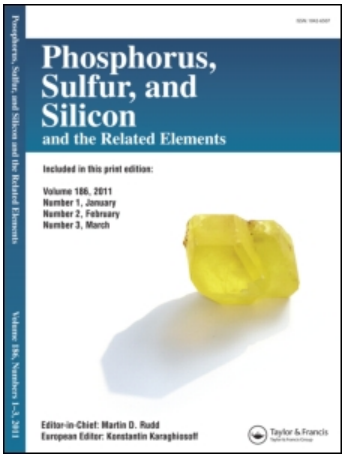


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Conformational Energies in Organic Six-Membered Cyclic Sulfoxides

Issa Yavari[ab]; Mina Haghdadi[ac]; Rahebeh Amiri[ad]

[a] Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran [b] Chemistry Department, Tarbiat Modarres University, Tehran, Iran [c] Chemistry Department, Islamic Azad University, Amol, Iran [d] Chemistry Department, Islamic Azad University, Tehran Central Branch, Tehran, Iran

To cite this Article Yavari, Issa , Haghdadi, Mina and Amiri, Rahebeh(2006) 'Conformational Energies in Organic Six-Membered Cyclic Sulfoxides', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 7, 1693 — 1705
To link to this Article: DOI: 10.1080/10426500500366913
URL: http://dx.doi.org/10.1080/10426500500366913

Phosphorus, Sulfur, and Silicon, 181:1693–1705, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500366913

Taylor & Francis
Taylor & Francis Group

Conformational Energies in Organic Six-Membered Cyclic Sulfoxides

Issa Yavari
Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran, and Chemistry Department, Tarbiat Modarres University, Tehran, Iran

Mina Haghdadi
Chemistry Department, Islamic Azad University, Amol, Iran, and Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran

Rahebeh Amiri
Chemistry Department, Islamic Azad University, Tehran Central Branch, Tehran, Iran, and Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran

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-oxo-thiane (**1**), 1-oxo-1,2-dithiane (**2**), 1-oxo-1,3-dithiane (**3**), 1-oxo-1,4-dithiane (**4**), 1,2-dioxo-1,2-dithiane (**5**), 1,3-dioxo-1,3-dithiane (**6**), and 1,4-dioxo-1,4-dithiane (**7**). According to the MP2/6-31G*//HF/6-31G* calculations, while the axial conformations of compounds **1**, **2**, and **4** are more stable than the equatorial forms by 6.0, 20.0, and 9.9 kJ mol^{-1}, respectively, the equatorial geometry of **3** is 3.0 kJ mol^{-1} more stable than the axial form. The diaxial conformations of **5** and **7** are calculated to have similar energies, but the diaxial form of **6** is about 43 kJ mol^{-1} less stable than that of **5** or **7**.*

Keywords Conformational energies; cyclic sulfoxides; oxo-thiane; stereochemistry

INTRODUCTION

The chemistry of organic cyclic sulfoxides continues to attract considerable attention due to their synthetic potential.[1] In recent decades, enantiomerically pure sulfoxides have become important asymmetric

Received May 10, 2005; accepted September 1, 2005.
Address correspondence to Issa Yavari, Chemistry Department, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran. E-mail: yavarisa@modares.ac.ir

synthons in organic synthesis.[2,3] The preference by most substituents to occupy the equatorial positions on chair conformations of monosubstituted cyclohexanes,[3,4] oxanes,[3,5] and thianes[3,6] is occationally reversed in certain substituted heterocyclic systems. Examples include stereoelectronic interactions, such as the anomeric effect and hyperconjugative orbital interactions, where an electron-withdrawing (electronegative) substituent at C2 in a heterocycle preferes the axial position.[7] Another example is the sulfinyl group (S=O), which prefers an axial orientation in 1-oxo-thiane (**1**) and in 1-oxo-1,2-dithiane (**2**).[8]

