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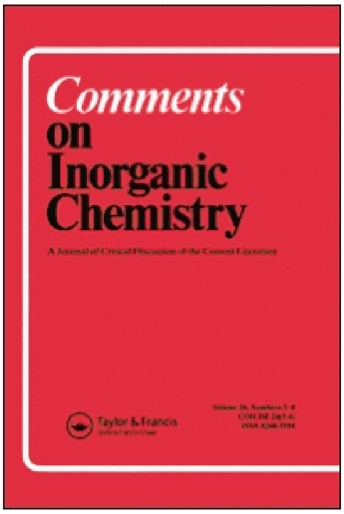

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Results and Perspectives in Sulfur and Nitrogen Chemistry

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Results and Perspectives in Sulfur and Nitrogen Chemistry

In view of the recent interest in sulfur nitrogen compounds some important aspects and studies involving polymers and metal complexes are briefly reviewed.

INTRODUCTION

There is no lack of reviews of the energy problems of the world. But we are also faced with the problem that we are running into a shortage of certain elements. Therefore it is a challenge to chemists to investigate the properties of those elements that are present in abundance. Two of these elements are sulfur and nitrogen. Sulfur has been known for more than 2500 years and its production was considerably increased when fertilizers were produced on a large scale. Nowadays sulfur is formed in large amounts in the purification of oil and coal.

The development of SN polymers as electrical conductors has interested chemists and physicists in this field. In the past few years the extraordinary properties of $(SN)_x$ have made it practical to do experiments with sulfur nitrogen compounds. It is well known that several transition metal complexes with ligands containing sulfur play an important role in biochemistry and the elucidation of the reactivity of model complexes may help to understand how reactions in living systems proceed. Some details of various experimental studies are given in this article along with a discussion of further investigations.

THE DIFFERENCE BETWEEN NITROGEN AND SULFUR

It is well known that the eight elements of the second period and the elements of the succeeding rows show significant chemical differences. There

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are various explanations in textbooks for these anomalies which use measured physical data as well as mathematically calculated properties. A summary of these data for nitrogen and sulfur is given in the table below.[1-3] It is quite obvious that the striking differences between nitrogen and sulfur are related to differences in their fundamental atomic properties.

N	S	
14.534	10.360	Ionization potential in electron volts
3.04	2.58	Electronegativities on the Pauling scale
0.70	1.04	Single-bond covalent radius in Å
0.52	0.85	Distance to the maximum of the radial distribution function of the outermost orbital in Å (from Hartree–Fock)
0.77	1.09	Average radial distance from the nucleas of the outermost p electrons in Å (from Hartree–Fock)
13.09	8.24	Total electrostatic potential at the covalent radius in electron volts
31.8	21.6	Internal potential at the covalent radius in electron volts
1.04	3.45	Polarizability in $Å^3$
−0.2	2.1	Electron affinity A_1 in electron volts
−8.3	−6.1	Electron affinity A_2 in electron volts
159	264	Average single-bond energy at 300 K in kJ mol^{-1}
2.54	0.901	Bond order for the homonuclear diatomic molecule
419	423	Average double bond energy at 300 K in kJ mol^{-1}
1.5	1.83	van der Waals radius in Å

The binding forces in S_2 are less than those in N_2. Politzer[3] calculated the binding forces in N_2 and P_2 taking into account the screening effect for a 2p electron in a nitrogen atom and a 3p electron for phosphorus. The overall bond order of P_2 (0.953) is approximately the same as in S_2, so that the results may also be valid for S_2.

The calculated pi and sigma forces are

N_2:	29.66 eV	65.30 eV
P_2:	15.23 eV	33.74 eV

From the calculation two interesting results were obtained: The pi and sigma forces of N_2 are nearly twice as large as those of P_2, and the binding force exerted by a pi valence electron in N_2 and P_2 is nearly half of that exerted by a sigma electron. From this calculation we have to conclude that there is significant $p\pi$–$p\pi$ bonding in S_2, though the bond order is 0.901. Also in sulfur–nitrogen compounds we can describe the bonding as a combination of sigma and pi contributions. But there is still no calculated

