Thioxoethenylidene C_2S: A Matrix-Spectroscopic Study[‡]

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Thioxoethenylidene C_2S (**5**), known for its high abundance in interstellar space, has been generated by irradiation of C_3S_2 (**4**) and C_3OS (**6**) in an argon matrix at 10 K. Its structural elucidation is based on comparison of the experimental and calculated IR and UV spectra.

Introduction

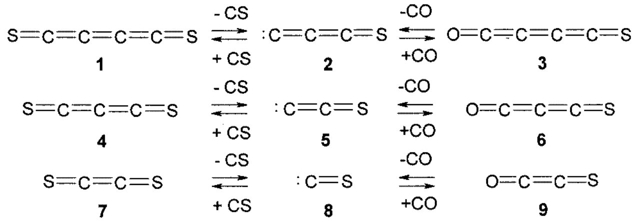
In 1999 chalcogeno-cumulenes were the topic of a special issue of the journal *Sulfur Reports*.[1] Compounds of this type have attracted considerable interest since they might be present in interstellar space. A peculiar example is thioxoethenylidene C_2S. Saito et al.[2a] identified this molecule in 1987 by means of its microwave spectrum and found that four lines could be assigned to transitions previously detected in the spectra of interstellar clouds.[2b] Structural details of C_2S were elucidated in Saito's microwave studies.[2c][2d] Additional confirmation for the existence of C_2S (**5**) in the gas phase was obtained from mass spectrometric investigations.[3,4]

In our review on matrix isolation spectroscopy of chalcogeno heterocumulenes we have already mentioned briefly that this method allows the determination of IR and UV/Vis data for C_2S.[5] The details of this investigation are given in the present report.

Results and Discussion

Synthesis of Thioxoethenylidene

In the gas phase experiments carried out to date, C_2S was generated either by glow-discharge of a mixture of carbon disulfide and helium[2a–2d] or by electron impact ionization of a suitable heterocyclic precursor molecule and neutralization of the corresponding radical cation.[3,4] Additionally, laser ablation of a carbon/sulfur pellet can be used. Vala et al. found that this latter procedure yields several small carbon-sulfur clusters, but no C_2S was found.[6] Therefore, matrix isolation of the title compound required a new synthetic strategy. The decisive insight came from our earlier observations on the photochemical behavior of related heterocumulenes. For instance, the initial reaction product upon photolysis of C_4S_2 (**1**) is C_3S (**2**).[7] In an analogous way, **2** is also accessible by matrix photolysis of C_4OS (**3**).[7] The same type of fragmentations occur on irradiation of the cumulenes **7** and **9**, which possess only two carbon atoms. In 1990 we showed that **7** is a stable molecule under matrix conditions.[8] Cleavage of **7** into two molecules CS (**8**) can be achieved by irradiation at the appropriate wavelength.[8] Irradiation of C_2OS (**9**) also leads to CS (**8**).[9] Since the fragments remain embedded in the matrix cage in all cases the reverse addition reactions can be triggered by irradiation with the correct wavelength.[5–9] Awareness of these results tempted us to generate C_2S (**5**), in the same manner, via irradiation of C_3S_2 (**4**) or C_3OS (**6**). This method was successful.[10]



Propadienedithione C_3S_2 (**4**), the most promising photoprecursor for C_2S (**5**), has been known for a long time and its synthesis is based on a discharge reaction in carbon disulfide.[11,12] This compound is quite stable under standard conditions and can be easily condensed with argon onto a spectroscopic window. In contrast, the second precursor molecule C_3OS (**6**) caused some difficulties. The routine

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[‡] Heterocumulenes, 13. For part 11 see: G. Maier, H. P. Reisenauer, K. Rademacher, *Chem. Eur. J.* **1998**, *4*, 1957–1963; for part 12 see: G. Maier, H. P. Reisenauer, R. Ruppel, *Eur. J. Org. Chem.* **2003**, 2695–2701.

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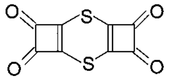
generation of C_3OS (**6**) is by the pyrolysis of heterocycle **10**.[13] Unfortunately, the volatility of **10** is not sufficient to prepare a suitable gas mixture of pure C_3OS (**6**) with argon. Therefore, the more volatile starting material **11**[8] was used. In an earlier study it was shown that this compound yields C_2S_2 (**7**) upon matrix irradiation.[8] Now we have found that, complementary to this procedure, flash pyrolysis of **11** gives C_3OS (**6**) in high yield. Only minor impurities (CO, COS, and CS_2) were present, which could be removed by vacuum distillation. By these means it was possible to prepare the desired stable gas mixture of C_3OS with argon. This variation offers an independent route to the target molecule C_2S (**5**).



