Synthesis of Reactive Sulfines by Flash Vacuum Thermolysis: Thioformyl Cyanide *S*-Oxide and Thioxoethanal *S*-Oxide

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Thioformyl cyanide *S*-oxide and thioxoethanal *S*-oxide were synthesized by retro Diels–Alder cleavage of their dimethylanthracene adducts under flash vacuum thermolysis conditions. They were characterized by low-temperature IR and NMR spectroscopy. The formation of thioformyl cyanide *S*-oxide was also confirmed by mass spectrometry.

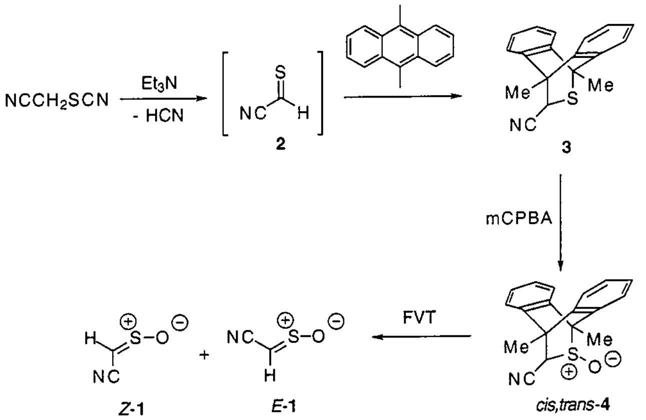
Introduction

Sulfines are the *S*-oxides of thiocarbonyl compounds. Thioketone *S*-oxides are generally stable.[1] This is not the case for thioaldehydes *S*-oxides which are more stable than the corresponding thioaldehydes, and yet are very reactive species.[2] The most studied sulfines are methanethial *S*-oxide,[3] the parent compound of the series, and propanethial *S*-oxide,[4] which has been identified as the lachrymatory factor of onion. We have been interested in the synthesis of α-functionalized thioaldehydes (thioxoethanal,[5] thioformyl cyanide,[6] α-iminothials[7]) and α-oxosulfines.[8] More recently, we have reported the synthesis of thioacrolein *S*-oxide.[9] In this paper, we present the first experimental observation of thioformyl cyanide *S*-oxide and some new results concerning thioxoethanal *S*-oxide. Some theoretical calculations are also reported.

Thioformyl Cyanide *S*-Oxide

The synthetic potential of sulfines is well established. In particular, they can be used in various reactions with nucleophiles[10] and in cycloadditions with 1,3-dienes[11][12] or dipolarophiles.[13] We thought that sulfines possessing a second functional group could be even more useful. This appears to be the case for thioformyl cyanide *S*-oxide **1**, which possess both the sulfine and cyano moieties. Furthermore, molecules containing simple fragments such as the cyano group or the formyl and thioformyl moieties are of special interest in the field of interstellar chemistry. This is the case for formyl cyanide (HCOCN)[14] and thioformyl cyanide (HCSCN),[15] which have been the subject of millimeter waves studies. Even though no sulfine has yet been found in the interstellar space, one can think of **1** as a potential interstellar molecule. In addition to its synthetic interest, this convinced us to study the sulfine **1**.

A precursor of **1** (Scheme 1) was obtained in two steps from 9,10-dimethylanthracene (DMA).[16] The reactive thioaldehyde **2** was generated by base-promoted elimination of HCN from $NCCH_2SCN$, and trapped by DMA. The resulting adduct **3** was oxidized by *m*-CPBA to yield sulfoxide **4** as a mixture of two isomers in the ratio 2:1. The configurations were assigned on the basis of the NMR shift of the HCCN proton. In the case of the major *cis*-isomer, this proton was affected by the shielding effect of the anisotropic magnetic field of the S−O group[17] and was observed at $\delta = 2.96$. The *trans* isomer was characterized by a singlet at $\delta = 4.04$. The same anisotropic effect was observed in the ^{13}C NMR spectrum in which the cyano carbon of the *trans* isomer was shielded: $\delta_{cis} = 114.7$; $\delta_{trans} = 111.9$.



Scheme 1. Synthesis of *Z*- and *E*-**1**

The first thermolyses were run using an FVT-MS (mass spectrometry) coupled apparatus. A scheme of this apparatus is presented in the Experimental Section. The thermolysis was effected at 550°C. The molecular ion gave the base peak (M^+: 87). Peaks corresponding to M−O (71, 11%) and M−OH (70, 20%) were also detected. Further evidence for the formation of **1** was obtained by determining the exact mass of the product. The measured mass was 86.9772, the calculated mass for **1** being 86.97788.

