ALKYL-SUBSTITUTED BENZO[1,2-*d* :3,4-*d'*]DIIMIDAZOLES. PREPARATION AND ANNULAR TAUTOMERISM

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Abstract- The treatment of 4-nitro-5-amino-2,1,3-benzothiadiazole (**3**) with tin/hydrochloric acid in the presence of a carboxylic acid having a C1-C3 chain gave the corresponding 2,5-dialkylbenzo[1,2-*d*:3,4-*d'*]diimidazoles (**1**). When the amount of tin was reduced to a half, **3** afforded only 5-alkylimidazolo[4,5-*d*]benzothiadiazoles (**2**). Unsymmetrical dialkyldiimidazoles (**1**) were obtained from **2** in a second step. Annular tautomers due to NH-proton exchange of the imidazole rings of **1** and **2** could be observed in ^{1}H NMR spectra in DMSO-d$_6$ at a low concentration (*ca.* 5 x 10^{-4} M).

INTRODUCTION

Annular tautomerism of 5-membered cyclic compounds with more than two nitrogen atoms has extensively been investigated[1] and NMR techniques have been employed in the investigation. For the direct observation[2,3] of the tautomers in a solid state where the tautomerism is either slow or frozen, ^{13}C NMR have been shown to provide a useful tool. In a neutral organic solvent, the tautomerism is extremely fast on the NMR time scale,[1] but tautomers of 1,2-diazole (pyrazole),[4-7] 1,2,x-triazole (x = 3 and 4)[8] and tetrazoles[9] could be detected by using ^{1}H and ^{13}C NMR spectroscopy. Also, in a limited number of cases and at low temperatures, ^{1}H NMR signals of the two tautomers of imidazoles in solution have been seen.[10-13] Recently, it has been shown that both a unimolecular and a bimolecular process are operative in the concentration- and solvent-dependent annular tautomerism of dihydropyrimidine (1,3-prototropic shift), though it is not a fully conjugated system.[14,15]

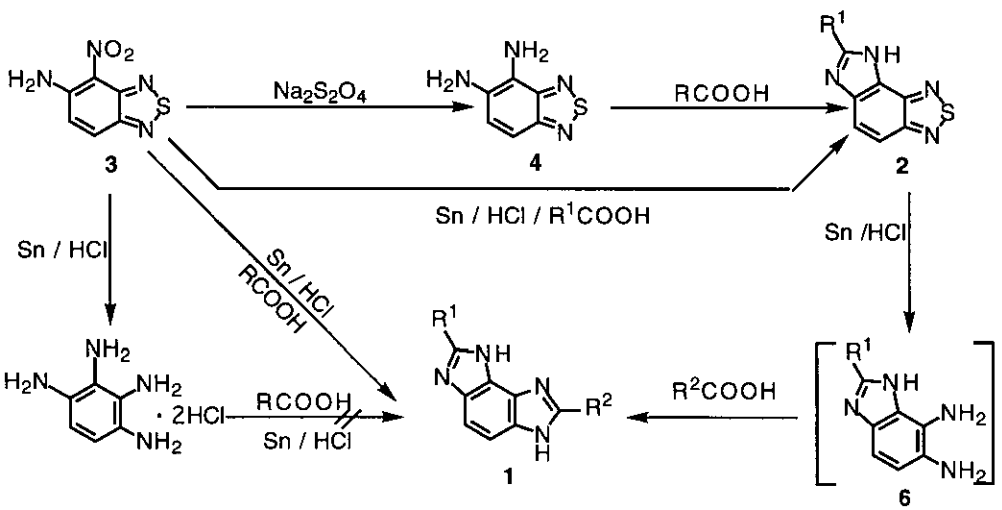
In the present article, it is shown that tautomers of 2,5-dialkylbenzo[1,2-*d*:3,4-*d'*]diimidazole (**1**) as well as

5-alkylimidazolo[4,5-*d*]benzo-2,1,3-thiadiazole (**2**) can be shown by ^{1}H NMR at a low concentration.

