W, 54.38; Rb, 22.26; $H_2O$, 5.40. IR (KBr pellet; $cm^{-1}$): 990 (m), 941 (s), 910 (s), 867 (vs), 816 (s), 738 (vs), 659 (sh), 552 (w), 525 (m), 480 (sh), 450 (sh), 395 (sh), 358 (s), 328 (m), 317 (m), 299 (sh).

**Aqueous solution of $\gamma$-$H_8SiW_{10}O_{36}$** was obtained by $K^+/H^+$ exchange on a strongly acidic cation exchanger with sulfonic groups based on styrene-DVB copolymer. A 12-g amount of $\gamma$-$K_8SiW_{10}O_{36}$ and 30 mL of water were agitated with 20 mL of a Dowex 50W-X2 resin ($H^+$ form). The resulting solution was passed through a column containing the same resin (45 cm × 1.2 cm). The effluent was checked by atomic absorption and contained less than 1‰ of the initial potassium.

**Physical Measurements.** Polarograms were recorded on a Tacussel PRG3 instrument with dropping or stationary mercury electrodes.

Absorption spectra were recorded on Perkin-Elmer 555 (UV) and Perkin-Elmer 283 (IR) spectrophotometers. $^{183}W$ NMR spectra were obtained at 297 K on a Bruker WM 250 spectrometer operating at 10.4 MHz. The samples were measured in 10 mm o.d. Pyrex tubes either in pure $D_2O$ or in $H_2O/D_2O$ (90/10) mixtures. Chemical shifts are referenced to external 2 M $Na_2WO_4$ in alkaline $D_2O$; a negative value means a high-field shift (low frequency) with respect to the reference.

**Structure Determination.** Preliminary oscillation and Weissenberg photographs showed a monoclinic lattice, and systematic absences indicated the space group $P2_1/c$. The intensities were collected at room temperature on a Philips PW 1100 four-circle diffractometer (Mo K$\alpha$ radiation, graphite monochromator and scintillation counter) in the $\theta$–$2\theta$ scan mode up to $2\theta_{max} = 48°$ (background measurement in fixed position before and after every scan for a time equal to half of the scan time). The intensities were corrected for the Lorentz and polarization factors and absorption ($\mu = 315$ $cm^{-1}$). The cell constants were determined from a least-squares fit of 25 reflections. Crystal data are given in Table V.

**Solution and Refinement of the Structure.** The 10 tungsten atoms of the asymmetric unit were located by using direct methods (MULTAN). The rubidium, silicon, and anionic oxygen atoms were located from alternate Fourier synthesis and full-matrix least-squares refinements. Refinements to convergences with isotropic thermal parameters for the oxygen atoms and anisotropic thermal parameters for the others gave $R = 0.070$ and $R_w = 0.073$.

As often occurs in structural determination of heteropolyanions, all cations were not found. Half of the rubidium atoms are missing. Water molecules were not located.

Calculations were carried out on the Gould UTX 32 computer of the university with SHELX programs.[17]

**Registry No.** $K_8SiW_{10}O_{36}$, 102073-48-3; $K_8SiW_{11}O_{39}$, 37300-95-1; $Rb_8SiW_{10}O_{36}$, 102073-49-4; $H_8SiW_{10}O_{36}$, 102073-50-7; $LiSiW_{10}O_{36}{}^{7-}$, 102073-51-8; $NaSiW_{10}O_{36}{}^{7-}$, 102073-52-9; $KSiW_{10}O_{36}{}^{7-}$, 102073-53-0; $RbSiW_{10}O_{36}{}^{7-}$, 102073-54-1; $MgSiW_{10}O_{36}{}^{6-}$, 102073-55-2; $CaSiW_{10}O_{36}{}^{6-}$, 102073-56-3; $SnSiW_{10}O_{36}{}^{6-}$, 102073-57-4.

**Supplementary Material Available:** A listing of anisotropic thermal parameters of W, Si, and Rb atoms (1 page). Ordering information is given on any current masthead page.

(17) Sheldrick, G. M. "SHELX 76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.
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Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4,
and Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560 São Carlos, SP, Brazil

# Synthesis and Electronic Structure of the $R_2NCS_2N_3$ Ring: X-ray Crystal Structure of the Bicyclic Compound $i$-$Pr_2NCS_3N_5$ and Preparation of $R_2NCS_2N_3 \cdot C_7H_8$ (R = Me, Et, $i$-Pr), $Et_2NCS_2N_2{}^+Cl^-$, and Salts of the $(R_2NCN)(NSCl)(NS)^+$ Cation

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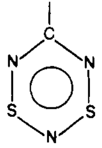
and Milan Trsic*[‡]

*Received November 21, 1985*

The crystal and molecular structures of $i$-$Pr_2NCS_3N_5$ have been determined by X-ray crystallography. The crystals are triclinic and belong to the space group $P\bar{1}$, with $a = 5.648$ (1) Å, $b = 9.162$ (2) Å, $c = 13.432$ (2) Å, $\alpha = 69.52$ (1)°, $\beta = 79.58$ (2)°, $\gamma = 76.66$ (2)°, $V = 629.7$ (5) Å$^3$, and $Z = 2$. The final $R$ and $R_w$ values were 0.042 and 0.040, respectively. The molecule is bicyclic and consists of an $-N{=}S{=}N-$ bridge ($d$(S–N) = 1.539 (3) Å) weakly bonded ($d$(S–N) = 1.748 (3) Å) to the sulfur atoms of a six-membered $i$-$Pr_2NCS_2N_3$ ring. The thermolysis and photolysis of this bicyclic compound and the reduction of $(RCN)(NSCl)_2$ (R = $Me_2N$, $Et_2N$, $i$-$Pr_2N$) have been investigated as possible routes to the six-membered rings, $RCS_2N_3$. The reduction of $(R_2NCN)(NSCl)_2$ (R = Et, $i$-Pr) with $(Me_3Si)_2Hg$ in diethyl ether at −78 °C produced dark purple solids that react with norbornadiene to give the adducts $R_2NCS_2N_3 \cdot C_7H_8$. In contrast, the reaction of $(Et_2NCN)(NSCl)_2$ with sodium azide in acetonitrile at 23 °C caused ring contraction to give $Et_2NCS_2N_2{}^+Cl^-$ ($\lambda_{max}$ 530 nm). The purple color of this product is attributed to the HOMO ($n\pi$) → LUMO ($\pi^*$) transition on the basis of ab initio level HFS-SCF MO calculations for $RCS_2N_2{}^+$ (R = H, $NH_2$). Similar calculations for the six-membered ring $RCS_2N_3$ (R = $NH_2$) indicate that the heterocyclic ring is an eight-$\pi$-electron system but reveal a quasi-degeneracy for the HOMO and LUMO (both $\pi^*$ orbitals). A single determinant ground-state representation could not be obtained for the planar rings $RCS_2N_3$ (R = H, $CH_3$, Cl). The compounds $(RCN)(NSCl)_2$ react with the halide ion acceptors $BCl_3$, $SbCl_5$, and $SnCl_4$ to give salts of the monocation $(RCN)(NSCl)(NS)^+$, whereas treatment of 1,5-$(Me_2NCN)_2(NSCl)_2$ with $SbCl_5$ yields the dication $(Me_2NCN)_2(SN_2)^{2+}$.

## Introduction

In the context of our studies of $\pi$-electron-rich S–N heterocycles,[1] ring system **1** represents an interesting target molecule since it is expected to be an eight-$\pi$-electron system on the basis of simple electron-counting rules[1a] (cf. **2**).[2] The trifluoromethyl derivative (**1**, R = $CF_3$) was described by Mews et al. in 1984, but the characterization is based only on mass spectroscopic evidence.[3] White this work was in progress,[4] Oakley et al. reported the preparation of **1** (R = Ph) as an air-stable buff-colored solid, "presumably not monomeric".[5]



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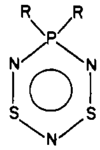

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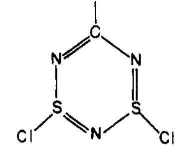

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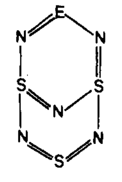

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[‡] Universidade de São Paulo.

