

2-Chloro-4,5-dihydroimidazole. Part VII.¹ Reactions with Carbon Disulfide and Potassium *O*-Alkyl Dithiocarbonates. Synthesis and Transformations of 2,3,7,8-Tetrahydro-5*H*-diimidazo[2,1-*b*:1',2'-*e*][1,3,5]thiadiazine-5-thione

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2-Chloro-4,5-dihydroimidazole **1** reacted with carbon disulfide to give 2,3,7,8-tetrahydro-5*H*-diimidazo[2,1-*b*:1',2'-*e*][1,3,5]thiadiazine-5-thione **5**. Acid hydrolysis of **5** gave imidazolidine-2-thione **6**, which reacted with amines, dialkylhydrazines, and alkoxides to give thioureas **9**, thiosemicarbazides **10** and thiocarbamates **11**, respectively. Reaction of the hemisulfate of **1** with excess of potassium *O*-alkyl dithiocarbonates afforded diesters of thiodicarbamic acid **13**.

Recently, Yasumoto *et al.* have reported² on the cyclocondensation of dialkylcyanamides with carbon disulfide at high pressure leading to the formation of 1,3,5-thiadiazine derivatives. We now wish to describe that 2-chloro-4,5-dihydroimidazole **1** containing a chloroamidino moiety reacted with CS₂ under mild conditions to give diimidazo[1,3,5]-thiadiazine **5**. The reaction outlines the value of compound **1** in the constructions of novel nitrogen-bridgehead heterocyclic systems.³

Results and Discussion

Treatment of the compound **1** with carbon disulfide in the presence of triethylamine at 20 °C for 48 h afforded the title 1,3,5-thiadiazine **5** in 54% yield. The mechanistic pathway for this reaction was deduced as shown in Scheme 1.

The initial step is the addition of the N-H group of **1** to the C=S double bond of the disulfide, followed by an internal nucleophilic substitution of the chlorine atom to give imidazothiazetidine **3**. Then, the intermediate **3** reacts with a second molecule of **1** yielding the chloro derivative **4**. The final product is formed by 1,3,5-thiadiazine ring closure in a second intramolecular displacement of the chlorine with a sulfur atom. It is noteworthy that the intermediate imidazothiazetidine **3** cannot be isolated from the reaction mixture, apparently due to its high susceptibility to the nucleophilic ring opening.

The ¹H NMR spectrum of **5** revealed two multiplets at δ 4.0 and 4.25, and a pattern typical of the AA'BB' system. The ¹³C NMR spectrum exhibits four resonances: two signals indicative of CH₂ groups at δ 51.1 and 53.0, as well as signals at δ 145.6 and 167.9 due to the C=N and C=S groups, respectively. Molecular structure obtained from X-ray analysis of compound **5** is shown in Fig. 1.

Examination of the reactivity of thiadiazine **5** revealed its relative inertness to basic hydrolysis with 5% NaOH. Acid hydrolysis, however, with 10% hydrochloric acid at 20 °C gave

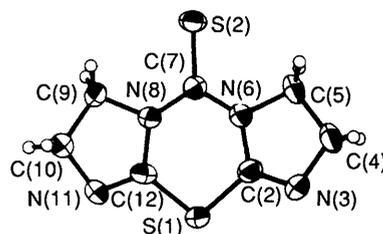


Fig. 1 Molecular structure of compound **5**

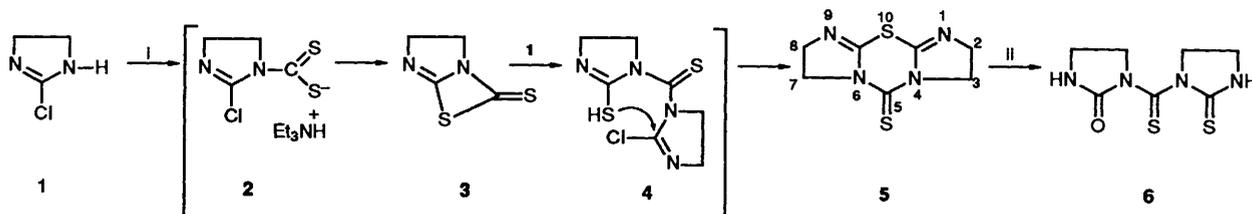
a high yield of imidazolidine-2-thione **6** as a result of C-S bond cleavage.

