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Trithiatetrazocine Cations, $[RCN_4S_3]^+$; Planar Sulfur−Nitrogen 10π Aromatics[†]

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The reaction of bicyclic sulfur−nitrogen heterocyles RCN_5S_3 (R = F_3C, Ph, Me_2N, 2-FC_6H_4, 2,6-$F_2C_6H_3$) with $[Hg(SO_2)_2][AsF_6]_2$ in liquid SO_2 yielded the corresponding trithiatetrazocinium-hexafluoroarsenates $[RCN_4S_3][AsF_6]$ as yellow solids and a red-brown insoluble byproduct with the approximate composition Hg_3N_2. Single crystal structure determinations of the salts and theoretical calculations on the trithiatetrazocine cations $[RCN_4S_3]^+$ revealed the cations to be planar eight-membered heterocycles. The $[RCN_4S_3]^+$ cations are the missing link in the series of known valence isoelectronic eight-membered 10π azocines, that is, $[S_4N_4]^{2+}$ and $RC(NSN)_2CR$. In contrast to neutral trithiatetrazocines and dithiatetrazocines $RC(NSN)_2CR$ carrying donor substituents, which have a folded butterfly structure with a transannular S−S bond, the positive charge on the $[RCN_4S_3]^+$ cations always stabilizes the planar structure independent of the nature of the substituent. Experimentally obtained structures and theoretical calculations (geometries, frequencies, charges, nucleus-independent chemical shifts (NICS)) are in agreement with the description of $[RCN_4S_3]^+$ as planar eight-membered 10π Hückel aromatic. The single crystal structure determinations of some 3,5-R-1,2,4,6-thiatriazinyl hexafluoroarsenates (R = Ph, 2-FC_6H_4, 4-FC_6H_4), which were isolated from the above reaction as well, are also included.

Introduction

The chemistry of sulfur−nitrogen heterocycles has been extensively investigated over the last decades.[1] Because of their interesting physical properties and bonding situations they still represent a modern research field of high interest.[1] In 1972 Banister introduced simple electron counting rules to predict the Hückel aromaticity and planarity of electron-rich sulfur−nitrogen heterocycles.[2] Classical representatives of the class of electron-rich sulfur−nitrogen heterocycles are the valence isoelectronic eight-membered azocines with 10π electrons (Scheme 1). Formally they are obtained by successive isolobal replacement of S^+ by R-C. The dication of sulfur nitride, $[S_4N_4]^{2+3}$ (**A**) and the neutral dithiatetrazocines, $RC(NSN)_2CR^{4,5}$ (**C**) have been known for many years and are well investigated. Indeed $[S_4N_4]^{2+}$ is planar in agreement with a 10π Hückel aromatic system.[3] For $RC(NSN)_2CR$ a

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planar and a folded butterfly structure with a transannular S−S bond have been found experimentally[4] and correlated theoretically to the electronic nature of the substituent R.[5] The missing link in this series of valence isoelectronic heterocycles is the trithiatetrazocine cation, $[RCN_4S_3]^+$ (**B**). A series of neutral trithiatetrazocines $RC(NSN)_2SR'$ ($R' =$ Cl, $NPPh_3$, $NAsPh_3$) have been prepared and structurally characterized, but they all possess a folded butterfly structure (**D**) with a transannular S−S bond (Scheme 1).[6,7] So far the planar cation $[F_3CCN_4S_3]^+$, which has been prepared as its $[S_3N_3O_4]^-$ salt from F_3CCN and $(NSCl)_3$ in liquid SO_2 in 4% yield[8] and has been isolated as its $[AsF_6]^-$ salt from the reaction of $F_3CCN_5S_3$ and AsF_5 as side-product (Scheme 2),[7] represents the only known example of this class of compounds.

In our investigations of structures and reactions of bicyclic sulfur−nitrogen heterocycles RCN_5S_3[7,9,10,11] we have shown their ability to act as donor ligands toward "naked" transition metal centers[10] and their potential as precursor for the formation of sulfur−nitrogen radicals.[11] Surprisingly, the reaction of RCN_5S_3 (**1**) with Hg^{2+} in liquid SO_2 yielded $[RCN_4S_3][AsF_6]$ as yellow solids containing trithiatetrazocine cations $[RCN_4S_3]^+$. Herein we will present the generation of $[RCN_4S_3][AsF_6]$ ($R = C_6H_5$ (**2b**), 2,6-$F_2C_6H_3$ (**2c**), Me_2N (**2d**), 2-FC_6H_4 (**2e**)), a crystallographic investigation of their structures, and a short discussion of the bonding situation within the cationic heterocycles.

2. Experimental Section

General Remarks. Solid reagents and crystals were manipulated in vacuum or using a drybox and an atmosphere of dry nitrogen. The reactions were carried out in glass vessels with Teflon valves and an incorporated frit. The solvent liquid sulfur dioxide was dried over P_4O_{10} and distilled prior to use. The starting materials RCN_5S_3 ($R =$ Ph,[12] 2-FC_6H_4,[9a] 2,6-$F_2C_6H_3$,[9a] Me_2N[6a]) were prepared according to published procedures. $[Hg(SO_2)_2(AsF_6)_2]$ was obtained from HgF_2 (prepared from $HgCl_2$ and F_2)[13] and a small excess of AsF_5[14] in liquid sulfur dioxide.[15] IR spectra were recorded on a Perkin-Elmer Paragon 500 FT-IR spectrometer using Nujol and Kel-F mulls, ^1H and ^{19}F NMR spectra in 5 mm NMR tubes on a Bruker DPX 200 spectrometer (chemical shifts are given with respect to TMS and $CFCl_3$), and ^{14}N NMR spectra in 5 mm NMR tubes on a Varian 400 spectrometer (chemical shifts are given with respect to $MeNO_2$), and melting/decomposition points on a Gallenkamp Melting Point Apparatus in sealed melting point capillaries. Elemental analyses were carried out by Mikroanalytisches Labor Beller, Göttingen, Germany.

