The Hetero-Diels–Alder Addition of Sulfur Dioxide to 1-Fluorobuta-1,3-dienes: The Sofa Conformations Preferred by 6-Fluorosultines (6-Fluoro-3,6-dihydro-1,2-oxathiin-2-oxides) Enjoy Enthalpic and Conformational Anomeric Effects

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Abstract: The reactivity of (*E*)- and (*Z*)-1-fluorobuta-1,3-diene ((*E*)- and (*Z*)-**11**), 2-fluorobutadiene (**12**), (*E*)- and (*Z*)-1-(fluoromethylidene)-2-methylidenecyclohexane ((*E*)- and (*Z*)-**13**) toward SO_2 has been explored and compared with that of (*Z*)- and (*E*)-1-(fluoromethylidene)-2-methylidene-3,4-dihydronaphthalene ((*Z*)-**8** and (*E*)-**8**). In agreement with quantum calculations, **12** is unreactive toward SO_2 (no cycloaddition, only polymerization), whereas (*E*)-1-fluoro-1,3-dienes react more rapidly than their (*Z*)-isomers to give the corresponding 6-fluorosultines following the *endo* (Alder rule) mode of hetero-Diels–Alder addition. No sulfolene has been observed following the cheletropic mode of addition with the fluorodienes, in contrast to other substituted dienes. In agreement with the calculations, *cis*-2-fluoro-3,4-oxathiabenzobicyclo[4.4.0]dec-1(6),9-diene-4-oxide (*cis*-**9**, the sultine obtained by SO_2 addition to (*Z*)-**8** under conditions of kinetic control) adopts a sofa conformation with the oxygen atom of the ring lying in the average plane of the four carbon atoms of its sultine moiety when it is in the crystalline state at $-100\,^{\circ}C$. A similar sofa conformation was found for its *trans*-isomer, *trans*-**9**, obtained by isomerization of *cis*-**9** or by hetero-Diels–Alder addition of SO_2 to (*E*)-**8**. Experiments (equilibrium constant for hetero-Diels–Alder additions, bond lengths, and bond angles in crystalline fluorosultines *cis*-**9** and *trans*-**9**) and high-level quantum calculations on *cis*- and *trans*-6-fluoro-3,6-dihydro-1,2-oxathiin-2-oxide (*cis*- and *trans*-**20**) confirm the existence of a stabilizing, enthalpic, anomeric (*gem*-disubstitution by sulfinyloxy and fluoro groups) effect, which is interpreted in terms of (lone pair) $n(O1) \rightarrow \sigma^*(C{-}F)$ hyperconjugative interactions. This effect is strongest in the sofa conformers with a *gauche* arrangement of the σ(O1,S2) and σ(C6,F) bonds. The calculations suggest also that $n(O1) \rightarrow \sigma^*(S2,O2')$, $\pi^*(S{=}O)$, and $n(S2) \rightarrow \sigma^*(O1,C6)$ interactions intervene and affect the relative stability of the conformers (sofa, boat, pseudo-chair) found for 6-fluorosultines *cis*- and *trans*-**20**.

Keywords: anomeric effects · conformation analysis · cycloaddition · heterocycles · quantum calculations

Introduction

Conjugate dienes are known to undergo cheletropic additions[1] with sulfur dioxide to generate the corresponding 2,5-dihydrothiophene-1,1-dioxides (sulfolenes),[2] or to generate polymers (polysulfones).[3] At low temperature and in the presence of a protic or Lewis acid catalyst, simple acyclic alkyl-substituted 1,3-dienes that can adopt the *s-cis*-conformation add reversibly to SO_2 by hetero-Diels–Alder additions to generate the corresponding 3,6-dihydro-1,2-oxathiin-2-oxides (sultines).[4, 5] The latter are unstable above $-50\,^{\circ}C$ and undergo fast cycloreversion to liberate the starting 1,3-dienes and SO_2, which can then undergo the expected cheletropic addition at higher temperature. The competition between the hetero-Diels–Alder and the cheletropic additions of SO_2 strongly depends on the nature of the substituents

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author: Tables S1, S2 and S3: calculations details.

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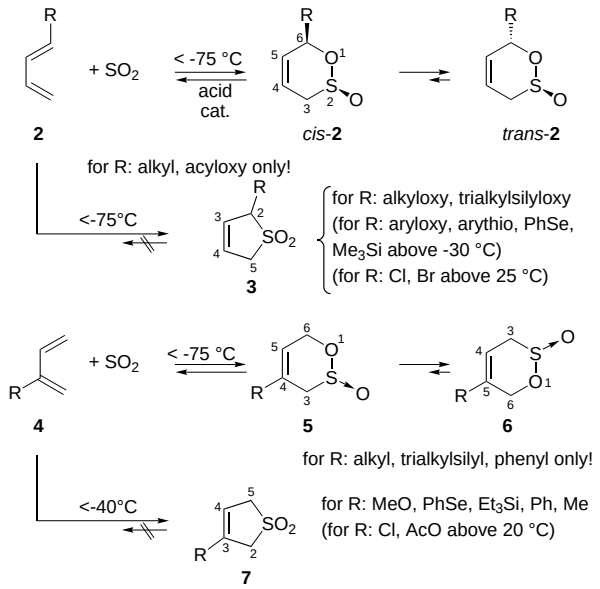
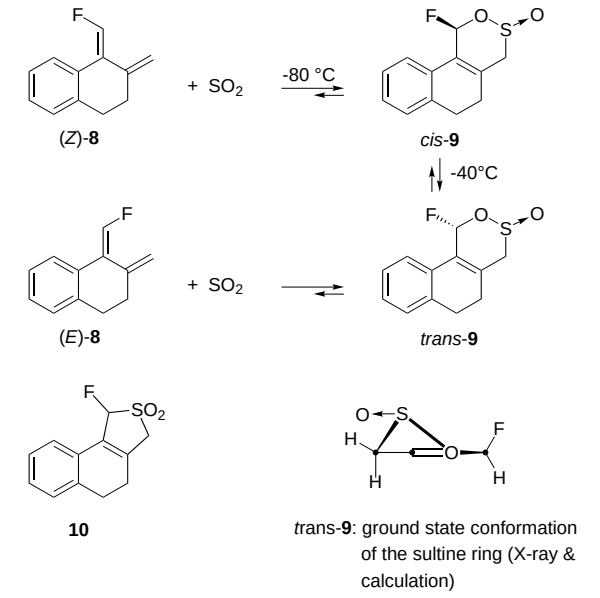
of the 1,3-dienes.[6] (*Z*)-1-Substituted buta-1,3-dienes do not add in the hetero-Diels–Alder mode, whereas their (*E*)-isomers **1** can be equilibrated below $-75\,^{\circ}C$ with the corresponding sultines (*cis*-**2** = *trans*-**2**) if substituted by methyl, ethyl, *tert*-butyl, cyclo-hexyl, benzyl, acyloxy, benzoyloxy, and β-naphthoyloxy groups.[5b] Surprisingly, the electron-richer (*E*)-1-substituted derivatives such as 1-cyclopropyl, 1-phenyl, 1-(4-methoxyphenyl), 1-(trimethylsilyl), 1-(aryloxy), 1-methylthio, 1-arylthio, and 1-phenylselenobuta-1,3-diene (Scheme 1) do not equilibrate with sultines between -100 and $-10\,^{\circ}C$, but undergo cheletropic additions to give the expected sulfolenes **3**.[5b] Similarly, (*E*)-1-(alkyloxy)- and (*E*)-1-(trialkylsilyloxy)-1,3-dienes, which can be combined with SO_2 and enoxysilanes in our one-pot, four-component synthesis of sulfones[7] and for which an asymmetrical version has been proposed,[8] generate the sulfolenes **3** in the absence of enoxysilanes.[9] Nevertheless, the corresponding sultines **2** are believed to be formed first and to be intermediates in our new carbon–carbon bond-forming reaction.[10]



Scheme 1. Competition between hetero-Diels–Alder and cheletropic additions of SO_2 to substituted dienes.

Abstract in French: *La réactivité du SO_2 face aux (E)- et (Z)-1-fluorobuta-1,3-diène ((E)- et (Z)-**11**), 2-fluorobuta-1,3-diène (**12**), (E) et (Z)-1-(fluorométhylidène)-2-méthylidènecyclohexane ((E)- et (Z)-**13**) est étudiée et comparée avec celle du SO_2 sur le (Z)- et (E)-1-(fluorométhylidène)-2-méthylidène-3,4-dihydronaphthalène ((Z)- and (E)-**8**). En concordance avec des calculs quantiques de haut niveau (pseudo-G3), **12** ne réagit pas avec le SO_2 en dehors de sa polymérisation (pas de cycloaddition) alors que les (E)-1-fluoro-1,3-diènes s'additionnent au SO_2 plus rapidement que leurs isomères (Z) en donnant des 6-fluorosultines. Ces additions du type hétéro-Diels–Alder suivent la règle (endo) d'Alder. En accord avec les calculs quantiques, le 4-oxide de cis-2-fluoro-3,4-oxathiabenzobicyclo[4.4.0]dec-1-(6),9-diène (cis-**9**, la sultine résultant de l'addition hetero-Diels–Alder du SO_2 sur (Z)-**8** sous conditions de contrôle cinétique) adopte une conformation sofa avec l'atome d'oxygène cyclique se plaçant dans le plan moyen des quatre atomes de carbone de l'entité sultine, à l'état cristallin à $-100\,^{\circ}C$. Une conformation sofa similaire est observée à l'état cristallin de l'isomère trans-**9**, obtenu par isomérisation de cis-**9** ou par addition selon Diels–Alder du SO_2 sur (E)-**8**. L'expérience (constantes d'équilibre pour les additions hétéro-Diels–Alder, les longueurs de liaisons et les angles de liaisons pour les fluorosultines cristallisées cis-**9** et trans-**9**) et les calculs quantiques sur les 2-oxydes de cis- et trans-6-fluoro-3,6-dihydro-1,2-oxathiine (cis-**20** and trans-**20**) confirment l'existence d'un effet anomère enthalpique (effet de gem-disubstitution par les groupements sulfinyloxy et fluoro) stabilisant et d'effets anomères conformationels qui sont dominés par une interaction hyperconjugative du type $n(O1) \rightarrow \sigma^*(C{-}F)$. Cet effet est le plus marqué dans les conformères sofa où les liaisons σ(O1,S2) et σ(C6,F) sont gauches. Les calculs suggèrent encore que des interactions du type $n(O1) \rightarrow \sigma^*(S2,O2')$, $\pi^*(S{=}O)$ et $n(S2) \rightarrow \sigma^*(O1,C6)$ interviennent également et affectent la stabilité relative des conformères sofa, bateau et pseudo-chaise que l'on trouve sur l'hypersurface d'énergie des 6-fluorosultines cis-**20** et trans-**20**.*

Recently, we reported that sulfur dioxide adds to (*Z*)-1-(fluoromethylidene)-2-methylidene-3,4-dihydronaphthalene ((*Z*)-**8**) at $-80\,^{\circ}C$ without acidic promoter giving the *cis*-fluorosultine *cis*-**9**. At $-40\,^{\circ}C$, *cis*-**9** isomerizes into the more stable *trans* isomer *trans*-**9**. Above $-30\,^{\circ}C$, the latter decomposes, and no trace of the corresponding sulfolene **10** (Scheme 2) could be detected.[11] Diene (*E*)-**8** is less reactive

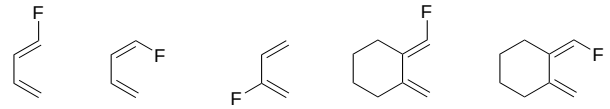


Scheme 2. The *endo* Alder rule is obeyed for the hetero-Diels–Alder addition of SO_2 to fluorodienes (*Z*)-**8** and (*E*)-**8**. Sofa conformation for fluorosultine *trans*-**9**.

than (*Z*)-**8**. It adds to SO_2 at $-40\,^{\circ}C$ to give fluorosultine *trans*-**9** directly. This sultine has been crystallized and analyzed by X-ray crystallography at $-100\,^{\circ}C$, thus allowing us to firmly establish for the first time the molecular structure of a sultine. All other derivatives are unstable above $-50\,^{\circ}C$;

their structures had been inferred from their NMR data only. In agreement with high-level quantum calculations on *trans*-6-fluorosultine, in the crystalline state, *trans*-**9** adopts a sofa conformation with the oxygen atom lying in the average plane of the four carbon atoms of its sultine moiety; its S=O bond resides in a pseudo-equatorial position (Scheme 2). This was a double surprise as high-level quantum calculations had predicted for unsubstituted and methyl-substituted sultines a pseudo-chair conformation in their ground state, in which the S=O bonds prefer pseudo-axial positions.

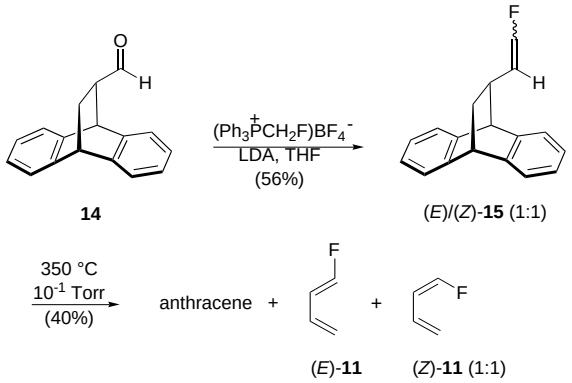
The results of the reactions of SO_2 with (*Z*)- and (*E*)-**8** demonstrated that fluoro substitution of a 1,3-diene definitively affects the competition between the hetero-Diels–Alder and cheletropic additions of SO_2 and renders 1-fluorobuta-1,3-dienes different from the other halogenobuta-1,3-dienes. In the cases of (*E*)-1-chloro- and (*E*)-1-bromobuta-1,3-diene, no sultines could be detected between −100 and 25 °C, with or without an acidic promoter. These dienes underwent slow cheletropic additions above 25 °C, equilibrating with the corresponding 2-halogenated sulfolenes exclusively.[6] In order to learn more about the fluoro substituent effects, we have now studied the reactions of SO_2 with (*E*)- and (*Z*)-1-fluorobuta-1,3-diene ((*E*)- and (*Z*)-**11**), with 2-fluorobuta-1,3-diene (**12**), and with two new fluorodienes, (*E*)- and (*Z*)-1-(fluoromethylidene)-2-methylidenecyclohexane ((*E*)- and (*Z*)-**13**). We have been able to crystallize the fluorosultine



(*E*)-**11** (*Z*)-**11** **12** (*E*)-**13** (*Z*)-**13**

cis-**9**, the adduct of (*Z*)-**8** and SO_2, obtained under conditions of kinetic control (*endo* Alder rule, see Scheme 2) and have compared its crystalline molecular structure, obtained by X-ray crystallography, with that predicted by high-level quantum calculations for *cis*-6-fluorosultine and with that found for *trans*-**9**. High-level quantum calculations have also been applied to ascertain the role of fluoro substitution on the competition between hetero-Diels–Alder and cheletropic additions of SO_2 and on the conformation of sultines. They suggest that the higher hetero-Diels–Alder reactivity of 1-fluorobuta-1,3-dienes compared with their 1-chloro and 1-bromo analogues might be due to the higher exothermicity for the formation of 6-fluorosultines than for the formation of 6-chloro and 6-bromosultines. The experiments (equilibrium constants for hetero-Diels–Alder addition, bond lengths and bond angles in crystalline sultines *cis*-**9** and *trans*-**9**) and calculations confirm the existence of stabilizing enthalpic anomeric effects (*gem*-disubstitution effects of sulfinyloxy and fluoro substituents). Conformational anomeric effects in 6-fluorosultines will also be discussed. The calculations suggest that 6-substituents are capable of deforming the pseudo-chair conformation of a sultine into a sofa conformation with the ring-oxygen atom lying in the plane of the four carbon atoms. Depending on the nature of the substituents, on the relative configuration (*cis* or *trans*), and on the conformation (pseudo-chair, sofa, boat), a delicate balance exists between destabilizing steric or electrostatic repulsions (*gauche* effects) on the one hand and stabilizing $n(O-1) \rightarrow \sigma^*(C-F)$, $n(O) \rightarrow \sigma^*(S-O)$, $n(O-1) \rightarrow \pi^*(S=O)$, and $n(S) \rightarrow \pi^*(O-C)$ interactions on the other.

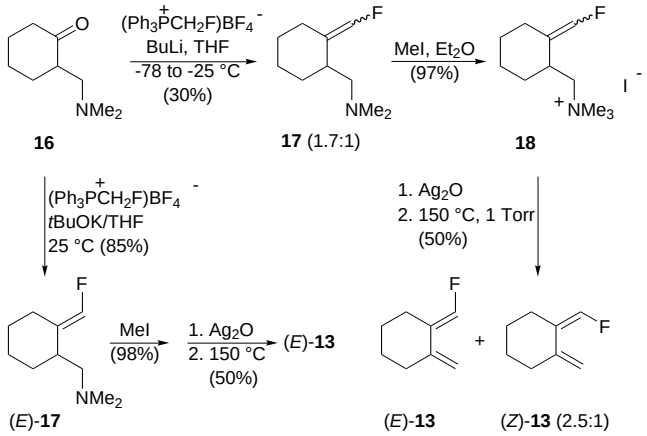
Synthesis of the 1-fluorodienes: The known syntheses of mixtures of (*E*)- and (*Z*)-1-fluorobutadiene[12] are lengthy and give low yields. Our synthesis is based on the fluoromethylenation[13] of the Diels–Alder adduct **14** of acrolein and anthracene,[14] followed by cycloreversion (Scheme 3).



14 (*E*)/(*Z*)-**15** (1:1) (*E*)-**11** (*Z*)-**11** (1:1)

Scheme 3. New synthesis of a 1:1 mixture of (*E*)- and (*Z*)-1-fluorobuta-1,3-diene.

