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From Fenestrindane Toward Saddle-Shaped Nanographenes Bearing a Tetracoordinate Carbon Atom

Wai-Shing Wong,[a] Chun-Fai Ng,[a] Dietmar Kuck*,[b] and Hak-Fun Chow*,[a]

Dedication ((optional))

Abstract: Two saddle-shaped polycyclic aromatic compounds **8a** and **8b** bearing an all-*cis*-[5.5.5.5]fenestrane core surrounded by an *o*,*p*,*o*,*p*,*o*,*p*,*o*,*p*-cyclooctaphenylene belt were synthesized and characterized by NMR spectroscopy and mass spectrometry. The key step featured four Scholl-type cycloheptatriene formation steps of the corresponding 1,4,9,12-tetraarylfenestrindane derivatives **7a** and **7b** bearing electron-rich substituents. The structural details of the D_{2d}-symmetrical saddle **8a** were determined by X-ray crystallography, and the photoelectronic and cyclovoltammetric properties of **8a** and **8b** were studied.

Fenestranes have been considered exotic in organic chemistry for a long time.[1] Nevertheless, they have attracted special interest owing to the presence of a quaternary, tetracoordinate carbon atom shared by all of the four rings of the centrotetracyclic framework.[2-7] Besides the fact that naturally occurring fenestranes are known and of increasing interest,[5,8] the intriguing possibility to synthesize purely organic compounds that would bear a planar tetracoordinate carbon atom with anti-Van't-Hoff-Le-Bel geometry has inspired scientists over several decades.[1,9-15] Small-ring fenestranes have been studied by experiment,[16] while fenestranes bearing a highly unsaturated π-electron periphery[11,12,13a] and fenestrane units embedded in the center of a rigidified three-dimensional carbon framework have been investigated by various theoretical approaches.[14] A number of low-strain [5.5.5.5]fenestrane hydrocarbons, such as the parent hydrocarbons **1**[17] and **2**,[18] and their four-fold benzoannelated analog **4** (fenestrindane)[19] are known, whereas the fully unsaturated congeners **3** and **5** ("fenestrindene") are not. Notably, the fenestrane motif has never been incorporated into the network of graphene sheets, as suggested in the hypothetical structure **6** (Figure 1).

Owing to the unique topography of the fenestrindane framework,[4,19a] fenestrane-based graphene sheets would adopt a highly warped profile[20,21] and suffer a strong perturbation of the extended conjugated π-electron system. Therefore, from the viewpoint of materials science, they would offer an unprecedented variation of the electronics of such chromophores. Both saturated fenestrane cores, as depicted in **6**, which would preserve the possibility of functionalization at the bridgeheads, and fully unsaturated, fenestrindene-based variants (cf. **5**) can be envisioned. In turn, it would be of high interest to elucidate the extent of planarization ("flattening") of the central carbon atom in such graphene networks.

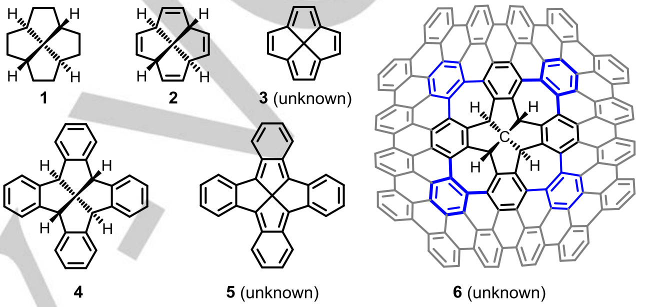

Figure 1. Known bridgehead-saturated [5.5.5.5]fenestranes **1**, **2** and **4**, yet unknown unsaturated congeners **3** and **5** ("fenestrindene") and the central motif of a hypothetical fenestrane-based graphene sheet (**6**). The colored extension in **6** emphasizes the novel four-fold bay-bridged fenestrindane framework achieved in the present work.

In the present work, we disclose the synthesis of the first fully bay-bridged fenestrindane derivatives, 8a and 8b, via a four-fold non-classical Scholl-type cycloheptatriene ring formation reaction[22] from two fenestrindanes, 7a and 7b, respectively, that bear electron-rich aryl groups at four of the eight inner (ortho-) positions of the bays (Figure 2). Compounds 8, on the one hand, can be considered as rigidified derivatives of o,p,o,p,o,p,o,p-cyclooctaphenylene 9,[23] on the other hand, due to their unique molecular geometry, they also represent important intermediates on the way to saddle-shaped fenestrane-based graphenes as well as potential building blocks for porous covalent organic frameworks.

