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Diazadioxa[8]circulenes: Planar Antiaromatic Cyclooctatetraenes

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Abstract: In this paper we describe a new class of antiaromatic planar cyclooctatetraenes: the diazadioxa[8]circulenes. The synthesis was achieved by means of a new acid-mediated oxidative dimerization of 3,6-dihydroxycarbazoles to yield the diazadioxa[8]circulenes in high yields. The synthetic protocol appears to be general, and is a one-pot transformation in which two C–C bonds and two C–O bonds are formed with the loss of two molecules of water. We also present a detailed characterization of the optical and electrochemical properties of this new class of stable planar cyclooctatetraenes. The properties of the diazadioxa[8]circulenes are compared with the properties of isoelectronic tetraoxa[8]circulenes and azatrioxa[8]circulenes. We discuss the antiaromatic nature of the planar central cyclooctatetraene moiety. The antiaromatic nature of the planar cyclooctatetraenes was studied by using computational methods (NICS calculations), and these calculations reveal that the central eight-membered ring has antiaromatic character.

Keywords: aromaticity · density functional calculations · electrochemistry · fluorescence · heterocycles

Introduction

Antiaromatic compounds that are chemically stable are rare. An attractive strategy to stabilize antiaromatics is to fuse them in larger π-conjugated systems, giving structures that contain formal aromatic- and antiaromatic regions.[1] The antiaromatic regions in these types of systems often impart unique electrochemical and optical properties on the entire conjugated system. This strategy has been applied by several teams for the preparation of large antiaromatic porphyrioids by the groups of Osuka, Sessler, and Latos-Grażyński,[2–4] indeno[1,2-b]fluorenes by Haley et al.,[5] and hetero-acenes by the group of Bunz.[6] A particular fundamental area that has attracted interest is the studies of the aromatic/antiaromatic properties of planarized conjugated cyclooctatetraenes.[7] Several experimental strategies have been explored and fully conjugated systems have been prepared by Osuka,[8] Nenajdenko,[9] and us.[10] Completely nonfused systems have been prepared by Komatsu and co-workers.[11] Analysis of the experimental and computational data collected on these systems suggest that planarized cyclooctatetraenes are antiaromatic.[8–10,12]

Högberg and Erdtman established that when 1,4-benzoquinones and naphthoquinones are treated with strong acid, tetrameric condensation products of the tetraoxa[8]circulene type (**1**) are formed.[13] Högberg showed that 3,6-dihydroxydibenzofurans are important intermediates in these condensation reactions, and that isolated 3,6-dihydroxydibenzofurans derived from naphthoquinone or benzoquinones react with an additional two equivalents of 1,4-quinones to give mixed tetraoxa[8]circulenes.[14] It has also been shown that substitution of a 1,4-benzoquinone in the 2- and 3 positions resulted in significantly improved yields of the tetraoxa[8]circulenes.[14] Inspired by these findings we showed that 2-*tert*-butyl-1,4-benzoquinone tetramerizes to yield tetra-*tert*-butyl-tetraoxa[8]circulene in a one-step procedure (Figure 1 a).[15]

Recently we extended this work to provide the first synthesis of azatrioxa[8]circulenes (**2**) by condensing a *N*-alkyl-2,3-di-*tert*-butyl-3,6-dihydroxycarbaxole (**4**) with a benzoquinone.[16] We reasoned that an *N*-alkyl-2,7-di-*tert*-butyl-3,6-dihydroxycarbaxole (**4**) would be ideal to (through a dimerization reaction) form the diazadioxa[8]circulene (**3**). The two *tert*-butyl-substituents serve to prevent polymerization. However, since the proposed mechanism requires a Michael-type reaction between a “hydroquinone”-type moiety and a “quinone”-type moiety, followed by acid-mediated dehydration, an oxidant was needed. We proposed the reaction pathway depicted in Scheme 1.

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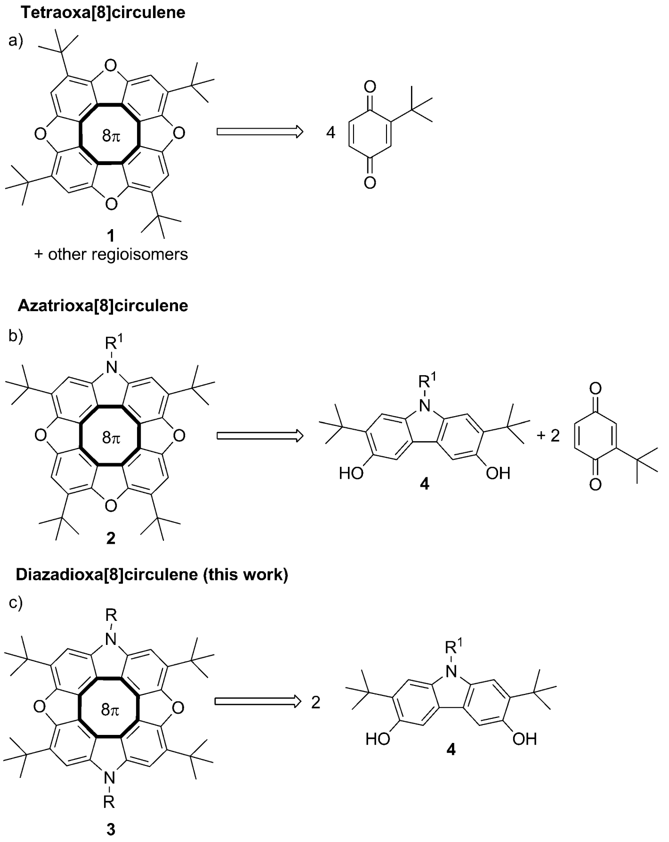
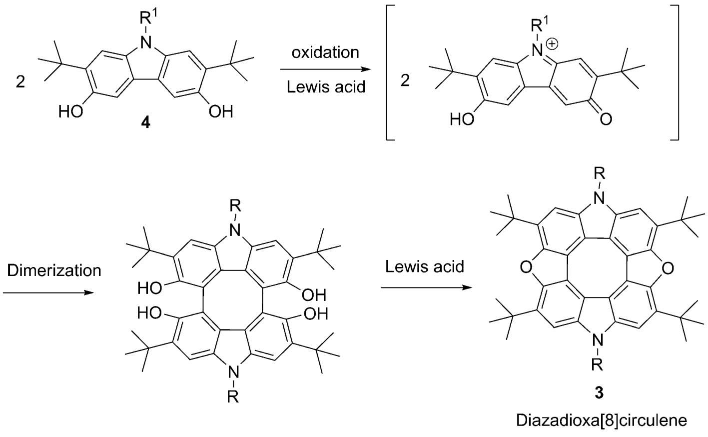


