Heteroatom Chemistry
Volume 10, Number 2, 1999

Ab Initio Conformational Analysis of 1,5-Dithiacyclooctane, 1,5-Diselenacyclooctane, and 1,5-Ditelluracyclooctane

Naofumi Nakayama,[1] Ohgi Takahashi,[1] Osamu Kikuchi,[1] and Naomichi Furukawa[2]

[1]*Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan*

[2]*Tsukuba Advanced Research Alliance Center, University of Tsukuba, Tsukuba 305-8577, Japan*

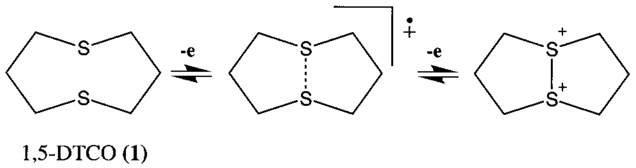
Received June 25, 1998

ABSTRACT: *Energy-minimum structures of 1,5-dithiacyclooctane (1,5-DTCO), 1,5-diselenacyclooctane (1,5-DSeCO), and 1,5-ditelluracyclooctane (1,5-DTeCO) were calculated by the ab initio molecular orbital method. Nine energy-minimum structures were obtained for each compound. A twist-boat–chair (TBC) structure is the most stable for 1,5-DTCO and 1,5-DSeCO, whereas a boat–boat (BB) structure is the most stable in 1,5-DTeCO. The TBC conformer of 1,5-DTCO has received little attention so far. The energy gap between HOMO and NHOMO in the TBC conformer of 1,5-DTCO is in good agreement with the experimental data (photoelectron spectrum). For 1,5-DTCO and 1,5-DSeCO, the boat–chair (BC) conformer in which two chalcogen atoms face each other has the highest HOMO energy among the nine conformers, and the energy barriers between the TBC and BC conformers were calculated to be relatively low for these compounds. Therefore, a conformational change from the TBC to the BC is predicted to occur before these compounds are oxidized in solution.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 159–166, 1999

INTRODUCTION

1,5-Dithiacyclooctane (1,5-DTCO, 1,5-dithiocane, **1**) is one of the best known molecules in heteroatom chemistry because of its unique chemical properties caused by the transannular interaction between the two sulfur atoms [1–3]. Its radical cation and dication, having a new bond between the two sulfur atoms (Scheme 1), are unusually stable [1,2,4]. The oxidation potential of **1** is extremely low as compared to ordinary sulfides, and its oxidation is electrochemically reversible unlike ordinary sulfides [5]. In spite of many studies on the radical cation and dication and the redox system shown in Scheme 1 [1,2,4–15], the structural details of the neutral state of **1** seem to be still rather open.

There has been no crystal structure determination of **1** itself, while the crystal structures of various metal complexes of **1** have been determined [3,16]. In most of these complexes, the molecules of **1** act as bidentate ligands and adopt the boat–chair (BC) or chair–chair (CC) conformation in which the two



1,5-DTCO (**1**)

SCHEME 1

Correspondence to: Osamu Kikuchi and Naomichi Furukawa

Contract Grant Sponsor: TARA project fund (University of Tsukuba).

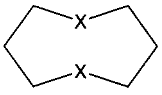
sulfur atoms face each other. It should be noted, however, that these two conformations were also found in bis(1,5-dithiacyclooctane)nickel(II) chloride, $Ni(1,5\text{-}DTCO)_2Cl_2$, where the molecules of **1** act as bridging ligands [17], and that the BC conformation was also adopted in *trans*-bis(1,5-dithiacyclooctane)tetrachlorotin(IV), *trans*-$SnCl_4(1,5\text{-}DTCO)_2$, where the molecules of **1** act as monodentate ligands [18]. Moreover, the BC and CC conformations were also found in $1,5\text{-}DTCO \cdot 2I_2$ [18]. In these cases, however, the molecules of **1** act as donors and do not represent the pure neutral state.

Setzer et al. [19] reported the photoelectron (PE) spectrum of **1** that shows a large splitting of the two sulfur lone pairs of 0.43 eV. Moreover, their molecular mechanics calculations showed that the most stable conformation of **1** is the BC conformation in which the sulfur lone pairs point toward each other. However, the values of the lone-pair–lone-pair splitting calculated for this conformation (and twist-chair–chair) by extended Hückel and semiempirical molecular orbital methods were much larger than the observed. This discrepancy can be attributed either to the limited conformations considered or to the levels of calculations in their study.

Serita et al. [20] reported the Raman and IR spectra of **1** in liquid and solid states. Based on molecular mechanics and normal-coordinate calculations, they concluded that the most probable structure of **1** in the solid state is the BC conformation as suggested by Setzer et al. [19] (which is called twisted-boat–boat in Ref. [20]) and that in the liquid state, there exist at least two structures including the BC and CC conformations. However, their assignments are not conclusive, especially for the liquid state.

