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Coupling Constants

Stereoelectronic Effects: Perlin Effects in Thiane-Derived Compounds

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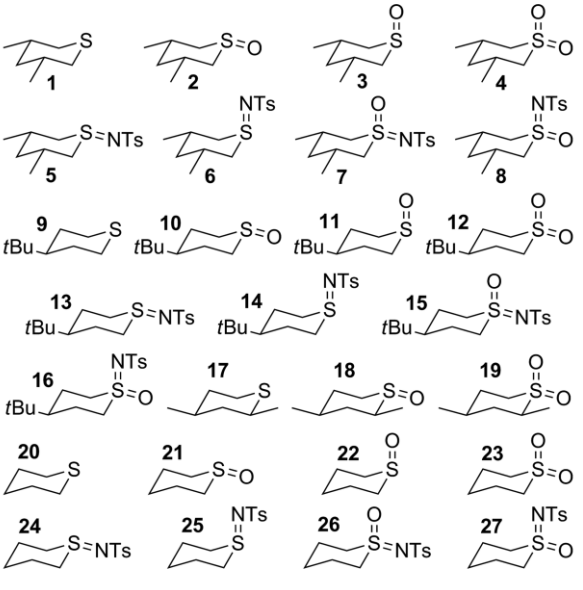
Dedicated to Rolf Huisgen on the occasion of his 100th birthday

Abstract: Stereoelectronic effects in thianes and thiane-derived sulfoxides, sulfones, sulfilimines, and sulfoximines were investigated by measuring $^1J_{C,H}$ coupling constants and by identification of normal and reversed Perlin effects, i.e., of differences in the coupling constants for equatorial and axial C–H bonds in the methylene groups of six-membered rings. The Perlin effects were correlated with results from natural bond orbital (NBO) analyses. NMR experiments were performed with conformationally restricted dimethyl- or *tert*-butyl-substituted derivatives, while the parent compounds were used for calculations. It turned out that the coupling constants are not only strongly influenced by stereoelectronic interactions with antiperiplanar C–H, C–C, C–O, and C–N bonds, but by the s character of the respective C–H bonds' carbon orbital as well.

Introduction

The stability, conformation, and reactivity, as well as various physical and in particular spectroscopic properties are significantly influenced by stereoelectronic effects.[1] We have investigated these effects especially in sulfur-based functional groups, *inter alia* in sulfides, sulfoxides, sulfones, and in their respective α-anions.[2] Stereoelectronic effects have, e.g., a strong influence on $^1J_{C,H}$ coupling constants and these can thus be used to quantify the underlying stereoelectronic interactions. Perlin and Casu[3] observed in tetrahydropyrans (actually in carbohydrates) that equatorial hydrogens next to the oxygen show a larger $^1J_{C,H}$ coupling than axial hydrogens. This so-called normal Perlin effect was attributed to an $n_O \rightarrow \sigma^*_{C,Hax}$ interaction weakening the axial C–H bond.[4] A reversed Perlin effect is observed in 1,3-dithianes: At position C-2, where the influence of two sulfur atoms is active, the $^1J_{C,Hax}$ coupling is larger than the $^1J_{C,Heq}$ coupling. This was explained by the relatively poor donor ability of the sulfur's lone pair and by the most relevant $\sigma_{C,S} \rightarrow \sigma^*_{C,Heq}$ and $\sigma_{C,Heq} \rightarrow \sigma^*_{S,C}$ interactions.[2c,5] While 1,3-dithianes,[5d,5e,6] 1,3-oxathianes,[5e] and related compounds have been investigated repeatedly, the simpler thiane derivatives have not been examined thoroughly. Only the Perlin effects of thiane and its sulfone derivative have been investigated by Juaristi with theoretical methods.[5d,6]

In this paper we examine $^1J_{C,H}$ coupling constants in thianes and in thiane-derived sulfoxides, sulfones, sulfilimines, and sulfoximines by experimental and by quantum chemical methods. For experimental investigations it is mandatory to use conformationally fixed substrates to allow for an unambiguous differentiation of axial and equatorial positions.[7] Herein we utilized 2,4-dimethyl, 3,5-dimethyl, or 4-*tert*-butyl groups as anchors.



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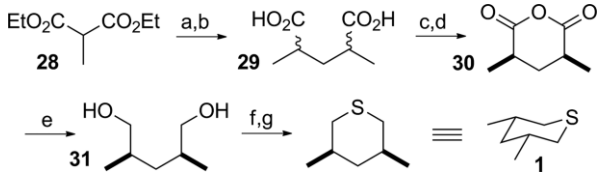
Compounds **1**–**19** were used for NMR spectroscopic investigations, where 2,4-dimethyl-substituted compounds **17**–**19** were investigated for comparison. Only the sulfide **17**, the equatorial sulfoxide **18**, and the respective sulfone **19** were synthesized with this substitution pattern. The parent compounds **20**–**27** were used for calculations.

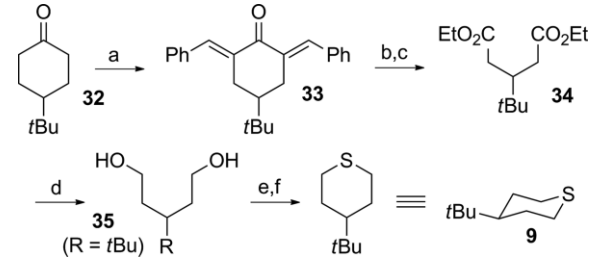
Results and Discussion

3,5-Dimethylthiane was prepared starting with diethyl methylmalonate (**28**), which was deprotonated and added to methyl methacrylate (Scheme 1). The resulting triester was hydrolyzed and decarboxylated yielding dicarboxylic acid **29** as a mixture of diastereoisomers.[8] Anhydride formation and basic equilibration furnished *cis*-dimethyl-substituted substrate **30**,[9] which was reduced with lithium aluminium hydride to yield diol **31**,[10] activated, and reacted with sodium sulfide[11] to thiane derivative **1**.



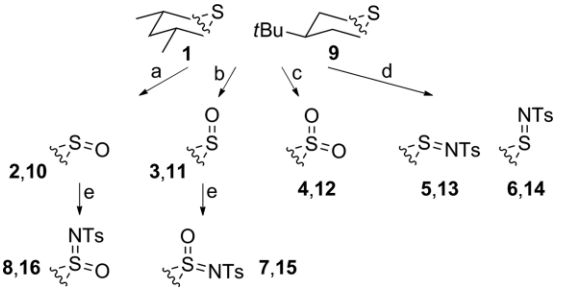
Scheme 1. Synthesis of thiane **1**. Conditions: a) methyl methacrylate, NaOMe, MeOH, 25 °C, 15 h; b) HCl, AcOH, reflux, 24 h (51 %, 2 steps); c) Ac_2O, reflux, 2 h (85 %); d) Et*N*iPr_2, EtOAc; recrystallization (67 %, 97 % de) e) $LiAlH_4$, THF, reflux (73 %); f) Et_3N, $MeSO_2Cl$, CH_2Cl_2, 0 °C (94 %); g) Na_2S, EtOH/H_2O, reflux (40 %).

4-*tert*-Butyl-substituted thiane **9** was prepared from 4-*tert*-butyl-cyclohexanone (**32**), which was subjected to a double aldol condensation to yield **33** (Scheme 2). Ozonolysis with oxidative workup furnished a dicarboxylic acid. Esterification to **34**[12] and reduction gave the diol **35** (R = *t*Bu)[13] which was again activated and reacted with sodium sulfide[11] to yield the *tert*-butyl-substituted thiane **9**.



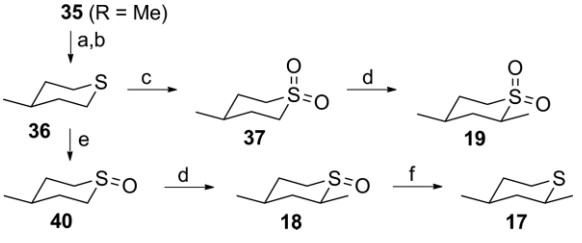
Scheme 2. Synthesis of thiane **9**. a) PhCHO, KOH, EtOH/H_2O (78 %); b) O_3, AcOH, 10 °C, 5 h, then H_2O_2, reflux, 3 h; c) EtOH, cat. H_2SO_4, PhMe; Dean–Stark trap, 16 h (46 %); d) $LiAlH_4$, Et_2O, r.t., 16 h (93 %); e) MsCl, Et_3N, CH_2Cl_2, r.t., 1 h (99 %); f) Na_2S, EtOH/H_2O, reflux, 2 h (78 %).

Functionalization of thianes **1** and **9** was achieved with proven methods (Scheme 3). Oxidation with ozone yielded the equatorial sulfoxides **2** and **10**, respectively, with good yields.[14] The axial sulfoxides (**3** and **11**) were obtained with a known protocol[14] by oxidation with *tert*-butyl hypochloride, albeit with quite poor yields. Excellent yields were observed in the preparation of sulfones **4** and **12**, which was achieved with potassium permanganate.[15] The sulfilimines **5**, **6** and **13**, **14**, respectively, were accessible by reaction of the respective thianes with chloramine-T (TsNClNa)[16] and subsequent separation of the isomers by medium pressure liquid chromatography (MPLC). Since only small fractions of the diastereomeric mixtures were separated, no reasonable yield can be given for these reactions. Reaction of the equatorial sulfoxides **2** or **10**, respectively, with *N*-tosyliminobenzyliodinane (PhINTs) and copper(II) triflate as catalyst[17] yielded the equatorial sulfoximines **8** and **16**, respectively, while the axial sulfoximines **7** and **15** were accessible from the axial sulfoxides **3** and **11**.



Scheme 3. Functionalization of thianes **1** and **9**. Conditions: a) O_3 (**2**: 69 %; **10**: 47 %[14]); b) *t*BuOCl (**3**: 10 %; **11**: 18 %[14]); c) $KMnO_4$ (**4**: 94 %; **12**: 86 %); d) TsNClNa, MeCN, r.t., 16 h, then separation by MPLC; e) PhINTs, cat. $Cu(OTf)_2$ (**7**: 94 %; **8**: 93 %; **15**: 63 %; **16**: 51 %).

