### Photochemical Formation and Reactivities of Substituted Oxathiiranes in Low-Temperature Argon Matrices

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Thiocarbonyl S-oxides (sulfines) derived from aliphatic and cycloaliphatic thioketones were irradiated in argon matrices at 10 K, and the resulting oxathiiranes were identified by comparison of computed and experimental IR spectra. Upon photolysis at 10 K, depending on the substitution pattern, the oxathiiranes underwent either H-shift reactions or regiose-lective ring enlargements to form the corresponding thio-

esters. After warming of the matrix material to 38–40 K, the oxathiiranes underwent fast desulfurization to yield the corresponding ketones. Density functional theory (DFT) computations at the B3LYP/6-311+G(3df,3pd) level suggest that the desulfurizations of oxathiiranes occurred as bimolecular processes with activation enthalpies near 0 kcalmol<sup>-1</sup>.

### Introduction

Dithiiranes,<sup>[1]</sup> thiaziridines,<sup>[2]</sup> and oxathiiranes<sup>[3]</sup> are key intermediates in sulfur transfer reactions, and the last of these parent systems has just recently been reported to be fleetingly existent under matrix isolation conditions. The current study aims at elucidating the fascinating reactivity of substituted oxathiirane derivatives, which to date are practically unknown compounds. It has been well established that the best method for the preparation of the parent dithiirane and its 3,3-dimethyl derivative is based on the photocyclization of matrix-isolated thiosulfines (thiocarbonyl *S*-sulfides) **1a** and **1b**, respectively (Scheme 1).<sup>[1d]</sup> In the case of thioformaldehyde *S*-sulfide (**1a**), photolytic ring closure leads to dithiirane (**2a**), which subsequently undergoes rearrangement to a mixture of rotamers of s-*cis* and s-*trans* dithioformic acid (**3**).<sup>[1a]</sup>

On the other hand, in the case of thioacetone S-sulfide (1b), the formation of the disulfane 4, by a thermal 1,4-H shift, was observed.<sup>[1b]</sup> In contrast to thiosulfines 1, sulfines (thiocarbonyl S-oxides) 5 in many cases can be isolated and used for experiments as shelf-stable substances.<sup>[4]</sup> To the best of our knowledge, the first photochemical study on sulfines, performed in an organic glass matrix, was de-

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Scheme 1. Thermal and photochemical conversions of thiocarbonyl *S*-sulfides (thiosulfines) **1**.

scribed by Carlsen et al.<sup>[5]</sup> In this case, thiobenzophenone *S*-oxide (**5a**) was irradiated at 85 K, and 2,2-diphenyloxathiirane (**6a**) was tentatively postulated as an intermediate. After warming the matrix to room temperature, benzophenone (**7a**) and sulfur are formed. The same result was obtained after irradiation of **5a** in various solvents at room temperature. An analogous course of sulfur elimination was reported for hexafluorothioacetone *S*-oxide (**5b**) upon irradiation with sunlight.<sup>[6]</sup> Sander et al. described convincing spectroscopic evidence for the photochemical formation of a spirooxathiirane from the sulfine generated in situ in an argon matrix at 10 K.<sup>[7]</sup>

The studies reported in our recent papers focused on the photolysis of the parent sulfine 5c.<sup>[3,8]</sup> Unexpectedly, the course of the reaction observed in an argon matrix at 10 K strongly depended on the wavelength applied in the photolytic reaction. Whereas irradiation with light at  $\lambda = 254$  nm led to the formation of compound **8**, which displays an unusual structure with a formal C=S triple bond

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(Scheme 2),<sup>[8,9]</sup> the photoreaction performed with light at  $\lambda$  = 313 nm yielded the parent oxathiirane (**6c**) as one of several photoproducts identified after the reaction.<sup>[3]</sup>



Scheme 2. Photochemical conversions of thiocarbonyl S-oxides (sulfines) 5.

