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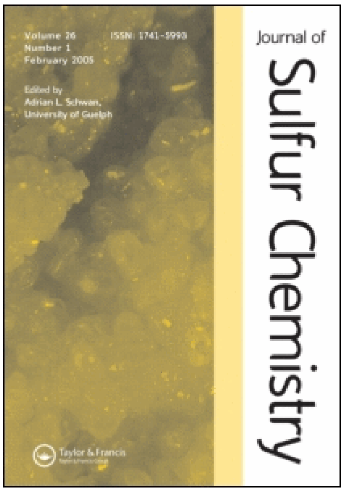

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The Thiosulfine-Dithiirane-Dithioester Manifold $R^1R^2(CS_2)$

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THE THIOSULFINE–DITHIIRANE–DITHIOESTER MANIFOLD $R^1R^2(CS_2)$

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The Thiosulfine–Dithiirane–Dithioester Manifold (TDDM) is described in detail, based on both theoretical and experimental findings, and its implications for synthetic organic chemistry discussed. Results of numerous new quantum chemical calculations obtained at the hybrid HF/DFT and beyond-HF *ab initio* level are reported, focusing particular attention upon the structure and the properties of thiosulfines.

Keywords: ab initio, quantum chemistry, density functional theory, dithiiranes, dithioesters, pericyclic reactions, thiosulfines

CONTENTS

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1. INTRODUCTION

In the light of recent dramatic developments in the chemistry of thiosulfines **1** and dithiiranes **2** (for selected reviews and other important source papers see Refs. [1–11]), including so far unpublished significant progress in our own laboratories, we wish to summarize and consolidate contemporary views on the Thiosulfine–Dithiirane–Dithioester Manifold (TDDM). The present status paper does not intend to give a chronographic overview of events, nor does it contain a complete

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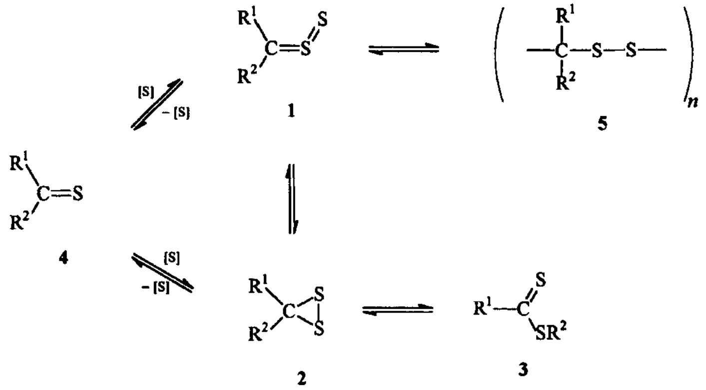
bibliography. However, adequate overall bibliographic coverage is provided by the cited papers and the literature cited therein. Also, online substructure searches in the CAS Registry File and in Beilstein Crossfire have been carried out (in July, 1997) to ensure up-to-date coverage. We have chosen to emphasize synthetic aspects of the TDDM while, for instance, spectroscopy and environmentally oriented work can be retrieved via the cited literature.

2. THE TDDM CONCEPT

Based on literature data as well as on own experimentation one of us systematized and defined the TDDM (Scheme 1).[1–3]



SCHEME 1

Its basic implications are:

(a) Thiosulfines **1** might be formed by thiation of thiocarbonyl compounds **4**:

$$\mathbf{4} + [\mathrm{S}] \rightarrow \mathbf{1} \tag{1}$$

(b) Dithiiranes **2** might be formed by thiation of thiocarbonyl compounds **4**:

$$\mathbf{4} + [\mathrm{S}] \rightarrow \mathbf{2} \tag{2}$$

(c) Thiosulfines **1** might decay to **4** by carrier mediated loss of the terminal sulfur atom:

$$\mathbf{1} \rightarrow \mathbf{4} + [\mathrm{S}] \tag{3}$$

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(d) Dithiiranes **2** might decay to **4** by carrier mediated loss of one sulfur atom:

$$\mathbf{2} \rightarrow \mathbf{4} + [\mathrm{S}] \tag{4}$$

(e) Thiosulfines **1** might be in equilibrium with the tautomeric dithiiranes **2**:

$$\mathbf{1} \leftrightarrows \mathbf{2} \tag{5}$$

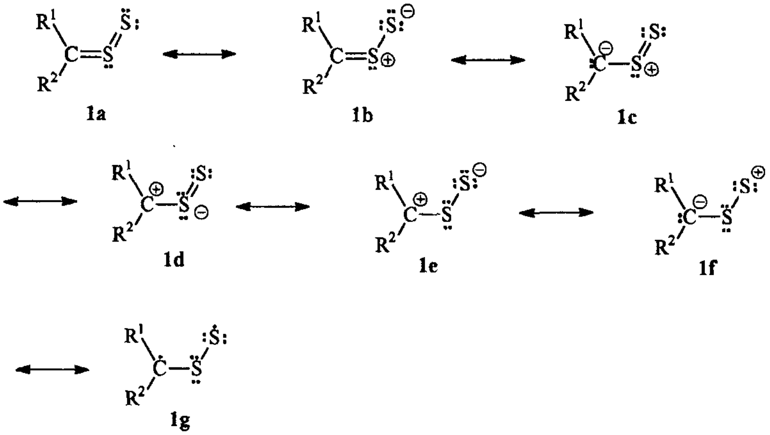
(f) Dithiiranes **2** might be in equilibrium with the tautomeric dithioesters **3**:

$$\mathbf{2} \leftrightarrows \mathbf{3} \tag{6}$$

(g) Thiosulfines **1** might be in equilibrium with their oligomers **5**:

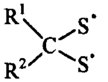
$$n\,\mathbf{1} \leftrightarrows \mathbf{5} \tag{7}$$

A theoretical follow-up by So[12] with MP2 calculations with HF/3-21G$^{(*)}$ optimized geometries gave the relative stabilities of the parent compounds ($R^1 = R^2 = H$) as **3** > **2** > **1**.



Moreover, resonance structures **1a-g** must be included in any consideration of thiosulfine **1** chemistry. For the sake of convenience and brevity in our subsequent discussions the class name thiosulfine and the single resonance structure **1a** will be used to symbolize the full set of resonance structures **1a-g** without any prejudice concerning the relative weights of these structures. When individual **1** are discussed *S*-sulfide names will frequently be used as the least cumbersome, again without any prejudice as to the relative weights of the resonance structures **1a-g** in the case in question. Also, it is understood that Scheme 1 and the derived Eqs. (1)–(7) do not imply any restrictions on the choice of R^1 and R^2. Thus, the dithioesters **3** include compounds which are not dithiocarboxylic acid esters, i.e. compounds where R^1 can contain a key atom different from hydrogen or carbon and/or R^2 a key atom different from carbon. By the same token, formula **4** for thiocarbonyl compounds comprises, but is by no means limited to, thioketones. For IUPAC's name recommendations for **1**, see Ref. [13].

The singlet and the triplet biradical species **6**, while closely related to **2**, do not appear to have been observed nor implied in any known preparative chemistry.



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3. THEORETICAL ASPECTS

3.1. Introductory Remarks

If the experimental geometries and the energetics of molecular structures are sufficiently known empirical forces can be defined to reproduce the experimental data quite well ("Force Field Methods", *Molecular Mechanics*, MM).[14] As long as the same types of bonds are present this approach is very successful in modeling the structures of unknown organic compounds. It is widely used for compounds of classical structure, i.e. structures describable by simple formulas without charge separation or free valencies.

The MM method may partially or completely fail, however, if the molecules are of non-classical structure or if the molecules contain atoms with non-standard valencies not considered in the parametrization. It generally fails for transition structures of chemical reactions.

In the latter case no experimental parameters are available to calibrate the empirical force field. Since the MM method does not treat electrons explicitly it is also unable to describe ionization, electron excitation, and other processes which are immediately caused by electrons. In these and other cases the application of quantum chemistry is required.

Semiempirical quantum chemical methods are a more generally applicable way to predict physical and chemical properties without high computational expenditure. In general, these methods are parametrized within a single configurational description. Methods dubbed with the acronyms MNDO, AM1, and PM3 have been successfully used for molecules containing first- and second-row element atoms.[15] Calculations of structures containing heavier elements provide less accurate results or cannot be carried out in want of appropriate parameters. Efforts have been made more recently to extend this approach by explicit consideration of d-orbitals in this approximation. Examples of this methodology are ZINDO,[16] SINDO,[17] and MNDO/d.[18] Since these methods are parametrized for the single configuration approach numerical predictions by more refined semiempirical methods beyond the single approximation approach are less useful unless reparametrization is performed. An alternative to this procedure is to avoid parametrization altogether by taking resort to purely theoretical quantum chemical methods.

Caution should be exercized when treating thiosulfines **1** and related compounds within the single configuration approach. The peculiar features of **1** are already obvious from their representation by structural formulas. Polar Lewis–Kekulé type structures (**1b-f**), the hypervalent type structure **1a**, and the singlet biradical structure **1g** need to be invoked.

As basically shown by Salem and Rowland[19] ylidic (ionic) and biradicaloid structures are two components of a unique theoretical description for cases where the single electron configuration approach is insufficient. Formula **1g** also suggests that the corresponding triplet molecule should lie close in energy to the singlet molecule. A singlet–triplet splitting is then expected to be lower in energy for thiosulfines than for any classical structure of the same molecular size. *Ab initio* quantum chemical calculations of thiosulfines show that the solution of the single configuration description is unstable with respect to the triplet state (“RHF/UHF instability”). This means that the simplest

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ab initio approach, i.e. RHF, should not be employed. There is a need to use the correlation method of quantum chemistry.

The theoretical results reported in the present paper have been obtained with "exact" first-principles methods which include electron correlation. The term "exact" refers to a strict nonempirical theoretical treatment based on quantum mechanics. Two, completely different, methods have proven themselves as valuable tools in chemistry. The first one is based on Schrödinger's wavefunction (the wavefunction based *ab initio* method, wavefunction theory, WFT[20]), the second on the electron density (density functional theory, DFT[21]). Much experience has been gathered concerning the first type of methods over the past years. Within *ab initio* methods it is well known how to improve the accuracy of the calculation. The only question is how expensive the calculation in question will be or if it can be carried out at all at present. DFT has only recently entered applied quantum chemistry. Here it is not yet known how to systematically improve the level of theory. However, recent calculations show that DFT computations are less expensive and can be performed with more modest computer resources than equally accurate conventional *ab initio* quantum chemical calculations.

The following paragraphs briefly explain the theoretical methods used in this study. Our *ab initio* calculations are based on the single-determinant Hartree–Fock (HF) approach. This means that the many-electron wavefunction refers to a single-electron configuration with the lowest-energy MOs occupied in the zeroth-order ground state. In order to remedy deficiencies due to the averaged electronic interaction in the HF scheme some mixing of the above-mentioned zeroth-order ground state configuration with excited-state configurations is introduced (post-HF methods). This is usually done with perturbation theory (Møller–Plesset perturbation theory of second order, MP2) or with configuration interaction (e.g. quadratic configuration interaction including triples perturbatively, QCSD(T)[20]). Thus, correlation energy is partially considered (correlation methods). Unfortunately, the computing time scales with N^4 (or even higher orders) where N is the number of electrons.

