

Azatrioxa[8]circulenes: Planar Anti-Aromatic Cyclooctatetraenes

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Abstract: We describe herein the first synthesis of a new class of anti-aromatic planar cyclooctatetraenes: the azatrioxa[8]circulenes. This was achieved by treating a suitably functionalised 3,6-dihydroxycarbazole with 1,4-benzoquinones or a 1,4-naphthoquinone. We fully characterised the azatrioxa[8]circulenes by using optical, electrochemi-

cal and computational techniques as well as by single-crystal X-ray crystallography. The results of a computational study (NICS) suggest that the central planar cyclooctatetraene is anti-aromatic when the molecules are in neutral or oxidised states (2+), and that the corresponding dianions are aromatic. We discuss the aromatic/anti-aromatic nature of the planar cyclooctatetraenes and compare them with the isoelectronic tetraoxa[8]circulenes.

Keywords: aromaticity • fluorescence • heterocycles • polycycles

Introduction

When benzoquinone is treated with strong acid it oligomerises to give a mixture of linear, branched and cyclic benzo-furan structures.^[1] A minor component of this mixture is the cyclisation product obtained by condensation of four molecules of benzoquinone: tetraoxa[8]circulene (**1**, R = H; Figure 1a).^[2] The yield of this cyclisation product is significantly improved by substituting one side of the benzoquinone with either two alkyl substituents or one *tert*-butyl substituent, or by using naphthoquinone.^[2a,3] When analysing the reaction mixture of this polymerisation/tetramerisation reaction with benzoquinone or naphthoquinone, Högberg showed that an important intermediate was 3,6-dihydroxydibenzofuran (Figure 1a).^[4] When 3,6-dihydroxydibenzofuran was isolated and allowed to react with a further 2 equiv of benzoquinone or naphthoquinone, it yielded the tetraoxa[8]circulenes in good yields (**1** and **2**).^[5] We have recently shown that a statistical

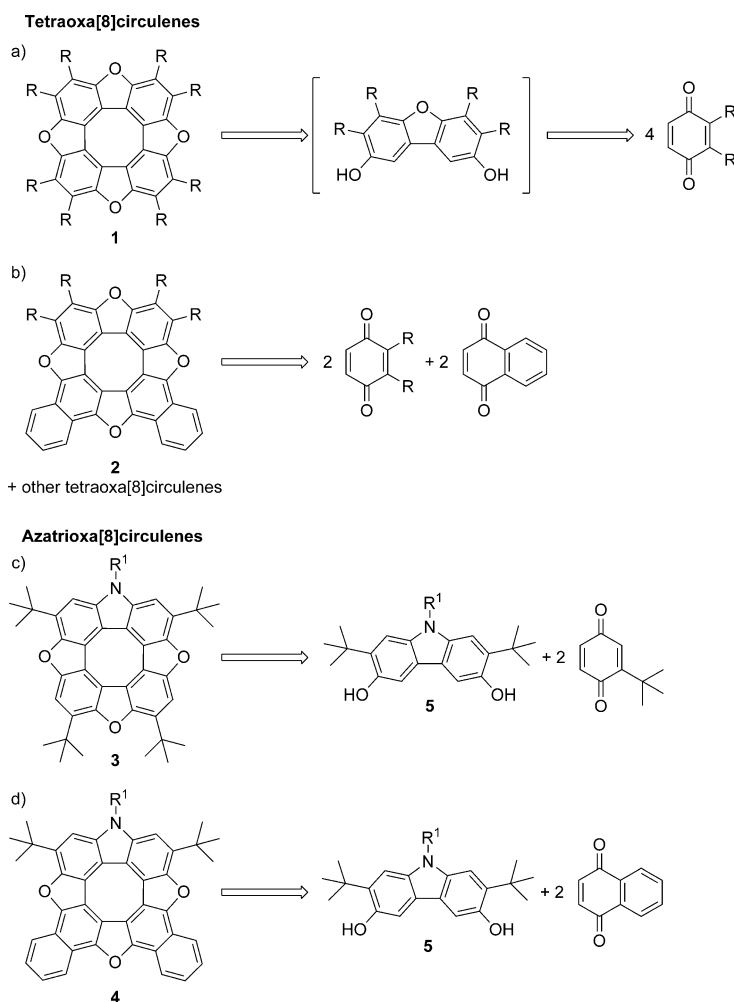


Figure 1. Structures and schematic retrosynthetic analyses of tetraoxa[8]circulenes **1** and **2**, and azatrioxa[8]circulenes **3** and **4** (R = C₁₁H₂₃, *tert*-butyl or H; R¹ = propyl).