Very recently, the conformational behavior of **1** in solution was studied closely by Nash et al. [21]. They have successfully analyzed the ^{1}H-NMR spectrum of **1**, which shows that **1** is fully fluxional in solution, by taking into account four types of conformations (a crownlike twist-chair–chair; two types of BC, and a twist-boat–chair (TBC)) that were obtained from their molecular mechanics calculations. Although their analysis explained well the observed NMR spectrum, we feel that it is not conclusive because there could be many sets of conformations that reproduce reasonably the experimental spectrum.

The selenium and tellurium analogues of **1**, 1,5-diselenacyclooctane (1,5-DSeCO, 1,5-diselenocane, **2**), and 1,5-ditelluracyclooctane (1,5-DTeCO, 1,5-ditellurocane, **3**) were also synthesized, and their dication salts were isolated [22,23]. Both **2** and **3** exhibited redox characteristics similar to **1**; the oxidation potentials are unusually low, and the oxidations are reversible [23,24]. Whereas the crystal structure of the dication $\mathbf{2}^{2+}$ was determined [25], the conformational properties of neutral **2** and **3** have not been studied.



2: X=Se
3: X=Te

Since the 1,5-dichalcogenacyclooctanes **1–3** are fundamental heterocycles and are important with respect to the role of the transannular interaction in controlling physical and chemical properties, it is essential to clarify their conformational properties. Although molecular mechanics calculations were performed to deduce possible conformations of **1** [19–21], those calculations do not directly take into account the effect of the transannular overlap between the sulfur lone-pair orbitals. The repulsive interaction between the two lone pairs undoubtedly affects the conformational properties of **1–3**. The only ab initio calculations performed for neutral **1** are STO-3G calculations by Tamaoki et al. [15], where only two conformations were taken into account. In the present study, we carried out ab initio molecular orbital calculations to study conformations of **1–3**. Energy minimums were searched for comprehensively based on known conformers of cyclooctane [26], and several new conformers were found that have not been found or mentioned in previous articles. It is shown that the PE spectrum of **1** can be attributed to a TBC conformer that has received little attention so far and is predicted to be the most stable by the present ab initio calculations.

CALCULATION

Calculations were carried out using SPARTAN 3.1 and 4.0 [27] on HP 735/125 workstations. The restricted Hartree–Fock (RHF) method was employed with the 3-21G$^{(*)}$ basis set that includes d-type polarization functions on sulfur, selenium, and tellurium atoms. The 6-31G* basis set was also used for **1** to compare the results obtained with both basis sets.

Initial structures for geometry optimizations were mostly constructed by referring to various conformations of cyclooctane [26]. We also located a transition structure for **1** and **2** (see the next section). Vibrational frequencies were calculated for each optimized structure to characterize stationary points as a minimum or a transition state.

The definition of the ω_1–ω_8 torsional angles with respect to the molecular skeleton is shown in Figure 1. Designations of conformations of **1** have been dependent on authors of articles, and this makes some confusion. Our nomenclature, which is based on that for cyclooctane and seems to be more general, is explained in the next section.

RESULTS AND DISCUSSION

Energy-Minimum Structures

Nine energy-minimum structures were found for each compound. Figure 2 shows the nine energy-minimum structures obtained for **1** with 6-31G*, and Figure 3 shows five conformations of cyclooctane that are related to those in Figure 2. Table 1 shows the calculated distances between two chalcogen atoms for each optimized structure of **1–3**, and Tables 2–5 show the torsional angles ω_1–ω_8.

It should be noted that three structures can be derived from the BC conformer of cyclooctane by replacing two methylene groups at 1,5-positions by sulfur atoms; the resulting three structures are designated as BC1, BC2, and BC3 (Figure 2). Likely, two structures are derived from each of the boat–boat

