1-(Hex-5-en-1-yl)-4-[[3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene]methyl]quinolin-1-ium iodide monohydrate

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The title thiazole orange derivative, bearing an alkene substituent, crystallized as a monohydrate of its iodide salt, namely, (Z)-1-(hex-5-en-1-yl)-4-[[3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene]methyl]quinolin-1-ium iodide monohydrate, C_{24}H_{25}N_{2}S^{+}/Cl^{-}C_{1}H_{2}O. The packing features aromatic π-stacking and van der Waals interactions. The water molecule of crystallization interacts with the cation and anion via O–H⋯N and O–H⋯I hydrogen bonds, respectively.

Structure description

Intercalating dyes are a standard means to detect duplex DNA or RNA in vitro and in vivo. The cyanine dye thiazole orange has been used extensively as a on/off fluorescent probe in a host of biological applications (Suss et al., 2021). The bis-intercalating dye based on thiazole orange has been shown to have an increased affinity towards duplexed oligomers and retains its fluorogenic characteristic (Rye et al., 1992). In an effort to enhance the binding affinity further, and essentially create a non-covalent interaction that is effectively permanent, we synthesized a thiazole orange dye bearing an alkene substituent that is capable of participating in polymerization reactions. Access to polymeric thiazole orange dye and other cyanine dyes will afford extremely bright, highly organized, and versatile fluorescent probes that can be attached to molecules of interest and mitigate the equilibrium the dye would establish with endogenous duplexes.

Herein we report the crystal structure of 4-hexenyl thiazole orange iodide monohydrate, C_{24}H_{35}N_{2}S^{+}I^{-}⋅H_{2}O, which crystallizes in the triclinic space group P1. In the cation (Fig. 1), the benzothiazole ring is titled by 3.32 (13)° with respect to the quinoline ring system: as a result the molecule is close to planar (excluding the hex-1-ene group)
data reports

Figure 1
A view of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

with an r.m.s. deviation of 0.048 Å for the non-hydrogen atoms; including the hex-1-ene group increases the r.m.s.d to 0.416 Å for the non-hydrogen atoms. The crystal structure contains a water molecule of crystallization bound to the cation via a weak O1—H1A···N1 hydrogen bond [O···N = 3.014 (10) Å] and the anion via an O1—H1B···I1 link [O1···I1 = 3.546 (10) Å] (Table 1). There is also a weak C2—H2···S1 intramolecular interaction with C···S = 3.128 (7) that helps to maintain the coplanarity of the two ring systems.

In the extended structure (Fig. 2), aromatic π–π stacking is observed with Cg1···Cg1i = 3.559 (6) Å [symmetry code: (i) 2 − x, 2 − y, 1 − z] and Cg1···Cg3i = 3.492 (5) Å, where Cg1 is the centroid of the phenyl ring of the benzothiazole group containing atoms C18–C23, Cg2 is the centroid of the phenyl ring of the quinoline group containing atoms C4–C9, and Cg3 is the centroid of the pyridyl ring of the quinoline groups containing atoms N1/C1–C4/C9. These π–π stacking interactions run along the [100] direction with neighboring layers held together with van der Waals interactions.

Synthesis and crystallization
All materials were purchased from Fisher Scientific or Sigma Aldrich and used as received. All flash chromatography was performed with 230 × 400 mesh silica gel. Pure samples were analyzed with a Joel 300 MHz NMR and HRMS of the title compound was acquired on a Shimadzu LCMS 9030 QToF operating in positive mode. The reaction scheme is shown in Fig. 3.

