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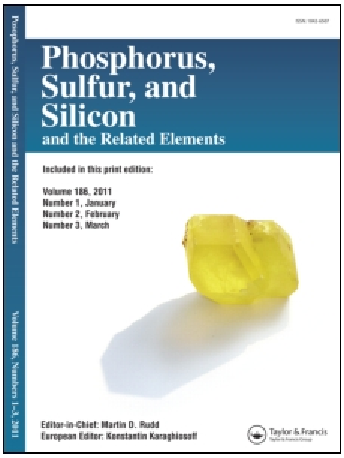

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New Oxides and Sulfides of Carbon

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NEW OXIDES AND SULFIDES OF CARBON

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Abstract Recent results from the literature about the chemistry of carbon oxides and sulfides are reviewed. The generation and characterization of elusive polycarbon oxides and sulfides XC_nY, $X,Y=O,S$ and $n \geqq 2$ by neutralization–reionization mass spectrometry or flash vacuum pyrolysis and matrix isolation techniques is described. The electronic ground state of dicarbon disulfide, C_2S_2, is discussed taking theoretical results and experimental observations into consideration. Finally, the sulfides CS_3 and C_6S_6 are presented.

INTRODUCTION

The aim of this lecture is to give an overview about recent developments in the field of carbon oxides and sulfides. The terms carbon oxides and sulfides are used to cover the whole range of neutral compounds which are formed by the elements carbon, oxygen and sulfur.

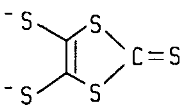
A number of new oxides and sulfides have been synthesized or experimentally proven to be capable of existence in recent years. Heterocyclic and cyclic oxides and sulfides have been synthesized by applying classical synthetic methods and characterized by modern analytical techniques, i.e. ^{13}C–NMR spectroscopy or X–Ray crystallography. The availability of carbon–fullerenes in macroscopic quantities allows now the investigation of the oxidation of the fullerene cage by a number of different methods leading to the formation of hitherto unknown carbon oxides. Thermal decomposition of heterocyclic carbon oxides and sulfides in a flash vacuum pyrolysis experiment or

[+] Present address: Schering AG, PCS, Postfach 650311, W-1000 Berlin 65, Germany their electron induced dissociation in the ion source of a mass spectrometer gives rise either to neutral fragment molecules or ionized fragments. The neutral molecules are usually trapped in noble gas matrices at low temperatures, and characterized by applying optical spectroscopical techniques like IR or UV/VIS spectroscopy. A different approach is taken in the mass spectrometric experiment to *synthesize* elusive neutral molecules. In a neutralization–reionization mass spectrometric experiment a beam of mass–selected accelerated ions is neutralized by collision–induced charge transfer between the fast moving ions and a thermalized target gas, i.e. xenon or oxygen. Remaining ions are deflected by applying an electrical field, and the newly generated beam of fast moving neutrals is reionized in a second collision experiment and analyzed by applying standard mass spectrometric techniques. Analysis of the collision–induced dissociation spectra obtained with and without the presence of the electrical deflection field reveals the presence of a neutral molecule as a stable entity between the two collision events. The charge–transfer processes are best described as vertical processes. Molecular lifetimes are typically of the order of 10^{-6} seconds[1].

HETEROCYCLIC CARBON OXIDES AND SULFIDES

Carbon sulfides

A key intermediate in the synthesis of heterocyclic carbon sulfides is the dianion of 1,3–dithiole–2–thione–4,5–dithiol[2], **1**, $C_3S_5{}^{2-}$. Compound **1** is formed in the reduction of carbon disulfide by alkali metals in aprotic solvents together with the trithiocarbonate dianion, $CS_3{}^{2-}$.



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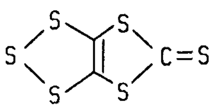

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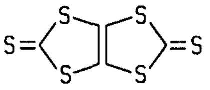

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A product of the electrochemical reduction of carbon disulfide is [1,3]dithiolo[4,5–d]–1,2,3–trithiole–5–thione[3], **2**, C_3S_6. The reaction of **1** with electrophiles according to equation (1a) gives rise either to 1,3,4,6–tetrathiapentalene–2,5–dithione[4] **3**, or according to (1b) to [1,3]dithiolo[4,5–f]–1,2,3,4,5–pentathiepine–7–thione[5], **4**, C_3S_8.

