



(*E*)-2,6-Dibromo-4-{2-[1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)pyridinium-4-yl]ethenyl}phenolate methanol disolvate, a fluoroponytailed solvatochromic dye

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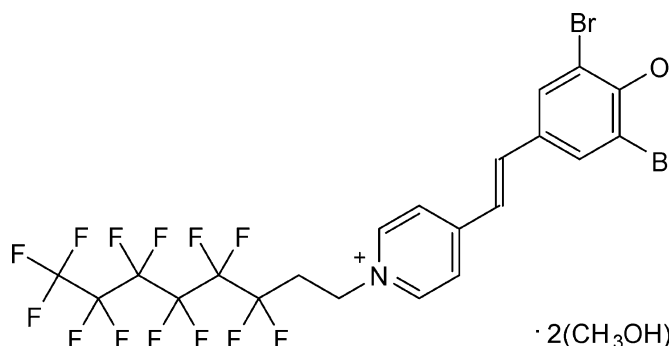
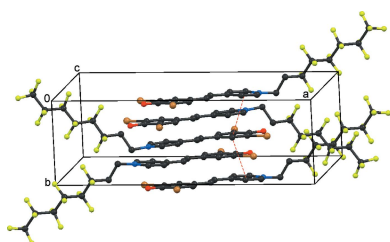
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The title compound, C₂₁H₁₂Br₂F₁₃NO·2CH₃OH, was obtained by condensation of 4-methyl-1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)pyridinium iodide and 3,5-dibromo-4-hydroxybenzaldehyde, followed by deprotonation. It crystallizes as a methanol disolvate and exhibits short O—H···O hydrogen bonds and a disordered perfluoroalkyl chain [occupancy ratio 0.538 (7):0.462 (7)]. Significant π – π stacking interactions are observed between the benzene and pyridine rings of neighbouring molecules along the *b*-axis direction.

1. Chemical context

Dyes with a fundamental type of conjugated system as in the title compound have long been known (Hünig & Rosenthal, 1955). It was intended to combine the structural features of a delocalized π -electron system with those of polyfluorinated compounds in order to derive a new material with advantageous properties such as altered solubility (Hoang & Mecozzi, 2004) and affinity (Wagner *et al.*, 2016) profiles, given that the physical and chemical properties of organic compounds are strongly affected by the introduction of fluorinated substituents. Fluorosurfactants have a tendency towards micelle formation in biphasic or ternary solvent mixtures. Thus, the utilization of solvatochromic surfactants as self-indicating micelle reporters (Kedia *et al.*, 2014) is an attractive analytical concept for fluorous-phase-related materials science.



2. Structural commentary

The title compound comprises a delocalized π -electron system, involving either a zwitterionic benzoid or a non-polar

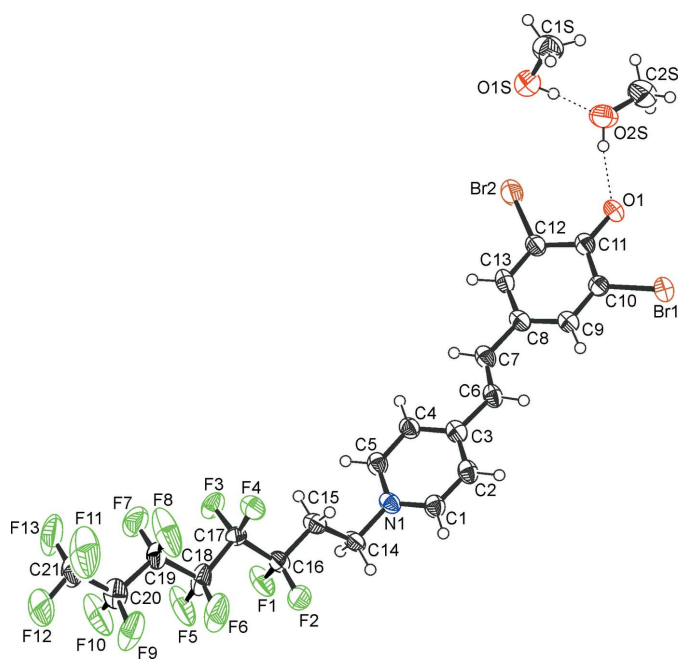


Figure 1
The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms. Dashed lines indicate hydrogen bonds. Only the major disorder component of the perfluoroalkyl chain is shown.

quinoid resonance structure. Inspection of bond lengths leads to the conclusion that it is not a typical cyclohexadienone system (Chandran *et al.*, 2008; Chiverton *et al.*, 1991) but rather a benzoid system similar to 2,6-dibromophenol predominant (Eriksson & Eriksson, 2001; Lu *et al.*, 2011; Lehmler & Parkin, 2005). The heterocyclic ring also resembles a typical pyridinium system. Furthermore, the shortest C=C bond in the bridge linking the two rings is between C6 and C7 with a length of 1.337 (6) Å, whereas the adjacent bonds are considerably longer. The framework thus is not quinoid but benzoid. The conjugated moieties of the dye molecule are