The goal of this paper is the investigation of photolyses of substituted sulfines **5d–f** under matrix-isolation conditions. All of them are known compounds. Thioacetone *S*oxide (**5d**) undergoes immediate decomposition at room temperature,<sup>[10]</sup> but three other sulfines, i.e., **5a**,<sup>[11]</sup> **5e**,<sup>[12a]</sup> and **5f**,<sup>[12a]</sup> which are available through oxidation of the corresponding thioketones, can be isolated and stored for a limited period of time at temperatures below –18 °C. However, slow decomposition to the corresponding ketone and elemental sulfur was observed upon standing.

#### **Results and Discussion**

The currently most advantageous method for the generation of matrix-isolated thioacetone *S*-oxide (**5d**) is the gasphase thermolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane 4oxide (**9**) (Scheme 3). In analogy to the thermolysis of 1,2,4-trithiolane 4-oxide described earlier,<sup>[13]</sup> substrate **9** was evaporated and subjected to high-vacuum flash thermolysis at 600 °C (Scheme 3).

The products formed in the gas phase were condensed with a large excess of argon at 10 K and subsequently analyzed by means of IR and UV spectroscopy. The recorded IR spectrum revealed the presence of a strong absorption band at  $1116.2 \text{ cm}^{-1}$ , which was attributed to sulfine **5d** formed as the major product side by side with thiosulfine **1b** (see Supporting Information, Figure S1). The latter underwent a secondary 1,4-H shift in the gas phase and gave rise to the unsaturated disulfane 4. In addition, a small amount of thioacetone was also detected. The transformation of 1b to 4 by a 1,4-H shift was extensively discussed in our earlier paper.<sup>[1b]</sup> The presence of the sulfine 5d and thiosulfine 1b in the obtained pyrolysate results from the retro-[2+3]-cycloaddition reaction of 9 in which 5d plays the dipolarophile role, while 1b acts as a 1,3-dipole. The characteristic strong absorption band found at 1116.2 cm<sup>-1</sup> is typical for the sulfine heterocumulene group (C=S=O stretching vibration) and fits well to the data reported for parent  $5c^{[14]}$  and to the computed value (see Supporting Information). In addition, the UV spectrum of the pyrolysate (Supporting Information, Figure S2) displays a strong absorption band at  $\lambda_{max} = 259.2$  nm, which belongs to sulfine 5d. This value is close to that reported for unsubstituted **5c** ( $\lambda_{\text{max}} = 242.6 \text{ nm}$ ).<sup>[15]</sup> On the other hand, a less intense band at  $\lambda = 370.6$  nm confirms the presence of thiosulfine 1b.<sup>[1b]</sup> In order to transform 1b into the known 3,3-dimethyldithiirane (2b), the pyrolysate was selectively irradiated at  $\lambda = 366$  nm, and the UV absorption band of 1b disappeared completely.

Subsequent irradiation of **5d** at  $\lambda = 254$  nm or  $\lambda = 313$  nm led to the disappearance of the strong heterocumulene absorption band, and 3,3-dimethyloxathiirane (**6d**) formed as the photocyclization product. The change of absorption bands observed in the experimental IR spectrum (Figure 1) confirms the formation of **6d** and fits well with the location of the computed absorption bands. The strongest bands attributed to **6d** were found at 1373.9, 1267.3, 1069.0, and 806.9 cm<sup>-1</sup>, respectively. The computations suggest that the most intense band located at 1267.3 cm<sup>-1</sup> corresponds to the symmetric C–O and C–S stretching vibrations in the oxathiirane ring.

Finally, oxathiirane **6d** present in the argon matrix was irradiated with visible light ( $\lambda > 395$  nm), and thereafter two new isomeric products, identified as *S*-methyl thioacetate (**10**), and very likely, isopropenyl hydrothioperoxide (**11**) were detected. The presence of both compounds is corroborated by comparison of the experimental and computed IR spectra in which strong bands located at 1700.7 cm<sup>-1</sup> and 1244.4 cm<sup>-1</sup> are attributed to **10** and **11**, respectively (Supporting Information, Figure S3).

