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Journal of Organic Chemistry

Competition between Hetero-Diels-Alder and Cheletropic Addition of Sulfur Dioxide. Theoretical and Experimental Substituent Effects on the Relative Stability of 3,6-Dihydro-1,2-oxathiin-2-oxides (Sultines) and 2,5-dihydrothiophene-1,1,-dioxides (Sulfolenes). Anomeric Effects in Sultine and 6-substituted Derivatives.

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SUPPLEMENTARY MATERIAL

2-Acetoxy-2,5-dihydrothiophene-1,1-dioxide (11d). IR (KBr) ν 2975, 2940, 1755, 1325, 1310, 1215, 1130, 1045 cm^{-1}. ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ_C 20.3 (q, ^1J(C,H) = 131, C(2')), 54.3 (t, ^1J(C,H) = 145, C(5)), 83.4 (d, ^1J(C,H) = 167, C(2)), 125.2 (d, ^1J(C,H) = 174, C(4)), 130.1 (d, ^1J(C,H) = 173, C(3)). CI-MS (NH_3): m/z 194 (0.1, M+NH_3), 166 (1.8), 164 (1.5), 117 (10), 113 (5), 112 (26), 99 (1.5), 89 (3), 83 (1.5), 71 (8), 70 (100). Anal. calc. for $C_6H_8O_4S$ (176.19): C 40.90, H 4.58, S 18.20; found: C 40.88, H 4.61, S 18.22.

Data for **2-Chloro-2,5-dihydrothiophene-1,1-dioxide (11e)**. IR (KBr) ν 1330, 1254, 1145, 1120, 795, 735, 645 cm^{-1}; CI-MS (NH_3) m/z 117 (4), 109 (12), 88 (100). Anal. calc. for $C_4H_5ClO_2S$ (152.45): C 31.59, H 3.32; found: C 31.53, H 3.26.

Data for **2-Bromo-2,5-dihydrothiophene-1,1-dioxide (11f)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 3.83 (dddd, ^2J(H-5,H'-5) = 16.9, ^3J(H-4,H-5) = ^4J(H-3,H-5) = 2.5, ^5J(H-2,H-5) = 1.5, H-C(5)), 3.88 (dddd, ^2J = 16.9, ^3J(H-4,H'-5) = 3.0, ^4J(H-3,H'-5) = 2.3, ^5J(H-2,H'-5) = 1.0, H'-C(5)), 5.36 (m, ^4J(H-2,H-4) = 1.2, H-C(2)), 6.23 (dddd, ^3J(H-3,H-4) = 8.5, ^3J(H-4,H-5) = 3.0, ^3J(H-4,H-5) = 2.5, ^4J(H-2,H-4) = 1.2, H-C(4)), 6.32 (dddd, ^3J(H-3,H-4) = 8.5, ^3J(H-2,H-3) = 2.3, ^4J(H-3,H-5) = 2.5, ^4J(H-3,H'-5) = 2.3, H-C(3)); ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ_C 57.7 (t, ^1J(C,H) = 145, C(5)), 58.3 (d, 155, C(2)), 126.6 (d, 176, C(4)), 129.5 (d, 176, C(3)). IR (film) ν 2975, 1325, 1250, 1140, 760 cm^{-1}. CI-MS (NH_3) m/z 197 ($M^{+\bullet}$, 1), 134 (90), 132 (100). Anal. calc. for $C_4H_5BrO_2S$ (197.1): C 24.50, H 2.57; found: C 24.55, H 2.66.

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Table 1. Crystal data and structure refinement for **11d**

Identification code	Frederic Monnat #1
Empirical formula	$C_6H_8O_4S$
Formula weight	176.18
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.0306(8) Å $\alpha = 90°$ b = 8.0766(10) Å $\beta = 90°$ c = 14.135 (2) Å $\gamma = 90°$
Volume	802.7 (2) $Å^3$
Z	4
Density (calculated)	1.458 Mg/m^3
Absorption coefficient	0.367 mm^{-1}
F(000)	368
θ range for data collection	2.88 to 23.29°
Index ranges	$-7 \le h \le 6$, $-8 \le k \le 8$, $-12 \le l \le 15$
Reflections collected	3077
Independent reflections	1141 (R_{int} = 0.0250)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1141 / 0 / 134
Goodness-of-fit on F^2	2.044
Final R indices [I>2σ(I)]	R1 = 0.0260, wR2 = 0.0518
R indices (all data)	R1 = 0.0283, wR2 = 0.0526
Absolute structure parameter	-0.04 (8)
Extinction coefficient	0.024 (2)
Largest diff. peak and hole	0.134 and –0.131 $eÅ^{-3}$