2.1. Generation and Characterization of Materials Containing the $[RCN_4S_3]^+$ Cations. General Procedure. A 10 mL portion of SO_2 was condensed onto a mixture of RCN_5S_3 (0.6 mmol) and $[Hg(SO_2)_2][AsF_6]_2$ (0.3 mmol) at −196 °C via a vacuum line. A red-brown precipitate formed during slow warming to room temperature. After stirring at room temperature for 2 h the red-brown insoluble precipitate was removed by filtration from the yellow solution and washed with SO_2 several times. Slow removal of the solvent using a temperature gradient by cooling one side of the reaction vessel with water yielded a partly crystalline yellow to orange material containing crystals suitable for X-ray diffraction. Single crystals of **2d** were prepared by dissolving **2d** in CH_2Cl_2 and slow removal of the solvent. The crystalline bulk materials (crystals were partly hand sorted) of the soluble fraction were characterized by decomposition point, ^1H and ^{19}F NMR, and IR spectroscopy.

Phenyl-trithiatetrazocinium-hexafluoroarsenate (2b[AsF$_6$]). Mp. 130−140 °C (dec.); ^1H NMR (200 MHz, CD_3CN, 20 °C): $\delta = 7.7$ (m); IR (KBr, 1700−600 cm^{-1}): 1675 m, 1650 sh, 1595 m, 1455 s, 1410 s, 1340 s, 1295 w, 1240 w, 1180 m, 1150 m, 1075 w, 1060 w, 1025 sh, 1005 m, 925 w, 785 m, 700 vs (ν_3 $[AsF_6]^-$), 670 sh; red insoluble side product: Found: Hg, 94.95, N, 4.89%.

2,6-Difluorophenyl-trithiatetrazocinium-hexafluoroarsenate (2c-[AsF$_6$]). Mp. 190−200 °C (dec.); ^1H NMR (200 MHz, SO_2/C_6D_6, 20 °C): $\delta = 6.92-7.05$ (m, 2H, m-$C_6F_2H_3$), 7.28−7.52 (m, 1H, p-$C_6F_2H_3$); ^{19}F NMR (188 MHz, SO_2/C_6D_6, 20 °C): $\delta = -61.3$ (qa, $^1J_{FAs} = 914$ Hz, 6F, AsF_6^-), −114.9 (dd, $^3J_{FH} = 7.8$ Hz, $^4J_{FH} = 6.2$ Hz, 2F); IR (KBr, 1700−450 cm^{-1}): 1699 sh, 1686 w, 1625 s, 1583 w, 1560 w, 1542 w, 1508 w, 1470 s, 1426 s, 1362 s, 1302 w, 1243 m, 1175 sh, 1148 m, 1122 sh, 1016 s, 977 w, 935 w, 928 m, 797 s, 768 w, 720 sh, 708 sh, 693 vs (ν_3 $[AsF_6]^-$), 680 sh, 584 w, 553 m, 525 sh, 516 s, 478 w.

Dimethylamino-trithiatetrazocinium-hexafluoroarsenate (2d[AsF$_6$]). Mp. 128 °C (dec.); ^1H NMR (200 MHz, CD_3CN, 20 °C): $\delta =$ 3,49 (s, 6H, Me_2N)); ^{19}F NMR (188 MHz, CD_3CN, 20 °C): $\delta =$

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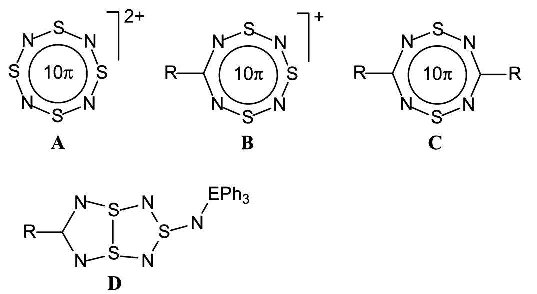
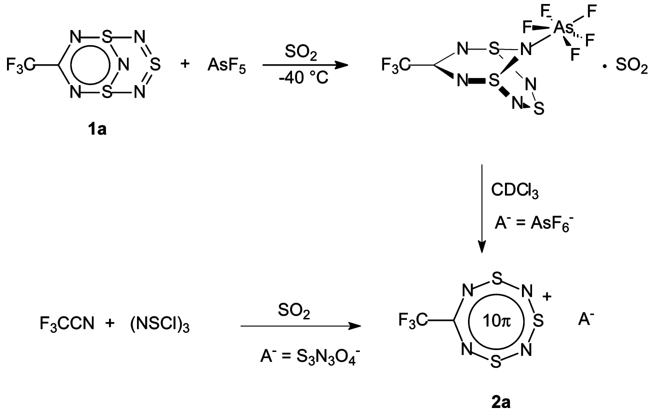
Scheme 1



Scheme 2



-67.0 (qa, $^{1}J_{FAs} = 931$ Hz, 6F, AsF_6^-); IR (KBr, 3000−650 cm^{-1}): 2950 w, 1650 w, 1585 s, 1550 s, 1410 s, 1365 m, 1270 w, 1205 w, 1160 w, 1130 w, 1025 m, 975 m, 900 m, 700 vs (ν_3 $[AsF_6]^-$).

2-Fluorophenyl-trithiatetrazocinium-hexafluoroarsenate (2e[AsF$_6$]). An NMR scale reaction of 2-$FC_6H_4CN_5S_3$ with $[Hg(SO_2)_2](AsF_6)_2$ in 2:1 ratio yielded among other products one yellow single crystal of $[2\text{-}FC_6H_4CN_4S_3][AsF_6]$ after several weeks. Attempts to repeat the reaction on a preparative scale to obtain pure material for analysis were unsuccessful. ^{14}N NMR (28.9 MHz, SO_2, 20 °C) of a dissolved yellow single crystal of $[2\text{-}FC_6H_4CN_4S_3][AsF_6]$ in liquid SO_2: $\delta = -77$ (s, $\nu_{1/2} = 850$ Hz), -133 (s, $\nu_{1/2} = 1000$ Hz).

