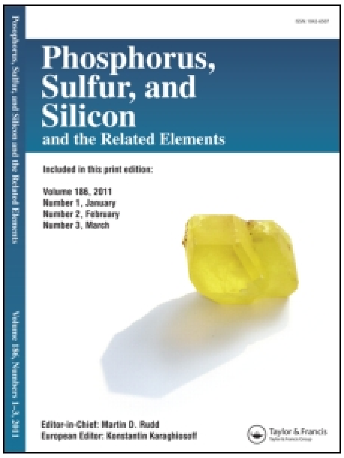

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Carbon Monosulfide Chemistry. Reactivity and Polymerization Studies

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CARBON MONOSULFIDE CHEMISTRY. REACTIVITY AND POLYMERIZATION STUDIES

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Abstract Carbon monosulfide can be generated by photolysis, thermolysis, or discharges of CS_2. We have found a high voltage AC discharge works well for production of synthetic quantities of CS. This method yields a mixture of mainly CS and CS_2 with small amounts of S_8 and C_3S_2. A stream of CS gas about 85% pure can be obtained if this mixture is passed through a -112°C trap. The ground state of CS is $X^1\Sigma^+$, and its spectroscopy is somewhat unique due to the similar energy levels of the first excited electronic configuration interspersed with the vibronic levels of the second excited state. The reactivity of CS is quite interesting. It will react with Lewis acids and Bronstead acids as well as Lewis bases. It is particularly reactive with halogens, basic amines and thiols, hydrogen halides, electron rich acetylenes, sulfenyl chlorides, and diazo compounds. This range of reactivity will be discussed with the aim of understanding reaction mechanisms and modes of attack. Another very favorable reaction is self polymerization of CS, which can occur explosively. A third body is necessary (wall reaction), and CS polymerization can be catalyzed by certain metals and organometallic compounds. The polymerization process and the structures of the polymer will be reviewed and discussed.

INTRODUCTION

Recently we comprehensively reviewed what is known about the properties and chemistry of carbon monosulfide (CS).[1] Revealed were hundreds of studies of CS dating back more than a century.[2-3] The initial work of Dewar and Jones[4-5] and Dyne and Ramsey[6] should be noted. Dewar and Jones demonstrated that CS could be produced from CS_2 by a "silent electric discharge", that CS could be condensed at -190°C, and upon warming polymerized with itself to form a dark brown solid. They hypothesized that the effect of the discharge had been to produce gaseous CS. In 1913, Martin confirmed their findings when he observed the band spectrum of gaseous CS as produced by the action of an electric discharge on CS_2 vapors.[7]

PRODUCTION OF CS

Since this original work a wide range of methods have been employed to produce CS. These include various discharges, arcs, photolysis, shock waves, thermolysis, partial combustion, and others.[1,8] Most workers have been interested in observing the spectroscopic and physical properties of CS, and such interest has been spurred by the early reports of CS as an intermediate in combustion of CS_2[9], and the discovery of CS in interstellar space[10].

Although much is known about CS, there are very few reports on the use of CS as a synthon. Presumably the difficulties in handling such a reactive molecule is the reason. On the other hand, it can be prepared from an inexpensive source, CS_2, and can be moved in a vacuum system rather long distances. With these thoughts in mind, in 1972 we began an investigation of CS as a synthon. Our first project was to devise a method of preparing CS safely on a multigram scale. After many attempts using radiowave and microwave discharges, we returned to the old method of Dewar and Jones, that of a high voltage AC discharge. With some improvements and rapid throughputs under vacuum we found that about 75% CS_2 decomposition was obtained and that the effluent consisted mainly of CS plus excess CS_2 plus smaller amounts of S_8 and C_3S_2[11].