Frederic Monnat #1: 2-Acetoxy-2,5-dihydrothiophene-1,1-dioxide Sulfolene **11d**

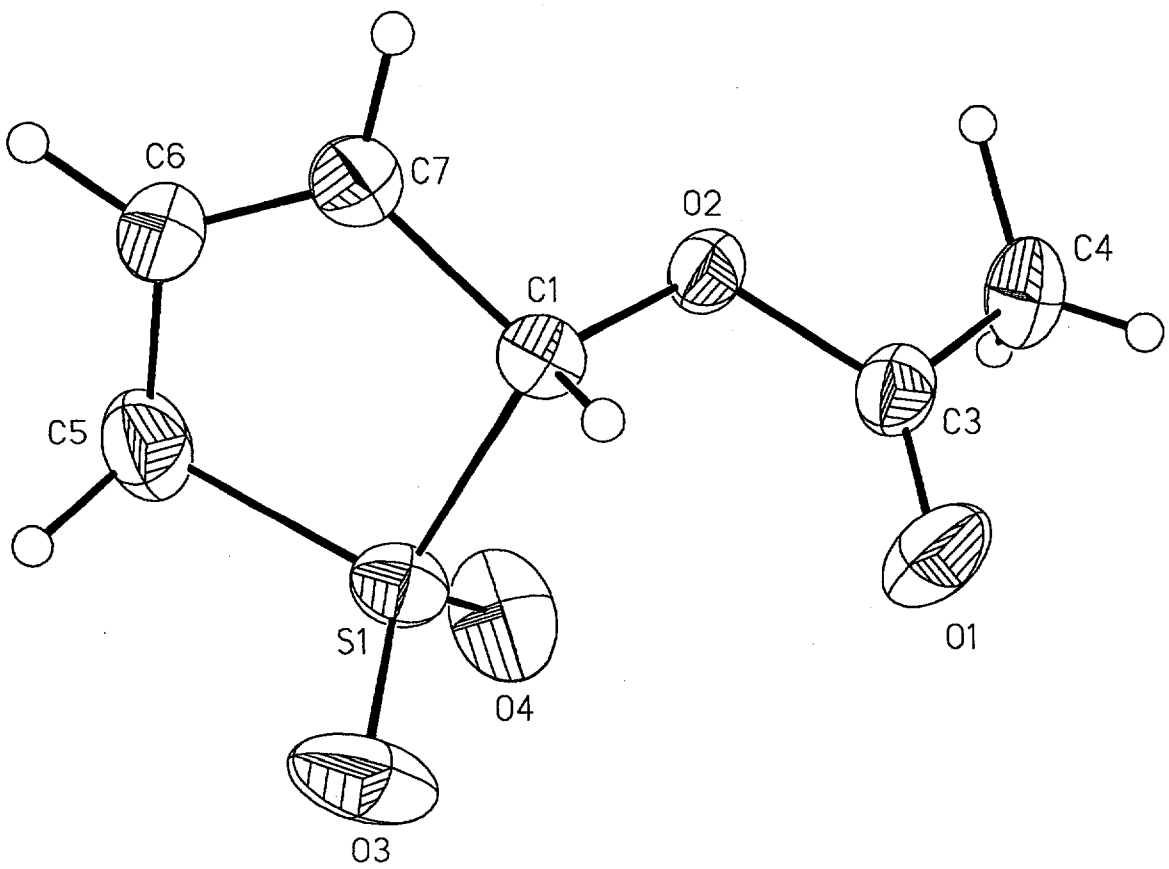


Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for **11d**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	1961(1)	510(1)	4758(1)	50(1)
O(3)	185(2)	-325(2)	4772(2)	89(1)
O(4)	2449(3)	1498(2)	3961(1)	90(1)
C(1)	3848(3)	-990(2)	4984(2)	43(1)
O(1)	3780(3)	-2081(2)	3233(1)	75(1)
O(2)	5403(2)	-737(2)	4360(1)	47(1)
C(3)	5170(4)	-1346(3)	3465(2)	51(1)
C(4)	6860(6)	-908(5)	2870(2)	70(1)
C(5)	2258(5)	1672(4)	5823(2)	73(1)
C(6)	3655(4)	676(4)	6372(2)	70(1)
C(7)	4445(4)	-605(4)	5964(2)	59(1)

Table 3. Bond lengths [Å] and angles [°] for **11d**.

S(1)-O(3)	1.419(2)	S(1)-O(4)	1.423(2)
S(1)-C(5)	1.787(3)	S(1)-C(1)	1.825(2)
C(1)-O(2)	1.419(2)	C(1)-C(7)	1.480(3)
C(1)-H(1)	0.98(2)	O(1)-C(3)	1.189(3)
O(2)-C(3)	1.367(3)	C(3)-C(4)	1.499(4)
C(4)-H(4B)	0.80(3)	C(4)-H(4C)	0.86(3)
C(4)-H(4D)	1.13(3)	C(5)-C(6)	1.488(4)
C(5)-H(5A)	1.02(4)	C(5)-H(5B)	0.86(3)
C(6)-C(7)	1.308(4)	C(6)-H(6)	0.93(3)
C(7)-H(7)	0.91(2)		

O(3)-S(1)-O(4)	119.33(13)	O(3)-S(1)-C(5)	109.9(2)
O(4)-S(1)-C(5)	110.2(2)	O(3)-S(1)-C(1)	108.76(10)
O(4)-S(1)-C(1)	109.65(11)	C(5)-S(1)-C(1)	96.64(13)
O(2)-C(1)-C(7)	109.4(2)	O(2)-C(1)-S(1)	110.83(13)
C(7)-C(1)-S(1)	103.4(2)	O(2)-C(1)-H(1)	113.5(12)
C(7)-C(1)-H(1)	113.6(13)	S(1)-C(1)-H(1)	105.7(12)
C(3)-O(2)-C(1)	115.5(2)	O(1)-C(3)-O(2)	122.2(2)
O(1)-C(3)-C(4)	127.9(3)	O(2)-C(3)-C(4)	109.8(3)
C(3)-C(4)-H(4B)	107(2)	C(3)-C(4)-H(4C)	111(2)
H(4B)-C(4)-H(4C)	100(3)	C(3)-C(4)-H(4D)	107.4(14)
H(4B)-C(4)-H(4D)	124(3)	H(4C)-C(4)-H(4D)	107(3)
C(6)-C(5)-S(1)	103.4(2)	C(6)-C(5)-H(5A)	107(2)
S(1)-C(5)-H(5A)	100(2)	C(6)-C(5)-H(5B)	122(2)
S(1)-C(5)-H(5B)	103(2)	H(5A)-C(5)-H(5B)	118(3)
C(7)-C(6)-C(5)	118.6(3)	C(7)-C(6)-H(6)	126(2)
C(5)-C(6)-H(6)	116(2)	C(6)-C(7)-C(1)	117.3(3)
C(6)-C(7)-H(7)	124(2)	C(1)-C(7)-H(7)	118(2)

