HETEROCYCLES, Vol. 62, 2004, pp. 235 - 249
Received, 17th December, 2002, Accepted, 27th January, 2003, Published online, 6th May, 2003

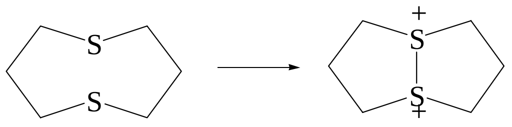
COMPUTATIONAL STUDY ON CONFORMATIONAL FEATURES OF PROTONATED 5*H*,7*H*-DIBENZO[*b,g*][1,5]DITHIOCIN OXIDES BY *ab initio* MO CALCULATIONS

Keiji Okada, Masato Tanaka, and Katsuo Ohkata*

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

Abstract – The *ab initio* MO calculations with HF/6-31G* basis set were performed in the neutral 5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocin 12-oxide (**1**), the mono-protonated (**1-H$^+$**) and the di-protonated (**1-2H$^+$**) sulfoxides. The calculations indicated that the protonation is very important process for the 1,5-oxygen shift and the oxygen atom approaches to another sulfur by protonation. The inside oxygen conformation (the TB_i or the BB_i) is important for the intramolecular oxygen shift to form the oxygen-bridged intermediate in **1-2H$^+$**-BB_b, and the outside oxygen conformation (the TB_o or the BB_o) is the most probable conformation to form the sulfurane intermediate in **1-2H$^+$**-BB_o and **2-2H$^+$**-BB_o, respectively.

Many interesting phenomena were observed in 1,5-dithiacyclooctane (**1,5-DTCO**) derivatives; for example very low oxidation potential compared with the related compounds and dicationic species formed by transannular bonding (Scheme 1).[1-4] Recently, theoretical investigation suggested a partial but significant S-S σ bond in the cationic species of ditiacyclooctane derivative.[5] We reported an acid-induced 1,5-oxygen shift in 5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocin 12-oxide (**1**) to produce the corresponding 6-oxide (**2**) (Scheme 2).[3] The transannular 1,5-oxygen shift in **1** proceeded smoothly in chloroform solution under acidic conditions but the reverse rearrangement from **2** to **1** was not observed. The oxygen isotope exchange experiments indicated that at least 70% of the 1,5-oxygen shift occurred intramolecularly through a direct path or coupling of intimate ion pair in the solvent cage (Scheme 3). Treatment of **1** with D_2SO_4 furnished the same dithiodication as that resulted from **2**. Quenching of the dithiodication with aqueous sodium carbonate gave **2**, quantitatively and the disproportionation was not observed (Scheme 4).[6]

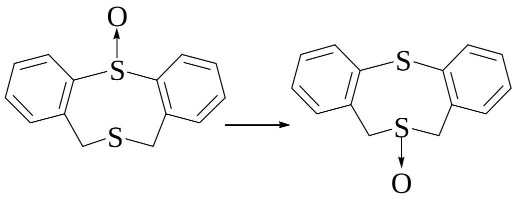


1,5-ditiacyclooctane

1,5-DTCO

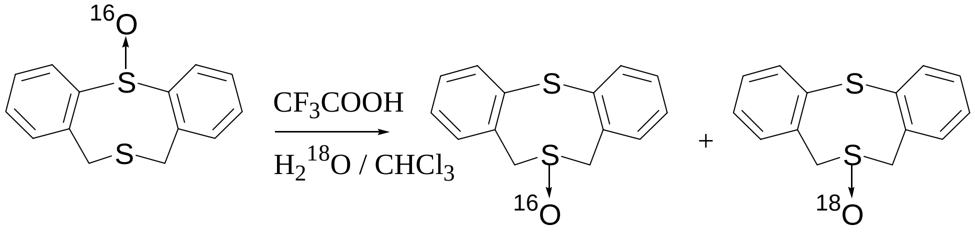
dthiadication

Scheme 1



1 **2**

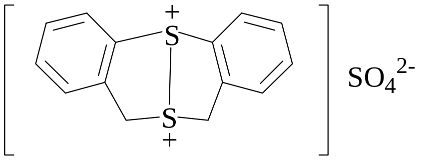
Scheme 2



1

2-^{16}O 70 : 30 **2-**^{18}O

Scheme 3



Dication
Scheme 4

In order to compare the stability between the protonated intermediates in the sulfoxides (**1** and **2**), the *ab initio* MO calculations with HF/6-31G* basis set were performed in various conformers of the intermediates. In this paper the conformational features and various intermediates in the 1,5-oxygen shift are discussed on the basis of the *ab initio* MO calculations.

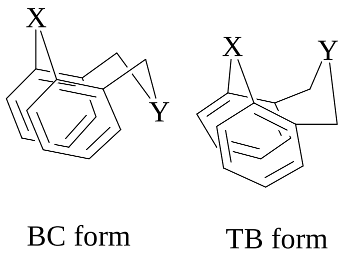
RESULTS AND DISCUSSION

Computational details

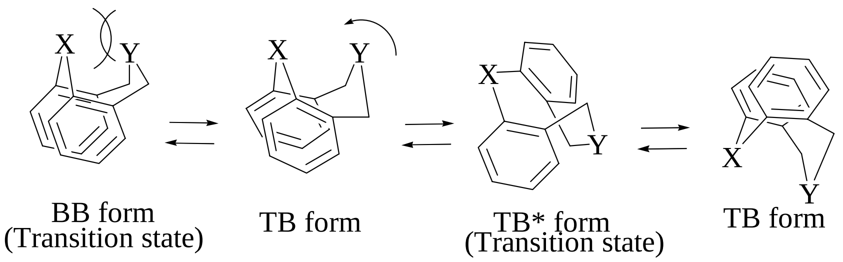
All the calculations were carried out at Hartree-Hock (HF) level with the 6-31G* basis set using the program packages of HONDO 2001.[7] The initial geometries of the molecules were assumed by the PM3 method. The frequency calculations were carried out for the optimized geometries in order to verify that they were minima and then the atomic charges were evaluated from the Mulliken population. All structures were optimized without geometrical constrains.

Conformational considerations of the dibenzodithiocin system and the 1,5-oxygen shift

There are at least two kinds of conformations available to dibenzo-1,4-cyclooctadiene system (eight-membered ring system). They are the *boat-chair* BC form and the *twist-boat* TB form (Scheme 5). The *boat-boat* BB form that is a transition state for interconversion between the TB forms is destabilized by the torsional strain caused by the van der Waals repulsion between the X (at 1-position) and Y (at 5-position) groups. When there is no extra stabilization factor such as 1,5-transannular attractive interaction,[8] usually the BB form is less stable than the BC and TB forms (Scheme 6).[9] Another interconversion between the TB forms is known as a ring-inversion and occurs *via* the C_2 symmetric TB* form (transition state).

