ELSEVIER

Journal of Fluorine Chemistry 92 (1998) 153–156

JOURNAL OF FLUORINE CHEMISTRY

Synthesis and characterization of fluoro azido-carbondisulfide, F–$SCSN_3$, and a new synthesis for azido-carbondisulfide, N_3SCS–$SCSN_3$[1]

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Received 10 July 1998; accepted 11 August 1998

Abstract

A new and improved synthesis for azido-carbondisulfide, N_3SCS–$SCSN_3$ (**1**), is reported from sodium azido-dithiocarbonate, $[Na][SCSN_3]$, and xenon difluoride in aqueous solution. Treatment of azido-carbondisulfide, N_3SCS–$SCSN_3$ (**1**), with elemental fluorine in SO_2ClF solution at -100°C yielded the new compound fluoro azido-carbondisulfide, F–$SCSN_3$ (**2**), as a pale yellow solid. F-$SCSN_3$ (**2**) was characterized by infrared and Raman spectroscopy and quantum chemical DFT computations. The structures of both compounds, N_3SCS–$SCSN_3$ (**1**) and F–$SCSN_3$ (**2**), have been elucidated by a combined theoretical (DFT) and experimental (IR, Raman) study. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ab initio computations; Azido-carbondisulfide; Density functional calculations; Fluoro azido-carbondisulfide; Raman spectra

1. Introduction

The 1,2,3,4-thiatriazole-5-thiolate ion (azido-dithiocarbonate) is a member of the interesting family of pseudohalides [1–16]. Sodium azido-dithiocarbonate, $[Na][SCSN_3]$, was first reported in 1915 (reaction (1)) [17] and structurally characterized in 1991 by X-ray diffraction methods [18] to consist of a pseudoaromatic 5-membered ring with an exocyclic sulfur atom. During an investigation of the properties of $[Na][SCSN_3]$ [17,19,20], it was found that the treatment of aqueous solutions of this salt with such oxidizing agents such as potassium permanganate or hydrogen peroxide (reaction (2)), resulted in the precipitation of an unstable white solid which exploded violently when heated under water at a temperature below 100°C [17,19]. This white solid was later shown to be azido-carbondisulfide (**1**) and to possess the molecular formula N_3SCS–$SCSN_3$ [21–23]. Both an open-chain and a heterocyclic structure have been discussed for compound **1** (cf. Fig. 1), however, prior to the work reported in this paper no structural investigations of this compound based on spectroscopic or diffraction data had been published [21]. In this contribution we want to report a new convenient synthesis for azido-carbondisulfide, N_3SCS–$SCSN_3$ (**1**), and its structural characterization based on a combined vibrational (IR and Raman) and quantum chemical study. We also report on the fluorination of compound **1** to yield the new compound fluoro azido-carbondisulfide, F–$SCSN_3$ (**2**), which was also characterized by a combined vibrational (IR and Raman) and DFT (density functional theory) study.

$$CS_2 + NaN_3 \rightarrow [Na][SCSN_3] \qquad (1)$$

$$2[Na][SCSN_3] + H_2O_2 \rightarrow N_3SCS\text{–}SCSN_3(\mathbf{1}) + 2NaOH \qquad (2)$$

2. Results and discussion

2.1. *Azido-carbondisulfide, N_3SCS–$SCSN_3$ (**1**)*

The reaction of $[Na][SCSN_3]$ with one equivalent of XeF_2, as shown in reaction (3), gave azido-carbondisulfide, N_3SCS–$SCSN_3$ (**1**), as a white solid in moderate yield. The compound can be stored for several days at -30°C in the freezer. The structure of **1** was elucidated from a combined IR/Raman and quantum chemical study (Fig. 1, Tables 1 and 2). A comparison between the DFT calculated vibrational frequencies and the observed IR and Raman data clearly indicates that **1** exists in the ring structure and not as

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[1] Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