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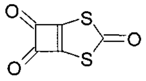

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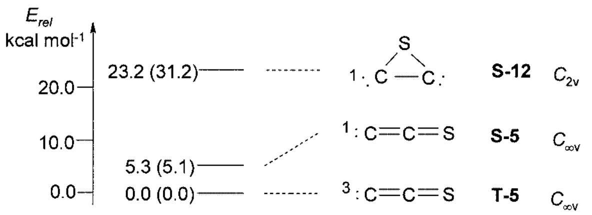
Calculations

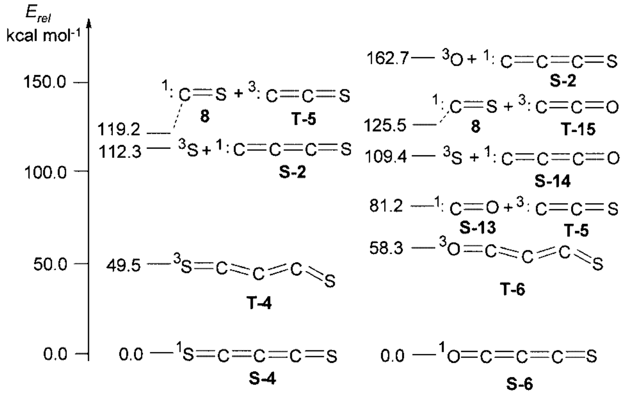
For the structural identification of the predicted species, it was necessary to obtain the calculated vibrational and UV/Vis spectra. In addition to earlier theoretical treatments,[6,14–17] we have also carried out some calculations. The structures, energies and vibrational spectra were mainly calculated with the density functional method B3LYP/6-311+G* using the Gaussian package of programs (Gaussian 94, Revision D 3,[18a] for standard calculations, Gaussian 98, Revision A 3 [18b] for TD calculations). All energy values were corrected using the zero point energies. The vibrational frequencies were calculated using the optimized geometries. On the one hand, theoretical vibrational spectra were needed for the identification of the unkown species, on the other hand they were necessary to decide which stationary point represents a minimum or a transition state. In the latter case the geometry was disturbed in the direction of the negative vibrational frequency and then reoptimized.

In 1992, Xie and Schaefer reported on the calculated (CISD/TZ2P+f) structures and IR spectra of linear and cyclic isomers of C_2S in different electronic states.[14] For linear chalcogeno-cumulenes with an even number of carbon atoms, such as C_2S (**5**), a triplet ground state is expected.[15,16] Indeed, linear **T-5** was calculated to be the global minimum on the C_2S energy surface, linear **S-5** and the cyclic isomer **12** are higher in energy.[14] On the basis of the theoretical IR spectra, Xie and Schaefer argued that an earlier report on the observation of IR bands, which were tentatively assigned to C_2S (unpublished research by L. Andrews, cited in ref.[14]), had to be erroneous. According to our experience, B3LYP/6-311+G* calculations are ideally suited for the comparison between theoretical and experimental IR spectra. So we applied this method to all three species (Scheme 1). Independently, the ground state **T-5** was also treated by Lee[15] within a density functional study of polycarbon sulfides (BLYP/6-311+G*: 1646, 815, 237 cm^{-1}), as well as by Janoschek[16] (B3LYP/cc-pVTZ: 1726, 863, 281 cm^{-1}), Vala et al.[6] (B3LYP/6-311G*: 1721, 860, 266 cm^{-1}), and Endo et al.[17] [CCSD(T)/cc-pVTZ: 1694, 857, 276 cm^{-1}).



Scheme 1. Calculated [CCSD(T)(full)/6-311+G*; in parentheses: B3LYP/6-311+G*] relative energies of the C_3S isomers **T-5**, **S-5** and **12**; zero point energies are included; point groups in italics

Another important parameter is the energy required for the fragmentation of C_3S_2 (**4**) or C_3OS (**6**). The calculated relative energies of the fragments compared to the starting material molecules are given in Scheme 2. In all cases intersystem crossing must occur. Apart from the detailed mechanism of the photofragmentation, light of the wavelength 254 or 248 nm (112.6 or 115.3 kcal·mol^{-1}) could be sufficient for the photochemical generation of **T-5** from **6**. In the case where C_3S_2 (**4**) is the precursor molecule, the light energies are still in the range of the calculated dissociation energies.