6-Iodohex-1-ene (1)
In a conical reaction vial with a magnetic stir bar, 3.0 g of 6-chlorohex-1-ene (25.4 mmol, 1 equiv) was dissolved in 50 ml of acetone. To this solution was added 11.36 g (76.3 mmol, 3 equiv.) of sodium iodide. The solution was warmed slightly to assist with dissolving the sodium iodide and then covered and stirred for 48 h. An equal portion of hexane was added to the reaction and then the solids were filtered. The volatiles were stripped and the product was purified on silica with 100% hexanes as the eluent. Yield 3.31 g (62%) NMR: 1HN M R [300 MHz, (CDCl3)] δ = 5.77 (m, 1H, –CH=CH2), 4.98 (m, 2H, –CH=CH2), 2.19 (t, 2H, –CH2CH2I), 2.07 (s, 2H, –CH2CH2CH3), 1.77 (t, 2H, –CH2CH2CH2I), 1.52 (t, 2H, –CH2CH2CH2) p.p.m.

1-(Hex-5-en-1-yl)-4-methylquinolin-1-ium iodide (2)
To a conical reaction vial with a magnetic stir bar was added 0.22 g (1.58 mmol, 1 equiv) of 4-methylquinoline and 0.5 g (2.38 mmol, 1.5 equiv.) of 6-iodohex-1-ene. The reaction was stirred at 70°C for 18 h. The reaction was then purified on silica eluting with 2% methanol in DCM. Yield 0.54 g (96%) NMR: 1H NMR [300 MHz, (CDCl3)] δ = 10.17 (d, 1H, Ar.), 8.37 (m, 2H, Ar.), 8.20 (t, 1H, Ar.), 8.01 (m, 2H, Ar.), 6.71 (m, 2H, CH=CH2), 5.28 (t, 2H, –CH2N), 4.96 (m, 2H, –CH=CH2), 2.12 (m, 4H, –CH2CH2CH3), 1.62 (t, 2H, –CH2CH2CH3) p.p.m.

2-Mercapto-3-methylbenzothiazol-3-ium iodide (3)
To a conical reaction flask was added 1 g (6.0 mmol, 1 equiv) of benzothiazole-2-thiol and 2.2 g (15.5 mmol, 2.6 equiv) of methyl iodide. The reaction was allowed to stir at 50°C for 24 h and then taken up in a minimal amount of methanol. The

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| C2—H2···S1 | 0.93 | 2.40 | 3.128 (7) | 135 |
| O1—H1A···N1 | 0.85 | 2.39 | 3.014 (10) | 131 |
| O1—H1B···I1 | 0.85 | 2.71 | 3.546 (10) | 169 |

Figure 2
Crystal packing diagram of the title compound viewed down the b-axis direction with H atoms omitted for clarity.

Figure 3
Reaction scheme.
concentrated solution was then titrated into ether to form a precipitate that was collected by filtration. This provided the product as a white solid that needed no further purification. Yield 0.75 g (69%) NMR: $^1$H NMR [300 MHz, (CD$_3$)$_2$SO]$ \delta$ = 8.80 (d, 1H, Ar.), 8.63 (d, 1H, Ar.), 8.15 (d, 1H, Ar.), 8.06 (d, 1H, Ar.), 7.99 (t, 1H, Ar.), 7.77 (q, 2H, Ar.), 7.62 (t, 1H, Ar.), 7.40 (m, 2H, Ar.), 5.77 (m, 1H, –CH≡CH$_2$), 4.97 (t, 2H, –CH$_2$N), 4.61 (t, 2H, –CH≡CH$_2$), 4.02 (s, 3H, –N–CH$_3$) 2.08 (q, 2H, –CH$_2$–CHCH$_2$), 1.85 (quin, 2H, –CH$_2$CH$_2$CH$_2$), 1.45 (t, 2H, –CH$_2$CH$_2$CH$_2$) p.p.m.

Crystal formation: the title compound was taken up in methanol and then allowed to crystallize as dark-red prisms by slow evaporation of the solvent.

