

## Substituent effects on the structure of hexacoordinate carbon bearing two thioxanthene ligands\*

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**Abstract:** In order to elucidate the electronic nature of our recently reported first hexacoordinated carbon (12-C-6), density functional theory (DFT) calculations of sulfide precursor, sulfone derivative, and S<sup>+</sup>-F derivative were carried out and compared with those of the reported S<sup>+</sup>-Me hexacoordinated carbon. Computations on the hexacoordinated carbon, indicating that four attractive C–O interactions with the central hexacoordinate carbon atom exist, also revealed that the interactions consist of two different types of three-center four-electron bonds, which can be regarded as electron donation by the lone pairs of the oxygen atoms to the empty low-lying  $\pi^*$ -orbitals of the allene. The optimized structures of the sulfide, sulfone, S<sup>+</sup>-F, and the original S<sup>+</sup>-Me suggested that the introduction of electron-withdrawing groups at the sulfur atoms would make the C–O attractive interactions stronger by a larger contribution of the carbon dication resonance structure.

Thus, allene compounds (sulfide, sulfone, sulfonium) with two different thioxanthene ligands (one with 1,8-dimethoxy groups as in the S<sup>+</sup>-Me compound and the other with 1,8-diphenoxy groups) were synthesized to confirm the predicted substituent effects on the C(central)–O interactions. Electron-withdrawing substituents at the sulfur atoms were found to give rise to strong C(central)–O attractive interactions; the average values of the four C–O distances were smaller as the electron-withdrawing ability of the sulfur atoms rose. Additionally, C(central)···OMe distances were shorter than the corresponding C(central)···OPh distances, reflecting the higher electron-donating ability of the oxygen atoms at these 1,8-positions of the thioxanthene skeleton.

**Keywords:** carbon; hypervalent compounds; synthesis; structures.

### INTRODUCTION

It is widely accepted that the transition state of the S<sub>N</sub>2 reactions of the carbon atom involves the pentacoordinate carbon with 10 valence electrons formally assignable around the central carbon [1]. Despite numerous attempts to isolate such pentacoordinate carbon species, especially by Breslow [2], Hojo [3], and Martin [4], their definitive characterization had not been established, although hypervalent compounds of heavier main-group elements, such as Si, S, P, and I are widely known. However, in 1999, we were able to report on the first structural determination of a pentacoordinate hypervalent carbon species with compound **1** (Fig. 1) [5], which exploited a sterically rigid anthracene skeleton. A second example with a flexible van Koten-type ligand **2** (Fig. 1) followed in 2005 [6].

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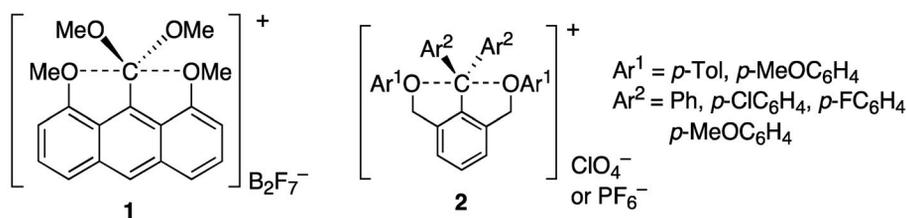


Fig. 1

The pentacoordinate carbon species **1** and **2** have three strong equatorial bonds and two weak apical bonds, the latter of which consists of a three-center four-electron bond of  $\text{O}\cdots\text{C}^+\cdots\text{O}$  composition. Since the apical bonds of **1** [2.43(1), 2.45(1) Å] and **2** (2.67–2.78 Å) were long relative to the usual C–O single bond (1.43 Å) [7], demonstration of the existence of attractive interactions became an issue. The key question was whether these short distances corresponded to attractive bonding interactions or the proximity was simply the consequence of fixation or steric crowding with no bonding [8]. Thus, electron density distribution studies based on accurate X-ray analysis [9] and theoretical calculations (atoms-in-molecules, AIM, [10] calculations) were exploited to elucidate the nature of the interaction between the oxygen atoms and the central carbon atom. Results showed distribution of electron density (bond path) [10] between the O and C atoms in **1** and **2**, thereby providing support for their pentacoordinate bonding scheme. Additionally, the  $\text{C}\cdots\text{O}$  distances in **2** were in good correlation with the electronic nature of the  $\text{Ar}^2$  group, that is, the more electrophilic carbocation was more strongly coordinated by the two O atoms. These results were in good agreement with the notion that the apical  $\text{C}\cdots\text{O}$  bonds of **1** and **2** were constituted by the interaction of the vacant p-orbital of the carbocations with lone pair electrons of the two ether O atoms. Similar aspects were observed in the case of pentacoordinate boron analogues of **1** [5b,11] and **2** [12].