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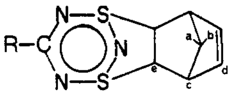
Recently, we discovered a high-yield synthesis of the mixed thiazyl–cyanuric rings **3** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$).[4,6a] These heterocycles could serve as precursors of **1** via reduction. We have also described the preparation of the bicyclic derivatives **4** (E = $Me_2NC$, $Et_2NC$, *i*-$Pr_2NC$) by the metathetical reaction of **3** with $Me_3SiNSNSiMe_3$.[4,6b] The thermolysis or photolysis of **4** (E = CR) might provide an alternative source of **1** via the reductive elimination of an NSN unit. The related ring system **2** (R = Ph) is produced in ca. 70% yield from the thermal decomposition of **4** (E = $PPh_2$), and thermally unstable derivatives of **2** (R = Me, F) have been obtained as adducts with norbornadiene via the same route.[7]

We report here the details of an X-ray structural analysis of **4** (E = *i*-$Pr_2NC$) and the behavior of **4** (E = $R_2NC$) upon thermal decomposition and photolysis. We also describe the reactions of **3** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$) with various reducing agents to give **1**, characterized as adducts with norbornadiene (NBD), **5** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$), or the five-membered ring, **6** (R = $Et_2N$). The reactions of **3** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$) with halide ion acceptors produced salts of the monocations $(RCN)(NSCl)(NS)^+$ rather than the dication of **1**. The experimental results are discussed in the context of discrete variational Hartree–Fock–Slater (HFS) SCF MO calculations of the electronic structure of the six-membered ring **1** (R = H, $CH_3$, $NH_2$, Cl).



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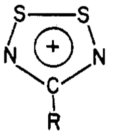

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## Experimental Section

**Reagents and General Procedures.** Solvents were dried [carbon tetrachloride and methylene dichloride ($P_2O_5$), *n*-pentane ($CaH_2$), diethyl ether ($CaH_2$), and acetonitrile ($CaH_2$ and $P_2O_5$)] and freshly distilled before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen (99.99% purity) or argon. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ.

The following reagents were prepared by literature procedures: $(R_2NCN)(NSCl)_2$ (R = Me, Et, *i*-Pr),[6a] $R_2NCS_3N_5$ (R = Me, Et, *i*-Pr),[6b] $(Me_3Si)_2Hg$.[8] The following chemicals were commercial products used as received: $NaN_3$ (Eastman), $Ph_3Sb$ (Eastman), norbornadiene (Aldrich), $BCl_3$ (Aldrich, 1 M solution in hexane). $SnCl_4$ (MCB) and $SbCl_5$ (Baker) were freshly distilled before use.

**Instrumentation.** Infrared spectra were recorded as Nujol mulls (CsI windows) on a Nicolet 5DX FT-IR spectrometer. UV–visible spectra were obtained by use of a Cary 219 spectrophotometer. NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (routine $^1H$), Bruker WH-90, or Varian XL-200 ($^1H$ and $^{13}C$) instrument. Chemical shifts are reported in ppm downfield from $Me_4Si$. Mass spectra were obtained on a Kratos MS80RFA instrument (EI/70 eV).

**Table I.** NMR Data for the Norbornadiene Adducts, $R_2NCS_2N_3{\cdot}C_7H_8$[a,b]

| | $Me_2NCS_2N_3{\cdot}C_7H_8$ | $Et_2NCS_2N_3{\cdot}C_7H_8$ | *i*-$Pr_2NCS_2N_3{\cdot}C_7N_8$ |
|---|---|---|---|
| $H_{a,b}$ | 1.06 (AB, 9.6) | 1.08 (AB, 9.0) | 1.04 (AB, 9.4) |
| | 2.00 (AB, 9.6) | 2.05 (AB, 9.0) | 2.03 (AB, 9.4) |
| $H_{c,c'}$ | 3.13 (m) | 3.12 (m)[c] | 3.13 (m) |
| $H_{d,d'}$ | 6.21 (t, 1.6) | 6.24 (t, 1.3) | 6.23 (t, 1.8) |
| $H_{e,e'}$ | 4.18 (d, 1.6) | 4.19 (d, 1.7) | 4.16 (d, 1.8) |
| $CH_3$ | 2.75 (s) | 1.02 (t, 7.0) | 1.12 (d, 6.8) |
| $CH_2$ | | 3.18 (q, 7.0) | |
| CH | | | 3.99[d] |
| $C_{a,b}$ | 36.7 | 39.7 | 43.5 |
| $C_{c,c'}$ | 40.7 | 40.5 | 40.6 |
| $C_{d,d'}$ | 138.9 | 138.6 | 138.6 |
| $C_{e,e'}$ | 81.0 | 82.3 | 82.5 |
| $C_{ring}$ | 145.7 | 150.4 | 150.7 |
| $CH_3$ | 43.7 | 13.4 | 20.9 |
| $CH_2$ | | 43.4 | |
| CH | | | 44.3 |

[a] The numbering scheme for H and C atoms is indicated in structure **5**. [b] $\delta(CDCl_3)$ relative to internal $Me_4Si$. Coupling constants (in parentheses) are quoted in Hz and refer to H–H coupling. [c] The signals of the $CH_2$ and $H_{c,c'}$ protons overlap. [d] Broad septet.

**Preparation of $(R_2NCS_2N_3)_n$. (a) Reaction of $(Et_2NCN)(NSCl)_2$ with $(Me_3Si)_2Hg$.** A solution of $(Me_3Si)_2Hg$ (1.66 g, 4.78 mmol) in diethyl ether (20 mL) was added during 5 min to a vigorously stirred solution of $(Et_2NCN)(NSCl)_2$ (1.25 g, 4.79 mmol) in diethyl ether (60 mL) at −78 °C. The color of the reaction mixture darkened rapidly to give a thick, purple-brown slurry that became darker purple and less viscous within 10 min. After 30 min at −78 °C the mixture was filtered through a coarse frit to give a purple solid (0.70 g) containing mercury, which was used for the preparation of an NBD adduct (vide infra). Solvent was removed from the filtrate at 0 °C in vacuo to give purple microcrystals of $(Et_2NCNS_2N_3)_n$ (0.35 g, 1.84 mmol). Anal. Calcd for $C_5H_{10}N_4S_2$: C, 31.55; H, 5.30; N, 29.45; S, 33.72. Found: C, 32.76; H, 5.90; N, 26.60; S, 34.74. IR: 1500 s, 1296 s, 1260 m, 1210 m, 1167 m, 1095 sh, 1074 m, 995 m, 950 w, 852 w, 804 w, 778 w, 722 m, 706 w, 580 w, 530 vw, 457 w, 360 w $cm^{-1}$. MS, *m/e* (relative intensity): 190 (72, $Et_2NCS_2N_3^+$), 176 (31, $Et_2NCS_2N_2^+$), 162 (16, $EtN(H)CS_2N_3^+$), 144 (17, $Et_2NCSN_2^+$), 119 (13, $HNCS_2N_2^+$), 112 (12, $Et_2NCN_2^+$), 98 (46, $Et_2NCN^+$), 83 (72, $EtN(CH_2)NCN$), 78 (61, $S_2N^+$), 72 (71, $Et_2N^+$), 55 (93, $HN(CH_2)NCN$), 46 (100, $SN^+$), 42 (50, $H_2NCN$). The product was further characterized by conversion to the NBD adduct (vide infra).

