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Soluble cycloannulated tetroxa[8]circulane derivatives: synthesis, optical and electrochemical properties, and generation of their robust cation–radical salts

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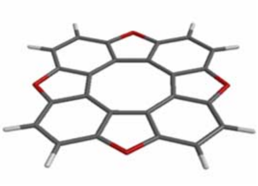
Abstract—Syntheses of soluble bicycloalkane-annulated tetraoxa[8]circulane derivatives via Lewis acid-catalyzed tetramerization of readily available cycloannulated benzoquinons is described. The ready availability of the soluble circulane derivatives allows the evaluation of their optical and electrochemical properties. These circulanes form stable (isolable) cation–radical salts upon 1-electron oxidation using antimony pentachloride and various aromatic oxidants.

Polycyclic aromatic hydrocarbons (PAH) have found widespread applications as building blocks for the preparation of materials that can hold potential usage as conductors, ferromagnets, wires, liquid crystalline materials, and in other electronic and optoelectronic devices.[1] The saddle-shaped tetraphenylene derivatives (see Structure **A**) are extensively studied for their novel conformational properties as well as for their usages as clatherate precursors.[2] Interestingly, these nonplanar polyaromatic hydrocarbons can be transformed to the corresponding planar structures (see Structure **B**) by introduction of the furan linkages, that is,

A



B

Such a planar tetraphenylene derivative (e.g. the parent tetraoxa[8]circulane, structure **B**) has been known since the early sixties, however, the potential of this planar PAH could not be readily exploited owing to its insolubility in most common organic solvents.[3] The lack of the solubility of the parent circulane is attributed to its planar structure, which allows it to pack in graphite-like stacks.

Mullen and co-workers[4] have recently demonstrated by synthesizing a variety of soluble (planar) graphitic fragments by substitution of free aromatic *p*-positions with bulky *t*-butyl groups to prevent graphite-like stacking. Moreover, Rathore et al.[5] and others[6] have recently noted that the structural modification of simple aromatic as well as polycyclic aromatic hydrocarbons with bulky bicycloalkane frameworks leads to the derivatives, which allow ready isolation of the reactive intermediates, such as the Wheland intermediates and cation–radical salts for spectral and structural characterization by X-ray crystallography.

Herein, we report the preparation of tetraoxa[8]circulane derivatives, annulated by bicyclo[2.2.2]octane and bicyclo[2.2.2]heptane frameworks, in excellent yields, from the Lewis-acid catalyzed tetramerization of readily-available cycloannulated quinones[7] **4a** and **4b** (see Scheme 1 below). These soluble bicyclo-annulated circulane derivatives allow their optical and electrochemical properties to be evaluated for the first time as well as generation of their highly robust cation–radical salts upon 1-electron oxidation using a variety of oxidants as follows.

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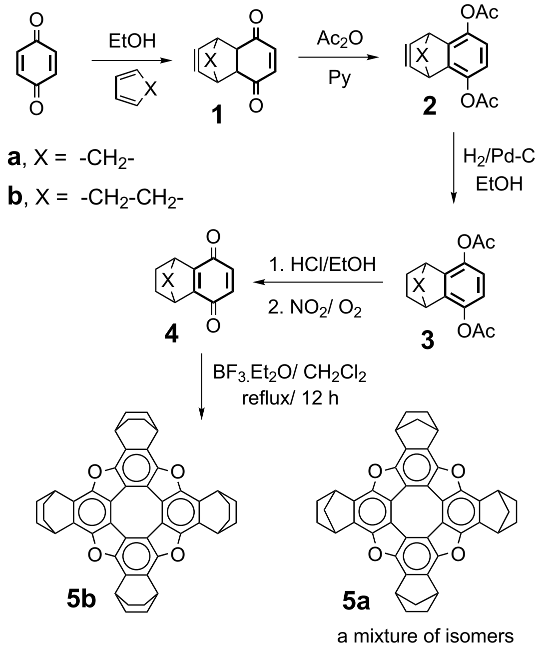


Scheme 1.

