Crystal structures of three $N,N,N'$-trisubstituted thioureas for reactivity-controlled nanocrystal synthesis

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The synthesis and single-crystal X-ray structures of three $N,N,N'$-trisubstituted thioureas are reported, namely $N,N,N'$-tribenzylthiourea, $C_{22}H_{22}N_{2}S(1)$, $N$-methyl-$N,N'$-diphenylthiourea, $C_{14}H_{14}N_{2}S(2)$, and $N,N$-di-$n$-butyl-$N'$-phenylthiourea, $C_{15}H_{24}N_{2}S(3)$. The influence of the different substituents on the thioureas is clear from the delocalization of the thiourea C—N and C=S bonds, while the crystal structures show infinite chains of $N,N,N'$-tribenzylthiourea (1), hydrogen-bonded pairs of $N$-methyl-$N,N'$-diphenylthiourea (2) and hexamer ring assemblies of $N,N$-di-$n$-butyl-$N'$-phenylthiourea (3) molecules.

The above-mentioned compounds were synthesized via a mild, general procedure, readily accessible precursors and with a high yield, providing straightforward access to a whole library of thioureas.

1. Chemical context

To control the size of colloidal nanocrystals, many traditional methods terminate the synthesis during the nanocrystal growth at the desired size. However, this leads to a lower yield, higher size dispersity, and it is difficult to get a good reproducibility (Owen *et al.*, 2010; Abe *et al.*, 2012, 2013). Therefore, Owen *et al.* suggest a new method that uses a library of substituted thioureas, whose substitution pattern tunes their conversion reactivity (Hendricks *et al.*, 2015; Hamachi *et al.*, 2017). By this, the nanocrystal concentration can be adjusted and the desired nanocrystal size can be obtained at full conversion, with a high degree of consistency. This control is obtained by varying the substitution pattern of the thiourea, and thus the conversion reactivity (Hens, 2015). This can be understood from the fact that the conversion reactivity is influenced by the number of substituents, and their electronic and steric properties. The conversion rate, i.e. reactivity, decreases as the number of substituents increases, or by replacing electron-withdrawing with electron-donating groups (e.g. substituting aryl for alkyl substituents). These thioureas are synthesized via a one-step click reaction between isothiocyanates and primary or secondary amines (Hendricks *et al.*, 2015). In addition, they have a long shelf-life and are air-stable after synthesis (Hendricks *et al.*, 2015). An additional advantage of these precursors is that the starting reagents are relatively cheap and widely commercially available, in large quantities. When added to a hot solution of metal oleate, such as lead, cadmium, zinc, etc., this results in the formation of highly reproducible, monodisperse, homogeneously capped
metal sulfide nanocrystals at a full yield (Hendricks et al., 2015; Hamachi et al., 2017; Dhaene et al., 2019).

Herein, we report the single-crystal X-ray structural analysis of the following trisubstituted thioureas: \( \text{N}_1\text{N}_2\text{N}_0\text{-tri-benzylthiourea (1)}, \text{N}-\text{methyl-N}_0\text{-diphenylthiourea (2)}, \) and \( \text{N}-\text{phenyl-N}_0\text{-di-n-butylthiourea (3)}, \) prepared via a simple, straightforward synthesis method making use of readily commercially available compounds, to a high purity (> 99%) and with a high yield (> 75%).

2. Structural commentary

Compound 1 crystallizes in the centrosymmetric monoclinic space group \( \text{P}_2_1/c \), with the asymmetric unit consisting of one \( \text{N}_1\text{N}_2\text{N}_0\text{-tribenzylthiourea molecule}. \) On the one hand, the secondary amine benzyl ring (C3–C8) is found to be almost completely parallel to one of the tertiary amine benzyl rings (C17–C22), subtending a dihedral angle of 8.92 (8)° between the best planes through the two benzene rings. On the other hand, the two tertiary amine benzyl rings (C10–C15 and C17–C22) are highly twisted to each other, with a dihedral angle of 76.96 (7)° between the best planes through the two benzene rings (Fig. 1a). The N1—C1 and C1—N2 bond distances are 1.3419 (18) and 1.3569 (18) Å, respectively, while the C1=S1 (double) bond distance is 1.6905 (14) Å.

Compound 2 crystallizes in the centrosymmetric triclinic space group \( \text{P}_{\text{T}} \), with two \( \text{N}-\text{methyl-N}_0\text{-diphenylthiourea molecules in the asymmetric unit}. \) The secondary and tertiary amine phenyl rings (C2–C7, C9–C14 and C22–C27, C29–C34, for the first and second molecules, respectively) subtend a dihedral angle of 69.39 (9)° and 75.70 (10)°, respectively, between the best planes through the two phenyl rings (Fig. 1b). The N1—C1 and C1—N2 bond distances are 1.359 (2) and 1.352 (3) Å, for molecule 1, while the respective N21—C21 and C21—N22 bond distances are 1.367 (2) and 1.345 (3) Å, for molecule 2. The C1=S1 and C21=S22 (double) bond distances are 1.6835 (17) and 1.6798 (19) Å, for molecule 1 and 2, respectively.

The influence of the two phenyl substituents on the delocalization of the N1—C1, C1—N2 and C1=S1 bonds is clear, in comparison with the structure of 1, i.e. the lone electron pair on N1/N21 is more delocalized towards the secondary amine phenyl ring substituent in 2, leading to an increased N1—C1/ N21—C22 distance of 1.359 (2)/1.367 (2) Å, which is even more pronounced for the second molecule in the asymmetric unit, because of higher planarity of the phenyl ring with the N—C(=S)—N plane (Fig. 2). However, the delocalization of

Figure 1
Molecular structures of (a) 1, (b) 2 and (c) 3, showing thermal displacement ellipsoids drawn at the 50% probability level and the atom-labelling scheme for the non-hydrogen atoms. For 2, both molecules of the asymmetric unit are shown.
N2/N22 is less pronounced towards the tertiary amine phenyl ring, with a C1—N2/C21—N22 distance of 1.352 (3)/1.345 (3) Å, because of the latter phenyl ring being almost perpendicular to the central N—C(═S)—N plane. As a consequence of the improved delocalization of N1/N21 in 2, the C1≡S1/C21≡S21 bond length decreases slightly — although less significantly in the case of C1≡S1 — to 1.6835 (17)/1.6798 (19) Å in comparison with 1.

The structure of 3 has very recently been deposited with the Cambridge Structural Database (CSD) (refcode OYOSIH; Rahman et al., 2021); however, the mentioned structure was determined at room temperature and showed disorder of both butyl substituents, as well as the presence of unknown solvent, which was treated by the SQUEEZE procedure in PLATON (Spek, 2015). Here, our reported structure was determined at 100 K and shows no signs of any kind of (solvent) disorder. The unknown solvate structure of Rahman et al. (2021) might be caused by the use of acetone as solvent and recrystallized by slow evaporation from EtOH, whereas we used toluene as solvent and recrystallized from a hot hexane:EtOH (10:1) mixture by slowly cooling down. Compound 3 crystallizes in the trigonal space group R3̅, with one N-phenyl,N’,N’-di-n-butylthiourea molecule in the asymmetric unit. The phenyl substituent on the secondary amine is twisted with respect to the central N—C—S—N plane, with a C1—N1—C2—C7 torsion angle of 55.54 (16)°, while the two butyl substituents are found completely staggered (Fig. 1c). The N1—C1 and C1—N2 bond distances are 1.3594 (15) and 1.3432 (15) Å, respectively, while the C1≡S2 (double) bond distance is 1.7004 (11) Å. The delocalization of N1 towards the secondary amine phenyl substituent is also noticed here, comparable to 2, while there is minimal delocalization of N2 towards the butyl substituents, consequently showing the shortest C1—N2 and the longest C1≡S1 distances.

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···S1' | 0.86 (3) | 2.47 (3) | 3.2044 (13) | 145 (3) |

Symmetry code: (i) x, −y + 1/2, z + 1/4

Table 2
Hydrogen-bond geometry (Å, °) for 2.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···S21 | 0.86 (3) | 2.58 (3) | 3.3360 (16) | 148 (3) |

3. Supramolecular features

Despite the presence of three benzyl moieties in the molecular structure of 1, only weak π—π interactions are present in the crystal packing, with rather large centroid-centroid distances ranging from 4.4279 (11) to 5.9248 (9) Å. However, clear intermolecular hydrogen bonds are found between the secondary amine N1—H1 hydrogen atoms and the thiourea S1 atoms [N1—H1···S1 = 2.47 (3) Å; Table 1], linking the N,N,N’-tribenzylthiourea molecules into infinite chains along the [001] direction, and forming columnar arrangements through alternating orientations of the molecules (Fig. 3). Non-classical intramolecular hydrogen bonds can be noticed between methyl C—H atoms of two benzyl groups and S1 atoms [C2—H2A···S1 = 2.70 Å; C9—H9A···S1 = 2.60 Å], as well as between benzene ring C—H atoms and tertiary amine N2 atoms [C15—H15···N2 = 2.51 Å; C22—H22···N2 = 2.58 Å]. Furthermore, several C—H···π contacts are observed in the range of 3.5419 (17)–3.8507 (19) Å, complementing the crystal packing.