Refrinement
Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements
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Table 2

| Crystal data | Chemical formula | C$_{24}$H$_{25}$N$_2$S$^+$·I$^-$·H$_2$O |
|--------------|------------------|--------------------------------------|
| Crystal system, space group | Triclinic, $PT$ | |
| Temperature (K) | 170 | |
| $\alpha$, $\beta$, $\gamma$ (°) | 95.810 (12), 105.762 (12), 110.651 (14) | |
| $\mu$ (mm$^{-1}$) | 1.51 | |
| Crystal size (mm) | 0.5 × 0.1 × 0.1 | |

Data collection
Diffractometer | XtaLAB Mini (ROW) |
Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2019) |

| $T_{\text{min}}$, $T_{\text{max}}$ | 0.332, 1.000 |
| No. of measured, independent and observed $|F| > 2\sigma(|F|)$ reflections | 6581, 4189, 2249 |
| $R_{\text{int}}$ (sin $\theta$$_{\text{max}}$/A$^{-1}$) | 0.043 |
| $S$ | 0.602 |

Refinement
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.060, 0.171, 1.03 |
| No. of reflections | 4189 |
| No. of parameters | 266 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta \rho_{\text{max}}$, $\Delta \rho_{\text{min}}$ (e A$^{-3}$) | 0.66, −0.60 |

The title compound was then purified using a gradient (2–5%) of methanol in DCM. Yield 45 mg (30%). NMR: 1H NMR [300 MHz, (CD$_3$)$_2$SO] $\delta$ = 8.43 (d, 1H, Ar.), 8.29 (d, 1H, Ar.), 7.90 (t, 2H, Ar.), 7.80 (t, 2H, Ar.), 4.20 (s, 3H, –CH$_3$), 3.17 (t, 3H, –SC$_2$H$_5$) p.p.m.

(Z)-1-(Hex-5-en-1-yl)-4-((3-methylbenzo[d]thiazol-2(3H)-ylidene)methyl)quinolin-1-ium iodide (4)

Into a conical reaction vial with a magnetic stir bar was added 106 mg (0.3 mmol, 1 eqv) of 2 that was dissolved in 2 ml of DMF. A total of 97 mg (0.3 mmol, 1 eqv) of 3 was added followed by the addition of 42 mg (0.3 mmol, 1 equiv.) of triethylamine. The solution immediately turned dark red and was allowed to stir for 48 h.

The solution was then added to ether, and the orange solid was collected.

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1-(Hex-5-en-1-yl)-4-([3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene]methyl)-quinolin-1-ium iodide monohydrate

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1-(Hex-5-en-1-yl)-4-([3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene]methyl)quinolin-1-ium iodide monohydrate

_Crystal data_

C_{24}H_{25}N_{2}S^{+}\cdot I^{-}\cdot H_{2}O

Mr = 518.43

Triclinic, P1

a = 8.4780 (11) Å
b = 10.5773 (17) Å
c = 14.5191 (19) Å

α = 95.810 (12)°
β = 105.762 (12)°
γ = 110.651 (14)°

V = 1144.1 (3) Å³

Z = 2

F(000) = 524

D_x = 1.505 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 644 reflections

θ = 2.1–21.1°

µ = 1.51 mm⁻¹

T = 170 K

Rect. prism, clear dark red

0.5 × 0.1 × 0.1 mm

_Data collection_

XtaLAB Mini (ROW)
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Rigaku (Mo) X-ray Source

Graphite monochromator

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2019)

T_min = 0.332, T_max = 1.000

6581 measured reflections

4189 independent reflections

2249 reflections with I > 2σ(I)

R_{int} = 0.043

θ_max = 25.4°, θ_min = 2.1°

h = −10→10

k = −12→11

l = −17→16

_Refinement_

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.060

wR(F²) = 0.171

S = 1.03

4189 reflections

266 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained

w = 1/σ²(F_c²) + (0.0622P)^2 + 0.1317P

where P = (F_c² + 2F_s²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.66 e Å⁻³

Δρ_{min} = −0.60 e Å⁻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.