(1) a) $C_3S_5{}^{2-} + Cl_2CS \rightarrow C_4S_6 + 2\,Cl^-$

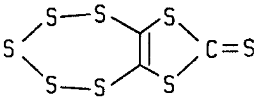
1 **3**

(1) b) $C_3S_5{}^{2-} + Cl_2Ti(C_5H_5)_2 \rightarrow C_3S_5Ti(C_5H_5)_2 + 2\,Cl^-$

1

$C_3S_5Ti(C_5H_5)_2 + S_2Cl_2 \rightarrow C_3S_8\ (!) + Cl_2Ti(C_5H_5)_2C_3S_5{}^{2-}$

4



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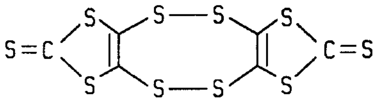

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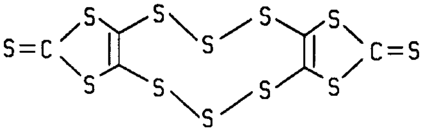

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Sulfide **4** is not stable in solution and decomposes into bis[1,3]dithiolo[4,5–d : 4′, 5′–i][1,2,3,6,7,8]hexathiecine–2,8–dithione, **6**, C_6S_{12} and elemental sulfur. The oxidation of **1** with sulfuryl chloride according to equation (2) leads to the formation of bis[1,3]dithiolo[4,5–c : 4′, 5′–g]tetrathiocine–2,7–dithione[6], **5**, C_6S_{10}.

(2) $2\,C_3S_5{}^{2-} + 2\,SO_2Cl_2 \rightarrow C_6S_{10} + 4\,Cl^- + 2\,SO_2$

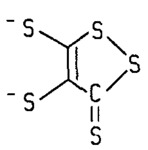
1 **5**

Whereas polymeric 1,3–dithiolo–2,4,5–trithione[7], **7**, $(C_3S_5)_x$ is formed in the oxidation of **1** with elemental iodine according to equation (3). The structure of **7** is not known.

(3) $x\,C_3S_5{}^{2-} + x\,I_2 \rightarrow (C_3S_5)_x + 2x\,I^-$

1 **7**

The thermal induced isomerization of **1** leads to the dianion of 1,2–dithiole–3–thione–4,5–dithiol[8], **8**, $C_3S_5{}^{2-}$. Reaction of **8** with thiophosgene according to reaction (1a) results in the formation of [1,3]dithiolo[4,5–f]–1,2–dithiole–3,5–dithione[9], **9**, C_4S_6.



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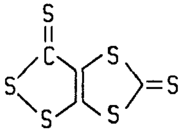

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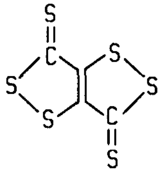

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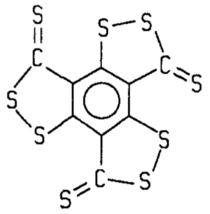
A third C_4S_6 isomer, [1,2]dithiolo[4,3−c]−1,2−dithiole−3,6−dithione[10], **10**, is generated in the reaction between hexachlorobutadiene and sodium pentasulfide in aprotic solvents according to equation (4).

(4) $$8\,C_4Cl_6 + 24\,Na_2S_5 \rightarrow \underset{\mathbf{10}}{8\,C_4S_6} + 48\,NaCl + 9\,S_8$$



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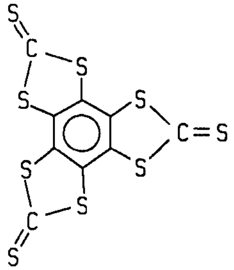

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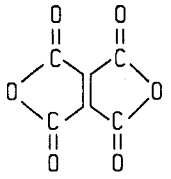
Formally oligomers of carbon monosulfide are the compounds benzo[1,2−c : 3,4−c′ : 5,6−c″]tris[1,2]dithiole−1,4,7−trithione[11], **11**, and benzo[1,2−d : 3,4−d′ : 5,6−d″]tris[1,3]dithiole−2,5,8−trithione[12], **12**. Both compounds are of the elemental composition C_9S_9. Compound **11** is formed in the reaction between polyhalogenomesitylenes and elemental sulfur in N,N−dimethylformamide. Compound **12** is formed by trapping the hexaanion of hexamercaptobenzene with thiophosgene in analogy to reaction (1a).

