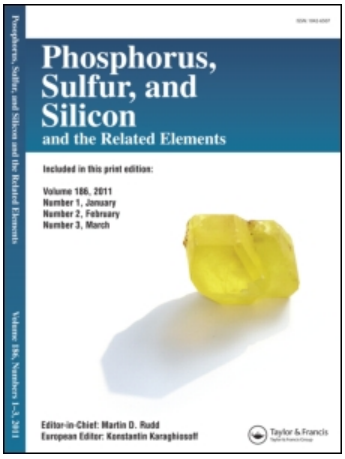

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An Ab Initio Study of Conformational Energies in Dioxo-, Trioxo-, and Tetroxo-Dithianes

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An Ab Initio Study of Conformational Energies in Dioxo-, Trioxo-, and Tetroxo-Dithianes

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Ab initio Hartree–Fock calculations at the HF/6-31G level of theory for geometry optimization and the MP2/6-31G*//HF/6-31G* and B3LYP/6-311G(2df,p)//HF/6-31G* levels for a single point total energy calculation are reported for the important energy-minimum conformations of 1,1-dioxo-thiane (**2**), 1,1-dioxo-1,2-dithiane (**3**), 1,1-dioxo-1,3-dithiane (**4**), 1,1-dioxo-1,4-dithiane (**5**), 1,1,2-trioxo-1,2-dithiane (**6**), 1,1,3-trioxo-1,3-dithiane (**7**), 1,1,4-trioxo-1,4-dithiane (**8**), 1,1,2,2-tetroxo-1,2-dithiane (**9**), 1,1,3,3-tetroxo-1,3-dithiane (**10**), and 1,1,4,4-tetroxo-1,4-dithiane (**11**). According to the MP2/6-31G*//HF/6-31G* calculations, compound **5** is more stable than **3** and **4** by 7.8 and 8.9 kJ mol^{-1}, respectively. The axial geometries of **6** and **8** are more stable than the equatorial forms by 21.4 and 19.1 kJ mol^{-1}, respectively, but the equatorial form of **7** is 4.1 kJ mol^{-1} more stable than the axial geometry. Compound **11** is more stable than **9** and **10** by 49.3 and 31.0 kJ mol^{-1}, respectively.*

Keywords Conformational energies; cyclic sulfoxides; dioxo-dithiane; stereochemistry

INTRODUCTION

The preference by most substituents to occupy the equatorial positions on the chair conformations of monosubstituted cyclohexanes,[1,2]

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oxanes,[1,3] and thianes[1,4] is occationally reversed in certain substituted heterocyclic systems.[1,5] Examples include stereoelectronic interactions, such as the anomeric effect and hyperconjugative orbital interactions, where an electron-withdrawing substituent at C2 in a heterocycle preferes the axial position.[6]

Conformations of organic six-membered cyclic sulfoxides have been investigated by many experimental and computational methods.[7] The normal equatorial orientation of substituents in the cyclohexane ring was reversed in 1-oxo-thiane (**1**), so the more stable chair conformation of **1** has the oxygen atom in the axial position (see Scheme 1). This conformational preference has been attributed to a destabilization of an equatorial conformer by four O/H gauche interactions.[8] There are only two such interactions plus two apparently attractive *syn*-axial interactions in the axial conformer. On the other hand, the proposed interaction of the sulfoxide 3*p* orbital with the σ^* orbitals of C(5)-C(6) and C(2)-C(3) moieties is better when the lone pair is equatorial and the oxygen atom is axial.[9]