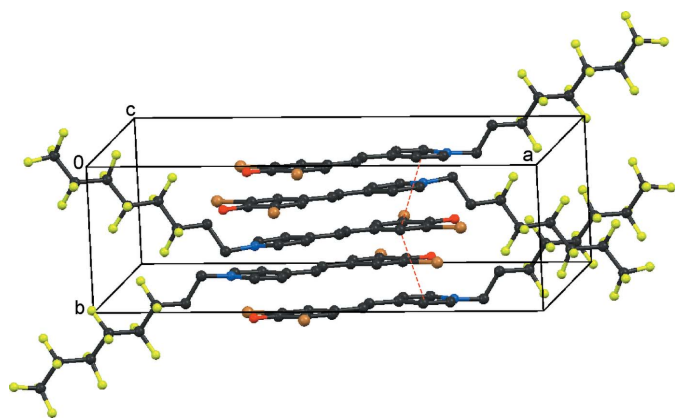


Figure 2
View of the planar chromophore moieties and the attached perfluoroalkyl chains. The π - π stacking interactions between the benzene and pyridine rings are shown in red dashed lines. Solvent molecules are omitted for clarity.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1S-H1S\cdots O2S$	0.85 (1)	1.83 (1)	2.674 (5)	176 (7)
$O2S-H2S\cdots O1$	0.84 (1)	1.85 (2)	2.675 (4)	167 (6)

almost planar and the mean planes of the benzene and pyridine rings form an angle of 2.97 (2)°, whilst the fluorinated chains protrude from the plane.

The carbon atoms C17–C21 and fluorine atoms F3–F13 of the polyfluorinated tail are disordered over sets of sites with an occupancy ratio for the two disorder fragments of 0.538 (7):0.462 (7). The chain adopts a slightly helical conformation (Fournier *et al.*, 2010) with an average C–C–C–C twist angle (deviation from 180°) of 3°. Typically, π -electron donor–acceptor-substituted conjugated systems exhibit solvatochromism. Solutions of the title compound display absorption maxima at 610 nm (blue) in THF and 502 nm (red) in MeOH. Here, increased solvent polarity leads to higher transition energy (negative solvatochromism). A quinoid system based on 2,6-dibromophenol displaying positive solvatochromism has been reported previously (Laus *et al.*, 2003).

3. Supramolecular features

The three components of the title compound are linked into a finite hydrogen-bonded chain. The two solvent molecules are connected by an $O1S-H1S\cdots O2S$ bond, and additionally the interaction $O2S-H2S\cdots O1$ links the second solvent molecule with the main molecule (Table 1, Fig. 1). In addition, there are significant π - π stacking interactions between the benzene and pyridine rings. These are weakly connecting in the b -axis direction. Centroid–centroid distances $Cg1\cdots Cg2^i$ and $Cg1\cdots Cg2^{ii}$ are 3.525 (3) and 3.605 (3) Å, respectively [$Cg1$ and $Cg2$ are the centroids of the benzene and pyridine rings, respectively; symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$]. The packing of the molecules is displayed in Fig. 2.

4. Database survey

The crystal structure of an acceptor-substituted conjugated 2,6-dibromophenol derivative (refcode SULSAV), displaying visible solvatochromism, has been reported (Stock *et al.*, 2015).

5. Synthesis and crystallization

4-Methyl-1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)pyridinium iodide (1): A solution of 4-methylpyridine (10.0 g, 107.4 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (66.2 g, 139.2 mmol) in CH_3CN (15 ml) was refluxed for 24 h. The mixture was diluted with Et_2O (250 ml) and allowed to rest at 249 K overnight. The product **1** was collected by filtration, washed with Et_2O (100 ml) and dried to give 59.3 g (97%) of a dark-red powder.

¹H NMR (300 MHz, CD₃OD): δ 8.97 (*d*, *J* = 6.5 Hz, 2H), 8.01 (*d*, *J* = 6.5 Hz, 2H), 5.01 (*t*, *J* = 7.2 Hz, 2H), 3.25–3.04 (*m*, 2H), 2.71 (*s*, 3H) ppm.

(E)-4-(2-(3,5-Dibromo-4-hydroxyphenyl)ethenyl)-1-(1H,1H,2H,2H-perfluorooctyl)pyridinium iodide (2): A solution of intermediate **1** (2.03 g, 3.57 mmol), 3,5-dibromo-4-hydroxybenzaldehyde (1.00 g, 3.57 mmol) and piperidine (0.5 ml, 5 mmol) in MeOH (10 ml) was refluxed for 4 h. After removal of the solvent, the residue was washed with CHCl₃ (50 ml) and H₂O (20 ml), dissolved in MeOH (70 ml) and precipitated with Et₂O (400 ml). The crude product (2.0 g) was redissolved in acetone (40 ml) and precipitated with H₂O (400 ml), filtered and dried to give 1.53 g (52%) of **2** as a red-brown powder, m.p. 497 K. ¹H NMR (300 MHz, CD₃OD): δ 8.52 (*d*, *J* = 6.7 Hz, 2H), 7.81 (*d*, *J* = 6.6 Hz, 2H), 7.73 (*s*, 2H), 7.63 (*d*, *J* = 15.8 Hz, 1H), 6.82 (*d*, *J* = 15.8 Hz, 1H), 4.78 (*t*, *J* = 7.2 Hz, 2H), 3.18–2.93 (*m*, 2H) ppm IR (neat): ν 3035(*w*), 3002(*w*), 2956(*w*), 1641(*w*), 1601(*m*), 1563(*m*), 1499(*m*), 1469(*m*), 1425(*w*), 1366(*w*), 1315(*w*), 1232(*m*), 1171(*s*), 1140(*vs*), 1075(*m*), 1041(*m*), 958(*m*), 916(*w*), 859(*m*), 809(*w*), 780(*w*), 745(*m*), 717(*m*), 695(*m*), 652(*m*), 616(*m*), 588(*m*), 551(*w*), 514(*m*), 488(*w*) cm⁻¹.