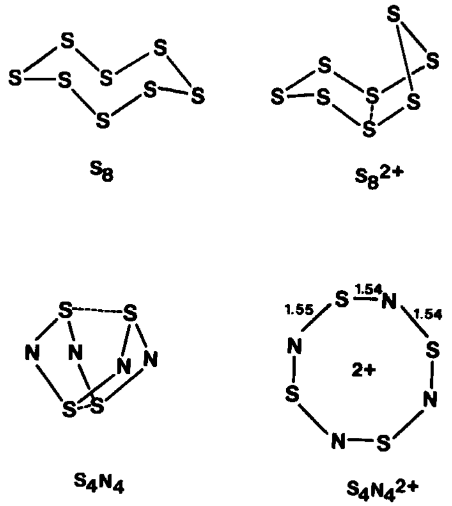


FIGURE 1 Structures of S_8, S_8^{2+}, S_4N_4 and $S_4N_4^{2+}$.

dependence of the pi and sigma forces on the coordination number of the nitrogen and sulfur atoms. These values would be very helpful for understanding the nature of the sulfur-nitrogen bond.

A RELATION BETWEEN STRUCTURE AND ELECTRON DENSITY

It is well known that replacement of sulfur atoms in S_8 by the isoelectronic NH groups yields structures completely analogous to that of S_8. This was found in S_7NH, $S_5N_3H_3$, $S_4N_4H_4$ and the isomers of $S_6N_2H_2$.[4,5] On the basis of MO calculations the structures of S_8, S_8^{2+}, S_4N_4, and $S_4N_4^{2+}$ (Figure 1) were interpreted. The different number of valence electrons—changing from 48 in S_8 to 42 in $S_4N_4^{2+}$—is the reason for the different structures. Each nitrogen atom contributes one and each sulfur atom two π electrons. Starting from $S_4N_4^{2+}$, this molecule can be described as a 10π electron system and compared with the 10π $C_8H_8^{2-}$ anion. Both molecules have a planar structure. The addition of two electrons yields S_4N_4, a molecule with two transannular S–S bonds and, in agreement with MO calculations, this D_{2d}-structure has the lowest energy.[6] Further addition of two electrons into the antibonding orbitals yields the structure of S_8^{2+} with only one transannular S–S bond. The completely filled molecular orbitals are reached with 16π electrons in the S_8 molecule which contains no transannular S–S interactions.

From this example we can conclude that S–S interactions and electron densities are closely related to each other and we can use this model for the

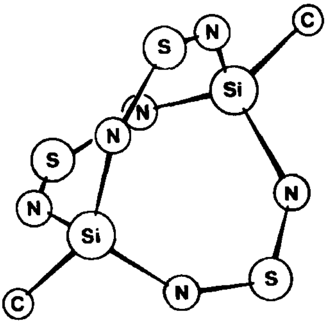


FIGURE 2 $CH_3Si(NSN)_3SiCH_3$ with D_{3h} symmetry.

description of various S–N heterocycles. In many examples we have shown that the bonding properties in S–N compounds can be best interpreted by using the 4π NSN building unit. The *cis*-NSN moiety has equal S–N bond distances when there are the same substituents attached to the nitrogen atoms. This was found in all symmetrically built S–N compounds, e.g., $SN_2NS_2O_4^-$ or $SN_2N_4P_4F_6$. Using this model for $S_4N_4^{2+}$, this molecule can be described in terms of two NSN fragments linked by two sulfur ions (S^+) of low electron density. $CH_3Si(NSN)_3SiCH_3$ (Figure 2), a molecule with three NSN units linked by two methyl-substituted silicon atoms, has D_{3h} symmetry and no S–S bonding was observed because the silicon atoms do not contribute electron density to the NSN skeleton.[7] The replacement of the two CH_3–Si groups by two electron-rich sulfur atoms leads to S_5N_6 (Figure 3), which has a basket-like structure. The increase in electron density in comparison to $CH_3Si(NSN)_3SiCH_3$ results in the formation of one S–S bond.[8] Removal of two electrons from S_5N_6 would yield the species $S_5N_6^{2+}$ which has not yet been identified and which is expected to have D_{3h} symmetry. Also, in the adducts of S_5N_6 with Lewis acids no S–S bonding would be expected. Unfortunately S_5N_6 is kinetically too unstable to be used to investigate the fluxional behavior of this molecule by ^{33}S NMR.

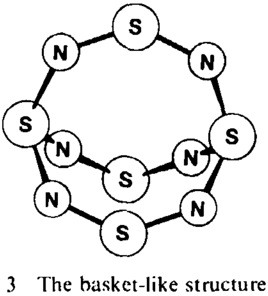


FIGURE 3 The basket-like structure of S_5N_6.