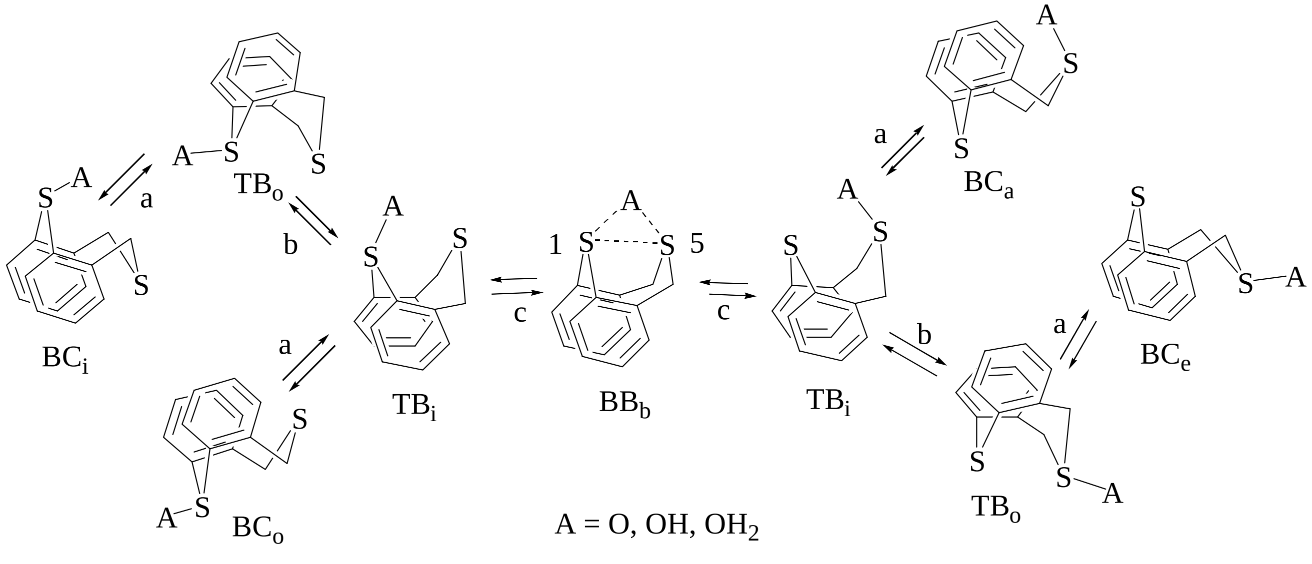


Scheme 5

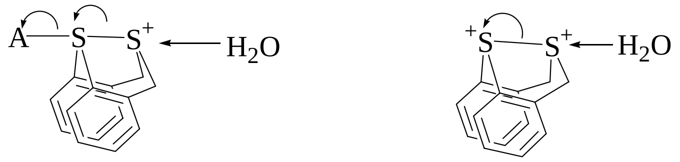


Scheme 6

For the dibenzodithiocin 12-*S*-oxide (**1**) (eight-membered ring), four stable conformations are capable of being populated (Scheme 7). These are the BC_i and BC_o forms and the TBi and TB_o forms where the orientation of the oxygen on sulfur can be described as inside or outside in these forms (subscript i or o). Similarly, for the 6-*S*-oxide derivative (**2**), four stable conformations are capable of being populated. These are the BC_a and BC_e forms and the TB_i and TB_o forms where the orientation of the oxygen on sulfur can be described as *axial-like* or *equatorial-like* in the BC forms (subscript a or e) and inside or outside in the TB forms (subscript i or o). Scheme 7 illustrated the pathway of interconversion between these conformations along with the transannular 1,5-oxygen shift *via* the *bridged boat-boat* (BB_b) conformation.



Scheme 7 Conformational interconversion: (a) ring inversion by rotation about the Ar-S-Ar bond; (b) ring inversion *via* the TB* form; (c) transannulation between S(1) and S(5)



Sulfurane type Dication type

Scheme 8

According to the isotope exchange experiments in **1** and **2**, definitely there existed the intramolecular and the intermolecular pathways in the 1,5-oxygen shift which proceeds through a protonated intermediate in chloroform/trifluoroacetic acid solution.[3] The oxygen atom of the sulfoxide (**1**) must approach to the sulfide moiety for the intramolecular 1,5-oxygen shift. Therefore, it is supposed that the intramolecular oxygen shift proceeds *via* TB or BB form and the inside position is more favorable for the oxygen atom in the TB or BB form than the outside position. Thus, the TB$_{i}$ or BB$_{i}$ form seems to be an important conformation for the intramolecular oxygen shift. It is speculated that this reaction proceeds through an oxygen-bridged BB form (BB$_{b}$). On the other hand, it is considered that the intermolecular 1,5-oxygen shift proceeded through a dicationic intermediate (dicationic type path) formed by elimination of the oxygen or a concerted mechanism (sulfurane type path) followed by a nucleophilic attack of water to another sulfur atom (Scheme 8).

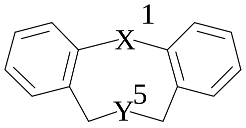
Conformational considerations of dibenzodithiocin oxides (1) and (2)

We performed *ab initio* molecular orbital calculations of various conformers in **1** and **2** at Hartree-Hock (HF) level with the 6-31G* basis set using the program packages of HONDO 2001.[7] The calculated total energies and relative energies along with the selected structural parameters around sulfur atom are summarized in Table 1.

The BC forms were more stable than the TB forms in both the sulfoxides (**1**) and (**2**). The difference of energy levels between the BC$_{o}$ form and the TB$_{o}$ form in **1** was 28 kJ/mol, while the difference was 13 kJ/mol in **2**. In the ^{1}H NMR spectra of **1** and **2**, only the signals assigned to the BC form was observed in the sulfoxide (**1**), while the signals for a mixture of the BC/TB form were observed in the sulfoxide (**2**) at 35 ℃ in $CDCl_3$.[3] The most stable conformation in **1** was calculated to be the BC$_{o}$ form and that in **2** was the BC$_{e}$ form that was only 5 kJ/mol more stable than the BC$_{o}$ form of the sulfoxide (**1**). However, the energy difference between **1**-BC$_{o}$ form and **2**-BC$_{e}$ form is too small to explain the fact that the equilibrium in 1,5-oxygen shift lies heavily to the side of 5-oxide derivative (**2**). Therefore, it is considered that the energy difference (20 kJ/mol) between TB forms in **1** and **2** affects the very large equilibrium ratio in the oxygen rearrangement.