Symmetry transformations used to generate equivalent atoms:

Torsional angles [°] for **11d**

Selected torsion angles		
136.34	(0.16)	O3 – S1 – C1 – O2
4.23	(0.18)	O4 – S1 – C1 – O2
-110.00	(0.19)	C5 – S1 – C1 – O2
106.50	(0.17)	O3 – S1 – C1 – C7
121.39	(0.17)	O4 – S1 – C1 – C7
7.16	(0.21)	C5 – S1 – C1 – C7
167.86	(0.21)	C7 – C1 – O2 – C3
-78.78	(0.19)	S1 – C1 – O2 – C3
-2.11	(0.31)	C1 – O2 – C3 – O1
176.66	(0.23)	C1 – O2 – C3 – C4
105.05	(0.22)	O3 – S1 – C5 – C6
-121.48	(0.22)	O4 – S1 – C5 – C6
-7.69	(0.25)	C1 – S1 – C5 – C6
6.60	(0.37)	S1 – C5 – C6 – C7
-1.34	(0.41)	C5 – C6 – C7 – C1
113.55	(0.25)	O2 – C1 – C7 – C6
-4.58	(0.29)	S1 – C1 – C7 – C6

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for **11d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + 2hka*b*U_{12}]

	U11	U22	U33	U23	U13	U12
S(1)	46(1)	43(1)	63(1)	6(1)	-4(1)	1(1)
O(3)	43(1)	65(1)	157(2)	-5(1)	-20(1)	-7(1)
O(4)	119(2)	72(1)	78(1)	36(1)	20(1)	29(1)
C(1)	41(1)	38(1)	49(2)	2(1)	0(1)	-1(1)
O(1)	81(2)	82(1)	61(1)	-18(1)	-14(1)	-22(1)
O(2)	45(1)	54(1)	43(1)	-12(1)	0(1)	-5(1)
C(3)	64(2)	44(2)	45(2)	-5(1)	-3(1)	7(1)
C(4)	83(2)	74(2)	52(2)	-12(2)	14(2)	0(2)
C(5)	70(2)	68(2)	80(2)	-16(2)	12(2)	10(2)
C(6)	61(2)	95(5)	52(2)	-17(2)	1(1)	2(2)
C(7)	52(2)	79(2)	47(2)	0(2)	0(1)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **11d**.

	x	y	z	U(eq)
H(1)	3256(28)	-2075(25)	4918(15)	57(6)
H(4B)	6876(46)	-1538(41)	2432(24)	105(13)
H(4C)	6677(45)	7(41)	2569(24)	102(13)
H(4D)	8098(43)	-698(36)	3365(21)	103(10)
H(5A)	954(51)	1479(37)	6123(23)	126(13)
H(5B)	2512(36)	2647(38)	5617(21)	95(12)
H(6)	3839(40)	1003(36)	6996(20)	98(10)
H(7)	5425(35)	-1198(29)	6216(17)	62(8)

Table 6. Crystal data and structure refinement for **11e**

Identification code	Elena Roversi #2
Empirical formula	$C_4H_5ClO_2S$
Formula weight	152.59
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.839(2) Å $\alpha = 90°$ b = 9.493(2) Å $\beta = 102.76(3)°$ c = 13.551(3) Å $\gamma = 90°$
Volume	1234.4 (4) $Å^3$
Z	8
Density (calculated)	1.642 Mg/m^3
Absorption coefficient	0.858 mm^{-1}
F(000)	624
θ range for data collection	2.12 to 23.90°
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 10$, $-15 \le l \le 10$
Reflections collected	4576
Independent reflections	1789 (R_{int} = 0.0502)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1789 / 0 / 186
Goodness-of-fit on F^2	1.675
Final R indices [I>2σ(I)]	R1 = 0.0567, wR2 = 0.1882
R indices (all data)	R1 = 0.0592, wR2 = 0.1917
Extinction coefficient	0.00 (3)
Largest diff. peak and hole	0.795 and –0.440 e $Å^{-3}$

Elena Roversi #2: 2-Chloro-2,5-dihydrothiophene-1, -dioxide 2-Chlorosulfolene **11e**

