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Synthesis, crystal structure and conformational analysis of an unexpected [1,5]dithiocine product of aminopyridine and thiovanillin

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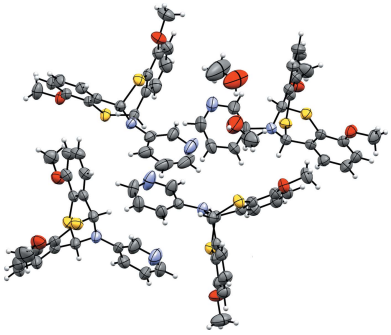
The condensation reaction of 2-mercapto-3-methoxybenzaldehyde with 3-aminopyridine afforded an unexpected *N*-alkylated [1,5]dithiocine instead of the *N*-salicylideneaniline. The proposed mechanism for this condensation involves a strong intramolecular hydrogen bond between the thiol and the amine groups, leading to a second condensation. The corresponding product, *i.e.* 4,10-dimethoxy-13-(pyridin-3-yl)-6*H*,12*H*-6,12-epiminodibenzo[*b*,*f*][1,5]dithiocine methanol 0.463-solvate, $C_{21}H_{18}N_2O_2S_2{\cdot}0.463CH_3OH$, was characterized by single-crystal X-ray diffraction analysis. The supramolecular structure shows π–π stacking and S$\cdots$S interactions in the crystal packing. Within the asymmetric unit, two geometries of the N atom are observed. Although a planar geometry should be expected, a pyramidal one is observed due to the crystal packing. The presence of the two geometries was further supported by density functional theory (DFT) calculations that show an electronic energy difference of less than 2 kJ mol^{-1} between the two conformers.

1. Introduction

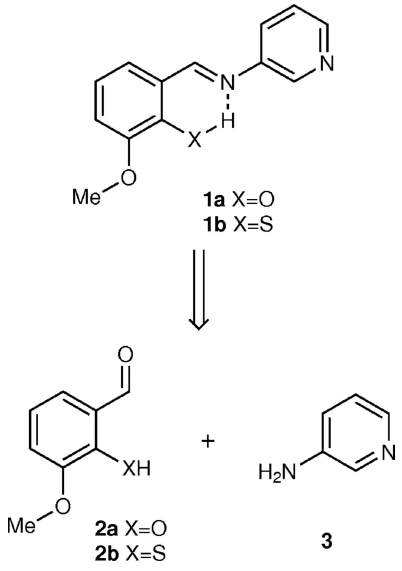
As part of our interest in photo- and thermochromic cocrystals (Carletta *et al.*, 2015, 2016, 2018), the investigation of compounds analogous to the already studied *N*-salicylideneaniline derivatives of *o*-vanillin could lead to a better understanding of the factors influencing photo- and thermochromic behaviour. Indeed, the impact of the intramolecular hydrogen bond with regard to external stimuli (temperature and light) should affect the properties of new analogues. For that purpose, 2-mercapto-3-methoxybenzaldehyde, referred to as *o*-thiovanillin in this article, was studied (see structure **1b** in Scheme 1). The significant difference between **1a** and **1b** lies in the possibility of forming a stronger intramolecular hydrogen bond (O—H$\cdots$N *versus* S—H$\cdots$N), as sulfur is a better base than oxygen.

Moreover, cocrystallization and salification are modern alternatives to chemical modification in order to induce the photochromic behaviour of *N*-salicylideneaniline derivatives (Hutchins *et al.*, 2014; Carletta *et al.*, 2016; Jacquemin *et al.*, 2015). In the case of the compound studied in this article, chalcogen bonding could be a possible interaction to increase the tendency of *N*-salicylideneaniline toward cocrystal formation. This noncovalent interaction has attracted much attention as it has been demonstrated that chalcogen bonds can be strong enough to be an effective tool in crystal engineering (Vogel *et al.*, 2019; Scilabra *et al.*, 2019).

Unexpectedly, our synthetic approach (Scheme 1 shows the structures and retrosynthesis of *N*-salicylideneaniline deriva-



tives) led to a product derived from the double condensation. [1,5]Dithiocine compounds, known for their V-shaped molecular cleft, were studied in the late 1990s for the purpose of applications in molecular recognition and supramolecular chemistry. They were then synthesized by an *ortho* formylation of the appropriate thiol *via* directed *ortho*-lithiation (Toste, 1995; Still *et al.*, 1999; Brieaddy & Donaldson, 1995). Recently, Dai *et al.* (2019) showed that double condensation can take place in phosphate-buffered saline with tris(2-carboxyethyl)phosphine at room temperature. In that respect, a new synthetic pathway for a novel [1,5]dithiocine derivative was discovered. We present here the synthesis, structure and conformational analysis of this product.



Scheme 1

2. Experimental

2.1. General information

All reagents were purchased from Sigma–Aldrich (Schnelldorf, Germany).

Reactions were monitored by thin-layer chromatography (TLC) on 2 mm silica coated (60 F_{254}) Merck aluminium plates revealed under UV light at 254 nm or with a solution of *para*-anisaldehyde (0.5 ml of *para*-anisaldehyde, 100 ml of acetic acid, 85 ml of methanol and 5 ml of concentrated sulfuric acid).

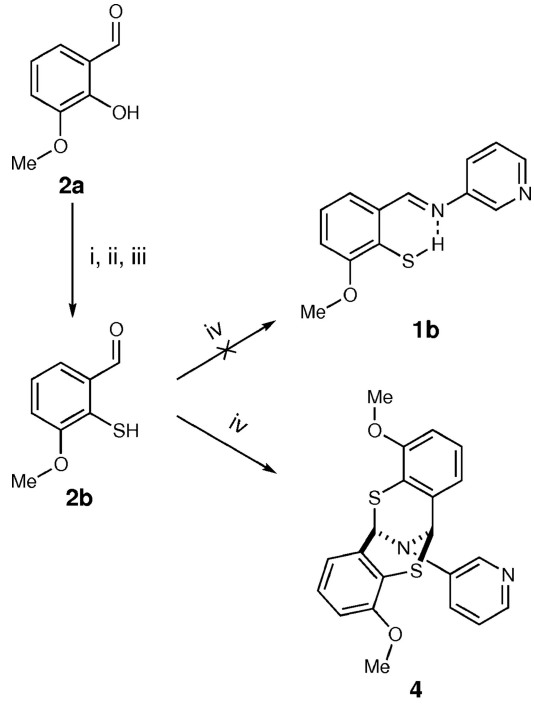
Flash chromatography was performed either on Silica gel 60 Merck (particle size 40–63 µm, 230–400 mesh) or on demetallated silica gel obtained through the protocol described by Hubbard & Harris (1981).

NMR spectra were recorded on a JEOL spectrometer (JNM EX-400). The samples were prepared in deuterated solvents at room temperature. Spectra were analysed with the *Delta* program (Jeol; https://www.jeol.co.jp/en/products/detail/Delta5.html). Chemical shifts (δ) – calibrated from the solvent – are given in ppm. The multiplicities are described as *s* (singlet), *d* (doublet), *t* (triplet) and *m* (multiplet).

LC–MS analysis was performed on an alliance HPLC Waters 2695 coupled with UV–Vis Waters 2489 and Acquity qda Water detectors. The apparatus was equipped with an XBridge C18 3.5 µM 2 ×1 × 50 mm Waters column. A water/acetonitrile mixture was used as solvent (gradient from 90/10 to 20/80). Masses were determined using electron spray ionisation (ESI) in positive mode. The program used was *MassLynx* (Version 4.2; https://www.waters.com/waters/).

Microwave (MW) reactions were performed in 10 ml sealed vials in a CEM Discover focused microwave oven with temperature and pressure monitoring.

Powder X-ray diffraction (PXRD) data were collected on a Stoe MP in transmission mode using Cu $K\alpha_1$ radiation (λ = 1.54060 Å). The data were collected at room temperature from a 4 to 40° 2θ angle. Calculated powder patterns were generated with *Mercury CSD* (Version 3.10.3; Macrae *et al.*, 2020).



(i) DMTCl, DABCO, DMF anh., 72%
(ii) MW, NMP, 58%
(iii) NaOH, 68%
(iv) 3-Aminopyridine, ETOH, reflux, 29%

Scheme 2

2.2. Synthesis and crystallization

2.2.1. *O*-(2-Formyl-6-methoxyphenyl) dimethylcarbamothioate. In an oven-dried round-bottomed two-necked flask, *o*-vanillin, **2a** (5.00 g, 32.9 mmol, 1.0 equiv.), *N*,*N*-dimethylthiocarbamoyl chloride (DMTCl; 12.2 g, 98.6 mmol, 3.0 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO; 11.1 g, 98.6 mmol, 3.0 equiv.) were dissolved in anhydrous *N*,*N*-dimethylformamide (DMF; 53.0 ml). The mixture was heated to 50 °C and stirred for 3 h. The reaction mixture was poured into cooled water, extracted with dichloromethane and washed consecutively with HCl (1 *M*), NaOH (0.1 *M*) and brine. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting crude product was purified by flash column chromatography

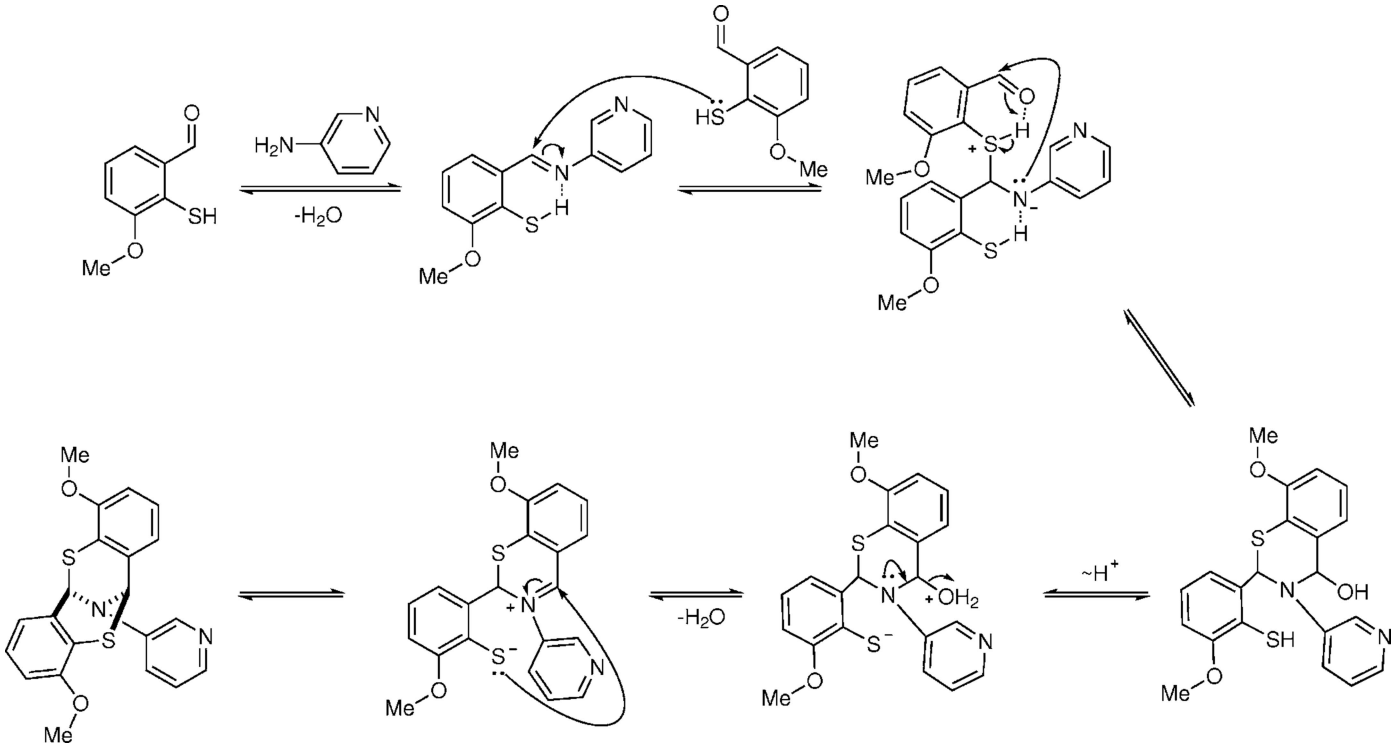


Figure 1
The proposed mechanism for the double condensation of *o*-vanillin and 3-aminopyridine.

over demetallated silica gel, eluting with cyclohexane/ethyl acetate (8:2 *v*/*v*) to yield a pale-yellow powder (yield 5.64 g, 72%). If the purity is not good enough, recrystallization from boiling cyclohexane is an alternative.

^{1}H NMR ($CDCl_3$): δ 3.43 (*s*, 3H, NCH_3), 3.48 (*s*, 3H, NCH_3), 3.86 (*s*, 3H, OCH_3), 7.21 (*dd*, 1H, H_{arom}), 7.34 (*t*, 1H, H_{arom}), 7.50 (*dd*, 1H, H_{arom}), 10.10 [*s*, 1H, H(C═O)].

Spectral data were in agreement with the reference (Stefański *et al.*, 2018).

2.2.2. *S*-(2-Formyl-6-methoxyphenyl) dimethylcarbamothioate. In a sealed 10 ml microwave vial, a solution of *O*-thiocarbamate (130 mg, 0.54 mmol) dissolved in *N*-methyl-2-pyrrolidone (1.2 ml) was irradiated in a microwave oven (power 200 W; temperature 230 °C; ramp time 2 min; time 3 min). The residue was then extracted with ethyl acetate and washed several times with water to remove *N*-methyl-2-pyrrolidone. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting crude product was purified by flash column chromatography over demetallated silica gel, eluting with cyclohexane/ethyl acetate (7:3 *v*/*v*) to yield a yellow–brown solid (yield 68.6 mg, 58%).

^{1}H NMR ($CDCl_3$): δ 3.02 (*s*, 3H, NCH_3), 3.21 (*s*, 3H, NCH_3), 3.92 (*s*, 3H, OCH_3), 7.20 (*dd*, 1H, H_{arom}), 7.53 (*t*, 1H, H_{arom}), 7.63 (*dd*, 1H, H_{arom}), 10.46 [*s*, 1H, H(C═O)].

