CHEMCOMM
Communication
www.rsc.org/chemcomm

The hetero-Diels–Alder addition of sulfur dioxide: structure of the first crystalline sultine. Quantum calculations on the conformations of 6-fluoro-3,6-dihydro-1,2-oxathiine 2-oxides†

Elena Roversi,[a] Rosario Scopelliti,[a] Euro Solari,[a] Raphaël Estoppey,[a] Pierre Vogel,*[a] Pedro Braña,[b] Bibiana Menéndez[b] and José Ángel Sordo*[b]

[a] *Section de chimie de l'Université de Lausanne, BCH, CH 1015 Lausanne-Dorigny, Switzerland. E-mail: pierre.vogel@ico.unil.ch; Fax: (+41) 21 692 3955*

[b] *Laboratorio de Química Computacional, Departamento de Química Física y Analítica, Universidad de Oviedo, Oviedo, Spain*

Received (in Cambridge, UK) 5th April 2001, Accepted 18th May 2001
First published as an Advance Article on the web 14th June 2001

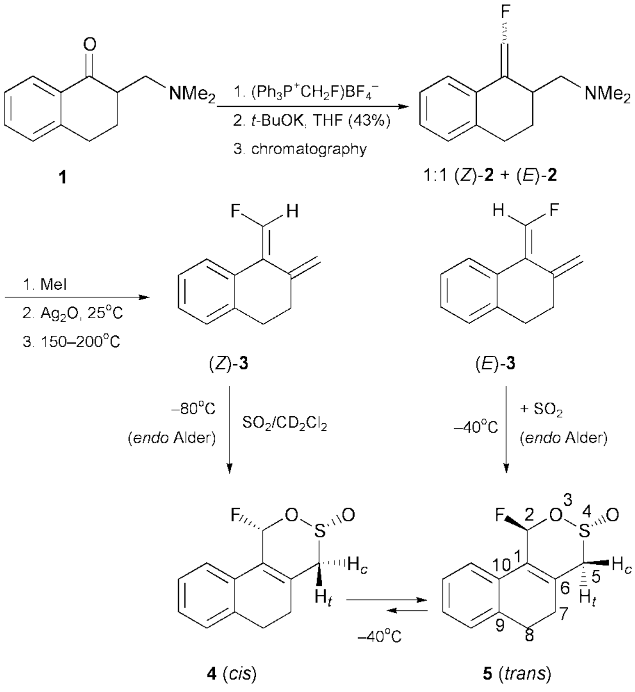
The hetero-Diels–Alder addition of sulfur dioxide to (*E*)- and (*Z*)-4-(fluoromethylidene)-3-methylene-2,3-dihydronaphthalene follows the *endo* Alder rule. The first example of a crystalline sultine has been obtained. In agreement with high level quantum calculations, (1*SR*,3*SR*)-1-fluoro-1,4,5,6-tetrahydronaphtho[2,1-*d*][1,2]oxathiine 3-oxide adopts a sofa conformation in its ground state.

At low temperature and in the presence of a catalyst, simple alkyl-substituted 1,3-dienes add reversibly to SO_2 *via* hetero-Diels–Alder additions to generate the corresponding 3,6-dihydro-1,2-oxathiine 2-oxides (sultines).[1] They are unstable above −50 °C and undergo fast cycloreversion liberating the starting 1,3-dienes and SO_2 that can undergo the expected chelotropic additions at higher temperature. Until now sultines have been characterised in solution by their NMR data only.[1,2] Because of their instability, none of them have been isolated and better characterised. We report here the successful crystallisation of a fluorosultine and its structure determination by X-ray radiocrystallography. Whereas cyclohexene adopts a *pseudo*-chair conformation in its ground-state that interconverts through sofa transition structures, 6-fluoro-3,6-dihydro-1,2-oxathiine 2-oxides seem to prefer sofa conformation in their ground state with the intra-ring oxygen atom lying in the plane of the four carbon centres. We demonstrate also that the hetero-Diels–Alder addition of SO_2 obeys the *endo* Alder rule.[3]