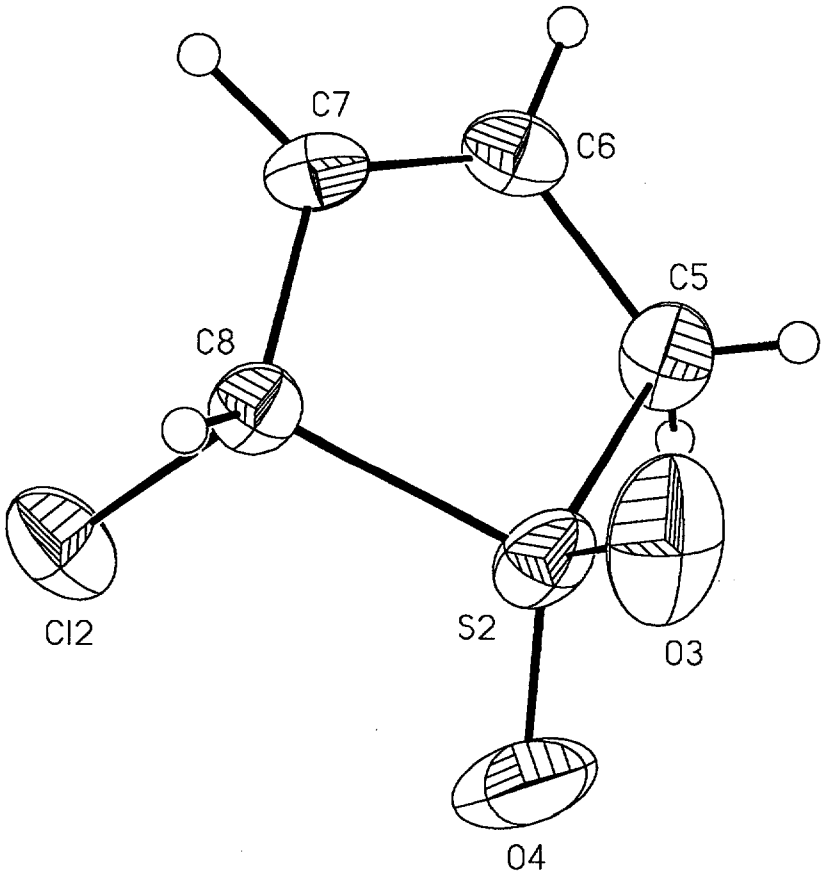


Table 7. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for **11e**. U(eq) is defined as one third of the trace of orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	3855(1)	2165(1)	9229(1)	48(1)
S(2)	1111(1)	1980(1)	6216(1)	55(1)
Cl(1)	5723(1)	855(1)	8058(1)	71(1)
Cl(2)	-1024(1)	1452(1)	7424(1)	74(1)
O(1)	2793(3)	3233(4)	9021(2)	71(1)
O(2)	3436(3)	740(3)	9260(3)	75(1)
O(3)	2354(3)	2819(4)	6391(3)	87(1)
O(4)	1237(4)	486(4)	6339(3)	96(1)
C(1)	4981(3)	2471(3)	8346(2)	45(1)
C(2)	6047(3)	3450(3)	8927(3)	51(1)
C(3)	6113(4)	3532(3)	9901(3)	54(1)
C(4)	5130(4)	2656(4)	10325(3)	55(1)
C(5)	26(4)	2457(5)	5028(3)	58(1)
C(6)	-890(3)	3566(3)	5312(3)	51(1)
C(7)	-891(3)	3715(3)	6265(3)	49(1)
C(8)	2(3)	2747(3)	6981(2)	44(1)

Torsional angles [°] for **11e**

Selected torsion angles		
-138.39	(0.23)	O2 – S1 – C1 – C2
90.08	(0.24)	O1 – S1 – C1 – C2
-21.43	(0.24)	C4 – S1 – C1 – C2
-18.93	(0.24)	O2 – S1 – C1 – C11
-150.47	(0.18)	O1 – S1 – C1 – C11
98.02	(0.20)	C4 – S1 – C1 – C11
102.03	(0.33)	C11 – C1 – C2 – C3
15.92	(0.35)	S1 – C1 – C2 – C3
-0.14	(0.47)	C1 – C2 – C3 – C4
-16.16	(0.40)	C2 – C3 – C4 – S1
138.96	(0.25)	O2 – S1 – C4 – C3
-87.77	(0.28)	O1 – S1 – C4 – C3
21.32	(0.27)	C1 – S1 – C4 – C3
134.06	(0.30)	O4 – S2 – C5 – C6
-92.17	(0.28)	O3 – S2 – C5 – C6
17.24	(0.29)	C8 – S2 – C5 – C6
-12.49	(0.42)	S2 – C5 – C6 – C7
-1.16	(0.47)	C5 – C6 – C7 – C8
-105.69	(0.31)	C6 – C7 – C8 – C12
13.90	(0.35)	C6 – C7 – C8 – S2
-134.62	(0.24)	O4 – S2 – C8 – C7
93.86	(0.25)	O3 – S2 – C8 – C7
-17.90	(0.26)	C5 – S2 – C8 – C7
-15.93	(0.25)	O4 – S2 – C8 – C12
-147.45	(0.21)	O3 – S2 – C8 – C12
100.79	(0.22)	C5 – S2 – C8 – C12

Table 8. Bond lengths [Å] and angles [°] for **11e**.