The structural features in the TB forms of **1** are interesting as compared with the interatomic distances between the two sulfur atoms. The interatomic distance S(1)-S(5) between two sulfur atoms in the **1**-TB$_{i}$ form (406 pm) was comparable to that of the BC forms (*ca.* 390 pm). These interatomic

Table 1. Calculated total energies of the neutral sulfoxides (**1**, **2**) and the sulfide (**3**), the relative energies from **1**-BC$_o$ and the selected structural parameters



compd.	X	Y
1	SO	S
2	S	SO
3	S	S

compd	form	total energy	relative energy		interatomic distance		
					S(1)-O	S(5)-O	S(1)-S(5)
		(a.u.)	(a.u.)	(kJ/mol)	(pm)	(pm)	(pm)
1	BC$_o$	-1406.96712	0.0 (std.)	0.0 (std.)	148.7	536.5	388.8
	BC$_i$	-1406.96288	0.00424	11.1	148.8	377.9	397.3
	TB$_o$	-1406.95645	0.01067	28.0	148.9	532.1	385.4
	TB$_i$	-1406.95123	0.01589	41.7	148.8	412.8	405.8
2	BC$_e$	-1406.96909	-0.00197	-5.2	506.1	148.9	387
	BC$_a$	-1406.96542	0.00170	4.5	443.5	148.3	389.4
	TB$_o$	-1406.96423	0.00289	7.6	516.8	148.8	405.8
3	BC	-1332.16646	0.0 (std.)	0.0 (std.)	-	-	387.2
	TB	-1332.15861	0.00785	20.6	-	-	409.6

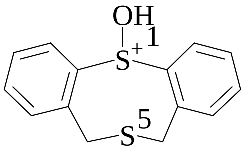
distances are almost the same as that in dibenzodithiocin (**3**). The interatomic distance between two sulfur atoms in the **1**-TB$_o$ form was slightly 20 pm shorter than that of **1**-TB$_i$ form. Furthermore, the interatomic distance between the oxygen and the sulfur atoms at 5-position in the **1**-TB$_i$ form (413 pm) is slightly longer than that (378 pm) of the BC$_i$ form. These structural features are very different from that of 1,5-dithiacyclooctane (**1,5-DTCO**). When **1,5-DTCO** is converted to the mono-sulfoxide, two sulfur atoms approach each other to result in about 40 pm shorter interatomic distance than that of **1,5-DTCO**.[10]

Conformational considerations of the mono-protonation sulfoxides (1-H$^+$) and (2-H$^+$)

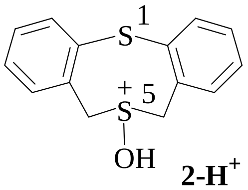
The calculated total energies and relative energies along with the selected structural parameters around sulfur atom in mono-protonated species (**1-H**$^+$) and (**2-H**$^+$) are summarized in Table 2.

The most stable conformer was the BC$_o$ form for **1-H**$^+$ and the BC$_e$ form for **2-H**$^+$, respectively. The TB forms of **1-H**$^+$ and **2-H**$^+$ were also extremely twisted in the same as the neutral sulfoxides (**1**-TB) and (**2**-TB). There are several interesting features in the conformations. The existence of the BB$_i$ conformation as a local minimum in the mono-protonated sulfoxide (**1-H**$^+$) suggests the possibility of 1,5-oxygen shift *via* this BB$_i$ form. The **2-H**$^+$-BC$_e$ form was 31 kJ/mol more stable than **1-H**$^+$-BC$_o$. The energy difference between **1-H**$^+$-BC$_o$ and **2-H**$^+$-BC$_e$ increased 6 times larger as compared with that (5 kJ/mol) of the neutral species (**1**-BC$_o$) and (**2**-BC$_e$). Judging from the energy difference (31 kJ/mol),

Table 2. Calculated total energies of the mono-protonated sulfoxides (**1-H**$^+$) and (**2-H**$^+$), the relative energies from (**1-H**$^+$-BC$_o$) and the selected structural parameters



1-H$^+$



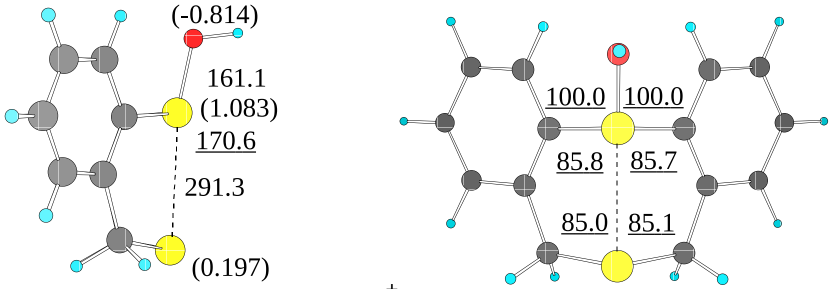
2-H$^+$

compd	form	total energy	relative energy		interatomic distance		
					S(1)-O	S(5)-O	S(1)-S(5)
		(a.u.)	(a.u.)	(kJ/mol)	(pm)	(pm)	(pm)
1-H$^+$	BC$_o$	-1407.33584	0.0 (std.)	0.0 (std.)	160.1	530.4	371.2
	BC$_i$	-1407.33339	0.00245	6.4	160.8	398.1	396.6
	TB$_o$	-1407.32639	0.00945	24.8	160.5	535.0	380.3
	TB$_i$	-1407.33162	0.00422	11.1	161.4	452.2	416.1
	BB$_o$	-1407.32920	0.00664	17.4	161.1	541.1	291.3
	BB$_i$	-1407.31694	0.01890	49.6	160.2	293.5	331.1
2-H$^+$	BC$_e$	-1407.34776	-0.01192	-31.3	498.1	161.2	374.6
	BC$_a$	-1407.34249	-0.00665	-17.5	427.8	160.0	379.7
	TB$_o$	-1407.33971	-0.00387	-10.1	475.3	159.3	409.0
	TB$_i$	-1407.34141	-0.00557	-14.6	327.0	158.7	346.3
	BB$_o$	-1407.33707	-0.00123	-3.2	447.6	162.8	284.9

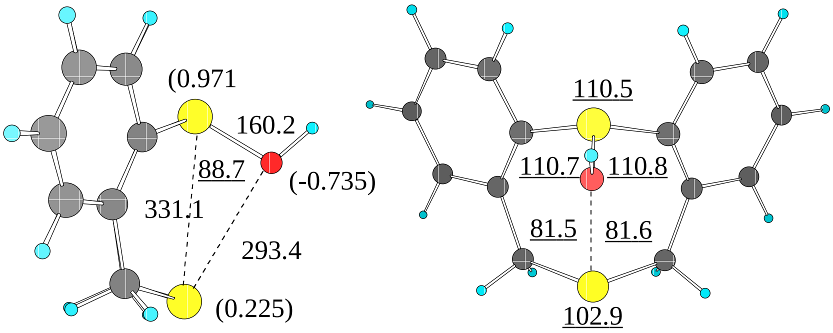
the equilibrium in the rearrangement between **1-H**$^+$ and **2-H**$^+$ can be expected to lie so far to **2-H**$^+$ thermodynamically.

There were found three types of local minimum for the BB forms, thus **1-H**$^+$-BB$_o$, **1-H**$^+$-BB$_i$ and **2-H**$^+$-BB$_o$. Optimized geometries of these conformers along with the selected structural parameters are illustrated in Figure 1. Expectably the distances between two sulfur atoms become shorter as changing from the **1-H**$^+$-TB$_o$ form (380 pm) to the **1H**$^+$-BB$_o$ form (291 pm). The S(1)-O lengths in **1-H**$^+$ were 160-161 pm, which were almost the same as that (159-163 pm) of S(5)-O lengths in **2-H**$^+$. These values were only 11 pm longer than that (149 pm) of the neutral species (**1**) and (**2**).