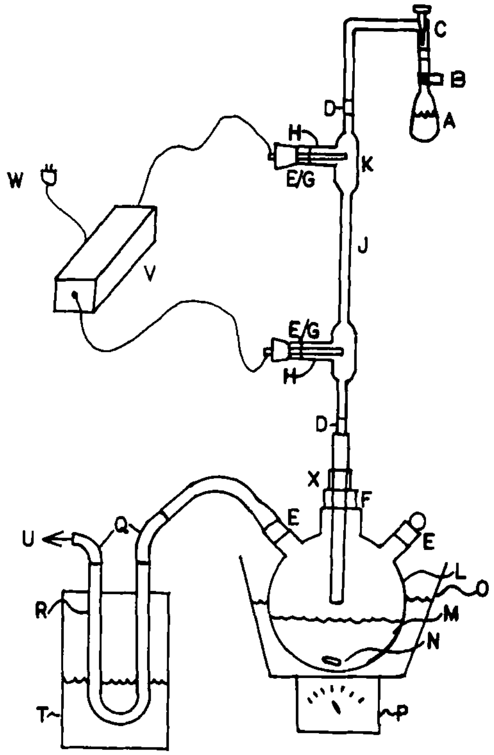


FIGURE 1 Apparatus for Production of CS on Multigram Scale (Without Purification Cold Trap)

A. Degassed carbon disulfide

B. Teflon o-ring stopcock

C. Needle valve

D. 14/35 joint

E. 24/40 joint

F. 34/45 to 24/40 joint

G. 6 cm side arm with 24/40 joint

H.	8 mm diameter polished brass electrode
J.	10 mm diameter, 35 cm length pyrex glass tubing
K.	22 mm diameter, 10 cm length pyrex glass tubing
L.	500 ml three neck round bottom flask
M.	Reactant/solvent solution
N.	Magnetic stirring bar
O.	Cold Bath (usually isopropanol/dry ice)
P.	Magnetic stirring motor
Q.	n-butyl rubber tubing
R.	3/8 in. inner diameter copper U-tube
T.	-196°C cold bath (liquid nitrogen)
U.	to vacuum (normally 10 microns)
V.	Transformer rated at 15,000 V at 30 mA
W.	to variac
X.	24/40 joint with inner member

Interestingly, most of the S_8 generated remained in the discharge tube:

$$\begin{tikzcd}
CS_2 \arrow[r, "\text{AC discharge}"] & CS + S \arrow[d, "\text{fast}"] & \\
& S_8 \arrow[r] & \text{sulfur}
\end{tikzcd}$$

A surprising feature of this experiment is that the CS could be moved large distances without polymerization. In fact, as it moved out of the reactor region it would slowly coat the inside walls of the entire vacuum system with $(CS)_n$. When it was purposely trapped at -196°C, CS monomer condensed, but small violent polymerizations took place periodically at the leading edge of this condensate. These small explosions yielded heat, light, and crackling noises, and destroyed many glass traps before we learned that a metal cold trap was necessary.

In order to purify the $CS/CS_2/C_3S_2/S_8$ effluent stream, we have employed a cold trap at -112°C[12]. In this way most of the

CS_2, C_3S_2, and S_8 were trapped, while the more volatile CS could be partially passed through, although serious losses of CS to wall polymerization were also experienced.

BONDING IN CS

A molecular orbital energy level diagrams for CS (and CO, Figure 2) shows its singlet configuration with 22 total electrons and 10 valence electrons[8,13]. Note the filled π levels and the unfilled π^* and σ^* levels. Of course this system is isoelectronic with CO and RNC. However, the M.O. diagram for CO is quite different owing to the much lower energy of atomic oxygen 2s and 2p levels vs. 3s and 3p for sulfur. This results in a very different type of orbital mixing and for CO the highest occupied molecular orbital is σ^* while for CS it is π. Thus, very different chemistry might be expected as the π- and σ-filled orbitals are at nearly the same energy level and the unfilled π^* and σ^* are also nearly the same energy and only slightly above the HOMO. From these considerations CS might be expected to behave as a reactive carbene possibly exhibiting electrophilic or nucleophilic character. Also, its π-bonds should be easily broken to form multiple single bonds.

It would be expected that spectroscopic properties may also be unusual. Indeed, they are somewhat unique[14]. The vibronic levels of the first excited electronic configuration $\pi^4\sigma\pi^*$ are interspersed among the vibronic levels of the second excited configuration $\pi^3\sigma^2\pi^*$, resulting in extensive spin-orbit perturbations, much more severe that with CO.

Ground state CS has a dipole moment for 1.958D, with the sign convention being C^-S^+. Since carbon and sulfur have the same electronegativities, the existence of any dipole moment must be due to the bonding hybridization (valence bond terminology).