(E)-2,6-Dibromo-4-(2-(1-(1H,1H,2H,2H-perfluorooctyl)pyridinium-4-yl)ethenyl)phenolate methanol disolvate (3): A solution of NaOH (2 ml 5%, 2.5 mmol) was added to intermediate **2** (1.0 g, 1.2 mmol) in MeOH (20 ml). The mixture was ultrasonicated for 25 min, then heated and diluted with H₂O (400 ml). After resting at 277 K overnight, the mixture was filtered and the dark-red product **3** was collected and dried: 0.57 g (68%). M.p. 513 K. Suitable crystals were obtained by diffusion of Et₂O into a solution of **3** in MeOH at 249 K. ¹H NMR (300 MHz, CD₃OD): δ 8.52 (*d*, *J* = 6.3 Hz, 2H), 7.81 (*d*, *J* = 6.3 Hz, 2H), 7.73 (*s*, 2H), 7.63 (*d*, *J* = 15.8 Hz, 1H), 6.90–6.75 (*m*, 1H), 4.78 (*t*, *J* = 7.2 Hz, 2H), 3.17–2.95 (*m*, 2H) ppm IR (neat): ν 3642(*w*), 3305(*w*), 3037(*w*), 2999(*w*), 2958(*w*), 2939(*w*), 1641(*m*), 1601(*m*), 1562(*s*), 1523(*s*), 1499(*s*), 1469(*m*), 1425(*m*), 1366(*w*), 1315(*w*), 1231(*m*), 1171(*vs*), 1140(*vs*), 1119(*s*), 1076(*m*), 1041(*m*), 996(*w*), 959(*m*), 916(*w*), 857(*m*), 809(*m*), 780(*w*), 745(*m*), 717(*s*), 707(*m*), 694(*s*), 653(*m*), 616(*m*), 589(*m*), 565(*w*), 551(*m*), 530(*m*), 516(*m*), 491(*w*) cm⁻¹.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were identified in difference maps. Methyl H atoms were idealized and included as rigid groups allowed to rotate but not tip and refined with *U*_{iso}(H) set to 1.5*U*_{eq}(C) of the parent carbon atom. All other H atoms bonded to carbon atoms were positioned geometrically and refined with *U*_{iso}(H) set to 1.2*U*_{eq}(C) of the parent carbon atom. Hydrogen atoms in OH groups were refined with restrained distances [O–H = 0.84 (1) Å] and their *U*_{iso} parameters were refined freely.

The terminal C₅F₁₁ unit of the polyfluorinated tail was found to be disordered over two orientations. The two

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₁ H ₁₂ Br ₂ F ₁₃ NO·2CH ₄ O
<i>M</i> _r	765.22
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	22.2362 (7), 6.7922 (18), 18.9098 (5)
β (°)	103.989 (3)
<i>V</i> (Å ³)	2771.3 (7)
<i>Z</i>	4
Radiation type	Cu Kα
μ (mm ⁻¹)	4.80
Crystal size (mm)	0.36 × 0.06 × 0.04
Data collection	
Diffractometer	Rigaku Xcalibur Ruby Gemini ultra
Absorption correction	Analytical [<i>CrysAlis PRO</i> (Rigaku Oxford Diffraction, 2015), based on expressions derived by Clark & Reid (1995)]
<i>T</i> _{min} , <i>T</i> _{max}	0.499, 0.853
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11115, 4314, 3371
<i>R</i> _{int}	0.035
(sin θ/λ) _{max} (Å ⁻¹)	0.576
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.106, 1.05
No. of reflections	4314
No. of parameters	516
No. of restraints	403
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.74, -0.72

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

disorder components, each consisting of 16 atomic positions, were refined using 401 distance restraints (SADI) for chemically equivalent C–C, C–F and F···F bonds, and the final occupancy ratio was 0.538 (7):0.462 (7). All disordered atoms were refined anisotropically. The extension of the modelled disorder increased the number of refined parameters substantially. Consequently, the obtained data/parameter ratio is lower than normally expected.

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Computing details

Data collection: *CrysAlis PRO* 1.171.38.43f (Rigaku Oxford Diffraction, 2015); cell refinement: *CrysAlis PRO* 1.171.38.43f (Rigaku Oxford Diffraction, 2015); data reduction: *CrysAlis PRO* 1.171.38.43f (Rigaku Oxford Diffraction, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2008).