**(b) Reaction of (*i*-$Pr_2NCN)(NSCl)_2$ with $(Me_3Si)_2Hg$.** A solution of $(Me_3Si)_2Hg$ (1.10 g, 3.17 mmol) in diethyl ether (30 mL) was added rapidly to a vigorously stirred solution of (*i*-$Pr_2NCN)(NSCl)_2$ (0.83 g, 2.85 mmol) in diethyl ether (100 mL) at −78 °C. The color of the reaction mixture rapidly darkened. The mixture was allowed to warm to ca. 0 °C. Solvent was removed from the filtrate under vacuum at 0 °C to give purple-black microcrystals of (*i*-$Pr_2NCS_2N_3)_n$ (0.42 g, 1.9 mmol) after washing with cold (ca. −30 °C) *n*-pentane (30 mL) and drying under vacuum. Anal. Calc for $C_7H_{14}N_4S_2$: C, 38.51; H, 6.46; N, 25.66. Found: C, 36.89; H, 6.46; N, 23.58. IR: 1473 s, 1360 s, 1335 vs, 1259 m, 1200 w, 1140 m, 1067 s, 1029 m, 945 w, 910 w, 758 s, 694 m, 534 m, 510 m, 437 m, 350 m $cm^{-1}$. MS, *m/e* (relative intensity): 218 (17, *i*-$Pr_2NCS_2N_3^+$), 204 (11, *i*-$Pr_2NCS_2N_2^+$), 172 (7, *i*-$Pr_2CSN_2^+$), 147 (17, $C_2H_5NCS_2N_2^+$), 134 (14), 130 (12), 126 (26, *i*-$Pr_2NCSN_2^+$), 111 (22, $(C_3H_7)(C_3H_6)NC^+$), 100 (15, *i*-$Pr_2N^+$), 92 (12, $S_2N_2^+$), 88 (45), 84 (42, $C_3H_7NCNH$), 78 (22, $S_2N^+$), 69 (82, $C_3H_7NC^+$), 64 (69, $S_2^+$), 58 (22, $C_3H_7NH$), 46 ($NS^+$, 72), 43 (100, $H_2NCNH^+$). The product was further characterized by conversion to the NBD adduct (vide infra).

**Preparation of the NBD Adducts of $R_2NCS_2N_3$. (a) Reaction of $(Et_2NCN)(NSCl)_2$ with Triphenylantimony in the Presence of NBD.** A mixture of triphenylantimony (3.63 g, 10.3 mmol) and norbornadiene (1.42 g, 15.5 mmol) in diethyl ether (20 mL) was added dropwise, with stirring, to a solution of $(Et_2NCN)(NSCl)_2$ (2.69 g, 10.3 mmol) in diethyl ether (50 mL) at −78 °C. The solution began to turn red-brown within 5 min, finally becoming dark red-purple after the addition was complete. The reaction mixture was then stirred at 23 °C for 30 min to give a yellow solution with a small amount of white precipitate, which was removed by filtration. The volume of the filtrate was reduced to ca. 35 mL, and then fractional crystallization at −20 °C yielded $Ph_3SbCl_2$

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(4) Preliminary results were presented at the symposium Horizons in the Chemistry and Properties of Low Dimensional Solids, PAC-CHEM conference, Honolulu, Dec 1984. For the proceedings of that meeting, see: Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Mol. Cyrst. Liq. Cryst.* **1985**, *125*, 447.

(5) (a) Boeré, R. T.; Cordes, A. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1985**, 929. (b) After the submission of this paper, the structure of this material was reported. It is a cofacial dimer in which $PhCN_3S_2$ units are linked by two long S–S (2.527 (3) Å) interactions: Boeré, R. T.; French, C. L.; Oakley, R. T.; Cordes, A. W.; Privett, J. A. J.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 7710.

(6) (a) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 47. (b) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 272.

(7) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. *Can. J. Chem.* **1984**, *62*, 712.

(8) Rösch, L.; Altnau, G.; Hahn, E.; Havemann, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1234.

**Table II.** Analytical and IR Spectroscopic Data for Salts of the $(RCN)(NSCl)(NS)^+$ (R = $Me_2N$, $Et_2N$, $i$-$Pr_2N$) and 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ Cations[a]

| | | % | | | $cm^{-1}$ | |
|---|---|---|---|---|---|---|
| compd | color | C | H | N | $\nu(CN_2)$ | $\nu$(S–Cl) |
| $[(Me_2NCN)(NSCl)(NS)][SbCl_6]$ | orange | 6.97 (6.76) | 1.25 (1.13) | 10.28 (10.53) | 1614 | 450 |
| $[(Et_2NCN)(NSCl)(NS)][SbCl_6]$ | orange | 10.01 (10.71) | 1.85 (1.78) | 9.33 (9.99) | 1589 | 449 |
| $[(Et_2NCN)(NSCl)(NS)][BCl_4]$ | pale cream | 15.46 (15.85) | 2.65 (2.64) | 14.45 (14.80) | 1596 | 455 |
| $[(Et_2NCN)(NSCl)(NS)]_2[SnCl_6]$[b] | orange | 14.67 (15.32) | 2.73 (2.55) | 13.87 (14.31) | 1595 | 446 |
| $[(i\text{-}Pr_2NCN)(NSCl)(NS)]_2[SnCl_6]$ | golden yellow | 20.11 (20.02) | 3.25 (3.34) | 13.05 (13.35) | 1575 | 444 |
| $[1,5\text{-}(Me_2NCN)_2(SN)_2][SbCl_6]_2$[c] | orange-red | 7.99 (7.99) | 1.88 (1.33) | 9.61 (9.33) | 1579 | |

[a] Calculated values in parentheses. [b] Found: Cl, 34.91; S, 15.59. Calcd: Cl, 36.26; S, 16.37. [c] Prepared by dropwise addition of $SbCl_5$ to a solution of 1,5-$(Me_2NCN)_2(NSCl)_2$[6] in methylene dichloride.

(3.0 g, 7.1 mmol) identified by IR and $^1H$ NMR spectra and $Et_2NCS_2N_3{\cdot}C_7H_8$ (0.7 g, 2.5 mmol). Anal. Calcd for $C_{12}H_{18}N_4S_2$: C, 51.03; H, 6.42; N, 19.84; S, 22.81. Found: C, 50.64; H, 6.76; N, 19.53; S, 23.07. MS, $m/e$ (relative intensity): 190 (70, $Et_2NCS_2N_3^+$), 176 (9, $Et_2NCS_2N_2^+$), 144 (27, $Et_2NCSN_2^+$), 98 (52, $Et_2NCN^+$), 92 [82, $C_7H_8^+$ (and $S_2N_2^+$)], 91 (92, $C_7H_7^+$), 78 (82, $S_2N^+$), 59 (100). NMR data are given in Table I.

**(b) Reaction of $(Me_2NCN)(NSCl)_2$ with Bis(trimethylsilyl)mercury in the Presence of NBD.** A solution of $(Me_3Si)_2Hg$ (1.66 g, 4.78 mmol) in diethyl ether (30 mL) was added rapidly to a vigorously stirred solution of $(Me_2NCN)(NSCl)_2$ (1.10 g, 4.72 mmol) in diethyl ether (80 mL) at −78 °C. The reaction mixture immediately became purple-brown, and after 5 min, an excess of norbornadiene (10 mL) was added and the mixture was allowed to warm to room temperature. After 1 h, the finely divided mercury was removed by filtration to give a pale yellow solution. Removal of solvent gave a pale yellow solid that was dissolved in toluene (50 mL). The solution was filtered, and solvent was removed under vacuum to give a pale yellow solid that was washed with $n$-pentane (20 mL) to give $Me_2NCS_2N_3{\cdot}C_7H_8$ (0.88 g, 3.54 mmol), mp 139 °C. The product was purified by recrystallization from $n$-hexane. Anal. Calcd for $C_{10}H_{14}N_4S_2$: C, 47.22; H, 5.51; N, 22.03. Found: C, 45.69; H, 5.63; N, 20.82. MS, $m/e$ (relative intensity): 162 (60, $Me_2NCS_2N_3^+$), 148 (5, $Me_2NCS_2N_2^+$), 116 (28, $Me_2NCSN_2^+$), 92 [60, $C_7H_8^+$ (and $S_2N_2^+$)], 91 (100, $C_7H_7^+$), 78 (19, $S_2N^+$), 70 (43, $Me_2NCN^+$), 69 (74, $CH_3(CH_2)NCN^+$), 66 (73), 64 (40, $S_2^+$), 46 (88, $NS^+$). NMR data are given in Table I.

