



## In search of aromatic seven-membered rings <sup>☆</sup>

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### ABSTRACT

A theoretical search for aromatic seven-membered rings has been carried out using density functional theory calculations with the B3LYP functional. The rings considered include the  $C_7H_7^+$  cation and its hetero-derivatives by replacing C, CH or CC units by B, Al, Ga, Si, Ge, N, P, As and BN group, the  $B_8^{2-}$  dianion, the  $CB_7^-$  anion, the neutral  $S_3N_4$  ring and its derivatives by substituting one or two N atoms by CH group, the  $S_4N_3^+$  cation and the all-metallic cycles  $M_7^{3-}$  and  $M_7T$  with  $M = Cu, Ag, Au$  and  $T = Y, Sc$ . Most molecules studied have planar structure in their electronic ground state. Vibrational spectra of some derivatives are plotted. Nucleus independent chemical shift (NICS) indices show that the parent molecule  $C_7H_7^+$  has a higher degree of aromaticity than its derivatives. Substitution of N in  $S_3N_4$  by CH marginally influences the aromaticity in such a way that  $S_3N_4$ ,  $S_3N_3(CH)$  and  $S_3N_2(CH)_2$  are similarly aromatic. The  $B_8^{2-}$  dianion and both  $D_{7h}$  and  $C_{2v}$  isomers of  $CB_7^-$  possess comparable aromatic character. As for the all-metal clusters  $Cu_7^{3-}$ ,  $Ag_7^{3-}$ ,  $Au_7^{3-}$ ,  $Cu_7Sc$ ,  $Cu_7Y$ ,  $Ag_7Y$  and  $Au_7Y$ , the binary clusters become more aromatic than the pure metal anions, and are thus characterized by  $\sigma$ -aromaticity.

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## 1. Introduction

Aromaticity, which is beyond any doubt one of the most fundamental and popular concepts in chemistry, is widely employed and successfully applied in many areas to interpret and predict the molecular structure, electronic and thermodynamic properties, as well as chemical reactivities of cyclic compounds [1]. The higher thermodynamic stability of planar aromatic rings is usually rationalized in terms of the number of delocalized electrons which satisfy the classical  $(4n + 2)$  Hückel rule. Although this was originally derived for organic  $\pi$ -delocalized rings, its applicability was later extended to  $\sigma$ - and also multiply  $\sigma$ -,  $\pi$ -aromatic systems [1b,2]. More recently, the concept of aromaticity was applied to planar cycles formed by metallic elements [3] but its origin and character remain a matter of discussion [1a,4] as these cycles could be considered as either  $\pi$ - or  $\sigma$ -aromatic or both. This concept can also be applied to three-dimensional cage-shaped atomic clusters [5]. Similar to the planar rings, a closed electronic shell (or subshell) often makes a cage aromatic according to the large negative NICS value at the center of the cage [5]. In the case of icosahedral cage-shaped

clusters, a closed electronic shell and aromaticity can be reached if the number of the delocalized electrons satisfies the  $2(n + 1)^2$  Hirsch rule [5].

As originally discovered by Kekulé from benzene, aromaticity usually implies a stabilizing effect in organic or inorganic compounds that commonly involve planar six-membered rings as building blocks. Aromaticity of five-membered cycles such as pyrrole derivatives is also well established. In contrast, aromatic seven-membered rings are rather scarce. The most well known representative for this class is the tropylium cation  $C_7H_7^+$  **1** (cf. Chart 1) which exhibits  $D_{7h}$  point group symmetry [6]. Replacement of a  $CH^+$  group in **1** by a BH and AlH leads to neutral  $C_6H_6BH$  **2** and  $C_6H_6AlH$  **3**, respectively. Earlier molecular orbital calculations [7] showed, however, that the parent borepin **2** is planar but only weakly aromatic. Spectroscopic data of the substituted borepins pointed out that steric hindrance and attenuated aromatic character induce significant non-planarity of the seven-membered skeleton [7]. More recently, the gallepin  $C_6H_6GaH$  **4**, which is the gallium analogue of **1**, has been prepared and quantum chemical calculations have shown that although gallepin **4** contains the expected  $6\pi$ -electron structure, it is even less aromatic than borepin **2** [8].