In comparison, no undisputable example of hypervalent second-row element compounds with *six* bonds had been reported. Hexacoordinate carbon compounds in a transition-metal cluster, such as  $(\text{Ph}_3\text{PAu})_6\text{C}^{2+}$ , were characterized experimentally [13], but orbital analysis did not support hypervalency.  $\text{CLi}_6$  was explored computationally [14] and detected by mass spectroscopy [15], but has not been structurally characterized. Computationally explored species such as  $\text{CH}_6^{2+}$ , which is diprotonated  $\text{CH}_4$ , are electron-deficient [16]. A hexacoordinate hypervalent boron species was reported [17], but characterization was based only upon NMR and no decisive evidence such as X-ray structure has been provided.

Recently, we succeeded in the synthesis and structural determination of hexacoordinate carbon dication **4** by the dimethylation of allene **3** bearing two sterically rigid thioxanthene ligands, as reported in a preliminary communication (Fig. 2) [18]. The structure of **4** was a distorted octahedral. The four

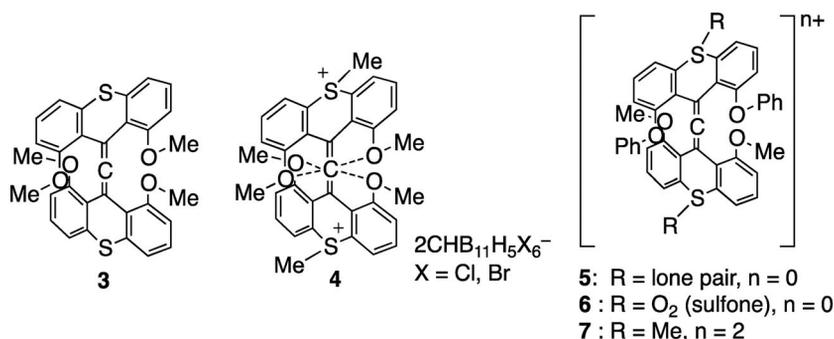
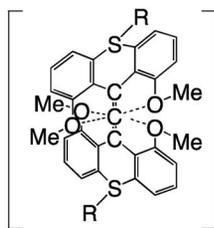


Fig. 2

**Table 1** Optimized structures for the estimation of substituent effects.


**3** : R = lone pair, n = 0  
**8** : R = O<sub>2</sub>, n = 0  
**4** : R = Me, n = 2  
**9** : R = F, n = 2



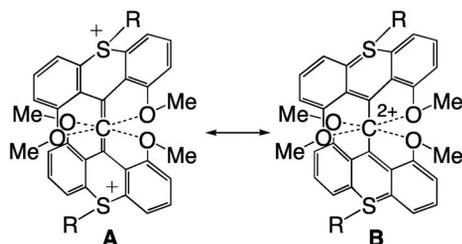
distances (Å)

	C(b)-C(a)	C(b)-C(a')	C(b)-O1	C(b)-O2	C(b)-O3	C(b)-O4
<b>3</b>	1.321	1.321	2.742	2.834	2.834	2.742
<b>3 (X-ray)</b>	1.319(5)	1.314(5)	2.663(1)	2.770(4)	2.815(4)	2.689(4)
<b>8</b>	1.321	1.321	2.707	2.789	2.789	2.707
<b>4</b>	1.325	1.325	2.705	2.735	2.735	2.709
<b>4 (X-ray)</b>	1.319(5)	1.310(6)	2.641(5)	2.706(5)	2.750(5)	2.673(5)
<b>9</b>	1.327	1.327	2.673	2.671	2.671	2.674

Angles (°)

	C(a)-C(b)-C(a')	O1-C(b)-O3	O2-C(b)-O4	O2-C(b)-O3	O1-C(b)-O4
<b>3</b>	169.9	76.9	76.9	58.3	168.9
<b>3 (X-ray)</b>	168.5(3)	76.7(1)	78.2(1)	58.9(1)	164.3(2)
<b>8</b>	168.0	78.5	78.5	59.5	159.4
<b>4</b>	172.7	74.3	74.1	61.7	158.8
<b>4 (X-ray)</b>	166.8(4)	76.5(1)	76.2(1)	60.7(1)	162.7(2)
<b>9</b>	171.2	76.8	76.8	65.3	147.3

