

Synthesis, characterization, and crystal structures
of *N,N'*-bis(2-dialkylaminophenyl)thioureas

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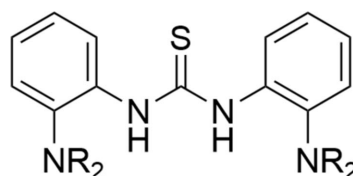
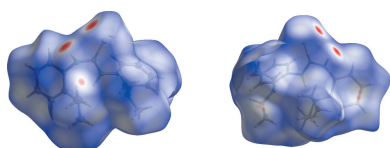
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Autónoma de México, México**Keywords:** crystal structure; aryl-substituted
thiourea; hydrogen bond.**CCDC references:** 2233350; 2233349**Supporting information:** this article has
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N,N'-Bis[2-(dimethylamino)phenyl]thiourea, C₁₇H₂₂N₄S (**1**), and *N,N'*-bis[2-(diethylamino)phenyl]thiourea, C₂₁H₃₀N₄S (**2**), were prepared by the treatment of 1,1'-thiocarbonyldiimidazole and 2 equivalents of 2-amino-*N,N'*-dialkylaniline. Both compounds exhibit intramolecular hydrogen bonds between the N–H(thiourea) and NR₂ (R = Me, Et) groups. The other N–H bonds face the sulfur atoms of S=C bonds in an adjacent molecule, which forms an intermolecular interaction in the packed structure. The structural details match the spectroscopic data acquired from NMR and IR spectroscopy.

1. Chemical context

Thioureas and their derivatives are found in numerous organic and biological molecules (Schroeder, 1955; Kožurková *et al.*, 2017; Khan *et al.*, 2021; Ronchetti *et al.*, 2021). Recent reviews pointed out that thioureas have been used in various research areas, such as catalysis (Doyle & Jacobsen, 2007; Zhang & Schreiner, 2009; Sun *et al.*, 2017; Parvin *et al.*, 2020), chemical sensing (Li *et al.*, 2010; Khan *et al.*, 2021; Al-Saidi & Khan, 2022), as ligands (Saeed *et al.*, 2014; Zahra *et al.*, 2022), *etc.* For example, strong hydrogen bonding in some thiourea compounds allows them to be used as organocatalysts in different chemical transformations. Furthermore, thioureas with chiral substituents are easily available and are used in asymmetric catalysis. Finally, thioureas substituted with functionalized aromatic rings can act as chemosensors.

Aryl-substituted thiourea compounds with amine groups in the *ortho* positions are expected to have versatile applications due to the unique hydrogen-bonding interactions, but so far, no such compounds have been reported. Diaryl thioureas with dimethylamine functional groups in the *meta* or *para* positions of the aryl substituents have been reported, but their crystal structures are unknown.

R = Me (**1**), Et (**2**)

This report describes the preparation and crystal structures of *N,N'*-bis(2-dimethylaminophenyl)thiourea (**1**) and *N,N'*-bis(2-diethylaminophenyl)thiourea (**2**). Compounds **1** and **2** were prepared by treating 1,1'-thiocarbonyldiimidazole and



two equivalents of 2-amino-*N,N'*-dialkylaniline in CH_2Cl_2 . Methyl and NH resonances for **1** were observed at δ 2.64 and 8.82 ppm in the ^1H NMR spectrum, whereas singlets at δ 43.99 and 178.66 ppm in the ^{13}C NMR spectrum match to methyl and $\text{C}=\text{S}$ resonances (Figs. S1 and S2 in the supporting information). Ethyl and NH resonances for **2** were found at δ 0.89, 2.89, and 9.14 ppm in the ^1H NMR spectrum, while resonances at δ 12.47, 48.07, and 176.68 ppm in ^{13}C NMR spectrum correspond to the ethyl and $\text{C}=\text{S}$ groups (Figs. S3 and S4). In the IR spectra, the NH stretches were observed at 3165 and 3226 cm^{-1} for **1** and **2**, respectively (Figs. S5 and S6). High-resolution ESI-MS data confirmed the formation of **1** and **2** with the desired isotopic patterns (Figs. S7 and S8).

2. Structural commentary

One of the most noticeable features in both **1** and **2** is the intramolecular hydrogen bonding between one of the thiourea NH moieties and the NR_2 group ($R = \text{Me}$ and Et) in the *ortho* position of the aromatic rings (Figs. 1 and 2). The $\text{N2}-\text{H2}$ bond distance of 0.896 (15) Å in **1** is slightly shorter (within error ranges) than the $\text{N2}-\text{H2}$ bond distance of 0.905 (15) Å in **2**, whereas the $\text{N3}\cdots\text{H2}$ distance of 1.957 (17) Å for **1** is more elongated than the $\text{N3}\cdots\text{H2}$ distance of 1.864 (15) Å for **2**. Bond distance analysis suggests that the hydrogen bonding interaction is stronger in **2**, due to the increased basicity of amine with longer chains. The increased hydrogen bonding was also observed in the solution, as demonstrated with the deshielded NH resonance of **2** at δ 9.14 ppm compared to that for **1** at δ 8.82 ppm. It is worth noting that, contrary to what is expected, there are no hydrogen bonds between N4 and H2 in both **1** and **2** even as the corresponding $\text{N}\cdots\text{H}$ distances are 2.707 (12) and 2.641 (14) Å for **1** and **2**, respectively.

Slightly asymmetric $\text{C1}-\text{N1}$ and $\text{C1}-\text{N2}$ bond distances are observed for the trigonal planar thiourea backbones, presumably due to the intramolecular hydrogen-bonding

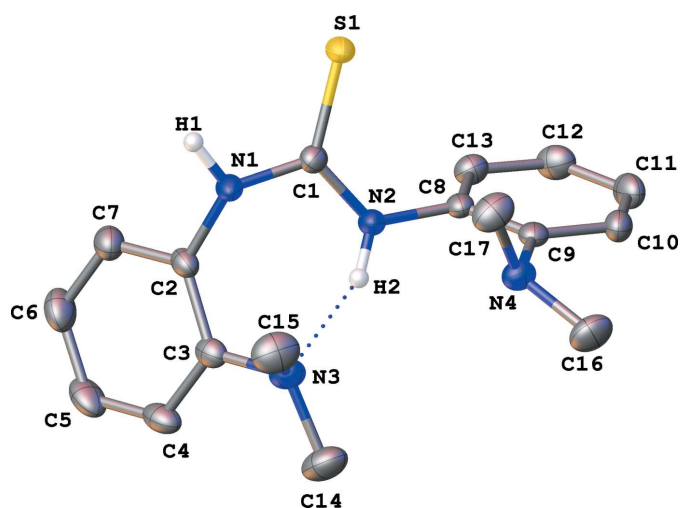


Figure 1
Molecular structure of **1** with displacement ellipsoids at the 50% probability level. Hydrogen atoms attached to carbon were omitted from the figure.