The synthesis of (*E*)- and (*Z*)-1-(fluoromethylidene)-2-methylidenecyclohexane ((*E*)-**13**, (*Z*)-**13**) follows the method of Bickelhaupt and co-workers reported for the synthesis of 1,2-dimethylidenecyclohexane[15] (Scheme 4). Fluoromethylenation[13] of the product of Mannich condensation with



Scheme 4. Synthesis of pure (*E*)-1-(fluoromethylidene)-2-methylidenecyclohexane, (*E*)-**13**, and of a 2.5:1 mixture of (*E*)-**13** and (*Z*)-**13**.

cyclohexanone, formaldehyde, and dimethylamine (**16**) with $(Ph_3PCH_2F)BF_4$ in the presence of BuLi produced a 1.7:1 mixture of the (*E*)- and (*Z*)-fluoroalkene **17** in mediocre yield (30%). Quaternization of **17** with MeI followed by Hoffman elimination provided a mixture of (*E*)-**13**/(*Z*)-**13** (2.5:1, 50%). Pure (*E*)-**13** could be obtained by using *t*BuOK/THF (25 °C)

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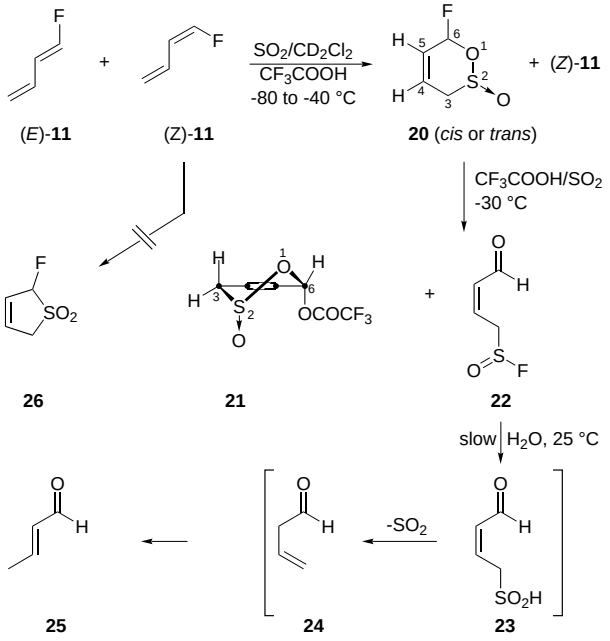
instead of BuLi/THF for the fluoromethylenation of ketone **16** (Scheme 4).

Reactions of fluorodienes with sulfur dioxide: In the absence of protic or Lewis acid, (*E*)- and (*Z*)-1-fluorobuta-1,3-diene did not react with SO_2 (1:1 mixture of SO_2/CD_2Cl_2) between -80 and $-10\,^{\circ}C$. At $25\,^{\circ}C$, (*E*)-**11** decomposed slowly into (*Z*)-crotonaldehyde whereas (*Z*)-**11** stayed stable, even upon heating in pure SO_2 up to $50\,^{\circ}C$ (Scheme 5). Unlike (*E*)-1-chloro- and (*E*)-1-bromobutadiene, which reacted at $50\,^{\circ}C$



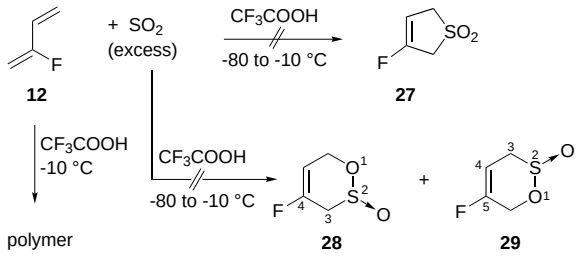
Scheme 5. The reactions of 1-fluorobutadienes (*E*)-**11** and (*Z*)-**11** with SO_2 (excess) and CF_3COOH (1 equiv).

with SO_2 to form the corresponding sulfolenes (Scheme 1),[6] (*Z*)-**11** did not add to SO_2 and generate the expected sulfolene **26** (2-fluoro-2,5-dihydrothiophene-1,1-dioxide). At higher temperature, only polymer formation was observed (Scheme 5).

In the presence of one equivalent of CF_3COOH, (*E*)-**11** added to SO_2 to form a single sultine **20** between -80 and $-40\,^{\circ}C$ (Scheme 5). An equilibrium constant ((*E*)-**11** + SO_2 = **20**) $K^{233\,K} \cong 3.5 \times 10^{-2}\,mol^{-1}dm^3$ was measured (by ^1H NMR, internal reference: toluene) at $-40\,^{\circ}C$. It is larger than the equilibrium constants evaluated for the hetero-Diels–Alder additions of SO_2 to (*E*)-piperilene[4a] ($K^{233\,K} \cong 5 \times 10^{-4}\,mol^{-1}dm^3$) and to isoprene[4a] ($K^{233\,K} \cong 4 \times 10^{-3}\,mol^{-1}dm^3$) at the same temperature. After standing at $-30\,^{\circ}C$ for 15 h, the mixture of fluorosultine **20** + (*Z*)-**11** + CF_3COOH in SO_2/CD_2Cl_2 (1:1) was half converted into a mixture containing the trifluoroacetoxysultine **21** and sulfinyl fluoride **22**. The former product probably arises from trifluoroacetolysis of **20** and the latter by reaction of the liberated fluoride anion, or alternatively, by direct 1,3-migration: **20** → **22**.[16] At $25\,^{\circ}C$, **20**, **21**, and **22** decomposed into crotonaldehyde (**25**) and other unidentified products. In the presence of CF_3COOH and SO_2, (*Z*)-**11** decomposed very slowly at $25\,^{\circ}C$. No trace of the expected 2-fluorosulfolene (**26**) could be detected by ^1H NMR spectroscopy of the crude reaction mixture after it had stood for several days. The formation of **25** probably arises from traces of water or from water formed during the decomposition. Hydrolysis of the sulfinyl fluoride **22** is expected to generate sulfinic acid, **23**, which undergoes a fast retro-ene reaction with elimination of SO_2. This forms enal **24**, which equilibrates with the more stable (*E*)-crotonaldehyde (**25**) (Scheme 5).

Our attempts to catalyze the hetero-Diels–Alder and cheletropic additions of SO_2 to 1-fluorobutadienes (*Z*)-**11** and (*E*)-**11** with Lewis acids all failed. With $BF_3 \cdot Et_2O$, Me_3SiOTf, $EtAlCl_2$, PCl_5, and Cp_2TiCl_2, the mixture of (*E*)-**11**/(*Z*)-**11** (1:1) in SO_2/CD_2Cl_2 (1:1) polymerized and decomposed to **25** at $-80\,^{\circ}C$. Decomposition was also observed in the presence of $BuBCl_2$ or $Sn(OTf)_2$ above $-50\,^{\circ}C$. With Cp_2ZrCl_2 above $-50\,^{\circ}C$, (*E*)-**11** added slowly to SO_2 to give 6-fluorosultine **20**. None of the above catalysts (up to 3 equivalents) induced the formation of 2-fluorosulfolene (**26**).

In the absence of acid catalysts, 2-fluorobutadiene (**12**)[17a] did not react with SO_2 between -80 and $+50\,^{\circ}C$. This is a surprise, as at least the cheletropic addition giving 3-fluorosulfolene (**27**) should occur at $50\,^{\circ}C$, since most 2-substituted butadienes generate the corresponding sulfolenes under these conditions (Scheme 6).[1, 2, 5c] At $-100\,^{\circ}C$, isoprene undergoes

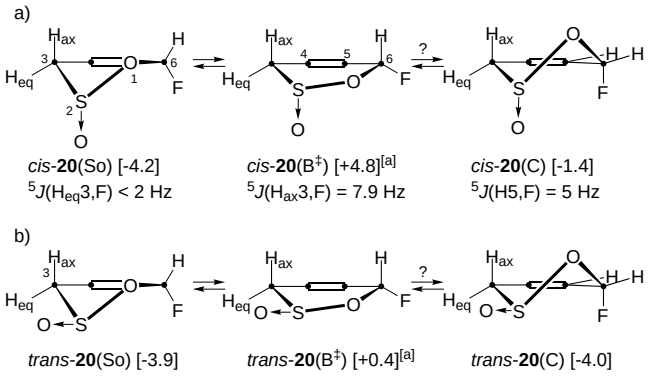


Scheme 6. Absence of reactivity of 2-fluorobuta-1,3-diene toward SO_2 in the presence of CF_3COOH.

hetero-Diels–Alder addition with SO_2 in the presence of CF_3COOH. In the presence of the same acid, 2-fluorobutadiene did not add to SO_2 after several days at various temperatures between -80 and $-10\,^{\circ}C$. Above $-10\,^{\circ}C$ it slowly polymerized. The expected sultines **28** and **29** (Scheme 6) could not be detected by ^1H NMR spectroscopy of the crude reaction mixtures.

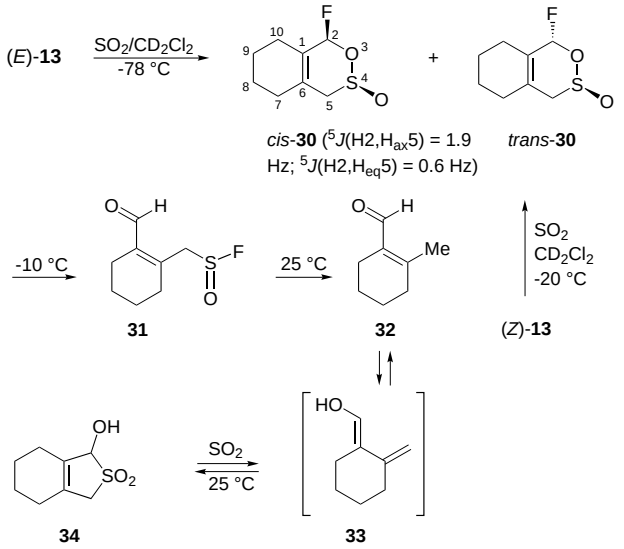
The structures of **20**–**22** were deduced from ^1H NMR and ^{13}C NMR data of the crude reaction mixtures and by comparison with data reported for derivatives *cis*-**9** (see below) and *trans*-**9**.[11] Because of the presence of unreacted (*Z*)-**11** and of polymeric material, selective TOCSY experiments were necessary to obtain the ^1H NMR spectra of sultines **20** and **21**. Unfortunately, the vicinal (^3J(H,H)) and homoallylic (^5J(H,H)) proton–proton coupling constants could not be measured. We are thus unable to propose preferred conformations and to tell whether *cis*-6-fluorosultine (*cis*-**20**), resulting from a preferred (see our quantum calculations below) *endo*-mode (Alder rule) of addition, or *trans*-6-fluorosultine (*trans*-**20**) is formed by reaction of (*E*)-**11** with SO_2. The ^{19}F NMR spectrum of fluorosultine **20**

showed a doublet of doublets of doublets for its fluorine atom assigned to ^2J(H6,F) = 51.1 Hz, ^3J(H5,F) = 8.0 Hz and $^5J(H_{ax}\text{-}3,F) = 7.9$ Hz; the assignment was confirmed by double irradiation experiments. The other ^nJ(H,F) coupling constants were smaller than 2 Hz. Assuming that the homoallylic coupling constants ^5J(H3,F) follow a relationship similar to that found for $^5J(H3,H6) = (5\text{ Hz})(\sin\theta)^2(\sin\theta')^2$ in cyclohexenes, in which θ and θ' are the angles that H3 and H6 make with the C1,C2,C3,C4 plane,[19] the data suggest that one of the two protons H3 of **20** always resides in a pseudo-equatorial position ($^5J(H_{eq}3,F) < 2$ Hz) and the other in a pseudo-axial position ($^5J(H_{ax}3,F) = 7.9$ Hz) and this independently of the relative configuration of **20**, which can be either *cis* or *trans*. These observations imply, therefore, that *cis*-**20** is either in a sofa conformation (*cis*-**23**(So)), as predicted by calculations,[11] or exists as an equilibrium between this conformer, the boat (*cis*-**20**(B)) and the pseudo-chair conformer (*cis*-**20**(C)), as shown in Scheme 7. The NMR data of **20** are also consistent with the *trans* isomer adopting the sofa conformation or existing as an equilibrium of conformers *trans*-**20**(So) = *trans*-**20**(B) = *trans*-**20**(C).



Scheme 7. Possible conformers of a) *cis*-**20** and b) *trans*-**20** that are consistent with the ^nJ(H,F) values. In square parenthesis the G3 calculated energies relative to SO_2 + (*E*)-**11**. [a] These conformers are not energy minima by calculations[11] (see Scheme 9).

Comparing the δ_H of 6-trifluoroacetoxysultine, **21**, with those reported for 6-acetoxysultines,[5b, 6] we suggest that **21** is the *cis*-diastereomer adopting a sofa or pseudo-chair conformation with pseudo-axial CF_3COO and S=O groups. As we had found that 1,2-dimethylidenecyclohexane[18] and other 1,2-dimethylidenecycloalkanes[5a] are much more reactive toward SO_2 than simpler alkyl-substituted buta-1,3-dienes, we explored the reactivity of (*E*)- and (*Z*)-1-(fluoromethylidene)-2-methylidenecyclohexane ((*E*)-**13**, (*Z*)-**13**) toward SO_2 under various conditions (Scheme 8). Without protic or Lewis acid catalyst, pure (*E*)-**13** added to SO_2 (1:1 mixture of SO_2/CD_2Cl_2) at $-78\,^\circ$C to give a mixture of fluorinated sultines *cis*-**30** and *trans*-**30** (93:7). The reaction was complete after 1 h at $-78\,^\circ$C. Diels–Alder adducts were stable between -80 and $-30\,^\circ$C, their proportion staying the same. Above $-10\,^\circ$C, no cycloreversion could be detected, but the sultines decomposed into the sulfinyl fluoride **31**. At 25 °C, the latter was completely converted into 2-methylcyclohex-1-ene-1-carbaldehyde (**32**), probably according to a mechanism



Scheme 8. The reactions of fluorodienes (*E*)- and (*Z*)-**13** with SO_2 under various conditions. The hetero-Diels–Alder reactions of SO_2 follow the *endo* Alder rule.[21]

similar to that proposed in Scheme 5 for the decomposition of the SO_2 adducts of (*E*)-1-fluorobutadiene. Enal **32** equilibrated with its dienol **33**, which underwent a cheletropic addition with SO_2 to give the 2-hydroxysulfolene **34**, which was unstable and could not be isolated, although it was visible by ^{1}H NMR spectroscopy.

In the presence of one equivalent of CF_3COOH, (*E*)-**13** added to SO_2 at $-80\,^\circ$C to give the same mixture of sultines *cis*-**30** and *trans*-**30** (93:7). Trifluoroacetic acid accelerated the decomposition of the fluorosultines **30** as they were converted into the sulfinyl fluoride **31** at $-50\,^\circ$C. The reaction was complete in 15 h at this temperature. Apparently, protonation of the sultines **30** accelerates the 1,3-migration of the fluoride. When a mixture 5:1 of dienes (*E*)-**13** and (*Z*)-**13** was allowed to react with SO_2/CD_2Cl_2 at $-80\,^\circ$C, only (*E*)-**13** added SO_2 and provided a mixture of fluorosultines *cis*-**30** and *trans*-**30** (93:7). As in the case of 1-fluorobuta-1,3-dienes, **11**, the fluorodiene (*Z*)-**13** is definitively less reactive than its (*E*)-isomer in the hetero-Diels–Alder addition with SO_2; this is in agreement with predictions based on quantum calculations[11] and as demonstrated for the hetero-Diels–Alder additions of SO_2 to piperilenes.[4a] Because of steric repulsions between the C–F and C–H groups (1,4-interactions) in the *s-cis* conformer of the (*Z*)-1-fluorobutadiene moiety, the 1,4-distance is increased and this retards the cycloaddition.[20] At $-20\,^\circ$C, (*Z*)-**13** added slowly to SO_2 with preferred formation of *trans*-**30**. Thus, an initial 5:1 mixture of (*E*)-**13**/(*Z*)-**13** gave a 5:1 mixture of *cis*-**30**/*trans*-**30** at $-20\,^\circ$C. This demonstrates that both (*E*)-**13** and (*Z*)-**13** prefer the *endo* mode (Alder rule[4a]) for these Diels–Alder additions with SO_2, in agreement with predictions based on quantum calculations[11] (see Scheme 9). In CD_2Cl_2/SO_2 (1:1) the conversion of dienes **13** into sultines **30** was complete (by ^{1}H NMR spectroscopy); this allowed a lower limit for the equilibrium constant to be set: $K^{253\,K}$ (**13** + $SO_2 \rightleftharpoons$ **30**) $> 50\ \text{mol}^{-1}\,\text{dm}^3$. This value is significantly larger than the equilibrium constant $K^{253\,K}$ (**35** + $SO_2 \rightleftharpoons$ **36**) $\cong 0.8\ \text{mol}^{-1}\,\text{dm}^3$ evaluated for the hetero-Diels–Alder addi-

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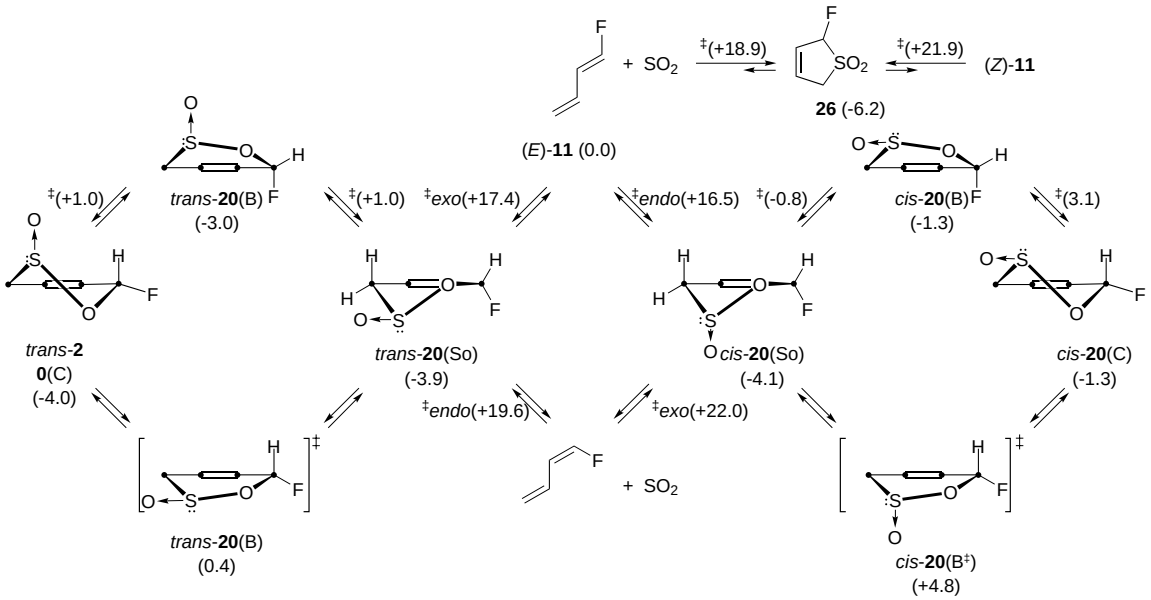
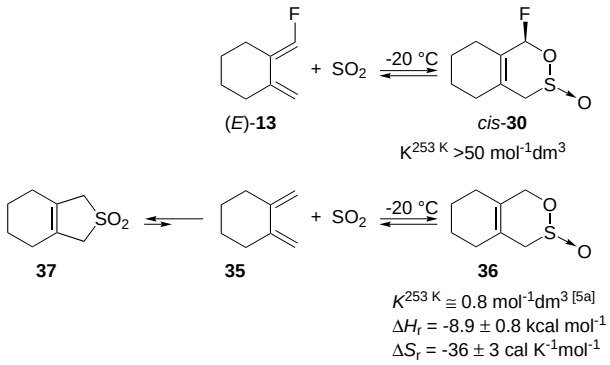


Scheme 9. G3 calculated energies (in kcal mol^{-1}) for the hetero-Diels–Alder and cheletropic additions of SO_2 to (*E*)- and (*Z*)-1-fluorobuta-1,3-diene. The *endo* mode (Alder rule)[21] of [4+2] cycloaddition is easier than the *exo* mode of addition; the cheletropic addition is more difficult than the hetero-Diels–Alder addition and the latter reaction is slightly more exothermic than the former reaction, by 2 kcal mol^{-1} (ca. 10 kcal mol^{-1} for alkyl-substituted dienes[5a, 6]).

tion of SO_2 to 1,2-dimethylidenecyclohexane (**35**) to give sultine **36**[5a] (Scheme 10). In fact sultine **36** is not stable at $-20\,^{\circ}C$; it undergoes fast cycloreversion giving SO_2 + **35**, which then adds slowly in the cheletropic mode to provide the corresponding sulfolene **37** quantitatively.[5a] As suggested by our quantum calculations (see below) the relatively large

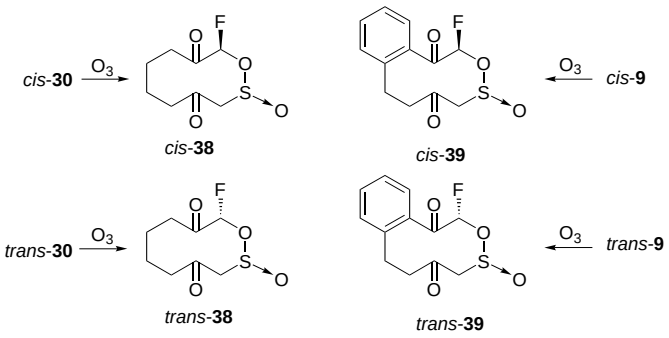


Scheme 10. The hetero-Diels–Alder addition of fluorodiene (*E*)-**13** to SO_2 is more exothermic than that of unsubstituted diene **35**.

equilibrium constant $K^{253\,K}$ (**13** + $SO_2 \rightleftharpoons$ **30**) compared with $K^{253\,K}$ (**35** + $SO_2 \rightleftharpoons$ **36**) shows the existence of an enthalpic anomeric effect[22] in the 6-fluorosultines **30** due to the *gem*-disubstitution F-C-OSO), an effect similar to that predicted for fluoromethanol.[23] Surprisingly, neither (*E*)- nor (*Z*)-**13** underwent the expected cheletropic additions with SO_2, only decomposition and polymerization products were observed when the reactants were treated with concentrated SO_2 at $0\,^{\circ}C$. This is a surprise as our calculations (Scheme 9) suggest that the energy barrier of the cheletropic addition (*E*)-**11** + $SO_2 \rightarrow$ **26** (18.9 kcal mol^{-1}) is not higher than that of the hetero-Diels–Alder addition (*Z*)-**11** + $SO_2 \rightarrow$ *trans*-**20** (19.6 kcal mol^{-1}).