Low-temperature NMR spectroscopy also confirmed the formation of the cyano sulfine **1**. The volatile products of thermolysis of **4** at 550°C were trapped on a $CFCl_3$−

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Table 1. Calculated [B3LYP/6−31 + G(d, p) + 2df (S)] and experimental IR data for sulfine **1**

$\tilde{\nu}$	Experimental values [cm^{-1}]	Calculated values [cm^{-1}] [scaled values]	
		E	*Z*
CH	3010	3186 [3068]	3189 [3071]
CN	2205	2312 [2226]	2317 [2231]
CSO	1260, 1130	1306 [1258], 1176 [1132]	1343 [1293], 1203 [1158]
CH (out-of-plane)	767	767 [738]	721 [694]

CD_2Cl_2 matrix. The matrix was allowed to melt and the ^{1}H-NMR spectra were recorded at −100 °C and −60 °C. At −100 °C, only a poorly-resolved singlet was observed in the sulfinic proton region ($\delta = 8.42$). Two well-resolved singlets were observed at −60 °C at $\delta = 8.39$ (major) and $\delta = 8.36$ (minor). The observed ratio was ca 3:2. We assigned these signals to the two isomers of **1**. By analogy with other sulfines, the upper field singlet could be assigned to the *Z* isomer. In this case, the difference between the two shifts is too small (even nonexistent at −100 °C!) for a definitive assignment. On the other hand, the fact that the *Z* isomer is more stable than the *E* isomer for aliphatic sulfines has been attributed to the existence of an interaction between the negatively charged oxygen and an α-hydrogen atom. There is no such possibility in the case of **1** and therefore no reason that *Z*-**1** should be more stable than *E*-**1**. The theoretical calculations presented below will confirm that the energy difference between the two isomers should be very weak. We think that the obtained ratio is largely due to thermodynamic control, i.e. the initial (kinetic) mixture of the *Z*- and *E*-sulfines (ratio 2:1 according to the *cis*/*trans* ratio of precursor **4**) tends to give a nearly 1:1 mixture in the oven under the thermolysis conditions. However, it cannot be ruled out that such an equilibrium occurs in sulfoxide **3** before the retro Diels−Alder reaction takes place.

The ^{13}C-NMR spectrum of **1** was recorded at −90 °C. Four peaks were observed. According to a DEPT experiment and by analysis of the relative heights of these peaks, the following assignments were tentatively proposed: major *Z* isomer: $\delta = 150.6$ (CHSO), 111.0 (CN); minor *E* isomer: $\delta = 142.5$ (CHSO), 110.2 (CN).

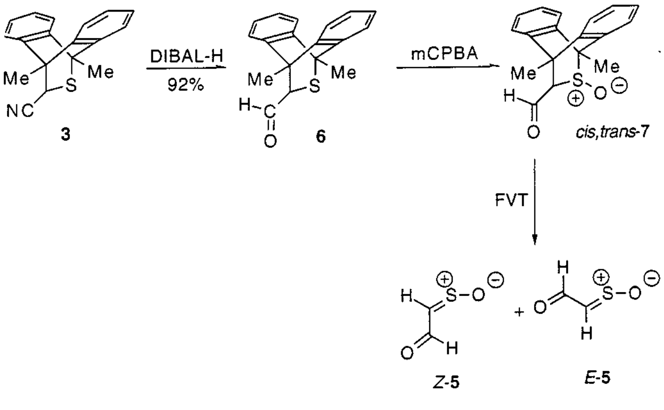
FVT-UV coupled experiments were also run. The volatile products obtained by thermolysis of precursor **4** were trapped at liquid-nitrogen temperature on a Suprasil plate. The UV/Vis spectrum of the obtained frozen product showed maxima at 262 and 278 nm and a shoulder at 256 nm. These bands disappeared upon warming the plate to −80 °C. Even though little information is available about the UV spectra of thioaldehyde *S*-oxides, these bands can be assigned to **1** with a reasonable degree of confidence. They are close to the absorptions reported for stable thioketone *S*-oxides.[18] Finally, the IR spectrum of the *E*/*Z* mixture of **1** was recorded. Bands were observed at 3010 [ν_{C-H}], 2205 [$\nu_{C\equiv N}$], 1260 and 1130 cm^{-1} (2 bands for the C=S−O function), further confirming the formation of the sulfine **1**. Furthermore, a band observed at 730 cm^{-1} was tentatively assigned to the C−H out-of-plane deformation. This band is similar to the one observed for the parent sulfine at 767 cm^{-1} (other bands for $H_2C{=}S{-}O$: 1357, 1165cm^{-1}).[19]

