Antiaromaticity

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Antiaromatic Supramolecules: F···S, F···Se, and F···π Intermolecular Interactions in 32π Expanded Isophlorins**

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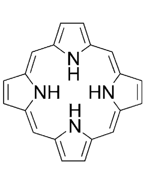
Dedicated to Professor T. K. Chandrashekar

Aromaticity[1] and antiaromaticity[2] are intriguing offshoots of π delocalization in cyclic conjugated systems. Their electronic effects and structural features are interdependent and crucial to conjugated macrocycles. The 18π porphyrin and 20π isophlorin (**1**)[3,4] are striking examples of cyclic conjugated systems with structural features akin to annulenes,[1] and have contrasting ring current effects. $4n\pi$ macrocycles can react quickly to lose their antiaromatic character.[5] The isophlorin/porphyrin redox couple further illustrates the unstable nature of isophlorin relative to porphyrin under ambient conditions.[3] Similar to the isophlorin π framework, the inherently antiaromatic tetraepoxy annulenes[6] are susceptible to oxidation/reduction to form the corresponding aromatic macrocyclic ions. Their large ring size induces structural flexibility leading to inseparable conformational isomers. Interestingly, steric hindrance favor macrocycles to undergo structure-induced loss of π delocalization.[7] Giant porphyrinoids are well studied examples for macrocycles which adopt figure-eight conformations.[8] Such nonplanar cyclic conjugated systems lack ring current effects and are considered to be nonaromatic in nature. Relative to aromatic systems, the experimental evidence reported for antiaromaticity is found to be far less than satisfactory. There are very limited reports to bridge theoretical predictions with experimental data, particularly for large antiaromatic systems.[9] In this context, the synthesis of stable quintessential planar $4n$ π molecules is crucial not only to understand the electronic effects of π conjugation but also imperative to the development of novel materials for applications in molecular electronics.



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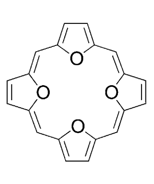

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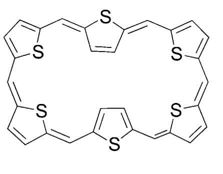

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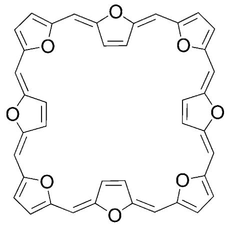

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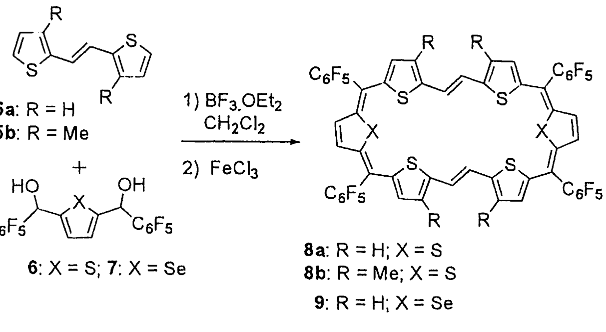
Expanding the π framework of either **1** or the modified isophlorin **2** is an attractive strategy for generating a variety of expanded isophlorins (**3** and **4**, respectively).[10] Its effective conjugation and rigid structural skeleton affords a unique opportunity to explore the chemistry of antiaromatic molecules. But the synthesis of stable antiaromatic isophlorinoids is hindered by the inherent unstable nature of $4n\pi$ systems.[10] Amongst a few isophlorins known so far,[11] the synthetic strategy employed for **2**[11d] is probably the simplest to obtain stable antiaromatic macrocycles from easy-to-make precursors. Adopting a similar synthetic strategy, with modified precursors, we describe the syntheses and structural features of novel and stable 32π vinylogous expanded isophlorins which display unprecedented short F···X (X = π/S/Se) and π–π intermolecular contacts for antiaromatic systems.

