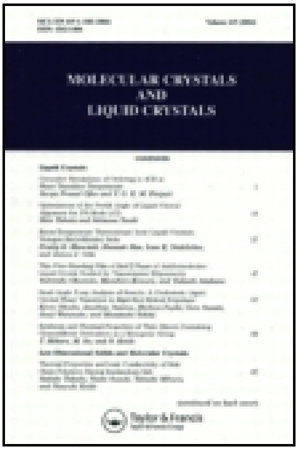

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Tristram Chivers [a], John F. Richardson [a] & Nigel R.M. Smith [a]
[a] Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

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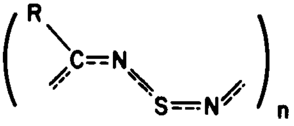
SYNTHETIC AND STRUCTURAL STUDIES OF PRECURSORS TO POLYMERS CONTAINING AN -(R)CNSN- BACKBONE

TRISTRAM CHIVERS, JOHN F. RICHARDSON, and NIGEL R.M. SMITH
Department of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4

Abstract The ring systems $(Me_2NCN)_x(NSCl)_2$ (x=1 or 2) are prepared by (a) the reaction of dimethylcyanamide with $(NSCl)_3$ in CCl_4 at 60°C and (b) the oxidative addition of Cl_2 to 1,5-$Me_2NC(NSN)_2CNMe_2$. Treatment of $(Me_2NCN)(NSCl)_2$ with $Me_3SiNSNSiMe_3$ or Me_3SiNSO produces the bicyclic compound $Me_2NCS_3N_5$. The latter reagent also yields 1,5-$Me_2NC(NSN)_2SCl$ shown by X-ray crystallography to be a folded eight-membered ring. The dications $(Me_2NCN)_x(SN)_2{}^{2+}$ (x=1 or 2) are readily obtained from $(Me_2NCN)_x(NSCl)_2$ and $SbCl_5$. The reduction of $(Me_2NCN)(NSCl)_2$ with azide ion is briefly described.

INTRODUCTION

The metallic, superconducting properties of $(SN)_x$ have spurred efforts to prepare structural variations of this polymer, which may also exhibit unusual conducting properties.[1] The most promising and versatile candidates for such behavior are those containing the repeating unit -(R)CNSN-, **1**.[2] However, only the cyclocondensation products, **2** or **3**, have been isolated in attempts to prepare such polymers from amidines, $RC(NH)NH_2$ (R = Ph,[3,4] Me_2N[4]), and SCl_2.



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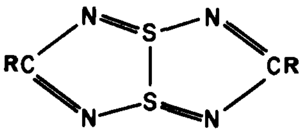

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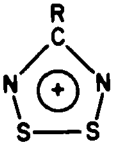

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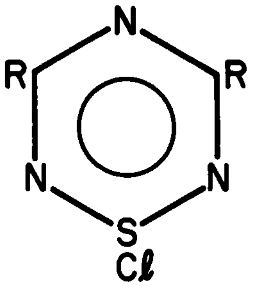
Linear polymers in which 3,4-dicyanothiophene[5] or p-phenylene[6] rings are bridged by -N=S=N- groups have been prepared. The base-catalyzed elimination of SO_2 from bis (sulfinylamino) derivatives was one of the more successful strategies employed in these syntheses.

$$\text{OSN-Ar-NSO} \xrightarrow[-SO_2]{\text{pyridine}} (\text{-Ar-N=S=N-})_x \qquad (1)$$

Concurrently alternative routes to $(SN)_x$, which avoid the necessity to isolate S_2N_2, have been discovered. These involve the reduction of the cyclothiazyl halides, $(NSCl)_3$ or $S_3N_2Cl_2$, with azides in acetonitrile at low temperatures[7] or the electrochemical reduction of the cation $S_5N_5^+$.[8,9] In view of these advances, high yield syntheses of the mixed cyanuric-thiazyl rings **5**-**7** have been developed and the reactions of these heterocycles with $Me_3SiNSNSiMe_3$, Me_3SiNSO, $SbCl_5$ and azides have been investigated.