**(c) Reaction of $(Et_2NCS_2N_3)_n$ with Norbornadiene.** An excess of norbornadiene (5 mL) was added by syringe to a stirred solution of $(Et_2NCS_2N_3)_n$ containing mercury (0.70 g) in diethyl ether (60 mL) at −20 °C. The dark olive-brown color of the solution disappeared in 5–10 s, and finely divided mercury was removed by filtration to give a pale yellow filtrate. The solid material was washed with diethyl ether (20 mL), and solvent was removed from the combined filtrates in vacuo to give a pale yellow solid (0.42 g). Recrystallization of this product from $n$-hexane (20 mL) at −20 °C produced white crystals of $Et_2NCS_2N_3{\cdot}C_7H_8$ (0.31 g, 1.10 mmol), mp 106 °C. Anal. Calcd for $C_{12}H_{18}N_4S_2$: C, 51.03; H, 6.42; N, 19.84. Found: C, 49.52; H, 6.44; N, 19.37. The $^1H$ NMR spectrum of this product was identical with that of an authentic sample.

**(d) Reaction of $(i\text{-}Pr_2NCS_2N_3)_n$ with Norbornadiene.** An excess of norbornadiene (5 mL) was added to a solution of $(i\text{-}Pr_2NCS_2N_3)_n$ (0.30 g, 1.4 mmol) in diethyl ether (30 mL) at −20 °C. After 2 h at 23 °C solvent and excess norbornadiene were removed under vacuum to give a sticky yellow residue. Recrystallization from $n$-hexane at −20 °C gave pale yellow needles of $i\text{-}Pr_2NCS_2N_3{\cdot}C_7H_8$ (0.25 g, 0.8 mmol), mp 145 °C. Anal. Calcd for $C_{14}H_{22}N_4S_2$: C, 54.16; H, 7.14; N, 18.05. Found: C, 53.92; H, 7.22; N, 17.81. NMR data are given in Table I.

**Reaction of $(Et_2NCN)(NSCl)_2$ with Sodium Azide.** Solid sodium azide (0.51 g, 7.9 mmol) was added to a solution of $(Et_2NCN)(NSCl)_2$ (2.07 g, 7.9 mmol) in acetonitrile (60 mL). The yellow solution rapidly became burgundy red, and vigorous evolution of a gas, presumably $N_2$, was observed. After 2 h at 23 °C the solution was filtered, reduced in volume to ca. 10 mL, treated with diethyl ether (55 mL), and then cooled to −20 °C. After 4 days purple-black crystals of $Et_2NCN_2S_2^+Cl^-$ (0.36 g, 1.7 mmol) were isolated by filtration and recrystallized from carbon tetrachloride (30 mL). Anal. Calcd for $C_5H_{10}ClN_3S_2$: C, 28.35; H, 4.72; Cl, 16.77; N, 19.85; S, 30.30. Found: C, 27.99; H, 5.04; Cl, 16.96; N, 19.59; S, 30.00. IR: 1561 ssh, 1546 vs, 1320 s, 1204 m, 1161 m, 1088 m, 1078 sh, 997 m, 904 m, 864 w, 780 m, 722 m, 713 s, 569 m $cm^{-1}$. MS, $m/e$ (relative intensity): 176 (40, $Et_2NCS_2N_2^+$), 119 (40, $HNCN_2S_2^+$), 98 (12, $Et_2NCN^+$), 78 (95, $S_2N^+$), 64 (38, $S_2^+$).

**Preparation of Salts of the Monocations $(RCN)(NSCl)(NS)^+$ (R = $Me_2N$, $Et_2N$, $i$-$Pr_2N$).** The procedure used for the preparation of these five salts was similar in each case. The dropwise addition of 2 molar equiv of the halide ion acceptor to a solution of $(RCN)(NSCl)_2$ in carbon tetrachloride or $n$-hexane at 23 °C resulted in the immediate formation of a precipitate. Analytical data and the characteristic IR bands of the products are listed in Table II. Full IR data are deposited with the supplementary material. The monocations are extremely moisture-sensitive, insoluble in organic solvents, but soluble in liquid $SO_2$. An example of a typical preparation is given below.

**Table III.** Crystallographic Parameters

| | |
|---|---|
| formula | $C_7H_{14}N_6S_3$ |
| fw | 278.42 |
| space group | $P\bar{1}$ |
| $a$, Å | 5.648 (1) |
| $b$, Å | 9.162 (2) |
| $c$, Å | 13.432 (2) |
| $\alpha$, deg | 69.52 (1) |
| $\beta$, deg | 79.58 (2) |
| $\gamma$, deg | 76.66 (2) |
| vol, Å$^3$ | 629.7 (5) |
| $Z$ | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.468 |
| $F(000)$ | 292 |
| radiation, (λ, Å) | Mo K$\alpha$ (0.71069, graphite monochromator) |
| temp, °C | 21 (1) |
| scan range, $\Delta\omega$, deg | 1.5(0.80 + 0.347 tan $\theta$) |
| scan speed, deg min$^{-1}$ | 0.5 + 3.3 |
| max $\theta$, deg | 25 |
| octants collcd | $+h{\pm}k{\pm}l$ |
| no. of unique reflctns | 2194 |
| no. of obsd reflctns | 1703 |
| cryst dimens, mm | 0.2 × 0.25 × 0.35 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 5.56 |
| min/max transmissn coeff | 0.67, 1.24 |
| weighting formula | $[\sigma^2(F) + 0.00002F^2]^{-1}$ |
| no. of obsd reflctns used in final cycle | 1703 |
| no. of variables in final cycle | 146 |
| resid electron density, e Å$^{-3}$ | 0.3 |
| GOF | 1.12 |
| $R$, $R_w$[a] | 0.042, 0.040 |

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**Reaction of $(Et_2NCN)(NSCl)_2$ with $BCl_3$.** Addition of a 1 M solution of $BCl_3$ in $n$-hexane (2.44 mL, 2.44 mol) to a solution of $(Et_2NCN)(NSCl)_2$ (0.32 g, 1.22 mmol) in $n$-hexane (30 mL) gave an immediate pale cream precipitate of $[(Et_2NCN)(NSCl)(NS)][BCl_4]$ (0.41 g, 1.08 mmol). The product was filtered off, washed with carbon tetrachloride (2 × 10 mL) and analyzed (Table II).

**X-ray Analysis of $i\text{-}Pr_2NCS_3N_5$.** The crystal and experimental conditions are given in Table III. The crystal chosen for data collection was a fragment cut from a larger crystal and sealed in a glass capillary under nitrogen. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurate reflections ($10 < \theta < 17°$). The final choice of space group $V\mathrm{p}\bar{1}$ was based on the centric distribution of $E$ values (K-curve)[9] and the successful solution of the structure. The data were collected on an Enraf-Nonius CAD 4F automated diffractometer using the $\omega$-$2\theta$ scan technique. The data were corrected for background, Lorentz, and polarization effects as well as crystal decay (18% drop in intensity of three standard reflections). The data were corrected for absorption by using the empirical method

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(9) All computations were performed with XRA 76 unless otherwise stated: Technical Report TR-446; Stewart, J. M., Ed.; Computer Science Center, University of Maryland: College Park, MD, 1976.

