

# Quantum-Chemical Ab Initio Calculations on Ala-(C<sub>5</sub>H<sub>5</sub>Al) and Galabenzene (C<sub>5</sub>H<sub>5</sub>Ga)

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Z. Naturforsch. **69a**, 349–359 (2014) / DOI: 10.5560/ZNA.2014-0015

Received February 2, 2014 / revised February 21, 2014 / published online July 15, 2014

*Dedicated to Professor Dr. Jörg Fleischhauer on the occasion of his 75th birthday*

Quantum-chemical ab initio and time-dependent density functional theory (TD-DFT) calculations employing various basis sets were used to elucidate the spatial as well as the electronic structure of C<sub>5</sub>H<sub>5</sub>Al (**1**) and C<sub>5</sub>H<sub>5</sub>Ga (**2**) (ala- and galabenzene). The lowest closed shell singlet states of both compounds were found to have a non-planar structure of C<sub>5</sub> symmetry with C–X–C bond angles of about 116° (MP2/6-311++G\*\*) and 125° (CCSD/aug-cc-pVDZ). At approximately 103°, the corresponding angles of the lowest triplets are significantly smaller. The lowest triplet state of alabenzene is also non-planar (C<sub>5</sub>) at the MP2 level while optimization with the CCSD and the CASPT2 method resulted in planar structures with C<sub>2v</sub> symmetry. The corresponding state of galabenzene has C<sub>2v</sub> symmetry at all levels of optimization. The relative stability of the lowest closed shell singlet and the lowest triplet ( $\Delta E(T_1 - S_0)$ ) state is small and its sign even strongly method-dependent. However, according to the highest levels of theory applied in this study the singlet states of both molecules are slightly lower in energy than the corresponding triplets with singlet/triplet gaps between about 0.5 and 5.8 kcal/mol in favour of the singlet states. Most of the applied methods give a slightly smaller splitting for ala- than for galabenzene.

Independent of the applied method (TD-DFT/CAM-B3LYP/6-311++G(3df,3pd)//MP2/6-311++G\*\* or SAC-CI/6-31++G(3df,3pd)//MP2/6-311++G\*\*), the general shape of the calculated UV/VIS spectral curves are quite similar for the lowest singlet states of ala- and galabenzene, and the same applies to the spectra of the normal modes. The calculated UV/VIS spectra of C<sub>5</sub>H<sub>5</sub>Al and C<sub>5</sub>H<sub>5</sub>Ga are featured by long wavelength bands of moderate intensity around 900 nm at the TD-DFT and between 1300 and 1500 nm at the SAC-CI level. According to both methods these bands are predominantly due to HOMO( $\pi$ ) → LUMO( $\sigma^*$ ) transitions.

The results of isodesmic bond separation reactions for the singlet states indicate some degree of stabilization due to delocalization in both of the title compounds. With our best values between 29 and 32 kcal/mol this stabilization appears to be only slightly less than the previously reported value for borabenzene (~ 38 kcal/mol).

*Key words:* Alabenzene; Galabenzene; Ab Initio Calculations; Time Dependent DFT; Singlet/Triplet Splitting.

## 1. Introduction

While borabenzene [1–12] and also the diborabenzenes [13–21] have been the subjects of several theoretical and also of some experimental studies, very little is known about ala- and galabenzene (C<sub>5</sub>H<sub>5</sub>Al, **1** and C<sub>5</sub>H<sub>5</sub>Ga, **2**) so far. To get some knowledge about these still elusive compounds, we performed quantum-chemical ab initio and time-dependent density functional theory (TD-DFT) calculations on the corresponding energy surfaces. Our first point of interest was whether compounds of sum formula C<sub>5</sub>H<sub>5</sub>X

(X=Al, Ga) are minima on the corresponding potential energy surfaces at all, and if so, whether their geometric and electronic structures are similar to that of previously studied borabenzene [12]. Closely related to latter point, we also posed the question whether the ground states of the title compounds are closed shell singlets or triplet states. Just like the ground state of borabenzene, those of the title compounds could be:

(i) aromatic with six electrons in three delocalized doubly occupied orbitals of  $\pi$  symmetry, three unoccupied  $\pi^*$  molecular orbitals (MOs), and in addition an energetically low-lying lowest unoccupied molecu-

lar orbital (LUMO) of  $\sigma$  symmetry oriented approximately parallel to the X–C3 axis (see Fig. 1). This would correspond to a closed shell singlet ground state. Another possibility would be

(ii) an anti-aromatic singlet state with only four electrons in doubly occupied  $\pi$  orbitals and two more in the  $\sigma$  orbital mentioned above. Finally

(iii) the molecule in its ground state could be a biradical with two unpaired electrons with parallel spin where five electrons occupy the  $\pi$  system and a single one the  $\sigma$  MO. This would correspond to a triplet. Another point of interest was the possible role that stabilization by delocalization plays in the ground states of these compounds and what predictions can be made regarding their reactivity.

Since calculated ultraviolet/visible (UV/VIS) and infrared (IR) spectra will be helpful for the experimentalist in attempts to identify the title compounds generated and trapped for example in rare gas matrices, we also calculated the 30 energetically lowest excited states employing TD-DFT. Additional calculations on the optical spectra were performed with the symmetry-adapted cluster-configuration interaction (SAC-CI) method. Approximate vibrational spectra emerged from diagonalization of the force constant matrix.

Finally, isodesmic bond separation reactions (Scheme 1) were performed in order to elucidate the possible role of stabilization by delocalization in  $C_5H_5Al$  and  $C_5H_5Ga$ , respectively.