RESULTS AND DISCUSSION

Preparation of benzodiimidazoles (1) and imidazolobenzothiadiazoles (2).

Recently 4-nitro-5-amino-2,1,3-benzothiadiazole (**3**)[16] was reported as a good precursor for 1,2,3,4-benzenetetraamine, which in turn gives benzo[1,2-*d*:3,4-*d'*]diimidazole (**1a**; $R^1 = R^2 = H$ in Scheme 1) in the reaction with *N*,*N*-dimethylformamide.[17] Thus, it was expected that the reduction of **3** in the presence of a carbonyl compound might provide a convenient and direct method for **1**. The above expectation was realized in the reduction of **3** by using tin/hydrochloric acid in the presence of C1-C3 carboxylic acids (Scheme 1 and Table 1).



Scheme 1

Dimethyl- (**1b**) and diethylbenzo[1,2-*d*:3,4-*d'*]diimidazoles (**1c**) were obtained in 68% and 52% yields, respectively. Dipropyl derivative (**1d**) was also prepared, albeit with a low yield (18%). Carboxylic acid with a longer alkyl chain, as well as formic and benzoic acids, did not give the expected diimidazoles. In these cases, only tarry materials were formed, probably due to oxidation of 1,2,3,4-tetraaminobenzene during the work-up.

Interestingly when the amount of tin was reduced to a half, imidazolobenzothiadiazoles (**2a-b**) were produced selectively. This finding opens the way to the synthesis of unsymmetric dialkyl derivative (**1e**). Thus, ethyl derivative (**2b**) was treated with tin/hydrochloric acid in the presence of acetic acid, giving methyl ethyl derivative (**1e**). Diimidazole (**1**) can be considered to form *via* a sequence of reduction of the nitro group, cyclization to imidazolothiadiazole (**2**), reduction of thiadiazole ring to **6**, and cyclization with acid. Treatment of 1,2,3,4-tetraaminobenzene, which shows little differentiation of the reactivity for its

amino groups, afforded tars under the reductive conditions mentioned above. In fact, **3** can be regarded as a suitably protected synthetic equivalent of 1,2,3,4-tetraaminobenzene.

Table 1. Preparation of **1** and **2**.

Entry	Substrate (mmol)	Time (h)	conc.HCl (mL)	Carboxylic acid (ml)	Sn (g)	Product (R^1, R^2) (Yield, %)
1	**3** (5)	2	10.2	Acetic acid (13)	3.03	**1b** (CH_3, CH_3)(25)
2	**3** (5)	24	10.2	Acetic acid (13)	3.03	**1b** (CH_3, CH_3)(68)
3	**3** (5)	27	10.2	Propionic acid (13)	3.03	**1c** (C_2H_5, C_2H_5)(52)
4	**3** (2.5)	25	5.0	Butyric acid (7.7)	1.50	**1d** (C_3H_7, C_3H_7)(18)
5	**3** (5)	2	5.0	Acetic acid (7)	1.50	**2a** (CH_3, -)(49)
6	**3** (2.5)	4	2.5	Propionic acid (4.3)	0.75	**2b** (C_2H_5, -)(54)
7	**2b** (1.12)	17	1.25	Acetic acid (1.75)	0.38	**1e** (CH_3, C_2H_5)(31)

Annular Tautomerism of 1 and 2.

Possible annular tautomers for **1** and **2** are shown in Fugure 1.