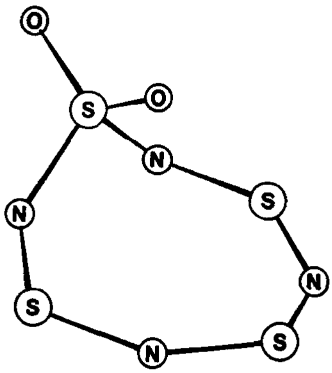


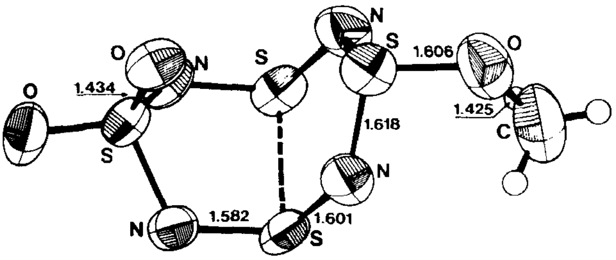
FIGURE 4 $S_4N_4O_2$.

The electron density of S_4N_4 can also be diminished by increasing the coordination number on one sulfur atom. In $S_4N_4O_2$ (Figure 4) two NSN fragments are linked by a sulfur atom of coordination number two and by a SO_2 bridge. Again no S–S interaction is observed.

From these investigations it can be seen that S–S interactions are a sensitive probe of electron densities. Even in biological systems S–S compounds may function as electron-releasing or -accepting reservoirs by forming S–S interactions.

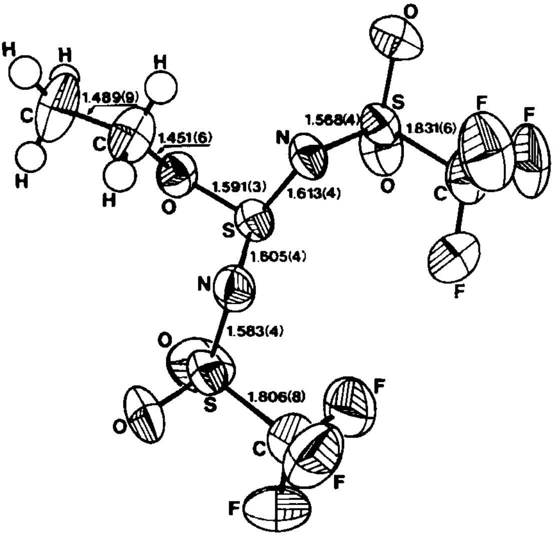
THREE-COORDINATED ANIONIC SPECIES OF SULFUR(IV)

The reaction between $S_4N_4O_2$ and nucleophiles[7,9] such as sodium methylate leads to the formation of anionic species with sulfur of coordination number three (Figure 5). The anion has an ideal C_s symmetry, the increas-



$[S_4N_4O_2OCH_3]^-$

FIGURE 5 The $S_4N_4O_2OCH_3^-$ anion.

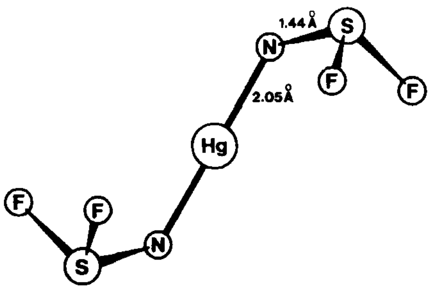


$(CF_3SO_2N)_2SOC_2H_5^-$

FIGURE 6 The molecular structure of an acyclic anion.

ing electron density again being compensated by forming an intramolecular S-S bond.

Sulfur anions of oxidation state (IV) and coordination number three were so far known only for the sulfite dianion and its derivatives with electron-withdrawing substituents such as FSO_2^- and $CF_3SO_2^-$. As it is well known that a change of electron density in S-N systems is easily achieved when both atoms have the coordination number two, it is obvious that the type of reaction described above can be used to synthesize acrylic anions



$Hg(NSF_2)_2$

FIGURE 7 $Hg(NSF_2)_2$.

employing open-chain sulfur diimides with bulky or electron-withdrawing groups attached to both nitrogen atoms (Figure 6).[10]

Systematic investigations in this field will point out the range in which three-coordinated sulfur atoms can exist. X-ray analysis of these anionic species show some interesting differences in S–N bond lengths. The strengthening of the S–N bonds in $Hg(NSF_2)_2$ (Figure 7) is probably due to an additional polar part of the bonding.[11] By contrast, since the bond distances between the triply coordinated sulfur and the neighboring nitrogens in $S_4N_4O_2OCH_3$ and $(CF_3SO_2N)_2SOC_2H_5^-$ lie between a single and a double bond, the negative charge should be delocalized over the whole N–S–N unit. This results in a lengthening of the S–N bonds, the pseudo-allenic N=S=N moiety is no longer preserved. Although the *cis–cis* configuration of N=S=N units as in $S_4N_4O_2$ and its ionic derivatives and the *trans–trans* configuration shown in the open-chain anions are kinetically not favored, these systems are rather stable.

