Starlike Aluminum–Carbon Aromatic Species

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Abstract: Is it possible to achieve molecules with starlike structures by replacing the H atoms in $(CH)_n^q$ aromatic hydrocarbons with aluminum atoms in bridging positions? Although D_{4h} $C_4Al_4^{2-}$ and D_2 C_6Al_6 are not good prospects for experimental realization, a very extensive computational survey of fifty $C_5Al_5^-$ isomers identified the starlike D_{5h} global minimum with five planar tetracoordinate carbon atoms to be a promising candidate for detection by photoelectron detachment spectroscopy. BOMD (Born–Oppenheimer molecular dynamics) simulations and high-level theoretical computations verified this conclusion. The combination of favorable electronic and geometric structural features (including aromaticity and optimum C–Al–C bridge bonding) stabilizes the $C_5Al_5^-$ star preferentially.
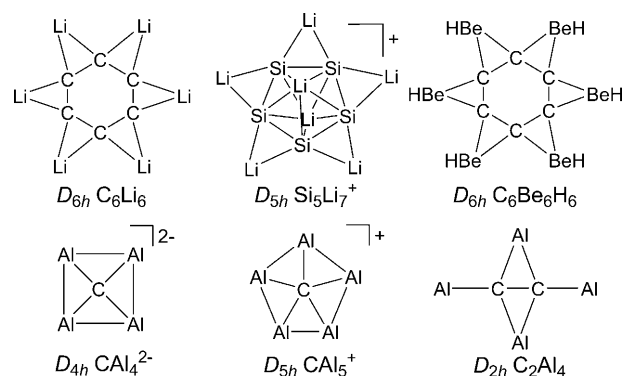
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Introduction

Substitution of the hydrogen atoms of typical planar sp^2-hybridized aromatic monocyclic hydrocarbons ($C_3H_3^+$, $C_4H_4^{2-}$, $C_5H_5^-$, and C_6H_6) by atoms prone to adopt bridging posi-

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tions favors starlike structures.[1] Lithium is noted for its bridging proclivity[2] and is a prime example. Indeed, Baran and Lagow claimed the conversion of hexachlorobenzene to hexalithiobenzene in over 60% yield in 1990[1a] and provided chemical, FTICR, and high-resolution mass spectrometric evidence for C_6Li_6 in 1992.[1b] Instead of a classical geometry, Xie and Schaefer proposed in 1991 that this complex could adopt the more stable starlike D_{6h} geometry (Scheme 1). This beautiful structure was the lowest energy minimum among the limited number of isomers they considered.[1c] However, Smith's subsequent extensive search of the C_6Li_6 potential energy surface identified a 62.1 kcal mol^{-1} more stable C_6Li_6 isomer not only lacking a starlike geometry, but even a six-membered carbon ring.[1d]

Scheme 1. Structures of some species mentioned in the text.

The starlike structures of $C_3Li_3^+$, $C_4Li_4^{2-}$, and $C_5Li_5^-$ have been identified.[1e,f] Jemmis and Schleyer established that $C_3Li_3^+$ has an unusually stable starlike structure.[1e] Minkin and co-workers found $C_4Li_4^{2-}$ and $C_5Li_5^-$ to be local, but not global minima.[1f] Winter and co-workers claimed the formation of the pertlithiation product of ruthenocene, Ru-$(C_5Li_5)_2$, but did not present experimental evidence to support this proposal.[3] Starlike molecules based on silicon rings have also been described.[4] Our recent detailed exploration of the potential energy surfaces of $Si_5Li_n^{n-6}$ ($n=5$–7) systems[5] demonstrated that it is feasible to design three-dimensional starlike silicon structures by using the appropriate type and number of ligands.

Our extensive computational exploration of starlike molecules by replacing the H atoms in $(CH)_n^q$ rings by BeH groups[6] revealed that D_{nh} $C_nBe_nH_n^q$ ($n=4$–9 and $q=0, \pm1, -2$) starenes are minima and aromatic.[7] Interestingly, further computations demonstrated how such $C_6Be_6H_6$ starbenzene (Scheme 1) building-block units might be used to construct new nanomolecular families by means of hydrogen-bridge bonds (HBBs). These nanomolecules resemble graphenes, carbon nanotubes, and fullerenes in shape. Although the "starbenzene" monomer is not the $C_6Be_6H_6$ global minimum, we predicted that the energetic benefits from inter-block HBBs bonding should result in rather stable nanomolecules.[7]