PII: S0022-1139(98)00275-9

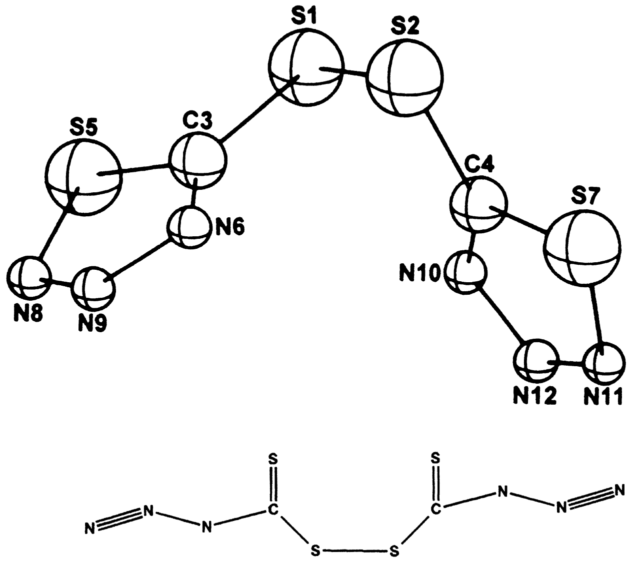

Fig. 1. Structure of the $N_3SCS–SCSN_3$ ring isomer **1a** (top), fully optimized at B3LYP/6-311++G* level of theory (within C_1 symmetry) to give C_2 symmetry; the atomic labeling corresponds to Tables 1 and 2. Structure of the $N_3SCS–SCSN_3$ chain isomer **1b** (bottom).

Table 1
B3-LYP/6-311++G* computed energies of the S–S bound dimer $N_3SCS–SCSN_3$

	1a	1b
Symmetry	C_2 (fully optimized within C_1)	C_1
E (a.u.)	−1997.546116	−1997.541716
$E_{\text{rel.}}$ (kcal mol^{-1}) (kJ mol^{-1})	0.0 (0.0)	2.8 (11.7)
NIMAG[a]	0	0
zpe (kcal mol^{-1}) (kJ mol^{-1})	27.2 (113.7)	25.0 (104.5)

[a] NIMAG: number of imaginary frequencies.

Table 2
Structural parameters of the $N_3SCS–SCSN_3$ ring isomer **1a**, fully optimized at B3-LYP/6-311++G* level of theory (within C_1 symmetry) to give C_2 symmetry

	d (Å)		$\varnothing \measuredangle$ (°)
S1-S2	2.096	S2-S1-C3	102.8
C3-S1	1.761	S1-C3-S5	121.7
S5-C3	1.725	S1-C3-N6	125.5
N6-C3	1.309	S5-C3-N6	112.8
N8-S5	1.751	C3-S5-N8	88.0
N9-N6	1.357	C3-N6-N9	111.0
N9-N8	1.257	S5-N8-N9	110.4
		C4-S2-S1-C3	79.5

an open-chain molecule. Although the difference in total energy between both isomers **1a** and **1b** is small (see below), it appears that exclusively isomer **1a** is formed in the oxidation reaction starting from the cyclic anion $[SCSN_3]^-$. Since the activation barrier for the interconversion of **1a** into **1b** is expected to be high the appearance of exclusively isomer **1a** in the IR and Raman spectra can easily be understood.

$$2[\mathrm{Na}][\mathrm{SCSN_3}]+\mathrm{XeF_2} \rightarrow \mathrm{N_3SCS{-}SCSN_3}(\mathbf{1}) + 2\mathrm{NaF} + \mathrm{Xe} \tag{3}$$

Prior to this investigation there have been no experimental or theoretical studies to determine or predict the molecular structure of the S–S bound compound **1**. In order to predict quantumchemically the different stabilities of both possible structural isomers, the total energies and vibrational frequencies of molecules **1a** (ring isomer) and **1b** (open-chain structure) were computed (structure **1b**, Fig. 1 and Table 1). (Note that at PM3/VSTO-3G* and at HF/6-311++G* level of theory, for the ring isomer **1a**, two local minima were established on its potential energy surface: (a) a planar molecule with C_s symmetry and (b) a non-planar C_2 molecule. As expected, the C_2 type molecule was shown to be more stable with ΔE^{PM3}=9.1 kcal mol^{-1}=38.0 kJ mol^{-1}.)