COMPLEXES WITH SULFUR-CONTAINING LIGANDS

Another way to stabilize the *trans–trans* arrangement in acyclic sulfur diimides is the reaction with transition metal carbonyl compounds to form stable 1 : 1 complexes. The N=S=N group can act as a mono- or a bidentate ligand.[12] (Figure 8)

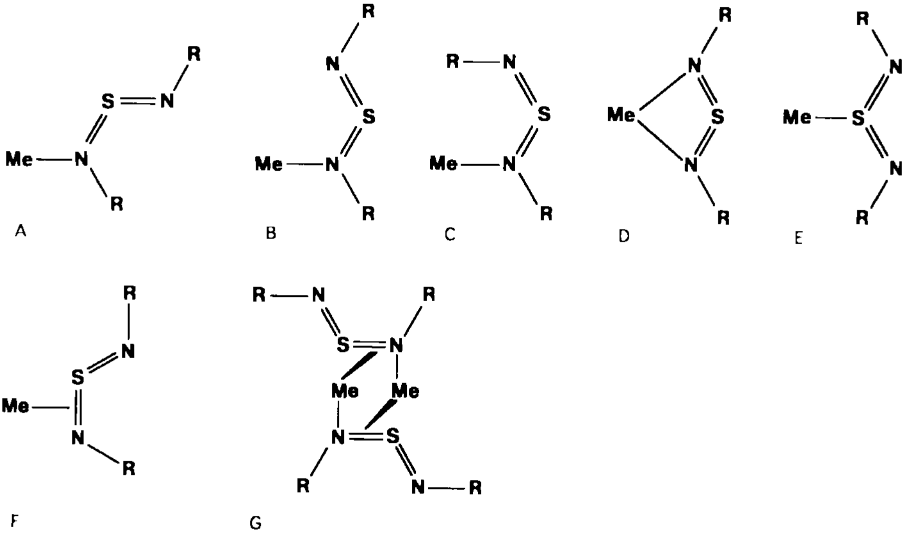


FIGURE 8 The different types of metal coordination to a sulfur diimide ligand.