As exemplified by CAl_4^{2-} (Scheme 1) and its analogues (CAl_4^-, CAl_3Si^-, CAl_3Ge^-, and CAl_2Si_2, etc.),[8] aluminum is known to be a suitable ligand for stabilizing unusual planar tetracoordinate carbon (ptC)[9] molecules due to the electron deficiency and proper size match of the atoms.[10] The metallic character of the ligands can weaken the sp^3 carbon tetrahedron rigidity and the nonmetallic character can provide stabilization by forming a peripheral partial covalent bond. The computed CAl_5^+ and C_2Al_4 global minima follow similar principles for their ptC or planar pentacoordinate carbon (ppC) preferences.[11] Recently, we proposed that C_2Al_4 species elaborated with bulky protecting groups, such as $C_2Al_4(tBu)_8$, might be possible targets for experimental realization.[12]

Analyses of the C_2Al_4 electronic structure revealed that Al only utilizes one of its three valence electrons for chemical bonding; the other two electrons form a lone pair.[12] This "inert-pair" effect is well known in second (and lower) row main-group elements, as exemplified by Group 14 divalency.[13] Monovalent electropositive aluminum is thus essentially equivalent to Li and BeH, which implies that the replacement of all the H atoms in monocyclic aromatic hydrocarbons with Al atoms also may result in binary carbon–aluminum starlike structures. We have now verified this possibility computationally.

Results and Discussion

Figure 1 displays the optimized, but point-group-restricted starlike structures D_{3h} $C_3Al_3^+$ (**1**), D_{4h} $C_4Al_4^{2-}$ (**2**), D_{5h}
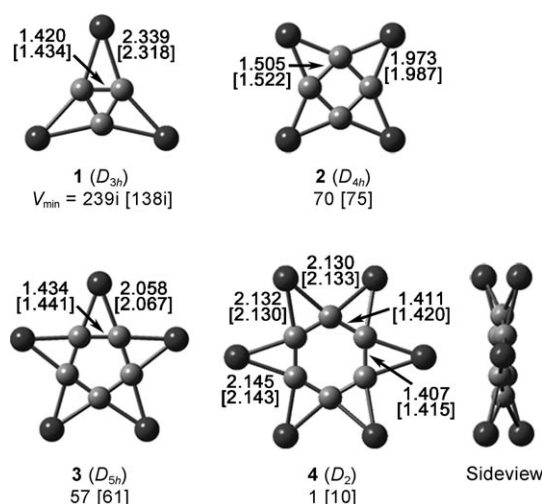

Figure 1. Optimized structures of C−Al starenes with necessary bond lengths [Å] and the smallest magnitude B3LYP and [MP2] vibrational frequencies (ν_{min}, cm^{-1}). Color versions of the figures in this paper are given in the Supporting Information.

$C_5Al_5^-$ (**3**), and D_2 C_6Al_6 (**4**). At the B3LYP/aug-cc-pVTZ level, **2** and **3** are minima. Interestingly, the unbridged D_{4h} counterpart of **2** is also a minimum, but is 18.8 kcal mol^{-1} less stable than **2**. The unbridged form of **3** is a third-order saddle point, 25.5 kcal mol^{-1} less stable than **3**. At the B3LYP/cc-pVTZ level, **1** is a transition state and is 17.0 kcal mol^{-1} less stable than unbridged D_{3h} minimum. The starlike D_{6h} C_6Al_6 has two degenerate imaginary frequencies, but it is 30.0 kcal mol^{-1} more stable than its unbridged D_{6h} isomer. Slight distortion of bridged D_{6h} C_6Al_6 gives the D_2 minimum (**4**, shown in Figure 1), but this is only 1.1 kcal mol^{-1} lower in energy. The somewhat shorter Al–Al separations (3.249 Å) may be responsible for this distortion (see below). The $C_nAl_n^q$ ($n>6$) structures are high-order saddle points and are not considered further herein. MP2 computations with corresponding basis sets confirmed the B3LYP structures and vibrational frequency analyses.