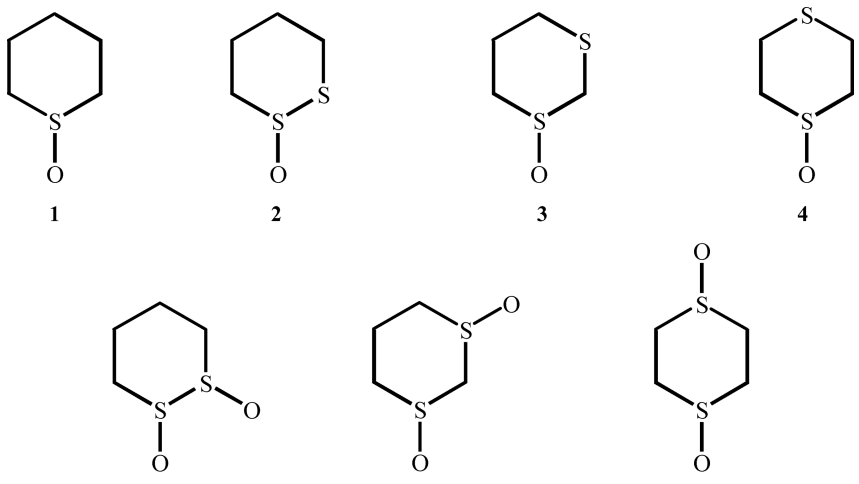
The conformational properties of sulfur-containning six-membered heterocycles may differ from those of cyclohexane. The thiane, dithianes, and sulfoxides derived from them adopt a chair conformation somewhat more puckered than of cyclohexane.[9] Generally, in heterocyclic systems, at least one polar group is in the ring, and parent compounds usually have dipole moments, so the electrostatic term in total strain energy of a molecule may be either attractive or repulsive depending on whether the dipoles within the molecules are aligned in an antiparallel or parallel orientation. 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.

In continuation of our interest in conformations of sulfur-containing heterocycles,[10] this study was undertaken in order to calculate the geometry-optimized structures and configurational isomer energy differences (ΔE) of organic six-membered cyclic sulfoxides, such as 1-oxo-thiane (**1**), mono-oxo-dithianes (**2–4**), and dioxodithianes (**5–7**) (Scheme 1) 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*). Results from MP2/6-31G*//HF/6-31G* calculations are used in the conformational energies discussions to follow. The calculated isomer energy differences (ΔE) and structural parameters of **1**, **2**, **3**, **6**, and **7** are compared with the available experimental data.

RESULTS AND DISCUSSION

1-Oxo-thiane (1)

Conformations of organic six-membered cyclic sulfoxides, 1-oxo-thiane (**1**), and its derivatives, have been investigated by many experimental and computational methods.[11] The normal equatorial orientation of substituents in the cyclohexane ring was reversed in **1**, so the more stable chair conformation of **1** has the oxygen atom in the axial position



1 **2** **3** **4** **5** **6** **7**

SCHEME 1

(see Scheme 2). This conformational preference has been attributed to a destabilization of an equatorial conformer by four O/H gauche interactions.[12] 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 $3p$ orbital with 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.[13]

1a **1e**

SCHEME 2

Conformational equilibria of six-membered cyclic sulfoxides have been shown to be strongly affected by the presence of a second heteroatom in the ring or substituents at the C-ring atoms and by the nature of the solvent.[11] Thus, for 1-oxo-thiane (**1**), a slight axial preference of the sulfinyl oxygene ($\Delta G^{\circ}_{-90^{\circ}C} = +0.73$ kJ mol^{-1}, CH_2Cl_2) has been determined by low-temperature ^{1}H and ^{13}C NMR spectroscopy,[14–17] but only an axial chair form of **1a** has been found in the gas phase by an electron diffraction study.[8] The higher stablity of the axial conformer as compared with the equatorial one was explained by an attractive

1,3-*syn*-axial interaction between the hydrogen atoms in the **1a** conformer and/or by a repulsion of the equatorial oxygen atom by its vicinal hydrogen atoms in **1e**.[11] The small conformational preference for an axial disposition of a sulfoxide oxygen is owing to the substitution of a heteroatom for a methylene group in such systems, which should lower the barrier to a chair–chair interconversion by reducing 1–2 rotational interactions. Moreover, Eliel and Hutchins have demonstrated that sulfur (presumably oxygen as well) with its lone pairs, has a smaller space requirment than a mathylene group.[18]

The results of ab initio calculations for the axial and equatorial geometries of 1-oxo-thiane (**1**) are shown in Table I. Although the ab initio methods predict the correct order of stabilities for **1a** and **1e** conformations, the free energy difference (6.0 kJ mol^{-1}) between two forms is higher than the experimental value. The molecular structure of **1** has been determined by gas-phase electron diffraction. According to the electron diffraction data, the molecule has a chair conformation with C_s symmetry. The oxygen atom takes the axial position. Bond distances and bond angles determined by electron diffraction are in good agreement with the results of ab initio studies (see Table I). Dihedral angles for chair conformations **1a** and **1e** (Scheme 2) show a rather puckered ring than cyclohexane.