The structures of the new compounds **30**, **31**, and **32** were inferred from their ^1H, ^{13}C, and ^{19}F NMR spectra. Assignment of structures *cis*-**30** and *trans*-**30** is consistent with the hypothesis that fluorodienes (*E*)-**13** and (*Z*)-**13** must have similar relative reactivity as their analogues (*Z*)-**8** and (*E*)-**8**, respectively, toward SO_2.[11] The coupling constants ^1J(C,H) and ^1J(C,F) for the anomeric center in α- and β-glycopyranosyl fluorides are remarkably different.[24] Since very similar values are found for ^1J(C2,H2) in *cis*-**30** (185 Hz) and *trans*-**30** (184 Hz), and for ^1J(C2,F) in *cis*-**30** (224 Hz) and *trans*-**30** (220 Hz), we must admit that both fluorosultines **30** adopt similar average conformations for their C1-C2-O3-S4 moieties. The data are consistent with sofa conformations analogous to *cis*-**20**(So) and *trans*-**20**(So) (Scheme 9), which correspond to energy minima calculated for the *cis*- and *trans*-6-fluorosultine,[11] and to the conformations observed in the crystalline state for fluorosultines *cis*-**9** (see below) and *trans*-**9**,[11] respectively. The homoallylic coupling constants $^5J(H2,H_{ax}5) = 1.9$ Hz and $^5J(H2,H_{eq}5) = 0.6$ Hz measured in the ^1H NMR spectrum of *cis*-**30** are also consistent with the sofa conformer analogous to *cis*-**20**(So). The same analysis could not be carried out for *trans*-**30** because the corresponding ^5J(H2,H5) coupling constants could not be measured due to spectral complexity arising from the numerous long-range ^nJ(H,H) couplings.

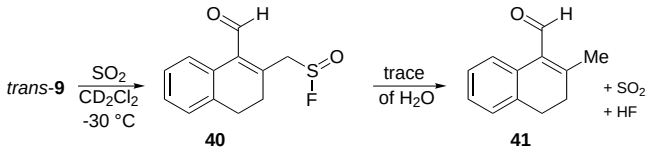
Further proof for the formation of sultines **30** was given by their ozonolysis.[9] When O_3 was bubbled through a mixture of *cis*-**30** and *trans*-**30** (93:7) in SO_2/CH_2Cl_2 (1:1) at $-78\,^{\circ}C$, a 93:7 mixture of diketones **38** and **39** was obtained (Scheme 11). These compounds could not be isolated as they decomposed on concentrating above $-10\,^{\circ}C$, providing a dark, sticky polymeric material. Their structures were de-



Scheme 11. Ozonolysis of fluorosultines *cis*-**30**, *trans*-**30**, *cis*-**9** and *trans*-**9** provides new medium-size ring heterocycles *cis*-**38**, *trans*-**38**, *cis*-**39**, and *trans*-**39**, respectively.

duced from the ^{1}H NMR of the crude reaction mixture (see Experimental Section).

As already described in our preliminary communication[11] the hetero-Diels–Alder additions of SO_2 to fluorodienes (*Z*)-**8** followed the *endo* Alder rule giving the 6-fluorosultines *cis*- and *trans*-**9** under conditions of kinetic control (see Scheme 2). We shall present below the crystalline and molecular structure of *cis*-**9** obtained by X-ray crystallography at $-100\,^\circ$C. The ozonolysis of *cis*-**9** and *trans*-**9** gave heterocycles *cis*-**39** and *trans*-**39**, respectively (Scheme 11). We have also studied the decomposition of *trans*-**9** (the most stable sultine) at $-30\,^\circ$C. Similarly to the decomposition of sultines **20** (Scheme 5) and **30** (Scheme 8), *trans*-**9** isomerized slowly at $-30\,^\circ$C into the sulfinyl fluoride **40**, which in its turn decomposed slowly into enal **41** (Scheme 12). The reaction *trans*-**9** → **40** was rapid and quantitative at 25 °C.



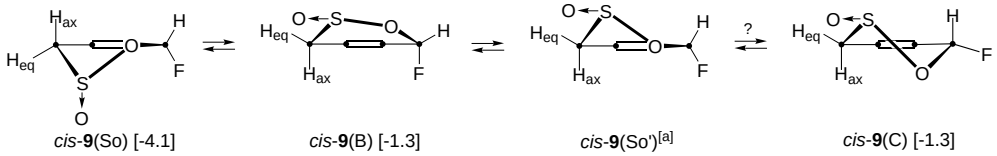
Scheme 12. Decomposition of sultine *trans*-**9** in SO_2/CD_2Cl_2.

Like the crystalline structure of *trans*-**9**, *cis*-**9** adopts a sofa conformation with the oxygen of the ring lying in the average plane of the four carbon atoms of the sultine moiety (Figure 1, below), as predicted by our calculations[11] for *cis*-6-fluorosultine (*cis*-**20**(So), Scheme 9). This may not be the unique conformation available for *cis*-**9** in solution as suggested by its ^{1}H NMR spectrum and by comparison with that of *cis*-**30** (Scheme 8). If the sofa conformation *cis*-**9**(So), analogous to *cis*-**20**(So), were the unique conformation available for *cis*-**9**, a small (0–1 Hz) value would be expected for the homoallylic coupling constant ^5J(H2,H$_{eq}$5) and a larger one (1.5–3.0 Hz[19, 25]) for ^5J(H2,H$_{ax}$5), as found for *cis*-**30** (^5J(H2,H$_{eq}$5) = 0.6 Hz, ^5J(H2,H$_{ax}$5) = 1.9 Hz). For *cis*-**9** we observe similar homoallylic coupling constants ^5J(H2,H5) = 1.5 and 1.7 Hz on the one hand and ^5J(F,H5) = 6.3 and 7.6 Hz on the other. Thus, for *cis*-**9** in solution we must admit that the sofa conformer *cis*-**9**(So) equilibrates with a boat (*cis*-**9**(B), another sofa *cis*-**9**(So′) and a pseudo-chair conformer (*cis*-**9**(C), Scheme 13). Such equilibrium interchanges the H5 proton *cis* with respect to F from a pseudo-equatorial to a pseudo-axial position, and the H5 proton *trans* with respect to F from a pseudo-axial to a pseudo-equatorial position.

As already commented in our preliminary communication,[11] fluorosultine *trans*-**9**, which adopts a sofa conformation in the crystalline state similar to that calculated for *trans*-**20**(So) (Scheme 9), must exist as an equilibrium of several conformers in solution as its ^{1}H NMR spectrum showed similar homoallylic coupling constants ^5J(H4,F) = 5.6 and 6.2 Hz and relatively small ^5J(H4,H2) values (0.8 Hz < 0.2 Hz). However, since the one-bond coupling ^1J(C2,H) = 184 Hz, ^1J(C2,F) = 226 Hz for *cis*-**9** and ^1J(C2,H) = 184 Hz, ^1J(C2, F) = 221 Hz for *trans*-**9** are similar, one most admit that both sultines adopt similar average conformations for their S-O-C-F moieties in solution.

Single crystal and molecular structure of fluorosultines *cis*-9: ORTEP representations[26] of *cis*-**9** at $-100\,^\circ$C are shown in Figure 1. The most significant interatomic distances and bond angles of this sultine are reported in Table 1 and the torsion angles in Table 2. Fluorosultine *cis*-**9** crystallizes with two equivalents of sulfur dioxide (Figures 1 and 2) that strongly coordinate the S=O moiety: (S3=O2 = 2.730(6) Å, S2=O2 = 2.788(5) Å) (Table 3). Nevertheless, the structural parameters of SO_2 in the crystal are only slightly affected by this interaction as the S=O bond lengths (S2−O4 = 1.432(6), S2−O3 = 1.429(7), S3−O5 = 1.428(7), S3−O6 = 1.419(6) Å) and the O-S-O angle (O3-S2-O4 = 117.3(4), O5-S3-O6 = 116.5(4)°—see Figure 1a for atom numbering) for both coordinated molecules are similar to those measured for pure SO_2.[27] Additional Lewis acid–base interactions between the molecules of the crystal are present (Figure 2) but do not affect the molecular parameters because of the rather long intermolecular interatomic distances (O5−S2 = 3.288(6), O4−S3 = 3.001(6) Å).

Interestingly, the C1−F1 distance (1.399(8) Å) in *cis*-**9** is similar to the average C−F value (1.40 Å) observed in several crystallized pyranosyl fluoride derivatives,[28] but slightly larger than the average value of paraffinic C−F bonds (1.38 Å).[29] This phenomenon may be associated with the conformational anomeric effect[22] allowing electron-donation



Scheme 13. Possible conformers for fluorosultine *cis*-**9** in solution as suggested by the homoallylic ^5J(H,H) and ^5J(H,F) values. Number in square parentheses give the G3 energies, in kcal mol^{-1}, calculated for the corresponding conformers *cis*-**20** relative to the cycloaddents (Scheme 9). [a] This conformer is not calculated to be an energy minimum in the case of *cis*-**20**.

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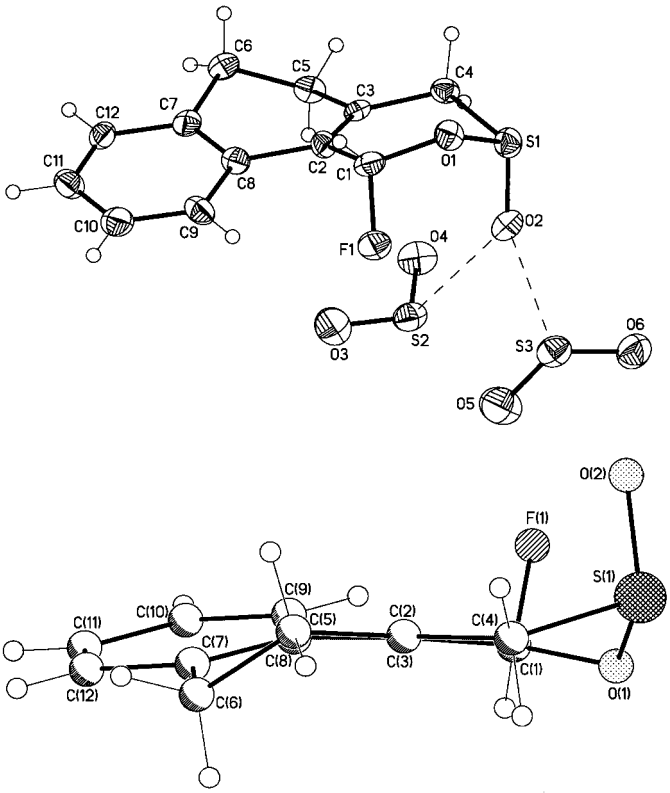

Figure 1. ORTEP representations of *cis*-**9** showing top: the two molecules of SO_2 and their coordination to the S=O group of the sultine, bottom: the sofa conformation. For reasons of commodity the atom numbering does not follow the IUPAC recommendations.

Table 1. Selected interatomic distances and bond angles for crystalline *cis*-**9**·$(SO_2)_2$.

Bond lengths [Å]		Angles [°]	
S1–O2	1.482-5	OS–S1–O1	108.8(3)
S1–O1	1.630-5	O2–S1–C4	105.2(3)
S1–C4	1.785-7	O1–S1–C4	96.9(3)
O1–C1	1.418-9	C1–O1–S1	120.0(4)
C1–C2	1.490-10	F1–C1–O1	106.4(6)
C2–C3	1.331-10	F1–C1–C2	110.4(6)
C3–C4	1.506-10	O1–C1–C2	116.3(6)
S2–O3	1.428-6	C3–C2–C8	119.7(7)
S2–O2	2.788-5	C3–C2–C1	122.5(6)
S3–O2	2.730-6	C8–C2–C1	117.6(7)
S2–O5	3.288-6	C2–C3–C5	121.9(6)
S2–O4	1.431-6	C2–C3–C4	123.6(7)
S3–O5	1.429-6	C5–C3–C4	114.5(5)
S3–O6	1.419-6	C3–C4–S1	115.1(5)
C1–F1	1.399-8		

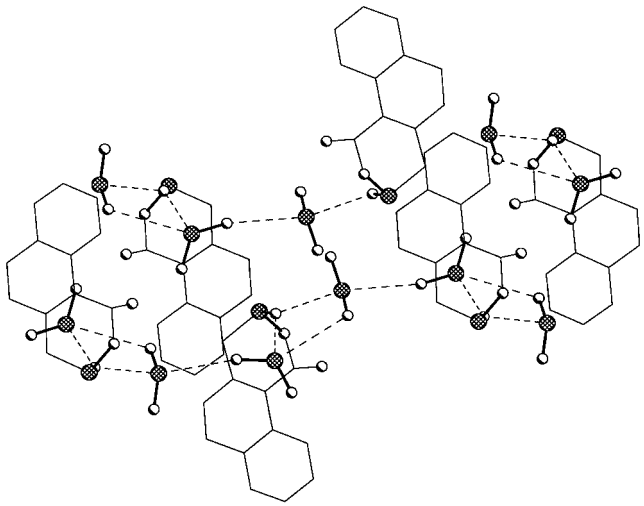

Figure 2. Organization of the SO_2 and *cis*-**9** molecules in the crystal at –100 °C.

Table 2. Torsion angles [°] of *cis*-**9** (for atom numbering see Figure 1).

O2-S1-O1-C1	179.11(18)	C4-S1-O1-C1	70.82(19)
S1-O1-C1-F1	73.4(2)	S1-O1-C1-C2	–49.5(3)
O1-C1-C2-C3	2.3(4)	F1-C1-C2-C3	–118.3(3)
O1-C1-C2-C8	–174.3(2)	F1-C1-C2-C8	65.1(3)
C8-C2-C3-C5	4.8(4)	C1-C2-C3-C5	–171.8(2)
C8-C2-C3-C4	–173.1(2)	C1-C2-C3-C4	10.4(4)
C2-C3-C4-S1	21.2(3)	C5-C3-C4-S1	–156.84(18)
O2-S1-C4-C3	–158.32(18)	O1-S1-C4-C3	–53.67(19)
C2-C3-C5-C6	27.4(3)	C4-C3-C5-C6	–154.6(2)
C3-C5-C6-C7	–45.7(3)	C5-C6-C7-C12	–147.7(2)
C5-C6-C7-C8	35.8(3)	C12-C7-C8-C9	0.1(4)
C6-C7-C8-C9	176.7(2)	C12-C7-C8-C2	179.0(2)
C6-C7-C8-C2	–4.4(3)	C3-C2-C8-C7	–17.4(3)
C1-C2-C8-C7	159.2(2)	C3-C2-C8-C9	161.4(2)
C1-C2-C8-C9	–21.9(3)	C7-C8-C9-C10	0.0(4)
C2-C8-C9-C10	–178.9(2)	C8-C9-C10-C11	0.0(4)
C9-C10-C11-C12	–0.1(4)	C10-C11-C12-C7	0.2(4)
C8-C7-C12-C11	–0.2(4)	C6-C7-C12-C11	–176.7(3)

from O1 into the C1–F1 axial bond (atom numbering of Figure 1). It has been well documented from experimental and computational data that the antiperiplanar disposition of the oxygen lone pair and the C–F bond in molecules containing the O-C-F moiety results in shortening of the C–O bond, elongation of the C–F bond and "opening" of the O-C-F bond angle.[28, 30, 31] The variation of these structural parameters associated with the conformational anomeric effect[22, 32] is clearly indicated by the theoretical structural data calculated for the different conformers of 2-fluorotetrahydropyran[30] and fluoromethanol.[23] Fluorosultine *trans*-**9** is "flatter" than *cis*-**9** and thus crystallizes easily without SO_2 molecules.