DFT differs from HF by its consideration to some extent of electron correlation by the correlation functionals. As shown by numerous benchmark calculations the results obtained by DFT methods may be comparable in accuracy or even superior to those of post-HF methods such as MP2. Moreover, the computation time scales with N^3.

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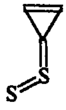
This allows calculations for larger compounds. There is, however, no generally accepted concept of how to define improved functionals. One of the best exchange-correlation functionals currently known is the B3LYP functional.[22,23] This functional has been used exclusively in the present study.

To the best of our knowledge neither post-HF nor DFT calculations of thiosulfines are on record. In the present paper the parent structure **1** ($R^1 = R^2 = H$) has been considered in most detail with high level quantum chemical methods. In addition, a number of derivatives, including several ones with conjugated carbocyclic rings, and several related compounds, have been investigated.

Thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) is formally derived from thioformaldehyde **4** ($R^1 = R^2 = H$) by the addition of a sulfur atom. Compound **1** ($R^1 = R^2 = H$) can also be regarded as a thio derivative of thioformaldehyde *S*-methylide **A** ($X = CH_2$, cf. Eq. (8)). By the same token, **1** ($R^1 = R^2 = H$) is a thio derivative of thioformaldehyde *S*-oxide **A** ($X = O$).

Our theoretical study also deals with the thiosulfine/dithiirane pairs **1**/**2** ($R^1 = R^2 = Me$), **1**/**2** ($R^1 = R^2 = Cl$), and **1**/**2** ($R^1 = Me$, $R^2 = Ph$), as well as with the thiosulfine/dithiirane pairs **7**/**8**, **9**/**10**, **11**/**12**, **13**/**14**.



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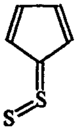

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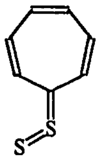

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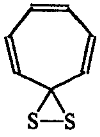

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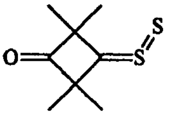

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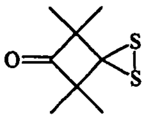

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3.2. Computational Methodology

Our compounds were investigated by conventional *ab initio* quantum theory and by DFT in the shape of the GAUSSIAN-94 suite of

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programs.[24] Pople basis sets were used throughout this study. Most of the calculations were performed with the 6-31+G(d,p) (=6-31+G**) basis set where "+" designates the inclusion of a set of diffuse functions on heavy atoms, "d" d-type polarization functions on heavy atoms, and "p" p-type polarization functions on hydrogen atoms. Higher angular-momentum functions are considered by the basis sets 6-31+G(3df,2pd). The polarization as well the diffuse functions affect the relative energies,[25] the molecular geometries,[26a] and the electronic charge distributions.[26b]

The *ab initio* calculations were performed at the beyond-Hartree–Fock level.[20] The Gaussian-1 (G1), Gaussian-2 (G2), and the more efficient G2(MP2) method make use of the Møller–Plesset perturbation method adding further corrections for basis set effects and for electron correlation contributions.[27] G2(MP2), for example, corresponds approximately to the QCISD(T)/6-31+G(3df, 2p) level of theory. These methods include the calculation of zero-point vibrational energies (ZPVE). The thermodynamic data are obtained by thermodynamic statistics based on the ideal-gas rigid-rotor harmonic-oscillator model. Some more expensive geometry optimizations at the QCISD(T)/6-31+G** level allowed the effect of electron correlation on geometry to be estimated. The geometries were fully optimized by analytical gradient techniques. The transition structures were found by the QST2 procedure. Stationary points, minima, and saddle points of the parent compounds were characterized by the number of negative eigenvalues of the Hessian matrix (0 for minima and 1 for saddle points, respectively). The connection between the transition structures, the reactants, and the products was established by the intrinsic reaction coordinate as cited in GAUSSIAN-94.

The DFT calculations were performed with gradient-corrected (non-local) hybrid HF functional B3LYP (Becke's three-parameter Lee–Yang–Parr functional).[22] Triplet molecules were optimized by means of the unrestricted Kohn–Sham DFT approximation. The spin contamination is indicated by the expectation values $\langle S^2 \rangle$. The calculated values are less than 2.01 for the triplet molecules before annihilation (exact value 2). The total energies of the geometry optimized singlets and triplets provide the adiabatic singlet/triplet (S_0/T_1) splitting energies. In contrast to RHF calculations DFT calculations do not generate spin contaminated singlet ground states.

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In other words, thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) is singlet/triplet stable.

The understanding of the electron structures of our molecules may also be increased by the knowledge of quantities such as atomic charges and bond orders. Because of the extensive basis sets utilized in the present study atomic charges are calculated according to Weinhold's natural population analysis (NPA)[28] and by Bader's "Atoms-in-Molecules" (AIM) topological theory[29] rather than to Mulliken population analysis. Bond orders are defined by Weinhold's Natural Resonance Theory[28] and Cioslowski's AOM-derived (atomic overlap matrix derived) covalent bond order within the AIM approach.[30] NRT provides a description in terms of Lewis structures. In the case of DFT the electronic distribution was derived from the SCF-converged Kohn–Sham orbitals.

The normal modes of the vibrational spectra are calculated with harmonic frequencies by means of the Hessian matrix.[31] In order to take into account systematic errors the frequencies are scaled down by a uniform factor.

The lowest-energy excitation energies in the UV/Vis region are calculated by configuration interaction between all singly-substituted determinants using the RHF reference states (RCIS).[32]

NMR chemical shifts are obtained by the GIAO (gauge invariant atomic orbital)-SCF method.[33] NICS (nucleus independent chemical shift) values have, more recently, been introduced by Schleyer *et al.*[34] These values given in ppm are calculated at the centers of conjugated ring systems and are the negative of the magnetic shielding at this position. They have proved themselves to be an effective probe for aromaticity and antiaromaticity.

The total energies of geometry optimized structures are collected in Tables A and B in the Appendix.

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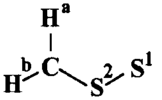
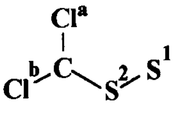
3.3. Results and Discussion

3.3.1. Structures

Table I contains the geometrical parameters of the parent thiosulfine **1** ($R^1 = R^2 = H$) and of **1** ($R^1 = R^2 = Cl$) calculated at two different levels of theory. As expected the skeleton is bent with a CSS angle of about

TABLE I Geometric parameters (bond lengths in Å, bond angles in deg.) of thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) and thiophosgene *S*-sulfide **1** ($R^1 = R^2 = Cl$) at different levels of theory[a,b]

	DFT (*B3LYP*)		*MP2* (*full*)	
	6-31+G(d,p)	6-311+G(3df,3pd)	6-31+G(d,p)	6-311+G(3df,2p)
				
S^1S^2	1.973	1.939	1.930	1.904
CS^2	1.639	1.620	1.638	1.619
CH^a	1.085	1.080	1.081	1.082
CH^b	1.086	1.081	1.080	1.082
S^1S^2C	114.4	115.0	114.8	115.4
SCH^a	122.8	122.9	122.3	122.6
SCH^b	116.5	116.3	116.2	115.6
$S^1S^2CH^a$	0.0	0.0	0.0	0.0
				
S^1S^2	1.970	1.939	1.925	1.947
CS	1.679	1.659	1.677	1.671
CCl^a	1.706	1.693	1.695	1.713
CCl^b	1.728	1.715	1.714	1.735
S^1S^2C	113.1	113.5	113.0	113.0
S^2CCl^a	124.6	124.6	123.5	124.3
S^2CCl^b	117.9	117.7	117.9	118.0
$S^1S^2CCl^a$	0.0	0.0	0.0	0.0

[a] Bond lengths of thioformaldehyde *S*-sulfide in Å calculated by post-Hartree–Fock methods: *QCISD*/6-31+G(d,p): CS 1.640, SS 1.973; *QCISD(T)*/6-31+G(d,p): CS 1.652, SS 1.972; *CCD*/6-31+G(d,p): CS 1.627, SS 1.949.

[b] CS bond lengths calculated by B3LYP/6-31+G(d,p) for comparison: $H_2C{=}S$ 1.614 Å (exp. 1.611 Å[35]); $H_2C{=}S^+{-}O^-$ 1.626 Å (exp. 1.610 Å[35]); S_2 1.929 Å; $Cl_2C{=}S$ 1.610 Å.

115°. The stretched conformation with a CSS angle of 180° is about 37 kcal/mol higher in energy (DFT). Especially revealing features are the CS and SS bond lengths. The CS bond length is 1.639 Å at the B3LYP/6-31+G** level and only about 0.02 Å longer than the corresponding bond in thioformaldehyde **4** ($R^1 = R^2 = H$) (calc. 1.618 Å, exp. 1.611 Å (MW)).[35] The SS bond length of 1.973 Å is shorter than that of disulfanes (H_2S_2: 2.055 Å),[35] but longer than the bond in S_2 (calc. (DFT) 1.929 Å, exp. 1.891 Å (MW)[35]). The latter formally results by the removal of CH_2 from **1** ($R^1 = R^2 = H$). These geometric

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data suggest a structure of **1** ($R^1 = R^2 = H$) with a CS bond of overwhelmingly double bond character. A similarly straightforward conclusion about the nature of the SS bond cannot be reached in want of a proper reference molecule.

Significantly different bond lengths are obtained depending on the choice of basis set, i.e. 6-31+G(3df,3pd) or 6-31+G(p,d), for the DFT (B3LYP) calculations. The SS bonds are most strongly affected with a contraction of about 0.3 Å. The geometric parameters predicted by DFT calculations are rather similar to those predicted by MP2 *ab initio* calculations. The DFT bond lengths are, in general, slightly larger than those obtained by MP2 theory, and probably somewhat overestimated. This is in accordance with the general experience with bonds involving third-row elements such as sulfur.[26] Increased consideration of electron correlation is expected to counteract the extended basis set's contraction of bond lengths. Thus, bond lengths of 1.63 Å for CS and 1.93 Å for SS appear most realistic. The only remarkable difference between the parent and the dichloro compound is a CS bond elongation of 0.04 Å in the latter.

Additional information concerning **1** ($R^1 = R^2 = H$) can be gained from natural population analysis (NPA) and natural resonance theory (NRT) based on the results of DFT and *ab initio* quantum chemical calculations, Table II and Figure 1.

