# 2-Hydroxy-1-naphthaldehyde 2-methylthiosemicarbazone

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The potentially tridentate O,N,S-donor ligand, 2-hydroxy-1-naphthaldehyde 2-methylthiosemicarbazone, $C_{13}H_{13}N_3OS$, has been structurally characterized and the molecule is found to exhibit a distorted planar structure with the thiosemicarbazide moiety being twisted slightly out of the plane defined by the naphthyl ring.

## Comment

Ligands of the aroylhydrazone class have shown much promise as potential chelators for treatment of iron overload disease and perhaps cancer (Johnson *et al.*, 1982; Baker *et al.*, 1992; Richardson *et al.*, 1995; Richardson & Milnes, 1997). Our previous investigations have demonstrated that 2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone, (II), and several other aroylhydrazone chelators possess antitumour activity due to their ability to bind intracellular iron (Richardson *et al.*, 1995; Richardson & Milnes, 1997; Darnell & Richardson, 1999; Richardson & Bernhardt, 1999). From these studies we have been able to identify structural components of the hydrazones which infer antineoplastic activity, namely the salicylaldehyde and 2-hydroxy-1-naphthaldehyde moieties (Richardson *et al.*, 1995).

Another related group of chelators known as the thiosemicarbazones also show high antitumour activity due to their ability to inhibit ribonucleotide reductase (Cory *et al.*, 1995; Liu *et al.*, 1995). Considering this, we have designed and synthesized a new group of ligands by condensation of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with a range of thiosemicarbazides. The parent compound of this new series of chelators is 2-hydroxy-1-naphthaldehyde thiosemicarbazone, (III). Substitution of a methyl group at the 2-position of (III) to give (I) results in a marked decrease in anti-proliferative activity and a decrease in iron chelation efficacy (Lovejoy *et al.*, 1999). These data may suggest that this latter substitution diminishes the metal ion binding capability of these chelators. Studies assessing the biological activity of this new class of compounds are underway and will be reported

elsewhere (Lovejoy *et al.*, 1999). In the present communication we report the X-ray crystal structure of 2-hydroxy-1-naphthaldehyde 2-methylthiosemicarbazone, (I).
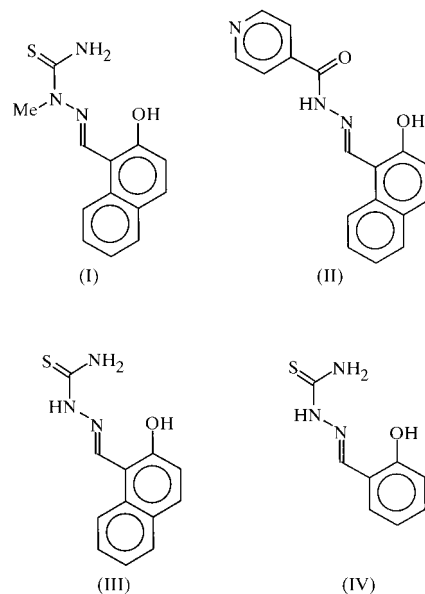


A view of (I) is shown in Fig. 1. The bond lengths are typical of a compound of this type (Table 1), and the angles are all close to 120°. The greatest deviation from an ideal trigonal planar geometry is at N2 where steric repulsion between the *N*-methyl group and S1 contracts the C13—N2—N1 angle to 116.1 (3)°. The naphthyl ring is planar, with atoms C1–C10 all lying within 0.05 Å of the least-squares plane of the ring system. The atoms deviating the most from the naphthyl ring moiety are C12 [0.428 (3) Å], C13 [−0.671 (7) Å], N3 [−1.288 (7) Å] and S1 [−0.452 (8) Å], which is also seen in the C11—N1—N2—C12 torsion angle of 9.7 (5)°. The conformation of the molecule finds S1 *anti* to N1. Generally, it has been found that ligands of the salicylaldehyde thiosemicarbazone class [such as (IV)] act as meridionally coordinating, tridentate S,N,O-donors, so there needs to be a *ca* 180° rotation about N2—C13 in (I) before a metal ion can be bound in this fashion. The potential donors O1 and N1 are found in a *syn* disposition, as a result of a strong intramolecular hydrogen bond [O1—H1···N1 1.89, O1···N1 2.603 (4) Å].