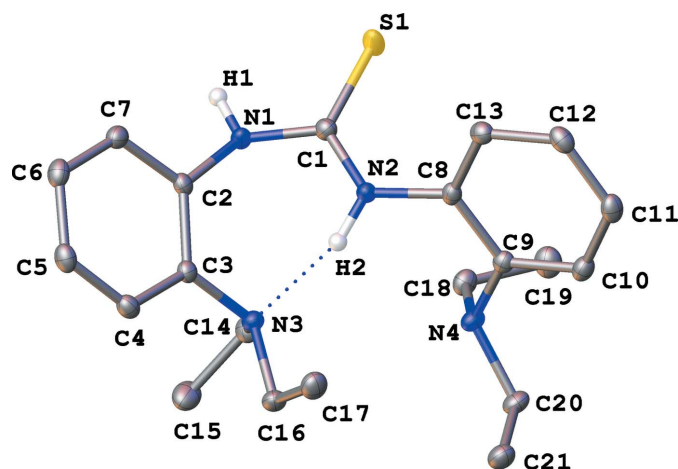


Figure 2
Molecular structure of **2** with displacement ellipsoids at the 50% probability level. Hydrogen atoms attached to carbon were omitted from the figure.

interactions. The $\text{C1}-\text{S1}$ bond distance of 1.6879 (11) Å in **1** is between the values for a double and a single bond, while the sum of bond angles around the thiourea carbon (C1) is 360.0° . In the thiourea backbone, the $\text{C1}-\text{N2}$ bond [1.3396 (14) Å] that is involved in intramolecular hydrogen bonding is slightly shorter than the $\text{C1}-\text{N1}$ bond [1.3621 (15) Å] without the intramolecular hydrogen bonding. The other $\text{C}-\text{N}$ bond distances, such as $\text{C1}-\text{N1}$, $\text{C3}-\text{N3}$, $\text{C8}-\text{N2}$, and $\text{C9}-\text{N4}$ range from 1.41 to 1.43 Å. Similar bond distances and angles were observed for **2**. The thiourea backbone contains the $\text{C1}-\text{S1}$ bond distance of 1.6921 (11) Å, and $\text{C1}-\text{N2}$ and $\text{C1}-\text{N1}$ bond distances of 1.3415 (14) and 1.3652 (14) Å, respectively, while the sum of the bond angles around C1 is 360.0° . Finally, the $\text{C1}-\text{N1}$, $\text{C3}-\text{N3}$, $\text{C8}-\text{N2}$, and $\text{C9}-\text{N4}$ bond distances range from 1.42 to 1.43 Å. Overall, a similar $\text{C1}-\text{S1}$ bond distance is observed within a variation of 0.01 Å between **1** and **2**, while both structures exhibit a trigonal-planar geometry around the central carbon (C1). Furthermore, the $\text{C1}-\text{N2}$ bonds involved in intramolecular hydrogen bonds are 0.02 Å shorter than the $\text{C1}-\text{N1}$ bonds in **1** and **2** that do not participate in the hydrogen bonding.

3. Supramolecular features

Supramolecular features for **1** and **2** were investigated using Hirshfeld surface analysis with *CrystalExplorer 21.5* (Spackman *et al.*, 2021). Hirshfeld surfaces for **1** and **2** were mapped over d_{norm} in the range of -0.27 to 1.29 and -0.18 to 1.48 a.u. for **1** and **2**, respectively (Figs. 3 and 4). The most intense red spots on the surface indicate the intermolecular $\text{H1}\cdots\text{S1}$ interactions (Tables 1 and 2) with the graph-set descriptor $R_2^2(8)$ (Bernstein *et al.*, 1995). The corresponding intermolecular distances of $\text{H1}\cdots\text{S1}$ were measured to be 2.506 (14) and 2.677 (16) Å for **1** and **2**, respectively. In addition, the acquired $\text{N}-\text{H}$ stretch from IR spectra red shifted for **1** (3165 cm^{-1}) when compared to that of **2** (3226 cm^{-1}).

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots S1^i$	0.905 (15)	2.506 (14)	3.3814 (10)	163.4 (14)
$N2-H2\cdots N3$	0.896 (15)	1.957 (17)	2.8018 (17)	156.8 (13)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

This matches the elongated $N1-H1$ bond distance of 0.905 (15) Å and shorter $H1\cdots S1$ interaction of 2.506 (14) Å for **1** when compared to those for **2** at 0.851 (16) and 2.677 (16) Å.

Some weaker interactions were observed as faint red spots on the Hirshfeld surface. The spots in **1** correspond to the short contacts of $C15-H15A\cdots H15A-C15$ and $C5-H5\cdots C9-C10$ (Fig. 3). In addition, the spots in **2** correspond to $C20-H20A\cdots C15-H15B$, $C4-H4\cdots C11$, and $C20-H20B\cdots C5-C6$ interactions (Fig. 4). No appreciable $\pi-\pi$ interactions or hydrogen bonding associated with $N4$ atoms

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots S1^i$	0.851 (16)	2.677 (16)	3.5017 (10)	163.6 (13)
$N2-H2\cdots N3$	0.905 (15)	1.864 (15)	2.7366 (14)	161.4 (13)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

are observed for either **1** or **2**. The Hirshfeld surface of **1** arises from $H\cdots H$ (64.8%), $C\cdots H/H\cdots C$ (22.9%), and $S\cdots H/H\cdots S$ (12.1%) contacts, whereas $H\cdots H$ (71.3%), $C\cdots H/H\cdots C$ (14.4%), and $S\cdots H/H\cdots S$ (11.4%) contacts contribute to the surface of **2**. The minor contributions include $N\cdots H/H\cdots N$ (0.2%) for **1** and $C\cdots C$ (2.0%) and $N\cdots H/H\cdots N$ (1.0%) for **2**.

4. Database survey

A search in the Cambridge Structural Database for structures **1** and **2** did not match any reported structures, including

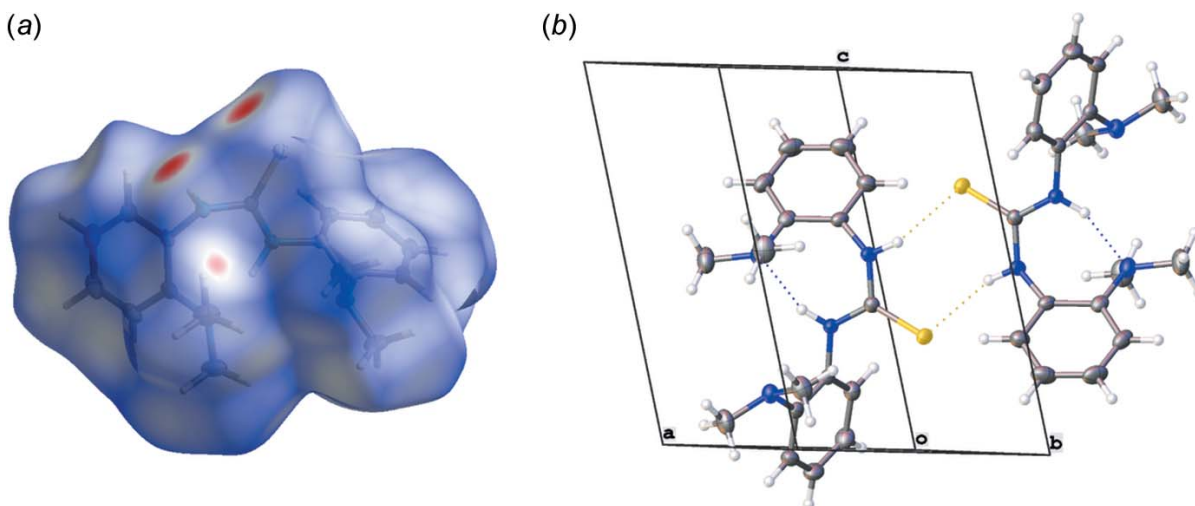


Figure 3
(a) Hirshfeld surface mapped over d_{norm} in the range -0.27 to 1.29 . (b) Partial packing plot of **1**.

