

Stereoelectronic Effects in Cyclic Sulfoxides, Sulfones, and Sulfilimines: Application of the Perlin Effect to Conformational Analysis

Tobias Wedel,^[a] Monika Müller,^[a] Joachim Podlech,^{*[a]} Helmut Goesmann,^[b] and Claus Feldmann^[b]

Dedicated to Professor Günter Szeimies on the occasion of his 70th birthday

Abstract: The $^1J_{\text{C-H}}$ coupling constants in conformationally constrained sulfoxides, bissulfoxides, sulfoxide-sulfones, and sulfilimines derived from 2-benzylidene-1,3-dithiane and 2-(2,2-dimethylpropylidene)-1,3-dithiolane were measured by means of HMQC and HSQC NMR experiments and the Perlin effects were calculated. The type and the relative configuration of S=X groups (X = O, NTos) in these compounds

have a strong influence on the magnitude of coupling constants for axial and equatorial C-H bonds, respectively. Axial S=O bonds give rise to a stereoelectronic effect on antiperiplanar axial

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C-H bonds. The resultant weakening of the respective C-H bonds leads to a smaller coupling constant than for a respective equatorial C-H bond. Equatorial S=O groups have an influence on β -C-H bonds through a homoanomeric effect. Here, the axial C-H bond is weakened and a smaller coupling constant is measured. Sulfilimine groups show similar effects to sulfoxide groups.

Introduction

Coupling constants give valuable information about the conformation and configuration especially in constrained molecules with fixed geometry. First to mention are $^3J_{\text{H-H}}$ coupling constants which are strongly dependent on the torsion angle of the respective vicinal hydrogens.^[1] Further information can be obtained from $^1J_{\text{C-H}}$ coupling constants though these are significantly less frequently measured or used for structure elucidation.^[2] Perlin and Casu recognized that $^1J_{\text{C-H}}$ coupling constants of geminal hydrogens differ when they are in the vicinity of heteroatoms when conformational fluctuation is inhibited.^[3] This has been explained by stereoelectronic effects in which orbitals (bonds or lone pairs) are interacting with antiperiplanar C-H bonds.^[4] The resultant

decrease of the bond order (as can be visualized by a double-bond–no-bond resonance)^[5] is accompanied by a decrease of the $^1J_{\text{C-H}}$ coupling constant.^[6] This observation has later been referred to as the Perlin effect.^[7]

The nature of the proximate heteroatoms or functional groups has a strong influence on which of the geminal hydrogen atoms shows a higher C-H coupling constant.^[8] In 1,3-dioxane, for example, the axial lone pair is in resonance with axial hydrogen atoms in the 2-, 4-, and 6-position leading to smaller coupling constants as for the respective equatorial hydrogens (normal Perlin effect, Figure 1, top).^[9–12] In other words, an $n_{\text{O}} \rightarrow \sigma_{\text{ax-C-H}}^*$ hyperconjugation leads to a weakening of the axial C-H bond.^[13]

An anomalous pattern in the magnitude of the coupling constants has been found for similar systems containing sulfur atoms.^[7,10–12,14] Here, a hyperconjugation from the $\sigma_{\text{C-S}}$ bond into the $\sigma_{\text{eq-C-H}}^*$ is responsible for smaller coupling constants of the adjacent equatorial C-H bonds (reverse Perlin effect, Figure 1, bottom).^[11,14–16] Alabugin calculated the influence of the converse $\sigma_{\text{eq-C-H}} \rightarrow \sigma_{\text{C-S}}^*$ interaction and found its contribution to be much smaller.^[10]

Perlin effects in cyclic sulfoxides and sulfones have been investigated occasionally (Figure 2).^[17–19] A $\sigma_{\text{ax-C-H}} \rightarrow \sigma_{\text{S=O}}^*$ hyperconjugation^[20,21] should lead to a normal Perlin effect. However, in cyclic substrates elongation of the respective

[a] Dr. T. Wedel, Dipl.-Chem. M. Müller, Prof. Dr. J. Podlech
Institut für Organische Chemie der Universität Karlsruhe (TH)
Fritz-Haber-Weg 6, 76131 Karlsruhe (Germany)
Fax: (+49) 721-608-7652
E-mail: joachim.podlech@ioc.uka.de

[b] Dr. H. Goesmann, Prof. Dr. C. Feldmann
Institut für Anorganische Chemie der Universität Karlsruhe (TH)
Engesserstrasse 15, 76131 Karlsruhe (Germany)

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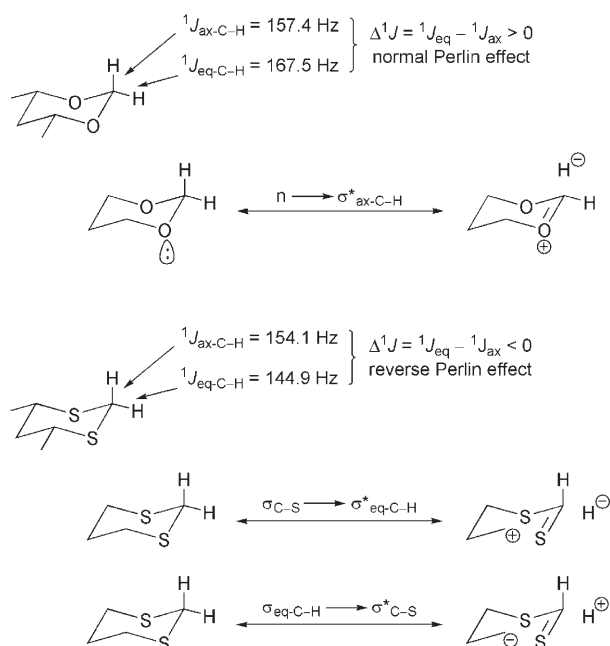


Figure 1. Stereoelectronic effects in 1,3-dioxanes and 1,3-dithianes visualized by a double-bond-no-bond resonance.

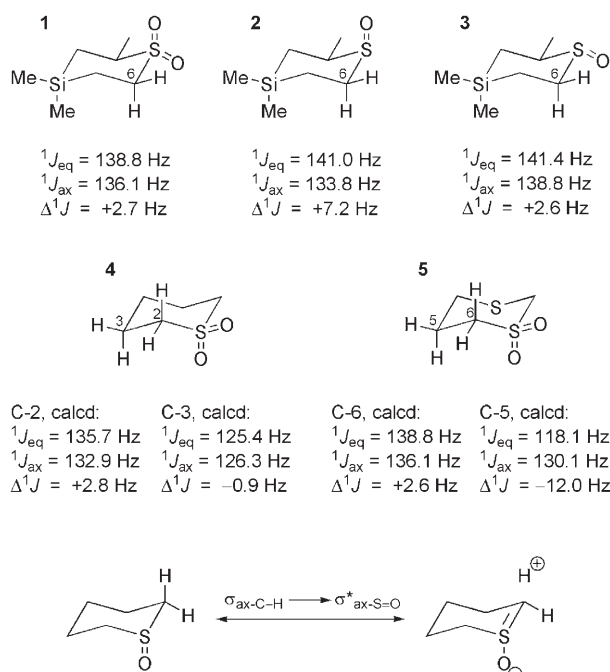


Figure 2. Normal Perlin effects in sulfoxides and sulfones with an axial S=O bond ($\Delta^1J = J_{eq} - J_{ax}$).^[17-19]

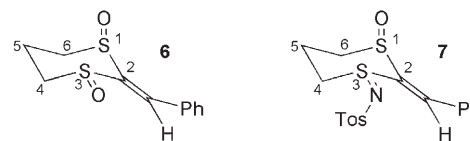
C-H bond is possible only with an axial, that is, antiperiplanar S=O bond, whereas equatorial S=O groups could lead to a reverse Perlin effect as observed for 1,3-dithianes. Experimental NMR spectroscopic data have been supplied for oxidized 1,4-thiasilinanones **1-3**, allocating a normal Perlin effect for compounds **1** and **2** in position C-6.^[17] Though the Perlin effect is not reversed at position C-6 for compound **3**

bearing an equatorial S=O group, the coupling constant here is significantly higher ($J_{ax-C-6} = 138.8$ Hz) than that for the isomeric compound **2** ($J_{ax-C-6} = 133.8$ Hz). Nevertheless, it has to be kept in mind, that interfering effects of the silicon might occur in these compounds. A normal Perlin effect in thiane-1,1-dioxide (**4**) and 1,3-dithiane-1,1-dioxide (**5**) was deduced from a calculated +2.8 and +2.6 Hz difference, respectively, for the coupling constants α to the sulfone group.^[18] Stereoelectronic effects and especially Perlin effects have to the best of our knowledge never been studied in sulfilimines.^[22]

In the course of our investigations on nucleophilic additions to alkylidenebissulfoxides^[23] we were able to synthesize several cyclic sulfoxides and sulfilimines which should give further insights in the stereoelectronic effects occurring in these compounds. These compounds are conformationally constrained due to allylic strain without an interfering effect arising from a bulky substituent in positions C-4, C-5, or C-6, respectively. In this paper we wish to report on these effects.