Compounds 7 were prepared from tetramethoxy-fenestrindane 10, a key intermediate which in turn was obtained in a multistep synthesis according to our established strategy

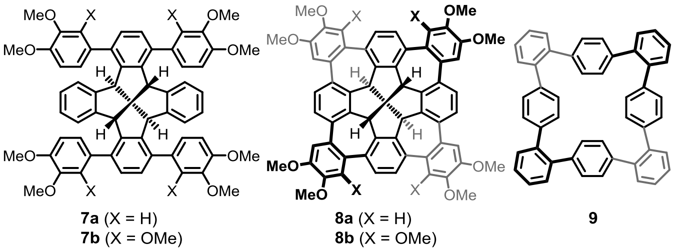

Figure 2. Fenestrindane derivatives **7**, bay-bridged fenestrindane compounds **8** and *o*,*p*,*o*,*p*,*o*,*p*,*o*,*p*-cyclooctaphenylene **9**.

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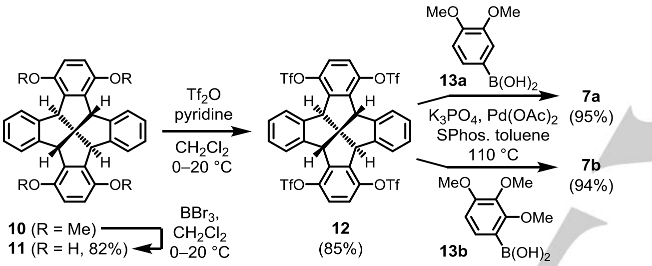
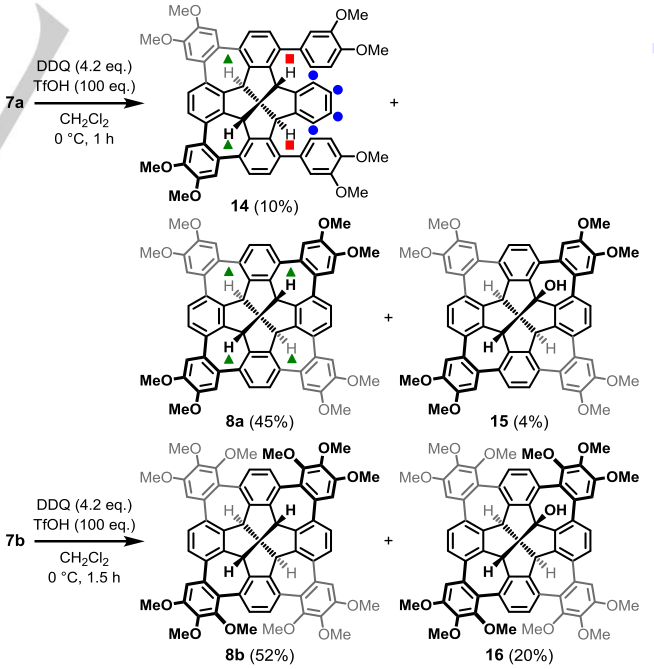
[see Supporting Information (SI) for details].[19,24] Compound **10** was then converted into the corresponding bis-hydroquinone **11** in 82% yield using an excess of BBr_3 (8 equiv.), followed by treatment of **11** with triflic anhydride to furnish the corresponding tetrakis(triflate) **12** in 85% yield (Scheme 1). Suzuki-Miyaura cross-coupling reactions of compound **12** with 3,4-dimethoxyphenylboronic acid (**13a**) and with 2,3,4-trimethoxyphenylboronic acid (**13b**) in the presence of $Pd(OAc)_2$, SPhos and K_3PO_4 then furnished the target 1,4,9,12-tetraaryl-substituted fenestrindanes **7a** and **7b** in 95 and 94% yield, respectively. The structures of all new compounds were determined by ^1H and ^{13}C NMR spectroscopy and by mass spectrometry. The structure of **7a** was further confirmed by X-ray crystallographic analysis (see Figure S11 in SI).[25] Compound **7b** showed signal broadening in both its ^1H and ^{13}C NMR spectra recorded at room temperature. This phenomenon was attributed to the restricted rotation of the 2,3,4-trimethoxyphenyl residues about the newly formed aryl-aryl bonds due to the presence of the *ortho*-methoxy groups. The signals were sharpened when the spectra were recorded at 45 °C (see SI for details).



Scheme 1. Synthesis of 1,4,9,12-tetraarylfenestrindanes **7**.