Spectral data were in agreement with the reference (Stefański *et al.*, 2018).

2.2.3. 2-Mercapto-3-methoxybenzaldehyde, 2b. In a round-bottomed flask containing a solution of *S*-thiocarbamate (550 mg, 2.30 mmol) in methanol (7.8 ml), NaOH (3 *M*, 8.2 ml) was added dropwise at room temperature. The mixture

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{18}N_2O_2S_2{\cdot}0.463CH_4O$
M_r	409.34
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, *b*, *c* (Å)	14.7387 (4), 16.6445 (3), 17.8970 (4)
α, β, γ (°)	84.662 (2), 73.498 (2), 68.886 (2)
V (Å^3)	3926.80 (17)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	2.64
Crystal size (mm)	0.46 × 0.27 × 0.06
Data collection	
Diffractometer	Rigaku Xcalibur Ruby Gemini Ultra
Absorption correction	Analytical [*CrysAlis PRO* (Rigaku OD, 2018), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.414, 0.865
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33207, 13626, 12152
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.598
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.102, 1.03
No. of reflections	13626
No. of parameters	1184
No. of restraints	838
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.34

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *ShelXle* (Hübschle *et al.*, 2011) and *Mercury* (Macrae *et al.*, 2020).

was then heated under reflux and stirred for 2 h. The resulting solution was cooled to room temperature, acidified with H_2SO_4 (3 *M*) to a pH of 5, extracted with ethyl acetate and washed with brine. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting crude product was purified by flash column chromatography over silica gel, eluting with cyclohexane/ethyl acetate (9:1 *v*/*v*) to yield a yellow pasty solid (yield 265 mg, 68%).

^{1}H NMR ($CDCl_3$): δ 3.96 (*s*, 3H, OCH_3), 5.72 (*s*, 1H, SH), 7.06 (*dd*, 1H, H_{arom}), 7.26 (*t*, 1H, H_{arom}), 7.40 (*dd*, 1H, H_{arom}), 10.10 [*s*, 1H, H(C═O)].

Spectral data were in agreement with the reference (Akine *et al.*, 2010).

2.2.4. 4,10-Dimethoxy-13-(pyridin-3-yl)-6*H*,12*H*-6,12-epiminodibenzo[*b*,*f*][1,5]dithiocine, 4. In an oven-dried round-bottomed flask fitted with a condenser, under an argon atmosphere, a solution of thiovanillin, **2b** (81.4 mg, 0.484 mmol, 1.0 equiv.), dissolved in absolute ethanol (1.0 ml) was added to a solution of 3-aminopyridine, **3** (46.2 mg, 0.490 mmol, 1.0 equiv.), dissolved in absolute ethanol (1.0 ml) under an argon atmosphere. The mixture was heated under reflux and stirred for 1 h. The resulting solution was cooled to room temperature and left in a fridge overnight. The precipitate was filtered off and washed with pentane. The resulting crude product was purified by flash column chromatography over silica gel, eluting with cyclohexane/ethyl acetate (3:1 *v*/*v*) to afford a white solid (yield 34.4 mg, 29%). The product, **4**, was crystallized by slow evaporation from methanol, which afforded colourless plates suitable for single-crystal X-ray diffraction analysis (SCXRD).

^{1}H NMR ($CDCl_3$): δ 3.80 (*s*, 6H, OCH_3), 6.15 (*s*, 2H, CH), 6.65 (*dd*, J_1 = 8.0, J_2 = 1.1 Hz, 2H, CH_{arom}), 7.04 (*dd*, J_1 = 7.8, J_2 = 1.1 Hz, 2H, CH_{arom}), 7.10 (*dd*, J_1 = 8.0, J_2 = 7.8 Hz, 2H, CH_{arom}), 7.24 (*m*, 1H, CH_{pyr}), 7.39 (*dd*, J_1 = 8.4, J_2 = 1.7 Hz, 1H, CH_{pyr}), 8.26 (*s*, 1H, CH_{pyr}), 8.48 (*s*, 1H, CH_{pyr}). ^{13}C NMR ($CDCl_3$): δ 56.1, 59.2, 108.9, 119.5, 121.4, 125.2, 126.8, 134.0, 141.5, 143.3, 154.9 LC–MS (ES^+): 395 (*M* + 1).

The batch product was characterized by powder X-ray diffraction (PXRD) and compared to the calculated pattern (see supporting information). The difference between the two patterns is most certainly caused by the solvate, obtained after recrystallization.

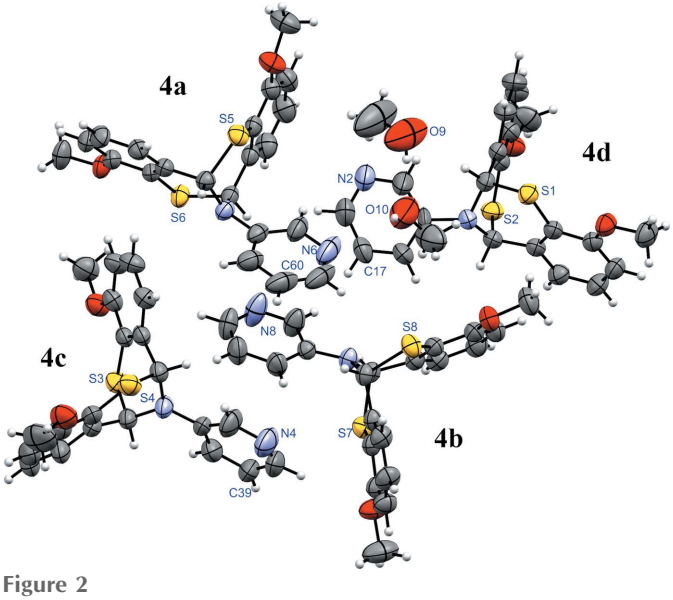


Figure 2
The asymmetric unit of the crystal structure of compound **4**, with displacement ellipsoids drawn at the 50% probability level. Disordered molecules are not shown for clarity. The four molecules in the asymmetric unit are labelled **4a**–**4d**.

2.3. Single-crystal X-ray diffraction (SCXRD)

Crystal data, data collection and structure refinement details are summarized in Table 1. Atoms N4, N6 and N2 were modelled in the same positions as C39, C60 and C17, respectively, because three of the four aminopyridine rings are disordered. In addition, H atoms were fixed for the methanol molecules. The occupancy factors of the two methanol molecules and atom N6 were fixed at the same value because they are involved in the same hydrogen-bond network. Some of the H atoms were localized according to electron-density difference maps and those bonded to disordered atoms were calculated geometrically. All H atoms were refined using a riding model, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.98 Å (tertiary carbon) and O—H = 0.82 Å. The isotropic atomic displacement parameters of the H atoms were set at $1.5U_{eq}$ of the parent atom for the methyl and alcohol groups, and at $1.2U_{eq}$ otherwise.

2.4. Computational details

Full structure optimizations were carried out with *GAUSSIAN16* (Frisch *et al.*, 2016) on the geometries obtained by SCXRD. The density functional theory (DFT) method was selected with exchange-correlation functional M06 (Zhao & Truhlar, 2008) and 6-31G* as basis set. The calculations were done in the gas phase with default parameters and a tight convergence criterion. Frequency calculations were performed on the optimized structure at the same level of approximation. The energies were taken after structure optimization.

3. Results and discussion

3.1. Synthesis

The synthesis of *o*-thiovanillin was achieved in three steps, shown in Scheme 2, and follows closely that reported by Romagnoli *et al.* (2010).

Commercially available *o*-vanillin was treated with *N*,*N*-dimethylthiocarbamoyl chloride (DMTCl) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in *N*,*N*-dimethylformamide (DMF) and gave the desired *O*-thiocarbamate. This reaction was followed by a Newman–Kwart rearrangement with heating under microwave irradiation. Initially, the reaction was performed without solvent (Romagnoli *et al.*, 2010), but with *N*-methyl-2-pyrrolidone (NMP) as solvent, less degradation was observed (Moseley *et al.*, 2006); thus, a better

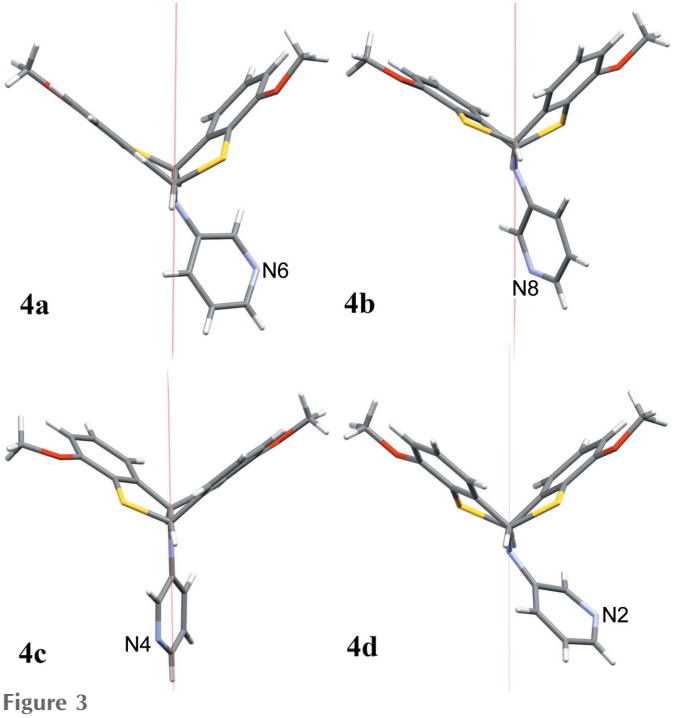


Figure 3
The four molecules (**4a**–**4d**) present in the asymmetric unit (viewed perpendicular to the red plane formed by two C atoms and the N atom of amine).

yield of the corresponding *S*-thiocarbamate was obtained. *o*-Thiovanillin, **2b**, was finally obtained by hydrolysis of the thiocarbamoyl group in the presence of sodium hydroxide.

In order to obtain the desired Schiff base, *i.e.* **1b**, a condensation with 3-aminopyridine in ethanol was performed. Unexpectedly, the reaction led to a double condensation, resulting in compound **4** instead of the desired molecule **1b**. The low yield could probably be caused by the instability of starting material **2b** but could be improved, as the reaction was not optimized since it was an unexpected product not needed for further study. The proposed mechanism is described in Fig. 1, where the key intermediates described by the group of Still can be found (Toste, 1995; Still *et al.*, 1999). The strong intramolecular hydrogen bond with the N atom, which increases the electrophilicity of the imine, leads to an attack and the formation of the first stereogenic centre. At that point, two nucleophilic entities could reversibly attack the benzaldehyde, *i.e.* the thiophenol or the amine. In the case of the amine, a more stable ring (six-membered *versus* eight-membered) is obtained. The last step should be the cyclization of the [3.3.1]bicyclic ring system, which leads to a diastereoselective product.

3.2. Crystal structure analysis

Compound **4** crystallizes in the space group $P\overline{1}$ as plate-like colourless crystals. The crystal data, the data collection and the structure refinement details are summarized in Table 1 and the asymmetric unit of the structure is shown in Fig. 2.

The asymmetric unit contains four molecules as a racemic mixture, where three of the four aminopyridine groups are disordered, and two molecules of methanol. The disorder is caused by two possible conformations of the aminopyridine group, differing by a 180° flip. Occupancy factors are provided in the supporting information.

Table 2
Interactions observed in the crystal structure.

Interaction type	Atoms involved	Distance (Å)	Angle (°)
Hydrogen bond	O9—H9···O10	1.757	166.9
Hydrogen bond	O10—H10*A*···N6	2.105	143.0
Chalcogen bond	C64—S8···S5	3.531	167.0
Chalcogen bond	C14—S2···S3	3.575	175.5
π-stacking	py**4a**···py**4b**	3.555*	4.2**

Notes: (*) distance between centroids; (**) angle between two planes formed by the pyridine rings.

In the case of atoms N2 and N4, the occupancy factors are around 0.5 because there are two possible conformations of the aminopyridine group with similar probability. For N6, the value is close to 1 due to the presence of methanol. Hence, for one of the two conformations, atom N6 is included in a hydrogen bond with one molecule of methanol. Apart from the weak hydrogen bonds presented in Table S1 of the supporting information, the other interactions observed in the crystal structure are summarized in Table 2. Figures highlighting these interactions are provided in the supporting information.

Contacts between pairs of S atoms are observed in the crystal packing as the S···S distance is shorter than the sum of the van der Waals radii. Besides, chalcogen bonds require angles close to 180° (Vogel *et al.*, 2019). This is the case for C14—S2···S3, with an angle of 175°, and to a lesser extent for the second C64—S8···S5 interaction, where the angle is 167°.

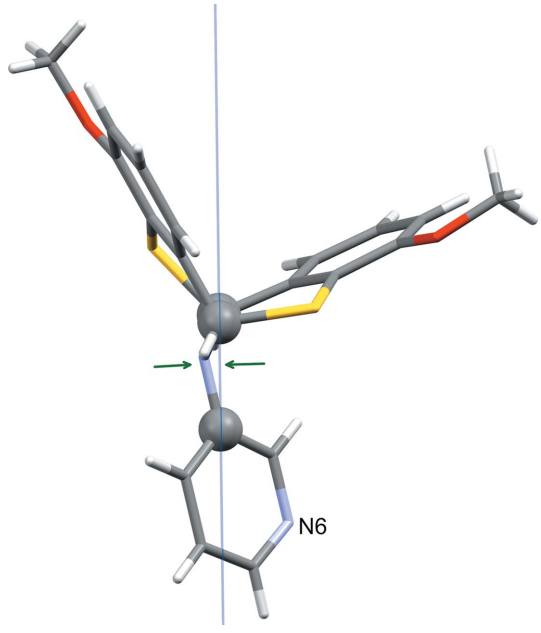


Figure 4
Representation of the deviation distance (in green) between the N atom of the amine group and the plane (in blue) formed by three atoms highlighted with grey balls. The numerical values are reported in Table 3.

3.3. Conformational study

Different geometries of the N atom are observed for the molecules in the asymmetric unit (Fig. 3). Interestingly, only molecule **4c** shows a planar geometry, while molecules **4a**, **4b** and **4d** show a pyramidal one.

