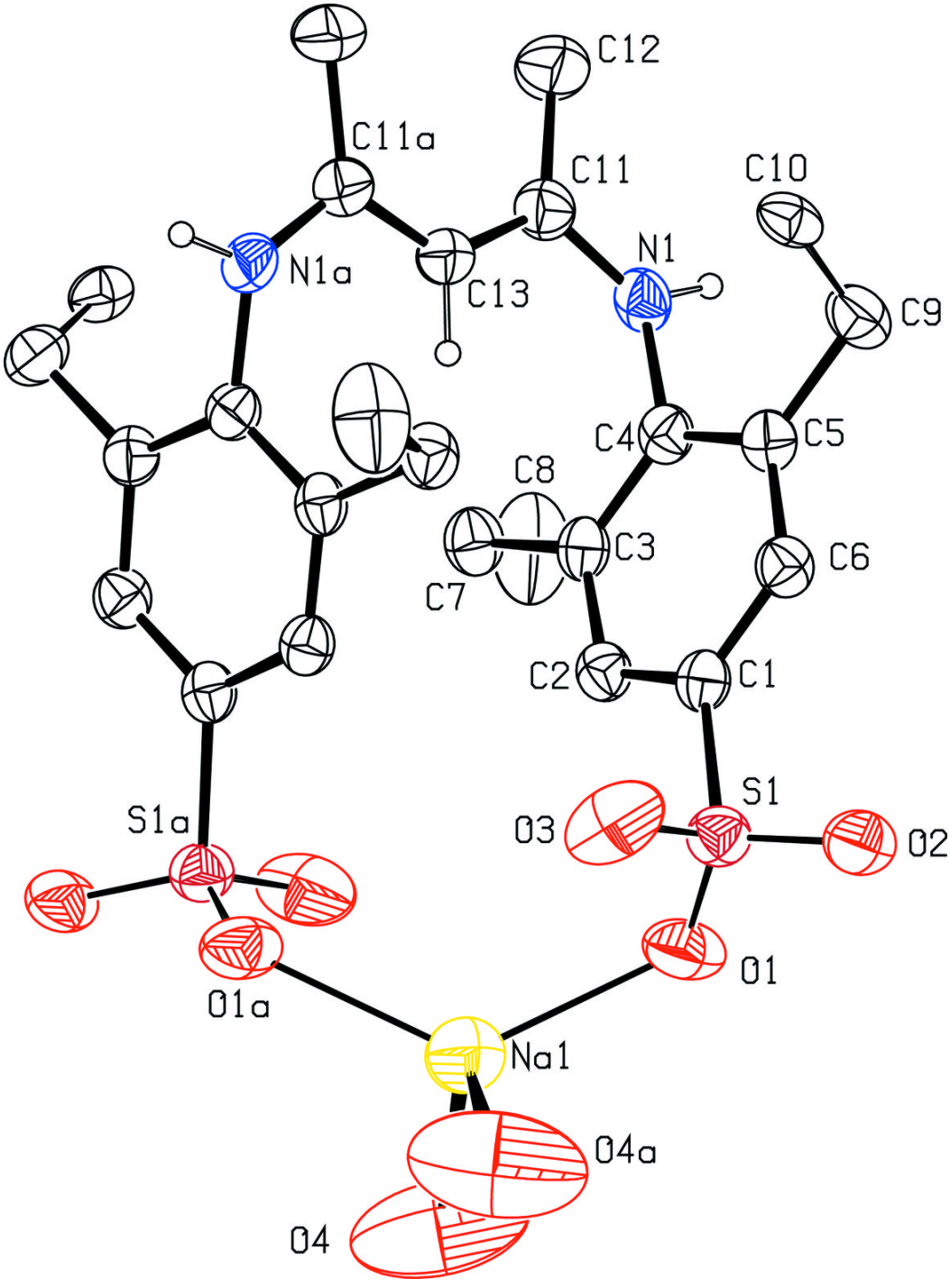
Symmetry codes: (i) −*x*+1, −*y*+1/2, *z*.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O2$^{ii}$ | 0.85 (4) | 2.01 (4) | 2.854 (6) | 175 (4) |
| N1—H1···O2A$^{ii}$ | 0.85 (4) | 2.08 (5) | 2.83 (3) | 148 (4) |

Symmetry codes: (ii) −*y*+1/4, *x*−3/4, −*z*+5/4.

**Fig. 1**


C12
C11a
C11
C10
N1a
C13
N1
C9
C4
C5
C8
C3
C6
C7
C2
C1
S1
S1a
O3
O2
O1
O1a
Na1
O4a
O4