According to the NRT analysis summarized in Figure 1 the contribution of the resonance structure **1b** to the electronic structure of **1** ($R^1 = R^2 = H$) amounts to 61%. The contribution of **1c** is considerably lower (15%). There are no appreciable contributions of the resonance structures **1d** to **1f**. 1,3-Charge separated structures of compounds related to **1e** were originally introduced to describe the 1,3-dipolar nature of the reactive species. However, structures like these were later refuted by Huisgen in favor of **1b**-type structures.[36] The charges in resonance structures correspond to π-charges rather than to total atomic charges. The reactive nature of the 1,3-dipole seems to be better indicated by the biradicaloid structure **1g**. This structure is related to a resonance structure with spin-pairing of the atoms in the 1- and 3-positions which contributes to an extent of 21% (cf. Figure 1). The presence of this resonance structure was also verified for related compounds of the series **A** except for **A**, X = O. Interestingly, the latter compound behaves differently in that no thermal electrocyclic ring

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TABLE II NPA charges q and NRT bond orders p and AIM charges q and AOM-based bond orders p of **1** ($R^1 = R^2 = H$)[a] calculated by DFT and *ab initio* quantum chemical calculations.[b] Dipole moments μ are given in Debye

	DFT (B3LYP)		*MP2(full)*		*QCISD*		*CCD*	
	NPA	AIM	NPA	AIM	NPA	AIM	NPA	AIM
q_{CH_2}	−0.16	−0.40	−0.23	−0.45	−0.14	−0.43	−0.19	−0.50
q_{S^2}	+0.51	+0.63	+0.55	+0.65	+0.50	+0.67	+0.58	+0.74
q_{S^1}	−0.35	−0.23	−0.32	−0.20	−0.36	−0.24	−0.39	−0.24
p_{CS}	1.62	2.01	1.44	1.93	1.52	1.81	1.78	1.87
p_{SS}	1.15	1.60	1.28	1.62	1.23	1.43	1.19	1.54
μ	3.42		2.77		3.55		3.47	

[a] CS bond orders for comparison (B3LYP/6-31+G**): thioformaldehyde p_{CS} (NRT) = 2.04, p_{CS} (AIM) = 2.01.

[b] Basis set 6-31+G**; MP2/QCI/CC densities.

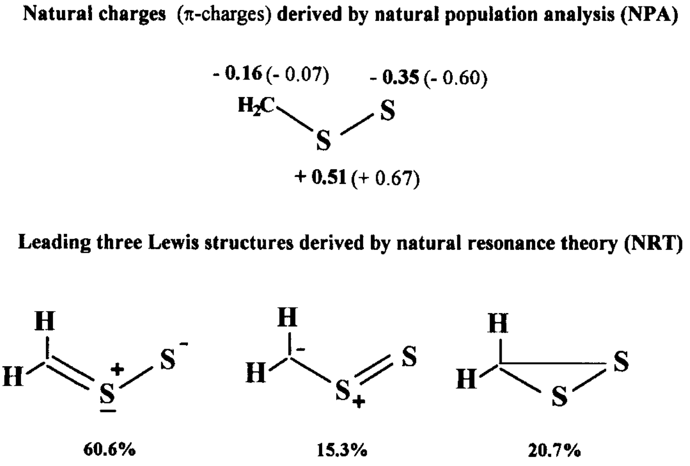

FIGURE 1 Charges and leading resonance structures of **1** ($R^1 = R^2 = H$) calculated from DFT electron densities (B3LYP/6-31+G**).

closure was found. In all cases considered, the NRT analysis (default option) does not support the hypervalent structure **1a**. The valency of the central sulfur atom is less than 3. The d-orbital participation to its valency is negligibly small.

Although AIM is a model completely different from NPA the main conclusions remain the same (cf. Table II). The CS bond is strong compared to the SS bond. However, the double-bond character of both

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bonds is more strongly developed than according to NRT calculations. Concomitant with the enhanced bond strengths the charge at the terminal sulfur atom, about −0.20, is remarkably small and the ionicity of the SS bond correspondingly feeble (about 20%).

A comparison of **1** ($R^1 = R^2 = H$) with **A** ($X = CH_2$) reveals substantial dissimilarities. In the latter case both CS bonds are relatively short and strong and only partially localized. The AOM localization procedure based on AIM predicts a delocalized allyl-type 4e–3c bond system. Such a three-center bond is absent in **1** ($R^1 = R^2 = H$) and a number of related compounds.

In spite of the ylidic nature of **1** ($R^1 = R^2 = H$) its calculated dipole moment (approximately 3 D, by DFT; cf. Table II) is rather small. As a consequence solvent effects must be expected to be negligible.

The calculated geometries of the thiosulfine groups of more complex thiosulfines differ only slightly from that of the parent compound; representative examples are shown in Figure 2. In general the CS bonds of these derivatives are somewhat elongated. The conjugated

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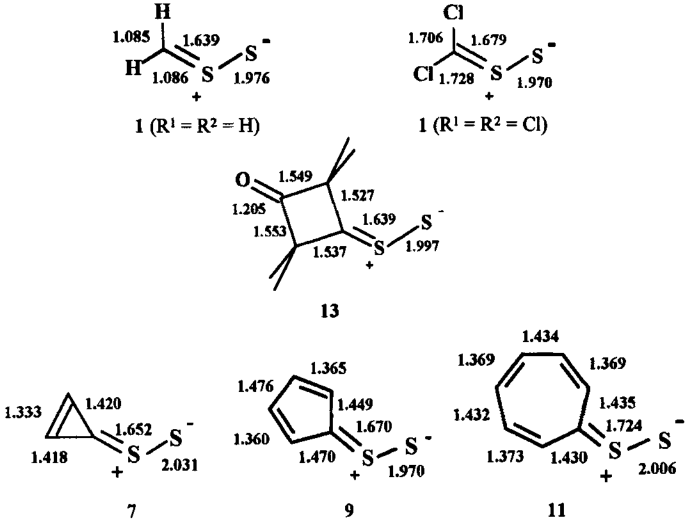

FIGURE 2 Selected bond lengths of thiocarbonyl *S*-sulfides in Å calculated at the B3LYP/6-31+G** level of theory. Calculated dipole moments: **7**: 7.9 D, **9**: 2.9 D.

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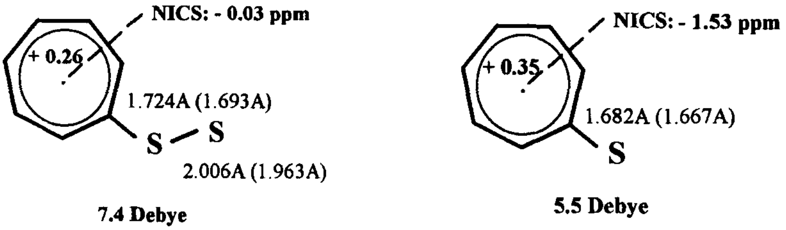
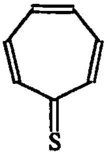


FIGURE 3 Selected bond lengths (B3LYP/6-31+G**, MP2/6-31+G** in parentheses), dipole moments and π-charges of the seven-membered rings (B3LYP/6-31+G**) and NICS (Nucleus Independent Chemical Shift) values of tropothione *S*-sulfide **11** and of tropothione **15** (SCF-GIAO/6-31+G*//B3LYP/6-31+G**).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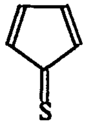
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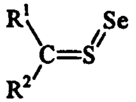
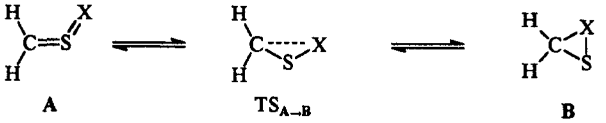

18

thiosulfines **7**, **9**, and **11** exhibit (as do their parent thiones **16**, **17** and **15**) a pronounced CC bond length alternation which decreases from the three-membered towards the seven-membered ring. Tropothione *S*-sulfide **11** contains the most elongated CS and SS bonds in this series.

Because of **11**'s particular features its data deserve a more detailed discussion. As shown in Figure 3 already the parent tropothione **15** contains a long CS bond. This prediction agrees well with **15**'s experimental CS bond length of 1.676 Å (determined by X-ray diffraction).[37] Nevertheless a tropylium thiolate-type structure for **15** is not indicated by the calculated total charge and the π-charge of the seven-membered ring which is far from +1 as expected of the zwitterion. As an indicator of possible aromatic delocalization in the carbocyclic rings of **11** and **15** we have applied Schleyer's NICS criterion of NMR chemical shift. With NICS values of about zero both compounds appear non-aromatic. However, in spite of their strong bond localizations and their small net charge shifts from the seven-membered ring to the exocyclic group the calculated dipole moments of **11** and **15** are remarkably large. In the case of **15**, where a comparison with the experimental dipole moment (4.42 D in benzene)[37c] is possible, the calculated value is overestimated.

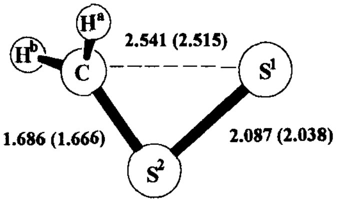
3.3.2. Pericyclic Reactions



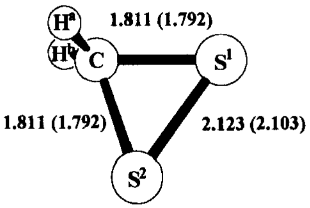
(8)

The ylides **A** as defined in Eq. (8) form upon electrocyclic ring closure the corresponding three-membered heterocycles **B**. This reaction is well documented for numerous thiocarbonyl *S*-methylides such as **A** ($X = CH_2$) which are known to form thiiranes (Eq. (8), $X = CH_2$).[38] Less is known about the analogous transformation of thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) to dithiirane **2** ($R^1 = R^2 = H$) (Eq. (8), X = S),[1–11] cf. Scheme 1.

The transition structure of Eq. (8) (X = S) has been calculated both at the DFT and the *ab initio* level. As shown in Figure 4 in this transition state the CH_2 group is partially twisted out of the original sp^2 plane



S^1S^2C 84.5 (83.3); $S^1S^2CH^a$ 53.7 (52.8); $S^1S^2CH^b$ - 128.6 (- 128.8)



S^1S^2C 54.1 (54.1); $S^1S^2CH^a$ 110.3 (110.3); $S^1S^2CH^b$ - 110.3 (- 110.3)

FIGURE 4 Selected atom–atom distances in Å and bond and dihedral angles in deg. of the thioformaldehyde *S*-sulfide-to-dithiirane transition structure ($TS_{A\to B}$, X = S) and dithiirane (**B**, X = S) of reaction (8) at the DFT B3LYP/6-31+G** and MP2(full)/6-31+G** level of theory (in parentheses).

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on the way to the distorted sp^3 tetrahedron of the product **2** ($R^1 = R^2 = H$). With a CS^1 distance of 3.040 Å (3.010 Å) and a CS^2S^1 angle of 114.4° (114.9°) of the reactant **1** ($R^1 = R^2 = H$) at the DFT (*ab initio*) level the transition structure in Figure 4 appears more product- than reactant-like.

The only crystalline **2** is substituted with an alkyl and an aryl substituent and has experimental bond lengths of 1.818 Å (average) for the CS bonds and 2.073 Å for the SS bond (determined by X-ray crystallography),[11] in good agreement with our theoretical predictions for the parent molecule, cf. Figure 4.