Normally, it would be expected that the geometry is planar because of the conjugation of the N-atom electron pair with π orbitals of the pyridine group. Thus, the difference in geometry could be explained by the different interactions present in the crystal packing.

Indeed, as mentioned above (Table 2), π-stacking is observed between molecules **4a** and **4b**, which could constrain the pyridine ring and force the pyramidal geometry. Indeed, other pyramidal N atoms involved in π-stacking for this type of molecule with a V-shaped molecular cleft have been observed (Aslam *et al.*, 2012). The pyramidal N atom in molecule **4d** could be explained by the presence of methanol.

The geometry can be characterized by the deviation distance between the N atom and the plane resulting from the three atoms highlighted in Fig. 4. A structure optimization was performed in order to compare the distances obtained after geometry optimization with those from the crystal structure (Table 3).

For molecules **4a**, **4b** and **4d**, similar deviation distances are observed after geometry optimization, compared with those in the crystal structures (a superposition of these structures is shown in the supporting information). Besides, after optimization, the molecules have converged into the same geometry of the N atom (deviation distance = 0.280 Å).

In contrast, after geometry optimization, molecule **4c** has a deviation distance slightly greater compared to that in the crystal structure. Moreover, after optimization, molecule **4c** appears to converge into a different geometry of the N atom (deviation distance = 0.123 Å), a more planar geometry compared to the other.

Interestingly, these results demonstrate that the four molecules converge into two distinct minima, with a difference in energy of less than 2 kJ mol^{-1}. This supports the presence of two geometries in the crystal structure as they have similar energies. A deeper study of this using more sophisticated computational approaches is now possible but beyond the scope of the present work.

Table 3
Free energy after geometry optimization and comparison of the deviation distance (see Fig. 4 for definition) in the crystal structure and after geometry optimization for the four molecules present in the asymmetric unit.

Molecule	Deviation distance in the crystal structure (Å)	Deviation distance after geometry optimization (Å)	ΔE after geometry optimization (kJ mol^{-1})
4a, **4b**, **4d**	0.304, 0.208, 0.329	0.280	0
4c	0.007	0.123	1.9

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References

Akine, S., Akimoto, A. & Nabeshima, T. (2010). *Phosphorus Sulfur Silicon*, **185**, 1000–1007.
Aslam, M., Anis, I., Afza, N., Ibrahim, M. & Yousuf, S. (2012). *Acta Cryst.* E**68**, o440.
Brieaddy, L. E. & Donaldson, K. H. (1995). *J. Heterocycl. Chem.* **32**, 1683–1686.
Carletta, A., Buol, X., Leyssens, T., Champagne, B. & Wouters, J. (2016). *J. Phys. Chem. C*, **120**, 10001–10008.
Carletta, A., Dubois, J., Tilborg, A. & Wouters, J. (2015). *CrystEngComm*, **17**, 3509–3518.
Carletta, A., Zbačnik, M., Van Gysel, M., Vitković, M., Tumanov, N., Stilinović, V., Wouters, J. & Cinčić, D. (2018). *Cryst. Growth Des.* **18**, 6833–6842.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Dai, Y., Weng, J., George, J., Chen, H., Lin, Q., Wang, J., Royzen, M. & Zhang, Q. (2019). *Org. Lett.* **21**, 3828–3833.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Frisch, M. J., *et al.* (2016). *GAUSSIAN16*. Revision A.3. Gaussian Inc., Wallingford, CT, USA. http://www.gaussian.com.
Hubbard, J. S. & Harris, T. M. (1981). *J. Org. Chem.* **46**, 2566–2570.
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.
Hutchins, K. M., Dutta, S., Loren, B. & MacGillivray, L. R. (2014). *Chem. Mater.* **26**, 3042–3044.
Jacquemin, P.-L., Robeyns, K., Devillers, M. & Garcia, Y. (2015). *Chem. Eur. J.* **21**, 6832–6845.
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.
Moseley, J. D., Sankey, R. F., Tang, O. N. & Gilday, J. P. (2006). *Tetrahedron*, **62**, 4685–4689.
Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Romagnoli, R., Baraldi, P. G., Carrion, M. D., Cruz-Lopez, O., Tolomeo, M., Grimaudo, S., Di Cristina, A., Pipitone, M. R., Balzarini, J., Brancale, A. & Hamel, E. (2010). *Bioorg. Med. Chem.* **18**, 5114–5122.
Scilabra, P., Terraneo, G. & Resnati, G. (2019). *Acc. Chem. Res.* **52**, 1313–1324.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Stefański, T., Mikstacka, R., Kurczab, R., Dutkiewicz, Z., Kucińska, M., Murias, M., Zielińska-Przyjemska, M., Cichocki, M., Teubert, A., Kaczmarek, M., Hogendorf, A. & Sobiak, S. (2018). *Eur. J. Med. Chem.* **144**, 797–816.
Still, I. W. J., Natividad-Preyra, R. & Toste, F. D. (1999). *Can. J. Chem.* **77**, 113–121.
Toste, F. D. (1995). *Tetrahedron Lett.* **36**, 6619–6622.
Vogel, L., Wonner, P. & Huber, S. M. (2019). *Angew. Chem. Int. Ed.* **58**, 1880–1891.
Zhao, Y. & Truhlar, D. G. (2008). *Theor. Chem. Acc.* **120**, 215–241.

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Synthesis, crystal structure and conformational analysis of an unexpected [1,5]dithiocine product of aminopyridine and thiovanillin

Kalina Mambourg, Laurie Bodart, Nikolay Tumanov, Steve Lanners and Johan Wouters

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009) and ShelXle (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015b).

4,10-Dimethoxy-13-(pyridin-3-yl)-6*H*,12*H*-6,12-epiminodibenzo[*b*,*f*][1,5]dithiocine methanol 0.463-solvate

Crystal data

$C_{21}H_{18}N_2O_2S_2 \cdot 0.463CH_4O$
$M_r = 409.34$
Triclinic, $P\overline{1}$
$a = 14.7387$ (4) Å
$b = 16.6445$ (3) Å
$c = 17.8970$ (4) Å
$\alpha = 84.662$ (2)°
$\beta = 73.498$ (2)°
$\gamma = 68.886$ (2)°
$V = 3926.80$ (17) Å^3
$Z = 8$
$F(000) = 1715$
$D_x = 1.385$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 18138 reflections
$\theta = 2.8$–$67.0°$
$\mu = 2.64$ mm^{-1}
$T = 295$ K
Plate, colourless
0.46 × 0.27 × 0.06 mm

Data collection

Rigaku Xcalibur Ruby Gemini Ultra diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance Ultra (Cu) X-ray Source
Detector resolution: 5.1856 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2018), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.414$, $T_{max} = 0.865$
33207 measured reflections
13626 independent reflections
12152 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 67.1°$, $\theta_{min} = 2.6°$
$h = -17 \rightarrow 16$
$k = -19 \rightarrow 17$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.03$
13626 reflections
1184 parameters
838 restraints
Primary atom site location: dual
Secondary atom site location: dual
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.8423P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

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

Refinement. A crystal of suitable size was mounted on an Oxford Diffraction Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Cu *Kα* (λ = 1.54184 Å). The data were collected at room temperature. Analytical absorption correction was performed on SCXRD data using *CrysAlis PRO* 1.171.40.16b (Rigaku, 2018). Analytical numeric absorption correction used a multifaceted crystal model based on expressions derived by R.C. Clark and J.S. Reid. (Clark *et al.*, 1995). Empirical absorption correction used spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved over $|F|^2$ using SHELXT (Sheldrick, 2015a) and then refined using SHELXL-2016/6 (Sheldrick, 2015b) within Olex2 (Dolomanov *et al.*, 2009) and ShelXle (Hubschle *et al.*, 2011).

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C64	0.08042 (14)	0.55515 (11)	0.75957 (10)	0.0463 (4)	
C65	0.09081 (15)	0.51419 (12)	0.83084 (10)	0.0511 (4)	
C66	0.02928 (16)	0.46910 (12)	0.86924 (11)	0.0574 (5)	
H66	0.037246	0.441494	0.915802	0.069*	
C67	−0.04446 (16)	0.46549 (13)	0.83752 (12)	0.0582 (5)	
H67	−0.087168	0.436143	0.863603	0.070*	
C68	−0.05554 (15)	0.50463 (12)	0.76803 (11)	0.0526 (4)	
H68	−0.105910	0.501757	0.747856	0.063*	
C69	0.00802 (13)	0.54882 (11)	0.72715 (10)	0.0450 (4)	
C70	−0.00116 (13)	0.58184 (11)	0.64687 (10)	0.0458 (4)	
H70	−0.004343	0.534895	0.619648	0.055*	
C71	0.10757 (13)	0.66314 (11)	0.63837 (10)	0.0453 (4)	
H71	0.159047	0.680088	0.599293	0.054*	
C72	0.01953 (14)	0.74484 (11)	0.66779 (10)	0.0454 (4)	
C73	0.04123 (16)	0.81288 (13)	0.69039 (11)	0.0552 (4)	
H73	0.107440	0.805774	0.688343	0.066*	
C74	−0.03465 (17)	0.88987 (14)	0.71552 (13)	0.0638 (5)	
H74	−0.019672	0.934065	0.731581	0.077*	
C75	−0.13350 (17)	0.90235 (13)	0.71717 (12)	0.0610 (5)	
H75	−0.184364	0.955144	0.732878	0.073*	
C76	−0.15560 (15)	0.83583 (12)	0.69533 (11)	0.0528 (4)	
C77	−0.07977 (14)	0.75541 (11)	0.67222 (10)	0.0464 (4)	
N7	0.08640 (11)	0.60072 (10)	0.60150 (8)	0.0475 (3)	
C78	0.11464 (13)	0.59155 (11)	0.51981 (10)	0.0447 (4)	
C79	0.13717 (19)	0.65327 (14)	0.46891 (12)	0.0648 (5)	
H79	0.129250	0.706458	0.487404	0.078*	
C80	0.1718 (2)	0.63497 (17)	0.38985 (12)	0.0755 (6)	
H80	0.188707	0.675518	0.354788	0.091*	
C81	0.1810 (2)	0.55816 (18)	0.36362 (12)	0.0747 (7)	

H81	0.203890	0.547246	0.310232	0.090*	
N8	0.1588 (2)	0.49789 (15)	0.41064 (11)	0.0880 (7)	
C82	0.1272 (2)	0.51496 (15)	0.48697 (12)	0.0710 (6)	
H82	0.112719	0.472366	0.520444	0.085*	
C83	−0.3312 (2)	0.91837 (19)	0.7212 (2)	0.0990 (10)	
H83A	−0.322271	0.964111	0.686469	0.149*	
H83B	−0.332718	0.932009	0.772619	0.149*	
H83C	−0.393688	0.911676	0.722560	0.149*	
C84	0.1859 (2)	0.48126 (18)	0.92531 (14)	0.0795 (7)	
H84A	0.204247	0.420287	0.919109	0.119*	
H84B	0.126588	0.501967	0.968095	0.119*	
H84C	0.240439	0.493004	0.935602	0.119*	
S5	0.65327 (3)	0.28897 (3)	0.32598 (3)	0.05113 (11)	
S6	0.40368 (3)	0.31152 (3)	0.23192 (2)	0.05010 (11)	
O5	0.74023 (12)	0.11954 (10)	0.36693 (10)	0.0697 (4)	
O6	0.47293 (10)	0.26822 (9)	0.07428 (7)	0.0538 (3)	
C43	0.58723 (14)	0.21625 (12)	0.35064 (9)	0.0472 (4)	
C44	0.64160 (15)	0.13350 (13)	0.37211 (11)	0.0547 (4)	
C45	0.59500 (19)	0.07344 (15)	0.39721 (13)	0.0667 (5)	
H45	0.631197	0.018676	0.411528	0.080*	
C46	0.4940 (2)	0.09562 (17)	0.40082 (14)	0.0743 (6)	
H46	0.462010	0.055796	0.418774	0.089*	
C47	0.44040 (17)	0.17546 (15)	0.37833 (13)	0.0645 (5)	
H47	0.372813	0.188846	0.380275	0.077*	
C48	0.48625 (14)	0.23688 (12)	0.35254 (10)	0.0492 (4)	
C49	0.42334 (13)	0.32295 (12)	0.32661 (10)	0.0487 (4)	
H49	0.356748	0.339943	0.364482	0.058*	
C50	0.56447 (13)	0.37215 (11)	0.27850 (10)	0.0460 (4)	
H50	0.580615	0.424716	0.275894	0.055*	
C51	0.58390 (13)	0.34496 (11)	0.19586 (10)	0.0430 (4)	
C52	0.51862 (12)	0.31686 (11)	0.17141 (9)	0.0422 (4)	
C53	0.54267 (13)	0.29329 (11)	0.09295 (10)	0.0450 (4)	
C54	0.63047 (15)	0.29682 (13)	0.04036 (10)	0.0543 (4)	
H54	0.646506	0.280161	−0.011329	0.065*	
C55	0.69404 (15)	0.32543 (14)	0.06568 (11)	0.0575 (5)	
H55	0.752688	0.328659	0.030461	0.069*	
C56	0.67177 (14)	0.34915 (12)	0.14208 (11)	0.0511 (4)	
H56	0.715437	0.368113	0.158142	0.061*	
C62	0.4914 (2)	0.24535 (17)	−0.00487 (12)	0.0712 (6)	
H62A	0.499768	0.292434	−0.037951	0.107*	
H62B	0.435243	0.232698	−0.010877	0.107*	
H62C	0.551666	0.195519	−0.019087	0.107*	
C63	0.8038 (2)	0.03451 (17)	0.37855 (19)	0.0895 (8)	
H63A	0.801031	−0.004582	0.343779	0.134*	
H63B	0.781318	0.017896	0.431438	0.134*	
H63C	0.872056	0.032860	0.368260	0.134*	
N5	0.46035 (11)	0.39317 (10)	0.32316 (8)	0.0494 (3)	
C58	0.4293 (4)	0.4427 (2)	0.3925 (2)	0.0570 (9)	0.927 (3)

