



Aromaticity Hot Paper

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# A Planar Five-Membered Aromatic Ring Stabilized by Only Two $\pi$ -Electrons

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Dedicated to Peter Göltz on the occasion of his 70th birthday

**Abstract:** Many chemicals known today are partially or fully aromatic, since a ring framework experiences additional stabilization through the delocalization of  $\pi$ -electrons. While aromatic rings with equal numbers of  $\pi$ -electrons and ring atoms such as benzene are particularly stable, those with the minimally required two  $\pi$ -electrons are very rare and yet remain limited to three- and four-membered rings if not stabilized in the coordination sphere of heavy metals. Here we report the facile synthesis of a dipotassium cyclopentagallene, a unique example of a five-membered aromatic ring stabilized by only two  $\pi$ -electrons. Single-crystal X-ray diffraction revealed a planar Ga<sub>5</sub> ring with almost equal gallium–gallium bond lengths, which together with computational and spectroscopic data confirm its aromatic character. Our results prove that aromatic stabilization goes far beyond what has previously been assumed as minimum  $\pi$ -electron count in a five-atom ring fragment.

While originally used to describe the odor, the term *aromatic* has been expanded to a chemical characteristic in 1855,<sup>[1]</sup> before, less than ten years later, August Kekulé proposed not only the correct structure of benzene but also introduced the concept of aromaticity.<sup>[2]</sup> Since then, aromaticity has become one of the most important theories in chemistry and researchers have been trying to provide a general definition.<sup>[3]</sup> Hückel's rule is probably the best

known concept, according to which planar unsaturated carbocyclic ring systems possessing  $4n + 2$   $\pi$ -electrons ( $n = 0, 1, 2, 3, \dots$ ) gain particular stability by electron delocalization,<sup>[4]</sup> with benzene possessing six  $\pi$ -electrons ( $n = 1$ ) being the most prominent example. In the past 100 years, a plethora of new aromatic compounds with six, ten, 14, and even more  $\pi$ -electrons have been reported, which do not remain limited to hydrocarbons but also include organometallic and purely inorganic ring systems.<sup>[5]</sup> However, while the discovery of ever-increasing ring sizes pushes the upper limit to systems with 162  $\pi$ -electrons ( $n = 40$ ),<sup>[6]</sup> examples of aromatic compounds at the lower end, i.e., those stabilized by only the minimally required two  $\pi$ -electrons ( $n = 0$ ) remain rare and limited to three- and four-membered rings.

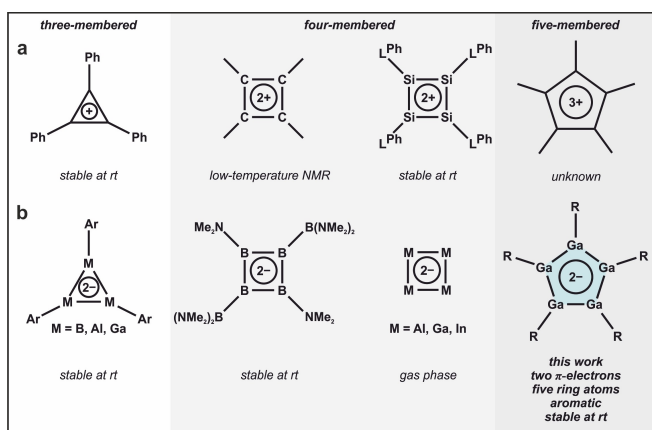
The decreasing stability with increasing ring sizes at a constant count of two  $\pi$ -electrons is in-line with Breslow's statement that aromatic stabilization is highest when the ring size is closest to the number of  $\pi$ -electrons<sup>[7]</sup> and also substantiated by experimental observations. The triphenylcyclopropenyl cation<sup>[8]</sup>—the most simple aromatic carbocycle—is stable at room temperature and could even be crystallographically characterized. Increasing the ring size from three to four atoms and consequently the overall charge from +1 to +2 significantly reduces the stability, which is why the cyclobutadiene dication has yet only been observed by low temperature nuclear magnetic resonance (NMR) experiments,<sup>[9]</sup> and the recently isolated tetrasilacyclobutadiene dication requires additional stabilization by a Lewis-basic ligand (Figure 1a).<sup>[10]</sup> An additional increase of the ring-size and consequently the overall charge in carbon-