Carbon oxides

The members of the family of heterocyclic carbon oxides are mainly cyclic anhydrides or oxalates. A well known example is the trisanhydride of benzenehexacarboxylic acid, **14**, $C_{12}O_9$. The anhydride **13**, C_6O_6, has not been isolated yet. It is only known in 1:1−Diels−Alder adducts, i.e. with 9,10−dimethoxyanthracene[13]. The only experimental proof so far for the existence of the free molecule **13** in the gas phase is a neutralization−reionization mass spectrometric experiment[14].



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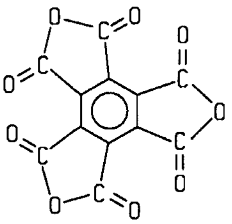

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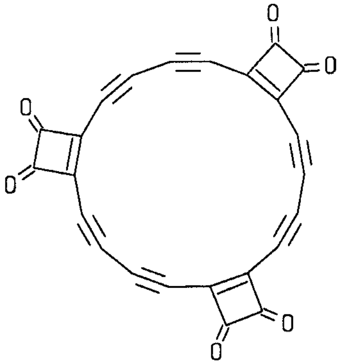
Two well characterized oxides (UV, IR, NMR) which are not heterocycles in a strict sense have been prepared by the Eglington–Glaser coupling of 3,4–dialkinyliden–cyclobutene–1,2–diones[15]. The two compounds obtained are tetracyclo[20.2.0.0^{6,9}.0^{14,17}]tetracosa–1(22),6(9),14(17)triene–2,4,10,12,18,20–hexayne–7,8,15,16,23,24–hexaone, **15**, $C_{24}O_6$, and pentacyclo[28.2.0.0^{6,9}.0^{14,17}.0^{22,25}]dotriaconta–1(30),6(9),14(17),22(25)–tetraene–2,4,10,12,18,20,26,28–octayne–7,8,15,16,23,24,31,3–octaone, **16**, $C_{32}O_8$. Both carbon oxides are described as very unstable.



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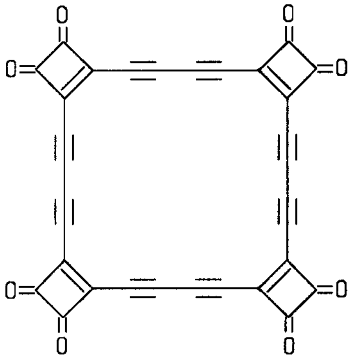

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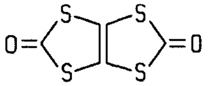
Carbon oxidosulfides

As in the case of the heterocyclic oxides and sulfides the known carbon oxidosulfides belong either to the class of anhydrides, thioanhydrides, carbonates, thiocarbonates or oxalates. Starting from the above–mentioned thiones it is possible by performing a mercury(II) induced $C{=}S \rightarrow C{=}O$ transformation to synthesize the mono– and diketones **17** – **20**. These compounds are of the elemental composition C_4S_5O and $C_4S_4O_2$[16,17], respectively.



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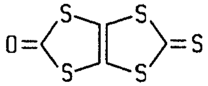

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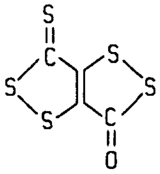

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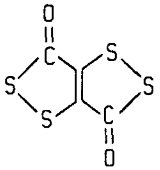
Noteworthy is the formation of 3–oxo–4–thioxo–1,2,5,6–tetrathiapentalene, **21**, in the reaction between diethyl ethoxyethylenemalonate and Lawesson reagent, followed by an oxidative cyclization and sulfuration[18]. Compound **22** is obtained in the reaction between **8** and phosgene[19] according to reaction (1a).



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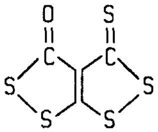

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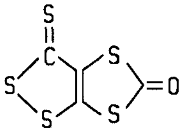

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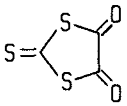
The reaction of trithiocarboxylic acid or the dianion $CS_3{}^{2-}$ with oxalyl chloride or 1,2,4,5–tetrachloro–p–benzoquinone, results in the formation of 1,3–dithiole–2–thione–4,5–dione[20], **23**, $C_3O_2S_3$, or 2,6–dithioxo–benzo[1,2–d : 4,5–d′]bis[1,3]dithiole–4,8–dione[21], **24**, $C_8O_2S_6$. The diketone **25** is synthesized starting from **24** by performing a mercury(II) induced $C{=}S \longrightarrow C{=}O$ transformation. Trapping of the hexaanion of hexamercaptobenzene with phosgene according to (1a) leads to the formation of the triketone benzo[1,2–d : 3,4–d′ : 5,6–d″]tris[1,3]dithiole–2,5,8–trione[22], **26**, $C_9O_3S_6$.