C59	0.4258 (3)	0.5261 (2)	0.3878 (2)	0.0748 (10)	0.927 (3)
H59	0.443452	0.550414	0.339409	0.090*	0.927 (3)
C60	0.3962 (3)	0.5741 (3)	0.4545 (3)	0.0966 (12)	0.927 (3)
H60	0.394054	0.630812	0.451940	0.116*	0.927 (3)
C61	0.3701 (3)	0.5368 (3)	0.5244 (2)	0.1037 (15)	0.927 (3)
H61	0.350115	0.569470	0.569488	0.124*	0.927 (3)
N6	0.3717 (2)	0.4559 (3)	0.53177 (16)	0.1016 (11)	0.927 (3)
C57	0.4013 (3)	0.4097 (3)	0.46604 (19)	0.0755 (10)	0.927 (3)
H57	0.403127	0.353044	0.469972	0.091*	0.927 (3)
C58A	0.450 (5)	0.446 (2)	0.389 (3)	0.052 (8)	0.073 (3)
C57A	0.460 (2)	0.5261 (16)	0.3681 (16)	0.047 (6)	0.073 (3)
H57A	0.486258	0.537772	0.316202	0.056*	0.073 (3)
N6A	0.433 (2)	0.5854 (16)	0.4228 (15)	0.061 (6)	0.073 (3)
C61A	0.384 (4)	0.570 (3)	0.4935 (17)	0.067 (7)	0.073 (3)
H61A	0.366828	0.611919	0.531351	0.081*	0.073 (3)
C60A	0.357 (3)	0.500 (2)	0.5171 (19)	0.068 (7)	0.073 (3)
H60A	0.320390	0.494027	0.567740	0.082*	0.073 (3)
C59A	0.387 (4)	0.438 (2)	0.460 (2)	0.061 (7)	0.073 (3)
H59A	0.365892	0.391251	0.469463	0.074*	0.073 (3)
S1	0.29790 (3)	0.22144 (3)	0.88911 (3)	0.05261 (11)	
S2	0.08595 (3)	0.13094 (3)	0.82255 (3)	0.05333 (12)	
O1	0.13071 (12)	−0.04312 (9)	0.83753 (10)	0.0679 (4)	
O2	0.23369 (10)	0.27155 (9)	1.04579 (8)	0.0596 (3)	
C1	0.17205 (13)	0.24770 (11)	0.94654 (10)	0.0457 (4)	
C2	0.15205 (14)	0.26946 (11)	1.02509 (10)	0.0489 (4)	
C3	0.05649 (16)	0.28763 (13)	1.07494 (11)	0.0571 (5)	
H3	0.044041	0.300911	1.127072	0.069*	
C4	−0.02084 (16)	0.28580 (14)	1.04622 (12)	0.0592 (5)	
H4	−0.085318	0.297210	1.079613	0.071*	
C5	−0.00336 (15)	0.26736 (12)	0.96908 (11)	0.0533 (4)	
H5	−0.056293	0.267326	0.950607	0.064*	
C6	0.09320 (13)	0.24866 (10)	0.91814 (10)	0.0447 (4)	
C7	0.10471 (13)	0.23246 (11)	0.83375 (10)	0.0468 (4)	
H7	0.050073	0.278954	0.818375	0.056*	
C8	0.28639 (14)	0.17615 (12)	0.80390 (10)	0.0498 (4)	
H8	0.345608	0.175048	0.761084	0.060*	
C9	0.29041 (14)	0.08360 (12)	0.81643 (10)	0.0487 (4)	
C10	0.38256 (15)	0.01951 (14)	0.81800 (12)	0.0607 (5)	
H10	0.438692	0.034613	0.813897	0.073*	
C11	0.39092 (17)	−0.06595 (14)	0.82557 (13)	0.0685 (6)	
H11	0.452768	−0.107831	0.826370	0.082*	
C12	0.30878 (17)	−0.09012 (13)	0.83199 (12)	0.0639 (5)	
H12	0.315318	−0.147930	0.836656	0.077*	
C13	0.21729 (16)	−0.02812 (12)	0.83142 (11)	0.0548 (4)	
C14	0.20750 (14)	0.05929 (11)	0.82362 (10)	0.0476 (4)	
C20	0.1297 (2)	−0.12809 (15)	0.85624 (18)	0.0842 (7)	
H20A	0.149385	−0.145938	0.903599	0.126*	
H20B	0.176160	−0.166966	0.814689	0.126*	

H20C	0.062889	−0.128516	0.863009	0.126*	
C21	0.2196 (2)	0.28976 (17)	1.12571 (13)	0.0749 (6)	
H21A	0.196715	0.247822	1.158202	0.112*	
H21B	0.170133	0.346187	1.139396	0.112*	
H21C	0.282451	0.287482	1.133160	0.112*	
N1	0.19848 (12)	0.23498 (10)	0.78101 (8)	0.0503 (3)	
C15	0.1964 (9)	0.2295 (8)	0.7014 (6)	0.049 (2)	0.565 (19)
C16	0.1250 (8)	0.2907 (7)	0.6706 (5)	0.068 (2)	0.565 (19)
H16	0.073597	0.334462	0.702519	0.082*	0.565 (19)
C17	0.1290 (6)	0.2879 (6)	0.5927 (4)	0.0727 (17)	0.565 (19)
H17	0.081151	0.329563	0.571950	0.087*	0.565 (19)
C18	0.2047 (5)	0.2225 (7)	0.5467 (3)	0.080 (2)	0.565 (19)
H18	0.207210	0.220860	0.494315	0.096*	0.565 (19)
N2	0.2749 (6)	0.1612 (6)	0.5736 (4)	0.080 (2)	0.565 (19)
C19	0.2696 (10)	0.1664 (8)	0.6492 (6)	0.0645 (19)	0.565 (19)
H19	0.318842	0.124247	0.668274	0.077*	0.565 (19)
C15A	0.2092 (13)	0.2456 (10)	0.6998 (7)	0.051 (3)	0.435 (19)
C16A	0.2788 (14)	0.1856 (11)	0.6454 (8)	0.080 (5)	0.435 (19)
H16A	0.326375	0.137337	0.660018	0.096*	0.435 (19)
C17A	0.2772 (11)	0.1982 (12)	0.5685 (7)	0.101 (4)	0.435 (19)
H17A	0.323737	0.159233	0.529757	0.121*	0.435 (19)
C18A	0.2042 (9)	0.2705 (13)	0.5513 (5)	0.101 (4)	0.435 (19)
H18A	0.203024	0.279209	0.499397	0.121*	0.435 (19)
N2A	0.1360 (8)	0.3280 (11)	0.6026 (5)	0.113 (5)	0.435 (19)
C19A	0.1387 (12)	0.3153 (11)	0.6765 (6)	0.085 (4)	0.435 (19)
H19A	0.091031	0.355333	0.713946	0.102*	0.435 (19)
S7	−0.11929 (3)	0.67424 (3)	0.65003 (3)	0.05137 (11)	
S8	0.16431 (4)	0.61018 (3)	0.71764 (3)	0.05265 (12)	
O7	0.16600 (11)	0.52340 (9)	0.85602 (8)	0.0611 (3)	
O8	−0.24999 (11)	0.84059 (10)	0.69471 (10)	0.0689 (4)	
S3	0.16816 (4)	0.73602 (3)	0.17146 (3)	0.05830 (13)	
S4	0.36065 (4)	0.87559 (3)	0.20142 (3)	0.05927 (13)	
O3	0.27865 (11)	0.56991 (9)	0.11139 (9)	0.0636 (3)	
O4	0.38711 (14)	0.99543 (10)	0.08896 (11)	0.0809 (5)	
C22	0.29443 (13)	0.67976 (11)	0.17353 (10)	0.0472 (4)	
C23	0.34053 (15)	0.59696 (12)	0.13919 (11)	0.0531 (4)	
C24	0.43987 (16)	0.54959 (13)	0.13520 (13)	0.0618 (5)	
H24	0.470126	0.495236	0.111905	0.074*	
C25	0.49446 (16)	0.58373 (13)	0.16627 (14)	0.0640 (5)	
H25	0.561941	0.552286	0.163125	0.077*	
C26	0.45007 (15)	0.66329 (13)	0.20156 (12)	0.0559 (4)	
H26	0.487715	0.684982	0.222437	0.067*	
C27	0.34923 (14)	0.71222 (12)	0.20662 (10)	0.0480 (4)	
C28	0.30499 (14)	0.79599 (13)	0.25160 (10)	0.0524 (4)	
H28	0.323617	0.783331	0.300919	0.063*	
C29	0.15567 (15)	0.84168 (13)	0.20586 (10)	0.0548 (4)	
H29	0.083078	0.873514	0.225135	0.066*	
C30	0.19693 (15)	0.89597 (13)	0.14223 (10)	0.0560 (5)	

C31	0.28102 (16)	0.91649 (12)	0.13911 (11)	0.0558 (5)	
C32	0.30480 (18)	0.97772 (14)	0.08506 (13)	0.0674 (6)	
C33	0.2477 (2)	1.01518 (17)	0.03347 (14)	0.0821 (7)	
H33	0.264183	1.055369	−0.002290	0.098*	
C34	0.1664 (2)	0.99236 (19)	0.03563 (14)	0.0871 (8)	
H34	0.128298	1.016764	0.000480	0.104*	
C35	0.14022 (19)	0.93385 (17)	0.08904 (12)	0.0731 (6)	
H35	0.084601	0.919424	0.089789	0.088*	
C41	0.4012 (3)	1.07159 (18)	0.0513 (2)	0.1141 (12)	
H41A	0.340842	1.120438	0.069477	0.171*	
H41B	0.415551	1.065343	−0.004017	0.171*	
H41C	0.456626	1.080006	0.063391	0.171*	
C42	0.3207 (2)	0.48624 (15)	0.07724 (16)	0.0769 (6)	
H42A	0.346186	0.444714	0.114036	0.115*	
H42B	0.374792	0.484398	0.031580	0.115*	
H42C	0.269447	0.473076	0.063018	0.115*	
N3	0.19655 (12)	0.83109 (12)	0.27132 (9)	0.0601 (4)	
C36	0.1396 (13)	0.8510 (19)	0.3493 (7)	0.054 (3)	0.57 (2)
C40	0.0396 (11)	0.8587 (15)	0.3744 (8)	0.072 (3)	0.57 (2)
H40	0.009405	0.847659	0.339235	0.087*	0.57 (2)
C39	−0.0178 (13)	0.8822 (17)	0.4503 (10)	0.084 (4)	0.57 (2)
H39	−0.085971	0.888941	0.467071	0.100*	0.57 (2)
C38	0.0325 (14)	0.8946 (17)	0.4982 (7)	0.091 (4)	0.57 (2)
H38	−0.002111	0.906415	0.550511	0.109*	0.57 (2)
N4	0.1265 (12)	0.8912 (12)	0.4762 (7)	0.107 (4)	0.57 (2)
C37	0.1816 (12)	0.8694 (12)	0.4033 (7)	0.084 (3)	0.57 (2)
H37	0.248561	0.866306	0.388318	0.101*	0.57 (2)
C36A	0.1322 (17)	0.855 (2)	0.3447 (10)	0.047 (3)	0.43 (2)
C37A	0.0333 (11)	0.8536 (17)	0.3654 (9)	0.055 (3)	0.43 (2)
H37A	0.007685	0.841030	0.327907	0.066*	0.43 (2)
N4A	−0.0234 (13)	0.8699 (18)	0.4387 (9)	0.073 (3)	0.43 (2)
C38A	0.0112 (15)	0.8852 (19)	0.4940 (10)	0.072 (3)	0.43 (2)
H38A	−0.032060	0.897735	0.544033	0.086*	0.43 (2)
C39A	0.1080 (16)	0.8837 (15)	0.4813 (9)	0.071 (3)	0.43 (2)
H39A	0.133258	0.891089	0.521289	0.085*	0.43 (2)
C40A	0.1650 (14)	0.8703 (13)	0.4052 (9)	0.063 (3)	0.43 (2)
H40A	0.230167	0.871283	0.393579	0.075*	0.43 (2)
O10	0.4006 (3)	0.3545 (3)	0.66304 (18)	0.1835 (19)	0.927 (3)
H10A	0.381772	0.366617	0.623160	0.275*	0.927 (3)
C86	0.3265 (3)	0.3825 (3)	0.7211 (2)	0.1127 (13)	0.927 (3)
H86A	0.265708	0.387530	0.708254	0.169*	0.927 (3)
H86B	0.322173	0.438001	0.735884	0.169*	0.927 (3)
H86C	0.334799	0.343374	0.763623	0.169*	0.927 (3)
O9	0.5502 (3)	0.2112 (3)	0.6408 (2)	0.248 (3)	0.927 (3)
H9	0.496918	0.252311	0.650218	0.372*	0.927 (3)
C85	0.5579 (4)	0.1672 (5)	0.5778 (4)	0.209 (4)	0.927 (3)
H85A	0.599446	0.184440	0.532174	0.314*	0.927 (3)
H85B	0.491928	0.179559	0.571032	0.314*	0.927 (3)