Although **2**, **3**, and **4** are minima on their corresponding potential energy surfaces (PES), this does not suffice for experimental viability predictions.[14] We first explored $C_4Al_4^{2-}$, $C_5Al_5^-$, and C_6Al_6 PESs by using the GXYZ stochastic search program,[11b,15] to generate random initial structures. These were optimized with Gaussian 03[16] at B3LYP/6-31+G* (for the $C_4Al_4^{2-}$ and $C_5Al_5^-$ anions) and at B3LYP/6-31G* (for neutral C_6Al_6). More than 100 $C_4Al_4^{2-}$ isomers were lower in energy than **2**! The global minimum **2A** (Figure 2) was 44.3 kcal mol^{-1} below **2**. A more refined Molpro 2008.1[17] computation[18] at CCSD(T)/aug-cc-pVTZ// B3LYP/aug-cc-pVTZ (CCSD(T)//B3LYP)+ΔZPE$_{B3LYP}$ that is, including the B3LYP/aug-cc-pVTZ zero-point energy, reduced the energy difference, but only to 32.4 kcal mol^{-1}. The relative energies of the five most stable C_6Al_6 isomers (**4A**–**E**) are shown in Figure 2. While **2** and **4** are aromatic, the four-membered ring strain in **2** and the Al–Al repulsions in
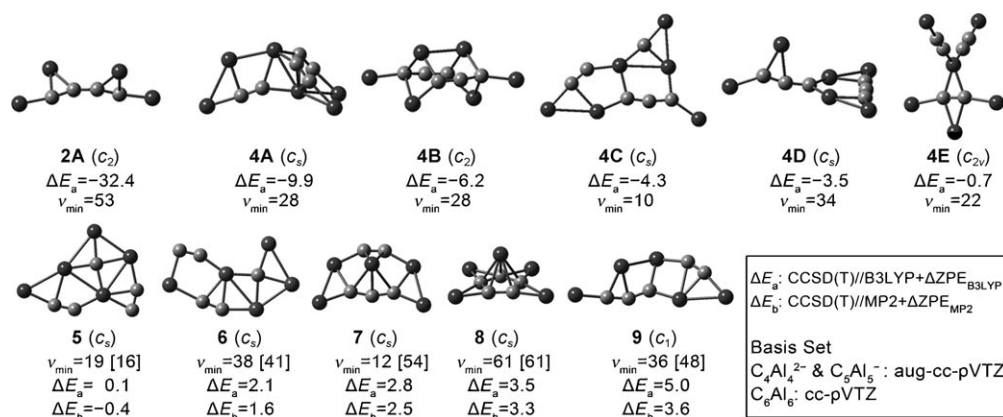
Figure 2. Optimized structures, relative energies (ΔE, kcal mol^{-1}, in comparison with corresponding starlike species), and lowest vibrational frequencies (ν_{min}, in cm^{-1}) of the selected low lying isomers of $C_4Al_4^{2-}$, $C_5Al_5^-$, and C_6Al_6.

4 are unfavorable. The results of these PES explorations exclude the possibility of viable starlike structures for **2** and **4**.

$C_5Al_5^-$ (**3**) is the best "molecular star" candidate. This minimum has the lowest electronic energy (barely) among hundreds of isomers identified by the random GXYZ searches[11b, 15] at the B3LYP/6-31+G* level. The PES of $C_5Al_5^-$ was further explored with the GEGA program[19] at the B3LYP/LANL2DZ level, but gave similar results. All but three of the 50 lowest-energy isomers from the GXYZ and GEGA searches, when reoptimized at the B3LYP/aug-cc-pVTZ level, were confirmed to be minima. The energies of the 20 best isomers, when refined by single-point CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ computations (including ΔZPE$_{B3LYP}$), predicted **3** to be the lowest-energy minimum, although **5** (Figure 2) was only 0.1 kcal mol^{-1} less stable. Figure 2 also shows the other $C_5Al_5^-$ isomers (**6–9**) within 5.0 kcal mol^{-1} of **3** (the remaining 14 isomers are given in the Supporting Information).

The triplet $C_5Al_5^-$ species also were considered by using the same search approach as for the singlets. The best triplet form is 17.1 kcal mol^{-1} higher in energy than the starlike **3** structure at the B3LYP level, which indicates that $C_5Al_5^-$ has a singlet ground state.

As a further refinement, re-optimization of the 20 singlet isomers at MP2/aug-cc-pVTZ gave geometries similar to those at B3LYP. The relative energies at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ (CCSD(T)//MP2)+ΔZPE$_{MP2}$ also are in excellent agreement with those at the CCSD(T)//B3LYP+ΔZPE$_{B3LYP}$ level. Nevertheless, the two levels of

theory rank **3** and **5** slightly differently; CCSD(T)//MP2 predicts **5** to be 0.4 kcal mol^{-1} more stable than **3**. Although the true global minimum cannot be predicted with certainty, the starlike $C_5Al_5^-$ structure **3** clearly is competitive. Both **3** and **5** are well separated energetically from the other isomers on the PES. Depending on the method of generation, either or both isomers might be detectable experimentally.