In another experiment, photolytically generated 3,3-dimethyloxathiirane (6d) (argon matrix, 10 K) was warmed to 39–40 K, and the changes were monitored by IR spectroscopy. After just 15 min, acetone (7d) was detected side by side with 6d, and, after ca. 60 min, the conversion was complete. The experiment showed that the elimination of sulfur from oxathiirane 6d, leading to 7d, occurred smoothly even at very low temperatures, probably as soon



Scheme 3. Products of high-vacuum flash thermolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane 4-oxide (9).



Figure 1. IR spectrum of matrix-isolated 3,3-dimethyloxathiirane (**6d**) after photolysis of thioacetone S-oxide (**5d**) (argon, 10 K). Upper and lower traces show computed [B3LYP/6-311+G(3df,3pd)] spectra, the middle trace is the difference of the spectra taken before and after irradiation at 254 nm.

as the reduced viscosity of the matrix material allowed diffusion of the guest molecules, which underwent a bimolecular desulfurization reaction with very low activation energy (vide infra). (7c), is a highly exothermic ( $-51.4 \text{ kcal mol}^{-1}$  with respect to S<sub>2</sub> triplet ground state) process (Supporting Information, Figure S4).

In order to provide more insight into the mechanism of the sulfur elimination process, we performed DFT computations for the parent oxathiirane (**6c**). It is well established that the elimination of a sulfur atom S<sub>1</sub> is highly endothermic (by  $\Delta H = +66.3 \text{ kcal mol}^{-1}$ ),<sup>[16]</sup> but this path is excluded under matrix-isolation conditions. On the other hand the computations show that a bimolecular reaction of **6c**, resulting in the formation of disulfur S<sub>2</sub> and formaldehyde

The analogous computations for **6d** show a very similar energy profile with an even higher exothermicity ( $\Delta H =$ -62.8 kcalmol<sup>-1</sup> with respect to the S<sub>2</sub> triplet ground state). The stepwise sulfur elimination process is presented in Figure 2. Very low activation enthalpy is required for the formation of activated complex TS-**6d**, in which both sulfur atoms of the oxathiirane ring interact to form a new S–S bond. This process leads to the formation of acetone (**7d**) and intermediate 3,3-dimethyloxathiirane *S*-sulfide (**12**)



Figure 2. Reaction profile (in kcalmol<sup>-1</sup>) for the desulfurization of 3,3-dimethyloxathiirane (**6d**) leading to acetone (**7d**) and disulfur S<sub>2</sub>; computed at the B3LYP/6-311+G(3df,3pd) level of theory, including zero-point vibrational energy (ZPVE) corrections. Energies of the excited singlet states of S<sub>2</sub> were derived from computed ground-state ( $^{3}\Sigma_{g}^{-}$ ) and experimental values.<sup>[17,18]</sup>

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 $(\Delta H = -39.1 \text{ kcal mol}^{-1})$ . Compound **12d** is not expected to be observable, because the excess energy of this process is more than six times higher than the computed activation barrier (5.9 kcalmol<sup>-1</sup>) of the subsequent fragmentation through TS-**12d** giving rise to another molecule of **7d** and disulfur S<sub>2</sub>. A similar mechanism was postulated for the desulfurization of the parent thiirane.<sup>[16]</sup> However, in that case, the computed energy profile showed that this process was endothermic and that the activation enthalpy needed for the first step of the reaction was much higher than in the case of oxathiirane **6d**. This activation enthalpy difference offers a convincing explanation of the relative stabilities of thiirane derivatives in comparison to the corresponding oxathiiranes.