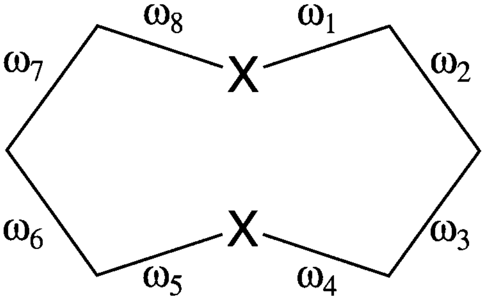
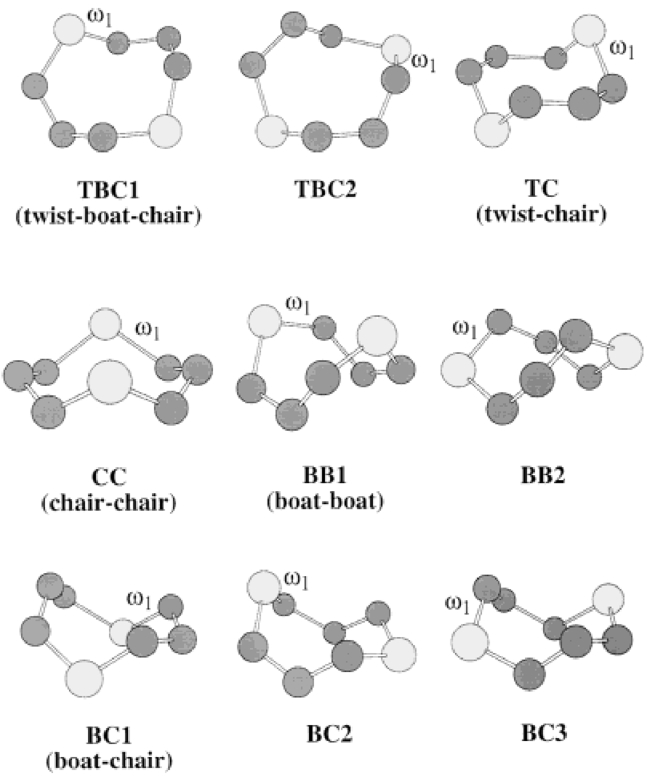
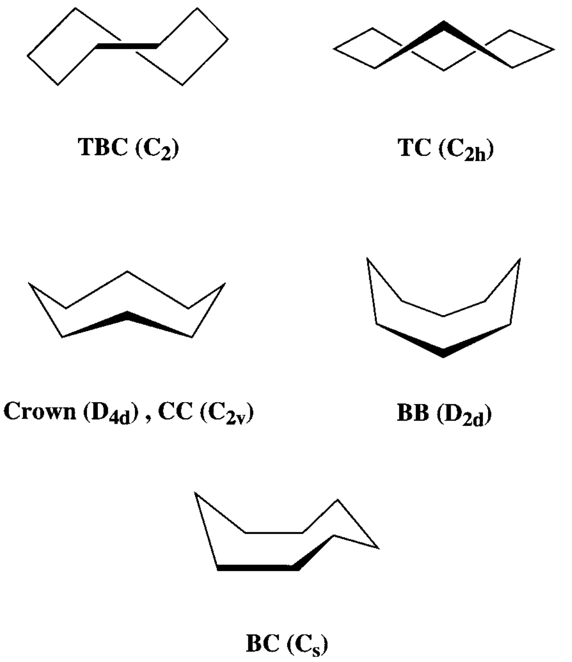


FIGURE 1 The definition of the torsional angles ω_1–ω_8. See also Figures 2 and 4.



TBC1 (twist-boat-chair)
TBC2
TC (twist-chair)
CC (chair-chair)
BB1 (boat-boat)
BB2
BC1 (boat-chair)
BC2
BC3

FIGURE 2 Energy-minimum structures of **1** obtained by RHF/6-31G*. Hydrogen atoms are omitted for clarity.



TBC (C_2)
TC (C_{2h})
Crown (D_{4d}) , CC (C_{2v})
BB (D_{2d})
BC (C_s)

FIGURE 3 The conformations of cyclooctane that have relation to those of **1–3** shown in Figure 2 and Tables 2–5.

TABLE 1 Calculated Distances (in Å) between Two Chalcogen Atoms in Nine Energy-Minimum Structures of **1–3**

Structure	*Symmetry*	**1** (*3-21G*$^{(*)}$)	**1** (*6-31G**)	**2**	**3**
TBC1	C_1	3.853	3.911	4.045	4.512
TBC2	C_1	4.235	4.012	4.479	4.973
TC	C_{2h}	3.571	3.665	3.749	4.211
CC	C_{2v}	3.669	3.772	3.625	4.043
BB1	C_2	3.331	3.402	3.428	3.903
BB2	D_2 or C_2	4.113[a]	4.171[b]	4.251[a]	4.539[b]
BC1	C_s or C_1	3.444[c]	3.537[c]	3.508[c]	4.102[d]
BC2	C_s	3.992	4.007	4.194	4.597
BC3	C_1	4.168	4.188	4.352	4.736

[a] C_2 symmetry.
[b] D_2 symmetry.
[c] C_s symmetry.
[d] C_1 symmetry.