The presence of the *N*-methyl group in (I) also has other consequences for the coordination chemistry of this potentially tridentate ligand. In the structures of unsubstituted thiosemicarbazones such as (IV), the aldimine and phenolic protons (attached at positions corresponding to O1 and N2 in the present structure) can be removed upon coordination of the S, N and O-donors. However, it is not essential that either the aldimine or the phenolic protons are lost upon coordination of ligands in this class. Examples of (IV) coordinated in its neutral (Zimmer *et al.*, 1991), mono anionic (Soriano-Garcia *et al.*, 1985) and dianionic (Gyepes *et al.*, 1981) forms are known. In the present case, the *N*-methyl group renders (I) incapable of losing more than one proton (at O1). In principle, this should not detract from the ability of (I) (or its anion) to coordinate to a metal ion, but the charge of the resulting

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# organic compounds

complex will not be as variable as those found for complexes of (IV). The charge of the ligand and its resulting complexes *in vivo* are important for determining the biological activity of these chelators. Passage across the cell membrane is inhibited if the compound is hydrophilic, so systems close to neutrality are generally desirable if high iron chelation activity is sought (Richardson *et al.*, 1990).

We are currently exploring the coordination chemistry and biological activity of these novel chelators.
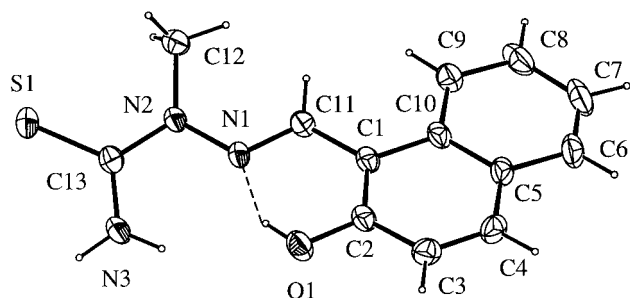


**Figure 1**
View of (I) showing 30% probability ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

## Experimental

The title compound was synthesized by refluxing equimolar amounts of the 2-hydroxy-1-naphthaldehyde and 2-methyl-3-thiosemicarbazide in ethanol. The compound was collected by filtration and crystals suitable for X-ray work were obtained by slow evaporation of an ethanolic solution of the compound.

*Crystal data*

| | |
|---|---|
| $C_{13}H_{13}N_3OS$ | $D_x = 1.388$ Mg m$^{-3}$ |
| $M_r = 259.32$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1$ | Cell parameters from 25 |
| $a = 8.0560 (10)$ Å | reflections |
| $b = 6.7586 (6)$ Å | $\theta = 10–14°$ |
| $c = 11.694 (3)$ Å | $\mu = 0.252$ mm$^{-1}$ |
| $\beta = 102.930 (10)°$ | $T = 295 (2)$ K |
| $V = 620.56 (19)$ Å$^3$ | Needle, yellow |
| $Z = 2$ | $0.50 \times 0.50 \times 0.13$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffract-ometer | $R_{int} = 0.048$ |
| | $\theta_{max} = 24.98°$ |
| $\omega$–$2\theta$ scans | $h = 0 \to 9$ |
| Absorption correction: $\psi$ scan | $k = 0 \to 8$ |
| (North *et al.*, 1968) | $l = -13 \to 13$ |
| $T_{min} = 0.732$, $T_{max} = 0.968$ | 3 standard reflections |
| 1278 measured reflections | frequency: 120 min |
| 1191 independent reflections | intensity decay: <5% |
| 1067 reflections with $I > 2\sigma(I)$ | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C2—O1 | 1.351 (4) | C13—N2 | 1.365 (5) |
| C11—N1 | 1.293 (5) | C13—S1 | 1.671 (4) |
| C12—N2 | 1.461 (5) | N1—N2 | 1.371 (4) |
| C13—N3 | 1.332 (5) | | |
| | | | |
| O1—C2—C1 | 122.7 (3) | N2—C13—S1 | 122.9 (3) |
| O1—C2—C3 | 115.2 (4) | C11—N1—N2 | 121.4 (3) |
| N1—C11—C1 | 120.3 (3) | C13—N2—N1 | 116.2 (3) |
| N3—C13—N2 | 116.6 (3) | C13—N2—C12 | 122.4 (3) |
| N3—C13—S1 | 120.5 (3) | N1—N2—C12 | 121.2 (3) |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0918P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $+ 0.0783P]$ where |
| $wR(F^2) = 0.121$ | $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.044$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1191 reflections | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |
| 164 parameters | $\Delta\rho_{min} = -0.24$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N3—H3$A\cdots$S1$^i$ | 0.86 | 2.90 | 3.472 (3) | 125.3 |
| N3—H3$B\cdots$O1$^{ii}$ | 0.86 | 2.21 | 3.033 (4) | 161.5 |
| O1—H1$\cdots$N1 | 0.82 | 1.89 | 2.603 (4) | 145.1 |

