^{17}O NMR Spectroscopy of Sulfolenes (2,5-Dihydrothiophene-1,1-dioxides) and Sultines (3,6-Dihydro-1,2-oxathiin-2-oxides)—Experiment and Quantum Calculations: Synthesis of 4,9-Dioxo-1,2-oxathiacyclodecane-2-oxide, a New Heterocycle

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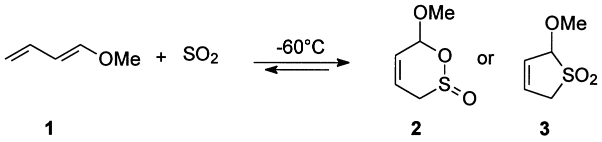
Dedicated to Professor Jean-Marie Lehn on the occasion of his 60th birthday

Abstract: The products of hetero-Diels–Alder reactions (sultines) and cheletropic addition reactions (sulfolenes) between 1,3-dienes and sulfur dioxide can be distinguished by their ^{17}O NMR shifts. Experimental data have been collected for derivatives of 3,6-dihydro-1,2-oxathiin-2-oxide and of 2,5-dihydrothiophene-1,1-dioxide. This data was then compared with that calculated by the gauge independent atomic orbital (GIAO) method at the HF/6-31+G(d,p) and HF/6-311+G(3df, 2p) levels of theory with geometries optimized by MP2/6-31G(d) calculations. GIAO-MBPT(2) calculations were also performed with the 6-31+G(d,p) basis set. The adduct between (*E*)-1-methoxybutadiene and SO_2 is sulfolene **3**, the ozonolysis of which in SO_2 followed by work-up with ethanol provided (2*RS*,3*SR*,6*SR*)-(**31**), (2*RS*,3*RS*,6*SR*)-(**32**), and (2*RS*,3*RS*, 6*RS*)-2,6-diethoxy-3-methoxy-1,4-oxathiane-4,4-dioxide (**33**). Single-crystal X-ray diffraction studies are reported for **32** and **33**. Ozonolysis of the hetero-Diels–Alder adduct of SO_2 with 1,2-dimethylidenecyclohexane produced 4,9-dioxo-1,2-oxathiacyclodecane-2-oxide (**34**), the first member of a new class of sulfur heterocycles.

Keywords: ab initio calculations · cycloadditions · NMR spectroscopy · ozonolysis · sulfur heterocycles

Introduction

Since 1914[1], conjugated dienes have been known to undergo cheletropic addition reactions[2] with sulfur dioxide to generate the corresponding 2,5-dihydrothiophene-1,1-dioxides (sulfolenes). Homoconjugated dienes can either rearrange into conjugated 1,3-dienes in the presence of SO_2 by means of ene reactions[3] or they can undergo homocheletropic additions.[4] At low temperature and in the presence of a protic or Lewis acid catalyst, simple 1,3-dienes add reversibly to SO_2 by a hetero-Diels–Alder addition to generate 3,6-dihydro-1,2-oxathiin-2-oxides (sultines).[5] These compounds are usually unstable above $-50\,^{\circ}C$ and undergo fast cycloreversion to liberate the starting dienes and SO_2 that can then undergo the expected cheletropic addition at higher temperatures.[6] Electron-rich 1,3-dienes, such as (*E*)-1-methoxybutadiene (**1**), react with SO_2 at $-60\,^{\circ}C$ without a catalyst to give a single adduct ($K = [\text{adduct}]/[\mathbf{1}][SO_2] > 3\ \text{mol}^{-1}\,\text{dm}^3$), the structure of which was assigned as sultine **2** on the basis of its ^{1}H and ^{13}C NMR data[7] (Scheme 1). The formation of sultine **2** was consistent with the fact that the cheletropic additions usually require temperatures above $-60\,^{\circ}C$ in order to take place. Furthermore, quantum calculations[8] suggested that sultine **2** can be as stable as sulfolene **3** because of a stabilizing thermodynamic anomeric effect (*gem*-disubstitution effect of



Scheme 1. Possible products from the cycloaddition of (*E*)-1-methoxybutadiene (**1**) and SO_2: either the hetero-Diels–Alder cycloaddition product sultine **2** or the cheletropic addition product sulfolene **3**.

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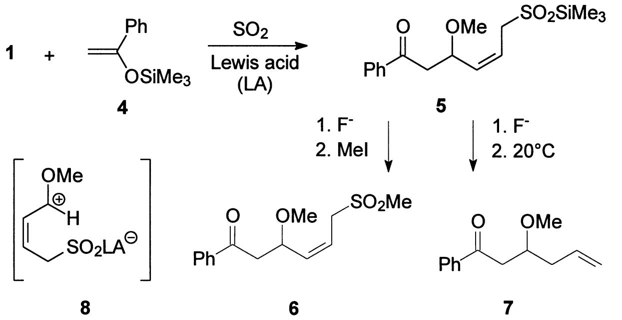
the sulfinate and methoxy group) in **2** and because of repulsive interactions between the methoxy group and sulfone moiety in **3**.[8] The calculations also predicted the hetero-Diels–Alder addition $\mathbf{1}+\mathrm{SO_2}\rightarrow\mathbf{2}$ to have a lower activation energy than the concurrent cheletropic addition $\mathbf{1}+\mathrm{SO_2}\rightarrow\mathbf{3}$.[8] For symmetrical 1,3-dienes, there is no ambiguity in the distinction between the structure of the corresponding sultines (C_1) and sulfolenes (C_{2v}). With 1,3-dienes (such as **1**) that are not substituted symmetrically and that generate only one adduct with SO_2, the distinction between sultine and sulfolene structure can be problematic. The adduct of **1** with SO_2 cannot be isolated; it is observed only at low temperature in the presence of a large excess of SO_2. The instability of this adduct probably arises from its reversibility (Scheme 1). The liberated diene **1** polymerizes quickly above −30 °C in the presence of SO_2.