Scheme 2. Calculated (B3LYP/6-311+G*) relative energies of the fragments expected upon photolysis of C_3S_2 (**4**) and C_3OS (**6**) together with the excited triplet states of **4** and **6**; zero point energies are included

Matrix Photolysis of Propadienedithione (4)

A gas mixture of **4** and argon (1:2000) was condensed on a spectroscopic window. A slow deposition rate and a temperature of 15 K (instead of the usual 10 K) were necessary to obtain an ideal isolation of the guest molecules (with no trapping of two molecules together in the same matrix cage). Upon irradiation of the matrix-isolated dithione **4** with light from low or high pressure mercury lamps no reaction could be observed. Only upon applying laser light of the wavelength 248 nm (KrF excimer laser) did the IR bands of **4** decrease with concurrent appearance of several new absorptions. A photochemical equilibrium was soon reached (Figure 1).

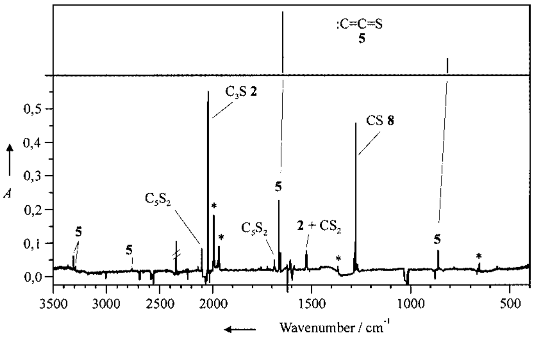


Figure 1. Top: calculated (B3LYP/6-311+G*) IR spectrum of triplet thioxoethenylidene C_2S **T-5**; bottom: difference IR spectrum (Ar, 10 K) of the photolysis of propadienedithione C_3S_2 **4** with 248 nm-light; positive bands increase and negative bands (not shown) diminish in intensity during irradiation. *: Unidentified absorptions

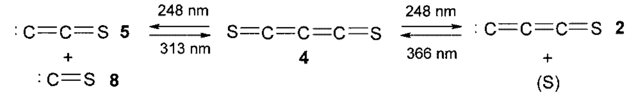
The new bands must be attributed to a mixture of CS, C_2S (**5**), C_3S (**2**), and C_5S_2. The bands of C_3S (**2**)[7,19] and C_5S_2 [20] could be identified by comparison with known spectra. The presence of C_2S (**5**) can be deduced from the comparison of the experimental and calculated IR absorptions (Table 1). The stretching vibration ν_1 is found at 1666.6 cm^{-1}, the vibration ν_2 at 862.7 cm^{-1}. From a weak combination band at 2763.4 cm^{-1} it can be deduced that the bending motion should be found at 230 to 240 cm^{-1}, in agreement with the theoretical prediction. The fourth experimental band at 3311.1 cm^{-1} corresponds to the overtone $2\nu_1$.

Table 1. Comparison of the theoretical (B3LYP/6-311+G*; relative intensities [km·mol^{-1}] in parentheses) IR absorptions of triplet C_2S **T-5** with the observed IR bands (bands are split and only the most intense line is given; Ar, 10 K; relative intensities in parentheses) of **5** after irradiation of C_3S_2 **4** with laser-light (248 nm)

		T-5, $\tilde{\nu}_{exp.}$ [cm^{-1}]	**T-5**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]
$2\nu_1$		3311.1 (14.8)	
$\nu_1 + \nu_2 + \nu_3$		2763.4 (2.3)	
ν_1	σ	1666.6 (100)	1645.2 (100)[a]
ν_2	σ	862.7 (18.9)	816.1 (24)
ν_3	π[b]	ca. 234[c]	237.7 (30)

[a] Absolute intensity: 54.5 km·mol^{-1}. [b] Doubly degenerate. [c] Calculated from combination band.