Two cycloaliphatic sulfines, **5e** and **5f**, derived from adamantanethione and 2,2,4,4-tetramethyl-3-thioxocyclobutanone, respectively, are relatively stable compounds that could be prepared and used as starting materials for matrixisolation studies.

Photolysis reactions of **5e** at  $\lambda = 254$  nm or  $\lambda = 313$  nm were monitored by UV spectroscopy, showing the disappearance of the absorption maximum at  $\lambda_{max} = 265.8$  nm. At the same time, a broad and very weak absorption band at ca. 425 nm formed, along with another, much stronger, absorption band at  $\lambda_{max} = 216.6$  nm (the relative intensities of both bands were established as ca. 1:20). Both absorption bands belong to oxathiirane **6e** (Figure 3). They compare well with the computed [TD-B3LYP/6-



Figure 3. UV/Vis spectra of matrix-isolated (argon, 10 K) oxathiirane **6e** and thiolactone **13a** obtained after photolysis of adamantanethione S-oxide (**5e**). (For **5e**, the value of  $\lambda_{max}$  was determined in another experiment by using a thinner matrix.).



Figure 4. IR spectrum of matrix-isolated oxathiirane **6e** after photolysis of adamantanethione *S*-oxide (**5e**) (argon, 10 K). The upper and lower traces show computed [B3LYP/6-311+G(3df,3pd)] spectra, the middle trace is the difference of the spectra taken before and after irradiation at 254 nm.

311+G(3df,3pd)] electronic transitions for **6e**, which give a very weak band at 424 nm and much stronger absorptions at 232 and 231 nm (see Supporting Information).

The IR spectrum after photolysis of **5e** reveals the presence of three relevant absorption bands at 1452.4, 1146.3, and 821.1 cm<sup>-1</sup>, respectively. Whereas the first band is attributed to the CH<sub>2</sub> scissoring vibration of the adamantane skeleton, the two other bands correspond to vibrations involving the oxathiirane ring (Figure 4). Upon photolysis with blue light ( $\lambda = 435 \pm 5$  nm), **6e** converts to an isomeric product displaying a strong IR absorption at 1675.8 cm<sup>-1</sup>. Based on comparison of computed and experimental IR spectra, this compound was identified as the known homothiaadamantanone **13a**.<sup>[19]</sup>

It seems likely that photolysis of **6e** leads, after homolytic cleavage of the S–O bond, to the formation of a diradical intermediate, which selectively forms the ring-expanded product **13a** by insertion of the sulfur atom into the adamantane skeleton. The computed IR spectrum of the alternative thiocarbonyl product, with the oxygen atom present in the seven-membered ring, was compared with the recorded IR spectrum, but no absorption bands characteristic for this product were found. Therefore, we concluded that the ring enlargement occurred regioselectively to yield **13a** exclusively (Scheme 4).



Scheme 4. Photochemical conversions of thiocarbonyl *S*-oxides **5**e-**f** and matrix-generated oxathiiranes **6**e-**f**.

An analogous treatment of 5f immobilized in an argon matrix at 10 K with light of  $\lambda = 245$  nm or  $\lambda = 313$  nm led to the formation of the corresponding oxathiirane derivative 6f with the absorption band of the C=O group slightly redshifted in the IR spectrum in comparison to that of the starting material ( $\tilde{v}_{CO}$  = 1805.2 cm<sup>-1</sup> for 5f vs.  $\tilde{v}_{CO}$  = 1792.3 cm<sup>-1</sup> for **6f**). Characteristically, photocyclization of 5f leading to 6f was accompanied by ring enlargement resulting in the formation of the five-membered thiolactone 13b, and complete conversion of 5f to 13b was smoothly achieved without having to change the wavelength (i.e.,  $\lambda =$ 313 nm). In the case of the latter, two carbonyl absorptions appeared at 1748.7 (less intense, in-phase C=O stretch) and 1711.5 cm<sup>-1</sup> (more intense, out-of phase C=O stretch), respectively. The computed IR spectrum of 6f matches the experimental data nicely (Supporting Information, Figure S5). Thus, after a 10 min irradiation of **5f** at  $\lambda = 313$  nm, oxathiirane 6f formed as the major component, but thiolactone 13b was also found in the matrix as a minor product.