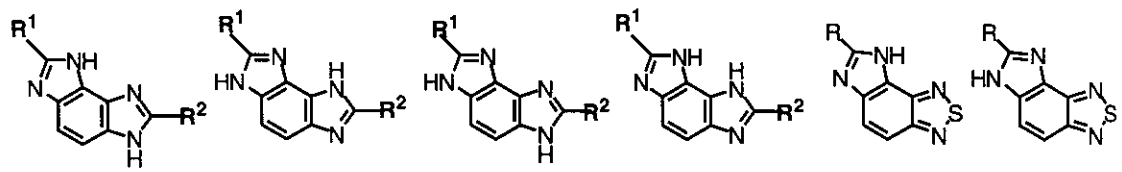


Figure 1. Annular tautomers of **1** and **2**.

It is well known that an intermolecular proton exchange process is responsible for a rapid annular tautomerization of 1,3-diazole (imidazole) in solution.[1,18] While benzodiimidazoles (**1b-1e**) are poorly soluble in most solvents, their ^{1}H NMR spectra could be assigned in DMSO-d_6 at the concentrations of 0.5 M, 0.05 M, 0.005 M, and 0.0005 M. Due to increasing dilution, the signals of the aromatic protons and the NH protons successively become broad, show coalescence, and give sharp well-separated signals, as represented by spectra of **1b** and **1e** (Figure 2).

For diimidazoles (**1**) where R^1=R^2, there exist three tautomers, one unsymmetric type **1-(A)** and two symmetric ones, **1-(B)** and **1-(C)**. In ^{1}H NMR spectrum of **1a** at the concentration of *ca.* 0.005 M, NH and imidazole-ring protons are observed each as a set of three singlet peaks of the relative intesities of 1.0:1.5:1.5; δ = 12.43, 12.56, and 12.98 ppm for NH protons and δ = 8.13, 8.07, and 8.18 ppm for imidazole-ring protons, respectively. The aromatic protons were shown as one singlet peak and the peaks of AB quartet pattern, the latter being assigned to unsymmetric tautomer **1a-(A)**. The similar spectra to that of **1a** were obtained for alkyl-substituted diimidazoles (**1b-d**), although the signals for NH and aromatic protons showed an up-field shift, as compared to those of **1a** and unsymmetric tautomer **1b-d(A)** could be

assigned.

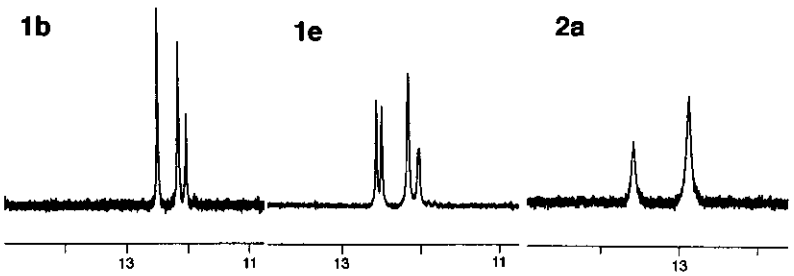


Figure 2. ^{1}H-NMR spectra of **1b**, **1e**, and **2a**.

The singlet peak due to aromatic protons of **1a-d** showed the presence of one symmetric isomer, either **1-(B)** or **1-(C)**. In each of the structures of **1-(B)** and **1-(C)**, two NH protons and two aromatic protons are equivalent. The chemical shift of NH protons of the observed symmetric tautomer is similar to that of the proton NH_A of **1-(A)**, which is shifted up-field, as compared to NH_B. As it seems unfavorable for **1-(C)** to accommodate two molecules of DMSO-d_6 in the bay-region, hydrogen-bonds between NH-proton and the solvent is supposed to be weaker in **1a-(B)** than **1a-(C)**. Thus, the symmetric tautomer observed is tentatively assigned as **1-(C)**.