We also examined the kinetic stability of **3** and **5** by carrying out two sets of Born–Oppenheimer molecular dynamic (BOMD)[20] simulations at B3LYP/6-31G* at 323 and 373 K. Figure 3 shows the RMSD structural evolutions (in terms of the root-mean-square deviations relative to the B3LYP/6-31G*-optimized structures). The small RMSD fluctuations indicate that both species have reasonable kinetic stability at least for 30 ps. The four trajectories reveal no isomerization or other structural alterations; **3** and **5** do not intercon-
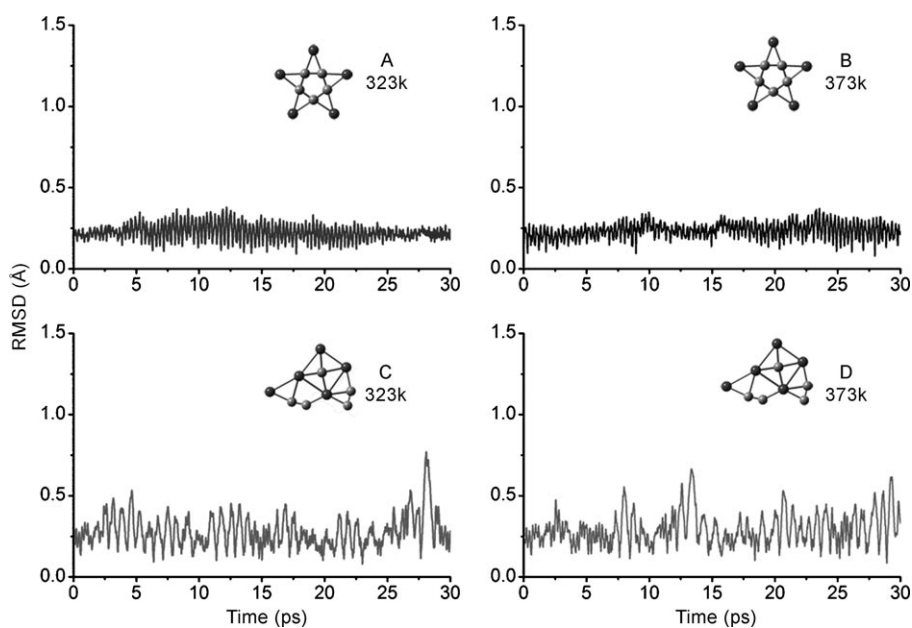

Figure 3. The structural evolutions of **3** and **5** described by RMSD during 30 ps at 323 and 373 K, respectively.

vert. Comparison of Figure 3A,B with 3C,D indicates the greater rigidity of **3**.

In contrast to the classical sp²-trigonal bonding in their hydrocarbon analogues, all carbon atoms in **2–4** adopt ptC arrangements. Nevertheless, their three π orbitals are similar to those of classical 6-π-electron aromatic systems (Figure 4). As documented by the computed total NBO π
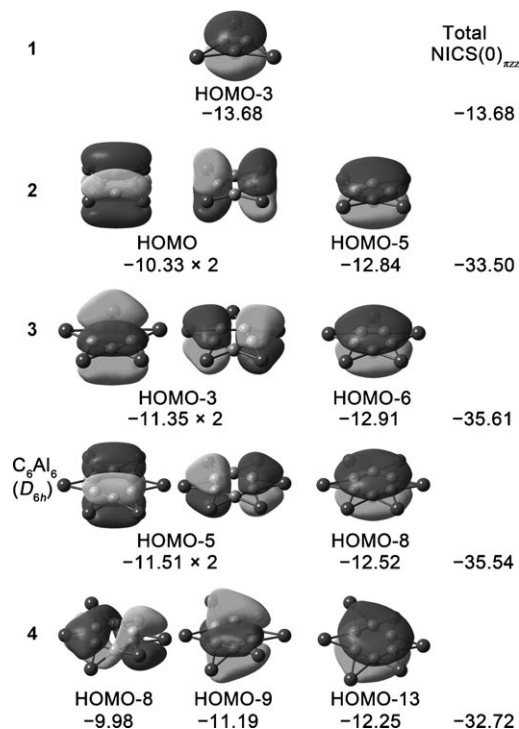

Figure 4. Occupied π MOs, dissected and total $NICS(0)_{\pi zz}$ values (ppm) of **1–4** and D_{6h} C_6Al_6.

Table 1. $NICS(0)_{\pi zz}$ values (PW91/IGLOIII) for bridged $C_nAl_n^q$ species and their hydrocarbon analogues.