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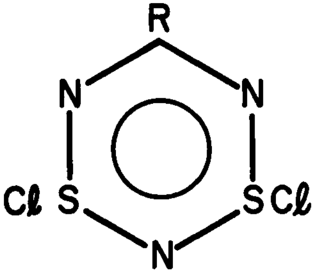

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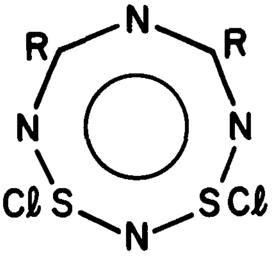

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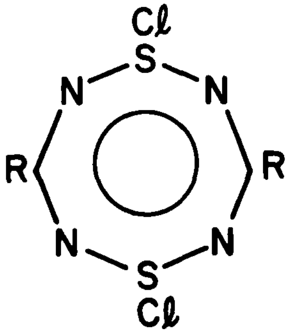

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PREPARATION OF MIXED CYANURIC-THIAZYL RINGS

The cycloaddition reaction of an organic nitrile with thiazyl units potentially represents a versatile synthesis of mixed cyanuric-thiazyl rings. Such reactions, however, usually produce the five-membered ring 3.[10] We found that,

$$xRCN + yNSCl \longrightarrow (RCN)_x(NSCl)_y \qquad (2)$$

in the specific case of R=Me_2N, equation (2) provides an excellent synthesis of both six- and eight-membered heterocycles, 5 and 6, respectively, when the appropriate reaction conditions are employed.

Heterocycle 5 is prepared by dropwise addition (ca. 2h) of dimethylaminocyanamide (10.4 mmol) in dry carbon tetrachloride (80 ml) to an intensely green solution of $(NSCl)_3$ (15.7 mmol) in carbon tetrachloride (125 ml) at 65°C. Yellow crystals of 5 are obtained in ca. 90% yield (based on Me_2NCN) after recrystallization from CCl_4:pentane (1:1). The product was identified by comparison of infrared and

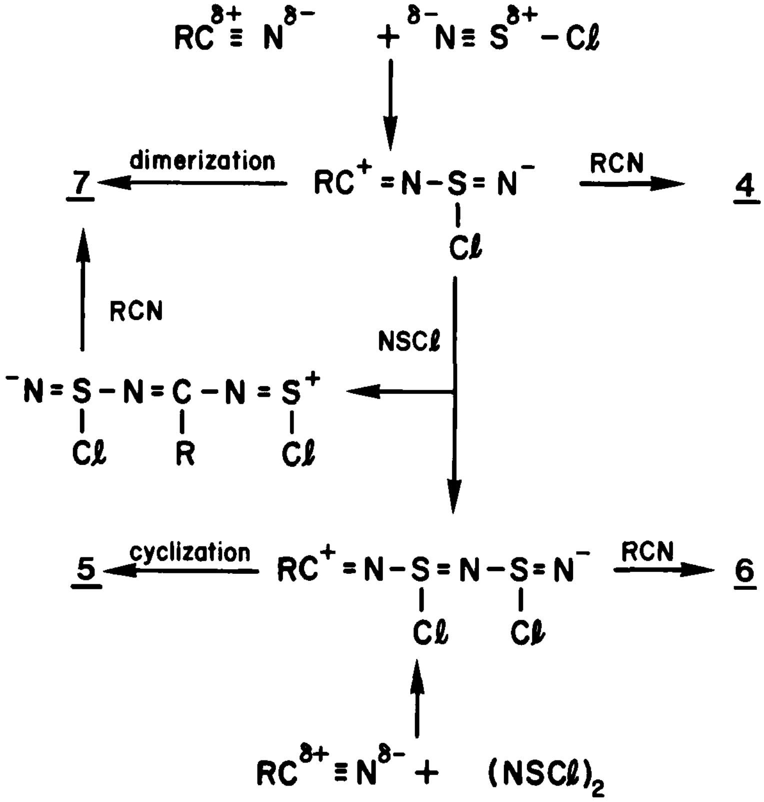
NMR spectra (in $CDCl_3$, ^1H, δ=3.24; ^{13}C, δ=36.70 pm, cf. lit. 3.2 and 36.7 ppm, respectively) with the literature values for 5 ($R=Me_2N$) prepared from dimethylguanidine hydrochloride and $S_3N_2Cl_2$.[11] The yield in the latter reaction is only 7%.