Replacing two methine carbon bridges in **3** by an equal number of ethylene bridges can convert a $(4n+2)\pi$ system into a $4n\pi$ system. McMurry coupling is widely used to couple dialdehydes of thiophene oligomers into macrocycles[12] with ethylene bridges. We adopted a modified Rothemund-type synthesis,[13] (Scheme 1), wherein diols of five-membered heterocycles were condensed with bis(thiophene)s under



Scheme 1. Synthesis of vinylogous expanded isophlorins **8a**,**b** and **9**.

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dilute conditions. (*E*)-1,2-Dithienylethylene (**5a**) was reacted with either the thiophene diol **6** or the selenophene diol **7** under acidic conditions with subsequent oxidation (see the Supporting Information). The reaction mixture was subjected to column chromatography using dichloromethane and hexanes (1:20) to obtain the ethylene bridged expanded isophlorins **8a** and **9** as brownish-yellow solutions. Even the β-methyl-substituted (*E*)-1,2-dithienylethylene **5b** afforded a similar product, **8b**, when reacted with **6** under similar reaction conditions.

Along with **8a**,**b** and **9**, trace amounts of larger macrocycles were detected by MALDI-TOF mass spectrum analysis of the reaction mixture. High-resolution mass spectroscopy confirmed the composition of **8a**,**b** and **9** (see the Supporting Information). The molecular structure was unambiguously determined from single-crystal X-ray diffraction studies (Figure 1). Good quality single crystals were grown from suitable solvents.[14] **8a**,**b** exhibit a planar structure with the sulfur atoms of all the thiophenes pointing towards the center of the macrocycle. The macrocycles adopt a rectangular shape because of the lengthy bis(thiophene) units. Both the ethylene bridges in these macrocycles sustain *E* conformation similar to that of the precursors **5a**,**b**. A comparison of the carbon–carbon (C-C) bond length in the precursors **5a**,**b** and their corresponding macrocycles substantiated the delocalization of π electrons in the cyclic systems. The C_β-C_β bond length of 1.46 Å in **5a** is reduced to 1.39 Å in the hexathiophene **8a**. The bonds connecting the two thiophene units also show a decrease in the bond lengths upon cyclization. Similar changes in bond lengths are also observed for **8b** and **9**. The two pairs of diagonally opposite pentafluorophenyl rings form a dihedral angle of 78° and 67° with the plane of the macrocycle defined by the eight carbon atoms which connect the six thiophene rings.

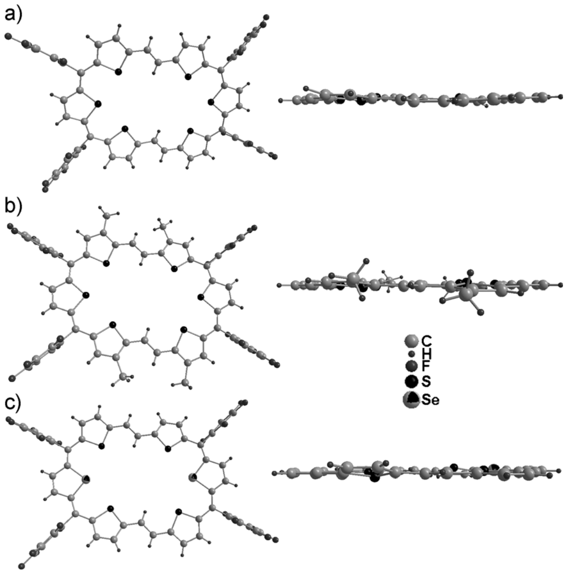

Figure 1. Molecular structure of a) **8a**, b) **8b**, and c) **9**. Both the top view and side view of each compound are shown. The solvent molecules and the pentafluorophenyl rings (in the side view) are omitted for clarity.

