Preparation and X-Ray Structure of $4\text{-BrC}_6\text{H}_4\overline{\text{CNSC(Cl)N}}$

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Z. Naturforsch. **52 b,** 557–559 (1997); received September 5, 1996

Crystal Structure, 1,2,4-Thiadiazole, Intramolecular Cyclization

The title compound was obtained in 82% yield by the intramolecular cyclization of $4\text{-BrC}_6\text{H}_4\text{C(NSCCl}_3)[\text{N(SiMe}_3)_2]$ in CH_2Cl_2 at 23°C. It crystallizes in the triclinic system, space group $P\bar{1}$, $a = 7.957(3)$ Å, $b = 10.864(5)$ Å, $c = 5.625(1)$ Å, $\alpha = 95.94(3)°$, $\beta = 97.79(2)°$, $\gamma = 100.72(3)°$, $V = 469.2(3)$ Å^3, and $Z = 2$. The bond lengths of the planar $\text{C}_2\text{N}_2\text{S}$ ring indicate partial π-delocalization.

Introduction

A variety of synthetic approaches to the 1,2,4-thiadiazole ring system is available [1]. For example, the cyclocondensation of carbamidines $\text{RC(NH}_2)(\text{NH}_2)^+\text{Cl}^-$ with Cl_3CSCl produces $\text{R}\overline{\text{CNSC(Cl)N}}$ [1]. In this note we report the synthesis and X-ray structure of 3-*p* -bromophenyl-5-chloro-1,2,4-thiadiazole (**2**), which was obtained by the spontaneous intramolecular cyclization of $4\text{-BrC}_6\text{H}_4\text{C(NSCCl}_3)[\text{N(SiMe}_3)_2]$ (**1**), according to eq. (1).

Results and Discussion

The monothiolated benzamidine **1** was prepared from $4\text{-BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ [2,3] and CCl_3SCl (1:1 molar ratio) *cf.* synthesis of $\text{PhC(SCCl}_3)[\text{N(SiMe}_3)_2]$ [4]. The ^{1}H NMR spectrum of **1** showed resonances for $4\text{-BrC}_6\text{H}_4$ (an AA'XX' pattern centred at δ 8.80 and 7.56) and SiMe_3 groups (δ 0.30) in the intensity ratio 4:18. In addition, a second weak AA'XX' pattern (δ 8.15 and 7.65) attributed to **2** was evident. A solution of **1** in CH_2Cl_2 was kept for 72 h at 23 °C and, after subsequent work-up, the heterocycle **2** was obtained in 82% yield. A small amount of $4\text{-BrC}_6\text{H}_4\text{C(NH)(NH}_2)$, the hydrolysis product of **1**, was also isolated.

The structure of **2** was determined by X-ray crystallography (see Fig. 1). The pertinent bond lengths, bond angles and torsion angles are summarized in Table I. In common with other 1,2,4-thiadiazoles [5-10], the heterocyclic ring in **2** is essentially planar and the bond lengths indicate some π-delocalization. Thus the S-N distance of 1.650(6) Å is significantly shorter than the predicted single bond value of 1.73 Å [11] and the sequence of C-N bond lengths is 1.331(7), 1.380(8) and 1.302(7) Å (*cf.* single and double bond values of *ca.* 1.29 and 1.47 Å, respectively [12]). The $4\text{-BrC}_6\text{H}_4$ substituent is coplanar with the heterocyclic ring and there are no significant intermolecular interactions.

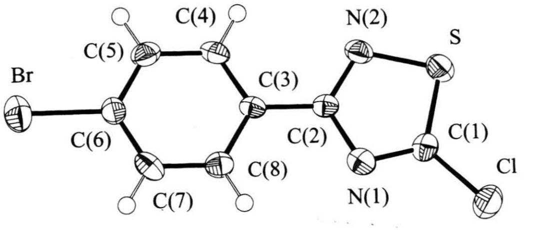

Fig. 1. ORTEP drawing and atomic numbering scheme for **2**.

The synthetic route represented by eq. (1) represents an alternative to the use of carbamidines [2] for the synthesis of 1,2,4-thiadiazoles containing a 5-Cl substituent that can be subsequently functionalized.