The calculated reaction energy for the electrocylic ring closure of **1** ($R^1 = R^2 = H$) to **2** ($R^1 = R^2 = H$) (Eq. (8), X = S) depends on the basis set used (Table III). The DFT reaction energy decreases by about 5 kcal/mol if the 6-31+G(d,p) basis set is replaced by the more extended 6-31+G(3df) basis set. On the other hand, the addition of polarization functions at hydrogen, i.e. going from the 6-31+G(3df) to the 6-31+G (3df,3dp) basis set, has only a minor effect on the relative energies. The additional functions obviously stabilize the open-chain compound **1** and the transition state more than the resulting **2**. Similar effects of higher-angular momentum atom functions have been observed for the electrocyclic ring closure of thioformaldehyde *S*-imide (Eq. (8), X = NH).[39] Another case of unexpectedly large effects of f-functions was encountered with the ethanedithial/1,2-dithiete valence isomers.[25]

TABLE III Reaction and activation energies in kcal/mol of the prototypical 1,3-electrocyclic ring closure reaction of thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$)

Theoretical model	ΔE	$\Delta E^{\neq}$
DFT		
B3LYP/6-31+G(d, p)	− 9.9	25.6
B3LYP/6-311+G(3df, 3pd)	**− 5.9**	**28.6**
ab initio		
MP2(full)/6-31+G(d, p)	− 14.6	28.8
MP2(full)/6-311+G(3df, 3pd)	− 11.2	30.6
CCSD(T)/6-31+G(d, p)//MP2(full)/6-31+G(d, p)	− 12.2	24.2
QCISD(T)/6-31+G(d, p)//MP2(full)/6-31+G(d, p)	− 11.7	25.5
QCISD(T)/6-311+G(3df, 3pd) //MP2(full)/6-31+G(d, p)	**− 9.1**	**27.3**
G1	− 10.1 (−9.2)[a]	25.3 (24.8)[a]
G2(MP2)	− 7.7 (−6.8)[a]	26.0 (26.5)[a]
G2	− 8.5 (−7.9)[a]	27.1 (26.0)[a]

[a] Data in parentheses: zero-point vibrational energy (ZVPE) included, calculated with RHF frequencies scaled by 0.8923.[20a]

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Here, however, the ring compound is more stabilized by extended basis sets than the acyclic compound. In the Gaussian-2(MP2) method f-functions are also considered. The G2(MP2) reaction energy therefore corresponds closely to the corresponding predictions by DFT calculations with extended basis sets. According to G2(MP2) calculations the energy barrier for the ring closure of **1** ($R^1 = R^2 = H$) to the more stable **2** ($R^1 = R^2 = H$) amounts to about 26 kcal/mol. The heat of the reaction is no more than about −18 kcal/mol. In other words, this reaction should be thermally allowed.

All ring closures of substituted thiosulfines (to dithiiranes **2** as well as **7**, **9**, **11**, and **13**, respectively) examined in this paper exhibit relatively low barriers of activation and thus the higher-energy isomer should be formed under thermal conditions. In fact, Ishii *et al.*[11] verified the formation of an open-chain alkyl aryl thioketone *S*-sulfide **1** from the corresponding dithiirane **2** by their observation of an intramolecular cycloaddition. As shown in Table IV substituted thiosulfines and dithiiranes may become nearly isoenergetic. One such example is **1**/**2** ($R^1 = R^2 = Cl$). If the higher-angular momentum function is considered the isomers differ in energy less than 2 kcal/mol (cf. Table IV,

TABLE IV Reaction and activation energies in kcal/mol of electrocyclic ring closure reactions of substituted thiocarbonyl *S*-sulfides calculated at the DFT B3LYP/6-31+G** and MP2/6-31+G** *ab initio* level of theory[a]

Compound	*DFT*		*ab initio*	
	ΔE	$\Delta E^{\neq}$	ΔE	$\Delta E^{\neq}$
Thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$)[b]	−9.9	25.6	−14.6	28.8
Thioacetone *S*-sulfide **1** ($R^1 = R^2 = Me$)	−5.1	26.4	−15.0	38.3
Thiophosgene *S*-sulfide **1** ($R^1 = R^2 = Cl$)[c]	−2.6	27.6	−7.9	31.4
Thioacetophenone *S*-sulfide **1** ($R^1 = R^2 = Ph$)	−6.0	20.7	—	—
Cyclopropenethione *S*-sulfide **7**	−1.7	17.0	−12.6	17.0
Cyclopentadienethione *S*-sulfide **9**	1.8	23.7	—	—
Tropothione *S*-sulfide **11**	10.0[d]	19.5	−2.1[e]	20.9

[a] $\Delta E < 0$ means dithiirane lower in energy than thiocarbonyl *S*-sulfide, without ZPVEs.

[b] $H_2C{=}S^+{-}Se^-$ (**18**, $R^1 = R^2 = H$), B3LYP/6-311G** reaction energy $\Delta E = -9.0$ kcal/mol, cf. **1** ($R^1 = R^2 = H$) $\Delta E = -10.3$ kcal/mol.

[c] Thiophosgene, B3LYP/6-311+G(3df)//B3LYP/6-31+G** energies in kcal/mol: $\Delta E = 1.4$ and $\Delta E^{\neq} = 29.5$.

[d] Calculations with more extended basis sets: B3LYP/6-31G(2df) energies with fully optimized geometries $\Delta E = 11.2$ and $\Delta E^{\neq} = 20.7$ kcal/mol.

[e] The table contains the results of MP2(full)/6-31+G**//B3LYP/6-31+G** single point calculations. Reaction energy ΔE with fully optimized geometries at the MP2(frozen)/6-31+G** and MP2 (frozen)/6-31 G(2df) level: −1.4 and 2.8 K cal/mol, respectively. QCISD(T)/6-31G*//MP2(full)/6-31+G** single point calculations resulted in $\Delta E = -3.3$ kcal/mol.

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footnote). The open-chain **11** is also favored with respect to its dithiirane isomer **12**. However, the isomerization energies of the MP2 and DFT calculations differ by more than 10 kcal/mol. Barone and Arnaud recently found the same type of error in the calculated reaction energy of Diels–Alder reactions.[40] According to QCISD(T) single-point calculations of **11**/**12** the prediction by MP2 appears more reliable than that by DFT. However, because of the high dipole moment of **11** the open-chain compound should be favored in polar solvents. A previous calculation by Machiguchi *et al.*[41] was performed at the RHF level with Pople's small split valence basis set 3-21G(*) and favored the thiosulfine by 3.9 kcal/mol.

For the sake of comparison the reactivity parameters of the electrocyclic reactions (8) ($X = CH_2$, O) have been calculated as well (Table V). In order to allow a proper consideration of basis set and correlation effects the calculations were performed at the G2(MP2) level of theory. Apparently thioformaldehyde *S*-sulfide ($X = S$) takes up a position intermediate between that of thioformaldehyde *S*-methylide ($X = CH_2$) and thioformaldehyde *S*-oxide ($X = O$). While **B** ($X = CH_2$) is strongly favored over **A** ($X = CH_2$) the opposite is true in the case of $X = O$. This is corroborated by experimental findings. Compound **A** ($X = O$) is well known and has been characterized spectroscopically.[42] The dithiirane ring is less favored than the thiirane ring relative to the corresponding

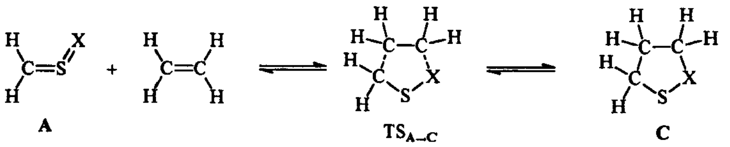
TABLE V Change in relative energies ΔE and $\Delta E^{\neq}$, enthalpies ΔH and $\Delta H^{\neq}$ and Gibbs free energies ΔG and $\Delta G^{\neq}$ in kcal/mol of the 1,3-electrocyclic ring closure (Eq. (1)) and the 1,3-dipolar cycloaddition to ethylene (Eq. (2)) of thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$), thioformaldehyde *S*-methylide **A** ($X = CH_2$) and thioformaldehyde *S*-oxide **A** ($X = O$) calculated at the G2(MP2) level of theory[a]

Reaction	*Reactant*	*Heat of reaction*			*Energy of activation*		
		ΔE	ΔH	ΔG	$\Delta E^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$
Ring closure (Eq. (1))[b]							
	A ($X = S$)	−6.8	−7.0	−6.2	26.5	26.3	26.6
	A ($X = O$)	15.5	15.4	15.6	54.8	54.6	54.8
	A ($X = CH_2$)	−34.6	−35.1	−34.3	16.3	16.0	16.5
Cycloaddition (Eq. (2))							
	C ($X = S$)	42.8	38.7	32.2	7.5	6.6	18.0
	C ($X = O$)	25.9	27.4	15.0	21.6	20.5	32.3
	C ($X = CH_2$)	68.1	73.8	61.2	5.7	4.6	15.8

[a] ZPVEs included.
[b] For comparison, G2(MP2) energies in kcal/mol: formaldehyde oxide $CH_2{=}O^{+}{-}O^{-}$ $\Delta E = -24.0$, $\Delta E^{\neq} = 17.7$; thioformaldehyde *S*-imide **A** ($X = NH$): $\Delta E = -8.7$, $\Delta E^{\neq} = 32.5$.

ylidic structures whereas the energy barrier for the ring closure is higher for **A** ($X = CH_2$). While **A** ($X = S$) differs in reactivity from **A** ($X = CH_2$) and **A** ($X = O$) it seems to bear a greater resemblance to thioformaldehyde *S*-imide **A** ($X = NH$), cf. Table V, footnote. Here, both barriers amount to about 30 kcal/mol and the heat of the two reactions does not exceed 10 kcal/mol. In addition also the reactivity data for formaldehyde *O*-oxide have been calculated in the same approximation. In all above-mentioned cases the thermodynamic parameters are virtually invariant between 0 and 298.15 K.

It appears obvious that more than two minima exist on the CH_2S_2 potential energy surface. There can be no doubt that the global minimum is dithioformic acid **3** ($R^1 = R^2 = H$). Attempts to locate unimolecular transformations between **3** ($R^1 = R^2 = H$) and **1** ($R^1 = R^2 = H$) or **2** ($R^1 = R^2 = H$) failed. Corresponding experimental efforts with **2** (R^1 = alkyl, R^2 = Ar)[11] and **1** ($R^1 = R^2$ = Ar)[10] were equally unsuccessful. However, earlier experimental work indicates that tautomerization of **1** and/or **2** to **3** is feasible when R^2 is an overall electron acceptor,[3] cf. Scheme 1. It seems likely that these tautomerizations are stepwise rather than concerted reactions (cf. Section 4.1.2).



(9)

Some early *ab initio* studies of **3** ($R^1 = R^2 = H$) should be mentioned.[12,43] Particular attention was paid in these studies to the barrier to rotation around the C–SH single bond resulting in the *syn*- or *anti*-conformer. Our calculations at the MP2(full)/6-31G* level show **3** ($R^1 = R^2 = H$) to be about 5 kcal/mol more stable than **2** ($R^1 = R^2 = H$). Both isomers are nearly isoenergetic at the G2(MP2) level with consideration of zero-point vibrational energies.

The ylides mentioned above belong to the category of 1,3-dipoles which are known to undergo [3+2] cycloadditions according to Eq. (9).[44] The prototypical cycloaddition of thioformaldehyde *S*-sulfide **A** ($X = S$) to ethene would thus yield 1,2-dithiolane **C** ($X = S$). While the formation of tetrahydrothiophenes from thiocarbonyl *S*-methylides (cf. Eq. (9), $X = CH_2$) is well established[38,45] much less

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is known about cycloaddition reactions of sulfines (cf. Eq. (2), $X = O$).[46]

The calculated data for the reactions of Eq. (9) are also presented in Table V. With the extended basis sets employed the *ab initio* and the DFT calculations lead to quite similar results. In the case of $X = S$ the energy barrier amounts to about 20 kcal/mol and the heat of reaction to about 5 kcal/mol, the Gibbs free energy of reaction being about 10 kcal/mol lower. With $X = CH_2$ the barrier is considerably higher and the exothermicity smaller.