Upon prolonged irradiation, complete conversion of the starting material into thiolactone **13b** was observed. An IRabsorption band at 2049.4 cm<sup>-1</sup> revealed the presence of COS formed in a secondary process. Moreover, a set of absorption bands located at 1777.5, 1327.9, and 1104.0 cm<sup>-1</sup>was also found in the IR spectrum. Comparison of their locations and intensities with the computed IR spectrum of **14**, leads to the conclusion that this regioisomer of the ring-enlarged product formed in competition with **13b**.

On the other hand, thermal desulfurization of **6e** was also observed when the argon matrix was slowly warmed to 40 K within 2 h. After that time, the argon had completely evaporated and the IR spectrum of the residue showed an additional broad band located at  $\tilde{v} = 1720 \text{ cm}^{-1}$ , which is characteristic for adamantanone (**7e**). This experiment confirmed the easy desulfurization of oxathiiranes in solution, even at very low temperature.

The photocyclization of thiobenzophenone S-oxide (5a) in argon at 10 K was also studied. A short (1 min) irradiation of 5a at  $\lambda = 366$  nm led to the appearance of a new, very weak absorption band at  $\lambda_{max} = 410$  nm. This absorption maximum fits well to the data reported by Carlsen et al.<sup>[5]</sup> for the experiment performed in an organic glass at 85 K. This band is characteristic of the presence of matrix-immobilized 3,3-diphenyloxathiirane (6a).

Additional support for the existence of **6a** was delivered in the IR spectrum taken after 1 min of irradiation with  $\lambda$ = 366 nm. The locations of the absorption bands found in the experimental spectrum were in good agreement with the computed values (see Supporting Information, Figure S6). Longer irradiation of matrix material resulted in the conversion of 3,3-diphenyloxathiirane (**6a**) into a complex mixture of products with unidentified structures.

In complete analogy to in-situ-generated oxathiiranes **6b–d**, the product **6a** was obtained from **5a** after  $\lambda = 366$  nm photolysis at 10 K, and easily underwent desulfurization upon warming of the matrix to 39–40 K (Scheme 2). In this experiment, the IR spectrum recorded after 15 h proved the exclusive presence of benzophenone (**7a**).

### Conclusions

The present study shows that irradiation of matrix-isolated sulfines **5** leads to the formation of oxathiiranes **6** as initial photocyclization products, and these intermediate products subsequently undergo further photochemical transformations. The substitution pattern determines the type of secondary products, which in the case of aliphatic and cycloaliphatic oxathiiranes **6d**-**f** were identified as the corresponding *S*-alkyl monothioesters (or closely related structures).

The investigated oxathiiranes 6a,d-f were stable only under matrix-isolation conditions. As soon as the matrix material was warmed to temperatures that allowed the diffusion of the immobilized molecules, bimolecular reactions of 6 led to the formation of the respective ketones 7, with disul-

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fur (S<sub>2</sub>) elimination. The proposed reaction pathway is well supported by DFT computations that show that the desulfurization of an oxathiirane is a highly exothermic two-step process with nearly 0 kcalmol<sup>-1</sup> activation enthalpy. This is a prototypical sulfur transfer reaction involving oxathiirane intermediates as sulfur donors.<sup>[20]</sup>

The desulfurization of putative oxathiirane intermediates appears also important in some biological transformations, e.g., in the context of oxidative stress damage of tRNA molecules containing 2-thiouridine nucleosides, which can be converted, inter alia to their uridine analogues.<sup>[21]</sup>