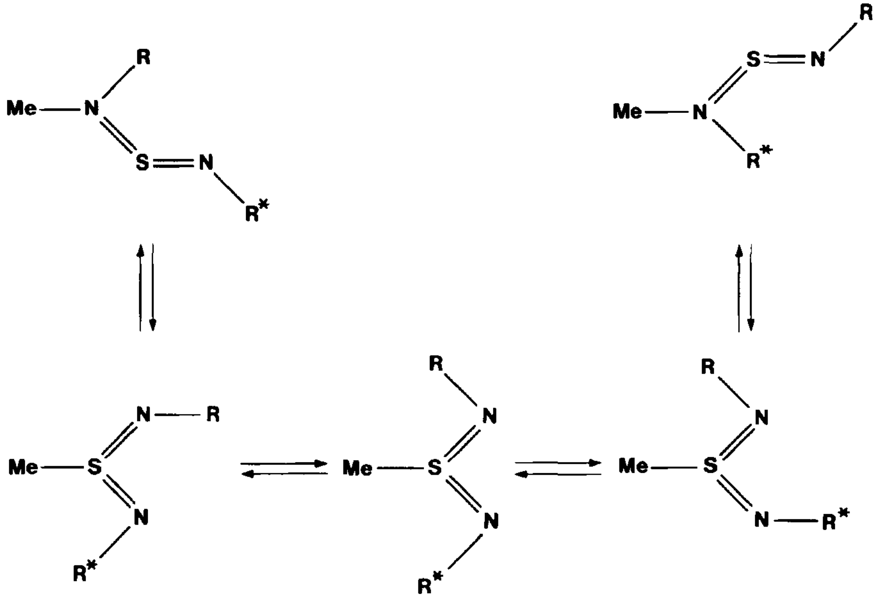


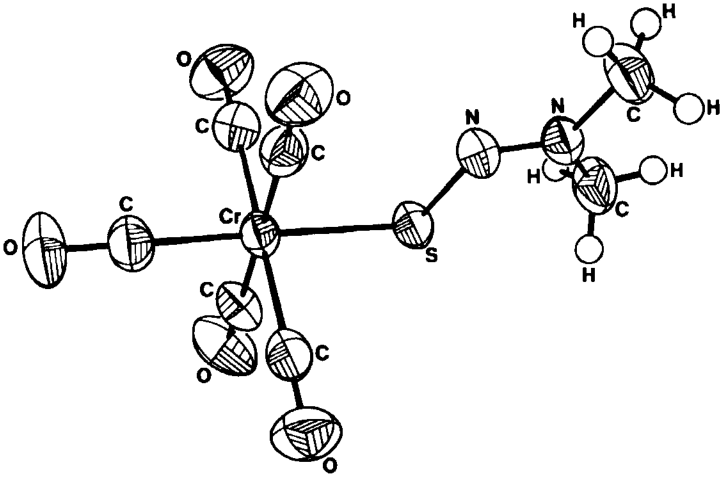
FIGURE 9 The dynamic behavior of sulfur diimide metal complexes.

In most cases the bonding is achieved by the lone pairs of the nitrogens; in the case of group VIIIb metals an ethylenic type π bonding is observed. There is no structural proof for a coordination of the sulfur to the metal atom in the solid state, but spectroscopic investigations show that the complexes are fluxional in solution, and NMR spectra indicate symmetric and asymmetric species. The rearrangement process probably involves a gliding movement of the metal along the NSN system.[13] (Figure 9)

This process is similar to rearrangements found in group VIIIb-metal allene complexes.

A sulfur coordination has been found only in two compounds, in a rhodium-*N*-sulfinylaniline complex[12] and a stable chromium complex of *dimethyl thionitrosamine (Figure 10), which is quite unstable in the free* state.[14]

In the last few years transition metal chalcogen clusters and polynuclear iron and molybdenum complexes with organosulfur ligands have raised both chemical and biological interest. Dithiolate-bridged dimeric molybdenum(III) complexes are useful substrates for the generation of olefins either in the catalytic reduction of acetylenes under mild conditions, or in reversible ligand-exchange reactions.[15,16] (Figure 11) These dithiolates undergo very easily two reversible one-electron oxidations at 0.13 and 0.79 V. (Fig-



$(CO)_5CrSNN(CH_3)_2$

FIGURE 10 The molecular structure of a thionitrosamine complex.

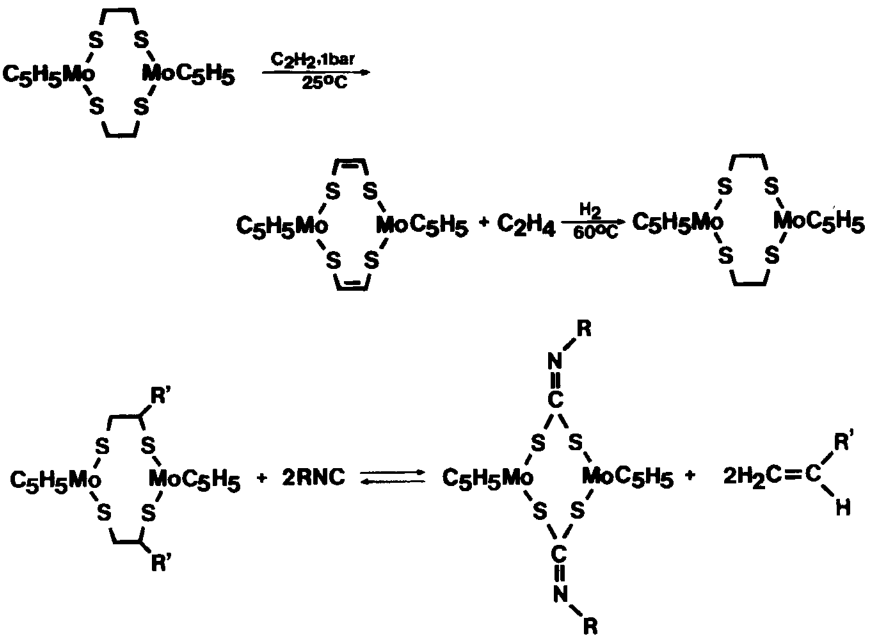


FIGURE 11 Exchanges in the coordinated ligands in a metal complex.