Table 4 shows the most significant interatomic distances and bond angles for *trans*-**9**. The C1–F1 bond is longer in this fluorosultine (1.414(3) Å) than in *cis*-**9** (1.399(8) Å); the C1–O1 bond is longer in the *cis* isomer, and the F1-C1-O1 bond angle is larger in *trans*-**9** (106.6°) than in the *cis* (106.4°). This suggests that the O-C-F conformational anomeric effect involving electron donation from O1 to the *trans* C1–F1 bond is stronger in *trans*-**9** than in *cis*-**9**. Moreover, the O1–S1 bond is longer in *trans*-**9** (1.6840(19) Å) than in *cis*-**9** (1.630(5) Å) while the S1–O2 bond is longer in *cis*-**9** (1.482(5) Å) than in *trans* (1.475(2) Å). The O1-S1-O2 angle is larger (108.8°) in *cis*-**9** than in *trans*-**9** (102.91°). This may be due to the additional O/S=O conformational anomeric effect in *cis*-**9** (axial S=O bond), in which the ring oxygen atom can donate electrons to both the C1–F1 and S1=O2 bonds. Alternatively, the opening of angle O1-S1-O2 in *cis*-**9** compared with that in *trans*-**9** could be due to more severe electrostatic repulsions between the C–F and S=O bonds in the former. This

Table 3. Crystal data and structure refinement for *cis*-**9**·$(SO_2)_2$ (*cis*-1-fluoro-1,4,9,10-tetrahydronaphth[2,1-d][2,3]oxathiin-3-oxide.

empirical formula	$C_{12}H_{11}FO_6S_3$
formula weight	366.39
temperature [K]	143(2)
wavelength [Å]	0.71073
crystal system	Monoclinic
space group	$P2(1)/c$
unit cell dimensions [Å]	a = 7.8848(12).
	b = 14.870(2)
	c = 12.667(2)
[°]	$\alpha = 90°$
	$\beta = 93.439(14)°$.
	$\gamma = 90°$.
volume [Å^3]	1482.5(4)
Z	4
density (calcd) [Mg m^{-3}]	1.642
absorption coefficient [mm^{-1}]	0.536
$F(000)$	752
θ range [°]	3.18 to 25.02
index ranges	$-9 \le h \le 9$
	$-17 \le k \le 15$
	$-14 \le l \le 15$
reflections collected	8245
independent reflections	2556 ($R_{int} = 0.1019$)
completeness to $\theta = 0.50°$	0.0 %
absorption correction	None
refinement method on F^2	Full-matrix least-squares
data/restraints/parameters	2556/0/200
goodness of fit on F^2	1.191
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0887$, w$R2 = 0.1527$
R indices (all data)	$R1 = 0.1377$, w$R2 = 0.1755$
extinction coefficient	0.0017(4)
largest diff. peak and hole [e Å^{-3}]	0.432 and −0.477

interpretation is consistent with the fact that the latter fluorosultine is more stable than the former in solution. The most striking observation with crystalline *cis*- and *trans*-**9** is that both adopt sofa conformations in which the oxygen atom of the ring lies in the average plane of the carbon atoms and the sulfur center is *gauche* with respect to the fluoro substituent of the sultine moieties. The cyclohexa-1,3-diene moieties of both *cis*- and *trans*-**9** adopt distorted boat conformations. Twist about the sultine double bond C2=C3 (atom numbering in Figure 1) is somewhat larger in *trans*-**9** than in *cis*-**9**.

Theoretical methods: The potential energy surfaces (PESs) for the reactions between (*E*) and (*Z*)-1-fluoro-1,3-butadiene ((*E*)-**11**, (*Z*)-**11**)[11] or 2-fluoro-1,3-butadiene (**12**) and sulfur dioxide to give sultines *cis*-**20**, *trans*-**20**, **28**, **29** and sulfolenes **26**, **27** (Schemes 5 and 6) were extensively explored by using high level ab initio methodologies. According to our previous experience on similar reactions[6, 33, 18] we carried out optimizations at the MP2/6–31G(d) level of theory. The structures located on the PES were characterized by computing the corresponding Hessian matrices at the MP2/6–31G(d) level. Further intrinsic reaction coordinate (IRC)[34] calculations allowed us to connect the different structures, thus identifying the several pathways on the PESs.[35]

It has been shown recently[36] that special care must be taken to choose a basis set with an appropriate number of polarization functions when studying processes involving several hypervalent molecules, each with some particular atom exhibiting different Lewis structures. Particularly, it should be expected that the polarization functions with contributions to the d symmetry must be much more important in sulfolenes (in which the sulfur atom has a formal electronic configuration $3s^1 3p^3 3d^2$ as in SO_3) than in sultines (in which the sulfur atom has a formal electronic configuration $3s^2 3p^3 3d^1$ as in SO_2). Therefore, basis sets with a number of polarization functions large enough to minimize the unbalanced description of sulfolenes and sultines should be employed.[36] Pople's Gaussian-n (Gn) theories,[37] in which corrections for higher polarization functions are included, are specially suited to that purpose.

Table 4. Selected interatomic distances and bond angles for crystalline *trans*-**9**.[11]

Bond lengths [Å]		Angles [°]	
S1–O2	1.475(2)	O2–S1–O1	102.91(11)
S1–O1	1.6840(19)	O2–S1–C4	106.94(13)
S1–C4	1.796(3)	O1–S1–C4	93.57(11)
O1–C1	1.413(3)	C1–O1–S1	113.98(16)
C1–F1	1.413(3)	F1–C1–O1	106.6(2)
C2–C3	1.351(3)	F1–C1–C2	110.8(2)
C3–C4	1.517(4)	O1–C1–C2	114.6(2)
C3–C5	1.514(4)	C3–C2–C8	119.9(2)
C1–C2	1.511(4)	C3–C2–C1	122.1(2)
		C8–C2–C1	117.9(2)
		C2–C3–C5	121.6(2)
		C2–C3–C4	123.3(2)
		C5–C3–C4	115.1(2)
		C3–C4–S1	110.68(18)

In this work, G2(MP2, SVP) calculations[38] were performed on all the structures located on the PESs. This method is a variant of Pople's G2 theory,[37c] in which the basis set extension correction, ΔE(MP2), is obtained at the MP2 level according to:

$$\Delta E(\text{MP2}) = E[\text{MP2/6-311+G(3df,2p)}] - E[\text{MP2/6-311G(d,p)}] \quad (1)$$

and the QCISD(T) component is computed by using the split-valence plus polarization (SVP) 6–31G(d) basis. The final expression for the G2(MP2, SVP) energy is:[38]

$$E[\text{G2(MP2,SVP)}] = E[\text{QCISD(T)/6-31G(d)}] + \Delta E(\text{MP2}) + E(\text{ZP}E) + \text{HLC} \quad (2)$$

in which E(ZPE) is the zero-point vibrational energy and HLC (higher-level correction) is an empirical parameter to account for remaining basis sets deficiencies.[37] In the present work, the geometry optimizations were performed by correlating only the valence electrons (previous tests have shown that the discrepancies with all-electron-correlated optimizations are negligible, and, given the great number of structures optimized in the present work, the resulting computational saving was considerable) and the zero-point energy corrections were estimated from frequencies computed at the MP2/6–31G(d) level of theory (they were scaled by a factor 0.96 to take into account the known deficiencies at this level).[39] In the present case, the HLC term in Equation (2) has no effect on the energy differences.

In a recent work, Pople and co-workers have shown that a new Gaussian-n theory (G3)[37d] leads to a considerable

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improvement in the case of hypervalent molecules (e.g. SO, SO_2). Therefore, in consequence of our previous findings,[36] we also estimated the energetics in the present work, where hypervalent molecules are involved (sultines, sulfolenes), using the G3 theory, in which the energy is expressed as:

$$E(\mathrm{G3}) = \Delta E(+) + \Delta E(\mathrm{2df,p}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{G3\ large}) + \Delta E(\mathrm{ZPE}) \quad (3)$$

here $\Delta E(+) = E[\mathrm{MP4/6-31+G(d)}] - E[\mathrm{MP4/6-31G(d)}]$, $\Delta E(\mathrm{2df,p}) = E[\mathrm{MP4/6-31G(2df,p)}] - E[\mathrm{MP4/6-31G(d)}]$, $\Delta E(\mathrm{QCI}) = E[\mathrm{QCISD(T)/6-31G(d)}] - E[\mathrm{MP4/6-31G(d)}]$, $\Delta E(\mathrm{G3\ large}) = E[\mathrm{MP2(full)/G3\ large}] - E[\mathrm{MP2/6-31G(2df,p)}] - E[\mathrm{MP2/6-31+G(d)}] + E[\mathrm{MP2/6-31G(d)}]$

A detailed description of the basis set employed can be found in the original reference.[37d] The computationally most demanding step in the G3 composite procedure is the one requiring MP4/6–31G(2df,p) calculations (a typical calculation on the sultines and sulfolenes considered in the present work took more than 20 h CPU time running on a NEC SX-4 supercomputer, employing 1.2 GB RAM, at the Swiss Center for Scientific Computing). As we will show below, a reasonably accurate estimate of ΔE(2df,p) in Equation (3) can be obtained at the much less computationally expensive MP2 level. We will refer to the energy computed by means of such an approach as E(pseudo-G3).

The G3 spin–orbit term was not included because of the lack of data for sultines and sulfolenes and, as mentioned above, the HLC term needs not be considered. The zero-point energy was computed from MP2/6–31G(d) harmonic frequencies scaled by a factor of 0.96.[39] The frozen-core approximation was employed to carry out the MP2/6–31G(d) geometry optimizations.

Solvation effects were estimated by performing single-point MP2/6–31G(d) calculations with the self-consistent reaction field (SCRF) Onsager model, in which the solvent is represented by a dielectric continuum characterized by its dielectric constant.[40] Density functional theory (DFT) with Becke's three-parameter hybrid functional[41] was employed in a series of SCRF optimizations to assess the effects of geometry relaxation on solvation calculations.

In order to estimate the importance of hyperconjugative interactions on the stabilization of structures, natural bond orbital (NBO)[42] analysis was used. In the NBO method, the atomic orbital basis set is orthogonalized and the canonical delocalized Hartree–Fock (HF) molecular orbitals are transformed into localized hybrids (NBOs). The filled NBOs describe covalency effects in molecules while unoccupied NBOs are used to describe noncovalency effects. Among the latter, the most important are the antibonds. Small occupancies of these antibonds correspond, in HF theory, to irreducible departures from the idealized Lewis picture and thus to small noncovalent corrections to the picture of localized covalent bonds. The energy associated with the antibonds can be numerically assessed by deleting these orbitals from the basis set and recalculating the total energy in order to determine the associated variational energy lowering. For a X-Y-Z system, the NBO-deletion procedure allows the energy (E_{XYZ}) to be computed after zeroing the off-diagonal Fock matrix elements connecting the lone pairs n on X with the Y-Z σ* antibonds. The difference $E_{total} - E_{XYZ}$ ($= E_{XYZ}$) is the energy corresponding to the $n \rightarrow \sigma^*$ interactions.[42]

All calculations were carried out by using the Gaussian 94[43] and 98[44] packages of programs.

We were tempted to compute[45] the ^nJ nuclear spin–spin coupling constants in order to complement the structural (conformational) information coming from the corresponding experimental values (see above). However, it is well-known that to describe spin–spin couplings properly one needs:[46] a) nonstandard basis sets that render appropriate electron densities close to the nuclei and b) sophisticated theoretical methods to account for correlation effects (some of the contributions to ^nJ involve triplet excitation operators which may render HF or second-order many-body perturbation theory results meaningless).[47] The Fermi contact term, in particular, is very sensitive to the basis set and electron-correlation effects.[48] The basis-set requirements are often accomplished by adding a number of s functions to the (already extended) standard basis sets used in correlation calculations. The appropriate treatment of the correlation effects calls for the use of multiconfigurational[46] or coupled-cluster[49] methodologies. The computational effort required to perform calculations on ^nJ nuclear spin–spin coupling constants, by using very extended basis sets together with high-level methods, for the systems dealt with in this work is not computationally tractable at present. The computational level affordable (CASSCF/6–31G(d,p) with a reduced active space including four occupied and four virtual orbitals) rendered unreliable coupling constants for sultines and sulfolenes.

Calculation results: The energies calculated for the minima and transition structures located on the potential energy hypersurfaces of the hetero-Diels–Alder additions of (*E*)-**11** and (*Z*)-**11** with SO_2 have been presented earlier,[11] and are summarized in Tables 5 and 6 and Scheme 9 together with the G3 calculated exothermicities and energy barriers for the cheletropic additions of SO_2 to (*E*)-**11** and (*Z*)-**11** (see Supporting Information for details).

Comparisons between geometrical data calculated for *cis*- and *trans*-6-fluoro-3,6-dihydro-1,2-oxathiin-2-oxide (*cis*- and *trans*-**20**) with those obtained by X-ray crystallography for *cis*-**9** and *trans*-**9** are given in Tables 7 and 8.[50] Scheme 14 gives the energies calculated for the minima and transition structures located on the potential energy hypersurfaces of the hetero-Diels–Alder and cheletropic additions of SO_2 to 2-fluorobutadiene (**12**) leading to regioisomeric sultines **28** and **29**, on one hand, and to sulfolene **27**, on the other. Representations of these calculated structures are shown in Figure 3, 4, and 5.

Very good agreement is found between the calculated geometrical parameters of *cis*-**20** and *trans*-**20** with those observed for *cis*-**9** and *trans*-**9**, in particular, the calculations predict stable sofa conformers for *cis*-**20** and *trans*-**20** in agreement with the crystalline structures of *cis*-**9** (Figure 1) and *trans*-**9**.[11]

The MP2 SCRF (solvation) results in Table 6 are single-point calculations on the MP2 in vacuum geometries. The effect of geometry relaxation has been assessed by performing

Table 5. Different contributions[a] to the G2(MP2,SVP), G3; and pseudo-G3 (see text for abbreviations) energies [kcal mol^{-1}] for the located minima and transition states of the hetero-Diels – Alder and the cheletropic addition of SO_2 to (*E*)- and (*Z*)-**11**. The energies corresponding to structures involving the (*Z*) isomer are referred to (*Z*)-**11** + SO_2. The rest are referred to (*E*)-**11** + SO_2.[f]

Structure[g]	ΔE(MP4)	$\Delta\Delta E(+)$	$\Delta\Delta E$(2df,p)[c]	$\Delta\Delta E$(2df,p)[d]	$\Delta\Delta E$(QCI)	$\Delta\Delta E$(G3L)	$\Delta\Delta E$(MP2)	$\Delta\Delta E$(ZPE)[e]	G2(MP2,SVP)	pseudo – G3	G3
cis-**20** (sofa)	– 6.8	– 0.1	– 2.2	– 2.4	– 3.6	4.1	1.5	4.4	– 4.5	– 4.2	– 4.7
+ *endo* (*E*)-**11** + SO_2 → *cis*-**20**	17.8	– 1.6	– 5.6		0.6	2.9	– 3.5	2.4	17.3	16.5	
+ *exo* (*E*)-**11** + SO_2 → *trans*-**20**	17.9	– 1.3	– 5.3		0.9	3.0	– 3.1	2.3	18.0	17.4	
cis-**20**(C)	– 2.3	– 0.6	– 3.2		– 3.5	3.9	– 0.3	4.3	– 1.8	– 1.4	
cis-**20**(B)	– 4.0	0.2	– 2.4		– 3.5	4.2	1.6	4.2	1.6	– 1.2	
+ (So → B)/*cis*-**20**	– 2.9	0.2	– 2.6		– 3.6	4.0	1.3	4.1	– 1.1	– 0.8	
+ (C → B)/*cis*-**20**	1.4	– 0.2	– 2.9		– 3.5	4.1	0.6	4.3	2.7	3.1	
cis-**20**(B)	3.4	0.6	– 3.4		– 3.6	4.0	– 0.5	3.8	3.2	4.8	
trans-**20** (sofa)	– 5.9	– 0.5	– 2.3		– 3.5	4.0	0.9	4.3	– 4.3	– 3.9	
endo (*Z*)-**11** + SO_2 → *trans*-**20**	20.9	– 1.8	– 5.5		0.6	3.3	– 3.2	2.2	20.4	19.6	
exo (*Z*)-**11** + SO_2 → *cis*-**20**	20.9	– 0.9	– 4.8		1.0	3.8	– 1.2	2.1	22.7	22.1	
trans-**20**(C)	– 5.3	– 0.4	– 2.6		– 3.9	3.8	0.3	4.5	– 4.4	– 4.0	
trans-**20**(B)	– 4.8	– 0.6	– 2.5		– 3.5	4.1	0.6	4.3	– 3.4	– 3.0	
+ (C → B)/*trans*-**20**	– 4.0	– 0.9	– 2.4		– 3.7	4.0	0.4	4.0	– 3.3	– 2.9	
+ (So → B)/*trans*-**20**	– 0.4	– 0.7	– 2.3		– 3.7	4.3	0.8	4.0	0.6	1.0	
trans-**20**(B)	– 0.7	– 0.5	– 2.6		– 3.5	3.8	0.3	3.9	0.1	– 1.0	
sulfolene **26**	3.9	0.5	– 11.4	– 11.7	– 2.4	– 1.2	– 10.4	4.6	– 4.3	– 6.0	– 6.7
+ (*E*)-**11** + SO_2 → **26**	25.6	– 1.5	– 9.5		1.5	0.4	– 8.7	2.3	20.7	18.9	
+ (*Z*)-**11** + SO_2 → **26**	27.3	– 1.0	– 9.2		1.6	0.8	– 7.5	2.3	23.8	21.9	

[a] $\Delta E(\text{MP4}) = E[\text{MP4/6-31G(d)}]_{\text{SYSTEM}} - E[\text{MP4/6-31G(d)}]_{\text{REACTANTS}}$; $\Delta\Delta E(\text{A}) = \Delta E(\text{A})_{\text{REACTANTS}}$, in which A stands for the different contributions in Equations (2) and (3). It should be noted that $\Delta E[\text{QCISD(T)/6-31G(d)}] = \Delta\Delta E(\text{QCI}) + \Delta E(\text{MP4})$ (this term is needed to compute ΔE[G2(MP2, SVP)] values from Equation (2). [b] Optimizations were carried out at the MP2/6 – 31G(d) level of theory. [c] Contribution estimated at the MP2 level of theory. [d] Contribution estimated at the MP4 level of theory. [e]MP2/6 – 31G(d) frequencies scaled by 0.96 (see Ref. [39]). [f] Table S1 of the Supporting Information contains the corresponding absolute energies. [g] See Scheme 9.