Pauling has interpreted the dipole by assigning % of contribution of various possible hydrids[15]:

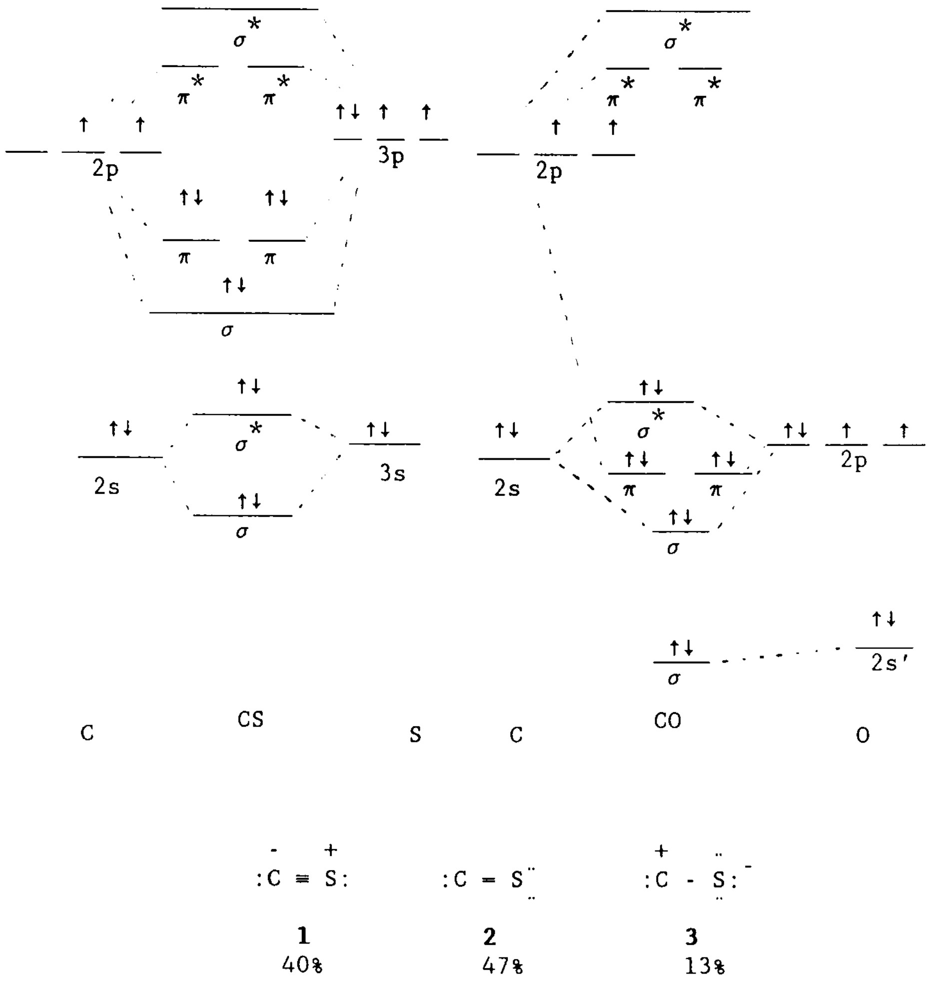


FIGURE 2 Simple Molecular Orbital Energy Level Diagrams for CS and CO,[13,16] and Resonance Forms for CS

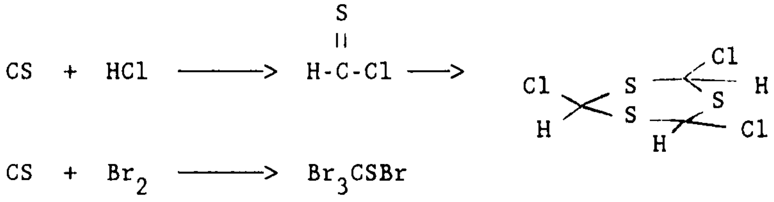
Mockler and Bird[17] established the bond length of CS to be 1.535Å with a bond order of 2.4. Pauling's estimate of the bond order was 2.27[15]. Also, Mockler and Bird[17] believed that resonance from **2** was most important (60% of total), and **3** was negligible.

REACTIVITY OF CS

Although certain predictions about CS reactivity can be made by studying the M.O. and valence bond pictures, when experiments are commenced many surprises present themselves.