H85C	0.587940	0.106547	0.585531	0.314*	0.927 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C64	0.0489 (9)	0.0441 (9)	0.0434 (9)	−0.0150 (7)	−0.0098 (7)	−0.0009 (7)
C65	0.0563 (11)	0.0470 (10)	0.0459 (9)	−0.0143 (8)	−0.0123 (8)	−0.0008 (7)
C66	0.0654 (12)	0.0508 (11)	0.0482 (10)	−0.0171 (9)	−0.0090 (9)	0.0053 (8)
C67	0.0603 (12)	0.0522 (11)	0.0569 (11)	−0.0237 (9)	−0.0034 (9)	0.0022 (8)
C68	0.0531 (10)	0.0502 (10)	0.0542 (10)	−0.0212 (8)	−0.0088 (8)	−0.0032 (8)
C69	0.0452 (9)	0.0423 (9)	0.0446 (9)	−0.0147 (7)	−0.0074 (7)	−0.0040 (7)
C70	0.0488 (9)	0.0477 (9)	0.0443 (9)	−0.0209 (8)	−0.0111 (7)	−0.0032 (7)
C71	0.0490 (9)	0.0518 (10)	0.0397 (8)	−0.0229 (8)	−0.0119 (7)	0.0001 (7)
C72	0.0534 (10)	0.0493 (9)	0.0391 (8)	−0.0221 (8)	−0.0157 (7)	0.0007 (7)
C73	0.0579 (11)	0.0592 (11)	0.0576 (11)	−0.0258 (9)	−0.0202 (9)	−0.0057 (8)
C74	0.0727 (14)	0.0567 (12)	0.0695 (13)	−0.0272 (10)	−0.0202 (11)	−0.0134 (9)
C75	0.0628 (12)	0.0533 (11)	0.0639 (12)	−0.0149 (9)	−0.0159 (10)	−0.0116 (9)
C76	0.0529 (11)	0.0554 (11)	0.0513 (10)	−0.0185 (9)	−0.0154 (8)	−0.0033 (8)
C77	0.0520 (10)	0.0498 (10)	0.0416 (9)	−0.0204 (8)	−0.0153 (7)	−0.0001 (7)
N7	0.0528 (8)	0.0546 (8)	0.0400 (7)	−0.0263 (7)	−0.0089 (6)	−0.0039 (6)
C78	0.0434 (9)	0.0494 (9)	0.0412 (8)	−0.0139 (7)	−0.0142 (7)	−0.0005 (7)
C79	0.0895 (16)	0.0530 (11)	0.0506 (11)	−0.0250 (11)	−0.0184 (10)	0.0051 (9)
C80	0.1017 (18)	0.0828 (16)	0.0465 (11)	−0.0411 (14)	−0.0191 (11)	0.0123 (10)
C81	0.0873 (16)	0.1109 (19)	0.0417 (10)	−0.0549 (15)	−0.0124 (10)	−0.0071 (11)
N8	0.1224 (19)	0.1004 (15)	0.0554 (11)	−0.0683 (15)	−0.0002 (11)	−0.0226 (10)
C82	0.0988 (17)	0.0679 (13)	0.0518 (11)	−0.0460 (13)	−0.0037 (11)	−0.0086 (9)
C83	0.0603 (15)	0.0874 (19)	0.141 (3)	−0.0016 (13)	−0.0319 (16)	−0.0450 (18)
C84	0.0902 (17)	0.0949 (18)	0.0597 (13)	−0.0319 (14)	−0.0368 (12)	0.0209 (12)
S5	0.0480 (2)	0.0589 (3)	0.0517 (2)	−0.0191 (2)	−0.02117 (19)	0.00163 (19)
S6	0.0435 (2)	0.0713 (3)	0.0375 (2)	−0.0216 (2)	−0.01090 (17)	−0.00263 (18)
O5	0.0623 (9)	0.0635 (9)	0.0868 (11)	−0.0152 (7)	−0.0372 (8)	0.0104 (7)
O6	0.0597 (8)	0.0674 (8)	0.0379 (6)	−0.0242 (6)	−0.0140 (5)	−0.0052 (5)
C43	0.0511 (10)	0.0578 (10)	0.0355 (8)	−0.0198 (8)	−0.0137 (7)	−0.0023 (7)
C44	0.0583 (11)	0.0594 (11)	0.0489 (10)	−0.0181 (9)	−0.0213 (8)	0.0002 (8)
C45	0.0807 (15)	0.0607 (12)	0.0645 (13)	−0.0265 (11)	−0.0289 (11)	0.0101 (10)
C46	0.0831 (16)	0.0782 (15)	0.0735 (14)	−0.0437 (13)	−0.0238 (12)	0.0161 (12)
C47	0.0590 (12)	0.0808 (15)	0.0593 (12)	−0.0334 (11)	−0.0144 (9)	0.0056 (10)
C48	0.0492 (10)	0.0634 (11)	0.0348 (8)	−0.0197 (8)	−0.0098 (7)	−0.0028 (7)
C49	0.0402 (9)	0.0663 (11)	0.0352 (8)	−0.0156 (8)	−0.0055 (7)	−0.0058 (7)
C50	0.0459 (9)	0.0472 (9)	0.0444 (9)	−0.0133 (7)	−0.0139 (7)	−0.0035 (7)
C51	0.0427 (9)	0.0411 (9)	0.0420 (8)	−0.0098 (7)	−0.0129 (7)	0.0004 (6)
C52	0.0406 (8)	0.0436 (9)	0.0370 (8)	−0.0089 (7)	−0.0100 (7)	0.0007 (6)
C53	0.0475 (9)	0.0450 (9)	0.0391 (8)	−0.0115 (7)	−0.0129 (7)	0.0003 (7)
C54	0.0553 (11)	0.0641 (11)	0.0357 (8)	−0.0152 (9)	−0.0079 (8)	0.0010 (8)
C55	0.0459 (10)	0.0722 (13)	0.0469 (10)	−0.0190 (9)	−0.0054 (8)	0.0071 (9)
C56	0.0447 (9)	0.0563 (11)	0.0512 (10)	−0.0175 (8)	−0.0124 (8)	0.0039 (8)
C62	0.0939 (17)	0.0881 (16)	0.0422 (10)	−0.0439 (13)	−0.0157 (10)	−0.0085 (10)
C63	0.0762 (16)	0.0721 (16)	0.115 (2)	−0.0106 (13)	−0.0446 (16)	0.0199 (14)

N5	0.0456 (8)	0.0568 (9)	0.0408 (7)	−0.0108 (7)	−0.0098 (6)	−0.0109 (6)
C58	0.042 (2)	0.0719 (16)	0.0508 (15)	−0.0035 (12)	−0.0173 (12)	−0.0201 (12)
C59	0.064 (2)	0.0718 (18)	0.080 (2)	−0.0018 (14)	−0.0265 (16)	−0.0256 (14)
C60	0.072 (3)	0.095 (2)	0.113 (3)	0.0091 (17)	−0.040 (3)	−0.057 (2)
C61	0.055 (2)	0.142 (4)	0.092 (2)	0.013 (2)	−0.0263 (19)	−0.072 (2)
N6	0.0713 (17)	0.156 (3)	0.0582 (14)	−0.010 (2)	−0.0139 (12)	−0.0437 (17)
C57	0.063 (2)	0.106 (2)	0.0453 (13)	−0.012 (2)	−0.0112 (12)	−0.0220 (15)
C58A	0.033 (15)	0.057 (10)	0.055 (11)	0.004 (9)	−0.011 (10)	−0.034 (9)
C57A	0.032 (13)	0.052 (9)	0.058 (11)	0.002 (9)	−0.023 (9)	−0.041 (8)
N6A	0.039 (12)	0.069 (10)	0.071 (11)	0.000 (9)	−0.017 (9)	−0.054 (9)
C61A	0.048 (12)	0.089 (12)	0.070 (11)	−0.015 (10)	−0.019 (11)	−0.056 (11)
C60A	0.041 (12)	0.094 (12)	0.068 (11)	−0.014 (11)	−0.009 (10)	−0.049 (10)
C59A	0.046 (12)	0.078 (12)	0.058 (11)	−0.012 (11)	−0.014 (9)	−0.032 (9)
S1	0.0466 (2)	0.0613 (3)	0.0469 (2)	−0.0161 (2)	−0.01069 (18)	−0.00248 (19)
S2	0.0484 (2)	0.0488 (2)	0.0601 (3)	−0.00791 (19)	−0.0207 (2)	−0.00444 (19)
O1	0.0693 (9)	0.0505 (8)	0.0843 (10)	−0.0185 (7)	−0.0246 (8)	0.0015 (7)
O2	0.0588 (8)	0.0713 (9)	0.0488 (7)	−0.0191 (7)	−0.0164 (6)	−0.0093 (6)
C1	0.0487 (9)	0.0397 (9)	0.0430 (9)	−0.0109 (7)	−0.0098 (7)	0.0016 (7)
C2	0.0531 (10)	0.0441 (9)	0.0471 (9)	−0.0131 (8)	−0.0146 (8)	−0.0007 (7)
C3	0.0618 (12)	0.0588 (11)	0.0439 (9)	−0.0171 (9)	−0.0063 (8)	−0.0086 (8)
C4	0.0511 (11)	0.0661 (12)	0.0516 (11)	−0.0184 (9)	−0.0008 (8)	−0.0074 (9)
C5	0.0475 (10)	0.0553 (11)	0.0530 (10)	−0.0147 (8)	−0.0105 (8)	−0.0024 (8)
C6	0.0475 (9)	0.0378 (8)	0.0437 (9)	−0.0095 (7)	−0.0120 (7)	0.0021 (7)
C7	0.0457 (9)	0.0431 (9)	0.0438 (9)	−0.0060 (7)	−0.0135 (7)	0.0019 (7)
C8	0.0458 (9)	0.0561 (10)	0.0398 (9)	−0.0115 (8)	−0.0086 (7)	0.0016 (7)
C9	0.0473 (10)	0.0506 (10)	0.0376 (8)	−0.0051 (8)	−0.0102 (7)	−0.0021 (7)
C10	0.0472 (10)	0.0642 (13)	0.0578 (11)	−0.0049 (9)	−0.0134 (9)	−0.0003 (9)
C11	0.0576 (12)	0.0559 (12)	0.0712 (13)	0.0059 (10)	−0.0188 (10)	−0.0009 (10)
C12	0.0688 (13)	0.0466 (11)	0.0619 (12)	−0.0029 (9)	−0.0178 (10)	−0.0013 (9)
C13	0.0613 (12)	0.0492 (10)	0.0463 (10)	−0.0096 (9)	−0.0150 (8)	−0.0018 (7)
C14	0.0481 (10)	0.0465 (9)	0.0385 (8)	−0.0050 (7)	−0.0116 (7)	−0.0015 (7)
C20	0.103 (2)	0.0554 (13)	0.103 (2)	−0.0337 (13)	−0.0358 (16)	0.0050 (12)
C21	0.0793 (15)	0.0918 (17)	0.0563 (12)	−0.0260 (13)	−0.0215 (11)	−0.0189 (11)
N1	0.0497 (8)	0.0518 (8)	0.0410 (8)	−0.0100 (7)	−0.0116 (6)	0.0061 (6)
C15	0.053 (4)	0.052 (4)	0.045 (2)	−0.024 (3)	−0.013 (2)	0.013 (2)
C16	0.077 (3)	0.060 (4)	0.056 (3)	−0.007 (3)	−0.025 (2)	0.005 (2)
C17	0.084 (3)	0.083 (4)	0.055 (3)	−0.026 (3)	−0.034 (3)	0.021 (3)
C18	0.093 (4)	0.099 (5)	0.045 (2)	−0.033 (4)	−0.019 (2)	0.009 (3)
N2	0.086 (3)	0.100 (5)	0.044 (2)	−0.025 (3)	−0.0117 (18)	0.004 (3)
C19	0.073 (4)	0.070 (4)	0.041 (3)	−0.020 (3)	−0.011 (2)	0.006 (2)
C15A	0.059 (5)	0.062 (6)	0.038 (3)	−0.032 (4)	−0.010 (3)	0.011 (3)
C16A	0.078 (6)	0.093 (9)	0.049 (4)	−0.012 (5)	−0.013 (4)	0.009 (4)
C17A	0.124 (8)	0.114 (9)	0.038 (4)	−0.023 (7)	−0.006 (4)	−0.002 (5)
C18A	0.123 (7)	0.132 (11)	0.044 (4)	−0.037 (7)	−0.034 (4)	0.020 (5)
N2A	0.121 (6)	0.131 (9)	0.061 (4)	−0.014 (6)	−0.033 (4)	0.028 (5)
C19A	0.098 (7)	0.083 (8)	0.044 (4)	0.001 (5)	−0.021 (4)	0.013 (4)
S7	0.0505 (2)	0.0523 (2)	0.0588 (3)	−0.0216 (2)	−0.0212 (2)	0.00005 (19)
S8	0.0537 (3)	0.0613 (3)	0.0527 (2)	−0.0277 (2)	−0.0224 (2)	0.0102 (2)