As shown in Scheme 1, the bicycloalkane-annulated quinones **4a** and **4b** were obtained by Diels–Alder cycloaddition of *p*-benzoquinone with cyclopentadiene (**a**-series) and 1,3-cyclohexadiene (**b**-series), respectively.[8] The cycloadducts (**1a**–**b**) were aromatized in the presence of acetic anhydride and pyridine and the resulting aromatic diesters (**2a**–**b**) were hydrogenated using catalytic amounts of palladium–carbon in ethyl acetate. The reduced diesters (**3a**–**b**) were then hydrolyzed in refluxing ethanol/hydrochloric acid mixture to the corresponding hydroquinones, which were in turn oxidized to the corresponding quinones (**4a**–**b**) using catalytic amounts of nitrogen dioxide in presence of air in quantitative yields.[7] The circulane derivatives **5a** and **5b** were conveniently obtained by tetramerization of cycloannulated benzoquinones **4a** and **4b**, respectively, in refluxing dichloromethane in the presence of boron-trifluoride–etherate complex as a Lewis acid catalyst, in 70% and 76% yields, respectively. The simplicity of ^{1}H and ^{13}C NMR spectra together with FAB mass spectrometric analysis confirmed the identity of the bicyclooctane-annulated circulane **5b** as a single compound.[9] However, both ^{1}H and ^{13}C NMR data[10] indicated that bicyclohepatane-annulated **5a** contained an inseparable mixture of isomers in which the methanobridges were up and down in various combinations.[11] Repeated attempts to separate the isomeric mixture of **5a** were unsuccessful and thus it was used as such.

The electronic absorption spectra of the yellow **5b** and the isomeric mixture of **5a**, obtained as dichloromethane solutions, are shown in Fig. 1a. The fine-structure in the UV–vis absorption spectra of **5a** and **5b** is typical to that observed in various planar polyaromatic hydrocarbons. Moreover, the slight red shift of the absorption maxima in the spectrum of bicycloheptane-annulated **5a** (as an isomeric mixture) as compared to the bicyclooctane-annulated **5b** as well as the larger extinction coefficient at the maximum of **5a** ($\lambda_{\max} = 268$, 279, 369, 382 nm, $\varepsilon_{382} = 73,200\ \mathrm{M^{-1}\,cm^{-1}}$) as compared to **5b** ($\lambda_{\max} = 263$, 274, 359, 377 nm, $\varepsilon_{377} = 62,300\ \mathrm{M^{-1}\,cm^{-1}}$) can be attributed to the smaller ring size of the bicycloalkane frameworks in **5a**.[12] The structured emission spectra of **5a** ($\lambda_{\max} = 507$, 541 nm) and **5b** ($\lambda_{\max} = 482$, 530 nm) recorded in benzene were of comparable intensity and they both show well-defined vibronic bands $\Delta\nu \sim 1300\ \mathrm{cm^{-1}}$ (see Fig. 1b). Moreover, keeping with the rigid structures of **5a** and **5b**, their excitation spectra were identical to their corresponding absorption spectra (compare Fig. 1a and b).

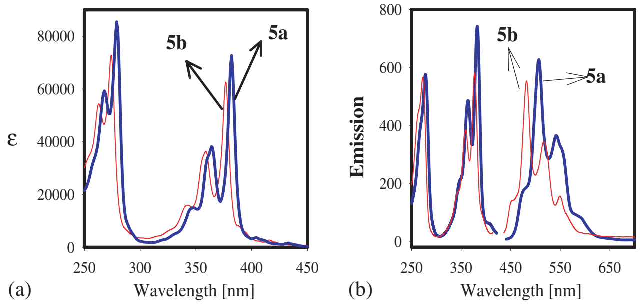


Figure 1. (a) The electronic absorption spectra of **5a** and **5b** in dichloromethane (left). (b) The excitation and emission spectra of **5a** and **5b** (as indicated) in toluene (right).