Structures were optimized at B3PW91/6-31G(d) level



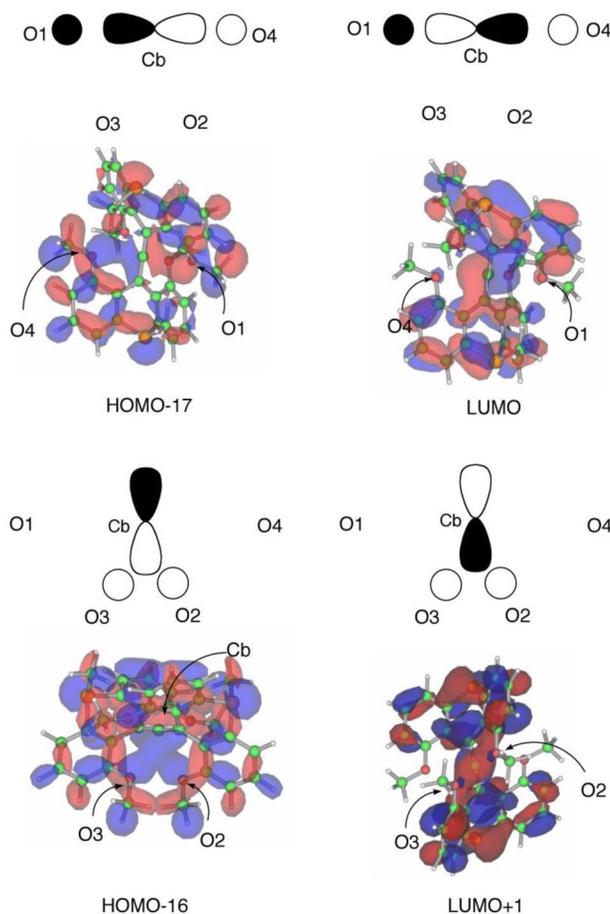
C(central)⋯O distances of **4** [2.641(5)–2.750(5) Å] were slightly shorter than those of **3** [2.663(4)–2.815(4) Å], consistent with the dipositive charge on **4**. The hexacoordinate nature of **4** was also supported by experimental charge density analysis based upon X-ray structure and AIM calculations based upon the structure optimized at the B3PW91/6-31G(d) [19] level (Table 1). The calculated

structure was very similar to the experimentally determined structure except that the C $\cdots$ O distances were on the average slightly longer, and more symmetrical. Consistent with the accurate X-ray analysis, AIM calculations of **4** showed bond paths between the central carbon atom and all four oxygen atoms. The calculated values of the electron density [ $\rho(r) = 0.015\text{--}0.014\text{ e/a}_0^3$ ] and the Laplacian values at the bond critical points [ $\nabla^2\rho(r) = 0.055\text{--}0.051\text{ e/a}_0^5$ ] agreed well with the values obtained experimentally [ $\rho(r) = 0.018\text{--}0.011\text{ e/a}_0^3$ ,  $\nabla^2\rho(r) = 0.067\text{--}0.050\text{ e/a}_0^5$ ] [18]. In order to gain a better understanding of the nature of the C $\cdots$ O interactions in the allene system with two thioxanthene skeletons (Fig. 2), in this article, we describe theoretical calculations on several other *S,S'*-disubstituted allene compounds and the synthesis of three new derivatives **5**, **6**, and **7**.

## RESULTS AND DISCUSSION

### Molecular orbitals (MOs) of **4**

MOs relevant to the hexacoordinate nature of **4** would be a combination of bonding or antibonding orbitals involving the central carbon atom and lone pairs of the four surrounding oxygen atoms. Previous calculations [18] on **4** indicate that MOs with large contributions of such orbitals can be found in HOMO(−16), HOMO(−17), LUMO, and LUMO(+1). A close look at these MOs suggests the presence of two modes of orbital interaction between the lone pairs of the oxygen atoms and the  $\pi^*$ -orbitals



**Fig. 3** MOs of **4** (above: simplified MOs).

of the allene moiety. HOMO(-17) and LUMO correspond to the bonding and antibonding orbitals of the two shorter C–O bonds, respectively, and can be depicted as a geometrically linear set of orbitals (see the simplified scheme). HOMO(-16) and LUMO(+1) correspond to the bonding orbital and antibonding orbital of the two longer C–O bonds, respectively, shown as the geometrically bent set (Fig. 3). Unfortunately, MOs with large contributions from the nonbonding orbitals of two C–O bonds could not be assigned due to the complexity of the whole orbital scheme.