In the crystal packing, the cavity of each macrocycle is sandwiched by the near-perpendicular orientation of the pentafluorophenyl rings from two other macrocycles, thus enforcing the *ortho*- and *meta*-fluorine atoms to be in close proximity to the cavity of the macrocycle. These four fluorines are involved in weak noncovalent interactions (two bifurcated hydrogen bonds per hydrogen; 2.53 Å and 138°; 2.6 Å and 147°) with the hydrogen atoms, on the ethylene bridge, pointing towards the center of the macrocycle. At the same time a distance of 3.11 Å and 3.24 Å has been observed for F···S contacts[15] for the *ortho*- and *meta*-fluorine atoms, respectively. These observations lead to four interesting scenarios: a) for the first time, either in porphyrinoids or isophlorinoids, intermolecular noncovalent interactions between two macrocycles are observed without hydrogen atoms; b) the heteroatoms from the core of the macrocycle are directly involved in the intermolecular contacts; c) the four fluorines are found within a distance of just 1.5 Å (above and below) from the mean macrocyclic plane, thus suggesting the possibility of F···π interactions[16] (Figure 2); d) offset-type π stacking between two macrocycles, which share the F···S contacts, are observed in the crystal packing of **8a**. The plane formed by the two thiophene rings adjacent to pentafluorophenyl ring (involved in F···S interactions) was found to overlap with a similar plane from another macrocycle with an interplanar distance of 3.6 Å. This distance is very similar to the value expected for offset-type π stacking in aromatic molecules.

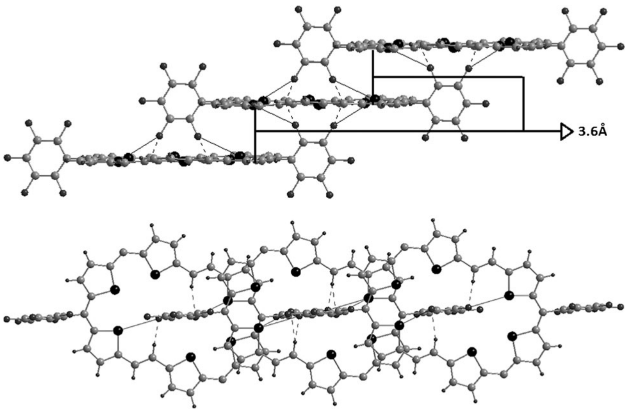

Figure 2. Side view (top) and top view (below) of the intermolecular F···S (grey lines), C–H···F (dotted lines), F···π, and π–π contacts in **8a**. Solvent molecules and pentafluorophenyl rings not involved in the interactions are omitted for clarity.

8b and **9** also exhibit noncovalent contacts similar to those observed for **8a** (Table 1). Further analysis of the crystal packing in **8b** revealed C_{sp^2}-F···H-C_{sp^3} hydrogen bonds (2.57 Å, 160°) involving the methyl substituents on the thiophene rings and the pentafluorophenyl rings which are not involved in F···S contacts (Figure 3). In **9**, F···Se contacts have been observed for selenium and fluoroarene.[17] The sum of the van der Waals radii of F and Se add up to 3.37 Å, and

Table 1: Intermolecular noncovalent contacts. All values given in Å.

Macrocycle	F⋯X	F⋯π	π–π
8a	X = S (3.11, 3.24)	1.5	3.6
8b	X = S (2.98)	1.5	3.6
9	X = S (2.99) X = Se (3.3)	1.35	3.6

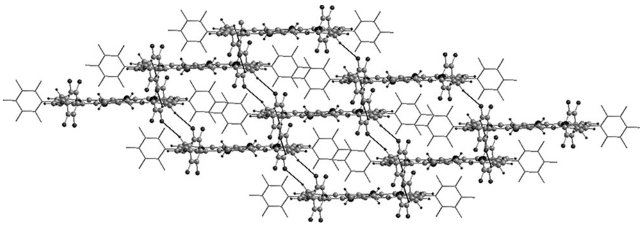

Figure 3. Thick black lines indicate the C_{sp^2}-F⋯H-C_{sp^3} intermolecular hydrogen bonds in **8b**. The wire framework represent pentafluorophenyl rings involved in F⋯π interactions. Solvent molecules are omitted for clarity.

the distance between these two atoms in **9** does not exceed this value. Both **8b** and **9** display similar π–π interactions with an interplanar distance of 3.6 Å in the solid state. We presume that these are the first examples for π–π interactions in planar 4*n*π macrocycles. Since it is known that fluorine[18] can change the type of interactions in molecular crystals, we embarked upon the synthesis of phenyl-substituted vinylogous expanded isophlorins. Unlike the pentafluorophenyl derivatives of **8a**,**b** and **9**, their analogous phenyl-substituted macrocycles were found to be unstable and underwent additional oxidation at the ethylene bridge carbon atoms.