Analogous to 1, the presence of two phenyl substituents in the molecular structure of 2, only leads to weak π—π interactions present in the crystal packing, with rather large centroid-centroid distances ranging from 4.8431 (13) to 5.9503 (12) Å. However, in this case, intermolecular hydrogen bonds are formed between the two distinct molecules in the asymmetric unit, i.e. between the secondary amine N1—H1 hydrogen atom of the first molecule and the thiourea S21 atom...
of the second molecule [N1—H1⋯S21 = 2.58 (3) Å; Table 2], assembling the N-methyl-N,N'-diphenylthiourea molecules into hydrogen-bonded pairs (Fig. 4). Non-classical intramolecular hydrogen bonds can be noticed between the two methyl group C—H atoms, as well as phenyl ring C—H atoms, and S1/S21 atoms [C8—H8B⋯S1 = 2.65 Å; C28—H28B⋯S21 = 2.58 Å; C27—H27⋯S21 = 2.67 Å]. Additionally, an intramolecular C=S⋯π contact is observed [C21=S21⋯Cg2 = 3.7115 (11) Å; Cg2 is the centroid of the C9–C14 ring]. Furthermore, several C—H⋯π contacts are observed in the range of 3.518 (2)–3.800 (2) Å, complementing the crystal packing.

Analogous to 1 and 2, for 3, only one type of weak π⋯π interaction is present in the crystal packing, i.e. between symmetry-equivalent phenyl substituents, with a centroid–centroid distance of 4.9098 (10) Å. Intermolecular hydrogen bonds are formed between the secondary amine N1—H1 hydrogen atoms and the thiourea S1 atoms [N1—H1⋯S1 = 3.4656 (11) Å; Table 3], leading to a hexamer ring assembly of molecules, around the threefold rotoinversion axes (Fig. 5). Non-classical intra- and intermolecular hydrogen bonds can be noticed between two butyl CH2 groups and S1 [C8—H8B⋯S1 = 2.65 Å; C12—H12A⋯S1; symmetry code: (i) y—1/3,−x+y+1/3,−z+1/3]. Only one C—H⋯π contact is observed [C4—H4⋯Cg1 = 3.6996 (17) Å; Cg1 is the centroid of the C2–C7 ring].

### 4. Database survey

A survey of compounds, closely related to 1, 2 and 3, deposited with the Cambridge Structural Database (CSD 2021.1, version 5.42, updates of September 2021; Groom et al., 2016) resulted in ten other thiourea compounds, containing (substituted) benzyl/phenyl rings on the secondary amine and (substituted) benzyl/phenyl rings or alkyl groups on the tertiary amine, with refcodes HIFTIX, HIFTOF, KUFQOS, KUFQOS01, KUFQOS02, POFJUR, QEMZOA, RAPNAA, RAQRAF and OYOSIH.

The structures with refcodes HIFTIX and HIFTOF are two unsymmetrical thiourea derivatives, 1,1-dimethyl-3-o-tolylthiourea and 1,1-diethyl-3-o-tolylthiourea (Ramnathan et al., 1996), containing o-tolyl groups as secondary amine substituents, while KUFQOS (Zhao et al., 2008), KUFQOS01 (Panda et al., 2017) and KUFQOS02 (Bhide et al., 2021) represent the same structure of 1,1-dimethyl-3-phenylthiourea. Halogen-substituted phenyl rings as secondary amine substituents are found for refcodes POFJUR and QEMZOA.

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**Table 3**

Hydrogen-bond geometry (Å, °) for 3.

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|--------|------|------|------|--------|
| N1—H1⋯S1 | 0.86 (2) | 2.62 (2) | 3.4656 (11) | 167 (2) |
| C12—H12A⋯S1 | 0.99 | 2.67 | 3.6888 (13) | 174 |

Symmetry code: (i) y—1/3,−x+y+1/3,−z+1/3.

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**Figure 4**

Packing in the structure of 2, viewed down the a axis, showing the assembly of hydrogen-bonded pairs of molecules, with one pair highlighted (green). Hydrogen atoms (except involved in hydrogen bonds) are omitted for clarity.

**Figure 5**

Packing in the structure of 3, (a) viewed down the c axis, showing the hexamer ring assembly of molecules, around the threefold rotoinversion axes, with one hexamer highlighted (green). (b) Detail of one hydrogen-bonded hexamer ring assembly. Hydrogen atoms (except involved in hydrogen bonds) are omitted for clarity.
which represent isomorphic structures of 3-(2-bromo-4-chlorophenyl)-1,1-dimethylthiourea (El-Hiti et al., 2014) and N'- (2-bromo-4-methylphenyl)-N,N-dimethylthiourea (El-Hiti et al., 2018), respectively, while RAPNAA and RAQRAF represent structures of 3-(2-bromophenyl)-1,1-dimethylthiourea (El-Hiti et al., 2017a) and 3-(4-chlorophenyl)-1,1-dimethylthiourea (El-Hiti et al., 2017b), respectively.

In all the above-mentioned structures, N—H ⋅⋅⋅ S hydrogen bonds link the molecules into infinite chains, similar to I. This makes the reported structures of 2 and 3 unique in the sense that they show assemblies of hydrogen-bonded pairs and hexamer rings of molecules, respectively.

As previously mentioned, OYOSIH (Rahman et al., 2021) represents the same structure as 3, although determined at room temperature and showed disorder of both butyl substituents, as well as the presence of unknown solvent, which was treated by the SQUEEZE procedure in PLATON (Spek, 2015).

5. Synthesis and crystallization

**General considerations** All manipulations were performed in air. All chemicals were used as received. Phenyl isothiocyanate (97.0%) was purchased from Alfa Aesar. Chloroform-d$_1$ (stabilized with Ag, 99.8%) was purchased from Carl Roth. Toluene (99.0%), acetonitrile (99.9%), n-hexane (99.0%), and abs. ethanol (99.8%) were purchased from Chem-Lab. Benzyl isothiocyanate (98.0%), dibenzylamine (97.0%), N-methylaniline (98.0%), and di-n-butylamine (99.5%) were purchased from Sigma-Aldrich. Dichloromethane-d$_2$ (99.8%) was purchased from VWR. The thioureas were synthesized according to the procedure by Hendricks and Co-workers on a 30 mmol scale with the addition of a recrystallization step to purify the thiourea (Hendricks et al., 2015; Hamachi et al., 2017).

**Synthesis of N,N,N-tribenzyllthiourea (1):** A 40 mL vial was loaded with benzyl isothiocyanate (4476.6 mg, 3.800 mL, 30 mmol, 1.0 eq.) in toluene (5 mL). To this, a solution of dibenzylamine (5918.4 mg, 5.800 mL, 30 mmol, 1.0 eq.) in toluene (5 mL) was added dropwise. The mixture was left to stir for 1 h at room temperature. Afterwards, the solvent was removed under reduced pressure, and the residual solid was recrystallized from hot acetonitrile which was cooled slowly (> 2 h) to room temperature and then to refrigerator temperature (275–281 K; > 2 h). The formed crystals were filtered off and extensively dried under dynamic vacuum to obtain white needle-like crystals (6.9 g, 75%), suitable for single-crystal X-ray diffraction analysis. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.55–7.50 (m, 2H), $\delta$ 7.45–7.35 (m, 3H), $\delta$ 7.32–7.27 (m, 4H), $\delta$ 7.20–7.12 (m, 1H), $\delta$ 7.00 (s, 1H), $\delta$ 3.70 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 181.92, 143.52, 140.04, 131.05, 129.03, 128.76, 127.44, 126.21, 126.12, 43.73. LC–MS (API–ES) calculated for C$_{14}$H$_{15}$N$_2$S $[M+H]^+$ 243.10, found 243.1.

**Synthesis of N,N-di-n-butyl-N′-phenylthiourea (3):** A 40 mL vial was loaded with phenyl isothiocyanate (4055.7 mg, 3.585 mL, 30 mmol, 1.0 eq.) in toluene (5 mL). To this, a solution of di-n-butylamine (3877.2 mg, 5.055 mL, 30 mmol, 1.0 eq.) in toluene (5 mL) was added dropwise. The mixture was left to stir for 1 h at room temperature. Afterwards, the solvent was removed under reduced pressure, and the residual solid was recrystallized from a hot hexane:ethanol (10:1) mixture which was cooled slowly (> 2 h) to room temperature and then to refrigerator temperature (275-281 K; > 2 h). The formed crystals were filtered off and extensively dried under dynamic vacuum to obtain white needle-like crystals (6.9 g, 87%), suitable for single-crystal X-ray diffraction analysis. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.40–7.28 (m, 4H), $\delta$ 7.23–7.15 (m, 1H), $\delta$ 7.00 (s, 1H), $\delta$ 3.67 (t, J = 7.9 Hz, 4H), $\delta$ 1.71 (quin, J = 7.7 Hz, 4H), $\delta$ 1.38 (six, J = 7.9 Hz, 4H), $\delta$ 0.97 (t, J = 7.5 Hz, 6H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 181.56, 140.65, 128.85, 128.25, 126.21, 125.84, 51.85, 29.95, 20.69, 14.06. LC–MS (API–ES) calc for C$_{14}$H$_{15}$N$_2$S $[M+H]^+$ 265.17, found 265.2.

