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# Benzyltributylammonium 6-hydroxynaphthalene-2-sulfonate

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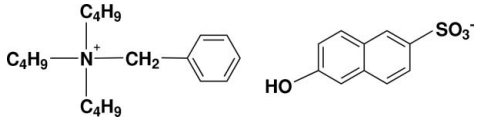
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.005 Å; disorder in main residue; $R$ factor = 0.055; $wR$ factor = 0.191; data-to-parameter ratio = 15.6.

The title compound, $C_{19}H_{34}N^+\cdot C_{10}H_7O_4S^-$, is a charge-control agent for toners used in electrophotography. Intermoleclar O—H···O hydrogen bonding between the OH group of one anion and the sulfonate O atom of a neighboring anion leads to the formation of one-dimensional chains along the *b* axis. In addition, C—H···O hydrogen bonds are observed. One of the *n*-butyl chains of the cation is disordered over two sites in a 0.88:0.12 ratio.

## Related literature

For general background to charge-control agents for toners, see: Nash *et al.* (2001). For a related structure, see: Mizuguchi *et al.* (2007).




## Experimental

### Crystal data

$C_{19}H_{34}N^+\cdot C_{10}H_7O_4S^-$
$M_r$ = 499.70
Monoclinic, $P2_1/c$
$a$ = 16.9616 (4) Å
$b$ = 10.4422 (2) Å
$c$ = 17.6700 (4) Å
$\beta$ = 116.2570 (11)°
$V$ = 2806.73 (11) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 1.28 mm$^{-1}$
$T$ = 296.1 K
0.50 × 0.25 × 0.04 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.720, $T_{max}$ = 0.954
24483 measured reflections
5103 independent reflections
2818 reflections with $F^2 > 2\sigma(F^2)$
$R_{int}$ = 0.032

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.191
$S$ = 1.10
5103 reflections
328 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.40 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H4*O*···O2$^{i}$ | 0.82 | 1.88 | 2.696 (3) | 177 |
| C12—H12*B*···O2$^{ii}$ | 0.96 | 2.52 | 3.470 (4) | 173 |
| C16—H16*B*···O3$^{i}$ | 0.98 | 2.34 | 3.251 (4) | 155 |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2006); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

The authors express their sincere thanks to Mr O. Yamate at Orient Chemical Industries, Ltd. for the preparation of the sample.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2755).

## References

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# supplementary materials

*Acta Cryst.* (2009). E**65**, o319 [ **doi:10.1107/S1600536809001329** ]

# Benzyltributylammonium 6-hydroxynaphthalene-2-sulfonate

**K. Uta, Y. Sato and J. Mizuguchi**

## Comment

Quaternary ammonium salts (for example, benzyltributylammonium 4-hydroxynaphthalene-1-sulfonate: P-51 from Orient Chemical Industries) are well known charge-control agents (CCAs) for toners used in electrophotography. CCAs are usually added to toners to create a desired charge level and polarity (Nash *et al.*, 2001). The above compounds are characterized by high melting point above 433 K. The present high thermal stability is required for the toner manufacturing process which includes kneading of various toner components such as polymer, colorant, wax and CCA at 403–453 K. However, ordinary quaternary ammonium salts used in electrochemistry as supporting electrolytes exhibit much lower melting points below 373 K. Previously, we have investigated why P-51 alone possesses such a high melting point from the standpoint of the crystal structure. Then, we found chains of O—H···O intermolecular hydrogen bonds between the OH group of one anion and the sulfonate O atom of the neighboring one (Mizuguchi *et al.*, 2007). The formation of the hydrogen bond is found to be responsible for the high thermal stability of P-51. A s an extension of this study, the present paper deals with the structure of the title compound, which is one of the P-51 derivatives.

Fig. 1 shows the *ORTEPIII* plot (Burnett & Johnson, 19966) of the title molecule. The ions have no crystallographically imposed symmetry. Fig. 2 shows a hydrogen-bonded anionic chain along the *b* axis between the OH group of one anion and the sulfonate O atom of the neighboring one. In addition, C—H···O hydrogen bonds are observed in the crystal structure (Table 1). The hydrogen-bonding network is found to greatly contribute to the high melting point of the title compound (433 K), just as in the case of P-51 (462 K).

## Experimental

The title compound was obtained from Orient Chemical Industries Ltd., and was recrystallized from a methanol solution. After 48 h, a number of colourless crystals were obtained in the form of platelets.

## Refinement

Atom C11 was found to be disordered over two sites. The site occupancies for C11A/C11B were initially refined and later fixed at 0.88/0.12. These atoms were anisotropically refined. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å (aromatic), 0.96 Å (methyl), or 0.97 Å (methylene), and O—H = 0.82 Å; $U_{iso}$(H) = 1.2–1.5$U_{eq}$(parent atom).

## Figures

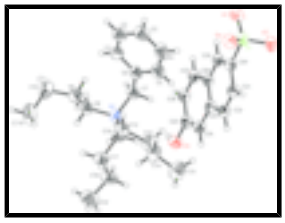


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Only the major disorder component is shown.

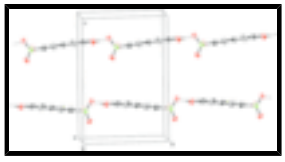


Fig. 2. The formation of a hydrogen-bonded (dashed lines) chain. Only anions are shown for clarity.