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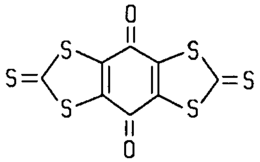

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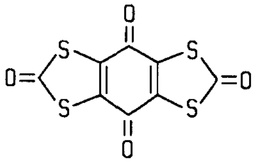

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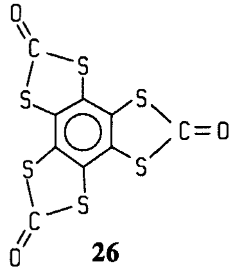

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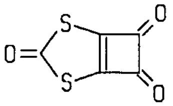
Unique for carbon oxidosulfides is the existence of heterocyclic compounds which are derivatives of squaric or croconic acid.The compounds **27** – **29** are synthesized either from the dianions of dithiosquaric acid or dithiocroconic acid or from the corresponding acid chlorides and Lawesson reagent[23,24].



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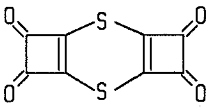

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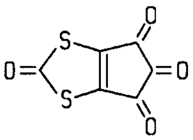
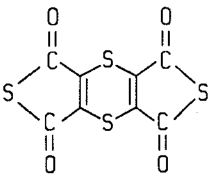


29

Unprecetented are the dithioanhydrides **30**, **31** and **32**. The 2,3:5,6–dithioanhydride **30** is synthesized from dichloromaleic thioanhydride and hydrogen sulfide. Dichloromaleic thioanhydride is easily available as the product of the reaction between tetrachlorothiophene and fuming nitric acid. Oxidation of **30** leads to 4–oxo–4H–4λ^4–ditheno[3,4–b : 3',4'–e]dithiine–1,3,5,7–tetraone, **31**, $C_8O_5S_4$, which upon thermolysis loses sulfur monoxide to generate the 2,3:4,5–dithioanhydride of thiophenetetracarboxylic acid[25], **32**, $C_8O_4S_3$.



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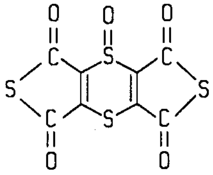

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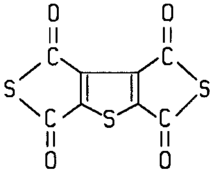

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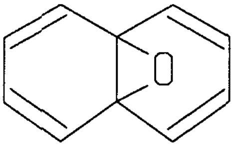
CARBON-FULLERENE OXIDES

Mass spectrometric studies of the reaction products of the photooxygenation of C_{60} and C_{70} in benzene revealed the formation of oxides of the elemental composition $C_{60}O_x, x=1-4$, $C_{70}O$ and $C_{70}O_2$[26]. It was possible to isolate $C_{60}O$ from the reaction mixture by preparative chromatography[27]. $C_{60}O$ is also formed in the reaction of C_{60} with dimethyldioxirane[28]. On the basis of the ^{13}C-NMR spectrum the epoxide structure **33** were assigned to $C_{60}O$ and not the annulene structure **34**.



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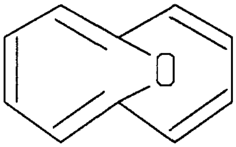

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$C_{60}O$ and $C_{70}O$ were also identified as byproducts in the carbon-arc synthesis of fullerenes[27,29]. In an electrochemical study it was shown that the dianion of C_{60}, C_{60}^{2-}, reacts with oxygen in the presence of water to form the oxides $C_{60}O_x, x=1-4$. Prolonged electrolytic reduction in the presence of oxygen and water leads to the loss of what appear to be C_{10} fragments[30].