Results and Discussion

(*R,S,R,S*)-2-Benzylidene-1,3-dithiane-1,3-dioxide (6) and *rac*-(*R,S,R,S,2Z*)-2-benzylidene-3-(4-methylphenylsulfonylimino)-1,3-dithian-1-oxide (7): Structure and conformation of di-

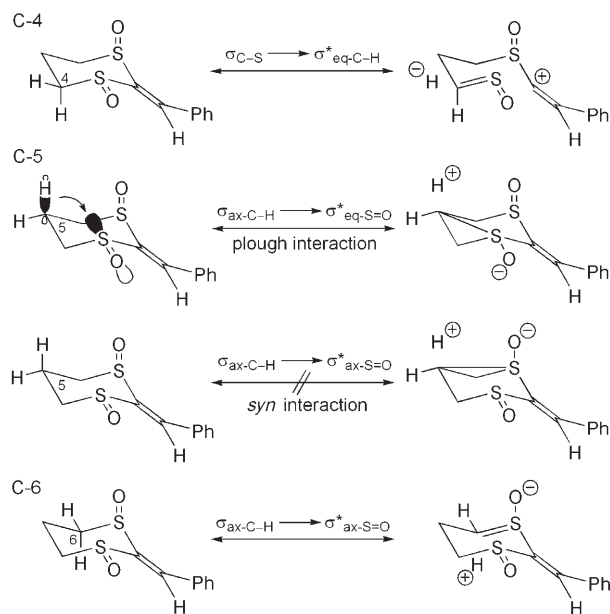


thiane-derived alkylidenebissulfoxide **6** were determined by X-ray crystallographic analysis.^[23a] This compound is conformationally not very flexible (flipping of the chair is equivalent to an interchange of substituents at the alkylidene moiety), the conformation bearing the phenyl substituent in the vicinity of the axial S=O group should be significantly more stable than the flipped-chair conformation. Though the alkylidene moiety might have a (presumably small) effect on the stereoelectronic interactions at C-4, C-5, and C-6, it is mandatory to achieve a conformationally rigid substrate. J_{C-H} coupling constants were determined by means of coupled HMQC^[24,25,26] and HSQC^[25,27] NMR experiments (Table 1). A small negative difference in the coupling constants ($\Delta J_{C-4-H} = -0.7$ Hz) at position C-4 of bissulfoxide **6** indicates a reverse Perlin effect which is explained by $\sigma_{C-2-S} \rightarrow \sigma_{eq-C-4-H}^*$ hyperconjugation (Figure 3, top row).^[7,21] Because a C-S(=O) bond is a poor donor (as compared with a C-S bond),^[18] this effect is only small. Nevertheless, X-ray crystallographic analysis revealed that S3-C2 (179.6 pm) is slightly longer than S1-C2 (178.6 pm).^[23]

The normal Perlin effect for position C-5 is quite unexpected ($\Delta J_{C-5-H} = +2.1$ Hz). In 1,3-dithiane a reverse Perlin

Table 1. $^1J_{\text{C-H}}$ coupling constants in dithiane-derived bissulfoxide **6**.

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	56.1	4-H _{eq}	3.75	141.1	−0.7
		4-H _{ax}	2.93	141.8	
C-5	14.9	5-H _{eq}	2.44	134.0	+2.1
		5-H _{ax}	3.19	131.9	
C-6	48.9	6-H _{eq}	3.31	140.6	+3.2
		6-H _{ax}	2.85	137.4	

Figure 3. Explanation of Perlin effects in bissulfoxide **6**.

effect is observed for this position resulting from $\sigma_{\text{eq-C-H}} \rightarrow \sigma^*_{\text{C-S}}$ interaction. By contrast, the axial C–H bond in position C-5 is significantly weakened in bissulfoxide **6**. The possibility and the quality of stereoelectronic effects towards a bond in the β position of heteroatoms (homoanomeric effect) has been calculated and discussed repeatedly.^[9,11,28,29] Alabugin and co-workers pointed out that hyperconjugation is possible from equatorial and axial lone pairs to equatorial and axial C–H bonds.^[29] W effects (interaction of two equatorial orbitals, one being the donor, one the acceptor) and *syn* effects (interaction of two axial orbitals) are not necessarily stronger than the so-called plough effects (interaction between equatorial and axial orbitals).^[30] The magnitude of the interaction is dependent on the donor and the acceptor orbital and, thus, from the heteroatoms and the atoms attached in the β position. Unfortunately, Alabugin and co-workers examined only substrates with lone pairs at the heteroatoms which unambiguously act as donors. The hyperconjugation occurring here from C–H bonds in position C-5 with acceptor bonds like the β -S=O bonds have never been studied. Nevertheless, the NMR spectroscopic data, that is, the $^1J_{\text{C-H}}$ coupling constants can supply some information. Alabugin and co-workers found that though homoanomeric

effects are often small they are additive in magnitude. The axial C-5–H is weakened, either by interaction with the axial S=O bond (*syn* effect, Figure 3, third row) or with the equatorial S=O bond (plough effect, second row). If the latter effect was working to a significant extent, the Perlin effect should be even larger in the sulfoxide-sulfone **10** bearing two axial S=O groups (see below). Because it is about the same, we assume in fact that interaction with the equatorial S=O group is the dominant effect. Nevertheless, further theoretical work on this topic seems to be mandatory for a conclusive argumentation. It has to be noted that though a normal Perlin effect is observed for position C-5 the equatorial C–H is also significantly weakened ($^1J = 134.0$ Hz), which might be due to a $\sigma_{\text{C-S}} \rightarrow \sigma^*_{\text{ax-C-H}}$ interaction.

A significant normal Perlin effect is observed for C-6 ($\Delta J_{\text{C-6-H}} = +3.2$ Hz). Hyperconjugation with the axial S=O bond leads to a weakening of the axial C–H bond at position C-6 (Figure 3, fourth row). The concomitant lengthening of this S=O bond is confirmed by X-ray crystallographic analysis and this bond is 1.4 pm longer than the equatorial S=O bond at position C-6. The competing $\sigma_{\text{C-2-S}} \rightarrow \sigma^*_{\text{eq-C-6-H}}$ interaction which is occurring at position C-4 seems to be too weak to impair the normal Perlin effect.

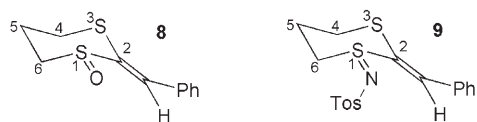
Sulfoxide-sulfilimine **7** was prepared from the corresponding sulfilimine **9** (see below) by oxidation with *meta*-chloroperbenzoic acid (mCPBA). Inspection of the $^1J_{\text{C-H}}$ coupling constants revealed that stereoelectronic effects arising from the sulfilimine group are quite similar to those observed for the corresponding bissulfoxide. While the very high $^1J_{\text{ax-C-4-H}}$ coupling constant at the axial C-4–H (149.9 Hz) virtually excludes any stereoelectronic effect working at this bond, the $^1J_{\text{eq-C-4-H}}$ coupling constant is somewhat reduced (145.6 Hz). Nevertheless, it is still significantly higher than that observed for the corresponding bond in sulfoxide **8** giving evidence that an S(=NR)–C bond is a less effective donor than an S(=O)–C bond (Table 2).