**NMR spectroscopy.** Nuclear Magnetic Resonance (NMR) spectra of the synthesized organics were recorded on a Bruker 400 MHz. Chemical shifts ($\delta$) are given in ppm and the residual solvent peak was used as an internal standard (CD$_2$Cl$_2$: $\delta$ H = 7.24 ppm, $\delta$ C = 77.06 ppm, CD$_2$Cl$_2$: $\delta$ H = 5.32 ppm, $\delta$ C = 53.84 ppm). The signal multiplicity is denoted as follows: s (singlet), d (doublet), t (triplet), qu (quartet), quint (quintet), sext (sextet), m (multiplet). Coupling constants are reported in Hertz (Hz). All resonances were corrected prior to integration by subtracting a background from the measured intensity. $^1$H, and $^{13}$C spectra were acquired using the standard pulse sequences from the Bruker library: zg30, and jmod (Attached Proton Test = APT), respectively.

**Mass spectroscopy.** Mass spectra (MS) were measured with an Agilent ESI single quadrupole detector type VL and an Agilent APCI single quadrupole detector type VL.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For all structures, the amine N–H hydrogen atoms could be located from a difference-Fourier
electron-density map, and were further refined with isotropic temperature factors fixed at 1.2 times \( U_{eq} \) of the parent atoms. All other hydrogen atoms were refined in the riding mode with isotropic temperature factors fixed at 1.2 times \( U_{eq} \) of the parent atoms (1.5 times for methyl groups).

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Crystal structures of three $N,N,N'$-trisubstituted thioureas for reactivity-controlled nanocrystal synthesis

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Computing details
For all structures, data collection: CrysAlis PRO (Rigaku OD, 2019); cell refinement: CrysAlis PRO (Rigaku OD, 2019); data reduction: CrysAlis PRO (Rigaku OD, 2019); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: Mercury (Macrae et al., 2020).

$N,N,N'$-Tribenzylthiourea (1)

Crystal data

$C_{22}H_{22}N_2S$
$M_r = 346.48$
Monoclinic, $P2_1/c$
$a = 11.2378 (4)$ Å
$b = 14.7792 (5)$ Å
$c = 11.3165 (5)$ Å
$\beta = 102.042 (3)^\circ$
$V = 1838.15 (12)$ Å$^3$
$Z = 4$

$F(000) = 736$
$D_x = 1.252$ Mg m$^{-3}$
Cu Ka radiation, $\lambda = 1.54184$ Å
Cell parameters from 8187 reflections
$\theta = 4.0$–74.0°
$\mu = 1.59$ mm$^{-1}$
$T = 100$ K
Plate, clear colourless
$0.24 \times 0.19 \times 0.06$ mm

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.4839 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2019)

$T_{\text{min}} = 0.750$, $T_{\text{max}} = 1.000$
16515 measured reflections
3589 independent reflections
3256 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{\text{max}} = 74.2^\circ$, $\theta_{\text{min}} = 4.0^\circ$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -11 \rightarrow 13$

Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.123$
$S = 1.06$
3589 reflections
229 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F^2) + (0.0753P)^2 + 0.4416P]$
where $P = (F^2 + 2F_c^2)/3$
$(\Delta\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.30$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.31$ e Å$^{-3}$
Absolute structure: -
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 ($\AA^2$)

| Atomic symbol | x          | y          | z          | U(eq) |
|---------------|------------|------------|------------|-------|
| S1            | 0.10482 (3)| 0.29165 (3)| 0.32245 (3)| 0.02217 (14) |
| N1            | 0.12474 (11)| 0.23113 (8)| 0.54565 (11)| 0.0198 (3) |
| N2            | 0.25536 (10)| 0.34685 (8)| 0.52442 (11)| 0.0191 (3) |
| C1            | 0.16633 (12)| 0.28879 (9)| 0.47205 (13)| 0.0177 (3) |
| C2            | 0.04085 (13)| 0.15697 (10)| 0.50233 (13)| 0.0209 (3) |
| H2A           | −0.024231| 0.179223| 0.435803| 0.025* |
| H2B           | 0.002213| 0.136546| 0.568717| 0.025* |
| C3            | 0.10428 (12)| 0.07750 (10)| 0.45767 (14)| 0.0215 (3) |
| C4            | 0.20059 (15)| 0.03591 (12)| 0.53478 (18)| 0.0358 (4) |
| H4            | 0.226181| 0.057328| 0.615227| 0.043* |
| C5            | 0.25996 (16)| −0.03682 (13)| 0.4954 (2)| 0.0519 (6) |
| H5            | 0.326738| −0.064616| 0.548228| 0.062* |
| H1            | 0.154 (3)| 0.2304 (18)| 0.622 (3)| 0.062* |
| C6            | 0.22149 (18)| −0.06872 (13)| 0.3786 (2)| 0.0494 (6) |
| H6            | 0.262381| −0.118215| 0.351143| 0.059* |
| C7            | 0.1240 (2)| −0.02889 (12)| 0.30214 (19)| 0.0433 (5) |
| H7            | 0.096928| −0.051638| 0.222546| 0.052* |
| H8            | −0.001553| 0.072197| 0.288476| 0.036* |
| C9            | 0.31744 (12)| 0.40391 (10)| 0.45137 (13)| 0.0202 (3) |
| H9A           | 0.313944| 0.374034| 0.372425| 0.024* |
| H9B           | 0.404170| 0.408858| 0.492068| 0.024* |
| C10           | 0.26494 (12)| 0.49838 (10)| 0.42917 (13)| 0.0190 (3) |
| C11           | 0.31752 (13)| 0.55802 (10)| 0.35960 (14)| 0.0242 (3) |
| H11           | 0.384844| 0.538845| 0.327235| 0.029* |
| C12           | 0.27248 (15)| 0.64526 (11)| 0.33705 (15)| 0.0281 (4) |
| H12           | 0.308310| 0.685134| 0.288571| 0.034* |
| C13           | 0.17537 (14)| 0.67414 (11)| 0.38522 (15)| 0.0276 (4) |
| H13           | 0.144508| 0.733810| 0.370034| 0.033* |
| C14           | 0.12353 (13)| 0.61561 (10)| 0.45559 (15)| 0.0249 (3) |
| H14           | 0.057692| 0.635536| 0.489717| 0.030* |
| C15           | 0.16720 (12)| 0.52792 (10)| 0.47662 (13)| 0.0211 (3) |
| H15           | 0.130022| 0.487852| 0.523739| 0.025* |
| C16           | 0.29405 (13)| 0.35662 (10)| 0.65564 (13)| 0.0209 (3) |
| H16A          | 0.222424| 0.347522| 0.692503| 0.025* |
| H16B          | 0.323109| 0.419334| 0.673830| 0.025* |
| C17           | 0.39376 (12)| 0.29173 (10)| 0.71478 (14)| 0.0195 (3) |
| C18           | 0.45690 (13)| 0.31034 (11)| 0.83213 (14)| 0.0230 (3) |
| H18           | 0.438430| 0.363493| 0.871962| 0.028* |
### Table 1: Atomic Displacement Parameters (Å²)

| Atom | U¹¹   | U¹²   | U¹³   | U¹²   | U¹³   |
|------|-------|-------|-------|-------|-------|
| S1   | 0.0224 (2) | 0.0317 (2) | 0.0112 (2) | 0.00067 (12) | 0.00060 (14) |
| N1   | 0.0220 (6) | 0.0250 (6) | 0.0118 (6) | 0.0008 (5) | 0.0020 (5) |
| N2   | 0.0202 (6) | 0.0220 (6) | 0.0136 (6) | 0.0015 (4) | 0.0006 (4) |
| C1   | 0.0162 (6) | 0.0215 (7) | 0.0153 (7) | 0.0052 (5) | 0.0028 (5) |
| C2   | 0.0195 (7) | 0.0251 (7) | 0.0181 (7) | −0.0015 (5) | 0.0041 (5) |
| C3   | 0.0189 (7) | 0.0240 (7) | 0.0222 (8) | −0.0037 (5) | 0.0057 (5) |
| C4   | 0.0274 (8) | 0.0291 (8) | 0.0444 (11) | 0.0016 (6) | −0.0073 (7) |
| C5   | 0.0243 (8) | 0.0301 (10) | 0.0956 (18) | 0.0028 (7) | −0.0003 (9) |
| C6   | 0.0427 (11) | 0.0253 (9) | 0.0929 (18) | −0.0065 (7) | 0.0434 (11) |
| C7   | 0.0719 (14) | 0.0292 (9) | 0.0394 (11) | −0.0185 (9) | 0.0362 (10) |
| C8   | 0.0434 (9) | 0.0277 (8) | 0.0196 (8) | −0.0080 (7) | 0.0090 (6) |
| C9   | 0.0175 (6) | 0.0251 (7) | 0.0184 (7) | 0.0009 (5) | 0.0044 (5) |
| C10  | 0.0178 (6) | 0.0236 (7) | 0.0141 (7) | −0.0007 (5) | −0.0002 (5) |
| C11  | 0.0242 (7) | 0.0289 (8) | 0.0194 (8) | −0.0031 (6) | 0.0048 (5) |
| C12  | 0.0333 (8) | 0.0272 (8) | 0.0226 (9) | −0.0079 (6) | 0.0029 (6) |
| C13  | 0.0277 (8) | 0.0216 (7) | 0.0286 (9) | −0.0007 (6) | −0.0054 (6) |
| C14  | 0.0190 (7) | 0.0253 (8) | 0.0283 (8) | 0.0023 (5) | 0.0001 (6) |
| C15  | 0.0180 (6) | 0.0245 (7) | 0.0196 (7) | −0.0009 (5) | 0.0012 (5) |
| C16  | 0.0215 (7) | 0.0251 (7) | 0.0142 (8) | 0.0027 (5) | −0.0003 (5) |
| C17  | 0.0166 (7) | 0.0261 (7) | 0.0156 (7) | −0.0013 (5) | 0.0027 (5) |
| C18  | 0.0226 (7) | 0.0285 (7) | 0.0167 (8) | −0.0028 (6) | 0.0010 (5) |
| C19  | 0.0218 (7) | 0.0373 (9) | 0.0173 (8) | −0.0031 (6) | −0.0020 (5) |
| C20  | 0.0169 (6) | 0.0340 (8) | 0.0264 (8) | 0.0020 (6) | 0.0012 (6) |
| C21  | 0.0200 (7) | 0.0279 (8) | 0.0261 (9) | 0.0030 (5) | 0.0064 (6) |
| C22  | 0.0192 (7) | 0.0296 (8) | 0.0167 (7) | 0.0010 (5) | 0.0019 (5) |