Replacement of a carbon atom in the typical hydrocarbon cation **1** by the heavier congeners Si and Ge leads to the silatropylium **5** ( $C_6H_6SiH^+$ ) and germatropylium **6** ( $C_6H_6GeH^+$ ) cations, respectively. It was predicted that they are higher in energy than the

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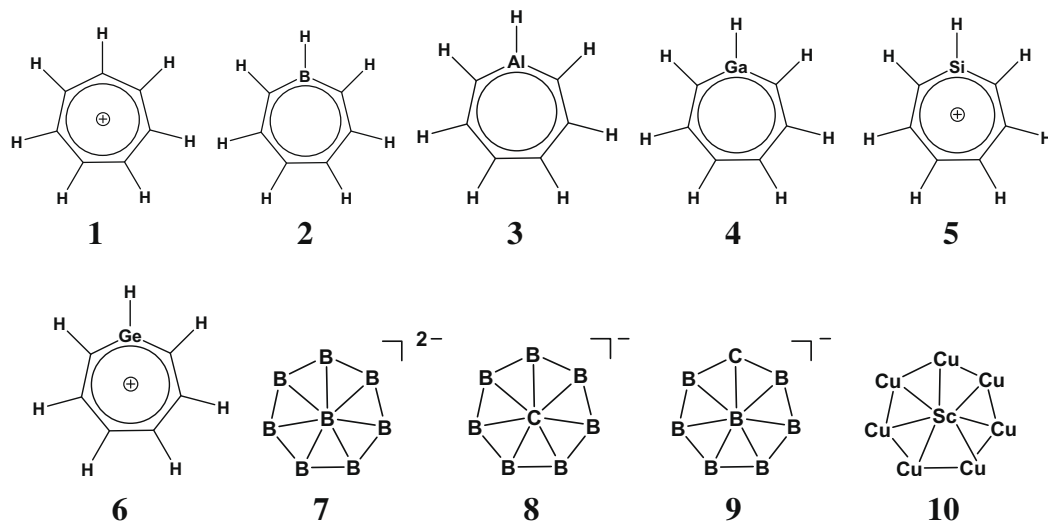


Chart 1.

silabenzyl and germabenzyl cations by  $\sim 9$  and  $\sim 16$  kcal/mol, respectively [9]. While  $D_{7h}$   $C_7H_7^+$  is the global minimum on the potential energy surface, and the nonclassical isomers have relatively higher energies, the nonclassical bridged isomers of  $C_6H_6GeH^+$  have been found to be more stable than the seven-membered counterpart. The situation of  $C_6H_6SiH^+$  is intermediated between  $C_7H_7^+$  and  $C_6H_6GeH^+$  in that both classical and nonclassical isomers of  $C_6H_6SiH^+$  tend to have comparable energy content [9c].

The  $B_8^{2-}$  anion **7** is a planar molecular wheel with  $D_{7h}$  point group [10], and it can be stabilized by a  $Li^+$  cation, forming a  $C_{7v}$  symmetric  $LiB_8^-$  complex [11]. Substitution of the central  $B^-$  unit of  $B_8^{2-}$  by one C results in the  $CB_7^-$  anion **8**, which maintains the  $D_{7h}$  symmetry [12]. Based on electron counts and analysis of the canonical molecular orbitals, it was indicated that both of them have a double  $\sigma$ - and  $\pi$ -aromaticity, even though that the  $\sigma$ -aromaticity is less pronounced for  $CB_7^-$  [13]. The  $D_{7h}$  aromatic  $CB_7^-$  anion bears a heptacoordinated carbon atom [12–14] but it was subsequently demonstrated that such a form is extremely unfavorable, and the lowest energy isomer **9** has a  $C_{2v}$  shape with a heptacoordinated boron atom at the ring center and the carbon atom in the outside ring [15].