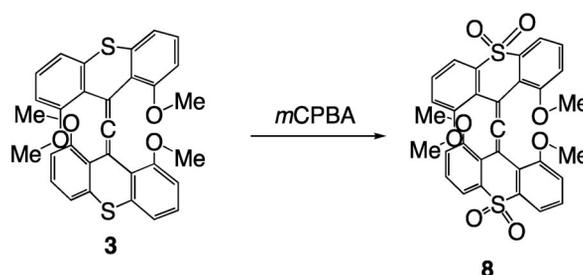
### Estimation of substituent effects at the two sulfur atoms on the structure by theoretical calculations

As summarized in Table 1, the structures of precursor sulfide **3** and two new compounds, sulfone **8** and fluorinated **9**, were optimized to estimate the influence of the substituents at the sulfur atoms on the four C–O bonds of the hexacoordinate carbon species. The calculated structures were similar to that of dimethylated allene **4** and showed distorted allene units. The bent frameworks would result from steric crowding of the two thioxanthene substituents. The separation of the four C–O distances into a short pair [C(b)–O1, C(b)–O4] and a long pair [C(b)–O2, C(b)–O3] reflects the existence of two types of three-center four-electron bonds for the O–C–O moiety, as predicted by MO analysis of **4**. Although small elongations of the C–C bonds of the allene framework are observed by the increase of the electron-withdrawing nature of the substituents at the sulfur atoms, the C–C bond lengths (1.321–1.327 Å) are too short to consider them as C–C single bonds. On the other hand, shortening of the C–O distances by the electron-withdrawing substituents such as F (**9**) is evident and the angles of O2–C(b)–O3 and O1–C(b)–O4 are approaching the ideal value of 90°. These results indicate that the introduction of electron-withdrawing groups at the sulfur atoms slightly enhances the contribution of resonance structure **B**, which has carbon dication character, and the structure of the compound becomes closer to the ideal octahedral. The X-ray structures of **3** and **4** are consistent with the calculations.

### Attempted introduction of electron-withdrawing groups at the sulfur atoms

Introduction of electron-withdrawing substituents at the sulfur atoms was attempted to explore their influence on the structure.

The oxidation of allene **3** using an excess amount of *m*CPBA (*m*-chloroperbenzoic acid) afforded sulfone **8** (Scheme 1), the <sup>1</sup>H NMR spectrum of which suggested high symmetry (one *MeO* signal and three Ar–H signals). However, the yield of **8** after purification by silica gel chromatography was low, and, furthermore, single crystals suitable for X-ray analysis could not be obtained. The poor solubility of **8** to organic solvents (e.g., CH<sub>2</sub>Cl<sub>2</sub>, MeCN, ether, EtOH, acetone, benzene) made purification difficult. Thus, the structure of **8** could not be confirmed experimentally. Additionally, all other attempts to introduce electron-withdrawing substituents at the sulfur atom were not successful: for instance, the



Scheme 1 Synthesis of sulfone **8**.

reaction of **3** with  $\text{XeF}_2$  gave a complex mixture, and the reaction with  $\text{RCH}_2\text{I}$  ( $\text{R} = \text{CF}_3, \text{Cl}$ ) in the presence of silver salts did not give the desired  $S,S'$ -disubstituted dications.

### Synthesis of allene compounds bearing two different thioxanthene ligands

Due to the difficulty in the synthesis of other  $S,S'$ -disubstituted derivatives of **3**, an alternative system, with two different ligands, one with 1,8-dimethoxy groups and the other with 1,8-diphenoxy groups, was examined (Fig. 4). The system was expected to show influence from not only the substituents at the sulfur atoms, but also from the difference in the electron-donating ability of the donor oxygen atoms. Since the electron-donating ability of the oxygen atom of the methoxy group is stronger than that of the phenoxy group, the C–O distance of C(central)–OMe was expected to be shorter than that of C(central)–OPh.

