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Chrysaorenes: Assembling Coronoid Hydrocarbons via the Fold-in Synthesis†

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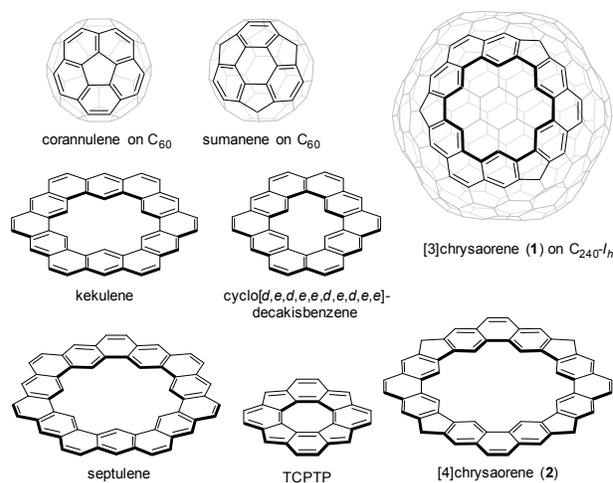
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Two coronoid hydrocarbons, [3]- and [4]chrysaorene were synthesized from fluorenophane precursors using the fold-in strategy. [3]Chrysaorene is a bowl-shaped fragment of the C_{240} - I_h fullerene, whereas [4]chrysaorene is planar and contains a uniquely large 24-membered internal ring. Chrysaorenes show geometry-dependent magnetic properties and are strongly fluorescent.

The continuing interest in polycyclic aromatic hydrocarbons (PAH's) has led to dramatic advances in molecular design and synthetic methodology.¹ In the case of benzenoid PAH's, band gaps and spin states can be tailored by judicious assembly of six-membered rings, usually arranged into subsections of graphene.² Nonbenzenoid PAH's are capable of providing additional structural diversity, notably by introducing curvature and unusual bonding topologies to the π -conjugated system. Positive (convex) curvature, typically achieved by embedding five-membered rings, is the hallmark of synthetic fullerene fragments (buckybowls), such as corannulene or sumanene (Scheme 1).³ Negatively curved (saddle-shaped) aromatic hydrocarbons⁴ can be built around 7-membered^{4a-e} or larger^{4f-h} rings. Examples of non-trivial conjugation effects in non-benzenoid frameworks range from classical simple systems (e.g. azulene) to carefully designed modern constructs, such as the recently reported TCPTP molecule.⁵

Fused ring systems in which a large ring is completely enclosed by a belt of six- or five-membered rings⁶ have been variously classified as circulenes,^{6a} cycloarenes,^{6b} coronoids,^{6c} or torands,^{6d} depending on the size of the central ring and fusion topology. In spite of considerable theoretical interest in such systems,^{5b} the synthetic chemistry of coronoid hydrocarbons is quite limited.⁷ In fact, since the seminal synthesis of kekulene by Staab and Diederich,^{7a-b} only two

other cycloarenes have been prepared: cyclodecabenzene from the Staab group^{7c} and septulene, reported recently by King et al.^{7d} This scarcity reflects difficulties associated with assembling *cata*-fused aromatic macrocycles.^{6b,7e} Here we introduce two homologous nonbenzenoid carbocyclic coronoids, [3]- and [4]chrysaorene, so named after their heterocyclic congener, chrysaorole^{8a} (**1** and **2**, Scheme 1). With a 24-atom internal ring, **2** is the largest coronoid framework synthesized to date. The bowl-shaped **1**, containing 45 carbon atoms forms a uniquely large, conformationally rigid fragment of the C_{240} - I_h fullerene.