(E)-2,6-Dibromo-4-{2-[1-(1H,1H,2H,2H-perfluorooctyl)pyridinium-4-yl]ethenyl}phenolate methanol disolvate

Crystal data

C₂₁H₁₂Br₂F₁₃NO·2CH₄O

M_r = 765.22

Monoclinic, *P*2₁/*c*

a = 22.2362 (7) Å

b = 6.7922 (18) Å

c = 18.9098 (5) Å

β = 103.989 (3)°

V = 2771.3 (7) Å³

Z = 4

F(000) = 1504

D_x = 1.834 Mg m⁻³

Melting point: 513 K

Cu *K*α radiation, λ = 1.54184 Å

Cell parameters from 3207 reflections

θ = 6.8–62.6°

μ = 4.80 mm⁻¹

T = 173 K

Needle, red

0.36 × 0.06 × 0.04 mm

Data collection

Rigaku Xcalibur Ruby Gemini ultra diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance Ultra (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.3575 pixels mm⁻¹

ω scans

Absorption correction: analytical

[*CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), based on expressions derived by Clark & Reid (1995)]

T_{min} = 0.499, *T_{max}* = 0.853

11115 measured reflections

4314 independent reflections

3371 reflections with *I* > 2σ(*I*)

R_{int} = 0.035

θ_{\max} = 62.7°, θ_{\min} = 4.1°

h = -25→22

k = -7→6

l = -14→21

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.106$
 $S = 1.05$
 4314 reflections
 516 parameters
 403 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 2.6693P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.74 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.72887 (2)	0.71430 (7)	0.85956 (2)	0.03986 (15)	
Br2	0.58110 (2)	0.70255 (10)	1.06685 (3)	0.06123 (19)	
O1	0.69939 (13)	0.7051 (4)	1.00942 (15)	0.0413 (7)	
N1	0.30370 (15)	0.7317 (5)	0.55358 (18)	0.0355 (8)	
C1	0.35778 (19)	0.7194 (6)	0.5334 (2)	0.0384 (10)	
H1	0.3574	0.7177	0.4830	0.046*	
C2	0.41297 (19)	0.7094 (6)	0.5841 (2)	0.0373 (10)	
H2	0.4505	0.7012	0.5686	0.045*	
C3	0.41516 (19)	0.7111 (6)	0.6584 (2)	0.0349 (9)	
C4	0.35844 (19)	0.7177 (6)	0.6781 (2)	0.0360 (9)	
H4	0.3575	0.7151	0.7280	0.043*	
C5	0.30411 (19)	0.7278 (6)	0.6247 (2)	0.0366 (10)	
H5	0.2658	0.7322	0.6386	0.044*	
C6	0.47455 (19)	0.7076 (6)	0.7121 (2)	0.0373 (10)	
H6	0.5111	0.6998	0.6946	0.045*	
C7	0.48119 (19)	0.7145 (6)	0.7842 (2)	0.0375 (10)	
H7	0.4440	0.7199	0.8005	0.045*	
C8	0.53856 (19)	0.7149 (6)	0.8404 (2)	0.0347 (9)	
C9	0.59774 (18)	0.7163 (6)	0.8264 (2)	0.0336 (9)	
H9	0.6016	0.7186	0.7775	0.040*	
C10	0.64987 (18)	0.7145 (6)	0.8824 (2)	0.0321 (9)	
C11	0.65004 (18)	0.7098 (6)	0.9584 (2)	0.0343 (9)	
C12	0.58882 (19)	0.7105 (6)	0.9690 (2)	0.0371 (9)	
C13	0.53587 (18)	0.7137 (6)	0.9137 (2)	0.0377 (10)	
H13	0.4966	0.7152	0.9254	0.045*	
C14	0.24393 (19)	0.7506 (6)	0.4984 (2)	0.0390 (10)	
H14A	0.2518	0.7731	0.4497	0.047*	
H14B	0.2205	0.8648	0.5103	0.047*	
C15	0.20596 (19)	0.5630 (6)	0.4972 (2)	0.0389 (10)	
H15A	0.2305	0.4488	0.4876	0.047*	