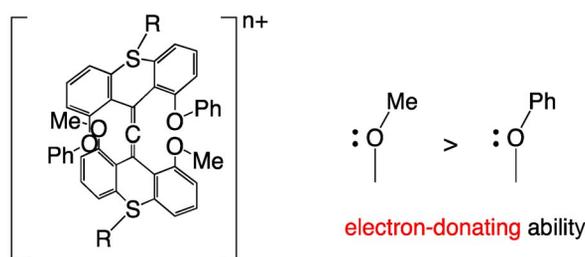
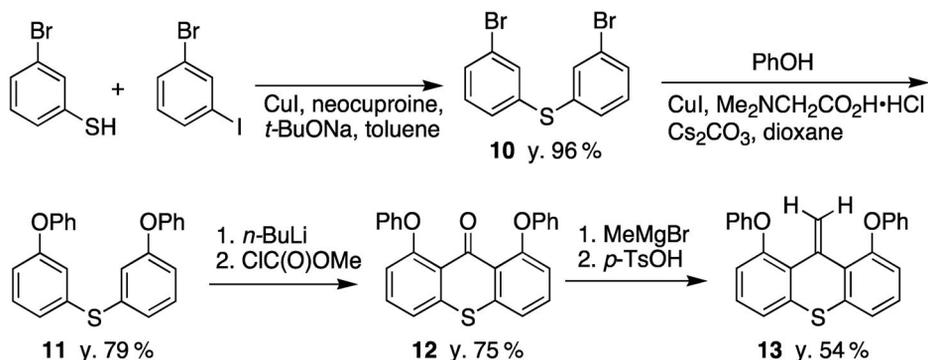


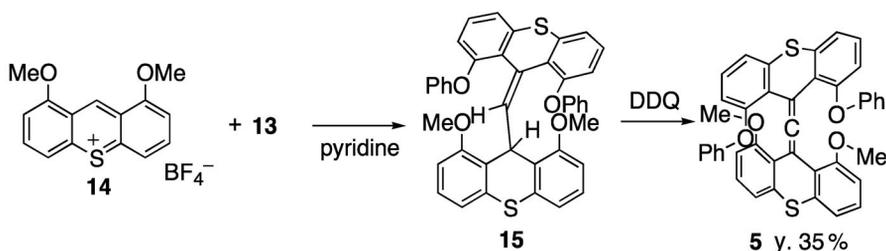
Fig. 4 Novel allene system with two different thioxanthene ligands.

The thioxanthene moiety with two PhO groups was constructed by a method similar to that for previously reported MeO derivatives [20] (Scheme 2). The Cu-catalyzed cross-coupling [21] of commercially available 3-bromobenzenethiol and 3-iodobromobenzene afforded bis(3-bromophenyl) sulfide **10** in good yield (96 %). The cross-coupling reaction [22] of **10** with phenol gave sulfide **11**. Thioxanthone **12** was synthesized by the selective dilithiation of sulfide **11** under previously reported conditions (using 2.2 equiv of  $n\text{-BuLi}$  and refluxing in  $n\text{-hexane}$ ) for the MeO analog [20], followed by treatment with  $\text{ClC(O)OMe}$  under high dilution. Olefin **13** was obtained by the reaction of **12** with  $\text{MeMgBr}$ , followed by treatment with  $p\text{-TsOH}$ .



Scheme 2 Synthesis of **13**.

Allene compound **5** bearing two different thioxanthene ligands was synthesized as shown in Scheme 3. The reaction of the thioxanthylum salt **14** [18] with olefin **13** in pyridine [23], followed by oxidation using 1,2-dichloro-4,5-dicyano-*p*-benzoquinone (DDQ), produced the desired allene **5**. Single crystals of **5** suitable for X-ray analysis were obtained from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The molecular structure of **5** is illustrated in Fig. 5.



Scheme 3 Synthesis of **5**.

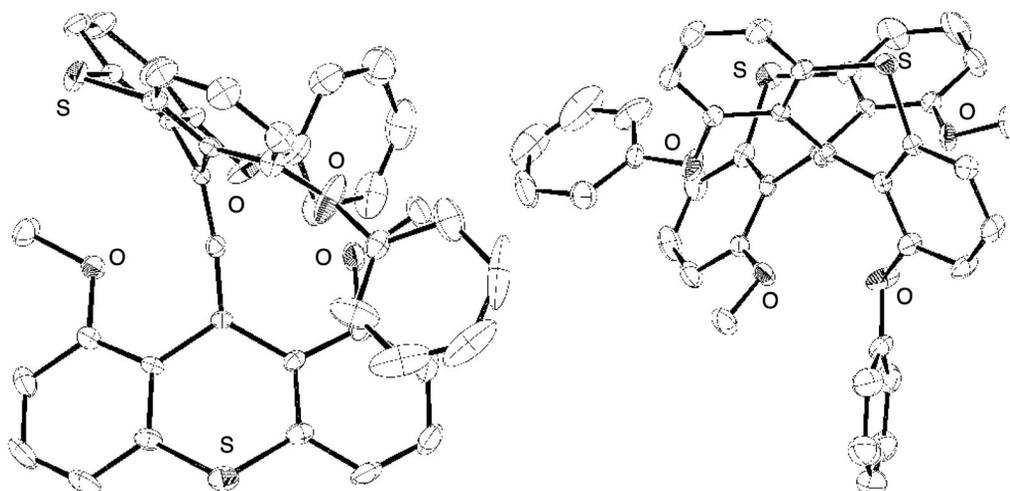
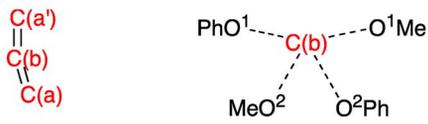


Fig. 5 ORTEP drawings of **5** (50 % thermal ellipsoids). Hydrogen atoms are omitted for clarity.