1a

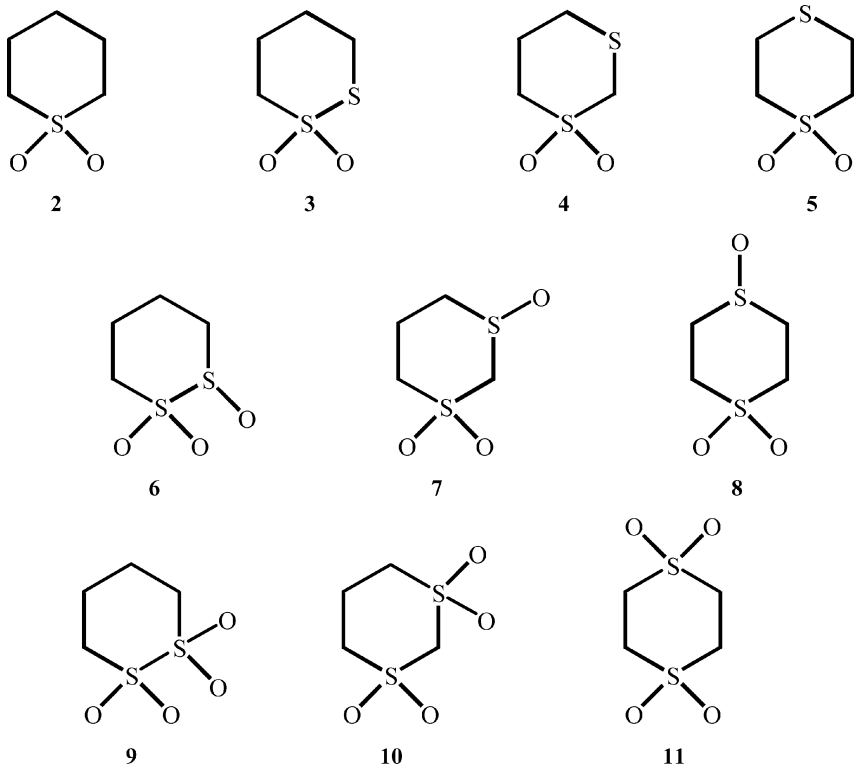
1e

SCHEME 1

Conformational properties of sulfur-containning six-membered heterocycles may differ from those of cyclohexane. The thiane, dithianes, and the sulfoxides derived from them adopt a chair conformation somewhat more puckered than of cyclohexane.[10] The axial–equatorial preference of oxygen in six-membered cyclic sulfoxides has been attributed to the interaction between the polar sulfoxide group and the axial C—H bonds of C3 and C5.

Even though some of the six-membered cyclic sulfoxides are not presently available for more studies, it is possible to carry out ab initio calculations at the Hartree–Fock level, from which many properties can be obtained with an accuracy that is competitive with experiments. In continuation of our interest in conformations of sulfur-containing heterocycles,[11] this study was undertaken in order to calculate geometry-optimized structures and configurational isomer energy differences (ΔE) of organic six-membered cyclic sulfoxides, such as dioxothiane (**2**), dioxo-dithianes (**3–5**), trioxo-dithianes (**6–8**), and tetroxodithianes (**9–11**) (Scheme 2) by comparing their geometries (HF/6-31G*)

and conformational energies (MP2/6-31G*//HF/6-31G* and B3LYP/6-311G(2df,p)//HF/6-31G*). The results from MP2/6-31G*//HF/6-31G* calculations are used in the conformational energies discussions to follow.



SCHEME 2

1,1-Dioxo-thiane (2), 1,1-Dioxo-1,2-dithiane (3), 1,1-Dioxo-1,3-dithiane (4), and 1,1-Dioxo-1,4-dithiane (5)

Selected geometrical data for 1,1-dioxo-thiane (**2**), 1,1-dioxo-1,2-dithiane (**3**), 1,1-dioxo-1,3-dithiane (**4**), and 1,1-dioxo-1,4-dithiane (**5**) are given in Table I. The oxidation of thiane and 1, *n*-dithianes to 1,1-dioxo-1,*n*-dithianes has been carried out using different oxidants under several different reaction conditions. The sulfur-33 NMR spectrum of **8** has been reported,[12] and a conformational preference in benzyloxy- and siloxy-substituted 1,1-dioxo-thiane has been reported.[13] The most significant structural difference obsereved among the compounds shown in Table I is the large variation in the ring torsion angle involving