In the spectrum of unsymmetric diimidazole (**1e**) in DMSO-d_6 at the concentration of 0.005 M, NH protons were observed as five singlet peaks with an intensity ratios of 1:1:4.5:2.25:2.25 in the region of ca. δ 12.0-12.6 ppm. The three peaks appeared at a lower magnetic field are assigned to NH protons of non-symmetric types, **1-(A-1)** and **1-(A-2)**, and the two in the higher magnetic field are assigned to NH protons of symmetric **1-(B)** tautomer, on the basis of the chemical shift. The aromatic protons of the two tautomers of type **1-(A)** could also be identified. The angular tautomerism of benzodiimidazoles (**1a-e**) favors the unsymmmetric form over the symmetric one as the tautomer ratios show in Table 2.

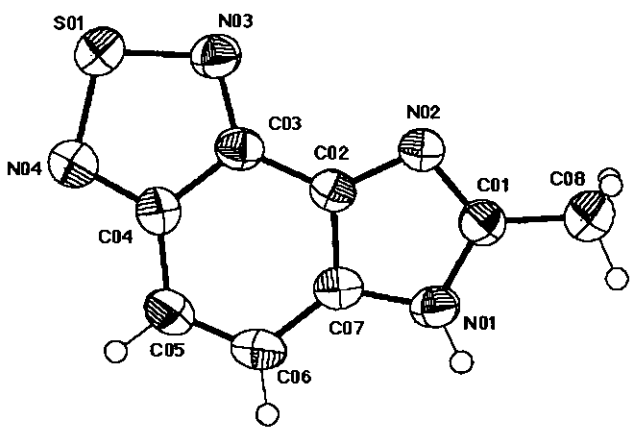


Figure 3. ORTEP View of **2a**.

Table 2. Ratios of tautomers of **1** and **2**.

Compd (R^1, R^2)	Concentration [10^{-4} M]	δ ppm (J Hz) Aromatic proton[a] / NH proton[b]	Ratio of (A)/(B)
1a (H, H)	6.5	7.33 and 7.50 (each d, J= 8.6 Hz), 7.37 /12.43, 12.56, 12.98	3/1
1b (CH_3, CH_3)	5.3	7.13 and 7.25 (each d, J=8.7 Hz), 7.14 /12.03, 12.16, 12.50	4.4/1
1c (C_2H_5, C_2H_5)	3.8	7.13 and 7.28 (each d, J=8.6 Hz), 7.14 /12.02, 12.16, 12.54	3.3/1
1d (C_3H_7, C_3H_7)	5.0	7.15 and 7.28 (each d, J=8.8 Hz), 7.16 /12.02, 12.16, 12.55	3.1/1
1e (CH_3, C_2H_5)	5.3	7.11-7.13 and 7.14-7.18 (each m), 7.26 (d, J=8.6 Hz), 7.50 (d, J=8.4 Hz) /12.02, 12.04, 12.16, 12.49, 12.57	4.5/1
2a (CH_3, --)	5.5	7.73 and 7.86 (each d, J=8.8 Hz), 7.85-7.95 (br s) /12.89, 13.59	2/1
2b (C_2H_5, --)	5.9	7.72 and 7.92 (each d, J=9.4 Hz), 7.50 and 7.86 (each d, J= 8.9 Hz) /12.87, 13.56	2.4/1

a) Singlet umless otherwise stated. b) Singlet.

Imidazolothiadiazoles (**2**) show a similar behavior in the variable-concentration ^{1}H NMR spectra (Figure 2), similar to **1** and the presence of two annular tautomers **2-(A)** and **2-(B)** could be ascertained in solution. In a solid state, **2a** takes the **2-(A)** form, as the X-Ray crystallographic analysis disclosed in Figure 3.

The tautomer ratios (**2-(A)/2-(B)**) of **2a,b** are small (Table 2). Assignment of the NH-protons to the tautomers was done on the basis of a reasoning similar to that presented above for **1**.

In conclusion, annular tautomers due to NH-proton exchange of the imidazole rings of **1** and **2** could be observed in ^{1}H NMR spectra measured at a low concentration (0.005 M). Finally, it must be noted that singlet peaks, albeit broad, can be observed for benzimidazole at a concentration of 0.005 M.