At B3-LYP level of theory the ring isomer **1a** was shown to be just slightly favored over the chain-like structure **1b** by 3 kcal mol^{-1} (12.5 kJ mol^{-1}) (Table 1, Fig. 1). Although both isomers **1a** and **1b** were calculated and fully optimized in C_1 symmetry, isomer **1a** was optimized during the calculation to C_2 symmetry (Table 2, Fig. 1). This result makes it very interesting to also look at a covalently bound "monomeric" $SCSN_3$ system in which a fluorine atom is coordinated to the sulfide sulfur, i.e. $F–SCSN_3$ (**2**, see below) (cf. Fig. 2)

Although it seems to be reasonable to assume from the previously reported results of the experimental studies that the compound $[Na]^+[SCSN_3]^-$ can be oxidized to give the neutral covalently bound dimer $N_3SCS–SCSN_3$ (**1**), prior to our work, it had been impossible to measure the vibrational frequencies of this elusive molecule. In Table 2 we now report the experimentally observed IR and Raman data of compound **1** and compare these values with the calculated vibrational frequencies of compound **1a** (Table 3) [24].

2.2. *Fluoro azido-carbondisulfide, $F–SCSN_3$ (**2**)*

The reaction of $N_3SCS–SCSN_3$ (**1**) with an excess of elemental fluorine, as shown in Eq. (4), gave fluoro azido-carbondisulfide, $F–SCSN_3$ (**2**), as a pale yellow solid in

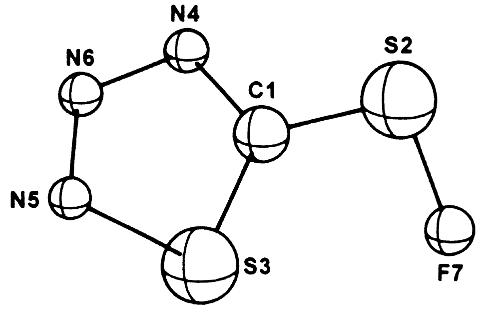

Fig. 2. Structure of the $F–SCSN_3$ (**2**) (top), fully optimized at B3LYP/6-311++G* level of theory (within C_1 symmetry) to give C_s symmetry.

Table 3
Calculated (B3-LYP/6-311++G*) and experimentally observed vibrational data (cm^{-1}) for compound **1a** (C_2 symmetry) [24]

Calculated (relative IR intensity in km mol^{-1})	IR	Raman (relative intensity)
27 (3)		
29 (9)		
43 (2)		
127 (0.5)		
144 (5)		156 (4)
215 (1)		
218 (1)		
243 (0.5)		236 (7)
307 (1)		326 (7)
411 (12)		
421 (13)		423 (4)
482 (2)		475 (3)
519 (10)		525 (8)
521 (15)		
543 (1)		
554 (1)		
643 (0.5)	630 w	633 (10)
647 (0.5)		
686 (1)	705 w	700 (1)
689 (11)		
915 (33)	909 m	
916 (2)		
1019 (0.5)	1017 m	1009 (5)
1020 (1.5)		
1069 (36)	1070 s	
1070 (190)		
1342 (120)	1342 s	1335
1344 (123)		
1399 (7)		
1399 (10)		

moderate yield. The compound, which is insoluble in most solvents (SO_2, $CFCl_3$, CS_2) and decomposes in others (pyridine) can be stored for several weeks at room temperature. The structure of **2** was elucidated from a combined IR/Raman and quantum chemical study (Fig. 1, Tables 4 and 5). A comparison between the DFT calculated vibrational frequencies and the observed IR and Raman data clearly indicates that **2** exists in the ring structure with an exocyclic S–F group attached to the pseudoaromatic 5-membered heterocycle.

Table 4
Structural parameters of F–$SCSN_3$ (**2**), fully optimized at B3-LYP/6-311++G* level of theory (within C_1 symmetry) to give C_s symmetry

	d (Å)		∅ ∡ (°)
C1-S2	1.739	S2-C1-S3	127.5
C1-S3	1.722	S2-C1-N4	119.0
C1-N4	1.312	S3-C1-N4	113.5
S3-N5	1.747	C1-S3-N5	87.5
N4-N6	1.361	C1-N4-N6	110.5
N5-N6	1.258	S3-N5-N6	111.2
S2-F7	1.663	N4-N6-N5	117.2
		C1-S2-Cl7	98.2