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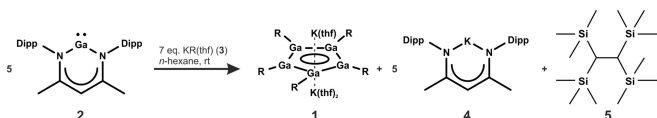
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**Figure 1.** Aromatic ring systems containing two  $\pi$ -electrons through the formal a) oxidation of unsaturated group 14 cycles or b) reduction of cyclic group 13 compounds.

based aromatic systems would derive the cyclopentadiene trication, which however remains elusive. In addition to oxidizing unsaturated rings consisting of group 14 elements, the reduction of electron-deficient cycles based on group 13 elements is an alternative approach to access aromatic systems possessing only two  $\pi$ -electrons (Figure 1b). However, examples are similarly rare and reflect well the lower stability of larger rings: While three-membered rings of

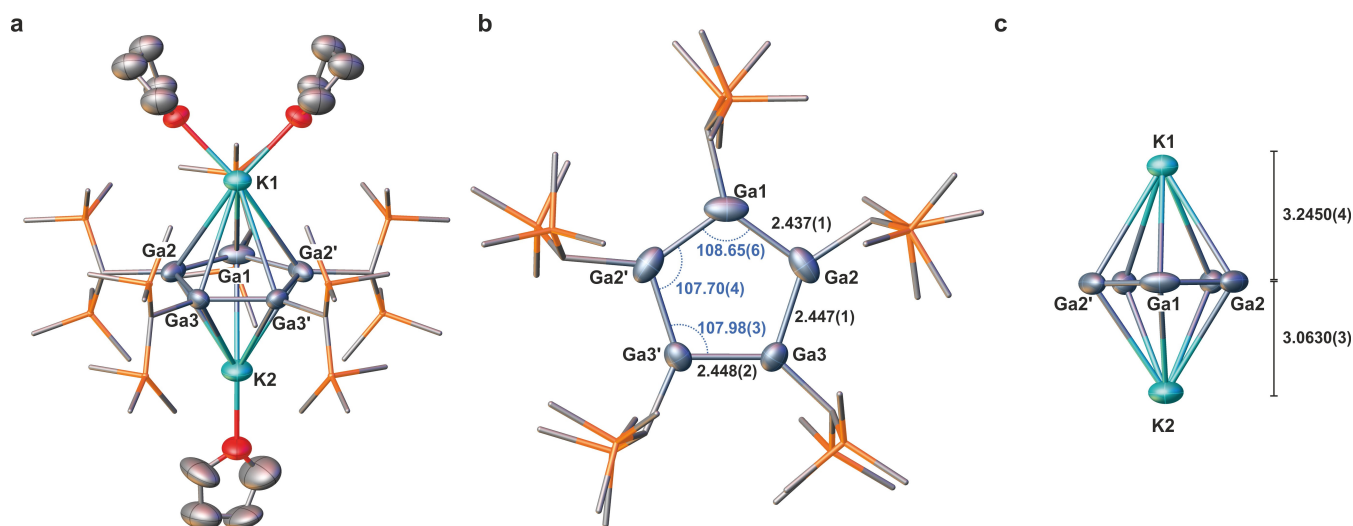


**Scheme 1.** Preparation of the dipotassium cyclopentagallene **1**; Dipp = 2,6-diisopropylphenyl, R = CH(SiMe<sub>3</sub>)<sub>2</sub>, thf = tetrahydrofuran.

boron,<sup>[11]</sup> aluminium,<sup>[12]</sup> and gallium<sup>[13]</sup> could be crystallographically characterized, only a puckered resonance-stabilized four-membered boracycle<sup>[14]</sup> and a dianionic In<sub>4</sub> cycle shielded by boryl ligands<sup>[15]</sup> have been isolated while reports of (M<sub>4</sub>)<sup>2-</sup> clusters (M = Al, Ga, In) remain limited to gas-phase experiments.<sup>[5a,16]</sup> In light of this elusive nature of four-membered rings, two  $\pi$ -electrons did not seem sufficient to derive aromatic rings with five or more atoms, except when stabilized in the coordination sphere of heavy metals.<sup>[17]</sup> Here, we report the synthesis and structure of a planar cyclopentagallane dianion **1**, which is valence-isoelectronic with the putative cyclopentadiene trication and a unique example of a five-membered  $2\pi$ -aromatic ring system.