The unsymmetrical nature of 2,4-dimethylthiane (**17**) and its derivatives prevented a comparably simple synthetic approach. 4-Methylthiane (**36**) is accessible from diol **35** (R = Me) by the proven activation and reaction with sodium sulfide (Scheme 4).[11] Oxidation with potassium permanganate[15] furnished the respective sulfone **37**, which could be deprotonated with butyllithium and methylated with methyl iodide. The pure isomer **19** was obtained after crystallization. Oxidation of thiane **36** with ozone gave the equatorial sulfoxide, which could similarly be methylated to furnish sulfoxide **18**. Reduction to the respective thiane **17** was achieved with phosphorus pentasulfide,[18] where this reaction was performed with an analytical sample in deuterated chloroform.



Scheme 4. Synthesis of 2,4-dimethylthiane derivatives. Conditions: a) MsCl, Et_3N, CH_2Cl_2, 0 °C, 45 min (quant.); b) Na_2S, MeOH/H_2O, reflux, 2 h (65 %); c) $KMnO_4$, CH_2Cl_2/H_2O, r.t., 16 h (94 %); d) BuLi, THF, 0 °C to r.t., 30 min, then MeI, 0 °C to r.t. (**19**: 17 %, **18**: 30 %, diastereomerically pure); e) O_3, CH_2Cl_2, –40 °C to r.t., 2 h (67 %, d.r. = 5.8:1); f) P_4S_{10}, $CDCl_3$.

Determination of $^1J_{C,H}$ Coupling Constants

$^1J_{C,H}$ coupling constants of the thiane-derived compounds **1**–**19** were determined and the experimental data are ordered in

three sets for the 3,5-dimethylthiane-derived compounds **1**–**8** in Figure 1, for 4-*tert*-butylthiane-derived compounds **9**–**16** in Figure 2, and for the 2,4-dimethylthiane-derived compounds **17**–**19** in Figure 3. $^1J_{C,H}$ coupling constants are here given as green data points with error bars for every C–H bond of the thiane rings. Perlin effects for methylene groups are given as vertical blue bars, where an upward bar indicates a (normal) Perlin effect ($^1J_{C,Heq}-{}^1J_{C,Hax} > 0$), while a downward bar denotes a reversed Perlin effect ($^1J_{C,Heq}-{}^1J_{C,Hax} < 0$). Numeric values for all measured coupling constants and Perlin effects are given in the Supporting Information.

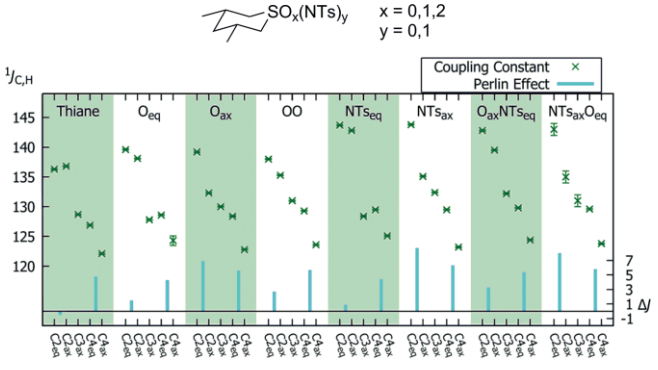


Figure 1. Experimental $^1J_{C,H}$ coupling constants of 3,5-dimethylthiane-derived compounds **1**–**8** (green, with error bars; left scale) and Perlin effects ($^1J_{C,Heq}-{}^1J_{C,Hax}$; blue; right scale).

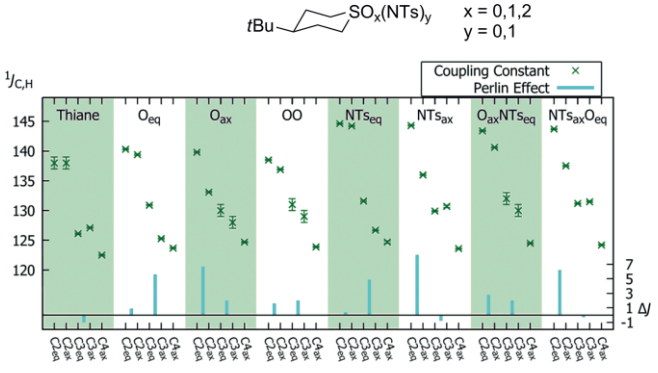


Figure 2. Experimental $^1J_{C,H}$ coupling constants of 4-*tert*-butylthiane-derived compounds **9**–**16** (green, with error bars; left scale) and Perlin effects ($^1J_{C,Heq}-{}^1J_{C,Hax}$; blue; right scale).

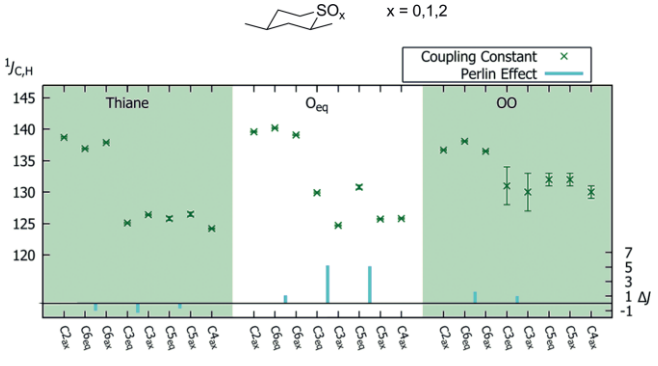


Figure 3. Experimental $^1J_{C,H}$ coupling constants of 2,4-dimethylthiane-derived compounds **17**–**19** (green, with error bars; left scale) and Perlin effects ($^1J_{C,Heq}-{}^1J_{C,Hax}$; blue; right scale).

The following general trends can be deduced for the investigated compounds:

1) Larger coupling constants are generally observed for the α positions.

2) Thianes show small reversed Perlin effects (except for C-4 in compound **1**).

3) Sulfoxides with equatorial S=O bonds and sulfilimines and sulfoximines with equatorial S=N bonds show similar patterns of the Perlin effects. Similar patterns are furthermore observed for sulfoxides with axial S=O bonds and for sulfilimines and sulfoximines with axial S=N bonds.

4) Virtually no Perlin effect is observed for the α positions of sulfoxides with equatorial S=O bonds and for sulfilimines and sulfoximines with equatorial S=N bonds.

5) Sulfilimines and sulfoximines with axial S=N bonds show a reversed Perlin effect for their β positions.

6) All substrates show only negligibly differing coupling constants at the 4-positions.

7) The conformationally constraining substituents (methyl and *tert*-butyl groups, respectively) seem to have no significant influence on the Perlin effects. Comparable carbon positions show comparable Perlin effects.

These trends are discussed in the next section together with results from natural bond orbital (NBO) analyses.

NBO Analyses

Already Alabugin[5e] and Juaristi[5f] concluded from their investigations that there is no obvious and simple correlation between resonance energies obtained from NBO analyses and coupling constants. Contreras et al. examined the influence of stereoelectronic effects on coupling constants,[19] where they gained a much deeper insight into the theoretical foundations. They could explain both the missing of correlations and some observed trends. They divided Fermi contact interactions (as the dominant coupling mechanism) into orbital contributions of occupied and unoccupied LMOs (localized molecular orbitals). This led to contributions to the coupling constant of a C–H bond from the respective σ orbital (J^b, with b: bond), from the respective σ* orbital (J^{ab}; ab: anti bond), and from further bonds at the coupling atoms (J^{ob}; ob: other bond). Contreras elegantly took advantage of model compounds, in which the "other bonds" are equivalent due to symmetry. The influence of "other bonds" is easily understood: Altering of the s character in an "other bond's" hybrid orbital by resonance has an immediate influence on the hybridization of the respective atom's other bonds, since there is a total of only one 2s orbital for every carbon. As the s character is of relevance for the Fermi contact, this must have an influence on the coupling constants. The subtle interplay of hybridization and hyperconjugation has similarly been reported in other systems and is of relevance e.g. in the blue-shifting hydrogen bonding.[20]

In the light of these findings we used multiple linear regressions to test for a random number of compounds, whether there is a correlation, when resonance energies [*E*(2) values],

occupation numbers of the bonding and of the antibonding orbitals (for the respective bond and for "other bonds") are considered. Nevertheless, satisfying linear correlations could be observed for neither of these combinations. The occurrence of saturation, when several effects coincide, has already been presumed by Juaristi et al.[5f]

Since the general trends of the coupling constants turned out to be not significantly affected by the methyl or *tert*-butyl groups, respectively, we used simplified compounds for computational studies, in which methyl or *tert*-butyl groups were omitted. Compounds with tosylimino groups were calculated in a conformation, which had been determined as the minimum conformation in the presence of the conformationally constraining substituents. We calculated bond lengths of the C–H bonds, s characters of the hybrid orbitals at the carbons, and summarized resonance energies [*E*(2) values] of all interactions, in which the respective C–H bonds are acting as donors or acceptors, respectively (using a threshold of 0.1 kcal/mol). The resulting sums immediately reveal, whether the considered bond is essentially acting as a donor or as an acceptor. In addition, resonance energies (NBO deletion energies E_{del}; Supporting Information) were calculated for all antiperiplanar donor/acceptor pairs. ^1J coupling constants for the parent compounds **20**–**27** were additionally calculated for comparison (Supporting Information). The highest observed coupling constants of C–H bonds in α positions come along with high s characters of the carbons' hybrid orbitals used to build up the respective C–H bond. The p character of the carbons' hybrid orbitals in the adjacent C–S bonds is increased, most probably to allow for a better overlap with orbitals at the sulfurs to compensate the increased bond lengths. This effect is somewhat more pronounced in the *S*-oxidized substrates, since the respective C–S bonds are here more polarized towards the S atoms (Table 1).[21]

Table 1. Bond lengths and *s* characters in thiane derivatives.