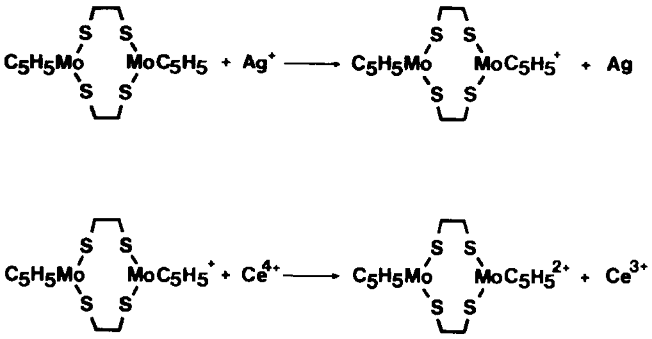


FIGURE 12 The oxidation of $C_5H_5Mo(SCH_2CH_2S)_2MoC_5H_5$.

ure 12) The magnetic moment for the monocation is consistent with a single unpaired electron and indicates a triplet ground state for the dication.

Molybdenum–sulfur clusters show low potential barriers for reversible electron-transfer reactions. This is best illustrated by the two species $Mo_3S_4cp_3$ and $Mo_3S_4cp_3^+$. Some Mo(IV)–sulfur compounds have biological activities: they are found in certain bacteria which are responsible for catalytic transfer of oxygen and nitrogen.[17]

An enzyme which contains both iron and molybdenum is nitrogenase.[18] Major efforts have been made to understand the fundamental biochemical process of nitrogen fixation, for the structure of this enzyme is not yet known. A combination of Mössbauer and ESR techniques has been used to investigate the oxidation states and the redox processes involved.

Another class of complexes which play a key role in metabolism are the iron–sulfur proteins, in which the iron is bound to the cysteinyl group of the polypeptide chain. A wide range of enzymes with different geometric structures at the active centers are known such as rubredoxins, desulfuredoxins, ferredoxins, etc. In common with the molybdenum complexes, these clusters undergo changes in oxidation state over a small range of

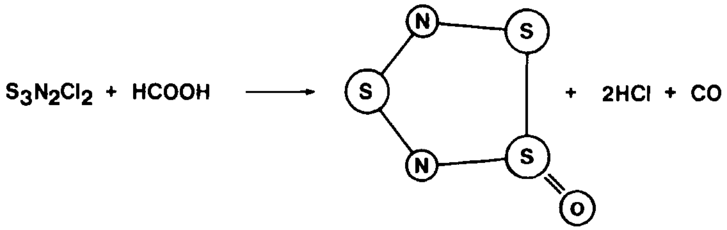


FIGURE 13 Hydrolysis of $S_3N_2Cl_2$.

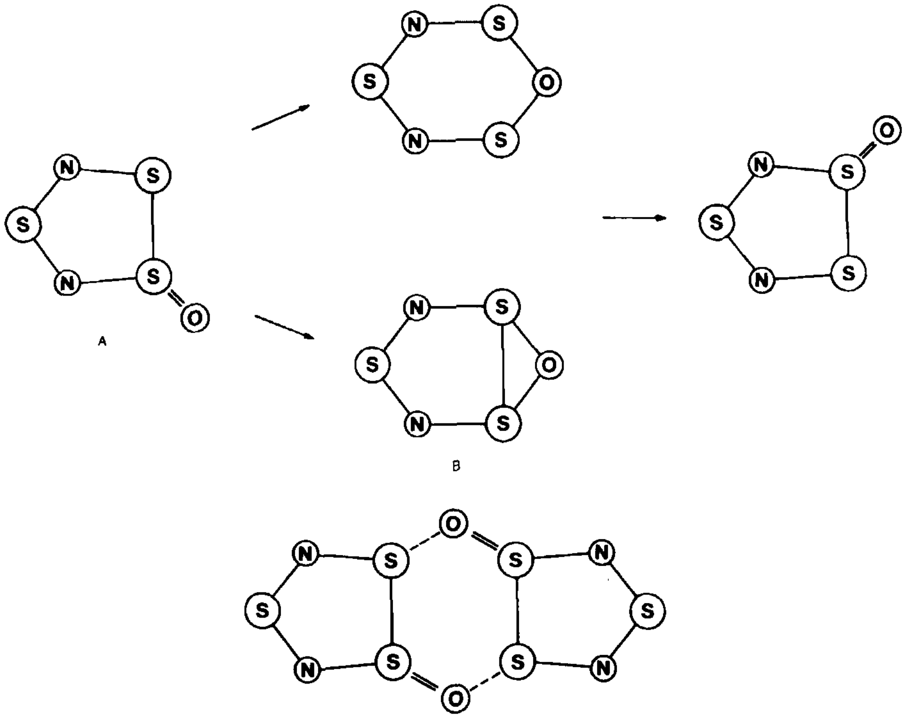


FIGURE 14 A possible intra- or intermolecular exchange of oxygen.

redox potentials, from +0.34 to −0.46 V. Analogous model compounds with the same active centers have been synthesized and show similar properties.