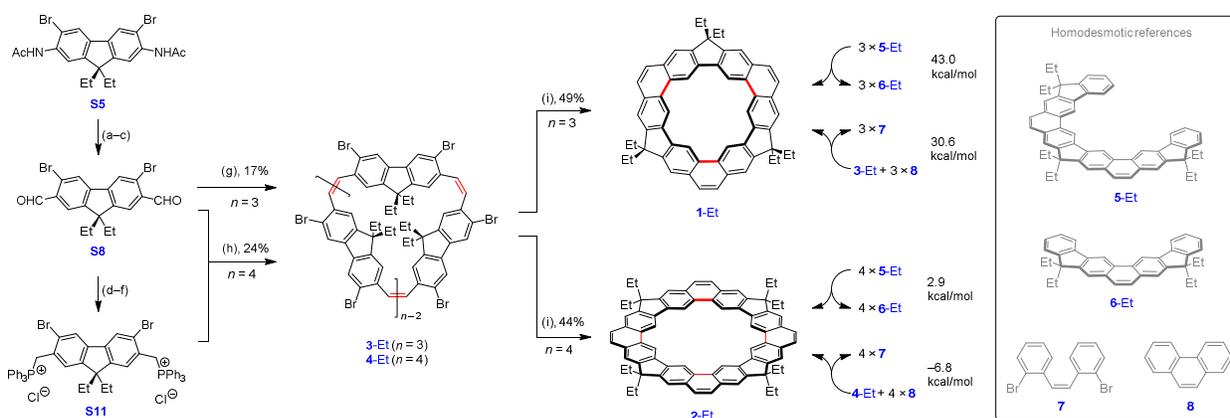


Scheme 1. Chrysaorenes and related hydrocarbons.

We surmised that chrysaorenes might be obtainable from bromo-functionalized fluorenophanes using the fold-in strategy, previously developed by us for the synthesis of carbazole-containing molecular bowls and belts.⁸ Similarly to sumanene, chrysaorenes contain cyclopentadiene rings with peripherally exposed CH_2 bridges. Double substitution of these bridges with ethyl groups was found necessary to secure proper solubility and reactivity of synthetic intermediates, without compromising the required conformational freedom

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Scheme 2. Synthesis of chrysaorenes and homodesmotic strain estimates. Reagents and conditions: (a) KOH, MeOH, reflux, 99%; (b) 1. $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, 2. NaNO_2 , 3. $\text{KI}/\text{H}_2\text{O}$, 62%. (c) 1. *i*-PrMgCl/THF, 2. DMF, 66%. (d) NaBH_4 , THF, 96%. (e) SOCl_2 , DCM, DMF, 96%. (f) PPh_3 , toluene, reflux, 90%. (g) TiCl_4 , CuI, Zn, THF, reflux. (h) 50% NaOH, DCM, (i) $\text{Ni}(\text{cod})_2$, bpy, DMF, 85 °C, 18 h. Calculation method: B3LYP/6-31G(d,p) in vacuo.

of the cyclophane precursors. The use of two chemically identical groups on each five-membered ring was needed to avoid stereoisomerism in the macrocyclic products.

The syntheses of halogenated fluorenohane precursors **3-Et** and **4-Et** employed macrocyclization strategies based respectively on McMurry and Wittig reactions (Scheme 2).^{8a,9} The key monofluorene building blocks, **S8** and **S11**, were more difficult to prepare than the corresponding carbazole precursors, because the required 3,6-dibromo substitution could not be achieved by direct bromination of the 2,7-diformylfluorenes. The desired substitution pattern was elaborated on the diacetamide **S5**, which was hydrolyzed, converted into the diolide using the Sandmeyer reaction, metallated with *i*-PrMgCl, and converted into the dialdehyde **S8** via reaction with DMF. The “gunshot” McMurry cyclization of **S8** produced **3-Et** with good ring-size selectivity. In contrast to the analogous carbazolophane cyclization,^{9a} the competing cyclodimer formation was suppressed in the synthesis of **3-Et**, possibly by the bulk of the 9-Et substituents. Likewise, in the Wittig reaction of **S8** and **S11**, cyclotetramer **4-Et** was formed as the principal macrocyclic product.