TABLE I Calculated Heats of the Formation (kJ mol^{-1}), Total and Zero-Point Vibrational (Zero-Point Vibrational Energy Is Scaled by a Factor of 0.9135 to Eliminate Known Systematic Errors in Calculations) Energies (Hartree), Relative Energy (Including Zero-Point Energy, kJ mol^{-1}), Dipole Moment, and Structural Parameters for Various Geometries of 1,1-Dioxo-Thiane (2) and 1,1-Dioxo-1,*n*-dithianes (3–5)

	2	**3**	**4**	**5**
HF/6-1G*//HF/631G*	−742.33944	−1100.80255	−1100.80302	−1100.80900
MP2/6-31G*//HF/6-31G*	−743.48757	−1101.94695	−1101.94400	−1101.94950
B3LYP/6-311G// HF/631G*	−744.94507	−1103.80762	−1103.80311	−1103.81088
ZPE	0.16418	0.13557	0.13483	0.13511
E^{a}_{rel}/kJ·mol^{-1}		18.0	10.1	0.0
E^{b}_{rel}/kJ·mol^{-1}		7.8	8.9	0.0
E^{c}_{rel}/kJ·mol^{-1}		9.7	19.7	0.0
μ (D)	5.67	6.14	5.46	3.59
r_{12}/Å	1.816	2.061	1.788	1.782
r_{23}/Å	1.518	1.831	1.804	1.528
r_{34}/Å	1.524	1.530	1.819	1.816
r_{45}/Å	1.524	1.534	1.529	1.816
r_{56}/Å	1.518	1.530	1.531	1.528
r_{61}/Å	1.816	1.780	1.780	1.782
S—O_{ax}/Å	1.469	1.434	1.439	1.440
S—O_{eq}/Å	1.472	1.431	1.435	1.436
θ_{123}/°	114.5	96.9	114.5	112.4
θ_{234}/°	112.0	113.2	99.6	113.5
θ_{345}/°	111.7	114.3	113.9	99.7
θ_{456}/°	112.0	114.5	113.3	113.5
θ_{561}/°	114.5	112.4	113.6	112.4
θ_{612}/°	100.1	102.0	102.7	103.7
ϕ_{1234}/°	58.3	61.9	56.7	65.2
ϕ_{2345}/°	−64.7	−65.6	−58.8	−59.9
ϕ_{3456}/°	64.7	61.2	66.7	59.9
ϕ_{4561}/°	−58.3	−62.3	−64.4	−65.2
ϕ_{5612}/°	46.1	61.5	56.1	57.3
ϕ_{6123}/°	−46.1	−56.4	−56.6	−57.3

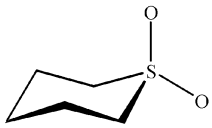
[a]The relative energy with respect to the most stable conformation from HF/6-31G*// HF/6-31G* calculations.

[b]The relative energy with respect to the most stable conformation from MP2/6-31G*// HF/6-31G* calculations.

[c]The relative energy with respect to the most stable conformation from B3LYP/6-311 G//HF/6-31G* calculations.

the S atom ($\phi_{5612} = 46.1$) in **2** relative to thiane ($\phi_{5612} = 53.4$). Dioxo-1,2-dithiane (**3**), namely thiosultone, undergoes a rapid chair–chair interconversion at −90°C because the second heteroatom, as expected, significantly lowers the energy barrier for ring inversion in **3**.[14,15]

According to ab initio calculations, 1,1-dioxo-1,4-dithiane (**5**) is more stable than **3** and **4** (see Scheme 3).