Recently, using quantum chemical calculations, we have shown that the bimetallic cluster  $Cu_7Sc$  **10** turns out to be a planar system bearing  $D_{7h}$  point group symmetry [16]. More importantly,  $Cu_7Sc$  represents a prototype of a class of metallic clusters featuring a high  $\sigma$ -aromaticity. The  $Cu_7^{3-}$  cluster is isoelectronic with  $Cu_7Sc$  with respect to the number of delocalized valence  $s$ -electrons, and it has been predicted to be similarly  $\sigma$ -aromatic with  $Cu_7Sc$  [16]. Although multiply charged anions are not electronically stable, the calculations of such species do make sense due to the repulsive Coulomb barrier, which prevents the autodetachment of electrons, as has been discussed in the case of  $Al_4^{2-}$  [17].

In view of the scarcity of this type of potentially interesting compounds, we set out to search for the seven-membered cycles containing different elements that possess a relative thermodynamic stability and a certain degree of aromaticity. In addition, we attempt to probe such aromaticity using the approaches derived from density functional theory.

## 2. Computational methods

Quantum chemical calculations were carried out making use of the density functional theory with the popular hybrid B3LYP

functional [18] in conjunction with the all electron augmented correlation consistent basis set aug-cc-pVTZ [19] for the non-metallic systems and aug-cc-pVDZ-PP [20] for all-metal systems  $M_7^{3-}$  and  $M_7T$  with  $M = Cu, Ag, Au, T = Sc, Y$ , where PP stands for an effective core potential. Harmonic vibrational frequencies were subsequently calculated to characterize the stationary points located as equilibrium structures having all real vibrational frequencies. A scale factor of 0.9614 was used to scale the frequencies [21]. To facilitate comparison and to obtain a certain spectroscopic signature of the rings considered, calculated vibrational spectra were folded with a Gaussian line width function of  $20\text{ cm}^{-1}$  full width at half maximum. All geometry optimizations were performed using the Gaussian 03 package [22]. We have considered a localization of the electron density in order to identify the chemical bonds and their origin. For this purpose, we have applied the electron localization function (ELF) [23], the electron localizability indicator (ELI-D) [24–26] and its canonical MO decomposition (partial p-ELI-D) [27], which have been proved to be valuable tools to study the structure and bonding in molecules. To ensure the accuracy of basin integrations, a threshold value of  $10^{-7}$  has been adopted for ELF. Both the ELI-D and p-ELI-D approaches were computed using the DGrid-4.2 program suite [28]. The isosurfaces were plotted with the graphical program gOpenMol [29]. To investigate further the electronic structure of the all-metal clusters, the total and the partial density of states (DOS, computed using the Pymolyze program [30]) were also plotted using the densities computed at the B3LYP/aug-cc-pVDZ-PP level of theory.

To evaluate the possible aromaticity of these systems, the nucleus independent chemical shift (NICS) indices [1b,31], which is defined as the negative value of the absolute shielding computed at certain point of the ring, were calculated. There has been much discussion about the validity of NICS as an index for aromaticity. Recent study [16] showed that it can be used to describe this property of planar seven-membered cycles. Accordingly, a ring with large negative NICS value in its center is considered aromatic, and usually the more negative the NICS value the ring has, the more aromatic the ring is. Since the NICS(0) value (the reference ghost atom being put at the center of the ring) is largely influenced by the central atom of the ring, and it is also influenced by the framework, the NICS(1), NICS(2) in which the reference dummy atom is placed at 1 and 2 Å above the ring center, respectively, instead of NICS(0), were evaluated for some molecules. The corre-

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