### Table 2: Geometric Parameters (Å, °)

| Bond | Length (Å) | Angle (°) |
|------|------------|-----------|
| S1—C1 | 1.6905 (14) | C10—C15 | 1.390 (2) |
| N1—C1 | 1.3419 (19) | C11—H11 | 0.9500 |
| N1—C2 | 1.4621 (18) | C11—C12 | 1.389 (2) |
| N1—H1 | 0.85 (3) | C12—H12 | 0.9500 |
| N2—C1 | 1.3569 (18) | C12—C13 | 1.385 (3) |
| N2—C9 | 1.4566 (19) | C13—H13 | 0.9500 |
| N2—C16 | 1.4648 (19) | C13—C14 | 1.384 (2) |
| C2—H2A | 0.9900 | C14—H14 | 0.9500 |

*Note: The values in parentheses indicate the estimated standard deviations.*

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*Acta Cryst. (2022). E78, 184-190*
| Bond          | Distance (Å) | Bond          | Distance (Å) | Temperature (K) |
|--------------|--------------|--------------|--------------|-----------------|
| C2—H2B       | 0.9900       | C14—C15      | 1.389 (2)    |                 |
| C2—C3        | 1.514 (2)    | C15—H15      | 0.9500       |                 |
| C3—C4        | 1.384 (2)    | C16—H16A     | 0.9900       |                 |
| C3—H8        | 1.385 (2)    | C16—H16B     | 0.9900       |                 |
| C4—H4        | 0.9500       | C16—C17      | 1.5199 (19)  |                 |
| C4—C5        | 1.387 (3)    | C17—C18      | 1.396 (2)    |                 |
| C5—H5        | 0.9500       | C17—C22      | 1.386 (2)    |                 |
| C5—C6        | 1.384 (3)    | C18—H18      | 0.9500       |                 |
| C6—H6        | 0.9500       | C18—C19      | 1.386 (2)    |                 |
| C6—C7        | 1.378 (3)    | C19—H19      | 0.9500       |                 |
| C7—H7        | 0.9500       | C19—C20      | 1.389 (2)    |                 |
| C7—C8        | 1.391 (3)    | C20—H20      | 0.9500       |                 |
| C8—H8        | 0.9500       | C20—C21      | 1.383 (2)    |                 |
| C9—H9A       | 0.9900       | C21—H21      | 0.9500       |                 |
| C9—H9B       | 0.9900       | C21—C22      | 1.393 (2)    |                 |
| C9—C10       | 1.5162 (19)  | C22—H22      | 0.9500       |                 |
| C10—C11      | 1.393 (2)    |              |              |                 |
| C1—N1—C2     | 123.48 (12)  | C15—C10—C11  | 118.84 (14)  |                 |
| C1—N1—H1     | 121.3 (18)   | C10—C11—H11  | 119.7        |                 |
| C2—N1—H1     | 114.6 (18)   | C12—C11—C10  | 120.66 (15)  |                 |
| C1—N2—C9     | 121.00 (12)  | C12—C11—H11  | 119.7        |                 |
| C1—N2—C16    | 122.75 (13)  | C11—C12—C11  | 120.0        |                 |
| C9—N2—C16    | 116.25 (11)  | C13—C12—C11  | 120.03 (15)  |                 |
| N1—C1—S1     | 120.99 (11)  | C13—C12—H12  | 120.0        |                 |
| N1—C1—N2     | 116.81 (13)  | C12—C13—C12  | 120.2        |                 |
| N2—C1—S1     | 122.13 (11)  | C14—C13—C12  | 119.64 (14)  |                 |
| N1—C2—H2A    | 109.2        | C14—C13—H13  | 120.2        |                 |
| N1—C2—H2B    | 109.2        | C13—C14—H14  | 119.8        |                 |
| N1—C2—C3     | 112.20 (11)  | C13—C14—C15  | 120.39 (15)  |                 |
| H2A—C2—H2B   | 107.9        | C15—C14—H14  | 119.8        |                 |
| C3—C2—H2A    | 109.2        | C10—C15—H15  | 119.8        |                 |
| C3—C2—H2B    | 109.2        | C14—C15—C10  | 120.43 (14)  |                 |
| C4—C3—C2     | 119.63 (14)  | C14—C15—H15  | 119.8        |                 |
| C4—C3—C8     | 119.56 (15)  | N2—C16—H16A  | 108.6        |                 |
| C8—C3—C2     | 120.79 (14)  | N2—C16—H16B  | 108.6        |                 |
| C3—C4—H4     | 119.8        | N2—C16—C17   | 114.82 (12)  |                 |
| C3—C4—C5     | 120.44 (18)  | H16A—C16—H16B| 107.5        |                 |
| C5—C4—H4     | 119.8        | C17—C16—H16A | 108.6        |                 |
| C4—C5—H5     | 120.1        | C17—C16—H16B | 108.6        |                 |
| C6—C5—C4     | 119.70 (19)  | C18—C17—C16  | 118.44 (13)  |                 |
| C6—C5—H5     | 120.1        | C22—C17—C16  | 122.47 (13)  |                 |
| C5—C6—H6     | 119.9        | C22—C17—C18  | 119.05 (14)  |                 |
| C7—C6—C5     | 120.19 (17)  | C17—C18—H18  | 119.7        |                 |
| C7—C6—H6     | 119.9        | C19—C18—C17  | 120.51 (15)  |                 |
| C6—C7—H7     | 120.0        | C19—C18—H18  | 119.7        |                 |
| C6—C7—C8     | 120.03 (18)  | C18—C19—H19  | 119.9        |                 |
| C8—C7—H7     | 120.0        | C18—C19—C20  | 120.19 (14)  |                 |
supporting information

C3—C8—C7 120.05 (17) C20—C19—H19 119.9
C3—C8—H8 120.0 C19—C20—H20 120.3
C7—C8—H8 120.0 C21—C20—C19 119.47 (14)
N2—C9—H9A 108.7 C21—C20—H20 120.8 (15)
N2—C9—H9B 108.7 C20—C21—C22 120.29 (14)
N2—C9—C10 114.29 (12) C21—C20—H20 120.3
H9A—C9—H9B 107.6 C17—C22—C21 119.9
N2—C9—C10 114.29 (12) C21—C20—H20 120.3
C10—C9—H9A 108.7 C17—C22—H22 119.9
C10—C9—H9B 108.7 C19—C20—C21 119.47 (14)
C11—C10—C9 118.69 (13) C20—C21—H21 120.3
C15—C10—C9 112.46 (13) C21—C22—C22 120.48 (15)

Hydrogen-bond geometry (Å, º)

| D—H···A   | D—H   | H···A   | D···A   | D—H···A |
|-----------|-------|--------|--------|--------|
| N1—H1···S1i | 0.86 (3) | 2.47 (3) | 3.2044 (13) | 145 (3) |

Symmetry code: (i) x, −y+1/2, z+1/2.

N-methyl-N,N'-Diphenylthiourea (2)

Crystal data

C14H14N2S  a = 65.913 (5)°
M_r = 242.33  β = 87.752 (4)°
Triclinic, P1  γ = 84.059 (5)°
a = 9.8379 (6) Å  V = 1276.82 (13) Å³
b = 10.8014 (6) Å  Z = 4
C = 13.2328 (6) Å  F(000) = 512

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Supporting information

$D_\varepsilon = 1.261$ Mg m$^{-3}$  
$\text{Cu }K\alpha$ radiation, $\lambda = 1.54184$ Å  
Cell parameters from 5889 reflections  
$\theta = 3.6\text{--}73.7^\circ$  

$\mu = 2.06$ mm$^{-1}$  
$T = 100$ K  
Block, clear colourless  
$0.26 \times 0.17 \times 0.13$ mm

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer  
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source  
Mirror monochromator  
Detector resolution: 10.4839 pixels mm$^{-1}$  
$\omega$ scans  
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2019)  
$T_{\text{min}} = 0.687, T_{\text{max}} = 1.000$  
12208 measured reflections  
4818 independent reflections  
4298 reflections with $I > 2\sigma(I)$  

Refinement

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.049$  
$wR(F^2) = 0.142$  
$S = 1.06$  
4818 reflections  
315 parameters  
0 restraints  
Primary atom site location: dual  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement  

