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Communication

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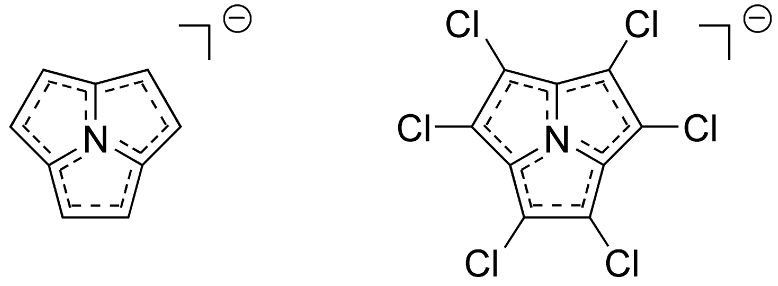

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# The Azaacepentalenide Anion: A New Aromatic, Bowl-Shaped Heterocycle

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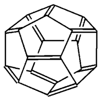
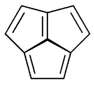
The immense interest surrounding the fullerenes has directed much attention toward concave polycycles which represent fragments of $C_{60}$, and these have become attractive targets for synthesis.[1] The smallest possible fullerene, $C_{20}$ (**1**), is composed entirely of five-membered rings and has been produced, albeit fleetingly, via its parent $C_{20}H_{20}$ hydrocarbon dodecahedrane.[2] However, long before the advent of **1** or indeed any fullerene, the smallest curved fragment of $C_{20}$, acepentalene (**2**), had been considered a theoretical curiosity and fundamental synthetic challenge in the field of nonbenzenoid polycycles.[3] Compound **2** is antiaromatic and to date has been observed only in mass spectrometry experiments,[4] but its dianion (**2**$^{2-}$) is a stable nonplanar aromatic species which was prepared by de Meijere and co-workers in a remarkable superbase-induced dehydrogenation of triquinacene (**3**).[5]

Recently, the achievement of azafullerenes on a macroscopic scale has opened up a new dimension in carbon cage research.[6] However, no convex aromatic polycycle including nitrogen in its framework appears to have yet been described. We have for some time been studying a class of rigid, hemispherical tricycles of the 10-azatricyclo[5,2,1,0$^{4,10}$]decane (or simply "azatriquinane"[7]) family[8] and have recently completed the synthesis of 10-azatriquinacene (**4**).[9] With **4** in hand and de Meijere's landmark synthesis of **2**$^{2-}$ in mind, we set sights on the analogous azaacepentalenide anion **5**, and herein we describe the preparation of both **5** and its perchloro derivative **8**.



**1**



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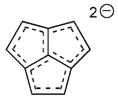
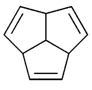
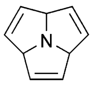


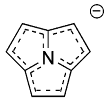
**2**$^{2-}$



**3**



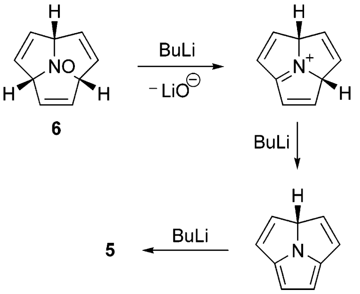
**4**



**5**

Hitherto, **5** had only been described in theory.[10] Schleyer and co-workers applied the nucleus-independent chemical shift criterion of aromaticity to **5** and concluded it would be more aromatic than **2**$^{2-}$. In addition to this, we reasoned that the monoanionic nature of **5** would make it easier to handle than **2**$^{2-}$. It seemed unlikely that the synthetic approach taken by de Meijere in the conversion of **3** to **2**$^{2-}$ would be successful for **4**, since the N is a better leaving group than hydride and ring opening would be expected. Indeed, treatment of **4** with a mixture of *n*-butyllithium and potassium *tert*-pentoxide[5] led only to decomposition. However, the nitrogen in **4** provides a functional handle by which to oxidize the ring system. Thus, treatment of **4** with *m*-chloroperbenzoic acid resulted in the stable *N*-oxide **6**. Addition of excess *n*-butyllithium in THF-$d_8$ to **6** at −78 °C led to the NMR signals of the *N*-oxide being cleanly replaced by a new set of signals which we could only attribute to the aromatic azaacepentalenide anion **5**. Likewise, treatment of hexachloroazatriquinacene *N*-oxide **7** with lithium hexamethyldisilazide gave **8**. The reaction apparently progresses as described in Scheme 1.

***Scheme 1***



The observed $^1$H and $^{13}$C NMR resonances of the new aromatics are shown in Figure 1, alongside those of the *N*-oxides from which they are derived. The expected downfield shift is seen in the $^1$H spectrum of **5**, and in the $^{13}$C spectrum there is a ca. 20 ppm downfield shift of the carbons α to nitrogen and a comparable upfield shift of the formerly olefinic carbons. The $\delta$ values in **5** and **8** are consistent with the ab initio calculated chemical shifts to within 0.1 ppm for $^1$H and an absolute mean error of 3.5 ppm for $^{13}$C.[11]

The structures of **5** and **8** modeled at the B3LYP/6-311G++(2d,p) level of theory are shown in Figure 2.[12] Both are $C_{3v}$ symmetric and electronically delocalized, with C−C and C−N bond lengths of 1.42 and 1.37 ± 0.01 Å, respectively. Visual comparison of **5** alongside its parent tricycle **4** shows how aromatization decreases the curvature: The summation of the CNC angles for acutely pyramidalized **4** is 325.9°, while for **5** it is 353.5°. The respective deviations of the N from the planes described by the six peripheral carbons of **4** and **5** are 1.31 and 0.41 Å.