Theoretical calculations were undertaken (see Experimental Section for details of the employed bases). They indicate that the *Z*-**1** and *E*-**1** isomers present almost the same stability. The electronic energy difference *Z*-**1** − *E*-**1** is equal to −0.5 kJ mol^{-1} and becomes −0.8 kJ mol^{-1} when a larger basis set is used. Zero-point energy correction inverts the order of the relative stabilities (*Z*-**1** more stable than *E*-**1** by 0.2 kJ mol^{-1}). Finally, the entropy term favors the *Z* isomer and $\Delta G(Z) - \Delta G(E)$ is again slightly negative (−0.2 kJ mol^{-1}). These results are in good agreement with the observed ^{1}H-NMR ratio, the 3:2 ratio corresponding to 1 kJ mol^{-1} at 25 °C.

Theoretical IR spectra have also been calculated. Theoretical and experimental values are presented in Table 1. Theoretical values are higher than the experimental ones. However, if one uses a scaling factor of 0.963,[20] the "scaled values" are in better agreement with the observed ones, except for the ν_{CH} vibration which is then underestimated. Furthermore, the resolution of the experimental spectra was not good enough to allow a clear assignment of the peaks to the *Z* and/or *E* isomers. It is probable, however, that like in the NMR spectra, a ca. 1:1 mixture was present.

Thioxoethanal *S*-Oxide

In 1991, we reported the first synthesis of thioxoethanal *S*-oxide (**5**).[8] It was obtained by FVT of 2,3-dihydro-1,4-oxathiin *S*-oxide at 850 °C. It was characterized by photoelectron spectroscopy and IR spectroscopy. However, we



