

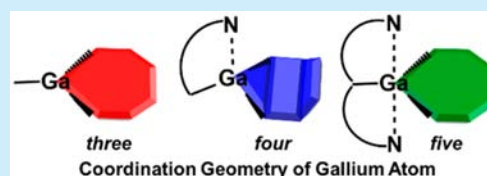
# Synthesis of Air- and Moisture-Stable Dibenzogallepins: Control of Planarity of Seven-Membered Rings in Solid States by Coordination to Gallium Atoms

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## S Supporting Information

**ABSTRACT:** Air- and moisture-stable dibenzo[*bf*]gallepins with planar seven-membered rings have been designed and synthesized. From X-ray single-crystal analyses, the effects of the coordination numbers were evaluated at the gallium atom on the planarity of the seven-membered rings with a series of the synthesized complexes. Accordingly, it was shown that the seven-membered ring of dibenzogallepin involving a three-coordinated gallium atom presented the highest planarity compared to other dibenzogallepins with four- or five-coordinated gallium atoms. In addition, from theoretical calculations, it was proposed that the electronic states of the gallium atom in the complexes contributed to the energy levels of LUMOs+1.



Seven-membered cycloheptatrienes have attracted attention as flexible  $\pi$ -conjugated building units<sup>1</sup> and as precursors to the tropylium ion.<sup>2</sup> Neutral cycloheptatriene usually forms a boatlike conformation in which flipping frequently occurs.<sup>1a,b</sup> In contrast, the one-electron oxidized form of cycloheptatriene such as the tropylium ion has a planar structure due to stabilization by the formation of a  $6\pi$ -electron aromatic system on the seven-membered ring.<sup>2a,b</sup> Heteropins are a class of cycloheptatrienes containing a heteroatom instead of an sp<sup>3</sup> carbon. The synthesis of heteropins involving group 14<sup>1c,d,2c,3</sup> and 15<sup>3e,4</sup> elements has been already established. In particular, the structures and optical and electrochemical properties of dibenzo[*bf*]silepins have been investigated in detail.<sup>1c,d,2c,3a,b</sup> Heteropins containing group 13 elements can be regarded as neutral analogues of the tropylium ion. The synthesis of various borepins has been achieved, and their structure and material properties have been examined.<sup>5,6</sup> In particular, the aromaticity in the seven-membered rings was observed in the tropylium ion. In addition, it was shown that dibenzo[*bf*]borepins possess the planar aromatic seven-membered ring and electron-accepting property.<sup>6</sup>

Compared to the number of reports on organoboron-conjugated heterocycles, those on heteroles,<sup>7</sup> heterorbenzenes,<sup>8</sup> and heteropins<sup>9,10</sup> containing heavier group 13 elements are still limited. The first synthesis of dibenzoaluminepin was reported by Uchiyama et al.,<sup>9</sup> and that of dibenzogallepin was accomplished by Robinson et al.<sup>10</sup> These reports show that aluminepin and gallepin accepted coordination with the Lewis base and solvent molecules and had boatlike seven-membered rings. These conformations were attributed to the four-coordinated structure of the group 13 elements.

The planar conformations of dibenzoheteropins involving the heavier group 13 atoms were predicted theoretically.<sup>9,10</sup> This means these compounds could be a building block for obtaining robust  $\pi$ -conjugations. Furthermore, information on

their electronic states should be significant for further comprehension of electronic structures of heavier atom-containing  $\pi$ -conjugated molecules. Thus, the next challenge is to establish the synthesis of these molecules and to clarify their conformations and electronic properties. Herein, we demonstrate the synthesis of dibenzo[*bf*]gallepins involving a series of three-, four-, and five-coordinated gallium atoms and compare their conformations. We obtained the planar dibenzogallepins, which are promised to be building units for constructing heteroatom-containing conjugation systems.