Subsequently, the tetrakis(3,4-dimethoxyphenyl)-substituted compound **7a** was treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 4.2 equiv.) in the presence of triflic acid (100 equiv.)[26] to furnish the C-shaped two-fold cyclization product **14** (10%), the four-fold cyclization product **8a** (45%) and the bridgehead-monohydroxylated four-fold cyclization product **15** (4%) after chromatography (Scheme 2). Use of a slightly excess of DDQ (4.6 equiv.) altered the product distribution to **14** (5%), **8a** (50%) and **15** (7%). In any attempts, neither products of single nor triple cyclization were observed. The three compounds were structurally elucidated by ^1H and ^{13}C NMR spectroscopy and mass spectrometry (see SI for details). The ^1H NMR spectrum of the two-fold cyclization product **14** showed two distinct singlets at δ 5.70 and 4.72 due to the two nonequivalent pairs of benzhydrylic protons (Figure 3b). The latter signal corresponds to those incorporated in the cycloheptatriene rings, in line with the previously reported upfield shift of bridgehead protons after Scholl cyclization in the TBTQ series.[22c,d] A priori, two-fold cyclization of **7a** could give rise to three possible regioisomers, yet the C-shaped heptaphenylene **14** was obtained exclusively, presumably because of the more rapid Scholl-type coupling between the two more electron-rich arene moieties formed by the first cyclization step. The ^1H NMR spectrum of **14** also showed the presence of an AA'BB' spin system (δ 6.77 and 5.95) similar to that found for the precursor molecule **7a** (δ 6.76 and 6.05), which is only consistent with the structure of this C-shaped regioisomer. Alongside with 2D ^1H-^1H ROESY and COSY techniques, the constitution of compound **14** could be established unambiguously (see SI for details). The highly symmetrical four-fold cyclization product **8a** gave ^1H and ^{13}C NMR spectra that were greatly simplified relative to **7a** (Figures 3a and 3c). In solution, **8a** may adopt either D_{2d} symmetry or it may exist as two degenerate S_4-conformers under rapid interconversion at room temperature.[4,19a,27] Hence, the four benzhydrylic protons and eight methoxy groups appeared as sharp singlets at δ 4.65 and 4.04, respectively, whereas the two different sets of aromatic protons gave rise to two singlets at δ 7.76 and 48. The unexpected monohydroxylated product **15** was unequivocally confirmed by various techniques including 2D ^1H-^1H ROESY (see SI for details). In particular, the hydroxyl proton resonance at δ 2.06 vanished upon H/D exchange with D_2O. In the ESI mass spectrum of compound **15**, the peaks at *m*/*z* 943.2865 ($[M + Na]^+$) and 903.2937 ($[M + H – H_2O]^+$) pinpointed the particularly facile loss of H_2O from the protonated molecule in the gas phase Independent experiment showed that the monohydroxylated compound **15** could be obtained in 39% yield when pure **8a** was treated with DDQ (2 equiv.) and triflic acid (100 equiv.) in CH_2Cl_2 for 2 h. Plausibly, the fully cyclized product **8a** might undergo hydride abstraction at a benzhydrylic position by the slight excess of DDQ[28] to produce a fairly stable tropylium ion which, upon aqueous workup, led to compound **15** as an oxidation side product.



Scheme 2. DDQ-mediated Scholl-type oxidative cycloheptatriene formation with 1,4,9,12-tetraarylfenestrindanes **7**.

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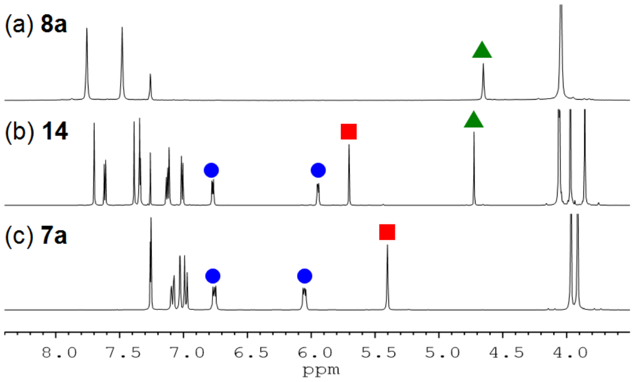

Figure 3. Stacked partial ^{1}H NMR spectra ($CDCl_3$, 22 °C) of (a) **8a** (400 MHz), (b) **14** (700 MHz), and (c) **7a** (400 MHz). The red squares and green triangles indicate the ^{1}H signals due to the benzhydrylic protons before and, respectively, after cycloheptatriene formation in the corresponding bay. The blue circles indicate the AA'BB' spin system(s) of the unreacted benzo unit(s). See Scheme 2 for signal assignments.