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 ($\AA^2$)

|    | $x$      | $y$       | $z$          | $U_{eq}$   |
|----|----------|-----------|--------------|------------|
| S1 | 0.87530  | 0.36219   | −0.10166     | 0.03871    |
| N1 | 0.74118  | 0.27410   | 0.09073      | 0.0352     |
| N2 | 0.78346  | 0.49902   | 0.01836      | 0.0385     |
| C1 | 0.79648  | 0.37896   | 0.00793      | 0.0344     |
| C2 | 0.74183  | 0.13995   | 0.09466      | 0.0339     |
| C3 | 0.61818  | 0.08717   | 0.09855      | 0.0370     |
| H3 | 0.534808 | 0.141270  | 0.096050     | 0.044*     |
| C4 | 0.61600  | −0.04473  | 0.10612      | 0.0415     |
| H4 | 0.531343 | −0.081517 | 0.110231     | 0.050*     |
| C5 | 0.73777  | −0.12244  | 0.10765      | 0.0431     |
| H5 | 0.736363 | −0.211941 | 0.111191     | 0.052*     |
| C6 | 0.8613   | −0.06994  | 0.10404      | 0.0419     |
| H6 | 0.944550 | −0.123412 | 0.104909     | 0.050*     |
| C7 | 0.86365  | 0.06084   | 0.09914      | 0.0383     |
| H7 | 0.948411 | 0.095870  | 0.098860     | 0.046*     |
| C8 | 0.8263   | 0.62333   | −0.06957     | 0.0466     |
|    | x     | y     | z     | Uiso  |
|----|-------|-------|-------|-------|
| H8A| 0.755527 | 0.661994 | -0.127069 | 0.070* |
| H8B| 0.912030 | 0.601735 | -0.101872 | 0.070* |
| H8C| 0.840149 | 0.689582 | -0.038711 | 0.070* |
| C9 | 0.71401 (18) | 0.51678 (17) | 0.11024 (14) | 0.0357 (4) |
| C10| 0.78585 (18) | 0.49184 (18) | 0.20553 (15) | 0.0379 (4) |
| H10| 0.879437 | 0.457338 | 0.212657 | 0.045* |
| C11| 0.7198 (2) | 0.51775 (19) | 0.29091 (15) | 0.0429 (4) |
| H11| 0.768623 | 0.501230 | 0.356392 | 0.052* |
| C12| 0.5839 (2) | 0.5672 (2) | 0.28090 (17) | 0.0461 (4) |
| H12| 0.539256 | 0.584186 | 0.339560 | 0.055* |
| C13| 0.5120 (2) | 0.5923 (2) | 0.18474 (19) | 0.0470 (4) |
| H13| 0.418349 | 0.626521 | 0.177738 | 0.056* |
| C14| 0.5773 (2) | 0.56728 (19) | 0.09959 (17) | 0.0420 (4) |
| H14| 0.528599 | 0.584619 | 0.033840 | 0.050* |
| S21| 0.52714 (5) | 0.19752 (5) | 0.30490 (4) | 0.04442 (16) |
| N21| 0.47106 (17) | 0.1816 (2) | 0.50962 (13) | 0.0464 (4) |
| N22| 0.69539 (17) | 0.14244 (18) | 0.47379 (14) | 0.0456 (4) |
| C21| 0.5669 (2) | 0.17492 (19) | 0.43396 (15) | 0.0408 (4) |
| C22| 0.33316 (19) | 0.23455 (19) | 0.49771 (14) | 0.0380 (4) |
| C23| 0.2535 (2) | 0.1894 (2) | 0.59315 (14) | 0.0438 (4) |
| H23| 0.292688 | 0.122901 | 0.660265 | 0.053* |
| C24| 0.1187 (2) | 0.2401 (2) | 0.59142 (16) | 0.0491 (5) |
| H24| 0.065365 | 0.208041 | 0.656896 | 0.059* |
| C25| 0.0610 (2) | 0.3379 (2) | 0.49387 (18) | 0.0520 (5) |
| H25| -0.031833 | 0.373337 | 0.492102 | 0.062* |
| C26| 0.1397 (2) | 0.3832 (2) | 0.39947 (17) | 0.0503 (5) |
| H26| 0.099883 | 0.449752 | 0.332619 | 0.060* |
| C27| 0.2752 (2) | 0.3338 (2) | 0.39998 (15) | 0.0431 (4) |
| H27| 0.328299 | 0.367067 | 0.334463 | 0.052* |
| C28| 0.8129 (2) | 0.1216 (2) | 0.4083 (2) | 0.0526 (5) |
| H28A| 0.862359 | 0.203300 | 0.379216 | 0.079* |
| H28B| 0.780515 | 0.104245 | 0.346634 | 0.079* |
| H28C| 0.874188 | 0.043352 | 0.455457 | 0.079* |
| C29| 0.72661 (18) | 0.1336 (2) | 0.58213 (15) | 0.0418 (4) |
| C30| 0.7548 (2) | 0.0084 (2) | 0.6690 (2) | 0.0541 (5) |
| H30| 0.756557 | -0.072996 | 0.657398 | 0.065* |
| C31| 0.7807 (3) | 0.0024 (2) | 0.7737 (2) | 0.0621 (6) |
| H31| 0.798209 | -0.083740 | 0.833900 | 0.074* |
| H1| 0.688 (3) | 0.290 (3) | 0.138 (3) | 0.074* |
| H21| 0.494 (3) | 0.135 (3) | 0.580 (3) | 0.074* |
| C32| 0.7813 (2) | 0.1195 (2) | 0.79115 (17) | 0.0497 (5) |
| H32| 0.798612 | 0.114241 | 0.862995 | 0.060* |
| C33| 0.7567 (2) | 0.2446 (2) | 0.70368 (16) | 0.0438 (4) |
| H33| 0.759655 | 0.325717 | 0.714838 | 0.053* |
| C34| 0.72752 (19) | 0.2523 (2) | 0.59942 (15) | 0.0430 (4) |
| H34| 0.708181 | 0.338601 | 0.539811 | 0.052* |
Atomic displacement parameters (Å²)