We selected Mes\* (2,4,6-tri-*tert*-butylphenyl),<sup>7b,e,f,h</sup> Mamx (2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl),<sup>11</sup> and NCN (2,6-bis[(dimethylamino)methyl]phenyl)<sup>12</sup> as protecting groups of gallium atoms to prevent the coordination of Lewis bases or solvents and improve the durability toward water. As described in Scheme 1, we synthesized three dibenzogallepins (3-Gapin, 4-Gapin, and 5-Gapin) with a method similar to that of the previous report by Robinson.<sup>10</sup> After formation of the dibenzogallepin frameworks in reactions with gallium chloride, the protecting groups were introduced. All of the synthesized dibenzogallepins had high stabilities to air and moisture. Therefore, general purification operations such as extraction with water and recrystallization under ambient atmosphere were applicable. The dibenzogallepins storable under air for at least 2 months without any decomposition. The bulky *tert*-butyl groups and the coordination of amine groups should be responsible for improvement of their stabilities.<sup>11a,b</sup> In particular, it is known that the compounds containing three-coordinated gallium atoms are sensitive to water.<sup>7e-h</sup> The formation of a  $6\pi$ -electron aromatic system could also contribute to enhancement of the durability of 3-Gapin.

Received: February 15, 2015

Published: March 4, 2015

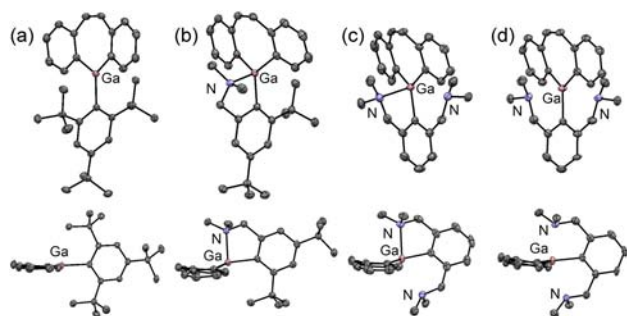
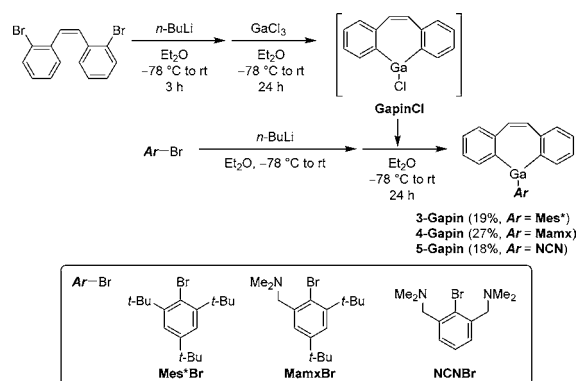
Scheme 1. Synthesis of Dibenzo[*b,f*]gallepins 3-Gapin, 4-Gapin, and 5-Gapin

Figure 1. ORTEP drawings of (a) 3-Gapin, (b) 4-Gapin, (c) A of 5-Gapin and (d) B of 5-Gapin (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3-Gapin, 4-Gapin, and 5-Gapin

lengths (Å) and angles (deg)	3-Gapin	4-Gapin	5-Gapin	
			A	B
Ga–N		2.120	2.275 2.735	2.371 2.573
$\sum$ C–Ga–C	359.98	356.01	359.50	359.97
$\sum$ inner angles <sup>a</sup>	899.14	890.48	894.42	896.70
$\theta_1$	5.15	11.63	10.11	5.06
$\theta_2$	5.05	24.70	19.14	13.93
Ga–N bond order <sup>b</sup>		0.2304	0.1825 0.1040	0.1629 0.1315

<sup>a</sup>Sum of inner angles of seven-membered rings. <sup>b</sup>Calculated at the B3LYP/6-31G(d,p) level by using the geometries of single crystals.



Figure 2. Bent angles  $\theta_1$  and  $\theta_2$  of the seven-membered rings.