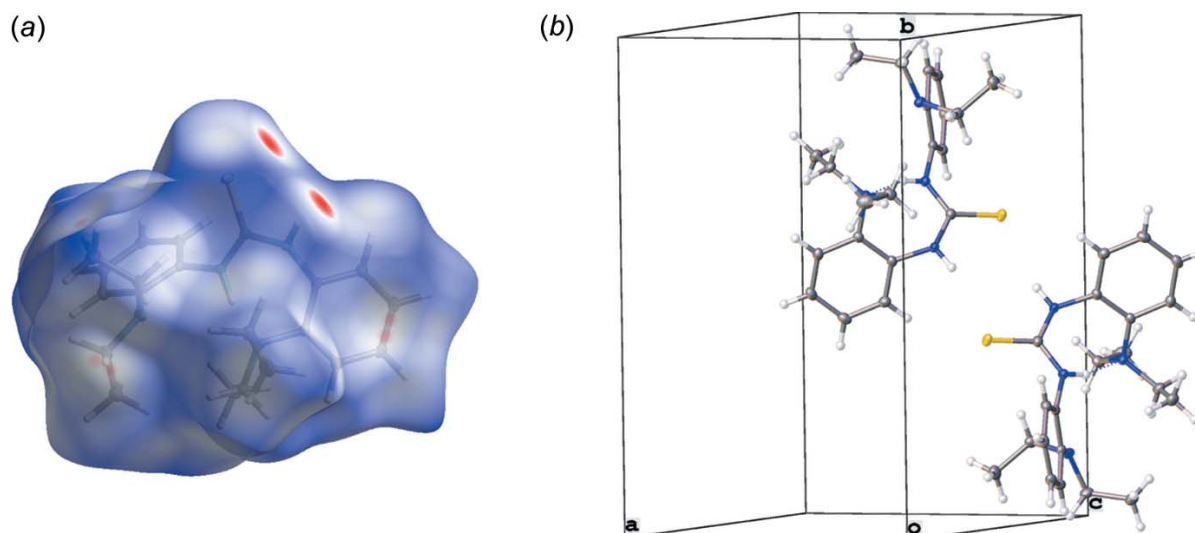


Figure 4
(a) Hirshfeld surface mapped over d_{norm} in the range -0.18 to 1.48 . (b) Partial packing plot of **2**.

Table 3
 Experimental details.

	1	2
Crystal data		
Chemical formula	C ₁₇ H ₂₂ N ₄ S	C ₂₁ H ₃₀ N ₄ S
<i>M_r</i>	314.44	370.55
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	173	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6486 (1), 10.8964 (2), 10.9266 (2)	9.6159 (7), 16.0524 (11), 12.9462 (8)
α , β , γ (°)	78.086 (1), 70.863 (1), 81.135 (1)	90, 96.724 (3), 90
<i>V</i> (Å ³)	838.10 (3)	1984.6 (2)
<i>Z</i>	2	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.20	0.18
Crystal size (mm)	0.41 × 0.33 × 0.16	0.63 × 0.46 × 0.33
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.705, 0.746	0.671, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	15212, 3820, 3496	19639, 4948, 4402
<i>R_{int}</i>	0.023	0.037
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.649	0.669
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.089, 1.04	0.037, 0.095, 1.04
No. of reflections	3820	4948
No. of parameters	209	245
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.24, -0.27	0.32, -0.26

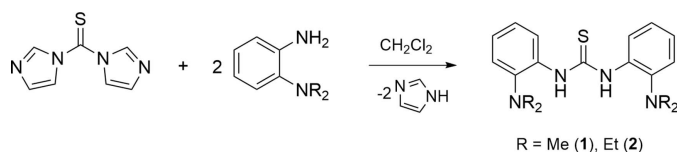
Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *OLEX2* (Dolomanov *et al.*, 2009).

derivative searches. Similar compounds with dimethylamine at the *meta* or *para* position have been prepared, but the structures are unknown.

5. Synthesis and crystallization

Compounds **1** and **2** were prepared by treating 1,1'-thiocarbonyldiimidazole with two equivalents of 2-amino-*N,N'*-dialkylaniline in CH₂Cl₂ (Fig. 5) following the reported procedures (Ren *et al.*, 2011; Thapa *et al.*, 2020). Detailed procedures are described below. Single crystals were grown by diffusion of pentane vapor into a solution of **1** in THF or **2** in Et₂O, respectively. The relative intensities of IR bands were described as *vw*, *w*, *m*, *s*, and *vs*, corresponding to very weak, weak, medium, strong, and very strong, respectively.

***N,N'*-Bis(2-dimethylaminophenyl)thiourea (1)**. To a stirred solution of 1,1'-thiocarbonyldiimidazole (0.38 g, 2.2 mmol) in CH₂Cl₂ (5 mL) was added a solution of 2-amino-*N,N'*-dimethylaniline (0.58 g, 4.3 mmol) in CH₂Cl₂ (5 mL). The


Figure 5

Preparation of *N,N'*-bis(2-dimethylaminophenyl)thiourea (**1**) and *N,N'*-bis(2-diethylaminophenyl)thiourea (**2**).

resulting solution was heated at 323 K overnight. CH₂Cl₂ (50 mL) was added to the pale-yellow solution, and the solution was washed with deionized (DI) water (60 mL) three times. The organic layer was dried over Na₂SO₄ and evaporated to dryness under vacuum. The obtained solid was solubilized in a minimum amount of CH₂Cl₂ (*ca* 5 mL) and excess amount of Et₂O was added before the solution was stored at 253 K. The product was obtained as an off-white powder. Yield: 0.47 g (70%). ¹H NMR (CDCl₃, 300 MHz): δ 8.82 (*br s*, NH, 2H), 7.96 (*s*, Ar, 2H), 7.19–7.13 (*m*, Ar, 2H), 7.13–7.06 (*m*, Ar, 4H), 2.64 (*s*, NMe₂, 12H). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 178.66 (*s*, C–S), 146.26 (*s*, Ar), 132.49 (*s*, Ar), 126.25 (*s*, Ar), 124.16 (*s*, Ar), 123.56 (*s*, Ar), 119.71 (*s*, Ar), 44.00 [*s*, N(CH₃)₂]. IR (ATR, cm⁻¹): 3165 *s* (N–H stretch), 3068 *w* (C–H stretch), 2984 *w* (C–H stretch), 2936 *w* (C–H stretch), 2834 *m* (C–H stretch), 2788 *w* (C–H stretch), 1596 *s*, 1583 *s*, 1552 *s*, 1525 *s*, 1489 *vs*, 1451 *m*, 1429 *w*, 1405 *w*, 1362 *s*, 1297 *m*, 1259 *s*, 1215 *s*, 1159 *w*, 1150 *m*, 1100 *s*, 1045 *vs*, 935 *vs*, 855 *vw*, 809 *m*, 751 *vs*, 735 *m*, 644 *m*, 623 *vs*, 566 *m*, 558 *m*, 531 *m*, 507 *m*, 493 *s*. ESI-MS *m/z*: calculated for C₁₇H₂₃N₄S 315.1643; found 315.1644.