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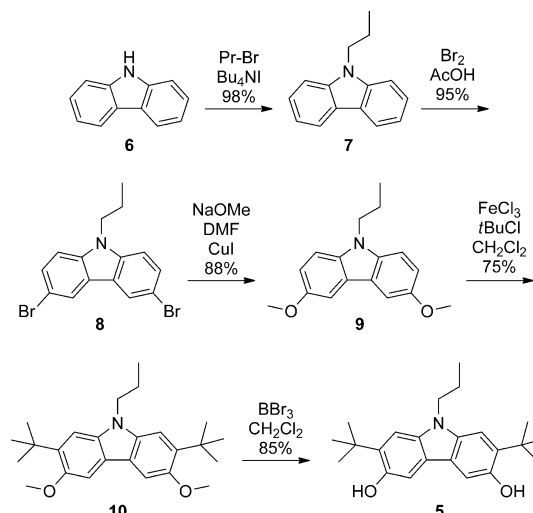
condensation of a 2,3-dialkyl-1,4-benzoquinone and naphthoquinone gives a mixture of π -extended tetraoxa[8]circulenes (e.g., **2**; Figure 1b).^[6] Inspired by the above findings, we decided to investigate whether a suitably functionalised *N*-alkyl-3,6-dihydroxycarbazole could replace 3,6-dihydroxydibenzofuran in the condensation reaction with benzoquinones or naphthoquinones to produce azatrioxa[8]circulenes. Herein we describe the synthesis of the first azatrioxa[8]circulenes **3** and **4** (Figure 1c,d) and compare their electrochemistry and photophysical properties with their iso-electronic tetraoxa[8]circulene analogues **1** and **2**. The results of a computational study (nuclear-independent chemical shift calculations) suggest that the central planar cyclooctatetraenes (COTs) are anti-aromatic when the molecules are in the neutral or oxidised states (2+) and that the corresponding dianions are aromatic.

[*n*]Circulenes are conjugated cyclic compounds that can formally be derived from [*n*]radialenes by connecting the termini of the semi-cyclic double bonds by etheno bridges.^[7] In heterocyclic [*n*]circulenes, heteroatoms such as oxygen, nitrogen, sulfur or selenium replace one or more of the etheno bridges. Although the parent [8]circulene is predicted to be saddle-shaped,^[7b] some of the heterocyclic [8]circulenes have been shown to be planar. Heteroatom substitution of [8]circulenes has only been achieved in a few instances since the seminal work on tetraoxa[8]circulenes by Erdtman and Högberg.^[8] These include the contribution of Christensen and co-workers for the synthesis of soluble tetraoxa[8]circulenes,^[3a] our own tetraoxa[8]circulenes and π -extended tetraoxa[8]circulenes,^[6] Nenajdenko and co-workers octathia[8]circulene and tetrathiatetraselena[8]circulene,^[9,10] and Osuka and co-workers formal tetraaza[8]circulene.^[11]

Polycyclic conjugated compounds are complex to understand in terms of aromaticity and anti-aromaticity as the simple Hückel rules do not apply. From a magnetic point of view, a diatropic ring current is a characteristic of aromatic rings, whereas paratropic ring currents are a characteristic of anti-aromatic rings. In computational chemistry, methods to measure aromaticity have been developed, and nuclear-independent chemical shift (NICS) calculations appear to be a reliable method for studying this kind of phenomena. In NICS calculations, large negative values indicate aromaticity and large positive values indicate anti-aromaticity.^[12] Heterocyclic [8]circulenes are good candidates for studying the aromaticity/anti-aromaticity of planar COTs in polycyclic structures that are placed in an environment of aromatic moieties. The seminal work by Osuka and co-workers on this topic focused on showing that a planar COT formed in a tetraporphyrin array with two diagonally metallated porphyrins connected by bidentate organic ligands displays paratropicity by measuring the ring current effects in ¹H NMR spectroscopy experiments.^[11,13]

Results and Discussion

The azatrioxa[8]circulenes **3** and **4** were synthesised from the common 3,6-dihydroxycarbazole precursor **5** (Scheme 1). Carbazole (**6**) was alkylated using a two-phase

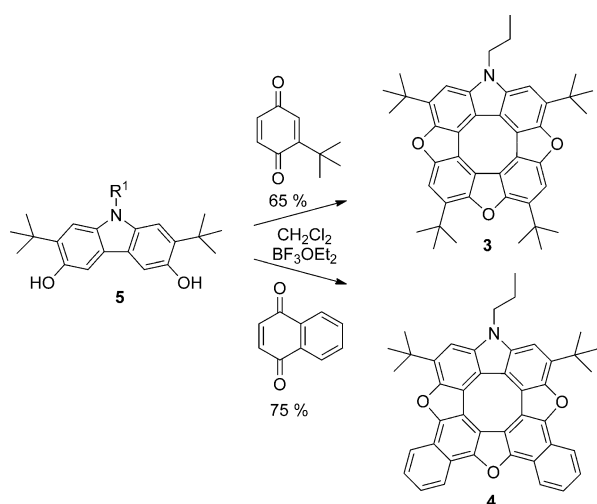


Scheme 1. Synthesis of the azatrioxa[8]circulene precursor **5**.

protocol to give the alkylcarbazole **7** in high yield. The *N*-propylcarbazole (**7**) was selectively brominated twice *para* to the nitrogen to yield the dibromide **8**, which was effectively transformed into the dimethoxy derivative **9** by treatment with NaOMe/MeOH and CuI in DMF.