## Benzyltributylammonium 6-hydroxynaphthalene-2-sulfonate

*Crystal data*

| | |
|---|---|
| $C_{19}H_{34}N^+ \cdot C_{10}H_7O_4S^-$ | $F_{000}$ = 1080.00 |
| $M_r$ = 499.70 | $D_x$ = 1.183 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Cu $K\alpha$ radiation<br>λ = 1.54187 Å |
| Hall symbol: -P 2ybc | Cell parameters from 15945 reflections |
| $a$ = 16.9616 (4) Å | θ = 3.0–68.2º |
| $b$ = 10.4422 (2) Å | μ = 1.28 mm$^{-1}$ |
| $c$ = 17.6700 (4) Å | $T$ = 296.1 K |
| β = 116.2570 (11)º | Plate, colourless |
| $V$ = 2806.73 (11) Å$^3$ | 0.50 × 0.25 × 0.04 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 2818 reflections with $F^2 > 2\sigma(F^2)$ |
| Detector resolution: 10.00 pixels mm$^{-1}$ | $R_{int}$ = 0.032 |
| ω scans | $\theta_{max}$ = 68.2º |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $h$ = −20→20 |
| $T_{min}$ = 0.720, $T_{max}$ = 0.954 | $k$ = −12→12 |
| 24483 measured reflections | $l$ = −21→21 |
| 5103 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.055 | $w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.689P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |

| | |
|---|---|
| $wR(F^2) = 0.191$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.10$ | $\Delta\rho_{max} = 0.27$ e Å$^{-3}$ |
| 5103 reflections | $\Delta\rho_{min} = -0.40$ e Å$^{-3}$ |
| 328 parameters | 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 $F^2 > \sigma(F^2)$ 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) |
|---|---|---|---|---|---|
| S1 | 0.72863 (6) | −0.06500 (8) | 0.72643 (5) | 0.0673 (2) | |
| O1 | 0.64931 (16) | −0.0460 (2) | 0.73670 (15) | 0.0775 (6) | |
| O2 | 0.79375 (17) | −0.1418 (2) | 0.79490 (15) | 0.0840 (7) | |
| O3 | 0.71380 (17) | −0.1121 (2) | 0.64457 (14) | 0.0805 (7) | |
| O4 | 0.89003 (16) | 0.6746 (2) | 0.76763 (17) | 0.0837 (7) | |
| N1 | 0.71413 (18) | 0.5740 (2) | 0.48646 (16) | 0.0636 (6) | |
| C1 | 0.5395 (2) | 0.3823 (4) | 0.4426 (2) | 0.0829 (10) | |
| C2 | 0.4932 (2) | 0.2707 (5) | 0.4115 (2) | 0.0948 (12) | |
| C3 | 0.5324 (3) | 0.1552 (5) | 0.4400 (3) | 0.1058 (14) | |
| C4 | 0.6187 (3) | 0.1490 (4) | 0.4993 (3) | 0.1091 (15) | |
| C5 | 0.6659 (2) | 0.2610 (4) | 0.5289 (2) | 0.0922 (12) | |
| C6 | 0.6279 (2) | 0.3792 (3) | 0.5014 (2) | 0.0729 (9) | |
| C7 | 0.6794 (2) | 0.4989 (3) | 0.5397 (2) | 0.0729 (9) | |
| C8 | 0.6398 (2) | 0.6301 (3) | 0.4083 (2) | 0.0691 (8) | |
| C9 | 0.5816 (2) | 0.7256 (3) | 0.4246 (2) | 0.0849 (10) | |
| C10 | 0.5138 (3) | 0.7839 (4) | 0.3429 (3) | 0.1152 (14) | |
| C11A | 0.5529 (5) | 0.8743 (7) | 0.3027 (4) | 0.145 (3) | 0.88 |
| C11B | 0.499 (2) | 0.774 (4) | 0.2541 (10) | 0.120 (8) | 0.12 |
| C12 | 0.7657 (2) | 0.4880 (3) | 0.4554 (2) | 0.0701 (9) | |
| C13 | 0.8520 (2) | 0.4368 (4) | 0.5213 (2) | 0.0877 (11) | |
| C14 | 0.8937 (3) | 0.3471 (4) | 0.4819 (3) | 0.1095 (14) | |
| C15 | 0.9840 (3) | 0.3085 (6) | 0.5412 (4) | 0.148 (2) | |
| C16 | 0.7723 (2) | 0.6785 (3) | 0.5429 (2) | 0.0736 (9) | |
| C17 | 0.8068 (2) | 0.7742 (3) | 0.5005 (2) | 0.0821 (10) | |
| C18 | 0.8740 (3) | 0.8608 (4) | 0.5651 (2) | 0.1039 (14) | |
| C19 | 0.8973 (4) | 0.9751 (5) | 0.5287 (3) | 0.142 (2) | |
| C20 | 0.7782 (2) | 0.0872 (2) | 0.73747 (19) | 0.0591 (7) | |
| C21 | 0.8585 (2) | 0.0989 (3) | 0.7323 (2) | 0.0686 (8) | |