***N,N'*-Bis(2-diethylaminophenyl)thiourea (2)**. To a stirred solution of 1,1'-thiocarbonyldiimidazole (0.40 g, 2.2 mmol) in CH₂Cl₂ (5 mL) was added a solution of 2-amino-*N,N'*-diethylaniline (0.74 g, 4.5 mmol) in CH₂Cl₂ (5 mL). The resulting solution was heated at 323 K overnight. CH₂Cl₂ (20 mL) was added to the pale-yellow solution, and the solution was washed with DI water (30 mL) three times. The

organic layer was dried over Na₂SO₄ and evaporated to dryness under vacuum. The obtained solid was solubilized in a minimum amount of CH₂Cl₂ (ca 5 mL) and excess amount of Et₂O was added before the solution was stored at 253 K. The product was obtained as an off-white powder. Yield: 0.51 g (61%). ¹H NMR (CDCl₃, 300 MHz): δ 9.14 (*br s*, NH, 2H), 8.27 (*s*, Ar, 2H), 7.20–7.10 (*m*, Ar, 6H), 2.89 (*q*, NCH₂, 8H), 0.89 (*t*, CH₃, 12H). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 176.68 (*s*, C–S), 141.93 (*s*, Ar), 135.14 (*s*, Ar), 125.03 (*s*, Ar), 124.59 (*s*, Ar), 123.19 (*s*, Ar), 121.78 (*s*, Ar), 48.07 [*s*, N(CH₂CH₃)₂], 12.47 [*s*, N(CH₂CH₃)₂]. IR (ATR, cm⁻¹): 3226 *s* (N–H stretch), 2977 *s* (C–H stretch), 2958 *w* (C–H stretch), 2936 *w* (C–H stretch), 2866 *m* (C–H stretch), 1600 *s*, 1577 *m*, 1556 *s*, 1523 *s*, 1485 *vs*, 1442 *s*, 1370 *vs*, 1347 *m*, 1336 *w*, 1302 *m*, 1285 *m*, 1275 *m*, 1257 *m*, 1236 *s*, 1203 *s*, 1162 *s*, 1088 *s*, 1066 *m*, 1015 *s*, 942 *w*, 901 *w*, 861 *w*, 828 *m*, 799 *m*, 766 *w*, 755 *vs*, 735 *m*, 692 *m*, 646 *s*, 623 *s*, 586 *m*, 555 *m*, 523 *m*, 506 *s*, 470 *m*, 463 *m*, 435 *w*. ESI–MS *m/z*: calculated for C₂₁H₃₁N₄S 371.2269; found 371.2273.

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. Upon scrutiny, no appreciable disorder was observed in either structure. The positions of hydrogen on nitrogen atoms were refined, whereas the other hydrogen atoms were optimized using riding models [C–H = 0.93–0.98 Å; *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C)].

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References

- Al-Saidi, H. M. & Khan, S. (2022). *Crit. Rev. Anal. Chem.* pp. 1–17.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2012). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Doyle, A. G. & Jacobsen, E. N. (2007). *Chem. Rev.* **107**, 5713–5743.
- Khan, E., Khan, S., Gul, Z. & Muhammad, M. (2021). *Crit. Rev. Anal. Chem.* **51**, 812–834.
- Kožurková, M., Sabolová, D. & Kristian, P. (2017). *J. Appl. Toxicol.* **37**, 1132–1139.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Li, A.-F., Wang, J.-H., Wang, F. & Jiang, Y.-B. (2010). *Chem. Soc. Rev.* **39**, 3729–3745.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Parvin, T., Yadav, R. & Choudhury, L. H. (2020). *Org. Biomol. Chem.* **18**, 5513–5532.
- Ren, P., Vechorkin, O., Csok, Z., Salihu, I., Scopelliti, R. & Hu, X. (2011). *Dalton Trans.* **40**, 8906–8911.
- Ronchetti, R., Moroni, G., Carotti, A., Gioiello, A. & Camaioni, E. (2021). *RSC Med. Chem.* **12**, 1046–1064.
- Saeed, A., Flörke, U. & Erben, M. F. (2014). *J. Sulfur Chem.* **35**, 318–355.
- Schroeder, D. C. (1955). *Chem. Rev.* **55**, 181–228.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Sun, Y.-L., Wei, Y. & Shi, M. (2017). *ChemCatChem*, **9**, 718–727.
- Thapa, P., Palacios, P. M., Tran, T., Pierce, B. S. & Foss, F. W. (2020). *J. Org. Chem.* **85**, 1991–2009.
- Zahra, U., Saeed, A., Abdul Fattah, T., Flörke, U. & Erben, M. F. (2022). *RSC Adv.* **12**, 12710–12745.
- Zhang, Z. & Schreiner, P. R. (2009). *Chem. Soc. Rev.* **38**, 1187–1198.

supporting information

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Synthesis, characterization, and crystal structures of *N,N'*-bis(2-dialkylamino-phenyl)thioureas

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

N,N'-Bis[2-(dimethylamino)phenyl]thiourea (1)

Crystal data

$C_{17}H_{22}N_4S$	$Z = 2$
$M_r = 314.44$	$F(000) = 336$
Triclinic, $P\bar{1}$	$D_x = 1.246 \text{ Mg m}^{-3}$
$a = 7.6486 (1) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 10.8964 (2) \text{ \AA}$	Cell parameters from 8859 reflections
$c = 10.9266 (2) \text{ \AA}$	$\theta = 2.5\text{--}27.5^\circ$
$\alpha = 78.086 (1)^\circ$	$\mu = 0.20 \text{ mm}^{-1}$
$\beta = 70.863 (1)^\circ$	$T = 173 \text{ K}$
$\gamma = 81.135 (1)^\circ$	BLOCK, colourless
$V = 838.10 (3) \text{ \AA}^3$	$0.41 \times 0.33 \times 0.16 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	3820 independent reflections
Multilayer monochromator	3496 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.0^\circ$
$T_{\text{min}} = 0.705$, $T_{\text{max}} = 0.746$	$h = -9 \rightarrow 9$
15212 measured reflections	$k = -14 \rightarrow 14$
	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.2821P]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3820 reflections	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
209 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.11704 (4)	0.46317 (3)	0.30114 (3)	0.02635 (10)
N2	0.38096 (14)	0.27534 (9)	0.32181 (9)	0.0225 (2)
H2	0.466 (2)	0.2452 (13)	0.3632 (14)	0.027*
N1	0.20935 (15)	0.34773 (9)	0.51263 (9)	0.0246 (2)
H1	0.115 (2)	0.4039 (14)	0.5467 (14)	0.030*
N4	0.71659 (14)	0.34986 (9)	0.14163 (10)	0.0256 (2)
N3	0.57747 (15)	0.21641 (10)	0.50554 (11)	0.0288 (2)
C9	0.59665 (16)	0.29364 (10)	0.09912 (11)	0.0216 (2)
C2	0.23764 (17)	0.23641 (10)	0.60252 (11)	0.0231 (2)
C3	0.41291 (17)	0.17201 (10)	0.60109 (11)	0.0241 (2)
C1	0.24274 (15)	0.35521 (10)	0.38108 (11)	0.0207 (2)
C8	0.42590 (15)	0.25953 (10)	0.18851 (11)	0.0206 (2)
C13	0.30914 (17)	0.19843 (11)	0.15256 (12)	0.0270 (3)
H13	0.193140	0.176791	0.214054	0.032*
C10	0.64498 (18)	0.26354 (11)	−0.02667 (12)	0.0280 (3)
H10	0.759573	0.286296	−0.089404	0.034*
C7	0.07808 (19)	0.19426 (12)	0.69835 (12)	0.0302 (3)
H7	−0.039053	0.239647	0.700428	0.036*
C4	0.4167 (2)	0.06285 (11)	0.69360 (12)	0.0319 (3)
H4	0.532617	0.015914	0.692284	0.038*
C12	0.36034 (19)	0.16861 (12)	0.02749 (13)	0.0329 (3)
H12	0.280371	0.126205	0.003170	0.039*
C11	0.5286 (2)	0.20110 (13)	−0.06139 (13)	0.0334 (3)
H11	0.564805	0.180434	−0.147111	0.040*
C17	0.65604 (19)	0.48128 (12)	0.15808 (15)	0.0360 (3)
H17A	0.677991	0.534802	0.071569	0.054*
H17B	0.726455	0.507818	0.207029	0.054*
H17C	0.523152	0.489167	0.206665	0.054*
C5	0.2567 (2)	0.02127 (12)	0.78690 (13)	0.0386 (3)
H5	0.263790	−0.053267	0.848686	0.046*
C16	0.91227 (18)	0.33728 (14)	0.06450 (15)	0.0385 (3)
H16A	0.951293	0.248938	0.054645	0.058*
H16B	0.987224	0.364986	0.109466	0.058*
H16C	0.929808	0.389445	−0.022427	0.058*
C6	0.0869 (2)	0.08720 (13)	0.79092 (13)	0.0385 (3)
H6	−0.023033	0.059693	0.856327	0.046*
C14	0.7454 (2)	0.12829 (15)	0.48739 (17)	0.0428 (3)
H14A	0.786992	0.115000	0.565347	0.064*
H14B	0.843493	0.163155	0.410108	0.064*