With the tetrakis(2,3,4-trimethoxyphenyl) analogue **7b**, four-fold cyclization proceeded smoothly to produce the desired product **8b** (52%) and the corresponding monohydroxylated derivative **16** (20%). Partially cyclized compounds were not observed in this case. The total four-fold cyclization yield of **7b** (72%) was superior to that of **7a** (49–57%) although the four additional *ortho*-methoxy groups in the former might incur torsional strain upon cyclization. It is believed that the lower oxidation potential of the trimethoxyphenyl group, as compared to that of the dimethoxyphenyl group, facilitates the oxidative cyclization of **7b**.[29] The structures of compounds **8b** and **16** were again confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see SI for details). Notably, the broad NMR signals found in the case of the precursor molecule **7b** were sharpened upon conversion into **8b** and **16** by virtue of the rigidification of the *para*-terphenyl substructures.

The saddle-shaped topography of compound **8a** was unambiguously confirmed by X-ray crystallography using a single crystal obtained from a 1,2-dichloroethane solution by slow evaporation.[25] The molecule assumes a conformation with D_{2d} molecular symmetry (Figure 4a). The depth of the saddle was found to be 3.41 ± 0.02 Å,[30] and the dihedral angles between two neighboring aromatic rings were in the range of 28.9–35.4° (Figure 4b). When compared to the parent *o*,*p*,*o*,*p*,*o*,*p*,*o*,*p*-cyclooctaphenylene **9**, which has a saddle depth of 3.74–3.97 Å and dihedral angles ranging within 33.2–65.5°,[23] compound **8a** possesses a shallower saddle structure. The C–C bond lengths between two adjacent aromatic rings in **8a** were found to be 1.48–1.51 Å, and thus typical for sp^2–sp^2 carbon–carbon single bonds. Among the six C–C–C bond angles around the central quaternary carbon, four are internal angles of the pentagons, the average of which is defined as θ. The remaining two bond angles (α and β) quantify the extent of planarization of the tetracoordinate carbon atom in a fenestrane (Figure 4a).[3,5,6] The larger the values of α and β, the more flattened is the central carbon. In **8a**, angles α and β were found to be 116.4 and 117.0°, respectively. These values were slightly larger than the corresponding bond angles of the precursor molecule **7a** (113.0, 114.2°) but were very close to those of the parent all-*cis*-fenestrindane **4** (116.4, 116.5°).[19a] Thus, the introduction of four *ortho*-phenylene units across the bays of **4** gives rise to only marginal flattening at the central quaternary carbon. As a possible consequence, the ^{13}C resonance of the central quaternary carbon shifted upfield from compound **7a** (δ 71.1) to compound **14** (δ 68.3) and to compound **8a** (δ 66.4). A similar upfield shift was found in the cyclization of tetrakis-(2,3,4-trimethoxyphenyl) compound **7b** (δ 72.3) to form compound **8b** (δ 65.4). More interestingly, the two opposite veratrole units within each moiety of structure **8a** possessed nearly orthogonal (88.9°) orientation to each other (Figure 4c),[31] suggesting that the molecule may be used to construct large-size molecular squares via tetramerization[32] or to form porous covalent organic frameworks.[33] On the other hand, the packing of molecules **8a** revealed that there is no π–π stacking interaction in the solid state (see SI for details).

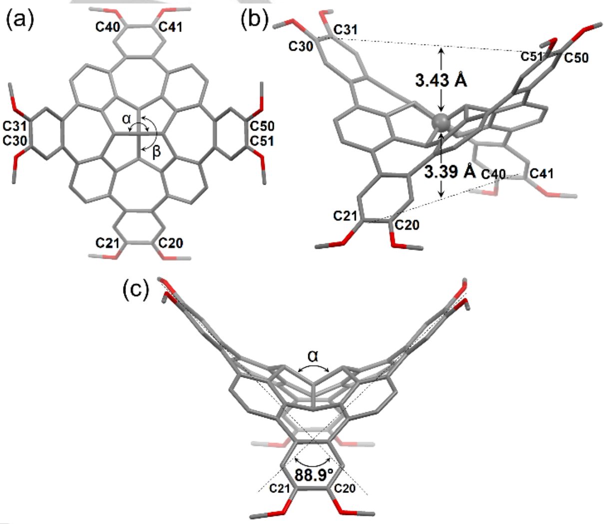

Figure 4. Crystal structure of compound **8a**: (a) top view, (b) oblique view showing the depth of the saddle, and (c) front view showing the nearly orthogonal disposition (88.9°) of two opposite veratrole moieties.