3.3.3. Spectral Characteristics

The theoretically derived infrared spectrum could be a powerful tool for the identification of the transient species when trapped in matrix at low temperature.[31] The spectra of **1** ($R^1 = R^2 = H$) predicted by *ab initio* and DFT calculations were closely similar and there is no difference in the nature of the vibrations on passing from smaller to larger wavenumbers. The SS stretch is the only normal mode numerically more at variance. The most intense vibrations are in the fingerprint region between 700 and 1000 cm^{-1}.

A prediction of the absorption wavenumbers of the UV/Vis absorption bands is known to be less reliable. The calculated electronic exitation energies are, in general, overestimated since CIS calculations neglect the dynamic correlation. Unexpectedly, the lowest-energy $\pi \rightarrow \pi^*$ transitions of sulfur-containing ylides were well reproduced.[50] In addition, the $n \rightarrow \pi^*$ excitation energies of thiocarbonyl compounds are only slightly overestimated. The results of the calculation of **1** ($R^1 = R^2 = H$) shown in Table VI imply that a weak absorption should occur at small wavenumbers and a more intensive one at larger ones.

NMR spectroscopy is less suited for identification purposes of transient species. However, the question has been asked as to whether the extremely strong ^{13}C NMR paramagnetic chemical shift in thiocarbonyl compounds is retained in thiocarbonyl *S*-sulfides. As shown by the calculated values assembled in Table VI the GIAO-SCF method predicts a less low-field δ ^{13}C shift of **1** ($R^1 = R^2 = H$) than in thioformaldehyde. However, compared with the heteroanalogs **A** with $X = CH_2$, NH, and O the δ ^{13}C shift of the parent thiosulfine to lower fields is relatively large.

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TABLE VI Spectral characteristics of thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) (C_{2v} symmetry)

	Ab initio		IR[a] *DFT*		*Approximative descriptors*
	In cm^{-1} (Int.)	*After scaling*[a]	*In* cm^{-1} (Int.)	*After scaling*[a]	
a′ modes					
ν_1	3336 (2.8)	3169	3290 (3.0)	3168	CH_2 antisymmetric stretch
ν_2	3204 (7.8)	3044	3168 (4.0)	3051	CH_2 symmetric stretch
ν_3	1467 (13.0)	1394	1454 (5.8)	1400	CH_2 scissors
ν_4	1013 (49.2)	962	1007 (11.9)	970	CS stretch
ν_5	980 (51.1)	931	954 (15.8)	919	CH_2 in-plane bend
ν_6	675 (44.8)	641	586 (33.7)	564	SS stretch
ν_7	309 (2.8)	294	299 (1.4)	288	CSS in-plane bend
a″ modes					
ν_8	754 (98.8)	716	798 (81.7)	768	CH_2 out-of-plane wag
ν_9	567 (2.1)	539	559 (0.8)	538	CH_2 out-of-plane twist

	UV/Vis[b]			**NMR**[c] (δ in ppm)	
	ν (cm^{-1})	λ (nm)	f	^{13}C	^{1}H
$A'' \leftarrow A'$ ($n \rightarrow \pi^*$)	26800	373	0.0004	204.9	9.6 (trans)
$A' \leftarrow A'$ ($\pi \rightarrow \pi^*$)	33300	300	0.32		9.8 (cis)

[a] *Ab initio* MP2(full)/6-31G* calculation, intensities in km/mol, uniform scaling of vibrational frequencies by 0.95,[20a] DFT B3LYP/6-31G* intensities in km/mol, uniform scaling of vibrational frequencies by 0.963,[47] the experimental frequencies of the heteroanalogous *S*-oxide ($H_2C{=}S^+{-}O^-$) are known[48] and well reproduced theoretically.

[b] RCIS/6-31+G*//MP2(full)/6-31G* intensities in oscillator strength in parentheses.

[c] GIAO-SCF B3LYP/6-311G(2df,p)//B3LYP/6-31+G**; ^{13}C of $H_2C{=}S$: 260.7 ppm; experimental $\delta(^{13}C{=}S)$ values in fact strongly low field shifted (250–280 ppm).[49]

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3.3.4. *Singlet/Triplet Splitting Energies*

Although the calculated bond lengths of **1** fail to provide arguments for a significant contribution of the singlet biradical resonance structure **1g** indirect support is rendered by the 1,3-bonding between C and S^2 predicted by NRT. The deeper nature of the structure of **1** is revealed by a calculation of the singlet/triplet (S_0/T_1) splitting. The geometry of the lowest-energy triplet state of **1** differs from that of the singlet ground state by the out-of-plane twisted CH_2 group. At the same time the CS and SS bonds are elongated. The DFT bond lengths between the skeletal atoms are again longer than those calculated by MP2 (cf. Figure 5). The electron distribution of the triplet molecules of **1** ($R^1 = R^2 = H$ or Cl) also differs greatly from that of the singlet molecules. As shown by the bond orders in Figure 5 the SS bond order of the triplet molecule is strongly increased relative to that of the singlet molecule while the CS

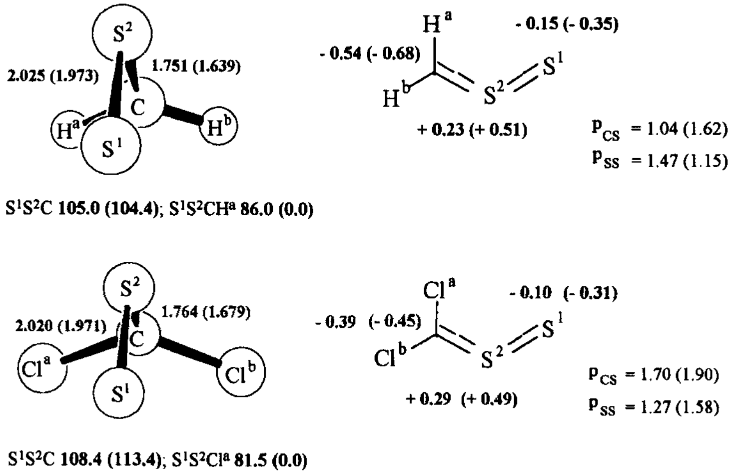

FIGURE 5 Structure of the relaxed lowest energy triplet molecule with bond lengths in Å and bond and dihedral angles in deg. calculated at the (U)B3LYP/6-31+G** level of theory, on the left, and selected natural atomic charges and bond orders (p), on the right. Values for the planar singlet ground state are given in parentheses.

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bond order is decreased. Concomitantly, the charge separation of the SS bond is reduced.

The adiabatic singlet/triplet energy gap of **1** ($R^1 = R^2 = H$) amounts to about 25 kcal/mol at the highest level of theory employed in the present study (QCISD(T)). The relaxed molecules are considerably lower in energy than their planar counterparts (adiabatic rather than transition energies). Our data are listed in Table VII together with corresponding data at the B3LYP/6-31+G** level. The agreement between *ab initio* QCISD(T) and DFT is surprisingly good. According to the DFT calculations the S_0/T_1 splitting energy of **1** ($R^1 = R^2 = H$) is clearly smaller than that of **A** ($X = O$), but of the same order of magnitude as that of **A** ($X = CH_2$).

The S_0/T_1 splitting energies commonly amount to a few kcal/mol for genuine biradicals. For cases with splitting energies of less than 25 kcal/mol the term "biradicaloid" has been coined.[51] Thus, thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) looks like a borderline case between biradicaloid and non-biradicaloid species. The lowest-energy

TABLE VII Singlet/triplet (S_0/T_1) splitting energies of thioformaldehyde *S*-sulfide **A** (X = S) and some related compounds in kcal/mol.[a] On the left: adiabatic S_0/T_1 splitting energies ΔE at (U)MP2(full)/6-31+G** optimum geometries. On the right: adiabatic (a) and vertical (v) S_0/T_1 splitting energies at the DFT B3LYP/6-31+G** level of theory[b,c]

Compound	*Method*	ΔE_a (S_0/T_1)	*Compound*	ΔE_a (S_0/T_1)	ΔE_v (S_0/T_1)
A (X = S)	(U)HF	−4.9	A (X = S)	**22.4**	46.2
	(U)MP2	27.9	A (X = O)	33.1	74.1
	(U)MP3	20.5	A (X = CH_2)	20.2	34.0
	(U)MP4SDQ	22.0			
	(U)QCISD	21.1			
	(U)QCISD(T)	**25.1**			

[a] Singlet ground state energy calculations based on the restricted Hartree–Fock and restricted Kohn–Sham theory, respectively, triplet molecules are calculated by the unrestricted versions.

[b] Nonplanar relaxed triplet state geometries (cf. Figure 4).

[c] In good agreement, (U)QCISD(T) optimized energies of **1** ($R^1 = R^2 = H$) predict ΔE_a (S_0/T_1) to 25.4 kcal/mol. Inclusion of higher angular atomic functions in the DFT calculations changes ΔE_a (S_0/T_1) only slightly: (B3LYP/6-311+G(3df,3pd) 25.9 kcal/mol. However, correlation method with extended basis sets resulted in higher energies, e.g. MP2/6-31G(3df,2p) (33.5 kcal/mol) and Gaussian-2 level of theory (32.2 kcal/mol).

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excited state imparts the partially ylidic thioformaldehyde *S*-sulfide some degree of biradical character.

3.3.5. Conclusions

The parent thiosulfine thioformaldehyde *S*-sulfide **1** ($R^1 = R^2 = H$) is a bent molecule dominantly presented by the ylidic resonance formula **1b** ($R^1 = R^2 = H$). An additional Lewis structure found by NRT indicates another characteristic feature of **1** ($R^1 = R^2 = H$). The 1,3-separated terminal main atoms C and S appear here linked, thus indicating the unsaturated nature of this open-chain compound. With regard to the singlet/triplet energy gap the compound does not appear strongly biradicaloid. The molecular and electronic structure of **1** ($R^1 = R^2 = H$) and various acyclic and cyclic derivatives are described consistently by non-local hybrid HF/DF and conventional *ab initio* quantum theory.

Our knowledge about minimum-energy structures on the CH_2S_2 hypersurface remains incomplete at present. The TDDM probably embraces the molecular structures of lowest energy. Only the **1**/**2** system could be calculated as being interconvertible in a unimolecular thermal reaction. The calculated barrier to isomerization was found at less than approximately 30 kcal/mol for the compounds considered. The reaction and activation energies depend markedly upon the substituents. The thiosulfine structure being more sensitive to consideration of electron correlation the relative DFT/B3LYP and G2(MP2) energies are markedly affected by additional polarization functions, including a set of f-functions. In general, the isomerization of thiosulfines to the corresponding dithiiranes is exothermic. However, in the case of tropothione *S*-sulfide **11** the thiosulfine and the dithiirane are nearly isoenergetic, even at high levels of *ab initio* quantum theory, as shown by QCISD(T) calculations, while DFT/B3LYP favors the open-chain thiosulfine structure.

Calculated spectral data are presented in order to facilitate future detection of the transient species **1** ($R^1 = R^2 = H$) and **2** ($R^1 = R^2 = H$) in inert matrices at low temperature.