Table 5
Calculated (B3-LYP/6-311++G*) and experimentally observed vibrational data (cm^{-1}) for the F–$SCSN_3$ (**2**) molecule

	Calculated	IR (Nujol)	Raman (relative intensity)
Symmetry	C_1 opt. to C_s		
$-E$ (a.u.)	−1098.612384		
NIMAG[a]	0		
zpe (kcal mol^{-1})	14.4	(60.2)	
(kJ mol^{-1})			
	75 (7)		
	145 (6)		
	217 (0.3)	221 w	205 (1)
	340 (0.2)	n.o.	316 (1)
	409 (8)	392 m	415 (3)
	529 (15)	480 w	496 (10)
	539 (1)	520 w	530 (2)
	639 (0.2)	645 w	650 (9)
	681 (5)	675 w	673 (2)
	724 (80)	728 s	722 (1)
	918 (10)	900 m	904 (1)
	1006 (27)	1015 m	1015 (4)
	1107 (75)	1070 m, br	1073 (3)
	1346 (145)	1320 w	1333 (5)
	1393 (8)	n.o.	1360 (2)

[a] NIMAG: number of imaginary frequencies.

$$N_3SCS-SCSN_3 + \text{xs.}\,F_2 \rightarrow 2\,F-SCSN_3 \qquad (4)$$

3. Experimental

3.1. Preparative part

Sodium azido-dithiocarbonate, [Na][$SCSN_3$] [17], was prepared according to the literature. XeF_2 (Fluorochem), and F_2 (Solvay) were commercially available and used as supplied, SO_2ClF (Aldrich) was dried over CaH_2. The experimental techniques and apparatus have been described elsewhere [25–28] – Raman: Perkin-Elmer R2000 system fitted with a Ventacon cold cell and a Nd-YAG IR laser (1064 nm). All spectra were recorded using the 180° geometry – IR: Perkin-Elmer spectrometer model PE 983. All spectra were recorded as Nujol mulls between KBr plates at 20°C.

3.1.1. *Preparation of azido-carbondisulfide, $N_3SCS–SCSN_3$ (**1**)*

A solution of 0.17 g (1.0 mmol) XeF_2 in 15 ml H_2O was reacted with a magnetically stirred solution of 0.43 g (2 mmol) [Na][$SCSN_3$] in 10 ml H_2O. Reaction occurred immediately yielding a white frothy precipitate and Xe gas was given off as the reaction mixture effervesced. After a few minutes, the white precipitate was filtered off at room temperature and the reaction product was dried at 0°C overnight under vacuum over P_4O_{10}. 0.15 g (63%) of **1a** was obtained as a white powder which can be stored for several days at or below −18°C.

1. $C_2N_6S_4$ (mol. wt. 236.32).
2. The thermal instability of the compound did not allow us to get reproducible microanalytical data.
3. IR (Nujol) see Table 2.
4. Raman (1064 nm, −120°C) see Table 2.

3.1.2. Preparation of fluoro azido-carbondisulfide, F–SCSN₃ (**2**)

0.12 g (0.5 mmol) of freshly prepared and dried **1a** were added to a dried and passivated Pyrex glass vessel fitted with a PTFE Young valve. In the next step, 10 ml of SO_2ClF were added and then 1 mmol F_2 (2-fold excess) was condensed into the reaction mixture at −196°C. The reaction mixture was then immediately warmed up to −100°C and allowed slowly to warm up overnight to room temperature and the SO_2ClF solvent and all other volatile material was then pumped off at room temperature. 0.055 g (40%) of **2** was recovered as a pale yellow solid.

1. CFN_3S_2 (137.16) calculated C 8.8, N 30.6; found C 8.5, N 30.2.
2. IR (Nujol) see Table 4.
3. Raman (1064 nm, 20°C) see Table 4.

3.2. Computations

The structure and frequencies of azido-carbondisulfide, $N_3SCS–SCSN_3$ (isomers **1a** and **1b**) and of fluoro azido-carbondisulfide, $F–SCSN_3$ (**2**), were computed at B3-LYP level of theory with the program package Gaussian 94 [29]. For all atoms a standard 6-311++G(d) basis was used [29]. For a concise definition of the B3-LYP functional see [30–34].

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG Kl 636/6-1), the University of Munich and the Fonds der Chemischen Industrie.

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