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# The molecular and electronic structures of a thioaroyl cation formed by borinium ion-mediated C=S double bond cleavage of CS<sub>2</sub>

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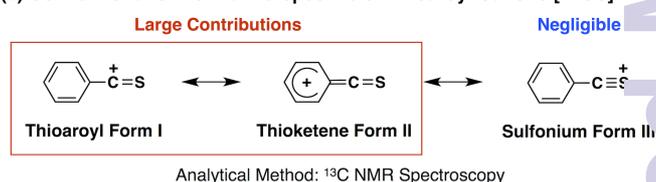
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The first crystallographic and electron density distribution analyses of a thioaroyl cation unveil its true structural perspective; this chemical species can be mainly expressed as the combination of the thioketene form (II) and sulfonium form (III) with a C=S<sup>+</sup> triple bond character (Fig. 1).

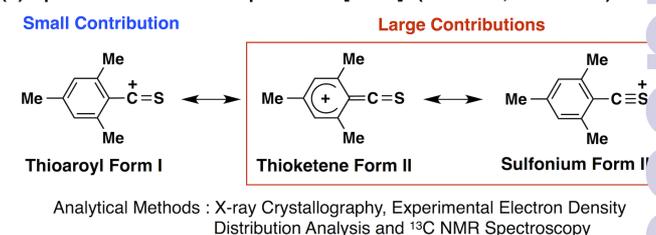
Thioaroyl cation, formulated as [ArCS]<sup>+</sup>, has scarcely been studied, in contrast to its oxygen congener (aroyl cation, [ArCO]<sup>+</sup>), which is widely recognized as the intermediate in Friedel-Crafts type reactions.<sup>1</sup> To date, only two examples have reported the synthesis and spectroscopic characterization of thioaroyl cations.<sup>2,3</sup> In 1968, Lindner and Karmann achieved the first synthesis of a thioaroyl cation ([PhCS]<sup>+</sup>[SbF<sub>6</sub>]<sup>-</sup>) by reacting thiobenzoyl chloride and AgSbF<sub>6</sub>.<sup>2</sup> According to this report, the C–S vibration of [PhCS]<sup>+</sup>[SbF<sub>6</sub>]<sup>-</sup> appears at 1332 cm<sup>-1</sup> in the infrared spectrum.<sup>2</sup> In 1980, Olah and coworkers showed that thiocarbonyl and aromatic carbons in a series of [ArCS]<sup>+</sup> salts are significantly deshielded in <sup>13</sup>C NMR spectroscopy,<sup>3</sup> and concluded that two resonance forms, thioaroyl cation (I) and thioketene (II) (Fig. 1a), mainly contribute to the electronic structure of [ArCS]<sup>+</sup>.<sup>3</sup> This structural perspective of [ArCS]<sup>+</sup> contrasts sharply with that of [ArCO]<sup>+</sup>, where the contribution of the oxonium ion form (ArC=O<sup>+</sup>), corresponding to III (Fig. 1a), is significantly large.<sup>3</sup> Nevertheless, the true structural perspective of thioaroyl cation remains obscure due to the lack of X-ray crystallographic data.

As a part of our study on the chemistry of a two-coordinate boron cation, *i.e.*, diarylborinium ion [Mes<sub>2</sub>B<sup>+</sup>; Mes (mesityl) = 2,4,6-trimethylphenyl],<sup>4</sup> we investigated the reaction of Mes<sub>2</sub>B<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**1**, Scheme 1) and carbon disulfide (CS<sub>2</sub>), which affords thioaroyl cation salt [MesCS]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**2**, Scheme 1) in moderate yield. In the course of this study, we successfully obtained high-quality single crystals of **2** suitable for X-ray crystallography, allowing us to unveil

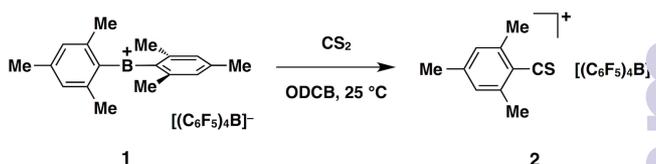
## (a) Conventional Structural Perspective of Thioaroyl Cations [ArCS]<sup>+</sup>



## (b) Updated Structural Perspective of [ArCS]<sup>+</sup> (Ar = Mes, This Work)



**Fig. 1.** (a) Conventional and (b) updated structural perspectives of [ArCS]<sup>+</sup> expressed by three resonance forms of thioaroyl cation form I, thioketene form II and sulfonium form III.