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 in *CAD-4 Software*; data reduction: *Xtal* (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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# supporting information

## 2-Hydroxy-1-naphthaldehyde 2-methylthiosemicarbazone

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### Computing details

Data collection: CAD4 (Enraf-Nonius, 1988); cell refinement: *SET4* in CAD4; data reduction: *Xtal* (Hall, 1992); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

### (I)

*Crystal data*

| | |
|---|---|
| $C_{13}H_{13}N_3OS$ | $F(000) = 272$ |
| $M_r = 259.32$ | $D_x = 1.388$ Mg m$^{-3}$ |
| Monoclinic, $P2_1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 8.056$ (1) Å | Cell parameters from 25 reflections |
| $b = 6.7586$ (6) Å | $\theta = 10$–$14°$ |
| $c = 11.694$ (3) Å | $\mu = 0.25$ mm$^{-1}$ |
| $\beta = 102.93$ (1)° | $T = 295$ K |
| $V = 620.56$ (19) Å$^3$ | Needle, yellow |
| $Z = 2$ | $0.50 \times 0.50 \times 0.13$ mm |

*Data collection*

| | |
|---|---|
| Enraf-Nonius CAD4 diffractometer | 1191 independent reflections |
| Radiation source: fine-focus sealed tube | 1067 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.048$ |
| $\omega$–$2\theta$ scans | $\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$ |
| Absorption correction: $\psi$ scan (North et al., 1968) | $h = 0 \rightarrow 9$ |
| | $k = 0 \rightarrow 8$ |
| | $l = -13 \rightarrow 13$ |
| $T_{min} = 0.732$, $T_{max} = 0.968$ | 3 standard reflections every 120 min |
| 1278 measured reflections | intensity decay: < 5% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.121$ | |
| $S = 1.04$ | H-atom parameters constrained |
| 1191 reflections | Calculated $w = 1/[\sigma^2(F_o^2) + (0.0918P)^2 + 0.0783P]$ |
| 164 parameters | |
| 1 restraint | where $P = (F_o^2 + 2F_c^2)/3$ |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} < 0.001$ |
| | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |

$\Delta\rho_{min} = -0.24$ e Å⁻³
Absolute structure: Flack (1983)

Absolute structure parameter: −0.03 (16)