***rac*-(*E*)-2-Benzylidene-1,3-dithiane-1-oxide (**8**) and *rac*-(*E*)-2-benzylidene-1-(4-methylphenylsulfonylimino)-1,3-dithiane (**9**):** Compound **8** was prepared by oxidation of 2-benzylidene-1,3-dithiane with four equivalents hydrogen peroxide in phenol as solvent.^[31] No over-oxidation was observed in this spot-to-spot reaction and monosulfoxide **8** was obtained

Table 2. $^1J_{\text{C-H}}$ coupling constants in dithiane-derived sulfoxide-sulfilimine **7**.

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	52.4	4-H _{eq}	3.54	145.6	−4.3
		4-H _{ax}	3.29	149.9	
C-5	15.5	5-H _{eq}	2.40–2.49	135 ^[a]	–
		5-H _{ax}	3.11–3.33	135 ^[b]	
C-6	47.7	6-H _{eq}	3.07	141.1	+3.3
		6-H _{ax}	2.89	137.8	

[a] Signals partly covered. [b] This value could only be measured with reduced accuracy.



with 81% yield after chromatography. The signals in the ^1H NMR spectrum are partly superimposed which made a detailed analysis impossible (Table 3). Nevertheless, the $^1J_{\text{C-H}}$ coupling constants were measured and the Perlin effects were calculated wherever the signals were sufficiently separated and were able to be assigned.

Table 3. $^1J_{\text{C-H}}$ coupling constants in dithiane-derived sulfoxide **8**.

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	31.8	4- H_{eq}	2.65	139.1	−3.3
		4- H_{ax}	2.82–2.91	142.4	
C-5	27.2	5- H_{eq}	2.46–2.57	$\approx 132^{[a]}$	≈ 0.0
		5- H_{ax}	2.46–2.57	$\approx 132^{[a]}$	
C-6	55.0	6- H_{eq}	3.43	139.9	−1.4
		6- H_{ax}	2.82–2.91	141.3	

[a] Signals partly obscured. A shallow analysis of the spectra revealed that ΔJ is close to zero.

Steric constraints and evaluation of the $^1J_{\text{C-H}}$ coupling constants (see above) confirmed that this compound bears an equatorial sulfoxide group *trans* to the phenyl substituent. Equatorial oxidation at the other sulfur would lead to a significant steric hindrance between the oxygen and the phenyl group and oxygen in one of the axial positions would lead to differing Perlin effects. Further evidence for the proposed configuration arises from the γ -*gauche* effect in this substrate (see below, Figure 7) and from the chemical shift of the vinylic proton ($\delta = 7.52$ ppm), which is exactly identical for the bissulfoxide **6** and the monosulfoxide **8**. Coupling constants for the equatorial hydrogen next to the equatorial sulfoxide are in the same range for both compounds (see Supporting Information). We think that oxidation is in fact occurring in the equatorial position, though axial oxidation with subsequent flipping of the chair cannot generally be excluded. Interaction of the axial sulfur lone pairs in alkylidene-1,3-dithiane with the alkene moiety should lead to a substantial reduction of the donor ability of these lone pairs as the equatorial lone pairs are available for oxidation.

A negative Perlin effect ($\Delta J_{\text{C-4-H}} = -3.3$ Hz) was determined for position C-4 next to the sulfide moiety. A hyperconjugation $\sigma_{\text{C-S}} \rightarrow \sigma_{\text{eq-C-H}}^*$ should be responsible for this observation as it has been calculated for the parent 1,3-dithiane (Figure 4). The measured negative Perlin effect of $\Delta J = -6.7$ Hz for position C-4 in 2-*tert*-butyl-1,3-dithiane should be due to similar effects.^[14b]

Discussion of the effects working at position C-5 is not possible because the ^1H NMR signals at this position are not resolved and the $^1J_{\text{C-H}}$ coupling constants are not as accurate as for the other protons. Nevertheless, the difference seems to be close to zero and both coupling constants are small

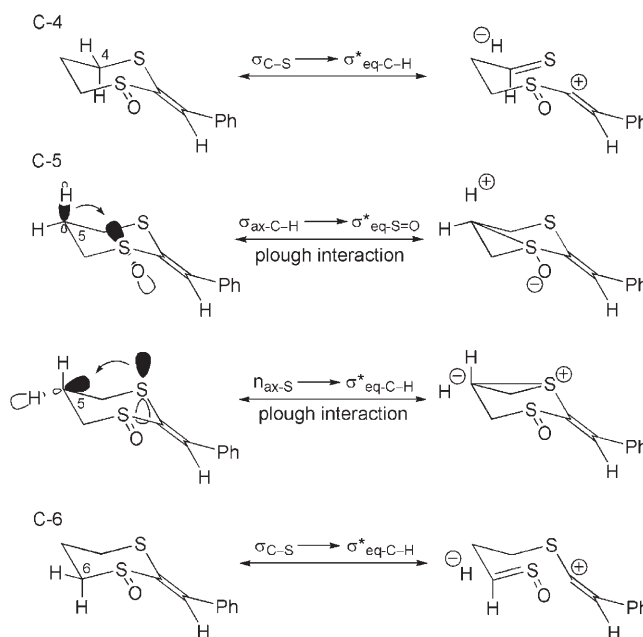


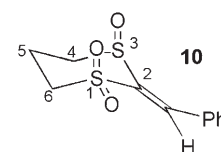
Figure 4. Explanation of Perlin effects in monosulfoxide **8**.

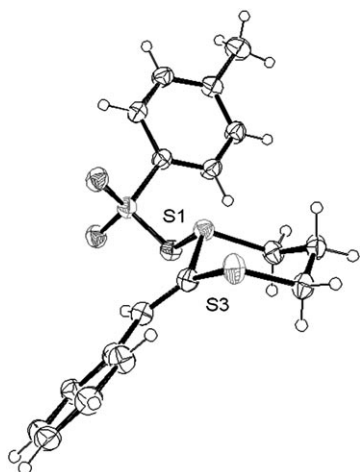
(≈ 132 Hz), meaning that a stereoelectronic effect is occurring for both C–H bonds. We assume that a homoanomeric effect from the axial sulfur lone pair to the equatorial C–H ($n_{\text{ax-S}} \rightarrow \sigma_{\text{eq-C-H}}^*$) similar to that calculated for thiane^[29] is responsible for a short equatorial bond. It is noteworthy that for this axial sulfur lone pair a 100% p character was calculated, resulting in more distinct donor ability.^[29] The axial C–H bond might be stabilized by $\sigma_{\text{ax-C-H}} \rightarrow \sigma_{\text{eq-S=O}}^*$ as it has been proposed for the axial C–H in bissulfoxide **6**.

Again a negative Perlin effect ($\Delta J_{\text{C-6-H}} = -1.4$ Hz) next to the equatorial sulfoxide group at position C-6 can be explained by $\sigma_{\text{C-2-S}} \rightarrow \sigma_{\text{eq-C-4-H}}^*$ hyperconjugation. Because a C–(S=O) bond will not be as effective a donor relative to the C–S bond, the effect is smaller than that observed for position C-4.

Sulfilimine **9** was prepared from 2-benzylidene-1,3-dithiane by sulfilimination with chloramine T. The structure of this substrate could unambiguously be confirmed by X-ray crystallographic analysis (Figure 5). The NMR spectra confirmed that the conformation present in the crystal is preferred similarly in solution. Evaluation of the $^1J_{\text{C-H}}$ coupling constants again revealed that sulfilimines and sulfoxides give rise to similar stereoelectronic effects. As has already been noted for sulfilimine **7** the axial $^1J_{\text{C-H}}$ coupling constant at position C-6 is very high and participation of the equatorial C-6-H in hyperconjugation is less effective than that of the corresponding sulfoxide **8** giving rise for a more distinct negative Perlin effect (Table 4).

(*R,S,E*)-2-Benzylidene-1,3-dithiane-1,1,3-trioxide (10): Bissulfoxide **6** was oxidized to the corresponding monosulfone **10** by using *m*CPBA. Selective oxi-



Figure 5. Structure of sulfilimine **9** in the crystal.^[23]Table 4. $^1J_{\text{C-H}}$ coupling constants in dithiane-derived sulfilimine **9**.