X					
bond length (C–X) [Å]	1.54	1.84	1.85	1.85	1.82
% s (C–X)	28	21	19	19	18

Thianes show reversed Perlin effects in α and β positions (albeit hardly pronounced), as it has similarly been observed for the thoroughly investigated 1,3-dithianes,[5e] where this has been explained with a significant $\sigma_{C,S} \rightarrow \sigma^*_{C,Heq}$ interaction.[5b,d,23] Evaluation of the NBO analyses showed that further parameters have to be considered. The bond length of C–H bonds is influenced by two effects: When a σ bond acts as donor, the hybridization is changed; the s character at the carbon is reduced.[21] If σ* is an acceptor, the bond is weakened and the bond length is increased. Both effects can have an influence on the respective coupling constants. Investigation of thiane (and of further thiane derivatives) revealed that coupling constants in the α positions are mainly influenced by $\sigma_{C,H}$ donor interactions. The axial C–H bonds in the α positions are weakened by $n_S \rightarrow \sigma^*_{C,Hax}$ interactions and thus elongated in comparison with the respective equatorial C–H bonds. However, the ^1J coupling constants of the axial C–H bonds are larger due to a smaller s character of the equatorial C–H bonds, which here is not a result of a distinct $\sigma_{C,H} \rightarrow \sigma^*_{S,C}$ interaction. The resonance energy of this interaction actually is significantly smaller than that of a $\sigma_{C,H} \rightarrow \sigma^*_{C,C}$ interaction. Nevertheless, the two possible stereoelectronic interactions, in which the equatorial C–H bond acts as donor ($\sigma_{C,Heq} \rightarrow \sigma^*_{S,C}$ and $\sigma_{C,Heq} \rightarrow \sigma^*_{C,C}$) exceed the single donor interaction of the axial C–H bond ($\sigma_{C,Hax} \rightarrow \sigma^*_{C,Hax}$). The axial C–H bonds in the β positions act as donors in two interactions, but the $\sigma_{C,Heq} \rightarrow \sigma^*_{C,S}$ stereoelectronic effect of the equatorial C–H bond is dominating the outcome at this position. The polarization of the C–S bond makes it a significantly better acceptor than a C–C bond, which itself is a better acceptor than an S–C bond.[1f] Homohyperconjugative interactions like the so-called homoanomeric effect ($n_S \rightarrow \sigma_{C3,H}$), which have been proposed by Alabugin et al. for thiane and other six-membered heterocycles,[22] might have a small influence on the Perlin effect in β position of the thianes [n_S (p-type) $\rightarrow \sigma_{C3,Heq}$: E_{del} = 2.10 kcal/mol]. Nevertheless, this type of interaction is actually only mentionable for the p-type lone pair of the parent thiane and is much less (E_{del} < 0.3 kcal/mol) in the sulfoxides and sulfilimines, where the sulfur's lone pairs have a pronounced s character. The respective values are given in the Supporting Information.

An essentially similar pattern for the axial C–H bonds can be deduced for the sulfoxides and sulfilimines with axial S=O or S=N bonds. The $\sigma_{C,Heq} \rightarrow \sigma^*_{S,C}$ interactions are even weaker as for the respective thianes. The $\sigma^*_{S,C}$ bonds in sulfoxides are higher occupied due to interaction with n_O orbitals and thus have reduced acceptor abilities towards further donors.[2m] A hardly pronounced reversed Perlin effect at the thiane's α positions thus turns into a weak normal Perlin effect in the equatorial sulfoxides. Since the thiane's β position is governed by a $\sigma_{C,Heq} \rightarrow \sigma^*_{C,S}$ interaction, the change in the acceptor ability of the C–S bond has an even stronger effect. The weak reversed Perlin effect (in the thianes) thus turns into a much more pronounced normal Perlin effect.

A strong normal Perlin effect is observed for the α positions in axial sulfoxides and sulfilimines due to the high acceptor ability of the $\sigma^*_{S,O}$ and $\sigma^*_{S,N}$ orbitals. A further contribution might arise from $n_{O/N} \rightarrow \sigma^*_{C2,Hax}$ interactions (Figure 4a), which are analogous to the homoanomeric effect (vide supra).[22] The donor ability of the oxygens' lone pair in direction of the C2–H_{ax} bond is here more pronounced than that of the nitrogens' lone pairs (cf. Supporting Information), since the latter can additionally interact with the respective tosyl groups. This leaves smaller shares for the C–H bonds. The $\sigma_{C2,Hax} \rightarrow \sigma^*_{C3,Hax}$ interaction is much weaker than for the equatorial analogues, while the $\sigma_{C3,Hax} \rightarrow \sigma^*_{C2,Hax}$ stereoelectronic effect is more pronounced. The former interaction results in an increased dipole moment, while the latter would reduce it (Figure 4b).

The reversed Perlin effects at the β positions of sulfilimines and sulfoximines with axial S=N bond cannot be explained sufficiently with the available data. The equatorial C–H bond is

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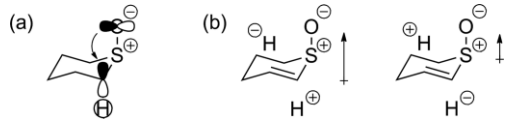

Figure 4. (a) nO → $\sigma^*_{C2,Hax}$ interaction; (b) influence of hyperconjugation on the dipole moment.

somewhat longer than the axial bond, but this cannot be traced back to specific orbital interactions. Nevertheless, an extremely weak resonance energy for the $\sigma_{C3,Heq} \rightarrow \sigma^*_{C2,S}$ interaction in the sulfoximine with equatorial S=N bond is notable. An insignificant deletion energy of 0.07 kcal/mol was determined for this interaction. The $\sigma^*_{C2,S}$ orbital is significantly occupied by interaction with n_O and n_N orbitals, making it a less effective acceptor for the interaction with other donor orbitals. It should be noted that a much higher *E*(2) energy (4.8 kcal/mol) was obtained for the $\sigma_{C3,Heq} \rightarrow \sigma^*_{C2,S}$ interaction, being an example that *E*(2) energies do not consider competing interactions and are thus less valuable in the explanation of resonance effects than deletion energies.

Comparatively weak normal Perlin effects are observed for the α and the β positions in the sulfones. The relevant interactions seem to have a balanced overall effect. The coupling constants at the γ positions of the investigated compounds show insignificant deviations, making long-range orbital interactions less likely. Small differences might be due to slightly differing local orbital interactions resulting from the different molecular dipoles.

Conclusion

Perlin effects observed in thiane-derived compounds can be qualitatively explained with the data obtained from NBO analyses, although it turned out that no direct correlation between coupling constants and calculated resonance energies is possible. It is noteworthy to emphasize that the donor ability of the sulfur's lone pairs is commonly underestimated. The reversed Perlin effects in thianes are in fact not (only) due to a better donor quality of the S–C bond in comparison with the n_S lone pair but are mostly due to the higher acceptor property of the σ^*_{S-C} orbital. The equatorial C–H bonds in thianes are acting as donors in this stereoelectronic interaction. This is in contrast to the respective tetrahydropyran (and 1,3-dioxane) derivatives, where the axial C–H bonds are acting essentially as acceptors for the oxygen's lone pair electrons and thus give rise to a normal Perlin effect. Again, it became obvious in this investigation that experimental findings are easily misinterpreted without consideration of NBO analyses.

When one and the same orbital takes part in competing interactions, it has again to be mentioned, that meaningful data of NBO analyses are only obtained from the deletion energies (E_{del}). The resonance in these cases is usually overestimated, when only *E*(2) energies are considered.

Experimental Section

NMR spectroscopic Investigations. $^1J_{C,H}$ coupling constants of the thiane-derived compounds **1**–**19** were measured on a Bruker Avance III HD 500 MHz spectrometer using CLIP-HSQC experiments[24] and analyzed using the Topspin software package.[25] CLIP-HSQC spectra result in clean inphase doublets in the directly detected dimension, so that accurate coupling constants can be determined without further phase correction. Spectra were acquired using broadband BEBOP excitation,[26] BIBOP inversion,[27] and BURBOP refocusing pulses.[28] When a signal overlap obscured the coupling constants, we used ω1-iINEPT experiments with BIP inversion pulses during the BIRD-element[29] for clarification.[30] Number of scans as well as acquisition times and spectral widths were optimized for each compound individually. In all cases, digital resolution in the dimension with coupling evolution was below 0.1 Hz for CLIP-HSQC experiments and below 1.0 Hz for the ω_1-iINEPT experiments. Due to highly symmetric multiplets and sufficient chemical shift difference of coupling partners second order contributions could be neglected in most cases. The individually estimated experimental errors of the coupling constants were generally on the order of the digital resolution, sometimes even below (see Figure 1–3).

Quantum Chemical Calculations. All structures were optimized at the B3LYP[31]/6-311++G(d,p)[32] level by using the Gaussian 09 software package.[33] Coupling constants were calculated with the GIAO (gauge-including atomic orbitals) method[34] at the same level. The NBO 3.1 program for natural bond orbital (NBO) analyses[35] was used as implemented in Gaussian 09.

Synthetic Procedures – General. Compounds **10**,[14] **11**,[14] **31**,[10] **35**[13] and **36**[11] were prepared according to published procedures. Tetrahydrofuran (THF), Et_2O and pentane were distilled from sodium benzophenone ketyl radical prior to use and CH_2Cl_2 was distilled from CaH_2. All moisture-sensitive reactions were carried out under oxygen-free argon using oven-dried glassware and a vacuum line (Schlenk technique). Ozone was generated with an ozone generator 300.5 (Erwin Sander Elektroapparatebau) from dry air. Flash column chromatography was carried out using Merck silica gel 60 (230–400 mesh) and thin-layer chromatography was carried out by using commercially available Merck F_{254} pre-coated sheets. Spots were detected by fluorescence quenching and staining in an iodine chamber. Medium pressure liquid chromatography (MPLC) on silica gel (LiChroprep Si 60 columns from Merck) was performed with a Laboprep MPLC pump and a Latek UVIS 200 detector. NMR spectra were recorded on Bruker Avance AV 300, Bruker Avance 400, or Bruker Avance III HD 500 spectrometers. ^{13}C NMR spectra were recorded with broad band decoupling and signals were assigned by HSQC experiments. The spectra were calibrated using the residual solvent signals. IR spectra were recorded on a Bruker FT-IR spectrometer "Alpha" using ATR on diamond. EI and FAB mass spectra were recorded with a Finnigan MAT-95 and ESI spectra were recorded with a Q Exactive Orbitrap (Thermo Fisher). Melting points were measured with an Optimelt MPA100 apparatus and are not corrected.