H15B	0.1971	0.5439	0.5456	0.047*	
C16	0.14596 (17)	0.5710 (6)	0.4401 (2)	0.0390 (10)	
F1	0.11416 (12)	0.7347 (4)	0.44718 (17)	0.0615 (8)	
F2	0.15626 (12)	0.5751 (5)	0.37277 (13)	0.0621 (8)	
C17	0.1052 (6)	0.3886 (19)	0.4512 (11)	0.032 (3)	0.538 (7)
F3	0.0880 (11)	0.395 (3)	0.5138 (13)	0.046 (3)	0.538 (7)
F4	0.1392 (9)	0.227 (2)	0.4520 (9)	0.047 (3)	0.538 (7)
C18	0.0443 (6)	0.398 (2)	0.3879 (6)	0.049 (5)	0.538 (7)
F5	0.0088 (6)	0.553 (2)	0.3897 (9)	0.096 (5)	0.538 (7)
F6	0.0511 (6)	0.380 (2)	0.3204 (6)	0.114 (6)	0.538 (7)
C19	0.0003 (5)	0.2195 (14)	0.3942 (5)	0.0466 (13)	0.538 (7)
F7	-0.0127 (5)	0.2142 (17)	0.4591 (4)	0.086 (4)	0.538 (7)
F8	0.0246 (3)	0.0455 (11)	0.3845 (7)	0.109 (4)	0.538 (7)
C20	-0.0657 (5)	0.2196 (13)	0.3402 (6)	0.049 (3)	0.538 (7)
F9	-0.0608 (7)	0.227 (2)	0.2719 (6)	0.096 (5)	0.538 (7)
F10	-0.0975 (3)	0.3771 (10)	0.3515 (4)	0.095 (3)	0.538 (7)
C21	-0.1086 (5)	0.0383 (14)	0.3430 (6)	0.0659 (17)	0.538 (7)
F11	-0.0834 (3)	-0.1257 (10)	0.3271 (7)	0.126 (4)	0.538 (7)
F12	-0.1620 (5)	0.063 (2)	0.2950 (6)	0.093 (4)	0.538 (7)
F13	-0.1200 (5)	0.020 (2)	0.4076 (5)	0.114 (6)	0.538 (7)
C17A	0.1030 (7)	0.396 (2)	0.4358 (14)	0.032 (3)	0.462 (7)
F3A	0.1343 (11)	0.230 (3)	0.4336 (12)	0.081 (7)	0.462 (7)
F4A	0.0912 (14)	0.406 (4)	0.5014 (16)	0.074 (8)	0.462 (7)
C18A	0.0435 (6)	0.3502 (19)	0.3801 (6)	0.034 (4)	0.462 (7)
F5A	0.0231 (6)	0.5312 (18)	0.3621 (8)	0.063 (3)	0.462 (7)
F6A	0.0670 (6)	0.2830 (18)	0.3267 (6)	0.055 (3)	0.462 (7)
C19A	-0.0047 (6)	0.2143 (16)	0.3974 (5)	0.0466 (13)	0.462 (7)
F7A	-0.0318 (5)	0.3151 (16)	0.4410 (6)	0.080 (4)	0.462 (7)
F8A	0.0262 (4)	0.0682 (13)	0.4367 (5)	0.070 (3)	0.462 (7)
C20A	-0.0509 (5)	0.1407 (16)	0.3308 (6)	0.051 (4)	0.462 (7)
F9A	-0.0241 (4)	-0.0059 (14)	0.3042 (5)	0.104 (4)	0.462 (7)
F10A	-0.0640 (8)	0.282 (2)	0.2817 (9)	0.110 (7)	0.462 (7)
C21A	-0.1099 (5)	0.0648 (16)	0.3461 (7)	0.0659 (17)	0.462 (7)
F11A	-0.1445 (3)	0.2054 (15)	0.3637 (7)	0.121 (4)	0.462 (7)
F12A	-0.0958 (6)	-0.061 (2)	0.4003 (7)	0.108 (6)	0.462 (7)
F13A	-0.1435 (7)	-0.028 (2)	0.2889 (7)	0.099 (5)	0.462 (7)
O1S	0.65266 (18)	0.2293 (6)	1.1488 (2)	0.0597 (9)	
H1S	0.678 (2)	0.321 (7)	1.146 (4)	0.10 (2)*	
C1S	0.6945 (3)	0.0714 (8)	1.1694 (3)	0.0690 (15)	
H1S1	0.7365	0.1231	1.1877	0.104*	
H1S2	0.6933	-0.0130	1.1270	0.104*	
H1S3	0.6827	-0.0057	1.2077	0.104*	
O2S	0.72828 (18)	0.5293 (6)	1.1399 (2)	0.0699 (11)	
H2S	0.713 (3)	0.582 (9)	1.0994 (17)	0.09 (2)*	
C2S	0.7847 (3)	0.5858 (10)	1.1829 (3)	0.0746 (16)	
H2S1	0.7859	0.7296	1.1876	0.112*	
H2S2	0.8178	0.5422	1.1605	0.112*	
H2S3	0.7906	0.5261	1.2312	0.112*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0307 (2)	0.0410 (3)	0.0472 (3)	-0.00156 (19)	0.00816 (18)	-0.0061 (2)
Br2	0.0379 (3)	0.1009 (5)	0.0449 (3)	-0.0003 (3)	0.0099 (2)	0.0052 (3)
O1	0.0285 (15)	0.0506 (18)	0.0395 (16)	-0.0031 (13)	-0.0018 (13)	0.0026 (13)
N1	0.0327 (18)	0.0273 (18)	0.041 (2)	-0.0018 (14)	-0.0013 (15)	0.0000 (14)
C1	0.036 (2)	0.036 (2)	0.043 (2)	-0.0035 (18)	0.0078 (19)	-0.0013 (18)
C2	0.031 (2)	0.031 (2)	0.048 (3)	-0.0014 (18)	0.0064 (18)	-0.0033 (19)
C3	0.033 (2)	0.0195 (19)	0.049 (3)	-0.0007 (17)	0.0035 (18)	-0.0019 (18)
C4	0.034 (2)	0.032 (2)	0.039 (2)	-0.0023 (18)	0.0025 (18)	0.0009 (18)
C5	0.033 (2)	0.031 (2)	0.045 (3)	-0.0029 (17)	0.0076 (18)	-0.0012 (18)
C6	0.029 (2)	0.031 (2)	0.049 (3)	-0.0020 (17)	0.0040 (18)	-0.0021 (19)
C7	0.031 (2)	0.029 (2)	0.049 (3)	-0.0009 (18)	0.0020 (18)	0.0005 (19)
C8	0.032 (2)	0.023 (2)	0.044 (2)	-0.0009 (17)	-0.0006 (18)	0.0005 (17)
C9	0.033 (2)	0.025 (2)	0.040 (2)	0.0000 (17)	0.0032 (17)	-0.0034 (17)
C10	0.032 (2)	0.0229 (19)	0.040 (2)	-0.0025 (16)	0.0058 (17)	0.0009 (17)
C11	0.031 (2)	0.024 (2)	0.046 (2)	-0.0028 (17)	0.0053 (19)	-0.0001 (18)
C12	0.032 (2)	0.036 (2)	0.041 (2)	-0.0006 (18)	0.0045 (18)	0.0013 (18)
C13	0.026 (2)	0.033 (2)	0.052 (3)	-0.0002 (17)	0.0058 (18)	-0.0008 (19)
C14	0.031 (2)	0.040 (3)	0.040 (2)	0.0012 (18)	-0.0048 (18)	0.0039 (18)
C15	0.039 (2)	0.035 (2)	0.038 (2)	0.0002 (19)	-0.0012 (18)	0.0013 (18)
C16	0.031 (2)	0.041 (3)	0.042 (2)	0.0029 (19)	0.0038 (18)	0.0035 (19)
F1	0.0363 (14)	0.0402 (15)	0.097 (2)	0.0058 (12)	-0.0057 (14)	-0.0023 (14)
F2	0.0504 (16)	0.094 (2)	0.0383 (15)	-0.0251 (15)	0.0026 (12)	0.0056 (14)
C17	0.037 (3)	0.045 (3)	0.014 (8)	-0.001 (2)	0.006 (3)	0.000 (3)
F3	0.057 (5)	0.061 (6)	0.026 (6)	-0.017 (5)	0.018 (4)	-0.006 (4)
F4	0.045 (5)	0.030 (5)	0.056 (5)	-0.005 (3)	-0.006 (3)	0.002 (3)
C18	0.049 (9)	0.059 (11)	0.041 (8)	-0.031 (7)	0.017 (6)	-0.022 (7)
F5	0.034 (5)	0.049 (4)	0.185 (15)	0.003 (3)	-0.011 (6)	0.010 (7)
F6	0.075 (9)	0.211 (18)	0.047 (5)	-0.084 (10)	-0.002 (5)	0.002 (9)
C19	0.036 (3)	0.051 (3)	0.052 (3)	-0.009 (2)	0.010 (2)	0.000 (2)
F7	0.071 (7)	0.129 (10)	0.050 (4)	-0.052 (7)	-0.001 (4)	0.020 (5)
F8	0.049 (4)	0.054 (4)	0.208 (11)	0.002 (3)	-0.002 (6)	-0.039 (6)
C20	0.050 (7)	0.054 (9)	0.042 (6)	-0.012 (6)	0.010 (5)	-0.020 (7)
F9	0.093 (8)	0.165 (11)	0.032 (6)	-0.081 (8)	0.019 (5)	-0.020 (6)
F10	0.045 (4)	0.081 (5)	0.140 (7)	0.006 (3)	-0.016 (4)	-0.024 (4)
C21	0.047 (3)	0.084 (5)	0.062 (4)	-0.028 (3)	0.006 (3)	-0.003 (4)
F11	0.088 (6)	0.070 (5)	0.220 (12)	-0.031 (4)	0.036 (7)	-0.028 (6)
F12	0.058 (7)	0.122 (11)	0.086 (6)	-0.041 (6)	-0.008 (4)	-0.004 (6)
F13	0.067 (8)	0.211 (17)	0.063 (5)	-0.073 (9)	0.015 (5)	0.000 (7)
C17A	0.037 (3)	0.045 (3)	0.014 (8)	-0.001 (2)	0.006 (3)	0.000 (3)
F3A	0.044 (7)	0.064 (9)	0.131 (18)	0.006 (6)	0.009 (10)	-0.042 (9)
F4A	0.068 (8)	0.116 (12)	0.034 (11)	-0.049 (7)	0.006 (7)	0.004 (6)
C18A	0.046 (9)	0.022 (6)	0.023 (8)	-0.004 (5)	-0.015 (6)	-0.003 (5)
F5A	0.033 (7)	0.052 (7)	0.085 (8)	0.002 (5)	-0.019 (5)	0.015 (5)
F6A	0.042 (5)	0.094 (7)	0.032 (5)	-0.014 (4)	0.014 (4)	-0.017 (4)
C19A	0.036 (3)	0.051 (3)	0.052 (3)	-0.009 (2)	0.010 (2)	0.000 (2)