1-Oxo-1,2-dithiane (2), 1-Oxo-1,3-dithiane (3), and 1-Oxo-1,4-dithiane (4)

The results of ab initio calculations for the axial and equatorial chair conformations of 1-oxo-1,2-dithiane (**2**), 1-oxo-1,3-dithiane (**3**), and 1-oxo-1,4-dithiane (**4**) are shown in Table II. According to these calculations, the axial conformation of **2** is more stable than the equatorial geometry. The ^1H and ^{13}C NMR spectra of **2** have been studied by Juaristi and colleagues.[19] The single most important chemical shift in the ^{13}C NMR spectrum of **2** is C(5) at $\delta = 16.2$ ppm. This value represents more than a 10 ppm upfield shift relative to the chemical shift of this carbon atom in 1,2-dithiane ($\delta = 27.8$ ppm),[20] which has been attributed to the γ-effect of the axial S—O bond.[21] This chemical shift had no change when the temprature was lowered to -90°C, so 1-oxo-1,2-dithiane exists exclusively in the axial conformation.[20] This strong preference for an axial oxygen results from a disfavorable electrostatic dipole repulsion between the S—O bond in the equatorial conformation (Scheme 3) with the adjacent sulfur atom bearing lone-pair electrons.[22]

1-oxo-1,3-dithiane (**3**) and its derivatives are used as chiral auxiliaries and asymmetric building blocks for an enantiocontrol of a range of organic reactions, including enolate alkylation,[23] Grignard

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, and kJ mol^{-1}), Dipole Moment, and Structural Parameters for the Axial and Equatorial Geometries of 1-Oxo-thiane (1)

	1a	**1e**
HF/6-1G*//HF/6-31G*	−667.486201	−667.484400
MP2/6-1G*//HF/6-31G*	−668.449605	−668.447130
B3LYP/6-311G//HF/6-31G*	−669.848907	−669.845630
ZPE	0.158071	0.157847
E^a_{rel}/kJ · mol^{-1}	0.0	4.2
E^b_{rel}/kJ · mol^{-1}	0.0	6.0
E^c_{rel}/kJ · mol^{-1}	0.0	8.1
μ (D)	4.37	5.09
r_{12}/Å	1.807 (1.816)[d]	1.803
r_{23}/Å	1.528 (1.538)	1.530
r_{34}/Å	1.530 (1.539)	1.531
r_{45}/Å	1.530 (1.539)	1.531
r_{56}/Å	1.528 (1.538)	1.530
r_{61}/Å	1.807 (1.816)	1.803
S—O_{ax}/Å	1.490 (1.483)	
S—O_{eq}/Å		1.486
θ_{123}/°	112.4	112.2
θ_{234}/°	112.6	112.6
θ_{345}/°	112.6	112.4
θ_{456}/°	112.6	112.6
θ_{561}/°	112.4	112.2
θ_{612}/°	96.9	96.5
ϕ_{1234}/°	−61.9	−62.5
ϕ_{2345}/°	58.4	57.9
ϕ_{3456}/°	−58.4	−57.9
ϕ_{4561}/°	61.9	62.5
ϕ_{5612}/°	−56.7	−57.8
ϕ_{6123}/°	56.7	57.8

[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 MP2/6-1G*// HF/6-31G* calculations.

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

[d]The gas-phase electron diffraction data for **1a**.[8]

reagent addition,[24] hydride reduction,[25] conjugate addition,[26] heterocycloaddition,[27] and the Mannich reaction. An X-ray crystallographic structure for 2-phenyl-1-oxo-1,3-dithiane has been reported.[9] NMR data have shown[28] the equatorial conformation being favored over the

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 and kJ mol^{-1}), Dipole Moment, and Structural Parameters for the Axial and Equatorial Geometries of 1-Oxo-1,*n*-Dithianes (2–4)