|     | $U_{11}$       | $U_{22}$       | $U_{33}$       | $U_{12}$       | $U_{13}$       | $U_{23}$       |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|
| S1  | 0.0441 (3)     | 0.0393 (3)     | 0.0306 (2)     | −0.00590 (17)  | 0.00684 (17)   | −0.01224 (18)  |
| N1  | 0.0400 (8)     | 0.0323 (7)     | 0.0335 (7)     | −0.0053 (5)    | 0.0067 (6)     | −0.0139 (6)    |
| N2  | 0.0462 (8)     | 0.0326 (7)     | 0.0349 (7)     | −0.0076 (6)    | 0.0072 (6)     | −0.0116 (6)    |
| C1  | 0.0316 (8)     | 0.0362 (9)     | 0.0331 (7)     | −0.0041 (6)    | 0.0001 (6)     | −0.0117 (6)    |
| C2  | 0.0425 (9)     | 0.0322 (8)     | 0.0262 (7)     | −0.0054 (6)    | 0.0031 (6)     | −0.0109 (6)    |
| C3  | 0.0413 (9)     | 0.0372 (9)     | 0.0303 (7)     | −0.0037 (7)    | −0.0002 (6)    | −0.0115 (6)    |
| C4  | 0.0521 (11)    | 0.0398 (9)     | 0.0326 (8)     | −0.0118 (8)    | −0.0010 (7)    | −0.0128 (7)    |
| C5  | 0.0642 (12)    | 0.0328 (9)     | 0.0318 (8)     | −0.0049 (8)    | 0.0016 (8)     | −0.0128 (7)    |
| C6  | 0.0506 (11)    | 0.0384 (9)     | 0.0323 (8)     | 0.0028 (7)     | 0.0058 (7)     | −0.0118 (7)    |
| C7  | 0.0419 (9)     | 0.0381 (9)     | 0.0314 (8)     | −0.0045 (7)    | 0.0036 (7)     | −0.0108 (7)    |
| C8  | 0.0462 (9)     | 0.0345 (9)     | 0.0402 (9)     | −0.0127 (8)    | 0.0105 (8)     | −0.0116 (7)    |
| C9  | 0.0397 (9)     | 0.0299 (8)     | 0.0378 (8)     | −0.0068 (6)    | 0.0046 (7)     | −0.0138 (7)    |
| C10 | 0.0365 (9)     | 0.0344 (9)     | 0.0385 (8)     | −0.0038 (6)    | 0.0026 (7)     | −0.0108 (7)    |
| C11 | 0.0516 (11)    | 0.0408 (10)    | 0.0353 (8)     | −0.0099 (8)    | 0.0040 (7)     | −0.0133 (7)    |
| C12 | 0.0507 (11)    | 0.0430 (10)    | 0.0485 (10)    | −0.0098 (7)    | 0.0144 (8)     | −0.0225 (8)    |
| C13 | 0.0361 (10)    | 0.0461 (11)    | 0.0633 (12)    | −0.0038 (7)    | 0.0051 (8)     | −0.0273 (9)    |
| C14 | 0.0402 (10)    | 0.0383 (9)     | 0.0501 (10)    | −0.0039 (7)    | −0.0037 (8)    | −0.0203 (8)    |
| S21 | 0.0442 (3)     | 0.0584 (3)     | 0.0392 (8)     | −0.0158 (2)    | 0.00781 (19)   | −0.0247 (2)    |
| N21 | 0.0393 (9)     | 0.0629 (11)    | 0.0288 (7)     | 0.0000 (7)     | 0.0020 (6)     | −0.0115 (7)    |
| N22 | 0.0390 (9)     | 0.0546 (10)    | 0.0426 (8)     | −0.0017 (7)    | 0.0057 (6)     | −0.0203 (7)    |
| C21 | 0.0415 (10)    | 0.0406 (9)     | 0.0395 (9)     | −0.0068 (7)    | 0.0062 (7)     | −0.0154 (7)    |
| C22 | 0.0373 (9)     | 0.0443 (9)     | 0.0324 (8)     | −0.0068 (7)    | 0.0013 (7)     | −0.0150 (7)    |
| C23 | 0.0438 (10)    | 0.0516 (11)    | 0.0301 (8)     | −0.0021 (8)    | 0.0011 (7)     | −0.0112 (7)    |
| C24 | 0.0422 (10)    | 0.0597 (12)    | 0.0366 (9)     | −0.0036 (8)    | 0.0076 (7)     | −0.0116 (8)    |
| C25 | 0.0364 (10)    | 0.0549 (12)    | 0.0515 (11)    | −0.0008 (8)    | 0.0011 (8)     | −0.0092 (9)    |
| C26 | 0.0444 (11)    | 0.0491 (11)    | 0.0417 (9)     | −0.0040 (8)    | −0.0022 (8)    | −0.0025 (8)    |
| C27 | 0.0417 (10)    | 0.0465 (10)    | 0.0340 (8)     | −0.0088 (7)    | 0.0034 (7)     | −0.0084 (7)    |
| C28 | 0.0433 (11)    | 0.0587 (12)    | 0.0612 (12)    | −0.0032 (9)    | 0.0114 (9)     | −0.0312 (10)   |
| C29 | 0.0321 (9)     | 0.0482 (10)    | 0.0412 (9)     | −0.0036 (7)    | 0.0010 (7)     | −0.0143 (8)    |
| C30 | 0.0559 (13)    | 0.0411 (11)    | 0.0601 (12)    | −0.0092 (9)    | −0.0146 (10)   | −0.0131 (9)    |
| C31 | 0.0719 (15)    | 0.0467 (12)    | 0.0534 (12)    | −0.0157 (10)   | −0.0225 (11)   | −0.0017 (9)    |
| C32 | 0.0472 (11)    | 0.0539 (12)    | 0.0407 (9)     | −0.0128 (8)    | −0.0050 (8)    | −0.0094 (8)    |
| C33 | 0.0395 (10)    | 0.0489 (11)    | 0.0407 (9)     | −0.0052 (7)    | 0.0061 (7)     | −0.0161 (8)    |
| C34 | 0.0399 (9)     | 0.0457 (10)    | 0.0356 (8)     | 0.0006 (7)     | 0.0055 (7)     | −0.0101 (7)    |
| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|---------------|------------|
| C2—C7         | 1.386 (2)  | C22—C27       | 1.395 (3)  | C2—H3         | 0.9500     |
| C3—H3         | 0.9500     | C23—H23       | 0.9500     | C3—C4         | 1.389 (3)  |
| C3—C4         | 1.389 (3)  | C23—C24       | 1.379 (3)  | C4—H4         | 0.9500     |
| C4—C5         | 1.385 (3)  | C24—H24       | 0.9500     | C5—H5         | 0.9500     |
| C5—C6         | 1.385 (3)  | C25—H25       | 0.9500     | C5—C6         | 1.385 (3)  |
| C6—H6         | 0.9500     | C26—H26       | 0.9500     | C6—C7         | 1.390 (3)  |
| C6—C7         | 1.390 (3)  | C26—C27       | 1.383 (3)  | C7—H7         | 0.9500     |
| C7—H7         | 0.9500     | C27—H27       | 0.9500     | C8—H8A        | 0.9800     |
| C8—H8A        | 0.9800     | C28—H28A      | 0.9800     | C8—H8B        | 0.9800     |
| C8—H8B        | 0.9800     | C28—H28B      | 0.9800     | C8—H8C        | 0.9800     |
| C9—C10        | 1.384 (3)  | C29—C30       | 1.381 (3)  | C9—C14        | 1.388 (3)  |
| C9—C14        | 1.388 (3)  | C29—C34       | 1.392 (3)  | C10—H10       | 0.9500     |
| C10—H10       | 0.9500     | C30—H30       | 0.9500     | C10—C11       | 1.393 (3)  |
| C10—C11       | 1.393 (3)  | C30—C31       | 1.393 (4)  | C11—H11       | 0.9500     |
| C11—H11       | 0.9500     | C31—H31       | 0.9500     | C11—C12       | 1.377 (3)  |
| C11—C12       | 1.377 (3)  | C31—C32       | 1.376 (4)  | C12—H12       | 0.9500     |
| C12—H12       | 0.9500     | C32—H32       | 0.9500     | C12—C13       | 1.394 (3)  |
| C12—C13       | 1.394 (3)  | C32—C33       | 1.379 (3)  | C13—H13       | 0.9500     |
| C13—H13       | 0.9500     | C33—H33       | 0.9500     | C13—C14       | 1.382 (3)  |
| C13—C14       | 1.382 (3)  | C33—C34       | 1.387 (3)  | C14—H14       | 0.9500     |
| C14—H14       | 0.9500     | C34—H34       | 0.9500     | C1—N1—C2      | 124.62 (14) |
| C1—N1—C2      | 124.62 (14)| C21—N21—C22  | 131.73 (16)| C1—N1—H1      | 120 (2)    |
| C1—N1—H1      | 120 (2)    | C21—N21—H21  | 116 (2)    | C2—N1—H1      | 114 (2)    |
| C2—N1—H1      | 114 (2)    | C22—N21—H21  | 112 (2)    | C1—N2—C8      | 121.52 (15) |
| C1—N2—C8      | 121.52 (15)| C21—N22—C28  | 122.70 (17)| C1—N2—C9      | 122.74 (14) |
| C1—N2—C9      | 122.74 (14)| C21—N22—C29  | 121.26 (16)| C9—N2—C8      | 115.42 (14) |
| C9—N2—C8      | 115.42 (14)| C29—N22—C28  | 115.95 (17)| N1—C1—S1      | 112.60 (13) |
| N1—C1—S1      | 112.60 (13)| N21—C21—S21  | 123.08 (15)| N2—C1—S1      | 121.65 (13) |
| N2—C1—S1      | 121.65 (13)| N22—C21—S21  | 122.99 (14)| N2—C1—N1      | 115.75 (15) |
| N2—C1—N1      | 115.75 (15)| N22—C21—N21  | 113.87 (17)| C3—C2—N1      | 118.94 (15) |
| C3—C2—N1      | 118.94 (15)| C23—C22—N21  | 116.39 (16)| C3—C2—C7      | 120.07 (17) |
| C3—C2—C7      | 120.07 (17)| C23—C22—C27  | 119.09 (17)| C7—C2—N1      | 120.94 (16) |
| C7—C2—N1      | 120.94 (16)| C27—C22—N21  | 124.39 (17)| C2—C3—H3      | 120.0       |
| C2—C3—H3      | 120.0      | C22—C23—H23  | 119.5      | C2—C3—C4      | 120.09 (17) |
| C2—C3—C4      | 120.09 (17)| C24—C23—C22  | 120.92 (17)| C4—C3—H3      | 120.0       |
| C4—C3—H3      | 120.0      | C24—C23—H23  | 119.5      | C3—C4—H4      | 120.1       |
| C3—C4—H4      | 120.1      | C23—C24—H24  | 120.1      | C5—C4—C3      | 119.83 (19) |
| C5—C4—C3      | 119.83 (19)| C23—C24—C25  | 119.87 (18)| C5—C4—H4      | 120.1       |
| C5—C4—H4      | 120.1      | C25—C24—H24  | 120.1      | C4—C5—H5      | 119.9       |
| C4—C5—H5      | 119.9      | C24—C25—H25  | 120.3      | C4—C5—C6      | 120.12 (18) |
| C4—C5—C6      | 120.12 (18)| C26—C25—C24  | 119.35 (19)| C6—C5—H5      | 119.9       |
| C6—C5—H5      | 119.9      | C26—C25—H25  | 120.3      | C5—C6—H6      | 119.9       |
| C5—C6—H6      | 119.9      | C25—C26—H26  | 119.3      | C5—C6—C7      | 120.13 (17) |
| C5—C6—C7      | 120.13 (17)| C25—C26—C27  | 121.47 (18)|
| Bond                  | Distance  | Bond                  | Distance  |
|-----------------------|-----------|-----------------------|-----------|
| C7—C6—H6             | 119.9     | C27—C26—H26          | 119.3     |
| C2—C7—C6             | 119.73 (18) | C22—C27—H27          | 120.3     |
| C2—C7—H7             | 120.1     | C26—C27—C22          | 119.30 (17) |
| C6—C7—H7             | 120.1     | C26—C27—H27          | 120.3     |
| N2—C8—H8A            | 109.5     | N22—C28—H28A         | 109.5     |
| N2—C8—H8B            | 109.5     | N22—C28—H28B         | 109.5     |
| N2—C8—H8C            | 109.5     | N22—C28—H28C         | 109.5     |
| H8A—C8—H8B           | 109.5     | H28A—C28—H28B        | 109.5     |
| H8B—C8—H8C           | 109.5     | H28B—C28—H28C        | 109.5     |
| C10—C9—N2            | 119.96 (16) | C30—C29—N22          | 120.46 (19) |
| C10—C9—C14           | 120.40 (16) | C30—C29—C34          | 119.83 (19) |
| C14—C9—N2            | 119.52 (16) | C34—C29—N22          | 119.71 (17) |
| C9—C10—H10           | 120.3     | C29—C30—H30          | 120.3     |
| C9—C10—C11           | 119.43 (17) | C29—C30—C31          | 119.4 (2) |
| C11—C10—H10          | 120.3     | C31—C30—H30          | 120.3     |
| C10—C11—H11          | 119.8     | C30—C31—H31          | 119.5     |
| C12—C11—C10          | 120.35 (18) | C32—C31—C30          | 120.9 (2) |
| C12—C11—H11          | 119.8     | C32—C31—H31          | 119.5     |
| C11—C12—H12          | 120.0     | C31—C32—H32          | 120.2     |
| C11—C12—C13          | 120.04 (17) | C31—C32—C33          | 119.6 (2) |
| C13—C12—H12          | 120.0     | C33—C32—H32          | 120.2     |
| C12—C13—H13          | 120.1     | C32—C33—H33          | 119.9     |
| C14—C13—C12          | 119.84 (18) | C32—C33—C34          | 120.2 (2) |
| C14—C13—H13          | 120.1     | C34—C33—H33          | 119.9     |
| C9—C14—H14           | 120.0     | C29—C34—H34          | 120.0     |
| C13—C14—C9           | 119.94 (18) | C33—C34—C29          | 120.03 (18) |
| C13—C14—H14          | 120.0     | C33—C34—H34          | 120.0     |
| N1—C2—C3—C4          | -177.86 (15) | N21—C22—C23—C24     | 176.9 (2) |
| N1—C2—C7—C6          | 179.34 (15) | N21—C22—C27—C26     | -176.8 (2) |
| N2—C9—C10—C11        | 175.88 (16) | N22—C29—C30—C31     | -178.1 (2) |
| N2—C9—C14—C13        | -176.16 (17) | N22—C29—C34—C33     | 179.60 (17) |
| C1—N1—C2—C3          | -120.49 (18) | C21—N21—C22—C23     | 161.2 (2) |
| C1—N1—C2—C7          | 62.2 (2)   | C21—N21—C22—C27     | -23.1 (4)  |
| C1—N2—C9—C10         | 89.0 (2)   | C21—N22—C29—C30     | 105.4 (2)  |
| C1—N2—C9—C14         | -95.1 (2)  | C21—N22—C29—C34     | -74.2 (3)  |
| C2—N1—C1—S1          | -0.6 (2)   | C22—N21—C21—S21     | -16.0 (3)  |
| C2—N1—C1—N2          | 178.92 (16) | C22—N21—C21—N22     | 166.9 (2)  |
| C2—C3—C4—C5          | -1.2 (3)   | C22—C23—C24—C25     | -0.4 (3)   |
| C3—C2—C7—C6          | 2.0 (2)    | C23—C22—C27—C26     | -1.2 (3)   |
| C3—C4—C5—C6          | 1.4 (3)    | C23—C24—C25—C26     | 0.1 (4)    |
| C4—C5—C6—C7          | 0.2 (3)    | C24—C25—C26—C27     | -0.4 (4)   |
| C5—C6—C7—C2          | -1.9 (3)   | C25—C26—C27—C22     | 0.9 (3)    |
| C7—C2—C3—C4          | -0.5 (2)   | C27—C22—C23—C24     | 1.0 (3)    |
| C8—N2—C1—S1          | 5.5 (2)    | C28—N22—C21—S21     | -1.0 (3)   |
| C8—N2—C1—N1          | -174.01 (17) | C28—N22—C21—N21     | 176.15 (19) |
| C8—N2—C9—C10         | -97.4 (2)  | C28—N22—C29—C30     | -78.0 (3)  |
C8—N2—C9—C14 78.5 (2)  C28—N22—C29—C34 102.4 (2)
C9—N2—C1—S1 178.71 (13) C29—C30—C31—C32 −1.4 (4)
C9—N2—C1—N1 −0.8 (2) C30—C29—C34—C33 0.0 (3)
C10—C9—C14—C13 0.3 (3) C32—C33—C34—C29 −1.7 (3)
C10—C9—C14—C13 −0.3 (3) C34—C29—C30—C31 1.5 (3)
C11—C12—C13—C14 0.1 (3) C30—C29—C34—C33 −0.3 (4)
C11—C12—C13—C14 −0.4 (3) C32—C33—C34—C29 1.9 (3)
C12—C13—C14—C9 0.2 (3) C34—C29—C30—C31 0.0 (3)
C14—C9—C10—C11 0.0 (3) C34—C29—C30—C31 1.5 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···S21 | 0.86 (3) | 2.58 (3) | 3.3360 (16) | 148 (3) |