### **Experimental Section**

**General:** A series of *S*-oxides **9** and sulfines **5** was prepared according to known protocols by oxidation of the corresponding 1,2,4-trithiolanes and thioketones with *m*-chloroperbenzoic acid (*m*-CPBA): 2,2,5,5-tetramethyl-1,2,4-trithiolane 4-oxide (**9**),<sup>[12b]</sup> thiobenzophenone *S*-oxide (**5a**),<sup>[22]</sup> adamantanethione *S*-oxide (**5e**),<sup>[12a]</sup> 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-oxide (**5f**).<sup>[12a]</sup>

Matrix-Isolation Experiments: The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF2 windows for UV/Vis measurements. Matrix temperatures were measured and controlled by a Scientific Instruments 9600-1 silicon diode temperature controller. For irradiations, a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used (band width ca. 10 nm). IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm<sup>-1</sup>, resolution 0.7 cm<sup>-1</sup>). UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer. For the combination of high-vacuum flash pyrolysis with matrix isolation, we employed a home-built, water-cooled oven directly connected to the vacuum shroud of the cryostat. The pyrolysis zone consisted of an empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a thermo-coax wire. The temperature was controlled by an Ni/CrNi thermocouple. In order to produce matrix-isolated thioacetone Soxide (dimethylsulfine, 5d), 1,2,4-trithiolane 4-oxide 9 was evaporated from a pre-cooled (0 °C) storage vessel and pyrolysed at ca. 600 °C. Thioketone S-oxides 5a,e-f were evaporated under high vacuum (5a at 35 °C, 5e at 25 °C, 5f at -10 °C) and condensed with a large excess of argon on a cold spectroscopic window. The obtained matrices were photolyzed, and the products formed were analyzed by means of FT-IR and UV/Vis spectroscopy.

**Computational Methods:** All geometries were fully optimized and characterized as minima or transition structures by means of analytical harmonic vibrational frequency computations at the B3LYP/ 6-311+G(3df,3pd) level of theory.<sup>[23]</sup> The Gaussian program suite was used for all computations.<sup>[24]</sup>

**Supporting Information** (see footnote on the first page of this article): Additional matrix spectra, comprehensive computational results.