The electron donor strength of **5a** and **5b** were evaluated by electrochemical oxidation at a platinum electrode as a 2×10^{-3} M solution in chloroform containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. The cyclic voltammogram of both **5a** and **5b** in Figure 2 showed two

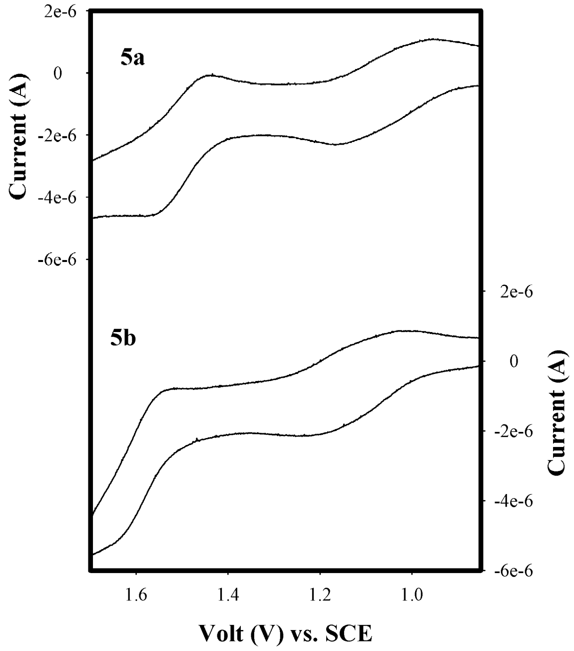
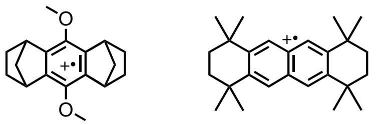


Figure 2. Cyclic voltammograms of 2 mM **5a** and **5b** (as indicated) in dichloromethane containing 0.2 M TBAPF$_6$ at a scan rate of 200 mV s^{-1} and at 22 °C.

chemically reversible oxidation waves at a potential of 1.09, 1.38, and 1.10, 1.49 V versus SCE, respectively. A quantitative evaluation of the CV peak currents of various waves in **5a** and **5b** (with added ferrocene as an internal standard) confirmed that all the waves corresponded to the removal of a single electron in their cyclic voltammograms. The similarity of the oxidation potentials for both **5a** and **5b** suggests that the redox properties are not significantly influenced by the size of bicycloalkane bridges.[13]

The reversibility of the cyclic voltammograms of **5a** and **5b** encouraged us to examine the stability of the cation radicals derived from these cycloannulated-circulane derivatives by 1-electron oxidation as follows. In order to examine the spectral characteristics of the cation radicals of **5a** and **5b**, they were generated using two stable organic oxidants **MA**$^{+\cdot}$ ($\lambda_{max} = 518$ nm, $\varepsilon_{518} = 7300\ \mathrm{M^{-1}\,cm^{-1}}$)[5a] and **NAP**$^{+\cdot}$ ($\lambda_{max} = 672$ nm, $\varepsilon_{672} = 9300\ \mathrm{M^{-1}\,cm^{-1}}$)[14] with reversible reduction potentials that differ by 230 mV (Fig. 3).



MA$^{+\cdot}$ **NAP**$^{+\cdot}$

E^{o}_{red} 1.11 1.34 (V *vs.* SCE)

Thus, Figure 3A shows the spectral changes attendant upon the reduction of 1.6×10^{-4} M **NAP**$^{+\cdot}$ $\mathrm{SbCl_6^-}$ ($\lambda_{max} = 672$ nm) by an incremental addition of 2.7×10^{-3} M **5a** to its cation radical **5a**$^{+\cdot}$ in dichloromethane at 22 °C. The presence of well-defined isosbestic points at $\lambda_{max} = 558$, 588, and 714 nm in Figure 3A established the clean electron transfer from **5a** to **NAP**$^{+\cdot}$. Furthermore, a plot of the depletion of **NAP**$^{+\cdot}$ (i.e. decrease of the absorbance at 672 nm) and formation of **5a**$^{+\cdot}$ (i.e. increase in the absorbance at 532 nm) against the increments of added **5a** (Fig. 3B), established that **NAP**$^{+\cdot}$ was completely consumed after the addition of 1 equiv of **5a**; and the resulting highly-structured absorption spectrum of **5a**$^{+\cdot}$ [$\lambda_{max} = 493$, 531, 593, 628, and a broad band extending beyond 1100 nm, $\varepsilon_{531} = 10,800 \pm 500\ \mathrm{M^{-1}\,cm^{-1}}$] remained unchanged upon further addition of neutral **5a** (i.e. Eq. 1).