N,N-Di-n-butyl-N′-phenylthiourea (3)

Crystal data

C15H24N2S
Mr = 264.42
Trigonal, R̅3
a = 25.5231 (3) Å
b = 12.6225 (2) Å
V = 7121.0 (2) Å³
Z = 18
F(000) = 2592

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.4839 pixels mm⁻¹
ω scans
Absorption correction: gaussian
(CrysAlisPro; Rigaku OD, 2019)

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.032
wR(F²) = 0.087
S = 1.06
3151 reflections
168 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

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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 (Å²)

|     | x     | y     | z     | Uiso* | Ueq  |
|-----|-------|-------|-------|-------|------|
| S1  | 0.52061 (2) | 0.89087 (2) | 0.56407 (2) | 0.03089 (10) |
| N1  | 0.54435 (4)  | 0.80126 (4)  | 0.59489 (8)  | 0.0307 (2)  |
| N2  | 0.60326 (4)  | 0.88769 (4)  | 0.69020 (7)  | 0.0277 (2)  |
| C1  | 0.55829 (5)  | 0.85861 (5)  | 0.61987 (8)  | 0.0269 (2)  |
| C2  | 0.50126 (5)  | 0.76273 (5)  | 0.51835 (9)  | 0.0300 (2)  |
| C3  | 0.45844 (5)  | 0.70441 (6)  | 0.54908 (10) | 0.0346 (3)  |
| H3  | 0.456357     | 0.692296     | 0.620843     | 0.041*      |
| C4  | 0.41868 (6)  | 0.66385 (6)  | 0.47470 (12) | 0.0409 (3)  |
| H4  | 0.389778     | 0.623828     | 0.495424     | 0.049*      |
| C5  | 0.42119 (6)  | 0.68178 (6)  | 0.37040 (11) | 0.0415 (3)  |
| H5  | 0.399836     | 0.654162     | 0.319656     | 0.050*      |
| C6  | 0.46357 (6)  | 0.73993 (7)  | 0.34018 (10) | 0.0404 (3)  |
| H6  | 0.464950     | 0.752227     | 0.268704     | 0.049*      |
| C7  | 0.50412 (5)  | 0.78049 (6)  | 0.41355 (10) | 0.0350 (3)  |
| H7  | 0.533631     | 0.820148     | 0.392150     | 0.042*      |
| C8  | 0.61573 (5)  | 0.94484 (5)  | 0.73935 (9)  | 0.0319 (2)  |
| H8A | 0.602928     | 0.966811     | 0.690774     | 0.038*      |
| H8B | 0.659778     | 0.970459     | 0.751515     | 0.038*      |
| C9  | 0.58233 (5)  | 0.93370 (5)  | 0.84445 (9)  | 0.0333 (3)  |
| H9A | 0.538255     | 0.909261     | 0.831385     | 0.040*      |
| H9B | 0.593836     | 0.910012     | 0.891379     | 0.040*      |
| C10 | 0.59590 (7)  | 0.99172 (6)  | 0.90032 (10) | 0.0426 (3)  |
| H10A| 0.582272     | 1.014382     | 0.855269     | 0.051*      |
| H10B| 0.640170     | 1.017203     | 0.910118     | 0.051*      |
| C11 | 0.56494 (7)  | 0.97991 (7)  | 1.00770 (12) | 0.0493 (3)  |
| H11A| 0.520992     | 0.956005     | 0.998160     | 0.074*      |
| H11B| 0.575502     | 1.018545     | 1.041429     | 0.074*      |
| H11C| 0.578367     | 0.957572     | 1.052685     | 0.074*      |
| H1  | 0.5540 (9)   | 0.7814 (9)   | 0.6385 (15)  | 0.059*      |
| C12 | 0.64531 (5)  | 0.86653 (5)  | 0.71978 (9)  | 0.0288 (2)  |
| H12A| 0.622637     | 0.821985     | 0.727847     | 0.035*      |
| H12B| 0.664311     | 0.884432     | 0.788746     | 0.035*      |
| C13 | 0.69452 (5)  | 0.88425 (6)  | 0.63577 (9)  | 0.0342 (3)  |
| H13A| 0.675206     | 0.869399     | 0.565789     | 0.041*      |
| H13B| 0.719121     | 0.928910     | 0.632074     | 0.041*      |
| C14 | 0.73574 (6)  | 0.85867 (6)  | 0.65902 (10) | 0.0359 (3)  |
| H14A| 0.711309     | 0.813967     | 0.661602     | 0.043*      |
| H14B| 0.754711     | 0.873062     | 0.729373     | 0.043*      |
| C15 | 0.78511 (6)  | 0.87735 (7)  | 0.57560 (12) | 0.0477 (3)  |
**supporting information**

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| H15A | 0.766520 | 0.863934 | 0.505610 | 0.071* |
| H15B | 0.809652 | 0.858661 | 0.591775 | 0.071* |
| H15C | 0.810909 | 0.921480 | 0.575771 | 0.071* |