## 2. Computational Methods

Most calculations were performed with the Gaussian09 [22] suite of quantum-chemical routines running on the facilities of the Computing and Communication Center of the RWTH Aachen University. All structures considered in this study were fully optimized at the MP2 level for the singlet and at the UMP2 level for the triplet states employing the valence triple zeta 6-311++G\*\* basis set. The nature of each of the stationary points located at this level was determined by diagonalization of the corresponding force constant

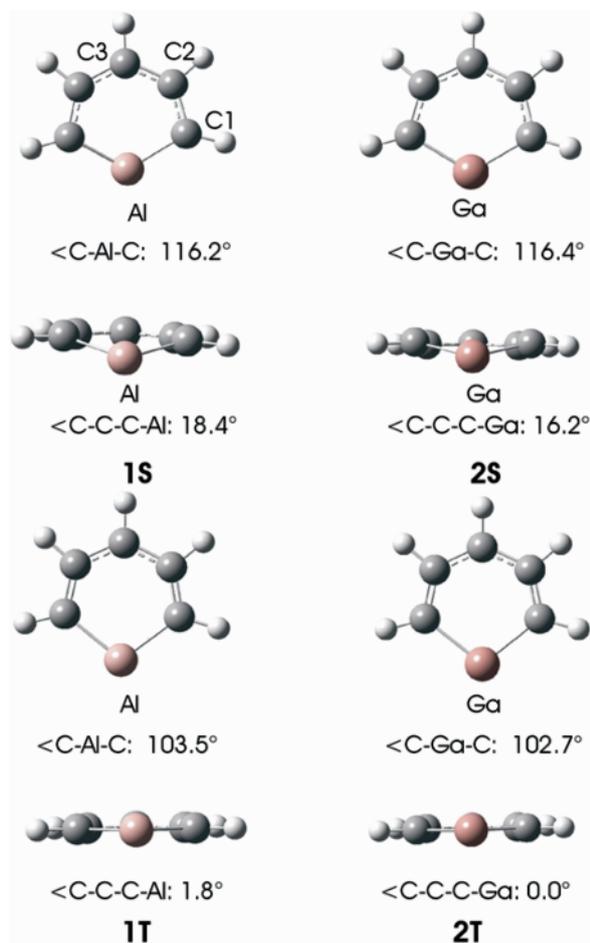
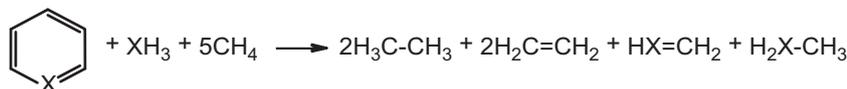


Fig. 1 (colour online). Structures of the singlet ground states of alabenzene ( $C_5H_5Al$ ) and galabenzene ( $C_5H_5Ga$ ) (**1S**, **2S**) as well as of the lowest triplet states (**1T**, **2T**) obtained at the MP2/6-311++G\*\* and UMP2/6-311++G\*\* level, respectively. For selected structural parameters see Table 1.

matrix. To obtain more reliable relative energies, these structures were then used to perform single point calculations at the coupled cluster level (CC) including single (S) and double (D) substitutions derived from the Hartree–Fock determinant as reference as well as a non-iterative inclusion of triple excitations (T) (CCSD(T)) [23–27]. Correlation-consistent basis sets



Scheme 1. Isodesmic bond separation reaction used to calculate the stabilization by delocalization in **1S** and **2S**.

(aug-cc-pVDZ and aug-cc-pVTZ [28–32]) were used in the coupled cluster calculations. The aug-cc-pVTZ basis set was also used in calculations with the Brueckner doubles method including a correction for triples (BD(T)) [33] and in quadratic singles/doubles configuration interaction also augmented by a correction for triple excitations (QCISD(T)) [34]. Additional geometry optimizations were performed at the CCSD/aug-cc-pVDZ level. However, the resulting structures could not be subjected to normal mode analyses (vide infra). Extrapolations to complete basis sets were performed employing the method by Truhlar et al. [35, 36] using  $\alpha = 3.39$  and  $\beta = 2.02$  [36]. The total energies of all compounds used in these extrapolations can be found in Table S1 of the supplementary material which can be obtained from the corresponding author (G. R.) upon request. CASSCF(6,7) calculations were performed with the 6-31G\* and the 6-31+G\* basis set where the corresponding Hartree–Fock (HF) and restricted open-shell Hartree–Fock (ROHF) wavefunctions provided the references. For the singlet states, the active space extended over the three doubly occupied ( $\pi$ -like) MOs which can be derived from the three doubly occupied  $\pi$  orbitals of benzene, those three least-diffuse unoccupied orbitals which can be derived from the three  $\pi^*$  orbitals of benzene, plus the LUMO of  $\sigma$  symmetry. The active space of the triplets contained two doubly and one singly occupied  $\pi$ -like MOs and their three unoccupied counterparts, plus the singly occupied LUMO of  $\sigma$  symmetry. Moreover, in order to include also dynamic correlation, CASPT2(8,8) calculations [37] including geometry optimizations were performed in a separate study using the program Molcas7.4 [38] and a CASSCF(8,8) wavefunction as reference. In these calculations we used a set of natural atomic orbitals [39] on the basis of a valence double-zeta set of contracted gaussians (ANO-RCC-VDZP) [40] for the geometry optimizations, while final single point calculations on the basis of these geometries were performed starting from a set of functions of valence-triple zeta quality (ANO-RCC-VTZP). Natural bond orbital (NBO) analyses of the wave functions from our MP2/6-311++G\*\* calculation were performed for the singlet state with the program NBO 3.0 [41, 42] as implemented in Gaussian09. Using the MP2/6-311++G\*\*-optimized structures UV/VIS spectra were calculated within the framework of TD-DFT [43] with the CAM-B3LYP hybrid functional [44–46] and the 6-311++G(3df,3pd)

basis set. In addition we performed SAC-CI calculations [47] at the MP2/6-311++G\*\* geometries with the 6-311++G(3df,3pd) basis set where the corresponding RHF wave function was used as a reference for the closed shell singlets. Eight excited states for each of the irreducible representations ( $A_1, A_2, B_1, B_2$ ) for the molecules of  $C_{2v}$  symmetry and fifteen for each of the irreducible representations ( $A$  and  $B$ ) of the species transforming like  $C_s$  were included into the calculation, while the active space comprised the occupied valence MOs and all virtual MOs of the correct symmetry. The spectral curves were generated using sums of Lorentzians each of which was centred at the corresponding transition wave length and multiplied with the associated oscillator strength. The half bandwidth  $\Gamma$  was calculated using the empirical formula  $\Gamma = k\lambda^{1.5}$  [48] with  $k = 0.00375$  [49].