First, we must clarify the experimental conditions. Since CS polymerizes with itself so readily, it must be generated under vacuum and swept into a reaction zone where it can be cocondensed at -196°C with excess reactant, or swept into a stirred solution containing reactant. In either case, generally low temperatures must be employed in the reaction zone in order to maintain a reasonable vacuum (so reactant/solvent evaporation is minimized). Due to these experimental restrictions only low Ea reactions proceed, and they always compete with CS polymerization. In effect, CS is a very selective reagent, but partially due to the conditions of the experiments.

First we determined that CS did not react as a typical carbene. It does not add to alkenes or unactivated acetylenes[11]. Nor did it react with alkanes, alkyl halides, acyl halides, or alcohols[18]. It was also inert to perfluoroalkenes. Eventually we learned that it reacted with acidic materials and halogens[11].



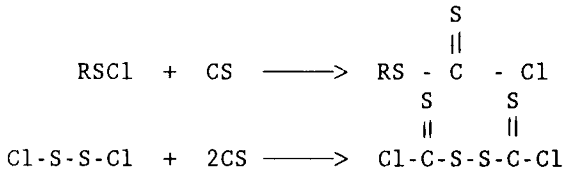
$$CS + HCl \longrightarrow H\text{-}\overset{\overset{S}{\|}}{C}\text{-}Cl \longrightarrow$$

$$CS + Br_2 \longrightarrow Br_3CSBr$$

Steudel[19-20] also found that CS would react with Te and Se to yield small amounts of CSTe and CSSe. And we showed that CS behaved as a mild deoxygenating agent such that cyclohexene oxide with CS yielded COS and cyclohexene[8].

These results were not very satisfying, since we believed CS should be a useful, new synthon in organosulfur chemistry. But after many failed attempts at introducing CS into alkenes, carboxylic acids, acetylenes, organohalides, and various metal compounds, we postponed further studies of CS, and did nothing more from 1974-1981. At that time Professor Senning suggested that we work together on further investigations of CS. This joint investigative approach proved very fruitful as Senning provided his organosulfur expertise, and we provided expertise in vacuum systems and CS generators. Students were recruited to jointly work on this NSF and NATO funded CS project, and very soon new interesting results were found.

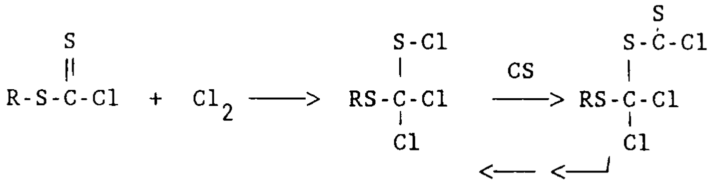
Sulfenyl chlorides proved to react very efficiently with CS by -S-Cl insertion[21-24]:



$$RSCl + CS \longrightarrow RS-\overset{\overset{S}{\|}}{C}-Cl$$

$$Cl-S-S-Cl + 2CS \longrightarrow Cl-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-Cl$$

By carrying out chlorination of the resulting products and further treatment with CS a method of adding CS units one at a time was established[22,25]:

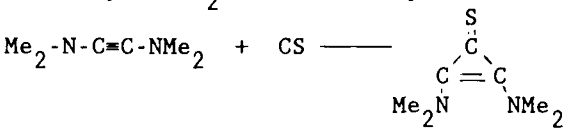


$$R-S-\overset{\overset{S}{\|}}{C}-Cl + Cl_2 \longrightarrow RS-\underset{\underset{Cl}{|}}{\overset{\overset{S-Cl}{|}}{C}}-Cl \xrightarrow{CS} RS-\underset{\underset{Cl}{|}}{\overset{\overset{S-\overset{S}{C}-Cl}{|}}{C}}-Cl$$

Interestingly the -S-Cl insertion reaction was not very sensitive to the nature of R, and even the relatively less reactive Cl_3S-Cl consumed CS efficiently.

Next, we found that -N-H and -S-H bonds were also susceptible to insertion by CS[12,18,25]. In these cases, especially with the amines, the reaction proved to be sensitive to electronic and steric effects. Highly basic secondary amines reacted best, morpholine reacting most efficiently (basic but with little steric congestion):

Further investigations by Krebs and coworkers, Senning and coworkers, and ourselves showed that CS will undergo cycloaddition reactions with highly electron rich acetylenes[26], and will displace N_2 in diazo compounds[8,25].

