The Hetero-Diels–Alder Addition of Sulfur Dioxide: The Pseudo-Chair Conformation of a 4,5-Dialkylsultine

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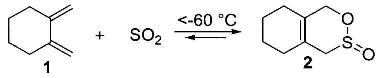
Abstract: Even unsubstituted butadiene adds to sulfur dioxide in the hetero-Diels–Alder mode more rapidly than in the chelotropic mode. The sultine can be observed in equilibrium with the diene and the sulfur dioxide only at low temperature and in the presence of CF_3COOH. Crystals of 4,5-dialkyl-sultine resulting from the SO_2 addition to 1,2-dimethylidenecyclohexane have been obtained at $-100\,^{\circ}C$ and analyzed by X-ray diffraction. Quantum chemical calculations have shown that hyperconjugative interactions within the sulfinyl moiety are responsible for the anomeric effects observed in sultines that prefer pseudo-chair conformations with pseudo-axial S=O bonds.

Keywords: ab initio calculations · conformation analysis · cycloadditions · heterocycles · sulfur

Introduction

Mono- and 2,3-dialkylbuta-1,3-dienes, which can adopt a *s-cis*-conformation, add to sulfur dioxide below $-50\,^{\circ}C$ giving the corresponding [1,2]oxathiin-3-oxides (sultines) that are unstable above $-40\,^{\circ}C$. The hetero-Diels–Alder additions are faster than expected chelotropic additions.[1–3] Except for 1,2-dimethylidenecycloalkanes,[3, 4] the reaction requires promotion by a protic or Lewis acid. With (*Z*)- and (*E*)-1-fluoromethylidene)-2-methylidene-3,4-dihydronaphthalene, the corresponding 6-fluorosultines have been recrystallized at $-100\,^{\circ}C$ and X-ray crystallography has shown sofa conformations with oxygen of the ring lying in average plane of the four carbon atoms and the S=O bond being either in a pseudo-equatorial[5] or a pseudo-axial position.[6] For simple non-fluorinated sultines, quantum chemical calculations predicted pseudo-chair conformations with the S=O bond preferring pseudo-axial positions.[7] Structures and conformations of the sultines in the solution were inferred from their NMR data.[1, 3, 4, 7] For the first time we have been able to recrystallize sultine **2** at $-100\,^{\circ}C$ (Scheme 1). We report now the first X-ray analysis of a non-fluorinated sultine. We also report a detailed computational analysis of the conformations which can be adopted by this sultine. The conformation observed for the crystalline sultine **2** was in fact found to be the most stable.



Scheme 1.

We have now established that:
1) the pseudo-chair is the more stable conformation of 1,2-dialkylsultine **2**,
2) the S=O bond prefers a pseudo-axial position,
3) pseudo-chair conformation of the sultine “communicates” with the pseudo chair of the cyclohexene unit in **2**,
4) anomeric effects are analyzed in terms of hyperconjugative interactions.

We report also for the first time that
5) butadiene itself adds slowly to SO_2 in the presence of CF_3COOH equilibrating with the parent sultine **3** at $-40\,^{\circ}C$.

Theoretical Methods

The potential energy surface for the hetero-Diels–Alder addition of sulfur dioxide to 2,3-dialkylbuta-1,3-dienes was

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Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author. Tables S4–S17, Figures S3–S6; X-ray analysis and calculations details.

DOI: 10.1002/chem.200304932

explored at the B3LYP/6-31G(d) level of theory,[8] which has been shown to provide reliable results on this type of systems.[3, 9]

The location of the minima on the potential energy surface was performed by means of standard algorithms as implemented in the GAUSSIAN 98 package of programs.[10] All stationary points located were characterized by computing the Hessian matrix and by checking the sign of the corresponding eigenvalues. This allowed us to perform the thermochemistry analysis using the ideal gas, rigid rotor, and harmonic oscillator approximations.[11]

The solvation effects were estimated by performing single-point B3LYP/6-31G(d) calculations with the self-consistent reaction field (SCFR) Onsager model, in which the solvent is represented by a dielectric constant.[12, 13] To obtain results applicable at the experimental concentration,[14] we computed the Gibbs free energies choosing the standard state in accordance with the condensed phase experimental conditions ($p = 272$).