Scheme 2. Synthesis of *Z*- and *E*-**5**

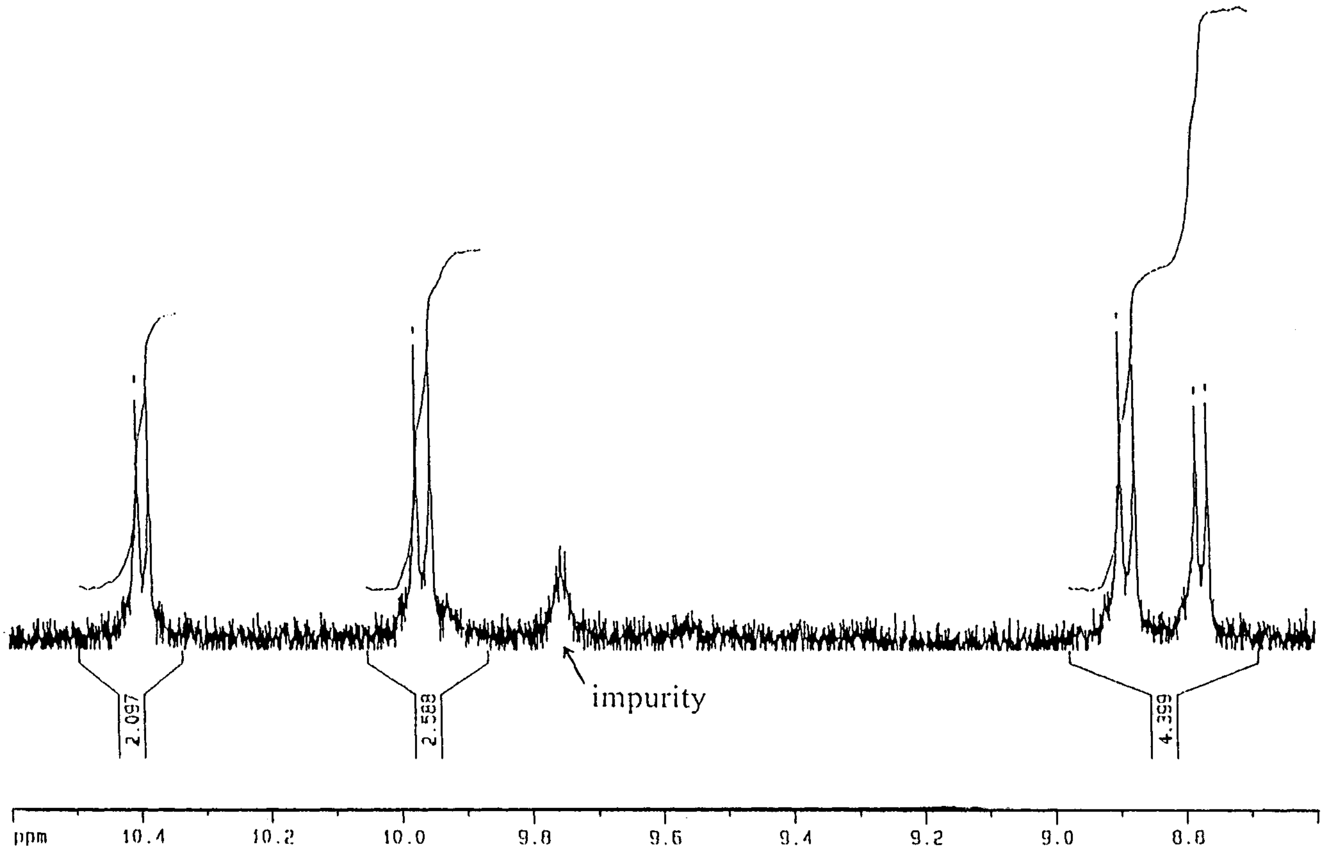


Figure 1. ^{1}H-NMR spectrum of sulfine **5** ($Z + E$) at 400 MHz

were unable to obtain a good NMR spectrum. We have now prepared the more efficient precursor **7** (Scheme 2) by oxidation of the corresponding sulfide **6**. As in the case of **4**, sulfoxide **7** was isolated as a mixture of isomers (*cis*/*trans* = 1:1).

The first experiments were run with an FVT-IR coupled apparatus, at an oven temperature of 600°C. Not surprisingly, the IR spectrum of the volatile product trapped on an NaCl plate at −196°C was similar to the spectrum described previously with major bands at 3020, 1660, 1230, 1120 and 1080 cm^{-1}. All these bands disappeared upon heating the plate to −50°C. The FVT-NMR experiments were more interesting. The spectrum obtained at −80°C is reported in Figure 1. Two doublets are observed, corresponding to the aldehyde proton ($\delta = 10.39$ and 9.96) and to the "sulfinic" proton ($\delta = 8.89$ and 8.77).

Theoretical calculations were carried out on two bases acting on the Z and E isomers (two conformers are possible in each case: *s-trans-Z*, *s-cis-Z* and *s-trans-E*, *s-cis-E*). The results are summarized in Figure 2. The *s-trans* isomers were found to be more stable than the corresponding *s-cis* ones. The energy difference between the two Z-sulfines is equal to 9 kJ mol^{-1} and to 17 kJ mol^{-1} for the E-sulfines. Overall, the *s-trans-E* conformer is predicted to be the most stable one. However, the energy difference between *s-trans-E*-**5** and *s-trans-Z*-**5** is rather small [at the B3LYP/6−31 + G(d,p) + 2df(S) level: $\Delta E = 0.6$ kJ mol^{-1}, $\Delta(E + ZPE) = 0.9$ kJ mol^{-1}, $\Delta(\Delta G) = 0.4$ kJ mol^{-1}]. This is in agreement with the nearly 1:1 ratio observed in the ^{1}H-NMR spectrum.