**Scheme 1.** Synthesis of thioaroyl cation salt [MesCS]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**2**) through the C=S double bond cleavage of CS<sub>2</sub> mediated by borinium ion salt Mes<sub>2</sub>B<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**1**).

the true structural perspective of [ArCS]<sup>+</sup>. Here we show that, contrary to the previous understanding, form II and sulfonium form III, rather than form I, mainly contribute to the electronic structure of [MesCS]<sup>+</sup> (Fig. 1b).

Very recently, we reported the first isolation and scalable synthesis of diarylborinium ion (Mes<sub>2</sub>B<sup>+</sup>) salts using chemically inert and weakly nucleophilic counterions, such as the undecachlorocborane anion ([HCB<sub>11</sub>Cl<sub>11</sub>]<sup>-</sup>) and tetrakis(pentafluorophenyl)borate ([C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup>.<sup>5,6</sup> Since Mes<sub>2</sub>B<sup>+</sup> is devoid of lone-pair donation from heteroatoms, the boron center is extremely electron deficient, causing unusual C=O double bond

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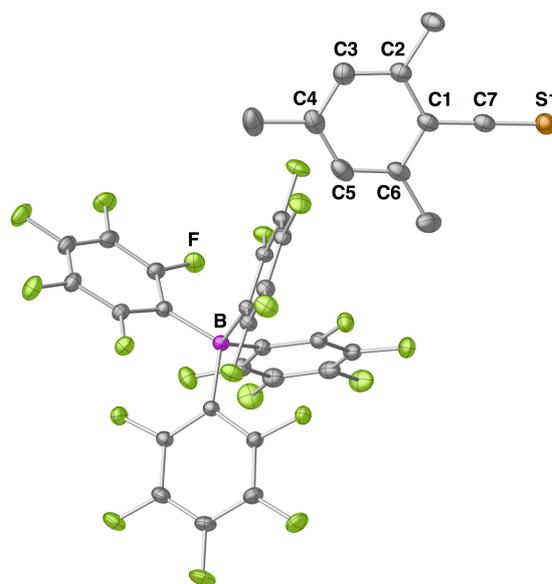
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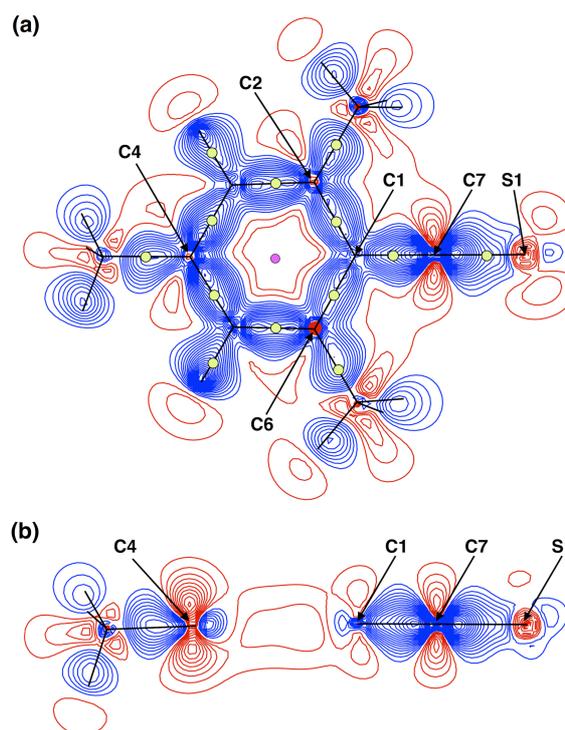
cleavage of CO<sub>2</sub> to yield aroyl cation [MesCO]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup>.<sup>4</sup> We extended this finding to the activation of CS<sub>2</sub> and found that C=S double bond cleavage likewise occurs to give [MesCS]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**2**). Typically, Mes<sub>2</sub>B<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B]<sup>-</sup> (**1**, Scheme 1) was added at 25 °C to an *o*-dichlorobenzene (ODCB) solution of CS<sub>2</sub> (one equivalent to **1**), and the mixture was stirred for 5 minutes. Upon slow diffusion of hexane vapour into the reaction mixture, yellow block-like crystals of **2** were obtained in 46% yield (ESI<sup>†</sup>). Although thioaroyl cation salt **2** decomposed immediately upon exposure to air, its crystalline sample showed no sign of decomposition after left standing for at least one year under argon at ambient temperatures. The formation of [MesCS]<sup>+</sup> likely proceeds via a mechanism similar to that which yields [MesCO]<sup>+</sup> by the reaction of CO<sub>2</sub> with Mes<sub>2</sub>B<sup>+</sup>.<sup>4</sup> Although a few transition metal complexes have been reported to cleave C=S double bond of CS<sub>2</sub>,<sup>7</sup> to the best of our knowledge, there is no example of CS transfer reaction from CS<sub>2</sub> mediated by non-transition-metal chemical species.