The above observations encouraged us to relook into the packing diagram of the molecular structures of modified isophlorins and expanded isophlorins (**2**–**4**) which we had reported earlier,[10d–e,11a] for possible F⋯π and F⋯S interactions (see the Supporting Information). As expected, in the modified isophlorin **2** two flourines, one above and one below the mean plane of macrocycle (defined by the meso-carbon atoms), are found at a distance of 2.64 Å. But those fluorines are not involved in any significant intermolecular C−H⋯F hydrogen bonds with the protons within the core of the macrocycle. In a similar fashion four flourines, two above and below the plane of the macrocycle **3**, are found at a distance of 1.87 Å and 2.32 Å. The distance between fluorine and the mean plane of the macrocycle in F⋯π contacts are found to vary from 2.06 Å to 2.97 Å in **4**. Even though these values are well within the range described for F⋯π interactions observed in molecular crystals,[16] they are not as short as those observed for vinylogous expanded isophlorins.

All three macrocycles, **8a**,**b** and **9**, formally account for 32π electrons along the conjugated pathway and are hence considered to be Hückel-type antiaromatic systems. The observation of only four signals in the ^{1}H NMR spectrum (298 K) of **8a**, indicated a highly symmetrical structure for the macrocycle in solution. The protons of the thiophene rings, connected by ethylene carbon atoms, resonate as two doublets at $\delta = 5.78$ and 5.29 ppm and correspond to four protons each. The four protons of the other thiophenes resonate as a singlet at $\delta = 5.15$ ppm. Compared to the chemical shift values in unsubstituted thiophenes, the protons of the macrocycle exhibit a marked upfield shift which can be attributed to paratropic ring current effects as expected for 4*n*π systems. The upfield shifts resulting from ring current effects also validates the planar structure of the macrocycle in solution, as well as that in the analysis of the solid-state structure. The protons on the carbon atoms of the ethylene bridge resonate as a broad singlet at $\delta = 8.4$ ppm. Ideally they should have resonated as two different signals, with ring current effects distinguishing the protons inside and outside the macrocycle. We suspected solution-state dynamics involving fast flipping of the two carbon atoms result in a time averaged spectrum. Upon reducing the temperature to 175 K, the broad signal at $\delta = 8.4$ ppm (298 K) split into two doublets at $\delta = 12.83$ and 5.37 ppm, and the rest of the signals also doubled thus indicating a stable conformation of the macrocycle. A difference of 7.5 ppm between these two peaks ascertained the paratropic ring current effect for the 32π system. Furthermore, the calculated coupling constant of 16 Hz, from ^{1}H-^{1}H COSY spectra, for the ethylene bridged protons confirmed the *E* conformation of the macrocycle in the solution state. The compound **9** also exhibits ^{1}H NMR spectrum similar to that of **8a**. A broad singlet at $\delta =$ 8.57 ppm corresponding to four protons of the ethylene bridge, two doublets at $\delta = 6.11$ and 5.76 ppm corresponding to two sets of four protons for the thiophene rings, and a singlet at $\delta = 5.63$ ppm for the selenophene protons were observed. Also, **8b** shows a symmetrical spectrum with three singlets between $\delta = 8.34$ and 5.11 ppm corresponding to protons of the thiophene. The β-methyl protons were found to resonate as a singlet at $\delta = 1.53$ ppm. Both **8b** and **9** show temperature-dependent ^{1}H NMR spectra akin to **8a**.