Optimized structural parameters of all compounds under consideration are given in Table 1, while the total energies obtained at different levels of theory are collected in Table S2 of the supplementary material. The corresponding singlet/triplet splittings are listed in Table 2, and the results of our isodesmic bond separation reactions [50] are compiled in Table 3.

### 3. Results and Discussion

#### 3.1. The Relative Energies and the Structures of the Lowest Singlet State and the Lowest Triplet State of Ala- and Galabenzene.

Cyclic borabenzene-like structures of both title compounds ( $C_5H_5Al$ , **1** and  $C_5H_5Ga$ , **2**) were found to be minima on the corresponding singlet and triplet potential energy surfaces. Geometry optimizations were performed at the MP2/6-311++G\*\*, the CCSD/aug-cc-pVDZ, and the CASPT2/ANO-VCC-VDZP level of theory. Since normal mode analyses for the obtained stationary points were feasible only with the Møller–Plesset method, exclusively the structures which proved to be local minima obtained at this level are shown in Figure 1, while selected structural parameters from optimizations with the MP2 and the CCSD method are listed in Table 1.

In the following discussion of ala- and galabenzene the CCSD-optimized structural parameters and the quantities derived thereof are given enclosed in parentheses together with the MP2 results.

Table 1. Selected structural parameters of the singlet and the lowest triplet state of of ala- (X=Al, **1S** and **1T**) and galabenzene (X=Ga, **2S** and **2T**) fully optimized (a) at the MP2/6-311++G\*\* and (b) at the CCSD/aug-cc-pVDZ level. Bond lengths in Å, bond angles and dihedral angles in °.

	<b>1S</b>	<b>1T</b>	<b>2S</b>	<b>2T</b>
X–C <sub>1</sub>				
(a)	1.876	1.952	1.901	1.985
(b)	1.891	1.977	1.852	1.982
C <sub>1</sub> –C <sub>2</sub>				
(a)	1.411	1.362	1.412	1.361
(b)	1.418	1.393	1.420	1.390
C <sub>2</sub> –C <sub>3</sub>				
(a)	1.417	1.424	1.418	1.425
(b)	1.426	1.438	1.425	1.438
C <sub>1</sub> –X–C <sub>1</sub>				
(a)	116.3	103.5	116.4	102.7
(b)	116.2	103.6	125.1	103.8
X–C <sub>1</sub> –C <sub>2</sub>				
(a)	105.2	117.7	105.2	117.4
(b)	105.2	117.5	102.9	117.2
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>				
(a)	128.4	126.4	128.9	126.8
(b)	128.5	126.4	129.9	126.4
C <sub>2</sub> –C <sub>3</sub> –C <sub>2</sub>				
(a)	128.7	128.4	129.3	128.9
(b)	128.8	128.6	129.2	128.6
X–C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>				
(a)	18.4	1.8	16.2	0.0
(b)	17.5	0.0	0.1	0.0
Symmetry				
(a)	C <sub>s</sub>	C <sub>s</sub>	C <sub>s</sub>	C <sub>2v</sub>
(b)	C <sub>s</sub>	C <sub>2v</sub>	C <sub>s</sub>	C <sub>2v</sub>

At the MP2/6-311++G\*\* level, the singlet/triplet splittings ( $\Delta E(T_1 - S_0)$ , Tab. 2) for both, ala- as well as for galabenzene are significantly smaller than the corresponding values for borabenzene at the same level of theory (53.8 kcal/mol before and 44.5 kcal/mol after spin projection [12]) and, as can be seen from the numbers in Table 2, in general the sign of  $\Delta E(T_1 - S_0)$  strongly depends on the applied method. At the UMP2/6-311++G\*\* level including zero point vibra-

Table 2. Energies of the lowest triplet states of ala- and galabenzene relative to the lowest singlet states  $\Delta E(T_1 - S_0)$  (in kcal/mol).

Method	$\Delta E(T_1 - S_0)$	
	C <sub>5</sub> H <sub>5</sub> Al	C <sub>5</sub> H <sub>5</sub> Ga
ZPE+UMP2/6-311++G**	17.76 <sup>a</sup>	19.59 <sup>a</sup>
ZPE+PUMP2/6-311++G** <sup>d</sup>	7.08 <sup>a</sup>	8.53 <sup>a</sup>
CASSCF(6,7)/6-31G*	-7.34 <sup>a</sup>	-7.05 <sup>a</sup>
CASSCF(6,7)/6-31+G*	-9.38 <sup>a</sup>	-7.23 <sup>a</sup>
CCSD(T)/aug-cc-pVTZ	3.02 <sup>a</sup>	5.17 <sup>a</sup>
	2.81 <sup>e</sup>	5.81 <sup>e</sup>
CCSD(T)/complete	3.41 <sup>a</sup>	5.44 <sup>a</sup>
B3LYP/VDZ	-1.10	2.57
BD(T)/aug-cc-pVTZ	1.86 <sup>a</sup>	4.80 <sup>a</sup>
QCISD(T)/aug-cc-pVTZ	2.49 <sup>a</sup>	5.61 <sup>a</sup>
CASPT2(8,8)/ANO-RCC-VDZP	1.61 <sup>b</sup>	3.83 <sup>b</sup>
CASPT2(8,8)/ANO-RCC-VTZP	0.53 <sup>b,c</sup>	5.08 <sup>b,c</sup>

<sup>a</sup>Total energies and zero point energies (ZPE) calculated at the MP2/6-311++G\*\* geometries for the singlet and UMP2/6-311++G\*\* geometry for the triplet.