***meso*-1,5-Bis(methanesulfonyloxy)-2,4-dimethylpentane.** This compound was prepared in analogy to a published procedure.[11] Et_3N (51.4 mL, 37.3 g, 369 mmol) was added to a solution of diol **31** (16.3 g, 123 mmol) in CH_2Cl_2 (660 mL). The mixture was cooled to 0 °C and $MeSO_2Cl$ (23.9 mL, 35.3 g, 308 mmol) was added within 30 min with stirring. The mixture was poured on ice/water (200 mL), the layers were separated, and the organic layer was washed with aq. 1M HCl (4 × 150 mL) and H_2O (200 mL). The organic layers were dried (Na_2SO_4), and concentrated at reduced pressure to yield the product (33.4 g, 116 mmol, 94 %) as a colorless solid, which was used without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (d, ^3J = 6.7 Hz, 6 H, 2-Me, 4-Me), 1.08–1.18 (m, 1 H, 3-H_a), 1.51–

1.63 (m, 1 H, 3-H_b), 1.90–2.12 (ddddq, $^3J = {}^3J = {}^3J = {}^3J = {}^3J = 6.8$ Hz, 2 H, 2-H, 4-H), 3.01 (s, 6 H, 2 × S-Me), 4.06 (d, $^3J = 5.6$ Hz, 4 H, 1-H_2, 5-H_2).

***meso*-3,5-Dimethylthiane (1).** This known[36] compound was prepared in analogy to a published procedure.[11] A solution of *meso*-1,5-bis(methanesulfonyloxy)-2,4-dimethylpentane (33.4 g, 116 mmol) in EtOH (650 mL) was warmed to 50 °C and added to a solution of $Na_2S{\cdot}9H_2O$ (55.7 g, 232 mmol) in H_2O (240 mL). The mixture was heated to reflux for 4 h, cooled to 0 °C, and H_2O (400 mL) was added. The mixture was extracted with pentane (6 × 150 mL) and the combined organic layers were washed with H_2O (150 mL) and brine (150 mL), dried (Na_2SO_4), concentrated at reduced pressure, and purified by fractioned distillation (68 °C, 33 mbar) to yield **1** (6.09 g, 46.8 mmol, 40 %) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.54$ (dt, $^2J = {}^3J = 12.2$ Hz, 1 H, 4-H_{ax}), 0.80 (d, $^3J = 6.6$ Hz, 6 H, 3-Me, 5-Me), 1.56–1.69 (m, 3 H, 4-H_{eq}, 3-H, 5-H), 2.06 (dd, $^2J = {}^3J = 12.3$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 2.30 (broad d, $^2J = 13.1$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.0 (3-Me, 5-Me), 34.3 (C-3, C-5), 35.2 (C-2, C-6), 43.9 (C-4); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3272, 2949, 2901, 2866, 1645, 1449, 1418, 1373, 1322, 1269, 1222, 1152, 1078, 1024, 942, 839, 825, 755, 733, 705, 577, 526, 442, 405; MS (EI, 20 °C): *m/z* (%) = 131.0 (15) [M + H]$^+$], 130.1 (62), 129.1 (17), 115.1 (76), 83.1 (100), 81.1 (37), 75.1 (24), 74.0 (66), 69.0 (53), 67.1 (13), 55.1 (80); HRMS (EI): calcd. for $C_7H_{14}{}^{32}S$ [M$^+$]: 130.0816, found 130.0810.

(1*S*,3*R*,5*S*)-3,5-Dimethylthiane 1-Oxide (2). This known[37] compound was prepared in analogy to a published procedure.[17] O_3 (100 mL/min, 380 s, ca. 3.77 mmol) was passed at –40 °C through a solution of thiane **1** (0.980 g, 7.52 mmol) in CH_2Cl_2 (150 mL). The mixture was concentrated at reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 50:1) to yield **3** (761 mg, 5.20 mmol, 69 %) as a colorless solid. M.p. 76 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.80$ (dt, $^2J = {}^3J = 12.6$ Hz, 1 H, 4-H_{ax}), 1.05 (d, $^3J = 6.70$ Hz, 6 H, 3-Me, 5-Me), 1.66 (broad d, $^2J = 13.5$ Hz, 1 H, 4-H_{eq}), 1.72–1.84 (m, 2 H, 3-H, 5-H), 2.20 (dd, $^2J = {}^3J = 12.4$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.27 (broad d, $^2J = 12.1$ Hz, 2 H, 2H_{eq}, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.9 (3-Me, 5-Me), 29.0 (C-3, C-5), 42.0 (C-4), 58.4 (C-2, C-6); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3441, 2951, 2921, 2868, 2824, 1648, 1450, 1374, 1345, 1254, 1164, 1087, 1019, 941, 844, 779, 738, 534, 484, 428, 394; MS (EI, 20 °C): *m/z* (%) = 147.1 (10) [[M + H]$^+$], 146.1 (51) [M$^+$], 131.0 (41), 129.3 (24), 104.0 (16), 97.1 (23), 96.1 (14), 83.1 (71), 63.0 (11), 56.0 (10), 55.0 (100); HRMS (EI): calcd. for $C_7H_{14}O^{32}S$ [M$^+$]: 146.0765, found 146.0759.

(1*R*,3*R*,5*S*)-3,5-Dimethylthiane 1-Oxide (3). This known[37] compound was prepared in analogy to a published procedure.[14] *t*BuOCl (1.06 g, 9.76 mmol) was added at –78 °C to a solution of thiane **1** (1.03 g, 7.91 mmol) in MeOH (77 mL), the mixture was stirred for 2 h at this temperature and warmed to r.t. A small amount of Na_2CO_3 was added and the mixture was concentrated at reduced pressure. CH_2Cl_2 (40 mL) was added, insoluble components were filtered off and rinsed with CH_2Cl_2 (40 mL). The filtrate was concentrated at reduced pressure and purified by column chromatography (silica gel, pentane/acetone, 5:1) to yield **3** (120 mg, 0.821 mmol, 10 %) as a colorless solid. M.p. 95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.83$ (dt, $^2J = {}^3J = 12.6$ Hz, 1 H, 4-H_{ax}), 1.01 (d, ^3J = 6.8 Hz, 6 H, 3-Me, 5-Me), 1.80 (broad d, $^2J = 13.5$ Hz, 1 H, 4-H_{eq}), 1.96 (dd, $^2J = {}^3J = 13.2$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 2.46–2.58 (m, 2 H, 3-H, 5-H), 2.94 (broad d, $^2J = 12.9$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.1 (3-Me, 5-Me), 22.4 (C-3, C-5), 42.5 (C-4), 51.9 (C-2, C-6); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3411, 2953, 2911, 2869, 2837, 1447, 1414, 1374, 1344, 1270, 1167, 1103, 1083, 1010, 882, 846, 708, 536, 452, 408; MS (EI, 20 °C): *m/z* (%) = 146.1 (48) [M$^+$], 129.1 (25), 104.1 (16), 97.1 (28), 76.1 (16), 83.1 (72), 69.1 (13), 63.0 (10), 56.1 (11), 55.1 (100); HRMS (EI): calcd. for $C_7H_{14}O^{32}S$ [M$^+$]: 146.0765, found 146.0766.

***meso*-3,5-Dimethylthiane 1,1-Dioxide (4).** This compound was prepared in analogy to a published procedure.[15] A solution of $KMnO_4$ (1.82 g, 11.5 mmol) in H_2O (25 mL) was added to a solution of thiane **1** (517 mg, 3.97 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred vigorously overnight. A saturated aq. $NaHSO_3$ solution (15 mL) was added, the precipitate was filtered off and rinsed with CH_2Cl_2 (100 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure to yield **4** (606 mg, 3.74 mmol, 94 %) as a colorless, spectroscopically pure solid. M.p. 111 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (dt, $^2J = 13.9$ Hz, $^3J = 12.0$ Hz, 1 H, 4-H_{ax}), 1.06 (d, $^3J = 6.8$ Hz, 6 H, 3-Me, 5-Me), 1.83 (broad d, ^2J = 13.9 Hz, 1 H, 4-H_{eq}), 2.25 (ddtdd, $^3J = {}^3J = 12.4$ Hz, $^3J = 6.3$ Hz, $^3J = {}^3J = 3.1$ Hz, 2 H, 3-H, 5-H), 2.53 (dd, $^2J = {}^3J = 13.1$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 2.97 (broad d, $^2J = 13.6$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5 (3-Me, 5-Me), 30.5 (C-3, C-5), 41.5 (C-4), 57.4 (C-2, C-6); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2964, 2921, 2901, 1442, 1645, 1414, 1348, 1331, 1288, 1263, 1216, 1164, 1130, 1094, 1069, 1009, 891, 848, 794, 554, 473, 442, 386; MS (EI, 20 °C): *m/z* (%) = 162.1 (41) [M$^+$], 97.1 (51), 96.1 (18), 69.1 (20), 57.1 (11), 56.1 (96), 55.1 (100); HRMS (EI): calcd. for $C_7H_{14}O_2{}^{32}S$ [M$^+$]: 162.0715, found 162.0709.