When butadiene **1** and enoxysilane **4** are mixed in SO_2 at −78 °C in the presence of a Lewis acid catalyst, a carbon–carbon bond is formed between the electron-rich alkene and the electron-rich diene to give the β-methoxyketone **5** after 4–5 h. This compound can be converted either into the methyl sulfone **6** (on treatment with TBAF, then with MeI) or into alkene **7** by retro-ene elimination of SO_2 (Scheme 2).[9, 10] It was hypothesized that the diene **1** generates the sultine intermediate **2**, which then undergoes heterolysis into a zwitterion of type **8** in the presence of the Lewis acid; this intermediate may then react with the enoxysilane **4** to generate the corresponding products of oxyallylation **5**. In order to put this hypothesis on firmer ground we ran a slightly different experiment. We first mixed diene **1** and SO_2 and waited for the full conversion into the corresponding adduct (**2** or **3**). Then we added, at −78 °C, the enoxysilane **4** together with the Lewis acid (0.1 to 1.5 M [Yb(OTf)$_3$] or (tBu)Me$_2$-SiOTf). We did not observe any condensation reaction even after several hours. On warming the mixture to −30 °C, polymerization was observed; the oxyallylation reaction (Scheme 2) could not be detected by ^{1}H and ^{13}C NMR of the crude reaction mixtures.



Scheme 2. Reaction of butadiene **1** and enoxysilane **4** in SO_2.

This showed that the adduct between **1** and SO_2 visible at −78 °C is not capable of generating any electrophilic species responsible for the oxyallylation of enoxysilane **4**! We were facing two alternatives: a) the observed adduct is not sultine **2** but sulfolene **3**; b) sultine **2** is incapable of undergoing the oxyallylation reaction and the reaction involves intermediates that are not derived from **2**. It was therefore necessary to reexamine the structure we had proposed[7] for the adduct formed between **1** and SO_2 above −78 °C. Because of the necessity to maintain a large excess of SO_2 and to analyze solutions at low temperature, we found the IR absorption spectra[11] did not provide conclusive evidence for one of the structures. Therefore, we decided to try ^{17}O NMR spectroscopy[12] to see whether it could give us a means to distinguish between the sultine (**2**) and the sulfolene (**3**) structures. Finally, ozonolysis proved that the adduct formed between (E)-1-methoxybutadiene (**1**) and SO_2, which is visible in the NMR spectrum at −78 °C (and which decomposes above −30 °C), is sulfolene **3** and not sultine **2**!

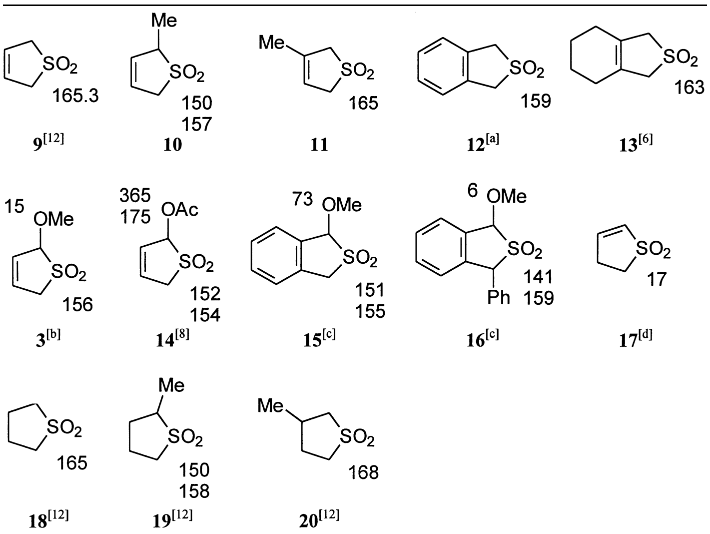
Abstract in French: *Les déplacements chimiques de l'oxygène-17 (δ(^{17}O)) permettent de distinguer entre les produits d'addition du type hétéro-Diels–Alder (sultines) et les produits d'addition chélétropique (sulfolènes) des 1,3-diènes et du dioxyde de soufre. Les valeurs expérimentales sont comparées avec celles obtenues par calculs quantiques pour les 2-oxyde de 3,6-dihydro-1,2-oxathiine (**28**), 2-oxyde de trans-6-méthoxy-3,6-dihydro-1,2-oxathiine (**2**), 1,1-dioxyde de 2,5-dihydrothiophène (**9**) et 1,1-dioxyde de 2-méthoxy-2,5-dihydrothiophène (**3**). Les bases de calcul HF/6-31 + G(d,p) et HF/6-311 + G(3df,2p) ont été utilisées pour des géométries optimalisées avec la méthode MP2/6-31G(d). Des calculs du type GIAO-MBPT(2) avec une base du type 6-31 + G(d,p) ont également été entrepris. L'adduit observé par réaction du (E)-1-méthoxybutadiène avec le SO$_2$ est le sulfolène **3** dont l'ozonolyse, suivie d'un traitement à l'éthanol, fournit les (2RS,3SR,6SR)-**31**, (2RS,3RS,6SR)-**32** et 4,4-dioxyde de (2RS,3RS,6RS)-2,6-diéthoxy-3-méthoxy-1,4-oxathiane (**33**). Les structures moléculaires obtenues par diffraction de rayons X sont décrites pour **32** et **33**. L'ozonolyse de l'adduit du type hétéro-Diels–Alder du 1,2-diméthylidènecyclohexane avec le SO$_2$ produit le 2-oxyde de 4,9-dioxo-1,2-oxathiacyclodécane (**34**), le premier membre d'une nouvelle famille de composés hétérocycliques du soufre.*

Results and Discussion

^{17}O NMR chemical shifts of sulfoxides, sulfones, sulfonic derivatives, sulfites, and sulfates have been reported for a large number of compounds.[12] Data for sulfinates are only reported for methyl methanesulfinate and methyl *para*-toluenesulfinate[13] (see Table 2 later). The literature does not provide sufficient data for α-alkoxy-substituted alkanesulfinates and sulfones, so that it is very difficult to make an empirical evaluation of the ^{17}O NMR shifts of **2** and **3** (on the basis of substituent effects on chemical shifts). We were thus forced to establish a basis of new data, as shown in Table 1, for the known sulfolenes **3**, **9**–**16** and derivatives **17**–**20**, and in Table 2 for the known sultines **21**–**23** and sulfinate derivatives **24**–**27**.