DYNAMIC STRUCTURES

A five-membered sulfur–nitrogen–oxygen compound was prepared from $S_3N_2Cl_2$ by hydrolysis with formic acid.[19] (Figure 13)

On the basis of IR investigations we assigned structure A to S_3N_2O. The SO stretching frequency was found for the liquid state at 1125 cm^{-1}. The absorption range for thionyl compounds is usually observed between (ν SO) 1100 and 1300 cm^{-1}. But, on the other hand, we cannot exclude an intra- or intermolecular exchange of the oxygen atom at elevated temperatures. (Figure 14)

^{33}S-NMR investigations would be a helpful tool to investigate this problem. For the preparative working chemist a general question arises, namely, whether compounds of sulfur, nitrogen, phosphorus, and other elements do

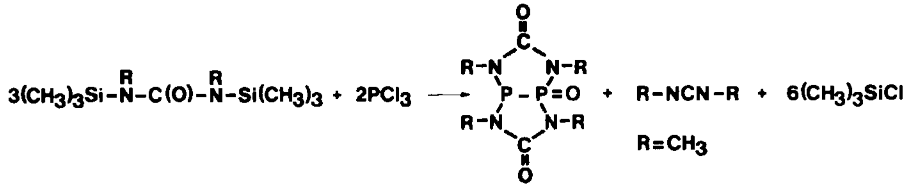


FIGURE 15 The reaction of a urea derivative with PCl_3.

exist which have an oxirane analogue structure like the formulated intermediate B. For this purpose we have prepared bicyclic compounds containing a phosphorus–phosphorus bond.[20] (Figure 15)

It was found by an x-ray crystal structure determination that this compound crystallizes in pairs of molecules which are related by a center of symmetry. (Figure 16)

The temperature dependent ^{31}P NMR spectra show no transfer of the oxygen atom between phosphorus atoms. From the solid-state structural features a bimolecular process could be suggested. Further studies to investigate the possible transition states for scrambling reactions are necessary.

An interesting example is $S_4N_4[N(CH_3)_2]_2$, which was prepared from $S_2N_4Cl_2$ and $(CH_3)_3Si\text{-}N(CH_3)_2$. The structure was determined by single-crystal x-ray diffraction. The molecule exhibits two non-equivalent dimethylamino groups, one in an exo and the other in an endo position.[21,22] (Figure 17)

On the basis of temperature-dependent ^{1}H-NMR spectra it was shown that this structure is also preserved in solution. The coalescence temperature for the exo dimethylamino group was found at 215 K. The ΔG^* value at this temperature was calculated using the Eyring equation ($\Delta G^* = 9.813$ kcal mol^{-1}). At elevated temperatures this molecule decomposes and one of the products is $[(CH_3)_2N]_2S$. Therefore the structure of $S_4N_4[N(CH_3)_2]_2$ can be considered as a "frozen" intermediate of the reaction coordinate for the formation of $[(CH_3)_2N]_2S$.

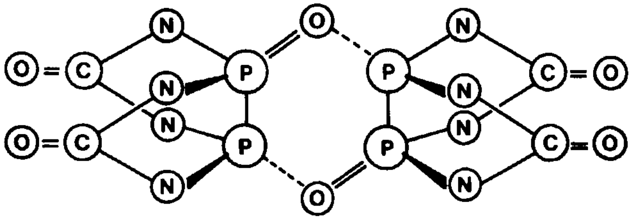


FIGURE 16 The x-ray structure of a bicyclic λ^3P- λ^5P compound. The methyl groups bonded to the nitrogen are omitted.