This experiment shows that upon irradiation with 248 nm laser light C_3S_2 (**4**) undergoes two parallel fragmentations, on the one hand into C_2S (**5**) and CS, and on the other hand into C_3S (**2**) and a sulfur atom. This behavior fits that predicted theoretically (Scheme 2). The reverse reactions can be initiated by irradiation with different wavelengths. As long as the fragments are in the same matrix cage, the bands of **5** diminish and those of **4** reappear upon irradiation at 313 nm (mercury lamp). In the same manner, the sulfur atom and **2** reform **4** by use of 366 nm light (mercury lamp).



Since C_3S_2 (**4**) is photostable under irradiation by the 254 nm line of a low pressure mercury light source one has to conclude that the high photon density is responsible for the effective fragmentation of **4** upon irradiation with the laser (2-photon process).

The detection of a small amount of C_5S_2 in the spectrum during laser photolysis (Figure 1) might be explained by recombination of a C_2S (**5**) and C_3S (**2**) molecule. This reaction is highly exothermic ($\Delta H_r = -133.8$ kcal·mol^{-1}; B3LYP/6-31G*).

Finally, it should be mentioned that the described IR spectrum of C_2S (**5**) corresponds closely to the dispersed fluorescence spectrum recently published by Endo et al. (vibrational frequencies at 1670.8, 857.8, and 266.6 cm^{-1}).[17a]

Matrix Photolysis of Thioxopropadienone 6

In contrast to C_3S_2 (**4**), oxocumulene C_3OS (**6**) did not decompose upon irradiation with an excimer KrF laser (248 nm). Instead, the desired fragmentation into C_2S (**5**) and CO was detected when the radiation of an ArF laser (193 nm) was used. In this case, the formation of small amounts of C_2S (**5**) and C_2O (**15**) was observed. A better yield of both species was achieved when the shorter 185 nm wavelength of a mercury lamp was applied. But again, even after a short irradiation time, a photoequilibrium was reached. The formation of C_2S (**5**) is indicated by absorptions at 3302.0, 1662.4, and 857.3 cm^{-1}. Two bands at 1972.5 and 1070.0 had to be assigned to C_2O (**15**). This oxygen analog of C_2S has been generated and identified using IR spectroscopy by Jacox et al. as early as 1965.[21] CS must also have been generated together with C_2O. This expectation was not confirmed by the IR spectrum, probably because the band of CS is obscured by a strong absorption of the starting material in that region. However, it was possible to prove the generation of CS using UV spectroscopy by the appearance of an absorption at 260 nm. The decomposition of C_3OS (**6**) into C_2O (**15**) and CS (**8**) is the first example of the generation of a CS fragment from a thioxocumulenone.

According to Scheme 2 a third possible pathway is the fragmentation of **6** into C_3O (**14**) and a sulfur atom. Experimental verification of this was not possible since the most intense IR absorption of **14** at 2243 cm^{-1} [22,23] is probably hidden by the stretching vibration ν_1 of the starting material **6**.

Similar to the C_3S_2 series, the photofragmentation of C_3OS **6** could be reversed. Upon irradiation of the matrix containing pairs of C_2S + CO and C_2O + CS with light of the wavelength 313 nm, **6** was reformed.

UV Spectrum of Thioxoethenylidene (5)

Additionally, formation of C_2S (**5**) upon irradiation of both the precursors **4** and **6** can be observed by UV spectroscopy. Matrix photolysis of **4** with λ = 248 and of **6** with λ = 193 or 185 nm leads to UV/Vis spectra which show, besides a broad intense band at 250 nm from the starting material and a signal for CS at 260 nm, a distinct absorption, with vibrational fine structure, in the range 280 to 340 nm (band origin at 335 nm) (Figure 2). We assign this absorption to C_2S **5**. In the long wavelength range a second, weak absorption between 750 and 1050 nm can be detected. Both absorptions are in accordance with the calculated spectrum of **T-5** (Table 2).