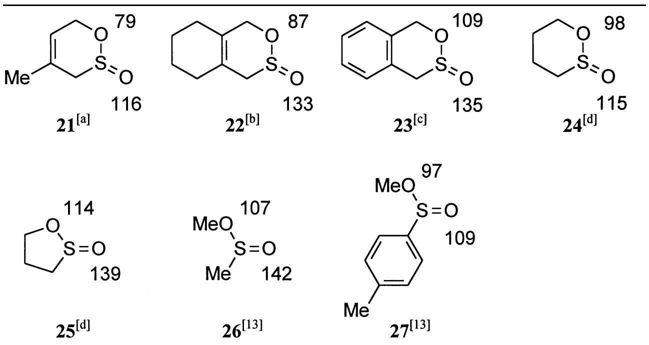
From the data reported in Table 1, it appears that δ(^{17}O) is nearly the same for a sulfolene and its corresponding sulfolane (cf. **9**/**18**, **10**/**19**, **11**/**20**). Annulation of sulfolene **9** with a benzo group to give **12** leads to a relatively small upfield shift (≈ −5 ppm), whereas annulation of **9** by a cyclohexeno ring to give **13** leads to an even smaller effect

Table 1. $\delta^{17}O$ NMR shifts (relative to 1,4-dioxane) for sulfolenes **3**, **9**–**16** and derivatives **17**–**20** in CD_2Cl_2 at 25 °C.



[a] At 25 °C, in CH_3CN, prepared according to ref. [15]. [b] At −70 °C, in CD_2Cl_2/SO_2 (1:1); 2.2 M. [c] At 25 °C, in $CDCl_3$; prepared from the corresponding alcohol[16] by acidic treatment in methanol. [d] At 80 °C, in toluene, see ref. [14].

Table 2. $\delta^{17}O$ NMR shifts (relative to internal 1,4-dioxane) for sultines **21**–**23** and sulfinates **24**–**27**, in CD_2Cl_2 at 25 °C or lower as indicated.

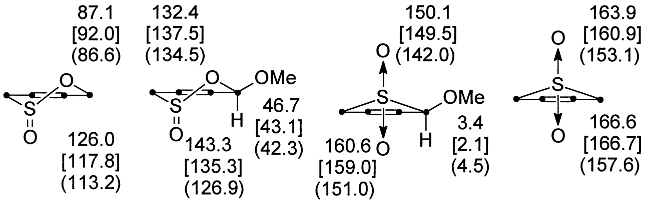


[a] In CD_2Cl_2/SO_2 (1:1), at −80 °C, see ref. [5]. [b] In CD_2Cl_2/SO_2 (1:1), at −40 °C, see ref. [6]. [c] Prepared according to ref. [15]. [d] At 25 °C, in $CHCl_3$; prepared according to ref. [17].

(≈ −2 ppm). Substitution of the α-carbon center by a methyl group makes the two sulfinyl groups of the sulfolene non-equivalent and induces average upfield shifts of ≈ −10 ppm. The effect is reminiscent of the well-known γ-substitution effect in ^{13}C NMR spectroscopy.[18] As seen from the comparison of $\delta(^{17}O)$ in **9**/**11** and in **18**/**20**, substitution of a β-carbon center has little effect, in contrast with the α-substitution (compare also **9**/**13**). The α-alkoxy substitution of sulfolenes (compare **12**/**15**), as well as the α-acetoxy substitution (compare **9**/**14**), induces upfield shifts as for the α-methyl substitution. On average, this upfield shift amounts to −6 ppm in the benzosulfolenes (cf. **12**/**15**). This first analysis suggested that the adduct between diene **1** and SO_2 is sulfolene **3**, as the average signal observed for its SO_2 moiety (broad signal on account of the low temperature) is $\delta(^{17}O) = 156$ (with half-height width of ≈22 ppm, ^{17}O NMR at 54.2 MHz), which is almost that expected ($\delta(^{17}O) = 159$ assuming an α-methoxy substituent effect of −6 ppm). This structural assignment is not definitive; as we shall see, sultine **2** could display a $\delta(^{17}O)$ similar to those observed for this adduct based on the available experimental data for sultines and alkanesulfinates (Table 2).

Contrary to what is observed with the sulfolenes, the $\delta(^{17}O)$ of the sulfinyl group in sultines **21**–**24** is strongly affected by β-alkyl substitution and by annulation of the alkene moiety. The $\delta(^{17}O)$ of the oxygen center in the S–O ring is also strongly affected by substitution and the degree of unsaturation. Considering the known β-alkoxy substitution effects on $\delta(^{17}O)$ (compare ethers with acetals[19]), we cannot exclude that the two oxygen centers of the sulfinate moiety in **2** have the same, or nearly the same, ^{17}O NMR shift and that it could be $\delta = 156$. At this stage we needed help from quantum calculations that have already been successfully used for the estimation of ^{17}O NMR shifts,[20] with satisfactory accuracy.[21] Geometries were optimized at the MP2/6-31G(d,p) level of theory. The NMR chemical shifts were estimated by means of the gauge-independent atomic orbital (GIAO) method[22] as implemented in the GAUSSIAN94 and GAUSSIAN98 program packages.[23, 24] The GIAO calculations were carried out at the selfconsistent field (SCF) level of theory with the standard 6-31 + G(d,p) and the extended 6-311 + G(3df,2p) basis sets.[23, 24] Bearing in mind the reported importance of electron correlation effects in the calculation of relative shifts,[25] especially in the case of molecules with multiple bonds,[26] GIAO-MBPT(2) calculations with the 6-31 + G(d,p) basis set were also performed. From the results (Table 3), one can conclude that for the systems we are dealing with (sulfolenes and sultines), the basis set used only causes moderate effects and correlation contributions are, in general, relatively small. In the following discussion we will use the GIAO-SCF/6-311 + G(3df,2p) and GIAO-MBPT(2)/6-31 + G(d,p) theoretical values (given in that order) of the chemical shifts.

Table 3. ^{17}O NMR chemical shifts computed by GIAO-SCF/6-311 + G(3df,2p) (in square brackets), 6-31 + G(d,p) (in round brackets) and GIAO-MBPT(2)6-31 + G(d,p) for the most stable diastereomers and conformers of sultines **2** and **28**, and sulfolenes **3** and **9**.[a]

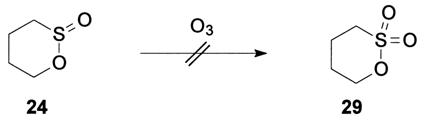


[a] ^{17}O NMR chemical shifts were estimated from MP2/6-31G(d)-optimized geometries and referenced to 1,4-dioxane [absolute shift, $\delta(O) = 325.1$ (GIAO-SCF/6-31 + G(d,p)), 313.9 (GIAO-SCF/6-311 + G(3df,2p)), 318.2 (GIAO-MBPT(2)/6-31 + G(d,p))].