F7A	0.063 (6)	0.106 (9)	0.087 (8)	-0.035 (5)	0.049 (6)	-0.060 (6)
F8A	0.055 (5)	0.058 (5)	0.084 (6)	-0.024 (4)	-0.010 (5)	0.016 (5)
C20A	0.057 (9)	0.060 (10)	0.035 (8)	-0.020 (7)	0.006 (6)	-0.026 (7)
F9A	0.077 (5)	0.139 (9)	0.103 (6)	-0.033 (6)	0.032 (5)	-0.074 (6)
F10A	0.070 (9)	0.135 (11)	0.091 (13)	-0.054 (7)	-0.048 (7)	0.055 (9)
C21A	0.047 (3)	0.084 (5)	0.062 (4)	-0.028 (3)	0.006 (3)	-0.003 (4)
F11A	0.037 (4)	0.149 (9)	0.178 (11)	-0.014 (5)	0.029 (5)	-0.058 (8)
F12A	0.066 (9)	0.145 (12)	0.100 (10)	-0.057 (8)	-0.005 (6)	0.049 (9)
F13A	0.075 (11)	0.140 (14)	0.073 (6)	-0.058 (8)	-0.002 (6)	-0.022 (7)
O1S	0.059 (2)	0.061 (2)	0.060 (2)	-0.001 (2)	0.0160 (18)	0.0056 (18)
C1S	0.075 (4)	0.058 (3)	0.072 (4)	0.006 (3)	0.012 (3)	0.010 (3)
O2S	0.065 (2)	0.070 (3)	0.063 (2)	-0.013 (2)	-0.0062 (19)	0.023 (2)
C2S	0.065 (4)	0.086 (4)	0.065 (4)	-0.006 (3)	-0.001 (3)	0.008 (3)