The structural assignment of compound **6** is based on the following evidence: the mass spectrum exhibits a molecular ion peak at *m/z* 230 (30.2%); in the IR spectrum, the N-H and C=O absorptions are observed at ν_{\max} 3215 and 1730 cm⁻¹, respectively; and the ¹³C NMR spectrum shows three peaks due to trigonal carbon atoms at δ 179.5 (C=S), 179.0 (C=S) and 152.5 (C=O).

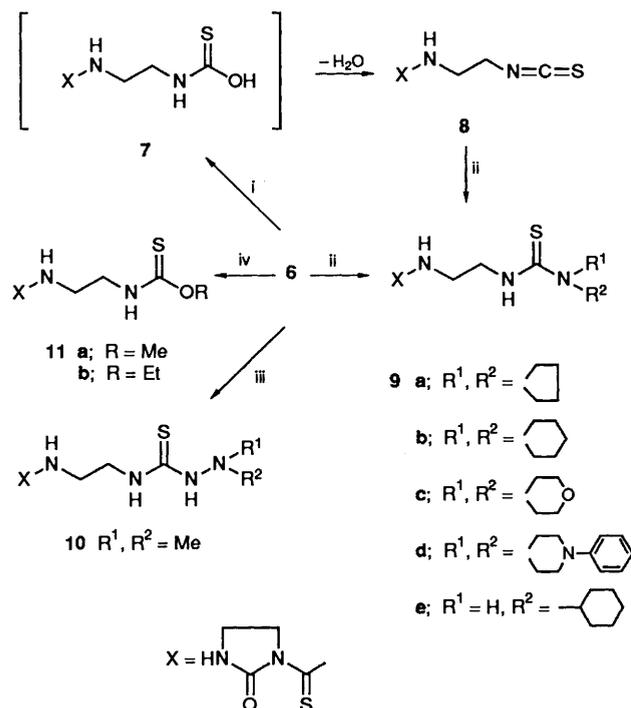
Compound **6** was applied to the synthesis of variously functionalized ethylenediamines **9**, **10** and **11** (Scheme 2). The method is based on our finding that **6**, which can be considered a dithiotriuret derivative, reacted selectively with nucleophilic reagents to give the products of the nucleophilic ring opening of the imidazolidine-2-thione moiety. Thus, refluxing of **6** in water for 10 min led to the formation of isothiocyanate **8** *via* elimination of water from the initially formed thiocarbamic acid **7**.

In the IR spectrum of **8**, characteristic bands for the N=C=S group are present (ν_{\max} 2120 and 2190 cm⁻¹) together with a band at ν_{\max} 1725 cm⁻¹ assignable to the C=O group.

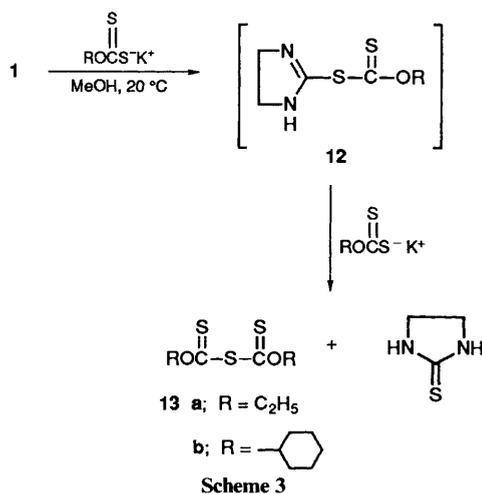
The reaction of **6** with primary and secondary amines, as well as *N,N*-dialkylhydrazines carried out in boiling ethanol afforded thioureas **9** and thiosemicarbazides **10**. In a related reaction compound **6** on treatment with sodium alkoxide at 20 °C was transformed into the thiocarbonate **11**.