tert-Butylation proved sensitive to the choice of reagents, but a mixture of anhydrous FeCl₃ and *tert*-butyl chloride gave a clean conversion to 2,7-di-*tert*-butyl-3,6-dimethoxycarbazole **10**. Demethylation with BBr₃ in CH₂Cl₂ gave the acid- and air-sensitive 3,6-dihydroxy-substituted carbazole **5** in good yield. Treatment of **5** with *tert*-butylbenzoquinone or naphthoquinone in CH₂Cl₂/BF₃·OEt₂ gave the azatrioxa[8]circulene **3** and the extended azatrioxa[8]circulene **4** in yields of 65 and 75%, respectively (Scheme 2). In the case of the tetra-*tert*-butylazatrioxa[8]circulene **3**, only one isomer with respect to the *tert*-butyl groups was observed. The symmetrical nature of **3** was evident in the NMR spectra, in which only two types of aromatic protons and only two types of *tert*-butyl groups were observed.

The azatrioxa[8]circulenes **3** and **4** possess cyclic 8 π electron conjugation of the central COT and the structures are almost completely planar, as can be seen in the single-crystal X-ray structures of **3** and **4** (Figure 2).^[14,15] The crystal structures also confirm the regiochemical outcome of the synthetic protocol. The crystal structure of **3** suggests there is little interaction between the π systems of neighbouring molecules, probably due to the steric bulk of the four *tert*-butyl substituents on the azatrioxa[8]circulene structure. The crystal packing of the π -extended azatrioxa[8]circulene **4** is dominated by π stacking, with each azatrioxa[8]circulene exhibiting significant π - π overlap with its closest neighbour.



Scheme 2. Synthesis of the azatrioxa[8]circulenes **3** and **4**.

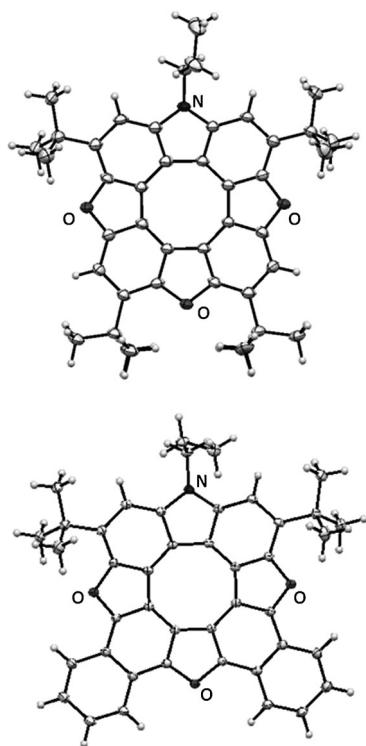


Figure 2. X-ray crystal structures of **3** (top) and **4** (bottom).

In addition, the nitrogen atom of every second azatrioxa[8]circulene is pointing in the opposite direction, probably to accommodate the space-filling *tert*-butyl substituents (Figure 3). The planarity of the tetrahetero[8]circulenes with four benzene rings, three furans and one pyrrole (e.g., azatrioxa[8]circulene) was anticipated on the basis of the Dopfer and Wynberg model, which predicts whether [*n*]circulenes are bowl-shaped, planar or saddle shaped.^[16]

Tetraoxa[8]circulenes **1** and **2** have shown promise as candidates for the blue fluorescent component of organic light-

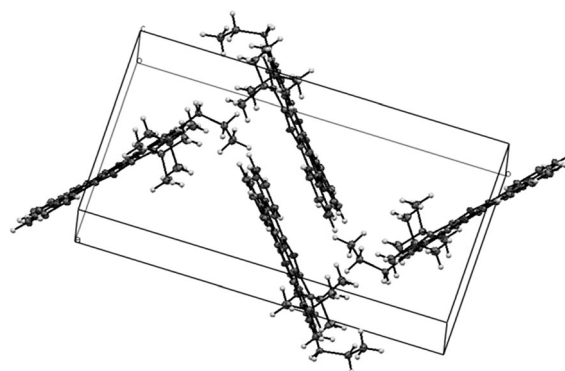


Figure 3. Packing observed in the X-ray crystal structure of **4**.

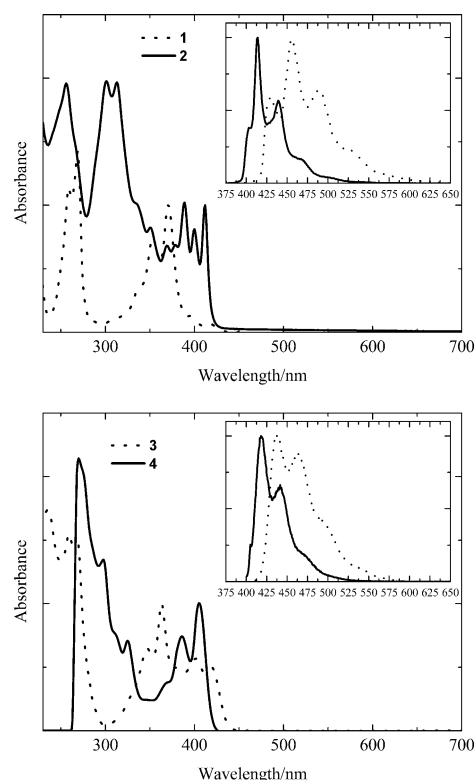


Figure 4. UV/Vis and fluorescence spectra (insert) of **1-4**.