Geometric parameters (Å, °)

Br1—C10	1.908 (4)	C17—C18	1.576 (9)
Br2—C12	1.900 (4)	C18—F6	1.325 (7)
O1—C11	1.274 (5)	C18—F5	1.326 (7)
N1—C5	1.344 (5)	C18—C19	1.579 (9)
N1—C1	1.350 (5)	C19—F7	1.328 (7)
N1—C14	1.484 (5)	C19—F8	1.331 (7)
C1—C2	1.365 (6)	C19—C20	1.573 (9)
C1—H1	0.9500	C20—F9	1.323 (7)
C2—C3	1.393 (6)	C20—F10	1.327 (7)
C2—H2	0.9500	C20—C21	1.566 (9)
C3—C4	1.400 (6)	C21—F13	1.313 (7)
C3—C6	1.459 (5)	C21—F11	1.314 (7)
C4—C5	1.375 (6)	C21—F12	1.319 (7)
C4—H4	0.9500	C17A—F3A	1.331 (7)
C5—H5	0.9500	C17A—F4A	1.331 (7)
C6—C7	1.337 (6)	C17A—C18A	1.513 (8)
C6—H6	0.9500	C18A—F6A	1.325 (7)
C7—C8	1.450 (5)	C18A—F5A	1.326 (7)
C7—H7	0.9500	C18A—C19A	1.509 (9)
C8—C13	1.401 (6)	C19A—F7A	1.322 (7)
C8—C9	1.404 (6)	C19A—F8A	1.328 (7)
C9—C10	1.368 (5)	C19A—C20A	1.506 (9)
C9—H9	0.9500	C20A—F10A	1.318 (7)
C10—C11	1.436 (6)	C20A—F9A	1.321 (7)
C11—C12	1.423 (6)	C20A—C21A	1.500 (9)
C12—C13	1.373 (6)	C21A—F12A	1.314 (7)
C13—H13	0.9500	C21A—F11A	1.319 (7)
C14—C15	1.526 (6)	C21A—F13A	1.319 (7)
C14—H14A	0.9900	O1S—C1S	1.411 (6)
C14—H14B	0.9900	O1S—H1S	0.845 (11)
C15—C16	1.501 (5)	C1S—H1S1	0.9800
C15—H15A	0.9900	C1S—H1S2	0.9800