The fluorodienes (*E*)-**3** and (*Z*)-**3** were derived from **1**[4] as shown in Scheme 1.[5] SO_2 added to (*Z*)-**3** at −80 °C (2 h) giving sultine **4**. When allowed to stand at −40 °C it isomerised into **5**. Above −30 °C, **5** was decomposed, no trace of the corresponding sulfolene could be detected! Diene (*E*)-**3** was less reactive than (*Z*)-**3**. It reacted with SO_2 at −40 °C (15 h) giving sultine **5** that could be crystallised at −50 °C and analysed by X-ray radiocrystallography at −100 °C (Fig. 1), thus establishing its structure unambiguously. That of the *cis*-sultine **4** was deduced from its NMR data and by its isomerization into the more stable *trans*-isomer **5**.[6]

Compound **5** represents the first example of a crystalline sultine.[7] The most striking observation is that it adopts a nearly sofa conformation in the crystalline state. This may not be the unique conformation available in solution as suggested by the ^1H NMR spectrum. Assuming validity of the relation $^5J_{H,H} = (5\ Hz)\ (\sin\theta)^2(\sin\theta')^2$ for the coupling constants between the homoallylic proton pairs[8] at C-2 and C-5, a larger value should be measured for ^5J(H-2,H$_t$-5) than for ^5J(H-2,H$_c$-5) since H$_t$ makes a greater angle with the C-2, 1, 6, 5 plane than H$_c$ (see Fig. 1). However, one finds similar values ^5J(H-2,H$_c$-5) < 0.2 Hz, ^5J (H-2,H$_t$-5) = 0.8 Hz and ^5J(F-2,H$_t$-5) = ^5J(H-2,H$_c$-3) = 6.2 Hz suggesting that **5** exists as an equilibrium of several conformers in solution.

We have explored using high-level quantum calculations the potential energy surface (PES) of the Diels–Alder additions of SO_2 to (*E*)- and (*Z*)-1-fluorobutadiene (Figs. 2 and 3). The relative energies were computed using G3 theory[9] with the ΔE(2df,p) contribution estimated at the MP2 level (while the



Scheme 1 Synthesis of fluorosultines.

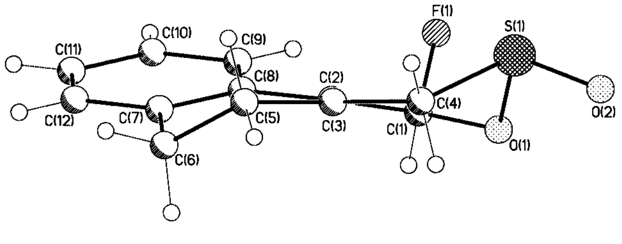


Fig. 1 ORTEP representation of **5** showing the nearly sofa conformation of this 6-fluorosultine. For reasons of commodity atom numbering does not follow IUPAC recommendations. Selected bond lengths (Å), bond angles (°) and torsion angles (°): S1–O2 1.475(2), S1–O1 1.6840(19), S1–C4 1.796(3), O1–C1 1.413(3), C1–F1 1.414(3), O2–S1–O1 102.91(11), O2–S1–C4 106.94(13), O1–S1–C4 93.57(11), O1–C1–F1 106.6, O2–S1–O1–C1 179.11(18), C1–C2–C3–C4 10.4(4).

---

† Electronic supplementary information (ESI) available: synthetic procedures, data for (*E*)-**3**, (*Z*)-**3**, **4** and **5**. Crystal and molecular structures of **5**, tables of calculated data and representations of calculated minima and transition structures. See http://www.rsc.org/suppdata/cc/b1/b103096p/