*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 (Å²)*

|      | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|------|-----|-----|-----|---------------------|
| C1   | −0.7419 (4)   | −0.6739 (7)   | −0.1715 (3)   | 0.0358 (7)   |
| C2   | −0.6693 (4)   | −0.8398 (6)   | −0.2108 (3)   | 0.0397 (8)   |
| C3   | −0.6255 (5)   | −1.0077 (6)   | −0.1409 (4)   | 0.0468 (9)   |
| H3   | −0.5803       | −1.1178       | −0.1708       | 0.056*       |
| C4   | −0.6487 (5)   | −1.0105 (7)   | −0.0301 (4)   | 0.0501 (10)  |
| H4   | −0.6198       | −1.1234       | 0.0154        | 0.060*       |
| C5   | −0.7164 (4)   | −0.8442 (7)   | 0.0182 (3)    | 0.0439 (9)   |
| C6   | −0.7310 (5)   | −0.8447 (10)  | 0.1368 (3)    | 0.0598 (13)  |
| H6   | −0.6987       | −0.9561       | 0.1831        | 0.072*       |
| C7   | −0.7915 (5)   | −0.6844 (12)  | 0.1826 (3)    | 0.0694 (15)  |
| H7   | −0.7967       | −0.6843       | 0.2612        | 0.083*       |
| C8   | −0.8469 (5)   | −0.5174 (9)   | 0.1130 (4)    | 0.0638 (14)  |
| H8   | −0.8920       | −0.4096       | 0.1452        | 0.077*       |
| C9   | −0.8347 (5)   | −0.5124 (8)   | −0.0024 (3)   | 0.0493 (10)  |
| H9   | −0.8710       | −0.4008       | −0.0476       | 0.059*       |
| C10  | −0.7671 (4)   | −0.6761 (7)   | −0.0530 (3)   | 0.0382 (8)   |
| C11  | −0.7930 (4)   | −0.5054 (6)   | −0.2464 (3)   | 0.0374 (8)   |
| H11  | −0.8649       | −0.4107       | −0.2259       | 0.045*       |
| C12  | −0.9362 (5)   | −0.2061 (7)   | −0.4052 (3)   | 0.0490 (10)  |
| H12A | −0.9698       | −0.2395       | −0.3338       | 0.073*       |
| H12B | −1.0308       | −0.2253       | −0.4706       | 0.073*       |
| H12C | −0.9009       | −0.0703       | −0.4023       | 0.073*       |
| C13  | −0.7210 (4)   | −0.3187 (6)   | −0.5125 (3)   | 0.0406 (8)   |
| N1   | −0.7393 (3)   | −0.4850 (5)   | −0.3420 (2)   | 0.0363 (7)   |
| N2   | −0.7951 (4)   | −0.3331 (5)   | −0.4187 (2)   | 0.0388 (7)   |
| N3   | −0.5897 (4)   | −0.4384 (6)   | −0.5126 (3)   | 0.0572 (10)  |
| H3A  | −0.5557       | −0.5193       | −0.4554       | 0.069*       |
| H3B  | −0.5389       | −0.4347       | −0.5699       | 0.069*       |
| O1   | −0.6391 (4)   | −0.8520 (4)   | −0.3196 (2)   | 0.0506 (7)   |
| H1   | −0.6686       | −0.7487       | −0.3553       | 0.061*       |
| S1   | −0.79038 (12) | −0.16331 (19) | −0.62414 (7)  | 0.0524 (3)   |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0352 (15) | 0.0387 (18) | 0.0357 (16) | −0.0064 (18) | 0.0128 (12) | 0.0023 (18) |
| C2 | 0.0390 (17) | 0.042 (2) | 0.0419 (18) | −0.0033 (18) | 0.0169 (14) | 0.0050 (19) |
| C3 | 0.0443 (19) | 0.039 (2) | 0.059 (2) | 0.0019 (17) | 0.0149 (16) | 0.0050 (19) |
| C4 | 0.044 (2) | 0.045 (2) | 0.060 (2) | −0.0005 (19) | 0.0106 (17) | 0.023 (2) |
| C5 | 0.0362 (17) | 0.056 (2) | 0.0404 (18) | −0.0081 (19) | 0.0102 (14) | 0.015 (2) |
| C6 | 0.051 (2) | 0.088 (4) | 0.043 (2) | −0.012 (3) | 0.0141 (17) | 0.025 (3) |
| C7 | 0.059 (2) | 0.120 (5) | 0.0352 (19) | −0.019 (3) | 0.0217 (17) | 0.006 (3) |
| C8 | 0.059 (3) | 0.093 (4) | 0.047 (2) | −0.004 (3) | 0.028 (2) | −0.013 (3) |
| C9 | 0.048 (2) | 0.063 (3) | 0.0388 (19) | 0.002 (2) | 0.0150 (16) | 0.001 (2) |
| C10 | 0.0314 (15) | 0.049 (2) | 0.0367 (16) | −0.0090 (18) | 0.0125 (12) | 0.003 (2) |
| C11 | 0.0418 (18) | 0.0346 (18) | 0.0390 (18) | −0.0008 (17) | 0.0157 (14) | 0.0001 (16) |
| C12 | 0.050 (2) | 0.048 (3) | 0.055 (2) | 0.0113 (18) | 0.0252 (16) | 0.0098 (18) |
| C13 | 0.0415 (18) | 0.041 (2) | 0.0422 (18) | −0.0044 (17) | 0.0144 (14) | 0.0059 (17) |
| N1 | 0.0408 (15) | 0.0374 (17) | 0.0340 (15) | 0.0010 (14) | 0.0152 (12) | 0.0087 (14) |
| N2 | 0.0420 (14) | 0.0402 (17) | 0.0394 (14) | 0.0051 (14) | 0.0202 (12) | 0.0101 (14) |
| N3 | 0.063 (2) | 0.063 (2) | 0.058 (2) | 0.0192 (19) | 0.0405 (16) | 0.0237 (19) |
| O1 | 0.0673 (17) | 0.0449 (17) | 0.0489 (14) | 0.0061 (15) | 0.0324 (14) | 0.0019 (14) |
| S1 | 0.0628 (6) | 0.0576 (6) | 0.0407 (5) | 0.0088 (6) | 0.0194 (4) | 0.0179 (5) |