<sup>b</sup>Using a CASSCF(8,8) reference.

<sup>c</sup>At the CASPT2/ANO-RCC-VDZP-optimized geometry.

<sup>d</sup>Projected MP2.

<sup>e</sup>Calculated at aug-cc-pVDZ-optimized geometries.

tional energy the lowest triplet state of alabenzene (**1T**) is 17.76 kcal/mol above the singlet ground state. At this level  $\langle S^2 \rangle$  is 2.390. Spin projection [51, 52] reduces this value to  $\langle S^2 \rangle = 2.068$ , and at this level the singlet/triplet gap is reduced by more than 50% and amounts to 7.08 kcal/mol. This energy difference is further reduced at the CCSD(T) level extrapolating the basis set to completeness where the singlet of alabenzene lies energetically 3.41 kcal/mol below the triplet. Moreover, performing a single point calculation with the CCSD(T) method and the aug-cc-pVTZ basis set at the CCSD/aug-cc-pVDZ-optimized geometry results in a singlet state 2.81 kcal/mol below **1T**. Calculations with the Brueckner doubles method gives a singlet/triplet splitting of 1.86 kcal/mol in favour of the singlet state, while according to our QCISD(T) calcu-

Table 3. Energies associated with the isodesmic bond separation reactions (Scheme 1, in kcal/mol). For total energies of educts and products see Table S2.

Molecule	<sup>a</sup> ZPE+MP2/6-311++G**//	ZPE+CCSD(T)/aug-cc-pVTZ//	ZPE+CCSD(T)/complete <sup>b</sup> //
	MP2/6-311++G**	MP2/6-311++G**	MP2/6-311++G**
C <sub>5</sub> H <sub>5</sub> Al ( <b>1S</b> )	36.52	29.03	29.30
C <sub>5</sub> H <sub>5</sub> Ga ( <b>2S</b> )	32.47	29.69	32.10
C <sub>5</sub> H <sub>5</sub> B	45.18	37.61	38.30
C <sub>5</sub> H <sub>5</sub> N	76.04	68.78	70.26
C <sub>6</sub> H <sub>6</sub>	73.52	63.53	64.90

<sup>a</sup>Zero point energies calculated at MP2/6-311++G\*\*-optimized geometries, <sup>b</sup>complete basis set approximation [35, 36].

lations the singlet is energetically 2.49 kcal/mol below the triplet.

The values obtained by  $T_1$  diagnostics [53] for the triplet states (0.03887 for X = Al, 0.03356 for X = Ga) which significantly exceed the recommended upper limit of 0.02 indicate, that non-dynamic correlation energy plays an important role for these states of the molecules under consideration. Therefore, the triplet states are probably not properly described by methods based on a single determinant as a reference. Performing CASSCF(6,7)/6-31+G\* calculations to estimate the importance of non-dynamic correlation employing the same geometry as above a different order of stability is obtained. At this level of theory the triplet of alabenzene is 9.38 kcal/mol energetically below the singlet. However, including non-dynamic as well as dynamic correlation (CASPT2(8,8)/ANO-RCC-VTZP) places the lowest triplet state of alabenzene 0.53 kcal/mol above the lowest singlet. An extension of the active space over all occupied and unoccupied orbitals is prohibitive for the molecules under consideration, and due to the non-planar structures of the singlet species the choice of the best limited active space is strongly encumbered especially when it comes to the virtual orbitals. Thus the possibility cannot be excluded that there was a better choice for the active space of **1S** than the one selected by us, and that the singlet/triplet gap is actually larger. CCSD(T), BD(T), and QCISD(T) calculations which are known to account for a certain amount of multiconfiguration character consistently predict a 1.86–3.41 kcal/mol lower energy for the singlet state of alabenzene.

At the UMP2/6-311++G\*\* level **2T** is energetically 19.59 kcal/mol above the molecule's lowest singlet state. At this level of theory  $\langle S^2 \rangle$  is 2.396. Spin projection reduces this value to 2.067 and the singlet/triplet splitting to 8.53 kcal/mol. Again, the energy difference is significantly smaller at the CCSD(T) level using a basis set extrapolated to completeness where it amounts to only 5.44 kcal/mol. A CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ calculation places **2S** energetically 5.81 kcal/mol below **2T**, and the corresponding values from our BD(T)/aug-cc-pVTZ and QCISD(T)/aug-cc-pVTZ calculations predict the singlet state to be 4.80 kcal/mol and 5.61 kcal/mol more stable than the triplet. Similar to alabenzene the triplet is energetically 7.23 kcal/mol below the singlet with the CASSCF(6,7) method employing the 6-31+G\* basis set. However, also at the

CASPT2(8,8) level the singlet lies 5.08 kcal/mol below the triplet.