DOI: 10.1039/b103096p

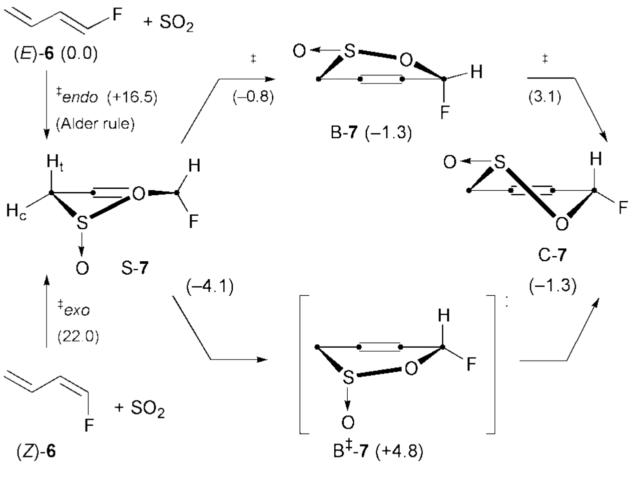


Fig. 2 G3 calculated energies for the hetero-Diels–Alder additions of SO$_2$ to **6** giving sultine **7** (*cis*). Values (kcal mol^{-1}) given relative to cycloaddends.

CPU times on a NEC SX-4 supercomputer were affected by a factor near 10, a difference of only 0.3 kcal mol^{-1} was found when computing this term for (*S*)-**7** at the MP4 level). The spin-orbit term was not included because of the lack of data for sultines, the zero-point energy was computed from MP2/6-31G(d) harmonic frequencies scaled by a factor of 0.96, and the frozen-core approximation was employed to carry out the geometry optimizations (see ESI†). Both dienes (*E*)-**6** and (*Z*)-**6** prefer the *endo* mode (Alder rule)[3] of addition and (*Z*)-**6** is less reactive than (*E*)-**6**, in agreement with our results with dienes (*Z*)-**3** and (*E*)-**3**, respectively. The calculations predict that *cis*-fluorosultine **7** prefers a sofa conformation S-**7** with *pseudo* axial S=O (Fig. 2). The interconversions of S-**7** and of the pseudo-chair conformer C-**7** can follow two paths. That with the lowest energy barrier involves equilibrium with a boat conformer B-**7**. In the case of the *trans*-fluorosultine **8** (Fig. 3) a sofa S-**8** with *pseudo*-equatorial S=O bond (corresponds to the X-ray structure of **5**) and a 'flattened' *pseudo*-chair conformer C-**8** of similar stabilities are found in agreement with our NMR data for **5**. A boat conformer B-**8** is only 1 kcal mol^{-1} above S-**8** and C-**8** and is reached with an energy barrier of 1.2 kcal mol^{-1}. Alternatively, interconversion S-**8** = C-**8** can operate through a boat transition structure B‡-**8** with an energy barrier of 4.3 kcal mol^{-1} only, suggesting that **8** is more flexible than **7**. If such a flexibility difference should prevail in the cases of **4** and **5**, it could contribute to make **5** more stable than **4**.

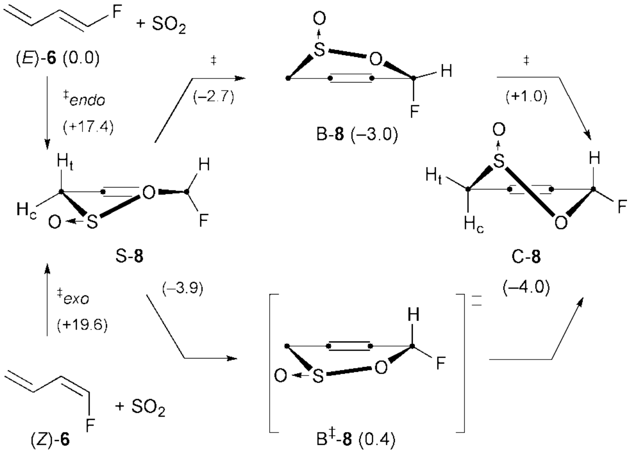


Fig. 3 G3 calculated energies for the hetero-Diels–Alder additions of SO$_2$ to **6** giving sultine **8** (*trans*). Values (kcal mol^{-1}) given relative to cycloaddends.

We have proposed that sultines are intermediates in our new carbon–carbon forming reaction between electron-rich dienes and enoxysilanes.[10] These species raise fundamental questions concerning their reactivity[11] and, as shown here, about their structure.

This work was supported by the Swiss National Science Foundation, the Centro Svizzero di Calcolo Scientifico (Manno), and by DGES (Madrid) under project PP97-0399-C03.03.