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	31.1	4-H _{eq}	2.72	140.7	−3.4
		4-H _{ax}	2.86	144.1	
C-5	26.5	5-H _{eq}	2.54	130.5	−0.6
		5-H _{ax}	2.69	131.1	
C-6	51.6	6-H _{eq}	3.34	142.9	−3.2
		6-H _{ax}	3.24	146.1	

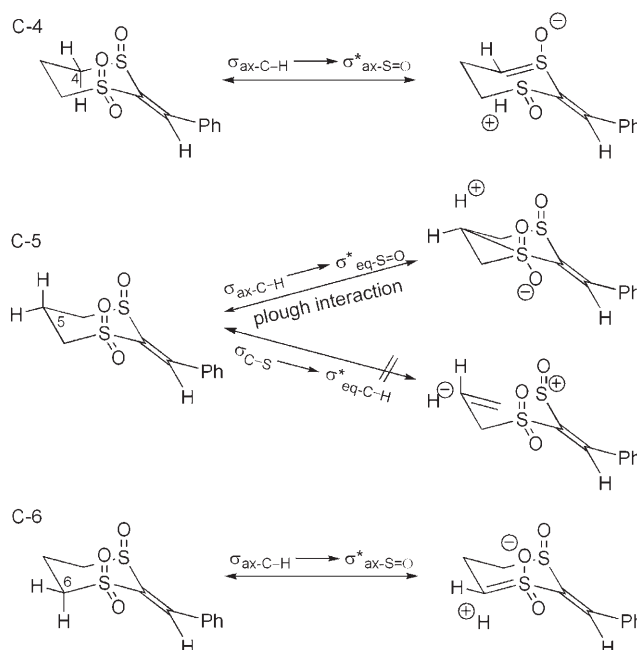
dation in the less sterically hindered position S-3 (S-1 in sulfone **10**) can be concluded for the following reasons: 1) The vinylic hydrogen is shifted in the ^1H NMR spectra from $\delta = 7.52$ ppm for sulfoxide **6** to $\delta = 8.19$ ppm for monosulfone **10**; 2) The axial 6-H (numbering as in sulfone **10**) is shifted from $\delta = 2.93$ ppm in sulfoxide **6** to $\delta = 3.31$ ppm; 3) The axial 5-H reaching in the direction of the new S=O bond is shifted from $\delta = 3.19$ ppm to $\delta = 3.48$ ppm (Table 5).

Table 5. $^1J_{\text{C-H}}$ coupling constants in dithiane-derived sulfoxide-sulfone **10**.

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	48.6	4-H _{eq}	3.35	140.3	+3.2
		4-H _{ax}	2.90	137.1	
C-5	16.5	5-H _{eq}	2.51	136.2	+1.8
		5-H _{ax}	3.48	134.4	
C-6	54.3	6-H _{eq}	3.55	139.0	+0.6
		6-H _{ax}	3.31	138.4	

The following Perlin effects resulted from the respective $^1J_{\text{C-H}}$ coupling constants (Table 5): For position C-4 again a normal Perlin effect ($\Delta J_{\text{C-4-H}} = +3.2$ Hz) was determined, which should again be due to a $\sigma_{\text{ax-C-4-H}} \rightarrow \sigma^*_{\text{ax-S=O}}$ interaction (Figure 6). The coupling constants are exactly the same as for C-6 in bissulfoxide **6**.

A normal Perlin effect was observed for position C-5 ($\Delta J_{\text{C-5-H}} = +1.8$ Hz). The poor donor ability of the C–(S=O)

Figure 6. Explanation of Perlin effects dithiane-derived sulfoxide-sulfone **10**.

and C–(SO₂) bonds is obviously more than counteracted by a plough β -interaction ($\sigma_{\text{ax-C-H}} \rightarrow \sigma^*_{\text{eq-S=O}}$), which has already been discussed for bissulfoxide **6** and monosulfoxide **8**. Nevertheless, it has to be noted that also the equatorial C-5–H is weakened significantly ($^1J_{\text{eq-C-5-H}} = 136.2$ Hz), most probably due to a double $\sigma_{\text{C-S}} \rightarrow \sigma^*_{\text{eq-C-5-H}}$ interaction with both antiperiplanar C–S bonds.

The positive Perlin effect ($\Delta J_{\text{C-6-H}} = +0.6$ Hz) at position C-6 might be explained by a $\sigma_{\text{ax-C-H}} \rightarrow \sigma^*_{\text{ax-S=O}}$ interaction. Shainyan and co-workers already observed that an axial S=O group part of a sulfone is a less effective acceptor compared with an S=O group which is part of a sulfoxide (see compounds **1** and **2**).^[17] The competing $\sigma_{\text{C-S}} \rightarrow \sigma^*_{\text{eq-C-5-H}}$ interaction, weakening the equatorial C-6–H bond consequently is in the same range giving rise to a negligible Perlin effect of only +0.6 Hz. Nevertheless, thiane-1,1-dioxide (**4**) and 1,3-dithiane-1,1-dioxide (**5**), the coupling constants of which have been calculated by Juaristi and co-workers,^[18] show significantly higher Perlin effects (**4**: $\Delta J_{\text{C-2-H}} = +2.8$ Hz, **5**: $\Delta J_{\text{C-6-H}} = +2.6$ Hz, Figure 2).

The conformation of monosulfone **10** avoids severe allylic strain which would arise from a flipped-chair conformation. This is supported by stereoelectronic effects described above and by evaluation of the ^{13}C NMR spectra: ^{13}C shifts in position C-5 of thiane- and 1,3-dithiane-derived S-oxides are strongly dependent from the number of β -sulfoxides with S=O groups in axial position (γ -gauche effect).^[32] Axial S=O groups which are part of a sulfone moiety do not contribute to this effect and compounds bearing a sulfilimine group behave inconsistently in that context.^[33] The ^{13}C shift of C-5 in monosulfone **10** is $\delta = 16.5$ ppm and is therefore comparable to the shift measured for *trans*-1,3-dithiane-1,3-

dioxide (**12**, $\delta=16.6$ ppm)^[34] and for bissulfoxide **6** ($\delta=14.9$ ppm) giving further evidence for the presence of a sulfoxide with an axial S=O group (Figure 7). On the other

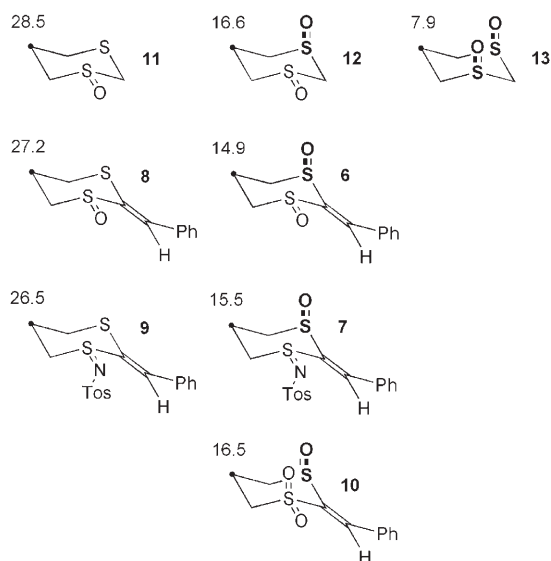
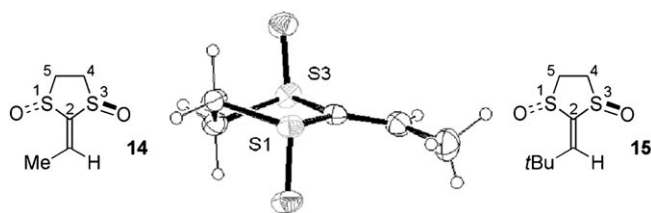


Figure 7. The γ -gauche effect. ^{13}C shifts are given in ppm.

hand, monosulfoxide **8** is present in a conformation without an axial S=O group as the chemical shift of C-5 ($\delta=27.2$ ppm) is comparable to that of 1,3-dithiane-1-oxide (**11**) with its S=O group in an equatorial orientation ($\delta=28.5$ ppm).^[35] Two axial S=O groups lead to a chemical shift of $\delta=7.9$ ppm as measured for compound **13**.^[35] Sulfilimines **7** and **9** fit in that scheme though it has to be kept in mind, that this empirical rule on the γ -gauche effect is not generally valid for this class of compounds.^[34]

(*R_S,R_S*)-2-Ethylidene-1,3-dithiolane-1,3-dioxide (14): Dithiolane-derived bissulfoxide **14** exhibits a C-2 half-chair



conformation with the sulfur atoms and the C=C double bond adopting a plane. This could be proven by X-ray crystallographic analysis^[23b] and by NMR spectroscopic investigations. Both sulfoxide groups are oriented, almost perfectly, in opposite directions. Hydrogens in position C-4 and C-5 are virtually axial and equatorial, respectively. This is in agreement with Kirby's rule,^[35] which designates that confor-

mation to be most stable in which the best donor lone pair (or the best donor bond) is antiperiplanar to the best acceptor bond. The ^1H NMR signals are fully resolved for the corresponding *tert*-butyl-substituted derivative **15**^[36] and the $^1J_{\text{C-H}}$ coupling constants were determined (Table 6).