S(1)-O(2)	1.418(3)	S(1)-O(1)	1.439(3)
S(1)-C(4)	1.781(3)	S(1)-C(1)	1.825(3)
S(2)-O(4)	1.429(4)	S(2)-O(3)	1.435(3)
S(2)-C(5)	1.782(4)	S(2)-C(8)	1.815(3)
Cl(1)-C(1)	1.779(3)	Cl(2)-C(8)	1.777(3)
C(1)-C(2)	1.489(4)	C(1)-H(1)	0.93(4)
C(2)-C(3)	1.310(6)	C(2)-H(2)	0.94(5)
C(3)-C(4)	1.484(6)	C(3)-H(3)	0.97(4)
C(4)-H(4A)	0.86(5)	C(4)-H(4B)	0.94(5)
C(5)-C(6)	1.491(6)	C(5)-H(5A)	0.98(4)
C(5)-H(5B)	0.80(6)	C(6)-C(7)	1.299(5)
C(6)-H(6)	0.93(4)	C(7)-C(8)	1.477(4)
C(7)-H(7)	0.94(4)	C(8)-H(8)	0.97(4)

O(2)-S(1)-O(1)	118.4(2)	O(2)-S(1)-C(4)	112.4(2)
O(1)-S(1)-C(4)	109.0(2)	O(2)-S(1)-C(1)	113.2(2)
O(1)-S(1)-C(1)	106.2(2)	C(4)-S(1)-C(1)	95.0(2)
O(4)-S(2)-O(3)	118.9(2)	O(4)-S(2)-C(5)	112.1(2)
O(3)-S(2)-C(5)	109.1(2)	O(4)-S(2)-C(8)	112.3(2)
O(3)-S(2)-C(8)	106.3(2)	C(5)-S(2)-C(8)	95.7(2)
C(2)-C(1)-Cl(1)	112.3(2)	C(2)-C(1)-S(1)	102.2(2)
Cl(1)-C(1)-S(1)	110.1(2)	C(2)-C(1)-H(1)	119(2)
Cl(1)-C(1)-H(1)	105(3)	S(1)-C(1)-H(1)	109(3)
C(3)-C(2)-C(1)	116.3(3)	C(3)-C(2)-H(2)	126(3)
C(1)-C(2)-H(2)	118(3)	C(2)-C(3)-C(4)	117.7(3)
C(2)-C(3)-H(3)	125(2)	C(4)-C(3)-H(3)	117(2)
C(3)-C(4)-S(1)	102.9(3)	C(3)-C(4)-H(4A)	115(3)
S(1)-C(4)-H(4A)	105(3)	C(3)-C(4)-H(4B)	114(3)
S(1)-C(4)-H(4B)	105(3)	H(4A)-C(4)-H(4B)	114(4)
C(6)-C(5)-S(2)	102.8(3)	C(6)-C(5)-H(5A)	121(2)
S(2)-C(5)-H(5A)	105(3)	C(6)-C(5)-H(5B)	119(4)
S(2)-C(5)-H(5B)	108(4)	H(5A)-C(5)-H(5B)	100(5)
C(7)-C(6)-C(5)	117.9(3)	C(7)-C(6)-H(6)	126(2)
C(5)-C(6)-H(6)	116(2)	C(6)-C(7)-C(8)	117.0(3)
C(6)-C(7)-H(7)	124(2)	C(8)-C(7)-H(7)	119(2)
C(7)-C(8)-Cl(2)	110.6(2)	C(7)-C(8)-S(2)	102.7(2)
Cl(2)-C(8)-S(2)	111.9(2)	C(7)-C(8)-H(8)	121(2)
Cl(2)-C(8)-H(8)	106(2)	S(2)-C(8)-H(8)	106(2)

Symmetry transformations used to generate equivalent atoms

Table 9. Anisotropic displacement parameters [$Å^2$ x 10^3] for **11e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + 2hka*b*U^{12}]

	U11	U22	U33	U23	U13	U12
S(1)	34(1)	53(1)	53(1)	-2(1)	5(1)	-10(1)
S(2)	37(1)	74(1)	49(1)	-6(1)	1(1)	16(1)
Cl(1)	66(1)	69(1)	77(1)	-24(1)	17(1)	2(1)
Cl(2)	70(1)	81(1)	68(1)	23(1)	13(1)	-11(1)
O(1)	40(1)	95(2)	74(2)	-7(2)	5(1)	13(1)
O(2)	68(2)	68(2)	87(2)	2(1)	15(1)	-34(1)
O(3)	35(1)	156(3)	68(2)	-12(2)	5(1)	-16(2)
O(4)	106(2)	84(2)	90(2)	-9(2)	3(2)	56(2)
C(1)	39(2)	49(2)	43(2)	0(1)	2(1)	-2(1)
C(2)	37(2)	40(2)	73(2)	7(1)	4(1)	-12(1)
C(3)	43(2)	40(2)	67(2)	-8(1)	-12(2)	-3(1)
C(4)	52(2)	59(2)	47(2)	-4(2)	-3(2)	1(2)
C(5)	45(2)	84(3)	43(2)	-4(2)	1(1)	4(2)
C(6)	42(2)	50(2)	54(2)	8(2)	-4(1)	-1(1)
C(7)	45(2)	40(2)	56(2)	-1(1)	2(1)	9(1)
C(8)	36(2)	50(2)	42(2)	-2(1)	3(1)	3(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **11e**.

	x	y	z	Ueq
H(1)	4432(42)	2776(40)	7735(34)	55(10)
H(2)	6636(44)	3914(43)	8576(33)	62(11)
H(3)	6755(39)	4122(37)	10372(30)	47(9)
H(4A)	5466(50)	1871(50)	10597(39)	69(13)
H(4B)	4630(46)	3166(43)	10722(37)	62(11)
H(5A)	-365(43)	1566(45)	4725(34)	59(11)
H(5B)	520(59)	2657(57)	4655(47)	95(18)
H(6)	-1404(43)	4102(41)	4782(33)	54(10)
H(7)	-1494(39)	4324(37)	6512(30)	55(10)
H(8)	632(40)	3109(37)	7580(32)	49(9)

Table 11. Total Energies (au) of the Reactants, Transition Structures and Products for the Cheletropic (CHE) and hetero Diels-Alder reactions (DA) between 1-X-butadiene (X=H, Cl, CH_3, OMe, OAc) and Sulfur Dioxide.