| | | | | | |
|---|---|---|---|---|---|
| C22 | 0.8973 (2) | 0.2154 (3) | 0.7391 (2) | 0.0711 (9) | |
| C23 | 0.8581 (2) | 0.3286 (3) | 0.75144 (19) | 0.0607 (7) | |
| C24 | 0.8940 (2) | 0.4517 (3) | 0.7557 (2) | 0.0662 (8) | |
| C25 | 0.8535 (2) | 0.5573 (3) | 0.7660 (2) | 0.0657 (8) | |
| C26 | 0.7749 (2) | 0.5462 (3) | 0.7738 (2) | 0.0679 (8) | |
| C27 | 0.7390 (2) | 0.4290 (3) | 0.7700 (2) | 0.0694 (8) | |
| C28 | 0.7778 (2) | 0.3164 (2) | 0.75807 (19) | 0.0600 (7) | |
| C29 | 0.7396 (2) | 0.1939 (3) | 0.7505 (2) | 0.0637 (8) | |
| H1 | 0.5117 | 0.4606 | 0.4249 | 0.107* | |
| H2 | 0.4349 | 0.2744 | 0.3713 | 0.121* | |
| H3 | 0.5001 | 0.0806 | 0.4187 | 0.134* | |
| H4 | 0.6455 | 0.0700 | 0.5191 | 0.138* | |
| H4O | 0.8599 | 0.7308 | 0.7740 | 0.134* | |
| H5 | 0.7246 | 0.2558 | 0.5688 | 0.117* | |
| H7A | 0.7295 | 0.4774 | 0.5924 | 0.094* | |
| H7B | 0.6427 | 0.5573 | 0.5532 | 0.094* | |
| H8A | 0.6026 | 0.5591 | 0.3754 | 0.092* | |
| H8B | 0.6643 | 0.6697 | 0.3744 | 0.092* | |
| H9A | 0.6195 | 0.7924 | 0.4617 | 0.110* | |
| H9B | 0.5529 | 0.6833 | 0.4544 | 0.110* | |
| H10A | 0.4837 | 0.7156 | 0.3035 | 0.138* | 0.88 |
| H10B | 0.4704 | 0.8296 | 0.3544 | 0.138* | 0.88 |
| H10C | 0.4579 | 0.7594 | 0.3413 | 0.138* | 0.12 |
| H10D | 0.5190 | 0.8753 | 0.3539 | 0.138* | 0.12 |
| H11A | 0.5899 | 0.8275 | 0.2843 | 0.217* | 0.88 |
| H11B | 0.5871 | 0.9381 | 0.3430 | 0.217* | 0.88 |
| H11C | 0.5066 | 0.9151 | 0.2551 | 0.217* | 0.88 |
| H11D | 0.4736 | 0.6916 | 0.2320 | 0.180* | 0.12 |
| H11E | 0.5535 | 0.7830 | 0.2511 | 0.180* | 0.12 |
| H11F | 0.4590 | 0.8400 | 0.2214 | 0.180* | 0.12 |
| H12A | 0.7296 | 0.4148 | 0.4277 | 0.090* | |
| H12B | 0.7775 | 0.5346 | 0.4148 | 0.090* | |
| H13A | 0.8416 | 0.3936 | 0.5644 | 0.112* | |
| H13B | 0.8904 | 0.5097 | 0.5475 | 0.112* | |
| H14A | 0.8585 | 0.2700 | 0.4617 | 0.144* | |
| H14B | 0.8968 | 0.3876 | 0.4337 | 0.144* | |
| H15A | 1.0082 | 0.2512 | 0.5147 | 0.233* | |
| H15B | 0.9832 | 0.2656 | 0.5898 | 0.233* | |
| H15C | 1.0206 | 0.3832 | 0.5609 | 0.233* | |
| H16A | 0.8213 | 0.6398 | 0.5893 | 0.096* | |
| H16B | 0.7382 | 0.7251 | 0.5667 | 0.096* | |
| H17A | 0.8322 | 0.7307 | 0.4688 | 0.104* | |
| H17B | 0.7582 | 0.8275 | 0.4611 | 0.104* | |
| H18A | 0.8514 | 0.8896 | 0.6034 | 0.128* | |
| H18B | 0.9261 | 0.8096 | 0.5965 | 0.128* | |
| H19A | 0.9420 | 1.0211 | 0.5738 | 0.226* | |
| H19B | 0.8478 | 1.0235 | 0.4979 | 0.226* | |
| H19C | 0.9225 | 0.9420 | 0.4920 | 0.226* | |
| H21 | 0.8853 | 0.0268 | 0.7241 | 0.087* | |