In order to estimate the importance of hyperconjugative interactions on the stabilization of structures, the natural bond orbital (NBO)[15] 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 to determine the associated variational energy lowering. For a X-Y-Z system, the NBO deletion procedure allows one to compute the energy (E_{XYZ}) after zeroing the off-diagonal Fock matrix elements connecting the lone pairs n on X with the Y–Z σ^* antibonds. The difference $E_{total} - E_{XYZ}$ is the energy corresponding to the $n \rightarrow \sigma^*$ interactions.[15]

Abstract in French: *Pour la première fois on montre que le dioxyde de soufre et le butadiène s'équilibrent avec le 2-oxyde de [1,2]oxathiine (sultine* **3** *non-substituée) en présence de* CF_3COOH. *Les calculs quantiques B3LYP/6-31G(d) prévoient qu'une sultine non-fluorée adopte une conformation pseudo-chaise avec la liaison exocyclique S=O en position pseudo-axiale. Ce conformère est estimé être plus stable que les conformères bateaux ou pseudo-chaises avec la liaison S=O pseudo-equatoriale. Les interactions* $n(S) \rightarrow \sigma^*(O\text{-}C)$ *et* $n(O) \rightarrow \sigma^*(S{=}O)$ *jouent un rôle décisif dans la stabilité du conformère pseudo-chaise avec S=O exocyclique en position pseudo-axiale. Ces prédictions sont verifiées par la structure crystalline à –100°C du 3-oxyde de (S)-1,4,5,6,7,8-hexahydrobenzo[d]-[1,2]oxathiine (sultine* **2** *résultant de l'addition hetero-Diels–Alder du 1,2-dimethylidenecyclohexane) à basse température. C'est la première fois qu'une sultine non-fluorée a été crystallisée et caractérisée par diffraction des rayons X.*

Results and Discussion

Homochiral crystals of $\mathbf{2}\cdot SO_2$ were obtained by reaction of diene **1**[16] in a 1:3.3 mixture of SO_2/MeOH at –78°C and cooling to –100°C.[17] X-ray diffraction at 140 K (Figure 1) showed that **2** exhibits a pseudo-chair conformation for the cyclohexane and the sultine units. Both pseudo-chairs have the pseudo P chirality with respect to the pseudo C_2 axis. Importantly, the S=O bond resides in a pseudo-axial position. Bond lengths involving sulfur atom are S–C 1.847(5) Å, S=O 1.520(4) Å and S–O 1.655(4) Å. Typical distorsion from tetrahedral geometry may be reflected by the O1–S–C4 bond angle of 98.1(2)°. The distances reflect an electronic delocalisation occurring in the O–S=O system. The crystal packing shows C–H···O hydrogen bonds (C···O 3.486(7) Å, C–H···O 157°). An important feature of the crystal packing is the weak interaction between the exocyclic S=O group and the SO_2 molecules. Each oxygen atom interacts with two sulfur atoms (O···S 2.841(4), 2.850(4) Å). These interactions are below the sum of the van der Waals radii for these two atoms (3.32 Å)[18] and form an infinite one-dimensional chain along the base vector [100] (see Supporting Information).

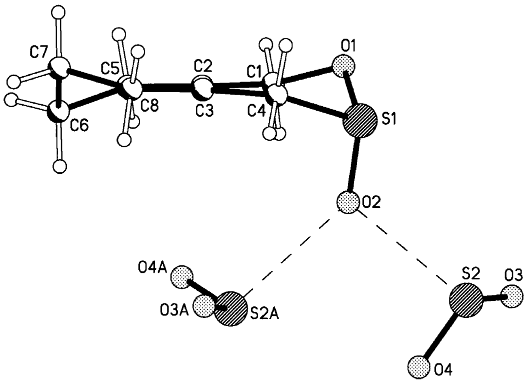

Figure 1. Ball and stick representation of (S)-1,4,5,6,7,8-hexahydrobenzo[d][1,2]oxathiin-3-oxide in $\mathbf{2}\cdot SO_2$.