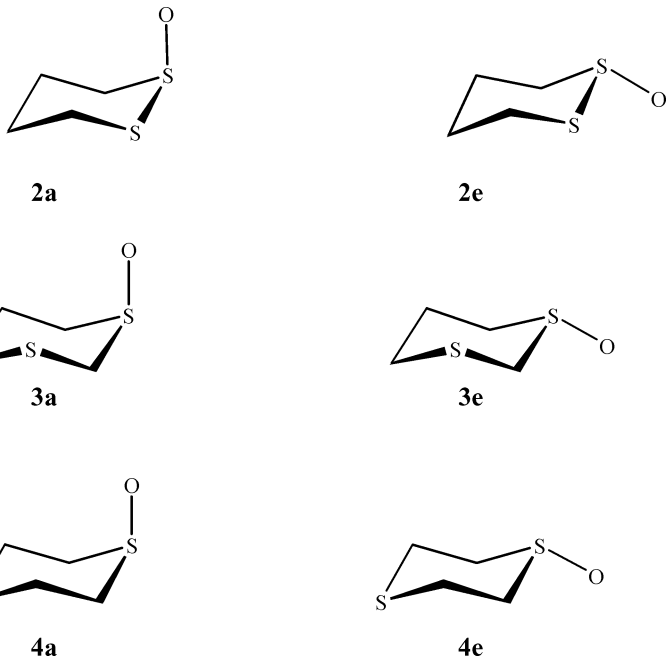
	2a	2e	3a	3e	4a	4e
HF/6-1G*//HF/6-31G*	−1025.95813	−1025.95120	−1025.95131	−1025.95321	−1025.95694	−1025.95343
MP2/6-1G*//HF/6-31G*	−1026.91624	−1026.90824	−1026.90748	−1026.90855	−1026.91222	−1026.90806
B3LYP/6-311G//HF/6-31G*	−1028.71581	−1028.72334	−1028.70869	−1028.71043	−1028.71705	−1028.71139
ZPE	0.12959	0.12917	0.12880	0.12872	0.12906	0.12874
E^a_{rel}/kJ · mol^{-1}	0.0	17.2	16.0	10.8	1.9	10.3
E^b_{rel}/kJ · mol^{-1}	0.0	20.0	21.1	18.1	9.3	19.4
E^c_{rel}/kJ · mol^{-1}	20.8	0.0	37.6	32.8	16.2	30.3
μ (D)	5.98	4.12	4.94	4.41	3.10	3.77
r_{12}/Å	2.085	2.103	1.812 (1.834)[d]	1.807 (1.830)	1.804	1.809
r_{23}/Å	1.827	1.823	1.803 (1.797)	1.803 (1.814)	1.527	1.524
r_{34}/Å	1.529	1.531	1.816 (1.812)	1.816 (1.808)	1.814	1.815
r_{45}/Å	1.530	1.532	1.528 (1.508)	1.530 (1.506)	1.814	1.815
r_{56}/Å	1.527	1.527	1.527 (1.512)	1.527 (1.519)	1.527	1.524
r_{61}/Å	1.811	1.804	1.813 (1.808)	1.812 (1.806)	1.804	1.809
S—O_{ax}/Å	1.479		1.481 (1.484)		1.489	
S—O_{eq}/Å		1.474	1.484 (1.497)	1.485 (1.497)		1.485
θ_{123}/°	98.2	97.4	116.2 (112.9)	113.2 (109.6)	113.0	113.2
θ_{234}/°	113.1	113.4	99.7 (99.2)	99.2 (100.5)	113.8	113.4
θ_{345}/°	113.8	113.6	113.8 (112.6)	113.4 (113.0)	99.5	99.3
θ_{456}/°	14.5	114.4	113.4 (113.0)	113.5 (113.3)	113.8	113.4
θ_{561}/°	113.0	113.0	114.0 (114.6)	114.7 (114.0)	113.0	113.2
θ_{612}/°	97.8	97.2	97.6 (98.7)	97.0 (98.2)	98.0	98.9
ϕ_{1234}/°	−63.5	−64.2	−53.1 (−61)	−63.2 (−63)	−68.3	−68.2
ϕ_{2345}/°	64.3	64.5	55.7 (62)	58.2 (61)	56.8	58.8
ϕ_{3456}/°	−60.6	−60.1	−65.3 (−68)	−63.1 (−64)	−56.8	−58.8
ϕ_{4561}/°	65.4	66.0	68.7 (67)	66.1 (67)	68.3	68.2
ϕ_{5612}/°	−63.9	−65.0	−60.1 (−58)	−61.3 (−63)	−62.4	−60.6
ϕ_{6123}/°	57.8	58.6	59.5 (59)	63.6 (63)	62.4	60.6

[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.