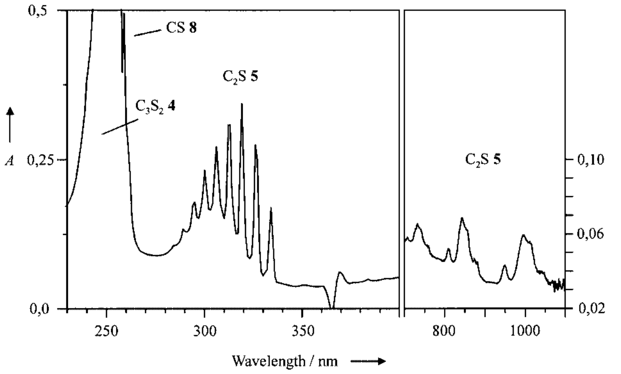


Figure 2. UV/Vis spectrum (Ar, 10 K) of thioxoethenylidene C_2S **T-5**, obtained after photolysis of propadienedithione C_3S_2 **4** with 248 nm-light

Our assignment of these bands to C_2S (**5**) is based on several facts. First, there is reasonable agreement with the calculated spectra. Second, all UV bands under discussion disappeared upon irradiation with 313 nm-light together with the corresponding IR absorptions. Third, the progression fits to the vibrational spectrum of **5**. For instance, the splitting of the short wavelength band (distances of 600 to 730 cm^{-1}) correlates with the expected stretching vibration ν_2* of the excited state of **5**. The vibrational fine structure of the long wavelength band of C_2S (**5**) (750 and 1050 nm) is even more complicated. Fortunately, this band has been analyzed in detail by Endo et al.,[17b] at least as far as the (1,0,0) ← (0,0,0), (2,0,0) ← (0,0,0), and (3,0,0) ← (0,0,0) transitions are concerned. The (0,0,0) ← (0,0,0) transition has not been reported by those authors. According to our spectra it lies in the range 950 to 1050 nm (Figure 2).

Van Der Waals Complexes of Thioxoethenylidene (5)

As can be seen in Figure 3 (bottom trace), the IR bands of C_2S (**5**) and CS (**8**), originating from matrix irradiation of C_3S_2 (**4**), are split. To find out whether this phenomenon is due to a matrix effect (different sites) annealing experiments were carried out. Warming of the matrix to 25 to 30 K for several minutes after photolysis with 248 nm-light resulted in decreases in the intensities of the bands of C_2S and CS, and of the additional fragment C_3S, while those of C_3S_2 became stronger. This means that the pairs C_2S + CS and C_3S + S recombine even at that very low temperature, and that the barrier for the thermal back reaction must be very low. A similar effect has already been observed by Jacox et al. for the recombination of C_2O (**15**) and CO (**13**).[21]

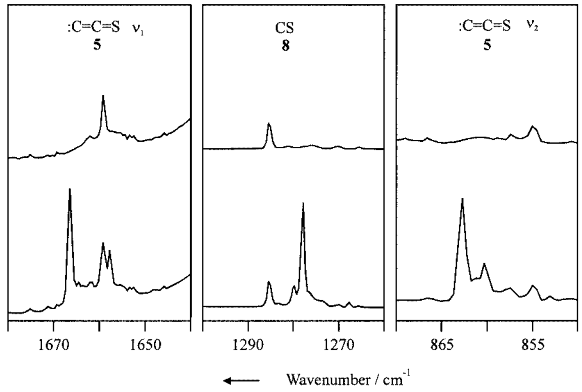


Figure 3. Portion of the IR spectrum (Ar, 10 K) of thioxoethenylidene C_2S **5**; bottom: IR spectrum directly after photolysis of propadienedithione C_3S_2 **4** with 248 nm-light; top: after secondary irradiation with λ > 660 nm

Exposure of the matrix to daylight after photofragmentation of C_3S_2 (**4**), resulted in a selective loss of some of the split signals. This process could be accelerated by irradiation with wavelengths λ > 600 nm. Under these conditions some signals remained unaffected (Figure 3, top trace), such as the band at 1659.1 cm^{-1}. This signal may be attributed to ν_1 of a specific C_2S molecule, which is not associated with the CS cofragment.

The same peculiarities were observed when C_3OS (**6**) was photolyzed in the matrix. Again the bands of C_2S and CO were split, but to a lesser extent. As described before, irradiation with daylight or long wavelength light (λ > 600 nm) led to the disappearance of some of the split signals.

All these observations can be explained by the assumption that, after photolysis, C_2S (**5**) exists in the form of different van der Waals complexes, which are isolated in the matrix cages. Some of them are preferred so that only a very small amount of energy (long wavelength light) is sufficient for the back reaction, while in other arrangements higher energies are necessary (for instance irradiation with 313 nm light).