The dipotassium cyclopentagallene **1** is obtained at room temperature from the reaction of the gallium(I)  $\beta$ -diketiminato **2**<sup>[18]</sup> and potassium bis(trimethylsilyl)methanide **3**<sup>[19]</sup> (Scheme 1). Here, **2** serves as a gallium(I) source yielding the respective potassium  $\beta$ -diketiminato **4** by salt metathesis. The potassium reagent **3** does not only provide the terminal substituent but also serves as a reducing agent through oxidative coupling of two bis(trimethylsilyl)methanide anions as evidenced by the formation of 1,1,2,2-tetrakis(trimethylsilyl)ethane **5**; see the Supporting Information for details. This is exceptional as the synthesis of group 13 dianions usually necessitates the use of strong reducing agents such as alkaline metals. Furthermore, this reaction is remarkable as the respective aluminium(I)  $\beta$ -diketiminato undergoes deprotonation of the ligand's backbone under the same reaction conditions.<sup>[20]</sup>

Cyclopentagallene **1** was isolated as green crystals and its molecular solid-state structure was established by X-ray diffraction analysis (Figure 2).<sup>[21]</sup> **1** features a planar five-membered ring. Consistent with an aromatic compound, the Ga–Ga distances are almost equal (2.437(1) to 2.447(1) Å) and significantly shorter than those of the non-aromatic

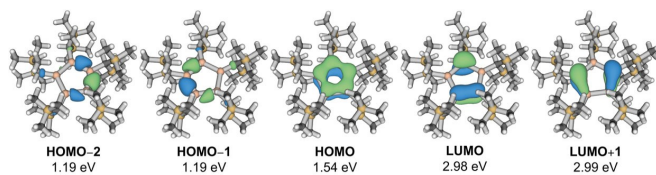


**Figure 2.** Molecular solid-state structure (hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level) of a) the dipotassium cyclopentagallene-3thf (**1**), b) the  $1^{2-}$  fragment, and c) the Ga<sub>5</sub>K<sub>2</sub> core with selected bond lengths (Å, given in black) and angles (°, given in blue); symmetry transformations used to generate equivalent atoms (marked with an '): +x, 3/2−y, +z; thf = tetrahydrofuran.

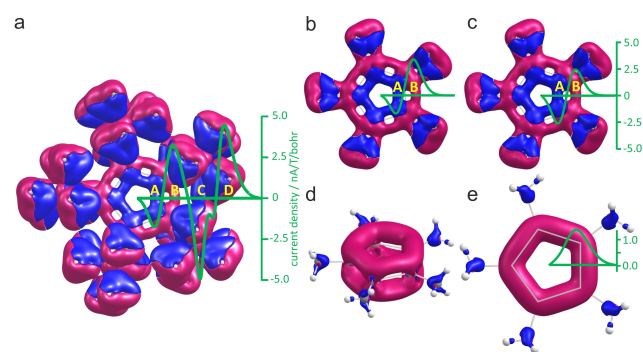
$[\text{Ga}_5(\text{dmap})_{10}]^{5+}$  pentacation (dmap = 4-(*N,N*-dimethylamino)pyridine)<sup>[22]</sup> or those in the neutral gallium(I) tetramer  $[\text{Ga}_4(\text{C}(\text{SiMe}_3)_3)_4]$ ,<sup>[23]</sup> which possess average Ga–Ga distances of 2.495(6) and 2.68 Å, respectively. However, they agree well with the gallium–gallium bond lengths of 2.441(1) Å reported for the valence-isoelectronic analogue of the cyclopropenyl cation, that is an alkali-metal mediated<sup>[24]</sup> dianionic cyclotrigallane,<sup>[13]</sup> which further substantiates the aromatic character of **1**.

To interrogate the aromatic character of **1** in more detail, density functional theory (DFT) calculations have been performed at the PBE-GD3BJ/def2-TZVP level of theory<sup>[25]</sup> for the free dianion  $\mathbf{1}^{2-}$ . In view of the frontier molecular orbitals (Figure 3), the  $\text{Ga}_5$  ring consists of five  $\text{sp}^2$ -hybridized gallium atoms. Each potassium atom donates one electron to the empty p-orbitals residing orthogonal to the ring plane, forming the highest occupied molecular orbital (HOMO) of  $\pi$ -character. The lowest unoccupied molecular orbital (LUMO) as well as the almost degenerate LUMO + 1 represent the antibonding  $\pi^*$ -orbitals as expected for an aromatic compound.