[d]The X-ray crystallographic data of 2-phenyl-1,3-dithiane.[9]



2a **2e**

3a **3e**

4a **4e**

SCHEME 3

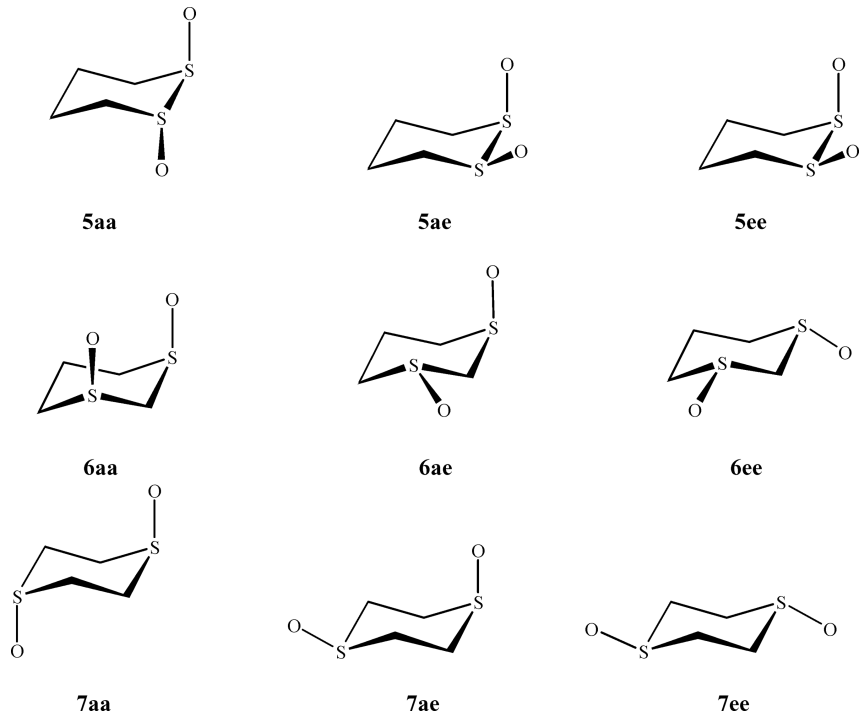
axial form by 2.7 kJ mol^{-1}, which is consistant with the ab initio results (3.0 kJ mol^{-1}) given in Table II. One reason for an equatorial preference in this structure has been related to the closer proximity of two sites of high electron density, namely, the sulfinyl oxygen and the cross-ring sulfur atom (Scheme 3). As shown in Table II, 1-oxo-1,3-dithiane is more puckered than cyclohexane, with the puckering most pronounced in the ring torsion angle involving the C5—C6 bond ($\phi_{4561} = 69°$). A longer S—O_{eq} bond distance indicates more of a single bond character and a more positive charge on the sulfur atom. The larger valence angle ($\theta_{123} = 116.2°$) in the axial oxide of **3** can be attributed to a repulsive gauche interaction between the S—O bond and C(2)-S(3) bonds. Polarizability of the C(2)—S(3) bond leads to this increased repulsion, but the interaction of an equatorial oxygen with the C(2)-S(3) bond is expected to be small because of their antiperiplanar relationship. The average endocyclic bond angles are smaller than those for 1,3-dithiane, which may indicate an additional attractive interaction of the sulfinyl sulfur atom with the electrons in the γ_{c-c} bond.

IR data show that both axial and equatorial conformations of 1-oxo-1,4-dithiane (**4**) exist in CS_2 solution,[29] but the axial form is the only conformation found in the solid state.[1]H NMR data have shown the

axial geometry to be 4.6 kJ mol^{-1} lower in energy than the equatorial form, and according to ^{13}C NMR spectra, the upfield shifts of C(3) and C(5) at $\delta = 19.6$ ppm in **4**, relative to the unoxidized 1,4-dithiane ($\delta = 29.1$ ppm), indicate the predominance of an axial orientation of the sulfinyl group.[19] The results of ab initio calculations for **4** show that the axial conformation is 8.4 kJ mol^{-1} more stable than the equatorial form (Scheme 3), which is in agreement with the experimental data.

1,2-Dioxo-1,2-dithiane (5), 1,3-Dioxo-1,3-dithiane (6), and 1,4-Dioxo-1,4-dithiane (7)

The results of ab initio calculations for axial-axial, axial-equatorial, and equatorial-equatorial conformations of 1,2-dioxo-1,2-dithiane (**5**), 1,3-dioxo-1,3-dithiane (**6**), and 1,4-dioxo-1,4-dithiane (**7**) (see Scheme 4) are shown in Table III. While the axial-axial conformation is the most stable form of **5** and **7**, the axial-equatorial conformation is calculated to be the global energy-minimum geometry for **6**.