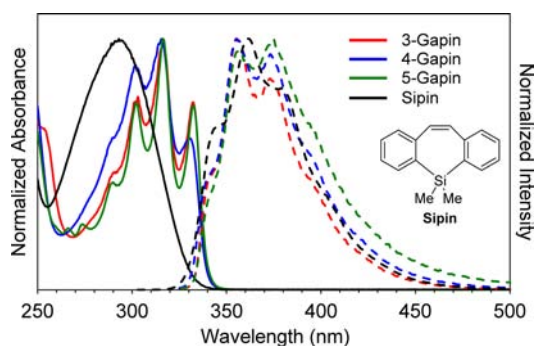
In Figure 1 and Table 1, we show results of X-ray crystallographic analyses. A gallium center of 3-Gapin was protected from coordination with any Lewis bases or solvents. The sum of internal angles of the seven-membered ring of 3-Gapin was 899.14°. As presented in Figure 2, two angles of  $\theta_1$  (5.15°) and  $\theta_2$  (5.05°) were bent angles of the seven-membered rings on the gallium sides and the C=C double bond sides, respectively. These facts indicate that the seven-membered ring of 3-Gapin has high planar conformation. The

planarity was comparable to reported planar dibenzoborepins.<sup>3a,6a–e</sup> The Ga–N bond length of 4-Gapin (2.120 Å) was within a typical coordination bond length between Ga and N (reported Ga–N bond lengths: 2.013–2.192 Å<sup>10,11a,b,d,13</sup>). The coordination with the Mamx group induced a bent conformation which was observed in the seven-membered rings involving four-coordinated gallium atoms.<sup>10</sup> The bent angles of 4-Gapin were 11.63° for  $\theta_1$  and 24.70° for  $\theta_2$ , respectively. The values of these angles were larger than those of 3-Gapin and smaller than those of the reported gallepin.<sup>10</sup> The higher planarity of 4-Gapin compared to the reported gallepin<sup>10</sup> could be attributed to the quasi-trigonal planar structures coordinated by nitrogen from the upper position.<sup>11a,b,d</sup>

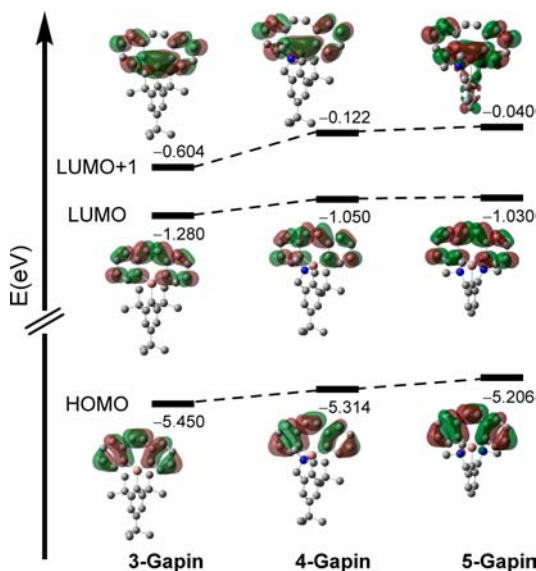
In a single crystal of 5-Gapin, it was found that two geometries A and B were involved. Two distances between Ga and N in A were obtained as 2.275 and 2.735 Å. The conformation of the gallium atom of A was similar to the four-coordinated structure of 4-Gapin including the bent geometry at the seven-membered ring. In contrast, the B conformation had more equivalent Ga–N bonds compared to A, and the bond lengths were determined as 2.371 and 2.573 Å. These mean that the gallium atom in B had a five-coordinated trigonal bipyramidal structure. The trigonal bipyramidal geometry of B showed a higher percentage of trigonal bipyramidal as 96% TBP<sub>a</sub> and 91% TBP<sub>e</sub> compared to A (88% TBP<sub>a</sub> and 90% TBP<sub>e</sub>), respectively.<sup>14</sup> The three equatorial carbons and gallium atoms of B revealed high symmetry, resulting in the higher planar seven-membered ring. Therefore, the smaller bent angles,  $\theta_1$  and  $\theta_2$ , than those of 4-Gapin and A of 5-Gapin were obtained as 5.06° and 13.93°, respectively. For investigation of the Ga–N bonds of the synthesized gallepins, we calculated WBI (Wiberg bond index) bond orders of the Ga–N bonds of the dibenzogallepins with density functional theory (DFT) method by using the geometries obtained by the X-ray crystallographic analyses (Table 1). The bond orders of two Ga–N bonds of A were 0.1825 and 0.1040. The bond order of the shorter one was similar to that of 4-Gapin (0.2304), while the longer one was lower than that of the shorter one. In contrast, similar bond orders of the two Ga–N bonds of B were observed (0.1629 and 0.1315). These results support the four-coordinated-like structure of A and the five-coordinated-like structure of B.