4. EXPERIMENTAL ASPECTS

4.1. Early Experimental Work

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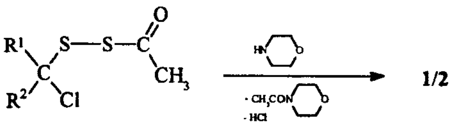
All early, i.e. pre-spectroscopy era, claims of isolated **1** or **2** based on stoichiometry determined by elemental analysis appear extremely naive in hindsight and invariably boil down to the corresponding dimers, the 1,2,4,5-tetrathianes, i.e. **5** ($n = 2$) or simply inseparable mixtures of unrelated organic sulfur compounds with S_8.[7,52,53] Nevertheless, considering that the elusive precursors of these and other 1,2,4,5-tetrathianes have been generated from widely different starting materials and under widely differing circumstances all of which appear conducive to the formation of **1** and/or **2**, it is certainly tempting to invoke their intermediacy whenever formal dimerizations of precursors lead to 1,2,4,5-tetrathianes.

So far, two fairly general methods appear especially useful to generate **1**/**2** under conditions which lend themselves to subsequent trapping of unstable **1**.



19

(10)

Reaction (10) was developed by Senning and co-workers[1–3] and allows considerable variation of R^1 and R^2. The required precursor **19** is prepared from the corresponding α-chloro sulfenyl chloride and

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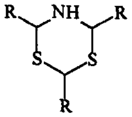
thioacetic acid or, if the sulfenyl chloride is unavailable, from the corresponding diazoalkane $R^1R^2CN_2$ and acetylchlorodisulfane $CH_3COSSCl$. Attempts to replace the secondary amine in reaction (10) with a tertiary amine such as triethylamine failed, presumably for steric reasons.[54] Moreover, attempts to modify reaction (10) by the use of less basic nucleophiles such as thiols remained equally unsuccessful.[54] Early experiments with reaction (10) did not include successful cycloadditions with **1**, but very recent experiments have closed this gap, cf. Sections 4.2.2.1 and 4.2.2.2.[55]

Reaction (1) which has been used by many authors has been consolidated and refined by Huisgen and co-workers, especially a recent streamlined version which uses the cheap and convenient S_8 as thiation agent and sodium benzenethiolate as a catalyst has led to significant progress. Earlier versions employ uncatalyzed S_8, arylthiiranes, and *in situ* formed thiaziridines as thiation reagents.[10]

It should be noted that even **4** can serve as the source of sulfur in Eq. (1), i.e. in a number of cases **1**/**2** are formed from **4** in the absence of extraneous sulfur.[10] We regard these reactions as outside the scope of the present paper.

4.1.1. *Alkyl and/or Aryl Substituted Thiosulfines/Dithiiranes*

Monosubstituted **1**/**2** (R^1 = alkyl or aryl, R^2 = H) appear to be intermediates in the formation of *cis*- and *trans*-isomers of 2,6-disubstituted 1,2,4,5-tetrathianes **5** ($n = 2$, R^1 = alkyl or aryl, R^2 = H) from the corresponding 2,4,6-trisubstituted dihydro-4*H*-1,3,5-dithiazines **20** by treatment with Lewis acids.[52] Although the mechanism of this intriguing reaction has not been elucidated it is interesting to note that the starting material's two sulfur atoms are situated in the 1- and 3-positions of a heterocycle, just like the two sulfur atoms of the starting materials **21** and **23** for Nakayama's syntheses, under similar conditions, of the isolable dithiiranes **22** and **24**, see Section 4.2.1, Eqs. (22) and (23).[11]



20

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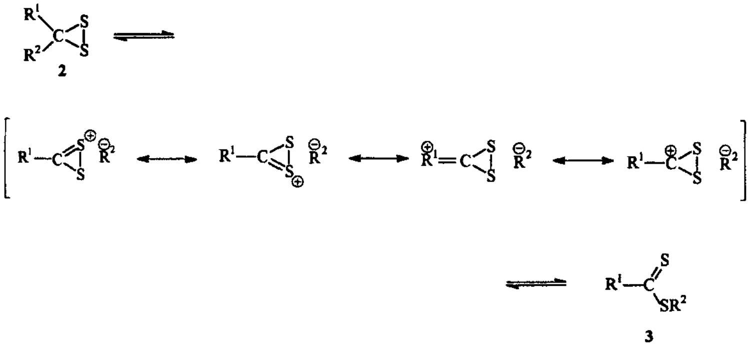
An attempt to prepare **1**/**2** ($R^1 = R^2 = Ph$) according to Eq. (10) remained inconclusive.[3]

Unisolable dialkyl, alkyl aryl and diaryl substituted **1** are accessible from thioketones by thiation according to Eq. (1).[10]

4.1.2. Thiosulfines/Dithiiranes Substituted with Good Leaving Groups

The thiation of thiophosgene **4** ($R^1 = R^2 = Cl$) with S_8 at elevated temperatures has been shown to lead to 3,3,6,6-tetrachloro-1,2,4,5-tetrathiane **5** ($n = 2$, $R^1 = R^2 = Cl$)[52] although the yield is extremely low.[56] It is a moot point whether this tetrathiane is formed by dimerization of **1** ($R^1 = R^2 = Cl$) or, after isomerization of **1** to **3**, by dimerization of the dithioester **3** ($R^1 = R^2 = Cl$) (sulfenyl chlorides are known to add to thiocarbonyl compounds in a thiophilic fashion[57]).

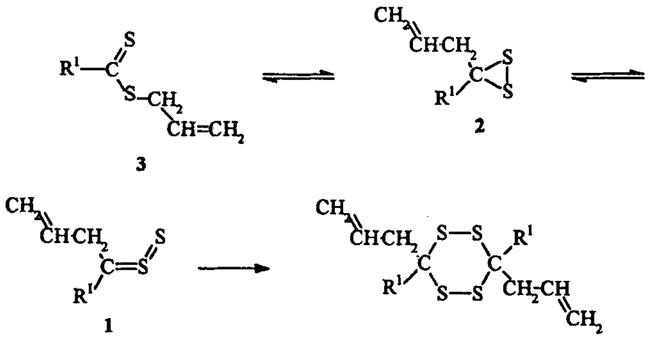
Employing reaction (10) to generate **1**/**2** Senning *et al.*[3] observed that in the two cases where the rearrangement **2** → **3** appeared to take place R^2 is a good anionic leaving group and R^1 has a key atom with lone electron pairs which could stabilize a remaining positive charge. Thus, the thermodynamically favored rearrangement **2** → **3** is especially facile when it can proceed as the two-step ionic process (11). The antiaromaticity of the resonance structures with charged sulfur atoms makes the donor properties of R^1 crucial for the stability of the ion pair in Eq. (11).



(11)

In keeping with this working hypothesis **2** ($R^1 = CCl_3$, $R^2 = Cl$) where the key atom of R^1 is devoid of lone electron pairs loses sulfur rather than rearranges like its close analog **2** ($R^1 = R^2 = Cl$).[3] In both cases the electron-withdrawing substituents should favor **2** over **1** (note, however, chlorine's mesomeric donor potential). This is also consistent with the observation by Nakayama *et al.*[11,58] that isolable **2** are extremely base sensitive with immediate sulfur loss. In the case of the pyrolytic formation of **1**/**2** ($R^1 = R^2 = CF_3$) from the corresponding α-chlorocarbonylthio sulfenyl chloride[52] which leads to **5** ($n = 2$, $R^1 = R^2 = CF_3$) no rearrangement to **3** is observed, in keeping with the above-said, nor can sulfur loss compete with the dimerization of **1**/**2**.

We are currently investigating the question of whether a concerted rearrangement **3** → **2**, followed by dimerization of **2** to **5** ($n = 2$), is feasible when R^2 is allyl or benzyl, cf. Eq. (12) (cf. Section 4.2.3.3). So far, our attempts have been unsuccessful.[54]



(12)

On the other hand, careful studies with diaryl substituted thiosulfines[10] and with sterically hindered alkyl(aryl)- and dialkyldithiiranes[11,58] failed to reveal any rearrangements to **3**. It seems safe to assume that the migratory aptitude of simple alkyl and aryl groups is insufficient to trigger this thermodynamically favored rearrangement (cf. Section 3.3.2).

4.1.3. Cumulated Thiosulfines/Dithiiranes

In a number of reactions where thiation of thioketenes is manifest or can be implied the corresponding 1,2,4-trithiolanes and/or 1,2,4,5-tetrathianes have been obtained. We interpret these findings as indicative of the intermediacy of the corresponding **1**/**2**, even in cases where the authors favor mechanisms not involving **1**/**2** (cf. Sections 4.1.5 and 4.2).

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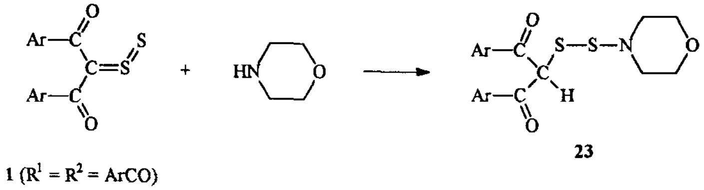
4.1.4. *α,β-Unsaturated Thiosulfines/Dithiiranes*

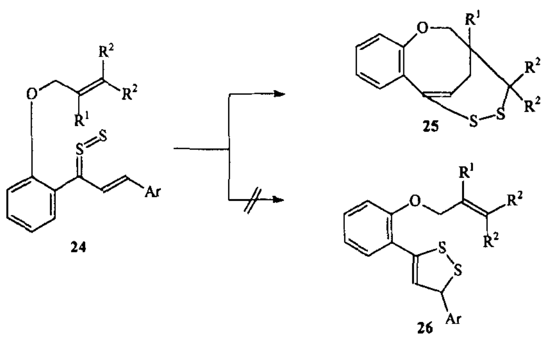
α-Oxo thiosulfines/dithiiranes seem to constitute a nontrivial variation of the **1**/**2** theme by virtue of their potential tautomerism with the so far unisolated thiosulfinoid **22** (X = R′C, Y = O), Eq. (13), as first pointed out by Franek.[59,60] The reaction of **1** ($R^1 = R^2 =$ ArCO) with morpholine, Eq. (14), can be interpreted either as an attack of the nucleophile on **22** (R = ArCO, X = ArC, Y = O) or, maybe more plausibly, by the predominance of the resonance formula **1f** ($R^1 = R^2 =$ ArCO). Similar peculiarities might be expected for analogous **1**/**2** with α,β-unsaturation other than C=O, cf. Eq. (13).

(13)



(14)

On the other hand, thiosulfines with a C=C double bond in the α,β-position behave as 1,5-dipoles and enter into [2+5] cycloadditions with alkenes.[61] We find it surprising that the intramolecular electrocyclic ring closure of e.g. **24** to **26** seems to be unable to compete with the intramolecular [2+5] cycloaddition **24** → **25**, Eq. (15).