In the solid state, **3-Et** and **4-Et** show highly nonplanar conformations (Figure 1A–B), different from those of the corresponding carbazolophanes.^{8a,9a} In **3-Et**, two fluorene subunits are in a relative anti arrangement, being tilted almost perpendicular to the average plane of vinylenes. The sp^3 carbon of the third fluorene points toward the centre of the macrocycle. The fluorene units in **4-Et**, arranged in an alternating up-and-down fashion, show noticeable bending (10–17° angles between benzene rings), unusual in such a large macrocycle. Apparently, adopting a more relaxed conformation is not possible for **4-Et** because of steric repulsions between alkyl substituents. DFT re-optimization of X-ray geometries leads to only minor structural variations. Sharp, fully symmetric ^1H NMR spectra are observed for **3-Et** and **4-Et** at 300 K (CDCl_3 , 600 MHz), indicating fast motions of the constituent fluorene subunits. GIAO ^1H shieldings corresponding to these DFT geometries are in good agreement

with experimental values, suggesting that the solid-state conformers are very similar to those present in solution.

The fold-in reaction was performed on each of the **3-Et** and **4-Et** cyclophanes using $\text{Ni}(0)$ reductive homocoupling under Yamamoto conditions, providing chrysaorenes **1-Et** (49%) and **2-Et** (44%) as pale yellow solids after column chromatography. In contrast to the extremely insoluble kekulene and septulene, Et-substituted chrysaorenes dissolve in CDCl_3 reasonably well, and their sharp ^1H NMR spectra indicate that π aggregation is insignificant. Both **1-Et** and **2-Et** have improved stability in solution relative to chrysaorene but unfortunately, neither compound formed crystals suitable for structural analysis. Chrysaorenes were thus characterized in detail using one- and two-dimensional ^1H and ^{13}C NMR spectroscopy, yielding excellent correlations between experimental and GIAO-DFT shifts (see the ESI). Resonances of the inner protons of **1-Et** and **2-Et** show downfield relocations relative to the peripheral signals (Figure 1), as previously observed for kekulene^{6b} and septulene.^{7d} **1-Et** shows two sets of ethyl signals, in accord with its rigid, non-planar geometry.

1-Et and **2-Et** absorb ultraviolet light up to ca. 400 nm (Figure 1G–H). The electronic spectra of both compounds are remarkably well resolved for such large molecules, reflecting the rigidity of chrysaorene frameworks. These distinct absorption patterns indicate that, while formally homologous, **1-Et** and **2-Et** have different electronic structures. In fact, the molecular orbital diagram determined for **1-Et** shows doubly degenerate HOMO and LUMO levels, which are both non-degenerate in **2-Et** (Figure S14). According to TD-DFT calculations (Tables S3–S4), the $\text{S}_0 \rightarrow \text{S}_1$ transitions in chrysaorenes are dipole-forbidden (in analogy to kekulene^{7b}) but they are nevertheless observed in the experimental spectra because of vibronic coupling. The vibronic progression associated with the S_1 transitions is also seen in the fluorescence emission spectra of **1-Et** ($\lambda_{\text{max}} = 437 \text{ nm}$, $\Phi_{\text{F}} = 30\%$) and **2-Et** ($\lambda_{\text{max}} = 447 \text{ nm}$, $\Phi_{\text{F}} = 41\%$). The fluorescence emissions of **1-Et** and **2-Et** exhibit single exponential decays with $\tau_{\text{F}} = 4$ and 8 ns, respectively.