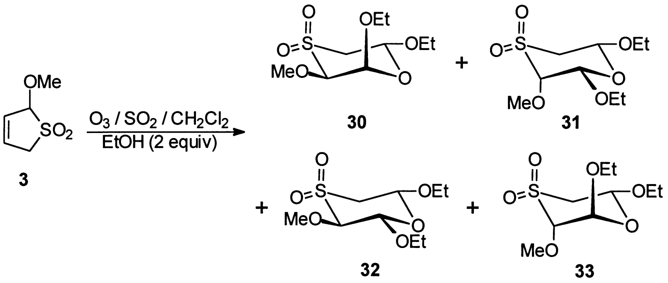
The calculated $\delta(^{17}O)$ value for sulfolene **9** (average $\delta(^{17}O) = 163.8$, 165.3) is the same as the experimental value (Table 1). For the parent sultine **28** (as yet unknown),[5] the calculations predict $\delta(^{17}O)$ values that are quite different from those of the parent sulfolene **9**, in agreement with data reported for alkyl-substituted derivatives in Tables 1 and 2.

For the substitution of **9** with a methoxy group, as in **3**, the calculations predict a shielding effect of ≈ -10 ppm (average $\delta(^{17}O)$ for the SO_2 moiety in $\mathbf{3} = 154.3$ and 155.4, and in $\mathbf{9} = 163.8$ and 165.3) to be compared with the α-methoxy substitution effect of -6 ppm found experimentally (cf. **12**/**15**, Table 1). Except for the $\delta(^{17}O)$ of the methoxy group (see below), the experimental $\delta(^{17}O)$ measured for the $\mathbf{1}+SO_2$ adduct are very similar to the calculated $\delta(^{17}O)$ values for sulfolene **3** (Table 3). Before concluding on this structural assignment, we must verify that sultine **2** should give significantly different $\delta(^{17}O)$ values. The calculations predict values (average $\delta(^{17}O) = 136.4$ and 137.9) that are the same for the two oxygen centers of the sulfinate moiety of **2** and that they differ by only ≈ 17 ppm from the calculated $\delta(^{17}O)$ (average: 154.3 and 155.4 ppm) for sulfolene **3**. The fact that the deviation between the calculated values ($\delta(^{17}O) = 3.4$, Table 3) and experimental values of the MeO group in **3** ($\delta(^{17}O) = 15$ ppm, Table 1) amounts to 11.6 ppm forced us to look for another proof for the sulfolene structure.

Since SO_2 is not oxidized by ozone[27] and since we found that sulfinate **24**[17] is not oxidized into sulfonate **29**[28] by O_3 at low temperature ($-78\,^{\circ}C$) (Scheme 3), we expected that ozone would cleave the olefinic moiety of **2** without affecting its sulfinate unit. Therefore, O_3 was bubbled through a reaction mixture of diene **1**, a large excess of SO_2, CH_2Cl_2, and two equivalents of EtOH. The reaction gave a 2:30:18:50 mixture of sulfones **30**/**31**/**32**/**33** in 65% yield from which **31**, **32**, and **33** were isolated (Scheme 4). Their structures were determined by their elemental analyses and their spectral data, including two-dimensional ^1H NMR (NOESY, COSY) spectra. Single-crystal diffraction studies were carried out on crystalline **32** and **33** (Table 4).



Scheme 3. Sulfonate **29** is not formed from the oxidation of sulfinate **24**.



Scheme 4. Reaction scheme for the formation of sulfones **30**, **31**, **32**, and **33**.

Table 4. Crystal data and structure refinement for (±)-(2*RS*,3*RS*,6*RS*)-2,6-diethoxy-3-methoxy-1,4-oxathiane-4,4-dioxide (**32**) and (±)-(2*RS*,3*RS*,6*RS*)-2,6-diethoxy-3-methoxy-oxathiane-4,4-dioxide (**33**).

	32	**33**
formula	$C_9H_{18}O_6S$	$C_9H_{18}O_6S$
M_w	254.29	254.29
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
crystal system	monoclinic	orthorhombic
space group	$C2/c$	$P2_12_12_1$
a [Å]	12.285(3)	8.293(2)
b [Å]	13.595(3)	8.772(2)
c [Å]	15.603(3)	17.562(4)
α [°]	90	90
β [°]	92.99(3)	90
γ [°]	90	90
V [Å^3]	2602.5(9)	1277.7(4)
Z	8	4
ρ_{calcd} [g cm^{-3}]	1.298	1.322
μ [mm^{-1}]	0.259	0.264
$F(000)$	1088	544
crystal size	n/a	600 × 500 × 400
θ range [°]	3.98–24.99	3.38–28.15
index ranges	$-18 \le h \le 18$ $-20 \le k \le 20$ $-23 \le l \le 23$	$-10 \le h \le 10$ $-11 \le k \le 11$ $-23 \le l \le 23$
reflections collected	12347	12116
independent reflections	2263 [$R_{int} = 0.1706$]	3057 [$R_{int} = 0.0477$]
absorption correction	None	None
refinement method	Full-matrix least-squares on F^2	
data/restraints/parameters	2218/0/145	3057/0/166
goodness-of-fit on F^2	1.468	2.127
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0879$, $wR_2 = 0.1982$	$R_1 = 0.0421$, $wR_2 = 0.0605$
R indices (all data)	$R_1 = 0.1032$, $wR_2 = 0.2251$	$R_1 = 0.0631$, $wR_2 = 0.0621$
weights	$[\sigma^2(F_o^2) + (0.1P)^2]^{-1}$[a]	$[\sigma^2(F^2)]^{-1}$
absolute structure parameter	–	0.34(7)
largest difference peak/hole [e Å^{-3}]	0.591/ –0.399	0.200/ –0.212

[a] $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

An accurate molecular structure was obtained for **33** ((2*RS*,3*RS*,6*RS*)-2,6-diethoxy-3-methoxy-1,4-oxathiane-4,4-dioxide) which does not differ significantly from the crystalline structure reported for (2*RS*,6*RS*)-2,6-dimethoxy-1,4-oxathiane-4,4-dioxide.[29] Interestingly, the O1–C2 bond in **33** is shorter (1.409(2) Å) than O1–C3 bond (1.421(2) Å) (Figure 1, Table 5). This is probably caused by a conformational anomeric effect[30] that allows electron donation from O1 into the axial C2–OEt bond and not into the equatorial C3–OEt bond (Figure 1). This is not accompanied by an elongation of the C2–OEt bond as this bond (1.379(2) Å) is not longer than the C3–OEt bond (1.378(2) Å). The above hypothesis (conformational anomeric effect) is confirmed on comparing this data with that obtained for **32** in which the two EtO groups are equatorial. Here the C2–O1 and C3–O1 bonds are equal and longer than C2–O1 in **33**.