Structures		HF/6-31G*	ZPVE	MP2/6-31G*	MP2/6-31G* SCRF (ε=13.3)	MP2/6-311+G(3df,2p) //MP2/6-31G*	QCISD(T)/6-31G*// //MP2/6-31G*
1,3-butadiene		-154.919654	0.091539	-155.422656	-155.424136	-155.619309	-155.487541
(*Z*)-piperilene		-193.959159	0.121669	-194.593852	-194.595540	-194.843079	-194.674055
SO_2		-547.169006	0.008020	-547.682480	-547.685632	-547.950983	-547.699245
butadiene + SO_2 (DA)	**TSIa**	-702.037148	0.103228	-703.076700	-703.082388	-703.547272	-703.153935
butadiene + SO_2 (CHE)	**TSIIa**	-702.027171	0.102988	-703.073853	-703.080235	-703.551602	-703.146920
butadiene + SO_2 (DA)	**9a**	-702.108831	0.107177	-703.111190	-703.117686	-703.575441	-703.196030
butadiene + SO_2 (DA)	**9'a**	-702.103306	0.106912	-703.105771		-703.571318	-703.190287
butadiene + SO_2 (CHE)	**11a**	-702.105565	0.107092	-703.113680	-703.123333	-703.595060	-703.192270
(*Z*)-piperilene + SO_2 (DA)	**TSIb**	-741.083696	0.132951	-742.252177	-742.257810	-742.775931	-742.345217
(*Z*)-piperilene + SO_2 (DA)	**TS'Ib**	-741.071081	0.133181	-742.243283	-742.248463	-742.767390	-742.336117
(*Z*)-piperilene + SO_2 (CHE)	**TSIIb**	-741.067432	0.132924	-742.246792	-742.253159	-742.778113	-742.334992

Table 11 (cont.)

Structures		HF/6-31G*	ZPVE	MP2/6-31G*	MP2/6-31G* SCRF (ε=13.3)	MP2/6-311+G(3df,2p) //MP2/6-31G*	QCISD(T)/6-31G*// //MP2/6-31G*
(*E*)-piperilene + SO_2 (DA)	**9b**	-741.146654	0.137032	-742.283348	-742.289511	-742.800185	-742.383670
(*E*)-piperilene + SO_2 (DA)	**9'b**	-741.143826	0.136729	-742.280154			
(*E*)-piperilene + SO_2 (DA)	**10b**	-741.148898	0.136952	-742.284983	-742.291151	-742.802263	-742.385214
(*E*)-piperilene + SO_2 (DA)	**10'b**	-741.141756	0.136714	-742.278334			
(*E*)-piperilene + SO_2 (CHE)	**11b**	-741.142925	0.137287	-742.285645	-742.294684	-742.819865	-742.379659
TS(9b→9'b)		-741.135641	0.136269	-742.272844			
TS(10b→10'b)		-741.136465	0.136114	-742.273668			
TS(9b→10'b)		-741.021384	0.134677	-742.165126			
TS(10b→9'b)		-741.022853	0.134677	-742.165942			

Table 11 (cont.)

Structures		HF/6-31G*	ZPVE	MP2/6-31G*	MP2/6-31G* SCRF (ε=13.3)	MP2/6-311+G(3df,2p) //MP2/6-31G*
(*E*)-1-MeO-butadiene		-268.799678	0.127257	-269.609280	-269.612984	-269.946438
(*E*)-1-MeO-butadiene + SO_2 (DA)	**TSIc**	-815.937736	0.139461	-817.276165	-817.282717	-817.887172
(*E*)-1-MeO-butadiene + SO_2 (DA)	**TS'Ic**	-815.917280	0.139194	-817.258906	-817.266241	-817.870714
(*E*)-1-MeO-butadiene + SO_2 (CHE)	**TSIIc**	-815.930522	0.139020	-817.270296	-817.227605	-817.881263
(*E*)-1-MeO-butadiene + SO_2 (DA)	**9c**	-815.992569	0.142537	-817.303450	-817.311821	-817.906200
(*E*)-1-MeO-butadiene + SO_2 (DA)	**9'c**	-815.989472	0.142402	-817.2988901		-817.904149
(*E*)-1-MeO-butadiene + SO_2 (DA)	**10c**	-815.994934	0.142674	-817.303315	-817.309808	-817.907607
(*E*)-1-MeO-butadiene + SO_2 (DA)	**10'c**	-815.992298	0.142472	-817.302757		-817.906265
(*E*)-1-MeO-butadiene + SO_2 (CHE)	**11c**	-815.974682	0.142931	-817.293392	-817.304187	-817.914723

Table 11 (cont.)