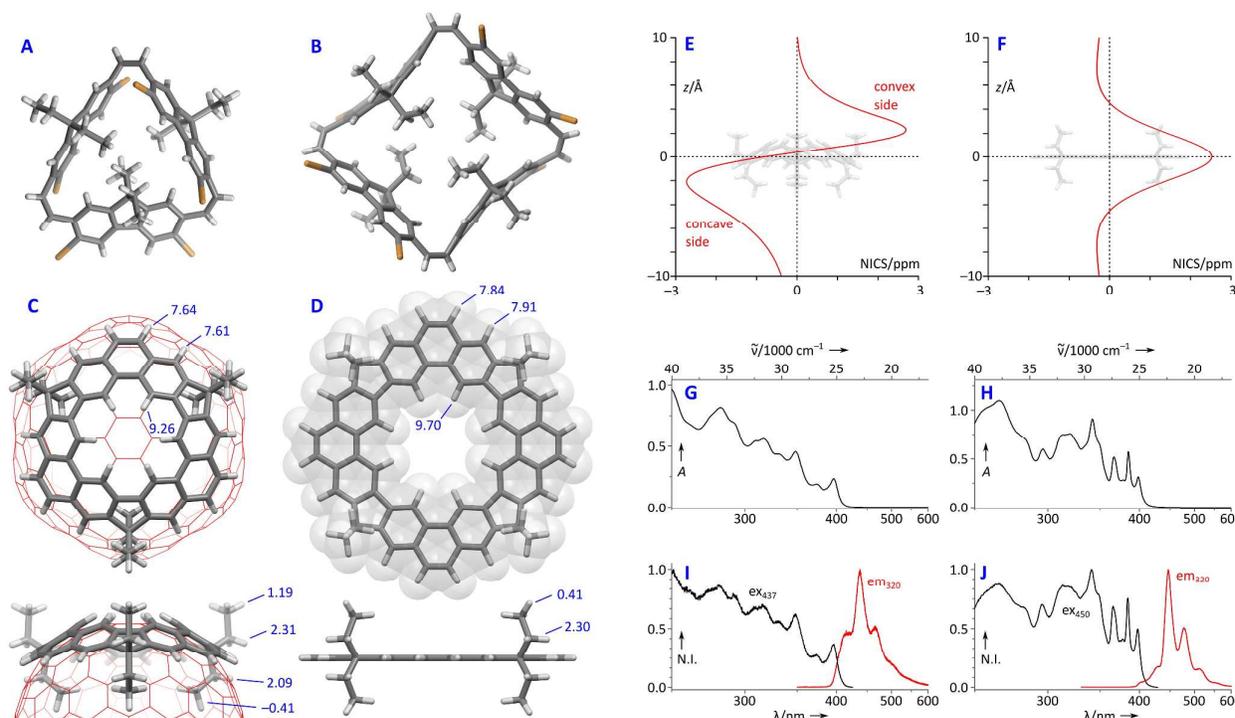


Figure 1. (A–B) Molecular geometries of 3-Et and 4-Et obtained from X-ray crystallographic analyses. (C–D) DFT-optimized geometries of 1-Et and 2-Et. The structure of 1-Et is overlaid with a DFT-optimized model of $C_{240}I_h$. 1H NMR shifts of 1-Et and 2-Et are shown in blue. (E–F) NICS scans along the symmetry axis for 1-Et and 2-Et. The models of 1-Et and 2-Et, scaled and positioned relative to the z axis, are superimposed with the plots. (G–H) Absorption spectra of 1-Et and 2-Et (295 K, dichloromethane). (I–J) Fluorescence emission (red), and excitation spectra (black) of 1-Et and 2-Et. Excitation and monitoring wavelengths are given in subscripts. N.I., normalized intensity.

The majority of reported buckybolls, including many corannulene^{3a,10a-b} and sumanene^{10c-e} derivatives, can be mapped onto the surface of buckminsterfullerene C_{60} . Several fragments of $C_{70}^{3a,10f-i}$ and C_{78}^{10j} have also been reported. **1** is not mappable onto any of the above fullerenes but it fits on the surface of $C_{240}I_h$, the still elusive higher homologue of C_{60} , postulated as a component of onion-type fullerene structures¹¹ (Figure 1C). Because of its fourfold symmetry, [4]chrysaorene will not map onto any [5,6]fullerene, although it is interestingly present in a theoretically investigated “wide-bridged” C_{60} dimer.¹² The fused framework of **2** contains the [4]cyclo(3,6)phenanthrene and [4]cyclo(3,6)fluorene substructures, neither of which has so far been synthesized. Furthermore, it provides a unique example of [8]cyclometaphenylene ([8]CMP)¹³ squeezed into a completely planar structure. In comparison, septulene, containing the smaller [7]CMP ring, has a slightly ruffled conformation.^{7d}