The results of our calculations on the relative stability of the singlet and the lowest triplet state of the title compounds can be summarized as follows. Definitive determination of the singlet/triplet splitting of the title compounds is hampered by several facts. First of all, the energy difference between these two states is quite small, and in addition description of the triplets requires methods that account for multireference character like for example CASSCF. However, the results of the CAS-based calculations might be biased by the non-planar structure of both **1S** and **2S** (Tab. 1) which significantly complicates the definition of the best active space for these species. And still the CASPT2 calculations predict a slightly lower energy for the closed shell singlets. Also other high level methods which are known to perform reasonably well in such cases (CCSD(T), BD(T), QCISD(T)) energetically favour **1S** and **2S** over **1T** and **2T**. We, therefore, conclude that both ala- as well as galabenzene has very likely a closed shell singlet ground state.

With all three methods and different from borabenzene [1, 2, 12], the lowest singlet states of both compounds (**1S**: X = Al, and **2S**: X = Ga) were found to be non-planar with a plane of symmetry passing through hetero atom X and the *para* C–H segment ( $C_s$ ). The corresponding planar structures ( $C_{2v}$ ) were found to be saddle points with one imaginary frequency in the spectra of their normal modes. The planar structures of the singlet species, which correspond to transition states connecting the two possible energetically degenerate local minima, were found to be 1.69 kcal/mol ( $C_5H_5Al$ ) and 0.89 kcal/mol ( $C_5H_5Ga$ ) higher in energy (MP2/6-311++G\*\*) than the non-planar local minima, indicating that inversion of these structures will be easy even at low temperatures. The carbon moieties (C1–C2–C3–C2'–C1') of both compounds are essentially planar, while the X–C1–C2–C3 dihedral angles are 18.4° for singlet ala- and 16.2° for singlet galabenzene at the MP2 level, while the structure of **2S** optimized with the CCSD method and the aug-cc-pVDZ basis set is almost planar. The length of the Al–C bond in **1S** is 1.876(1.891) Å while the corresponding bond distances in  $H_3C–AlH_2$  and  $H_2C=AlH$  are 1.960(1.985) Å and 1.805(1.839) Å. Thus, according to both methods the length of the Al–C bond in **1S** is slightly shorter than the average value obtained from the lengths of an Al–C single and a double bond.

This situation is similar to non-planar **2S**, where the Ga–C bond has a length of 1.901(1.852) Å and the Ga–C bond distances in H<sub>3</sub>C–GaH<sub>2</sub> and H<sub>2</sub>C=GaH are 1.991(1.987) Å and 1.820(1.811) Å, respectively. In both cases the shortening relative to the average value for a double and a single bond is more pronounced with the CCSD than with the MP2 method. At 116.3(116.2)° in **1S** and 116.4(125.1)° in **2S** the C–X–C bond angles are much closer to 120° than the corresponding angle in borabenzene (142.2°(141.2°)) at the same level of theory [12]. NBO analyses [41, 42] of the wavefunctions from our MP2/6-311++G\*\* geometry optimizations of the lowest closed shell singlet states of both ala- and galabenzene gave results in part similar to those obtained in a previous study for the singlet ground state of borabenzene [12]. Thus for alabenzene two of the valence orbitals of the heteroatom combine to form an approximate *sp* hybrid involving the 3*s* natural atomic orbital plus the corresponding 3*p* orbital which is oriented perpendicularly to the plane that bisects the C1–X–C1' and the C2–C3–C2' angles and extends parallelly to the C1–C1' axis. In the case of galabenzene an analogous hybrid is formed from the corresponding 4*s* and the 4*p* orbitals. These hybrid orbitals overlap with *sp*<sup>*n*</sup> hybrids of the neighbouring carbon atoms to form the X–C σ bonds, where *n* is 2.48, 2.71, and 1.71 for X = Al, Ga, and B, respectively. The differences between the electronegativities of carbon on the one and of boron, aluminium, and gallium on the other hand are larger for the last two elements. And, as a result, at 76.8% for X = Al and 72.6% for X = Ga the X–C bonds are stronger polarized to carbon than in the case of borabenzene (67.6%). Similarly, shortening of the X–C bonds in C<sub>5</sub>H<sub>5</sub>X relative to the values for the corresponding single bonds in H<sub>3</sub>C–AlH<sub>2</sub> and H<sub>3</sub>C–GaH<sub>2</sub> is 4.3% and 4.5% and, therefore, significantly less than those in borabenzene where it amounts to 7.9%. Moreover, different from latter molecule, the NBO analyses using the standard settings of the program parameters did not give an additional X–C π bond for the optimized structures of the title compounds. However, using the CHOOSE option it was possible to define benzene-like Lewis structures with three double bonds in the rings, and these structures reproduce the total density to a very similar degree (~ 97%) as those without the additional π bond. Therefore, both sets of Lewis structures describe the singlet states of **1S** and **2S** equally well. In addition numerical calculation of the C–X–C bond an-

gle deformation constants<sup>1</sup> in the minimum structures gave values of 0.82 and 0.94 kcal/(mol·deg<sup>2</sup>) for ala- and galabenzene, while a significantly higher value of 1.57 kcal/(mol·deg<sup>2</sup>) was obtained for borabenzene, indicating that deformation of the C–X–C angle is much easier for X = Al and Ga than for X = B. Schulman and Disch [3] found a value of 178.4° for the C–B–C angle in 2-borabuta-1,3-diene (H<sub>2</sub>C=B–CH=CH<sub>2</sub>). Fixing this angle at the corresponding value found for borabenzene (140.6° [3]) they obtained an approximate strain energy for that compound of 15.4 kcal/mol [3]. Similar calculations can be performed for the title compounds. However, due to the smaller C1–X–C1' angles in the rings the closest distances between two of the terminal hydrogen atoms in those H<sub>2</sub>C=X–CH=CH<sub>2</sub> structures where the C–X–C angles are fixed at the values for the C<sub>5</sub>H<sub>5</sub>X cycles are significantly shorter (2.058 Å and 2.098 Å for X = Al and Ga, respectively) compared with those in the boron compound (2.393 Å) and they are clearly below the twofold van der Waals radius of hydrogen (1.20 Å [54]). Strain energies for ala- and galabenzene calculated following the scheme proposed by Schulman and Disch [3] are, therefore, contaminated by non-bonding repulsion energy between the terminal hydrogens and cannot be compared with the corresponding value obtained for borabenzene.