| | | | | |
|---|---|---|---|---|
| H22 | 0.9508 | 0.2212 | 0.7367 | 0.091* |
| H24 | 0.9464 | 0.4604 | 0.7511 | 0.085* |
| H26 | 0.7479 | 0.6192 | 0.7816 | 0.089* |
| H27 | 0.6870 | 0.4229 | 0.7760 | 0.089* |
| H29 | 0.6873 | 0.1859 | 0.7549 | 0.083* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0846 (6) | 0.0493 (4) | 0.0677 (5) | −0.0029 (4) | 0.0336 (4) | −0.0039 (3) |
| O1 | 0.0811 (15) | 0.0723 (15) | 0.0930 (17) | −0.0088 (12) | 0.0512 (13) | −0.0066 (12) |
| O2 | 0.1071 (18) | 0.0523 (13) | 0.0804 (16) | 0.0101 (13) | 0.0304 (14) | 0.0063 (11) |
| O3 | 0.1080 (18) | 0.0711 (15) | 0.0679 (14) | −0.0156 (13) | 0.0438 (13) | −0.0229 (12) |
| O4 | 0.0858 (16) | 0.0560 (14) | 0.1050 (19) | −0.0103 (12) | 0.0383 (14) | −0.0062 (13) |
| N1 | 0.0717 (16) | 0.0652 (17) | 0.0576 (15) | −0.0036 (13) | 0.0320 (13) | −0.0055 (13) |
| C1 | 0.081 (2) | 0.090 (2) | 0.080 (2) | −0.012 (2) | 0.038 (2) | −0.003 (2) |
| C2 | 0.091 (2) | 0.104 (3) | 0.087 (2) | −0.029 (2) | 0.036 (2) | −0.012 (2) |
| C3 | 0.127 (4) | 0.093 (3) | 0.095 (3) | −0.036 (3) | 0.047 (3) | −0.016 (2) |
| C4 | 0.135 (4) | 0.074 (2) | 0.102 (3) | −0.013 (2) | 0.037 (3) | 0.005 (2) |
| C5 | 0.104 (3) | 0.079 (2) | 0.080 (2) | −0.011 (2) | 0.029 (2) | 0.003 (2) |
| C6 | 0.089 (2) | 0.071 (2) | 0.0592 (19) | −0.013 (2) | 0.0332 (18) | −0.0043 (17) |
| C7 | 0.084 (2) | 0.078 (2) | 0.062 (2) | −0.0089 (19) | 0.0364 (18) | −0.0029 (17) |
| C8 | 0.073 (2) | 0.073 (2) | 0.0627 (19) | 0.0024 (17) | 0.0304 (17) | 0.0008 (16) |
| C9 | 0.086 (2) | 0.085 (2) | 0.094 (2) | 0.009 (2) | 0.048 (2) | 0.002 (2) |
| C10 | 0.097 (3) | 0.115 (3) | 0.115 (3) | 0.029 (2) | 0.030 (2) | −0.003 (2) |
| C11A | 0.181 (6) | 0.158 (6) | 0.108 (4) | 0.075 (4) | 0.077 (4) | 0.051 (4) |
| C11B | 0.106 (16) | 0.120 (18) | 0.102 (5) | 0.004 (16) | 0.017 (11) | 0.009 (13) |
| C12 | 0.079 (2) | 0.070 (2) | 0.066 (2) | 0.0034 (18) | 0.0360 (18) | −0.0059 (17) |
| C13 | 0.088 (2) | 0.094 (2) | 0.076 (2) | 0.014 (2) | 0.032 (2) | −0.001 (2) |
| C14 | 0.103 (3) | 0.107 (3) | 0.105 (3) | 0.029 (2) | 0.034 (2) | −0.003 (2) |
| C15 | 0.106 (3) | 0.157 (5) | 0.168 (5) | 0.037 (3) | 0.050 (3) | 0.019 (4) |
| C16 | 0.081 (2) | 0.071 (2) | 0.070 (2) | −0.0148 (18) | 0.0341 (18) | −0.0136 (18) |
| C17 | 0.088 (2) | 0.079 (2) | 0.084 (2) | −0.016 (2) | 0.041 (2) | −0.015 (2) |
| C18 | 0.116 (3) | 0.102 (3) | 0.102 (3) | −0.043 (2) | 0.055 (2) | −0.025 (2) |
| C19 | 0.157 (4) | 0.117 (4) | 0.144 (4) | −0.057 (3) | 0.060 (3) | −0.012 (3) |
| C20 | 0.0646 (18) | 0.0539 (18) | 0.0538 (16) | 0.0011 (14) | 0.0217 (14) | −0.0009 (14) |
| C21 | 0.071 (2) | 0.057 (2) | 0.080 (2) | 0.0049 (16) | 0.0356 (18) | −0.0071 (16) |
| C22 | 0.0642 (19) | 0.062 (2) | 0.084 (2) | 0.0008 (16) | 0.0307 (18) | −0.0062 (17) |
| C23 | 0.0586 (17) | 0.0566 (19) | 0.0607 (18) | 0.0021 (15) | 0.0208 (14) | −0.0031 (14) |
| C24 | 0.0625 (19) | 0.057 (2) | 0.073 (2) | −0.0037 (15) | 0.0250 (16) | −0.0088 (16) |
| C25 | 0.072 (2) | 0.0512 (19) | 0.0646 (19) | −0.0051 (16) | 0.0217 (16) | −0.0048 (15) |
| C26 | 0.078 (2) | 0.0503 (19) | 0.078 (2) | 0.0024 (16) | 0.0371 (18) | −0.0069 (16) |
| C27 | 0.074 (2) | 0.0540 (19) | 0.085 (2) | 0.0023 (16) | 0.0389 (18) | −0.0032 (17) |
| C28 | 0.0641 (18) | 0.0514 (18) | 0.0622 (18) | 0.0035 (14) | 0.0259 (15) | −0.0006 (14) |
| C29 | 0.0685 (19) | 0.0508 (18) | 0.073 (2) | 0.0033 (15) | 0.0320 (16) | 0.0022 (15) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—O1 | 1.449 (3) | C5—H5 | 0.933 |