Refinement. All H atoms were placed in idealized locations (C—H = 0.93–0.97, O—H = 0.85 Å) and refined as riding atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x      | y      | z      | Uiso/*Ueq |
|-----|--------|--------|--------|-----------|
| I1  | 0.04034 (9) | 0.55965 (6) | 0.30846 (5) | 0.0920 (3) |
| S1  | 0.7927 (3)   | 0.81364 (17) | 0.36094 (14) | 0.0577 (5)  |
| N2  | 0.8314 (7)   | 1.0670 (5)   | 0.3757 (4)   | 0.0495 (14) |
| N1  | 0.6019 (8)   | 0.6852 (5)   | 0.6841 (5)   | 0.0579 (15) |
| C23 | 0.8637 (9)   | 1.0327 (7)   | 0.2901 (5)   | 0.0511 (17) |
| C4  | 0.6594 (9)   | 0.9170 (7)   | 0.6522 (5)   | 0.0498 (17) |
| C16 | 0.7461 (9)   | 0.9748 (7)   | 0.5082 (5)   | 0.0537 (17) |
| H16 | 0.746994     | 1.060734     | 0.530348     | 0.064*      |
| C3  | 0.7026 (9)   | 0.8785 (6)   | 0.5662 (5)   | 0.0486 (17) |
| C17 | 0.7876 (8)   | 0.9617 (6)   | 0.4235 (5)   | 0.0467 (16) |
| C9  | 0.6078 (9)   | 0.8171 (7)   | 0.7091 (5)   | 0.0549 (18) |
| C2  | 0.6923 (9)   | 0.7436 (7)   | 0.5470 (5)   | 0.0559 (18) |
| H2  | 0.716781     | 0.713601     | 0.492143     | 0.067*      |
| C1  | 0.6479 (9)   | 0.6548 (7)   | 0.6053 (5)   | 0.0590 (19) |
| H1  | 0.649126     | 0.567645     | 0.590268     | 0.071*      |
| C18 | 0.8509 (9)   | 0.8971 (7)   | 0.2716 (5)   | 0.0544 (18) |
| C22 | 0.9072 (10)  | 1.1178 (8)   | 0.2252 (6)   | 0.066 (2)   |
| H22 | 0.918042     | 1.209023     | 0.236988     | 0.080*      |
| C10 | 0.5465 (10)  | 0.5769 (7)   | 0.7392 (6)   | 0.067 (2)   |
| H10A| 0.515625     | 0.487592     | 0.698316     | 0.080*      |
| H10B| 0.439612     | 0.576184     | 0.751890     | 0.080*      |
| C5  | 0.6653 (10)  | 1.0472 (7)   | 0.6860 (5)   | 0.0609 (19) |
| H5  | 0.701850     | 1.115918     | 0.652057     | 0.073*      |
| C11 | 0.6831 (11)  | 0.5937 (7)   | 0.8340 (6)   | 0.066 (2)   |
| H11A| 0.705991     | 0.678282     | 0.878000     | 0.079*      |
| H11B| 0.793698     | 0.601946     | 0.822871     | 0.079*      |
| C6  | 0.6208 (11)  | 1.0797 (8)   | 0.7658 (6)   | 0.072 (2)   |
| H6  | 0.624418     | 1.167804     | 0.783995     | 0.086*      |
| C24 | 0.8400 (10)  | 1.2008 (7)   | 0.4111 (6)   | 0.064 (2)   |
| H24A| 0.927482     | 1.239531     | 0.475373     | 0.096*      |
| H24B| 0.725376     | 1.193066     | 0.414159     | 0.096*      |
| H24C| 0.872977     | 1.259910     | 0.367520     | 0.096*      |
| C8  | 0.5616 (11)  | 0.8527 (8)   | 0.7912 (6)   | 0.071 (2)   |
| H8  | 0.524265     | 0.786504     | 0.826843     | 0.085*      |
| O1  | 0.2316 (12)  | 0.5102 (8)   | 0.5443 (7)   | 0.138 (3)   |
| H1A | 0.291275     | 0.581291     | 0.590880     | 0.207*      |
| H1B | 0.192515     | 0.534755     | 0.491739     | 0.207*      |
C19  0.8832 (11)  0.8450 (8)  0.1895 (6)  0.073 (2)
H19  0.877847  0.755232  0.177902  0.087*
C12  0.6232 (11)  0.4721 (8)  0.8818 (6)  0.071 (2)
H12A  0.512182  0.464089  0.892323  0.085*
H12B  0.599653  0.387829  0.837227  0.085*
C20  0.9230 (12)  0.9296 (9)  0.1268 (6)  0.081 (2)
H20  0.943321  0.895594  0.071436  0.097*
C21  0.9340 (11)  1.0618 (9)  0.1423 (6)  0.075 (2)
H21  0.959534  1.115594  0.097174  0.090*
C7  0.5706 (12)  0.9825 (9)  0.8191 (7)  0.080 (3)
H7  0.542670  1.005128  0.874551  0.095*
C13  0.7538 (14)  0.4843 (11)  0.9753 (8)  0.110 (3)
H13A  0.770531  0.565495  1.020756  0.132*
H13B  0.867061  0.50099  0.965176  0.132*
C14  0.7080 (18)  0.3633 (12)  1.0222 (8)  0.113 (4)
H14  0.790099  0.376037  1.083381  0.136*
C15  0.585 (2)  0.2529 (12)  0.9957 (10)  0.146 (6)
H15A  0.496588  0.231168  0.935308  0.175*
H15B  0.578332  0.188806  1.035348  0.175*