Single-crystal X-ray crystallography provides great insights into the structure of **2** (Fig. 2 and ESI<sup>†</sup>). In the [MesCS]<sup>+</sup> moiety, the thiocarbonyl (CS) group has a linear geometry [ $\angle C_{ipso}-C-S = 179.93(5)^\circ$ ], as expected for an sp-hybridized carbon. The C<sub>ipso</sub>-C(S) bond length [1.3785(7) Å] is much shorter than the typical C-C single bond length (1.507 ± 0.039 Å),<sup>8,9</sup> reflecting the C<sub>ipso</sub>=C(S) double bond character through the π-donation from the aromatic ring to the CS moiety. Consistent with this, the mean length of the C<sub>ipso</sub>-C<sub>ortho</sub> bonds [1.4290(7) Å] in the mesityl group is longer than those of the other C-C bonds in the aromatic ring [1.3833(8) and 1.4051(9) Å for C<sub>ortho</sub>-C<sub>meta</sub> and C<sub>meta</sub>-C<sub>para</sub> bonds, respectively]. These structural features of [MesCS]<sup>+</sup> are similar to those of the previously reported aroyl cations<sup>4,10</sup> and indicate that the aromatic ring has a quinoid character, *i.e.*, form II (Fig. 1b). Importantly, the C-S bond length of **2** [1.5039(5) Å] is much shorter than a typical C=S double bond (1.63 Å)<sup>9,11</sup> and even those of the CS groups in transition metal complexes (1.57 Å).<sup>12,13</sup> These observations strongly suggest the large contributions of the thioetene (II) as well as sulfonium (III) forms (Fig. 1b). This perspective is very different from that proposed previously, where thioaroyl cations lack the contribution of form III (Fig. 1a).<sup>3</sup>

Experimental electron density distribution analysis using a multipole expansion method<sup>14</sup> further confirms the above structural perspective of [MesCS]<sup>+</sup> (ESI<sup>†</sup>). A 3D plot of the static model density of **2** (Fig. S1, ESI<sup>†</sup>) shows that all the covalent bonds, except for the C1-C7-S1 moiety, are characterized by normal σ- and π-bonds. Fig. 3 illustrates cross sections of the static model density map of **2** viewed along the in-plane and out-of-plane directions relative to the mesitylene ring. The largely delocalized bonding electrons between C7 and S1 atoms are clearly visualized both in the in-plane and out-of-plane directions relative to the mesitylene ring. This observation indicates the C≡S<sup>+</sup> triple bond character and thus the significant contribution of form III to [MesCS]<sup>+</sup>. Although the ellipticity<sup>15</sup> of the C-S bond (0.21, Fig. S2, ESI<sup>†</sup>) deviates from that expected for an undistorted triple bond (0.0), this is reasonable because form II also contributes to [MesCS]<sup>+</sup>, as represented by the presence of π-bonding electrons on C1-C7 (C<sub>ipso</sub>-CS) (Fig. 3b). Meanwhile, the contour level of the vacant 2p orbital on C7 is much shallower than expected for thioaroyl cation form I (Fig. 3b). Furthermore, the Stockholder population analysis<sup>16</sup> shows that C7