Table 2. Comparison of the theoretical UV transitions (oscillator strengths in parentheses) of triplet C_2S **T-5** with the observed UV bands (Ar, 10 K) of **5** after irradiation of C_3S_2 **4** with laser-light (248 nm)

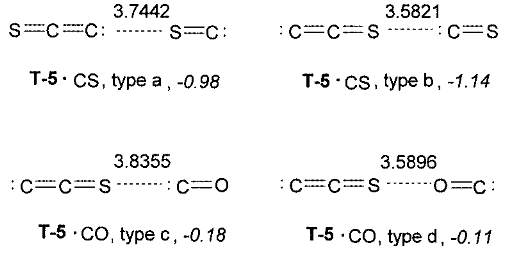
CIS-B3LYP/6-311+G* [nm]	TD-B3LYP/6-311+G* [nm]	Experiment [nm]
245.2 (0.2104) 502.7 (0.0092)	280.3 (0.0081) 850.4 (0.0002)	280−340 (strong) 750−1050 (weak)

Table 3. Theoretical (B3LYP/6-311+G*) IR band shifts $\Delta\nu$ (relative to the separated components; [cm^{-1}]) of van der Waals complexes between triplet **T-5** with CS and CO in comparison with the observed shifts (Ar, 10 K) of **5**, after irradiation of C_3S_2 (**4**) and C_3OS (**6**)

	$\Delta\tilde{\nu}_{calcd.}$ [cm^{-1}]		$\Delta\tilde{\nu}_{exp.}$ [cm^{-1}]		$\Delta\tilde{\nu}_{calcd.}$ [cm^{-1}]		$\Delta\tilde{\nu}_{exp.}$ [cm^{-1}]
type a	$\Delta\nu_1$	+1.9		type c	$\Delta\nu_1$	−2.1	
	$\Delta\nu_2$	+2.3			$\Delta\nu_2$	−2.1	
	$\Delta\nu_{CS}$	+2.2			$\Delta\nu_{CO}$	+6.3	
type b	$\Delta\nu_1$	−4.3		type d	$\Delta\nu_1$	−1.9	
	$\Delta\nu_2$	−3.8			$\Delta\nu_2$	−1.4	
	$\Delta\nu_{CS}$	+10.3			$\Delta\nu_{CO}$	−5.7	
$\Delta\Delta\nu$[a]	$\Delta\nu_1$	6.2	7.5	$\Delta\Delta\nu$[b]	$\Delta\nu_1$	0.2	1.0
	$\Delta\nu_2$	6.1	7.8		$\Delta\nu_2$	0.7	0.0
	$\Delta\nu_{CS}$	5.8	7.6		$\Delta\nu_{CO}$	12.0	4.0

[a] Type a − type b. [b] Type c − type d.

In order to get a rough idea about the kind of aggregations involved, we checked computationally whether, and to what degree, C_2S would be stabilized by complexation with CS and CO. It turned out that altogether four types of mutual interactions for **T-5** need to be considered (Scheme 3). Nonlinear atomic arrangements did not lead to computational minima. The frequencies of the calculated adducts in relation to the separated partners can be higher or lower. If one compares the calculated and experimental shifts (Table 3) one gets the impression that, in the case of CS complexation, the most intense lines belong to adduct **5**/CS, type a, and that the remaining species after $\lambda >$ 600 nm-irradiation is probably the differently oriented complex **5**/CS, type b.



Scheme 3. Calculated (B3LYP/6-311+G*) distances and stabilization energies of van der Waals complexes between **T-5** and CS or CO relative to the separated partners; distances are given in Å and energies (italics) in kcal·mol^{-1}

Conclusions

Photolysis of matrix-isolated propadienedithione **4** or thioxopropadienone **6** leads to thioxoethenylidene (**5**). The IR and UV/Vis spectra of **5** were measured for the first time in an argon matrix. The observations are in agreement with theoretical predictions and also agree with findings derived from laser induced fluorescence studies in the gas phase.[17] Under matrix conditions a special feature of C_2S (**5**) is its tendency to form van der Waals complexes with the accompanying partner molecules CS and CO.

Experimental Section

A Displex Closed-Cycle Refrigeration System CSW 202 from Air Products was used as the cryostat for matrix isolation. The matrix window was CsI and the spectrometer was a FTIR instrument (Bruker IFS 85). The light sources used were a mercury high pressure lamp (HBO, 200 from Osram) equipped with a monochromator (Bausch and Lomb), a mercury low pressure spiral lamp with a Vycor filter (Gräntzel), or an excimer laser LPX 105 MC from Lambda Physik.