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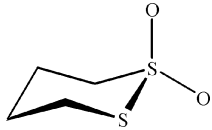

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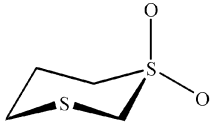

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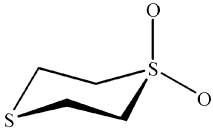


5

SCHEME 3

Trioxo-1,1,2-dithiane (6), Trioxo-1,1,3-dithiane (7), and Trioxo-1,1,4-dithiane (8)

The molecular structure of trioxo-1,*n*-dithianes **6–8** (see Scheme 4), as calculated by ab initio methods, are shown in Table II. The synthesis and spectral studies of 3-aryl-5-phenyl-trioxo-1,4-dithiane have been reported.[16] As shown in Table II, axial conformations of trioxo-1,2-dithiane (**6a**) and trioxo-1,4-dithiane (**8a**) are more stable than the equatorial isomers **6e** and **8e**. However, the equatorial conformation of trioxo-1,3-dithiane (**6e**) is calculated to be more stable than the axial conformation (**7a**). The isomer **8a** of trioxo-1,4-dithiane is the most stable compound among trioxo-1,*n*-dithianes. The significant structural difference observed in Table II is the variation in the dihedral angle involving the $-SO_2-$ moiety of **8a**. There is a compensation of dipoles in compound **8**, so the total dipole moment of **8e** is even less than the S—O moment of 3.03 D.

Tetroxo-1,1,2,2-dithiane (9), Tetroxo-1,1,3,3-dithiane (10), and Tetroxo-1,1,4,4-dithiane (11)

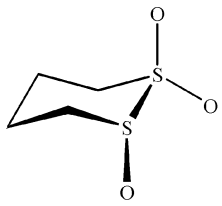
The results of ab initio calculations for tetroxo-1,*n*-dithianes **9–11** (Scheme 5) are given in Table III. One-bond C—H coupling constants of

TABLE II Calculated Heats of the Formation (kJ mol^{-1}), Total and Zero-Point Vibrational (Zero-Point Vibrational Energy is Scaled by a Factor of 0.9135 to Eliminate Known Systematic Errors in Calculations) Energies (Hartree), Relative Energy (Including Zero-Point Energy, kJ mol^{-1}), Dipole Moment, and Structural Parameters for Axial and Equatorial Geometries of Trioxo-1,*n*-dithianes (6–8)

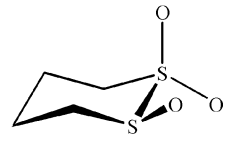
	6a	6e	7a	7e	8a	8e
HF/6-1G*//HF/6-31G*	−1175.59506	−1175.58536	−1175.59623	−1175.59959	−1175.61195	−1175.60477
MP2/6-1G*//HF/6-31G*	−1176.93251	−1176.92408	−1176.92753	−1176.92979	−1176.94131	−1176.93374
B3LYP/6-311G//HF/6-31G*	−1178.91725	−1178.90837	−1178.89180	−1178.89745	−1178.91563	−1178.90458
ZPE	0.13947	0.13915	0.13895	0.13886	0.1394	0.1390
E^{a}_{rel}/kJ·mol^{-1}	44.5	69.2	40.1	31.1	0.0	18.0
E^{b}_{rel}/kJ·mol^{-1}	23.3	44.7	33.1	29.0	0.0	19.1
E^{c}_{rel}/ kJ·mol^{-1}	0.0	22.6	65.3	50.5	4.1	32.1
μ (D)	5.66	8.28	6.92	5.10	3.65	2.74
r_{12}/Å	2.123	2.142	1.793	1.779	1.781	1.784
r_{23}/Å	1.816	1.809	1.819	1.817	1.526	1.527
r_{34}/Å	1.533	1.532	1.808	1.808	1.811	1.809
r_{45}/Å	1.533	1.532	1.529	1.530	1.811	1.809
r_{56}/Å	1.530	1.529	1.528	1.531	1.526	1.527
r_{61}/Å	1.782	1.781	1.780	1.782	1.781	1.784
S_1-O_{ax}/Å	1.437	1.431	1.435	1.432	1.440	1.437
S_1-O_{eq}/Å	1.428	1.433	1.430	1.436	1.433	1.434
S_2-O_{ax}/Å	1.478					