emitting diodes (OLEDs).^[6] The optical and electrochemical properties of azatrioxa[8]circulenes **3** and **4** were examined to assess the possibility of their use in this application. The UV/Vis spectra of **1-4** are shown in Figure 4 together with their fluorescence spectra. The emission spectra of the dinaphthyl-based [8]circulenes **2** and **4** are blue-shifted compared with the all-benzene-based [8]circulenes **1** and **3**. An increase in the conjugation length and the substitution of an oxygen atom by a nitrogen atom leads to an increase in the quantum yield (**1**=0.1, **2**=0.5, **3**=0.3, **4**=0.9). The azatrioxa[8]circulenes, therefore, could prove to be even better suited for applications in blue OLEDs than the tetraoxa[8]circulenes.

By comparing the absorption and fluorescence properties it can be seen that the effect of substituting an oxygen atom with a nitrogen atom outweighs the effect of extending the conjugation length because a pronounced redshift occurs for the lowest excited state of **1** compared with **2**. This effect is less dominant for **3** and **4**. The absorption spectra also show bands at higher energies that can be ascribed to transitions to higher electronic states. In addition, strong couplings to the vibrational degrees of freedom are evident by the significant fine structure in the spectra.

The fact that substitution of an oxygen atom outweighs the effect of extending the conjugation length is further supported by the oxidation and reduction potentials of **1–4** (see Table 1). In previous work, it was found that the first oxida-

G(d,p) level of theory by using geometries obtained from B3LYP/6-31+G(d) calculations. The results suggest that in the neutral form, the planar COTs of both tetraoxa[8]circulene and azatrioxa[8]circulene are anti-aromatic (positive values). Meanwhile, the benzene and furan rings are aromatic, which is in accordance with our previous work.^[17] In the case of the doubly oxidised (2+) tetraoxa[8]circulene and azatrioxa[8]circulene, our calculations indicate that the COTs retain their anti-aromaticity, whereas in the doubly reduced (2-) species the COTs are aromatic (large negative values). The benzene, furan and pyrrole rings appear to retain their aromaticity in all the oxidation states studied.

To further address the question of (anti)aromaticity, the bond lengths in the inner eight-membered ring of the tetraoxa[8]circulene and azatrioxa[8]circulene were examined (Table 2) by performing B3LYP calculations. The observed

Table 1. Reduction and oxidation potentials for **1–4** referenced against the Fc/Fc⁺ couple obtained by using square wave voltammetry.^[a]

Species	Potential [V] vs. Fc/Fc ⁺					
1		-2.71	-2.40	1.09		
2	-2.71	-2.55	-2.39	0.72	0.97	
3			-2.52	0.67	1.41	
4			-2.58	0.65	1.22	1.46

[a] Conditions: 1 mm in MeCN with Bu₄NBF₄ as the electrolyte.

tion potentials of a series of tetraoxa[8]circulenes decrease almost exponentially with the number of benzene rings in the molecule. At the same time, the first reduction potentials for this series of molecules have identical values. This trend is not observed for the two azatrioxa[8]circulenes studied, with both the first reduction and oxidation potentials relatively unaffected by the number of benzene rings in the molecule.

NICS calculations were performed on both the tetraoxa[8]circulene **1** and the azatrioxa[8]circulene **3** (NH) to address the question of the aromaticity/anti-aromaticity of the central planar COTs (Figure 5).^[12] Both the NICS(0) and NICS(1)_{zz} values were calculated at the B3LYP/6-311+

Table 2. Selected bond lengths for **1** and **3**.^[a]

Bond	1					
	-2	0	+2	-2	0	+2
a	1.4084	1.4319	1.3872	1.4260	1.4352	1.3855
b	1.4229	1.3973	1.4376	1.4290	1.4049	1.4483
c				1.4109	1.4351	1.3881
d				1.4239	1.3978	1.4370
e				1.4068	1.4306	1.3865

[a] See Figure 5 for labels. The bond lengths were determined by B3LYP calculations.

bond-length alternations in the eight-membered ring of **1** are 0.0145, 0.0346, and 0.0505 for the charge states -2, 0, and +2, respectively. A similar trend is observed for **3** in which the bond-length alternations are 0.013–0.018, 0.030–0.037, and 0.046–0.063 for -2, 0, and +2. Therefore the bond-length alternations were found to be significantly lower for the aromatic species. Thus, the structural information (calculated bond lengths) corroborates the conclusions regarding (anti)aromaticity inferred from the NICS calculations.