Table 6. $^1J_{\text{C-H}}$ coupling constants in dithiolane-derived bissulfoxide **14**

Carbon	δ [ppm]	Proton	δ [ppm]	$^1J_{\text{C-H}}$ [Hz]	Perlin effect ΔJ [Hz]
C-4	31.1	4- H_{eq}	3.52	146.2	+6.2
		4- H_{ax}	3.63	140.0	
C-5	26.5	5- H_{eq}	3.73	147.9	+7.6
		5- H_{ax}	2.82	140.3	

In summary, all coupling constants are above 140 Hz and the Perlin effects are much larger than for the six-membered heterocycles discussed above. The weakening of the axial C-H bonds can be explained by a $\sigma_{\text{ax-C-H}} \rightarrow \sigma_{\text{ax-S=O}}^*$ hyperconjugation. Obviously no appreciable stereoelectronic effect is able to weaken the equatorial C-H bonds. The 146.2 and 147.9 Hz coupling constants are among the highest measured in the systems presented here. Remarkably, a 5J long-range coupling of 1.1 Hz between the vinylic hydrogen and the eq-5-C-H could be resolved for this compound.

Conclusion

Orbital interactions of sulfoxides and sulfilimines have been elucidated for the first time by measuring $^1J_{\text{C-H}}$ coupling constants in conformationally constrained substrates without interfering heteroatoms other than sulfur. The strongest effects arise from the interaction of axial S=O bonds with antiperiplanar C-H bonds, but other consistent effects, for example, homoanomeric effects can be rationalized similarly. Because stereoelectronic effects have not only an effect on coupling constants, but also on conformation and especially on chemical reactivity, this knowledge should be of substantial interest for determining the chemistry of sulfoxides and related compounds.

Experimental Section

The synthesis of (*R_S,R_S*)-2-benzylidene-1,3-dithiane-1,3-dioxide (**6**)^[23a] (*R_S,R_S*)-2-ethylidene-1,3-dithiolane-1,3-dioxide (**14**)^[23b] and 2-benzylidene-1,3-dithiane-1,3-dioxide^[37b] has been published elsewhere. All moisture-sensitive reactions were carried out under oxygen-free argon by using oven-dried glassware and a vacuum line. Flash column chromatography was carried out by using Merck silica gel 60 (230–400 mesh), and thin-layer chromatography was carried out by using commercially available Merck F₂₅₄ pre-coated sheets. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-400, DRX 500, and AV-600 instruments, respectively. Chemical shifts are given in ppm downfield of tetramethylsilane. ^{13}C NMR spectra were recorded with broad-band proton decoupling and were assigned by using DEPT experiments. $^1J_{\text{C-H}}$ coupling constants were measured by using coupled HMQC experiments^[24,25] or coupled HSQC experiments (Bruker

pulse program hsqcetgpi2; power level pl12 set to 120 dB to prevent decoupling).^[25,27] Melting points were measured on a Büchi apparatus and were not corrected. IR spectra were recorded on a Bruker IFS-88 spectrometer. Elemental analyses were performed on a Heraeus CHN-O-rapid machine. EI, FAB, and high-resolution mass spectra were recorded on a Finnigan MAT-90 spectrometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter.

rac-(E)-2-Benzylidene-1,3-dithiane-1-oxide (8): 2-Benzylidene-1,3-dithiane (210 mg, 1.00 mmol) was dissolved in fresh molten PhOH (12.0 mmol, 1.13 g) and H₂O₂ (30%, 4 mmol, 450 µL) was slowly added at room temperature. The mixture was quenched after 10 min with saturated Na₂SO₃ solution (1 mL) and was washed with aqueous NaOH solution (10%, 12 mmol, 4.35 mL). The aqueous phase was extracted with CH₂Cl₂ (3 ×) and dried (Na₂SO₄). The solvent was removed and the residue was purified by chromatography on SiO₂ (hexane/ethyl acetate 2:1 → 1:4) yielding ketene dithioacetal **8** (182 mg, 0.811 mmol, 81%) as a colorless waxy solid: m.p. 70°C (ethyl acetate/hexane); *R*_f = 0.19 (hexane/ethyl acetate 1:4); ¹H NMR (400 MHz, CDCl₃): δ = 2.46–2.57 (m, 2H; 5-H_{eq}, 5-H_{ax}), 2.65 [dddd, ²J(4-H_{eq}–4-H_{ax}) = 13.1, ³J(4-H_{eq}–5-H) = 4.3, ³J(4-H_{eq}–5-H) = 3.7, ⁴J(4-H_{eq}–6-H_{eq}) = 1.3, ⁴J(4-H_{eq}–6-H_{ax}) = 0.8 Hz, 1H; 4-H_{eq}], 2.87 (m, 1H; 4-H_{ax}), 2.90 (m, 1H; 6-H_{ax}), 3.43 [dddd, ²J(6-H_{ax}–6-H_{eq}) = 12.1, ³J(6-H_{eq}–5-H) = 5.4, ³J(6-H_{eq}–5-H) = 3.0, ⁴J(6-H_{eq}–4-H_{eq}) = 1.3 Hz, 1H; 6-H_{eq}], 7.35–7.45 (m, 3H; Ph), 7.52 (s, 1H; =CH), 7.74–7.79 ppm (m, 2H; Ph); ¹³C NMR (100 MHz, CDCl₃): δ = 27.2 (t; C-5), 31.8 (t; C-4), 55.0 (t; C-6), 128.5 (d), 129.0 (d), 130.2 (d), 133.7 (s), 134.6 (d), 136.7 ppm (s); selected ¹J(C–H) coupling constants (HSQC, 600 MHz, CDCl₃): ¹J(C–4-H_{eq}) = 139.1, ¹J(C–4-H_{ax}) = 142.4, ¹J(C–6-H_{eq}) = 139.9, ¹J(C–6-H_{ax}) = 141.3 Hz; IR (DRIFT): $\tilde{\nu}$ = 3067 (m), 3050 (m), 3023 (m), 2953 (m), 2921 (s), 2904 (m), 2843 (m), 1484 (s), 1445 (s), 1423 (s), 1339 (m), 1222 (s), 1204 (m), 1173 (m), 1153 (m), 1058 (s, S=O), 1045 cm^{–1} (s); MS (EI, 80°C): *m/z* (%): 224 (56) [*M*⁺], 135 (12), 134 (100), 122 (12), 118 (22), 108 (13), 106 (84), 102 (15), 90 (24), 89 (20); HRMS (EI) calcd for C₁₁H₁₂OS₂: 224.0330; found: 224.0326.