Table 6. In a vacuum and solvation[a] (SCRF) MP2/6 – 31G(d) and B3LYP/6 – 31G(d) relative energies (kcal mol^{-1})[b] of products and transition structures for the Diels – Alder and cheletropic additions of (*E*)-**11** and (*Z*)-**11** with SO_2 (see Scheme 9).[c]

Structure	ΔE(MP2)	ΔE(MP2/SCRF)	ΔE_{solv}(MP2)	ΔE(B3LYP)	ΔE(B3LYP/SCRF)	ΔE_{solv}(B3LYP)
cis-**20** (sofa)	– 8.2	– 9.7	– 1.5	– 10.3	– 11.9	– 1.6
+ *endo* (*E*)-**11** + SO_2 → *cis*-**20**	15.4	14.8	– 0.6			
+ *exo* (*E*)-**11** + SO_2 → *trans*-**20**	15.4	15.1	– 0.3			
cis-**20**(C)	– 3.9	– 5.7	– 1.8	– 6.5	– 8.6	– 2.1
cis-**20**(B)	– 5.4	– 7.7	– 2.3	– 7.9	– 9.8	– 1.9
+ (So → B)/*cis*-**20**	– 4.1	– 5.8	– 1.7			
+ (C → B)/*cis*-**20**	– 0.2	– 1.6	– 1.4			
cis-**20**(B +)	2.3	– 0.2	– 2.5			
trans-**20** (sofa)	– 7.4	– 9.2	– 1.8	– 10.0	– 11.7	– 1.7
+ *endo* (*Z*)-**11** + SO_2 → *trans*-**20**	18.7	18.8	0.1			
+ *exo* (*Z*)-**11** + SO_2 → *cis*-**20**	18.7	17.1	– 1.6			
trans-**20**(C)	– 6.8	– 7.2	– 0.4	– 9.0	– 9.6	– 0.6
trans-**20**(B)	– 6.4	– 6.6	– 0.2	– 8.3	– 8.4	– 0.1
+ (C → B)/*trans*-**20**	– 5.6	– 5.8	– 0.2			
+ (So → B)/*trans*-**20**	– 1.5	– 3.0	– 1.5			
trans-**20**(B +)	– 2.1	– 3.9	– 1.8			
sulfolene **26**	0.0	– 1.8	– 1.8			
+ (*E*)-**11** + SO_2 → **26**	21.9	20.6	– 1.3			
+ (*Z*)-**11** + SO_2 → **26**	23.7	23.1	– 0.6			

[a] A relative permittivity of 13.3 to simulate the experimental conditions was used. [b] ΔE(MP2) and ΔE(B3LYP) values correspond to vacuum-optimized structures, and ΔE(B3LYP/SCRF) values correspond to SCRF fully optimized structures. ΔE(MP2/SCRF) values correspond to single-point MP2 SCRF/6 – 31G(d)//MP2 (in a vacuum)/6 – 31G(d) calculations. [c] Table S2 of the Supporting Information collects the corresponding absolute energies.

DFT(B3LYP)/6 – 31G(d) in a vacuum and SCRF calculations on all the minimum structures allowing for a full geometry optimization. As a general result, the DFT(B3LYP) method consistently renders more stable structures than MP2 (by about 2 – 3 kcal mol^{-1}) in all cases. Furthermore, solvent effects obtained at the MP2 (by using vacuum-optimized geometries) and DFT (by using both vacuum-optimized and SCRF fully optimized geometries) levels are quite similar—they differ in less than 0.4 kcal mol^{-1} in the worst case: see ΔE_{SOLV}(MP2) and ΔE_{SOLV}(B3LYP) in Table 6. Therefore, we can conclude that the estimates of the electrostatic solvent effects carried out at the MP2 SCRF/6 – 31G(d)//MP2 (in a vacuum)/6 – 31G(d) level (ΔE_{SOLV}(MP2) in Table 6) are plausible.

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A first comment on the theoretical results collected in Table 5 is that the estimate of the G3 ΔE(2df,p) term in Equation (3) at the MP2 level is really good. Indeed, Table 5 shows that the $\Delta\Delta E$(2df,p) contribution to the ΔE(G3) relative energies computed at the MP2 level for sultine *cis*-**20**, g-So_{ax} and sulfolene **26** (−2.2 and −11.4 kcal mol^{-1}, respectively) differ only slightly from those computed at the MP4 level following G3 (−2.4 and −11.7 kcal mol^{-1}, respectively). However, the two CPU times differ by a factor near to 100 (on a NEC SX-4 supercomputer). Therefore, we conclude that the pseudo-G3 values in Table 5, computed with the MP2 estimate of $\Delta\Delta E$(2df,p), seem to be rather good estimates of the corresponding real G3 values, obtained at a reasonable computational cost.

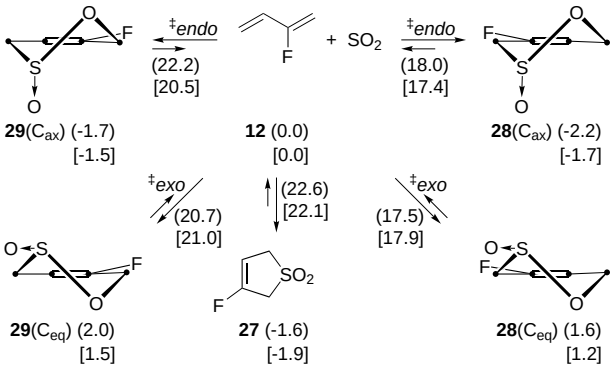
On the other hand, it is very encouraging to observe in Table 5 that the G2(MP2,SVP) theory used in this and previous[6, 18, 34] work provides, in general, energetics in quite good agreement with the G3 (pseudo-G3) theory, thus reinforcing the reliability of the present and previous results.[6, 18, 34] There are, however, some cases in which the differences become appreciable (see, for example, the energies for sulfolene **26** of transition states the cheletropic addition of (*E*)- and (*Z*)-1-fluorobutadiene). The sophisticated correction for larger basis set effects (diffuse and polarization functions) through the ΔE(G3 large) term[37d] [Eqs. (2) and (3)] should lead, according to our previous findings,[36] to more reliable results, especially in the case of the cheletropic reaction as mentioned in the Theoretical Methods section.

Table 7. Selected geometrical data for *cis*-fluorosultine *cis*-**9**; the atom numbering is given in Figure 1 (X-ray). The corresponding MP2/6–31G(d) computed values for the most stable sofa conformer of *cis*-**20** are given in square brackets.

Bond lengths [Å]					
C1–C2	1.490(10)	[1.49554]	S1–O1	1.630(5)	[1.71716]
C2–C3	1.331(10)	[1.33864]	S1–O2	1.482(5)	[1.48363]
C3–C4	1.506(10)	[1.4990]	O1–C1	1.418(9)	[1.41249]
C4–S1	1.785(7)	[1.82077]	C1–F1	1.399(8)	[1.38775]
Bond angles [°]					
C1-C2-C3	122.5(6)	[123.827]	O1-S1-O2	108.8(3)	[112.228]
C2-C3-C4	123.6(7)	[122.776]	S1-O1-C1	120.0(4)	[118.750]
C3-C4-S1	115.1(5)	[110.435]	O1-C1-F1	106.4(6)	[109.789]
C4-S1-O1	96.9(3)	[92.537]	F1-C1-C2	110.4(6)	[108.311]
C4-S1-O2	105.2(3)	[106.540]	O1-C1-C2	116.3(6)	[115.342]
Torsional angles [°]					
C1-C2-C3-C4	10.4(4)	[3.057]	S1-C4-C3-C2	21.2(3)	[33.116]
O1-C1-C2-C3	2.3(4)	[3.610]	F1-C1-C2-C3	−118.3(3)	[−127.067]

Table 8. Selected geometrical data for fluorosultine *trans*-**9** (atom numbering given in [11]). Corresponding MP2/6–31G(d) computed values for the most stable sofa conformer of *trans*-**20** in square brackets.

Bond lengths [Å]					
C1-C2	1.511(4)	[1.49875]	S1-O1	1.6840(19)	[1.73761]
C2-C3	1.351(3)	[1.34153]	S1-O2	1.475(2)	[1.48173]
C3-C4	1.517(4)	[1.50250]	O1-C1	1.413(2)	[1.39927]
C4-S1	1.796(3)	[1.80908]	C1-F1	1.414(3)	[1.39718]
Bond angles [°]					
C1-C2-C3	122.1(2)	[123.478]	O1-S1-O2	102.9(11)	[105.189]
C2-C3-C4	123.3(2)	[123.280]	S1-O1-C1	113.98(16)	[113.840]
C3-C4-S1	110.68(18)	[108.565]	O1-C1-F1	106.6(2)	[110.306]
C4-S1-O1	93.57(11)	[91.095]	F1-C1-C2	110.8(2)	[107.836]
C4-S1-O2	106.94(13)	[107.802]	O1-C1-C2	114.6(2)	[113.841]
Torsional angles [°]					
C1-C2-C3-C4	10.4(4)	[2.975]	S1-C4-C3-C2	21.2(3)	[31.480]
O1-C1-C2-C3	2.3	[3.880]	F1-C1-C2-C3	−118.3(3)	[−118.856]



Scheme 14. In a vacuum and in solution (permittivity of 13.3 to simulate experimental conditions) relative energies in kcal mol^{-1} for the reactions of 2-fluorobuta-1,3-diene (**12**) with SO_2. In parentheses: vacuum-optimized structures; in square brackets: single-point MP2SCRF/6–31G(d)//MP2 (in a vacuum)/6–31G(d) calculations. See Supporting Information for the corresponding absolute energies.

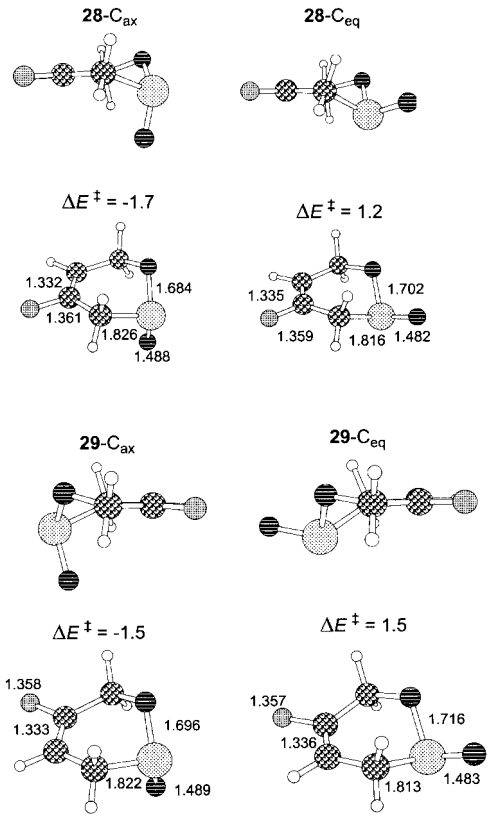


Figure 3. Calculated structures for sultines **28** and **29**. Energies (kcal mol^{-1}) relative to 2-fluorobuta-1,3-diene + SO_2, single-point MP2 SCRF/6–31G(d)//MP2 (in vacuum)/6–31G(d), see also Scheme 14.

Discussion

In agreement with our experimental results for (*E*)-**11**, (*Z*)-**11**, (*E*)-**13**, (*Z*)-**13**, (*E*)-**8**, and (*Z*)-**8**, which showed lower hetero-Diels–Alder reactivity toward SO_2 for (*Z*)-1-fluorobutadienes than for the corresponding (*E*)-isomers, our calculations predicted that (*E*)-1-fluorobutadiene ((*E*)-**11**) is more

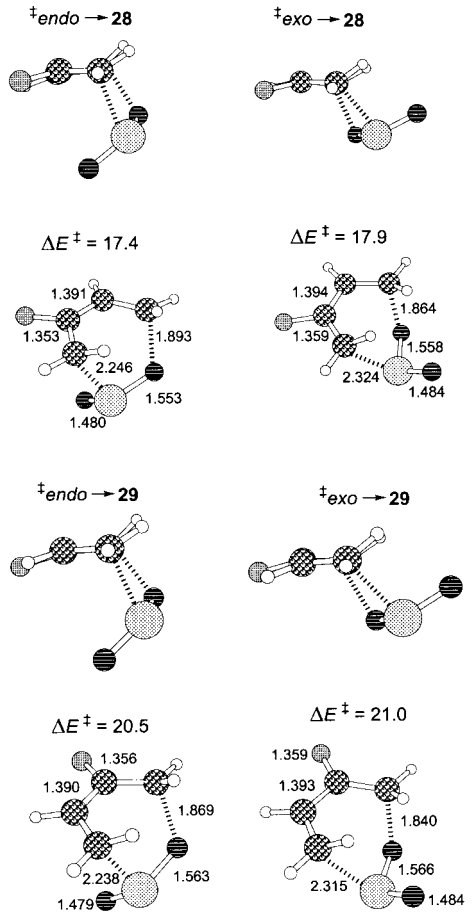


Figure 4. Calculated transition structures for the hetero-Diels–Alder addition of 2-fluorobutadiene + SO_2 giving 4-fluorosultine (**28**) or 5-fluorosultine (**29**). Energies in kcal mol^{-1}, see also Scheme 14.

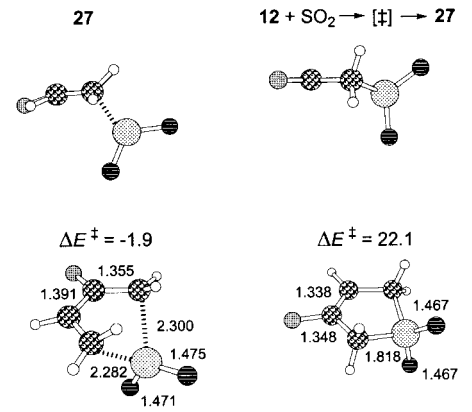


Figure 5. Calculated structure of 3-fluorosulfolene (**27**) and of the transition structure of the cheletropic addition **12** + $SO_2 \rightarrow$ **27**. Energies in kcal mol^{-1}, see also Scheme 14.

reactive than its (*Z*)-isomer in the absence of protic acid catalyst. The calculations must be compared with the experimental data obtained for the uncatalyzed reactions of (*E*)-**8** and (*Z*)-**8** (Scheme 2). As established experimentally for these hetero-Diels–Alder additions, the *endo* mode of cycloaddition is predicted to be favored for (*E*)-**11** + SO_2 and (*Z*)-**11** + SO_2. In the light of these predictions, the sultine observed by NMR for the reaction SO_2 + (*E*)-**11** in the presence of CF_3COOH might well be *cis*-**20**. Similarly, the major sultines formed by hetero-Diels–Alder additions of (*E*)-**13** and (*Z*)-**13** might well be *cis*-**30** and *trans*-**30**, respectively, both arising from favored *endo* mode cycloadditions.

Our calculations for 2-fluorobuta-1,3-diene (**12**) (Scheme 14) predict an energy barrier ($\Delta E = 17.4$ kcal mol^{-1}) for the formation of sultine **28** that is similar to that calculated ($\Delta E = 16.5$ kcal mol^{-1}) for the hetero-Diels–Alder addition (*E*)-**11** + $SO_2 \rightarrow$ *cis*-**20**. However the energy of reaction **12** + $SO_2 \rightarrow$ **28** ($\Delta E = -1.7$ kcal mol^{-1}) appears too low for that equilibrium to exist under our experimental conditions (−100 to −10 °C). The same prediction is made concerning the cheletropic addition **12** + $SO_2 \rightarrow$ **27** for which $\Delta E = -1.9$ kcal mol^{-1} is calculated, thus explaining that no product of addition is observed for SO_2 to **12** (compare with the exothermicities calculated for the reactions of (*E*)-**11** + SO_2, Scheme 9). The prediction that ΔE(**12** + $SO_2 \rightarrow$ **27**) is similar to ΔE(**12** + $SO_2 \rightarrow$ **28**) is unexpected. We must admit that it could be due to imperfections of our calculations method.

Compared with isoprene or (*E*)-piperylene, (*E*)-1-chloro- and (*E*)-1-bromobutadiene are much less reactive toward SO_2, both for the hetero-Diels–Alder and cheletropic additions.[6] In fact, no trace of sultines could be detected for the reactions of 1-chloro and 1-bromobutadiene with SO_2. Only slow and incomplete formation of the corresponding chloro- and bromosulfolenes was observed.[6] In contrast, none of our 1-fluoro-1,3-dienes underwent the cheletropic addition, although our calculations predicted similar heats of reaction for the hetero-Diels–Alder and for the cheletropic additions of SO_2 to (*E*)-**11** to give fluorosultine *cis*-**20** and fluorosulfolene **26**, respectively (Table 6). The calculations predict, however, that the energy barrier for the hetero-Diels–Alder addition (*E*)-**11** + $SO_2 \rightarrow$ *cis*-**20** is significantly lower than that for the cheletropic addition (*E*)-**11** + $SO_2 \rightarrow$ **26**, and that the latter is higher that the energy barrier of the cheletropic addition of SO_2 to (*E*)-1-chlorobutadiene; this is consistent with our experiments.

With the tricyclic fluorosultines *cis*-**9** and *trans*-**9** we have demonstrated that the latter isomer is more stable in solution than the former. The calculations do not predict any significant stability difference between *cis*-**20** and *trans*-**20** (Table 5). It is thus possible that the greater stability of *trans*-**9** compared with *cis*-**9** arises from the substitution of the fluorosultines at their C4,5 olefinic centers, or/and from differential solvation effects, or/and from differences in the flexibility (entropy factor) of these sultines. Similar relative stabilities are calculated for the chair (*trans*-**20**(C)), the boat (*trans*-**20**(B)) and sofa (*trans*-**20**(So)) conformers of 6-fluorosultine *trans*-**20** (see Scheme 15). This confers a greater flexibility on *trans*-**20** relative to *cis*-**20** and thus could make the former sultine more stable than the latter in solution.

Except for 6-methoxy-3,6-dihydro-1,2-oxathiin-2-oxide (**42**) and 2-methoxy-2,5-dihydrothiophene-1,1-dioxide (**43**), which were calculated to have similar relative stabilities,[6] all the sulfolenes are generally more stable than their isomeric sultines by about 10 kcal mol^{-1}.[5a, 8] In the case of the chlorinated derivatives, 2-chloro-2,5-dihydrothiophene-1,1-dioxide (**44**) is calculated to be −5.6 kcal mol^{-1} more stable than *cis*-6-chloro-3,6-dihydro-1,2-oxathiin-2-oxide (*cis*-**45**) (Table 9). As for *cis*-**20**, it is calculated that the latter adopts

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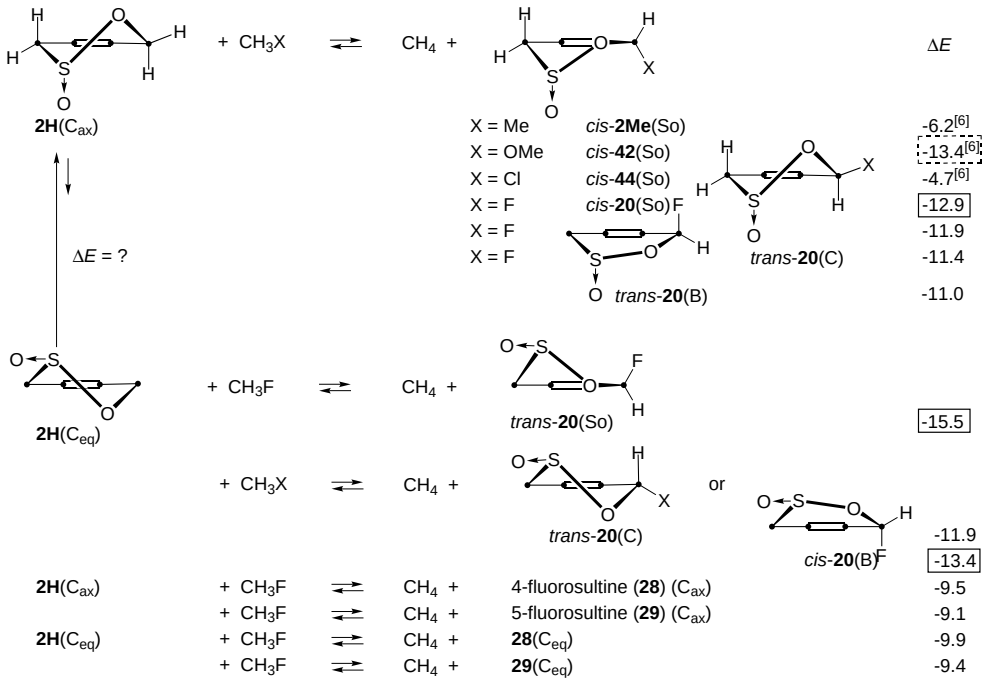
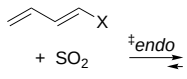
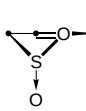


Scheme 15. Evaluated (MP2/6–31G(d)) energies (ΔE in kcal mol^{-1}) of isodesmic reactions involving sultines. Values in boxes are the largest enthalpic anomeric effects.