The ¹H NMR data of kekulene suggest that the peculiar downfield shift of the inner protons is an argument against viewing kekulene as an annulenic ring system. Instead, kekulene should be considered as a benzenoid system in which the magnetic field in the inner ring should be considered as arising from six linked benzene rings.^[18] A similar hypothesis could in principle be considered for tetraoxa[8]circulene, that is, the observed (by NICS calculations) anti-aromaticity in the neutral state is not due to an annulenic ring system. The NICS values suggest the anti-aromaticity can be explained by viewing the molecule as four linked benzene rings. This hypothesis can, however, be rejected by considering the magnetic field at a point surrounded by benzene rings. NICS calculations were carried out in which the dummy atom was placed at an identical distance from the benzene ring, as in the NICS calculations on tetraoxa[8]circulene, which resulted in a NICS(0) value of around 1. A similar calculation was carried out with two benzene rings

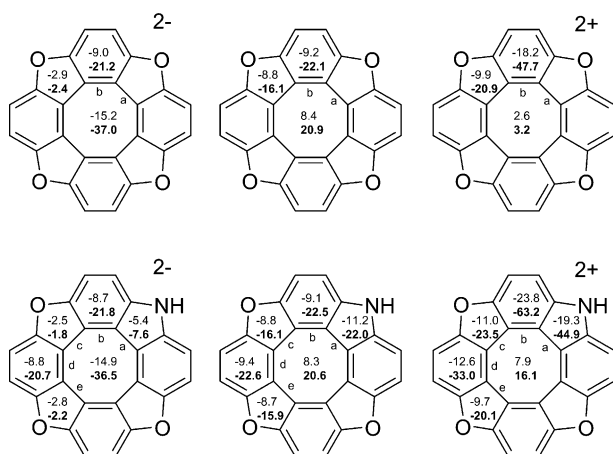


Figure 5. NICS(0) and NICS(1)_{zz} (bold) values calculated for tetraoxa[8]circulene **1** and azatrioxa[8]circulene **3**. The letters a–e refer to the bond lengths in Table 2.

with the benzene rings and dummy atom placed in a geometry identical to that of two opposite-lying benzene rings in tetraoxa[8]circulene and the dummy atom placed equidistant from the centre of the two rings. The calculated NICS(0) value of around 2 is in accordance with the addition of two magnetic field vectors of the same magnitude. If the electronic structure of tetraoxa[8]circulene is best described as four benzene rings linked to a benzenoid system, a NICS(0) value of around 4 should be expected, whereas a value of about 8 was found. Invoking such an additivity scheme on other fragments (benzofuran, dibenzofuran, phenol and 3-hydroxydibenzofuran) of the tetraoxa[8]circulene molecule resulted in values significantly lower than 8 (the largest value found was about 6).

The electronic structures of tetraoxa[8]circulene and azatrioxa[8]circulene are visualised with HOMO and LUMO density plots (Figures 6 and 7). In particular, the HOMO or-



Figure 6. LUMO (top) and HOMO (bottom) density plots for azatrioxa[8]circulene with charge state -2 (left), 0 (middle) and $+2$ (right).



Figure 7. LUMO (top) and HOMO (bottom) density plots for tetraoxa[8]circulene with charge state -2 (left), 0 (middle) and $+2$ (right).

bitals of azatrioxa[8]circulene in oxidation states 0 and $+2$ suggest that the electronic structure cannot be represented by four linked benzene rings as the orbitals indicate that the electron density is spread over two benzene rings for electrons in the HOMO orbitals.

The HOMO of tetraoxa[8]circulene in the $+2$ oxidation state also indicates that the electronic structure is better represented by an annulene electronic structure inasmuch as there is a mirror plane intersecting the heteroatoms.

Conclusions

We have developed the first protocol for the synthesis of azatrioxa[8]circulenes. The two azatrioxa[8]circulenes prepared have excellent blue emission properties and we are

currently investigating their properties for use in OLEDs as well as their electrical conductivity. Our computational results indicate that the planar COT in the heteroatom-substituted circulenes are anti-aromatic and become aromatic upon two-electron reduction.

Experimental Section

General experimental procedures: TLC was carried out by using aluminium sheets precoated with silica gel 60F (Merck 5554). Dry column vacuum chromatography was carried out with silica gel 60 (Merck 9385, 0.015–0.040 mm). Melting points were determined with a Büchi melting point apparatus and are uncorrected. ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded with a Bruker spectrometer (500 MHz CryoProbe). Samples were prepared in deuterated solvents (CDCl_3 , $[\text{D}_6]\text{DMSO}$, CD_2Cl_2) purchased from Cambridge Isotope Labs. FAB-MS was performed with a JEOL JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode with 3-nitrobenzyl alcohol (NBA) as the matrix. EI-MS spectra were recorded with a ZAB-EQ (VG-Analytical) spectrometer. Microanalyses were performed with a FlashEA 1112. UV/Vis spectra were recorded with a Cary 5E spectrophotometer (Varian Inc.) with pure solvent as the baseline.