2.2. Crystal Structure Determinations. Single-crystal X-ray structure determinations were carried out on a Siemens P4 diffractometer (**2b,c,d** and **3b,e,f**) or a Bruker AXS P4/SMART 1000 diffractometer (**2e**) using Mo-K$_\alpha$ (0.71073 Å) radiation with a graphite monochromator. The crystals were mounted onto a thin glass fiber using Kel-F or Paratone-N oil and frozen in the cold nitrogen stream of the goniometer. Details of the data collection and refinement are given in Table 1. The structures were solved by direct methods (SHELXS).[16] Subsequent least-squares refinement on F^2 (SHELXL 97−2) located the positions of the remaining atoms in the electron density maps.[16] All atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model. The data were corrected for absorption.[17] Graphical representations of the structures were prepared with the program DIAMOND.[18]

The asymmetric unit of the crystal structure of **2d** contains, beside a well defined $[Me_2NCN_4S_3]^+$ cation, two $[AsF_6]^-$ anions and an incorporated disordered CH_2Cl_2 solvent molecule, a disordered flat species (a figure of the unit cell is included with the Supporting Information). This species has to be a cation for electrical neutrality reasons and is believed to be a second $[Me_2NCN_4S_3]^+$ cation. The disorder of this second $[Me_2NCN_4S_3]^+$ cation could not be resolved. Therefore discussion has been restricted to the nondisordered and well refined $[Me_2NCN_4S_3]^+$ cation in the asymmetric unit. Several attempts to obtain better crystals of **2d** were unsuccessful. A figure of the molecular structures, selected bond length and angles, and details of the data collection and refinement for the 3,5-R-1,2,4,6-thiatriazinyl hexafluoroarsenats **3b**[AsF$_6$], **3e**[AsF$_6$], and **3f**[AsF$_6$] are given in the Supporting Information.

2.3. Quantum Chemical Calculations. All calculations have been carried out using the PBE0 DFT hybrid functional[19] with a 6−311+G** basis set as implemented in Gaussian 03.[20] Calculated structures and orbitals were visualized using ChemCraft.[21] Nucleus-Independent Chemical Shifts (NICS) were calculated according to the known procedure.[22] All calculated species represent minima on the respective hypersurface as shown by frequency analyses.

3. Results and Discussion

3.1. Generation and Characterization of Salts Containing the $RCN_4S_3^+$ Cation. A few years ago, we reported the reactions of the bicyclic sulfur nitrogen heterocycle $F_3CCN_5S_3$ with H^+ and naked metal cations Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} in liquid sulfur dioxide, which resulted in the formation of the respective complexes.[7,10] The bicyclic sulfur−nitrogen heterocycle exhibited a very versatile coordination chemistry acting as terminal ligand via the nitrogen atom N1 or N5 or as bridging ligand via nitrogen atoms N1 and N5 (Scheme 3). All attempts to introduce heterocycles with substituents other than trifluoromethyl into metal complexes failed and resulted in complete or partial decomposition. This confirms the exceptional stability of $F_3CCN_5S_3$ compared to other bicycles of this type, which has been noted and discussed before.[7,9a,23]

Surprisingly, the reaction of $F_3CCN_5S_3$ and other derivatives (R = Ph, 2,6-$F_2C_6H_3$, 2-FC_6H_4, Me_2N) with naked Hg^{2+} (as in $[Hg(SO_2)_2][AsF_6]_2$) in liquid SO_2 as a solvent lead to the isolation of yellow to orange solids containing the hexafluoroarsenate salts of the cationic eight-membered sulfur−nitrogen heterocycles $[RCN_4S_3]^+$ in a reproducible

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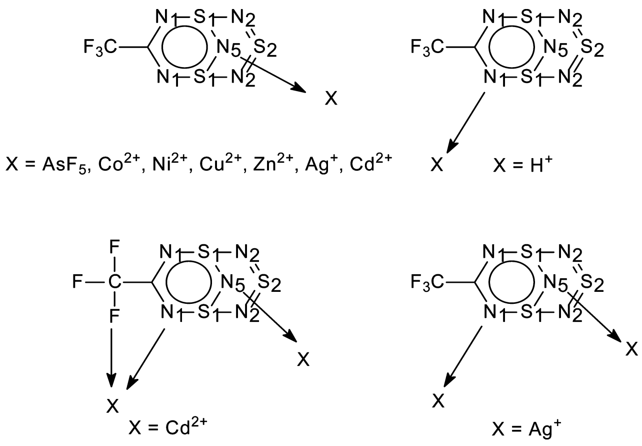
Table 1. Crystal Data and Structure Refinement for **2b**, **2c**, **2d**, and **2e**[a]