EXPERIMENTAL

Melting points were determined on a Yanaco micromelting point apparatus (MP 500D) and are uncorrected. IR spectra were recorded on KBr pellets on a JASCO IR-700 spectrophotometer. ^{1}H NMR spectra were

obtained on a JEOL JNM-LA 300 in a DMSO-d_6 solution and ratios of tautomers were determined according to the intensites of NH and aromatic proton signals obtained from the accumulation of 7200 scans at 30 °C. MS spectra were obtained at 75 eV by using a JMS-01SA-2. Elemental analyses were performed on Yanaco CHN corder MT-5.

2,5-Dimethylbenzo[1,2-*d*:3,4-*d'*]diimidazole (1b): To a stirred mixture of **3** (1.00 g, 5 mmol) and tin powder (3.03 g, 25.5 mmol) in acetic acid (13 mL) under reflux, concentrated hydrochloric acid (10.2 mL) was added dropwise for 1 h. The reaction mixture was heated under reflux for 24 h and cooled to rt. The hydrochloride precipitated was filtered, treated with saturated aqueous sodium hydrogen carbonate, and dissolved into boiling ethanol (80 mL). Insoluble materials were filtered off and the solvent was evaporated *in vacuo*, leaving the residue which, on recrystallization from water, gave **1b** (0.73 g, 68%) as colorless needles (water), mp 300-303 °C. IR: 3346-2918, 1619, 1533, 1019, 806; ^{1}H NMR: 2.51 (6H, s), 7.21 (2H, s); MS: m/z 187 (MH^+). *Anal.* Calcd for $C_{10}H_{10}N_4$+ $2H_2O$: C, 54.07; H, 6.35; N, 25.21. Found: C, 54.04; H, 6.59; N, 25.16.
On heating at 80 °C *in vacuo* for 24 h, **1b** was made to be water-free. *Anal.* Calcd for $C_{10}H_{10}N_4$; C, 62.65; H, 5.62; N, 29.22. Found; C, 62.57; H, 5.85; N, 29.32.

2,5-Diethylbenzo[1,2-*d*:3,4-*d'*]diimidazole (1c): To a stirred mixture of **3** (1.00 g, 5 mmol) and tin powder (3.03 g, 25.5 mmol) in propionic acid (13 mL) under reflux, concentrated hydrochloric acid (10.2 mL) was added dropwise for 1 h. The reaction mixture was heated under reflux for 27 h and cooled to rt. The hydrochloride precipitated was filtered, treated with saturated aqueous sodium hydrogen carbonate, and dissolved into boiling ethanol (80 mL). Insoluble materials were filtered off and the solvent was evaporated *in vacuo*, leaving the residue which, on recrystallization from aqueous ethanol, gave **1c** (0.57 g, 52%) as colorless needles; mp 254-257 °C; IR: 3300-2800, 1614, 1527, 1415, 1309, 1244, 845; ^{1}H NMR: 1.47 (6H, t, J= 7.6 Hz), 3.21 (4H, q, J= 7.6 Hz), 7.77 (2H, s); MS: m/z 214 (M^+). *Anal.* Calcd for $C_{12}H_{14}N_4$ + $2H_2O$: C, 57.58; H, 7.25; N, 22.38. Found; C, 58.07; H, 7.33; N, 22.39.