C15—H15B	0.9900	C1S—H1S3	0.9800
C16—F1	1.342 (4)	O2S—C2S	1.374 (6)
C16—F2	1.348 (4)	O2S—H2S	0.838 (11)
C16—C17A	1.515 (8)	C2S—H2S1	0.9800
C16—C17	1.578 (9)	C2S—H2S2	0.9800
C17—F4	1.329 (6)	C2S—H2S3	0.9800
C17—F3	1.330 (6)		
C5—N1—C1	119.4 (3)	F6—C18—F5	107.6 (7)
C5—N1—C14	119.6 (4)	F6—C18—C17	116.8 (14)
C1—N1—C14	120.9 (4)	F5—C18—C17	114.8 (13)
N1—C1—C2	121.0 (4)	F6—C18—C19	102.9 (11)
N1—C1—H1	119.5	F5—C18—C19	102.9 (10)
C2—C1—H1	119.5	C17—C18—C19	110.3 (11)
C1—C2—C3	121.0 (4)	F7—C19—F8	106.9 (7)
C1—C2—H2	119.5	F7—C19—C20	102.9 (9)
C3—C2—H2	119.5	F8—C19—C20	104.9 (8)
C2—C3—C4	117.0 (4)	F7—C19—C18	111.6 (9)
C2—C3—C6	120.5 (4)	F8—C19—C18	112.9 (9)
C4—C3—C6	122.5 (4)	C20—C19—C18	116.7 (9)
C5—C4—C3	119.7 (4)	F9—C20—F10	107.3 (7)
C5—C4—H4	120.2	F9—C20—C21	105.0 (10)
C3—C4—H4	120.2	F10—C20—C21	106.0 (7)
N1—C5—C4	121.8 (4)	F9—C20—C19	110.5 (10)
N1—C5—H5	119.1	F10—C20—C19	110.2 (7)
C4—C5—H5	119.1	C21—C20—C19	117.2 (9)
C7—C6—C3	124.6 (4)	F13—C21—F11	108.8 (7)
C7—C6—H6	117.7	F13—C21—F12	107.8 (7)
C3—C6—H6	117.7	F11—C21—F12	108.2 (7)
C6—C7—C8	127.5 (4)	F13—C21—C20	111.3 (9)
C6—C7—H7	116.3	F11—C21—C20	111.3 (7)
C8—C7—H7	116.3	F12—C21—C20	109.4 (10)
C13—C8—C9	116.9 (4)	F3A—C17A—F4A	107.1 (7)
C13—C8—C7	119.0 (4)	F3A—C17A—C18A	100.4 (15)
C9—C8—C7	124.1 (4)	F4A—C17A—C18A	108.8 (18)
C10—C9—C8	120.7 (4)	F3A—C17A—C16	109.8 (16)
C10—C9—H9	119.6	F4A—C17A—C16	100 (2)
C8—C9—H9	119.6	C18A—C17A—C16	129.3 (15)
C9—C10—C11	124.9 (4)	F6A—C18A—F5A	107.3 (7)
C9—C10—Br1	118.6 (3)	F6A—C18A—C19A	112.8 (11)
C11—C10—Br1	116.5 (3)	F5A—C18A—C19A	114.0 (11)
O1—C11—C12	124.8 (4)	F6A—C18A—C17A	99.2 (15)
O1—C11—C10	123.5 (4)	F5A—C18A—C17A	100.1 (13)
C12—C11—C10	111.7 (3)	C19A—C18A—C17A	121.5 (13)
C13—C12—C11	124.5 (4)	F7A—C19A—F8A	106.9 (7)
C13—C12—Br2	118.6 (3)	F7A—C19A—C20A	111.8 (9)
C11—C12—Br2	116.9 (3)	F8A—C19A—C20A	112.1 (10)
C12—C13—C8	121.3 (4)	F7A—C19A—C18A	105.9 (10)

C12—C13—H13	119.4	F8A—C19A—C18A	106.3 (9)
C8—C13—H13	119.4	C20A—C19A—C18A	113.4 (10)
N1—C14—C15	109.6 (3)	F10A—C20A—F9A	108.9 (7)
N1—C14—H14A	109.7	F10A—C20A—C21A	109.4 (13)
C15—C14—H14A	109.7	F9A—C20A—C21A	108.1 (8)
N1—C14—H14B	109.7	F10A—C20A—C19A	109.7 (11)
C15—C14—H14B	109.7	F9A—C20A—C19A	106.8 (9)
H14A—C14—H14B	108.2	C21A—C20A—C19A	113.8 (10)
C16—C15—C14	111.9 (3)	F12A—C21A—F11A	108.6 (7)
C16—C15—H15A	109.2	F12A—C21A—F13A	107.9 (7)
C14—C15—H15A	109.2	F11A—C21A—F13A	107.7 (7)
C16—C15—H15B	109.2	F12A—C21A—C20A	108.7 (10)
C14—C15—H15B	109.2	F11A—C21A—C20A	113.0 (9)
H15A—C15—H15B	107.9	F13A—C21A—C20A	110.8 (11)
F1—C16—F2	106.9 (3)	C1S—O1S—H1S	100 (5)
F1—C16—C15	110.9 (3)	O1S—C1S—H1S1	109.5
F2—C16—C15	110.9 (3)	O1S—C1S—H1S2	109.5
F1—C16—C17A	108.4 (9)	H1S1—C1S—H1S2	109.5
F2—C16—C17A	102.4 (11)	O1S—C1S—H1S3	109.5
C15—C16—C17A	116.7 (8)	H1S1—C1S—H1S3	109.5
F1—C16—C17	107.7 (8)	H1S2—C1S—H1S3	109.5
F2—C16—C17	112.0 (9)	C2S—O2S—H2S	121 (5)
C15—C16—C17	108.4 (6)	O2S—C2S—H2S1	109.5
F4—C17—F3	107.5 (6)	O2S—C2S—H2S2	109.5
F4—C17—C18	114.9 (14)	H2S1—C2S—H2S2	109.5
F3—C17—C18	107.2 (15)	O2S—C2S—H2S3	109.5
F4—C17—C16	107.8 (12)	H2S1—C2S—H2S3	109.5
F3—C17—C16	113.0 (17)	H2S2—C2S—H2S3	109.5
C18—C17—C16	106.5 (12)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1S—H1S...O2S	0.85 (1)	1.83 (1)	2.674 (5)	176 (7)
O2S—H2S...O1	0.84 (1)	1.85 (2)	2.675 (4)	167 (6)