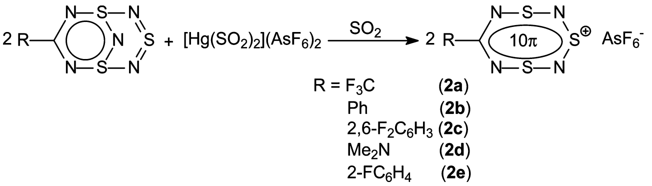
	[$PhCN_4S_3$][AsF_6] (**2b**[AsF_6])	[2,6-F_2**$C_6H_3CN_4S_3$**] **[AsF_6]** (**2c**[AsF_6])	[Me_2**NCN_4S_3**] **[AsF_6](2d**[AsF_6])	**[2-$FC_6H_4CN_4S_3$]** **[AsF_6](2e**[AsF_6])
empirical formula	$C_7H_5AsF_6N_4S_3$	$C_7H_3AsF_8N_4S_3$	$C_{23}H_{40}As_7Cl_4F_{42}N_{35}S_{21}$	$C_7H_4AsF_7N_4S_3$
formula weight	430.25	466.23	2944.40	448.24
crystal size (mm)	0.70 × 0.50 × 0.30	0.60 × 0.40 × 0.40	0.70 × 0.30 × 0.30	0.33 × 0.25 × 0.10
temperature	173(2) K	173(2) K	173(2) K	173(1) K
crystal color	Yellow	Yellow	Red	Yellow
space group	*Pbca*	$P\bar{1}$	$P\bar{3}$	$P\bar{1}$
a (Å)	824.2(2)	665.69(8)	1869.0(1)	652.40(5)
b (Å)	1185.8(2)	797.82(7)	1839.0(1)	791.84(7)
c (Å)	2753.0(4)	1432.71(10)	776.6(1)	1437.98(12)
α (deg)	90	85.892(7)	90	83.467(1)
β (deg)	90	83.377(9)	90	84.680(1)
γ (deg)	90	66.603(9)	120	66.607(1)
volume (Å^3)	2690.6(9)	693.41(11)	2349.3(4)	676.45(10)
Z	8	2	1	2
D_{calcd} (g cm^{-3})	2.124	2.233	2.081	2.201
μ	30.59 cm^{-1}	29.96 cm^{-1}	31.74 cm^{-1}	30.57 cm^{-1}
$2\theta_{max}$ (deg)	27.50	27.50	27.51	27.49
reflections collected	3267	6418	12407	4743
independent reflections	2417 [R_{int} = 0.0212]	3190 [R_{int} = 0.0304]	3609 [R_{int} = 0.0415]	2952 [R_{int} = 0.0151]
final R indices $R1$, $wR2$ [b]	0.0350, 0.0830	0.0255, 0.0690	0.0615, 0.1723	0.0313, 0.0898
goodness-of-fit	1.052	1.063	1.021	1.085

[a] Structural data for [$F_3CCN_4S_3$][AsF_6] has been included in ref 9d. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4])^{1/2}$.

Scheme 3. Coordination Modes for $F_3CCN_5S_3$



Scheme 4



straightforward way (Scheme 4). Bicycles with electron-donating substituents reacted faster than bicycles with electron-withdrawing groups. It may be assumed that coordination of the bridging nitrogen atom N5 to Hg^{2+} is the first step based on structures found in the solid state for $F_3CCN_5S_3$ coordinated to a metal cation via the bridging nitrogen atom N5 (Scheme 3).[10] However, detailed NMR studies have shown that RCN_5S_3 bicycles are fluxional in $CHCl_3$ solution and undergo a pseudodegenerate rearrangement,[24] which could also be the starting point for the observed reaction. Formally, oxidation of the sulfur–nitrogen heterocycle by Hg^{2+} might be expected, which should give elemental mercury and nitrogen as byproduct. However, elemental mercury has not been observed. Alternatively, nitride extrusion catalyzed by Hg^{2+} may be considered as possible reaction mechanism.

The reactions, although straightforward and reproducible, did not yield very pure products. Crystallization from the yellow solutions gave partly crystalline yellow to orange materials, from which the crystalline material was separated for further characterization. The soluble fraction usually contained (all components identified by X-ray diffraction) [RCN_4S_3][AsF_6] and in some cases unreacted RCN_5S_3 and 1,2,4,6-thiatriazinyl cations (**3**) (see below). Characterization of the crystalline bulk material by ^{1}H NMR spectroscopy showed the characteristic signals for the corresponding organic substituents and ^{19}F NMR showed the typical quartet for $[AsF_6]^-$. The IR spectra are dominated by the very strong As–F vibration at 700 cm^{-1}. A strong vibration at about 1410 cm^{-1} can be assigned to the symmetric C–N stretch (see Supporting Information for an analysis of the vibrations of the parent compound $[HCN_4S_3]^+$).

In all reactions an insoluble red to brown solid formed, which turned black immediately on contact to air. The color and the amount of this insoluble byproduct differed from reaction to reaction. An elemental analysis of this insoluble byproduct showed a composition of 94.95% mercury and 4.89% nitrogen (which add up to 99.84%), which formally corresponds to mercury nitride "Hg_3N_2". Hg_3N_2 has been described as chocolate-colored metastable very explosive substance, but has not been structurally characterized as a pure compound yet.[25] Thus, it is more likely that the insoluble byproduct is a mixture consisting of different yet unidentified compounds.

Attempts to follow the reaction by ^{14}N NMR showed (see Supporting Information for actual spectra and further details) that the characteristic peaks for the bicycle (e.g., for **1e**: −55

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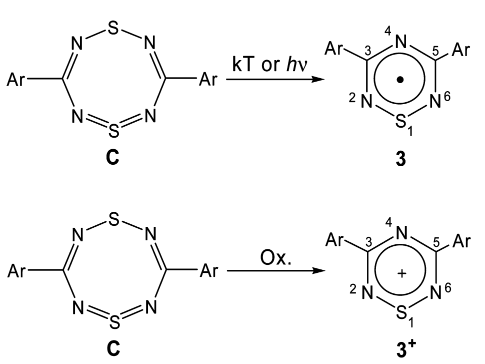
(24) Bestari, K. T.; Boere, R. T.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 1579–1584.

(25) (a) Fischer, F.; Schröter, F. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1465–1479. (b) Gumiñski, C. *J. Phase Equilib. Diffus.* **1997**, *18*, 101–103.

Scheme 5



R = Ph ($\mathbf{3b}[AsF_6]$)
= 2-FC_6H_4 ($\mathbf{3e}[AsF_6]$)
= 4-FC_6H_4 ($\mathbf{3f}[AsF_6]$)

ppm (N5), −196 ppm (N1/N4), −327 ppm (N2/N3))[26] disappeared while the reaction proceeded and two new main signals at about −80 and −135 ppm appeared, which may be assigned to the two pairs of equivalent nitrogen atoms in the cation **2e**. It is also evident from these investigations that the reactions produce a mixture with $[RCN_4S_3]^+$ being one of the major components.