X-ray crystallography: All single-crystal X-ray diffraction data were collected at 122(1) K on a Nonius-KappaCCD area-detector diffractometer equipped with an Oxford Cryostreams low-temperature device using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS97) and refined by using SHELXL97^[19]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located in the difference Fourier map and refined isotropically as riding on their parent atom in a fixed geometry. The molecular structure diagrams were prepared by using the Ortep-3^[20] and Mercury^[21] 3.0.1 programs.

Calculations: The Gaussian 03 suite^[22] of programs was used for the DFT calculations. Initially, geometry optimisations were carried out at the B3LYP/6-31G(d) level of theory, with all the structures constrained to C_{2v} symmetry. Frequency calculations were then carried out to assure that the structures were indeed minima on the potential energy surface (no imaginary frequencies). TDDFT and single-point calculations on the anion radicals were then carried out at the B3LYP/6-31G(d) level of theory on these optimised structures. The Gaussian archive entries for these calculations are included in the Supporting Information. GaussView 3.0 was used for generating the orbital plots.

Cyclic voltammetry: Tetrabutylammonium tetrafluoroborate (Aldrich, 98%) and acetonitrile (Lab-Scan, HPLC grade) were used as received. The cell was a cylindrical vial equipped with a Teflon top with holes to accommodate the platinum working electrode, the platinum counter electrode and Fc/Fc^+ . The electrochemical equipment was purchased from CHI instruments (CH630) with iR compensation. The solutions for voltammetry were 1 mM in substrate and made by dissolving an accurately weighed amount of the substrate in the required volume of a MeCN/ Bu_4NBF_4 (0.1 M) solution. The volumes of the resulting solutions were typically between 5 and 10 mL. The solutions were purged with nitrogen saturated with MeCN for at least 10 min prior to the measurements.

Synthesis of azatrioxa[8]circulene 3: 2-*tert*-Butyl-1,4-benzoquinone (697 mg, 4.24 mmol) and **5** (500 mg, 1.41 mmol) were dissolved in dichloromethane (40 mL) in a flame-dried flask under an atmosphere of nitrogen. Freshly distilled $\text{BF}_3 \cdot \text{OEt}_2$ (1 mL) was added to the solution and the reaction mixture was stirred over night at room temperature. Then 2 M aq. HCl (30 mL) was added and the phases separated. The aqueous phase was extracted with CH_2Cl_2 ($3 \times 30 \text{ mL}$) and the combined organic extracts were dried over MgSO_4 , filtered and concentrated. The crude product was purified by dry column chromatography on silica eluting with heptane/toluene mixtures (from pure heptane to pure toluene with a 10% gradient). Yield: 575 mg, 65%; m.p. 303–304 °C; ^1H NMR (500 MHz, CDCl_3): $\delta = 0.95\text{--}1.05$ (m, 3H), 1.67 (s, 18H), 1.69 (s, 18H),

1.94–2.07 (m, 2H), 4.45 (t, $J=7.5$ Hz, 2H), 7.34 (s, 2H), 7.67 ppm (s, 2H); ^{13}C NMR (126 MHz, CDCl_3): $\delta=12.11, 23.31, 30.36$ (2C), 35.16, 35.25, 45.42, 105.07, 107.23, 112.21, 115.01, 116.56, 116.94, 133.93, 134.47, 136.98, 150.77, 151.10, 152.71 ppm; MS (MALDI-TOF): m/z : 625; elemental analysis calcd (%) for $\text{C}_{43}\text{H}_{47}\text{NO}_3$: C 82.52, H 7.57, N 2.24; found: C 82.50, H 7.41, N 2.35.

Synthesis of azatrioxa[8]circulene 4: Naphthoquinone (4.24 mmol) and **5** (500 mg, 1.41 mmol) were dissolved in dichloromethane (40 mL) in a flame-dried flask under an atmosphere of nitrogen. Freshly distilled $\text{BF}_3\cdot\text{OEt}_2$ (1 mL) was added to the solution and the reaction mixture was stirred over night at room temperature. Then 2 M aq. HCl (30 mL) was added and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (3 \times 30 mL) and the combined organic extracts were dried over MgSO_4 , filtered and concentrated. The crude product was purified by dry column chromatography using heptane/toluene mixtures as the eluent. Yield: 651 mg, 75%; m.p. 285–286 °C; ^1H NMR (500 MHz, CDCl_3): $\delta=1.11$ (t, $J=7.4$ Hz, 3H), 1.86 (s, 18H), 2.13 (sext., $J=7.4$ Hz, 2H), 4.59 (t, $J=7.4$ Hz, 2H), 7.53 (s, 2H), 7.69–7.75 (m, 4H), 8.62–8.68 ppm (m, 4H); ^{13}C NMR (126 MHz, CDCl_3): $\delta=150.09, 148.67, 148.61, 137.26, 133.65, 125.99, 125.82, 122.13, 121.67, 120.79, 120.61, 117.17, 113.90, 112.93, 112.08, 104.47, 45.46, 35.41, 30.59, 23.24, 12.14$ ppm; MS (MALDI-TOF): m/z : 613; elemental analysis calcd (%) for $\text{C}_{45}\text{H}_{35}\text{NO}_3$: C 84.15, H 5.75, N 2.28; found: C 84.35, H 7.85, N 2.22.