SCHEME 4

TABLE III Calculated Heats of 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 and kJ mol^{-1}), Dipole Moment, and Structural Parameters for Various Geometries of 1,*n*-Dioxo-1,*n*-Dithianes (5–7)

	5aa	5ae	5ee	6aa	6ae	6ee	7aa	7ae	7ee
HF/6-31G*//HF/6-31G*	−1100.75576	−1100.74635	−1100.74354	−1100.74405	−1100.75073	−1100.74753	−1100.76280	−1100.75562	−1100.75211
MP2/6-31G*//HF/6-31G*	−1101.90677	−1101.89915	−1101.89407	−1101.88968	−1101.89455	−1101.89133	−1101.90684	−1101.89962	−1101.89512
B3LYP/6-311G// HF/6-31G*	−1103.83908	−1103.82772	−1103.82134	−1103.79709	−1103.80851	−1103.80308	−1103.82647	−1103.81422	−1103.80943
ZPE	0.13360	0.13338	0.13311	0.13278	0.13287	0.13270	0.13348	0.13310	0.13276
E^a_{rel}/kJ · mol^{-1}	18.8	42.9	49.7	47.5	30.2	38.2	0.0	17.9	26.3
E^b_{rel}/kJ · mol^{-1}	0.45	19.94	32.6	43.3	30.8	37.1	0.0	18.0	29.0
E^c_{rel}/kJ · mol^{-1}	0.0	29.3	45.4	108.3	78.5	92.3	32.8	64.1	75.8
μ (D)	2.74	6.69	7.87	7.45	5.20	5.03	0.0	5.40	0.0
r_{12}/Å	2.154	2.147	2.143	1.817	1.814 (1.804)[d]	1.807 (1.800)	1.808 (1.82)	1.809	1.806
r_{23}/Å	1.808	1.802	1.810	1.817	1.805 (1.799)	1.803 (1.817)	1.523	1.526	1.526
r_{34}/Å	1.529	1.533	1.528	1.806	1.810 (1.794)	1.807 (1.810)	1.808 (1.80)	1.804	1.806
r_{45}/Å	1.532	1.530	1.530	1.526	1.527 (1.534)	1.530 (1.510)	1.808	1.804	1.806
r_{56}/Å	1.529	1.531	1.528	1.526	1.529 (1.495)	1.530 (1.520)	1.523	1.526	1.526
r_{61}/Å	1.808	1.814	1.810	1.806	1.806 (1.794)	1.803 (1.820)	1.808	1.809	1.806
S_1—O_{ax}/Å	1.483	1.479		1.476	1.485 (1.511)		1.491(1.48)	1.486	
S_1—O_{eq}/Å			1.475			1.481 (1.487)			1.482
S_n—O_{ax}/Å	1.483			1.476			1.491		
S_n—O_{eq}/Å		1.475	1.475		1.484 (1.498)	1.481 (1.509)		1.482	1.482
θ_{123}/°	96.0	94.6	95.5	121.7	115.8 (113.0)	114.3 (120.2)	112.4	113.0	113.2
θ_{234}/°	113.1	111.7	114.3	98.4	97.7 (96.1)	96.6 (97.9)	112.4 (113.3)	112.6	113.2
θ_{345}/°	113.7	114.2	113.0	114.0	113.0 (111.8)	112.9 (113.2)	97.9 (97.9)	97.1	97.0
θ_{456}/°	113.7	114.0	113.0	112.5	113.3 (112.7)	114.1 (113.5)	112.4 (111.2)	112.6	113.2
θ_{561}/°	113.1	112.3	114.3	114.0	114.0 (113.7)	112.9 (113.8)	112.4	113.0	113.2
θ_{612}/°	96.0	94.4	95.5	98.4	97.1 (97.4)	96.6 (98.4)	97.9	97.6	97.0
ϕ_{1234}/°	65.9	69.2	66.7	50.9	61.9 (65.9)	65.1 (54.3)	70.7	70.9	70.8
ϕ_{2345}/°	−66.8	−66.7	−67.0	−54.9	−59.5 (−63.6)	−60.0 (−56.7)	−61.8	−62.5	−61.0
ϕ_{3456}/°	60.6	58.1	59.3	71.4	67.6 (69.6)	66.8 (71.4)	61.8	62.5	61.0
ϕ_{4561}/°	−66.8	−65.7	−67.0	−71.4	−67.7 (−67.2)	−66.8 (−70.2)	−70.7	−70.9	−70.8
ϕ_{5612}/°	65.9	68.3	66.7	54.9	58.7 (59.6)	60.0 (54.8)	61.8	60.3	61.0
ϕ_{6123}/°	−59.8	−64.1	−59.2	−50.9	−61.2 (−63.7)	−65.1 (−53.4)	−61.8	60.3	−61.0