Orbital localization procedures<sup>[26]</sup> yield two-centre two-electron bonds plus one additional orbital which is essentially identical with the delocalized HOMO. This situation is the same as e.g. in  $(\text{ThBi}_{12})^{4-}$ , where a large ring current and also large nucleus independent chemical shifts (NICS) values<sup>[27]</sup> were found for this  $2\pi$  aromatic system.<sup>[17b]</sup> The aromatic character of the free dianion  $\mathbf{1}^{2-}$  was investigated



**Figure 3.** Isosurface plot ( $\pm 0.04$  a.u.) of representative frontier molecular orbitals of the free cyclopentagallane dianion  $\mathbf{1}^{2-}$ .

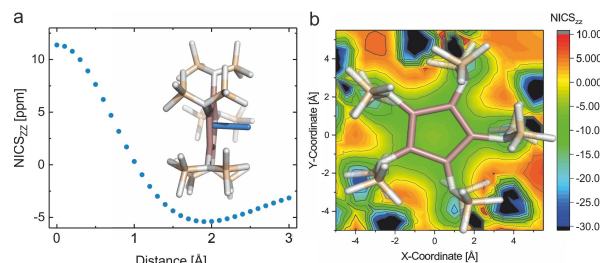


**Figure 4.** Contour plots of signed absolute values of current densities, and current profiles for a)  $\mathbf{1}^{2-}$ , b)  $(\text{Ga}_5\text{Me}_5)^{2-}$ , c)  $\text{Ga}_5\text{Me}_5$ , and d), e) of the current density difference between the latter two. Contours are drawn at 0.02 a.u., for the difference plots at 0.005 a.u. Paramagnetic regions (A,C) are shown in blue, diamagnetic regions (B,D) in red. The plane for current profiles (and for integration to get the current strength) is oriented perpendicular to the ring, from the centre to the right.

with the same tools. Magnetically induced ring currents were calculated<sup>[28]</sup> (see also Figure S15 and Table S4 in the Supporting Information) for  $\mathbf{1}^{2-}$  as well as for model compounds  $(\text{Ga}_5\text{Me}_5)^{2-}$ , where the HOMO again is the delocalized  $\pi$ -orbital, and—without further structure optimization—for  $\text{Ga}_5\text{Me}_5$ , where this orbital is unoccupied. Contour plots and current profiles for the three compounds are shown in Figure 4.

$\mathbf{1}^{2-}$  exhibits a paramagnetic current of  $-2.7 \text{ nA T}^{-1}$  in region A and a diamagnetic current of  $6.0 \text{ nA T}^{-1}$  in region B, and thus a small diamagnetic net current of  $3.3 \text{ nA T}^{-1}$ . This indicates (weak) aromaticity. Further, one observes currents in the region of the  $\text{C}(\text{SiMe}_3)_3$  groups (C:  $-7.9 \text{ nA T}^{-1}$ , D:  $+9.0 \text{ nA T}^{-1}$ ), which are not relevant for the discussion of the aromaticity of the ring. For the model compound  $(\text{Ga}_5\text{Me}_5)^{2-}$  the latter do not occur, but the situation in regions A ( $-2.5 \text{ nA T}^{-1}$ ) and B ( $+7.3 \text{ nA T}^{-1}$ ) is very similar to that in  $\mathbf{1}^{2-}$ , resulting in a net current of  $4.4 \text{ nA T}^{-1}$ . In contrast, for  $\text{Ga}_5\text{Me}_5$ , where the delocalized  $\pi$ -orbital is unoccupied, para- and diatropic currents cancel (A:  $-5.0 \text{ nA T}^{-1}$ , B:  $+5.1 \text{ nA T}^{-1}$ ), revealing a clearly non-aromatic situation. Matters become even more evident from the contour plot of the difference of current densities of the dianionic and the neutral model compound (Figure 4d, e), which almost exactly reflects the shape of the HOMO of the dianion (Figure 3). The corresponding current is purely diatropic. It is weaker than that in benzene by almost a factor of three, but also the number of electrons responsible for the current is smaller by this factor. The system may be considered as clearly  $\pi$ -aromatic.