H14C	0.718103	0.047721	0.474562	0.064*
C15	0.6169 (2)	0.33902 (13)	0.52041 (17)	0.0435 (4)
H15A	0.504137	0.397587	0.530400	0.065*
H15B	0.715220	0.372392	0.442398	0.065*
H15C	0.657686	0.329057	0.598368	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02772 (17)	0.02673 (16)	0.02053 (15)	0.00853 (11)	-0.00787 (12)	-0.00237 (11)
N2	0.0221 (5)	0.0251 (5)	0.0180 (5)	0.0051 (4)	-0.0064 (4)	-0.0037 (4)
N1	0.0283 (5)	0.0220 (5)	0.0182 (5)	0.0087 (4)	-0.0052 (4)	-0.0030 (4)
N4	0.0226 (5)	0.0245 (5)	0.0292 (5)	-0.0008 (4)	-0.0079 (4)	-0.0042 (4)
N3	0.0261 (5)	0.0299 (5)	0.0324 (6)	0.0031 (4)	-0.0124 (4)	-0.0081 (4)
C9	0.0227 (6)	0.0182 (5)	0.0218 (5)	0.0038 (4)	-0.0080 (4)	-0.0014 (4)
C2	0.0313 (6)	0.0199 (5)	0.0174 (5)	0.0030 (4)	-0.0088 (5)	-0.0036 (4)
C3	0.0321 (6)	0.0209 (5)	0.0227 (5)	0.0027 (4)	-0.0127 (5)	-0.0074 (4)
C1	0.0203 (5)	0.0193 (5)	0.0199 (5)	-0.0006 (4)	-0.0044 (4)	-0.0015 (4)
C8	0.0218 (5)	0.0189 (5)	0.0191 (5)	0.0052 (4)	-0.0064 (4)	-0.0035 (4)
C13	0.0231 (6)	0.0274 (6)	0.0298 (6)	0.0005 (4)	-0.0080 (5)	-0.0055 (5)
C10	0.0283 (6)	0.0300 (6)	0.0201 (6)	0.0034 (5)	-0.0036 (5)	-0.0030 (5)
C7	0.0342 (7)	0.0288 (6)	0.0232 (6)	0.0025 (5)	-0.0053 (5)	-0.0041 (5)
C4	0.0462 (8)	0.0232 (6)	0.0307 (6)	0.0080 (5)	-0.0214 (6)	-0.0064 (5)
C12	0.0351 (7)	0.0337 (7)	0.0368 (7)	0.0016 (5)	-0.0179 (6)	-0.0134 (5)
C11	0.0409 (7)	0.0369 (7)	0.0237 (6)	0.0073 (6)	-0.0121 (5)	-0.0123 (5)
C17	0.0326 (7)	0.0269 (6)	0.0475 (8)	-0.0036 (5)	-0.0078 (6)	-0.0105 (6)
C5	0.0628 (10)	0.0221 (6)	0.0276 (7)	0.0026 (6)	-0.0155 (6)	0.0013 (5)
C16	0.0230 (6)	0.0416 (7)	0.0498 (8)	-0.0017 (5)	-0.0086 (6)	-0.0106 (6)
C6	0.0506 (9)	0.0308 (7)	0.0252 (6)	-0.0046 (6)	-0.0020 (6)	0.0001 (5)
C14	0.0306 (7)	0.0474 (8)	0.0546 (9)	0.0098 (6)	-0.0180 (7)	-0.0195 (7)
C15	0.0392 (8)	0.0329 (7)	0.0593 (10)	-0.0069 (6)	-0.0154 (7)	-0.0069 (7)

Geometric parameters (Å, °)

S1—C1	1.6879 (11)	C7—H7	0.9500
N2—H2	0.896 (15)	C7—C6	1.3862 (17)
N2—C1	1.3396 (14)	C4—H4	0.9500
N2—C8	1.4235 (14)	C4—C5	1.380 (2)
N1—H1	0.905 (15)	C12—H12	0.9500
N1—C2	1.4316 (14)	C12—C11	1.380 (2)
N1—C1	1.3621 (15)	C11—H11	0.9500
N4—C9	1.4152 (15)	C17—H17A	0.9800
N4—C17	1.4645 (16)	C17—H17B	0.9800
N4—C16	1.4583 (17)	C17—H17C	0.9800
N3—C3	1.4233 (16)	C5—H5	0.9500
N3—C14	1.4636 (17)	C5—C6	1.376 (2)
N3—C15	1.4657 (17)	C16—H16A	0.9800
C9—C8	1.4004 (16)	C16—H16B	0.9800