(15)

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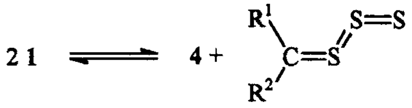
4.1.5. Rearrangements

A number of now classical reactions between carbon disulfide and diazoalkanes, with 3,6-bisalkylidene-1,2,4,5-tetrathianes as the end products[52] most likely involve the **3** → **1** part of the TDDM. While the reaction conditions (high temperature and pressure) are unconducive to kinetic and mechanistic subtlety the assumption of intermediate α-dithiolactones which subsequently rearrange to **1** which in turn dimerize to **5** ($n = 2$) appears extremely well founded. Whether the first reaction steps consist of [2+3] cycloaddition of the diazoalkane to the C=S bond, attack of the diazoalkane-derived carbene on a sulfur lone pair (leading to a labile thiocarbonyl *S*-methylide), or [1+3] cycloaddition of the carbene to the C=S bond is, in this context, of secondary importance.

A particularly neat case is the reaction between tetraethoxyallene $(EtO)_2C{=}C{=}C(OEt)_2$ and disulfur dichloride under extremely mild conditions where the corresponding 1,2,4,5-tetrathiane **5** ($n = 2$, $R^1 = R^2 = COOEt$), formed by dimerization of the corresponding **1**, is the end product of the mechanistic scenario.[52]

4.1.6. Sulfur Loss from thiosulfines/dithiiranes

Sulfur loss from **1**/**2** according to Eqs. (3) and (4) is a rather common reaction. In the absence of extraneous sulfur carriers **1** has been assumed to serve as sulfur acceptor according to Eq. (16).[10] For early attempts to generate and trap thiocarbonyl *S*-disulfides **27** and their tautomers, see [62,63]. As a rule of thumb, sulfur loss competes successfully with less efficient cycloadditions (or in the absence of 1,3-dipolarophiles) as well as the other TDDM options of **1** when these are slow.



27 (16)

Considering the severity of conditions under which trappable **1** have been generated heating *per se* does not seem to induce significant loss of sulfur.

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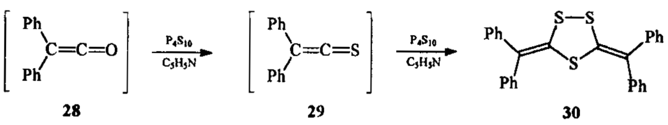
4.2. Recent Experimental Findings

The recent years have seen striking advances in the experimental verification of the TDDM, most notably the isolation of representative **2** (cf. Section 4.2.1). Remarkably individual behavior of diphenylketene **28** (generated *in situ* from diphenylacetyl chloride), dimesitylketene **31**, and bis(2,4,6-triisopropylphenyl)ketene **36** upon thiation with tetraphosphorus decasulfide in pyridine has been observed by Selzer and Rappoport.[64]

While **36** yielded the corresponding 1,3-dithietane **38** (the dimer of thioketene **37**) as the only sulfur-containing product **28** formed, *inter alia*, the corresponding 1,2,4-trithiolane **30**. Finally, from **30**, the corresponding 1,3-dithietane **33**, the 1,2,4-trithiolane **34**, and the 1,2,4,5-tetrathiane **35** were obtained.



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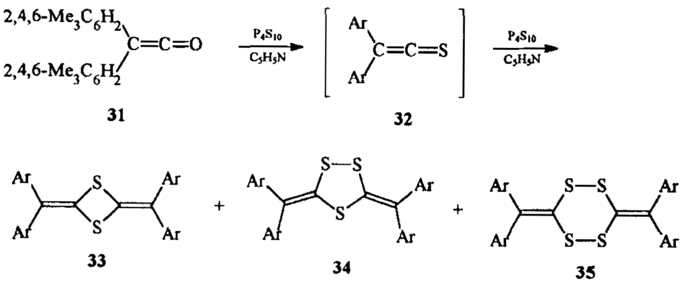

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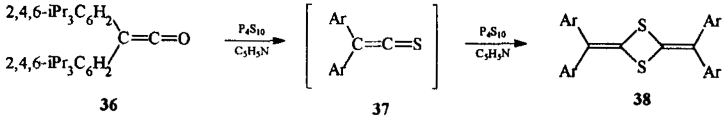

(19)

We strongly disagree with the authors' mechanistic proposals which, at least as far as the formation of the 1,2,4,5-tetrathiane is concerned, require the close approach of two anions in a sterically highly demanding fashion as indicated in Eq. (20). These objections apply

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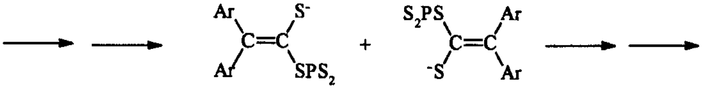
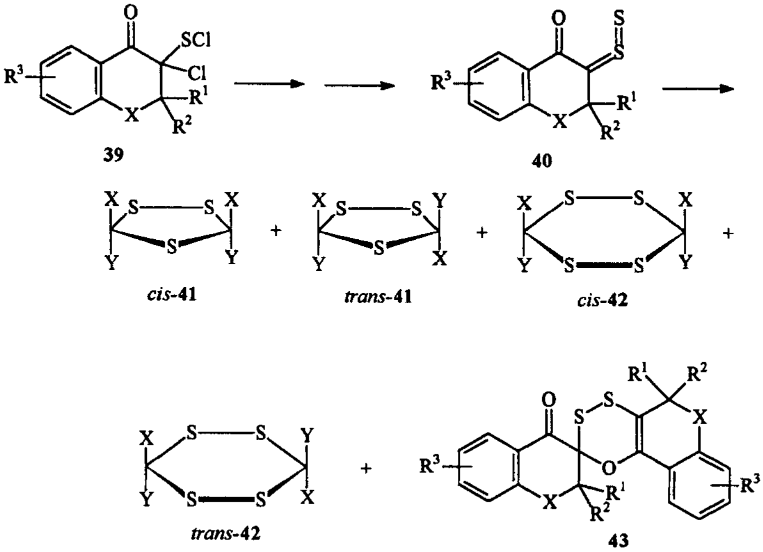
regardless of whether reaction (20) is formulated as a concerted or as a two-step reaction, a question which the authors leave open. In the absence of more compelling alternatives we prefer to regard the corresponding **1** as the key intermediate en route to the observed 1,2,4,5-tetrathiane **35**.

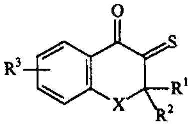


(20)

We have very recently investigated the behavior of α-monooxo substituted **1**/**2**, i.e. **40** prepared from the α-chloro sulfenyl chlorides **39** according to Eq. (10).[52] The isolated products do not include morpholine adducts corresponding to **23**. It thus appears that reactions such as (14) require the presence of two electron-withdrawing groups in the starting **1**. Depending on the substitution pattern of our *in situ* generated **40** we obtained, in modest and varying yields, the *cis*- and *trans*-isomers of the corresponding 1,2,4-trithiolanes **41**, the *cis*- and *trans*-isomers of the corresponding 1,2,4,5-tetrathianes **42**, and finally, the Diels–Alder dimers **43** of the corresponding thiones **44**, cf. Eq. (21).



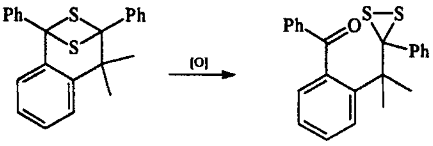
(21)



44

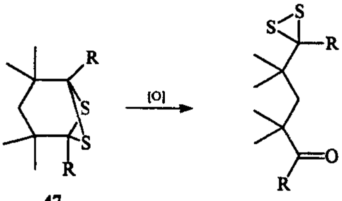
4.2.1. Dithiiranes

Major progress was made with the successful isolation and characterization of three dithiiranes, **46** and **48** (R = CMe$_3$, Ph), whose kinetic stability must be ascribed to steric hindrance.[11,58] It should be noted that the discovery of isolable dithiiranes was preceded by the serendipitous observation of dithiirane 1-oxides,[11] but we consider their chemistry as lying outside the scope of our presentation.



45 **46**

(22)



47 **48**

(23)

Isolable dithiiranes **2**, i.e. **46** and **48**, have been prepared by oxidation of a 1,3-dithietane **45**, Eq. (22), and also by oxidation of, respectively, the 1,5-diphenyl and 1,5-di-*tert*-butyl substituted 2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptanes **47** (R = CMe$_3$, Ph) according to Eq. (23).[11,58]

This is the most significant progress so far with respect to the TDMM. Unfortunately, the required starting materials are relatively cumbersome to prepare and thus a more readily generalized approach to **2** would be highly desirable.

The characteristic yellow to orange color of **46** and **48** (R = CMe$_3$, Ph) is in keeping with the theoretical predictions for torsion strained disulfides. It is interesting to note that in **48** (R = Ph) the crucial angle

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between C^3 of the dithiirane ring and the two adjacent carbon atoms amounts to 117.2°, far from the ideal tetrahedral angle and only insignificantly smaller than the ideal 120° angle in the corrresponding thiosulfine. Also the S^1–C^3–S^2 angle of 69.55° is expanded at the expense of the S^1–S^2–C^3 angle and the C^3–S^1–S^2 angle of 55.37° and 55.07°, respectively.[11]

The reactions of these isolable **2** include rearrangement to **1** which can be trapped by cycloaddition reactions (cf. Section 4.2.3), but not to **3** (cf. however, Section 4.1.2).[11,58]

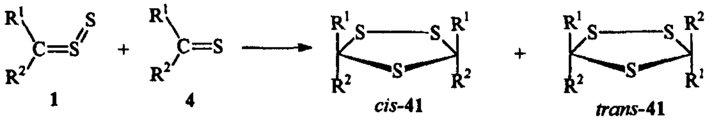
It should also be noted that so far no syntheses of isolable **2** by rearrangement of discrete **1** or **3** are on record.

Off hand, one would expect the stability of **2**, apart from by steric hindrance, to be favored by substitution with electron acceptors, i.e. **2** (R^1 = EWG, R^2 = EWG) should be isolable and protected from rearrangement to **1** and/or **3**. We are not aware of any extant work along these lines. Neither **2** ($R^1 = R^2$ = COOEt) (cf. Section 4.1.5) nor **2** ($R^1 = R^2 = PhSO_2$) (cf. Section 4.1.2) appear to be competitive in the TDDM.

4.2.2. Thiosulfines

While no isolable **1** have emerged during the prolific last years, their chemistry has been substantially enriched by the development of new modes of generation of **1** and, especially, by a painstaking charting of their behavior in a plethora of cycloaddition reactions.

Especially the formation of 1,2,4-trithiolanes **41** by [2+3] cycloaddition of **1**, generated by thiation of **4**, to unconsumed **4**, Eq. (24), is a typical feature of contemporary **1**/**2** chemistry. The [3+3] dimerization of **1**, generated in a number of ways, to 1,2,4,5-tetrathianes **5** ($n = 2$) appears to us almost as archetypical, although several authors deny the feasibility of this dimerization, especially when it would have to compete with reaction (24), and favor alternative mechanisms for the observed formation of **5** ($n = 2$) in reaction sequences starting from **4**. Some of these mechanistic alternatives suffer from considerable conceptual shortcomings (cf. Section 4.2.2.1).