$$\mathbf{NAP}^{+\cdot} + \mathbf{5a} \rightarrow \mathbf{5a}^{+\cdot} + \mathbf{NAP} \tag{1}$$

A similar redox titration of **NAP**$^{+\cdot}$ cation radical with neutral **5b** yielded **5b**$^{+\cdot}$ [$\lambda_{max} = 492$, 532, 584, 619, and a broad band extending beyond 1100 nm, $\varepsilon_{532} = 11,000 \pm 400\ \mathrm{M^{-1}\,cm^{-1}}$] quantitatively. [It is noteworthy that the absorption spectrum of cation radicals **5a**$^{+\cdot}$ and **5b**$^{+\cdot}$ (see Fig. 3C) obtained above were identical to that obtained by an oxidation of **5a** and **5b** using either **MA**$^{+\cdot}$ $\mathrm{SbCl_6^-}$ or an equivalent electrochemical method.[15]]

It is noteworthy that the solutions **5a**$^{+\cdot}$ and **5b**$^{+\cdot}$ obtained above are highly persistent at room temperature and did not show any decomposition during a 24 h period at 22 °C. The high stability of these cation radical salts allowed their isolation as microcrystalline powders by a treatment of a solution of **5a** or **5b** with $\mathrm{SbCl_5}$ in anhydrous dichloromethane at −20 °C followed by a precipitation using anhydrous ether, in nearly quantitative yield, according to the stoichiometry in Eq. 2.[15]

$$2\ \mathbf{5b} + \mathbf{3}\ \mathrm{SbCl_5} \rightarrow 2[\mathbf{5b}^{+\cdot}\mathrm{SbCl_6^-}] + \mathrm{SbCl_3} \tag{2}$$

The purity of the hexachloroantimonate salts of **5a**$^{+\cdot}$ and **5b**$^{+\cdot}$ were determined by iodometric titrations[15] and was found to be of greater than 99% purity. The identity of cation radicals **5a**$^{+\cdot}$ and **5b**$^{+\cdot}$ was further confirmed by the oxidation of a solution of cycloannulated cyclooctatetraene[16] (**COT**, $E_{red} = 0.8$ V vs SCE) with 1 equiv of [**5a**$^{+\cdot}$ $\mathrm{SbCl_6^-}$] or [**5b**$^{+\cdot}$ $\mathrm{SbCl_6^-}$] in dichloromethane to a emerald green cation radical **COT**$^{+\cdot}$ ($\lambda_{max} = 442$, 745 nm, $\varepsilon_{745} = 4600\ \mathrm{M^{-1}\,cm^{-1}}$)[16] in quantitative yield, as determined by the UV–vis spectral analysis (Eq. 3).

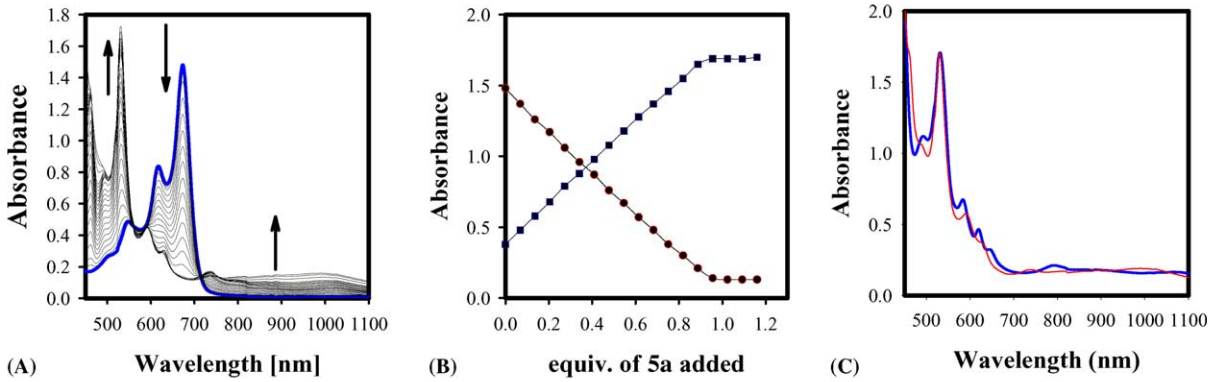
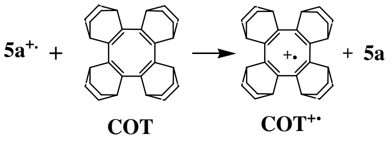