Additional support for the antiaromatic character of these macrocycles was obtained by computing the nucleus-independent chemical shift (NICS)[19] values by employing Gaussian 03.[20] NICS is a well-accepted index for quantitative evaluation of antiaromaticity or aromaticity in cyclic conjugated systems. The computed NICS(0) values for the hexathiophenes **8a**,**b** were found to be $\delta = 11.8$ and 11.99 ppm, while a value of $\delta = 10.98$ ppm was obtained for **9**. These large NICS values are in complete agreement with Hückel's 4*n*π-electron rules for planar, cyclic, π-conjugated systems and are in line with the experimental results obtained from ^{1}H NMR spectroscopy.

As a result of the extended conjugation, they form dark-brown solutions in organic solvents and exhibit absorptions in the visible region. The expansion of the delocalized π-electron network is well demonstrated by the large red-shift absorptions in comparison to the 20π-isophlorin derivatives.[10] The hexathia expanded isophlorin **8a** was found to have an intense absorptions at $\lambda = 495$ ($\varepsilon = 11 \times 10^4$) and 446 nm ($10 \times 10^4$), while **8b** was found to have less-intense absorptions at $\lambda = 494$ and 447 nm. The selenium derivative **9** shows intense absorptions at $\lambda = 485$ (13×10^4) and 445 nm (12×10^4). Interestingly, these relatively small macrocycles have much more intense and red-shifted absorptions than the giant cyclo[*n*]thiophenes.[12] Antiaromatic macrocycles are known to undergo redox chemistry in the presence of common oxidizing and reducing agents, but **8a**,**b** and **9** do not show any change in absorption spectra upon addition of DDQ (DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) or $NaBH_4$, thus conforming the stable nature of the 32π systems. Typical of antiaromatic systems, a low-intensity broad absorption is observed in the region between $\lambda = 600$ and 900 nm. Accordingly, DFT calculations also suggested a HOMO–LUMO gap of 1.41 eV for **8a**, thus corresponding to $\lambda = 880$ nm in the electromagnetic spectrum.[9]

In summary, we have described the synthesis of the novel 32π antiaromatic expanded isophlorinoids **8a**,**b** and **9**, which display unprecedented intermolecular interactions. Significant paratropic ring current effects in the ^1H NMR spectrum confirmed the antiaromatic nature of these molecules. They demonstrate identical features for F···X (X = S/Se/π), C−H···F, and π–π intermolecular interactions in the solid state, irrespective of the substituents within the core or on the periphery of the macrocycle. The multiple F···π interactions are extremely short and strongly indicate its decisive role in the crystal packing. This work substantiates that noncovalent interactions in antiaromatic systems can be as similar to those observed for aromatic molecules. In comparison to the earlier reported modified isophlorins and their expanded derivatives, **2**–**4**, the cavity sizes of **8a**,**b** and **9** are appropriate enough to accommodate two fluorines on either side of the molecular plane. These findings clearly suggest that size of macrocyclic cavity, planarity, and the role of substituents play a vital role in F···X intermolecular interactions.

Experimental Section

General synthetic procedure: An equimolar concentration of **5a**,**b** and the diol (**6** or **7**) were dissolved in 100 mL dichloromethane and degassed with nitrogen for ten minutes. A catalytic amount of boron trifluoride diethyl etherate was then added in the dark and the resulting solution was stirred for 1 h. After adding five equivalents of anhydrous $FeCl_3$, the solution was exposed to the air and stirred for an additional 2 h. A few drops of triethylamine were then added and the reaction mixture passed through a short basic alumina column. This mixture was further separated by silica gel column chromatography by using CH_2Cl_2/petroleum ether as eluent.