CUMULATED CARBON OXIDES AND SULFIDES

The title compounds are of the general composition $X{=}C(C)_n{=}Y$, $X{\neq}Y{=}O$, S, *electron pair*, $n=0-6$. The general formula covers also the well known carbon oxides, sulfides and oxidosulfides CO, CS, CO_2, COS, CS_2, C_3O_2, C_3OS and C_3S_2. Also included are the polycarbon oxides and sulfides which are only capable of existence as transient species. The photolysis of CO/C_n-mixtures in solid neon at 4 K leads to the formation of $C_{n+1}O$ for $n=3$ and $n=5$[31,32]. The even-numbered carbon oxides are identified on the basis of their characteristic ESR spectra. The electronic ground state of these compounds is the triplet state $^3\Sigma^-$. C_3O has been identified as a free molecule with the help of microwave spectroscopy[33]. The electronic ground state of the odd-numbered carbon oxides is the singlet state $^1\Sigma^+$. The presence of polycarbon monosulfides C_2S

and C_3S in He/CS_2 mixtures, which were subject to electrical discharges, has been shown by microwave spectroscopy. The experimentally determined electronic ground states of CS[34], C_2S[35] and C_3S[36] are $^1\Sigma^+$, $^3\Sigma^-$ and $^1\Sigma^+$.

Polycarbon dioxides, disulfides and oxidosulfides

A basic requirement for the detection and analysis of transient species by microwave spectroscopy is that the molecule of interest is provided with a permanent dipole moment. Accordingly, polycarbon dioxides or disulfides can not been characterized by microwave spectroscopy.

Dicarbon disulfide

The existence of a molecule $S{=}C{=}C{=}S$ as the global minimum on the $[C_2,S_2]$ potential energy hypersurface was predicted on the basis of results from CI/DZ+P calculations as early as 1983[37]. The electronic ground state of the C_2S_2 molecule according to the aforementioned calculations is the $^3\Sigma_g^-$ state. The reason for the stability of C_2S_2 is seen in the spin−forbidden nature and the unfavourable energetics of reaction (5).

$$(5) \qquad {}^3\Sigma_g^-\ C_2S_2 \rightarrow {}^1\Sigma^+CS + {}^1\Sigma^+CS$$

The calculated endothermicity of reaction (6) is 39.4 kcal/mol, and the endothermicity of the spin−allowed reaction (6) is 118.5 kcal/mol. The calculated energy difference of 78.1 kcal/mol is in good agreement with the experimentally determined value of 79.1 kcal/mol for the $^3\Pi-{}^1\Sigma$ splitting of CS[38].

$$(6) \qquad {}^3\Sigma_g^-\ C_2S_2 \rightarrow {}^3\Pi\ CS + {}^1\Sigma^+CS$$

In line with the theoretical prediction, C_2S_2 was *synthesized* in a neutralization−reionization mass spectrometric experiment in 1988[39]. Starting from the ion $C_2S_2^{+\cdot}$, which was generated upon electron impact induced dissociation of **17**, it was possible to generate neutral C_2S_2. The observed fragmentation pattern, especially the loss of neutral CS and atomic S from the radical cation in the collision−induced dissociation and charge transfer experiments, are in agreement with the connectivity $S{-}C{-}C{-}S$ for neutral and ionic dicarbon disulfide. C_2S_2 is perfectly stable under the conditions of the mass spectrometric experiment.

A different point of view about the electronic ground state of C_2S_2 is taken by the authors of reference 23. They generated neutral C_2S_2 in a flash vacuum pyrolysis experiment starting from **27** or **29**. On the basis of their results from CASSCF(6,6)/3−21G(d) calculations the authors of reference 23 claim that the electronic ground state of C_2S_2 is the $^1\Delta_g$ state. At this level of theory $^1\Delta_g$ C_2S_2 is 0.7 kcal/mol more stable than $^3\Sigma_g^-$ C_2S_2. The decomposition of $^1\Delta_g$ C_2S_2 into two $^1\Sigma^+CS$ molecules according to equation (7) should not be hampered by the presence of a spin−inversion barrier as it is the case in reaction (5).

$$(7) \qquad {}^1\Delta_g\, C_2S_2 \rightarrow {}^1\Sigma^+CS + {}^1\Sigma^+CS$$

Conclusively, C_2S_2 is described as a highly reactive species which polymerizes as a neat substance at 77 K and at a pressure of ca 10^{-4} mbar in the gas phase. Independently, however, the gas phase IR spectrum of C_2S_2 has been observed[40].