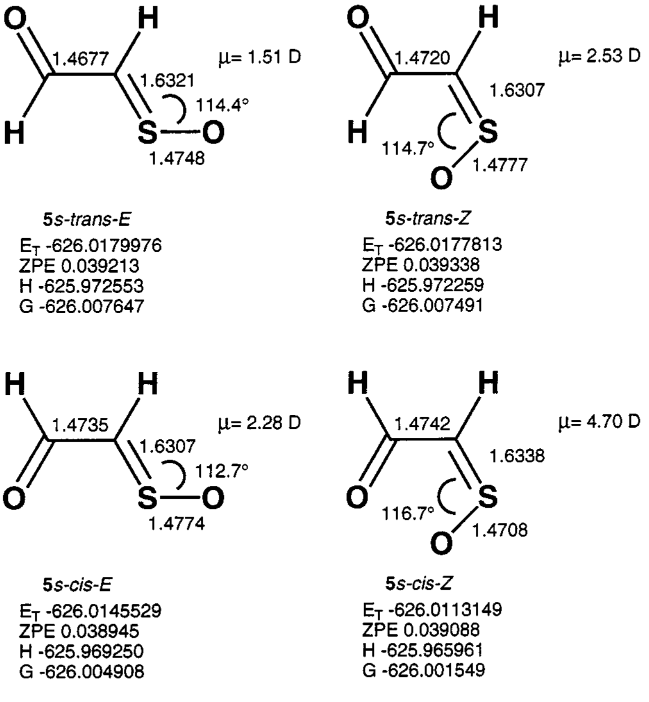


Figure 2. Optimized geometries and energetics of sulfine **5** at the B3LYP/6-31 + G(d,p) + 2df(S) level

Table 2. Calculated (B3LYP/6−31 + G(d, p) + 2df (S)) and experimental IR data for sulfine **5**

ṽ	Experimental values [cm^{-1}]	Calculated values [cm^{-1}] [scaled values]	
		E	*Z*
C(SO)−H	[a]	3198 [3080]	3189 [3071]
C(O)−H	3020	2951 [2841]	3017 [2905]
C=O	1660	1747 [1682]	1741 [1677]
CSO	1230, 1120, 1080	1266 [1219], 1169 [1125]	1294 [1246], 1182 [1138]
C(SO)−H (out-of-plane)	[a]	829 [798]	787 [758]

[a] Not detected.

Finally, theoretical and experimental IR data for **5***s-trans-E* and **5***s-trans-Z* are summarized in Table 2. If one takes into account the scaling factor (0.963), the theoretical bands are in good agreement with the experimental ones.

Experimental Section

The syntheses of **3** and **6** have been reported earlier.[21]

Oxidation of Sulfides 3 and 6. − General Procedure: Sulfide **3** or **6** (1 equiv.) was dissolved in dry dichloromethane. The resulting solution was cooled at 0°C and *m*-CPBA (1 equiv.) in dichloromethane was slowly added. The mixture was stirred for 1 h at room temperature. The solution was then treated with aqueous sodium hydroxide (7.5%) and extracted with CH_2Cl_2. The organic layer was separated, washed with water and dried with $MgSO_4$. Evaporation of the solvent and purification of the residue by column chromatography on silica gel (ethyl acetate/dichloromethane, 1:4) gave the expected sulfoxide as a mixture of stereoisomers. − The reported spectra are those of mixtures of *cis*/*trans* isomers. In the case of the ^{1}H-NMR spectra of **4** and **7**, we were able to clearly differentiate the two isomers. This was also the case in the ^{13}C-NMR spectrum of **4** but not in the ^{13}C-NMR spectrum of **7** for which we were unable to unambiguously assign all the peaks to each isomer.

Compound 4: Yield 76%. − IR (film): ṽ = 1078 cm^{-1} (S=O). − ^{1}H NMR (200 MHz, $CDCl_3$): ***cis*-4:** δ = 2.24 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.96 (s, 1 H, CH), 7.4−7.5 (m, 8 H, Ar-H); ***trans*-4:** δ = 2.26 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.04 (s, 1 H, CH), 7.4−7.5 (m, 8 H, Ar-H). − ^{13}C NMR (50 MHz, $CDCl_3$): ***cis*-4:** δ = 13.45, 17.27, 44.50, 66.63, 114.71 (CN), 122−140 (C-Ar); ***trans*-4:** δ = 13.56, 18.16, 44.72, 61.41, 111.87 (CN), 122−140 (C-Ar). − MS; *m*/*z* (%): 206 (100) [dimethylanthracene$^{\cdot+}$].

Compound 7: Yield 44%. − ^{1}H NMR (200 MHz, $CDCl_3$): ***cis*-7:** δ = 2.01 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.92 (d, 1 H, CH), 7.2−7.3 (m, 8 H, Ar-H), 9.19 (d, 1 H, CHO); ***trans*-7:** δ = 1.94 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 3.38 (d, 1 H, CH), 7.2−7.3 (m, 8 H, Ar-H), 8.63 (d, 1 H, CHO). − ^{13}C NMR (50 MHz, $CDCl_3$): **7:** δ = 13.65, 13.79, 43.90, 70.49, 85.64, 121−141 (C-Ar), 195.69, 198.70. − MS; *m*/*z* (%):296 (1) [M$^{\cdot+}$], 206 (100) [dimethylanthracene$^{\cdot+}$], 90 (8) [M$^{\cdot+}$−dimethylanthracene].