C9—C10	1.3960 (16)	C16—H16C	0.9800
C2—C3	1.4109 (16)	C6—H6	0.9500
C2—C7	1.3903 (17)	C14—H14A	0.9800
C3—C4	1.3963 (16)	C14—H14B	0.9800
C8—C13	1.3843 (17)	C14—H14C	0.9800
C13—H13	0.9500	C15—H15A	0.9800
C13—C12	1.3855 (18)	C15—H15B	0.9800
C10—H10	0.9500	C15—H15C	0.9800
C10—C11	1.3835 (19)		
C1—N2—H2	115.8 (9)	C5—C4—H4	119.1
C1—N2—C8	124.84 (10)	C13—C12—H12	120.3
C8—N2—H2	117.6 (9)	C11—C12—C13	119.35 (12)
C2—N1—H1	115.3 (9)	C11—C12—H12	120.3
C1—N1—H1	111.8 (9)	C10—C11—H11	119.7
C1—N1—C2	125.90 (10)	C12—C11—C10	120.53 (12)
C9—N4—C17	113.86 (10)	C12—C11—H11	119.7
C9—N4—C16	115.07 (10)	N4—C17—H17A	109.5
C16—N4—C17	110.25 (10)	N4—C17—H17B	109.5
C3—N3—C14	116.65 (11)	N4—C17—H17C	109.5
C3—N3—C15	113.45 (10)	H17A—C17—H17B	109.5
C14—N3—C15	110.35 (11)	H17A—C17—H17C	109.5
C8—C9—N4	119.15 (10)	H17B—C17—H17C	109.5
C10—C9—N4	122.93 (11)	C4—C5—H5	119.8
C10—C9—C8	117.82 (11)	C6—C5—C4	120.36 (12)
C3—C2—N1	124.50 (11)	C6—C5—H5	119.8
C7—C2—N1	115.61 (11)	N4—C16—H16A	109.5
C7—C2—C3	119.87 (11)	N4—C16—H16B	109.5
C2—C3—N3	120.27 (10)	N4—C16—H16C	109.5
C4—C3—N3	122.17 (11)	H16A—C16—H16B	109.5
C4—C3—C2	117.53 (12)	H16A—C16—H16C	109.5
N2—C1—S1	123.65 (9)	H16B—C16—H16C	109.5
N2—C1—N1	116.15 (10)	C7—C6—H6	120.4
N1—C1—S1	120.19 (8)	C5—C6—C7	119.19 (13)
C9—C8—N2	119.51 (10)	C5—C6—H6	120.4
C13—C8—N2	119.31 (10)	N3—C14—H14A	109.5
C13—C8—C9	120.82 (10)	N3—C14—H14B	109.5
C8—C13—H13	119.8	N3—C14—H14C	109.5
C8—C13—C12	120.45 (12)	H14A—C14—H14B	109.5
C12—C13—H13	119.8	H14A—C14—H14C	109.5
C9—C10—H10	119.5	H14B—C14—H14C	109.5
C11—C10—C9	121.03 (12)	N3—C15—H15A	109.5
C11—C10—H10	119.5	N3—C15—H15B	109.5
C2—C7—H7	119.4	N3—C15—H15C	109.5
C6—C7—C2	121.18 (12)	H15A—C15—H15B	109.5
C6—C7—H7	119.4	H15A—C15—H15C	109.5
C3—C4—H4	119.1	H15B—C15—H15C	109.5
C5—C4—C3	121.79 (12)		

N2—C8—C13—C12	-172.36 (10)	C1—N1—C2—C7	-115.29 (13)
N1—C2—C3—N3	-0.24 (17)	C8—N2—C1—S1	-8.08 (16)
N1—C2—C3—C4	-178.48 (11)	C8—N2—C1—N1	173.53 (10)
N1—C2—C7—C6	179.76 (12)	C8—C9—C10—C11	-0.54 (17)
N4—C9—C8—N2	-3.56 (15)	C8—C13—C12—C11	-0.39 (19)
N4—C9—C8—C13	-176.63 (10)	C13—C12—C11—C10	-0.40 (19)
N4—C9—C10—C11	175.69 (11)	C10—C9—C8—N2	172.81 (10)
N3—C3—C4—C5	179.22 (11)	C10—C9—C8—C13	-0.25 (16)
C9—C8—C13—C12	0.72 (17)	C7—C2—C3—N3	-178.31 (11)
C9—C10—C11—C12	0.88 (19)	C7—C2—C3—C4	3.45 (17)
C2—N1—C1—S1	150.72 (10)	C4—C5—C6—C7	1.4 (2)
C2—N1—C1—N2	-30.83 (17)	C17—N4—C9—C8	-74.41 (13)
C2—C3—C4—C5	-2.57 (18)	C17—N4—C9—C10	109.41 (13)
C2—C7—C6—C5	-0.5 (2)	C16—N4—C9—C8	156.94 (11)
C3—C2—C7—C6	-2.01 (19)	C16—N4—C9—C10	-19.25 (16)
C3—C4—C5—C6	0.2 (2)	C14—N3—C3—C2	-164.03 (11)
C1—N2—C8—C9	114.58 (13)	C14—N3—C3—C4	14.13 (17)
C1—N2—C8—C13	-72.26 (15)	C15—N3—C3—C2	66.05 (15)
C1—N1—C2—C3	66.56 (17)	C15—N3—C3—C4	-115.79 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots S1 ⁱ	0.905 (15)	2.506 (14)	3.3814 (10)	163.4 (14)
N2—H2 \cdots N3	0.896 (15)	1.957 (17)	2.8018 (17)	156.8 (13)

Symmetry code: (i) $-x, -y+1, -z+1$.

N,N'-Bis[2-(diethylamino)phenyl]thiourea (2)

Crystal data

C₂₁H₃₀N₄S

M_r = 370.55

Monoclinic, *P*2₁/*n*

a = 9.6159 (7) Å

b = 16.0524 (11) Å

c = 12.9462 (8) Å

β = 96.724 (3)°

V = 1984.6 (2) Å³

Z = 4

F(000) = 800

D_x = 1.240 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 8945 reflections

θ = 2.5–28.4°

μ = 0.18 mm⁻¹

T = 296 K

Block, colourless

0.63 × 0.46 × 0.33 mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.671, *T_{max}* = 0.746

19639 measured reflections

4948 independent reflections

4402 reflections with *I* > 2σ(*I*)

R_{int} = 0.037

θ_{\max} = 28.4°, θ_{\min} = 2.0°

h = -12→12

k = -21→21

l = -17→17

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.095$ $S = 1.04$

4948 reflections

245 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.8116P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$ *Special details*

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.02729 (3)	0.62006 (2)	0.58639 (3)	0.02352 (9)
N2	0.24439 (10)	0.69094 (6)	0.50659 (7)	0.01290 (18)
H2	0.2836 (15)	0.6950 (9)	0.4466 (11)	0.015*
N3	0.33323 (10)	0.67098 (6)	0.31488 (7)	0.01359 (19)
N1	0.17251 (10)	0.56268 (6)	0.44080 (7)	0.01455 (19)
H1	0.1150 (15)	0.5228 (10)	0.4448 (11)	0.017*
N4	0.20893 (10)	0.85320 (6)	0.42949 (7)	0.01425 (19)
C3	0.37577 (11)	0.58724 (7)	0.33846 (8)	0.0127 (2)
C9	0.25294 (11)	0.84099 (7)	0.53724 (8)	0.0131 (2)
C2	0.29696 (11)	0.53669 (7)	0.39875 (8)	0.0127 (2)
C8	0.25996 (11)	0.75917 (7)	0.57688 (8)	0.0129 (2)
C4	0.49907 (12)	0.55411 (7)	0.30729 (8)	0.0157 (2)
H4	0.554145	0.587217	0.269367	0.019*
C7	0.33721 (12)	0.45419 (7)	0.41875 (8)	0.0156 (2)
H7	0.281572	0.420032	0.454924	0.019*
C5	0.54073 (12)	0.47335 (8)	0.33161 (9)	0.0172 (2)
H5	0.624257	0.453287	0.311572	0.021*
C16	0.44184 (12)	0.72933 (7)	0.28857 (9)	0.0176 (2)
H16A	0.398226	0.781294	0.264119	0.021*
H16B	0.488678	0.706059	0.232742	0.021*
C10	0.29015 (12)	0.90660 (7)	0.60646 (9)	0.0164 (2)
H10	0.289327	0.960906	0.581382	0.020*
C12	0.32860 (12)	0.81178 (8)	0.75043 (9)	0.0168 (2)
H12	0.350995	0.802119	0.821254	0.020*
C13	0.29531 (11)	0.74547 (7)	0.68286 (8)	0.0152 (2)
H13	0.296695	0.691408	0.708783	0.018*
C1	0.15685 (11)	0.62606 (7)	0.50880 (8)	0.0142 (2)
C6	0.45841 (12)	0.42208 (7)	0.38581 (9)	0.0177 (2)
H6	0.484168	0.367023	0.399816	0.021*
C18	0.05902 (12)	0.83248 (7)	0.40160 (9)	0.0165 (2)