Besides the hybrids mentioned above, there are two further natural hybrid orbitals with low occupation numbers<sup>2</sup> of σ symmetry at the heteroatom X. These orbitals lie in the mirror plane passing through X and the *para* C–H segment and are approximately perpendicular to each other. One of these orbitals is approximately perpendicular to the X–C3 axis and occupied by about half an electron (X=Al: 0.52 e; X=Ga: 0.48 e). The other hybrid approximately coincides with this axis and is essentially empty. Within the framework of the NBO method latter hybrid corresponds to the low-lying LUMO of σ symmetry mentioned initially.

Different from **1S** the triplet state of alabenzene (**1T**) has an only slightly non-planar geometry with an Al–C1–C2–C3 dihedral angle of 1.8° at the UMP2/6-311++G\*\* level, while a CCSD/aug-cc-pVDZ optimization gives a planar structure with C<sub>2v</sub> symmetry. The C–Al–C angle is 103.5(103.6)° and, therefore, even smaller than in **1S**. Moreover, at 1.952(1.977) Å

<sup>1</sup>The second derivatives in the minimum.

<sup>2</sup>Labelled Lp\* by the NBO 3.0 program.

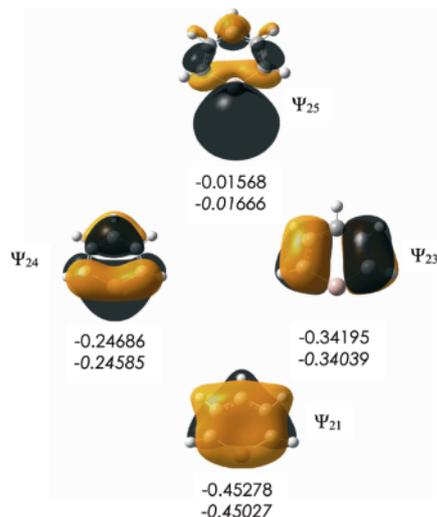


Fig. 2 (colour online). The three energetically highest orbitals ( $\psi_{21}$ ,  $\psi_{23}$ ,  $\psi_{24}$ ) of alabenzene ( $C_5H_5Al$ ) which can be derived from the corresponding orbitals of  $\pi$  symmetry of the planar system and the energetically lowest unoccupied orbital ( $\psi_{25}$ ,  $\sigma^*$ ) of the MP2/6-311++G\*\* -optimized structure of the singlet state of  $C_5H_5Al$ . The shapes of the corresponding molecular orbitals from the CCSD/aug-cc-pVDZ calculation are essentially the same. The numbers are the orbital energies from the MP2 and the CCSD (in italics) calculation.

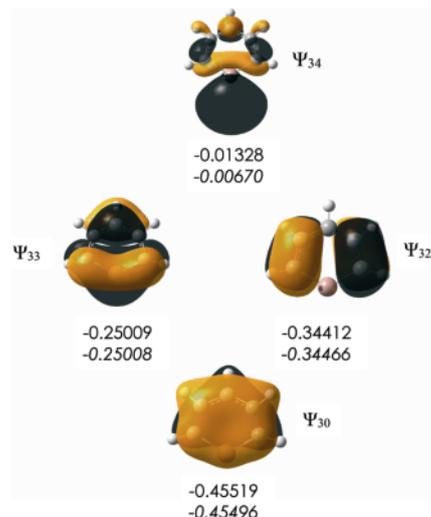


Fig. 3 (colour online). The three energetically highest orbitals ( $\psi_{30}$ ,  $\psi_{32}$ ,  $\psi_{33}$ ) of galabenzene ( $C_5H_5Ga$ ) which can be derived from the corresponding orbitals of  $\pi$  symmetry of the planar system and the energetically lowest unoccupied orbital ( $\psi_{34}$ ,  $\sigma^*$ ) of the MP2/6-311++G\*\* -optimized structure of the singlet state of  $C_5H_5Ga$ . The shapes of the corresponding molecular orbitals from the CCSD/aug-cc-pVDZ calculation are essentially the same. The numbers are the orbital energies from the MP2 and the CCSD (in italics) calculation.

the Al–C bond length is almost identical with the single bond of 1.960(1.985) Å in  $H_3C-AlH_2$ .

Things are somewhat different in the case of galabenzene. Here the UMP2 method gives a planar triplet state (**2T**) of  $C_{2v}$  symmetry. The Ga–C bond length is 1.985(1.982) Å and, therefore, almost also identical with the value for the single bond in  $H_3C-GaH_2$  (1.991(1.987) Å). Like for **1T** the angle of 102.7(103.8)° at the hetero atom in triplet galabenzene is much smaller than in the singlet state of  $C_5H_5Ga$  and in singlet borabenzene.

The singlet states of both molecules have three doubly occupied canonical MOs of  $\pi$ -like symmetry which can be derived from the  $a_u$  and  $e_g$  orbitals of planar benzene. These orbitals are shown in Figures 2 and 3. The LUMOs of both compounds are of  $\sigma$  symmetry with largest coefficients either at the aluminum or the gallium atom. The energies of these orbitals are  $-0.01568(-0.01666)$  and  $-0.01328(-0.00670)$  Hartree and, therefore, even lower than the value for borabenzene of 0.02410(0.02865) [12] Hartree obtained at the same level of theory. It is assumed that these low-lying orbitals will cause significant accep-

tor properties and, therefore, a high reactivity for both compounds which probably exceeds that of borabenzene.