(1*S*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluenesulfonylimino)thiane (5) and (1*R*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluenesulfonylimino)thiane (6). These known[38] compounds were prepared in analogy to a published procedure.[16] TsNClNa (Chloramine-T, 1.05 g, 4.62 mmol) was added to a solution of thiane **1** (497 mg, 3.82 mmol) in MeCN (13 mL). The mixture was stirred at r.t. overnight, poured on H_2O (100 mL) and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with H_2O (2 × 50 mL), dried (Na_2SO_4), and concentrated at reduced pressure. A fraction (100 mg) of the crude diastereomeric mixture (978 mg, 3.27 mmol, 85 %) was purified and separated by MPLC (silica gel, CH_2Cl_2/MeOH, 100:1) to yield the sulfilimines **6** (18 mg, 0.060 mmol) and **5** (72 mg, 0.240 mmol). (1*R*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluolsulfonylimino)thian (**6**): m.p. 138 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.78$ (dt, $^2J = {}^3J = 12.8$ Hz, 1 H, 4-H_{ax}), 0.97 (d, $^3J = 6.8$ Hz, 6 H, 3-Me, 5-Me), 1.79 (broad d, ^2J = 13.7 Hz, 1 H, 4-H_{eq}), 2.12 (dd, $^2J = {}^3J = 13.0$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 2.38 (s, 3 H, Ar-Me), 2.62–2.73 (m, 2 H, 3-H, 5-H), 2.80 (broad d, ^2J = 12.8 Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.23 (d, $^3J = 8.0$ Hz, 2 H, Ar-H), 7.77 (d, $^3J = 8.2$ Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5 (Ar-Me), 21.8 (3-Me, 5-Me), 23.2 (C-3, C-5), 41.3 (C-4), 47.4 (C-2, C-6), 126.4 (Ar-CH), 129.4 (Ar-CH), 141.7 (Ar-C), 171.7 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952, 2919, 2850, 1713, 1457, 1376, 1264, 1135, 1106, 1080, 1020, 975, 932, 841, 815, 769, 695, 647, 578, 550, 512, 493, 460, 429, 393, 380; MS (FAB): *m/z* (%) = 302.1 (11), 301.1 (19) [[M + H]$^+$], 300.1 (100) [M$^+$], 154.0 (13), 136.0 (19), 132.9 (98), 107.1 (22), 97.1 (29), 95.1 (38), 91.0 (42); HRMS (EI): calcd. for $C_{14}H_{22}NO_2{}^{32}S_2$ [[M + H]$^+$]: 300.1092, found 300.1088. (1*S*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluenesulfonylimino)thiane (**5**): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.87$ (dt, $^2J = {}^3J = 12.8$ Hz, 1 H, 4-H_{ax}), 1.04 (d, $^3J = 6.7$ Hz, 6 H, 3-Me, 5-Me), 1.71 (broad d, $^2J = 13.8$ Hz, 1 H, 4-H_{eq}), 1.78–1.89 (m, 2 H, 3-H, 5-H), 2.38 (s, 3 H, Ar-Me), 2.52 (dd, $^2J = {}^3J = 12.6$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.15 (broad d, $^2J = 12.4$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.22 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.78 (d, $^3J = 8.2$ Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6 (Ar-Me), 21.8 (3-Me, 5-Me), 30.1 (C-3, C-5), 41.2 (C-4), 53.3 (C-2, C-6), 126.4 (Ar-CH), 129.4 (Ar-CH), 141.7 (Ar-C), 141.8 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2965, 2917, 2876, 1713, 1598, 1494, 1453, 1424, 1381, 1279, 1137, 1109, 1082, 1024, 951, 936, 840, 810, 758, 657, 570, 546, 508, 461, 434; MS (EI, 140 °C): *m/z* (%) = 299.2 (26),

181.1 (15), 155.1 (10), 144.1 (23), 131.1 (14), 130.1 (12), 129.1 (100), 97.1 (16), 83.1 (10), 69.0 (17), 55.1 (10); HRMS (EI): calcd. for $C_{14}H_{21}NO_2{}^{32}S_2$ [M^+]: 299.1014, found 299.1007.

(1*R*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluenesulfonylimino)thiane 1-Oxide (7). This compound was prepared in analogy to a published procedure.[17] TsN=IPh (141 mg, 378 mmol) was added to a stirred solution of sulfoxide **3** (50 mg, 0.342 mmol) and $Cu(OTf)_2$ (14 mg, 0.039 mmol) in MeCN (4.2 mL). The mixture was stirred for 10 min, concentrated at reduced pressure, and purified by column chromatography (silica gel, cyclohexane/AcOEt, 3:1) to yield **7** (101 mg, 0.320 mmol, 94 %) as a colorless solid. M.p. 190–200 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (dt, ^2J = ^3J = 12.6 Hz, 1 H, 4-H_{ax}), 1.08 (d, ^3J = 6.8 Hz, 6 H, 3-Me, 5-Me), 1.85 (broad d, ^2J = 14.0 Hz, 1 H, 4-H_{eq}), 2.20–2.31 (m, 2 H, 3-H, 5-H), 2.39 (s, 3 H, Ar-Me), 2.82 (dd, ^2J = ^3J = 13.3 Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.62 (broad d, ^2J = 13.7 Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.26 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.85 (d, ^3J = 8.3 Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4 (3-Me, 5-Me), 21.6 (Ar-Me), 29.0 (C-3, C-5), 41.2 (C-4), 58.1 (C-2, C-6), 126.7 (Ar-CH), 129.4 (Ar-CH), 104.9 (Ar-C), 142.9 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3353, 3258, 2957, 2926, 2870, 1598, 1452, 1402, 1299, 1286, 1232, 1201, 1149, 1104, 1086, 1018, 888, 849, 817, 759, 712, 702, 653, 579, 545, 497, 465, 428; MS (EI, 180 °C): *m*/*z* (%) = 317.3 (11), 615.3 (89) [M^+], 313.3 (20), 219.1 (15), 181.1 (14), 171.1 (11), 156.1 (45), 155.1 (41), 145.1 (19), 131.0 (12), 97.1 (99), 96.1 (15), 92.1 (16), 91.1 (34), 69.0 (27), 55.0 (100); HRMS (EI): calcd. for $C_{14}H_{21}NO_3{}^{32}S_2$ [M^+]: 315.0963, found 315.0957.

(1*S*,3*R*,5*S*)-3,5-Dimethyl-1-(4-toluenesulfonylimino)thiane 1-Oxide (8). This compound was prepared in analogy to a published procedure.[17] TsN=IPh (283 mg, 0.758 mmol) was added to a stirred solution of sulfoxide **2** (101 mg, 0.691 mmol) and $Cu(OTf)_2$ (25 mg, 0.069 mmol) in MeCN (4.2 mL). The mixture was stirred for 10 min, concentrated at reduced pressure, and purified by column chromatography (silica gel, cyclohexane/AcOEt, 3:1) to yield **8** (202 mg, 0.640 mmol, 93 %) as a colorless solid. M.p. 182 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (dt, ^2J = 14.0 Hz, ^3J = 12.1 Hz, 1 H, 4-H_{ax}), 1.07 (d, ^3J = 6.7 Hz, 6 H, 3-Me, 5-Me), 1.85 (broad d, ^2J = 14.1 Hz, 1 H, 4-H_{eq}), 2.34–2.46 (m, 2 H, 3-H, 5-H), 2.39 (s, 3 H, Ar-Me), 2.57 (dd, ^2J = ^3J = 12.8 Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.78 (broad d, ^2J = 13.6 Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.26 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.84 (d, ^3J = 8.3 Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2 (3-Me, 5-Me), 21.6 (Ar-Me), 30.8 (C-3, C-5), 41.1 (C-4), 58.0 (C-2, C-6), 126.7 (Ar-CH), 129.4 (Ar-CH), 140.9 (Ar-C), 142.9 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3353, 3258, 2959, 2919, 1598, 1495, 1452, 1385, 1297, 1233, 1200, 1147, 1101, 1082, 1057, 1016, 889, 844, 814, 774, 692, 649, 586, 557, 519, 497, 479, 428, 403; MS (EI, 150 °C): *m*/*z* (%) = 315.2 (39) [M^+], 181.0 (19), 171.1 (16), 160.1 (15), 156.1 (22), 155.1 (24), 144.1 (27), 131.0 (11), 97.1 (100), 96.1 (21), 92.1 (13), 91.1 (19), 69.0 (18), 55.0 (41); HRMS (EI): calcd. for $C_{14}H_{21}NO_3{}^{32}S_2$ [M^+]: 315.0963, found 315.0959.

3-*tert*-Butyl-1,5-bis(methanesulfonyl)pentane. This compound was prepared in analogy to a published procedure.[11] $MeSO_2Cl$ (13.0 mL, 19.2 g, 168 mmol) was added dropwise within 10 min at 0 °C to a solution of diol **35** (R = *t*Bu)[13] (10.8 g, 67.4 mmol) and Et_3N (28.0 mL, 20.3 g, 201 mmol) in CH_2Cl_2 (330 mL). The mixture was stirred for 15 min at 0 °C and for 1 h at r.t., washed with 1M aq. HCl (3 × 100 mL) and half-concentrated brine (100 mL), dried (Na_2SO_4), and concentrated at reduced pressure to yield the product (21.2 g, 67.0 mmol, 99 %) as a colorless oil, which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (s, 9 H, *t*Bu), 1.18–1.28 (m, 1 H, 3-H), 1.41–1.56 (m, 2 H, 2-H_a, 4-H_a), 1.95–2.09 (m, 2 H, 2-H_b, 4-H_b), 3.03 (s, 6 H, 2 × SMe), 4.18–4.32 (m, 4 H, 1-H_2, 5-H_2).

4-*tert*-Butylthiane (9). This compound was prepared in analogy to a published procedure.[11] A solution of $Na_2S{\cdot}9H_2O$ (23.0 g, 95.8 mmol) in H_2O (130 mL) was added to a solution of 3-*tert*-butyl-1,5-bis(methanesulfonyl)pentane (21.2 g, 67.0 mmol) in EtOH (530 mL) and the mixture was heated for 2 h to reflux and cooled to 0 °C. H_2O (400 mL) was added and the mixture was extracted with pentane (4 × 200 mL). The combined organic layers were washed with H_2O (2 × 150 mL) and brine (150 mL), dried (Na_2SO_4), concentrated at reduced pressure, and purified by fractional distillation (80–82 °C, 10 mbar) to yield **9** (8.23 g, 52.0 mmol, 78 %) as a light yellow, foul-smelling liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (s, 9 H, *t*Bu), 0.98 (tt, $^3J_{4\text{-}H,3/5\text{-}Hax}$ = 11.8 Hz, $^3J_{4\text{-}H,3/5\text{-}Heq}$ = 2.7 Hz, 1 H, 4-H), 1.36 (dddd, $^2J_{3\text{-}Hax,3\text{-}Heq} \approx {}^3J_{3\text{-}Hax,2\text{-}Hax} \approx {}^3J_{3\text{-}Hax,4\text{-}H} \approx$ 12.2 Hz, $^3J_{3\text{-}Hax,2\text{-}Heq}$ = 4.2 Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.08 (broad dd, $^2J_{3\text{-}Heq,3\text{-}Hax}$ = 13.4 Hz, ^3J = 2.8 Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.60–2.69 (m, 4 H, 2-H_2, 6-H_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.3 [C(CH_3)$_3$], 29.0 (C-3, C-5), 29.8 (C-2, C-6), 32.9 [*C*(CH_3)$_3$], 47.9 (C-4); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3334, 2935, 1477, 1427, 1393, 1364, 1304, 1275, 1232, 1157, 1028, 968, 926, 898, 811, 665; MS (EI, 20 °C): *m*/*z* (%) = 159.1 (26) [[M + H]$^+$], 158.1 (100) [M^+], 157.1 (15), 143.1 (17), 102.1 (60), 101.1 (28) [(M – *t*Bu)$^+$], 87.0 (57), 69.0 (13), 57.1 (60) [*t*Bu$^+$]; HRMS (EI): calcd. for $C_9H_{18}{}^{32}S$ [M^+]: 158.1129, found 158.1125.