H18A	0.042289	0.777080	0.427390	0.020*
H18B	0.039633	0.830878	0.326388	0.020*
C14	0.20097 (12)	0.67896 (8)	0.24495 (9)	0.0177 (2)
H14A	0.161228	0.733438	0.255343	0.021*
H14B	0.135428	0.637633	0.264764	0.021*
C11	0.32826 (12)	0.89210 (8)	0.71185 (9)	0.0174 (2)
H11	0.353513	0.936423	0.756383	0.021*
C20	0.24384 (12)	0.93418 (7)	0.38573 (9)	0.0180 (2)
H20A	0.210396	0.978289	0.427696	0.022*
H20B	0.195027	0.939178	0.316070	0.022*
C17	0.54904 (13)	0.74644 (8)	0.38189 (10)	0.0211 (2)
H17A	0.614692	0.787422	0.363685	0.032*
H17B	0.597900	0.695884	0.402564	0.032*
H17C	0.502305	0.766842	0.438405	0.032*
C21	0.39972 (13)	0.94621 (8)	0.38091 (10)	0.0213 (2)
H21A	0.430684	0.908551	0.330719	0.032*
H21B	0.449937	0.935165	0.448033	0.032*
H21C	0.416989	1.002519	0.360919	0.032*
C15	0.21500 (15)	0.66843 (8)	0.13015 (9)	0.0251 (3)
H15A	0.123605	0.667487	0.091349	0.038*
H15B	0.262470	0.617064	0.119600	0.038*
H15C	0.267808	0.714092	0.106882	0.038*
C19	-0.04336 (13)	0.89250 (8)	0.44342 (10)	0.0229 (3)
H19A	-0.036737	0.946001	0.411224	0.034*
H19B	-0.020992	0.897916	0.517347	0.034*
H19C	-0.136942	0.871446	0.428077	0.034*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02364 (16)	0.01920 (16)	0.03137 (18)	-0.00753 (12)	0.01852 (13)	-0.00934 (12)
N2	0.0141 (4)	0.0115 (4)	0.0137 (4)	-0.0010 (3)	0.0045 (3)	-0.0009 (3)
N3	0.0141 (4)	0.0124 (5)	0.0147 (4)	-0.0004 (3)	0.0032 (3)	0.0012 (3)
N1	0.0136 (4)	0.0124 (5)	0.0188 (5)	-0.0030 (4)	0.0068 (3)	-0.0025 (4)
N4	0.0146 (4)	0.0123 (4)	0.0155 (4)	-0.0017 (4)	0.0001 (3)	0.0017 (3)
C3	0.0131 (5)	0.0134 (5)	0.0115 (5)	0.0001 (4)	0.0011 (4)	-0.0020 (4)
C9	0.0108 (5)	0.0131 (5)	0.0156 (5)	0.0000 (4)	0.0020 (4)	-0.0006 (4)
C2	0.0124 (5)	0.0142 (5)	0.0116 (5)	0.0002 (4)	0.0018 (4)	-0.0025 (4)
C8	0.0106 (5)	0.0122 (5)	0.0162 (5)	-0.0003 (4)	0.0034 (4)	-0.0022 (4)
C4	0.0143 (5)	0.0182 (6)	0.0150 (5)	-0.0018 (4)	0.0035 (4)	-0.0024 (4)
C7	0.0184 (5)	0.0141 (5)	0.0144 (5)	-0.0014 (4)	0.0021 (4)	-0.0007 (4)
C5	0.0137 (5)	0.0194 (6)	0.0183 (5)	0.0032 (4)	0.0015 (4)	-0.0043 (4)
C16	0.0204 (6)	0.0149 (5)	0.0187 (5)	-0.0030 (4)	0.0070 (4)	0.0004 (4)
C10	0.0157 (5)	0.0125 (5)	0.0210 (5)	-0.0008 (4)	0.0027 (4)	-0.0014 (4)
C12	0.0132 (5)	0.0230 (6)	0.0141 (5)	0.0026 (4)	0.0013 (4)	-0.0020 (4)
C13	0.0143 (5)	0.0151 (5)	0.0168 (5)	0.0021 (4)	0.0038 (4)	0.0013 (4)
C1	0.0134 (5)	0.0138 (5)	0.0159 (5)	0.0006 (4)	0.0038 (4)	0.0001 (4)
C6	0.0192 (6)	0.0148 (5)	0.0184 (5)	0.0039 (4)	-0.0008 (4)	-0.0020 (4)

C18	0.0152 (5)	0.0153 (5)	0.0184 (5)	-0.0009 (4)	-0.0011 (4)	-0.0011 (4)
C14	0.0168 (5)	0.0172 (6)	0.0186 (5)	0.0030 (4)	0.0003 (4)	0.0005 (4)
C11	0.0138 (5)	0.0182 (6)	0.0203 (5)	-0.0014 (4)	0.0016 (4)	-0.0064 (4)
C20	0.0203 (6)	0.0132 (5)	0.0202 (5)	-0.0014 (4)	0.0017 (4)	0.0035 (4)
C17	0.0195 (6)	0.0189 (6)	0.0255 (6)	-0.0044 (5)	0.0047 (5)	-0.0030 (5)
C21	0.0227 (6)	0.0164 (6)	0.0255 (6)	-0.0032 (5)	0.0061 (5)	0.0010 (5)
C15	0.0354 (7)	0.0219 (6)	0.0169 (6)	-0.0012 (5)	-0.0016 (5)	0.0007 (5)
C19	0.0163 (6)	0.0243 (7)	0.0281 (6)	0.0005 (5)	0.0031 (5)	-0.0038 (5)

Geometric parameters (Å, °)