Compared to the reported gallepin,<sup>10</sup> silepins,<sup>1d,3a</sup> and aluminepin,<sup>9</sup> all of the synthesized dibenzogallepins include high planar seven-membered rings, as shown in Table S5 (Supporting Information).

Figure 3 illustrates UV–vis absorption and photoluminescence spectra of the synthesized dibenzogallepins and dibenzosilepin Sipin. Their optical data are listed in Table S6 (Supporting Information). All the synthesized dibenzogallepins presented similar shapes of their absorption spectra. Absorption bands with the peaks at 302, 316, 332 nm attributed to vibrational structures were observed. In contrast, a broad absorption band with the peak at 293 nm without vibrational structures was observed from Sipin in the shorter wavelength region compared to the synthesized dibenzogallepins. These facts suggest that the conjugation system could be extended in dibenzogallepins because of their higher planar structures even in solution states, whereas Sipin vigorously flipped, resulting in the weak conjugation on the bent conformation. The synthesized dibenzogallepins provided photoluminescent spectra with the peaks at around 360 nm similar to Sipin. It is



**Figure 3.** UV-vis absorption (solid lines) and photoluminescence (dashed lines, excited at  $\lambda_{\text{max,abs}}$ ) spectra of  $1.0 \times 10^{-4}$  M **3-Gapin** (red), **4-Gapin** (blue), **5-Gapin** (green), and **Sipin** (black) in  $\text{CHCl}_3$ .



**Figure 4.** Energy diagram and selected molecular orbitals of **3-Gapin**, **4-Gapin**, and **5-Gapin** calculated by the DFT method. Hydrogen atoms are omitted for clarity.

implied that their heteropin rings including **Sipin** might have planar conformations in their excited states.

To assign their absorption bands, time-dependent DFT (TD-DFT) calculation was conducted. It is shown that all of the absorption bands observed around 315 nm should be mainly attributed to transitions from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied MOs (LUMOs). These frontier orbitals are localized only on *cis*-stilbene units, while the LUMOs+1 seems to be affected by the electronic states of gallium. Therefore, slight differences of the absorption bands of the dibenzogallepins are observed. As described in Figure 4, the energy level of LUMOs+1 of **3-Gapin** is stabilized relative to those of **4-Gapin** and **5-Gapin**. The larger stabilization should be ascribed to electronic interaction between the *cis*-stilbene unit and the vacant p-orbital of the gallium atom of **3-Gapin**. In **4-Gapin** and **5-Gapin**, the coordination of the nitrogen atoms to the gallium atoms interrupts the electronic interaction in the seven-membered rings, resulting in the higher energy levels of LUMOs+1.

In conclusion, we demonstrated the synthesis and structural investigation of a series of dibenzo[*b,f*]gallepins with various coordination numbers of gallium atoms. The synthesized dibenzogallepins showed high durability toward air and

moisture. The three-, four-, and five-coordinated structures were precisely determined with single crystals. Accordingly, the seven-membered rings in all dibenzogallepins showed higher planarity compared to other heteropin rings such as silepin. In particular, **3-Gapin** had the highest planar heteropin rings of the synthesized dibenzogallepins. Two geometries of **5-Gapin** originating from four- and five-coordinated-like structures were observed. Dibenzogallepins presented absorption bands owing to their high planar structures. Their frontier orbitals localized at *cis*-stilbene units. From the computer calculation, it was proposed that the conformations of gallium atoms significantly influenced LOMOs+1. We accomplished the construction of a planar structure based on heteropin rings by modulating the coordination geometries of gallium atoms.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental, measurement, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was partially supported by the “Adaptable and Seamless Technology Transfer Program” through target-driven R&D, Japan Science and Technology Agency (JST), and a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No. 2401)” (24102013) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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