In some cases beside the main products (**2**) 1,2,4,6-thiatriazinyl cations (**3**) were identified by X-ray crystallography as well. **3e** and **3f** were isolated from the reaction of the respective bicycles with $[Hg(SO_2)_2](AsF_6)_2$). Recently, we published electron spin resonance (ESR) spectroscopic investigations of the thermal and photochemical decomposition of several bicycles **1**.[11] Besides the corresponding 4-R-1,2,3,5-dithiadiazolyl radicals as the main product 3,5-R-1,2,4,6-thiatriazinyl radicals were always observed as a minor byproduct. An impurity of dithiatetrazocines (**C**) was suggested as the most likely source for the formation of the 3,5-R-1,2,4,6-thiatriazinyl radicals. A similar explanation could hold for the formation of the corresponding 3,5-R-1,2,4,6-thiatriazinyl cations under oxidizing conditions in this case (Scheme 5). The obtained structures are not significantly different from the known structure of $[(PhCN)_2SN][PF_6]$.[27] Figures, bond lengths and angles, and details of the crystal structure determination of **3e** and **3f** (together with the data of **3b**, which was isolated from the reaction of $PhCN_5S_3$ with $[Co(SO_2)_4](AsF_6)_2$), are included with the Supporting Information.

3.2. Structures of $[RCN_4S_3]^+$ Cations in the Solid State. The trithiatetrazocine cations **2a**,**b**,**c**,**e** are crystallographically found to be almost planar, while **2d** is significantly bent (Figure 1, Table 2). The bending is illustrated best by defining a plane through the four nitrogen atoms in the heterocycle. Then the carbon atom C1 and the sulfur atom S2 are located above the plane, the sulfur atoms S1 and S3 are located below the plane. Deviation from planarity in **2a**,**b**,**c**,**e** is small (distances from the plane of C1, S1, S2, and S3 are about 1−8 pm). The situation is different for the dimethylamino substituted compound **2d**, which is significantly bent. C1 (35.8 pm) and S2 (21.3 pm) are located above the plane through the four nitrogen atoms, while the sulfur atoms S1 and S3 are located about 21 pm below the plane (Figure 1). The transannular S−S distances in the $[RCN_4S_3]^+$ cations (393 pm (**2d**) − 400 pm (**2c**))[4] are about 20 pm longer than in the neutral planar dithiatetrazocines (ca. 380 pm)[4] reflecting the positive charge on the heterocycle. Folded structures with transannular S−S bonds (typically about 240−245 pm) have been found in the neutral dithiatetrazocine $Me_2NC(NSN)_2CNMe_2$[4f] and in neutral trithiatetrazocines RCN_4S_3X (R = Me_2N, *t*-Bu, X = Cl; R = Ph, F_3C, Me_2N, X = $NZPh_3$ Z = P, As).[6,7] All S−N bond distances (153.2−158.8 pm) are in the range for aromatic S−N bonds and similar to those in $[S_4N_4]^{2+}$ (154−156 pm)[3] (Table 2). The C−N bond distances (130.6−134.0 pm) are comparable with the bond distance in s-triazine (131.9(5)).[28] Substituting the acceptor for a donor substituent has only a minor influence on the bond distances within the heterocycle. The C1−N1/C1−N4 (130.6 pm (**2a**) versus 134.0 pm (**2d**) and the N2−S2/N3-S2 bonds (155.0 pm (**2a**) versus 158.8 pm (**2d**) elongate slightly, while the N1−S1/N4−S3 (155.0 (**2a**) versus 153.2 (**2d**)) and the S1−N2/S3/N3 (156.6 (**2a**) versus 153.8 (**2d**)) contract slightly. The experimentally found geometries are in agreement with planar delocalized 10π aromatics.

3.3. Theoretical Considerations. The $[RCN_4S_3]^+$ cations carry a positive charge of +1, which is mainly located on the sulfur atoms (Table 3). Electron donating substituents reduce the positive charge on the heterocyclic part of the cation as shown by calculated Mulliken charges for $[F_3CCN_4S_3]^+$ (+1.03) and $[Me_2NCN_4S_3]^+$ (+0.57). The positive charge located on the heterocycle stabilizes the planar structure over a folded butterfly structure with a transannular S−S bond found for neutral trithiatetrazocines. This is also demonstrated by a comparison of calculated relative energies for folded butterfly and planar structures (Table 3). Our calculations are in good agreement with recently published calculated comparative energies for a series of neutral and negatively charged dithiatetrazocines.[31] Only neutral trithiatetrazocines and the neutral dithiatetrazocine carrying Me_2N donor groups distort from planarity under formation of a transannular S−S bond, while for all positively charged species the planar structure is preferred. This distortion has been explained by a second-order Jahn−Teller effect, and the delicate balance between planar and folded structures has been extensively investigated by theory for neutral dithiatetrazocines.[5]

DFT calculations reveal the free $[RCN_4S_3]^+$ cations to be planar or almost planar in the gas phase. Depending on the substituent a planar or slightly puckered structure has been found as the total minimum. For **2d** a bent structure in agreement with the experimentally found structure is the total minimum, the planar structure is a transition state (Figure 2). However, it has to be noted that energy differences are very small (0.13 kJ/mol for **2d** between planar and bent