Synthesis of dihydroxycarbazole 5: Under an atmosphere of nitrogen, **10** (5.0 g, 13.1 mmol) was added to dry dichloromethane (50 mL) in a flame-dried round-bottomed flask. The solution was cooled to -78°C in an acetone/dry-ice bath. At this temperature, BBr_3 (27 mL, 27 mmol, 1 M in CH_2Cl_2) was added dropwise over the course of 1 h. After stirring for 2 h at -78°C , the reaction mixture was allowed to warm to room temperature with stirring overnight. The reaction was quenched with 2 M aq. HCl (40 mL) and the resulting two-phase system extracted with dichloromethane (3 \times 50 mL). After drying over anhydrous MgSO_4 and filtration, the solvent was removed under reduced pressure and the crude product was purified by dry column chromatography (EtOAc/heptane mixtures) to yield a white powder that turns slightly pink when left in air. Yield: 3.94 g, 85%; m.p. 213–214 °C; ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): $\delta=0.87$ (t, $J=7.5$ Hz, 3H), 1.47 (s, 18H), 1.76 (sext., $J=7.5$ Hz, 2H), 4.21 (t, $J=7.5$ Hz, 2H), 7.20 (s, 2H), 7.24 (s, 2H), 8.85 ppm (s, 2H; OH); ^{13}C NMR (126 MHz, $[\text{D}_6]\text{DMSO}$): $\delta=11.67, 22.10, 29.75, 34.95, 43.46, 105.55, 106.16, 119.37, 134.49, 134.71, 148.88$ ppm; MS (GCMS): m/z : 353.2; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{31}\text{NO}_2$: C 78.15, H 8.84, N 3.96; found: C 78.30, H 8.85, N 3.91.

Synthesis of *N*-propylcarbazole (7): 9*H*-Carbazole (50.0 g, 280 mmol) was suspended in a mixture of toluene (400 mL) and 12 M aq. NaOH (400 mL). After stirring for 10 min, tetrabutylammonium iodide (11.2 g, 30 mmol) was added to the orange reaction mixture. Propyl bromide (100 mL) was added and the reaction mixture was heated at reflux for 16 h. The reaction mixture was cooled to room temperature, the phases were separated and the aqueous phase extracted with toluene (3 \times 150 mL). The combined organic phases were dried over anhydrous MgSO_4 and filtered. The solvent was removed under reduced pressure and the resulting yellow crude product was recrystallised from ethanol. Yield: 61.3 g, 98%; m.p. 47–48 °C; ^1H NMR (500 MHz, CDCl_3): $\delta=1.02$ (t, $J=7.4$ Hz, 3H), 1.97 (sext., $J=7.4$ Hz, 2H), 4.32 (t, $J=7.4$ Hz, 2H), 7.25–7.30 (m, 2H), 7.46 (d, $J=8.3$ Hz, 2H), 7.48–7.53 (m, 2H), 8.15 ppm (d, $J=7.2$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3): $\delta=140.52, 125.56, 122.81, 120.34, 118.71, 108.70, 44.64, 22.34, 11.85$ ppm; MS (GCMS): m/z : 209.2; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{15}\text{N}$: C 86.08, H 7.22, N 6.69; found: C 86.00, H 7.11, N 6.82.

Synthesis of 3,6-dibromo- *N*-propylcarbazole (8): *N*-Propyl-9*H*-carbazole (**7**; 50 g, 239 mmol) was suspended in glacial acetic acid (500 mL). Bromine (76.4 g, 476 mmol) in glacial acetic acid (500 mL) was added dropwise to the mixture over the course of 1 h at room temperature. After stirring for 2 h, the reaction product was filtered and the crystals washed with cold glacial AcOH. The crude product was crystallised from glacial AcOH (50 mL) and washed several times with cold glacial AcOH to yield a white solid material. Yield: 83.3 g, 95%; m.p. 83–84 °C; ^1H NMR (500 MHz, CDCl_3): $\delta=0.87$ (t, $J=7.4$ Hz, 3H), 1.81 (sext., $J=7.4$ Hz,

2H), 4.15 (t, $J=7.3$ Hz, 2H), 7.20 Hz, (d, $J=8.9$ Hz, 2H), 7.48 (dd, $J=8.9$ Hz, $J=2.1$ Hz, 2H), 8.07 ppm (d, $J=2.1$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3): $\delta=139.40, 129.01, 123.44, 123.26, 111.95, 110.44, 44.88, 22.23, 11.73$ ppm; MS (GCMS): m/z : 367.0; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{N}$: C 49.08, H 3.57, N 3.82; found: C 48.92, H 3.68, N 3.96.