Polycarbon disulfides

The higher member of the family of polycarbon disulfides are accessible by mass spectrometric experiments. Upon electron impact induced dissociation **32** generates the ions $C_nS_2^{+\cdot}$ for $n=2-6$, which can be neutralized and reionized. The observed fragmentation pattern of the radical cations of the higher member of this series in collision−induced dissociation and charge transfer experiments are characteristic for the connectivities $S-C-C-C-C-S$, $S-C-C-C-C-C-S$ und $S-C-C-C-C-C-C-S$. The spectra are dominated by the loss of neutral CS or atomic sulfur from the molecular ions[41].The radical cation $C_4S_2^{+\cdot}$ is also available upon electron impact from the compound **28**. Upon thermolysis **28** generates neutral C_4S_2 as well which can be trapped in argon matrices at 12 K[42]. Also for this compound the question has been raised whether the $^3\Sigma_g^-$ state is the electronic ground state. C_5S_2 is available in matrix isolation experiments upon photolysis or flash vacuum pyrolysis of benzo[1,2−d:3,4−d':5,6−d"]tris[1,2,3]thiadiazole[43]. The cumulenes are easily recognized in the IR spectra of the matrix isolated molecules on the basis of their intense out−of−phase stretching vibrations. Furthermore, photolytic studies of the trapped cumulenes show that photo−equilibria exist between the cumulenes and their decomposition products. Whereas no difference between the stability of even−

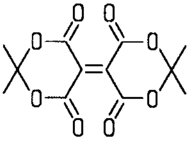
and odd–numbered cumulenes could be detected in the mass spectrometric experiments, the matrix isolation experiments clearly indicate that the even–numbered cumulenes are more prone to polymerization upon annealing than the odd–numbered ones.

Dicarbon oxidosulfide and the polycarbon oxidosulfides

The healthy rivalry between the two experimental techniques resulted in the formation of not only dicarbon oxidosulfide, C_2OS, by the mass spectrometric method[46], but also in the generation of a number of polycarbon oxidosulfides, C_nOS, for $n=3$, 4 and 5, by mass spectrometric and matrix isolation techniques[42,47]. C_3OS was synthesized before from C_3O_2 and P_4S_{10}[44] or identified as a fragment molecule in the pyrolysis of **28** by photo electron spectroscopy[45]. Noteworthy, the intensities of the radical anions, $C_nOS^{-\cdot}$, formed upon electron impact induced dissociation of the precursor molecules **28** or **30** in the presence of an electron moderator gas in the ion source, i. e. ammonia, are nearly as high as the intensities of the corresponding radical cations, $C_nOS^{+\cdot}$, formed under electron impact induced dissociation[48]. The major fragmentation pathway of the ions of interest in collision–induced dissociation and charge transfer experiments is the energetically favoured loss of carbon monoxide from the molecular ion. Flash vacuum pyrolysis of **32** leads to the isolation of C_5OS in a cryogenic matrix.

Polycarbon dioxides

With one exception all known polycarbon dioxides contain a odd–number of carbon atoms. C_5O_2 and C_7O_2 have been identified as fragment molecules formed in flash vacuum pyrolysis experiments starting from 1,3,5–trisdiazo–cyclohexane–2,4,6–trione[49] or **14**[50]. The known even–numbered polycarbon oxide is C_4O_2. The neutral molecule is generated upon photolysis of 1,2–bisdiazo–cyclopentane–1,3,4–trione in argon matrices at low temperatures[51]. The corresponding radical anions and cations are easily generated upon electron impact induced dissociation from **35**[52]. On the basis of results from CASSCF–CI(SD)/3–21G(d) calculations the authors of reference 51 argue that the equilibrium geometry of C_4O_2 belongs to the point group C_{2h}, and that the electronic ground state is the ^1A_g state. The energy difference between the excited $^3\Sigma_g^-$ state and the ground state was calculated to be 4.9 kcal/mol[53].



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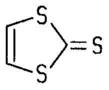
CARBON TRISULFIDE

Applying the technique of neutralization–reionization mass spectrometry[54] to $[C,S_3]$–ions, which were generated from specifically labelled 1,3–dithiole–2–^{34}S–thione, **36**, or 1,2–dithiole–3–^{34}S–thione, **37**, it was possible to show that at least two different isomers exist on the $[C,S_3]$ potential energy hypersurface of the neutral species and the radical cation.



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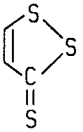

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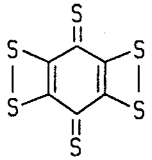
According to the mass spectrometric analysis one isomer belongs to the point group C_s and the other belongs either to the point group D_{3h} or to the point group C_{2v}. These observations are in line with a recent theoretical study of the lowest singlet and triplet potential energy hypersurfaces of the reaction between atomic sulfur and carbon disulfide[55].