The geometric parameters of **5** are shown in Table 2. Although the structure of **5** is similar to that of **3**, which has four methoxy groups, the C(b)–O<sup>Ph</sup> distances are longer than the C(b)–O<sup>Me</sup> distances [C(b)–O<sup>1</sup>Ph: 2.854(4) Å, C(b)–O<sup>2</sup>Ph: 2.878(3) Å, C(b)–O<sup>1</sup>Me: 2.662(3) Å, C(b)–O<sup>2</sup>Me: 2.739(3) Å]. This should be due to the difference in the electron-donating ability between methoxy groups and phenoxy groups, favoring the former.

**Table 2** Geometric parameters of **5**, **6**, and **7**.


distances (Å)

	C(b)-C(a)	C(b)-C(a')	C(b)-O <sup>1</sup> Ph	C(b)-O <sup>1</sup> Me	C(b)-O <sup>2</sup> Ph	C(b)-O <sup>2</sup> Me
<b>5</b>	1.317(3)	1.318(3)	2.854(4)	2.662(3)	2.878(3)	2.739(3)
<b>6 (MolA)</b>	1.319(5)	1.321(5)	2.707(4)	2.671(4)	2.904(5)	2.699(4)
<b>6 (MolB)</b>	1.315(5)	1.322(5)	2.677(5)	2.673(4)	2.894(5)	2.692(4)
<b>7</b>	1.322(7)	1.325(7)	2.673(7)	2.665(7)	2.833(7)	2.758(7)

average distances (Å)

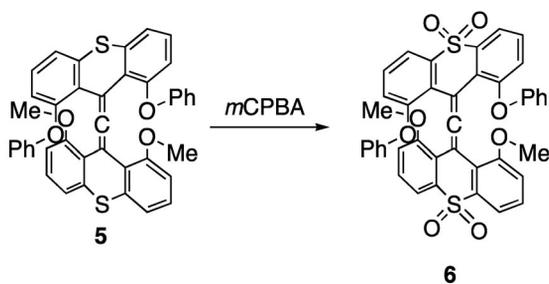
	C(b)-O (All)	C(b)-OPh	C(b)-OMe
<b>5</b>	2.79	2.87	2.70
<b>6 (MolA)</b>	2.74	2.81	2.69
<b>6 (MolB)</b>	2.73	2.79	2.68
<b>7</b>	2.73	2.75	2.71

Angles (°)

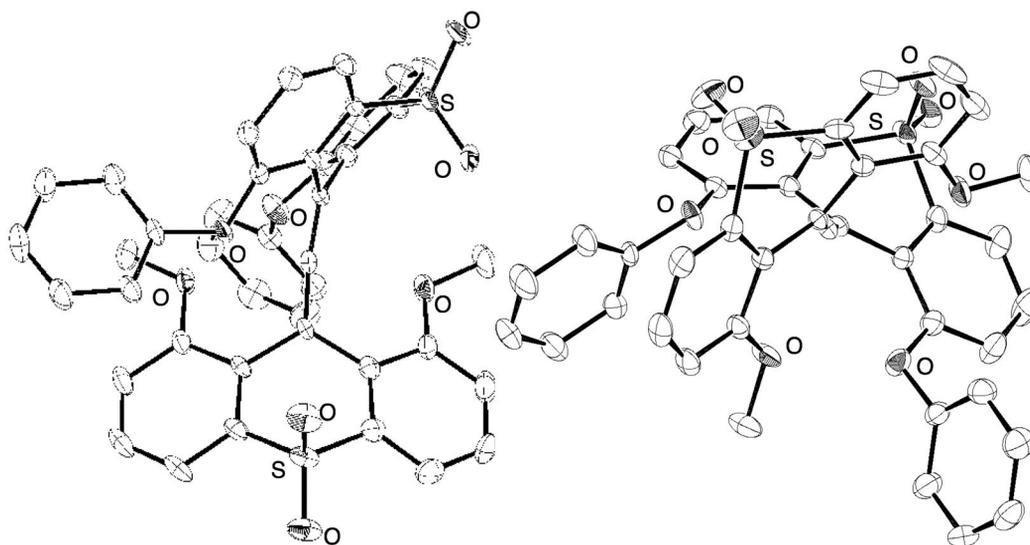
	C(a)-C(b)-C(a')	PhO <sup>1</sup> -C(b)-O <sup>2</sup> Me	PhO <sup>2</sup> -C(b)-O <sup>2</sup> Me	MeO <sup>1</sup> -C(b)-O <sup>2</sup> Ph	PhO <sup>1</sup> -C(b)-O <sup>1</sup> Me
<b>5</b>	171.0(3)	68.1(1)	60.4(1)	76.0(1)	168.1(1)
<b>6 (MolA)</b>	169.9(3)	74.8(1)	59.7(1)	81.0(1)	159.1(2)
<b>6 (MolB)</b>	167.7(4)	77.5(1)	59.8(1)	82.6(1)	155.8(2)
<b>7</b>	166.6(6)	76.6(2)	61.6(2)	79.8(2)	156.9(3)