Acknowledgments

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[1] *Sulfur Reports* **1999**, volume 21(4) (Guest Ed.: C. Th. Pedersen).

[2] [2a] S. Saito, K. Kawaguchi, S. Yamamoto, M. Ohishi, H. Suzuki, N. Kaifu, *Astrophys. J.* **1987**, *317*, L115−119. [2b] H. Suzuki, N. Kaifu, T. Miyaji, M. Morimoto, M. Ohishi, S. Saito, *Astrophys. J.* **1984**, *282*, 197−199. [2c] S. Yamamoto, S. Saito, K. Kawaguchi, Y. Chikada, H. Suzuki, N. Kaifu, S. Ichikawa, M. Ohishi, *Astrophys. J.* **1990**, *361*, 318−324. [2d] Summary: S. Saito, *Sulfur Reports* **1999**, *21*, 401−421.

[3] D. Sülzle, H. Schwarz, *Chem. Ber.* **1989**, *122*, 1803−1805.

[4] [4a] R. Flamming, Y. Van Haverbeke, M. W. Wong, C. Wentrup, *Rapid Commun. Mass Spectr.* **1995**, *9*, 203−208. [4b] Summary: R. Flamming, C. Wentrup, *Sulfur Reports* **1999**, *21*, 357−371.

[5] G. Maier, H. P. Reisenauer, R. Ruppel, *Sulfur Reports* **1999**, *21*, 335−355.

[6] J. Szepanski, R. Hodyss, J. Fuller, M. Vala, *J. Phys. Chem. A* **1999**, *103*, 2975−2981.

[7] G. Maier, J. Schrot, H. P. Reisenauer, R. Janoschek, *Chem. Ber.* **1991**, *124*, 2617−2622.

[8] G. Maier, H. P. Reisenauer, J. Schrot, R. Janoschek, *Angew. Chem.* **1990**, *102*, 1475−1477; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1464−1466.

[9] G. Maier, H. P. Reisenauer, R. Ruppel, *Angew. Chem.* **1997**, *109*, 1972−1973; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1862−1864.

[10] R. Ruppel, *Dissertation*, University of Giessen, **1999**.

[11] B. V. Lengyel, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 2960−2968.

[12] D. Koschel (Ed.), *Gmelin Handbuch der anorganischen Chemie, Kohlenstoff D4, 8th ed.,* p. 1, Springer Verlag, Heidelberg, **1977**.

[13] H. Bock, R. Dammel, D. Jaculi, *J. Am. Chem. Soc.* **1986**, *108*, 7844−7846.

[14] Y. Xie, H. F. Schaefer III, *J. Chem. Phys.* **1992**, *96*, 3714−3717.

[15] S. Lee, *Chem. Phys. Lett.* **1997**, *268*, 69−75.

[16] R. Janoschek, *Sulfur Reports* **1999**, *21*, 373−400.

[17] [17a] A. J. Schoeffler, H. Kohguchi, K. Hoshina, Y. Ohshima, Y. Endo, *J. Chem. Phys.* **2001**, *114*, 6142−6150. [17b] M. Nakajima, Y. Sumiyoshi, Y. Endo, *J. Chem. Phys.* **2002**, *117*, 9327−9338.

[18] [18a] Gaussian 94 (Revision D.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. W. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**. [18b] Gaussian 98 (Revision A.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

[19] S. Seeger, P. Botschwina, J. Flügge, H. P. Reisenauer, G. Maier, *J. Mol. Struct. (Theochem)* **1994**, *303*, 213−225.

[20] G. Maier, J. Schrot, H. P. Reisenauer, R. Janoschek, *Chem. Ber.* **1990**, *123*, 1753−1756.

[21] M. E. Jacox, D. E. Milligan, N. G. Moll, W. E. Thompson, *J. Chem. Phys.* **1965**, *43*, 3734−3746.

[22] G. Maier, H. P. Reisenauer, H. Balli, W. Brandt, R. Janoschek, *Angew. Chem.* **1990**, *102*, 920−923; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 905−908.

[23] P. Botschwina, H. P. Reisenauer, *Chem. Phys. Lett.* **1991**, *183*, 217−222.

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