Although anion **5** appears to be indefinitely stable in THF solution at room temperature, attempts to isolate its lithium salt by precipitation with hexane have yet to result in a clean product. We note that de Meijere experienced similar difficulties with the purification of **2**$^{2-}$ but was able to unambiguously confirm the structural assignment by trapping it with an electrophile (chlorotri-

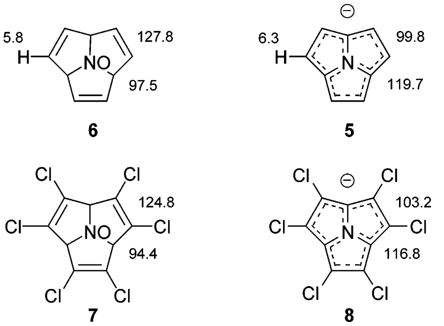


***Figure 1.*** $^1$H and $^{13}$C NMR shift comparisons in **5**−**8**.

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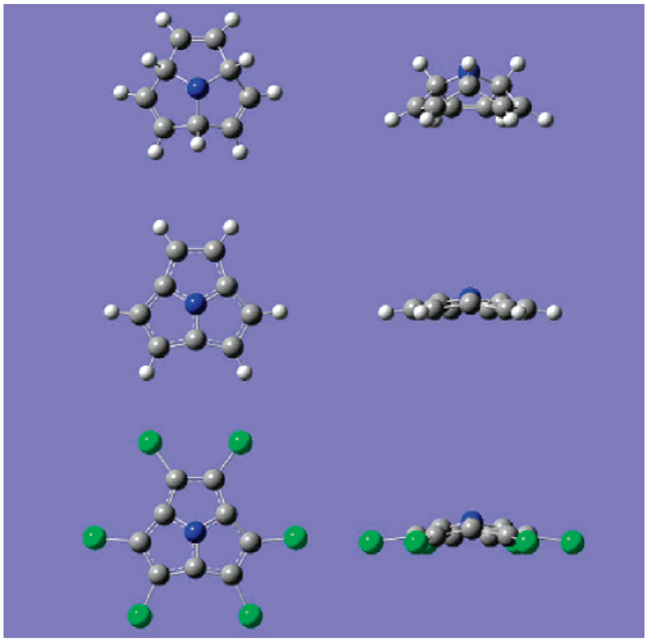
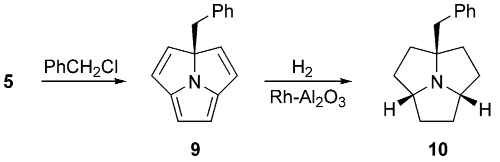


***Figure 2.*** Frontal and side views of the ab initio modeled structures of **4** (top), **5** (center), and **8** (bottom).

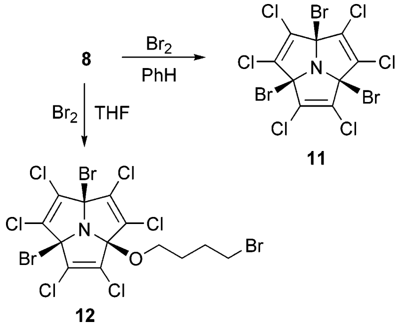
***Scheme 2***



methylsilane).[5a] For our purposes, we had better results trapping **5** with carbon electrophiles. Thus, treatment of a solution of **5** in THF with excess benzyl chloride resulted in the observation of the rather unstable α-alkylated product **9**. Catalytic hydrogenation of **9** provided the stable, isolable substituted azatriquinane **10** (Scheme 2).

Anion **8**, on the other hand, is stable in the absence of acids. It can be isolated and chromatographed on alumina in the form of its tetrabutylammonium salt. **8** is not sufficiently nucleophilic to be alkylated like **5**, but it reacts readily with molecular bromine at low temperature to give the α,α,α-tribromide **11** (Scheme 3) in good yield. Bromination of **8** apparently begins much like the alkylation of **5**, i.e., preferentially at an α-position, but the intermediate pyrrole then undergoes 1,4-addition of $Br_2$. Support for this mode of reaction is gained by performing the bromination in the presence of THF, which leads to $\omega$-bromoether **12** as the main product, while **11** itself does not react with THF even on extended standing in solution. High-resolution negative-ion MALDI-TOF mass spectrometry of **8** shows a strong $C_9Cl_6N^-$ signal alongside a range of dimer and trimer artifacts of the ionization process. Air-sensitive anion **5**, however, gives no interpretable spectrum under the same conditions.

***Scheme 3***



In conclusion, we report here in brief the synthesis and structural characterization of azaacepentalenide **5** and its perchloro derivative **8**. We look forward to probing the reactivity of these novel, nonplanar aromatic anions in detail, particularly the intriguing possibility of forming sandwich complexes with divalent transition metal ions.

**Supporting Information Available:** Experimental details for the preparation of compounds **5**−**8**; $^1$H and $^{13}$C NMR spectra for compounds **5**−**12**; mass spectra for compounds **6**−**8**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Calculations performed with the Gaussian 03 program, revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003. Default optimization procedures were used, and frequency calculations were performed at the stated level of theory to confirm stationary points as minima.

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