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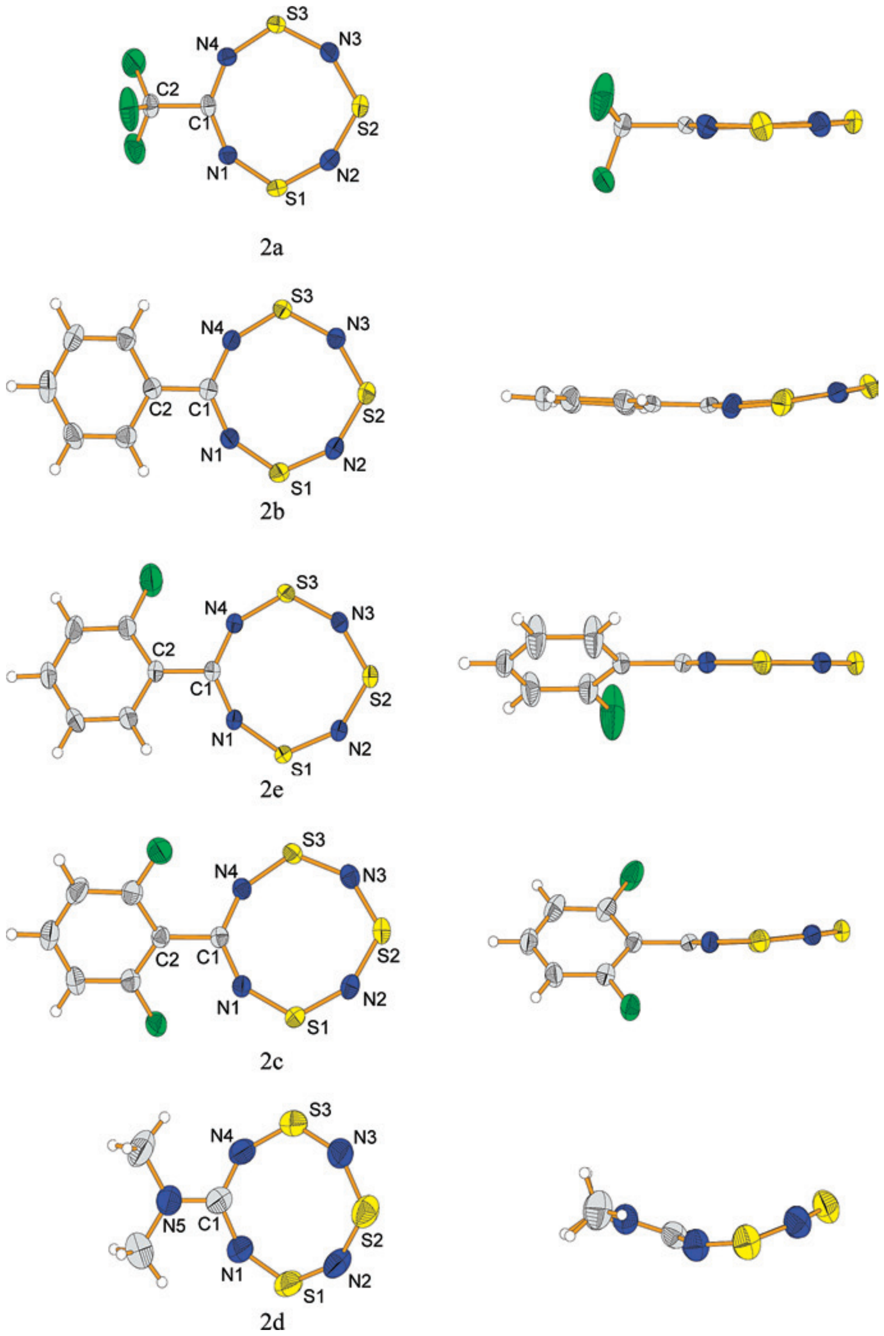
(26) Assigned by comparison with Boeré, R. T.; Oakley, R. T.; Shevalier, M. *J. Chem. Soc., Chem. Commun.* **1987**, 110–112.

(27) Boeré, R. T.; Cordes, A. W.; Hayes, P. J.; Oakley, R. T.; Reed, R. W.; Pennington, W. T. *Inorg. Chem.* **1986**, *25*, 2445–2450.

(28) Wheatley, P. J. *Acta Crystallogr.* **1955**, *8*, 224–226.



2a

2b

2e

2c

2d

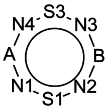
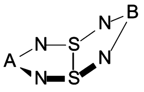
Figure 1. Crystal structures of **2a-e**. The left column shows a top view and the right column a side view of the $[RCN_4S_3]^+$ cations. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Experimental and Calculated (PBE0/6-311+G**) Averaged Bond Length for $[RCN_4S_3]^+$ Cations **2a-e**

		R−C1	av. (C1−N1, C1−N4)	av. (N1−S1, N4−S3)	av. (S1−N2, S3−N3)	av. (N2−S2, N3−S2)	N1−C1−C2−C3 torsion angle	point group
$[F_3CCN_4S_3]^+$ (**2a**)	exp.	152.3(13)	130.6	155.0	156.6	155.0		
	calc.	154.9	131.1	155.1	158.1	157.1		C_s
$[PhCN_4S_3]^+$ (**2b**)	exp.	148.7 (3)	132.3	153.7	156.4	156.0	9.6	
	calc.	146.2	133.3	154.4	157.6	158.1	1.1	C_s
$[2,6\text{-}F_2C_6H_3CN_4S_3]^+$ (**2c**)	exp.	148.0 (5)	133.1	153.2	156.0	156.5	44.0	
	calc.	146.6	132.7	154.4	158.1	157.7	39.5	C_2
$[Me_2NCN_4S_3]^+$ (**2d**)	exp.	132.8(7)	134.0	153.2	153.8	158.8		
	calc.	133.5	134.2	154.4	156.0	159.3		C_1
$[2\text{-}FC_6H_4CN_4S_3]^+$ (**2e**)	exp.	148.0(4)	132.6	153.8	156.5	156.5	29.3	
	calc.	146.2	133.1	154.4	157.7	158.0	19.2	C_1

structure) and all calculated structures show a very low-energy bending mode. The calculated minimum structure can be expected to be method and basis set dependent. Thus, on the basis of calculations, no definitive statement can be made about whether the gas phase structure is totally planar or bent. Therefore, experimentally found deviations from

Table 3. Calculated (PBE0/6-311+G**) Energy Differences (kJ/mol) between Planar and Folded Transannular-Bonded Structures and Mulliken Charges and Nucleus-Independent Chemical Shifts (NICS) for the Planar Structures