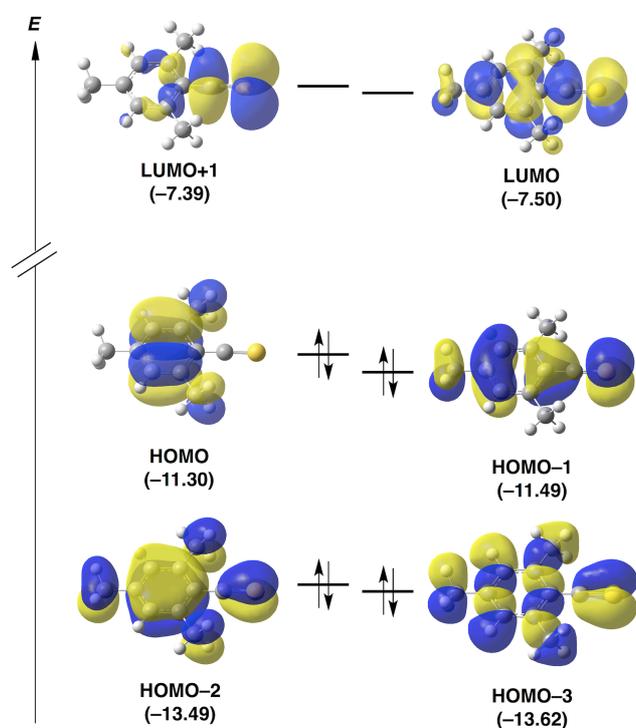
**Fig. 2.** Crystal structure of **2** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity. Boron, carbon, fluorine and sulfur atoms are colored in magenta, gray, yellow-green and orange, respectively. Selected bond lengths (Å) and angle (°) for **2**: C1-C2 = 1.4278(7), C1-C6 = 1.4303(6), C1-C7 = 1.3785(7), C2-C3 = 1.3857(7), C3-C4 = 1.4071(8), C4-C5 = 1.4031(9), C5-C6 = 1.3809(8), C7-S1 = 1.5039(5), C1-C7-S1 = 179.93(5).



**Fig. 3.** Experimentally obtained electron density distribution of **2**. Cross sections of the static model density map of **2** viewed along the in-plane (a) and out-of-plane (b) directions relative to the mesitylene ring. Red and blue curves represent positive and negative electron densities, respectively. The contours are drawn at a 0.05 eÅ<sup>-3</sup> interval. Bond critical points (BCPs) and a ring critical point (RCP) are depicted as yellow-green and pink circles, respectively.

(+0.138) is charged only moderately, while a large positive charge is located on S1 (+0.300) (Fig. S3). Hence, the contribution of thioaroyl cation form **I** to the electronic structure of  $[\text{MesCS}]^+$  is considered much smaller than those of forms **II** and **III**.

We also performed DFT calculations on counterion-free cation  $[\text{MesCS}]^+$  (a singlet state in vacuum) at the B3LYP/6-31G+(d,p) level of theory (ESI<sup>†</sup>).<sup>17</sup> Fig. 4 (see also Fig. S5, ESI<sup>†</sup>) shows the optimized structure of  $[\text{MesCS}]^+$ . The bond lengths and angles are consistent with those observed in the crystal structure of **2** (Fig. 2), except that the calculated C–S bond length (1.523 Å) is slightly longer than the experimental value [1.5039(5) Å]. The LUMO and LUMO+1 of  $[\text{MesCS}]^+$  involve the  $\pi^*$ -type orbitals at the CS moiety, while the HOMO is localized exclusively on the Mes group (Fig. 4). The HOMO–1 reflects the  $\pi$ -donation from the mesityl ring to the carbon atom of the CS group, while the HOMO–2 and HOMO–3 represent the two  $\pi$ -type orbitals at the CS moiety (Fig. 4). Importantly, the natural population analysis (NPA)<sup>18</sup> charge distribution indicates that the charge on the carbon atom of the CS group is very small (+0.021, Fig. S6, ESI<sup>†</sup>). Instead, the positive charges are predominantly located on the sulfur (+0.541), *C<sub>ortho</sub>* (+0.102) and *C<sub>para</sub>* (+0.119) atoms (Fig. S6, ESI<sup>†</sup>). Atoms in Molecules (AIM) analysis<sup>18</sup> of  $[\text{MesCS}]^+$  confirms that the calculated electron density at the bond critical points (Fig. S7, ESI<sup>†</sup>) agree well with the experimental results (Figs. 3 and S4, ESI<sup>†</sup>). All the above structural features in the theoretical model are consistent with those obtained in the X-ray crystal structure of **2** and its Stockholder population analysis (Figs. S3 and S4, ESI<sup>†</sup>), supporting our conclusion that thioketene form **II** and sulfonium form **III**, rather than form **I**, mainly contribute to the electronic structure of  $[\text{MesCS}]^+$  (Fig. 1b).