S1—C1	1.6921 (11)	C10—C11	1.3903 (16)
N2—H2	0.905 (15)	C12—H12	0.9300
N2—C8	1.4206 (14)	C12—C13	1.3910 (16)
N2—C1	1.3415 (14)	C12—C11	1.3826 (17)
N3—C3	1.4277 (14)	C13—H13	0.9300
N3—C16	1.4722 (14)	C6—H6	0.9300
N3—C14	1.4779 (14)	C18—H18A	0.9700
N1—H1	0.851 (16)	C18—H18B	0.9700
N1—C2	1.4335 (14)	C18—C19	1.5217 (17)
N1—C1	1.3652 (14)	C14—H14A	0.9700
N4—C9	1.4231 (14)	C14—H14B	0.9700
N4—C18	1.4822 (14)	C14—C15	1.5174 (17)
N4—C20	1.4724 (14)	C11—H11	0.9300
C3—C2	1.4072 (15)	C20—H20A	0.9700
C3—C4	1.4013 (15)	C20—H20B	0.9700
C9—C8	1.4089 (15)	C20—C21	1.5198 (17)
C9—C10	1.4018 (15)	C17—H17A	0.9600
C2—C7	1.3955 (16)	C17—H17B	0.9600
C8—C13	1.3919 (15)	C17—H17C	0.9600
C4—H4	0.9300	C21—H21A	0.9600
C4—C5	1.3822 (17)	C21—H21B	0.9600
C7—H7	0.9300	C21—H21C	0.9600
C7—C6	1.3865 (16)	C15—H15A	0.9600
C5—H5	0.9300	C15—H15B	0.9600
C5—C6	1.3879 (17)	C15—H15C	0.9600
C16—H16A	0.9700	C19—H19A	0.9600
C16—H16B	0.9700	C19—H19B	0.9600
C16—C17	1.5186 (17)	C19—H19C	0.9600
C10—H10	0.9300		
C8—N2—H2	118.1 (9)	N1—C1—S1	119.00 (8)
C1—N2—H2	113.5 (9)	C7—C6—C5	119.00 (11)
C1—N2—C8	127.18 (9)	C7—C6—H6	120.5
C3—N3—C16	117.08 (9)	C5—C6—H6	120.5
C3—N3—C14	114.65 (9)	N4—C18—H18A	108.5
C16—N3—C14	112.71 (9)	N4—C18—H18B	108.5
C2—N1—H1	112.4 (10)	N4—C18—C19	114.99 (10)

C1—N1—H1	113.5 (10)	H18A—C18—H18B	107.5
C1—N1—C2	128.45 (10)	C19—C18—H18A	108.5
C9—N4—C18	112.15 (9)	C19—C18—H18B	108.5
C9—N4—C20	116.34 (9)	N3—C14—H14A	108.5
C20—N4—C18	111.31 (9)	N3—C14—H14B	108.5
C2—C3—N3	120.14 (10)	N3—C14—C15	114.93 (10)
C4—C3—N3	121.78 (10)	H14A—C14—H14B	107.5
C4—C3—C2	118.01 (10)	C15—C14—H14A	108.5
C8—C9—N4	118.78 (10)	C15—C14—H14B	108.5
C10—C9—N4	123.20 (10)	C10—C11—H11	120.0
C10—C9—C8	118.02 (10)	C12—C11—C10	119.99 (11)
C3—C2—N1	124.79 (10)	C12—C11—H11	120.0
C7—C2—N1	115.56 (10)	N4—C20—H20A	108.9
C7—C2—C3	119.63 (10)	N4—C20—H20B	108.9
C9—C8—N2	119.24 (9)	N4—C20—C21	113.48 (10)
C13—C8—N2	120.32 (10)	H20A—C20—H20B	107.7
C13—C8—C9	120.14 (10)	C21—C20—H20A	108.9
C3—C4—H4	119.2	C21—C20—H20B	108.9
C5—C4—C3	121.52 (11)	C16—C17—H17A	109.5
C5—C4—H4	119.2	C16—C17—H17B	109.5
C2—C7—H7	119.3	C16—C17—H17C	109.5
C6—C7—C2	121.37 (11)	H17A—C17—H17B	109.5
C6—C7—H7	119.3	H17A—C17—H17C	109.5
C4—C5—H5	119.9	H17B—C17—H17C	109.5
C4—C5—C6	120.27 (11)	C20—C21—H21A	109.5
C6—C5—H5	119.9	C20—C21—H21B	109.5
N3—C16—H16A	109.3	C20—C21—H21C	109.5
N3—C16—H16B	109.3	H21A—C21—H21B	109.5
N3—C16—C17	111.40 (9)	H21A—C21—H21C	109.5
H16A—C16—H16B	108.0	H21B—C21—H21C	109.5
C17—C16—H16A	109.3	C14—C15—H15A	109.5
C17—C16—H16B	109.3	C14—C15—H15B	109.5
C9—C10—H10	119.3	C14—C15—H15C	109.5
C11—C10—C9	121.32 (11)	H15A—C15—H15B	109.5
C11—C10—H10	119.3	H15A—C15—H15C	109.5
C13—C12—H12	120.1	H15B—C15—H15C	109.5
C11—C12—H12	120.1	C18—C19—H19A	109.5
C11—C12—C13	119.72 (10)	C18—C19—H19B	109.5
C8—C13—H13	119.6	C18—C19—H19C	109.5
C12—C13—C8	120.71 (11)	H19A—C19—H19B	109.5
C12—C13—H13	119.6	H19A—C19—H19C	109.5
N2—C1—S1	124.35 (9)	H19B—C19—H19C	109.5
N2—C1—N1	116.61 (10)		
N2—C8—C13—C12	171.57 (10)	C4—C3—C2—N1	176.86 (10)
N3—C3—C2—N1	-0.16 (16)	C4—C3—C2—C7	-4.85 (15)
N3—C3—C2—C7	178.13 (9)	C4—C5—C6—C7	-2.64 (17)
N3—C3—C4—C5	179.08 (10)	C16—N3—C3—C2	157.09 (10)

N1—C2—C7—C6	-177.58 (10)	C16—N3—C3—C4	-19.82 (14)
N4—C9—C8—N2	9.69 (15)	C16—N3—C14—C15	56.20 (13)
N4—C9—C8—C13	-176.53 (10)	C10—C9—C8—N2	-170.21 (10)
N4—C9—C10—C11	177.90 (10)	C10—C9—C8—C13	3.57 (16)
C3—N3—C16—C17	-67.54 (12)	C13—C12—C11—C10	2.17 (17)
C3—N3—C14—C15	-81.12 (12)	C1—N2—C8—C9	-128.51 (12)
C3—C2—C7—C6	3.98 (16)	C1—N2—C8—C13	57.73 (15)
C3—C4—C5—C6	1.66 (17)	C1—N1—C2—C3	-60.21 (16)
C9—N4—C18—C19	69.76 (13)	C1—N1—C2—C7	121.44 (12)
C9—N4—C20—C21	68.56 (13)	C18—N4—C9—C8	68.45 (13)
C9—C8—C13—C12	-2.13 (16)	C18—N4—C9—C10	-111.66 (12)
C9—C10—C11—C12	-0.65 (17)	C18—N4—C20—C21	-161.30 (10)
C2—N1—C1—S1	-153.44 (9)	C14—N3—C3—C2	-67.53 (13)
C2—N1—C1—N2	28.65 (17)	C14—N3—C3—C4	115.56 (11)
C2—C3—C4—C5	2.11 (16)	C14—N3—C16—C17	156.26 (10)
C2—C7—C6—C5	-0.18 (17)	C11—C12—C13—C8	-0.78 (17)
C8—N2—C1—S1	10.13 (16)	C20—N4—C9—C8	-161.81 (10)
C8—N2—C1—N1	-172.09 (10)	C20—N4—C9—C10	18.08 (15)
C8—C9—C10—C11	-2.20 (16)	C20—N4—C18—C19	-62.54 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...S1 ⁱ	0.851 (16)	2.677 (16)	3.5017 (10)	163.6 (13)
N2—H2...N3	0.905 (15)	1.864 (15)	2.7366 (14)	161.4 (13)

Symmetry code: (i) $-x, -y+1, -z+1$.