2,5-Dipropylbenzo[1,2-*d*:3,4-*d'*]diimidazole (1d):To a stirred mixture of **3** (0.500 g, 2.5 mmol) and tin powder (1.50 g, 12.5 mmol) in butyric acid (7.7 mL) under reflux, concentrated hydrochloric acid (5 mL) was added dropwise for 1 h. The reaction mixture was heated under reflux for 27 h and cooled to rt. The hydrochloride precipitated was filtered, treated with saturated aqueous sodium hydrogen carbonate, and dissolved into boiling ethanol (40 mL). Insoluble materials were filtered off and the solvent was evaporated *in vacuo*, leaving the residue which, on recrystallization from aqueous ethanol, gave **1c** (0.10g, 18%) as colorless prisms; mp 340-344 °C; IR: 3200-2700, 1614, 1524, 1414, 1308, 1281, 837; ^{1}H NMR: 0.95 (6H, t, J= 7.4 Hz), 1.98-1.84 (4H, m), 2.81 (4H, t, J= 7.4 Hz), 7.22 (2H, s); MS: m/z 242 (M^+).
On heating at 80 °}C *in vacuo* for 24 h, **1d** was made to be water-free. *Anal.* Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49; N, 23.12. Found; C, 69.41; H, 7.50; N, 23.02.

2-Ethyl-5-methylbenzo[1,2-*d*:3,4-*d'*]diimidazole (1e): To a stirred mixture of **2b** (0.250 g, 1.22 mmol), tin powder (0.83 g, 7 mmol), and acetic acid (1.75 mL) under reflux, concentrated hydrochloric

acid (1.25 mL) was added dropwise for 10 min. The reaction mixture was heated under reflux for 17 h and cooled to rt. Precipitates formed was filtered, treated with saturated aqueous sodium hydrogen carbonate, and extracted with hot ethanol. The extract was evaporated and the residue was recrystallized from water, gave **1e** (0.075 g, 31%) as colorless prisms; mp 250-280 °C; IR: 3500-2500, 1642, 1604, 1550, 1402, 1318, 1244, 1060, 1016, 786; ^{1}H NMR: 1.35 (3H, t, J= 7.6 Hz), 2.52 (3H, s), 2.87 (2H, q, J= 7.6 Hz), 7.23 (2H, s), 12.34 (1H, br s); MS: m/z 200 (M^+).
On heating at 100 °C *in vacuo* for 48 h, **1e** was made to be water-free. *Anal.* Calcd for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found; C, 66.35; H, 6.12; N, 28.37.

5-Methylimidazolo[4,5-*d*]benzo-2,1,3-thiadiazole (2a): To a stirred mixture of **3** (1.00 g, 5 mmol), tin powder (3.03 g, 25.5 mmol), and acetic acid (7 mL) under reflux, concentrated hydrochloric acid (5 mL) was added dropwise for 10 min. The reaction mixture was heated under reflux for 2 h and cooled to rt. Precipitates formed was filtered, washed with saturated aqueous sodium hydrogen carbonate and recrystallized from aqueous ethanol, giving **2a** (0.47 g, 49%) as yellowish green needles; mp 272-275 °C; IR: 3234-2900, 1574, 1476, 1305, 1065, 818; ^{1}H NMR: 2.62 (3H, s), 7.75 (1H, d, J= 9.2 Hz), 7.90 (1H, d, J= 9.2 Hz); MS: m/z 190 (M^+). *Anal.* Calcd for $C_8H_6N_4S$: C, 50.51; H, 3.18; N, 29.45. Found; C, 50.22; H, 3.35; N, 29.44.

5-Ethylimidazolo[4,5-*d*]benzo-2,1,3-thiadiazole (2b): To a stirred mixture of **3** (0.50 g, 2.5 mmol), tin powder (0.75 g, 6 mmol), and propionic acid (4.3 mL) under reflux, concentrated hydrochloric acid (2.5 mL) was added dropwise for 10 min. The reaction mixture was heated under reflux for 4 h, cooled to rt, and neutralized with saturated aqueous sodium hydrogen carbonate. Precipitates formed was filtered, washed with hot methanol, and recrystallized from aqueous ethanol, giving **2b** (0.275 g, 54%) as pale yellow needles; mp 192-193 °C; IR: 3162-2794, 1604, 1528, 1325, 1275, 1175, 808; ^{1}H NMR: 1.38 (3H, t, J= 7.6 Hz), 2.94 (2H, q, J= 7.6 Hz), 7.76 (1H, d, J= 9.2 Hz), 7.90 (1H, d, J= 9.2 Hz); MS: m/z 204 (M^+). *Anal.* Calcd for $C_9H_8N_4S$: C, 52.92; H, 3.95; N, 27.43. Found; C, 52.87; H, 4.08; N, 27.30.