Scheme 1 Reagents and conditions: i, CS₂/Et₃N, CH₂Cl₂, 20 °C; ii, 10% HCl, 20 °C



Scheme 2 Reagents and conditions: i, H₂O, reflux; ii, R¹R²NH; iii, R¹R²NNH₂; iv, RO⁻Na⁺



The spectral properties of compounds **9**, **10** and **11** are in full accord with the assigned structures. Moreover, the reactions of isothiocyanate **8** with suitable amines gave the products **9** with identical spectroscopic and physicochemical characteristics to those obtained from **6**.

We further investigated the reaction of **1** with potassium *O*-alkyl dithiocarbonates (xanthates) and found that it provides a versatile method for preparation of the diesters of thiodicarbonyl acid of type **13** (Scheme 3).

The reaction involves formation of the unstable 2-imidazoline derivative **12**, which *in situ* undergoes reaction with a second molecule of the xanthate to give products **13**. The best results were obtained when the hemisulfate of **1** was treated with a three-fold excess of the xanthate in methanol at room temperature for 0.5 h.

Compounds of type **13** are the well known thioacylating agents.^{4,5}

Experimental

Melting points were determined with a Büchi capillary

apparatus and are uncorrected. Instrumentation: ¹H NMR, Varian VXR 300 instrument at 300 MHz using tetramethylsilane as the internal standard; ¹³C NMR, Varian XL 200 instrument using the resonance of solvent for calibration; MS, LKB 900 S instrument (electron impact at 70 eV); IR, Specord M-80 instrument.

2,3,7,8-Tetrahydro-5H-diimidazo[2,1-b:1',2'-e][1,3,5]thiadiazine-5-thione 5.—To a solution of **1**⁶ (5 g, 0.05 mol) in CH₂Cl₂ (60 cm³), carbon disulfide (6 cm³, 0.1 mol) and triethylamine (6.9 cm³, 0.05 mol) were added. The mixture was kept at room temperature for 48 h, after which the triethylamine hydrochloride that had precipitated was filtered off using suction. The filtrate was evaporated to dryness and the residue obtained was washed with water and Et₂O. The resulting crude compound **5** was purified by recrystallization from benzene (2.8 g, 54%), m.p. 191–192 °C (Found: C, 39.9; H, 3.7; N, 26.2. C₇H₈N₄S₂ requires C, 39.6; H, 3.8; N, 26.4%); δ_H[(CD₃)₂SO] 4.0 (m, 4 H) and 4.25 (m, 4 H); δ_C[(CD₃)₂SO] 51.1, 53.0, 145.6 and 167.9; *m/z* 212 (M⁺, 45%).

1-[(2-Thioxoimidazolidin-1-yl)thiocarbonyl]imidazolidin-2-one 6.—Compound **5** (5 g, 23 mmol) was dissolved in 10% hydrochloric acid (50 cm³) and the reaction mixture was stirred at room temperature for 0.5 h. The product **6** that precipitated was collected by filtration, washed with water and dried in a desiccator over P₂O₅, yield 5 g (93%), m.p. 161–164 °C (Found: C, 36.8; H, 4.4; N, 24.1. C₇H₁₀N₄OS₂ requires C, 36.5; H, 4.4; N, 24.3%); δ_H[(CD₃)₂SO] 3.4 (m, 4 H) and 4.0 (m, 4 H); δ_C[(CD₃)₂SO] 36.0, 41.1, 48.6, 52.4, 152.5, 179.0 and 179.5; ν_{max}/cm⁻¹ 3215 (NH), 1730 (C=O), 1535, 1350, 1245 and 1215; *m/z* 230 (M⁺, 30), 171 (48), 170 (20), 145 (100), 129 (58) and 112 (35).