**Table IV.** Positional Parameters ($\times 10^4$) and $B_{eq}$ ($\times 10$ Å$^2$) for Non-Hydrogen Atoms

| atom | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| S(1) | −1101 (2) | 7949 (1) | 3020 (1) | 42.2 (5) |
| S(2) | 290 (2) | 7675 (1) | 1076 (1) | 34.7 (4) |
| S(3) | −4128 (2) | 9847 (1) | 1396 (1) | 41.4 (5) |
| N(1) | −2054 (5) | 6342 (3) | 3275 (2) | 36 (4) |
| N(2) | 975 (5) | 8239 (3) | 1987 (2) | 40 (1) |
| N(3) | −429 (5) | 5981 (3) | 1564 (2) | 30 (1) |
| N(4) | −3630 (6) | 9392 (3) | 2563 (2) | 43 (2) |
| N(5) | −2441 (6) | 8950 (3) | 676 (2) | 40 (1) |
| N(6) | −2325 (5) | 4136 (3) | 2899 (2) | 27 (1) |
| C(1) | −1620 (6) | 5547 (3) | 2564 (3) | 26 (1) |
| C(2) | −3582 (7) | 3533 (4) | 3996 (3) | 35 (2) |
| C(3) | −6260 (8) | 3744 (6) | 3972 (3) | 64 (3) |
| C(4) | −2435 (9) | 1849 (5) | 4569 (3) | 56 (2) |
| C(5) | −2205 (6) | 3224 (3) | 2162 (3) | 30 (2) |
| C(6) | 380 (7) | 2473 (4) | 1861 (3) | 46 (2) |
| C(7) | −3561 (7) | 4144 (4) | 1197 (3) | 41 (2) |

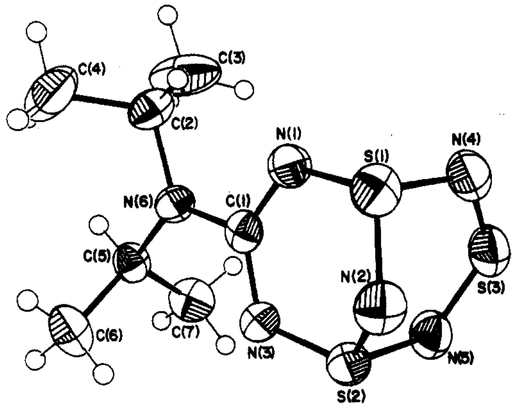

**Figure 1.** Perspective view (ORTEP) of $i$-$Pr_2NCS_3N_5$ showing the atomic labeling scheme. Non-hydrogen atoms are drawn at the 50% probability level, and hydrogen atoms are included as spheres of radius 0.1 Å.

(DIFABS)[10] in order to account for the irregular crystal shape and the use of a capillary. Details concerning data collection and reduction can be found in ref 11.

Atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann,[12] the H scattering factors were taken from ref 13, and real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[14] All non-hydrogen atoms of the model were clearly determined by using MULTAN 78.[15] Refinement was carried out by full-matrix least-squares techniques based on $F$, minimizing the function $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were unambiguously located on a difference Fourier map. These hydrogen atoms were included in the positions located and given an isotropic thermal parameter $1.1B_{eq}$ of the bonded atom but not refined. In the final cycles all non-hydrogen atoms were refined anisotropically, and it was possible to refine an isotropic extinction coefficient to a value of $1.12\ (7) \times 10^{-5}$. The model converged with a maximum shift/error of 0.7. The final atomic coordinates of the non-hydrogen atoms are given in Table IV.

**Theoretical Method.** The quantum-chemical approach is a discrete variational version of the Hartree–Fock–Slater (HFS) equations.[16] This procedure has been successfully applied to the description of the electronic structures of binary sulfur nitrides[17,18] and cyclothiaphosphazenes.[1b,2,19] The atomic basis set employed for the calculations is the atom-optimized double-$\zeta$ basis of Clementi and Roetti[20] augmented with 3d orbitals on sulfur.[21] The core orbitals are kept "frozen" and orthogonal to the valence orbitals during the SCF interactions in the manner described in ref 16a.

**Table V.** Bond Lengths (Å) and Angles (deg) for Non-Hydrogen Atoms

| | | | |
|---|---|---|---|
| S(1)–N(1) | 1.588 (3) | N(3)–C(1) | 1.355 (4) |
| S(1)–N(2) | 1.633 (3) | N(6)–N(1) | 1.341 (4) |
| S(1)–N(4) | 1.745 (3) | N(6)–C(2) | 1.487 (4) |
| S(2)–N(2) | 1.620 (4) | N(6)–C(5) | 1.488 (5) |
| S(2)–N(3) | 1.577 (3) | C(2)–C(3) | 1.485 (6) |
| S(2)–N(5) | 1.750 (3) | C(2)–C(4) | 1.510 (5) |
| S(3)–N(4) | 1.536 (3) | C(5)–C(6) | 1.512 (5) |
| S(3)–N(5) | 1.543 (3) | C(5)–C(7) | 1.507 (5) |
| N(1)–C(1) | 1.350 (5) | | |
| N(1)–S(1)–(2) | 112.1 (2) | C(1)–N(6)–C(2) | 120.3 (3) |
| N(1)–S(1)–N(4) | 103.0 (2) | C(1)–N(6)–C(5) | 122.0 (2) |
| N(2)–S(1)–N(4) | 103.7 (1) | C(2)–N(6)–C(5) | 117.2 (3) |
| N(2)–S(2)–N(3) | 111.4 (1) | N(1)–C(1)–N(3) | 127.0 (3) |
| N(2)–S(2)–N(5) | 104.4 (2) | N(1)–C(1)–N(6) | 116.7 (3) |
| N(3)–S(2)–N(5) | 104.3 (1) | N(3)–C(1)–N(6) | 116.2 (3) |
| N(4)–S(3)–N(5) | 118.8 (2) | N(6)–C(2)–C(3) | 110.9 (3) |
| S(1)–N(1)–C(1) | 121.9 (2) | N(6)–C(2)–C(4) | 111.6 (3) |
| S(1)–N(2)–S(2) | 110.3 (2) | C(3)–C(2)–C(4) | 113.1 (4) |
| S(2)–N(3)–C(1) | 119.4 (3) | N(6)–C(5)–C(6) | 112.8 (3) |
| S(1)–N(4)–S(3) | 119.3 (2) | N(6)–C(5)–C(7) | 113.6 (3) |
| S(2)–N(5)–S(3) | 121.9 (2) | C(6)–C(5)–C(7) | 112.2 (3) |

**Table VI.** Comparison of Mean S–N Bond Lengths (Å) in the Bicyclic Molecules $ES_3N_5$

| | E | | |
|---|---|---|---|
| bond[a] | $F_2P$[b] | PhC[c] | $i$-$Pr_2NC$[d] |
| S(1)–N(1)<br>S(2)–N(3) | 1.594 (7) | 1.622 (2) | 1.583 (3) |
| S(1)–N(2)<br>S(2)–N(2) | 1.622 (6) | 1.630 (2) | 1.626 (4) |
| S(1)–N(4)<br>S(2)–N(5) | 1.692 (8) | 1.728 (2) | 1.748 (3) |
| S(3)–N(4)<br>S(3)–N(5) | 1.550 (9) | 1.547 (2) | 1.539 (3) |

[a] See Figure 1 for numbering scheme. [b] Reference 22. [c] Reference 5. [d] This work.