A	B			Calculated Mulliken charge					NICS(0)[d]	NICS(1)[d]
				A	N1/N4	S1/S3	N2/N3	B		
S^+	S^+	0	-[c]	0.82	-0.32	0.82	-0.32	0.82	-17.0	-14.5
F_3C-C	S^+	0	-[c]	-0.22	-0.12	0.78	-0.37	0.67	-17.2	-14.3
H-C	S^+	0	-[c]	0.21	-0.22	0.61	-0.33	0.64	-16.7	-14.1
H_2N-C	S^+	0	+81	0.11	-0.28	0.69	-0.40	0.58	-12.2	-10.1
Me_2N-C	S^+	0[a]	+68	-0.09	-0.29	0.75	-0.42	0.58	-10.4	-8.2
H-C	S-F	+15[b]	0	-	-	-	-	-	-	-
F_3C-C	C-CF_3	0	+62	-0.41	-0.19	0.67	-0.19	-0.41	-16.4	-13.9
H-C	C-H	0	+49	-0.14	-0.21	0.39	-0.21	-0.14	-15.9	-13.4
H_2N-C	C-NH_2	+33[e]	0	-0.10	-0.28	0.50	-0.28	-0.10	-13.0	-10.7

[a] The planar minimum structure is slightly bent, the planar structure corresponds to a transition state (see Figure 2). [b] The calculated structure is slightly folded, but does not show a transannular S−S contact. [c] The folded butterfly structure with a transannular S−S bond does not correspond to a minimum on the hypersurface. [d] Nucleus-independent shifts (NICS), NICS(0) at the ring center, NICS(1) 100 pm above the ring center. [e] A value of 34.3 kJ/mol has been previously calculated (B3LYP/6−31G(d) for $Me_2NC(NSN)_2CNMe_2$.[31]

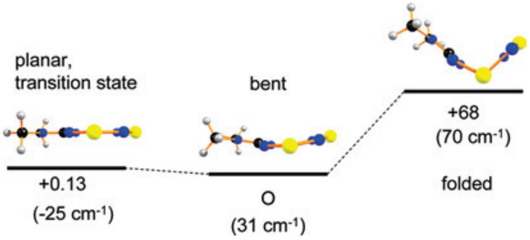


Figure 2. Calculated (PBE0/6−311+G**) geometries (left: planar, middle: bent, right: folded with transannular S−S bond) for $[Me_2NCN_4S_3]^+$ with relative energies in kJ/mol and frequency of the bending vibration.

planarity for the cations result from cation−anion interactions and packing effects (see below) rather than electronic reasons.

In recent years the aromatic character of sulfur−nitrogen heterocycles has received some theoretical attention with the development of new aromaticity criteria.[29] Ring currents are a probe for aromaticity in inorganic hetreocycles, and nucleus-independent chemical shifts (NICS)[22] are an easily accessible quantitative measure for diatropic ring currents. Calculated NICS values for $[RCN_4S_3]^+$ cations (Table 3) are in good agreement with those calculated previously for other 10π sulfur−nitrogen heterocycles (e.g., NICS(0) $[S_4N_4]^{2+}$ −20.6, $[S_4N_3]^+$ −12.1)[29a] indicating the aromatic character. $[RCN_4S_3]^+$ cations carrying electron donating groups show reduced NICS values and thus reduced aromaticity (cf. NICS(0) for $[F_3CCN_4S_3]^+$ is −17.2 and for $[Me_2NCN_4S_3]^+$ is −10.4).

In conclusion theoretical calculations are in agreement with the description of $[RCN_4S_3]^+$ as planar 10π aromatics. π donor substituents (e.g., Me_2N) decrease the positive charge on the heterocyclic part of the cation, reduce the aromatic character (NICS), and thus favor the cation to distort slightly because of the occurrence of a weak second-order Jahn−Teller effect.

3.4. Crystal Packing of $[RCN_4S_3][AsF_6]$. Exemplarily, the crystal packing of **2e**$[AsF_6]$ is shown in Figure 3. Previously, we investigated the crystal packing of the parent bicycles **1** and their respective co-crystals with C_6F_6.[9a,c] In all cases the packing of the sulfur−nitrogen heterocycles was strongly influenced by interactions between the corresponding substituents. The phenyl group lead to a herringbone structure with a perpendicular arrangement of the phenyl groups, the partly fluorinated derivatives formed π-type stacks. A similar behavior is observed for $[AsF_6]^-$ salts of the $[RCN_4S_3]^+$ cations. For instance for (**2e**) (Figure 3) π-stacking of the substituents significantly contributes to the structure, resulting in two different domains, one for the organic substituent and one for the sulfur−nitrogen part of the cation and the $[AsF_6]^-$ anion. Figure 4 shows the coordination sphere around the $[2\text{-}FC_6H_4CN_4S_3]^+$ cation (**2e**). The cation is surrounded by five $[AsF_6]^-$ anions, two of which are located above and below the center of the cation and three anions are approximately lying in the plane. There are in total nine contacts between the anion and the partially positively charged sulfur atoms (303.4−325.6 pm) and one contact to the carbon atom (312.6 pm) shorter than the sum of the van der Waals radii (S−F 330 pm, C−F 320 pm).[30] The two anions above and below the cation form three and four contacts respectively to the cation, while the three anions in plane only form one S−F contact each. Different solid state packing for each $[RCN_4S_3][AsF_6]$ salt depending on the substituent (see Supporting Information for figures) results in different surroundings around the $[RCN_4S_3]^+$ cations and

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(29) (a) De Proft, F.; Fowler, P. W.; Havenith, R. W. A.; von Ragué Schleyer, P.; Van Lier, G.; Geerlings, P. *Chem.−Eur. J.* **2004**, *10*, 940–950. (b) Fowler, P. W.; Rees, C. W.; Socini, A. *J. Am. Chem. Soc.* **2004**, *126*, 11202–11212. (c) Van Droogenbroeck, J.; Van Alsenoy, C.; Blockhuys, F. *J. Phys. Chem. A* **2005**, *109*, 4847–4851.