| | | | |
|---|---|---|---|
| S1—O2 | 1.465 (2) | C7—H7A | 0.969 |
| S1—O3 | 1.441 (2) | C7—H7B | 0.972 |
| S1—C20 | 1.768 (3) | C8—H8A | 0.981 |
| O4—C25 | 1.367 (4) | C8—H8B | 0.961 |
| N1—C7 | 1.530 (5) | C9—H9A | 0.978 |
| N1—C8 | 1.517 (3) | C9—H9B | 0.967 |
| N1—C12 | 1.515 (5) | C10—H10A | 0.970 |
| N1—C16 | 1.513 (4) | C10—H10B | 0.970 |
| C1—C2 | 1.376 (6) | C10—H10C | 0.970 |
| C1—C6 | 1.398 (4) | C10—H10D | 0.970 |
| C2—C3 | 1.361 (7) | C11A—H11A | 0.960 |
| C3—C4 | 1.375 (6) | C11A—H11B | 0.960 |
| C4—C5 | 1.383 (6) | C11A—H11C | 0.960 |
| C5—C6 | 1.377 (5) | C11B—H11D | 0.960 |
| C6—C7 | 1.503 (5) | C11B—H11E | 0.960 |
| C8—C9 | 1.518 (6) | C11B—H11F | 0.960 |
| C9—C10 | 1.519 (5) | C12—H12A | 0.966 |
| C10—C11A | 1.500 (10) | C12—H12B | 0.959 |
| C10—C11B | 1.48 (2) | C13—H13A | 0.966 |
| C12—C13 | 1.509 (4) | C13—H13B | 0.975 |
| C13—C14 | 1.515 (7) | C14—H14A | 0.971 |
| C14—C15 | 1.478 (6) | C14—H14B | 0.974 |
| C16—C17 | 1.513 (6) | C15—H15A | 0.957 |
| C17—C18 | 1.507 (5) | C15—H15B | 0.973 |
| C18—C19 | 1.490 (8) | C15—H15C | 0.962 |
| C20—C21 | 1.410 (5) | C16—H16A | 0.960 |
| C20—C29 | 1.362 (4) | C16—H16B | 0.982 |
| C21—C22 | 1.362 (5) | C17—H17A | 0.959 |
| C22—C23 | 1.419 (5) | C17—H17B | 0.983 |
| C23—C24 | 1.410 (4) | C18—H18A | 0.961 |
| C23—C28 | 1.423 (5) | C18—H18B | 0.969 |
| C24—C25 | 1.355 (5) | C19—H19A | 0.952 |
| C25—C26 | 1.406 (6) | C19—H19B | 0.923 |
| C26—C27 | 1.354 (4) | C19—H19C | 0.983 |
| C27—C28 | 1.408 (5) | C21—H21 | 0.924 |
| C28—C29 | 1.413 (4) | C22—H22 | 0.930 |
| O4—H4O | 0.817 | C24—H24 | 0.932 |
| C1—H1 | 0.926 | C26—H26 | 0.930 |
| C2—H2 | 0.930 | C27—H27 | 0.936 |
| C3—H3 | 0.931 | C29—H29 | 0.928 |
| C4—H4 | 0.931 | | |
| O2···O4$^{i}$ | 2.696 (3) | C11B···H2$^{iv}$ | 2.896 |
| O4···O2$^{ii}$ | 2.696 (3) | C25···H7A | 2.970 |
| C2···C11B$^{iii}$ | 2.99 (3) | H2···O1$^{v}$ | 2.993 |
| C11B···C2$^{iv}$ | 2.99 (3) | H2···O3$^{v}$ | 2.947 |
| S1···H4O$^{i}$ | 2.925 | H2···C11B$^{iii}$ | 2.896 |
| O1···H2$^{v}$ | 2.993 | H3···O1$^{v}$ | 2.817 |