The six minima conformations of 1,2-dialkylsultine **2** located on the potential energy hypersurface are collected in Figure 2. Such structures correspond to the three conformers **C2**, **B2**, **S2** and their "diastereomeric species" **C2′**, **B2′**, **S2′**, in which the sultine adopts a pseudo-chair (C) conformation with pseudo-axial S=O bond, a boat conformation (B) with pseudo-axial S=O bond, and another pseudo-chair conformation (S) with pseudo-equatorial S=O bond (see further details of the calculations in the Supporting Information).

In all these conformers the cyclohexene moiety adopts pseudo-chair conformations. Table 1 gives the most representative geometrical parameters for **C2** as computed at the B3LYP/6-31G(d) level. Comparison with the corresponding experimental values shows the reliability of the level of theory employed. The calculated relative (to reactants) enthalpies for the reaction $\mathbf{1}+SO_2 \rightleftharpoons \mathbf{2}$ are given in Table 2. They show that conformer **C2**, which corresponds to that found in the crystalline state with $\mathbf{2}\cdot\mathbf{SO_2}$, is the most stable. The calculations predict that **C2′** is 0.6 kcal mol^{-1} less stable than **C2**,

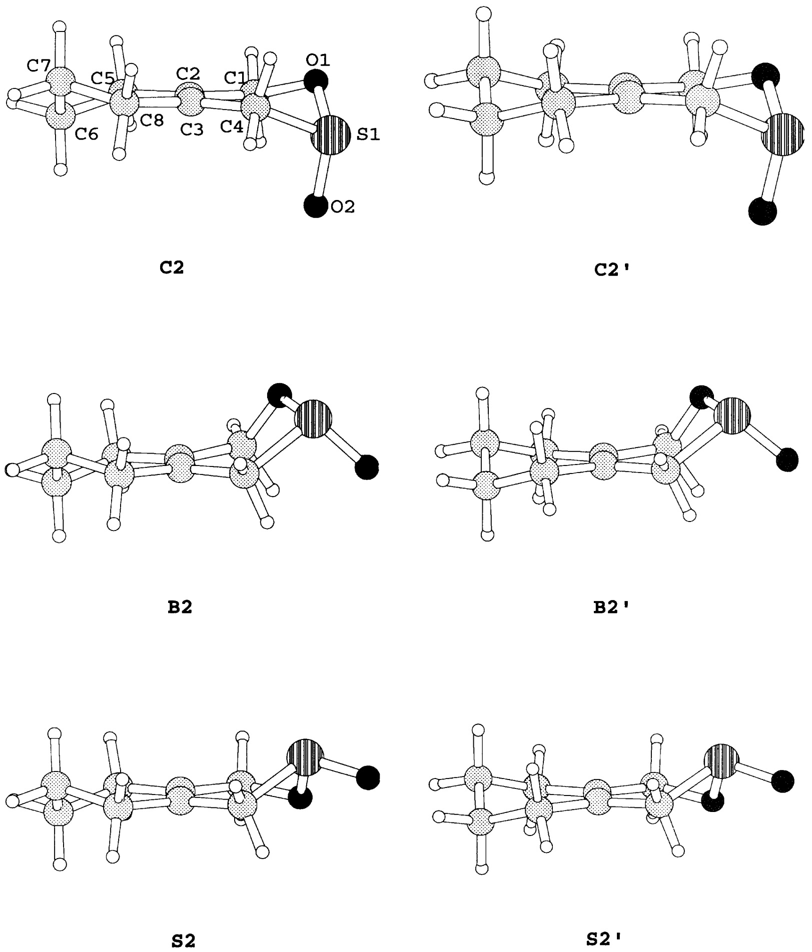

Figure 2. Different conformations of **2** as computed at the B3LYP/6-31G(d) level.

Table 1. Some representative bond lengths [Å] and angles [°] for 1,4,5,6,7,8-hexahydro-2,3-benzoxathiin-3-oxide (**2**).