4-*tert*-Butylthiane 1,1-Dioxide (12). This compound was prepared in analogy to a published procedure.[15] A solution of thiane **9** (2.71 g, 17.1 mmol) in CH_2Cl_2 (45 mL) was added to a solution of $KMnO_4$ (8.11 g, 51.3 mmol) in H_2O (110 mL) and the mixture was stirred vigorously at r.t. overnight. Excess $KMnO_4$ was destroyed by addition of saturated aq. $NaHSO_3$ solution, precipitated MnO_2 was filtered off and rinsed with CH_2Cl_2 (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, pentane/acetone, 10:1→2:1) to yield **12** (2.81 g, 14.8 mmol, 86 %) as a colorless solid. R_f = 0.47 (CH_2Cl_2/MeOH, 50:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (s, 9 H, *t*Bu), 1.23 (tt, $^3J_{4\text{-}H,3/5\text{-}Hax}$ = 12.2 Hz, $^3J_{4\text{-}H,3/5\text{-}Heq}$ = 2.8 Hz, 1 H, 4-H), 1.87 (broad ddd, $^2J_{3\text{-}Hax,3\text{-}Heq} \approx {}^3J_{3\text{-}Hax,2\text{-}Hax} \approx {}^3J_{3\text{-}Hax,4\text{-}H} \approx$ 13.2 Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.14 (broad ddddd, $^2J_{3\text{-}Heq,3\text{-}Hax}$ = 14.2 Hz, $^3J_{3\text{-}Heq,2\text{-}Hax} \approx {}^3J_{3\text{-}Heq,2\text{-}Heq} \approx {}^3J_{3\text{-}Heq,4\text{-}H} \approx J \approx$ 3.3 Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.93 (broad ddd, $^2J_{2\text{-}Hax,2\text{-}Heq} \approx {}^3J_{2\text{-}Hax,3\text{-}Hax} \approx$ 13.6 Hz, $^3J_{2\text{-}Hax,3\text{-}Heq}$ = 3.5 Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.06 (broad d, $^2J_{2\text{-}Heq,2\text{-}Hax} \approx$ 13.8 Hz, 2 H, 2-H_{eq}, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4 (C-3, C-5), 27.6 [C(CH_3)$_3$], 32.6 [*C*(CH_3)$_3$], 46.3 (C-4), 51.7 (C-2, C-6); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2953, 2866, 1477, 1406, 1367, 1330, 1277, 1232, 1157, 1111, 1060, 1008, 979, 963, 895, 857, 762, 712, 672; MS (EI, 80 °C): *m*/*z* (%) = 191.3 (11) [[M + H]$^+$], 135.0 (29), 134.1 (38) [(M + H-*t*Bu)$^+$], 117.1 (34), 111.1 (10), 109.1 (100), 106.0 (25), 81.1 (18), 70.1 (45), 69.1 (91), 67.1 (76), 57.1 (26) [*t*Bu$^+$], 55.0 (24), 43.0 (13), 42.0 (20), 41.0 (88); HRMS (EI): calcd. for $C_9H_{19}O_2{}^{32}S$ [[M + H]$^+$]: 191.1106, found 191.1102.

***trans*-4-*tert*-Butyl-1-(4-toluenesulfonylimino)thiane (13) and *cis*-4-*tert*-Butyl-1-(4-toluenesulfonylimino)thiane (14).** These compounds were prepared in analogy to a published procedure.[16] TsNClNa (Chloramine-T, 2.03 g, 8.92 mmol) was added to a solution of thiane **9** (951 mg, 6.01 mmol) in MeCN (20 mL). The mixture was stirred at r.t. overnight, poured on H_2O (250 mL), and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (2 × 50 mL), dried (Na_2SO_4), and concentrated at reduced pressure. A small fraction of the crude diastereomeric mixture (quant.) was purified and separated by MPLC (silica gel, CH_2Cl_2/MeOH, 100:1) to yield the sulfilimines. **14** (1st fraction): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (s, 9 H, *t*Bu), 1.09 (tt, $^3J_{4\text{-}H,3/5\text{-}Hax}$ = 12.1 Hz, $^3J_{4\text{-}H,3/5\text{-}Heq}$ = 2.5 Hz, 1 H, 4-H), 2.14 (broad d, $^2J_{3\text{-}Heq,3\text{-}Hax}$ = 13.6 Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.25 (broad ddd, $^2J_{3\text{-}Hax,3\text{-}Heq} \approx {}^3J_{3\text{-}Hax,2\text{-}Hax} \approx$

$^3J_{3\text{-Hax},4\text{-H}} \approx 13.3$ Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.38 (s, 3 H, Ar-Me), 2.63 (broad ddd, $^2J_{2\text{-Hax},2\text{-Heq}} \approx {}^3J_{2\text{-Hax},3\text{-Hax}} \approx 13.7$ Hz, $^3J_{2\text{-Hax},3\text{-Heq}} = 2.8$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 2.97 (broad d, $^2J_{2\text{-Heq},2\text{-Hax}} \approx 14.8$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.22 (broad d, $^3J = 7.2$ Hz, 2 H, Ar-H), 7.78 (d, $^3J = 8.3$ Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.9 (C-3, C-5), 21.6 (Ar-CH_3), 27.3 [C(CH_3)$_3$], 33.1 [C(CH_3)$_3$], 43.4 (C-2, C-6), 46.3 (C-4), 126.4 (Ar-CH), 129.4 (Ar-CH), 141.7 (Ar-C), 141.8 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954, 1597, 1467, 1426, 1366, 1272, 1134, 1090, 1020, 1008, 990, 959, 900, 811, 768, 745, 710, 649; MS (EI, 180 °C): *m/z* (%) = 327.2 (10) [M^+], 312.2 (14), 157.1 (100) [(M-HNTs)$^+$], 155.1 (14), 101.1 (17) [(M-HNTs – *t*Bu)$^+$], 91.1 (34), 87.0 (16), 69.1 (13), 57.1 (35) [*t*Bu$^+$], 55.1 (15); HRMS (EI): calcd. for $C_{16}H_{25}NO_2N^{32}S_2$ [M^+]: 327.1327, found 327.1325. **13** (2nd fraction): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (s, 9 H, *t*Bu), 1.17 (tt, $^3J_{4\text{-H},3/5\text{-Hax}} = 12.1$ Hz, $^3J_{4\text{-H},3/5\text{-Heq}} = 2.8$ Hz, 1 H, 4-H), 1.46 (broad ddd, $^2J_{3\text{-Hax},3\text{-Heq}} \approx {}^3J_{3\text{-Hax},2\text{-Hax}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx 13.5$ Hz, 2 H, 3-H_{ax}, 5-H_{ax}]), 2.14 (broad d, $^2J_{3\text{-Heq},3\text{-Hax}} = 14.6$ Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.37 (s, 3 H, Ar-Me), 2.87 (broad dd, $^2J_{2\text{-Hax},2\text{-Heq}} \approx {}^3J_{2\text{-Hax},3\text{-Hax}} \approx 13.0$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.28 (broad d, $^2J_{2\text{-Heq},2\text{-Hax}} \approx 11.7$ Hz, 2 H, 2-H_{eq},6-H_{eq}), 7.22 (d, $^3J = 8.1$ Hz, 2 H, Ar-H), 7.77 (d, $^3J = 8.2$ Hz, 2 H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5 (Ar-CH_3), 25.1 (C-3, C-5), 27.4 [C(CH_3)$_3$], 32.6 [C(CH_3)$_3$], 45.7 (C-4), 48.0 (C-2, C-6), 126.4 (Ar-CH), 129.4 (Ar-CH), 141.8 (Ar-C), 141.8 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 1598, 1418, 1365, 1277, 1230, 1140, 1090, 1020, 953, 809, 773, 757, 707, 650; MS (EI, 180 °C): *m/z* (%) = 327.3 (12) [M^+], 312.2 (15), 181.0 (13), 157.1 (100) [(M-HNTs)$^+$], 155.1 (11), 131.0 (14), 101.1 (14) [(M–HNTs – *t*Bu)$^+$], 91.1 (24), 87.0 (15), 69.0 (31), 57.1 (31) [*t*Bu$^+$], 55.1 (18); HRMS (EI): calcd. for $C_{16}H_{25}NO_2N^{32}S_2$ [M^+]: 327.1327, found 327.1328.

***cis*-4-*tert*-Butyl-1-(4-toluenesulfonylimino)thiane 1-Oxide (15).** This compound was prepared in analogy to a published procedure.[17] $Cu(OTf)_2$ (8.9 mg, 25 μmol) was added to as suspension of sulfoxide **11** (42.7 mg, 0.245 mmol) and PhI=NTs (101 mg, 0.271 mmol) in MeCN (1.5 mL). The mixture was stirred for 15 min at r.t., concentrated at reduced pressure, and purified by column chromatography (silica gel, cyclohexane/AcOEt, 2:1) to yield **15** (53.0 mg, 0.154 mmol, 63 %) as a colorless solid. R_f = 0.31 (cyclohexane/AcOEt, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 9 H, *t*Bu), 1.31 (tt, $^3J_{4\text{-H},3/5\text{-Hax}} = 12.2$ Hz, $^3J_{4\text{-H},3/5\text{-Heq}} = 2.6$ Hz, 1 H, 4-H), 1.86 (broad ddd, $^2J_{3\text{-Hax},3\text{-Heq}} \approx {}^3J_{3\text{-Hax},2\text{-Hax}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx 13.6$ Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.18 (broad d, $^2J_{3\text{-Heq},3\text{-Hax}} = 14.3$ Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.39 (s, 3 H, Ar-Me), 3.21 (ddd, $^2J_{2\text{-Hax},2\text{-Heq}} \approx {}^3J_{2\text{-Hax},3\text{-Hax}} \approx 13.9$ Hz, $^3J_{2\text{-Hax},3\text{-Heq}} = 3.0$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.70 (broad d, $^2J_{2\text{-Heq},2\text{-Hax}} \approx 13.4$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.26 (d, $^3J = 8.1$ Hz, 2 H, Ar-H), 7.85 (d, $^3J = 8.2$ Hz, 2 H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Ar-CH_3), 23.6 (C-3, C-5), 27.4 [C(CH_3)$_3$], 32.8 [C(CH_3)$_3$], 45.8 (C-4), 52.9 (C-2, C-6), 126.7 (Ar-CH), 129.4 (Ar-CH), 140.9 (Ar-C), 142.9 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928, 1399, 1301, 1282, 1229, 1204, 1180, 1145, 1092, 1053, 1003, 962, 891, 849, 807, 768, 755, 705, 670, 653; MS (EI, 150 °C): *m/z* (%) = 344.3 (14) [[M + H]$^+$], 343.1 (72) [M^+], 330.3 (10), 329.3 (20), 328.3 (100), 286.2 (12) [(M – *t*Bu)$^+$], 181.1 (26), 155.1 (19), 150.1 (11) [Ts$^+$], 131.0 (30), 91.1 (33), 69.0 (58), 57.1 (25) [*t*Bu$^+$], 55.1 (17); HRMS (EI): calcd. for $C_{16}H_{25}NO_3N^{32}S_2$ [M^+]: 343.1276, found 343.1271.