[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/6-311G//HF/6-31G* calculations.
[d]The X-ray crystallographic data.[31]

Carbon-13 NMR data have been used in assessing the degree of oxidation of the —S—S— component of a disulfide by observing the magnitudes of the ^{13}C NMR shift differences e.g., the oxidation of 1,2-dithiane to the thiosulfonate **5** leads to a downfield shift (from 41.4 to 65.1 ppm) at a carbon atom adjacent to the electron-withdrawing $-SO_2-$ group.[11]

The oxidation of 1,3-dithiane with different oxidizing agents results in *cis*- and *trans*-1,3-di-sulfoxides.[30] The S—C—S bond angle in **6aa** is expanded relative to other isomers shown in Table III. This expansion of the bond angle is caused by a repulsion between the two negatively polarized axial oxygens. X-ray crystallographic analysis reveals a distortion of the axial sulfinyl oxygen towards the equatorial sulfoxide, and this suggests a favorable dipole-dipole interaction between the two sulfoxide groups in **6ae**. Such an interaction may explain why the **6ae** geometry is more stable than **6aa** or **6ee** (Table III). The X-ray structures of **6ee** and **6ae** conformations of 1,3-disulfoxide reveal intermolecular attractions between one of the sulfoxide groups and one of the C(2) protons. It is thus hydrogen bonding that is responsible for the high lattice energy, high melting point, and poor solubility of the two isomers. The structure of **7aa**, which is the most stable isomer among the geometries shown in Table III, has been determined by X-ray diffraction. A comparison of bond lengths, bond angles and torsion angles shows fairly small differences between the cis- and trans-isomers of 1,4-di-sulfoxide **7**, but the C—S—C angles are closely similar to that (97.9°) reported experimentally for the **7aa** conformer.[31]

CONCLUSIONS

We have examined a number of organic six-membered cyclic sulfoxides (**1–7**) using ab initio calculations from both structural and energetic points of view. These compounds prefer a chair conformation. For 1-oxa-thiane (**1**), a slight axial preference of the sulfinyl oxygen has been predicted, which is in agreement with the results of dynamic NMR spectreoscopic data and gas phase electron diffraction. While 1-oxo-1,2-dithiane (**2**) or 1-oxo-1,4-dithiane (**4**) show an axial preference of the S═O bond, the equatorial conformation of 1-oxo-1,3-dithiane (**3**) is calculated to be more stable than the axial form. The axial geometry of **3** is destabilized as a result of the closer proximity of the sulfinyl oxygen and the cross-ring sulfur atom. The di-axial conformations of 1,2-dioxo-1,2-dithiane (**5**) or 1,4-dioxo-1,4-dithiane (**7**) are predicted to be the most stable geometries of these isomers; the axial-equatorial conformation of 1,3-dioxo-1,3-dithiane (**6**) is the energy-minimum geometry of **6**. 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 **3** and **6**, can play a rule.

C—C bond distances in all structures are significantly shorter than standard Csp^3—Csp^3 bond length of 1.54 Å. While the S—O_{ax} bonds in compounds **1**, **2**, **4**, **5**, and **7** are slightly longer than the S—O_{eq} bonds, the reverse order is observed in **3** and **6**. The present calculations indicate that 1-oxo-1,2-dithiane is the most stable compound among the 1-oxo-1,*n*-dithianes. Dioxo-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.[32] Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints.[33] 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.[34] Single point energy calculations at MP2/6-31G*//HF/6-31G* and B3LYP/6-311G(2df,p)[35] 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.[36]

REFERENCES

[1] (a) S. Chambert, J. Desire, and J.-L. Decout, *Synthesis*, 2319 (2002); (b) E. Block and M. Aslam, *Tetrahedron*, **44,** 281 (1988).
[2] H. B. Kagan and F. Rebiere, *Synlett*., 643 (1990).
[3] E. L. Eliel and S. H. Wilen, In *Stereochemistry of Organic Compounds* (Wiley, New York, 1994).
[4] C. H. Bushweller, In *Conformational Behavior of Six-Membered Rings*, E. Juaresti Ed., pp. 25–58 (VCH, New York, 1995).
[5] F. G. Ridell, *The Conformational Analysis of Heterocyclic Compounds* (Academic Press, New York, 1980).
[6] F. Freeman, A. Phornvoranunt, and W. J. Hehre, *J. Phys. Org. Chem*., **12,** 176 (1999).