| | | | |
|---|---|---|---|
| O1···H3$^{v}$ | 2.817 | H4···O3 | 2.757 |
| O1···H8A$^{vi}$ | 2.893 | H4O···S1$^{ii}$ | 2.925 |
| O1···H8B$^{vi}$ | 2.665 | H4O···O2$^{ii}$ | 1.880 |
| O1···H10B$^{vii}$ | 2.989 | H7A···C25 | 2.970 |
| O1···H12B$^{vi}$ | 2.930 | H8A···O1$^{ix}$ | 2.893 |
| O2···H4O$^{i}$ | 1.880 | H8B···O1$^{ix}$ | 2.665 |
| O2···H12B$^{vi}$ | 2.516 | H9B···C1$^{vii}$ | 2.961 |
| O2···H17A$^{vi}$ | 2.992 | H9B···C2$^{vii}$ | 2.846 |
| O2···H26$^{i}$ | 2.593 | H10B···O1$^{vii}$ | 2.989 |
| O3···H2$^{v}$ | 2.947 | H11D···C2$^{iv}$ | 2.949 |
| O3···H4 | 2.757 | H11E···C2$^{iv}$ | 2.624 |
| O3···H16B$^{i}$ | 2.336 | H11F···C1$^{iv}$ | 2.942 |
| O3···H18A$^{i}$ | 2.736 | H11F···C2$^{iv}$ | 2.895 |
| O4···H15B$^{viii}$ | 2.661 | H12B···O1$^{ix}$ | 2.930 |
| O4···H16A | 2.859 | H12B···O2$^{ix}$ | 2.516 |
| O4···H22$^{viii}$ | 2.777 | H15B···O4$^{x}$ | 2.661 |
| C1···H9B$^{vii}$ | 2.961 | H16A···O4 | 2.859 |
| C1···H11F$^{iii}$ | 2.942 | H16B···O3$^{ii}$ | 2.336 |
| C2···H9B$^{vii}$ | 2.846 | H17A···O2$^{ix}$ | 2.992 |
| C2···H11D$^{iii}$ | 2.949 | H18A···O3$^{ii}$ | 2.736 |
| C2···H11E$^{iii}$ | 2.624 | H22···O4$^{x}$ | 2.777 |
| C2···H11F$^{iii}$ | 2.895 | H26···O2$^{ii}$ | 2.593 |
| O1—S1—O2 | 111.98 (17) | C9—C10—H10B | 108.9 |
| O1—S1—O3 | 114.40 (15) | C9—C10—H10C | 104.0 |
| O1—S1—C20 | 106.62 (16) | C9—C10—H10D | 103.9 |
| O2—S1—O3 | 112.04 (15) | C11A—C10—H10A | 108.9 |
| O2—S1—C20 | 104.67 (13) | C11A—C10—H10B | 108.9 |
| O3—S1—C20 | 106.32 (17) | C11B—C10—H10C | 103.9 |
| C7—N1—C8 | 111.5 (2) | C11B—C10—H10D | 103.9 |
| C7—N1—C12 | 111.1 (2) | H10A—C10—H10B | 107.7 |
| C7—N1—C16 | 106.3 (2) | H10C—C10—H10D | 105.4 |
| C8—N1—C12 | 106.2 (2) | C10—C11A—H11A | 109.5 |
| C8—N1—C16 | 111.0 (2) | C10—C11A—H11B | 109.5 |
| C12—N1—C16 | 110.7 (2) | C10—C11A—H11C | 109.5 |
| C2—C1—C6 | 120.8 (3) | H11A—C11A—H11B | 109.5 |
| C1—C2—C3 | 120.3 (3) | H11A—C11A—H11C | 109.5 |
| C2—C3—C4 | 120.3 (4) | H11B—C11A—H11C | 109.5 |
| C3—C4—C5 | 119.4 (4) | C10—C11B—H11D | 109.5 |
| C4—C5—C6 | 121.5 (3) | C10—C11B—H11E | 109.5 |
| C1—C6—C5 | 117.6 (3) | C10—C11B—H11F | 109.5 |
| C1—C6—C7 | 122.3 (3) | H11D—C11B—H11E | 109.5 |
| C5—C6—C7 | 119.9 (2) | H11D—C11B—H11F | 109.5 |
| N1—C7—C6 | 117.0 (3) | H11E—C11B—H11F | 109.5 |
| N1—C8—C9 | 115.4 (3) | N1—C12—H12A | 108.4 |

| | | | |
|---|---|---|---|
| C8—C9—C10 | 111.4 (3) | N1—C12—H12B | 108.4 |
| C9—C10—C11A | 113.3 (4) | C13—C12—H12A | 107.0 |
| C9—C10—C11B | 133.1 (18) | C13—C12—H12B | 107.8 |
| N1—C12—C13 | 116.7 (3) | H12A—C12—H12B | 108.5 |
| C12—C13—C14 | 110.8 (3) | C12—C13—H13A | 108.7 |
| C13—C14—C15 | 113.0 (4) | C12—C13—H13B | 107.8 |
| N1—C16—C17 | 115.6 (3) | C14—C13—H13A | 111.0 |
| C16—C17—C18 | 110.5 (3) | C14—C13—H13B | 110.5 |
| C17—C18—C19 | 114.2 (3) | H13A—C13—H13B | 107.9 |
| S1—C20—C21 | 119.8 (2) | C13—C14—H14A | 110.2 |
| S1—C20—C29 | 120.9 (2) | C13—C14—H14B | 110.5 |
| C21—C20—C29 | 119.4 (3) | C15—C14—H14A | 108.0 |
| C20—C21—C22 | 120.9 (3) | C15—C14—H14B | 107.4 |
| C21—C22—C23 | 121.1 (3) | H14A—C14—H14B | 107.4 |
| C22—C23—C24 | 123.1 (3) | C14—C15—H15A | 111.0 |
| C22—C23—C28 | 117.9 (3) | C14—C15—H15B | 109.7 |
| C24—C23—C28 | 119.0 (3) | C14—C15—H15C | 109.6 |
| C23—C24—C25 | 121.0 (3) | H15A—C15—H15B | 108.7 |
| O4—C25—C24 | 118.7 (3) | H15A—C15—H15C | 109.6 |
| O4—C25—C26 | 120.9 (3) | H15B—C15—H15C | 108.2 |
| C24—C25—C26 | 120.4 (3) | N1—C16—H16A | 109.0 |
| C25—C26—C27 | 119.6 (3) | N1—C16—H16B | 107.7 |
| C26—C27—C28 | 122.2 (3) | C17—C16—H16A | 108.8 |
| C23—C28—C27 | 117.7 (3) | C17—C16—H16B | 108.4 |
| C23—C28—C29 | 119.2 (3) | H16A—C16—H16B | 107.2 |
| C27—C28—C29 | 123.1 (3) | C16—C17—H17A | 110.4 |
| C20—C29—C28 | 121.5 (3) | C16—C17—H17B | 109.7 |
| C25—O4—H4O | 109.9 | C18—C17—H17A | 110.0 |
| C2—C1—H1 | 119.9 | C18—C17—H17B | 108.2 |
| C6—C1—H1 | 119.3 | H17A—C17—H17B | 107.9 |
| C1—C2—H2 | 119.7 | C17—C18—H18A | 108.5 |
| C3—C2—H2 | 120.0 | C17—C18—H18B | 107.1 |
| C2—C3—H3 | 119.3 | C19—C18—H18A | 108.6 |
| C4—C3—H3 | 120.4 | C19—C18—H18B | 109.9 |
| C3—C4—H4 | 120.4 | H18A—C18—H18B | 108.4 |
| C5—C4—H4 | 120.2 | C18—C19—H19A | 107.9 |
| C4—C5—H5 | 118.8 | C18—C19—H19B | 110.3 |
| C6—C5—H5 | 119.7 | C18—C19—H19C | 106.2 |
| N1—C7—H7A | 107.2 | H19A—C19—H19B | 113.4 |
| N1—C7—H7B | 107.0 | H19A—C19—H19C | 108.2 |
| C6—C7—H7A | 109.2 | H19B—C19—H19C | 110.6 |
| C6—C7—H7B | 108.9 | C20—C21—H21 | 119.8 |
| H7A—C7—H7B | 107.2 | C22—C21—H21 | 119.3 |
| N1—C8—H8A | 107.8 | C21—C22—H22 | 119.8 |
| N1—C8—H8B | 108.6 | C23—C22—H22 | 119.1 |
| C9—C8—H8A | 107.9 | C23—C24—H24 | 119.5 |
| C9—C8—H8B | 109.4 | C25—C24—H24 | 119.5 |
| H8A—C8—H8B | 107.4 | C25—C26—H26 | 119.8 |
| C8—C9—H9A | 107.8 | C27—C26—H26 | 120.6 |