Table 9. Comparison of the G2(MP2,SVP) calculated heat of reaction (ΔH_r) and energy barriers ($\Delta E^{\neq}$) for the hetero-Diels–Alder and cheletropic additions of SO_2 to (*E*)-1-X-butadiene (X = F, Cl) [kcal mol^{-1}].[a,b]

Reactants	Products	X = F	X = Cl[b]
		*cis*-**20**[c]	*cis*-**45**[c]
		$\Delta H_r = -4.0\ (-1.5)$	$-4.4\ (-0.8)$
		$\Delta E^{\neq} = 17.3\ (-0.6)$[d]	23.6 (0.1)[d]
		**26**	**44**
		$\Delta H_r = -3.8\ (-1.8)$	$-10.0\ (-2.6)$
		$\Delta E^{\neq} = 20.7\ (-1.3)$	19.6 (0.5)

[a] MP2 SCRF/6–31G(d) estimates of the electrostatic solvent effect by using a relative permittivity of 13.3 to simulate the experimental conditions in parentheses. [b] Taken from Ref. [6]. [c] Both sultines *cis*-**20** and *cis*-6-chloro-3,6-dihydro-1,2-oxathiin-2-oxide (*cis*-**45**) prefer sofa So_{ax} conformations (ring oxygen atom in the four carbon atom plane, pseudo-axial S=O). [d] Lowest barriers calculated for the *endo* mode of cycloaddition in both cases.

a sofa conformation (ring oxygen in the carbon plane, *gauche* O–S and Cl–C bonds, pseudo-axial positions of the S=O moiety).[6] Thus, our calculations, which predict similar stabilities for 6-fluorosultine *cis*-**20** and 2-fluorosulfolene **26**, suggest the intervention of special electronic interactions in sultines, such as the *gem*-fluoro sulfinyloxy substitution effect (enthalpic anomeric effect), as also suggested by our experiments (Scheme 10). In order to evaluate such a possibility, we have estimated the heats of the isodesmic reactions, shown in Scheme 15, for the three conformers located on the potential energy hypersurfaces of *cis*-**20** and *trans*-**20**, and compared them with those calculated for other isodesmic reactions involving 4-fluoro (**28**), 5-fluoro (**29**), *cis*-6-methoxy- (*cis*-**42**), *cis*-6-chlorosultine (*cis*-**44**), and *cis*-6-methyl-3,6-dihydro-1,2-oxathiin-2-oxide. The calculations suggest the existence of enthalpic anomeric effects[51] that stabilize the 6-fluorosultines and 6-methoxysultines relative to the 4-fluoro and 5-fluorosultines and to the 6-methyl and 6-chlorosultines. This effect is the largest for *trans*-**20**, which takes up the sofa conformation (Scheme 7), then in the boat and in the sofa conformer of *cis*-**20**. The origin of these effects has been researched by evaluating the total hyperconjugative contributions arising from $n \rightarrow \sigma^*$ interactions[51] in the three conformers located on the potential energy hypersurface of *cis*-**20** and *trans*-**20** (Scheme 9, Table 10). Particularly significant are the contributions due to the $n(O1) \rightarrow \sigma^*(C6,F)$ electron transfer, which is commonly associated with the conformational anomeric effect.[52] It is found to be more important in the sofa and boat conformers, which authorize a better alignment between the n(O1) electron pair and the empty $\sigma^*(C6,F)$ orbitals than for the pseudo-chair conformations of *cis*-**20** and *trans*-**20** (Figure 6).

The data in Table 10 suggest that the $n(O1) \rightarrow \sigma^*(C6,F)$ interaction is not the only hyperconjugative interaction affecting the relative stability of the various conformers of the 6-fluorosultines.

Sultines *cis*-**20**(C) and *trans*-**20**(So) with pseudo-equatorial S=O moieties are less stabilized by the $n(O1) \rightarrow \sigma^*(S2,O2')$ interaction than the other conformers with a pseudo-axial S=O group. This is also calculated for the mother sultine (3,6-dihydro-1,2-oxathiin-2-oxide 2H) and alkyl substituted derivatives.[6] For sofa and pseudo-chair conformers, the calculations show that the $n(S2) \rightarrow \sigma^*(O1,C6)$ interaction is less stabilizing in sultines with pseudo-equatorial S=O than in conformers with pseudo-axial S=O moieties. Conformers with pseudo-equatorial S=O have their n(S2) electron pair at the sulfur center *gauche* with respect to the $\sigma(O1,C6)$ bond whereas in conformers with pseudo-axial S=O it is antiperi-

Table 10. Different hyperconjugative contributions (ΔE, kcal mol^{-1}) calculated at the MP2/6–31G(d) level of theory for the electron transfers from lone pairs (n) to empty σ* and π* orbitals in the conformers of *cis*-**20** and *trans*-**20**.[b]

Structure[a]	relative energy[c]	ΔE[d]	n(O1) → σ*(C6,F)	n(O1) → σ*(S2,O2′), π*(S=O)	n(O2′) → σ*(S′2,O1)	n(O2′) → σ*(S2,C3)
cis-**20**(So)	–4.2	–12.9	–15.9	–10.3	–1.5	–14.1
cis-**20**(C)	–1.4	–11.9	–4.9	–9.0[e]	–2.2	–12.7
cis-**20**(B)	–1.2	–13.4	–13.1	–13.8	–1.4	–13.0
trans-**20**(So)	–3.9	–15.5[f]	–16.7[f]	–8.2[e]	–2.1	–13.0
trans-**20**(C)	–4.0	–11.4	–4.9	–10.6	–1.8	–12.8
trans-**20**(B)	–3.0	–11.0	–16.1	–13.2	–1.7	–13.9

n(S2) → σ*(O1,C6)	n(F) → σ*(C6,O1)	n(F) → σ*(C6,C5)	ΔE total
–4.3	–12.8	–5.7	–64.6
–0.9[d]	–12.1	–6.2	–48.0
–4.0	–12.4	–5.9	–63.6
–1.0[d]	–12.1	–5.5	–58.6
–4.0	–12.2	–6.1	–52.4
–4.1	–11.7	–5.5	–66.2

[a] See Schemes 9 and 15 (So = sofa with ring oxygen atom in the four-carbon plane, C = pseudo-chair, B = boat). [b] See text for the method. [c] See Table 5 (pseudo-G3 values). [d] Estimated energies of isodesmic reactions. [e] Conformers with pseudo-equatorial S=O. [f] The largest conformational and enthalpic anomeric effect is found for the sofa conformer *trans*-**20**(So) and corresponds to the most stable sultine *trans*-**9** and its conformation in the crystal.

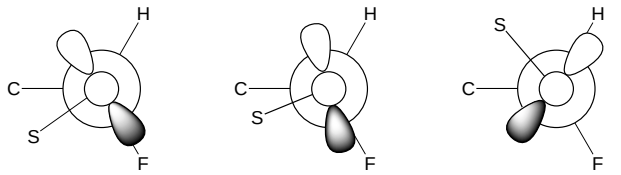


Figure 6. Orientation of the n(O) 2p orbital of the ring oxygen atom with the σ(C–F) bond in the various conformers of 6-fluoro-3,6-dihydro-1,2-oxathiine-2-oxides (6-fluorosultines).

planar with respect to σ(O1,C6). We must bear in mind that this analysis (Table 10) does not consider possible differential effects due to electrostatic repulsions between the polar groups of the fluorosultines, and steric factors.

Comparison of the crystalline structures of fluorosultines *cis*-**9** and *trans*-**9**,[11] which both adopt sofa conformations, had suggested that the ring oxygen in *cis*-**20**(So) must share its n electron lone-pair with both the C–F and S=O moieties, whereas in *trans*-**20**(So) the ring oxygen atom has all its n electrons available for the hyperconjugative n(O1) → σ*(C6,F) interaction. Accordingly, a larger enthalpic anomeric effect is expected for the latter 6-fluorosultine in agreement with the calculations on the isodesmic reaction in Scheme 15 and the stabilizing n(O1) → σ*(C6,F) contributions in Table 10 that predict the largest effect for *trans*-**20**(So).

Calculations show only two minima on the energy hypersurfaces of both 4-fluorosultine **28** and 5-fluorosultine **29**, which correspond to C_{ax} and C_{eq} pseudo-chair conformations, as in the case of the parent sultine.[6] As expected for stereoelectronic reasons (n(O1) → σ*(S2,O2′), π*(SO)), the C_{ax} conformers with pseudo-axial S=O moieties are more stable than C_{eq} conformers with pseudo-equatorial S=O groups by about 3 kcal mol^{-1} (Scheme 14). The finding of sofa conformations in the crystalline fluorosultines *cis*-**9** and *trans*-**9** is corroborated by our calculations for *cis*-**20** and *trans*-**20**. It suggests that 6-substitution is capable of deforming the pseudo-chair conformers into the corresponding sofa conformers. Calculations on 6-methyl, 6-chloro-, and 6-methoxysultines[6] suggest the same phenomenon in these sultines. In the case of the *cis*-sultines, steric repulsion (*gauche* interactions) between the pseudo-axial substituent at C6 and the pseudo-axial S=O group in the pseudo-chair conformers might be responsible for their deformation into sofa conformers.[53, 54]

Conclusion

Unlike 1-chloro- and 1-bromobuta-1,3-diene, 1-fluoro-1,3-dienes can undergo hetero-Diels–Alder addition with sulfur dioxide to give the corresponding 6-fluoro-3,6-dihydro-1,2-oxathiin-2-oxides (6-fluorosultines). (*E*)-1-fluoro-1,3-dienes are more reactive than their (*Z*)-isomers and tend to undergo the *endo* (Alder rule) mode of cycloaddition, as proven for the reaction of SO_2 with (*Z*)- and (*E*)-1-(fluoromethylidene)-2-methylidene-1,2,3,4-tetrahydronaphthalene (*E*)-**8**, (*Z*)-**8**) that provides crystalline *cis*-2-fluoro-3,4-oxathiabenzobicyclo[4.4.0]dec-1(6)-9-diene-4-oxide (*cis*-**9**) and its *trans*-isomer (*trans*-**9**),[11] respectively, and as predicted by high-level quantum calculations. Unlike 1-chloro-, 1-bromo- and other 1-substituted buta-1,3-dienes (Scheme 1), 1-fluoro-1,3-dienes (**8**, **11**, **13**) do not undergo cheletropic additions to give the corresponding 2-fluoro-2,5-dihydrothiophen-1,1-dioxides (2-fluorosulfolenes). The greater hetero-Diels–Alder reactivity of 1-fluoro-1,3-dienes relative to their 1-chloro and 1-bromo analogues might be due to the higher exothermicity for the formation of the corresponding 6-fluorosultines than for 6-chloro or 6-bromosultines and to the barriers involved in the last two. Experiments—equilibrium constant for the hetero-Diels–Alder addition of (*E*)-1-(fluoromethylidene)-2-methylidenecyclohexane (*E*)-**13** + SO_2 → *cis*-2-fluoro-3,4-oxathiabicyclo[4.4.0]dec-1(6)-ene-4-oxide (*cis*-**30**) compared with that for 1,2-dimethylidenecyclohexane (**35**) + SO_2 → 3,4-oxathiabicyclo[4.4.0]dec-1(6)-ene-4-oxide (**36**)—bond lengths and bond angles in crystalline fluorosultines *cis*-**9** and *trans*-**9**, and high-level quantum calculations confirm the existence of stabilizing enthalpic anomeric (*gem*-disubstitution) effects, which can be interpreted in terms of n(O1) → σ*(C6,F) hyperconjugative interaction. This effect is strongest in the sofa conformer (*gauche* arrangement of σ(O1,S2) and σ(C6,F) bonds, ring oxygen in the plane of the four carbon atoms of

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the sultine moiety, pseudo-axial S=O bond) *cis*-**20**(So), the most stable conformer calculated for *cis*-6-fluorosultine and found in the crystalline state of *cis*-**9**. Similarly the sofa conformer *trans*-**20**(So), calculated for *trans*-6-fluorosultine and corresponding to the conformation observed in the crystalline state of *trans*-**9**, experiences the strongest $n(O1) \rightarrow \sigma^*(C6,F)$ hyperconjuative interaction. The calculations also suggest that $n(O1) \rightarrow \sigma^*(S2,O2')$, $\pi^*(S{=}O)$, and $n(S2) \rightarrow \sigma^*(O1,C6)$ interactions intervene and affect the relative stability of the conformers (sofa, boat, pseudo-chair) found for the 6-fluorosultines *cis*-**20** and *trans*-**20**.

Experimental Section

The ^{1}H NMR were recorded on Bruker DPX 400 FT, ARX 400 FT, and DRX 400 FT spectrometers. The signals of residual solvents were used as references ($\delta(CHCl_3) = 7.27$, $\delta(MeOH) = 3.35$, $\delta(CH_2Cl_2) = 5.35$, $\delta(C_6H_6) = 7.20$). When necessary, the ^{1}H signal assignments were confirmed by COSY-45 spectra. The ^{13}C NMR spectra were recorded on Bruker DPX 400 FT, ARX 400 FT, and DRX 400 FT spectrometers at 100.6 MHz. The signals of residual solvents were used as references ($\delta(CHCl_3) = 77.0$, $\delta(MeOH) = 49.0$, $\delta(CH_2Cl_2) = 53.8$, $\delta(C_6H_6) = 128.5$). When necessary, the ^{13}C signal assignments were confirmed by XHCORR or HMQC spectra. The ^{19}F NMR spectra were recorded on a Bruker ARX-400 spectrometer at 376.5 MHz. $CFCl_3$ was used as internal reference.

NMR sample preparation and thermochemical parameters: CD_2Cl_2 and toluene were distilled over anhydrous CaH_2; CF_3COOH and MeCN over P_2O_5. Sulfur dioxide was filtered through a column of alkaline aluminum oxide 90 (activity I, Merck) before use. Diene (0.05–0.3 mmol), toluene or acetonitrile (internal reference, 5–10 mg), and CD_2Cl_2 (0.2–0.3 g) were mixed in a weighed, dry, 5 mm NMR Pyrex tube under Ar atmosphere at 20 °C. If viscous solutions were obtained at very low temperatures, mixtures of CD_2Cl_2 and $CFCl_3$ were used instead of pure CD_2Cl_2. The solution was degassed by several freeze–thaw cycles at 10^{-2} mbar. Degassed SO_2 (0.1–0.4 mL) and CF_3COOH (stoichiometric amount, if any) were transferred to the above mixture on the vacuum line, and the NMR tube was sealed under vacuum at −196 °C (liquid nitrogen). The NMR tube was then warmed to −80 °C (acetone/dry ice bath) and transferred into the spectrometer probe, which had been pre-cooled to the desired temperature for the analyses. Other tubes were left in thermostated EtOH baths at various temperatures until equilibria were reached, then cooled to −80 °C and transferred to the spectrometer. When the equilibrium constant measurements were terminated, the NMR tube was allowed to reach 25 °C and was weighed with the piece of tube left over after sealing; this allowed verification of the exact amount of SO_2 introduced in the diene solution.

1:1 Mixture of (*E*)- and (*Z*)-7-(2-Fluoroethenyl)dibenzobicyclo[2.2.2]octa-2,5-diene (15): A freshly prepared solution of *i*Pr_2NLi (from *i*Pr_2NH, 5.7 mL) in anhydrous THF (30 mL) was added slowly to a stirred suspension of (fluoromethyl)triphenylphosphonium tetrafluoroborate (13.8 g, 36 mmol) in anhydrous THF (250 mL) cooled to −78 °C under N_2 atmosphere. The mixture was stirred at 0 °C for 15 min and then cooled to −78 °C. A solution of dibenzobicyclo[2.2.2]octa-2,5-diene-7-carbaldehyde (**14**; 8.5 g, 36 mmol)[14] in anhydrous THF (15 mL) was added under stirring, and the mixture was allowed to warm up to 25 °C. After the mixture had been stirred at 25 °C for 12 h, the precipitate was filtered off, and the filtrate concentrated in vacuo. Flash chromatography on silica gel (EtOAc/light ether petroleum 9:1) afforded a 1:1 mixture of (*E*)- and (*Z*)-**15** as a pale yellow oil. Yield: 5 g (50 %); IR (film): $\tilde{\nu} = 3070$, 2945, 1670, 1470, 1095, 995, 920, 760 cm^{-1}; UV (MeCN): λ_{max} (ε) = 271 (3700), 264 (3500), 250 (7300), 223 nm (7000 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{18}H_{15}F$ (250.32): H 6.04, C 86.32; found: H 5.89, C 86.23.

Data for (*E*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.16$–6.96 (m, 8H), 6.09 (ddd, ^2J(H,F) = 85.1, ^3J(H,H) = 11.1, ^4J(H,H) = 0.4 Hz, HCF), 4.80 (ddd, ^3J(H,F) = 18.3, ^3J(H,H) = 11.1, 10.0 Hz, 1H), 3.91 (dd, ^3J(H,H) = 2.9, 2.5 Hz, H4), 3.52 (d, ^3J(H,H) = 2.5 Hz, H1), 2.10 (tddd, ^3J(H7,H_{syn}-8) = 10.0, ^3J(H7,H-C(ethylidene)) = 10.0, ^3J(H7,H_{anti}-8) = 4.5, ^3J(H1,H7) = 2.5, ^4J(H7,HCF(ethenyl) = 0.4 Hz, H7), 1.73 (ddd, ^2J = 12.5, ^3J = 10.0, 2.9 Hz, H_{syn}-8), 1.07 (ddd, ^2J = 12.5, ^3J = 4.5, 2.5 Hz, H_{anti}-8); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 148.2$ (dd, ^1J(C,H) = 198, ^1J(C,F) = 255 Hz, FCH), 145–120 (12 C_{arom}), 115.8 (d, ^1J(C,H) = 150 Hz, HC-C7), 50.5 (d, ^1J(C,H) = 141 Hz, C1), 44.1 (d, ^1J(C,H) = 137 Hz, C4), 35.2 (d, ^1J(C,H) = 132 Hz, C7), 35.1 (t, ^1J(C,H) = 132 Hz, C8); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -130.6$ (dd, ^2J(H,F) = 85.1, ^3J(H,F) = 18.3 Hz).