## Results and Discussion

**Crystal and Molecular Structure of $i$-$Pr_2NCS_3N_5$ (4, E = $i$-$Pr_2NC$).** The bicyclic structure suggested for **4** (E = $R_2NC$) on the basis of chemical and spectroscopic evidence[6b] has been confirmed by X-ray crystallography. An ORTEP drawing of **4** (E = $i$-$Pr_2NC$) is shown in Figure 1. Table V contains the bond lengths and bond angles for non-hydrogen atoms. The molecule consists of a six-membered $CS_2N_3$ ring bridged across the sulfur atoms by an −N=S=N− unit. The structures of the related molecules **4** (E = $PF_2$,[22] PhC[5]) have been reported previously, and the mean S–N bond lengths in these bicyclic molecules are compared with those in **4** (E = $i$-$Pr_2NC$) in Table VI. The bonds connecting the −NSN− bridge to the six-membered ring in the latter derivative are even longer than the corresponding distances in the other two molecules, suggesting a weaker interaction. This S–N bond length of 1.748 (3) Å is also significantly longer than that in $S_5N_6$ ($d$(S–N) = 1.702 (3) Å, which is known to readily lose the −NSN− bridge on heating.[23]

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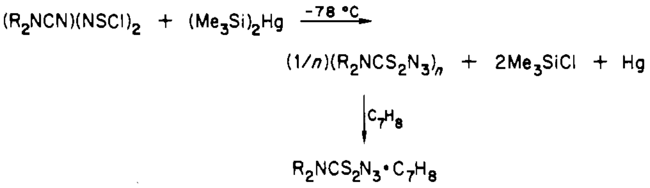
**Thermolysis and Photolysis of $R_2NCS_3N_5$ (4, E = $Me_2NC$, $Et_2NC$, *i*-$Pr_2NC$).** In the solid state, 4 (E = *i*-$Pr_2NC$) sublimed unchanged at 70–80 °C/$10^{-2}$ torr, whereas the other derivatives of 4 (E = $Me_2NC$, $Et_2NC$) decomposed to give a red melt at ca. 75 °C. Yellow toluene solutions of 4 (E = $Me_2NC$, $Et_2NC$) become orange-red after heating at ca. 100 °C for 2–3 h, but only unidentified oily products could be isolated from these reaction mixtures in either the presence of absence of NBD. A similar lack of success was observed in the attempted preparation of 1 by the photolysis of 4 (E = *i*-$Pr_2NC$). Consequently, we turned our attention to the generation of 1 by the reduction of 3 (R = $R_2N$) at low temperatures.

**Preparation of $(R_2NCS_2N_3)_n$ (R = Et, *i*-Pr).** Several reagents have been successfully employed for the reduction of cyclothiazyl halides. These include $Ph_3Sb$,[24,25] metals (e.g. iron[26a] or mercury[26b]), and azide ion, which also causes polymerization to give $(SN)_x$.[27] The reduction of 3 (R = $CF_3$) with zinc in $SO_2$ is reported to produce either 1 (R = $CF_3$) (vide supra) at 0 °C or the neutral five-membered ring 6 (R = $CF_3$) at room temperature.[3] Treatment of 3 (R = Ph) with triphenylantimony gives the dimer $(PhCS_2N_3)_2$.[5]

Stereochemical consideration of the ring systems 3, in which the chlorine substituents adopt a cis configuration.[6a,28] suggested the linear molecule $Me_3Si$–Hg–$SiMe_3$[29] would be an effective reagent for the transformation 3 → 1. The high reactivity toward element–chlorine bonds and anticipated ease of separation of byproducts were additional attractive features of this reagent. Indeed, we found that the reaction of $(R_2NCN)(NSCl)_2$ with $(Me_3Si)_2Hg$ occurs readily in diethyl ether at low temperatures to give dark purple solids formulated as $(R_2NCS_2N_3)_n$ (R = Et, *i*-Pr). The use of low temperatures in the reaction and workup procedure was essential for the isolation of these thermally unstable compounds. The existence of the six-membered $R_2NCS_2N_3$ ring in these products is indicated by elemental analyses, the presence of $R_2NCS_2N_3^+$ as the ion with the highest *m*/*e* in the mass spectra, and the formation of adducts with NBD (vide infra).



$$(R_2NCN)(NSCl)_2 + (Me_3Si)_2Hg \xrightarrow{-78\ ^\circ C} (1/n)(R_2NCS_2N_3)_n + 2Me_3SiCl + Hg$$

$$\downarrow C_7H_8$$

$$R_2NCS_2N_3 \cdot C_7H_8$$

In comparison to the case of $(PhCS_2N_3)_2$,[5] the intense colors and higher solubility of $(R_2NCS_2N_3)_n$ in organic solvents suggest a monomer ($n = 1$). However, the colors may be due to $n_\pi(R_2N) \rightarrow \pi^*$ transitions (vide infra) and we cannot rule out the possibility of a weakly associated structure. Attempts to grow crystals suitable for an X-ray structural determination are in progress, but the purple compounds decompose at room temperature in most solvents.

**Preparation of the Adducts $R_2NCS_2N_3 \cdot C_7H_8$ (R = Me, Et, *i*-Pr).** The reaction of 3 (R = $Et_2N$) with triphenylantimony or 3 (R = $Me_2N$) with $(Me_3Si)_2Hg$ in diethyl ether at −78 °C in the presence of NBD produced the adducts $R_2NCS_2N_3 \cdot C_7H_8$ in high yield. When the reaction of 3 (R = $Et_2N$) with triphenylantimony was carried out in the absence of NBD, the purple compound $(Et_2NCS_2N_3)_n$ was formed, but it was not possible to separate it from $Ph_3SbCl_2$ without decomposition.

Table VII. UV–Visible Spectroscopic Data for $RCN_2S_2^+Cl^-$[a]

| R | $\lambda_{max}$, nm | $\epsilon$,[b] L mol$^{-1}$ |
|---|---|---|
| Ph[c,d] | 222 | $2.1 \times 10^3$ |
| | 276 | $1.0 \times 10^3$ |
| | 370 | 85 |
| *t*-Bu[c] | 250 | $2.6 \times 10^3$ |
| | 300 sh | $4.3 \times 10^2$ |
| | 355 | $2.0 \times 10^2$ |
| | 454 | $1.2 \times 10^2$ |
| $CCl_3$[e] | 228 | $7.5 \times 10^3$ |
| | 262 sh | $2.3 \times 10^3$ |
| $Et_2N$ | 230 | $1.5 \times 10^3$ |
| | 388 | $2.0 \times 10^2$ |
| | 533 | $2.4 \times 10^2$ |

[a] In $CH_3CN$ solution. [b] The numerical values of $\epsilon$ are not very reliable due to rapid decomposition of ca. $10^{-3}$ M solutions. [c] Prepared according to the literature method.[30] [d] Literature values (in $CH_2Cl_2$): 396 nm ($6.9 \times 10^{-2}$ L mol$^{-1}$).[30] [e] Data taken from ref 30.

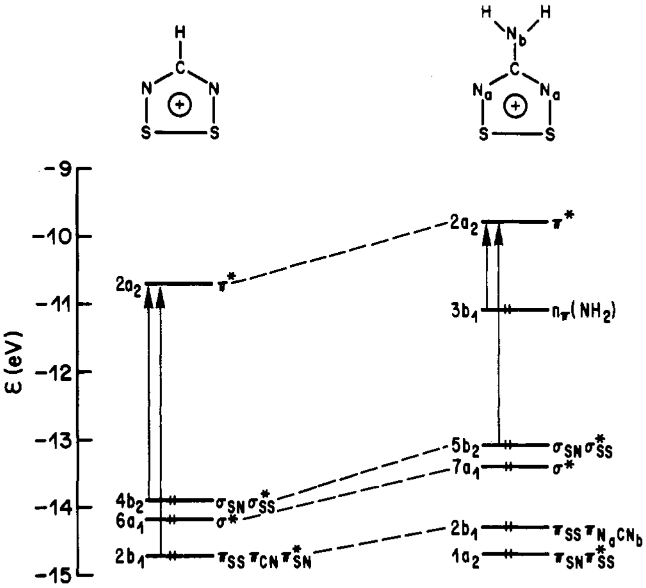


**Figure 2.** Highest occupied MOs and the LUMO for $RCN_2S_2^+$ (**6**, R = H, $NH_2$) showing the lowest energy transitions. The dashed lines link corresponding orbitals.