TABLE 2 Calculated Torsional Angles (in degrees) of **1** (3-21G$^{(*)}$)[a]

Structure	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
TBC1	−123.1	52.6	55.0	−95.1	91.5	−103.2	47.6	46.4
TBC2	54.9	−98.3	94.4	−94.8	50.4	47.4	−128.5	47.4
TC	−109.9	44.6	ω_2	ω_1	$-\omega_1$	$-\omega_2$	$-\omega_2$	$-\omega_1$
CC	−100.0	79.4	$-\omega_2$	$-\omega_1$	$-\omega1$	$-\omega2$	$-\omega_2$	$-\omega_1$
BB1	−23.7	−75.2	31.3	69.3	ω_1	ω_2	ω_3	ω_4
BB2	45.0	−69.0	−41.5	68.2	ω_1	ω_2	ω_3	ω_4
BC1	103.9	−73.2	$-\omega_2$	$-\omega_1$	43.3	67.2	$-\omega_6$	$-\omega_5$
BC2	−67.0	−41.5	111.7	−69.9	$-\omega_4$	$-\omega_3$	$-\omega_2$	$-\omega_1$
BC3	74.3	−68.4	−53.0	106.6	−67.8	78.6	−107.4	41.4

[a] For the definition of ω_1–ω_8, see Figure 1.

TABLE 3 Calculated Torsional Angles (in degrees) of **1** (6-31 G*)[a]

Structure	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
TBC1	−119.1	52.0	55.4	−93.3	88.4	−101.8	49.0	44.2
TBC2	67.7	−91.8	81.9	−96.8	59.4	44.8	−113.1	31.1
TC	−106.9	44.8	ω_2	ω_1	$-\omega_1$	$-\omega_2$	$-\omega_2$	$-\omega_1$
CC	−96.7	79.8	$-\omega_2$	$-\omega_1$	ω_1	ω_2	$-\omega_2$	$-\omega_1$
BB1	−24.9	−73.8	33.6	66.6	ω_1	ω_2	ω_3	ω_4
BB2	57.3	−55.4	ω_2	ω_1	ω_1	ω_2	ω_2	ω_1
BC1	101.1	−73.3	$-\omega_2$	$-\omega_1$	41.7	67.3	$-\omega_6$	$-\omega_5$
BC2	−65.4	−41.8	109.6	−67.6	$-\omega_4$	$-\omega_3$	$-\omega_2$	$-\omega_1$
BC3	72.8	−66.6	−53.3	104.7	−66.6	77.9	−105.6	40.5

[a] For the definition of ω_1–ω_8, see Figure 1.

TABLE 4 Calculated Torsional Angles (in degrees) of **2**[a]

Structure	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
TBC1	−124.9	54.8	55.0	−94.7	93.1	−108.6	48.5	44.7
TBC2	52.8	−101.0	100.3	−94.3	46.5	51.2	−135.9	50.3
TC	−110.7	46.3	ω_2	ω_1	$-\omega_1$	$-\omega_2$	$-\omega_2$	$-\omega_1$
CC	−103.4	76.8	$-\omega_2$	$-\omega_1$	ω_1	ω_2	$-\omega_2$	$-\omega_1$
BB1	−21.2	−77.9	34.0	68.8	ω_1	ω_2	ω_3	ω_4
BB2	51.9	−66.8	−44.5	67.7	ω_1	ω_2	ω_3	ω_4
BC1	105.0	−73.9	$-\omega_2$	$-\omega_1$	43.5	68.6	$-\omega_6$	$-\omega_5$
BC2	−65.6	−43.3	116.1	−70.4	$-\omega_4$	$-\omega_3$	$-\omega_2$	$-\omega_1$
BC3	77.2	−67.8	−55.8	108.0	−65.5	81.3	−109.8	40.9

[a] For the definition of ω_1–ω_8, see Figure 1.

(BB) and TBC conformations of cyclooctane (BB1, BB2, TBC1, and TBC2 in Figure 2). Our nomenclature of the conformations of **1**–**3** are based on the correspondence to those of cyclooctane and is partly different from those used in previous articles.

Other structural parameters were calculated as follows. The bond lengths of C–X are 1.81–1.83 Å (X = S, with both basis sets), 1.96–1.98 Å (X = Se), and 2.17–2.20 Å (X = Te); and those of C–C are 1.53–1.56 Å (X = S, 3-21G$^{(*)}$), 1.52–1.55 Å (X = S, 6-31G*), 1.53–1.56 Å (X = Se); and 1.53–1.56 Å (X = Te). The bond angles of C-X-C are 100–108° (X = S, 3-21G$^{(*)}$), 101–109° (X = S, 6-31G*), 98–108° (X = Se), and 95–104° (X = Te); those of X-C-C are 111–120° (X = S, 3-21G$^{(*)}$), 113–120° (X = S, 6-31G*), 112–119° (X = Se), and 113–121° (X = Te); and those of C-C-C are 112–118° (X = S, 3-21G$^{(*)}$), 114–119° (X = S, 6-31G*), 112–117° (X = Se), and 112–117° (X = Te).