Experimental Section

Preparation of $4\text{-BrC}_6\text{H}_4\overline{\text{CNSC(Cl)N}}$ (**2**)

A solution of Cl_3CSCl (0.60 g, 3.22 mmol) in 25 ml of CH_2Cl_2 was added dropwise to $4\text{-BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$, (1.37 g, 3.30 mmol) in 25 ml of CH_2Cl_2 at 23°C under an atmosphere of N_2. The reaction mixture was stirred for 72h and then solvent and Me_3SiCl were removed by vacuum transfer to give a viscous yellow oil containing a small amount of white powder. The oil was dissolved

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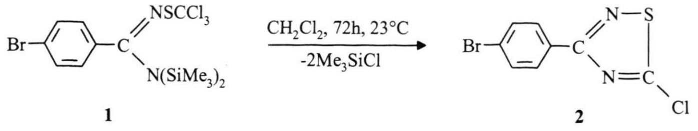

(1)

Table I. Selected bond lengths (Å) and bond angles (deg) for **2**.

Bond lengths		Bond angles	
S-N(2)	1.650(6)	N(2)-S-C(1)	91.8(3)
S-C(1)	1.709(7)	C(1)-N(1)-C(2)	107.9(5)
N(1)-C(1)	1.302(7)	S-N(2)-C(2)	108.4(5)
C(2)-N(1)	1.380(8)	Cl-C(1)-S	122.8(4)
N(2)-C(2)	1.331(7)	Cl-C(1)-N(1)	123.5(5)
Cl-C(1)	1.706(7)	S-C(1)-N(1)	113.6(5)
C(2)-C(3)	1.467(8)	N(1)-C(2)-N(2)	118.3(6)

Torsion angles	
Cl-C(1)-S-N(2)	-178.8(4)
Cl-C(1)-N(1)-C(2)	178.8(4)
S-N(2)-C(2)-N(1)	0.0(7)
S-N(2)-C(2)-C(3)	179.8(4)
S-C(1)-N(1)-C(2)	-0.6(6)
C(1)-S-N(2)-C(2)	-0.3(5)

in CH_2Cl_2:diethyl ether and the insoluble white solid was removed by filtration. Solvent was removed from the filtrate. Slow evaporation of a diethyl ether solution of the residue gave pale yellow rectangular crystals of 4-$BrC_6H_4\overline{CNSC(Cl)N}$ (0.73 g, 82%). M.p. 85°C.

Analysis for $C_8H_4BrClN_2S$

Calcd C 34.87 H 1.46 N 10.17%,
Found C 35.39 H 1.50 N 9.33%.

^1H NMR (in $CDCl_3$): δ 8.15 and 7.65 (4-BrC_6H_4, AA'XX' pattern). ^{13}C NMR (in $CDCl_3$): δ 173.3 and 171.2 (NC(S)Cl and CN_2), 132.1, 130.8, 129.6 and 125.6 (C_6H_4). The white solid was identified as 4-$BrC_6H_4C(NH)(NH_2)$ (0.10 g, 16%) by EI-MS (m/z = 198 and 200, M^+).

X-ray analysis

The crystal structure of **2** was determined by using a Rigaku AFC6S diffractometer. Experimental details are summarized in Table II*. The structure was solved by the heavy atom method [13] and expanded using Fourier techniques [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions. Scattering factors were taken from Cromer and Waber [15] and allowance was made for anomalous dispersion [16]. All calculations were performed using teXsan [17].

Table II. Crystal data for 4-$BrC_6H_4\overline{CNSC(Cl)N}$ **2**.

Formula	$C_8H_4N_2SBrCl$
Fw.	275.55
Crystal System	triclinic
Space Group	$P\bar{1}$ (No. 2)
a [Å]	7.957(3)
b [Å]	10.864(5)
c [Å]	5.625(1)
α [deg]	95.94(3)
β [deg]	97.79(2)
γ [deg]	100.72(3)
V [Å^3]	469.2(3)
Z	2
d_{calc} [g cm^{-3}]	1.950
Crystallogr. Dim. [mm]	0.50 × 0.40 × 0.20
Cell detn, refls	25
Cell detn, 2θ range, [deg]	18.50 - 29.97
Radiation, MoK_α [Å]	$\lambda = 0.71069$
Temperature [K]	170(1)
Scan type	ω - 2θ
Scan rate [deg min^{-1}]	16.0
Scan width [deg]	1.57 + 0.34 tan θ
2θ max [deg]	50.1
μ [cm^{-1}]	48.48
Absorption correction	empirical
Absorption, range	0.32 - 1.00
Total reflections	1797
Unique reflections	1666
Data with I > 3σ(I)	1149
Parameters refined	118
R	0.042
R_w	0.041
GOF	2.54
Largest Δ/σ	0.00
Final diff. map [e Å^{-3}]	0.53, -1.22
F(000)	268

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Ignacio Vargas-Baca for recording the ^{13}C NMR spectrum.

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* Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry No. CSD-406259.

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[17] *teXsan*: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).