The adducts $R_2NCS_2N_3 \cdot C_7H_8$ (R = Et, *i*-Pr) were also obtained in high yields by the direct reaction of $(R_2NCS_2N_3)_n$ with NBD in diethyl ether at −20 °C. The identities of the NBD adducts were established on the basis of elemental analyses, mass spectra, and their characteristic $^1H$ and $^{13}C$ NMR spectra (Table I.)[2,5] The latter spectra show that the NBD molecule is bound symmetrically to the two sulfur atoms of the heterocyclic ring.

**Preparation of $Et_2NCS_2N_2^+Cl^-$.** The reaction of a solution of 3 (R = $Me_2N$ or $Et_2N$) with 2 mol of sodium azide in acetonitrile at 23 °C produced a reddish purple solution ($\lambda_{max}$ 520–530 nm) within 15 min, but the color of the solution became orange on prolonged stirring and only oils could be isolated. When the reaction was carried out in a 1:1 ratio, the purple color of the solution persisted and workup gave purple crystals of 6 (R = $Et_2N$) as its chloride salt in ca. 20% yield. This product was identified on the basis of complete elemental analyses and spectroscopic data (IR and mass spectra). Thus, the reaction of 3 (R = $Et_2N$) with sodium azide brings about a ring contraction similar to that described by Mews et al. for the reaction of 3 (R = $CF_3$) with zinc at room temperature.[3]

**UV–Visible Spectra of $RCN_2S_2^+$.** Numerous derivatives of 6 (R = *t*-Bu,[29-31] $CCl_3$,[29,30] $CF_3$,[3,34] $CH_3$,[32] Ph,[29-31,34] F,[33] Cl,[34] Br[34])

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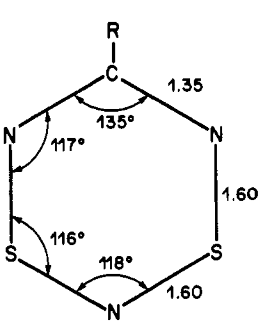

**Figure 3.** Bond distances (Å) and angles (deg) used for HFS-SCF MO calculations of planar $RCS_2N_3$ (**1**, R = H, $CH_3$, $NH_2$, Cl): $d(C-H)$ = 1.08 Å, $d(C-CH_3)$ = 1.53 Å, $d(C-NH_2)$ = 1.38 Å, $d(C-Cl)$ = 1.72 Å.

are known, but **6** (R = $Et_2N$) is the first example in which the exocyclic substituent is an electron-releasing $R_2N$ group. Since the known dithiadiazolium salts are usually yellow, orange, or red (when $X^-$ = $Cl^-$), the purple color of **6** (R = $Et_2N$; X = $Cl^-$) was unexpected.[35] There is very little information on the UV-visible spectra of $RCN_2S_2^+$ salts in the literature, so we have measured the spectra of several derivatives in order to compare them with that of **6** (R = $Et_2N$). The data are summarized in Table VII. The purple color of **6** (R = $Et_2N$) as its chloride salt can be attributed to the absorption band at ca. 530 nm in the visible spectrum. However, the extinction coefficient for this absorption is 1 order of magnitude smaller than the typical values found for $\pi$ (or $\pi^*$) $\rightarrow$ $\pi^*$ transitions of cyclothiazenes.[36] HFS-SCF MO calculations for **6** (R = H, $NH_2$) have been carried out,[37] and the upper energy levels are depicted in Figure 2. A comparison of the highest occupied MOs for **6** (R = H) with those of **6** (R = $NH_2$) reveals a significant difference. The HOMO for **6** (R = $NH_2$) is an $n_\pi$ orbital located on the exocyclic $NH_2$ group, and a low-energy $n_\pi \rightarrow \pi^*$ transition is expected for this derivative. By contrast, no such transition is available for **6** (R = H). Consequently, we tentatively attribute the purple color ($\lambda_{max} \sim$ 530 nm) of **6** (R = $Et_2N$; $X^-$ = $Cl^-$) to the HOMO ($n_\pi$) $\rightarrow$ LUMO ($\pi^*$) transition ($3b_1 \rightarrow 2a_2$).

**Electronic Structure of the 1,3,2,4,6-Dithiatriazine Ring, $RCS_2N_3$.** It is instructive to compare the electronic structure of **1** with those of **2**[2] and $S_3N_3^+$,[38] both of which are eight-$\pi$-electron systems. For that purpose we performed HFS-SCF MO calculations for various derivatives of **1** (R = H, Cl, $NH_2$, $CH_3$) with the bond distances and angles given in Figure 3.[37] For R = H, $CH_3$, and Cl we were unable to obtain a single determinant ground state. In the case of R = H we explored all possible configurations and obtained an excited-state configuration in each case (see Figure 4). Configurations $a_1^{14}a_2^4b_1^4b_2^{10}$ and $a_1^{14}a_2^2b_1^6b_2^{10}$ exhibit eight $\pi$-electrons. Configurations $a_1^{12}a_2^4b_1^6b_2^{10}$ has 10 $\pi$-electrons, but it is a highly excited state with the empty $7a_1$ orbital buried deep in the energy level stack. Thus, one may tentatively attribute eight $\pi$-electrons to ring **1** (R = H), but this assignment is not conclusive, since a ground state function was not obtained.

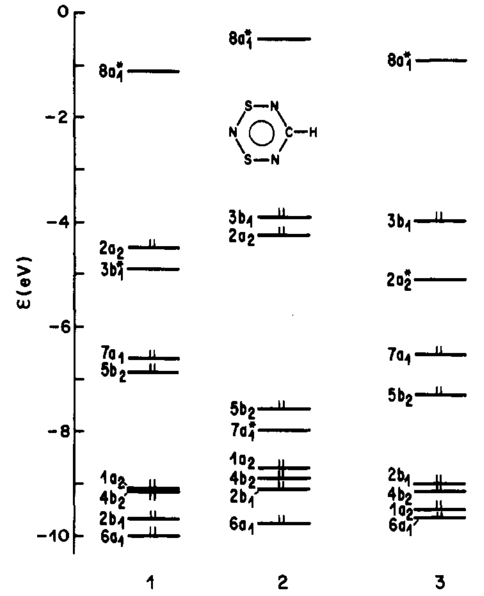

**Figure 4.** Highest MOs for three configurations of $HCS_2N_3$ showing the occupied orbitals. The unoccupied orbitals are indicated with an asterisk. The valence orbitals for the three configurations are **1** ($a_1^{14}a_2^4b_1^4b_2^{10}$), **2** ($a_1^{12}a_2^4b_1^6b_2^{10}$), and **3** ($a_1^{14}a_2^2b_1^6b_2^{10}$).