Table 6 shows the calculated relative energies of the nine structures in each compound. The TBC1 structure is the most stable in **1** and **2**, while the BB2 structure is the most stable in **3**. Relative energies of

TABLE 5 Calculated Torsional Angles (in degrees) of **3**[a]

Structure	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
TBC1	−119.7	57.6	56.6	−91.4	88.2	−117.2	61.0	31.6
TBC2	47.1	−104.7	111.1	−89.1	33.0	62.3	−145.8	55.0
TC	−107.8	49.0	ω_2	ω_1	$-\omega_1$	$-\omega_2$	$-\omega_2$	$-\omega_1$
CC	−99.9	81.7	$-\omega_2$	$-\omega_1$	ω_1	ω_2	$-\omega_2$	$-\omega_1$
BB1	−8.4	−89.5	39.9	60.6	ω_1	ω_2	ω_3	ω_4
BB2	63.9	−56.4	ω_2	ω_1	ω_1	ω_2	ω_2	ω_1
BC1	100.5	−77.1	88.9	−88.6	−6.9	103.1	−53.8	−60.5
BC2	−56.1	−51.7	121.5	−65.8	$-\omega_4$	$-\omega_3$	$-\omega_2$	$-\omega_1$
BC3	77.3	−64.2	−60.5	104.2	−55.8	81.9	−118.4	44.5

[a] For the definition of ω_1–ω_8, see Figure 1.

TABLE 6 Calculated Relative Energies (in kcal mol^{-1}) of Nine Structures of **1–3**

Structure	**1** (*3-21G$^{(*)}$*)	**1** (*6-31G**)	**2**	**3**
TBC1	0.0[a]	0.0[b]	0.0[c]	0.8
TBC2	3.7	3.7	4.6	4.9
TC	1.9	1.6	0.1	0.1
CC	2.1	0.9	1.6	2.7
BB1	8.5[d]	8.7[e]	7.7[f]	8.2[g]
BB2	4.5[h]	3.4	4.0[i]	0.0[j]
BC1	3.6	3.2	2.7	4.1[k]
BC2	2.3	2.5	3.3	4.7
BC3	0.6	0.2	1.2	1.0

[a] The total energy is −1024.228561 a.u.
[b] The total energy is −1029.207667 a.u.
[c] The total energy is −5010.279077 a.u.
[d] 10.4 kcal mol^{-1} for C_{2v} structure.
[e] 9.8 kcal mol^{-1} for C_{2v} structure.
[f] 9.6 kcal mol^{-1} for C_{2v} structure.
[g] 11.1 kcal mol^{-1} for C_{2v} structure.
[h] 4.7 kcal mol^{-1} for D_2 structure.
[i] 4.1 kcal mol^{-1} for D_2 structure.
[j] The total energy is −13399.418233 a.u
[k] 4.5 kcal mol^{-1} for C_s structure.

all structures were within 5 kcal mol^{-1}, except for BB1 in all compounds. The BB1 structures of **1–3** are considerably unstable (by 7–9 kcal mol^{-1}).

The highest possible symmetry for the BB1 structure is C_{2v}. However, the optimized C_{2v} structures have one imaginary vibrational frequency of a_2 symmetry in all cases. Thus, the minimum structures for the BB1 conformation were found in C_2 symmetry. The energy differences between the C_{2v} and C_2 structures are 1.9 (**1**, 3-21G$^{(*)}$), 1.2 (**1**, 6-31G*), 1.9 (**2**), and 2.9 (**3**) kcal mol^{-1}. One reason for these distortions from C_{2v} to C_2 can be a relaxation of the transannular lone-pair–lone-pair repulsion; the overlap between the p_π lone-pair orbitals decreases by the distortion (the HOMO energies of the C_{2v} BB1 structures are extremely high, as shown in Table 7). Also, the distances between two chalcogen atoms increase by 0.04–0.06 Å on going from C_{2v} to C_2. Nevertheless, the C_2 BB1 structures have the shortest distance between the two chalcogen atoms among the nine conformers (see Table 1). Moreover, in the C_{2v} structures, there exists a very short nonbonding H ⋯ H interaction between the methylene groups of the 3,7-positions: 1.870 (**1**, 3-21G$^{(*)}$), 1.929 (**1**, 6-31G*), 1.858 (**2**), and 1.892 (**3**) Å. This would give rise to a substantial steric distress, considering that the sum of van der Waals radii for two H atoms is usually taken to be 2.4 Å. These interactions are relaxed by the distortion to C_2 symmetry; the H ⋯ H distances increase to 2.079, 2.092, 2.102, and 2.184 Å, respectively. As mentioned earlier, the BB1 conformer is calculated to be the highest-energy conformer in all three compounds (Table 6). This is thus attributable to (1) a strong repulsive transannular interaction between the two lone-pair orbitals, (2) existence of the short H ⋯ H interaction, and (3) ring strain induced to relax these interactions. It should

TABLE 7 Energies of HOMO of Nine Structures of **1–3** (in eV)