(24)

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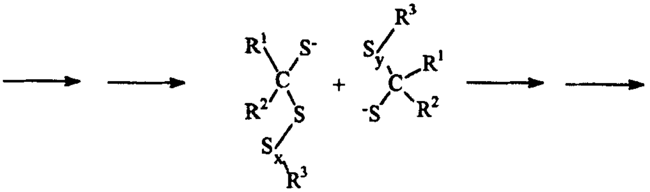
4.2.2.1. Dimerization of thiosulfines

The symmetry forbiddenness of the concerted [3+3] head-to-tail dimerization of **1**, Eq. (7) ($n = 2$), is no serious obstacle to the formation of a 1,2,4,5-tetrathiane **5** ($n = 2$) from **1** since even the slightest asynchronization of this dimerization process converts it to a legitimate nonconcerted reaction. While no examples appear to be on record the corresponding head-to-head dimerization to a 1,2,3,4-tetrathiane deserves consideration as well and needs to be ruled out in every single case. It should be noted that purely spectroscopic evidence will often be inadequate to discern between these two heterocyclic systems.

In a recent, painstaking investigation Huisgen and Rapp[65] treated thiobenzophenone **4** ($R^1 = R^2 = Ph$) with cyclooctasulfur and sodium benzenethiolate in acetone as solvent to obtain a 95% yield of **5** ($n = 2$, $R^1 = R^2 = Ph$). Considering the fact that the same thione, when treated with 2,2-diphenylthiirane as the sulfur source, affords a 92% yield of **41** ($R^1 = R^2 = Ph$) the authors ruled out the intermediacy of **1** ($R^1 = R^2 = Ph$) in the former reaction. Instead they prefer a mechanism whose key step is the close approach of two highly congested anions in a sterically demanding fashion, cf. Eq. (25).

 (25)

We find this suggestion unattractive, no matter if the interaction is conceived as a concerted or a two-step reaction (the authors do not specify their preference), and regard this matter as still open to debate. In our own experience concomitant formation of **41** and **5** ($n = 2$) from **1** is possible, cf. Section 4.2., Eq. (21).[55]

Selzer and Rappoport[64] formulated equivalent ideas about reaction (19) and the same objections as above apply to their Eq. (20), see Section 4.2.

Moreover, in their discussions of the attack of sulfur anions RS^- upon **4** most authors[10,64,65] do not hesitate to assume carbophilic attack of RS^- at the thiocarbonyl group of **4**. Since thiophilic attack of nucleophiles on thiocarbonyl groups is a well-known phenomenon, this should be considered as well.

4.2.2.2. Cycloadditions with thiosulfines

The many well-executed cycloaddition experiments with **1** which have become known in recent years have added substantially to our understanding of the TDDM. However, in cases where **1** are generated by thiation of **4** the facile (and reversible) formation of 1,2,4-trithiolanes **41** from **1** and **4** can diminish the preparative value of this approach to **1**. In fact, the absence of 1,2,4-trithiolanes **41** in reaction mixtures including **4** has been used as an argument for the absence of even transient **1** in such mixtures. It should be noted that 1,2,4-trithiolane formation has also been observed in cases where **1** was generated in ways not involving **4** as starting material. It has been suggested[10] that **1** can assume the role of sulfur carrier by virtue of equilibria such as (16), cf. Section 4.1.6.

In principle, for every single 1,2,4-trithiolane observed the alternative 1,2,3-trithiolane structure must be expressly excluded. So far, no cases of the latter appear to be on record.

Also additions of **1** to alkenes and alkynes appear facile and straightforward. In a number of cases the regiochemistry of these additions has been proven by classical degradation studies of the adducts.[10]

The corresponding cycloreversions, especially of **41**, can serve as a convenient source of **1**.[10] However, the concomitant formation of **4** may pose practical problems in a synthetic context. The cycloreversion of 1,2,4,5-tetrathianes appears attractive as a potential source of **1** considering the ready availability of a large variety of **5** ($n = 2$).[52]

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4.2.3. Rearrangements

Very recent work, although interpreted otherwise by the authors, suggests to us that **1**/**2**, generated by thiation of **4**, do indeed rearrange to **3** in a concerted manner provided that an additional driving force comes into play such as the relief of ring strain in **1**/**2** by ring expansion en route to the corresponding rearrangement product **3**,[66] cf. Section 4.2.3.2.

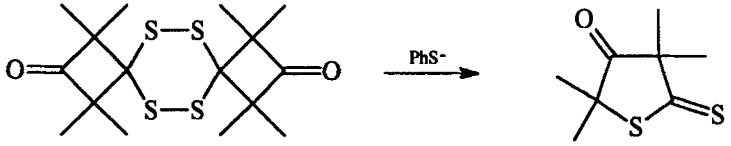
The authors go out of their way to formulate a mechanism which circumvents the intermediacy of **1**/**2** on the way from **4** to **3**, but we consider this matter as far from settled.

4.2.3.1. ***Rearrangements of dithiiranes to thiosulfines***

The three known isolable dithiiranes **2**, two alkyl aryl substituted, one dialkyl substituted, have been shown to rearrange to the thermodynamically less stable thiosulfine **1**. These rearrangements are probably made possible by the immediate scavenging of **1** by intramolecular cycloadditions.[11,58]

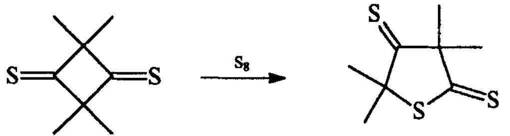
4.2.3.2. ***Rearrangements of thiosulfines/dithiiranes to dithioesters***

Huisgen *et al.* report the formation of the dithiolactone **50** by treatment of the 1,2,4,5-tetrathiane **49** with benzenethiolate, Eq. (26), while the analogous dithiolactone **52** is formed by thiation of 2,2,4,4-tetramethylcyclobutane-1,3-dithione **51** with S_8, Eq. (27).[66] The authors prefer a thiolate driven mechanism which avoids the intermediacy of the corresponding **1**/**2**, but we remain unconvinced that the attractive hypothesis of ring strain driven rearrangement of the corresponding **2** (in turn formed by rearrangement of the corresponding **1**) has really been ruled out.



49 **50**

(26)



51 **52**

(27)

4.2.3.3. ***Rearrangements of dithioesters to thiosulfines/dithiiranes***

We are unaware of any recent experiments addressing this question. Considering the unfavorable thermodynamics of this process we assume that an extraneous driving force (such as trapping of the **1**/**2** formed) would be required to realize this part of the TDDM.

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4.3. Unsolved Experimental Problems

One obvious white spot on the TDDM map is the conspicuous absence of a directly observable **1**. According to conventional wisdom electron donating substituents should stabilize the thiosulfine system, but it appears more likely that the first **1** to be isolated will be a sterically encumbered compound.

5. OUTLOOK

5.1. What Do We Know?

Most spectacularly, the stability of appropriately substituted **2** has been demonstrated. The existence of non-isolable **1** seems established beyond reasonable doubt while their equilibria, if any, with the corresponding **2** remain largely uncharted as far as experimentation is concerned. On the other hand, the computational picture of the **1** ⇄ **2** equilibrium is reasonably clear and the nature of its transition state has been fully elucidated.

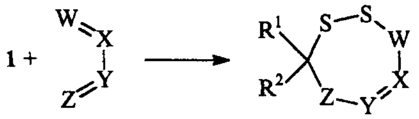
We feel that the postulated rearrangement of **1**/**2** to **3** has been experimentally secured while the computational search for its transition state in a unimolecular reaction failed.

5.2. What Do Wpe Think?

We believe that the thiation of thiocarbonyl compounds **4** other than non-enethiolizable thioketones will contribute substantially to the exploration of the TDDM.

We assume that the controlled oxidation of 1,3-dithia heterocycles (cf. Sections 4.1.1 and 4.2.1) will find even broader application as an access to **2** (and **1**).

We expect that [3+4] cycloadditions of **1** according to Eq. (28) should be feasible and amenable to the construction of interesting heterocyclic systems, i.e. **53**.



53

(28)

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We think that a full appreciation of the TDDM is a prerequisite for rational work and further progress in the area of **1** and **2** chemistry.

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APPENDIX

TABLE A Total energies of thiocarbonyl *S*-sulfides, isomers and transition structures in atomic units (hartrees[a]) calculated at the DFT and MP2 level of theory

Compound	*Becke*3LYP/6-31+G**	MP2(full)/6-31+G**
1 ($R^1 = R^2 = H$)	−835.64839	−834.41794
3	−835.67229	−834.44913
1 ($R^1 = R^2 = Me$)	−914.30193	−912.81420
1 ($R^1 = R^2 = Cl$)	−1754.82773	−1752.48184
1 ($R^1 = H$, $R^2 = Ph$)	−1106.04280	—
7	−911.77908	−910.32592
9	−989.26929	−987.54152[b]
11	−1066.70341	−1064.71601
13	−1183.66147	—
$TS_{A\rightarrow B}$	−835.60764	−834.37210
2 ($R^1 = R^2 = H$)	−835.66424	−834.44117
$TS_{A\rightarrow C}$	−914.23647	—
C	−914.32220	—
TS_{Me}	−914.25988	−912.75320
2 ($R^1 = R^2 = Me$)	−914.31000	−912.83818
TS_{Cl}	−1754.78373	−1752.43166
2 ($R^1 = R^2 = Cl$)	−1754.83187	−1752.49447
TS_{Ph}	−1106.00989	—
2 ($R^1 = R^2 = Ph$)	−1106.05243	—
$TS_{7\rightarrow 8}$	−911.75193	−910.29877
8	−911.78180	−910.34613
$TS_{9\rightarrow 10}$	−989.23157	—
10	−989.26638	−987.55182[b]
$TS_{11\rightarrow 12}$	−1066.67239	—
12	−1066.68750	−1064.71818

[a] 1 hartree = 627.51 kcal/mol.

[b] MP2(frozen) rather than MP2(full).

TABLE B Total energies of singlet thioformaldehyde *S*-sulfides, isomeric dithiiranes and transition structures and of the lowest energy triplet thioformaldehyde *S*-sulfides in atomic units (hartrees[a]) calculated at different levels of theory

Method	**1** ($R^1 = R^2 = H$)	$TS_{A\rightarrow B}$	**2**
B3LYP/6-31+G**	−835.64839	−835.60764	−835.66424
UB3LYP/6-31+G**[b]	−835.61284		
B3LYP/6-311+G(3df,3pd)	−835.73507	−835.68956	−835.74448
MP2(full)/6-311+G(3df,3pd)	−834.07799	—	−834.96949
CCSD(T)/6-31+G**//MP2(full)/6-31+G**	−834.44277	−834.40414	−834.46217
QCISD(T)/6-31+G**//MP2(full)/6-31+G**	−834.44386	−834.40322	−834.46246
UQCISD(T)/6-31+G**//UMP2(full)/6-31+G**[c]	−834.40391		
QCISD(T)/6-311+G(3df,3pd)//MP2(full)/ 6-31+G**	−834.65839	−834.61481	−834.67287
G1 (including ZPVE)	−834.67479	−834.63533	−834.68950
G2 (including ZPVE)	−834.67527	−834.63330	−834.68738
G2(MP2) (including ZPVE)	−834.66474	−834.62244	−834.67559

[a] Cf. footnote to Table A.

[b] Triplet molecule, UKS-based calculation, $\langle S^2\rangle = 2.008$ rather than 2.0.

[c] Triplet molecule, UHF-based calculation, $\langle S^2\rangle = 2.028$ rather than 2.0.

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