**Atomic displacement parameters (Å²)**

|     | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|-----|------|------|------|------|------|------|
| S1  | 0.03175 (16) | 0.03319 (16) | 0.03491 (17) | 0.02161 (12) | 0.00062 (10) | 0.00343 (10) |
| N1  | 0.0290 (5) | 0.0276 (5) | 0.0384 (5) | 0.0163 (4) | 0.0062 (4) | 0.0022 (4) |
| N2  | 0.0267 (4) | 0.0242 (4) | 0.0329 (5) | 0.0133 (4) | 0.0008 (4) | 0.0005 (4) |
| C1  | 0.0244 (5) | 0.0266 (5) | 0.0307 (5) | 0.0136 (4) | 0.0036 (4) | 0.0030 (4) |
| C2  | 0.0241 (5) | 0.0301 (6) | 0.0394 (6) | 0.0164 (5) | 0.0024 (4) | 0.0056 (4) |
| C3  | 0.0294 (6) | 0.0314 (6) | 0.0453 (6) | 0.0170 (5) | 0.0027 (5) | 0.0012 (5) |
| C4  | 0.0296 (6) | 0.0315 (6) | 0.0594 (8) | 0.0137 (5) | 0.0045 (5) | 0.0067 (5) |
| C5  | 0.0308 (6) | 0.0444 (7) | 0.0491 (7) | 0.0186 (6) | 0.0067 (5) | 0.0172 (6) |
| C6  | 0.0331 (6) | 0.0525 (8) | 0.0360 (6) | 0.0217 (6) | 0.0004 (5) | 0.0085 (5) |
| C7  | 0.0270 (5) | 0.0380 (6) | 0.0384 (6) | 0.0150 (5) | 0.0030 (4) | 0.0026 (5) |
| C8  | 0.0339 (6) | 0.0232 (5) | 0.0374 (6) | 0.0134 (5) | 0.0031 (5) | 0.0099 (4) |
| C9  | 0.0316 (6) | 0.0290 (6) | 0.0391 (6) | 0.0151 (5) | 0.0025 (5) | 0.0028 (5) |
| C10 | 0.0620 (9) | 0.0358 (7) | 0.0368 (6) | 0.0294 (6) | 0.0076 (6) | 0.0041 (5) |
| C11 | 0.0566 (9) | 0.0548 (8) | 0.0453 (7) | 0.0344 (7) | 0.0024 (6) | 0.0111 (6) |
| C12 | 0.0263 (5) | 0.0261 (5) | 0.0338 (5) | 0.0130 (4) | 0.0032 (4) | 0.0016 (4) |
| C13 | 0.0315 (6) | 0.0361 (6) | 0.0365 (6) | 0.0180 (5) | 0.0006 (5) | 0.0029 (5) |
| C14 | 0.0347 (6) | 0.0396 (6) | 0.0372 (6) | 0.0214 (5) | 0.0042 (5) | 0.0046 (5) |
| C15 | 0.0337 (7) | 0.0558 (8) | 0.0531 (8) | 0.0220 (6) | 0.0010 (6) | 0.0082 (6) |

**Geometric parameters (Å, °)**

|     |      |      |      |
|-----|------|------|------|
| S1—C1 | 1.7004 (11) | C9—H9A | 0.9900 |
| N1—C1 | 1.3594 (15) | C9—H9B | 0.9900 |
| N1—C2 | 1.4241 (15) | C9—C10 | 1.5157 (17) |
| N1—H1 | 0.86 (2) | C10—H10A | 0.9900 |
| N2—C1 | 1.3432 (15) | C10—H10B | 0.9900 |
| N2—C8 | 1.4663 (14) | C10—C11 | 1.521 (2) |
| N2—C12 | 1.4705 (14) | C11—H11A | 0.9800 |
| C2—C3 | 1.3907 (17) | C11—H11B | 0.9800 |
| C2—C7 | 1.3885 (17) | C11—H11C | 0.9800 |
| C3—H3 | 0.9500 | C12—H12A | 0.9900 |
| C3—C4 | 1.3901 (18) | C12—H12B | 0.9900 |
| C4—H4 | 0.9500 | C12—C13 | 1.5293 (16) |
| C4—C5 | 1.385 (2) | C13—H13A | 0.9900 |
| C5—H5 | 0.9500 | C13—H13B | 0.9900 |
| C5—C6 | 1.383 (2) | C13—C14 | 1.5186 (17) |
| C6—H6 | 0.9500 | C14—H14A | 0.9900 |
| C6—C7 | 1.3888 (18) | C14—H14B | 0.9900 |
| C7—H7 | 0.9500 | C14—C15 | 1.5242 (18) |
| C8—H8A | 0.9900 | C15—H15A | 0.9800 |
| C8—H8B | 0.9900 | C15—H15B | 0.9800 |
| C8—C9   | 1.5249 (17) | C15—H15C   | 0.9800 |
|----------|-------------|-------------|--------|
| C1—N1—C2 | 126.66 (10) | C10—C9—H9B | 109.0  |
| C1—N1—H1  | 119.1 (13)  | C9—C10—H10A | 109.2 |
| C2—N1—H1  | 112.1 (13)  | C9—C10—H10B | 109.2 |
| C1—N2—C8  | 121.99 (9)  | C9—C10—C11  | 112.25 (12) |
| C1—N2—C12 | 122.95 (9)  | H10A—C10—H10B | 107.9 |
| C8—N2—C12 | 115.00 (9)  | C11—C10—H10A | 109.2 |
| N1—C1—S1  | 121.22 (8)  | C11—C10—H10B | 109.2 |
| N2—C1—S1  | 122.70 (8)  | C10—C11—H11A | 109.5 |
| N2—C1—N1  | 116.68 (10) | C10—C11—H11B | 109.5 |
| C3—C2—N1  | 118.18 (11) | C10—C11—H11C | 109.5 |
| C7—C2—N1  | 121.64 (11) | H11A—C11—H11B | 109.5 |
| C7—C2—C3  | 120.00 (11) | H11A—C11—H11C | 109.5 |
| C2—C3—H3  | 120.0        | H11B—C11—H11C | 109.5 |
| C4—C3—C2  | 119.94 (12) | N2—C12—H12A | 109.4 |
| C4—C3—H3  | 120.0        | N2—C12—H12B | 109.4 |
| C3—C4—H4  | 120.0        | N2—C12—C13  | 110.96 (9) |
| C5—C4—C3  | 120.01 (12) | H12A—C12—H12B | 108.0 |
| C5—C4—H4  | 120.0        | C13—C12—H12A | 109.4 |
| C4—C5—H5  | 120.0        | C13—C12—H12B | 109.4 |
| C6—C5—C4  | 119.94 (12) | C12—C13—H13A | 109.1 |
| C6—C5—H5  | 120.0        | C12—C13—H13B | 109.1 |
| C5—C6—H6  | 119.8        | H13A—C13—H13B | 107.8 |
| C5—C6—C7  | 120.48 (13) | C14—C13—C12 | 112.46 (10) |
| C7—C6—H6  | 119.8        | C14—C13—H13A | 109.1 |
| C2—C7—C6  | 119.61 (12) | C14—C13—H13B | 109.1 |
| C2—C7—H7  | 120.2        | C13—C14—H14A | 109.2 |
| C6—C7—H7  | 120.2        | C13—C14—H14B | 109.2 |
| N2—C8—H8A | 109.4        | C13—C14—C15  | 111.96 (11) |
| N2—C8—H8B | 109.4        | H14A—C14—H14B | 107.9 |
| N2—C8—C9  | 111.07 (9)  | C15—C14—H14A | 109.2 |
| H8A—C8—H8B | 108.0      | C15—C14—H14B | 109.2 |
| C9—C8—H8A | 109.4        | C14—C15—H15A | 109.5 |
| C9—C8—H8B | 109.4        | C14—C15—H15B | 109.5 |
| C8—C9—H9A | 109.0        | C14—C15—H15C | 109.5 |
| C8—C9—H9B | 109.0        | H15A—C15—H15B | 109.5 |
| H9A—C9—H9B | 107.8      | H15A—C15—H15C | 109.5 |
| C10—C9—C8 | 112.91 (10) | H15B—C15—H15C | 109.5 |
| C10—C9—H9A | 109.0      |                      |        |
| N1—C2—C3—C4 | −174.90 (10) | C3—C4—C5—C6 | 0.45 (19) |
| N1—C2—C7—C6 | 175.74 (11)  | C4—C5—C6—C7 | 0.57 (19) |
| N2—C8—C9—C10 | 177.68 (10)  | C5—C6—C7—C2 | −1.16 (19) |
| N2—C12—C13—C14 | −175.23 (10) | C7—C2—C3—C4 | 0.27 (17) |
| C1—N1—C2—C3 | −129.37 (12) | C8—N2—C1—S1 | 11.78 (15) |
| C1—N1—C2—C7 | 55.54 (16)   | C8—N2—C1—N1  | −168.43 (10) |
| C1—N2—C8—C9 | 92.75 (12)   | C8—N2—C12—C13 | −97.50 (11) |
Hydrogen-bond geometry (Å, °)

|        | D—H—A        | D—H  | H—A  | D···A    | D—H···A |
|--------|---------------|------|------|----------|----------|
| N1—H1···S1<sup>i</sup> | 0.86 (2) 2.62 (2) 3.4656 (11) 167 (2) |      |      |          |          |
| C12—H12···S1<sup>i</sup> | 0.99 2.67 3.6588 (13) 174 |      |      |          |          |

Symmetry code: (i) y−1/3, −x+y+1/3, −z+4/3.