Notes and references

1 B. Deguin and P. Vogel, *J. Am. Chem. Soc.*, 1992, **114**, 9210; B. Deguin and P. Vogel, *Tetrahedron Lett.*, 1993, **34**, 6269; T. Fernández, J. A. Sordo, F. Monnat, B. Deguin and P. Vogel, *J. Am. Chem. Soc.*, 1998, **120**, 13 276.

2 T. Fernández, D. Suárez, J. A. Sordo, E. Roversi, A. Estrella de Castro, K. Schenk and P. Vogel, *J. Org. Chem.*, 1998, **63**, 9490; E. Roversi, F. Monnat, K. Schenk, P. Vogel, P. Braña and J. A. Sordo, *Chem. Eur. J.*, 2000, **6**, 1858.

3 K. Alder and G. Stein, *Angew. Chem.*, 1937, **50**, 510; J. Sauer and R. Sustmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 779; R. Gleiter and M. C. Böhm, *Pure Appl. Chem.*, 1983, **55**, 237.

4 D. S. Black and L. M. Johnstone, *Aust. J. Chem.*, 1984, **37**, 117.

5 D. Burton and D. Wiemers, *J. Fluorine Chem.*, 1985, 85.

6 Selected data of **4**: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$–SO$_2$–CFCl$_3$, 203 K): δ = 7.25 (m, 4H), 6.37 (dddd, ^2J(H,F) = 52.0 Hz, ^5J(H-2,H$_t$-5) = 1.55 Hz, ^5J(H-2,H$_t$-7) = 1.50 Hz, ^5J(H-2,H$_c$-7) = 1.45 Hz, H-2), 3.89 (ddddd, ^2J = 17.7 Hz, ^5J(H,F) = 7.6 Hz, ^4J(H$_t$-5,H$_t$-7) ≅ ^4J(H$_t$-5,H$_c$-7) ≅ ^5J(H$_t$-5,H-2) = 1.5 Hz, H$_t$-5), 3.40 (br dd, ^2J = 17.7, ^5J(H,F) = 6.3 Hz, H$_c$-5), 2.91 (m, 2H), 2.50 (m, 2H) (H$_c$ ≙ *cis*, H$_t$ ≙ *trans* with respect to F). Selected data of **5**: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$–SO$_2$–CFCl$_3$, 233 K): δ = 7.28 (m, 4H), 6.65 (br d, ^2J(H,F) = 53.0 Hz, H-2), 3.82 (dd, ^2J = 16.3 Hz, ^5J(H,F) = 6.2 Hz, ^5J(H-2,H$_c$-5) < 0.2 Hz, H$_c$-5), 3.63 (ddd, ^2J = 16.3 Hz, ^5J(H,F) = 5.6 Hz, ^5J(H-2,H$_t$-5) = 0.8 Hz, H$_t$-5), 2.91, 2.47 (2m, 4H).

7 C$_{12}$H$_{11}$FO$_2$S (238.27), monoclinic, a = 7.8271(9) Å, α = 90°, b = 13.982(2) Å, β = 106.577(12)°, c = 10.1237(15) Å, γ = 90°; V 1061.9(3) Å^3, 143(2) K, $P2(1)/n$, Z = 4, μ = 0.299 mm^{-1}, 1795 independent reflexion [R(int) = 0.0459], reflexion collected: 5521, final R indices (all data): $R1$ = 0.0572, $wR2$ = 0.1293. CCDC 157490. See http://www.rsc.org/suppdata/cc/b1/b103096p/

8 M. Barfield and S. Sternhell, *J. Am. Chem. Soc.*, 1972, **94**, 1905; J. Kowalewski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1978, **11**, 1.

9 L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov and J. A. Pople, *J. Chem. Phys.*, 1998, **109**, 7764.

10 J.-M. Roulet, G. Puhr and P. Vogel, *Tetrahedron Lett.*, 1997, **38**, 6201; V. Narkevitch, K. Schenk and P. Vogel, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 1806.

11 S. Megevand, J. Moore, K. Schenk and P. Vogel, *Tetrahedron Lett.*, 2001, **42**, 673.