### 3.2. The Calculated UV/VIS Spectra of $C_5H_5Al$ and $C_5H_5Ga$

The electronic excitation spectra of the lowest singlet states of the title compounds calculated at the CAM-B3LYP/6-311++(3df,3pd)//MP2/6-311++G\*\* level of TD-DFT together with the spectral curves obtained with the SAC-CI method and the 6-311++(3df,3pd) basis set are shown in Figures 4 and 5. At the SAC-CI level the optical spectra of the title compounds have broad bands of moderate intensity between 1300 nm and 1500 nm, at 1425 ( $A'$ ,  $f = 0.0280$ )<sup>3</sup> for alabenzene and at 1332 nm ( $A'$ ,  $f = 0.0230$ ) for galabenzene. For both compounds the bands are caused by a single state governed by the HOMO  $\rightarrow$  LUMO transition. No transition occurs between these states and the first state of  $A''$  symmetry and of vanishing inten-

<sup>3</sup>The capital letter in italics denotes the corresponding irreducible representation, and  $f$  is the oscillator strength.

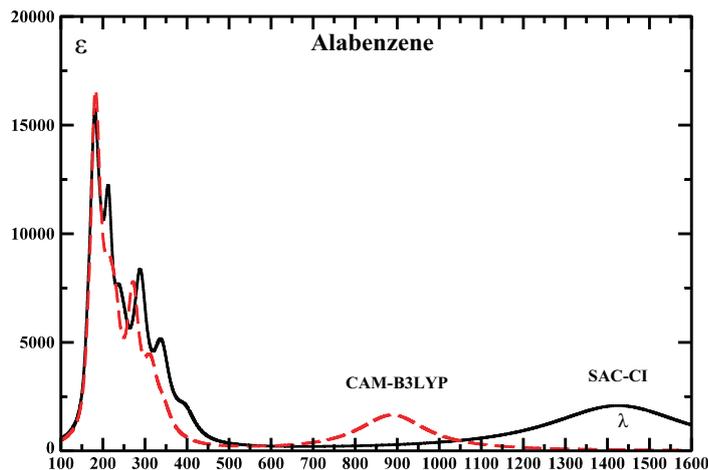


Fig. 4 (colour online). UV/VIS spectra of the lowest singlet state of  $C_5H_5Al$  calculated at the SAC-CI (SAC-CI/6-311++G\*\*//MP2/6-311++G(3df,3pd), black, solid) and at the TD-DFT level of theory (CAM-B3LYP//MP2/6-311++G(3df,3pd) red, dashed). Wavelengths are in nm,  $\epsilon$  in  $1000 \text{ cm}^2/\text{mol}$ .

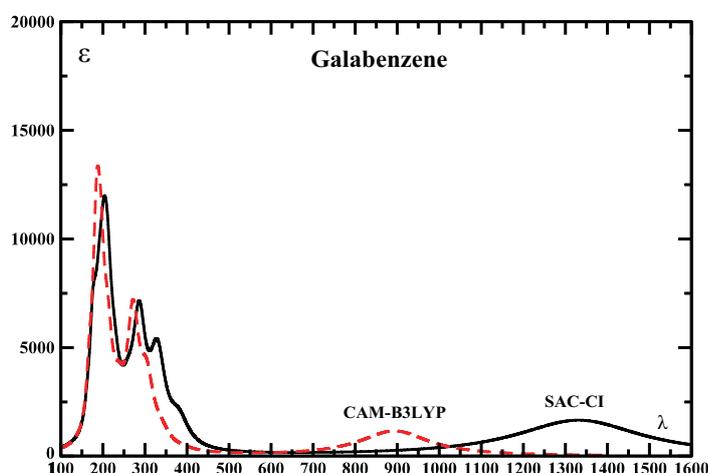


Fig. 5 (colour online). UV/VIS spectra of the lowest singlet state of  $C_5H_5Ga$  calculated at the SAC-CI (SAC-CI/6-311++G\*\*//MP2/6-311++G(3df,3pd), black, solid) and at the TD-DFT level of theory (CAM-B3LYP//MP2/6-311++G(3df,3pd) red, dashed). Wavelengths are in nm,  $\epsilon$  in  $1000 \text{ cm}^2/\text{mol}$ .

sity ( $f = 0.0000$ ) at  $\lambda = 478 \text{ nm}$  for **1S** and  $453 \text{ nm}$  for **2S**. Below about  $400 \text{ nm}$  a group of states of in part high intensity causes a system of overlapping bands. The most intense bands occur at  $181 \text{ nm}$  for the aluminum and at  $204 \text{ nm}$  for the gallium compound. The state of highest intensity is of  $A'$  symmetry for **1S** and the transition wavelength is  $179 \text{ nm}$ . The most intense state of **2S** transforms like  $A''$  and occurs at  $212 \text{ nm}$  ( $f = 0.14870$ ). Further relatively intense states between  $180$  and  $200 \text{ nm}$  contribute to the intensity of the strong bands at  $177$  and  $186 \text{ nm}$ .