2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethyl Isothiocyanate 8.—Compound **6** (1 g, 4.3 mmol) was suspended in H₂O (20 cm³) and the mixture was refluxed for 10 min. The insoluble material was filtered off, and the filtrate cooled to room temperature. The solid that precipitated was collected by suction to give compound **8** (0.7 g, 70%), m.p. 109–111 °C (Found: C, 36.4; H, 4.7. C₇H₁₀N₄OS₂ requires C, 36.5; H, 4.4%; ν_{max}/cm⁻¹ 3175 (N–H), 2190, 2120 (N=C=S), 1725 (C=O), 1535, 1390, 1345 and 1265; δ_H(CDCl₃) 3.45 (t, 2 H), 3.9 (m, 4 H) and 4.25 (t, 2 H).

Reactions of 6 with Aliphatic Amines and N,N-Dialkylhydrazines. General Procedure.—Compound **6** (1 g, 4.3 mmol) and suitable amine or hydrazine (6 mmol) were heated in boiling ethanol (10 cm³) for 0.5 h. Then the reaction mixture was cooled to 5 °C and the resulting product **9** or **10** was separated by suction filtration and purified by recrystallization.

According to the above procedure the following were prepared.

1-2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethylthiocarbamoyl}pyrrolidine 9a.—This was prepared from **6** and pyrrolidine in 92% yield, m.p. 198–200 °C (methanol) (Found: C, 43.5; H, 6.1. C₁₁H₁₉N₅OS₂ requires C, 43.8; H, 6.3%); ν_{max}/cm⁻¹ 3185, 1725 (C=O), 1550, 1470, 1400 and 1265; δ_H[(CD₃)₂SO] 2.0 (m, 4 H), 3.6 (m, 6 H), 3.8 (m, 4 H), 4.2 (t, 2 H), 7.5 (s, 1 H, N–H), 8.1 (s, 1 H, N–H) and 10.5 (s, 1 H, N–H); *m/z* 301 (M⁺, 15%), 230(16), 171(48), 170(11), 145(100), 129(13), 71(25) and 70(39).

1-2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethylthiocarbamoyl}piperidine 9b.—This was prepared from **6** and piperidine in 71% yield, m.p. 182–184 °C (methanol) (Found: C, 49.5; H, 6.7. C₁₂H₂₁N₅OS₂ requires C, 45.7; H, 6.7%);

Table 1 Crystal data for compound 5

| | |
|------------------------|---|
| Formula | C ₇ H ₈ N ₄ S ₂ |
| <i>M</i> | 212.29 |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>a</i> |
| Unit cell parameters | |
| <i>a</i> | 8.230(1) Å |
| <i>b</i> | 14.634(2) Å |
| <i>c</i> | 8.254(1) Å |
| β | 116.80(1) Å |
| <i>v</i> | 4 |
| <i>Z</i> | 1.59 g cm ⁻³ |
| μ (Cu-K α) | 50.1 cm ⁻¹ |

$\nu_{\max}/\text{cm}^{-1}$, 3185, 1725 (C=O), 1550, 1455, 1390, 1310 and 1265; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.7 (m, 6 H), 3.5 (t, 2 H), 3.9 (m, 8 H), 4.2 (t, 2 H), 7.9 (s, 1 H, NH), 8.1 (s, 1 H, N-H) and 10.6 (s, 1 H, N-H).

4-{2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethylthiocarbamoyl}morpholine **9c**.—This was prepared from **6** and morpholine in 52% yield, m.p. 185–187 °C (methanol) (Found: C, 41.4; H, 6.2; C₁₁H₁₉N₅O₂S₂ requires C, 41.6; H, 6.0%). $\nu_{\max}/\text{cm}^{-1}$ 3230, 1725 (C=O), 1630, 1550, 1395 and 1265; $\delta_{\text{H}}[(\text{CO}_3)_2\text{SO}]$ 3.4 (m, 4 H), 3.8 (m, 10 H), 4.2 (t, 2 H), 8.0 (s, 1 H, N-H), 8.1 (s, 1 H, N-H) and 10.5 (s, 1 H, N-H).