*Geometric parameters (Å, º)*

| C1—C2 | 1.389 (6) | C7—C8 | 1.404 (9) |
|---|---|---|---|
| C1—C11 | 1.440 (5) | C8—C9 | 1.375 (6) |
| C1—C10 | 1.445 (4) | C9—C10 | 1.420 (6) |
| C2—O1 | 1.351 (4) | C11—N1 | 1.293 (5) |
| C2—C3 | 1.397 (5) | C12—N2 | 1.461 (5) |
| C3—C4 | 1.350 (6) | C13—N3 | 1.332 (5) |
| C4—C5 | 1.421 (6) | C13—N2 | 1.365 (5) |
| C5—C10 | 1.413 (6) | C13—S1 | 1.671 (4) |
| C5—C6 | 1.417 (5) | N1—N2 | 1.371 (4) |
| C6—C7 | 1.348 (9) |  |  |
|  |  |  |  |
| C2—C1—C11 | 121.4 (3) | C9—C8—C7 | 120.3 (5) |
| C2—C1—C10 | 118.0 (4) | C8—C9—C10 | 120.5 (5) |
| C11—C1—C10 | 120.6 (4) | C5—C10—C9 | 117.9 (3) |
| O1—C2—C1 | 122.7 (3) | C5—C10—C1 | 119.3 (4) |
| O1—C2—C3 | 115.2 (4) | C9—C10—C1 | 122.8 (4) |
| C1—C2—C3 | 122.1 (3) | N1—C11—C1 | 120.3 (3) |
| C4—C3—C2 | 120.1 (4) | N3—C13—N2 | 116.6 (3) |
| C3—C4—C5 | 121.3 (4) | N3—C13—S1 | 120.5 (3) |
| C10—C5—C6 | 120.1 (4) | N2—C13—S1 | 122.9 (3) |
| C10—C5—C4 | 119.2 (3) | C11—N1—N2 | 121.4 (3) |
| C6—C5—C4 | 120.7 (4) | C13—N2—N1 | 116.2 (3) |
| C7—C6—C5 | 120.2 (5) | C13—N2—C12 | 122.4 (3) |
| C6—C7—C8 | 120.8 (4) | N1—N2—C12 | 121.2 (3) |

| | | | |
|---|---|---|---|
| C11—C1—C2—O1 | 1.4 (5) | C4—C5—C10—C1 | −2.7 (5) |
| C10—C1—C2—O1 | −179.4 (3) | C8—C9—C10—C5 | 1.2 (6) |
| C11—C1—C2—C3 | −177.3 (3) | C8—C9—C10—C1 | −176.1 (3) |
| C10—C1—C2—C3 | 1.8 (5) | C2—C1—C10—C5 | 0.5 (5) |
| O1—C2—C3—C4 | 179.3 (3) | C11—C1—C10—C5 | 179.7 (3) |
| C1—C2—C3—C4 | −1.9 (5) | C2—C1—C10—C9 | 177.8 (3) |
| C2—C3—C4—C5 | −0.4 (6) | C11—C1—C10—C9 | −3.0 (5) |
| C3—C4—C5—C10 | 2.7 (5) | C2—C1—C11—N1 | −15.4 (5) |
| C3—C4—C5—C6 | −176.3 (4) | C10—C1—C11—N1 | 165.5 (3) |
| C10—C5—C6—C7 | −0.7 (6) | C1—C11—N1—N2 | 175.6 (3) |
| C4—C5—C6—C7 | 178.4 (4) | N3—C13—N2—N1 | −7.5 (5) |
| C5—C6—C7—C8 | 2.4 (7) | S1—C13—N2—N1 | 171.5 (3) |
| C6—C7—C8—C9 | −2.2 (7) | N3—C13—N2—C12 | 177.8 (4) |
| C7—C8—C9—C10 | 0.4 (6) | S1—C13—N2—C12 | −3.2 (5) |
| C6—C5—C10—C9 | −1.1 (5) | C11—N1—N2—C13 | 175.7 (3) |
| C4—C5—C10—C9 | 179.9 (3) | C11—N1—N2—C12 | −9.5 (5) |
| C6—C5—C10—C1 | 176.4 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N3—H3A···S1[i] | 0.86 | 2.90 | 3.472 (3) | 125 |
| N3—H3B···O1[ii] | 0.86 | 2.21 | 3.033 (4) | 162 |
| O1—H1···N1 | 0.82 | 1.89 | 2.603 (4) | 145 |

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