rac-(E)-2-Benzylidene-1-(4-methylphenylsulfonylimino)-1,3-dithiane (9): Sodium *p*-toluenesulfonylchloramide (chloramine T, 369 mg, 1.40 mmol) was added to a stirred solution of 2-benzylidene-1,3-dithiane^[57b] (244 mg, 1.17 mmol) in acetonitrile (4 mL) and stirring was continued for 2 h at room temperature. Precipitated NaCl was removed by filtration and the solvent was removed at reduced pressure. The residue was purified by chromatography on SiO₂ (CH₂Cl₂/MeOH 50:1) to yield sulfilimine **9** as white crystals (343 mg, 0.910 mmol, 78%): m.p. 140–142°C; *R*_f = 0.29 (CH₂Cl₂/MeOH 20:1); ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3H; CH₃), 2.40–2.56 (m, 1H; H-5_{eq}), 2.57–2.73 (m, 2H; H-4_{eq}, H-5_{ax}), 2.74–2.87 (m, 1H; H-4_{ax}), 3.20 (ddd, ²J = 12.6, ³J = 11.5, ³J = 2.8 Hz, 1H; H-6_{ax}), 3.30 (dddd, ²J = 12.6, ³J = 5.7, ³J = 3.1, ⁴J = 1.3 Hz, 1H; H-6_{eq}), 7.12–7.23 (m, 2H; arom_{ph}), 7.28–7.37 (m, 3H; arom_{ph}), 7.40 (s, 1H; =CH), 7.46–7.55 (m, 2H; arom_{tol}), 7.75–7.83 ppm (m, 2H; arom_{tol}); ¹³C NMR (100 MHz, CDCl₃): δ = 21.4 (q), 26.4 (t; C-5), 31.1 (t; C-4), 51.5 (t; C-6), 126.3 (d, 2C), 127.4 (s), 128.5 (d, 2C), 129.1 (d), 129.4 (d, 2C), 130.0 (d), 130.4 (d), 132.6 (s), 139.4 (d), 141.5 (s), 141.9 ppm (s); selected ¹J(C–H) coupling constants (HSQC, 600 MHz, CDCl₃): ¹J(C–H-5_{eq}) = 130.5, ¹J(C–H-5_{ax}) = 131.1, ¹J(C–H-4_{eq}) = 140.7, ¹J(C–H-4_{ax}) = 144.1, ¹J(C–H-6_{eq}) = 142.9, ¹J(C–H-6_{ax}) = 146.1 Hz; IR (DRIFT): $\tilde{\nu}$ = 1279 (s), 1137 (s), 975 cm^{–1} (s); MS (EI, 190°C): *m/z* (%): 378.1 [(*M*+1)⁺]; HRMS (FAB) calcd for C₁₈H₂₀NO₂S₃: 378.0657; found: 378.0661; elemental analysis calcd (%) for C₁₈H₁₉NO₂S₃ (337.5): C 57.26, H 5.07, N 3.71; found: C 57.01, H 5.00, N 3.71.

rac-(R_sR_s2Z)-2-Benzylidene-3-(4-methylphenylsulfonylimino)-1,3-dithiane-1-oxide (7): Freshly purified *m*CPBA (129 mg, 0.75 mmol) in CH₂Cl₂ (6 mL) was transferred within 30 min through a syringe pump to a pre-cooled (0°C) solution of sulfilimine **9** (189 mg, 0.500 mmol) in CH₂Cl₂ (6 mL) whereupon a white solid precipitated. Satd NH₄Cl solution (15 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3 × 15 mL) and the combined organic layers were extracted with brine (25 mL) and dried (Na₂SO₄), and the solvent was removed at reduced pressure. The oily residue (224 mg) was purified by chromatography on SiO₂ (hexane/ethyl acetate 1:4–0:1) to yield sulfoxide **7** (132 mg, 0.336 mmol, 68%) as white crystals: m.p. 174–

175°C; *R*_f = 0.06 (hexane/ethyl acetate 1:4); ¹H NMR (400 MHz, CDCl₃): δ = 2.37 (s, 3H; CH₃), 2.40–2.48 (m, 1H; H-5_{eq}), 2.89 (ddd, ²J = 13.5, ³J = 12.2, ³J = 3.1 Hz, 1H; H-6_{ax}), 3.11–3.33 (m, 3H; H-6_{eq}, H-5_{ax}, H-4_{ax}), 3.51 (dddd, ²J = 11.7, ³J = 2.9, ³J = 2.9, ³J = 2.7, ³J = 1.2 Hz, 1H; H-4_{eq}), 7.15–7.20 (m, 2H; arom_{tol}), 7.21–7.27 (m, 2H; arom_{ph}), 7.35–7.45 (m, 3H; arom_{ph}), 7.53 (s, 1H; =CH), 7.77–7.82 ppm (m, 2H; arom_{tol}); ¹³C NMR (100 MHz, CDCl₃): δ = 15.6 (t; C-5), 21.5 (q), 47.8 (t; C-4), 52.4 (t; C-6), 126.3 (d), 128.9 (d), 129.6 (d), 131.0 (d), 131.2 (s), 136.5 (s), 140.2 (d), 141.1 (s), 142.4 ppm (s); selected ¹J(C–H) coupling constants (HSQC, 600 MHz, CDCl₃): ¹J(C–H-5_{ax}) = 137.6, ¹J(C–H-4_{ax}) = 138.1, ¹J(C–H-4_{eq}) = 141.1, ¹J(C–H-6_{ax}) = 148.4, ¹J(C–H-6_{eq}) = 144.2 Hz; IR (DRIFT): $\tilde{\nu}$ = 1146 (s), 969 cm^{–1} (s); MS (FAB): *m/z* (%): 306 [(*M*+1)⁺]; elemental analysis calcd (%) for C₁₁H₁₅NO₃S₃ (393.5): C 54.93, H 4.87, N 3.56; found: C 54.72, H 5.04, N 3.67.

(R_sE)-2-Benzylidene-1,3-dithiane-1,1,3-trioxide (10): Freshly purified *m*CPBA (553 mg, 3.20 mmol) in CHCl₃ (8 mL) was added within 30 min to a cooled (–20°C) solution of bissulfoxide **6** (480 mg, 2.00 mmol) in CHCl₃ (10 mL). The solution was stored for 12 h at –23°C (e.g., in a fridge) and filtered without warming through a column filled with Alox (pH 10). The column was rinsed with CH₂Cl₂ (50 mL) and the washings were concentrated in vacuum. Chromatography of the residue on SiO₂ (MPLC, CH₂Cl₂/MeOH 100:1) yielded monosulfone **10** (244 mg, 0.952 mmol, 48%) and recovered starting material (180 mg, 0.750 mmol, 38%): [α]_D²⁰ = –189 (*c* = 1.0 in CHCl₃); *R*_f = 0.68 (CH₂Cl₂/acetone 2:1); ¹H NMR (500 MHz, CDCl₃): δ = 2.51 (dddd, ²J(5-H_{eq}–5-H_{ax}) = 15.5, ³J(5-H_{eq}–6-H_{eq}) = 5.2, ³J(5-H_{eq}–4-H_{eq}) = 4.9, ³J(5-H_{eq}–6-H_{ax}) = 3.1, ³J(5-H_{eq}–4-H_{ax}) = 2.5 Hz, 1H; 5-H_{eq}), 2.90 (ddd, ²J(4-H_{ax}–4-H_{eq}) = 14.5, ³J(4-H_{ax}–5-H_{ax}) = 12.7, ³J(4-H_{ax}–5-H_{eq}) = 2.5 Hz, 1H; 4-H_{ax}), 3.31 (ddd, ²J(6-H_{ax}–6-H_{eq}) = 13.8, ³J(6-H_{ax}–5-H_{ax}) = 12.1, ³J(6-H_{ax}–5-H_{eq}) = 3.1 Hz, 1H; 6-H_{ax}), 3.35 (dddd, ²J(4-H_{eq}–4-H_{ax}) = 14.5, ³J(4-H_{eq}–5-H_{eq}) = 4.9, ³J(4-H_{eq}–5-H_{ax}) = 2.4, ⁴J(4-H_{eq}–6-H_{eq}) = 1.2 Hz, 1H; 4-H_{eq}), 3.48 (dddd, ²J(5-H_{ax}–5-H_{eq}) = 15.5, ³J(5-H_{ax}–4-H_{ax}) = 12.7, ³J(5-H_{ax}–6-H_{ax}) = 12.1, ³J(5-H_{ax}–6-H_{eq}) = 2.9, ³J(5-H_{ax}–4-H_{eq}) = 2.4 Hz, 1H; 5-H_{ax}), 3.55 (dddd, ²J(6-H_{eq}–6-H_{ax}) = 13.8, ³J(6-H_{eq}–5-H_{eq}) = 5.2, ³J(6-H_{eq}–5-H_{ax}) = 2.9, ⁴J(6-H_{eq}–4-H_{eq}) = 1.2 Hz, 1H; 6-H_{eq}), 7.48–7.55 (m, 3H; arom), 7.62–7.65 (m, 2H; arom), 8.19 ppm (s, =CH); ¹³C NMR (125 MHz, CDCl₃): δ = 16.5 (t; C-5), 48.6 (t; C-4), 54.3 (t; C-6), 129.1 (d), 130.4 (s), 131.1 (d), 131.9 (d), 139.1 (s), 147.1 ppm (s); selected ¹J_{C–H} coupling constants: ¹J(C–H-5_{eq}) = 136.2, ¹J(C–H-5_{ax}) = 134.4, ¹J(C–H-4_{eq}) = 140.3, ¹J(C–H-4_{ax}) = 137.1, ¹J(C–H-6_{eq}) = 139.0, ¹J(C–H-6_{ax}) = 138.4 Hz; IR (DRIFT): $\tilde{\nu}$ = 3002 (m), 2922 (m), 1601 (m), 1443 (m), 1311 (s, SO₂), 1179 (m), 1136 (s, SO₂), 1112 (m), 1049 (s, S=O), 924 cm^{–1} (m); MS (EI, 25°C): *m/z* (%): 256 (14) [*M*⁺], 171 (23), 153 (54), 147 (18), 141 (13), 136 (31), 134 (24), 129 (27), 118 (16), 115 (13), 108 (20), 107 (50), 106 (31), 105 (56), 102 (30), 91 (23), 90 (23), 89 (52), 87 (18), 79 (28), 28 (32), 77 (100), 75 (69); UV/Vis (EtOH): $\lambda_{\max}$ (ϵ) = 192 (12100), 201 (12000), 271 nm (11200 mol^{–1} dm³ cm^{–1}); HRMS (EI) calcd for C₁₁H₁₂O₃S₂: 256.0228; found: 256.0219; elemental analysis calcd (%) for C₁₁H₁₂O₃S₂ (256.3): C 51.54, H 4.72; found: C 51.74, H 4.75.