Bridged $C_nAl_n^q$	P.G. (N_{IMAG})	$NICS(0)_{\pi zz}$ [ppm]	Hydrocarbon analogue	P.G. (N_{IMAG})	$NICS(0)_{\pi zz}$ [ppm]
$C_3Al_3^+$ (**1**)	D_{3h} (1)	−13.68	$C_3H_3^+$	D_{3h} (0)	−14.16
$C_4Al_4^{2-}$ (**2**)	D_{4h} (0)	−33.50	$C_4H_4^{2-}$	D_{4h} (4)[a]	−29.88
$C_5Al_5^-$ (**3**)	D_{5h} (0)	−35.61	$C_5H_5^-$	D_{5h} (0)	−35.50
C_6Al_6 (**4**)	D_2 (0)	−32.72[b]	C_6H_6	D_{6h} (0)	−35.63

[a] The $C_4H_4^{2-}$ minimum (C_{2h} symmetry) is strongly distorted from planarity. [b] The value is −35.54 for the D_{6h} geometry with $N_{IMAG}=2$.
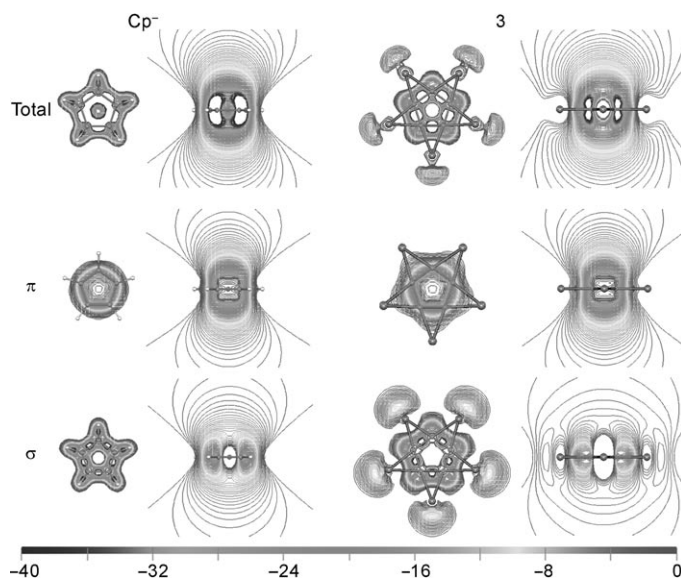

Figure 5. Molecular-orbital contributions to the B^{ind} ($NICS_{zz}$) component (for simplicity only the diatropic regions are depicted). The external field applied is $|B^{ext}|=1T$ and B^{ind} magnitude is in ppm. A color version of this figure is provided in the Supporting Information.

occupancies of **3**, 5.98 (5.65 for the five C atoms and 0.33 $|e|$ for the five Al atoms) and 5.99 $|e|$ for the cyclopentadienyl anion Cp^- (5.96 for the five C atoms and 0.03 $|e|$ for the five H atoms), the bridging aluminum atoms affect the π framework insignificantly. Thus, the computed total $NICS(0)_{\pi zz}$[21] values (NICS = nuclear-independent chemical shift) for all the $C_nAl_n^q$ (**1–4**) compounds agree reasonably with those of their hydrocarbon analogues. $NICS(0)_{\pi zz}$ is the most refined NICS index, which extracts the out-of-plane tensor component of the isotropic NICS and includes only the π MO contributions for quantifying aromaticity. The dissected contributions from each π MO are given in Figure 4. Based on $NICS(0)_{\pi zz}$ criteria, **3** (−35.61 ppm) is nearly as aromatic as Cp^- (−35.50 ppm) and benzene (−35.63 ppm; see Table 1); the $NICS(0)_{\pi zz}$ value for **4** (−32.72, −35.54 ppm for D_{6h}) is slightly lowered by the twisting of its π orbitals. Since **1** has only two π electrons, its $NICS(0)_{\pi zz}$ (−13.68 ppm) is less than half as aromatic as those of the other species in the series, which have six π electrons.

Figure 5 shows the diatropic region of the z-component of the induced magnetic field (B^{ind})[22] due to an external field

applied perpendicularly to the molecular plane of **3** and Cp^-. A magnetic field in this direction can induce a ring current in and parallel to the molecular plane. Like NICS, the B^{ind} can also be dissected into core σ and π orbital contributions.[21e,23] The core electrons generally contribute very little to B^{ind} except in very close vicinity of nuclei. The π orbital contributions to B^{ind} of both **3** and Cp^- show the typical response of aromatic systems, which generate a long-range shielding cone perpendicular to the molecular planes. Interestingly, the σ orbital contributions of **3** are a little different to that of Cp^-. As shown in Figure 5, the peripheral "inert pairs" of Al atoms contribute to the diatropic magnetic response of σ electrons.