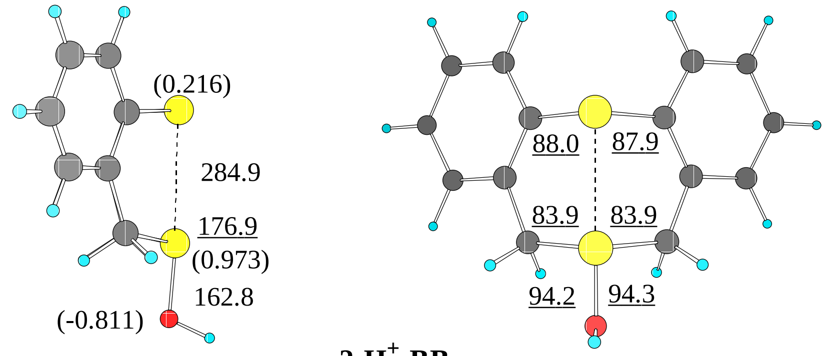
The **1-H**$^+$-BB$_i$ form seems to be a possible intermediate of the 1,5-oxygen shift from the mono-protonated species (**1-H**$^+$) to (**2-H**$^+$) because the interatomic distance between the oxygen and the sulfur atom at 5-position is the shortest (294 pm) among the mono-protonated sulfoxide (**1-H**$^+$). The positive charge at the S(1) in the **1-H**$^+$-BB$_i$ decreases and the positive charge at the S(5) increases compared with that of **1-H**$^+$-BB$_o$. Although the oxygen atom of **1-H**$^+$-BB$_b$ form was located at the equidistant position between the two sulfur atoms as the BB$_b$ shown in Scheme 7 in the initial optimization at PM3 level, the oxygen atom moved to return to a typical S-O bond at 1-position (the **1-H**$^+$-BB$_i$ form in Figure 1) as the result of 6-31G* calculation. The optimized geometries for **1-H**$^+$-BB$_o$ and **2-H**$^+$-BB$_o$ showed the angle CSO is 100° and 94° , respectively. The distances between two sulfur atoms in the **2-H**$^+$-BB$_o$ form (285 pm)



1-H$^+$-BB$_o$



1-H$^+$-BB$_i$

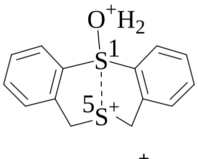


2-H$^+$-BB$_o$

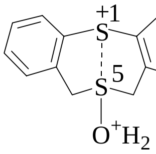
Figure 1. Optimized geometries of boat-boat conformations of the mono-protonated sulfoxide **1-H$^+$** and their selected structural parameters**;** the figures refer to bond lengths, the figures refer to bond angles, and (figures) refer to atomic charges

and of **1-H$^+$**-BB$_o$ form (291 pm) were shorter than the sum of van der Waals radii (360 pm) of two sulfur atoms,[12] although the S-O bond lengths were 161.1 and 162.8 pm which were almost the same as the other conformers. The angles of O-S-S in **2-H$^+$**-BB$_o$ form (177°) and **1-H$^+$**-BB$_o$ form (171°) were almost linear. The sulfur atoms bearing the oxygen atom in the **1-H$^+$**-BB$_o$ form and the **2-H$^+$**-BB$_o$ form composed the distorted structure of trigonal bipyramid in sulfurane.[8] More interestingly, the interatomic distance between two sulfur atoms increased, when the conformation changed from the **1-H$^+$**-BB$_o$ form to the **1-H$^+$**-BB$_i$ form. Notwithstanding, the bond lengths of the protonated sulfoxides (*ca.* 160 pm) were almost similar to those of all forms. The positive charge at the S(5) atom in **1-H$^+$**-BB$_o$ was calculated to be 0.197 that indicates a very weak interaction between S(1) and S(5).

Table 3. Calculated total energies of the di-protonated sulfoxides (**$1\text{-}2H^+$** and **$2\text{-}2H^+$**), the relative energies from (**$1\text{-}2H^+$**-BC_o) and selected structural parameters along with atomic charges



$1\text{-}2H^+$



$2\text{-}2H^+$

compd	form	total energy	relative energy			interatomic distance			atomic charge	
					S(1)-O	S(5)-O	S(1)-S(5)	S(1)	S(5)	O
		(a.u.)	(a.u.)	(kJ/mol)	(pm)	(pm)	(pm)			
$1\text{-}2H^+$	BC_o	-1407.45931	0 (std.)	0 (std.)	187.8	514.2	327.7	0.989	0.272	-0.858
	BC_i	-1407.49989	-0.04058	-106.5	287.5	469.8	383.9	0.802	0.274	-0.914
	BB_o	-1407.55548	-0.09618	-252.5	296.8	499.8	210.6	0.737	0.590	-0.910
$1\text{-}2H^+$	BB_b	-1407.55264	-0.09333	-245.0	308.7	311.1	210.5	0.744	0.636	-0.910
$2\text{-}2H^+$	BB_o	-1407.56341	-0.10411	-273.3	477.6	266.7	210.9	0.667	0.637	-0.927

Conformational considerations of di-protonation sulfoxides ($1\text{-}2H^+$ and $2\text{-}2H^+$)

The calculated total energies and relative energies along with the selected structural parameters and atomic charges around sulfur atom in di-protonated species (**$1\text{-}2H^+$** and **$2\text{-}2H^+$**) are summarized in Table 3. The most stable conformation was calculated to be the **$2\text{-}2H^+$**-BB_o in the di-protonated sulfoxides. The characteristic features of di-protonated sulfoxides (**$1\text{-}2H^+$** and **$2\text{-}2H^+$**) were very different from the neutral sulfoxides (**1** and **2**) and the mono-protonated sulfoxides (**$1\text{-}H^+$**) and (**$2\text{-}H^+$**). A series of calculations of **$1\text{-}2H^+$** and **$2\text{-}2H^+$** indicated that the S-S bond formation was clarified by means of the approaching of two sulfur atoms each other. The BB_o conformer strongly prefers to the BC_o form in the di-protonated sulfoxide (**$1\text{-}2H^+$**).[3] According to the calculations, the BB_o form was 253 kJ/mol more stable than the BC_o form.

The optimized geometries of some conformers of **$1\text{-}2H^+$** and **$2\text{-}2H^+$** are illustrated in Figure 2 where some structural parameters and atomic charges around sulfur atoms are also shown. The bond distance (297 pm) between oxygen and sulfur of the BB_o form was increased relative to that (188 pm) of the BC_o form in the di-protonated sulfoxide (**$1\text{-}2H^+$**), though the corresponding value (160 pm) of the mono-protonated sulfoxide (**$1\text{-}2H^+$**) was only 11 pm longer than that (149 pm) of the neutral sulfoxide in which there was no difference of the bond distance between the BC form and the TB or BB form. The S(1)-S(5) interatomic distances in the BB_o series (**$1\text{-}H^+$**) and (**$2\text{-}2H^+$**) became much shorter according to the increase of electronegative character of the apical moiety ($\text{-}O^+H_2$), that is from 291 pm for the mono-protonated sulfoxide (**$1\text{-}H^+$**) to 211 pm for the di-protonated intermediate (**$1\text{-}2H^+$**), while the S(1)-O distances of the same series became longer from 161 to 297 pm. The optimized geometries for **$1\text{-}2H^+$**-BB_o and **$2\text{-}H^+$**-BB_o showed the angle CSO were close to a right angle (96-98°) and another sulfur atom was along the axis of the S(1)-O bond.