Atomic displacement parameters (Å²)

|     | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|-----|------|------|------|------|------|------|
| I1  | 0.1378 (6) | 0.0665 (4) | 0.0968 (5) | 0.0488 (4) | 0.0612 (4) | 0.0317 (3) |
| S1  | 0.0704 (12) | 0.0407 (9) | 0.0605 (12) | 0.0162 (9) | 0.0271 (10) | 0.0111 (9) |
| N2  | 0.057 (4) | 0.041 (3) | 0.055 (4) | 0.019 (3) | 0.024 (3) | 0.018 (3) |
| N1  | 0.058 (4) | 0.041 (3) | 0.072 (4) | 0.011 (3) | 0.029 (3) | 0.016 (3) |
| C23 | 0.045 (4) | 0.048 (4) | 0.056 (5) | 0.010 (3) | 0.019 (4) | 0.014 (4) |
| C4  | 0.053 (4) | 0.043 (4) | 0.061 (5) | 0.019 (3) | 0.028 (4) | 0.017 (3) |
| C16 | 0.060 (5) | 0.046 (4) | 0.061 (5) | 0.021 (4) | 0.028 (4) | 0.017 (4) |
| C3  | 0.048 (4) | 0.043 (4) | 0.055 (4) | 0.016 (3) | 0.018 (3) | 0.016 (3) |
| C17 | 0.038 (4) | 0.042 (4) | 0.058 (5) | 0.010 (3) | 0.018 (3) | 0.014 (3) |
| C9  | 0.050 (4) | 0.058 (4) | 0.064 (5) | 0.024 (4) | 0.025 (4) | 0.020 (4) |
| C2  | 0.069 (5) | 0.048 (4) | 0.057 (5) | 0.019 (4) | 0.033 (4) | 0.018 (4) |
| C1  | 0.069 (5) | 0.047 (4) | 0.060 (5) | 0.018 (4) | 0.027 (4) | 0.008 (4) |
| C18 | 0.057 (5) | 0.047 (4) | 0.055 (5) | 0.013 (4) | 0.023 (4) | 0.013 (4) |
| C22 | 0.066 (5) | 0.068 (5) | 0.075 (6) | 0.028 (4) | 0.033 (4) | 0.027 (5) |
| C10 | 0.084 (6) | 0.050 (4) | 0.070 (5) | 0.016 (4) | 0.042 (5) | 0.024 (4) |
| C5  | 0.078 (5) | 0.057 (4) | 0.062 (5) | 0.031 (4) | 0.035 (4) | 0.022 (4) |
| C11 | 0.080 (5) | 0.059 (5) | 0.073 (6) | 0.030 (4) | 0.039 (5) | 0.024 (4) |
| C6  | 0.101 (6) | 0.062 (5) | 0.083 (6) | 0.045 (5) | 0.059 (5) | 0.026 (4) |
| C24 | 0.073 (5) | 0.054 (4) | 0.077 (6) | 0.027 (4) | 0.036 (4) | 0.027 (4) |
| C8  | 0.088 (6) | 0.078 (5) | 0.082 (6) | 0.043 (5) | 0.060 (5) | 0.042 (5) |
| O1  | 0.121 (7) | 0.111 (6) | 0.159 (8) | 0.044 (6) | 0.020 (6) | 0.009 (5) |
| C19 | 0.091 (6) | 0.058 (5) | 0.066 (5) | 0.015 (5) | 0.043 (5) | 0.006 (4) |
| C12 | 0.081 (6) | 0.063 (5) | 0.078 (6) | 0.028 (5) | 0.039 (5) | 0.025 (5) |
| C20 | 0.093 (7) | 0.078 (6) | 0.068 (6) | 0.016 (5) | 0.048 (5) | 0.009 (5) |
| C21 | 0.084 (6) | 0.072 (5) | 0.070 (6) | 0.017 (5) | 0.040 (5) | 0.028 (5) |
### Geometric parameters (Å, °)