[7] (a) A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects of Oxygen*, (Springer, Berlin, 1983); (b) P. P. Graczky and M. Mikolajczky, *Top. Stereochem*., **21,** 159 (1994); (c) E. Juareisti and G. Cuevas, *Tetrahedron*, **48,** 5019 (1992).
[8] G. Forgács, I. Hargittai, I. Jalsovszky, and Á. Kucsman, *J. Mol. Struct*., **243,** 123 (1991).
[9] F. A. Carey, P. M. Smith, R. J. Maher, and R. F. Bryan, *J. Org. Chem*., **42,** 961 (1977).
[10] (a) I. Yavari, H. Fallah-Bagher-Shaidaii, and D. Nori-Shargh, *J. Mol. Struct. (Theochem)*, **364,** 79 (1996); (b) I. Yavari, A. Jabbari, and Sh. Moradi, *J. Mol. Struct. (Theochem)*, **631,** 225 (2003); (c) I. Yavari, A. Jabbari, and Sh. Moradi, *Lect. Notes Comput. Sci*., **3044,** 432 (2004); (d) I. Yavari, M. Haghdadi, and R. Amiri, *Phosphorus, Sulfur, and Silicon*, **179,** 2015 (2004).
[11] E. Juaristi and M. Ordonez, In *Organosulfur Chemistry*, P. Page Ed., pp. 64–95, (Academic Press, London, 1998), and references therein.
[12] C. R. Johnson and D. McCants, *J. Am. Chem. Soc*., **86,** 2935 (1964).
[13] F. A. Carey, O. D. Dailey, and W. C. Hutton, *J. Org. Chem*., **43,** 96 (1978).
[14] (a) J. B. Lambert and R. G. Keske, *J. Org. Chem*., **31,** 3429 (1966); (b) J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem*., **37,** 377 (1972).
[15] G. W. Buchanan and T. Dorst, *Tetrahedron Lett*., **16,** 1683 (1975).
[16] R. J. Abraham, L. Pollock, and F. Sancassan, *J. Chem. Soc., Perkin Trans. 2*, 2329 (1994).
[17] G. Barbarella, P. Dembech, and V. Tognoli, *Org. Magn. Reson*., **22,** 402 (1984).
[18] E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc*., **91,** 2703 (1969).
[19] E. Juaristi, J. Guzman, V. V. Kane, and R. S. Glass, *Tetrahedron*, **40,** 1477 (1984).
[20] (a) S. W. Bass and S. A. Evans, *J. Org .Chem*., **45,** 710 (1980); (b) T. Takata, K. Iida, and S. A. Oae, *Heterocycles*, **15,** 847 (1981).
[21] D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc*., **89,** 5315 (1967).
[22] K. Muler, *Helv. Chim. Acta*, **53,** 1112 (1970).
[23] P. C. B. Page, D. Westwood, A. M. Z. Slawin, and D. J. Williams, *J. Chem. Soc*., *Perkin Trans. 1*, 18 (1989).
[24] P. C. B. Page, D. Westwood, A. M. Z. Slawin, and D. J. Williams, *J. Chem. Soc*., *Perkin Trans. 1*, 1158 (1989).
[25] P. C. B. Page and J. C. Prodger, *Synlett*., 460 (1990).
[26] P. C. B. Page, J. C. Prodger, M. Hursthouse, and M. Mazid, *J. Chem. Soc., Perkin Trans 1*, 167 (1990).
[27] P. C. B. Page and J. C. Prodger, *Synlett*., 84 (1991).
[28] L. Van Acker and M. Anteunis, *Tetrahedron Lett*., **15,** 225 (1974).
[29] N. Yoshimitsu, G. Michimasa, K. Kiyoshi, and Sh. Motoo, *Heterocycles*, **41,** 419 (1995).
[30] V. K. Aggarwal, I. W. Davies, R. Franklin, J. Maddock, M. F. Mahon, and K. C. Molloy, *J. Chem. Soc. Perkin Trans. 1*, 2363 (1994).
[31] H. M. M. Shearer, *J. Chem. Soc*., 1394 (1959).
[32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rubuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Oritz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L.

Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN 98, Revision A*.6, Gaussian. Inc., Pittsburgh, PA, 1998.
[33] F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999).
[34] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28,** 213 (1973).
[35] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2000).
[36] R. S. Grev, C. L. Janssen, and H. F. Schaefer, *Chem. Phys*., **95,** 5128 (1991).