The five Al bridges in **3** are analogous to the two-bridged Al atoms of D_{2h} C_2Al_4 (Scheme 1).[11b] Both have comparable C–Al bond lengths (2.067 in **3**, 2.155 Å in C_2Al_4), C–Al Wiberg bond indices (WBI_{C-Al}; 0.27 in **3**, 0.25 in C_2Al_4), and NBO Al natural charges (+0.70 in **3**, +0.69 in C_2Al_4). Aromaticity and favorable C–Al bonding are key stabilizing features for the starlike structure of **3**.

Isomer **5** of $C_5Al_5^-$ is also quite stable thermodynamically. Interestingly, although its five carbon atoms do not form a five-membered ring, **5** also has three occupied π MOs (see the Supporting Information). HOMO-3 of **5** mainly involves the CAl_4 moiety, whereas HOMO-6 and HOMO-8 result from combinations of two C−C π bonds. An orbital similar to HOMO-3 was important in stabilizing D_{4h} CAl_4^{2-}.[8b] That the carbon in the CAl_4 fragment of **5** has a similar bonding environment as that in D_{4h} CAl_4^{2-} is indicated by the following comparisons: WBI_C (2.24 vs. 2.24), WBI_{C-Al} (average 0.51 vs. 0.56), and Q_C (−2.66 vs. −2.72 $|e|$ in CAl_4^{2-}). In addition, the C_2Al_3 fragment shown at the left of **5** resembles the C_{2v} $C_2Al_3^-$ global minimum species.[24] This is also reflected in comparisons: WBI_C (3.58 average in the C_2Al_3 fragment vs. 3.46 in $C_2Al_3^-$), WBI_{C-C} (2.67 in the fragment vs. 2.33 in $C_2Al_3^-$), WBI_{C-Al} (0.49 average for the terminal and 0.26 for Al bridges in the fragment vs. 0.56 and 0.42 in C_2Al_3, respectively), and Q_C (−0.83 average in the fragment vs. −0.98 $|e|$ in $C_2Al_3^-$). The six-π-electron system and the rigid subfragment contribute to the stability of isomer **5**. The similar bonding could be found in the third lowest isomer **6**.

The discussion above implicates the C−Al−C bridge bonding and aromaticity as being responsible for the high stability of the $C_5Al_5^-$ star (**3**). Although **2** and **4** also are aromatic, this advantage alone does not suffice to result in viable starlike geometries. Destabilizing effects offset the favorable electronic structures. Cyclic (D_{3h}) C_6 is a relevant example; despite its double-aromaticity (π and σ),[25a] its linear C_6 triplet isomer is the global minimum.[25b]

Although **2** is a local minimum, it is destabilized both due to the strain of its four-membered ring and to the greater Coulomb repulsion of its two negative charges in its compact starlike shape. Consequently, the lowest-energy $C_4Al_4^{2-}$ isomer **2A** (Figure 2) adopts a more extended geometry. Note that D_{4h} $C_4H_4^{2-}$ is a fourth-order saddle point for similar reasons, despite its six-π-electron character.[26]

The D_{6h} C_6Al_6 star is not even a local minimum. It is destabilized by the Coulomb repulsions among its highly positively charged Al atoms ($Q_{Al}=0.73$ $|e|$), which approach one another more closely than in **2** or **3**, and distorts to D_2 symmetry (**4**). But even **4** is only a local C_6Al_6 minimum as its Al–Al distances, 3.280/3.327 Å, are still shorter than those (3.428 Å) in **3**. The Al atom crowding in **4** also stretches and weakens the C−Al bonds ($r_{C-Al}=2.130/2.132/2.145$ in **4** vs. 2.058 Å in **3**). The larger starlike C_nAl_n ring structures with $n>6$ also suffer from similar destabilization and all are high-order saddle points.

Therefore, aromaticity and electronic stabilization help achieve the starlike structures, but they may not be the main determinant. As in the realization of ptC arrangements,[8,10] geometric features can be critical. Only **3** is optimum both electronically and geometrically among **1**–**4**.

We computed the vertical detachment energies (VDE) and the ionization potentials (IP) of **3** and **5**–**9** to aid experimental identification by using outer-valence Green's function (OVGF)[27] with the aug-cc-pVTZ basis set as imple-mented in Gaussian 03. The IP values only range narrowly (from 2.26 to 2.50 eV) and would be hard to differentiate with certainty, but the VDE values, which are important for photoelectron spectroscopy, are divided into two distinguishable groups. The group with higher VDE's includes **3** (3.98 eV; more intense since the MO is doubly degenerate) and **7** (3.88 eV) with a C_5 ring; the other group with lower VDE values (3.59, 3.33, 3.12, and 2.84 eV) includes isomers without a C_5 ring **5**, **6**, **8**, and **9**, respectively.