| Bond/Angle | Distance/ Angle Value |
|------------|-----------------------|
| S1—C17     | 1.750 (7)             |
| S1—C18     | 1.726 (7)             |
| N2—C23     | 1.383 (8)             |
| N2—C17     | 1.366 (8)             |
| N2—C24     | 1.426 (8)             |
| N1—C9      | 1.385 (8)             |
| N1—C1      | 1.349 (9)             |
| N1—C10     | 1.478 (8)             |
| C23—C18    | 1.392 (9)             |
| C23—C22    | 1.400 (10)            |
| C4—C3      | 1.453 (9)             |
| C4—C9      | 1.427 (9)             |
| C4—C5      | 1.393 (9)             |
| C16—H16    | 0.9300 (9)            |
| C16—C3     | 1.399 (9)             |
| C3—C2      | 1.392 (9)             |
| C9—C8      | 1.408 (10)            |
| C2—H2      | 0.9300 (9)            |
| C2—C1      | 1.351 (9)             |
| C1—H1      | 0.9300 (9)            |
| C18—C19    | 1.397 (10)            |
| C22—H22    | 0.9300 (9)            |
| C22—C21    | 1.396 (11)            |
| C10—H10A   | 0.9700 (9)            |
| C10—H10B   | 0.9700 (9)            |
| C10—C11    | 1.485 (10)            |
| C5—H5      | 0.9300 (9)            |
| C5—C6      | 1.360 (10)            |