O7	0.0694 (9)	0.0700 (9)	0.0513 (7)	−0.0276 (7)	−0.0264 (7)	0.0114 (6)
O8	0.0502 (8)	0.0632 (9)	0.0912 (11)	−0.0108 (7)	−0.0215 (7)	−0.0182 (7)
S3	0.0506 (3)	0.0678 (3)	0.0560 (3)	−0.0145 (2)	−0.0222 (2)	0.0014 (2)
S4	0.0629 (3)	0.0503 (3)	0.0648 (3)	−0.0161 (2)	−0.0217 (2)	−0.0009 (2)
O3	0.0693 (9)	0.0560 (8)	0.0716 (9)	−0.0203 (7)	−0.0305 (7)	0.0013 (6)
O4	0.0865 (12)	0.0570 (9)	0.0919 (12)	−0.0263 (8)	−0.0156 (9)	0.0137 (8)
C22	0.0485 (10)	0.0514 (10)	0.0393 (8)	−0.0149 (8)	−0.0146 (7)	0.0101 (7)
C23	0.0601 (11)	0.0518 (10)	0.0513 (10)	−0.0219 (9)	−0.0214 (9)	0.0121 (8)
C24	0.0634 (12)	0.0459 (10)	0.0726 (13)	−0.0112 (9)	−0.0246 (10)	0.0051 (9)
C25	0.0532 (11)	0.0534 (12)	0.0811 (14)	−0.0095 (9)	−0.0259 (10)	0.0085 (10)
C26	0.0543 (11)	0.0543 (11)	0.0610 (11)	−0.0169 (9)	−0.0234 (9)	0.0078 (9)
C27	0.0499 (10)	0.0515 (10)	0.0407 (9)	−0.0157 (8)	−0.0153 (7)	0.0108 (7)
C28	0.0533 (10)	0.0607 (11)	0.0408 (9)	−0.0140 (9)	−0.0172 (8)	0.0013 (8)
C29	0.0475 (10)	0.0679 (12)	0.0396 (9)	−0.0079 (9)	−0.0131 (8)	−0.0012 (8)
C30	0.0548 (11)	0.0594 (11)	0.0393 (9)	−0.0041 (9)	−0.0098 (8)	−0.0044 (8)
C31	0.0602 (12)	0.0460 (10)	0.0462 (10)	−0.0042 (8)	−0.0089 (8)	−0.0049 (7)
C32	0.0719 (14)	0.0510 (11)	0.0596 (12)	−0.0075 (10)	−0.0063 (10)	0.0003 (9)
C33	0.0846 (18)	0.0744 (15)	0.0615 (14)	−0.0108 (13)	−0.0078 (12)	0.0161 (11)
C34	0.0872 (18)	0.1011 (19)	0.0510 (12)	−0.0096 (15)	−0.0214 (12)	0.0183 (12)
C35	0.0685 (14)	0.0935 (16)	0.0468 (11)	−0.0149 (12)	−0.0196 (10)	0.0086 (11)
C41	0.126 (3)	0.0622 (16)	0.142 (3)	−0.0353 (17)	−0.021 (2)	0.0258 (17)
C42	0.0884 (17)	0.0643 (14)	0.0861 (16)	−0.0225 (12)	−0.0388 (14)	−0.0065 (11)
N3	0.0517 (9)	0.0833 (12)	0.0368 (8)	−0.0123 (8)	−0.0126 (7)	−0.0033 (7)
C36	0.062 (5)	0.048 (6)	0.036 (4)	−0.002 (4)	−0.009 (4)	−0.003 (4)
C40	0.073 (5)	0.080 (5)	0.054 (5)	−0.009 (4)	−0.025 (4)	0.000 (4)
C39	0.077 (5)	0.092 (7)	0.047 (5)	0.006 (4)	−0.008 (4)	−0.008 (4)
C38	0.104 (9)	0.100 (8)	0.042 (4)	−0.003 (7)	−0.017 (4)	−0.014 (4)
N4	0.105 (6)	0.138 (8)	0.058 (4)	−0.012 (5)	−0.020 (4)	−0.034 (5)
C37	0.085 (6)	0.110 (7)	0.054 (4)	−0.022 (4)	−0.018 (3)	−0.031 (4)
C36A	0.055 (5)	0.042 (6)	0.039 (5)	−0.009 (5)	−0.016 (4)	0.006 (4)
C37A	0.042 (4)	0.074 (6)	0.032 (4)	−0.005 (4)	−0.004 (3)	0.003 (4)
N4A	0.064 (4)	0.091 (8)	0.038 (5)	−0.007 (4)	−0.002 (3)	−0.005 (4)
C38A	0.070 (6)	0.080 (6)	0.046 (6)	−0.016 (5)	0.001 (5)	−0.006 (5)
C39A	0.080 (7)	0.092 (6)	0.043 (4)	−0.037 (6)	−0.005 (4)	−0.013 (4)
C40A	0.066 (5)	0.070 (6)	0.054 (6)	−0.028 (4)	−0.012 (3)	−0.005 (4)
O10	0.134 (3)	0.243 (4)	0.0893 (19)	0.035 (3)	−0.0257 (18)	−0.024 (2)
C86	0.088 (2)	0.109 (3)	0.118 (3)	−0.028 (2)	−0.012 (2)	0.034 (2)
O9	0.181 (3)	0.314 (5)	0.191 (4)	0.089 (3)	−0.140 (3)	−0.158 (4)
C85	0.130 (4)	0.292 (8)	0.185 (5)	0.012 (4)	−0.078 (4)	−0.140 (6)

Geometric parameters (Å, º)

C64—C69	1.389 (3)	C3—C4	1.387 (3)
C64—C65	1.411 (3)	C3—H3	0.9300
C64—S8	1.7585 (18)	C4—C5	1.373 (3)
C65—O7	1.369 (2)	C4—H4	0.9300
C65—C66	1.378 (3)	C5—C6	1.396 (3)
C66—C67	1.382 (3)	C5—H5	0.9300

C66—H66	0.9300	C6—C7	1.510 (2)
C67—C68	1.373 (3)	C7—N1	1.448 (2)
C67—H67	0.9300	C7—H7	0.9800
C68—C69	1.400 (3)	C8—N1	1.456 (2)
C68—H68	0.9300	C8—C9	1.518 (3)
C69—C70	1.515 (2)	C8—H8	0.9800
C70—N7	1.440 (2)	C9—C14	1.389 (3)
C70—S7	1.8522 (19)	C9—C10	1.399 (3)
C70—H70	0.9800	C10—C11	1.380 (3)
C71—N7	1.446 (2)	C10—H10	0.9300
C71—C72	1.511 (3)	C11—C12	1.380 (3)
C71—S8	1.8437 (17)	C11—H11	0.9300
C71—H71	0.9800	C12—C13	1.374 (3)
C72—C77	1.389 (3)	C12—H12	0.9300
C72—C73	1.403 (3)	C13—C14	1.407 (3)
C73—C74	1.373 (3)	C20—H20A	0.9600
C73—H73	0.9300	C20—H20B	0.9600
C74—C75	1.388 (3)	C20—H20C	0.9600
C74—H74	0.9300	C21—H21A	0.9600
C75—C76	1.378 (3)	C21—H21B	0.9600
C75—H75	0.9300	C21—H21C	0.9600
C76—O8	1.368 (2)	N1—C15A	1.418 (12)
C76—C77	1.405 (3)	N1—C15	1.446 (10)
C77—S7	1.7665 (18)	C15—C16	1.379 (10)
N7—C78	1.409 (2)	C15—C19	1.391 (10)
C78—C79	1.377 (3)	C16—C17	1.382 (9)
C78—C82	1.383 (3)	C16—H16	0.9300
C79—C80	1.383 (3)	C17—C18	1.370 (10)
C79—H79	0.9300	C17—H17	0.9300
C80—C81	1.351 (3)	C18—N2	1.333 (9)
C80—H80	0.9300	C18—H18	0.9300
C81—N8	1.321 (3)	N2—C19	1.341 (9)
C81—H81	0.9300	C19—H19	0.9300
N8—C82	1.334 (3)	C15A—C16A	1.368 (13)
C82—H82	0.9300	C15A—C19A	1.374 (13)
C83—O8	1.418 (3)	C16A—C17A	1.378 (13)
C83—H83A	0.9600	C16A—H16A	0.9300
C83—H83B	0.9600	C17A—C18A	1.374 (12)
C83—H83C	0.9600	C17A—H17A	0.9300
C84—O7	1.419 (2)	C18A—N2A	1.310 (11)
C84—H84A	0.9600	C18A—H18A	0.9300
C84—H84B	0.9600	N2A—C19A	1.329 (11)
C84—H84C	0.9600	C19A—H19A	0.9300
S5—C43	1.7641 (19)	S3—C22	1.7660 (18)
S5—C50	1.8598 (18)	S3—C29	1.846 (2)
S6—C52	1.7603 (17)	S4—C31	1.764 (2)
S6—C49	1.8360 (17)	S4—C28	1.838 (2)
O5—C44	1.364 (2)	O3—C23	1.370 (2)

O5—C63	1.423 (3)	O3—C42	1.421 (3)
O6—C53	1.368 (2)	O4—C32	1.369 (3)
O6—C62	1.426 (2)	O4—C41	1.433 (3)
C43—C48	1.393 (3)	C22—C27	1.393 (3)
C43—C44	1.403 (3)	C22—C23	1.409 (3)
C44—C45	1.382 (3)	C23—C24	1.375 (3)
C45—C46	1.382 (3)	C24—C25	1.386 (3)
C45—H45	0.9300	C24—H24	0.9300
C46—C47	1.370 (3)	C25—C26	1.370 (3)
C46—H46	0.9300	C25—H25	0.9300
C47—C48	1.396 (3)	C26—C27	1.395 (3)
C47—H47	0.9300	C26—H26	0.9300
C48—C49	1.514 (3)	C27—C28	1.508 (3)
C49—N5	1.447 (2)	C28—N3	1.437 (3)
C49—H49	0.9800	C28—H28	0.9800
C50—N5	1.444 (2)	C29—N3	1.433 (2)
C50—C51	1.505 (2)	C29—C30	1.515 (3)
C50—H50	0.9800	C29—H29	0.9800
C51—C52	1.392 (2)	C30—C31	1.385 (3)
C51—C56	1.397 (3)	C30—C35	1.401 (3)
C52—C53	1.404 (2)	C31—C32	1.407 (3)
C53—C54	1.384 (3)	C32—C33	1.380 (4)
C54—C55	1.383 (3)	C33—C34	1.372 (4)
C54—H54	0.9300	C33—H33	0.9300
C55—C56	1.373 (3)	C34—C35	1.378 (4)
C55—H55	0.9300	C34—H34	0.9300
C56—H56	0.9300	C35—H35	0.9300
C62—H62A	0.9600	C41—H41A	0.9600
C62—H62B	0.9600	C41—H41B	0.9600
C62—H62C	0.9600	C41—H41C	0.9600
C63—H63A	0.9600	C42—H42A	0.9600
C63—H63B	0.9600	C42—H42B	0.9600
C63—H63C	0.9600	C42—H42C	0.9600
N5—C58	1.423 (4)	N3—C36A	1.380 (14)
N5—C58A	1.47 (4)	N3—C36	1.408 (10)
C58—C59	1.367 (4)	C36—C40	1.375 (11)
C58—C57	1.387 (5)	C36—C37	1.394 (11)
C59—C60	1.371 (5)	C40—C39	1.386 (11)
C59—H59	0.9300	C40—H40	0.9300
C60—C61	1.362 (6)	C39—C38	1.355 (11)
C60—H60	0.9300	C39—H39	0.9300
C61—N6	1.332 (6)	C38—N4	1.309 (10)
C61—H61	0.9300	C38—H38	0.9300
N6—C57	1.342 (4)	N4—C37	1.329 (10)
C57—H57	0.9300	C37—H37	0.9300
C58A—C59A	1.370 (16)	C36A—C40A	1.378 (13)
C58A—C57A	1.393 (16)	C36A—C37A	1.409 (13)
C57A—N6A	1.328 (14)	C37A—N4A	1.332 (11)

C57A—H57A	0.9300	C37A—H37A	0.9300
N6A—C61A	1.318 (15)	N4A—C38A	1.316 (11)
C61A—C60A	1.367 (15)	C38A—C39A	1.371 (12)
C61A—H61A	0.9300	C38A—H38A	0.9300
C60A—C59A	1.382 (15)	C39A—C40A	1.372 (12)
C60A—H60A	0.9300	C39A—H39A	0.9300
C59A—H59A	0.9300	C40A—H40A	0.9300
S1—C1	1.7620 (18)	O10—C86	1.252 (4)
S1—C8	1.8372 (19)	O10—H10A	0.8200
S2—C14	1.7629 (18)	C86—H86A	0.9600
S2—C7	1.8447 (19)	C86—H86B	0.9600
O1—C13	1.359 (3)	C86—H86C	0.9600
O1—C20	1.427 (3)	O9—C85	1.358 (5)
O2—C2	1.368 (2)	O9—H9	0.8200
O2—C21	1.431 (2)	C85—H85A	0.9600
C1—C6	1.389 (3)	C85—H85B	0.9600
C1—C2	1.406 (2)	C85—H85C	0.9600
C2—C3	1.379 (3)		

C69—C64—C65	119.44 (16)	C1—C6—C7	123.73 (16)
C69—C64—S8	124.90 (13)	C5—C6—C7	117.00 (16)
C65—C64—S8	115.65 (14)	N1—C7—C6	114.21 (15)
O7—C65—C66	124.99 (17)	N1—C7—S2	111.21 (12)
O7—C65—C64	114.07 (16)	C6—C7—S2	110.75 (12)
C66—C65—C64	120.94 (18)	N1—C7—H7	106.7
C65—C66—C67	119.02 (18)	C6—C7—H7	106.7
C65—C66—H66	120.5	S2—C7—H7	106.7
C67—C66—H66	120.5	N1—C8—C9	115.38 (16)
C68—C67—C66	120.92 (18)	N1—C8—S1	108.97 (12)
C68—C67—H67	119.5	C9—C8—S1	112.20 (12)
C66—C67—H67	119.5	N1—C8—H8	106.6
C67—C68—C69	120.86 (19)	C9—C8—H8	106.6
C67—C68—H68	119.6	S1—C8—H8	106.6
C69—C68—H68	119.6	C14—C9—C10	118.49 (18)
C64—C69—C68	118.76 (16)	C14—C9—C8	122.93 (15)
C64—C69—C70	123.33 (15)	C10—C9—C8	118.54 (18)
C68—C69—C70	117.77 (16)	C11—C10—C9	120.6 (2)
N7—C70—C69	112.25 (14)	C11—C10—H10	119.7
N7—C70—S7	111.65 (12)	C9—C10—H10	119.7
C69—C70—S7	112.77 (12)	C12—C11—C10	120.92 (19)
N7—C70—H70	106.6	C12—C11—H11	119.5
C69—C70—H70	106.6	C10—C11—H11	119.5
S7—C70—H70	106.6	C13—C12—C11	119.5 (2)
N7—C71—C72	116.08 (15)	C13—C12—H12	120.3
N7—C71—S8	108.84 (12)	C11—C12—H12	120.3
C72—C71—S8	110.52 (11)	O1—C13—C12	125.39 (19)
N7—C71—H71	107.0	O1—C13—C14	114.26 (16)
C72—C71—H71	107.0	C12—C13—C14	120.3 (2)