(R_sR_s)-2-(2,2-Dimethylpropylidene)-1,3-dithiolane-1,3-dioxide (15): Ethane-1,2-dithiol (2.83 g, 30 mmol) was added dropwise at 0°C to 3,3-dimethylbutyric chloride (30 mmol) and stirring was continued for 30 min at this temperature. Perchloric acid (70%, 3.1 mL, 36 mmol) was carefully added dropwise. An exothermic reaction started after 0.5–5 min. The mixture was stirred for 30 min at room temperature, cooled to 0°C, and freshly distilled Ac₂O (15 mL) was carefully added dropwise. The dithiolanium salt was precipitated with anhydrous Et₂O (50 mL) and filtered under argon. The red needles were washed with Et₂O (3 × 20 mL) and dissolved in anhydrous MeCN (30 mL). Et₃N was added until the red color disappeared and the solvents were removed under reduced pressure. The resulting oil was dissolved in saturated aqueous NH₄Cl solution (40 mL) and the solution was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried (Na₂SO₄ and K₂CO₃), the solvents were removed, and the residue was distilled by bulb-to-bulb distillation yielding 2-(2,2-dimethylpropylidene)-1,3-dithiolane (2.09 g, 12.0 mmol, 40%) as a pale yellow oil: ¹H NMR (250 MHz, CDCl₃): δ = 1.11 (s, 9H; *t*Bu), 3.14–3.19, 3.37–3.42 (2 m, 2 × 2H; 4-H₂, 5-H₂), 5.61 ppm (s, 1H; =CH).

(+)-Diethyl tartrate (24.0 mmol, traces of water were removed by azeotropic distillation with toluene) and freshly distilled $\text{Ti}(\text{O}-i\text{Pr})_4$ (6.00 mmol) were dissolved at room temperature under argon in anhydrous CH_2Cl_2 (120 mL) and the mixture was stirred for 30 min. 2-(2,2-Dimethylpropylidene)-1,3-dithiolane (2.09 g, 12.0 mmol) in CH_2Cl_2 (12 mL) was added, the mixture was cooled to -40°C and was stirred for 2 h. Cumene hydroperoxide (technical grade, 80%, 48 mmol, diluted with CH_2Cl_2 to twice the volume) was added within 1 h. The solution was warmed to -20°C and stored for 15 h in a freezer ($<-20^\circ\text{C}$). H_2O (4.32 mL) was added and the mixture was stirred vigorously for 1 h at room temperature. The slurry was kept for 1 h in an ultrasonication bath and the resulting suspension was filtered through a glass sinter (G2) covered with a Celite pad (1.5 cm). The filter cake was washed repeatedly with small amounts of CH_2Cl_2 . The solvents were removed and chromatography on SiO_2 ($\text{CH}_2\text{Cl}_2/\text{acetone}$ 2:1) yielded sulfoxide **15** (1.57 g, 7.61 mmol, 63%) as colorless crystals; m.p.: $165\text{--}166^\circ\text{C}$ ($\text{CH}_2\text{Cl}_2/\text{hexane}$); $R_f=0.19$ ($\text{CH}_2\text{Cl}_2/\text{acetone}$ 2:1); $[\alpha]_D^{20}=-226$ ($c=1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta=1.39$ (s, 9H; $t\text{Bu}$), 3.52 (ddd, $^3J(4\text{-H}_{\text{eq}}-4\text{-H}_{\text{ax}})=13.6$, $^3J(4\text{-H}_{\text{eq}}-5\text{-H}_{\text{ax}})=4.5$, $^3J(4\text{-H}_{\text{eq}}-5\text{-H}_{\text{eq}})=1.8$ Hz, 1H; 4-H_{eq}), 3.63 (ddd, $^2J(4\text{-H}_{\text{ax}}-4\text{-H}_{\text{eq}})=13.6$, $^3J(4\text{-H}_{\text{ax}}-5\text{-H}_{\text{ax}})=13.3$, $^3J(4\text{-H}_{\text{ax}}-5\text{-H}_{\text{eq}})=4.3$ Hz, 1H; 4-H_{ax}), 3.72 (dddd, $^2J(5\text{-H}_{\text{eq}}-5\text{-H}_{\text{ax}})=14.2$, $^3J(5\text{-H}_{\text{eq}}-4\text{-H}_{\text{ax}})=4.3$, $^3J(5\text{-H}_{\text{eq}}-4\text{-H}_{\text{eq}})=1.8$, $^2J(5\text{-H}_{\text{eq}}=\text{CH})=1.1$ Hz, 1H; 5-H_{eq}), 3.82 (ddd, $^2J(5\text{-H}_{\text{ax}}-5\text{-H}_{\text{eq}})=14.2$, $^2J(5\text{-H}_{\text{ax}}-4\text{-H}_{\text{ax}})=13.3$, $^3J(5\text{-H}_{\text{ax}}-4\text{-H}_{\text{eq}})=4.5$ Hz, 1H; 5-H_{ax}), 7.28 ppm (s, 1H, $=\text{CH}$). Assignment of the protons was made with the assumption that the $^3J(5\text{-H}_{\text{eq}}=\text{CH})$ coupling is a *trans* coupling; ^{13}C NMR (100 MHz, CDCl_3): $\delta=29.6$ (q, 3C), 37.8 (s), 48.4 (t), 51.9 (t), 153.5 (s), 164.5 ppm (d); selected $^1J(\text{C-H})$ coupling constants (HMOC, 500 MHz, CDCl_3): $^1J(\text{C-H}_{4\text{eq}})=146.2$, $^1J(\text{C-H}_{4\text{ax}})=140.0$, $^1J(\text{C-H}_{5\text{eq}})=147.9$, $^1J(\text{C-H}_{5\text{ax}})=140.3$ Hz; IR (DRIFT): $\tilde{\nu}=2973$ (m), 1593 (m), 1477 (m), 1086 (m), 1027 cm^{-1} (s, S=O); MS (EI, 30°C): m/z (%): 206 (23) [M^+], 163 (100) [$(\text{M}-\text{C}_3\text{H}_7)^+$], 113 (22), 112 (13), 104 (14), 103 (11), 77 (13), 76 (11), 57 (17); HRMS (EI) calcd for $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$: 206.0435; found: 206.0426; elemental analysis calcd (%) for $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$ (206.3): C 46.57, H 6.84; found: C 46.50, H 6.80.