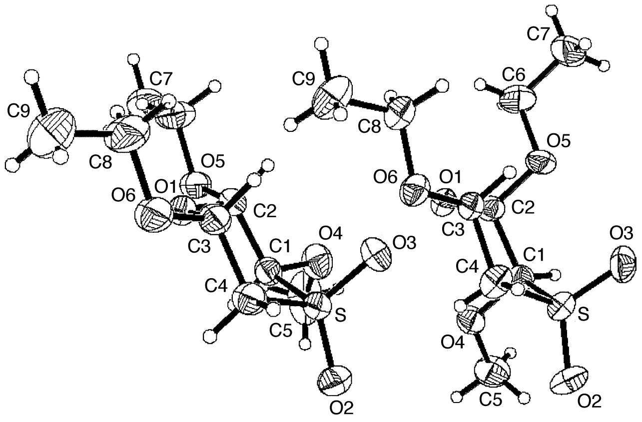


Figure 1. ORTEP representation of **32** and **33** showing atoms with 50% probability.[31]

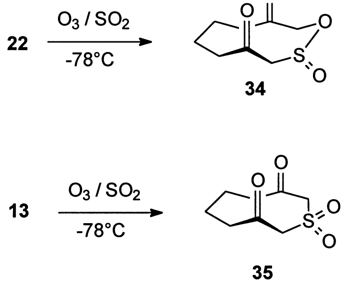
Table 5. Selected bond lengths [Å] and angles [°] for **32** and **33** (see atom numbering in Figure 1).

	C1-O4	C1-S	C4-S	S-O3	S-O2	
32	1.397(4)	1.815(3)	1.772(3)	1.440(2)	1.434(2)	
33	1.392(2)	1.804(2)	1.771(2)	1.433(2)	1.4297(14)	
	C1-C2	C2-O1	C2-O5	C3-O1	C3-O6	C3-C4
32	1.528(4)	1.428(4)	1.384(4)	1.428(4)	1.395(4)	1.516(4)
33	1.538(3)	1.409(2)	1.379(2)	1.421(2)	1.378(2)	1.512(3)
	O2-S-O3	C1-S-C4	C2-O1-C3	S-C1-C2	C1-C2-O1	
32	118.7(2)	102.4(2)	114.4(2)	109.2(2)	109.5(2)	
33	118.41(9)	101.21(12)	115.5(2)	111.8(2)	111.7(2)	

The crystalline structure of **33** shows a slightly longer C1–S bond length (1.804(2) Å) than the C4–S bond (1.771(2) Å). This can be interpreted in terms of repulsive interactions between the SO$_2$ and MeO–C1 moieties. This is also the case with isomer **32** (C1–S: 1.815(3) Å; C4–S: 1.772(3) Å, atom numbering given in Figure 1).

In order that the above ozonolysis experiment can be taken as the definitive proof for the sulfolene structure **3**, we had to verify that the ozonolysis of isomeric sulfolenes and sultines is much faster than their interconversion.

We thus subjected sulfolene **13**[6] and isomeric sultine **22**[6] to ozonolysis at $-78\,^{\circ}$C in the presence of excess SO$_2$ (without EtOH) and checked for completion of the reaction by ^{1}H NMR. We found that **13** and **22** were both oxidized at similar rates (the reactions were over in less than 5 min at $-78\,^{\circ}$C). Sultine **22** gave the asymmetrical diketone **34**, whereas sulfolene **13** produced the known isomeric, symmetrical compound **35**[32] (Scheme 5).



Scheme 5. Ozonolysis of sultine **22** and sulfolene **13**.

The ^{1}H NMR spectra of **34** demonstrated that the sulfinate moiety of **22** is not oxidized into a sulfonate moiety. This was evidenced by the CH$_2$ groups positioned α to the SO$_2$ moiety; they displayed two pairs of signals (diastereotopic protons). The mass spectrum of **34** also confirmed that the sulfinate moiety was not oxidized. Diketone **34** is the first member of a new kind of sulfur heterocycle, the 1,2-oxathiacyclodecane-2-oxides.

Conclusions

This work demonstrates that the adduct formed between (*E*)-1-methoxybutadiene (**1**) and SO$_2$ is not sultine **2**[7] but sulfolene **3**. The oxyallylation reaction between diene **1** and enoxysilanes is retarded if sulfolene **3** is generated. It must therefore be formed via the less stable sultine **2**, which is expected[8] to be formed faster than sulfolene **3**, or via another type of intermediate. We cannot exclude that reaction $\mathbf{1}+\mathbf{4}+\mathrm{SO_2}\rightarrow\mathbf{5}$ (Scheme 2) is a concerted process that is catalyzed by Lewis acids. Our work demonstrates that ^{17}O NMR spectroscopy can be applied to distinguish between sultines and isomeric sulfolenes. The fact that **2** was not observed, although the quantum calculations suggested it to be as stable as **3**,[8] remains unexplained. One possibility could be that specific solvent effects and SO$_2$ interactions stabilize the sulfolene **3** and the diene **1** more than sultine **2**.

Experimental Section

General methods: See ref. [33]. The ^{17}O NMR spectra were recorded on Bruker spectrometers DPX400 and DRX400 at 54.2 MHz, and AMX600 at 81.3 MHz, with a 5 mm observed broad band probehead (DPX400, DRX400) or a 10 mm ^{17}O probehead (AMX600). A 90° high-power pulse, calibrated with a D_2O sample, was used for all samples. Generally, a sweep width of 700 ppm was used. For unstable compounds measured at low temperature in the presence of SO_2, the sulfur dioxide signal ($\delta = 510$) was set outside the spectral window. Since digital filtering was used, this allowed a better signal-to-noise ratio. Since the ^{17}O nucleus relaxes very rapidly, a short time of 10 ms was set between 2 scans (d1). The free induction decays (FIDs) were accumulated over a period of 12 h. External calibration was carried out with a sample of dioxane in $CDCl_3$. The FIDs were typically processed with a decaying exponential by using a 100 Hz line broadening (1b) factor.