HEXACARBON HEXASULFIDES

The application of the above–mentioned techniques to **32** results not only in the formation of neutral and ionized polycarbon disulfides. It was also possible to characterize a sulfide of the elemental composition $[C_6,S_6]$ which is formed together with the polycarbon disulfides. Whereas in the neutralization–reionization study[56] primarily the existence of neutral C_6S_6 has been proven, the structure of the starting material and the applied method for the generation of the corresponding radical anion $C_6S_6^{-\cdot}$

suggested that minor structural changes are taking place during the ion formation process. In the matrix isolation study the presence of a photo–equilibrium between the compounds **38** and **39** was established upon prolonged photolysis of the trapped species[57]. Applying the technique of flash vacuum pyrolysis and matrix isolation to **25** it was also possible to generate the 1,4–dioxo derivative of **38**, $C_6O_2S_4$.



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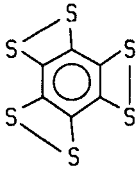

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REFERENCES

1. McLafferty, F. W. *Science* 1990, 247, 925.
2. Steimecke, G.; Sieler, H.–J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* 1979, 7, 49.
3. Hurley, M. F.; Chambers, J. Q. *J. Org. Chem.* 1981, 46, 775.
4. Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* 1977, 99, 5521.
5. Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* 1989, 111, 3465.
6. Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* 1990, 34.
7. Neiland, O. Ya.; Katsew, Ya. Ya.; Kreitsberga, Ya. N. *Zh. Org. Khim.* 1989, 25, 658.
8. Papavassiliou, G. C. *Chem. Scr.* 1985, 25, 67.
9. Lu, F. L.; Keshavarz–K., M.; Srdanov, G.; Jacobson, R. H.; Wudl, F. *J. Org. Chem.* 1989, 54, 2165.
10. Poleschner, H.; John, W.; Hoppe, F.; Fanghänel, E. *J. Prakt. Chem.* 1983, 325, 957.
11. a) Hansen, L. K.; Hardvik, A. *J. Chem. Soc., Chem. Commun.* 1974, 800.
    b) Brown, J. P.; Gay, T. B. *J. Chem. Soc., Perkin Trans. I* 1974, 866.
12. Richter, A. M.; Beye, N.; Fanghänel, E. *Z. Chem.* 1988, 28, 284.
13. a) Schröder, B. "*Präparative und mechanistische Untersuchungen an hochreaktiven Dienophilen*",Dissertation, München, 1965

b) Sauer, J.; Schröder, B.; Wiemer, R. *Chem. Ber.* 1967, 100, 306.

c) Sauer, J.; Schröder, B.; Mielert, A. *Chem. Ber.* 1967, 100, 315.

14. Sülzle, D.; Schwarz, H. unpublished.

15. Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* 1990, 112, 1607.

16. Poleschner, H.; John, W.; Hoppe, F.; Fanghänel, E. *J. Prakt. Chem.* 1983, 325, 957.

17. Fanghänel, E.; Richter, A. M.; Kordts, B.; Beye, N. *Phosphorus, Sulfur and Silicon* 1989, 43, 165.

18. Closs, F.; Srdanov, G.; Wudl, F. *J. Chem. Soc. Chem. Commun.* 1989, 1716.

19. Rauchfuss, T. B. 1990, personal communication.

20. Schönberg, A.; König, B.; Frese, E. *Chem. Ber.* 1965, 98, 3303.

21. a) Demetriadis, N. G.; Huang, S. J.; Samulski, E. T. *Tetr. Lett.* 1977, 26, 2223.
    b) Suzuki, T.; Kabuto, C.; Yamashita, Y.; Miyashi, T. *Bull. Chem. Soc. Jpn.* 1987, 60, 3459.

22. Richter, A. M.; Beye, N.; Fanghänel, E. *Z. Chem.* 1988, 28, 284.

23. Maier, G.; Reisenauer, H. P.; Schrot, J.; Janoschek, R. *Angew. Chem.* 1990, 102, 1475.

24. Seitz, G.; Gerecht, B. *Chem.–Ztg.* 1983, 107, 105.

25. Scherer, O.; Kluge, F. *Chem. Ber.* 1966, 99, 1973.

26. Wood, J. M.; Kahr, B.; Hoke, S. H.; Dejarme, L.; Cooks, R. G.; Ben–Amotz, D. *J. Am. Chem. Soc.* 1991, 113, 5907.

27. Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith III, A. B.; McCauley, Jr.; J. P.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* 1992, 114, 1103.