Structures		HF/6-31G*	ZPVE	MP2/6-31G*	MP2/6-31G* SCRF (ε=13.3)	MP2/6-311+G(3df,2p) //MP2/6-31G*
(*E*)-1-AcO-butadiene		-381.568290	0.137903	-382.675314	-382.679296	-383.127665
(*E*)-1-AcO-butadiene + SO_2 (DA)	**TSId**	-928.695804	0.149090	-930.335517	-930.342704	-931.062623
(*E*)-1-AcO-butadiene + SO_2 (DA)	**TS'Id**	-928.685584	0.149020	-930.328481	-930.337362	-931.055295
(*E*)-1-AcO-butadiene + SO_2 (CHE)	**TSIId**	-928.675386	0.149023	-930.326480	-930.335064	-931.060843
(*E*)-1-AcO-butadiene + SO_2 (DA)	**9d**	-928.850843	0.152910	-930.360870	-930.367900	-931.080233
(*E*)-1-AcO-butadiene + SO_2 (DA)	**9'd**	-928.753821	0.152770	-930.361539		
(*E*)-1-AcO-butadiene + SO_2 (DA)	**10d**	-928.758827	0.152938	-930.365712	-930.374180	-931.085975
(*E*)-1-AcO-butadiene + SO_2 (DA)	**10'd**	-928.756517	0.152751	-930.365503		
(*E*)-1-AcO-butadiene + SO_2 (DA)	**9d***	-928.737503	0.152687	-930.352126		
(*E*)-1-AcO-butadiene + SO_2 (DA)	**9'd***	-928.741871	0.152758	-930.351801		
(*E*)-1-AcO-butadiene + SO_2 (DA)	**10d***	-928.748451	0.153062	-930.356904		
(*E*)-1-AcO-butadiene + SO_2 (DA)	**10'd***	-928.745223	0.152847	-930.356026		
(*E*)-1-AcO-butadiene + SO_2 (CHE)	**11d**	-928.743860	0.153072	-930.359071	-930.369021	-931.096140

Table 11 (cont.)

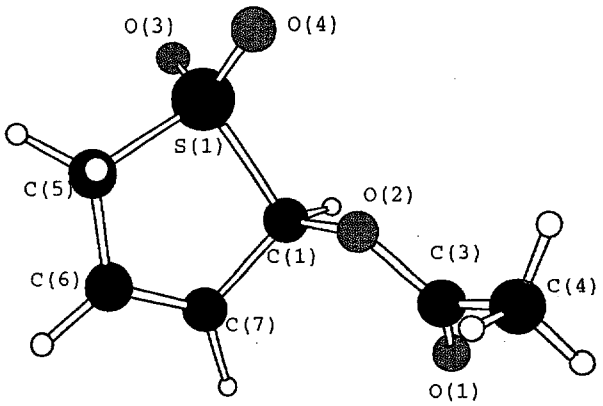
Structures		HF/6-31G*	ZPVE	MP2/6-31G*	MP2/6-31G* SCRF (ε=13.3)	MP2/6-311+G(3df,2p) //MP2/6-31G*	QCISD(T)/6-31G*// //MP2/6-31G*
(*E*)-1-Cl-butadiene		-613.820811	0.082350	-614.454433	-614.456792	-614.730985	-614.529749
(*E*)-1-Cl-butadiene + SO_2 (DA)	**TSIe**	-1160.934280	0.093621	-1162.107729	-1162.113904	-1162.659525	-1162.195156
(*E*)-1-Cl-butadiene + SO_2 (DA)	**TS'Ie**	-1160.922165	0.093407	-1162.099459	-1162.104896	-1162.651862	-1162.186717
(*E*)-1-Cl-butadiene + SO_2 (CHE)	**TSIIe**	-1160.922533	0.093434	-1162.103284	-1162.109534	-1162.662819	-1162.185984
(*E*)-1-Cl-butadiene + SO_2 (DA)	**9e**	-1161.003778	0.097221	-1162.140735	-1162.149463	-1162.684907	-1162.235782
(*E*)-1-Cl-butadiene + SO_2 (DA)	**9'e**	-1160.999898	0.097008	-1162.135516			
(*E*)-1-Cl-butadiene + SO_2 (DA)	**10e**	-1161.006069	0.097231	-1162.140419	-1162.147202	-1162.685650	-1162.235829
(*E*)-1-Cl-butadiene + SO_2 (DA)	**10'e**	-1161.003721	0.097045	-1162.140139			
(*E*)-1-Cl-butadiene + SO_2 (CHE)	**11e**	-1160.994884	0.097542	-1162.137612	-1162.147223	-1162.701185	-1162.226356

Table 12. ΔE [QCISD(T)/6-31G*]- ΔE [MP2/6-31G*] (δ) Calculated Energies (kcal/mol) of the MP2/6-31G* Optimized Transition Structures and Products Relative to Reactants for the Diels-Alder (DA) and Cheletropic (CHE) Reactions of (*E*)-1-X-butadiene (X=H, CH_3 and Cl) and Sulfur Dioxide.

Reactions	TS	δ	Products	δ
butadiene + SO_2 (Ia) DA	**TSIa**	2.8	**9a**	-2.0
(*E*)-piperilene + SO_2 (Ib) DA	**TSIb**	2.5	**9b**	-2.1
(*E*)-piperilene + SO_2 (I'b) DA	**TS'Ib**	2.6	**10b**	-2.0
(*E*)-Cl-butadiene + SO_2 (Ie) DA	**TSIe**	2.9	**9e**	-1.8
(*E*)-Cl-butadiene + SO_2 (I'e) DA	**TS'Ie**	3.0	**10e**	-2.0
DA Averaged Value		2.8		-2.0
butadiene + SO_2 (IIa) CHE	**TSIIa**	5.4	**11a**	2.0
(*E*)-piperilene + SO_2 (IIb) CHE	**TSIIb**	5.5	**11b**	1.8
(*E*)-1-Cl-butadiene + SO_2 (IIe) CHE	**TSIIe**	5.9	**11e**	2.0
CHE Averaged Value		5.6		1.9

Table 13. Atomic Coordinates [Å] of the MP2/6-31G* optimized structure for **11d**.