The rapid addition of a ten-fold excess of Me_2NCN in carbon tetrachloride (ca. 8M) to a solution of $(NSCl)_3$ in CCl_4 (ca. 0.3M) at 65°C produces the eight-membered ring 6 ($R=Me_2N$) as moisture-sensitive yellow crystals in 90% yield.[12] Attempts to obtain NMR spectral data in $CDCl_3$ or CH_3CN solution results in decomposition to 5 ($R=Me_2N$) via loss of Me_2NCN. This behaviour is in distinct contrast to that of the related heterocycle 1,3-$(Ph_2PN)_2(NSCl)_2$, which undergoes ring contraction via loss of NSCl to give $(Ph_2PN)_2(NSCl)$.[13] However, compound 6 ($R=Me_2N$) can be recrystallized from CH_3NO_2/diethyl ether (1:2) at -20°C without decomposition.

Heterocycle 7 ($R=Me_2N$), the structural isomer of 6, is obtained as thermally stable, orange crystals in almost quantitative yield by the oxidative addition of Cl_2 (as SO_2Cl_2) across the S-S bond of 2 ($R=Me_2N$).[12] The reaction of 2 with bromine yields 1,5-$(Me_2NCN)_2(NSBr)(NS)^+Br_3^-$ as dark red crystals.[12]

MECHANISM OF THE CYCLOADDITION REACTION

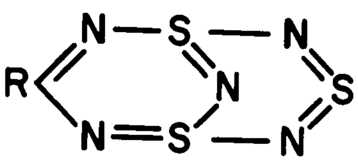
Although the reaction between dimethylcyanamide and $(NSCl)_3$ in carbon tetrachloride at 60°C was conducted using a wide range of reagent stoichiometries and concentrations, we were unable to detect significant amounts of 4 or 7 ($R=Me_2N$) among the products. The former ring system is well known[14] and the phenyl derivative, 4 (R=Ph), has been prepared recently by the reaction between benzamidine and $(NSCl)_3$.[15]



Pale yellow solutions of $(NSCl)_3$ become mint green above 55°C.[16] Although NSCl monomer is a candidate,[17] the species responsible for this green color has not been conclusively identified. The predominant formation of 5 and 6 in the cycloaddition reaction strongly suggests the involvement of a linear intermediate $(Me_2NCN)(NSCl)_2$ in which the thiazyl groups are juxtaposed. The Scheme shows that the interaction of Me_2NCN with NSCl monomer is expected to give rise to 4 and 7, in addition to 5 and 6. We propose, therefore, that linear $(Me_2NCN)(NSCl)_2$ is formed from the nitrile and a dimeric species $(NSCl)_2$.

REACTIONS OF $(Me_2NCN)(NSCl)_2$ WITH $Me_3SiNSNSiMe_3$ OR Me_3SiNSO

The reaction of 5 ($R=Me_2N$) with $Me_3SiNSNSiMe_3$ in CCl_4 is conveniently monitored by ^1H NMR spectroscopy, which shows that the reaction is complete after 15h at 23°C. The orange bicyclic compound 8 ($R=Me_2N$) was isolated in ca. 60% yield.[12]



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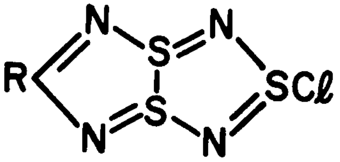

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The slow reaction of 5 ($R=Me_2N$) with Me_3SiNSO at 23°C was also followed by ^1H NMR spectroscopy. The signal due to 5 at 3.25 ppm disappeared gradually while that for 8 at 3.03 ppm increased steadily over a period of 24 days. During the latter stages of the reaction the formation of an additional product was indicated by the appearance of a small signal at 3.17 ppm. Yellow crystals of this compound were isolated by recrystallization from acetonitrile and identified as the bicyclic, eight-membered ring 9 ($R=Me_2N$) by X-ray crystallography. Thus the reagent Me_3SiNSO has accomplished a six- to eight-membered ring expansion.