S_2-O_{eq}/Å		1.469				
S_3-O_{ax}/Å			1.475			
S_3-O_{eq}/Å				1.479		
S_4-O_{ax}/Å					1.480	
S_4-O_{eq}/Å						1.489
θ_{123}/°	95.0	94.3	118.9	114.7	112.0	112.5
θ_{234}/°	113.0	113.6	98.0	96.9	112.7	113.0
θ_{345}/°	114.5	114.2	113.5	114.5	98.3	97.5
θ_{456}/°	114.0	113.4	112.7	113.7	112.7	113.0
θ_{561}/°	111.9	112.7	113.3	112.2	112.0	112.5
θ_{612}/°	101.0	100.7	103.4	102.4	90.4	102.6
ϕ_{1234}/°	63.6	64.4	51.6	59.2	67.7	67.5
ϕ_{2345}/°	−68.1	−69.2	−59.4	−60.4	−62.3	−63.3
ϕ_{3456}/°	61.9	61.6	73.2	68.6	62.3	63.3
ϕ_{4561}/°	−63.4	−63.3	−66.6	−63.8	−67.7	−67.5
ϕ_{5612}/°	62.9	63.0	50.9	56.1	81.8	56.4
ϕ_{6123}/°	−58.0	−57.7	−49.3	−59.5	−81.8	−56.4

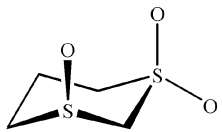
[a]The relative energy with respect to the most stable conformation from HF/6-31G*//HF/6-31G* calculations.
[b]The relative energy with respect to the most stable conformation from MP2/6-31G*//HF/6-31G* calculations.
[c]The relative energy with respect to the most stable conformation from B3LYP/6-311G//HF/6-31G* calculations.



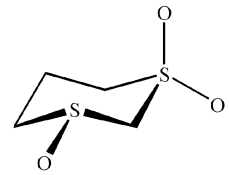
6a



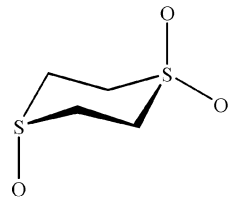
6e



7a



7e



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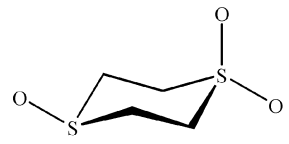
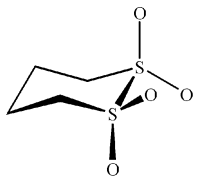


8e

SCHEME 4

anionic carbon of anions derived from **10** in the presence of a base provided unequivocal evidence for the trigonal hybridization of the charged carbon, which was previously assigned as a tetrahedral.[17]

One of the derivatives of **11**, namely 2,3-di-vinyl-tetroxo-1,4-dithiane, has been employed as an electron-deficient diene in the



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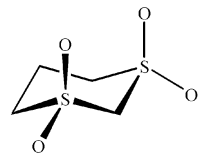
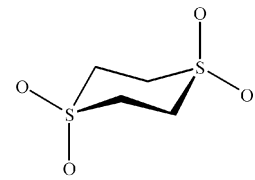


10



11

SCHEME 5

TABLE III Calculated Heats of the Formation (kJ mol^{-1}), Total and Zero-Point Vibrational (Zero-Point Vibrational Energy Is Scaled by a Factor of 0.9135 to Eliminate Known Systematic Errors in Calculations) Energies (Hartree), Relative Energy (Including Zero-Point Energy, kJ mol^{-1}), Dipole Moment, and Structural Parameters for the Most Stable Conformations of Tetroxo-1,*n*-dithianes (9–11)