***trans*-4-*tert*-Butyl-1-(4-toluenesulfonylimino)thiane 1-Oxide (16).** This compound was prepared in analogy to a published procedure.[17] $Cu(OTf)_2$ (33 mg, 91 μmol) was added to as suspension of sulfoxide **10** (160 mg, 0.918 mmol) and PhI=NTs (377 mg, 1.01 mmol) in MeCN (6 mL). The mixture was stirred for 15 min at r.t., concentrated at reduced pressure, and purified by column chromatography (silica gel, cyclohexane/AcOEt, 3:1) to yield **16** (160 mg, 0.466 mmol, 51 %) as a colorless solid. R_f = 0.29 (cyclohexane/AcOEt, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 9 H, 4-*t*Bu), 1.28 (tt, $^3J_{4\text{-H},3/5\text{-Hax}} = 12.2$ Hz, $^3J_{4\text{-H},3/5\text{-Heq}} = 2.8$ Hz, 1 H, 4-H), 1.99 (broad ddd, $^2J_{3\text{-Hax},3\text{-Heq}} \approx {}^3J_{3\text{-Hax},2\text{-Hax}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx 13.2$ Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.18 (broad d, $^2J_{3\text{-Heq},3\text{-Hax}} = 14.5$ Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.39 (s, 3 H, Ar-Me), 3.00 (ddd, $^2J_{2\text{-Hax},2\text{-Heq}} \approx {}^3J_{2\text{-Hax},3\text{-Hax}} \approx 13.5$ Hz, $^3J_{2\text{-Hax},3\text{-Heq}} = 2.9$ Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.88 (broad d, $^2J_{2\text{-Heq},2\text{-Hax}} \approx 13.6$ Hz, 2 H, 2-H_{eq}, 6-H_{eq}), 7.26 (d, $^3J = 8.1$, 2 H, Ar-H), 7.85 (d, $^3J = 8.3$, 2 H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (Ar-CH_3), 25.8 (C-3, C-5), 27.6 [C(CH_3)$_3$], 32.7 [C(CH_3)$_3$], 45.9 (C-4), 53.0 (C-2, C-6), 126.6 (Ar-CH), 129.4 (Ar-CH), 141.0 (Ar-C), 142.9 (Ar-C); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2934, 1398, 1369, 1298, 1283, 1254, 1203, 1145, 1055, 966, 891, 848, 810, 771, 743, 710, 666; MS (EI, 130 °C): *m/z* (%) = 343.3 (43) [M^+], 328.3 (37), 287.2 (16), 218.2 (10), 181.1 (17) 156.1 (17), 155.1 (40) [Ts$^+$], 131.0 (17), 125.2 (31), 109.1 (11), 97.1 (17), 91.1 (42), 83.1 (18), 69.1 (100), 67.1 (14). 58.1 (14), 57.1 (50) [*t*Bu$^+$], 55.1 (30); HRMS (EI): calcd. for $C_{16}H_{25}NO_3N^{32}S_2$ [M^+]: 343.1276, found 343.1268.

4-Methylthiane 1,1-Dioxide (37). This compound was prepared in analogy to a published procedure.[15] A solution of $KMnO_4$ (7.45 g, 47.1 mmol) in H_2O (100 mL) was added dropwise to a solution of 4-methylthiane **36**[11] (1.83 g, 15.7 mmol) in CH_2Cl_2 (40 mL) and the mixture was stirred overnight at r.t. Excess $KMnO_4$ was destroyed by addition of saturated aq. $NaHSO_3$ solution, CH_2Cl_2 (100 mL) was added, precipitated MnO_2 was filtered off and was rinsed with CH_2Cl_2 (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure to yield **37** as a colorless solid (2.18 g, 14.7 mmol, 94 %). R_f = 0.93 (CH_2Cl_2/MeOH, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, $^3J_{4\text{-Me},4\text{-H}} = 6.5$ Hz, 3 H, 4-Me), 1.69 (tqt, $^3J_{4\text{-H},3/5\text{-Heq}} = 3.5$ Hz, $^3J_{4\text{-H},4\text{-Me}} = 6.9$ Hz, $^3J_{4\text{-H},3/5\text{-Hax}} = 10.8$ Hz, 1 H, 4-H), 1.85 (broad dddd, $^3J_{3\text{-Hax},2\text{-Hax}} = 2.7$ Hz, $^3J_{3\text{-Hax},2\text{-Hax}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx 11.5$ Hz, $^2J_{3\text{-Hax},3\text{-Heq}} = 13.9$ Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 2.02 (broad d, $^2J_{3\text{-Heq},3\text{-Hax}} = 14.1$ Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.90–3.04 (m, 4 H, 2-H_2, 6-H_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (4-Me), 30.5 (C-4), 31.9 (C-3, C-5), 51.0 (C-2, C-6); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952, 2920, 1460, 1409, 1367, 1318, 1277, 1240, 1197, 1115, 1066, 933, 917, 842, 708, 663; MS (FAB, 30 °C): *m/z* (%) = 148.1 (100) [M^+], 131.1 (11) [(M-OH)$^+$], 83.1 (46) [(M-HSO_2)$^+$], 82.1 (12), 69.1 (38), 56.0 (58), 55.0 (62), 41.0 (25), 38.9 (13); HRMS (EI): calcd. for $C_6H_{12}O_2{}^{32}S$ [M^+]: 148.0558, found 148.0553. The ^{1}H NMR data are in full agreement with published data.[39]

***rac*-(2*R*,4*R*)-2,4-Dimethylthiane 1,1-Dioxide (19).** BuLi (2.5M in hexane, 3.3 mL, 8.25 mmol) was added at 0 °C to a solution of sulfone **37** (1.00 g, 6.75 mmol) in THF (16 mL). The mixture was stirred for 30 min at r.t. and transferred at 0 °C into a solution of MeI (0.85 mL, 1.94 g, 13.7 mmol) in THF (16 mL). The mixture was warmed to r.t., concentrated at reduced pressure. H_2O (50 mL) was added and the mixture was extracted with CH_2Cl_2 (100 mL and 3 × 50 mL). Brine (50 mL) was added to the aqueous layer, which was additionally extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure to yield a mixture of diastereoisomers (1.08 g, 6.66 mmol, 99 %). Recrystallization (2x) from cyclohexane furnished sulfone **19** (182 mg, 1.12 mmol, 17 %) as long colorless needles. R_f = 0.05 (CH_2Cl_2/MeOH, 10:1); ^{1}H NMR (500 MHz, CDCl): δ = 0.92 (d, $^3J_{4\text{-Me},4\text{-H}} = 6.5$ Hz, 3 H, 4-Me), 1.23 (d, $^3J_{2\text{-Me},2\text{-H}} = 6.8$ Hz, 3 H, 2-Me), 1.52 (ddd $^2J_{3\text{-Hax},3\text{-Heq}} \approx {}^3J_{3\text{-Hax},2\text{-H}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx 12.1$ Hz, 1 H, 3-H_{ax}), 1.65 (ddqdd, $^2J_{4\text{-H},3\text{-Hax}} \approx {}^2J_{4\text{-H},5\text{-Hax}} \approx 12.0$ Hz, $^3J_{4\text{-H},4\text{-Me}} = 6.0$ Hz, $^2J_{4\text{-H},3\text{-Heq}} \approx {}^2J_{4\text{-H},5\text{-Heq}} \approx 3.0$ Hz, 1 H, 4-H), 1.71–1.83 (m, 2 H, 3-H_{eq}, 5-H_{ax}), 1.98 (ddddd, $^2J_{5\text{-Heq},5\text{-Hax}} = 14.0$ Hz, $^3J_{5\text{-Heq},4\text{-Hax}} \approx {}^3J_{5\text{-Heq},6\text{-Hax}} \approx {}^3J_{5\text{-Heq},6\text{-Heq}} \approx {}^4J_{5\text{-Heq},3\text{-Heq}} \approx 3.3$ Hz, 1 H, 5-H_{eq}), 2.85 (ddd, $^2J_{6\text{-Hax},6\text{-Heq}} \approx {}^3J_{6\text{-Hax},5\text{-Hax}} \approx 13.8$ Hz, $^3J_{6\text{-Hax},5\text{-Heq}} = 3.8$ Hz, 1 H, 6-H_{ax}, partly covered), 2.90 (dqd, $^3J_{2\text{-Hax},3\text{-Hax}} = 12.8$ Hz, $^3J_{2\text{-H},2\text{-Me}} = 6.5$ Hz, $^3J_{2\text{-Hax},3\text{-Heq}} = 3.5$ Hz, 1 H, 2-H, partly covered), 2.97 (ddd, $^2J_{6\text{-Heq},6\text{-Hax}} = 14.2$ Hz, $^3J_{6\text{-Heq},5\text{-Hax}} \approx {}^3J_{6\text{-Heq},5\text{-Heq}} \approx 3.6$ Hz, 1 H, 6-

H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.8 (4-Me), 21.5 (2-Me), 31.6 (C-4), 32.2 (C-5), 40.4 (C-3), 51.0 (C-6), 56.0 (C-2); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2976, 2960, 2919, 2876, 1456, 1417, 1384, 1316, 1280, 1234, 1202, 1165, 1118, 1092, 1069, 1045, 913, 842, 798, 730, 645, 574, 514, 489, 458, 434, 405; MS (ESI): *m/z* (%) = 163.1 (100) [[M + H]$^+$]; HRMS (EI): calcd. for $C_7H_{15}O_2{}^{32}S$ [[M + H]$^+$]: 163.0793, found 163.0787.