Data for (*Z*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.16$–6.96 (m, 8H), 5.96 (ddd, ^2J(H,F) = 85.6, ^3J(H,H) = 4.7, ^4J(H,H) = 1.0 Hz, HCF), 4.01 (ddd, ^3J(H,F) = 42.8, ^3J(H,H) = 10.0, 4.7 Hz, HC-C7), 3.99 (d, ^3J = 2.5 Hz, H1), 3.89 (dd, ^3J = 2.9, 2.5 Hz, H4), 3.17 (tddd, ^3J = 10.0, 4.5, 2.5, ^4J = 1.0 Hz, H7), 1.89 (ddd, ^2J = 12.5, ^3J = 10.0, 2.9 Hz, H_{syn}-8), 1.13 (ddd, ^2J = 12.5, ^3J = 4.5, 2.5 Hz, H_{anti}-8); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 146.8$ (dd, ^1J(C,H) = 203 Hz, ^1J(C,F) = 253 Hz, FCH), 145–120 (12 C_{arom}), 115.3 (d, ^1J(C,H) = 169 Hz, HC-C7), 49.5 (d, ^1J(C,H) = 140 Hz, C1), 44.1 (d, ^1J(C,H) = 137 Hz, C4), 35.1 (t, ^1J(C,H) = 132 Hz, C8), 32.3 (d, ^1J(C,H) = 132 Hz, C7); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -130.6$ (dd, ^2J(H,F) = 85.6, ^3J(H,F) = 42.8 Hz); CI-MS (NH_3): *m*/*z* (%): 268 (100) [M^++18], 252 (6) [M^++1], 178 (100), 152 (8), 84 (11).

1:1 Mixture of (*E*)- and (*Z*)-1-Fluorobutadiene ((*E*)-11, (*Z*)-11): Compound **15** (400 mg, 1.6 mmol) was placed in a 10 mL round-bottom flask connected through a short Vigreux column to the vacuum line. Heating to 350 °C (heating mantle) under 10^{-2} Torr generated a 1:1 mixture of (*E*)-**11** and (*Z*)-**11** as a colorless, volatile oil, which was collected in a 5 mm NMR tube connected to the vacuum line and immersed in liquid N_2. Yield: 30 mg (25 %).

Data for (*E*)-**11**: ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 6.89$ (ddd, ^2J(H,F) = 83.1, ^3J(H,H) = 11.0, ^4J(H,H) = 0.6 Hz, H1), 6.24 (dddd, ^3J = 16.8, 11.4, 11.0, ^4J(H3,F) = 1.6 Hz, H3), 6.08 (ddd, ^3J(H2,F) = 17.1, ^3J(H2,H3) = 11.4, ^3J(H1,H2) = 11.0 Hz, H2), 5.25 (dm, ^3J = 16.8 Hz, H(*Z*)4), 5.12 (dm, ^3J = 11.0 Hz, H(*E*)4); ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 152.9$ (dd, ^1J(C,F) = 261, ^1J(C,H) = 200 Hz, C1), 129.5 (dd, ^1J(C,H) = 156, ^3J(C,F) = 9 Hz, C3), 117.9 (t, ^1J(C,H) = 156 Hz, C4), 114.9 (d, ^1J(C,H) = 158 Hz, C2); ^{19}F NMR (376.5 MHz, CD_2Cl_2): $\delta = 125.9$ (dd, ^2J(F,H) = 83.1, ^3J(F,H2) = 17.1 Hz).

Data for (*Z*)-**11**: ^{1}H NMR (400 MHz, CD_2Cl_2) $\delta = 6.68$ (dddd, ^3J = 17.2, 11.2, 10.9, ^4J = 1.0 Hz, H3), 6.49 (ddd, ^2J(H,F) = 83.3, ^3J(H1,H2) = 4.7, ^4J(H1,H3) = 1.0, ^5J(H1,H(*E*)4) = 1.8, ^5J(H1,H(*Z*)4) = 1.0 Hz, H1), 5.50 (ddddd, ^3J(H2,F) = 40.9, ^3J(H2,H3) = 10.9, ^3J(H1,H2) = 4.7, ^4J(H2,H(*E*)4) = ^4J(H2,H(*Z*)4) = 0.7 Hz, H2), 5.30 (dm, ^3J(H3,H(*E*)4) = 11.2 Hz, H(*E*)4), 5.15 (dm, ^3J(H3,H4) = 17.2 Hz, H(*Z*)4); ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 148.5$ (dd, ^1J(C,H) = 280, ^1J(C,H) = 204 Hz, C1), 127.3 (d, ^1J(C,H) = 157 Hz, C3), 117.5 (t, ^1J(C,H) = 156 Hz, C4), 112.3 (d, ^1J(C,H) = 158 Hz, C2); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = 125.2$ (dd, ^2J(F,H) = 83.3, ^3J(F,H2) = 40.9 Hz).

(*E*)-1-[(Dimethylamino)methyl]-2-fluoromethylidenecyclohexane ((*E*)-17): *t*BuOK (2.4 g, 21 mmol) and [18]crown-6 (5 mg) were added to a stirred suspension of (fluoromethyl)triphenylphosphonium tetrafluoroborate (8.3 g, 22 mmol) in anhydrous THF (40 mL) under Ar atmosphere. After stirring at 25 °C for 15 min, the mixture was cooled to 0 °C, and a solution of 2-[(dimethylamino)methyl]cyclohexanone (**16**;[15] 19 mmol) in anhydrous THF (10 mL) was added dropwise under stirring. After the mixture had been stirred at 0 °C for 30 min, then at 25 °C for 2 h, the precipitate was filtered off, and the solution was concentrated in vacuo. Bulb-to-bulb distillation (0.4 Torr, 130 °C) afforded pure (*E*)-**13** as a colorless oil. Yield: 2.5 g (85 %); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 6.48$ (d, ^2J(H,F) = 88.0 Hz, HC-C2), strong NOE with CH_2-C1), two-dimensional ^{1}H NOESY spectrum), 2.35 (m, H3), 2.00 (s, Me_2N), 2.16–1.89 (m, CH_2-C1), H1, H3), 2.16–1.20 (m, 6H); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 142.3$ (dd, ^1J(C,H) = 201, ^1J(C,F) = 250 Hz, FCH), 123.5 (d, ^2J(C,F) = 5 Hz, C2), 61.8 (t, ^1J(C,H) = 130 Hz, CH_2-C1), 45.6 (q, ^1J(C,H) = 127 Hz, Me_2N), 38.8 (dd, ^1J(C,H) = 124, ^3J(C,F) = 6 Hz, C1), 31.3 (t, ^1J(C,H) = 129 Hz), 27.2 (t, ^1J(C,H) = 128 Hz), 24.0 (t, ^1J(C,H) = 132 Hz), 23.1 (td, ^1J(C,H) = 129, ^3J(C,F) = 7 Hz, C6); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -142.0$ (d, ^2J(CH,F) = 88.0 Hz); IR (film): $\tilde{\nu} = 2930$, 2770, 1685, 1460, 1450, 1265, 1185, 1095, 1060, 1035, 860, 805, 645 cm^{-1}; UV (MeCN): λ_{max} (ε) = 199 nm (5400 mol^{-1} dm^3 cm^{-1}); CI-MS (NH_3): *m*/*z* (%): 171 (8) [M^+], 170 (60), 150 (10), 138 (8), 123 (16), 110 (50), 98 (100), 91 (62), 79 (53), 70 (32); elemental analysis calcd (%) for $C_{10}H_{18}FN$ (171.26): C 70.13, H 10.59; found: C 70.03, H 10.52.

Data for 2-[(Dimethylamino)methyl]cyclohexanone (16): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (dd, ^2J = 12.4, ^3J = 6.0 Hz, CH_2-C2), 2.45 (dddd, ^2J = 13.0, ^3J = 7.0, 6.9, 6.8 Hz, H2), 2.32, 2.25, 2.15 (3m, 5H),

2.14 (s, Me_2N), 1.87, 1.82, 1.65, 1.34 (4m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 212.6$ (s, C1), 59.0 (t, $^1J(C,H) = 131$ Hz, CH_2-C2), 49.0 (d, $^1J(C,H) = 124$ Hz, C2), 45.9 (q, $^1J(C,H) = 133$ Hz, Me_2N), 41.9, 32.5, 28.0, 24.5 (4t, $^1J(C,H) = 130$ Hz, 4 C); IR (film): $\tilde{\nu} = 2940$, 2860, 1710, 1460, 1310, 1385, 1220, 1130, 1030, 875 cm^{-1}; UV (MeCN): λ_{max} (ε) = 206 nm (7100 $mol^{-1} dm^3 cm^{-1}$); CI-MS (NH_3): m/z (%): 156 (10) [M^++1], 136 (25), 123 (20), 111 (20), 94 (10), 82 (16).

1:1.7 Mixture of (*Z*)- and (*E*)-17: *n*BuLi (1.6 M) in hexane (48 mL, 77 mmol) was added with a syringe to a stirred suspension of (fluoromethyl)triphenylphosphonium tetrafluoroborate (30 g, 77 mmol) in anhydrous THF (250 mL) cooled to $-78\,^\circ C$ under N_2 atmosphere. The resulting orange solution was stirred at $-78\,^\circ C$ for 4 h, then **16** (12.0 g, 77 mmol) in THF (20 mL) was added slowly under stirring at $-78\,^\circ C$. The mixture was allowed to warm up to 25 °C and stirred for 15 h. The brown precipitate was filtered off (*Celite*), and the solution was concentrated in vacuo. The residue was extracted with ether, and the extracts were concentrated in vacuo. Flash chromatography on silica gel (CH_2Cl_2/MeOH 9:1) afforded a 1:1.7 mixture of (*Z*)-**17** and (*E*)-**17**. Yield: 4.0 g (31 %).

Data for (*Z*)-**17**: ^1H NMR (400 MHz, C_6D_6): $\delta = 6.28$ (d, $^2J(H,F) = 87.7$ Hz, HCF-C2; no NOE with CH_2-C1), 3.25 (m, 1H), 2.30 (dd, $J = 8.5$, 4.3 Hz, 1H), 2.18 (s, Me_2N), 2.00 – 1.10 (m, 9H); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta =$ 142.2 (dd, $^1J(C,H) = 200$, $^1J(C,F) = 252$ Hz, CH-F), 123.7 (s, C2), 60.9 (t, $^1J(C,H) = 130$ Hz, CH_2-N), 45.6 (q, $^1J(C,H) = 127$ Hz, 2 C; Me_2N), 31.4 (d, $^1J(C,H) = 124$ Hz, C1), 28.7 (t, $^1J(C,H) = 129$ Hz), 28.5 (t, $^1J(C,H) =$ 128 Hz), 25.3 (td, $^1J(C,H) = 130$, ^3J (C,F) = 10 Hz, C3), 22.1 (t, $^1J(C,H) =$ 126 Hz); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -140.1$ (d, $^2J(F,H) = 87.7$ Hz).

Data for the 1:1.7 mixture of (*E*)-**17** and (Z)-**17**: IR (film): $\tilde{\nu} = 3000$, 2855, 2765, 1685, 1460, 1445, 1265, 1185, 1095, 1060, 1040, 805, 650, 605 cm^{-1}; UV (MeCN): λ_{max} (ε) = 202 nm (2300 $mol^{-1} dm^3 cm^{-1}$).

***(E)*-1-(Fluoromethylidene)-2-methylidenecyclohexane ((*E*)-13)**: A solution of (*E*)-**17** (2.0 g, 12 mmol) and MeI (1.6 mL, 3.9 g, 27 mmol) in anhydrous Et_2O (25 mL) was stirred at 25 °C for 8 h. The precipitate was collected and washed with Et_2O (5 mL), affording (*E*)-**18** (3.6 g, 98 %) as white solid; m.p. 177 – 178 °C. A solution of (*E*)-**18** (2.5 g, 8 mmol) and Ag_2O (2.3 g, 10 mmol) in H_2O (40 mL) was stirred at 25 °C for 15 h. The water was evaporated (20 Torr, 35 °C),and the residue was heated in a bulb-to-bulb distillation apparatus to 150 °C under 0.1 Torr. The volatile product collected at $-78\,^\circ C$ was dissolved in pentane (5 mL) and dried ($MgSO_4$). Solvent evaporation (35 °C, 700 mbar) afforded (*E*)-**13** as a colorless liquid. Yield: 500 mg (50 %); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.65$ (ddd, $^2J(H,F) = 86.9$, $^4J(H,H) = 1.6$, $^nJ(H,F) = 1.55$ Hz, H-CF), 4.77 and 4.63 (2 brs, H_2C=C2)), 2.26 (m, 4H), 1.63 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 143.7$ (d, $^3J(C,F) = 8$ Hz, C2), 141.6 (dd, $^1J(C,H) = 203$, $^1J(C,F) = 259$ Hz, H*C*F-C1), 124.2 (d, $^2J(C,F) = 9$ Hz, C1), 108.0 (t, $^1J(C,H) = 157$ Hz, CH_2=C2), 35.0 (t, $^1J(C,H) = 127$ Hz, C3), 26.8 (t, $^1J(C,H) = 124$ Hz), 25.3, 24.6 (2t, $^1J(C,H) = 126$ Hz); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -138.0$ (d, $^2J(H,F) = 86.9$ Hz); IR (film): $\tilde{\nu} =$ 2935, 2860, 1670, 1630, 1445, 1260, 1125, 1085, 1065, 895, 815, 735, 630 cm^{-1}; UV (MeCN): λ_{max} (ε) = 216 nm (3300 $mol^{-1} dm^3 cm^{-1}$); CI-MS (NH_3): m/z (%): 126 (100) [M^+], 111 (40), 102 (20), 97 (26), 93 (50), 85 (36), 77 (31), 71 (25).

2.5:1 Mixture of (*E*)-13 and (*Z*)-13: When the procedure described above for the preparation of pure (*E*)-**13** was applied to a 1.7:1 mixture of (*E*)-**17** and (*Z*)-**17**, a 2.5:1 mixture of (*E*)-**13** and (*Z*)-**13** was obtained (50 %) as a colorless oil.

Data for (*Z*)-**13**: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.47$ (dt, $^2J(H,F) = 85.7$, $^4J(H,H) = 1.3$ Hz, HCF), 5.09, 5.04 (2 brs, H_2C=C2), 2.80 – 1.60 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 141.6$ (dd, $^1J(C,H) = 203$, $^1J(C,F) =$ 259 Hz, F*C*H), 140.6 (s, C2), 122.7 (s, C1), 112.9 (dt, $^1J(C,H) = 160$, $^4J(C,F) = 5$ Hz, CH_2=C2), 35.4 (t, $^1J(C,H) = 126$ Hz), 28.7 (t, $^1J(C,H) =$ 128 Hz), 26.4 (t, $^1J(C,H) = 126$ Hz), 22.3 (t, $^1J(C,H) = 124$ Hz); ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -136.0$ (d, $^2J(H,F) = 85.7$ Hz).

***cis*- or *trans*-6-Fluoro-3,6-dihydro-1,2-oxathiin-2-oxide (20)**: On the vacuum line, a 1:1 mixture of (*E*)- and (*Z*)-1-fluorobutadiene ((*E*)-**11**, (*Z*)-**11**; 40 mg), was condensed in a 5 mm NMR tube containing CD_2Cl_2 (0.2 mL), SO_2 (0.2 mL), and CF_3COOH (50 μL). The NMR tube was sealed under vacuum in liquid N_2 and allowed to reach $-70\,^\circ C$ in the probe of the NMR machine. A single diastereomeric adduct was formed at the expense of (*E*)-**11**, exclusively between -70 and $-40\,^\circ C$ (toluene as internal reference). At $-40\,^\circ C$ equilibrium (*E*)-**11** + $SO_2 \rightleftharpoons$ **20** was reached after 48 h, giving $K^{233\,K} =$ **20**) $\cong 0.035$ $mol^{-1} dm^3$. Data for **20**: ^1H NMR (400 MHz, CD_2Cl_2/SO_2): $\delta = 6.24$ (m, H4, H5), 5.92 (dm, $^2J(H,F) = 51.1$ Hz, H6), 3.55 (m, H_2C3); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2) $\delta = 120.5$ (dd, $^1J(C,H) = 170$, $^3J(C,F) = 22$ Hz, C5), 98.4 (dd, $^1J(C,H) = 188$, $^1J(C,F) = 236$ Hz, C6), 46.5 (t, $^1J(C,H) = 141$ Hz, C3); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 233 K): $\delta =$ -103.0 (ddd, $^2J(H,F) = 51.1$, $^nJ(H,F) = 8.0$, 7.9 Hz).

***cis*-6-(Trifluoroacetoxy)-3,6-dihydro-1,2-oxathiin-2-oxide (21)**: In the presence of CF_3COOH, compound **20** as obtained above was converted into **21** and **22** at $-30\,^\circ C$. ^1H NMR (400 MHz, CD_2Cl_2/SO_2, 243 K) of **21**: $\delta = 6.87$ (m, H6), 6.30 (m, H4), 6.10 (dddd, $^3J(H5,H4) = 11.0$, $^3J(H5,H6) = 2.0$, $^4J(H3,H5) = 2.0$, 1.8 Hz, H5), 3.88 (dddd, $^2J = 17.0$, $^3J = 4.7$, $^4J = 1.8$, $^5J(H_{eq}3,H6) = 1.8$ Hz, $H_{eq}3$), 3.49 (dddd, $^2J = 17.0$, $^3J = 4.6$, $^4J = 2.0$, $^5J(H_{ax}3,H6) = 2.0$ Hz, $H_{ax}6$).

Data for (*Z*)-4-Oxobut-2-ene-1-sulfinyl fluoride (22): ^1H NMR (400 MHz, CD_2Cl_2/SO_2, 243 K): $\delta = 9.71$ (d, $^3J = 8.0$ Hz, H4), 6.85 (ddd, $^3J = 11.0$, 8.8, 8.4 Hz, H2), 6.72 (dddd, $^3J = 11.0$, 8.0, $^4J(H'1,H3) = 1.3$, $^4J(H1,H3) = 1.0$ (chirality of S) Hz, H3), 4.44 (dddd, $^2J = 13.9$, $^3J = 8.4$, $^3J(H,F) = 6.2$, $^4J(H1,H3) = 1.0$ Hz, H1), 4.28 (dddd, $^2J = 13.9$, $^3J(H,F) = 22.5$, $^3J(H'1,H2) = 8.8$, $^4J(H'1,H3) = 1.3$ Hz, H′1); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 243 K): $\delta = -22.4$ (dd, $^3J(H'1,F) = 22.5$, $^3J(H1,F) = 6.2$ Hz).