| Bond/Angle | Distance/ Angle Value |
|------------|-----------------------|
| C18—S1     | 123.1 (5)             |
| C17—N1     | 114.8 (5)             |
| C17—N2     | 122.1 (6)             |
| C9—N1      | 123.0 (6)             |
| C1—N1      | 118.1 (6)             |
| N2—C23     | 112.7 (6)             |
| N2—C2—C2   | 119.8 (7)             |
| C9—C4      | 119.4 (6)             |
C5—C4—C3 125.1 (6)  
C5—C4—C9 115.5 (7)  
C3—C16—H16 115.1  
C17—C16—H16 115.1  
C16—C3—C4 119.3 (6)  
C2—C3—C4 115.6 (6)  
C2—C3—C16 125.1 (7)  
N2—C17—S1 110.0 (5)  
N2—C17—C16 123.3 (6)  
C16—C17—S1 126.8 (5)  
N1—C9—C4 120.7 (7)  
N1—C9—C8 119.7 (6)  
C8—C9—C4 119.6 (6)  
C3—C2—C3 122.4 (7)  
C1—C2—H2 118.8  
C2—C1—H1 118.1  
C23—C18—S1 120.8 (7)  
C19—C18—S1 128.3 (5)  
C23—C18—C19 120.8 (7)  
C21—C22—H22 120.9  
C23—C22—H22 120.9  
N1—C10—H10A 108.6  
N1—C10—H10B 108.6  
H10A—C10—H10B 107.5  
C11—C10—H10A 108.6  
C11—C10—H10B 108.6  
C4—C5—H5 118.1  
C6—C5—C4 123.9 (7)  
C6—C5—H5 118.1  
C10—C11—H11A 109.3  
C10—C11—H11B 109.3  
S1—C18—C19—C20 178.2 (6)  
N2—C23—C18—S1 15.8 (8)  
N2—C23—C18—C19 −178.5 (6)  
N2—C23—C22—C21 −179.8 (7)  
N1—C9—C8—C7 178.2 (7)  
N1—C10—C11—C12 −174.8 (6)  
C23—N2—C17—S1 1.7 (7)  
C23—N2—C17—C16 −178.1 (6)  
C23—C18—C19—C20 −1.7 (12)  
C23—C22—C21—C20 −1.9 (12)  
S2—C24—C25—C26 178.2 (6)  
N3—C25—C24—S1 15.8 (8)  
N3—C25—C24—C26 −178.5 (6)  
N3—C25—C22—C21 −179.8 (7)  
N1—C9—C8—C7 178.2 (7)  
N1—C10—C11—C12 −174.8 (6)  
C23—N2—C17—S1 1.7 (7)  
C23—N2—C17—C16 −178.1 (6)  
C23—C18—C19—C20 −1.7 (12)  
C23—C22—C21—C20 −1.9 (12)
C4—C3—C2—C1 −1.1 (11)  C22—C23—C18—S1 −179.1 (5)
C4—C9—C8—C7 −2.1 (12)  C22—C23—C18—C19 0.8 (11)
C4—C5—C6—C7 1.6 (13)  C10—N1—C9—C4 −178.9 (6)
C16—C3—C2—C1 −179.3 (7)  C10—N1—C9—C8 0.8 (11)
C3—C4—C9—N1 1.2 (10)  C10—N1—C1—C2 176.7 (7)
C3—C4—C9—C8 −178.5 (7)  C10—C11—C12—C13 180.0 (8)
C3—C4—C5—C6 178.7 (7)  C5—C4—C3—C16 −3.2 (11)
C3—C16—C17—S1 1.7 (11)  C5—C4—C3—C2 178.4 (7)
C3—C16—C17—N2 −178.5 (7)  C5—C4—C9—N1 −178.2 (6)
C3—C2—C1—N1 3.1 (12)  C5—C4—C9—C8 2.1 (10)
C17—S1—C18—C23 −0.5 (6)  C5—C6—C7—C8 −1.4 (14)
C17—S1—C18—C19 179.6 (7)  C7—C6—C5—C4 −3.2 (11)
C17—N2—C23—C18 −2.1 (8)  C7—C6—C5—C3 178.4 (7)
C17—N2—C23—C22 178.6 (7)  C7—C6—C5—C2 178.4 (7)
C17—C16—C3—C4 −178.6 (7)  C7—C6—C5—C16 178.4 (7)
C17—C16—C3—C2 −0.3 (12)  C7—C6—C5—C17 178.4 (7)
C9—N1—C1—C2 −2.8 (11)  C12—C13—C14—C15 3 (2)
C9—N1—C10—C11 −76.4 (9)  C12—C13—C14—C15 3 (2)
C9—C4—C3—C16 177.4 (6)

**Hydrogen-bond geometry (Å, °)**

| D—H···A   | D—H | H···A | D···A  | D—H···A |
|-----------|------|-------|--------|---------|
| C2—H2···S1 | 0.93 | 2.40  | 3.128 (7) | 135     |
| O1—H1A···N1 | 0.85 | 2.39  | 3.014 (10) | 131     |
| O1—H1B···I1 | 0.85 | 2.71  | 3.546 (10) | 169     |