Conclusion

We suggest that the $C_5Al_5^-$ system could be a good candidate for capturing a molecular "star". Replacing the H atoms in monocyclic aromatic $(CH)_n^q$ rings ($n=3$–6) by Al atoms can result in fully bridged starlike $(CAl)_n^q$ structures with hardly any diminution of aromaticity, based on $NICS(0)_{\pi zz}$ and the B^{ind} comparisons. However, D_{5h} **3** is the only good candidate among the starlike alternatives for possible experimental realization, for example, by photoelectron detachment. However, another $C_5Al_5^-$ isomer, **5**, featuring a planar tetracoordinate carbon (ptC) in its rigid CAl_4 substructure, may also be viable in the gas phase. Extensive PES searches and detailed analyses indicate that both **3** and **5** are the $C_5Al_5^-$ global minimum candidates. Favorable C−Al bonding and aromaticity contribute to their stability. Alongside lithium, aluminum is now well-established to favor bridged structures. We are exploring this proclivity in other chemical elements and in other situations.

[1] a) J. R. Baran, R. J. Lagow, *J. Am. Chem. Soc.* **1990**, *112*, 9415–9416; b) J. R. Baran, C. Hendrickson, D. A. Laude, R. J. Lagow, *J. Org. Chem.* **1992**, *57*, 3759–3760; c) Y. M. Xie, H. F. Schaefer, *Chem. Phys. Lett.* **1991**, *179*, 563–567; d) B. J. Smith, *Chem. Phys. Lett.* **1993**, *207*, 403–406; e) E. D. Jemmis, G. Subramanian, A. J. Kos, P. von R. Schleyer, *J. Am. Chem. Soc.* **1997**, *119*, 9504–9512; f) V. I. Minkin, R. M. Minyaev, A. G. Starikov, T. N. Gribanova, *Russ. J. Org. Chem.* **2005**, *41*, 1289–1295.

[2] a) P. von R. Schleyer, *Pure Appl. Chem.* **1983**, *55*, 355–362; b) P. von R. Schleyer, *Pure Appl. Chem.* **1984**, *56*, 151–162; c) A. M. Sapse, P. von R. Schleyer in *Lithium Chemistry: A Theoretical and Experimental Overview*, Wiley, New York, **1995**.

[3] A. Bretschneider-Hurley, C. H. Winter, *J. Am. Chem. Soc.* **1994**, *116*, 6468–6469.

[4] a) J. C. Santos, P. Fuentealba, *Chem. Phys. Lett.* **2007**, *443*, 439–442; b) A. D. Zdetsis, *J. Chem. Phys.* **2007**, *127*; c) A. D. Zdetsis, P. W. Fowler, R. W. A. Havenith, *Mol. Phys.* **2008**, *106*, 1803–1811.

[5] W. Tiznado, N. Perez-Peralta, R. Islas, A. Toro-Labbe, J. M. Ugalde, G. Merino, *J. Am. Chem. Soc.* **2009**, *131*, 9426–9431.

[6] Z. X. Wang, C. G. Zhang, Z. F. Chen, P. von R. Schleyer, *Inorg. Chem.* **2008**, *47*, 1332–1336.

[7] Y. B. Wu, J. L. Jiang, R. W. Zhang, Z. X. Wang, *Chem. Eur. J.* **2010**, *16*, 1271–1280.

[8] a) X. Li, L. S. Wang, A. I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* **1999**, *121*, 6033–6038; b) X. Li, H. F. Zhang, L. S. Wang, G. D. Geske, A. I. Boldyrev, *Angew. Chem.* **2000**, *112*, 3776–3778; *Angew. Chem. Int. Ed.* **2000**, *39*, 3630–3633; c) L. S. Wang, A. I. Boldyrev, X. Li, J. Simons, *J. Am. Chem. Soc.* **2000**, *122*, 7681–7687.

[9] a) R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993; b) K. Sorger, P. von R. Schleyer, *J. Mol. Struct.* **1995**, *344–373*, 317–346, and references therein; c) D. Röttger, G. Erker, *Angew. Chem.* **1997**, *109*, 840–856; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 812–827, and references therein; d) W. Siebert, A. Gunale, *Chem. Soc. Rev.* **1999**, *28*, 367–371, and references therein; e) R. Keese, *Chem. Rev.* **2006**, *106*, 4787–4808, and references therein; f) G. Merino, M. A. Mendez-Rojas, A. Vela, T. Heine, *J. Comput. Chem.* **2007**, *28*, 362–372, and references therein.