	X	Y	Z
S(1)	1.4092	-0.6245	0.1421
O(1)	-2.6633	0.7374	1.0055
O(2)	-1.1556	-0.2679	-0.2699
O(3)	1.1522	-1.8447	-0.5588
O(4)	2.1551	-0.6347	1.3690
C(1)	-0.1192	0.2981	0.4886
C(2)	-2.4098	0.0016	0.1108
C(3)	-3.4026	-0.7378	-0.7376
C(4)	2.1229	0.6116	-0.9440
C(5)	1.3178	1.8491	-0.6486
C(6)	0.2167	1.6997	0.0636
H	-0.3231	0.2039	1.5434
H	-0.4396	2.5027	0.3393
H	1.6561	2.8007	-1.0148
H	3.1700	0.7104	-0.6892
H	2.0282	0.2815	-1.9707
H	-3.2699	-0.4626	-1.7772
H	-3.2268	-1.8036	-0.6546
H	-4.4034	-0.4966	-0.4129



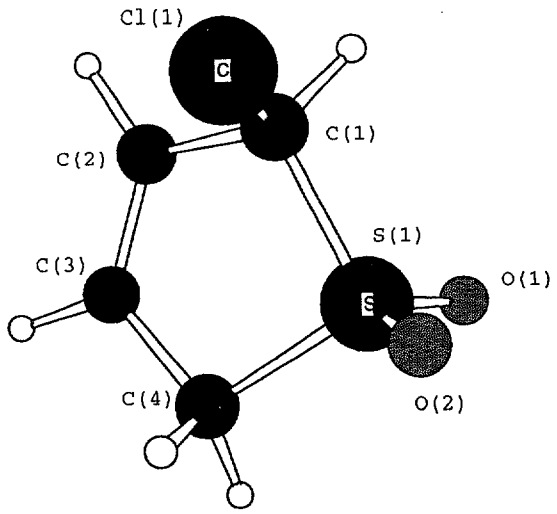
Bond lengths [Å] and angles [°] for **11d**.

S(1)-O(3)	1.469	S(1)-O(4)	1.465
S(1)-C(5)	1.811	S(1)-C(1)	1.832
C(1)-O(2)	1.435	C(1)-C(7)	1.493
C(1)-H(1)	1.094	O(1)-C(3)	1.217
O(2)-C(3)	1.371	C(3)-C(4)	1.501
C(4)-H(4B)	1.084	C(4)-H(4C)	1.092
C(4)-H(4D)	1.092	C(5)-C(6)	1.500
C(5)-h(5A)	1.095	C(5)-H(5B)	1.094
C(6)-C(7)	1.345	C(6)-H(6)	1.086
C(7)-H(7)	1.085		

O(3)-S(1)-O(4)	121.7	O(3)-S(1)-C(5)	108.3
O(4)-S(1)-C(5)	111.3	O(3)-S(1)-C(1)	105.7
O(4)-S(1)-C(1)	111.8	C(5)-S(1)-C(1)	94.4
O(2)-C(1)-S(1)	112.3	O(2)-C(1)-S(1)	106.8
C(7)-C(1)-S(1)	103.4	O(1)-C(3)-O(2)	123.0
C(3)-O(2)-C(1)	113.7	O(2)-C(3)-C(4)	110.1
O(1)-C(3)-C(4)	127.0	C(6)-C(7)-C(7)	115.7
C(6)-C(5)-S(1)	103.3		
C(7)-C(6)-C(5)	117.0		

Table 14. Atomic Coordinates [Å] of the MP2/6-31G* optimized structure for **11e**.

	X	Y	Z
S(1)	0.8329	-0.5622	0.0578
O(1)	1.7541	-0.5592	1.2017
O(2)	0.5990	-1.7666	-0.7404
C(1)	-0.7304	0.1771	0.6993
C(2)	-0.5123	1.6387	0.4945
C(3)	0.4628	1.9777	-0.3669
C(4)	1.2244	0.8530	-0.9999
Cl(1)	-2.1645	-0.4197	-0.1613
H	-0.8084	-0.1251	1.7462
H	-1.1335	2.3588	1.0176
H	0.7117	3.0088	-0.5988
H	2.3098	0.9886	-0.9787
H	0.9006	0.6264	-2.0211



Bond lengths [Å] and angles [°] for **11e**.

S(1)-O(2)	1.464	S(1)-O(1)	1.469
S(1)-C(4)	1.810	S(1)-C(1)	1.844
Cl(1)-C(1)	1.776	C(1)-H(1)	1.092
C(1)-C(2)	1.492	C(2)-H(2)	1.085
C(2)-C(3)	1.344	C(3)-H(3)	1.086
C(3)-C(4)	1.499	C(4)-H(4A)	1.095
		C(4)-H(4A)	1.094

O(2)-S(1)-O(1)	121.8	O(2)-S(1)-C(4)	111.1
O(1)-S(1)-C(4)	108.5	O(2)-S(1)-C(1)	112.6
O()-S(1)-C(1)	105.1	C(4)-S(1)-C(1)	94.2
C(2)-C(1)-Cl(1)	112.4	C(2)-C(1)-S(1)	102.8
Cl(1)-C(1)-S(1)	112.4	C(2)-C(3)-C(4)	116.7
C(3)-C(2)-C(1)	116.2		
C(3)-C(4)-S(1)	103.3		