| | | | |
|---|---|---|---|
| C8—C9—H9B | 109.2 | C26—C27—H27 | 118.8 |
| C10—C9—H9A | 110.3 | C28—C27—H27 | 119.0 |
| C10—C9—H9B | 110.4 | C20—C29—H29 | 119.3 |
| H9A—C9—H9B | 107.5 | C28—C29—H29 | 119.2 |
| C9—C10—H10A | 108.9 | | |
| O1—S1—C20—C21 | 178.7 (2) | C8—C9—C10—C11A | −70.7 (5) |
| O1—S1—C20—C29 | −1.7 (2) | C8—C9—C10—C11B | −6(2) |
| O2—S1—C20—C21 | 59.9 (3) | N1—C12—C13—C14 | 177.0 (3) |
| O2—S1—C20—C29 | −120.5 (2) | C12—C13—C14—C15 | 171.9 (4) |
| O3—S1—C20—C21 | −58.9 (2) | N1—C16—C17—C18 | −171.6 (3) |
| O3—S1—C20—C29 | 120.8 (2) | C16—C17—C18—C19 | −167.4 (4) |
| C7—N1—C8—C9 | 61.7 (3) | S1—C20—C21—C22 | 178.9 (2) |
| C8—N1—C7—C6 | 65.9 (3) | S1—C20—C29—C28 | −178.9 (2) |
| C7—N1—C12—C13 | −68.0 (3) | C21—C20—C29—C28 | 0.7 (4) |
| C12—N1—C7—C6 | −52.5 (3) | C29—C20—C21—C22 | −0.8 (4) |
| C7—N1—C16—C17 | −173.9 (3) | C20—C21—C22—C23 | −0.2 (4) |
| C16—N1—C7—C6 | −173.0 (2) | C21—C22—C23—C24 | −177.5 (3) |
| C8—N1—C12—C13 | 170.5 (3) | C21—C22—C23—C28 | 1.3 (4) |
| C12—N1—C8—C9 | −177.1 (3) | C22—C23—C24—C25 | 178.8 (3) |
| C8—N1—C16—C17 | −52.4 (4) | C22—C23—C28—C27 | −179.8 (2) |
| C16—N1—C8—C9 | −56.6 (4) | C22—C23—C28—C29 | −1.3 (4) |
| C12—N1—C16—C17 | 65.3 (3) | C24—C23—C28—C27 | −1.1 (4) |
| C16—N1—C12—C13 | 49.8 (4) | C24—C23—C28—C29 | 177.5 (2) |
| C2—C1—C6—C5 | −2.0 (7) | C28—C23—C24—C25 | 0.1 (3) |
| C2—C1—C6—C7 | −177.1 (4) | C23—C24—C25—O4 | −178.4 (2) |
| C6—C1—C2—C3 | 2.3 (8) | C23—C24—C25—C26 | 0.8 (4) |
| C1—C2—C3—C4 | −0.7 (9) | O4—C25—C26—C27 | 178.5 (3) |
| C2—C3—C4—C5 | −1.0 (9) | C24—C25—C26—C27 | −0.8 (4) |
| C3—C4—C5—C6 | 1.2 (9) | C25—C26—C27—C28 | −0.2 (4) |
| C4—C5—C6—C1 | 0.3 (7) | C26—C27—C28—C23 | 1.1 (4) |
| C4—C5—C6—C7 | 175.5 (5) | C26—C27—C28—C29 | −177.4 (3) |
| C1—C6—C7—N1 | −79.8 (5) | C23—C28—C29—C20 | 0.3 (4) |
| C5—C6—C7—N1 | 105.2 (4) | C27—C28—C29—C20 | 178.8 (3) |
| N1—C8—C9—C10 | 175.5 (3) | | |