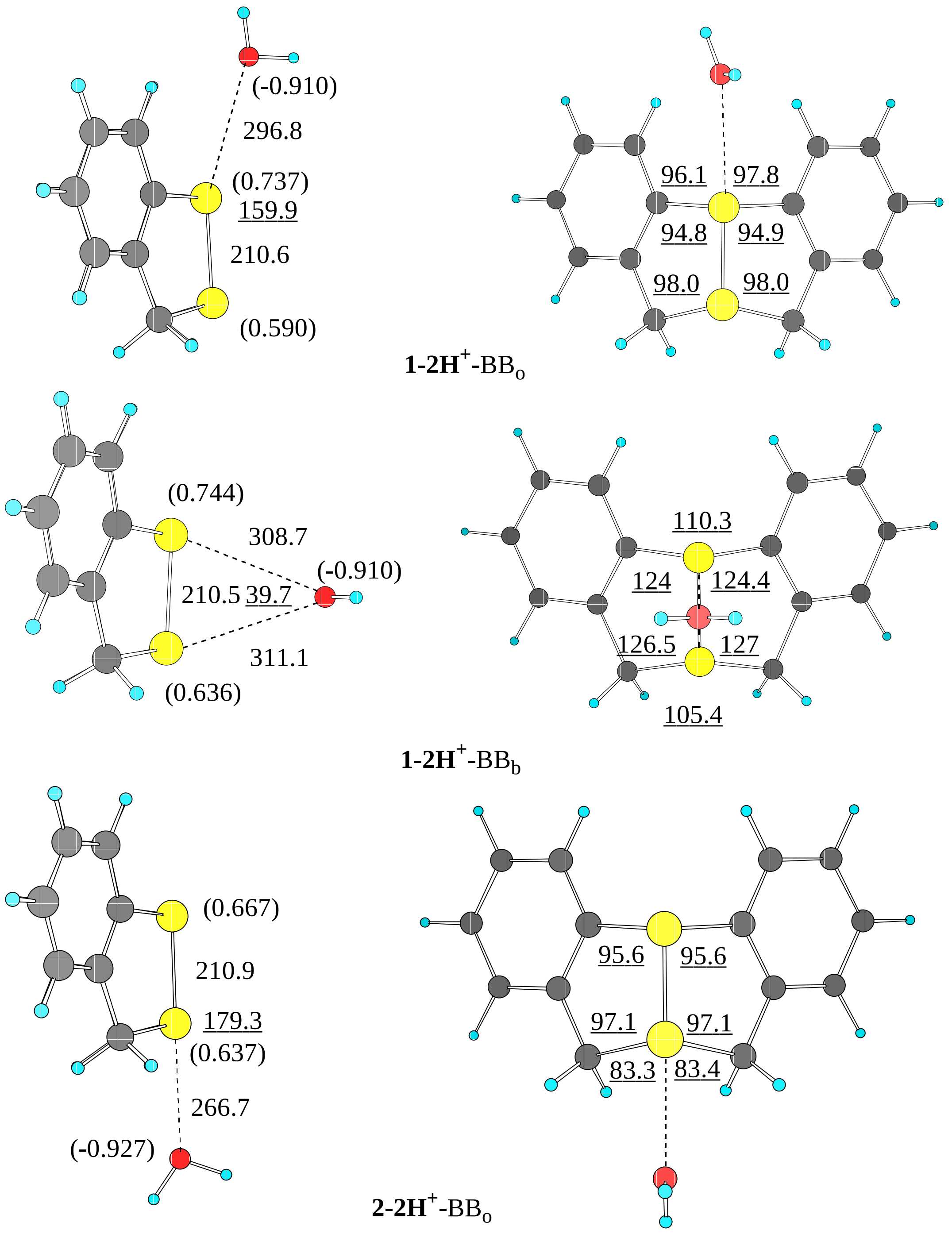


Figure 2. Optimized geometries of boat-boat conformations of the mono-protonated sulfoxides (**1-2H**$^+$ and **2-2H**$^+$) and their selected structural parameters**;** the figures refer to bond lengths, the figures refer to bond angles, and the (figure)s refer to atomic charges

The distances between two sulfur atoms in the **1-2H**$^+$-BB$_o$ form (211 pm) and of **2-2H**$^+$-BB$_o$ form (211 pm) were much shorter than the sum of van der Waals radii (360 pm) of two sulfur atoms as well as the S-O bond lengths were stretched to be 297 and 267 pm as shown in Figure 3, respectively.[12] The angles of O-S-S in **1-2H**$^+$-BB$_o$ form (160°) and **2-2H**$^+$-BB$_o$ form (179°) were almost linear, respectively. The sulfur atom bearing the oxygen atom in the **1-2H**$^+$-BB$_o$ form and the **2-2H**$^+$-BB$_o$ form was composed a typical structure of trigonal bipyramid in sulfurane.[11] When the conformation in **1-2H$^+$** was changed from the BC$_o$ to the BB$_o$ form, the positive charge at S(5) atom increased from 0.272 to 0.590 due to the S(1)-S(5) bond formation.

Furthermore, the local minimum for the BB$_b$ form in **1-2H$^+$** which formed a bridged structure by the oxygen atom was found in the present optimization (Figure 2). The S(1)-S(5) interatomic distance was 211 pm and the S(5)-O distances are 311 pm. These distances are less than the sum of van der Waald radii (S = 1.80 and O = 1.52 pm, respectively).[12] The BB$_b$ is regarded as a hydrated dithiodication. In this conformation, the negative charge (-0.910) increased at the oxygen and the positive charges at two sulfur atoms were 0.744 at S(1) and 0.636 at S(5), respectively.