Structure	**1** (*3-21G$^{(*)}$*)	**1** (*6-31G**)	**2**	**3**
TBC1	−8.837	−8.891	−8.210	−7.596
TBC2	−8.866	−8.963	−8.202	−7.622
TC	−8.785	−8.855	−8.145	−7.552
CC	−8.382	−8.548	−7.459	−6.952
BB1	−8.156[a]	−8.249[b]	−7.353[c]	−6.991[d]
BB2	−9.021[e]	−9.161	−8.330[f]	−7.667
BC1	−8.076	−8.248	−7.237	−7.157[g]
BC2	−8.739	−8.828	−8.093	−7.527
BC3	−8.933	−8.990	−8.289	−7.674

[a] −7.836 eV for C_{2v} structure.
[b] −8.022 eV for C_{2v} structure.
[c] −7.026 eV for C_{2v} structure.
[d] −6.596 eV for C_{2v} structure.
[e] −9.122 eV for D_2 structure.
[f] −8.386 eV for D_2 structure.
[g] −6.788 eV for C_s structure.

be noted that the C_2 BB1 structures can also be regarded as derived from the twist-boat (TB) conformation of cyclooctane, which has S_4 symmetry [26].

For the BB2 conformation, the highest possible symmetry is D_2. However, the optimized D_2 structures have one imaginary frequency for the cases of **1** (3-21G$^{(*)}$) and **2**. The minimum structures have C_2 symmetry in these cases, although the energy lowerings are very small (see Table 6). These distortions can also be ascribed to short H ⋯ H interactions. There are two short transannular H ⋯ H interactions in each D_2 structure: 1.882 (**1**, 3-21G$^{(*)}$), 1.948 (**1**, 6-31G*), 1.895 (**2**), and 2.016 (**3**) Å. For the case of **1** (3-21G$^{(*)}$), the two H ⋯ H distances become 2.005 and 1.896 Å in the C_2 structure; in **2**, these distances become 2.003 and 1.872 Å.

In compound **3**, the BC1 structure of C_s symmetry also has one imaginary frequency, and the minimum BC1 structure is of C_1 symmetry (the energy differences between the C_s and C_1 structures is 0.4 kcal mol^{-1}). This can be attributed to a stronger repulsive interaction between the Te atoms in **3** than the corresponding interactions in **1** and **2**. The Te ⋯ Te distance is 3.961 Å in the C_s structure, whereas it is 4.102 Å in the C_1 minimum.

The TC structures of **1**–**3** are relatively stable, despite the fact that the TC conformation of cyclooctane has a high energy and does not represent a local minimum [26]. In these structures, the overlap between the p_π lone-pair orbitals of the two chalcogen atoms is relatively small as reflected in the HOMO–LUMO splitting (see the next section). Interestingly, a TC structure was observed for a derivative of **1**, 1,5-dithiacyclooctane-3,7-dione bis(ethylene acetal) [28]. Its S ⋯ S distance (3.576 Å) is close to our calculated values for **1**, 3.571 (3-21G$^{(*)}$), and 3.665 (6-31G*) Å.

As mentioned in the Introduction, the BC1 and CC conformations were usually found in complexes containing **1** (even when the molecules of **1** do not act as bidentate ligands, i.e., when they act as monodentate or bridging ligands). Although these conformations do not correspond to the most stable one calculated here (TBC1), their relative energies to TBC1 are small. Moreover, the BC1 and CC structures have higher HOMO energies (see below) and can act as a stronger donor. Another view for the case of *trans*-$SnCl_4$(1,5-DTCO)$_2$ (where only one sulfur atom coordinates to Sn) is as follows. The coordination of one sulfur atom induces a positive charge on that atom, which in turn induces the approach of the other sulfur atom. It is interesting to note that the S ⋯ S distances observed in Ni(1,5-DTCO)$_2$$Cl_2$, *trans*-$SnCl_4$(1.5-DTCO)$_2$, and 1,5-DTCO·2$I_2$ [18] are appreciably shorter than our calculated values for BB1 or CC. This is consistent with the antibonding character of the HOMO between the two sulfur atoms.

TABLE 8 The Energy Differences between HOMO and NHOMO in Each Structure of **1** (in eV)

Structure	*3-21G$^{(*)}$*	*6-31G**
TBC1	0.434	0.419
TBC2	0.371	0.194
TC	0.515	0.488
CC	1.096	0.929
BB1	1.438	1.348
BB2	0.170	0.038
BC1	1.546	1.342
BC2	0.688	0.595
BC3	0.306	0.285

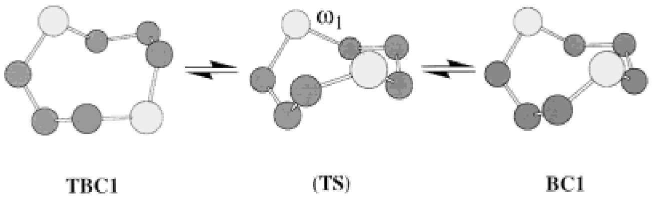


FIGURE 4 Interconversion between the TBC1 and BC1 conformers of the compound **1**. The structures shown are those calculated by RHF/6-31G*.