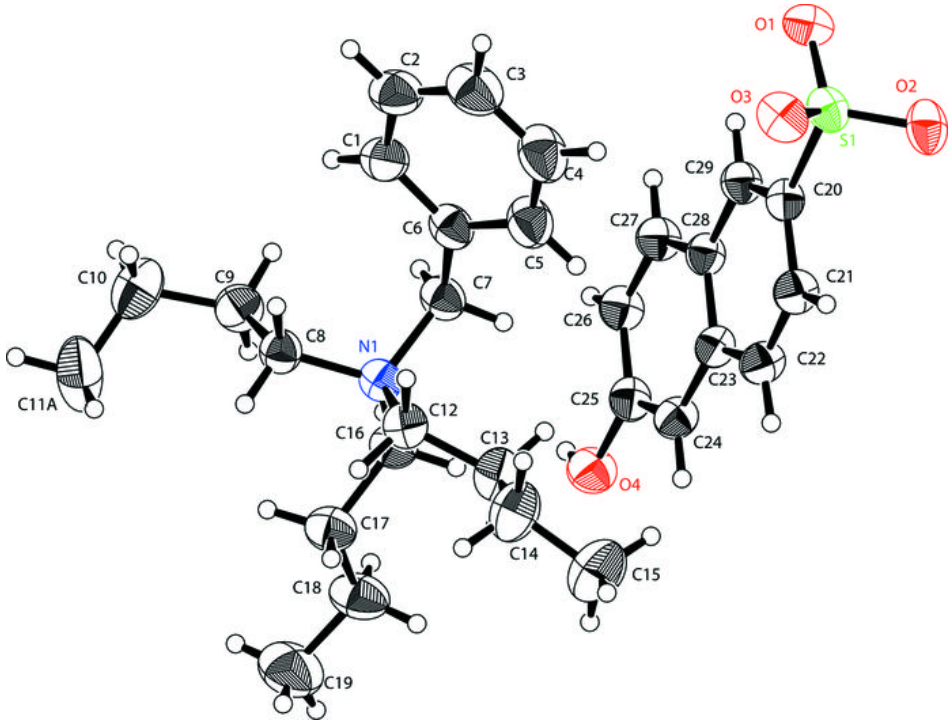
Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+1/2; (iv) −*x*+1, *y*+1/2, −*z*+1/2; (v) −*x*+1, −*y*, −*z*+1; (vi) *x*, −*y*+1/2, *z*+1/2; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+2, *y*+1/2, −*z*+3/2; (ix) *x*, −*y*+1/2, *z*−1/2; (x) −*x*+2, *y*−1/2, −*z*+3/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O4—H4O···O2$^{ii}$ | 0.82 | 1.88 | 2.696 (3) | 177 |
| C12—H12B···O2$^{ix}$ | 0.96 | 2.52 | 3.470 (4) | 173 |
| C16—H16B···O3$^{ii}$ | 0.98 | 2.34 | 3.251 (4) | 155 |

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

**Fig. 1**


O1
O2
O3
S1
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11A
N1
C12
C13
C14
C15
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C23
C24
C25
C26
C27
C28
C29
O4
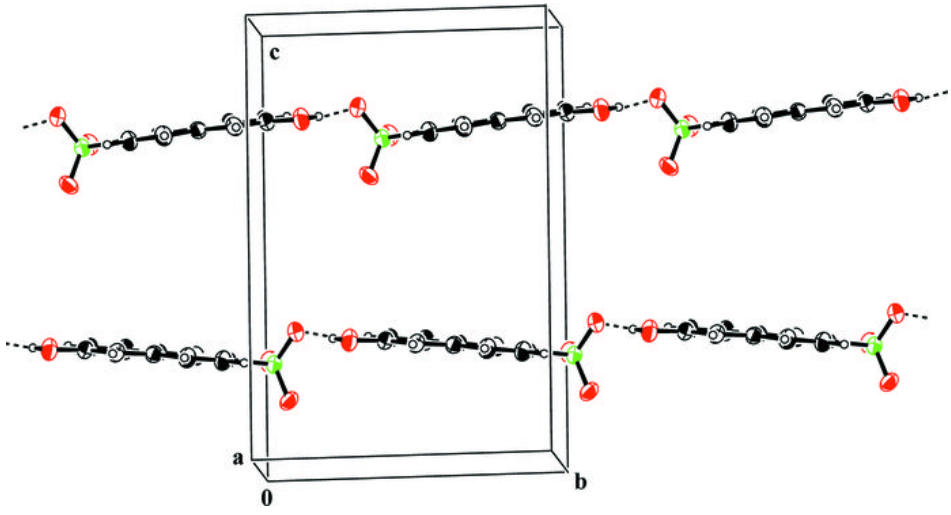
Fig. 2