Comparisons of stability of the neutral, mono- and di-protonated sulfoxides by MO calculations

In order to compare with the energy levels of **1**, **2**, **1-H$^+$**, **2-H$^+$**, **1-2H$^+$**, **2-2H$^+$** and the naked dication (**4**) each other, the potential energy values of two equivalent molecules of H_2O (-76.01075 a.u.) and/or H_3O^+ (-76.28934 a.u.) were added to the corresponding energy values to make isodesmic reactions.

$$
\begin{aligned}
[\mathbf{1} \text{ or } \mathbf{2}] + 2\,[H_3O^+] &\rightarrow [\mathbf{1} \text{ or } \mathbf{2\text{-}H^+}] + [H_2O] + [H_3O^+] \\
&\rightarrow [\mathbf{1} \text{ or } \mathbf{2\text{-}2H^+}] + 2\,[H_2O] \\
&\rightarrow [\mathbf{1} \text{ or } \mathbf{2\text{-}H^+(H_2O)}] + [H_3O^+] \\
&\rightarrow [\mathbf{1} \text{ or } \mathbf{2\text{-}2H^+(H_2O)}] + [H_2O] \\
&\rightarrow [\text{naked dication } (\mathbf{4})] + 3\,[H_2O]
\end{aligned}
$$

Table 4 shows the selected relative energy of the model species along with H_2O and/or H_3O^+ molecules. Furthermore, we carried out an optimization at HF/6-31G* level on some possible stable conformers as the protonated sulfoxides together with a water molecule (**1-H$^+$(H$_2$O)**, **2-H$^+$(H$_2$O)**, **1-2H$^+$(H$_2$O)** and **2-2H$^+$(H$_2$O)**) where the water is coordinated to the sulfur atom.

The stabilized energy (83.7 kJ/mol) by hydration in the di-protonated sulfoxide (**1-2H$^+$**-BB$_o$) is 72.9 kJ/mol more than that (10.8 kJ/mol) of the mono-protonated sulfoxide (**1-H$^+$**-BB$_o$) as shown in Table 4. But the hydrated (**1-H$^+$(H$_2$O)**-BB$_o$) is 64.5 kJ/mol more stable than the hydrated (**1-2H$^+$(H$_2$O)**-BB$_o$).

Table 4. Calculated total enegies containing H_2O and/or H_3O^+ and the relative energies from **1**-$BC_o(2H_3O^+)$

compd	form	H_2O [a]	H_3O^+ [a]	total energy	relative energy	
		-76.01075	-76.28934			
		(a.u.)	(a.u.)	(a.u.)	(a.u.)	(kJ/mol)
1	BC_o	0	2	-1559.5458	0.0 (std.)	0.0 (std.)
2	BC_e	0	2	-1559.54776	-0.00197	-5.2
1-H$^+$	BC_o	1	1	-1559.63593	-0.09013	-236.6
	TB_o	1	1	-1559.62648	-0.08068	-211.8
	TB_i	1	1	-1559.6317	0.0859	-225.5
	BB_o	1	1	-1559.62929	0.08349	-219.2
	BB_i	1	1	-1559.61702	0.07122	-187.0
2-H$^+$	BC_e	1	1	-1559.64785	-0.10205	-267.9
	TB_o	1	1	-1559.63979	-0.09399	-246.7
	TB_i	1	1	-1559.64149	-0.09569	-251.2
	BB_o	1	1	-1559.63716	-0.09136	-239.8
1-2H$^+$	BB_o	2	0	-1559.57698	-0.03118	-81.8
	BB_b	2	0	-1559.57413	-0.02833	-74.4
2-2H$^+$	BB_o	2	0	-1559.58491	-0.3911	-102.7
1-H$^+$(H_2O)	BB_o	0	1	-1559.63343	-0.08763	-230.0
2-H$^+$(H_2O)	BB_o	0	1	-1559.64608	-0.10028	-263.2
1-2H$^+$(H_2O)	BB_o	1	0	-1559.60885	-0.06305	-165.5
2-2H$^+$(H_2O)	BB_o	1	0	-1559.60842	-0.06263	-164.4
Naked dication (**4**)	BB	3	0	-1559.55158	-0.00579	-15.2

[a] the number of molecules.

Intramolecular oxygen shift

When the present 1,5-oxygen shift proceeds *via* intramolecular process from the mono-protonated sulfoxide (**1-H$^+$**), the stable BC_o form would be converted into the **1-H$^+$**-TB_i form, followed by twisting of the ring to form the **1-H$^+$**-BB_i form which is a favorable intermediate for the oxygen shift. The **2-H$^+$**-TB_i form produced after the oxygen shift in **1-H$^+$**-BB_i would result in the most stable **2-H$^+$**-BC_e form. Although the S-O bond lengths in every conformers were almost the same values (159-161 pm) in the present calculations, there would be a possibility occurring from the mono-protonated sulfoxide in the present 1,5-oxygen shift according to the relative stability as shown in Tables 2, 4 and Figure 1.

Comparisons of the energy differences of conformers and intermediate in Table 4 indicate that the di-protonated sulfoxide (**1-2H$^+$**-BB_o) might convert more smoothly into **1-2H$^+$**-BB_b (7.4 kJ/mol) than the mono-protonated sulfoxide (**1-H$^+$**-BB_o) into **1-H$^+$**-BB_i (32.2 kJ/mol) (Figure 3). However, the bridged structure (**1-2H$^+$**-BB_b) is regarded as a hydrated dithiodication in which a water molecule coordinated to the two sulfur atoms weakly. The bridged (**1-2H$^+$**-BB_b) was 113 kJ/mol less stable than **1-H$^+$**-BB_i form.

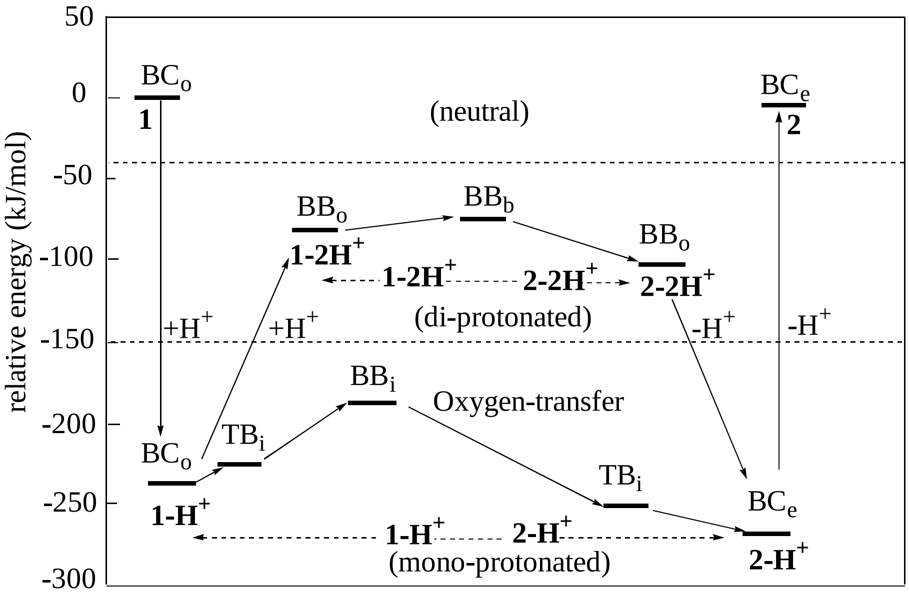


Figure 3. Relative energy level in various conformers during the intramolecular 1,5-oxygen shift of **1-H**$^+$ and **1-2H**$^+$

Intermolecular oxygen shift

The present MO calculations suggest that the 1,5-oxygen shift occurs *via* a transannular bonding intermediate, which is a quasi-sulfurane structure in the mono-protonated sulfoxide (**1-H**$^+$) and di-protonated sulfoxide (**1-2H**$^+$). In the both case, the TB$_o$ or the BB$_o$ form seems to be an intermediate precursor during the intermolecular oxygen shift. In the intermolecular shift, the oxygen shift proceeds in the process *via* various intermediates as schematically shown in Figure 4 and 5. The **1-H**$^+$-BB$_o$ is about 137 kJ/mol more stable than the **1-2H**$^+$-BB$_o$. There were found four types of local minimum for the intermediates (**1-H**$^+$**(H$_2$O)**-BB$_o$, **2-H**$^+$**(H$_2$O)**-BB$_o$, **1-2H**$^+$**(H$_2$O)**-BB$_o$ and **2-2H**$^+$**(H$_2$O)**-BB$_o$), respectively.