8a: **5a** (192 mg, 1 mmol) and **6** (476 mg, 1 mmol) were reacted in presence of $BF_3·OEt_2$, (0.13 mL, 1 mmol), as described above to yield **8a** in 4% yield. ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 8.4$(s, 4H), 5.78 (d, $J = 5.0$ Hz, 4H), 5.29 (d, $J = 5.0$ Hz, 4H), 5.15 ppm (s, 4H). ^1H NMR (500 MHz, $(CD_3)_2CO$, 175 K): $\delta = 12.83$ (d, 2H, 16 Hz), 5.98 (d, 2H, 4 Hz), 5.60–5.56 (m, 6H), 5.51 (d, 2H, 4 Hz), 5.42 (d, 2H, 4 Hz), 5.37 ppm (d, 2H, 16 Hz). UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ $L\,mol^{-1}cm^{-1} = 495$ (112000) and 446 (109000). HRMS *m/z*: calcd. For $C_{56}H_{16}F_{20}S_6$: 1259.9258; Observed: 1259.9291 (100.0%) M^+.

8b: **5b** (220 mg, 1 mmol) and **6** (476 mg, 1 mmol) were reacted, in presence of $BF_3·OEt_2$, (0.13 mL, 1 mmol), as described above to yield **8b** in 6% yield. ^1HNMR (400 MHz, $CDCl_3$, 298 K): $\delta = 8.34$ (s, 4H), 5.11 (s, 8H), 1.53 ppm (s, 12H). UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ $L\,mol^{-1}cm^{-1} = 494$ (67000) and 447 (59100). HRMS *m/z* calcd. for $C_{60}H_{24}F_{20}S_6$:1315.9883; Observed 1315.9863(100.0%).

9: **5a** (192 mg, 1 mmol) and **7** (523 mg, 1 mmol) were reacted, in presence of $BF_3·OEt_2$, (0.13 mL, 1 mmol), as described above to yield **9** in 2.5% yield. ^1H NMR (400 MHz, $[D_8]$THF, 298 K): $\delta = 8.50$ (s, 4H), 6.05 (d, $J = 4.0$ Hz, 4H), 5. 62 (d, $J = 4.0$ Hz, 4H), 5.47 ppm (s, 4H). UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ $L\,mol^{-1}cm^{-1} = 485$ (131000) and 445 (121000): HRMS *m/z* calcd. for $C_{56}H_{16}F_{20}S_4Se_2 = 1355.8146$: Observed = 1355.8141 (100%).

The Supporting Information detailing, characterization, intermolecular interactions, and coordinates for the DFT optimized structures for this article is available on the WWW under http://www.angewandte.org.

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[14] a) Crystal data for **8a**: $C_{74}H_{58}F_{20}S_6$ ($M_r = 1519.62$), monoclinic, space group *P21/c* (No.14), $a = 10.695(2)$, $b = 30.975(6)$, $c = 10.070(2)$ Å, $\beta = 98.003(4)°$, $V = 3303.5(11)$ Å^3, $Z = 2$, $\rho_{calcd} =$

$1.528\ \mathrm{g\,cm^{-3}}$, $T = 100$ K, R_{int} (all data) = 0.0609, R_1 (all data) = 0.084, R_{W} (all data) = 0.1997, GOF = 1.12. b) Crystal data for **8b**: $C_{61}H_{24}Cl_5F_{20}S_6$ ($M_r = 1506.47$), monoclinic, space group $P21/n$, $a = 9.564(7)$, $b = 11.231(9)$, $c = 30.12(2)$ Å, $\beta = 94.723(14)°$, $V = 3224(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.552\ \mathrm{g\,cm^{-3}}$, $T = 100$ K, R_{int} (all data) = 0.0954, R_1(all data) = 0.0694, R_{W} (all data) = 0.2120, GOF = 1.281. c) Crystal data for **9**: $C_{56}H_{16}F_{20}S_4Se_2$, ($M_r = 1354.85$), monoclinic, space group $P21/c$, $a = 10.652(3)$, $b = 9.675(3)$, $c = 24.894(6)$ Å, $\beta = 99.151(5)°$, $V = 2532.9(12)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.776\ \mathrm{g\,cm^{-3}}$, $T = 150$ K, R_{int} (all data) = 0.0562, R_1 (all data) = 0.0610, R_{W} (all data) = 0.1516, GOF = 1.286. CCDC 878689 (**8a**), 878690 (**8b**), and 878691 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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