	9	**10**	**11**
HF/6-1G*//HF/6-31G*	−1250.42941	−1250.44491	−1250.45922
MP2/6-1G*//HF/6-31G*	−1251.95534	−1251.96208	−1251.97423
B3LYP/6-311G//HF/6-31G*	−1253.99151	−1253.98032	−1254.00153
ZPE	0.14525	0.14498	0.14537
E_{rel}^{a}/kJ· mol^{-1}	78.0	36.6	0.0
E_{rel}^{b}/ kJ mol^{-1}	49.3	31.0	0.0
E_{rel}^{c}/ kJ mol^{-1}	26.0 (−2.55)	54.7 (3.1)	0.0 (0.0)
μ (D)	7.73	6.24	0.0
r_{12}/Å	2.127	1.795	1.786
r_{23}/Å	1.782	1.795	1.528
r_{34}/Å	1.534	1.781	1.786
r_{45}/Å	1.534	1.531	1.786
r_{56}/Å	1.534	1.531	1.528
r_{61}/Å	1.782	1.781	1.786
S_1-O_{ax}/Å	1.432	1.429	1.438
S_1-O_{eq}/Å	1.425	1.432	1.432
S_2-O_{ax}/Å	1.425		
S_2-O_{eq}/Å	1.432		
S_3-O_{ax}/Å		1.429	
S_3-O_{eq}/Å		1.432	
S_4-O_{ax}/Å			1.432
S_4-O_{eq}/Å			1.438
θ_{123}/°	99.4	116.9	112.3
θ_{234}/°	112.4	102.9	112.3
θ_{345}/°	114.7	113.2	103.0
θ_{456}/°	114.7	113.4	112.3
θ_{561}/°	112.4	113.2	112.3
θ_{612}/°	99.4	102.9	103.0
ϕ_{1234}/°	−60.8	−49.6	−64.5
ϕ_{2345}/°	65.2	54.6	59.0
ϕ_{3456}/°	−63.0	−68.6	−59.0
ϕ_{4561}/°	65.2	68.0	64.5
ϕ_{5612}/°	−60.8	−54.6	−59.0
ϕ_{6123}/°	78.8	49.6	59.0

[a]The relative energy with respect to the most stable conformation from HF/6-31G*// HF/6-31G* calculations.

[b]The relative energy with respect to the most stable conformation from MP2/6-31G*// HF/6-31G* calculations.

[c]The relative energy with respect to the most stable conformation from B3LYP/6-311 G//HF/6-31G* calculations.

synthesis of functionalized ring systems via Diels–Alder reactions. The introduction of hetero substituents has a significant influence on the reactivity and regioselectivity of the diene.[18] According to Table III, compound **11** is more stable than **9** and **10**. Cook and Tonge suggested that intramolecular dipole–dipole interactions contribute in some measure to the observed stabilization.[19]

CONCLUSIONS

We have examined a number of organic six-membered cyclic sulfoxides (**2–11**) using ab initio calculations from both structural and energetic points of view. These compounds prefer a chair conformation. The calculated conformational energy differences for the axial and equatorial geometries of the 1,*n*-trioxo-1,*n*-dithianes **6–8** are similar to those obtained for 1-oxo-1,*n*-dithianes. Thus, in addition to the attractive 1,3-*syn*-axial interaction between the oxygen and the hydrogen atoms in the axial conformation and/or repusion of the equatorial oxygen atom by its vicinal hydrogen atoms in the equatorial form, other stereoelectronic factors, such as a repulsive interaction between the sulfinyl oxygen and the cross-ring sulfur atom in **7** and **10**, can play a rule.

The C—C bond distances in all structures are significantly shorter than the standard Csp^3-Csp^3 bond length of 1.54 Å. The present calculations indicate that dioxo-, trioxo-, and tetroxo-derivatives of 1,4-dithiane are more stable than the corresponding oxidation forms of 1,2-dithiane or 1,3-dithiane.

METHODS

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 program.[20] Geometries for all structures were fully optimized by means of analytical energy gradients by a Berny optimizer with no geometrical constraints.[21] The restricted Hartree–Fock calculations with the split-valence 6-31G* basis set, which includes a set of d-type polarization functions on all nonhydrogen atoms, were used in these calculations.[22] Single point energy calculations at MP2/6-31G*//HF/6-31G* and B3LYP/6-311G(2df,p)[23] levels were used to evaluate the electron correlation effect in the energies and the order of the stability of conformers. Vibrational frequencies were calculated at the 6-31G* level for all geometries, which were confirmed to have zero imaginary frequency. The frequencies were scaled by a factor of 0.9135 and used to compute the zero-point vibrational energies.[24]

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