FVT of Compounds 4 and 7: The precursors (ca 30 mg) were thermolyzed at 550 or 600°C under 10^{-5} hPa in an empty quartz tube (dimensions: *l* = 10 cm, i.d. = 14 mm). The precursor was introduced into the warmed oven using a sliding spatula. − For mass analysis, the whole thermolysis system can slide into the direct introduction port of the mass spectrometer (Jeol GCmate) such that the oven is connected directly to the ionization chamber (Figure 3). For UV/Vis (Jobin−Yvon 201) or IR analysis (Perkin−Elmer 1420), the oven was coupled to the suitable cryostat allowing direct recording of spectra between −196 and 25°C. For NMR experiments (Bruker DRX 400), the volatile products of thermolysis were trapped at −196°C on a cold finger coated with a 50:50 CD_2Cl_2/$CFCl_3$ mixture.

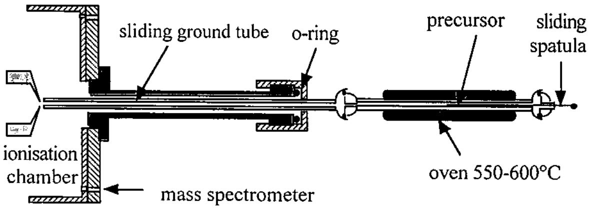


Figure 3. Coupling device used for the generation and mass analysis of thioformyl cyanide *S*-oxide **1**

Thioformylcyanide *S*-Oxide *Z*- and *E*-1: HR MS (C_2HNSO): calcd. 86.977876; found 86.977227; *m*/*z* (%) = 87 (M$^+$, 100), 76 (67), 71 (11), 70 (20), 64 (36), 60.5 (68), 59.5 (59), 56 (16), 55 (7). − UV/Vis (−196°C): 256 (sh), 262, 278 nm. − IR (−196°C): ṽ = 3010 (ν_{C-H}), 2205 ($\nu_{C\equiv N}$), 1260, 1130, 730 cm^{-1}. − ^{1}H NMR (−60°C, CD_2Cl_2/$CFCl_3$): δ = 8.39 (s, 1 H, *Z* isomer), 8.36 (s, 1 H, *E* isomer). − ^{13}C NMR (−90°C, CD_2Cl_2/$CFCl_3$): δ = 150.6 (d, CHSO, *Z* isomer), 142.5 (d, CHSO, *E* isomer), 111.0 (s, CN, *Z* isomer), 110.2 (s, CN, *E* isomer).

Thioxoethanal *S*-Oxide *Z*- and *E*-5: IR (−196°C): ṽ = 1160, 1230, 1120, 1080 cm^{-1}. − ^{1}H NMR (−80°C, CD_2Cl_2/$CFCl_3$): δ = 10.39 (d, *J* = 7.1 Hz, 1 H, CHO), 9.96 (d, *J* = 8.9 Hz, 1 H, CHO), 8.89 (d, *J* = 8.9 Hz, 1 H, HCSO), 8.77 (d, *J* = 7.1 Hz, 1 H, HCSO).

Calculations: Geometry optimizations and frequency calculations have been executed at the B3LYP/6−31 + G(d, p) + 2df (S) level of theory; large sets of polarization functions on the sulfur atom are necessary in order to obtain reliable geometries. The effect of basis set truncation on the relative energies has been tested by means of single-point calculations at the B3LYP/6-311 + G(3df, 2p) level.

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[1] [1a] B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1−27. − [1b] P. Metzner, *Phosphorus Sulfur Silicon* **1991**, *59*, 1−16.

[2] [2a] N. Pelloux-Léon, Y. Vallée, in *Gas Phase Reactions in Organic Synthesis* (Ed.:Y. Vallée), Gordon and Breach Publishers, Amsterdam, **1997**, pp. 275−303. − [2b] Y. Vallée, *Rev. Heteroatom Chem.* **1993**, *8*, 1−20.