(30) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(31) Boeré, R. T.; Bond, A. M.; Chivers, T.; Feldberg, S. W.; Roemmele, T. L. *Inorg. Chem.* **2007**, *46*, 5596–5607.

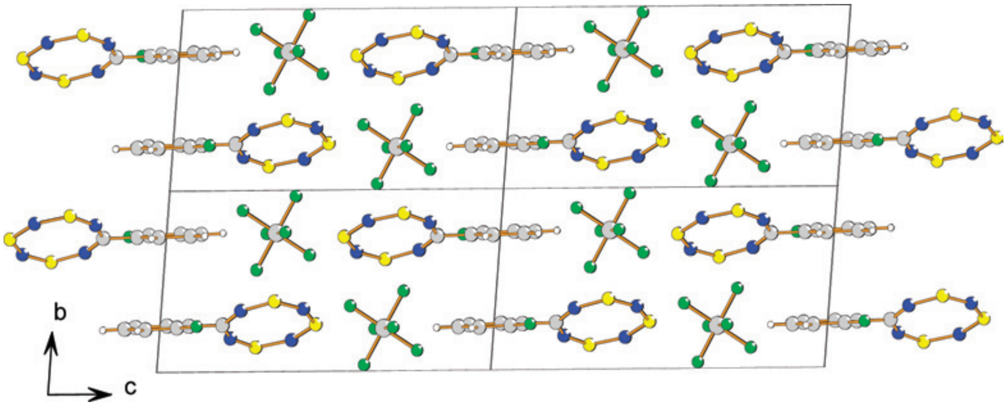

Figure 3. 1 × 2 × 2 cell of [2-$FC_6H_4CN_4S_3$][AsF_6] (**2e**[AsF_6]).

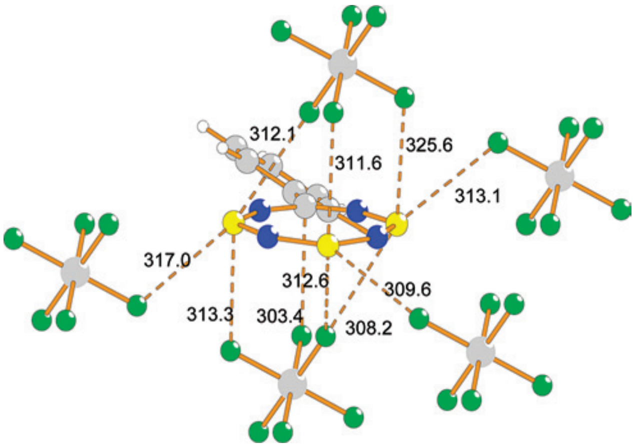

Figure 4. Coordination sphere of [2-$FC_6H_4CN_4S_3$]$^+$ (**2e**) showing cation−anion contacts [pm]. All S−F (sum of the van der Waals radii 330 pm)[30] and C−F (320 pm)[30] contacts below the sum of the van der Waals radii are given.

thus contributes to the experimentally found distortions from planarity.

Conclusion

Trithiatetrazocine cations [RCN_4S_3]$^+$ (**B**), the missing link between the long known valence isoelectronic 10π eight-membered heterocycles [S_4N_4]$^{2+}$ (**A**) and dithiatetrazocines RC(NSN)$_2$CR (**B**), were prepared as their [AsF_6]$^-$ salts from the reaction of bicyclic sulfur−nitrogen heterocycles RCN_5S_3 and [Hg(SO_2)][AsF_6]$_2$ in liquid SO_2. In contrast to previously published syntheses, which were limited to the trifluoromethyl substituted $F_3CCN_5S_3$, the reaction of bicyclic RCN_5S_3 with [Hg(SO_2)][AsF_6]$_2$ can be applied to generate various [RCN_4S_3]$^+$ cations with both electron-donating (e.g., Me_2N) and electron-withdrawing (e.g., F_3C) substituents. Crystal structure determinations and theoretical calculations revealed the [RCN_4S_3]$^+$ cations to be planar or almost planar 10π Hückel aromatics. In contrast to neutral dithiatetrazocines they remain planar even when carrying the electron-donating Me_2N group and do not fold to a butterfly like structure with a transannular S−S bond. Nevertheless, in the solid state all cations slightly deviate from ideal planarity because of solid state effects. According to theoretical calculations the planar [RCN_4S_3]$^+$ cations possess a low-energy bending mode, with a very small energy difference between totally planar and slightly bent structures. Electron donating groups reduce the positive charge on the sulfur−nitrogen heterocycle, reduce the aromatic character as shown by NICS calculations, and introduce a small second-order Jahn−Teller effect. For [$Me_2NCN_4S_3$][AsF_6] a slightly bent structure is found by calculations and experimental structure determination. Recently the 11π radical anions of some dithiatetrazocines (**C**) have been generated electrochemically and, despite half-lives of a few seconds, characterized by ESR spectroscopy.[31] Thus, the corresponding neutral 11π trithiatetrazocine radicals represent a worthwhile target for future investigations.

Acknowledgment. Financial support by the BFK NaWi, Universität Bremen is gratefully acknowledged. The authors are also grateful to Dr. Grigory Nikiforov for measuring ^{14}N NMR spectra.

Supporting Information Available: Crystallographic data (CIF) for **2b**, **2c**, **2d**, **2e**, **3b**, **3e**, **3f**. Figures, selected bond length and angles, and details of the data collection and refinement for the 3,5-R-1,2,4,6-thiatriazinyl hexafluoroarsenats [(RCN)$_2$SN][AsF_6] (R = Ph (**3b**), 2-FC_6H_4 (**3e**), 4-FC_6H_4 (**3f**)), solid state packing diagrams for **2b,c,d**, preliminary ^{14}N NMR scale experiment of 2-$FC_6H_4CN_5S_3$ with [Hg(SO_2)$_2$][AsF_6]$_2$, visualization of calculated π orbitals of the parent structure [HCN_4S_3]$^+$, geometries for all calculated species, frequency analysis and assignment of vibrations for calculated structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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