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- a) G. Mlostoń, J. Romański, H. P. Reisenauer, G. Maier, Angew. Chem. Int. Ed. 2001, 40, 393–395; b) G. Maier, H. P. Reisenauer, J. Romański, H. Petzold, G. Mlostoń, Eur. J. Org. Chem. 2006, 3721–3729; c) J. Romański, H. P. Reisenauer, H. Petzold, W. Weigand, P. R. Schreiner, G. Mlostoń, Eur. J. Org. Chem. 2008, 2998–3003; d) for a review, see: G. Mlostoń, J. Romański, H. P. Reisenauer, P. R. Schreiner, Phosphorus, Sulfur Silicon Relat. Elem. 2011, 186, 1175–1188.
- [2] a) G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* 1995, 78, 1298–1310; b) G. Mlostoń, H. Heimgartner, J. Romański, *Pol. J. Chem.* 1996, 70, 437–445; c) G. Mlostoń, J. Romański, A. Linden, H. Heimgartner, *Pol. J. Chem.* 1996, 70, 880–890.
- [3] P. R. Schreiner, H. P. Reisenauer, J. Romanski, G. Mloston, J. Am. Chem. Soc. 2010, 132, 7240–7241.
- [4] a) B. Zwanenburg, *Rev. Heteroat. Chem.* 1988, *1*, 218–234; b)
  B. Zwanenburg, T. J. G. Damen, H. J. F. Philipse, R. C. De Laet, A. C. B. Lucassen, *Phosphorus, Sulfur, Silicon Relat. Elem.* 1999, *153–154*, 119–136.
- [5] L. Carlsen, N. Harrit, A. Holm, J. Chem. Soc. Perkin Trans. 1 1976, 1404–1407.
- [6] A. Elsaβer, W. Sundermeyer, Chem. Ber. 1985, 118, 4553–4560.
- [7] a) W. Sander, A. Strehl, A. R. Maguire, S. Collins, P. G. Kelleher, *Eur. J. Org. Chem.* **2000**, 3329–3335; b) O. C. M. O'Sulivan, S. G. Collins, A. R. Maguire, M. Böhm, W. Sander, *Eur. J. Org. Chem.* **2006**, 2918–2924.
- [8] P. R. Schreiner, H. P. Reisenauer, J. Romański, G. Mlostoń, Angew. Chem. Int. Ed. 2009, 48, 8133–8136.
- [9] H. S. Rzepa, J. Chem. Theory Comput. 2011, 7, 97-102.
- [10] W. A. Shepard, J. Dickmann, J. Am. Chem. Soc. 1964, 86, 1891–1892.
- [11] a) R. Huang, J. H. Espenson, J. Org. Chem. 1999, 64, 6935–6936; b) F. Cerreta, A. M. Lenocher, C. Leriverend, P. Metzner, T. N. Pham, Bull. Soc. Chim. Fr. 1995, 132, 67–74.
- [12] a) B. Zwannenburg, A. Wagenaar, L. Thijs, J. Strating, J. Chem. Soc. Perkin Trans. 1 1973, 73–75; b) H. Petzold, S. Bräutigam, H. Görls, W. Weigand, U. Uhlemann, R. Geßner, W. Kiefer, J. Popp, A. Majchrzak, G. Mloston, Inorg. Chim. Acta 2004, 357, 1897–1908.
- [13] G. Mlostoń, J. Romański, M. L. McKee, H. P. Reisenauer, P. R. Schreiner, Eur. J. Org. Chem. 2010, 2132–2137.
- [14] a) D. E. Powers, C. A. Arrington, W. C. Harris, E. Block, V. F. Kalasinsky, J. Phys. Chem. 1979, 83, 1890–1892; b) E. Suzuki, R. Ishiguro, F. Watanabe, J. Mol. Struct. 1990, 238, 71–77; c) E. Suzuki, F. Watanabe, Spectrochim. Acta 1995, 51A, 779–785.
- [15] M. Petian, J. Fabian, P. Prasmus, *Phys. Chem. Chem. Phys.* 1999, 1, 5547–5554.
- [16] Y. Steudel, R. Steudel, M. W. Wong, Chem. Eur. J. 2002, 8, 217–228.
- [17] E. H. Fink, H. Kruse, D. A. Ramsay, J. Mol. Spectrosc. 1986, 119, 377–387.
- [18] V. E. Bondybey, J. H. English, J. Chem. Phys. 1980, 72, 3113– 3122.
- [19] T. Tabuchi, M. Nojima, S. Kusabayashi, J. Chem. Soc. Perkin Trans. 1 1991, 3043–3046.
- [20] a) R. Huisgen, G. Mloston, K. Polborn, F. Palacios-Gambra, *Liebigs Ann./Recueil* 1997, 187–192; b) W. Adam, R. M. Bargon, G. Mloston, *Eur. J. Org. Chem.* 2003, 4012–4015.
- [21] a) E. Sochacka, I. Fratczak, *Tetrahedron Lett.* 2004, 45, 6729–6731; b) E. Sochacka, K. Kraszewska, M. Sochacki, M. Sobczak, M. Janicka, B. Nawrot, *Chem. Commun.* 2011, 47, 4914–4916.
- [22] G. Mloston, A. Linden, H. Heimgartner, *Helv. Chim. Acta* 1996, 79, 31–40.
- [23] a) A. D. Becke, *Phys. Rev. A* 1988, 38, 3098–3100; b) C. Lee,
  W. Yang, R. G. Parr, *Phys. Rev. B* 1993, 37, 785–789; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 1989, 157, 200–206.
- [24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. Montgomery, J. A., T. Vreven,



K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, revision D.03, Pittsburgh, **2003**.

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