1 possesses several formal $[4n + 2]$ annulene circuits ($n = 4-7$), which might in principle provide “superaromatic” contributions to π -conjugation (Scheme S4). Interestingly, analogous circuits in **2** are of the $[4n]$ type ($n = 6-10$), corresponding to formal Hückel antiaromaticity. NICS(1)^{14a} scans performed for phenanthrene, 6-Et, and 2-Et show that nuclear shieldings above the C_{24} ring in the latter system (2.2 ppm at the center) are an effective superposition of shieldings induced by individual phenanthrene moieties (Figure S16). The axial shielding profile^{14b} of 2-Et (Figure 1F) is symmetric with a

maximum of 2.5 ppm at the center of the macrocycle. The analogous profile in 1-Et is remarkably different, with a well-defined shielding zone on the concave side of the bowl, and corresponds with the experimental 1H shifts of ethyl substituents. In spite of these differences, the shielding magnitudes in 1-Et and 2-Et show no significant macrocyclic di- or paratropic contributions. In terms of their magnetic properties, $[n]$ chrysaorenes are therefore best represented as unions of n weakly interacting phenanthrene π systems.

Structural consequences of fusing the fluorene units are demonstrated by bond length variations observed in the DFT geometries of 1-Et and 2-Et. In comparison with the central fluorene unit of 5-Et, rim C–C bonds in 1-Et are systematically elongated by up to 0.018 Å, whereas the hub and spoke bonds are slightly compressed (up to –0.009 Å, Table S1). In 2-Et, the overall distortion is reversed, leading to the expansion of the hub bonds. There is no structural evidence for “superaromatic” conjugation contributions in either 1-Et or 2-Et.

Homodesmotic internal strain in the bowl-shaped 1-Et, calculated relative to fused oligofluorenes 5-Et and 6-Et, is 43.0 kcal/mol (Scheme 2), lower than the value reported for unsubstituted [3]chrysaorene (53.4 kcal/mol^{8a}). For the planar 2-Et, a value of only 2.9 kcal/mol was obtained, likely corresponding to the small lateral bending of fluorenes that is needed to fit four such units into a planar cyclic structure (Figure S15). The strain increase due to homocoupling is 30.6

kcal/mol for 1-Et, well below the currently known limit of strain-inducing efficiency of the Yamamoto coupling (at least 48 kcal/mol/bond¹⁵). The negative homocoupling strain obtained for 2-Et (−6.8 kcal/mol) indicates that some energy, likely associated with the observed distortion of fluorene units in 4-Et, is actually released during the fold-in process.

In summary, we have demonstrated the synthesis of two new coronoids: the bowl-shaped [3]chrysaorene and the planar, uniquely large [4]chrysaorene, thus extending the fold-in approach to carbocyclic systems. Good solubility and stability characteristics of chrysaorenes are likely to facilitate further research on this new class of aromatic hydrocarbons. The simultaneous synthesis of two ring sizes provides the first opportunity to compare the aromatic properties of two homologous coronoids possessing formal $4n+2$ and $4n$ macrocyclic conjugation. The relevance of chrysaorenes comes from their extended carbocyclic frameworks, which can be used to develop systems with unusual electronic structure. In particular, achieving complete π conjugation in some or all of the five-membered rings is expected to bring out a range of desirable features, such as macrocyclic aromaticity, visible and near-IR absorptions, high-spin electronic states, and π complexation of transition metals. Efforts to achieve these goals are currently underway.

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