Parameter	B3LYP/6-31G(d)	Exptl
S1–O2	1.492	1.520(4)
S1–O1	1.687	1.655(4)
S1–C4	1.844	1.847(5)
O1–C1	1.439	1.461(6)
O2-S1-O1	110.1	107.6(2)
O2-S1-C4	106.6	105.9(2)
O1-S1-C4	94.0	98.1(2)
C1-O1-S1	114.2	114.9(3)
O1-C1-C2	115.1	115.5(4)
O2-S1-O1-C1	43.7	48.2(4)
C4-S1-O1-C1	−65.7	−61.4(4)
S1-O1-C1-C2	55.6	52.5(5)
O1-C1-C2-C3	−15.4	−14.0(7)
O2-S1-C4-C3	−65.0	−68.8(4)
O1-S1-C4-C3	47.4	42.1(4)

indicating that the pseudo-chairs of the sultine and cyclohexene moiety "communicate" with each other.

Contrary to what has been found for 6-fluorosultines[5, 6] sofa conformers of the sultines with intra-ring oxygen atom lying in the plane of four carbon atoms of the sultine are not energy minima. Conformers **S2** and **S2′** with pseudo-equatorial S=O bonds are calculated to be about 2–3 kcal mol^{-1} less stable than the pseudo-chair conformers **C2** and **C2′** with pseudo-axial S=O bonds. Interestingly, the boat conformers **B2** and **B2′** with pseudo-axial S=O bond are only 1–2 kcal mol^{-1} less stable than **C2** and **C2′**. Applying the natural bond orbital (NBO)[15] analysis we obtain the different hyperconjugative contributions shown in Table 3.

Interestingly, the total contribution ($n \rightarrow \sigma^*$) is higher in the boat conformers **B2** and **B2′** than in the pseudo-chair conformers **C2** and **C2′**; this suggests that the latter result from competition between stabilizing anomeric effects and avoided eclipsing interactions (steric effect). The calculations show that pseudo-chairs **S2** and **S2′** cannot enjoy hyperconjugative interactions as much as **C2** and **C2′**. The $n(\mathrm{S1}) \rightarrow \sigma^*(\mathrm{O1\text{-}C1})$ interaction as well as the $n(\mathrm{O1}) \rightarrow \sigma^*(\mathrm{S} \rightarrow \mathrm{O})$ are playing decisive roles.

Butadiene is much less reactive than 2,3-dialkylbuta-1,3-dienes toward SO_2 (Figure 3) and up to now the parent sultine **3** had never been observed. When a 2.5 mol^{-1} dm^{-3} solution of butadiene in $SO_2/CD_2Cl_2/CF_3COOH$ was left at −40 °C, equilibrium with **3** was observed after a week (K(butadiene+SO_2 $\rightleftharpoons$ **3**) $\cong 4.4 \times 10^{-3}$ mol^{-1} dm^{-3} at −40 °C (CH_3CN as internal reference).

Using an entropy of reaction of −42 cal K^{-1} mol^{-1} for this cycloaddition,[7] one estimates K(butadiene+SO_2 $\rightleftharpoons$ **3**) = 0.02 dm^3 mol^{-1} at −60 °C to be compared with K(isoprene+SO_2 $\rightleftharpoons$ 4-methylsultine) = 0.03 dm^3 mol^{-1} at the same temperature.[7] The ^{1}H NMR spectrum of **3** is consistent with a pseudo-chair conformation as for **2** (Figure 4).

Table 2. Thermodynamic data[a] (relative to reactants) as computed at 213.15 K for the different conformers of the 1,4,5,6,7,8-hexahydro-2,3-benzoxathiin-3-oxide. ΔE, ΔH and ΔG in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}.

Structure	ΔE	ΔH	ΔS	ΔG[b]
C2	−8.5	−9.4	−45.2	−2.1
C2′	−7.5	−8.8	−44.6	−1.7
B2	−6.5	−7.3	−43.5	−0.4
B2′	−6.3	−7.1	−43.5	−0.2
S2	−5.0	−5.8	−44.9	1.4
S2′	−5.6	−6.5	−45.2	0.8

[a] Solvation energy as estimated by means of the Onsager model is included. [b] ΔG includes the correction factor for changing the standard state function from 1 atm to 272 atm [passing from gas phase to condensed phase; see R. L. Martin, P. J. Hay, L. R. Pratt, *J. Phys. Chem. A* **1998**, *102*, 3565].