S8—C71—H71	107.0	C9—C14—C13	120.21 (16)
C77—C72—C73	119.49 (17)	C9—C14—S2	124.76 (14)
C77—C72—C71	123.25 (15)	C13—C14—S2	115.02 (15)
C73—C72—C71	117.25 (16)	O1—C20—H20A	109.5
C74—C73—C72	120.41 (19)	O1—C20—H20B	109.5
C74—C73—H73	119.8	H20A—C20—H20B	109.5
C72—C73—H73	119.8	O1—C20—H20C	109.5
C73—C74—C75	120.60 (19)	H20A—C20—H20C	109.5
C73—C74—H74	119.7	H20B—C20—H20C	109.5
C75—C74—H74	119.7	O2—C21—H21A	109.5
C76—C75—C74	119.40 (19)	O2—C21—H21B	109.5
C76—C75—H75	120.3	H21A—C21—H21B	109.5
C74—C75—H75	120.3	O2—C21—H21C	109.5
O8—C76—C75	124.57 (18)	H21A—C21—H21C	109.5
O8—C76—C77	114.45 (16)	H21B—C21—H21C	109.5
C75—C76—C77	120.98 (18)	C15A—N1—C7	120.9 (7)
C72—C77—C76	119.02 (16)	C15—N1—C7	109.6 (5)
C72—C77—S7	124.62 (14)	C15A—N1—C8	116.3 (7)
C76—C77—S7	116.36 (14)	C15—N1—C8	117.4 (5)
C78—N7—C70	119.21 (14)	C7—N1—C8	112.19 (13)
C78—N7—C71	121.27 (14)	C16—C15—C19	115.3 (8)
C70—N7—C71	113.27 (14)	C16—C15—N1	121.8 (9)
C79—C78—C82	116.45 (17)	C19—C15—N1	122.8 (8)
C79—C78—N7	123.73 (17)	C15—C16—C17	120.8 (8)
C82—C78—N7	119.70 (16)	C15—C16—H16	119.6
C78—C79—C80	119.0 (2)	C17—C16—H16	119.6
C78—C79—H79	120.5	C18—C17—C16	118.8 (7)
C80—C79—H79	120.5	C18—C17—H17	120.6
C81—C80—C79	119.9 (2)	C16—C17—H17	120.6
C81—C80—H80	120.0	N2—C18—C17	122.9 (6)
C79—C80—H80	120.0	N2—C18—H18	118.5
N8—C81—C80	122.7 (2)	C17—C18—H18	118.5
N8—C81—H81	118.6	C18—N2—C19	116.8 (8)
C80—C81—H81	118.6	N2—C19—C15	125.4 (10)
C81—N8—C82	117.3 (2)	N2—C19—H19	117.3
N8—C82—C78	124.6 (2)	C15—C19—H19	117.3
N8—C82—H82	117.7	C16A—C15A—C19A	119.2 (11)
C78—C82—H82	117.7	C16A—C15A—N1	123.1 (12)
O8—C83—H83A	109.5	C19A—C15A—N1	117.3 (12)
O8—C83—H83B	109.5	C15A—C16A—C17A	118.7 (13)
H83A—C83—H83B	109.5	C15A—C16A—H16A	120.6
O8—C83—H83C	109.5	C17A—C16A—H16A	120.6
H83A—C83—H83C	109.5	C18A—C17A—C16A	117.5 (11)
H83B—C83—H83C	109.5	C18A—C17A—H17A	121.3
O7—C84—H84A	109.5	C16A—C17A—H17A	121.3
O7—C84—H84B	109.5	N2A—C18A—C17A	124.7 (8)
H84A—C84—H84B	109.5	N2A—C18A—H18A	117.6
O7—C84—H84C	109.5	C17A—C18A—H18A	117.6

H84A—C84—H84C	109.5	C18A—N2A—C19A	117.2 (9)
H84B—C84—H84C	109.5	N2A—C19A—C15A	122.7 (11)
C43—S5—C50	98.21 (8)	N2A—C19A—H19A	118.7
C52—S6—C49	98.56 (8)	C15A—C19A—H19A	118.7
C44—O5—C63	118.35 (18)	C77—S7—C70	97.69 (8)
C53—O6—C62	117.70 (15)	C64—S8—C71	98.01 (8)
C48—C43—C44	119.49 (17)	C65—O7—C84	118.59 (17)
C48—C43—S5	124.48 (15)	C76—O8—C83	117.60 (18)
C44—C43—S5	116.00 (14)	C22—S3—C29	97.93 (9)
O5—C44—C45	124.65 (19)	C31—S4—C28	97.56 (9)
O5—C44—C43	114.78 (17)	C23—O3—C42	117.01 (17)
C45—C44—C43	120.56 (19)	C32—O4—C41	117.9 (2)
C44—C45—C46	119.3 (2)	C27—C22—C23	119.36 (17)
C44—C45—H45	120.4	C27—C22—S3	124.14 (14)
C46—C45—H45	120.4	C23—C22—S3	116.50 (14)
C47—C46—C45	120.9 (2)	O3—C23—C24	124.70 (19)
C47—C46—H46	119.5	O3—C23—C22	114.55 (17)
C45—C46—H46	119.5	C24—C23—C22	120.75 (18)
C46—C47—C48	120.6 (2)	C23—C24—C25	119.3 (2)
C46—C47—H47	119.7	C23—C24—H24	120.4
C48—C47—H47	119.7	C25—C24—H24	120.4
C43—C48—C47	119.09 (18)	C26—C25—C24	120.72 (19)
C43—C48—C49	123.08 (17)	C26—C25—H25	119.6
C47—C48—C49	117.83 (17)	C24—C25—H25	119.6
N5—C49—C48	116.41 (15)	C25—C26—C27	120.94 (19)
N5—C49—S6	109.24 (12)	C25—C26—H26	119.5
C48—C49—S6	110.28 (12)	C27—C26—H26	119.5
N5—C49—H49	106.8	C22—C27—C26	118.90 (18)
C48—C49—H49	106.8	C22—C27—C28	124.00 (16)
S6—C49—H49	106.8	C26—C27—C28	117.04 (17)
N5—C50—C51	113.47 (14)	N3—C28—C27	113.38 (16)
N5—C50—S5	112.61 (12)	N3—C28—S4	111.30 (14)
C51—C50—S5	109.57 (12)	C27—C28—S4	111.75 (13)
N5—C50—H50	106.9	N3—C28—H28	106.6
C51—C50—H50	106.9	C27—C28—H28	106.6
S5—C50—H50	106.9	S4—C28—H28	106.6
C52—C51—C56	119.53 (16)	N3—C29—C30	112.91 (17)
C52—C51—C50	123.08 (15)	N3—C29—S3	110.34 (14)
C56—C51—C50	117.39 (16)	C30—C29—S3	113.90 (13)
C51—C52—C53	119.08 (15)	N3—C29—H29	106.4
C51—C52—S6	124.42 (13)	C30—C29—H29	106.4
C53—C52—S6	116.47 (13)	S3—C29—H29	106.4
O6—C53—C54	124.39 (16)	C31—C30—C35	119.1 (2)
O6—C53—C52	114.72 (15)	C31—C30—C29	123.33 (17)
C54—C53—C52	120.89 (17)	C35—C30—C29	117.2 (2)
C55—C54—C53	119.16 (17)	C30—C31—C32	119.27 (19)
C55—C54—H54	120.4	C30—C31—S4	125.35 (15)
C53—C54—H54	120.4	C32—C31—S4	115.31 (18)

C56—C55—C54	120.92 (17)	O4—C32—C33	124.7 (2)
C56—C55—H55	119.5	O4—C32—C31	114.4 (2)
C54—C55—H55	119.5	C33—C32—C31	121.0 (2)
C55—C56—C51	120.42 (18)	C34—C33—C32	119.1 (2)
C55—C56—H56	119.8	C34—C33—H33	120.4
C51—C56—H56	119.8	C32—C33—H33	120.4
O6—C62—H62A	109.5	C33—C34—C35	121.1 (2)
O6—C62—H62B	109.5	C33—C34—H34	119.5
H62A—C62—H62B	109.5	C35—C34—H34	119.5
O6—C62—H62C	109.5	C34—C35—C30	120.4 (3)
H62A—C62—H62C	109.5	C34—C35—H35	119.8
H62B—C62—H62C	109.5	C30—C35—H35	119.8
O5—C63—H63A	109.5	O4—C41—H41A	109.5
O5—C63—H63B	109.5	O4—C41—H41B	109.5
H63A—C63—H63B	109.5	H41A—C41—H41B	109.5
O5—C63—H63C	109.5	O4—C41—H41C	109.5
H63A—C63—H63C	109.5	H41A—C41—H41C	109.5
H63B—C63—H63C	109.5	H41B—C41—H41C	109.5
C58—N5—C50	116.8 (2)	O3—C42—H42A	109.5
C58—N5—C49	117.03 (19)	O3—C42—H42B	109.5
C50—N5—C49	113.08 (14)	H42A—C42—H42B	109.5
C50—N5—C58A	105 (2)	O3—C42—H42C	109.5
C49—N5—C58A	127.3 (13)	H42A—C42—H42C	109.5
C59—C58—C57	117.7 (3)	H42B—C42—H42C	109.5
C59—C58—N5	119.8 (3)	C36A—N3—C29	119.6 (11)
C57—C58—N5	122.5 (3)	C36—N3—C29	125.4 (8)
C58—C59—C60	120.1 (4)	C36A—N3—C28	126.4 (10)
C58—C59—H59	119.9	C36—N3—C28	120.6 (8)
C60—C59—H59	119.9	C29—N3—C28	114.00 (15)
C61—C60—C59	118.4 (4)	C40—C36—C37	117.2 (9)
C61—C60—H60	120.8	C40—C36—N3	122.1 (11)
C59—C60—H60	120.8	C37—C36—N3	120.6 (11)
N6—C61—C60	123.6 (3)	C36—C40—C39	122.2 (11)
N6—C61—H61	118.2	C36—C40—H40	118.9
C60—C61—H61	118.2	C39—C40—H40	118.9
C61—N6—C57	117.3 (3)	C38—C39—C40	115.2 (12)
N6—C57—C58	122.9 (4)	C38—C39—H39	122.4
N6—C57—H57	118.6	C40—C39—H39	122.4
C58—C57—H57	118.6	N4—C38—C39	124.6 (10)
C59A—C58A—C57A	119 (2)	N4—C38—H38	117.7
C59A—C58A—N5	118 (3)	C39—C38—H38	117.7
C57A—C58A—N5	115 (3)	C38—N4—C37	120.3 (10)
N6A—C57A—C58A	119.9 (19)	N4—C37—C36	120.4 (11)
N6A—C57A—H57A	120.0	N4—C37—H37	119.8
C58A—C57A—H57A	120.0	C36—C37—H37	119.8
C61A—N6A—C57A	117.5 (18)	C40A—C36A—N3	122.1 (14)
N6A—C61A—C60A	126.9 (19)	C40A—C36A—C37A	115.5 (11)
N6A—C61A—H61A	116.5	N3—C36A—C37A	121.7 (13)

C60A—C61A—H61A	116.5	N4A—C37A—C36A	120.0 (13)
C61A—C60A—C59A	114.7 (18)	N4A—C37A—H37A	120.0
C61A—C60A—H60A	122.6	C36A—C37A—H37A	120.0
C59A—C60A—H60A	122.6	C38A—N4A—C37A	121.8 (12)
C58A—C59A—C60A	120 (2)	N4A—C38A—C39A	123.0 (11)
C58A—C59A—H59A	120.1	N4A—C38A—H38A	118.5
C60A—C59A—H59A	120.1	C39A—C38A—H38A	118.5
C1—S1—C8	98.63 (9)	C38A—C39A—C40A	114.9 (13)
C14—S2—C7	98.13 (8)	C38A—C39A—H39A	122.6
C13—O1—C20	118.18 (18)	C40A—C39A—H39A	122.6
C2—O2—C21	117.41 (16)	C39A—C40A—C36A	124.6 (13)
C6—C1—C2	119.31 (16)	C39A—C40A—H40A	117.7
C6—C1—S1	123.64 (13)	C36A—C40A—H40A	117.7
C2—C1—S1	117.05 (14)	C86—O10—H10A	109.5
O2—C2—C3	124.56 (17)	O10—C86—H86A	109.5
O2—C2—C1	114.53 (16)	O10—C86—H86B	109.5
C3—C2—C1	120.90 (18)	H86A—C86—H86B	109.5
C2—C3—C4	119.04 (18)	O10—C86—H86C	109.5
C2—C3—H3	120.5	H86A—C86—H86C	109.5
C4—C3—H3	120.5	H86B—C86—H86C	109.5
C5—C4—C3	120.83 (18)	C85—O9—H9	109.5
C5—C4—H4	119.6	O9—C85—H85A	109.5
C3—C4—H4	119.6	O9—C85—H85B	109.5
C4—C5—C6	120.59 (18)	H85A—C85—H85B	109.5
C4—C5—H5	119.7	O9—C85—H85C	109.5
C6—C5—H5	119.7	H85A—C85—H85C	109.5
C1—C6—C5	119.25 (16)	H85B—C85—H85C	109.5

C69—C64—C65—O7	178.62 (16)	C1—C6—C7—S2	113.15 (16)
S8—C64—C65—O7	−0.5 (2)	C5—C6—C7—S2	−68.27 (18)
C69—C64—C65—C66	−0.9 (3)	C14—S2—C7—N1	47.09 (13)
S8—C64—C65—C66	179.98 (15)	C14—S2—C7—C6	−81.03 (13)
O7—C65—C66—C67	179.49 (18)	C1—S1—C8—N1	48.42 (13)
C64—C65—C66—C67	−1.0 (3)	C1—S1—C8—C9	−80.63 (14)
C65—C66—C67—C68	1.3 (3)	N1—C8—C9—C14	−14.3 (2)
C66—C67—C68—C69	0.4 (3)	S1—C8—C9—C14	111.27 (17)
C65—C64—C69—C68	2.6 (3)	N1—C8—C9—C10	163.28 (16)
S8—C64—C69—C68	−178.43 (14)	S1—C8—C9—C10	−71.11 (19)
C65—C64—C69—C70	−172.93 (17)	C14—C9—C10—C11	0.8 (3)
S8—C64—C69—C70	6.1 (3)	C8—C9—C10—C11	−176.96 (18)
C67—C68—C69—C64	−2.3 (3)	C9—C10—C11—C12	−0.2 (3)
C67—C68—C69—C70	173.41 (17)	C10—C11—C12—C13	−0.5 (3)
C64—C69—C70—N7	14.1 (2)	C20—O1—C13—C12	8.7 (3)
C68—C69—C70—N7	−161.45 (16)	C20—O1—C13—C14	−171.62 (19)
C64—C69—C70—S7	−113.07 (17)	C11—C12—C13—O1	−179.8 (2)
C68—C69—C70—S7	71.39 (18)	C11—C12—C13—C14	0.6 (3)
N7—C71—C72—C77	10.7 (2)	C10—C9—C14—C13	−0.7 (3)
S8—C71—C72—C77	−113.83 (16)	C8—C9—C14—C13	176.95 (16)