Especially, two oxygens and two sulfur atoms arranged linealy in **2-2H**$^+$**(H$_2$O)**-BB$_o$. Furukawa *et al.* found the similar experimental characteristics in which a nearly collinear interaction of O---S$^+$-S$^+$---O was observed in the X-Ray structural analysis of the dication of **1,5-DTCO**.[4] Figure 4 shows the interatomic distances of S(1)-O and S(1)-S(5) in various conformers in which the oxygen is oriented to the outside. The representation suggests the formation of sulfurane intermediate during the 1,5-oxygen shift in **1**. In the BB form of the di-protonated sulfoxide (**1-2H**$^+$), the S(1)-O distance was extremely elongated and the S(1)-S(5) distance was extremely shortened, though there only a little charge (0.272) appeared at S(5) in the BC form of the di-protonated sulfoxide.

The stabilized energy (83.7 kJ/mol) by hydration in the di-protonated sulfoxide (**1-2H**$^+$-BB$_o$) is 72.9 kJ/mol more than that (10.8 kJ/mol) of the mono-protonated sulfoxide (**1-H**$^+$-BB$_o$) (Figure 5). But the hydrated **1-H**$^+$**(H$_2$O)**-BB$_o$ is 64.5 kJ/mol more stable than the hydrated **1-2H**$^+$**(H$_2$O)**-BB$_o$. Judging from the comparisons of the energy levels of the intermediates, it is considered that the process from mono-protonated sulfoxide (**1-H$^+$**) prefers to that from di-protonated species (**1-2H$^+$**) in both intra- and inter-molecular 1,5-oxygen shift.

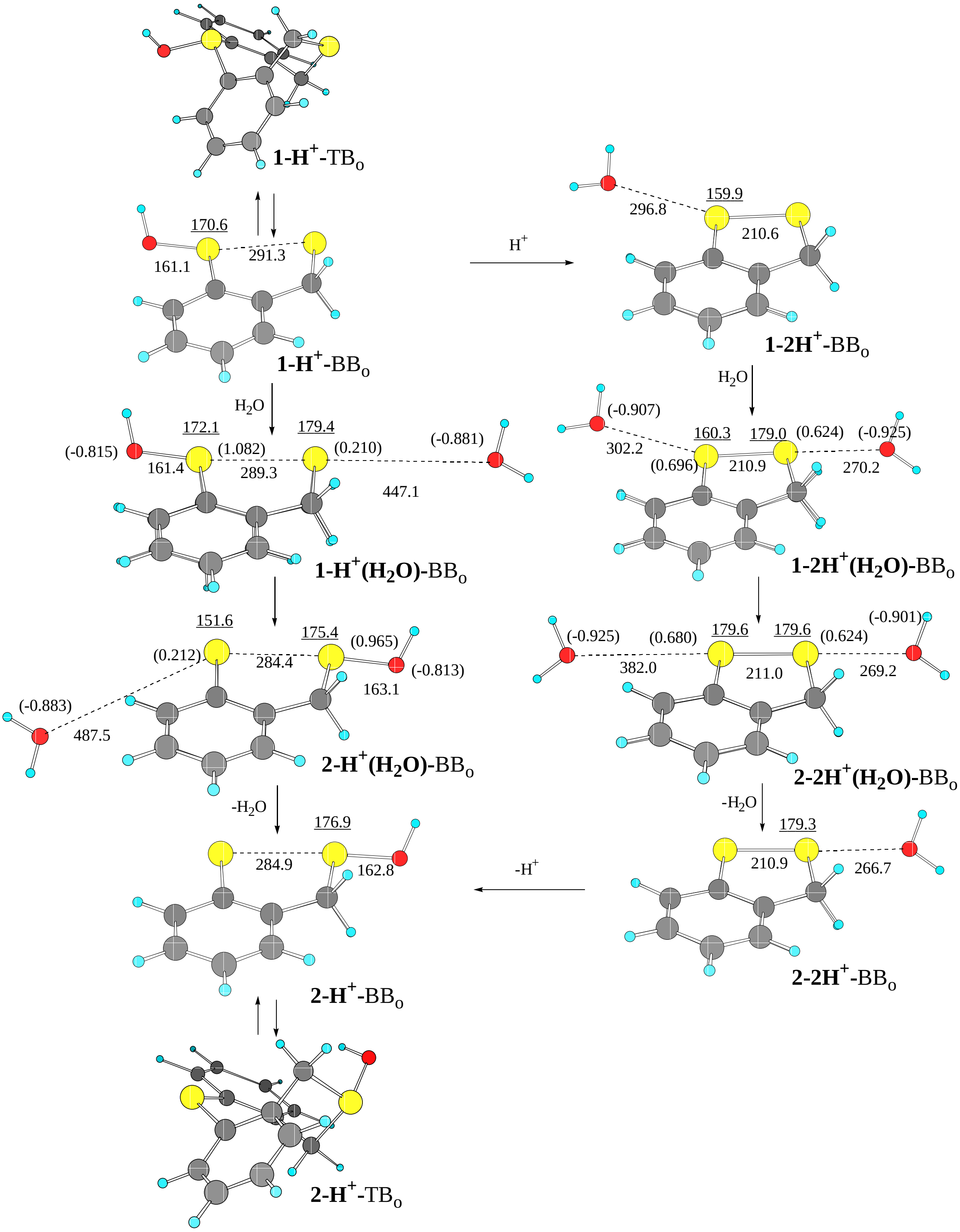


Figure 4. Optimized geometries of the intermediates in the intermolecular 1,5-oxygen shift in mono- and di-protonated sulfoxides (**1-H$^+$** and **1-2H$^+$**) and their selected structural parameters**;** the figures refer to bond lengths (pm), the figures refer to bond angles and the (figure)s refer to atomic chargs