Synthesis of (*2RS*,*3SR*,*6SR*)-(31), (*2RS*,*3RS*,*6SR*)-(32), and (*2RS*,*3RS*, *6RS*)-2,6-diethoxy-3-methoxy-1,4-oxathiane-4,4-dioxide (33): In a 100 mL 3-necked flask, 1-methoxy-1,3-butadiene (**1**, 1.5 g, 0.0175 mol) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled in a liquid nitrogen bath and SO_2 (35 mL, 50 g, 0.78 mol) was condensed in under vacuum. The mixture was then warmed to −78 °C (acetone/dry-ice bath) and stirred under Ar until the yellow color of the solution had completely disappeared (48 h). Anhydrous ethanol (3.5 mL, 2.7 g, 0.035 mol) was then added with a syringe and ozone was passed through the solution until it turned pale blue (40 min). The solution was warmed to 25 °C and stirred for 20 min. Sulfur dioxide was then completely removed under vacuum and CH_2Cl_2 (200 mL) added to the residue. The resulting solution was washed with a saturated aqueous solution of Na_2CO_3 and then with brine. The organic layer was dried ($MgSO_4$), and the solvent evaporated under vacuum to yield 3.5 g of a 1:15:9:25 mixture of **30**/**31**/**32**/**33** (by ^{1}H NMR (400 MHz)). Chromatography of this mixture on silica gel (Et_2O/light petroleum 2:3) gave a first fraction (1.0 g) that contained a 1:1 mixture of **31**/**32** from which **32** crystallized (Et_2O/light petroleum). A second fraction yielded pure **31** (30 mg). A third fraction yielded pure **32** (30 mg). A fourth fraction gave pure **33** (180 mg) that crystallized from Et_2O/light petroleum. A fifth fraction gave a mixture of **30** and **33** (1.9 g). Overall yield: 65%.

Compound 31: Pale yellow oil; UV (CH_3CN): λ (ε) = 210 nm (490 mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.91$ (d, $^3J_{\text{2ax, 3eq}} = 1.1$ Hz, H2), 4.72 (dd, $^3J_{\text{6ax, 5eq}} = 1.9$ Hz, $^3J_{\text{6ax, 5ax}} = 9.4$ Hz, H6), 3.99 (dd, $^3J_{2,3} = 1.1$ Hz, $^4J_{\text{3eq, 5eq}} = 2.0$ Hz, H3), 3.88 (m, CH_2(Et)), 3.71 (s, OMe), 3.56 (m, CH_2(Et)), 3.25 (dd, $^2J_{5,5} = 13.7$ Hz, $^3J_{\text{5ax, 6ax}} = 9.4$ Hz, H5$_{\text{ax}}$), 3.03 (ddd, $^2J = 13.7$, $^3J_{\text{5eq, 6ax}} = 1.9$ Hz, $^4J_{\text{3eq, 5eq}} = 2.0$ Hz, H5$_{\text{eq}}$), 1.29, 1.27 (2t, $^3J = 7.0$ Hz, 2Me(Et)); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 95.9$ (t, $J = 162$ Hz, C2), 94.9 (d, $J = 162$ Hz, C6), 91.2 (d, $J = 156$ Hz, C3), 65.9 (t, $J = 145$ Hz, CH_2(Et), 65.1 (t, $J = 145$ Hz, CH_2(Et)), 62.1 (q, $J = 145$ Hz, MeO), 51.7 (t, $J = 142$ Hz, C5), 15.0, 14.9 (2q, $J = 127$ Hz, 2Me(Et)); IR (KBr): $\tilde{\nu} = 2980$, 2900, 1445, 1360, 1375, 1355, 1315, 1250, 1160, 1120, 1035, 990, 865 cm^{-1}; CI-MS (NH_3): *m*/*z* (%): 272 (87) $[M+NH_4]^+$, 226 (20), 147 (17), 116 (14), 102 (51), 89 (58); elemental analysis calcd (%) for $C_9H_{18}SO_6$ (254.29): C 42.51, H 7.13; found C 42.52, H 7.16.

Compound 32: Colorless needles (pentane/Et_2O); m.p. 120–121 °C; UV (CH_3CN): λ (ε) = 210 nm (747 mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.98$ (dd, $^3J_{\text{6ax, 5ax}} = 9$ Hz, $^3J_{\text{6ax, 5eq}} = 2.3$ Hz, H6$_{\text{ax}}$), 4.72 (d, $^3J_{\text{2ax, 3ax}} = 7.1$ Hz, H2$_{\text{ax}}$), 4.16 (d, $^3J_{2,3} = 7.1$ Hz, H3$_{\text{ax}}$), 3.95 (m, CH_2(Et)), 3.82 (s, OMe), 3.65 (m, CH_2(Et)), 3.41 (dd, $^2J_{\text{5ax, 5eq}} = 13.8$ Hz, $^3J_{\text{5ax, 6ax}} = 9.0$ Hz, H5$_{\text{eq}}$), 1.29, 1.27 (2t, $^3J = 7$ Hz, 2Me(Et)); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 98.0$ (d, $J = 164$ Hz, C2), 94.7 (d, $J = 165$ Hz, C6), 94.1 (d, $J = 153$ Hz, C3), 65.9 (t, $J = 143$ Hz, CH_2(Et)), 65.3 (t, $J = 141$ Hz, CH_2(Et)), 62.6 (q, $J = 145$ Hz, MeO), 57.1 (t, $J = 141$ Hz, C5), 15.0, 14.9 (2q, $J = 127$ Hz, 2Me(Et)); IR (KBr): $\tilde{\nu} = 2980$, 2935, 1380, 1360, 1340, 1320, 1245, 1170, 1130, 1110, 1040, 1025, 1000, 525 cm^{-1}; CI-MS (NH_3): *m*/*z* (%): 272 (30) $[M+NH_4]^+$, 226 (4), 147 (3), 118 (7), 102 (21), 89 (36); elemental analysis calcd (%) for $C_9H_{18}SO_6$ (254.29): C 42.51, H 7.13; found C 42.47, H 7.17.