***cis*- and *trans*-2-Fluoro-3,4-oxathiabicyclo[4.4.0]dec-1(6)-ene-4-oxide (*cis*/*trans*-30)**: (*E*)-**13** (40 mg, 0.32 mmol), CD_2Cl_2 (0.25 mL), $CFCl_3$ (100 mg), and SO_2 (0.15 mL, 4.6 mmol) were mixed in a 5 mm NMR tube (vacuum line) at $-100\,^\circ C$, warmed up to $-80\,^\circ C$ and left at this temperature for 2 h. ^1H NMR at $-70\,^\circ C$ showed complete conversion of (*E*)-**13** into a 93:7 mixture of *cis*-**30** and *trans*-**30**.

Data for *cis*-**30**: ^1H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): $\delta = 5.66$ (dddd, $^2J(H,F) = 53.3$, $^5J(H2,H_{trans}5) = 1.9$, $^5J(H2,H_{cis}5) = 1.0$, $^5J(H2,H7) =$ 1.0 Hz, H2), 3.50 (dddm, $^2J = 16.8$, $^5J(H_{trans}5,F) = 8.6$, $^5J(H2,H_{trans}5) =$ 1.9 Hz, $H_{trans}5$), 3.05 (dddt, $^2J = 16.8$, $^5J(H_{cis}5,F) = 5.8$, $^4J(H_{cis}5,H_{cis}7) = 0.7$, $^4J(H_{cis}5,H_{trans}7) = 0.7$, $^5J(H_{cis}5,H2) = 0.65$ Hz, $H_{cis}5$), 2.25 (ddm, $^2J = 16.4$, $^5J(H_{cis}5,H10) = 0.7$ Hz, H10), 2.12 (m, $^4J(H2,H7) = 1.0$ Hz, H_2C5), 2.04 (dm, $^2J = 16.4$ Hz, H′10), 1.87 – 1.61 (m, H_2C8), H_2C9); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): $\delta = 124.3$ (d, $^2J(C,F) = 21$ Hz, C1), 122.9 (s, C6), 100.3 (dd, $^1J(C,H) = 186$, $^1J(C,F) = 226$ Hz, C2), 29.6 (t, $^1J(C,H) = 129$ Hz, C7), 49.2 (t, $^1J(C,H) = 140$ Hz, C5), 24.0 (t, $^1J(C,H) = 128$ Hz, C10), 21.5, 21.1 (2t, $^1J(C,H) = 129$ Hz, C8, C9); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2/ $CFCl_3$, 203 K): $\delta = -109.3$ (dm, $^2J(H,F) = 53$ Hz).

Data for *trans*-**30**: ^1H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): $\delta = 5.90$ (dm, $^2J(H,F) = 55$ Hz, H2), 3.50 (dm, $^2J = 16.5$ Hz, $H_{trans}5$), 3.25 (dm, $^2J =$ 16.5 Hz, $H_{cis}5$), 2.30 – 1.60 (m, 8H); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2/ $CFCl_3$, 203 K): $\delta = 132.1$ (d, $^2J(C,F) = 10$ Hz, C1), 131.2 (s, C6), 106.9 (dd, $^1J(C,H) = 182$, $^1J(C,H) = 218$ Hz, C2), 49.2 (t, C5), 26.7 (t, C7), 25.7 (C10), 22.0 – 23.0 (C8, C9); ^{19}F NMR (376.5 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): $\delta =$ -116.1 (dm, $^2J(H,F) = 55$ Hz). Structure assignments of *cis*-**30** and *trans*-**30** are based on comparison of the reactivity of (*E*)- and (*Z*)-**13** toward SO_2 with that of (*Z*)-**8** and (*E*)-**8**, and by comparing the NMR data of sultines *cis*-**30** and *trans*-**30** with those of *cis*-**9** and *trans*-**9**. IUPAC names for *cis*-**30** and *trans*-**30**: (1*RS*,3*SR*)- and (1*RS*,3*RS*)-1-fluoro-1,4,5,6,7,8-hexahydro-2,3-benzoxathiin-3-oxide.

(2-Formylcyclohexen-2-yl)methanesulfinyl fluoride (31): When a solution of *cis*-**30** and *trans*-**30** obtained above in CD_2Cl_2 (0.25 mL), $CFCl_3$ (100 mg), and SO_2 (0.15 mL) was allowed to stand at $-10\,^\circ C$ for 15 h, complete conversion of **30** into **31** took place. ^1H NMR (400 MHz, CD_2Cl_2/SO_2/ $CFCl_3$, 203 K): $\delta = 9.65$ (s, HCO), 4.24 (dd, $^2J = 13.6$, $^3J(H,F) = 13.9$ Hz, H1), 4.16 (dd, $^2J = 13.6$, $^3J(H,F) = 13.5$ Hz, H′1), 2.27 (m, H_2C3'), H_2C6'), 1.71 (m, H_2C4'), H_2C5'); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 263 K): $\delta = 192.2$ (d, $^1J(C,H) = 175$ Hz, CHO), 144.3 (s, C1′), 140.3 (s, C2′), 62.3 (td, $^1J(C,H) = 140$, $^2J(C,F) = 7$ Hz, C1), 34.8 (t, $^1J(C,H) = 127$ Hz), 22.0, 21.8, 21.3 (3t, $^1J(C,H) = 129$ Hz); ^{19}F NMR (376.5 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 263 K): $\delta = -17.0$ (dd, $^3J(H,F) = 13.9$, 13.5 Hz).

2-Methylcyclohex-1-ene-1-carbaldehyde (32): The above solution of **31** was left at 25 °C for 15 h. The NMR tube was opened, and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/light petroleum ether 1:4) affording **32** as a pale yellow oil. Yield: 20 mg (51 %); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 10.41$ (s), 2.20 (m, 4H), 2.14 (s, Me), 1.65 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 191.1$ (d, $^1J(C,H) = 170$ Hz, CHO), 156.2 (s, C2), 133.7 (s, C1), 34.2 (t, $^1J(C,H) = 128$ Hz, C3), 22.1, 22.0 (2t, $^1J(C,H) =$ 132 Hz), 21.7 (t, $^1J(C,H) = 128$ Hz), 18.3 (q, $^1J(C,H) = 127$ Hz, Me-C2);

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IR (film): $\tilde{\nu}$ = 2940, 2860, 1665, 1640, 1450, 1235, 1145, 1070, 735 cm^{-1}; UV (MeCN): λ_{max} (ε) = 240 nm (3000 mol^{-1}dm^{3}cm^{-1}); CI-MS (NH_3): *m*/*z* (%): 124 (100) [M^+], 109 (22), 95 (40), 81 (22).

***cis*- and *trans*-4,9-Dioxo-10-fluoro-1,2-oxathiacyclodecane-2-oxide (*cis*-/*trans*-38)**: The solution of the 93:7 mixture of *cis*-**30** and *trans*-**30** in CD_2Cl_2 (0.25 mL), $CFCl_3$ (100 mg), and SO_2 (0.15 mL) obtained at −80 °C was ozonolyzed (2% O_3 in O_2, bubbling for 20 min) at −78 °C (completion of reaction checked by ^{1}H NMR) to afford a 93:7 mixture of *cis*-**38** and *trans*-**38**, which was analyzed at −70 °C.

Data for *cis*-**38**: ^{1}H NMR (400 MHz, CD_2Cl_2/SO_2, 203 K): δ = 6.13 (d, ^2J(H,F) = 57.0 Hz, H10), 4.49 (d, ^2J = 12.6 Hz, H3), 4.05 (d, ^2J = 12.6 Hz, H′-3), 3.03 (ddd, ^2J = 15.3, ^3J = 9.8, 2.3 Hz), 2.50 (m, 3H), 2.23–1.10 (m, 4H); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): δ = 203.9 (d, C4), 200.3 (d, ^2J(C,F) = 20 Hz, C9), 104.3 (dd, ^1J(C,H) = 178, ^1J(C,F) = 242 Hz, C10), 68.8 (t, ^1J(C,H) = 143 Hz, C3), 42.9, 35.8, 22.5 (3t, ^1J(C,H) = 129 Hz), 21.1 (t, ^1J(C,H) = 132 Hz); ^{13}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 203 K): δ = −130.2 (d, ^2J(H,F) = 57.0 Hz).

Data for *trans*-**38**: ^{1}H NMR (400 MHz, CD_2Cl_2/SO_2, 203 K): δ = 5.91 (d, ^2J(H,F) = 57.0 Hz, H10), 4.40 (d, ^2J = 12.9 Hz, H3), 3.78 (d, ^2J = 12.9 Hz, H′3), 3.0–1.1 (m, 8H); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 203 K): δ = 204.0 (s, C4), 200.6 (d, ^2J(C,F) = 20.0 Hz, C9), 98.2 (dd, ^1J(C,H) = 177, ^1J(C,H) = 240 Hz, C10), 64.5 (t, ^1J(C,H) = 142 Hz, C3), 41.9, 38.6 (2t, ^1J(C,H) = 123 Hz), 23.0–20.0 (2t); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 203 K): δ = −137.6 (d, ^2J(H,F) = 57.0 Hz).

***cis*-2-Fluoro-3,4-oxathiabenzobicyclo[4.4.0]dec-1(6)-9-diene-4-oxide (*cis*-9)**: The same procedure was used as for the preparation of *cis*-**30**, starting with pure (*Z*)-**8** (40 mg, 0.23 mmol). ^{1}H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): δ = 7.25 (m, 4H), 6.37 (dddd, ^2J(H,F) = 52.0, ^5J(H2,H$_{trans}$5) = 1.55, ^5J(H2,H$_{trans}$7) = 1.50, ^5J(H2,H$_{cis}$7) = 1.45 Hz, H2), 3.89 (ddddd, ^2J = 17.7, ^5J(H,F) = 7.6, ^4J(H$_{trans}$5,H$_{trans}$7) ≅ ^4J(H$_{trans}$5,H$_{cis}$7) ≅ ^5J(H$_{trans}$5,H2) = 1.5 Hz, H$_{trans}$5), 3.40 (br dd, ^2J = 17.7, ^5J(H,F) = 6.3 Hz, H$_{cis}$5), 2.91 (m, 2H), 2.50 (m, 2H) (H$_{cis}$ = *cis*, H$_{trans}$ = *trans* with respect to F); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): δ = 135.9, 130.1 (2s), 128.44, 128.40, 127.1, 123.1 (4d, ^1J(C,H) = 162 Hz), 127.0 (d, ^3J(C,F) = 6.0 Hz, C6), 122.7 (d, ^2J(C,F) = 21 Hz, C1), 98.7 (dd, ^1J(C,H) = 184, ^1J(C,F) = 226 Hz, C2), 50.9 (t, ^1J(C,H) = 139 Hz, C5), 28.4 (t, ^1J(C,H) = 129 Hz, C8), 26.3 (t, ^1J(C,H) = 133 Hz, C7); ^{19}F NMR (376.5 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 203 K): δ = −104.1 (d, ^2J(H,F) = 52.0 Hz).

***trans*-2-Fluoro-3,4-oxathiabenzobicyclo[4.4.0]dec-1(6)-9-diene-4-oxide (*trans*-9)**: The solution of *cis*-**9** obtained above was warmed to −40 °C. After 15 h at −40 °C complete conversion of *cis*-**9** (<2%) into *trans*-**9** (>98%) was observed. Alternatively, (*E*)-**8** (40 mg) was mixed with CD_2Cl_2 (0.25 mL), $CFCl_3$ (0.1 g), and SO_2 (0.15 mL), and the mixture was allowed to react at −40 °C for 2 h. ^{1}H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 233 K): δ = 7.28 (m, 4H), 6.65 (br d, ^2J(H,F) = 53.0 Hz, H2), 3.82 (dd, ^2J = 16.3, ^5J(H,F) = 6.2, ^5J(H2,H$_{cis}$5) < 0.2 Hz, H$_{cis}$5), 3.63 (ddd, ^2J = 16.3, ^5J(H,F) = 5.6, ^5J(H2,H$_{trans}$5) = 0.8 Hz, H$_{trans}$5), 2.91, 2.47 (2m, 4H); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 233 K): δ = 136.1, 130.5 (2s), 130.1 (d, ^3J(C,F) = 6 Hz, C6), 128.9, 128.8, 127.6, 123.2 (4d, ^1J(C,H) = 158–160 Hz), 126.3 (d, ^2J(C,F) = 20 Hz, C1), 103.5 (dd, ^1J(C,H) = 184, ^1J(C,F) = 221 Hz, C2), 54.5 (t, ^1J(C,H) = 142 Hz, C5), 29.6 (t, ^1J(C,H) = 130 Hz, C8), 27.0 (t, ^1J(C,H) = 125 Hz, C7); ^{19}F NMR (376.5 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 233 K): δ = −110.6 (d, ^2J(H,F) = 53 Hz). Other (IUPAC) names for *cis*-**9** and *trans*-**9**: (1*RS*,3*SR*)- and (1*RS*,3*RS*)-1-fluoro-1,4,9,10-tetrahydronaphth[2,1-d] [2,3]oxathiin-3-oxide.

(1-Formyl-3,4-dihydronaphth-2-yl)methanesulfinyl fluoride (41): The above solution of *cis*- and *trans*-**9** was allowed to stand at −10 °C for 15 h. Compound *trans*-**9** was completely converted into a 1:1 mixture of **40** and **41**.

Data for **40**: ^{1}H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 263 K): δ = 10.2 (s, HCO), 7.62 (m, 1H), 7.25 (m, 3H), 4.43 (dd, ^2J(H,H) = 12.8, ^3J(H,F) = 12.9 Hz, H1), 4.31 (t, ^2J(H,H) = 12.9, ^3J(H,F) = 12.9 Hz, H′1), 2.83 (dd, ^3J = 10.3, 8.4 Hz, H$_2$C3), 2.60 (dd, ^3J = 10.3, 8.4 Hz, H$_2$C4); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 263 K): δ = 191.8 (d, ^1J(C,H) = 178 Hz, HCO) 142.3, 136.7 (2s), 128.9, 127.7, 127.0, 124.8 (4t), 64.7 (d, ^1J(C,H) = 136, ^2J(C,F) = 7 Hz, C1), 32.6 (t, ^1J(C,H) = 129 Hz, C3), 26.6 (t, ^1J(C,H) = 126 Hz, C4); ^{19}F NMR (376.5 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 263 K): δ = −15.7 (t, ^3J(H,F) = 12.9 Hz).

3,4-Dihydro-2-methylnaphthalene-1-carbaldehyde (40): The NMR tube from the above reaction (mixture of **40** + **41**) was opened, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (EtOAc/light petroleum ether 1:4) affording **41** as a pale yellow oil. Yield: 28 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.41 (s), 7.93 (m, 1H), 7.21 (m, 3H), 2.77, 2.46 (2dd, ^3J = 7.45, 7.40 Hz), 2.41 (s, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 190.2 (d, ^1J(C,H) = 173 Hz, CHO), 158.4 (s, C2), 135.4, 131.4, 130.9 (3s), 127.7 (2 C), 126.5, 125.7 (4d, ^1J(C,H) = 160 Hz), 33.2 (t, ^1J(C,H) = 123 Hz), 27.3 (t, ^1J(C,H) = 128 Hz), 14.2 (q, ^1J(C,H) = 128 Hz, Me); IR (film): $\tilde{\nu}$ = 2940, 1675, 1490, 1300, 1140, 1070, 760, 610 cm^{-1}; UV (MeCN): λ_{max} (ε) = 227 (11 000), 209 (13 500), 188 nm (4000 mol^{-1}dm^{3}cm^{-1}); CI-MS (NH_3): *m*/*z* (%): 172 (50) [M^+], 128 (100), 115 (56), 91 (27).

***cis*-4,9-Dioxo-10-fluoro-1,2-oxathiabenzocyclodec-7-ene-2-oxide (*cis*-39)**: Degassed (freeze–thaw cycles) SO_2 (0.5 mL) was transferred (vacuum line) to a frozen solution of (*E*)-**8** and (*Z*)-**8** (1:4, 40 mg, 0.23 mmol) in anhydrous CD_2Cl_2 (0.3 mL). The mixture was warmed up to −78 °C and allowed to stand at this temperature for 2 h. Then 2% O_3 in O_2 was bubbled through it at −78 °C for 20 min. ^{1}H NMR measurements showed complete conversion of (*Z*)-**8** into *cis*-**39**. ^{1}H NMR (400 MHz, CD_2Cl_2/SO_2, 203 K): δ = 7.49 (m, 2H), 7.37 (m, 1H), 7.22 (m, 1H), 6.32 (d, ^2J(H,F) = 57.0 Hz, H10), 4.42 (d, ^2J = 13.3 Hz, H3), 3.99 (d, ^2J = 13.3 Hz, H′-3), 3.00 (m, 3H), 2.78 (m, 1H); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 203 K): δ = 202.3 (s, C4), 195.3 (d, ^2J(C,F) = 24 Hz, C9), 136.4 (s), 131.5 (d, ^1J(C,H) = 159 Hz), 130.4 (d, ^1J(C,H) = 160 Hz), 129.8 (s), 127.4 (d, ^1J(C,H) = 158 Hz), 126.3 (d, ^1J(C,H) = 160 Hz), 104.6 (dd, ^1J(C,H) = 180, ^1J(C,F) = 246 Hz, C10), 69.1 (t, ^1J(C,H) = 140 Hz, C3), 44.7 (t, ^1J(C,H) = 132 Hz, C5), 27.2 (t, ^1J(C,H) = 131 Hz, C6); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 203 K): δ = −126.9 (br d, ^2J(H,F) = 57.0 Hz).

***trans*-4,9-Dioxo-10-fluoro-1,2-oxathiabenzocyclodec-7-ene-2-oxide (*trans*-39)**: Degassed SO_2 (0.5 mL) was transferred to a frozen solution of pure (*E*)-**8** (40 mg, 0.23 mmol) in anhydrous CD_2Cl_2. The mixture was allowed to stand at −40 °C for 15 h. After cooling to −78 °C, 2% O_3 in O_2 was bubbled through the solution at −78 °C for 20 min. ^{1}H NMR analysis showed complete conversion of (*E*)-**8** into *trans*-**39**. ^{1}H NMR (400 MHz, CD_2Cl_2/SO_2, 233 K): δ = 7.55 (m, 1H), 7.47 (d, 1H), 7.28 (m, 2H), 6.41 (d, ^2J(H,F) = 55.0 Hz, H11), 4.28, 3.93 (2d, ^2J = 13.9 Hz, H$_2$C3), 3.10 (m, 3H), 2.82 (m, 1H); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 233 K): δ = 202.6 (s, C4), 195.9 (d, ^2J(C,F) = 21 Hz, C9), 137.5, 135.3 (2s), 132.7, 130.6, 128.1, 127.4 (4d, ^1J(C,H) = 158–160 Hz), 99.1 (dd, ^1J(C,H) = 192, ^1J(C,F) = 242 Hz, C10), 66.0 (t, ^1J(C,H) = 141 Hz, C3), 44.9 (t, ^1J(C,H) = 133 Hz, C5), 27.4 (t, ^1J(C,H) = 132 Hz, C6); ^{19}F NMR (376.5 MHz, CD_2Cl_2/SO_2, 203 K): δ = −132.4 (d, ^2J(H,F) = 55.0 Hz).

CCDC-173479 (*cis*-**9**·$(SO_2)_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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