28. Elemes, Y.; Silvermann, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem.* 1992, 104, 364.

29. Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sehsharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* 1991, 252, 548.

30. Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* 1991, 314, 363.

31. Van Zee, R. J.; Smith, G. R.; Weltner, W. *J. Am. Chem. Soc.* 1988, 110, 609.

32. Ewing, D. W. *J. Am. Chem. Soc.* 1989, 111, 8809.

33. a) DeKock, R. D.; Weltner, W. *J. Am. Chem. Soc.* 1971, 93, 7106.
    b) Brown, R. D.; Eastwood, F. W.; Elmes, P. S.; Godfrey, P. D. *J. Am. Chem. Soc.* 1983, 105, 6496.
    c) Brown, R. D.; Rice, E. H. N. *J. Am. Chem. Soc.* 1984, 106, 6475.
    d) Brown, R. D. *Int. Rev. Phys. Chem.* 1986, 5, 101.

34. Moltzen, E. K.; Klabunde, K. J.; Senning, A. *Chem. Rev.* 1988, 88, 391.

35. Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *The Astrophysical Journal* 1987, 317, L115.

36. Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifu, N.; Suzuki, H.; Ohishi, M. *The Astrophysical Journal* 1987, 317, L119.
37. Raine, G. P.; Schaefer III, H. F.; Haddon, R. C. *J. Am. Chem. Soc.* 1983, 105, 194.
38. Huber, K. G.; Herzberg, G. "*Constants of Diatomic Molecules*" Van Nostrand Reinhold, New York, 1979.
39. Sülzle, D.; Schwarz, H. *Angew. Chem.* 1988, 100, 1384.
40. Wentrup, C.; Kambouris, P.; Evans, R. A.; Owen, D.; Macfarlane, G.; Chuche, J.; Pommelet, J. C.; BenCheikh, A.; Plisnier, M.; Flammang, R. *J. Am. Chem. Soc.* 1991, 113, 3130.
41. Sülzle, D.; Beye, N.; Fanghänel, E.; Schwarz, H. *Chem. Ber.* 1989, 123, 2069.
42. Maier, G.; Schrot, J.; Reisenauer, H. P.; Janoschek, R. *Chem. Ber.* 1991, 124, 2617.
43. Maier, G.; Schrot, J.; Reisenauer, H. P.; Janoschek, R. *Chem. Ber.* 1990, 123, 1753.
44. Winnewisser, M.; Peau, E. W. *Acta Phys. Hung.* 1984, 55, 33.
45. Bock, H.; Dammel, R.; Jacobi, D. *J. Am. Chem. Soc.* 1986, 108, 7844.
46. Sülzle, D.; Terlouw, J. K.; Schwarz, H. *J. Am. Chem. Soc.* 1990, 112, 628.
47. Maier, G.; Schrot, J.; Reisenauer, H. P. *Chem. Ber.* 1991, 124, 2613.
48. Sülzle, D.; Schwarz, H. *J. Am. Chem. Soc.* 1991, 113, 48.
49. Maier, G.; Reisenauer, H. P.; Schäfer, Balli, H. *Angew. Chem.* 1988, 100, 590.
50. Maier, G.; Reisenauer, H. P.; Ulrich, A. *Tetrahedron Lett.* 1991, 32, 4469.
51. Maier, G.; Reisenauer, H. P.; Balli, H.; Brandt, W.; Janoschek, R. *Angew. Chem.* 1990, 102, 920.
52. Sülzle, D.; Schwarz, H. *Angew. Chem.* 1990, 102, 920.

53. Janoschek, R. *Chem. unserer Zeit* 1991, 25, 59.
54. Sülzle, D.; Egsgaard, H.; Carlsen, L.; Schwarz, H. *J. Am. Chem. Soc.* 1990, 112, 3750–3754.
55. Froese, R. D. J.; Goddard, J. D. *J. Chem. Phys.* 1992, 96, 7449.
56. Sülzle, D.; Beye, N.; Fanghänel, E.; Schwarz, H. *Chem. Ber.* 1989, 122, 2411.
57. Maier, G.; Schrot, J.; Reisenauer, H. P.; Frenking, G.; Jonas, V. *Chem. Ber.* 1992, 125, 265.