Table 3. Different hyperconjugative contributions (ΔE/kcal mol^{-1})[a] calculated at the B3LYP/6-31G(d) level of theory for the electron transfers from lone pair (n) to empty σ^* and π^* orbitals in the conformers of sultine.

Structure	n(O1) → σ*(S1,O2)	n(O2) → σ*(S1,O1)	n(O2) → σ*(S1,C4)	n(S1) → σ*(O1,C1)	ΔE_{total}
C2	7.17	43.0	21.8	4.58	76.5
C2′	7.29	43.1	22.1	4.70	$\boxed{77.3}$
B2	10.6	42.2	22.1	4.95	$\boxed{79.9}$
B2′	10.7	42.3	22.1	4.92	80.0
S2	2.84	42.2	22.1	1.37	68.6
S2′	2.69	42.3	21.8	1.36	68.2

[a] See Figure 2 for notation.

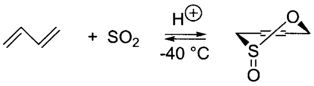

Figure 3.

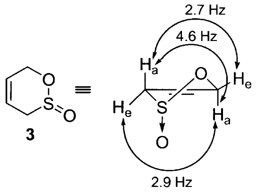

Figure 4.

Conclusion

Butadiene and alkylsubstituted derivatives undergo hetero-Diels–Alder additions with SO_2 activated with protic or Lewis acid below −40 °C, a reaction that is faster than the well-known chelotropic addition of SO_2.[19] X-ray diffraction data confirm predictions of quantum chemical calculations that the non-fluorinated sultine prefer pseudo-chair conformations with pseudo-axial S=O bonds. The sulfinate moiety of the non-fluorinated sultine manifests a conformational anomeric effect that our computational approach shows is due to hyperconjugative interactions.

Experimental Section

For general methods, see ref. [6].

1,4,5,6,7,8-Hexahydro-2,3-benzoxathiin-3-oxide (2): On the vacuum line, dry SO_2 (1.4 mL) was transferred to a frozen (liq. N_2) solution of 1,2-dimethylidenecyclohexane (**1**)[16] (436 mg, 4.03 mmol) in anhydrous methanol (5 mL). Dry SO_2 was obtained by degassing SO_2 and filtering (gas) through a column of alkaline aluminium oxide 90 (act. I, Merck). It was then mixed with quinoline and iodine and distilled from that mixture on the vacuum line. The mixture of **1**+SO_2 and MeOH was allowed to warm slowly to −78 °C and was kept at this temperature for 5 d. The crystals of **2**·SO_2 were collected at this temperature and measured at −100 °C. Data for **2**: ^1H NMR (400 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 193 K): $\delta = 1.56$ (m, 2H), 1.79 (m, 2H), 1.86 (m, 2H), 1.91 (m, 2H), 2.75/3.39 (2d, $^2J = 17.3$, 2H, $H_2C(5)$), 4.14/4.25 (2d, $^2J = 15.9$ Hz, 2H, $H_2C(2)$); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CFCl_3$, 193 K): $\delta = 21.3$ (t, $^1J(C,H) = 129$ Hz), 22.1 (t, $^1J(C,H) = 131$ Hz), 24.7 (t, $^1J(C,H) = 126$ Hz), 29.0 (t, $^1J(C,H) = 128$ Hz), 49.3 (t, $^1J(C,H) = 138$ Hz, C(5)), 60.0 (t, $^1J(C,H) = 150$ Hz, C(2)), 117.8 (s, C(6)), 125.9 (s, C(1)).

The same mixture allowed to stand at −40 °C for 5 d gave crystalline 1,3,4,5,6,7-hexahydrobenzo[c]thiophene 2,2-dioxide, white solid. ^1H NMR (400 MHz, CD_2Cl_2/SO_2, 294 K): $\delta = 1.78$ (m, 4H), 2.10 (m, 4H), 3.68 (m, 4H); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 294 K): $\delta = 22.7$ (t, $^1J(C,H) = 129$ Hz), 26.4 (t, $^1J(C,H) = 127$ Hz), 60.3 (t, $^1J(C,H) = 142$ Hz), 128.9 (s, C(1), C(5)).