1-{2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethylthiocarbamoyl}-4-phenylpiperazine **9d**.—This was prepared from **6** and *N*-phenylpiperazine in 51% yield, m.p. 195–197 °C (ethanol) (Found: C, 52.2; H, 6.5; C₁₇H₂₄N₆OS₂ requires C, 52.0; H, 6.2%). $\nu_{\max}/\text{cm}^{-1}$ 3185, 1725 (C=O), 1600, 1545, 1390, 1315 and 1265; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 3.3 (m, 6 H), 3.5–4.2 (m, 10 H), 7.0 (m, 3 H), 7.35 (m, 2 H), 8.0 (s, 2 H, N-H) and 10.5 (s, 1 H, N-H).

1-Cyclohexyl-3-{2-[(2-oxoimidazolidin-1-yl)thiocarbonylamino]ethyl}thiourea **9e**.—This was prepared from **6** and cyclohexylamine in 48% yield, m.p. 197–199 °C (DMF-H₂O) (Found: C, 47.1; H, 7.1; C₁₃H₂₃N₅OS₂ requires C, 47.4; H, 7.0%). $\nu_{\max}/\text{cm}^{-1}$ 3215, 1725 (C=O), 1535, 1470, 1390, 1265, 1230 and 1170; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.3–2.3 (m, 10 H), 3.6 (m, 3 H), 3.8 (m, 4 H), 4.25 (m, 2 H), 7.6 (s, 2 H, N-H), 8.1 (s, 1 H, N-H) and 10.7 (s, 1 H, N-H).

1,1-Dimethyl-4-{2-[(2-oxoimidazolidin-1-yl)thiocarbonylamino]ethyl}thiosemicarbazide **10**.—This was prepared from **6** and *N,N*-dimethylhydrazine in 71% yield, m.p. 168–170 °C (ethanol) (Found: C, 37.0; H, 6.0. C₉H₁₈N₆OS₂ requires C, 37.2; H, 6.2%). $\nu_{\max}/\text{cm}^{-1}$ 3215, 1715 (C=O), 1550, 1390, 1265 and 1210; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 2.6 (s, 6 H), 3.5 (m, 2 H), 3.8 (m, 4 H), 4.25 (m, 2 H), 8.1 (s, 1 H, N-H), 8.25 (s, 1 H, N-H), 8.8 (s, 1 H, N-H) and 10.5 (s, 1 H, N-H); m/z 290 (M⁺, 56%), 172 (22), 171 (69), 170 (16), 146 (23), 145 (56), 103 (20), 102 (43) and 60 (100).

O-Methyl *N*-{2-[(2-Oxoimidazolidin-1-yl)thiocarbonylamino]ethyl}thiocarbamate **11a**.—Compound **6** (1 g, 4.3 mmol) was added to a solution of sodium methoxide (0.54 g, 10 mmol) in methanol (10 cm³) and the reaction mixture was stirred at room temperature for 10 min. Water (10 cm³) was then added and the solution was neutralized with 10% hydrochloric acid. After being cooled to 5 °C, the solid that precipitated was collected by suction and recrystallized from methanol (0.9 g, 79%), m.p. 163–165 °C (ethanol) (Found: 36.3; H, 5.1. C₈H₁₄N₄O₂S₂ requires C, 36.6; H, 5.4%). $\nu_{\max}/\text{cm}^{-1}$ 3260, 1700, 1535, 1375, 1330, 1265 and 1185; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 3.2–3.9 (m, 6 H), 3.6 (s, 3 H, OCH₃) and 4.4