X-RAY STRUCTURE OF 1,5-$Me_2NC(NSN)_2SCl$, 9 ($R=Me_2N$)

The heterocycle 9 can be considered as a hybrid of 1,5-

$Me_2NC(NSN)_2CNMe_2$, 2 (R=Me_2N) and 1,5-$ClS(NSN)_2SCl$.[18] It has a similar folded structure with d(S-S) = 2.434(4)Å and the chlorine atom in an endo position, d(S-Cl) = 2.233(4)Å. The geometries at C(1) and N(5) are essentially planar but the five-membered rings, CS_2N_2 and S_3N_2, deviate significantly from planarity.

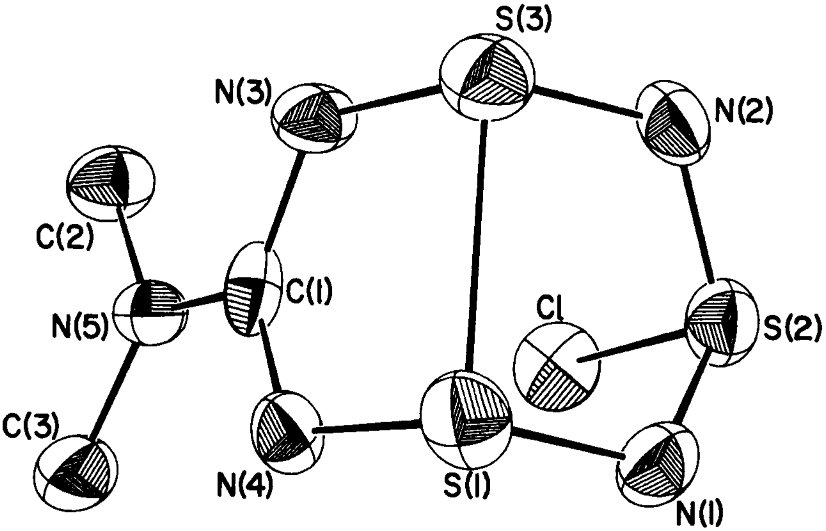

FIGURE 1 ORTEP plot (50% probability ellipsoids) for 1,5-$Me_2NC(NSN)_2SCl$

REACTIONS OF $(Me_2NCN)_x(NSCl)_2$ WITH $SbCl_5$

The dications $(Me_2NCN)_x(SN)_2{}^{2+}$ (x=1 or 2) are readily prepared by treatment of the heterocycles 5 or 7 with a slight excess of $SbCl_5$ in carbon tetrachloride.[12]

REACTIONS OF $(Me_2NCN)_x(NSCl)_2$ WITH AZIDES

The reaction of $(Me_2NCN)(NSCl)_2$ with sodium azide in acetonitrile at 23°C produces an intense reddish-purple solution (λ_{max} 520 nm), but no tractable products were isolated.

SUMMARY AND CONCLUSIONS

High yield syntheses of the mixed cyanuric-thiazyl rings $(Me_2NCN)_x(NSCl)_2$ (x=1 or 2) and the corresponding dications $(Me_2NCN)_x(SN)_2{}^{2+}$ have been developed. These ring systems are potential precursors to polymers containing a -(R)CNSN- backbone via chemical or electrochemical reduction. The heterocycle $(Me_2NCN)(NSCl)_2$ undergoes an unusual six- to eight-membered ring expansion reaction with Me_3SiNSO to give 1,5-$Me_2NC(NSN)_2SCl$.

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