Compound 33: Colorless needles (pentane/Et_2O); m.p. 81–82 °C; UV (CH_3CN): λ (ε) = 210 nm (220 mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.24$ (dd, $^3J_{\text{5eq, 6ax}} = 2.4$ Hz, $^3J_{\text{5ax, 6ax}} = 8.7$ Hz, H6$_{\text{ax}}$), 5.15 (d, $^3J_{\text{2eq, 3eq}} = 2.7$ Hz, H2$_{\text{eq}}$), 4.00 (dd, $^3J_{\text{2eq, 3eq}} = 2.7$ Hz, $^4J_{\text{3eq, 5eq}} = 2.3$ Hz, H3$_{\text{eq}}$), 3.90 (m, CH_2(Et)), 3.79 (s, OMe), 3.63 (m, CH_2(Et)), 3.38 (dd, $^2J_{\text{5ax, 5eq}} = 13.9$ Hz, $^3J_{\text{5ax, 6ax}} = 8.7$ Hz, H5$_{\text{ax}}$), 3.22 (ddd, $^2J = 13.9$ Hz, $^3J_{\text{5eq, 6ax}} = 2.4$ Hz, $^4J_{\text{3eq,5eq}} = 2.3$ Hz, H5$_{\text{eq}}$), 1.30, 1.25 (2t, $^3J = 7.0$ Hz, 2Me(Et)); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 97.7$ (d, $J = 172$ Hz, C2), 92.9 (d, $J = 169$ Hz, C6), 91.1 (d, $J = 157$ Hz, C3), 65.1 (t, $J = 145$ Hz, CH_2(Et)), 64.8 (t, $J = 143$ Hz, CH_2(Et)), 61.6 (q, $J = 150$ Hz, MeO), 53.1 (t, $J = 141$ Hz, C5), 14.9, 14.7 (2q, $J = 126$ Hz, 2Me(Et)); IR (KBr): $\tilde{\nu} = 2985$, 2930, 1380, 1315, 1145, 1035, 990, 950, 760, 540, 440 cm^{-1}; CI-MS (NH_3): *m*/*z* (%): 272 (98) $[M+NH_4]^+$, 226 (28), 209 (16), 147 (34), 118 (27), 102 (74); elemental analysis calcd (%) for $C_9H_{18}SO_6$ (254.29): C 42.51, H 7.13; found C 42.72, H 7.21.

4,9-Dioxo-1,2-Oxathiacyclodecane-2-oxide (34): Degassed (freeze–thaw cycles) SO_2 (2 mL) was transferred (vacuum line) to a solution of 1,2-dimethylidenecyclohexane[34] (0.2 g, 1.8 mmol) in anhydrous CH_2Cl_2 (2 mL). The mixture was left to stand at −78 °C (acetone/dry-ice bath) for 24 h. Ozone was bubbled through the solution at −78 °C. An aliquot (0.4 mL) was transferred by cannulation into a 5 mm NMR tube that contained CD_2Cl_2 (0.2 mL). The ^{1}H NMR spectrum showed complete conversion of the Diels–Alder adduct of SO_2 (1,4,5,6,7,8-hexahydro-2,3-benzoxathiine-3-oxide (**22**)) into diketone **34**, which was stable up to −20 °C. Slow polymerization occurred at 0 °C. ^{1}H NMR (400 MHz, CD_2Cl_2/CH_2Cl_2/SO_2 1:1:1, 273 K): $\delta = 4.51$ (d, $^2J = 16.5$ Hz, H10), 4.41 ($^2J = 16.5$ Hz, H10), 4.08 (d, $^2J = 11.8$ Hz, H3), 3.87 (d, $^2J = 11.8$ Hz, H3), 3.05 (ddd, $^2J = 16.9$ Hz, $^3J_{7,8} = 11.4$ Hz, $^3J_{7,8} = 3.2$ Hz, H8), 2.54 (ddd, $^2J = 12.7$ Hz, $^3J_{4,5} = 8.0$ Hz, $^3J_{4,5} = 3.6$ Hz, H5), 2.46 (ddd, $^2J = 16.9$ Hz, $^3J_{7,8} = 6.2$ Hz, $^3J_{7,8} = 3.6$ Hz, H8′), 2.27 (ddd, $^2J = 12.7$ Hz, $^3J_{5,6} = {}^3J_{5,6} = 8.6$ Hz, H5′), 1.92 (m, H7), 1.62 (m, H6), 1.51 (m, H7′), 1.21 (m, H6′); ^{13}C NMR (100.6 MHz, CD_2Cl_2/CH_2Cl_2/SO_2 1:1:1, 273 K): $\delta = 207.8$ (s, C9), 202.1 (s, C4), 72.7 (t, $J = 149$ Hz, C10), 70.2 (t, $J = 142$ Hz, C3), 41.1 (t, $J = 127$ Hz, C8), 36.9 (t, $J = 131$ Hz, C5), 24.3 (t, $J = 129$ Hz, C7), 20.6 (t, $J = 128$ Hz, C6); CI-MS (NH_3): *m*/*z* (%): 222 (92) $[M+NH_4]^+$, 205 (40), 204 ($[M^+]$, 51), 187 (34), 176 (73), 159 (45), 141 (23), 123 (43), 109 (35), 98 (51), 81 (100).

The NMR assignments were confirmed by HSQC, COSY, NOESY, and COLOC two-dimensional NMR experiments.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-134472 (**32**) and CCDC-134327 (**33**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] G. De Bruin, *K. Proc. Ned. Akad. Wet.* **1914**, *17*, 585; see also: H. J. Backer, J. Strating, *Recl. Trav. Chim. Pays-Bas* **1934**, *53*, 525–543.

[2] S. D. Turk, R. L. Cobb in, *1,4-Cycloaddition Reactions* (Ed.: J. Hammer), Academic Press, New York, **1967**, pp. 13–45; R. B. Woodward, R. Hoffmann in, *The Conservation of Orbital Symmetry* Academic Press, New York, **1970**, p. 152; M. J. S. Dewar, *J. Am. Chem. Soc.* **1984**, *106*, 209–219 and preceding papers.

[3] M. Rogic, D. Masilamani, *J. Am. Chem. Soc.* **1997**, *99*, 5219; see also: G. Capozzi, V. Lucchini, F. Marcuzzi, G. Melloni, *Tetrahedron Lett.* **1980**, *21*, 3289–3292.

[4] O. De Lucchi, V. Lucchini, *J. Chem. Soc. Chem. Commun.* **1982**, 1105–1106; J.-M. Roulet, B. Deguin, P. Vogel, *J. Am. Chem. Soc.* **1994**, *116*, 3639–3640; J.-M. Roulet, P. Vogel, *Bull. Soc. Chim. Fr.* **1994**, *131*, 822–828; J.-M. Roulet, P. Vogel, F. Wiesemann, A. A. Pinkerton, *Tetrahedron* **1995**, *51*, 1685–1696.