TABLE 9 Relative Energies (in kcal mol^{-1}) and Distances between Chalcogen Atoms (in Å) of the Transition States between TBC1 and BC1 in Compounds **1** and **2**

Compound	*Relative Energy*^{a}	*Distance between Two Chalcogen Atoms*
1 (3-21G$^{(*)}$)	4.3	3.625
1 (6-31G*)	3.9	3.694
2	4.9	4.143

^{a}Relative to the TBC1 structure.

TABLE 10 The Torsional Angles (in degrees) of the Transition States between TBC1 and BC1 in Compounds **1** and **2**^{a}

Compound	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
1 (3-21G$^{(*)}$)	−104.6	73.3	−82.9	89.1	−2.3	−93.9	50.9	62.4
1 (6-31G*)	−101.9	73.3	−82.0	87.3	−2.9	−92.7	52.0	59.8
2	−99.5	85.4	−95.3	70.4	31.4	−117.8	46.5	60.3

^{a}For the definition of ω_1–ω_8, see Figure 1.

Energies of HOMO and NHOMO

Table 7 shows the HOMO energies of **1**, **2**, and **3**, and Table 8 shows the energy gaps between the HOMO and next HOMO (NHOMO) in **1**. These orbitals are composed mainly of the p_π lone-pair orbitals of the two chalcogen atoms. Therefore, the energy gaps reflect the interaction between the two π lone pairs of the two chalcogen atoms.

In **1** and **2**, the BC1 has the highest HOMO energy, and the BB2 has the lowest. In **3**, the HOMO energy of the BC1 structure of C_s symmetry (which has one imaginary frequency) is higher than those of other minimum structures, and that of the BB2 is relatively low. The BC1 structure corresponds to the most stable structure of the radical cation of **1** and the dications of **1–3** [29]. The BB2 structures have the smallest HOMO–NHOMO splitting because there is little overlap between the two lone-pair orbitals. It may be seen from Tables 1 and 7 that there is a rough correlation between the HOMO energies and the distances between chalcogen atoms. However, the correlation is not good, because the HOMO energies are determined by not only the distances between the chalcogen atoms but also the relative directions of the lone pairs of the chalcogen atoms. The TC conformers have a relatively short chalcogen–chalcogen distance, but their HOMO energies are relatively low, because the overlap between the two chalcogen p_π lone-pair orbitals is small.

The energy differences between HOMO and NHOMO in TBC1 of **1** is 0.434 eV (3-21G$^{(*)}$) and 0.419 eV (6-31G*). These values are nearly the same as the experimental value (0.43 eV) for the difference between the first and second vertical ionization potentials [19]. This strongly supports that the TBC1 structure, which has received little attention in previous studies and was calculated to be the most stable in the present calculations, is indeed the most stable structure of **1** (in the gas phase). The stability of the TBC1 conformer is due to a relatively weak repulsion between the two sulfur lone pairs.

Transition Structures between TBC1 and BC1 of **1** *and* **2**

In **1** and **2**, the BC1 structure has the highest HOMO energy, while the TBC1 structure, which is the most stable structure, has the HOMO energy that is lower than the BC1 HOMO energy by 0.761 eV (**1**, 3-21G$^{(*)}$), 0.643 eV (**1**, 6-31G*), and 0.973 eV (**2**) (see Table 7). Thus, the BC1 structures are expected to be responsible for the facile oxidation of the 1,5-dichalcogenacyclooctanes. The energy differences between TBC1 and BC1 of **1** are 3.6 kcal mol^{-1} (3-21G$^{(*)}$) and 3.2 kcal mol^{-1} (6-31G*) and that of **2** is 2.7 kcal mol^{-1}, and it is reasonable to suppose that a conformational change from TBC1 to BC1 in the neutral state occurs before oxidation in solution, if the barrier to the conformational change is low. Therefore, we have located the transition states between TBC1 and BC1 for **1** and **2**.

Figure 4 shows the transition state for **1** located by 6-31G*. Tables 9 and 10 show the relative energies and structural parameters for the transition states of **1** and **2**. The barriers to the TBC1 → BC1 conversions are calculated to be 4.3 kcal mol^{-1} (**1**, 3-21G$^{(*)}$), 3.9 kcal mol^{-1} (**1**, 6-31G*), and 4.9 kcal mol^{-1} (**2**). These are small enough to allow the oxidation via the BC1 structure.