Both spectral curves obtained with the TD-DFT method have absorptions of moderate intensity at a somewhat higher energy slightly below  $900 \text{ nm}$ . Thus, relative to the transition wavelengths obtained at the SAC-CI level the underlying transitions are shifted to the blue by  $0.53 \text{ eV}$  in the case of ala- and  $0.46 \text{ eV}$  in

the case of galabenzene. In the case of the TD-DFT calculations these bands are due to transitions at  $889 \text{ nm}$  ( $A'$ ,  $f = 0.0280$ ) for ala- and  $893 \text{ nm}$  ( $A'$ ,  $f = 0.0196$ ) for galabenzene. In both cases the dominating contribution to these bands comes from the HOMO  $\rightarrow$  LUMO transition where, as mentioned above, the highest occupied molecular orbital (HOMO) is of  $\pi$  and the LUMO of  $\sigma$  symmetry. The transitions with the highest oscillator strengths occur at  $272 \text{ nm}$  for both  $X = Al$  ( $A''$ ,  $f = 0.1844$ ) and  $X = Ga$  ( $A''$ ,  $f = 0.1714$ ) causing bands with the corresponding absorption maxima at essentially the same wavelength for both compounds. In both cases the dominating contributions come to approximately equal degrees from  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  excitations. The most intense bands are calculated slightly below  $200 \text{ nm}$  ( $X=Al$ :  $181 \text{ nm}$ ,  $X=Ga$ :  $168 \text{ nm}$ ). These bands are caused by the combined in-

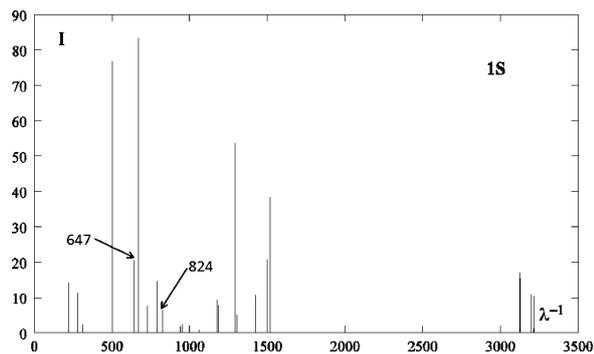


Fig. 6. Spectrum of the normal vibrations of the lowest singlet state of  $C_5H_5Al$  calculated at the MP2/6-311++G\*\* level of theory. Wave numbers are in  $cm^{-1}$ , intensities in  $km \cdot mol^{-1}$ .

tensities of a multitude of states with the most intense ones at 187 nm ( $A'$ ,  $f = 0.1445$ ) for  $C_5H_5Al$  and at 196 nm ( $A''$ ,  $f = 0.1507$ ) for  $C_5H_5Ga$ . While the position of the long wavelength bands differ significantly at the TD-DFT and SAC-CI level the systems of the short wavelengths band which start at about 400 nm for both compounds overlap fairly well not only as far as their positions are concerned but also with respect to their intensities.

In a previous study on the pyridine–borabenzene adduct ( $C_5H_5N-BC_5H_5$ , [55]) we found that for this particular compound the long-wavelength transition was predicted to be strongly blue-shifted ( $\sim 0.41$  eV) relative to the experimental values<sup>4</sup> when the CAM-B3LYP functional was used. SAC-CI calculations for the adduct gave a similar blue shift which, however, could be attributed to the very small basis set (6-31G\*) used in those calculations. Unfortunately, no experimental spectra are available for the title compounds of this study. However, here we were able to use a much larger basis set (6-311++G(3df,3pd)) in our SAC-CI calculations. We, therefore, suggest that in the present study priority should be given to the results of our SAC-CI calculations whose long wavelengths bands are shifted strongly to the red compared with the CAM-B3LYP results.

### 3.3. Normal Modes of the Singlet States of $C_5H_5Al$ and $C_5H_5Ga$

The spectra of the normal modes of both compounds are shown in Figures 6 and 7. Stretching of the X–

<sup>4</sup>And also relative to the values obtained with the B3LYP functional.

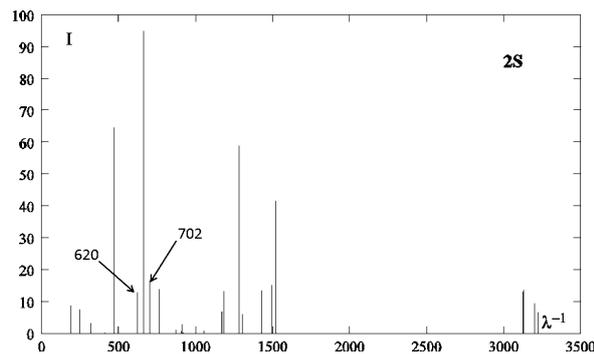


Fig. 7. Spectrum of the normal vibrations of the lowest singlet state of  $C_5H_5Ga$  calculated at the MP2/6-311++G\*\* level of theory. Wave numbers are in  $cm^{-1}$ , intensities in  $km \cdot mol^{-1}$ .

C bonds strongly mixes with other deformations of the molecular skeletons. Symmetric and antisymmetric stretching vibration of the Al–C bond with the largest amplitudes and significant intensity of **1S** occur at  $647$   $cm^{-1}$  and  $824$   $cm^{-1}$ . As to be expected due to the higher mass of gallium the corresponding vibrations of **2S** were calculated at lower wave numbers, i. e.  $620$  and  $702$   $cm^{-1}$ . These values might be compared to similar normal modes of borabenzene which occur at  $1346$  and  $1636$   $cm^{-1}$ .

### 3.4. Isodesmic Bond Separation Reactions

Isodesmic bond separation reactions [50] (see Scheme 1) for the closed shell singlets have been performed in order to approximately elucidate the possible role of conjugative stabilization in **1S** and **2S**. At the highest level of theory employed in this study the values are  $29.3$  kcal/mol for alabenzene and  $32.1$  kcal/mol for galabenzene. Both values are lower than the corresponding result for borabenzene at the same level of theory ( $38.3$  kcal/mol) and significantly lower than the corresponding energies for benzene ( $64.9$  kcal/mol) and pyridine ( $70.3$  kcal/mol). Nevertheless, the energies associated with the hypothetical bond separation reactions of ala- and galabenzene indicate that the singlet states of both title compounds are stabilized by conjugative interactions relative to their fragments.

### Acknowledgement

Most of the calculations were performed with computing resources granted by JARA-HPC from RWTH Aachen University under project jara0075.

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