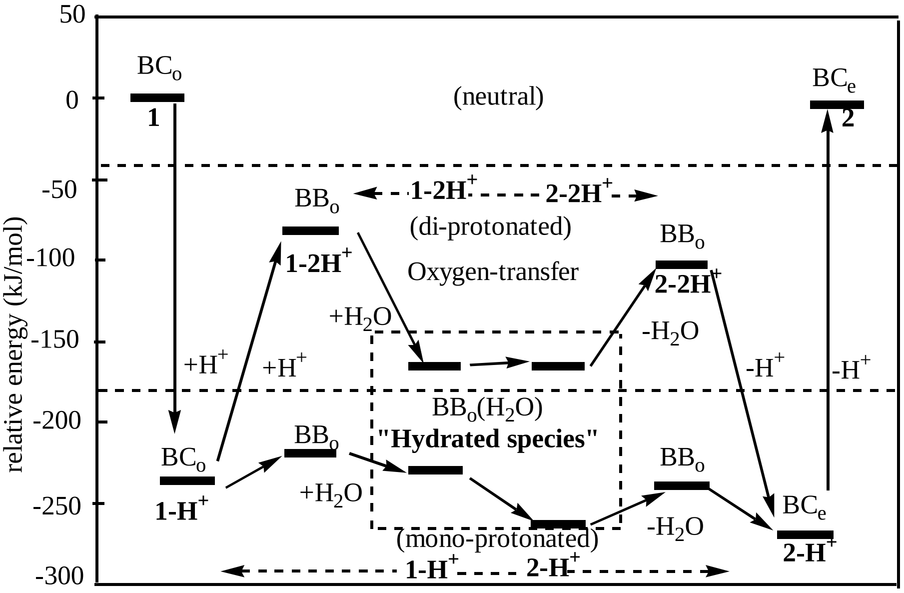


Figure 5. Relative energy level in various conformers during the intermolecular 1,5-oxygen shift of **1-H$^+$** and **1-2H$^+$**

SUMMARY

The *ab initio* MO calculations were performed in the neutral **1**, mono-protonated **1-H$^+$** and di-protonated **1-2H$^+$** sulfoxides. The calculations indicated that the protonation is very important process for the 1,5-oxygen shift and the oxygen atom approaches to another sulfur by protonation. The inside oxygen conformation (the $\mathrm{TB_i}$ or the $\mathrm{BB_i}$) is important for the intramolecular oxygen shift to form the oxygen-bridged intermediate in **1-2H$^+$**-$\mathrm{BB_b}$, and the outside oxygen conformation (the $\mathrm{TB_o}$ or the $\mathrm{BB_o}$) is the most probable conformation to form the sulfurane intermediate in **1-2H$^+$**-$\mathrm{BB_o}$ and **2-2H$^+$**-$\mathrm{BB_o}$, respectively, in order to occur the intermolecular 1,5-oxygen shift.

ACKNOWLEDGEMENTS

The authors are grateful to Professor M. Aida for her helpful advice of MO calculations. The calculations were carried out in part at the Research Center for Computational Science, Okazaki National Research Institute.

REFERENCES

1. K.-D. Asumus, *Acc. Chem. Res.*, 1979, **12**, 436; W. K. Musker, *Acc. Chem. Res.*, 1980, **13**, 200; J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, 1981, **103**, 1159; H. Fujihara and N. Furukawa, *Rev. Heteroatom Chem.*, 1992, **6**, 263; N. Furukawa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2571.
2. J.-G. Gourcy, G. Jeminet, and J. Simonet, *J. Chem. Soc., Chem. Commun.*, **1974**, 634; B. C. Gilbert,

D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1748; W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc*., 1976, **98**, 3055; N. Furukawa, A. Kawada, and T. Kawai, *J. Chem. Soc., Chem. Commun*., **1984**, 1151; H. Fujihara, A. Kawada, and N. Furukawa, *J. Org. Chem*., 1987, **52**, 4254; M. D. Ryman, D. D. Awanson, R. S. Glass, and G. S. Wilson, *J. Phys. Chem*.,1981, **85**, 1069; T. Brown, A. Hirschon, and W. K. Musker, *J. Phys. Chem*., 1981, **85**, 3767; M. Tamaoki, M. Serita, Y. Shiratori, and K. Itoh, *J. Phys. Chem*., 1989, **93**, 6052.

3. K. Ohkata, K. Okada, and K.-y. Akiba, *Tetrahedron Lett*., 1985, **26**, 4491; K. Ohkata, K. Okada, and K.-y.Akiba, *Heteroatom Chem*., 1995, **6**, 145.
4. F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn*., 1988, **61**, 2563.
5. R. Stowasser, R. S. Glass, and R. Hoffmann, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1559.
6. H. Fujihara, N. Toyoda, H. Miura, and N. Furukawa, *Chem. Lett*., **1994**, 619.
7. M. Dupuis, A. Marquez, and E. R. Davidson, HONDO 2001, based on HONDO 95, available from the Quantum Chemistry Program Exchange, Indiana University.
8. K. Ohkata, K. Takee, and K.-y. Akiba, *Tetrahedron Lett*., 1983, **24**, 4859; K. Ohkata, K. Takee, and K.-y. Akiba, *Bull. Chem. Soc. Jpn*., 1985, **58**, 1946; K.-y. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, *J. Am. Chem. Soc*., 1986, **108**, 6320; K. Ohkata, M. Ohnishi, K. Yoshinaga, K.-y. Akiba, J. C. Rongione, and J. C. Martin, *J. Am. Chem. Soc*., 1991, **113**, 9270 ; K.-y. Akiba, K. Okada, and K. Ohkata, *Tetrahedron Lett*., 1986, **27**, 5221; K. Ohkata, M. Ohnishi, and K.-y. Akiba, *Tetrahedron Lett*., 1988, **29**, 5401; K. Ohkata, S. Takemoto, M. Ohnishi, and K.-y. Akiba, *Tetrahedron Lett*., 1989, **30**, 4841.
9. R. P. Gellatly, W. D. Ollis, and I. O. Sutherlamd, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 913; N. L. Allinger, J. F. Jr. Viskocil, U. Burkert, and Y. Yuh, *Tetrahedron*, 1976, **32**, 33; R. N. Renaud and L. B. Layton, *Can. J. Chem*., 1973, **51**, 3380; R. R. Fraser, M. A. Raza, R. N. Renaud, and L. B. Layton, *Can. J. Chem*., 1975, **53**, 167; L. E. Brieaddy, B. S. Hurbert, and N. B. Metha, *J. Org. Chem*., 1981, **46**, 1630.
10. J. T. Doi, R. M. Kessler, D. L. de Leeuw, M. M. Olmrtead, and W. K. Musker, *J. Org. Chem*., 1983, **48**, 3707; G. S. Wilson, D. D. Awanson, J. T. Klug, R. S. Glass, M. D. Ryman, and W. K. Musker, *J. Am. Chem. Soc*., 1979, **101**, 1040.
11. R. A. Hayes and J. C. Martin in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, ed. by F. Bernardi, I. G. Csizmadia, and A. Mangini, Elsevier Scientific Publishing Company, Amsterdam, 1985, p. 408; T. A. Albright, J. K. Burdett, and M.-H. Whangbo in *Orbital Interactions in Chemistry*, John Wiley & Sons, Inc. New York, 1985, p. 258.
12. A. Bondi, *J. Phys Chem*., 1964, **68**, 441.