The oxidation of **5** was carried out using *m*CPBA to afford sulfone **6** (Scheme 4). The reaction proceeded cleanly, and **6** was obtained as a compound with high solubility in organic solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF. Although the tetra-methoxy derivative **8** was difficult to purify because of its poor solubility, **6** could easily be purified by silica gel chromatography. Single crystals of **6** suitable for X-ray analysis were obtained from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The crystals contained two solvent molecules of CH<sub>2</sub>Cl<sub>2</sub> per molecule of **6** in its X-ray structure, and **6** was found as two independent molecules (Mol A, Mol B). Since the structures of Mol A and Mol B were essentially the same, one of the two structures is represented in Fig. 6. The geometric parameters are shown in Table 2.

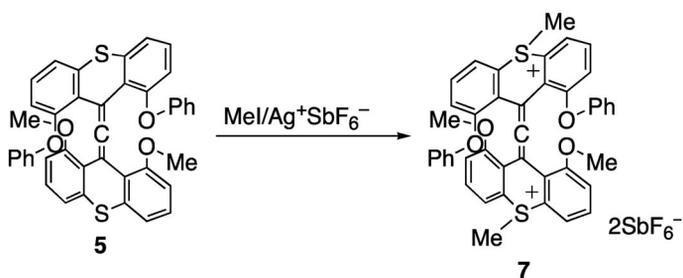
The dimethylation of **5** was carried out by the reaction with MeI and Ag<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (Scheme 5). Single crystals of **7** suitable for X-ray analysis were obtained from a mixture of tetrahydrofuran (THF) and hexane. The X-ray structure of **7** is shown in Fig. 7, and the geometric parameters are shown in Table 2.



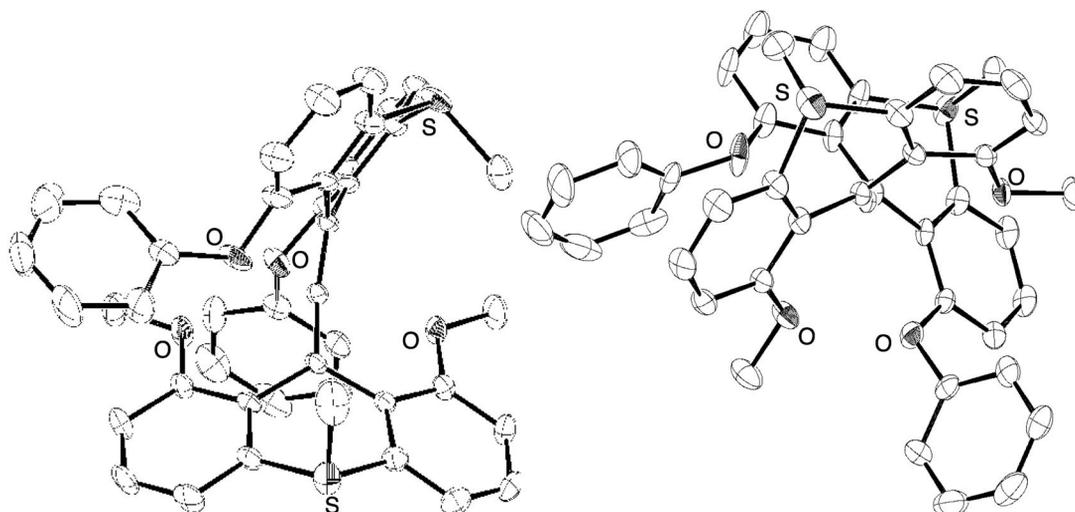
Scheme 4 Synthesis of 6.