Table 2 Fractional atomic co-ordinates with esd's in parentheses

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|------------|------------|
| S(1) | -0.2654(2) | 0.4910(1) | 0.0118(2) |
| S(2) | 0.0651(2) | 0.2078(1) | 0.2588(2) |
| C(2) | -0.0492(9) | 0.4748(4) | 0.1950(9) |
| N(3) | 0.0392(7) | 0.5412(4) | 0.2885(8) |
| C(4) | 0.2097(10) | 0.5032(5) | 0.4318(10) |
| C(5) | 0.1982(9) | 0.3995(4) | 0.4153(8) |
| N(6) | 0.0240(7) | 0.3876(3) | 0.2450(7) |
| C(7) | -0.0401(8) | 0.3056(4) | 0.1670(8) |
| N(8) | -0.1937(6) | 0.3072(3) | 0.0051(6) |
| C(9) | -0.2878(8) | 0.2242(4) | -0.0979(8) |
| C(10) | -0.4425(8) | 0.2668(5) | -0.2661(8) |
| N(11) | -0.4499(6) | 0.3639(3) | -0.2267(6) |
| C(12) | -0.3080(8) | 0.3812(4) | -0.0797(8) |

(m, 2 H); m/z 262 (M⁺, 100%), 161 (34), 103 (20), 102 (66), 88 (24) and 85 (18).

O-Ethyl *N*-{2-[(2-oxoimidazolidin-1-yl)thiocarbonylamino]ethyl}thiocarbamate **11b**.—This compound was prepared from **6** and sodium ethoxide according to the procedure described for **11a**, yield 66%, m.p. 149–151 °C (methanol-water) (Found: C, 38.8; H, 5.5. C₉H₁₆N₄O₂S₂ requires C, 39.1; H, 5.8%). $\nu_{\max}/\text{cm}^{-1}$ 3310, 1700, 1525, 1430, 1375, 1330, 1265 and 1185; $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.25 (t, 3 H), 3.2–3.8 (m, 6 H), 4.1 (q, 2 H) and 4.4 (m, 2 H).

Thiodicarbonate *O,O*-Diethyl Ester **13a**.—To a solution of potassium *O*-ethyl dithiocarbonate (12.3 g, 75 mmol) in methanol (50 cm³) was added hemisulfate of compound **1** (5 g, 25 mmol) and the reaction mixture was stirred at room temperature for 0.5 h. Water (50 cm³) was added and the crude product that precipitated was separated by suction filtration. Recrystallization from methanol gave 4.4 g (91%) of **13a**, m.p. 52 °C (lit.⁴ 52–53 °C); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.5 (t, 6 H) and 4.65 (q, 4 H).

Thiodicarbonate *O,O*-Dicyclohexyl Ester **13b**.—This was prepared from hemisulfate of compound **1** and potassium *O*-cyclohexyl dithiocarbonate according to the procedure described for **13a**, yield 85%, m.p. 78–79 °C (methanol) (Found: C, 52.7; H, 6.6. C₁₄H₂₂O₂S₃ requires C, 52.8; H, 6.9%). $\delta_{\text{H}}(\text{CDCl}_3)$ 1.2–1.5 (m, 6 H), 1.55–1.7 (m, 5 H), 1.8 (m, 4 H), 2.1 (m, 4 H) and 5.5 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3)$ 23.8, 25.1, 30.9, 84.3 and 204.5; m/z 318 (M⁺, 2%), 236 (11), 177 (20), 95 (17), 84 (53), 82 (100) and 80 (50).