[5] B. Deguin, P. Vogel, *J. Am. Chem. Soc.* **1992**, *114*, 9210–9211.

[6] Sulfur dioxide promotes both its Diels–Alder and cheletropic addition: T. Fernandez, J. A. Sordo, F. Monnat, B. Deguin, P. Vogel, *J. Am. Chem. Soc.* **1998**, *120*, 13276–13277.

[7] B. Deguin, P. Vogel, *Helv. Chim. Acta* **1993**, *76*, 2250–2253.

[8] T. Fernández, D. Suárez, J. A. Sordo, F. Monnat, E. Roversi, A. Estrella de Castro, K. Schenk, P. Vogel, *J. Org. Chem.* **1998**, *63*, 9490–9499.

[9] B. Deguin, J.-M. Roulet, P. Vogel, *Tetrahedron Lett.* **1997**, *38*, 6197–6200.

[10] J.-M. Roulet, G. Puhr, P. Vogel, *Tetrahedron Lett.* **1997**, *38*, 6201–6204.

[11] L. J. Bellamy in, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, **1964**, chapter 22, pp. 357–366; R. F. Heldeweg, H. Hogeveen, *J. Am. Chem. Soc.* **1976**, *98*, 2341–2342; F. Jung, M. Molin, R. Van den Elzen, T. Durst, *J. Am. Chem. Soc.* **1974**, *96*, 935–936.

[12] S. A. Evens in, *^{17}O NMR Spectroscopy in Organic Chemistry* (Ed.: D. W. Boykin), CRC Press, Boca Raton, **1991**, Chapt. 10, pp. 263–319; A. R. Bassindale, J. N. Iley in, *Supplement S: The Chemistry of Sulphur-Containing Functional Groups* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1993**, chapter 5, pp. 245–289.

[13] G. Barbarella, *J. Mol. Struct.* **1989**, *186*, 197–209.

[14] H. Tarek, Sammakia, D. L. Harris, S. A. Evans, Jr., *J. Magn. Reson.* **1984**, *22*, 747–752.

[15] M. D. Hoey, D. C. Dittmer, *J. Org. Chem.* **1991**, *56*, 1947–1948.

[16] T. Durst, E. C. Kozma, J. L. Charlton, *J. Org. Chem.* **1985**, *50*, 4829–4833.

[17] D. N. Harpp, J. G. Gleason, D. K. Ash, *J. Org. Chem.* **1971**, *36*, 322–326.

[18] E. Breitmaier, W. Voelter in, *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH, New York, **1987**; F. M. Wehrli, A. P. Marchand, S. Wehrli in, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., Wiley, New York, **1988**; J. B. Stothers, C. T. Tan, K. C. Teo, *Can. J. Chem.* **1973**, *51*, 2893–2901.

[19] S. Chandrasekaran in, *^{17}O NMR Spectroscopy in Organic Chemistry* (Ed.: D. W. Boykin), CRC, Boca Raton, **1991**, chapter 7, pp. 141–203.

[20] M. Schindler, W. Kutzelnigg, *Mol. Phys.* **1983**, *48*, 781–798; T. W. Weller, Meiler, H.-J. Köhler, H. Lischka, R. Höller, *Chem. Phys. Lett.* **1983**, *98*, 541–544; R. E. Wasylishen, J. O. Friedrich, S. Mooibroek, J. B. Macdonald, *J. Chem. Phys.* **1985**, *83*, 548–551; W. Kutzelnigg, U. Fleischer, M. Schindler in, *NMR Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, H. Günther, R. Kosfeld), Springer, Berlin, **1990**, *23*, 165–262.

[21] R. T. C. Brownlee, M. Sadek, D. J. Craik, *Org. Magn. Reson.* **1983**, *21*, 616–620; A. Barszczewicz, M. Jaszunski, K. Jackowski, *Chem. Phys. Lett.* **1993**, *203*, 404–408; J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497–5509; L. Olsson, M. Cremer, *J. Phys. Chem.* **1996**, *100*, 16881–16891; H. Dahn, P.-A. Carrupt, *Magn. Reson. Chem.* **1997**, *35*, 577–588.

[22] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8265.

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. I. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, Gaussian, Pittsburgh PA, **1995**.

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98*, *Revision A.6 and A.7*, Gaussian, Pittsburgh PA, **1998**; W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople in, *Ab initio Molecular Orbital Theory*, Wiley, NY, **1987**.

[25] T. Helgaker, M. Jaszunshi, K. Ruud, *Chem. Rev.* **1999**, *99*, 293–352.

[26] J. Gauss, *J. Chem. Phys.* **1993**, *99*, 3629–3643.

[27] *Gmelin Handbuch der Anorganischen Chemie*, Springer, Berlin, **1980**, 8th ed, Ergänzungsband 3, System-No. 9, pp. 70–246; W. E. Noland, R. D. DeMaster, *Org. Synth.* **1972**, *52*, 976–979.

[28] D. N. Harpp, J. G. Gleason, *J. Org. Chem.* **1971**, *36*, 1314–1316.

[29] M. D. Estrada, A. López-Castro, *Acta Crystallogr. Sect. C* **1991**, *47*, 1030–1032.

[30] P. Deslongchamps in, *Stereoelectronic Effects in Organic Chemistry*, Wiley, New York, **1983**; A. J. Kirby in, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer, Berlin, **1983**; A. J. Kirby, *Pure Appl. Chem.* **1987**, *59*, 1605–1612; C. L. Perrin, *Tetrahedron* **1995**, *51*, 11901–11935.

[31] C. K. Johnson, Report *ORNL-5138*, **1976**, Oak Bridge National Laboratory, Tennesse, USA.

[32] L. D. Quin, J. Leimert, E. D. Middlemas, R. W. Miller, A. T. McPhail, *J. Org. Chem.* **1979**, *44*, 3496–3500.

[33] J. Cossy, J.-L. Ranaivosata, V. Bellosta, J. Ancerewicz, R. Ferritto, P. Vogel, *J. Org. Chem.* **1995**, *60*, 8351–8359.

[34] N. A. Le, M. Jones, Jr., F. Bickelhaupt, W. H. de Wolff, *J. Am. Chem. Soc.* **1989**, *111*, 8491–8493.

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