Figure 3. (A) Spectral changes attendant upon the reduction of 1.6×10^{-4} M naphthalene cation radical **NAP**$^{+\cdot}$ (thick line) by incremental addition of 2.7×10^{-3} M **5a** to its cation radical **5a**$^{+\cdot}$ in dichloromethane at 22 °C. (B) A plot of depletion of absorbance (data from panel A) of **NAP**$^{+\cdot}$ (circles, monitored at 672 nm) and an increase of the absorbance of **5a**$^{+\cdot}$ (diamonds, monitored at 532 nm) against the equivalent of added **5a** showed a complete consumption of **NAP**$^{+\cdot}$ after addition of 1 equiv of **5a**. (C) UV–vis absorption spectra of cation radicals **5a**$^{+\cdot}$ (thick line) and **5b**$^{+\cdot}$ (thin line) in dichloromethane at 22 °C.



(3)

In a similar vein, a variety of aromatic and olefinic donors such as octamethylbiphenylene, octamethylanthracene, and tetraanisylethylene were quantitatively oxidized to their brightly colored cation radicals[14,16] using dichloromethane solutions of either $[\mathbf{5a}^{+\cdot}\ \mathrm{SbCl}_6^-]$ or $[\mathbf{5b}^{+\cdot}\ \mathrm{SbCl}_6^-]$, according to the stoichiometry in Eq. 3. [Note that our repeated attempts to obtain the single crystals of the cation radical salt of bicyclooctane-annulated **5b** thus far have been unsuccessful.]

In summary, we have developed an efficient synthesis of soluble circulane derivatives from readily available precursors and have shown that their stable cation–radical salts can be obtained in pure form. We are presently attempting the crystallization of $\mathbf{5b}^{+\cdot}$ with different donors (to obtain mixed-valence salts) as well as different counter anions to obtain single crystals for X-ray crystallography and for the study of their solid-state properties.

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9. Compound **5b**: Yellow solid, mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 1.67 (d, 16H), 2.03 (d, 16H), 3.96 (s, 8H); ^{13}C NMR δ 26.93, 28.72, 114.51, 126.60, 147.95. FAB Mass: *m*/*z* 680.8 (M^+), 680.8 calcd for $C_{48}H_{40}O_4$. Anal. Calcd for $C_{48}H_{40}O_4$: C, 84.68; H, 5.92. Found: C, 84.52; H, 5.78.
10. Compound **5a**: Yellow solid, mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (m, 8H), 1.79 (m, 4H), 2.02 (m, 4H), 2.13 (m. 8H), 4.10 (br s, 8H); ^{13}C NMR d 27.84, 41.52, 50.57, 115. 68, 130.04, 146.90. (Note that in the ^{13}C spectrum of **5a** all signals appear to be singlets, however they are consisted of multiple peaks as can be seen upon expansion of the spectrum.[11]) FAB Mass: *m*/*z* 624.7 (M^+), 624.7 calcd for $C_{44}H_{32}O_4$. Anal. Calcd for $C_{44}H_{32}O_4$: C, 84.59; H, 5.16. Found: C, 84.32; H, 5.04.
11. Note that the four different isomers of **5a** are possible.
12. The annulation of benzene by bicycloalkane rings induces a significant bond alternation, for example, see: Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.
13. It is noteworthy that the electron-donor properties of various *tris*-annulated benzenes were singularly constant within ±30 mV irrespective of the ring size of the bicycloalkane annulation; see: Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012.
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