Crystal of **2**·SO_2: orthorhombic, $a = 8.294(2)$, $b = 8.4181(2)$, $c = 16.066(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 12121.7(5)$ Å^3, $\rho = 1.399$ Mg m^{-3}, data/restraints/parameter = 1945/0/127, *ab* 140(2) K.

CCDC-198362 (**2**·SO_2) and -198363 (1,3,4,5,6,7-hexahydrobenzo[c]thiophene 2,2-dioxide) contain 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 CB21EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

3,6-Dihydro-1,2-oxathiin 2-oxide (3): A 1:1 mixture of butadiene and CF_3COOH (80 mg) in $CDCl_3$ (0.15 mL) containing 2% CH_3CN (internal reference) was placed in a 5 mm pyrex NMR tube and degassed (freeze/thaw cycles) on the vacuum line. Sulfur dioxide (0.3 mL) dried as above was transferred to this mixture (liq. N_2). The NMR tube was sealed off from the vacuum line and immersed in a EtOH bath maintained at −40 °C for 7 d until equilibrium was reached (control by ^1H NMR). An equilibrium constant $K \cong 4.4 \times 10^{-3}$ mol^{-3} dm^3 was evaluated at −40 °C for butadiene+SO_2 $\rightleftharpoons$ sultine **3**. ^1H NMR (400 MHz, $CD_2Cl_2/SO_2/CF_3COOH$, CH_3CN, 233 K): $\delta = 5.88$ (dm, $^3J(H\text{-}4,H\text{-}5) = 11.6$ Hz, H-5), 5.66 (ddddd, $^3J(H\text{-}4,H\text{-}5) = 11.6$, $^3J(H_e\text{-}3,H\text{-}4) = 6.4$, $^3J(H_a\text{-}3,H\text{-}4) = 2.2$, $^4J(H\text{-}4,H_e\text{-}6) = {}^4J(H_a\text{-}6,H\text{-}4) = 2.2$ Hz, H-4), 4.53 (ddddd, $^2J = 16.7$, $^3J(H\text{-}5,H_a\text{-}6) = {}^4J(H\text{-}4,H_a\text{-}6) = 2.2$, $^5J(H_a3,H_a\text{-}6) = 4.6$, $^5J(H_e\text{-}3,H_a\text{-}6) = 2.9$ Hz, H_a-6), 4.38 (dddd, $^2J = 16.7$, $^3J(H\text{-}5,H_e\text{-}6) = 2.7$, $^4J(H\text{-}4,H_e\text{-}6) = 2.2$, $^5J(H_a\text{-}3,H_e\text{-}6) = 2.7$ Hz, H_e-6), 3.43 (dm, $^2J = 17.1$ Hz, H_a-3), 3.07 (ddd, $^2J = 17.1$, $^3J(H_e\text{-}3,H\text{-}4) = 6.4$, $^5J(H_e\text{-}3,H_a\text{-}6) = 2.9$ Hz, H_e-3); ^{13}C NMR (100.6 MHz, $CD_2Cl_2/SO_2/CF_3COOH$, CH_3CN, 233 K): $\delta = 124.3$ ((d, $^1J(C,H) = 163$ Hz, C-5), 113.8 (d, $^1J(C,H) = 170$ Hz, C-4) 59.1 (t, $^1J(C,H) = 153$ Hz, C-6), 45.3 (t, $^1J(C,H) = 141$ Hz, C-3).

Acknowledgement

This work was supported by the Swiss National Science Foundation, the Centro Svizzero di Calcolo Scientifico (Manno), the SOCRATES (Oviedo/Lausanne) program, the Office Fédéral de l'Enseignement et de la Science (Bern, European COST D13/010/01 action), and by DGI (BQU 2001-3600-CO2-01, Madrid, Spain).

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Received: March 10, 2003 [F4932]