**Fig. 6** ORTEP drawings of **6** (50 % thermal ellipsoids, one of two independent molecules). Hydrogen atoms and four  $\text{CH}_2\text{Cl}_2$  molecules as a crystallization solvent are omitted for clarity.



Scheme 5 Synthesis of 7.



**Fig. 7** ORTEP drawings of **7** (50 % thermal ellipsoids). Hydrogen atoms and two  $\text{SbF}_6^-$  molecules are omitted for clarity.

### Comparison of the structures of **5**, **6**, and **7**

Although the C–C bond lengths of the allene frameworks [C(a)–C(b), C(a')–C(b)] of these three structures are nearly the same, the angles of C(a)–C(b)–C(a') are gradually bent as the electron-withdrawing ability of the substituents increases. As predicted by theoretical calculation as shown in Table 1, the orbital scheme consists of two types of three-center four-electron bonds: C(b)–O<sup>1</sup>Ph and C(b)–O<sup>1</sup>Me make up one of the pairs, and C(b)–O<sup>2</sup>Ph and C(b)–O<sup>2</sup>Me pair for the other. In all of these compounds, the C(b)–O<sup>1</sup>Ph distance is longer than that of C(b)–O<sup>1</sup>Me, and the C(b)–O<sup>2</sup>Ph distance is also longer than that of C(b)–O<sup>2</sup>Me. This tendency can be explained by the difference in the electron-donating ability of the oxygen atoms, that is, the more electron-donating OMe groups can coordinate more strongly to the central carbon atom.

The average of the four C–O distances of unsubstituted **5** is larger than those of **6** and **7**. The averages of the two C–OMe distances of the three compounds are about the same (2.68–2.71 Å), while those of the two C–OPh distances gradually become smaller as the electron-withdrawing ability of the substituents at the sulfur atoms rises (**5**: 2.87 Å; **6**: 2.81, 2.79 Å; **7**: 2.75 Å). These results indicate that the contribution of resonance structure **B**, which has carbon dication character, becomes larger as the electron-withdrawing ability of the substituents at the sulfur atoms increases as predicted by theoretical calculations. Although the bond lengths C(b)–C(a) [C(a')] of the allene moiety of all three compounds show little differences, thus suggesting that the contribution of resonance structure **B** may be weak, there is an obvious difference in the average distances between C(b) and O [especially C(b)–OPh], which can be attributed to structure **B**.

The <sup>13</sup>C NMR data of these compounds also agree with the X-ray structures: the chemical shifts of C(a) and C(a') are about the same (**5**: 95.1, 95.2; **6**: 92.5, 93.0; **7**: 94.2, 94.5 ppm in CD<sub>2</sub>Cl<sub>2</sub>), while the value for C(b) is gradually shifted to higher field as the electron-withdrawing ability of the substituents at the sulfur atoms increases (**5**: 216.1; **6**: 220.9; **7**: 222.2 ppm in CD<sub>2</sub>Cl<sub>2</sub>). These chemical shifts suggest that the electron density of the C(b) atom decreases accordingly, even though the electron densities of the C(a) and C(a') atoms of these three compounds are about the same.

## CONCLUSION

In conclusion, density functional theory (DFT) calculations of dimethylated allene **4** demonstrating the identity of the four C–O attractive interactions at the central hexacoordinate carbon atom as those with large contributions from the central carbon atom and lone pairs of the four surrounding oxygen atoms also revealed that dication **4** has two different modes of three-center four-electron bonds. Based on the orbital overlaps, the four C–O interactions of **4** can be considered as electron donation from the lone pairs of the oxygen atoms to the empty  $\pi^*$ -orbital of the allene moiety. Additionally, the optimized structures of **3**, **4**, **8**, and **9** suggested that the introduction of electron-withdrawing groups at the sulfur atoms would give rise to stronger C–O attractive interactions which can be attributed to larger contributions of resonance structure **B** which has carbon dication character.

The effects of the substituents at the sulfur atoms were experimentally confirmed in a series of allene compounds bearing two different thioxanthene ligands (**5–7**). As predicted by theoretical calculations, the average of the four C–O distances decreased more as the electron-withdrawing ability of the substituents at the sulfur atoms increased (sulfide **5** > sulfone **6** > sulfonium **7**). This system also revealed the influence of the electron-donating ability of oxygen atoms; the C–OMe distances were shorter than the corresponding C–OPh distances. These results clearly agree with the presence of attractive C–O interactions, which was indicated by theoretical calculations.

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