X-RAY CRYSTAL STRUCTURE DETERMINATION

Crystal data on 2a. $C_8H_6N_4S$, Mw = 190.23, orthorhombic, space group $P2_1/c$, a = 9.140(1), b = 11.639(3), c = 7.640(1) Å, β= 97.95°, V = 804.9(8) Å^3, Z = 4, Dc = 1.570 g cm^{-3}, F (000) = 392. Yellowish green needles, dimensions 0.27 x 0.13 x 0.10 mm, μ(Cu-Ka) = 3.173 cm^{-1}.

Data collection and analysis.
All crystallographic measurements were carried out at 296°K on a Enraf-Nonius FR-590 diffractometer operating in the ω-2θ scan mode; 4.89 < θ < 64.97°, using graphite monochromated CuKα-irradiation (λ = 1.54184 Å), 1480 measured, 1366 unique reflections. Structure (**2a**) was solved by direct methods using SIR 92[19] and refined by full-matrix least squares calculation for F^2 (246 parameters) using SHELXL93.[20]

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. $R = 0.0679$ ($Rw = 0.1803$, for F^2). The weighting scheme $w=1/[\sigma^2 (Fo^2)+(0.0650P)^2+0.5911P]$ where $P=(Fo^2+2Fc^2)/3$ was used.

Selected bond distances and angles are given in Tables 3 and 4.

The supplementary materials have been deposited at the Cambridge Crystallographic Data Center.

Table 3. Selected bond distances (Å) for **2a**.

C (1) - N (2)	1.329 (5)	C (1) - N (1)	1.358 (5)	C (1) - C (8)	1.481 (6)
C (2) - N (2)	1.367 (5)	C (2) - C (7)	1.380 (5)	C (2) - C (3)	1.423 (5)
C (3) - N (3)	1.342 (5)	C (3) - C (4)	1.441 (5)	C (4) - N (4)	1.345 (5)
C (4) - C (5)	1.430 (5)	C (5) - C (6)	1.347 (5)	C (6) - C (6)	1.407 (5)
C (7) - N (1)	1.367 (5)	N (3) - S (1)	1.615 (5)	N (4) - S (1)	1.624 (5)

Table 4. Selected bond angles for **2a**.

N (2)-C (1)-N (1)	111.6 (4)	N (2)-C (1)-C (8)	125.4 (4)	N (1)-C (1)-C (8)	123.0 (4)
N (2)-C (2)-C (7)	112.0 (4)	N (2)-C (2)-C (3)	130.6 (4)	C (7)-C (2)-C (3)	117.3 (4)
N (3)-C (3)-C (2)	128.6 (4)	N (3)-C (3)-C (4)	113.4 (4)	C (2)-C (3)-C (4)	118.0 (3)
N (4)-C (4)-C (5)	125.5 (4)	N (4)-C (4)-C (3)	112.9 (4)	C (5)-C (4)-C (3)	121.5 (4)
C (6)-C (5)-C (4)	118.9 (4)	C (5)-C (6)-C (7)	119.6 (4)	N (1)-C (7)-C (2)	103.9 (3)
N (1)-C (7)-C (6)	131.4 (4)	C (2)-C (7)-C (6)	124.7 (4)	C (1)-C (1)-C (7)	108.3 (3)
C (1)-N (2)-C (2)	104.1 (3)	C (3)-N (3)-S (1)	106.4 (3)	C (4)-N (4)-S (1)	106.3 (3)
N (3)-S (1)-N (4)	100.9 (2)				

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Received, 8th October, 1997