N7—C71—C72—C73	−168.39 (15)	C10—C9—C14—S2	−179.75 (14)
S8—C71—C72—C73	67.06 (18)	C8—C9—C14—S2	−2.1 (2)
C77—C72—C73—C74	−1.1 (3)	O1—C13—C14—C9	−179.68 (16)
C71—C72—C73—C74	178.08 (18)	C12—C13—C14—C9	0.0 (3)
C72—C73—C74—C75	−1.6 (3)	O1—C13—C14—S2	−0.5 (2)
C73—C74—C75—C76	1.8 (3)	C12—C13—C14—S2	179.16 (15)
C74—C75—C76—O8	179.9 (2)	C7—S2—C14—C9	−12.75 (16)
C74—C75—C76—C77	0.7 (3)	C7—S2—C14—C13	168.13 (14)
C73—C72—C77—C76	3.4 (3)	C6—C7—N1—C15A	−161.9 (8)
C71—C72—C77—C76	−175.67 (16)	S2—C7—N1—C15A	71.8 (8)
C73—C72—C77—S7	−177.04 (14)	C6—C7—N1—C15	−172.9 (5)
C71—C72—C77—S7	3.9 (2)	S2—C7—N1—C15	60.9 (5)
O8—C76—C77—C72	177.42 (16)	C6—C7—N1—C8	54.79 (19)
C75—C76—C77—C72	−3.3 (3)	S2—C7—N1—C8	−71.44 (16)
O8—C76—C77—S7	−2.2 (2)	C9—C8—N1—C15A	−92.1 (7)
C75—C76—C77—S7	177.16 (16)	S1—C8—N1—C15A	140.6 (7)
C69—C70—N7—C78	149.67 (15)	C9—C8—N1—C15	−75.4 (5)
S7—C70—N7—C78	−82.57 (17)	S1—C8—N1—C15	157.3 (5)
C69—C70—N7—C71	−57.75 (19)	C9—C8—N1—C7	52.9 (2)
S7—C70—N7—C71	70.01 (16)	S1—C8—N1—C7	−74.32 (16)
C72—C71—N7—C78	102.29 (18)	C7—N1—C15—C16	60.9 (9)
S8—C71—N7—C78	−132.31 (14)	C8—N1—C15—C16	−169.6 (6)
C72—C71—N7—C70	−49.7 (2)	C7—N1—C15—C19	−123.9 (8)
S8—C71—N7—C70	75.75 (16)	C8—N1—C15—C19	5.7 (11)
C70—N7—C78—C79	131.6 (2)	C19—C15—C16—C17	−0.6 (11)
C71—N7—C78—C79	−18.8 (3)	N1—C15—C16—C17	175.0 (8)
C70—N7—C78—C82	−52.7 (3)	C15—C16—C17—C18	0.6 (10)
C71—N7—C78—C82	157.02 (19)	C16—C17—C18—N2	0.1 (10)
C82—C78—C79—C80	−1.0 (3)	C17—C18—N2—C19	−0.8 (11)
N7—C78—C79—C80	174.9 (2)	C18—N2—C19—C15	0.8 (15)
C78—C79—C80—C81	1.4 (4)	C16—C15—C19—N2	−0.2 (15)
C79—C80—C81—N8	−0.5 (4)	N1—C15—C19—N2	−175.7 (10)
C80—C81—N8—C82	−0.8 (4)	C7—N1—C15A—C16A	−118.8 (10)
C81—N8—C82—C78	1.2 (4)	C8—N1—C15A—C16A	23.1 (13)
C79—C78—C82—N8	−0.3 (4)	C7—N1—C15A—C19A	54.3 (12)
N7—C78—C82—N8	−176.4 (2)	C8—N1—C15A—C19A	−163.9 (9)
C50—S5—C43—C48	−16.77 (16)	C19A—C15A—C16A—C17A	1.2 (14)
C50—S5—C43—C44	165.55 (14)	N1—C15A—C16A—C17A	174.2 (12)
C63—O5—C44—C45	8.3 (3)	C15A—C16A—C17A—C18A	−0.7 (14)
C63—O5—C44—C43	−172.6 (2)	C16A—C17A—C18A—N2A	−0.2 (19)
C48—C43—C44—O5	178.93 (16)	C17A—C18A—N2A—C19A	1 (2)
S5—C43—C44—O5	−3.3 (2)	C18A—N2A—C19A—C15A	0.1 (19)
C48—C43—C44—C45	−1.9 (3)	C16A—C15A—C19A—N2A	−0.9 (18)
S5—C43—C44—C45	175.88 (16)	N1—C15A—C19A—N2A	−174.3 (12)
O5—C44—C45—C46	179.2 (2)	C72—C77—S7—C70	12.72 (16)
C43—C44—C45—C46	0.2 (3)	C76—C77—S7—C70	−167.72 (14)
C44—C45—C46—C47	1.4 (4)	N7—C70—S7—C77	−47.12 (13)
C45—C46—C47—C48	−1.2 (4)	C69—C70—S7—C77	80.36 (13)

C44—C43—C48—C47	2.1 (3)	C69—C64—S8—C71	9.10 (17)
S5—C43—C48—C47	−175.47 (15)	C65—C64—S8—C71	−171.86 (14)
C44—C43—C48—C49	−176.89 (16)	N7—C71—S8—C64	−45.45 (13)
S5—C43—C48—C49	5.5 (2)	C72—C71—S8—C64	83.13 (13)
C46—C47—C48—C43	−0.6 (3)	C66—C65—O7—C84	2.4 (3)
C46—C47—C48—C49	178.5 (2)	C64—C65—O7—C84	−177.08 (19)
C43—C48—C49—N5	−19.3 (2)	C75—C76—O8—C83	−2.5 (3)
C47—C48—C49—N5	161.69 (16)	C77—C76—O8—C83	176.8 (2)
C43—C48—C49—S6	105.87 (17)	C29—S3—C22—C27	9.62 (16)
C47—C48—C49—S6	−73.15 (19)	C29—S3—C22—C23	−170.48 (13)
C52—S6—C49—N5	46.58 (13)	C42—O3—C23—C24	1.0 (3)
C52—S6—C49—C48	−82.55 (13)	C42—O3—C23—C22	−179.02 (18)
C43—S5—C50—N5	45.89 (14)	C27—C22—C23—O3	177.36 (15)
C43—S5—C50—C51	−81.41 (13)	S3—C22—C23—O3	−2.5 (2)
N5—C50—C51—C52	−19.0 (2)	C27—C22—C23—C24	−2.7 (3)
S5—C50—C51—C52	107.84 (16)	S3—C22—C23—C24	177.40 (15)
N5—C50—C51—C56	160.65 (15)	O3—C23—C24—C25	−179.30 (19)
S5—C50—C51—C56	−72.54 (18)	C22—C23—C24—C25	0.8 (3)
C56—C51—C52—C53	0.0 (2)	C23—C24—C25—C26	0.8 (3)
C50—C51—C52—C53	179.60 (15)	C24—C25—C26—C27	−0.5 (3)
C56—C51—C52—S6	−177.95 (13)	C23—C22—C27—C26	3.0 (2)
C50—C51—C52—S6	1.7 (2)	S3—C22—C27—C26	−177.11 (13)
C49—S6—C52—C51	−14.35 (16)	C23—C22—C27—C28	−173.90 (16)
C49—S6—C52—C53	167.67 (13)	S3—C22—C27—C28	6.0 (2)
C62—O6—C53—C54	−0.9 (3)	C25—C26—C27—C22	−1.4 (3)
C62—O6—C53—C52	178.55 (17)	C25—C26—C27—C28	175.66 (18)
C51—C52—C53—O6	−178.75 (14)	C22—C27—C28—N3	12.2 (2)
S6—C52—C53—O6	−0.7 (2)	C26—C27—C28—N3	−164.77 (16)
C51—C52—C53—C54	0.7 (3)	C22—C27—C28—S4	−114.61 (17)
S6—C52—C53—C54	178.81 (14)	C26—C27—C28—S4	68.46 (18)
O6—C53—C54—C55	178.29 (17)	C31—S4—C28—N3	−42.99 (14)
C52—C53—C54—C55	−1.1 (3)	C31—S4—C28—C27	84.90 (14)
C53—C54—C55—C56	0.8 (3)	C22—S3—C29—N3	−45.32 (15)
C54—C55—C56—C51	−0.2 (3)	C22—S3—C29—C30	82.88 (14)
C52—C51—C56—C55	−0.3 (3)	N3—C29—C30—C31	13.9 (3)
C50—C51—C56—C55	−179.90 (17)	S3—C29—C30—C31	−112.94 (19)
C51—C50—N5—C58	−162.0 (2)	N3—C29—C30—C35	−159.42 (19)
S5—C50—N5—C58	72.8 (3)	S3—C29—C30—C35	73.7 (2)
C51—C50—N5—C49	57.70 (19)	C35—C30—C31—C32	2.9 (3)
S5—C50—N5—C49	−67.50 (16)	C29—C30—C31—C32	−170.36 (18)
C51—C50—N5—C58A	−160 (2)	C35—C30—C31—S4	179.69 (17)
S5—C50—N5—C58A	75 (2)	C29—C30—C31—S4	6.5 (3)
C48—C49—N5—C58	−88.2 (3)	C28—S4—C31—C30	7.35 (18)
S6—C49—N5—C58	146.1 (3)	C28—S4—C31—C32	−175.72 (15)
C48—C49—N5—C50	51.98 (19)	C41—O4—C32—C33	15.9 (4)
S6—C49—N5—C50	−73.70 (15)	C41—O4—C32—C31	−164.1 (2)
C48—C49—N5—C58A	−80 (4)	C30—C31—C32—O4	177.68 (18)
S6—C49—N5—C58A	154 (4)	S4—C31—C32—O4	0.5 (2)

C50—N5—C58—C59	67.2 (5)	C30—C31—C32—C33	−2.3 (3)
C49—N5—C58—C59	−154.2 (3)	S4—C31—C32—C33	−179.44 (18)
C50—N5—C58—C57	−113.2 (4)	O4—C32—C33—C34	−179.6 (2)
C49—N5—C58—C57	25.5 (6)	C31—C32—C33—C34	0.4 (4)
C57—C58—C59—C60	0.6 (6)	C32—C33—C34—C35	1.0 (4)
N5—C58—C59—C60	−179.8 (4)	C33—C34—C35—C30	−0.4 (4)
C58—C59—C60—C61	−0.5 (6)	C31—C30—C35—C34	−1.6 (3)
C59—C60—C61—N6	0.0 (5)	C29—C30—C35—C34	172.0 (2)
C60—C61—N6—C57	0.3 (5)	C30—C29—N3—C36A	123.5 (16)
C61—N6—C57—C58	−0.2 (6)	S3—C29—N3—C36A	−107.8 (16)
C59—C58—C57—N6	−0.2 (7)	C30—C29—N3—C36	125.3 (14)
N5—C58—C57—N6	−179.9 (4)	S3—C29—N3—C36	−106.0 (14)
C50—N5—C58A—C59A	−144 (5)	C30—C29—N3—C28	−55.5 (2)
C49—N5—C58A—C59A	−9 (8)	S3—C29—N3—C28	73.22 (19)
C50—N5—C58A—C57A	66 (5)	C27—C28—N3—C36A	126.8 (17)
C49—N5—C58A—C57A	−159 (3)	S4—C28—N3—C36A	−106.2 (17)
C59A—C58A—C57A—N6A	18 (8)	C27—C28—N3—C36	124.9 (13)
N5—C58A—C57A—N6A	167 (4)	S4—C28—N3—C36	−108.0 (13)
C58A—C57A—N6A—C61A	−9 (6)	C27—C28—N3—C29	−54.3 (2)
C57A—N6A—C61A—C60A	−1 (7)	S4—C28—N3—C29	72.70 (19)
N6A—C61A—C60A—C59A	2 (7)	C29—N3—C36—C40	20 (3)
C57A—C58A—C59A—C60A	−16 (9)	C28—N3—C36—C40	−159 (2)
N5—C58A—C59A—C60A	−165 (5)	C29—N3—C36—C37	−155.9 (17)
C61A—C60A—C59A—C58A	7 (8)	C28—N3—C36—C37	25 (3)
C8—S1—C1—C6	−12.88 (16)	C37—C36—C40—C39	−1 (4)
C8—S1—C1—C2	167.76 (14)	N3—C36—C40—C39	−177 (2)
C21—O2—C2—C3	3.2 (3)	C36—C40—C39—C38	−2 (4)
C21—O2—C2—C1	−177.46 (18)	C40—C39—C38—N4	5 (4)
C6—C1—C2—O2	−176.22 (15)	C39—C38—N4—C37	−4 (4)
S1—C1—C2—O2	3.2 (2)	C38—N4—C37—C36	1 (3)
C6—C1—C2—C3	3.1 (3)	C40—C36—C37—N4	2 (4)
S1—C1—C2—C3	−177.47 (15)	N3—C36—C37—N4	178 (2)
O2—C2—C3—C4	178.06 (18)	C29—N3—C36A—C40A	−161 (2)
C1—C2—C3—C4	−1.2 (3)	C28—N3—C36A—C40A	18 (4)
C2—C3—C4—C5	−0.9 (3)	C29—N3—C36A—C37A	29 (4)
C3—C4—C5—C6	1.0 (3)	C28—N3—C36A—C37A	−152 (2)
C2—C1—C6—C5	−2.9 (2)	C40A—C36A—C37A—N4A	3 (5)
S1—C1—C6—C5	177.72 (14)	N3—C36A—C37A—N4A	174 (3)
C2—C1—C6—C7	175.62 (16)	C36A—C37A—N4A—C38A	−2 (5)
S1—C1—C6—C7	−3.7 (2)	C37A—N4A—C38A—C39A	−2 (5)
C4—C5—C6—C1	0.9 (3)	N4A—C38A—C39A—C40A	4 (4)
C4—C5—C6—C7	−177.75 (17)	C38A—C39A—C40A—C36A	−3 (4)
C1—C6—C7—N1	−13.3 (2)	N3—C36A—C40A—C39A	−171 (2)
C5—C6—C7—N1	165.25 (15)	C37A—C36A—C40A—C39A	−1 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C28—H28···O9^{i}	0.98	2.41	3.222 (3)	140
C29—H29···S2^{ii}	0.98	2.88	3.601 (2)	131
C41—H41*A*···O2^{iii}	0.96	2.51	3.367 (3)	148
O10—H10*A*···N6	0.82	2.11	2.804 (5)	143
O9—H9···O10	0.82	1.76	2.569 (5)	167

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