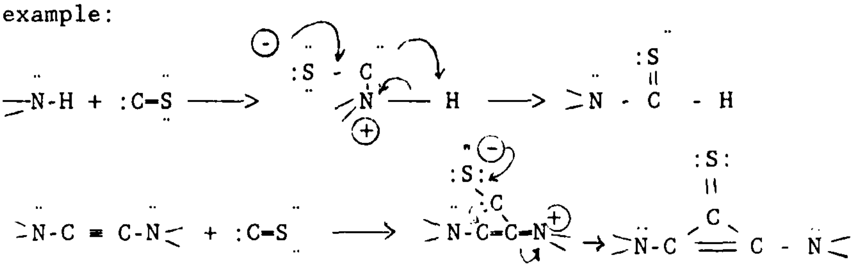


$(Me_3C)_2CN_2 + CS \longrightarrow (Me_3C)_2C{=}C{=}S$

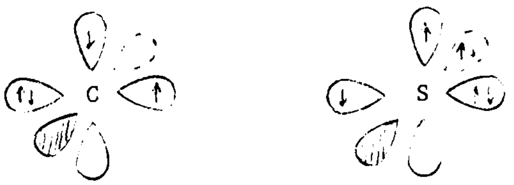
From this series of successful reactions we can conclude that CS is very selective. It seeks out electron rich substrates in the case of insertion into -N-H bonds and in cycloaddition reactions. It is interesting to note that in the successful CS reactions encountered, analogous isocyanide reactions are known[27]. Thus, the reactivity of isocyanides can be used somewhat as a rough guideline to judge CS reactivity.

This electrophilic behavior of CS suggests that the LUMO of CS (π^*) is very important in the initial attack of CS on the reagent.[28] This becomes increasingly apparent when we compare the dipole moments of CO (0.1 Debye) with CS (1.96 Debye, most electron density toward carbon). Thus, the dipole moment would suggest just the opposite behavior --- that of carbon of CS behaving as a nucleophile.

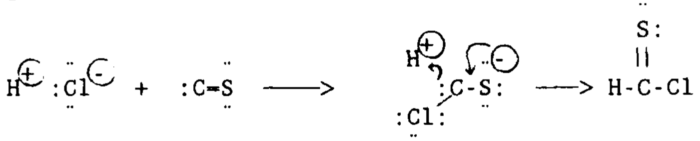
Perhaps it is easier to understand this unexpected reactivity behavior if we consider the resonance hybrids **2** and **3**. Unoccupied orbitals on carbon may initiate the attack, for example:



In resonance hybrid **2** we can see that in valence bond terminology the carbon is sp hybridized and one empty p-orbital remains available to attack by the electron rich substrate.



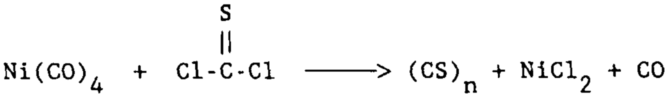
It is possible that the same mode of attack is operating for hydrogen halides, as shown below:



So generally CS should be considered as somewhat electron seeking, but it quite selective and will react with strong acids and oxidizers as well as electron rich thiols, sulfenyl chlorides, and acetylenes. And, of course, bond strengths and thermodynamics come into play as well. For example, -S-H bonds will react while -O-H bonds, which are stronger, will not.

POLYMERIZATION OF CS

What really sets CS apart from CO and RNC is its ability to spontaneously polymerize. The first observations of this were reported by Loew[2] and Sidot[3], who isolated CS polymer from the photolysis of CS_2, although at that time they could not know that CS was an intermediate. Dewar and Jones reported the first detailed investigations[4]. They produced CS (or a CS precursor) by treatment of thiophosgene with nickel carbonyl:



$$Ni(CO)_4 + Cl\text{-}\overset{\overset{S}{\|}}{C}\text{-}Cl \longrightarrow (CS)_n + NiCl_2 + CO$$

They also prepared it by trapping CS at -196°C (from an electrical discharge) followed by warming:

$$CS_2 \xrightarrow{\text{discharge}} CS \longrightarrow (CS)_n$$

the two polymers were similar but not identical in their properties. The brown-black powder was insoluble in alkanes, ethers, alcohols, benzene and dilute H_2SO_4. It was slightly soluble in nitrobenzene, CS_2, ethylene dibromide, napthalene, and phenol. It was very soluble in concentrated H_2SO_4, HNO_3, and aqueous or alcoholic solutions of NaOH or NH_3. Generally the discharge prepared $(CS)_n$ was less soluble, and this was attributed to a higher degree of polymerization.