[10] P. v. R. Schleyer, A. I. Boldyrev, *J. Chem. Soc. Chem. Commun.* **1991**, 1536–1538.

[11] a) Y. Pei, W. An, K. Ito, P. von R. Schleyer, X. C. Zeng, *J. Am. Chem. Soc.* **2008**, *130*, 10394–10400; b) Y. B. Wu, H. G. Lu, S. D. Li, Z. X. Wang, *J. Phys. Chem. A* **2009**, *113*, 3395–3402.

[12] Y. B. Wu, J. L. Jiang, H. Li, Z. F. Chen, Z. X. Wang, *Phys. Chem. Chem. Phys.* **2010**, *12*, 58–61.

[13] M. Kaupp, P. von R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 1061–1073.

[14] R. Hoffmann, P. von R. Schleyer, H. E. Schaefer, *Angew. Chem.* **2008**, *120*, 7276–7279; *Angew. Chem. Int. Ed.* **2008**, *47*, 7164–7167.

[15] a) GXYZ, a random Cartesian coordinates generating program, H. G. Lu, Y. B. Wu, Shanxi University, Taiyuan, **2008**; b) P. P. Bera, K. W. Sattelmeyer, M. Saunders, H. F. Schaefer, P. von R. Schleyer, *J. Phys. Chem. A* **2006**, *110*, 4287–4290.

[16] Gaussian 03, Revision E.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[17] Molpro 2008.1, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklab, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf, University College Cardiff Consultants Limited: 2008.

[18] The T1-diagnostics from converged CCSD wavefunctions were checked to gauge the degree of multireference character. The values for all species studied in this work are all less than 0.025 (see Figure S1 in the Supporting Information for the values of the 20 lowest isomers of $C_5Al_5^-$), which indicates that they can be well-described by a single-reference wavefunction-based method.

[19] a) A. N. Alexandrova, A. I. Boldyrev, Y. J. Fu, X. Yang, X. B. Wang, L. S. Wang, *J. Chem. Phys.* **2004**, *121*, 5709–5719; b) A. N. Alexandrova, A. I. Boldyrev, *J. Chem. Theory Comput.* **2005**, *1*, 566–580.

[20] a) K. Bolton, W. L. Hase, G. H. Peshlherbe, *Modern Methods for Multidimensional Dynamics Computation in Chemistry*, World Scientific, Singapore, **1998**; b) W. Chen, W. L. Hase, H. B. Schlegel, *Chem. Phys. Lett.* **1994**, *228*, 436–442; c) J. M. Millam, V. Bakken, W. Chen, W. L. Hase, H. B. Schlegel, *J. Chem. Phys.* **1999**, *111*, 3800–3805; d) X. S. Li, J. M. Millam, H. B. Schlegel, *J. Chem. Phys.* **2000**, *113*, 10062–10067.

[21] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H.-J. Jiao, N. J. R. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) P. von R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669–12670; c) Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888; d) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. V. Schleyer, *Org. Lett.* **2006**, *8*, 863–866; e) T. Heine, P. von R. Schleyer, C. Corminboeuf, G. Seifert, R. Reviakine, J. Weber, *J. Phys. Chem. A* **2003**, *107*, 6470–6475.

[22] T. Heine, R. Islas, G. Merino, *J. Comput. Chem.* **2007**, *28*, 302–309.

[23] G. Merino, T. Heine, G. Seifert, *Chem. Eur. J.* **2004**, *10*, 4367–4371.

[24] X. Li, L. S. Wang, N. A. Cannon, A. I. Boldyrev, *J. Chem. Phys.* **2002**, *116*, 1330–1338.

[25] a) P. von R. Schleyer, H. Jiao, M. N. Glukhovtsev, J. Chandrasekhar, E. Kraka, *J. Am. Chem. Soc.* **1994**, *116*, 10129–10134; b) H. Massó, M. L. Senent, *J. Phys. Chem. A* **2009**, *113*, 12404–12410.

[26] M. Balci, M. L. McKee, P. von R. Schleyer, *J. Phys. Chem. A* **2000**, *104*, 1246.

[27] J. V. Ortiz, V. G. Zakrzewski, O. Dolgounircheva, *Conceptual Perspectives in Quantum Chemistry*, Kluwer Academic, New York, **1997**, pp. 465–518.