Crystal Structure Analysis of Compound 5.—Colourless crystals obtained from methanol solution were twinned plates. A single crystal of dimensions 0.5 × 0.5 × 0.05 mm was cut from a twinned specimen. The lattice parameters given in Table 1 were determined by a least-squares fitting of the setting angles of 15 reflections (2 θ in the range 17 to 27°). Intensities of reflections were measured on a Syntex *P*2₁ diffractometer with graphite monochromatized Cu-K α radiation ($\lambda = 1.54178$ Å) to $2\theta_{\max} = 115^\circ$. Lorentz and polarization corrections were applied to the net intensities, absorption was ignored. Integrated intensities were obtained by peak profile analysis according to Lehmann and Larsen.⁷ No significant intensity variation was observed for two standard reflections. Out of 1361 measured reflections 1092 had $I > 2\sigma(I)$ and they were considered observed. The structure was solved straightforwardly by direct methods with program MULTAN80.⁸ The positions and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares method. The positions of the hydrogen atoms were calculated from

Table 3 Bond distances and angles with esd's in parentheses

| Distance/Å | | Bond angles/° | |
|-------------|----------|-------------------|----------|
| S(1)–C(2) | 1.756(6) | C(2)–S(1)–C(12) | 100.2(3) |
| S(2)–C(7) | 1.668(6) | S(1)–C(2)–N(3) | 120.6(6) |
| C(2)–N(6) | 1.392(8) | C(2)–N(3)–C(4) | 106.3(6) |
| C(4)–C(5) | 1.523(9) | C(4)–C(5)–N(6) | 101.2(5) |
| N(6)–C(7) | 1.352(7) | C(5)–N(6)–C(7) | 123.6(5) |
| N(8)–C(9) | 1.485(7) | S(2)–C(7)–N(6) | 122.3(5) |
| C(9)–C(10) | 1.531(8) | S(2)–C(7)–N(8) | 121.5(5) |
| N(11)–C(12) | 1.274(6) | C(7)–N(8)–C(9) | 124.1(5) |
| S(1)–C(12) | 1.743(6) | N(8)–C(9)–C(10) | 101.1(5) |
| C(2)–N(3) | 1.250(8) | C(10)–N(11)–C(12) | 107.0(5) |
| N(3)–C(4) | 1.477(8) | S(1)–C(12)–N(11) | 121.0(5) |
| C(5)–N(6) | 1.498(7) | S(1)–C(2)–N(6) | 121.0(5) |
| C(7)–N(8) | 1.364(6) | N(3)–C(2)–N(6) | 118.4(6) |
| N(8)–C(12) | 1.398(7) | N(3)–C(4)–C(5) | 107.8(6) |
| C(10)–N(11) | 1.465(9) | C(2)–N(6)–C(5) | 106.0(5) |
| | | C(2)–N(6)–C(7) | 130.5(6) |
| | | N(6)–C(7)–N(8) | 116.2(5) |
| | | C(7)–N(8)–C(12) | 128.4(5) |
| | | C(9)–N(8)–C(12) | 106.7(5) |
| | | C(9)–C(10)–N(11) | 107.1(5) |
| | | N(8)–C(12)–N(11) | 116.4(5) |
| | | C(1)–C(12)–N(8) | 122.6(5) |

geometrical conditions [$d(\text{C}–\text{H})$ 1.08 Å]. The H atoms contributed to F_c but their parameters were not refined. Empirical isotropic extinction parameter x was used to correct F_c according to $F' = F_c(1 - xF_c^2/\sin \theta)$; x converged at $2(1) \times 10^{-6}$. Final values of R and R_w are 0.091 and 0.111, respectively. The weights were $w = 1/[\sigma^2(F_o) + 0.00005F_o^2]$. The highest peak in the final difference map of $1.21 \text{ e } \text{Å}^{-3}$ was located near S(2), the lowest peak was $-0.67 \text{ e } \text{Å}^{-3}$.

* See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

Å^{-3} . The scattering factors used in calculations were those included in SHELX76.⁹ Calculations were performed using programs: SHELX76 for the refinement of the structure, ORTEP¹⁰ for drawings and programs written by Jaskólski¹¹ for molecular geometry analysis.

Final positional parameters of **5** are given in Table 2, molecular dimensions in Table 3. Hydrogen atom co-ordinates and thermal parameters are deposited at the CCDC.*

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