The polymerization of monomeric CS does not take place in the gas phase very readily. A surface is required, and a high surface area of, for example, carbon can help control the polymerization[4-5]. However, in the absence of an ameliorating high surface area, the polymerization is usually violent. If CS monomer collects at a low temperature spot sudden detonations can (usually) take place[4,5,11]. Heat and light are released and glassware is often cracked.

$$CS + CS \xrightarrow[\text{(often violent)}]{\text{wall}} (CS)_n + h\nu + \text{heat}$$

It would be expected that the degree of polymerization and perhaps even the stiochiometry of the solid would vary with method of preparation. Explosive polymerization might produce some graphite and/or sulfur and/or C_3S_2. Polymerization on a high surface and polymerization by halide abstraction from $(Cl)_2$ C=S might give quite different products. Unfortunately little has been done to elucidate the structure of any CS polymer, let alone a series of variously prepared ones. Dewar and Jones[4-5] report some preliminary experiments but nothing structurally elucidating (heating to 360° yielded CS_2 and carbon; heating with H_2 yielded H_2S and carbon; heating with Cl_2 yielded sulfur chlorides, thiophosgene, and carbon). The mp of $(CS)_n$ varies but is much greater than 300°C[8]. Pyrolysis at higher temperatures yielded H_2O, SO_2, CS_2, COS, CO, S_2, and C_2S.

Thus we see that no selective degradation studies have been carried out. In order to structurally elucidate the polymer(s) selective bond cleavages must be carried out, for example S-S and C-S.

Conclusions about the true structure of the polymer are not possible at this time. A variety of polymerization modes leading to various polymer products have been proposed. For example, Steudel has reported low temperature IR studies of CS polymerization and believes that C_2S is a key intermediate[19,29]:

$$2\ CS \longrightarrow C_2S + S$$

$$C_2S + CS \longrightarrow C_3S_2$$

$$C_3S_2/C_2S + S_n \longrightarrow C_xS_y$$

Richardson and coworkers and Breckenridge and coworkers believe that CS and carbon react[30,31]:

$$2CS + C_n \longrightarrow CS_2 + C_{n+1}$$

Moltzen and Senning[1,32] report XPS studies of the polymer, which showed one peak for C(1s) at 285.6ev and one C(2p) peak at 164.8

ev which are suggestive of aromatic like carbons. X-ray analyses shows that the material was amorphous, IR shows weak bands due to C-S, C=S, and C=C. No ^{13}C signals were found in the NMR (solid state).

Thus, possible structures are still unproven. Even reproducing the polymer synthesis to give the same properties and stoichometries has not really been worked out. Fig. 3 shows some of the possible polymer structures. The quest goes on for true understanding.

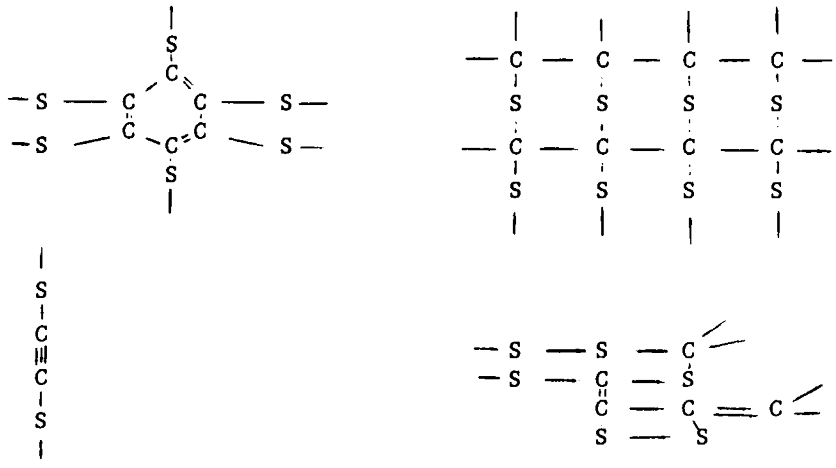


FIGURE 3 Possible Structures for $(CS)_n$

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