[3] For instance: [3a] E. Block, R. E. Penn, R. J. Olsen, P. F. Sherwin, *J. Am. Chem. Soc.* **1976**, *98*, 1264−1265. − [3b] R. E. Penn, R. J. Olsen, *J. Mol. Spectrosc.* **1976**, *61*, 21−28.

[4] E. Block, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1135−1178; and references therein.

[5] F. Bourdon, J.-L. Ripoll, Y. Vallée, S. Lacombe, G. Pfister-Guillouzo, *J. Org. Chem.* **1990**, *55*, 2596−2600.

[6] G. Pfister-Guillouzo, F. Gracian, A. Senio, F. Bourdon, Y. Vallée, J.-L. Ripoll, *J. Am. Chem. Soc.* **1993**, *115*, 324−327.

[7] R. Arnaud, N. Pelloux-Léon, J.-L. Ripoll, Y. Vallée, *J. Chem. Soc., Perkin Trans. 2* **1995**, 1077−1086.

[8] F. Bourdon, J.-L. Ripoll, Y. Vallée, S. Lacombe, G. Pfister-Guillouzo, *New J. Chem.* **1991**, *15*, 533−537.

[9] N. Pelloux-Léon, R. Arnaud, J.-L. Ripoll, P. Beslin, Y. Vallée, *Tetrahedron Lett*. **1997**, *38*, 1385−1388.

[10] For instance: [10a] A. G. Schultz, R. H. Schlessinger, *J. Chem. Soc., Chem. Commun.* **1970**, 747−748. − [10b] G. E. Veenstra, B. Zwanenburg, *Tetrahedron* **1978**, *34*, 1585−1592. − [10c] C. Alayrac, F. Cerreta, F. Corbin, I. Chapron, P. Metzner, *Tetrahedron Lett*. **1996**, *37*, 4507−4510. − [10d] C. Leriverend, P. Metzner, A. Capperucci, A. Degl′Innocenti, *Tetrahedron* **1997**, *53*, 1323−1342.

[11] B. Zwanenburg, L. Thijs, J. B. Broens, J. Strating, *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 443−451.

[12] Unsaturated sulfines as dienes: S. Braverman, D. Grinstein, H. E. Gottlieb, *J. Chem. Soc., Perkin Trans. 1* **1998**, 103−107.

[13] B. F. Bonini, G. Maccagnani, G. Mazzanti, G. Rosini, E. Foresti, *J. Chem. Soc., Perkin Trans. 1* **1981**, 2322−2327.

[14] M. Bogey, J. L. Destombes, Y. Vallée,. J.-L. Ripoll, *Chem. Phys. Lett.* **1988**, *146*, 227−229.

[15] M. Bogey, C. Demuynck, J. L. Destombes, A. Gaumont, J. M. Denis, Yo. Vallée, J.-L. Ripoll, *J. Am. Chem. Soc.* **1989**, *111*, 7399−7402.

[16] N. Pelloux, Y. Vallée, V. Duchenet, *Phosphorus Sulfur Silicon* **1994**, *89*, 17−23.

[17] 17.Tangerman, B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 2* **1975**, 352.

[18] B. Zwanenburg, A. Wazenaar, L. Thijs, J. Streting, *J. Chem. Soc., Perkin Trans. 1* **1973**, 73−75.

[19] [19a] Y. Vallée, J. L. Ripoll, C. Lafon, G. Pfister-Guillouzo, *Can. J. Chem.* **1987**, *65*, 290−291. − [19b] D. L. Joo, D. J. Clouthier, C. P. Chan, W. M. Laï, E. S. F. Ma, A. Merer, *J. Mol. Spectr.* **1995**, *171*, 113−124. − [19c] E. Suzuki, R. Ishiguro, F. Watari, *J. Mol. Struct.* **1990**, *238*, 71−77.

[20] This value (0.963) was proposed by G. Rauhut, P. Pulay, *J. Chem. Phys.* **1995**, *99*, 3093. Other values have been proposed: L. Bauschlicher, *Chem. Phys. Lett.* **1995**, *246*, 40−43 (scaling factor: 0.98); A. S. Skokov, R. Wheeler, *J. Phys. Chem. A* **1999**, *103*, 4261−4269 (scaling factor 0.9614).

[21] R. Arnaud, N. Pelloux-Léon, J. L. Ripoll, Y. Vallée, *Tetrahedron Lett*. **1994**, *35,* 8389−8392.

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