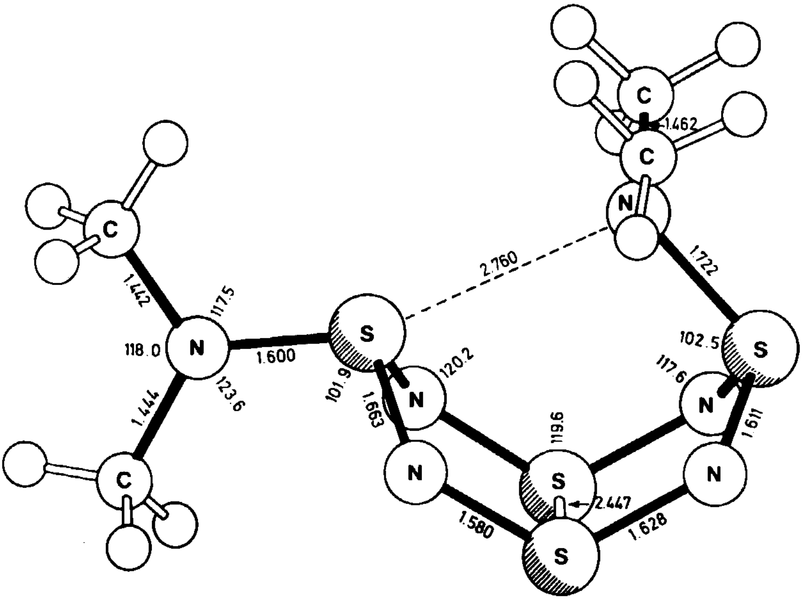


FIGURE 17 $S_4N_4[N(CH_3)_2]_2$.

CONDUCTIVE POLYMERS

Several reviews on the preparation and properties of $(SN)_x$ have been written.[23,24] Sulfur–nitrogen conjugation is of considerable current interest. Polysulfur nitride $(SN)_x$ has proved to be a strong anisotropic metal and the first superconducting polymer. Powdered S_4N_4 polymerizes at room temperature in the presence of Br_2 or ICl vapor to form a series of highly conducting metallic solid compounds of approximate composition $[SNBr_{0.4}]_x$ and $[SN(ICl)_{0.4}]_x$, respectively. Recently the first direct chemical synthesis of $(SN)_x$ from solution was reported. Trichlorotrithiatriazene $(NSCl)_3$ and trimethylsilylazide or sodium azide were used and reacted in acetonitrile[25] to yield 40%–50% $(SN)_x$. Furthermore, there is considerable interest in the possibility of obtaining analogues of $(SN)_x$ such as $(SCH)_x$ or $(SCR)_x$, where the nitrogen atoms are replaced by C–H or C–R groups.[26]

The most widely studied polymer with an unsaturated backbone is $(CH)_x$, polyacetylene. The two possible structural forms are shown in Figure 18.

The chain of carbon atoms has alternating single and double bonds. The π electron occupies a p orbital perpendicular to the plane of the carbon chain. The p orbitals combine to form a filled π and an empty π^* orbital.

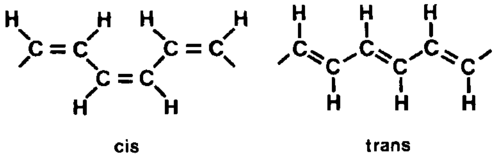


FIGURE 18 *cis* and *trans* $(CH)_x$.

In $(CH)_x$ these molecular orbitals broaden into filled and unfilled bands. In the case of complete π electron delocalization a constant carbon–carbon bond length would be observed and this would result in a zero separation between the π and π^* bands and lead to metallic properties of $(CH)_x$. However, in reality, bond alternation exists and this results in a gap between the π and π^* bands. $(CH)_x$ is a semiconductor with a p-type conductivity of 10^{-5} to 10^{-6} $(\text{ohm cm})^{-1}$. By doping with the Lewis acid AsF_5 or with halogens the p-type conductivity was raised to 1000 $(\text{ohm cm})^{-1}$. This conductivity is comparable to that of mercury. Adding electron donors such as alkali metals results in n-type materials of comparable conductivity.

Up to this time CN polymers, like paracyanogen $(CN)_x$, have not been extensively investigated. It was shown that $(CN)_x$ is a semiconductor but no doping experiments have been done.[27]

Conductive polymers have a broad technical application, e.g., in the electrophotographic industry. Polymers that are electrically insulating in the dark but can transport non-equilibrium carriers produced by light can function as photoreceptor elements. The ability to produce n- and p-type conductors in these solids by appropriate doping holds some promise to form contiguous regions of n- and p-type materials, which results in a p–n junction. Many questions still remain about the long term stability of these layers.

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