The same conclusion can be drawn from the calculated NICS values: A suitable height above the  $\text{Ga}_5$  ring plane to probe the induced  $\pi$ -electron ring current was obtained by a height scan of the  $\text{NICS}_{\text{ZZ}}$  component orthogonal to the ring plane (Figure 5).<sup>[27c,29]</sup> This scan revealed a dominating paratropic induced ring current by the  $\sigma$ -scaffold of the  $\text{Ga}_5$  ring at heights up to 1 Å above the ring plane. In contrast, the  $\text{NICS}_{\text{ZZ}}$  analysis at heights between 1.7 and 2.0 Å show an induced diatropic ring current caused by the aromatic  $2\pi$ -electron system of the cyclopentagallane. Two-dimensional  $\text{NICS}_{\text{ZZ}}$  XY scans at 1.8 Å above the  $\text{Ga}_5$  ring center further support the aromatic character of the free dianion with homogeneously negative  $\text{NICS}_{\text{ZZ}}$  values of ca.  $-10$  ppm (Figure 5b) that are in agreement with a set of comparable, carbon-based  $2\pi$ -aromatics theoretically investigated in this

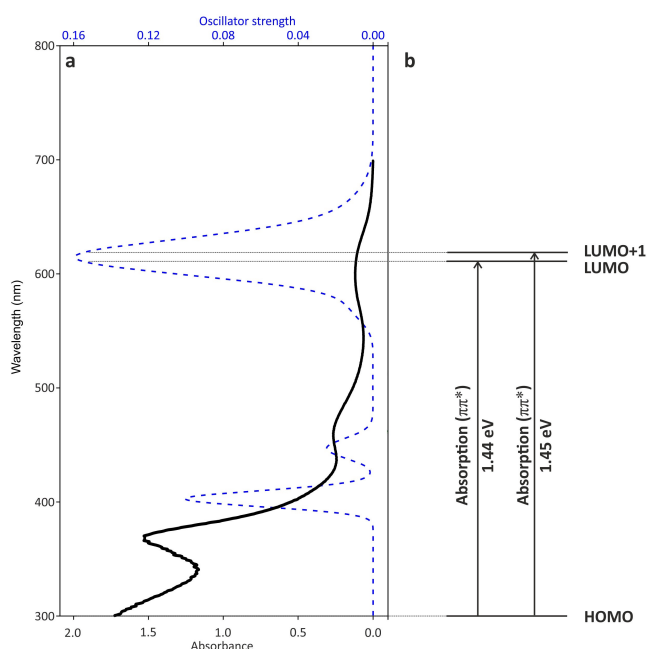


**Figure 5.** a) Height scan of the  $\text{NICS}_{\text{ZZ}}$  component orthogonal to the ring plane of  $\mathbf{1}^{2-}$ . b)  $\text{NICS}_{\text{ZZ}}$  2D plot at 1.8 Å above the cyclopentagallane ring-plane of  $\mathbf{1}^{2-}$ .

study, i.e., the cyclopropenyl cation, the cyclobutadienyl dication, and the cyclopentadienyl trication (see the Supporting Information, Figures S11 and S12 as well as Table S3). The calculated anisotropy of the induced ring current density (ACID)<sup>[30]</sup> in the free dianion underscores the aromaticity induced by the two  $\pi$ -electrons with a circular diatropic vector field along the five gallium atoms (Figure S13 and S14).

The low HOMO–LUMO gap of 1.44 eV agrees well with the observed colour of **1** and time-dependent DFT (TD-DFT) calculations allowed assigning the experimentally observed absorption events at 366, 460, and 602 nm (Figure 6). The long-wavelength absorption accounts for  $\pi$ – $\pi^*$  transitions from the HOMO to the LUMO and to the LUMO+1, as expected from an aromatic compound, while the absorptions at shorter wavelength originate from metal–metal-bonding  $\sigma$ -orbitals (HOMO–1 and HOMO–2, Figure S2) as previously reported for gallium clusters such as  $[\text{Ga}_4(\text{C}(\text{SiMe}_3)_3)_4]$ .<sup>[23]</sup>

In summary, the data we report here substantiate the aromatic nature of the cyclopentagallane dianion **1**. The synthesis and characterization of a  $2\pi$ -aromatic five-membered ring is, to our knowledge, unprecedented. The existence and stability of **1** proves the concept of aromaticity in its most minimalistic and purest form while expanding the hitherto known structural space of cyclic molecules.



**Figure 6.** a) Experimental (in black, solid line) and simulated (in blue, dashed line, PBE-GD3Bj/def2-TZVP) absorption spectra of **1** in *n*-hexane. b) Energy levels associated with the long-wavelength absorption of  $\pi$ – $\pi^*$ -nature.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** Aromaticity · Gallium · Inorganic Ring Systems · NICS

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