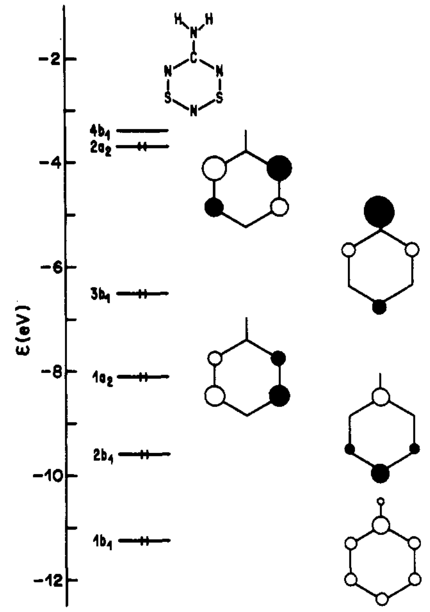

**Figure 5.** Composition and energies of the $\pi$-MOs of $H_2NCS_2N_3$ (**1**, R = $NH_2$).

A singlet ground state for **1** (R = $NH_2$) was obtained, and the $\pi$ energy levels are illustrated in Figure 5. A quasi-degeneracy between the HOMO and LUMO (both $\pi^*$ orbitals) is observed. Thus the $\pi$-manifold of **1** resembles more closely that of $S_3N_3^+$[17,38] than that of **2**. In **2** the replacement of S in $S_3N_3^-$ by $R_2P$ results in removal of the degeneracy of the $\pi$-levels.[2] By contrast, the replacement of S by RC has little effect on the $\pi$-structure of the six-membered ring. For comparison, MNDO molecular orbital calculations on model $RCS_2N_3$ systems (R = H, $NH_2$, F, $C_6H_5$) yield heats of formation that favor the triplet state over the singlet by 12–15 kcal mol$^{-1}$.[5b] The singlet/triplet separation is minimized, however, for the strong $\pi$-donor ligand $NH_2$, which led Oakley et al. to conclude that singlet ground states for $RCS_2N_3$ are most

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likely to be found when R is a strongly electron-releasing group.[5b]

The composition of the $\pi$-MOs of **1** (R = $NH_2$) is also shown in Figure 5. There are five occupied $\pi$-type orbitals, of which three are entirely associated with the heterocyclic ring. The other two orbitals have contributions from both endocyclic and exocyclic atoms. The $1b_1$ orbital is totally bonding with respect to the CNSNSN ring but also exhibits some electron density on the exocyclic $NH_2$ group. Conversely, the $3b_1$ orbital is primarily a lone pair located on the exocyclic nitrogen atom with smaller contributions from the three endocyclic nitrogen atoms. To a first approximation the $3b_1$ orbital can be regarded as an $n_\pi$ ($NH_2$) orbital, and the contribution of the exocyclic nitrogen to $1b_1$ can be neglected with the result that the ring in **1** (R = $NH_2$) can be regarded as an eight-$\pi$-electron system.

**Reactions of $(R_2NCN)(NSCl)_2$ with Halide Ion Acceptors.** The dication of **1**, $(RCN)(SN)_2^{2+}$, should be an electron-precise six-$\pi$-electron system.[1] The treatment of solutions of **3** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$) in carbon tetrachloride or *n*-hexane with various halide ion acceptors resulted in the immediate precipitation of yellow-orange solids, e.g.

$$(R_2NCN)(NSCl)_2 + SbCl_5 \rightarrow [(R_2NCN)(NSCl)(NS)][SbCl_6]$$

As indicated in Table II, these products were identified as monocations rather than dications on the basis of elemental analyses and IR spectroscopic data. The infrared band at 1550–1570 cm$^{-1}$ attributed to $\nu(CN_2)$ in **3** (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$)[6] is shifted by 40–45 cm$^{-1}$ in the monocations, which also exhibit a strong band in the 445–455-cm$^{-1}$ region assigned to $\nu$(S–Cl).

In contrast to the reactions of **3** with halide ion acceptors, the addition of antimony pentachloride to a solution of the eight-membered ring, 1,5-$(Me_2NCN)_2(NSCl)_2$,[6a] in carbon tetrachloride produces the dication 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ (Table II).

## Summary and Conclusions

The six-membered rings $(RCS_2N_3)_n$ (R = $Et_2N$, *i*-$Pr_2N$) were obtained as dark purple solids characterized as adducts with norbornadiene. HFS-SCF MO calculations for **1** (R = $NH_2$) indicate that the heterocyclic ring is an eight-$\pi$-electron system and reveal a quasi-degeneracy of the HOMO ($\pi^*$) and LUMO ($\pi^*$) levels ($\Delta\epsilon$ = 0.3 eV). The first example of the $RCS_2N_2^+$ ring in which R is an electron-releasing substituent was prepared by the azide reduction of **3** (R = $Et_2N$). The purple color of such derivatives ($\lambda_{max}$ ~530 nm) is attributed to an $n_\pi(R_2N) \rightarrow \pi^*$ transition. The cations $(RCN)(NSCl)(NS)^+$ (R = $Me_2N$, $Et_2N$, *i*-$Pr_2N$) and 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ are readily produced by treatment of the appropriate mixed thiazyl–cyanuric ring with a halide ion acceptor. The resulting salts are soluble in $SO_2$ and could serve as precursors of polymers containing an –(R)CNSN– backbone via electrochemical reduction (cf. preparation of $(SN)_x$ from $S_5N_5^+$ salts).[40]

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**Supplementary Material Available:** Listings of positional and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths, and bond angles associated with hydrogen atoms in *i*-$Pr_2NCS_3N_5$, and IR spectral data for salts of the $(R_2NCN)(NSCl)(NS)^+$ and 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ cations (4 pages). Ordering information is given on any current masthead page.

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# Crystal and Molecular Structures of *mer*-$Ph_3TeF_3$ and Stereoselective Fluorine Exchange in the *mer*-$Ph_3TeF_3$–$Ph_3TeF_2^+$ System

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Triphenyltellurium(VI) trifluoride, $(C_6H_5)_3TeF_3$, was prepared by the reaction of triphenyltellurium(IV) fluoride with xenon difluoride. The crystal and molecular structures of *mer*-$Ph_3TeF_3$ were determined by X-ray diffraction techniques. *mer*-$Ph_3TeF_3$ crystals are monoclinic, $P2_1/n$, $Z = 4$, with unit cell dimensions of $a$ = 10.640 (2) Å, $b$ = 12.144 (2) Å, $c$ = 12.445 (2) Å, and $\beta$ = 100.10 (1)°. The structure has been refined by full-matrix least-squares methods to values of $R$ and $R_w$ of 0.031 and 0.020, respectively. The molecule has Te with a slightly distorted octahedral coordination and has an approximate $C_2$ symmetry axis. The phenyl groups are rotated with respect to each other as a result of intramolecular steric repulsion. Te–F and Te–C bond distances lie in the ranges 1.915 (2)–1.954 (2) and 2.110 (3)–2.129 (3) Å, respectively. Crystals contain molecules packed in a chainlike pattern. The *mer* structure is retained in solution, as confirmed by $^{19}F$ and $^{125}Te$ NMR. Reaction of *mer*-$Ph_3TeF_3$ with $PF_5$ gave $Ph_3TeF_2^+PF_6^-$, which was characterized by $^{19}F$ and $^{125}Te$ NMR and chemical reaction. Intermolecular fluorine exchange occurred on addition of $Ph_3TeF_2^+$ to *mer*-$Ph_3TeF^aF^b_2$. On the basis of both $^{19}F$ and $^{125}Te$ NMR, it was possible to demonstrate that only the $F^a$ ligand undergoes fluorine exchange, consistent with a mechanism involving five- and six-coordinate tellurium species and the fluorine-bridged intermediate $[Ph_3TeF^b_2–F^a–TeF^b_2Ph_3]^+$, in which only the $F^a$ ligand occupies the bridging position. The intermolecular (bond-breaking) process is not accompanied by an intramolecular scrambling of $F^a$ and $F^b$ ligands. An intermolecular exchange process involving only the $PF_6^-$ anion can be initiated by adding $PF_5$ to $Ph_3TeF_2^+PF_6^-$.

## Introduction

The synthesis of a variety of phenyltellurium(VI) fluorides by the oxidative fluorination of Te(I), Te(II), and Te(IV) compounds with xenon difluoride[2]

$$Ph_3TeF + XeF_2 \rightarrow Ph_3TeF_3 + Xe$$

has made these compounds available for structural and NMR studies. In this paper we describe the crystal structure of *mer*-$Ph_3TeF_3$, which is the first example of an organotellurium(VI) crystal structure investigation, as far as we know, and correlate our findings with NMR studies of fluorine exchange in *mer*-$Ph_3TeF_3$.

Intermolecular fluorine exchange is known to be rapid in systems such as $SiF_5^-$–$SiF_6^{2-}$,[3] $PhPF_3H$–$PhPF_4H^-$,[4] and

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