**Fig. 4.** Molecular orbitals of  $[\text{MesCS}]^+$  in the optimized geometry [B3LYP/6-31G+(d,p)]. Energy levels (eV) are given in parentheses.

Analogous to  $\text{Mes}_2\text{B}^+$ ,<sup>4</sup>  $[\text{MesCS}]^+$  in ODCB-*d*<sub>4</sub> at 25 °C is heavily subject to the coordination of  $[(\text{C}_6\text{F}_5)_4\text{B}]^-$  anion. Thus, <sup>11</sup>B, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy (Figs. S9–S11, ESI<sup>†</sup>) of **2** show that the chemical shifts of the signals due to  $[(\text{C}_6\text{F}_5)_4\text{B}]^-$  are identical to those observed for **1**.<sup>4</sup> Note that the <sup>13</sup>C NMR signals of *C<sub>ortho</sub>* and *C<sub>para</sub>* of the  $[\text{MesCS}]^+$  moiety of **2** (157.0 and 161.2 ppm, Fig. S9, ESI<sup>†</sup>) are more downfield than those of the corresponding carbons of  $[\text{MesCO}]^+[(\text{C}_6\text{F}_5)_4\text{B}]^-$  [154.9 (*C<sub>ortho</sub>*) and 160.3 (*C<sub>para</sub>*) ppm].<sup>4</sup> This means that the degree of  $\pi$ -donation from the mesityl ring to the CS group in  $[\text{MesCS}]^+$  is stronger than that to the CO group in  $[\text{MesCO}]^+$ . The <sup>13</sup>C NMR signal due to the CS group of  $[\text{MesCS}]^+$  appears at the downfield region (204.0 ppm), which is consistent with the previous report on thioaroyl cations (195.1 to 198.3 ppm at –65 °C in  $\text{SO}_2$ ). Olah and coworkers ascribed the large deshielding of the CS group in several thioaroyl cations to the contribution of form **I** as well as the paramagnetic term of the cations.<sup>3,20</sup> However, as described above, the experimentally obtained and calculated charges on the carbon atom of the CS group of  $[\text{MesCS}]^+$  are small (+0.138 and +0.021, respectively, Figs. S3 and S6, ESI<sup>†</sup>). Furthermore, the calculation on  $[\text{MesCS}]^+$  at the B3LYP/6-311+G(2d,p) level virtually reproduces the <sup>13</sup>C NMR chemical shift (228 ppm in vacuum) observed for the CS group (204.0 ppm in ODCB-*d*<sub>4</sub>, Fig. S9, ESI<sup>†</sup>). Therefore, the significant deshielding of the CS groups in the <sup>13</sup>C NMR spectroscopy of thioaroyl cations is better explained by the paramagnetic term,<sup>20</sup> rather than the contribution of thioaroyl cation form **I**.

In conclusion, X-ray crystallographic studies and experimental electron density distribution analysis, along with theoretical calculations, on  $[\text{MesCS}]^+[(\text{C}_6\text{F}_5)_4\text{B}]^-$  (**2**, Scheme 1) unveiled the electronic structure of thioaroyl cation; this chemical species can be mainly expressed as the combination of thioketene form **II** and sulfonium form **III**, while the contribution of thioaroyl cation form **I** is small (Fig. 1b). Accordingly, the structural perspective of thioaroyl cation is now updated. This work also highlights the remarkable reactivity of diarylborinium ion  $\text{Mes}_2\text{B}^+$  to induce C=S double bond cleavage of  $\text{CS}_2$  (Scheme 1). The highly Lewis acidic and chalcogenophilic nature of  $\text{Mes}_2\text{B}^+$  should be useful for exploring new chemical transformations.

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