***trans*-4-Methylthiane 1-Oxide (40).** This compound was prepared in analogy to a published procedure.[14] O_3 (100 mL/min, 470 s, ca. 3.03 mmol) was passed at –40 °C through a solution of 4-methylthiane **36**[11] (705 mg, 6.07 mmol) in CH_2Cl_2 (120 mL). The mixture was let stand for 2 h at r.t., concentrated at reduced pressure, and purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 100:1→50:1) to yield **40** (536 mg, 4.05 mmol, 67 %, dr = 5.8:1) as a colorless solid. R_f = 0.49 (CH_2Cl_2/MeOH, 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{4\text{-Me},4\text{-H}}$ = 6.6 Hz, 3 H, 4-Me), 1.38 (broad ddd, $^2J_{3\text{-Hax},3\text{-Heq}} \approx {}^3J_{3\text{-Hax},2\text{-H}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx$ 12.8 Hz, 2 H, 3-H_{ax}, 5-H_{ax}), 1.54–1.71 (m, 1 H, 4-H), 2.02 (broad d, $^2J_{3\text{-Heq},3\text{-Hax}}$ = 14.1 Hz, 2 H, 3-H_{eq}, 5-H_{eq}), 2.63 (broad dd, $^2J_{2\text{-Hax},2\text{-Heq}} \approx {}^3J_{2\text{-Hax},3\text{-Hax}} \approx$ 12.9 Hz, 2 H, 2-H_{ax}, 6-H_{ax}), 3.28 (broad d, $^2J_{2\text{-Heq},2\text{-Hax}}$ = 11.7 Hz, 2 H, 2-H_{eq}, 6-H_{eq}). These ^1H NMR data systematically deviate by 0.1 ppm in comparison with published data.[39]

***rac*-(1*R*,2*R*,4*R*)-2,4-Dimethylthiane 1-Oxide (18).** BuLi (2.5M in hexane, 1.75 mL, 4.38 mmol) was added dropwise at 0 °C to a solution of sulfoxide **40** (525 mg, 3.97 mmol) in THF (4 mL) and the mixture was stirred for 30 min at r.t., and cooled to 0 °C. A solution of MeI (0.62 mL, 1.41 g, 9.96 mmol) in THF (2 mL) was added dropwise, the mixture was warmed to r.t. and concentrated at reduced pressure. The remnant was dissolved in CH_2Cl_2 (30 mL) and washed with half-concentrated brine (20 mL). The aqueous layer was extracted with CH_2Cl_2 (30 mL) and the combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, separated by column chromatography (silica gel/CH_2Cl_2→CH_2Cl_2/MeOH, 100:3), dissolved in pentane (3 mL), and crystallized overnight at –18 °C. The recrystallization was repeated twice and the crystals were purified by chromatography (Alox-N, Et_2O/MeOH, 40:1) to yield **18** (174 mg, 1.19 mmol, 30 %) as colorless crystals. R_f = 0.53 (CH_2Cl_2/MeOH, 10:1); ^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{4\text{-Me},4\text{-H}}$ = 6.6 Hz, 3 H, 4-Me or 2-Me), 1.19 (ddd, $^2J_{3\text{-Hax},3\text{-Heq}}$ = 14.8, $^3J_{3\text{-Hax},2\text{-H}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx$ 12.2 Hz, 1 H, 3-H_{ax}), 1.37–1.46 (m, 1 H, 5-H_{ax}, partly covered), 1.41 (d, $^3J_{2\text{-Me},2\text{-H}}$ = 6.8 Hz, 3 H, 2-Me or 4-Me, partly covered), 1.64–1.74 (m, 1 H, 4-H), 1.88 (dddd, $^2J_{3\text{-Heq},3\text{-Hax}}$ = 14.9, $^3J_{3\text{-Heq},2\text{-H}} \approx {}^3J_{3\text{-Heq, 4-H}} \approx {}^4J_{3\text{-Heq, 5-Heq}} \approx$ 3.0 Hz, 1 H, 3-H_{eq}), 1.98 (ddddd, $^2J_{5\text{-Heq},5\text{-Hax}}$ = 14.9, $^3J_{5\text{-Heq},6\text{-Heq}^*}$ = 4.3, $^3J_{5\text{-Heq},4\text{-H}^*} \approx {}^3J_{5\text{-Heq},6\text{-Heq}^*} \approx {}^4J_{3\text{-Heq, 5-Heq}} \approx$ 3.4 Hz, 1 H, 5-H_{eq}, * couplings not unambiguously assignable), 2.60–2.69 (m, 2 H, 2-H_{ax}, 6-H_{ax}), 3.34 (ddd, $^2J_{6\text{-Heq},6\text{-Hax}}$ = 12.1 Hz, $^3J_{6\text{-Heq},5\text{-Heq}}$ = 4.4 Hz, $^3J_{6\text{-Heq},5\text{-Hax}}$ = 2.8 Hz, 1 H, 6-H_{eq}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5 (2-Me), 21.4 (4-Me), 31.5 (C-5), 32.0 (C-4), 39.9 (C-3), 51.3 (C-6), 58.7 (C-2); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3480, 2954, 2914, 1451, 1380, 1257, 1026, 904, 688, 625; MS (EI, 20 °C): *m/z* (%) = 146.1 (40) [M$^+$], 129.1 (20), 97.1 (42) [(M-HSO)$^+$], 69.1 (15), 55.1 (100); HRMS (EI): calcd. for $C_7H_{14}O^{32}S$ [M$^+$]: 146.0765, found 146.0766.

***rac*-(2*R*,4*R*)-2,4-Dimethylthiane (17).** This known compound[36] was prepared according to a published protocol.[18] P_4S_{10} (133 mg, 0.299 mmol) was added to a solution of sulfoxide **18** (73.0 mg, 0.499 mmol) in $CDCl_3$ (2.0 mL). The mixture was stirred for 5 h at 80 °C and cooled to r.t. Saturated aq. $NaHCO_3$ solution (2.0 mL) was added and the mixture was stirred for 5 min at r.t. The precipitate was removed by filtration, the layers were separated, and the organic layer was dried (Na_2SO_4). The ill-smelling compound **17** was not isolated, but was investigated in solution. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (d, $^3J_{4\text{-Me},4\text{-H}}$ = 6.6 Hz, 3 H, 4-Me or 2-Me), 1.04 (ddd, $^2J_{3\text{-Hax},3\text{-Heq}}$ = 12.7, $^3J_{3\text{-Hax},2\text{-H}} \approx {}^3J_{3\text{-Hax},4\text{-H}} \approx$ 12.0 Hz, 1 H, 3-H_{ax}), 1.14–1.24 (m, 1 H, 5-H_{ax}, partly covered), 1.19 (d, $^3J_{2\text{-Me},2\text{-H}}$ = 6.8 Hz, 3 H, 2-Me or 4-Me, partly covered), 1.34–1.44 (m, 1 H, 4-H), 1.89–1.96 (m, 2 H, 3-H_{eq}, 5-H_{eq}), 2.60 (ddd, $^2J_{6\text{-Heq},6\text{-Hax}}$ = 13.5 Hz, $^3J_{6\text{-Heq},5\text{-Heq}} \approx {}^3J_{6\text{-Heq},5\text{-Hax}}$ = 3.5 Hz, 1 H, 6-H_{eq}), 2.72 (ddd, $^2J_{6\text{-Hax},6\text{-Heq}} \approx$ Hz, $^3J_{6\text{-Hax},5\text{-Hax}} \approx$ 13.0 Hz, $^3J_{6\text{-Hax},5\text{-Heq}}$ = 2.6 Hz, 1 H, 6-H_{ax}), 2.81 (dqd, $^3J_{2\text{-Hax},3\text{-Hax}}$ = 11.2 Hz, $^3J_{2\text{-H},2\text{-Me}}$ = 6.9 Hz, $^3J_{2\text{-Hax},3\text{-Heq}}$ = 2.4 Hz, 1 H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8 (2-Me), 23.1 (4-Me), 29.7 (C-6), 32.9 (C-4), 35.2 (C-5), 37.8 (C-2), 45.4 (C-3). The data are in full agreement with published data.[36]

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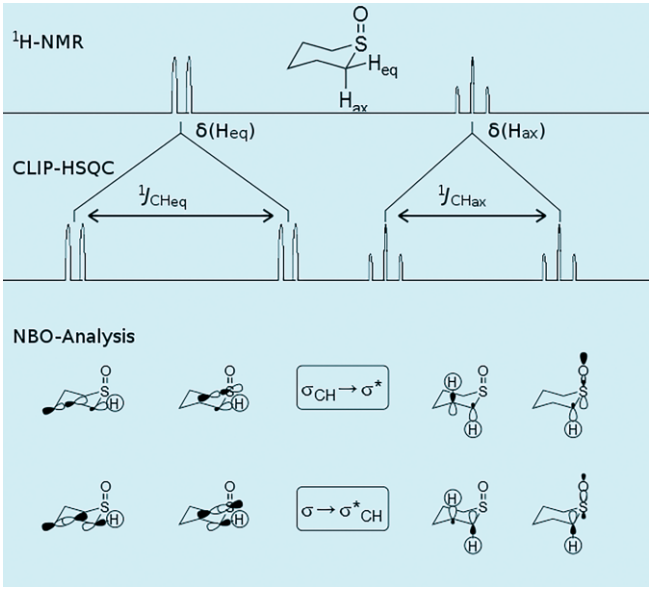
Coupling Constants



Equatorial and axial hydrogens in methylene groups of six-membered rings show differing coupling constants (Perlin effects) dependent on the adjacent functional groups. The coupling constants are influenced by stereoelectronic effects and by the hybridizations of the carbons.

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