Compounds **8a** and **8b** are soluble in most organic solvents, resulting in orange solutions with weak violet fluorescence when irradiated with UV light. Their photoelectronic and cyclic voltammetric (CV) data are collected in Table 1. For the octamethoxy compound **8a**, the long-wavelength absorption edge was estimated to be at 382 nm (see SI Figure S13a), which translates into an optical gap of 3.25 eV. The value for compound **8a** is noticeably smaller than that for the doubly cyclized compound **14** (3.79 eV) and the starting material **7a** (3.94 eV). In addition, the fluorescence wavelength of **8a** (424 nm) is red shifted from those of **14** (390 nm) and of **7a** (370 nm) (see SI Figure S14a). Together with the drastic increase in fluorescence intensity accompanying cyclization, both the absorption and emission data are consistent with the more extended π–conjugation in **8a**. The CV profile of **8a** in CH_2Cl_2 exhibited one quasi-reversible oxidation wave with a half-wave oxidation potential of +0.76 V vs the ferrocene/ferrocenium

(Fc/Fc$^+$) couple. The HOMO and LUMO energies of **8a** were estimated to be −5.90 and −2.65 eV, respectively (see SI for details). In comparison to **8a**, the dodecamethoxy derivative **8b** has a similar absorption edge (371 nm, 3.33 eV) and fluorescence wavelength (416 nm) (see SI Figure S13b and S14b), and a similar half-wave oxidation potential (+0.75 V). Likewise, the HOMO and LUMO levels of compound **8b** were estimated to be −5.91 and −2.58 eV, respectively.

Table 1. Photoelectronic and cyclic voltammetric properties of compounds **8**.

Compound	8a	8b
Low-energy absorption edge, λ_{edge} (nm)	382	371
Fluorescence emission (nm)[a]	424	416
HUMO-LUMO gap (eV)[b]	3.25	3.33
Half-wave oxidation potential (V)[c]	+0.76	+0.75
First oxidation onset, E_{ox1}^{onset} (V)	+0.80	+0.81
HOMO level (eV)[d]	–5.90	–5.91
LUMO level (eV)[e]	–2.65	–2.58

[a] Excitation at 280 nm. [b] Approximated by the long-wavelength UV absorption edge by 1239.8/λ_{edge}. [c] Supporting electrolyte: 0.1 M *n*-Bu_4PF_6 in CH_2Cl_2, scan rate 50 mV/s, Fc/Fc$^+$ as reference. [d] Estimated from the onset potential of the first oxidation wave by $E_{HOMO} = -(5.10 + E_{ox1}^{onset})$ eV.[34] [e] Estimated by the HOMO level and HOMO-LUMO gap.

In summary, we reported here the synthesis of two novel saddle-shaped polycyclic aromatic compounds **8a** and **8b** based on the fenestrindane framework using a four-fold Scholl-type cycloheptatriene formation reaction. The structural features of these compounds and their optical and electronic properties were examined. With the peripheral methoxy groups being available for further functionalization and C–C cross coupling reactions, these molecules should provide access to various novel π–extended saddle-shaped nanographenes.

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Keywords: fenestrane • polyaromatic compounds • Scholl cyclization • nanographene • saddle-shaped structures

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[25] CCDC-1528880 and CCDC-1528883 contain the supplementary crystallographic data for **7a** and **8a**, respectively. Due to the presence of a large amount of disordered solvent, both structures were treated using the SQUEEZE function of PLATON to remove the electron density of the solvent molecules. In the crystal structure of **8a**, there are 1.5 molecules in the asymmetric unit. Structural parameters were extracted from the complete molecule occupying a general position, instead of the half molecule occupying a special position.

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[30] The depth of the saddle is defined as the distance between the centroid of the molecule, which happens to coincide with the central quaternary carbon, and the centroid of the four carbons defined by C20, C21, C40 and C41, or by C30, C31, C50 and C51.

[31] The angle between the two least-squares mean planes generated by C18–C23 and by C38–C43 is 88.8° and that between the two planes generated by C28–C33 and by C48–C53 is 89.0°.

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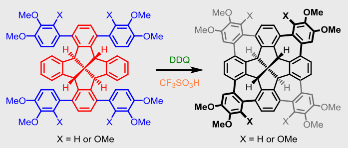

Two four-fold bay-bridged fenestrindane derivatives were prepared in good yields using a non-classical Scholl-type cyclization, paving the way to saddle-shaped nanographenes

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From Fenestrindane Toward Saddle-Shaped Nanographenes Bearing a Tetracoordinate Carbon Atom