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- [1] a) M. Karplus, *J. Chem. Phys.* **1959**, *30*, 11–15; b) M. Karplus, *J. Am. Chem. Soc.* **1963**, *85*, 2870–2871.
- [2] E. Kleinpeter, A. Koch, K. Pihlaja, *Tetrahedron* **2005**, *61*, 7349–7358.
- [3] A. S. Perlin, B. Casu, *Tetrahedron Lett.* **1969**, *10*, 2921–2924.
- [4] E. Juaristi, G. Cuevas, *Tetrahedron* **1992**, *48*, 5019–5087.
- [5] J. D. Roberts, R. L. Webb, E. A. McElhill, *J. Am. Chem. Soc.* **1950**, *72*, 408–411.
- [6] It has recently been shown that the $^1J_{\text{C-H}}$ value is not necessarily a consequence of $n_{\text{O}}\rightarrow\sigma^*_{\text{C-H}}$ delocalization: G. Cuevas, K. Martínez-Mayorga, M. d. C. Fernández-Alonso, J. Jiménez-Barbero, C. L. Perrin, E. Juaristi, N. López-Mora, *Angew. Chem.* **2005**, *117*, 2412–2416; *Angew. Chem. Int. Ed.* **2005**, *44*, 2360–2364.
- [7] S. Wolfe, B. M. Pinto, V. Varma, R. Y. N. Leung, *Can. J. Chem.* **1990**, *68*, 1051–1062.
- [8] a) S. David in *Anomeric Effect: Origin and Consequences* (Eds.: W. A. Szarek, D. Horton), American Chemical Society Symposium Series, Washington, DC, **1979**; b) E. Juaristi, G. Cuevas, *The Anomeric Effect*, CRC, Boca Raton, **1992**; c) E. Juaristi, M. Ordoñez in *Organosulfur Chemistry — Synthetic and Stereochemical Aspects*, Vol. 2 (Ed.: P. Page), Academic Press, San Diego, **1998**, pp. 63–95.
- [9] J. E. Anderson, A. J. Bloodworth, J. Cai, A. G. Davies, N. A. Tallant, *J. Chem. Soc. Chem. Commun.* **1992**, 1689–1691.
- [10] I. V. Alabugin, *J. Org. Chem.* **2000**, *65*, 3910–3919.
- [11] a) G. Cuevas, E. Juaristi, A. Vela, *J. Phys. Chem. A* **1999**, *103*, 932–937; b) E. Juaristi, G. Cuevas, A. Vela, *J. Am. Chem. Soc.* **1994**, *116*, 5796–5804.
- [12] S. Wolfe, C.-K. Kim, *Can. J. Chem.* **1991**, *69*, 1408–1412.
- [13] a) A. S. Cieplak, *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552; b) A. S. Cieplak, B. D. Tait, C. R. Johnson, *J. Am. Chem. Soc.* **1989**, *111*, 8447–8462.
- [14] a) W. F. Bailey, A. D. Rivera, K. Rossi, *Tetrahedron Lett.* **1988**, *29*, 5621–5624; b) E. Juaristi, G. Cuevas, *Tetrahedron Lett.* **1992**, *33*, 1847–1850; c) E. Juaristi, G. Cuevas, A. Flores-Vela, *Tetrahedron Lett.* **1992**, *33*, 6927–6930.
- [15] The sulfur lone pairs and especially a sulfoxide lone pair are hardly effective as donors: a) E. Juaristi, M. Ordoñez, *Tetrahedron* **1994**, *50*, 4937–4948; b) V. K. Aggarwal, J. M. Worrall, H. Adams, R. Alexander, B. F. Taylor, *J. Chem. Soc. Perkin Trans. 1* **1997**, 21–24.
- [16] Participation of sulfur d orbitals has been considered repeatedly but was found to have minor influence on stereoelectronic effects: a) A. E. Reed, P. von R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434–1445; b) N. D. Epiotis, R. L. Yates, F. Bernardi, S. Wolfe, *J. Am. Chem. Soc.* **1976**, *98*, 5435–5439.
- [17] B. A. Shainyan, I. A. Ushakov, E. N. Suslova, *J. Sulfur Chem.* **2006**, *27*, 3–13.
- [18] R. Notario, M. V. Roux, G. Cuevas, J. Cardenas, V. Leyva, E. Juaristi, *J. Phys. Chem. A* **2006**, *110*, 7703–7712.
- [19] B. A. Shainyan, S. V. Kirpichenko, *Russ. J. Gen. Chem.* **2003**, *73*, 1709–1714; B. A. Shainyan, S. V. Kirpichenko, *Zh. Obshch. Khim.* **2003**, *73*, 1806–1811.
- [20] A sulfoxide S=O group is not properly described by an S=O double bond. This picture is used herein anyway. a) D. B. Chesnut, L. D. Quin, *J. Comput. Chem.* **2004**, *26*, 734–738; b) V. M. Bzhezovskii, N. N. Il'chenko, M. B. Chura, L. G. Gorb, L. M. Yagupol'skii, *Russ. J. Gen. Chem.* **2005**, *75*, 86–93; V. M. Bzhezovskii, N. N. Il'chenko, *Zh. Obshch. Khim.* **2005**, *75*, 96–104.
- [21] a) S. Wolfe, A. Stolow, L. A. LaJohn, *Tetrahedron Lett.* **1983**, *24*, 4071–4074; b) S. Wolfe in *Organic Sulfur Chemistry—Theoretical and Experimental Advances* (Eds.: F. Bernardi, I. G. Csizmadia, A. Mangini), Elsevier, Amsterdam, **1985**, pp. 133–190.
- [22] The nature of the S=N double bond has been studied: a) S. Tsuchiya, S. Mitomo, M. Seno, H. Miyamae, *J. Org. Chem.* **1984**, *49*, 3556–3559; b) P. S. Kumar, P. Singh, P. Uppal, P. V. Bharatam, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1417–1424.
- [23] a) T. Wedel, J. Podlech, *Org. Lett.* **2005**, *7*, 4013–4015; b) T. Wedel, J. Podlech, *Synlett* **2006**, 2043–2046.
- [24] a) L. Müller, *J. Am. Chem. Soc.* **1979**, *101*, 4481–4484; b) A. Bax, R. H. Griffey, B. L. Hawkins, *J. Magn. Reson. Ser. A* **1983**, *55*, 301–315.
- [25] S. Berger, S. Braun, *200 and More NMR Experiments: A Practical Course*, Wiley-VCH, Weinheim, **2004**.
- [26] Spectra and coupling constants are given in the Supporting Information.
- [27] G. Bodenhausen, D. J. Ruben, *Chem. Phys. Lett.* **1980**, *69*, 185–189.
- [28] J. Cai, A. G. Davies, C. H. Schiesser, *J. Chem. Soc. Perkin Trans. 2* **1994**, 1151–1156.
- [29] I. V. Alabugin, M. Manoharan, T. A. Zeidan, *J. Am. Chem. Soc.* **2003**, *125*, 14014–14031.
- [30] An explanation of this term is given in footnote 33 of reference [29]: Plough is another name for the star constellation Ursa Major, also known as the big dipper.
- [31] W. L. Xu, Y. Z. Li, Q. S. Zhang, H. S. Zhu, *Synthesis* **2004**, 227–232.
- [32] Details on the crystallographic analysis of sulfilimine **9** are given in the Supporting Information. CCDC-622411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [33] a) H. Duddeck, U. Korek, D. Rosenbaum, J. Drabowicz, *Magn. Reson. Chem.* **1986**, *24*, 792–797; b) H. Duddeck, *Top. Stereochem.* **1986**, *16*, 219–324.
- [34] a) I. Jalsovszky, F. Ruff, M. Kajtár-Peredy, I. Kövesdi, Á. Kucsman, *Tetrahedron* **1986**, *42*, 5649–5656; b) I. Jalsovszky, Á. Kucsman, F.

- Ruff, T. Koritsánszky, G. Argay, A. Kálmán, *J. Mol. Struct.* **1987**, 156, 165–192.
- [35] S. Bien, S. K. Celebi, M. Kapon, *J. Chem. Soc. Perkin Trans. 2* **1990**, 1987–1990.
- [36] A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer, Berlin, **1983**.
- [37] Prepared in accordance with published procedures: a) T. Okuyama, W. Fujiwara, T. Fueno, *Bull. Chem. Soc. Jpn.* **1986**, 59, 453–456; b) V. K. Aggarwal, R. M. Steele, Ritmaleni, J. K. Barrell, I. Grayson, *J. Org. Chem.* **2003**, 68, 4087–4090.

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