Synthesis of 3,6-dimethoxy-*N*-propylcarbazole (9): Dibromocarbazole **8** (50 g, mmol) was dissolved in dry DMF (200 mL) under an atmosphere of nitrogen. NaOMe in methanol (500 mL, 25% in MeOH) was added over 10 min during which time Cu^{I} (20 mol-%) was added in small portions. The reaction mixture was maintained under nitrogen and heated at reflux overnight. The resulting brown suspension was treated with aqueous ammonia (24% in H_2O) to give a blue suspension. The suspension was extracted with dichloromethane (3 \times 500 mL) and the combined organic extracts were washed with water (2 \times 200 mL). The organic phase was dried over anhydrous MgSO_4 , filtered and the solvent removed under reduced pressure. The crude product was crystallised from methanol. Yield: 32.3 g, 88%; m.p. 73–74 °C; ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): $\delta=0.85$ (t, $J=7.5$ Hz, 3H), 1.76 (sext., $J=7.5$ Hz, 2H), 3.88 (s, 6H), 4.29 (t, $J=7.5$ Hz, 2H), 7.06 (d, $J=9.0$ Hz, 2H), 7.47 (d, $J=9.0$ Hz, 2H), 7.73 ppm (s, 2H); ^{13}C NMR (126 MHz, $[\text{D}_6]\text{DMSO}$): $\delta=152.67, 135.57, 122.14, 114.80, 109.98, 103.07, 55.60, 43.81, 21.99, 11.36$ ppm; MS (GCMS): m/z : 269.2; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C 75.81, H 7.11, N 5.20; found C 75.67, H 6.89, N 5.30.

Synthesis of 2,7-di-*tert*-butyl-3,6-dimethoxy-*N*-propylcarbazole (10): Under an atmosphere of nitrogen, dimethoxycarbazole **9** (10 g, 37.1 mmol) was dissolved in dry dichloromethane (100 mL). Anhydrous iron(III) chloride (6 g, 37.1 mmol) was then added to the solution. The reaction mixture was cooled to 0 °C and 2-chloro-2-methylpropane (40 mL) was added. The reaction mixture was stirred overnight. Another portion of iron(III) chloride (3 g) was then added. The reaction was stirred under an atmosphere of nitrogen for another 2 h. The reaction was quenched with 2 M aq. HCl (100 mL) and the phases were separated. The aqueous phase was extracted with dichloromethane (3 \times 100 mL) and the combined organic phases were dried over anhydrous MgSO_4 , filtered and concentrated. The crude product was crystallised from 96% ethanol and the resulting off-white crystals were washed several times with cold 96% ethanol. Yield: 10.6 g, 75%; m.p. 256–258 °C; ^1H NMR (500 MHz, CDCl_3): $\delta=0.90$ (t, $J=7.4$ Hz, 3H), 1.41 (s, 18H), 1.81 (sext., $J=7.4$ Hz, 2H), 3.90 (s, 6H), 4.07–4.23 (m, 2H), 7.18 (brs, 2H), 7.39 ppm (brs, 2H); ^{13}C NMR (126 MHz, CDCl_3): $\delta=152.69, 137.10, 135.59, 120.13, 106.67, 102.48, 55.83, 53.43, 44.28, 35.48, 30.18, 11.99$ ppm; MS (GCMS): m/z : 381.3; elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{35}\text{NO}_2$: C 78.70, H 9.25, N 3.67; found: C 79.02, H 9.43, N 3.48.

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- [14] a) Crystal data for **3**: C₄₃H₄₇NO₃, *M* = 625.82, triclinic, *a* = 11.277(5), *b* = 17.084(5), *c* = 19.853(14) Å, *α* = 93.293(36), *β* = 104.813(40), *γ* = 105.77(4)°, *V* = 3525(3) Å³, *T* = 122(1) K, space group *P* $\bar{1}$, *Z* = 4, $\mu(\text{Mo}_{\text{K}\alpha})$ = 0.073 mm⁻¹, 102 729 reflections measured, 12 375 independent reflections (*R*_{int} = 0.1792), *R*₁ = 0.0715 [*I* > 2σ(*I*)], *R*₁ = 0.1320 (all data), *wR*(*F*²) = 0.1294 [*I* > 2σ(*I*)], *wR*(*F*²) = 0.1554 (all data), GOF on *F*² = 1.096. b) CCDC-876617 (**3**) and CCDC-876618 (**4**) contains the supplementary crystallographic data for this paper. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [15] Crystal data for **4**: C₄₃H₃₅NO₃, *M* = 613.72, monoclinic, *a* = 14.8632(12), *b* = 20.273(3), *c* = 10.728(4) Å, *β* = 108.780(11)°, *V* = 3060.4(13) Å³, *T* = 122(1) K, space group *P*2₁/*c*, *Z* = 4, $\mu(\text{Mo}_{\text{K}\alpha})$ = 0.083 mm⁻¹, 87 868 reflections measured, 8915 independent reflections (*R*_{int} = 0.1129), *R*₁ = 0.0536 [*I* > 2σ(*I*)], *R*₁ = 0.0915 (all data), *wR*(*F*²) = 0.1142 [*I* > 2σ(*I*)], *wR*(*F*²) = 0.1370 (all data), GOF on *F*² = 1.072.^[14b]
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