CONCLUSION

Energy-minimum structures of the three 1,5-dichalcogenacyclooctanes, 1,5-DTCO (**1**), 1,5-DSeCO (**2**), and 1,5-DTeCO (**3**), were obtained by ab initio molecular orbital calculations. The most stable structure of **1** and **2** is TBC1, whereas that of **3** is BB2. In **1** and **2**, the HOMO energy of the BC1 structure of C_s symmetry is the highest among the nine conformers.

The calculated energy gaps between HOMO and NHOMO in TBC1 of **1** are in very good agreement with experiment [19], which strongly suggests that the most stable structure of **1** is actually TBC1. Only one recent article [21] described this conformation in the literature.

The energy barriers between TBC1 and BC1 of **1** and **2** are predicted to be considerably low. Therefore, a conformational change in the neutral state of these compounds is expected to occur prior to their one- and two-electron oxidations in solution.

REFERENCES

[1] Asmus, K.-D. Acc Chem Res 1979; 12, 436.
[2] Musker, W. K. Acc Chem Res 1980; 13, 200.
[3] Musker, W. K. Coord Chem Rev 1992; 117, 133.
[4] Fujihara, H.; Furukawa, N. J Mol Struct (Theochem) 1989; 186, 261.
[5] (a) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. J Am Chem Soc 1979; 101, 1040. (b) Ryan, M. D.; Swanson, D. D.; Glass, R. S.; Wilson, G. S. J Phys Chem 1981; 85, 1069.
[6] Musker, W. K.; Wolford, T. L. J Am Chem Soc 1976; 98, 3055.
[7] Musker, W. K.; Roush, P. B. J Am Chem Soc 1976; 98, 6745.
[8] Musker, W. K.; Wolford, T. L.; Roush, P. B. J Am Chem Soc 1978; 100, 6416.

[9] Musker, W. K.; Gorewit, B. V.; Roush, P. B.; Wolford, T. L. J Org Chem 1978; 43, 3235.

[10] Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. J Am Chem Soc 1979; 101, 5322.

[11] Brown, T. G.; Hirschon, A. S.; Musker, W. K. J Phys Chem 1981; 85, 3767.

[12] (a) Furukawa, N.; Kawada, A.; Kawai, T. J Chem Soc Chem Commun 1984; 1151 (b) Fujihara, H.; Kawada, A.; Furukawa, N. J Org Chem 1987; 52, 4254.

[13] Bonazzola, L.; Michaut, J. P.; Roncin, J. Can J Chem 1988; 66, 3050.

[14] Iwasaki, F.; Toyoda, N.; Akaishi, R.; Fujihara, H.; Furukawa, N. Bull Chem Soc Jpn 1988; 61, 2563.

[15] Tamaoki, M.; Serita, M.; Shiratori, Y.; Itoh, K. J Phys Chem 1989; 93, 6052.

[16] Setzer, W. N.; Glass, R. S. Conformational Analysis of Medium-sized Sulfur-Containing Heterocycles. In Glass, R. S., Ed.; Conformational Analysis of Medium Sized Heterocycles; VCH Publishers: New York, 1988; pp. 151–179.

[17] Hill, N. L.; Hope, H. Inorg Chem 1974; 13, 2079.

[18] Olmstead, M. M.; Williams, K. A.; Musker, W. K. J Am Chem Soc 1982; 104, 5567.

[19] Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. Tetrahedron 1981; 37, 2743.

[20] Serita, M.; Tamaoki, M.; Itoh, K. J Phys Chem 1988; 92, 1747.

[21] Nash, C. P.; Toto, S. D.; Musker, W. K. Tetrahedron 1997; 53, 7461.

[22] (a) Fujihara, H.; Akaishi, R.; Erata, T.; Furukawa, N. J Chem Soc Chem Commun 1989; 1789 (b)] Fujihara, H.; Akaishi, R.; Furukawa, N. Tetrahedron 1993; 26, 1605.

[23] Fujihara, H.; Ninoi, T.; Akaishi, R.; Erata, T.; Furukawa, N. Tetrahedron Lett 1991; 32, 4537.

[24] Fujihara, H.; Akaishi, R.; Furukawa, N. Chem Lett 1990; 549.

[25] Iwasaki, F.; Morimoto, M.; Yasui, M.; Akaishi, R.; Fujihara, H.; Furukawa, N. Acta Cryst 1991; C47, 1463.

[26] Burkert, U.; Allinger, N. L. Molecular Mechanics; American Chemical Society: Washington DC, 1982 and references cited therein.

[27] SPARTAN, Versions 3.1 and 4.0: Wavefunction, Inc., Irvine, CA.

[28] Olmstead, M. M.; Musker, W. K. Acta Cryst., 1981; B37, 261.

[29] Nakayama, N.; Takahashi, O.; Kikuchi, O.; Furukawa, N. unpublished work.