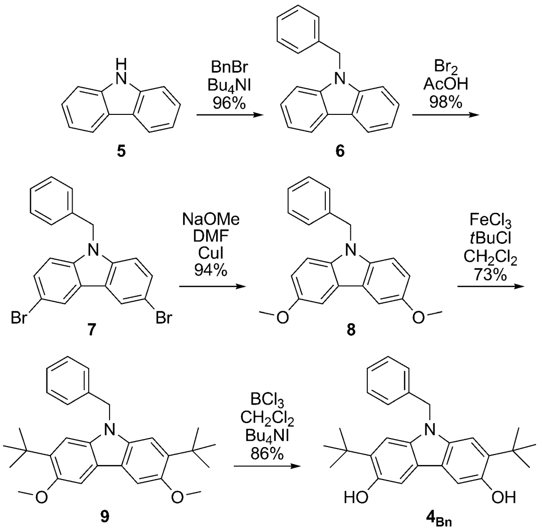
Figure 1. Structures and schematic retrosynthetic analyses of tetraoxa[8]circulenes (**1**), azatrioxa[8]circulenes (**2**), and the new diazadioxa[8]circulenes (**3**).



Scheme 1. Proposed reaction pathway for the oxidative acid-mediated formation of a diazadioxa[8]circulene (**3**).

Results and Discussion

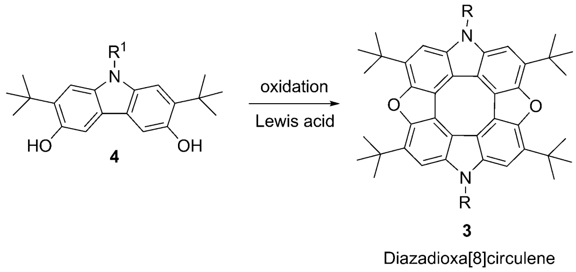
To test the hypothesis regarding the synthetic pathway we used two different *N*-alkyl-2,7-di-*tert*-butyl-3,6-dihydroxycarbaxoles (**4**, R = propyl or benzyl). The *N*-propyl ($\mathbf{4_{Pro}}$) we prepared previously, and the *N*-benzyl ($\mathbf{4_{Bn}}$) derivative was prepared by using the protocol depicted in Scheme 2. Carbazol (**5**) was benzylated by using a two-phase protocol to give the *N*-benzyl carbazol (**6**) in high yield. The *N*-benzyl carbazol (**6**) was brominated selectively twice in the position *para* to the nitrogen to yield the dibromide (**7**), which was effectively transformed into the dimethoxy derivative **8** by treatment with NaOMe/MeOH and CuI in DMF. The *tert*-butylation proved sensitive to the choice of reagents, but a mixture of anhydrous $FeCl_3$ and *tert*-butyl chloride gave a clean conversion to the 2,7-bis-*tert*-butyl-3,6-dimethoxy carbazole (**9**). The procedure is chromatography free up to this point. Selective demethylation of **9** proved difficult due to competitive debenzylation with most acidic (e.g., BBr_3 or $AlCl_3$ in CH_2Cl_2) and nucleophilic reagents (e.g., LiI in pyridine, NaSBu in DMF, PhSeNa in DMF). It turned out that a combination of BCl_3 and Bu_4NI in CH_2Cl_2 selectively cleaved the methyl groups and left the benzyl substituent on the nitrogen intact, and thus yielded the desired dihydroxy compound $\mathbf{4_{Bn}}$.



Scheme 2. Synthesis of *N*-benzyl-2,7-di-*tert*-butyl-3,6-dihydroxycarbaxole ($\mathbf{4_{Bn}}$).

We were delighted to find that when a *N*-alkyl-2,7-di-*tert*-butyl-3,6-dihydroxycarbaxole was treated with an oxidizing agent (e.g., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or chloranil) and a Lewis acid (e.g., $BF_3{\cdot}OEt_2$, $FeCl_3$, or $AlCl_3$) diazadioxa[8]circulenes (**3**) form in 71–85 % yield (Scheme 3).

Unambiguous evidence for the synthetic outcome came from the single-crystal X-ray crystallography (Figure 2). The crystals of $\mathbf{3_{Pro}}$ and $\mathbf{3_{Bn}}$ were grown by slow evaporation of CH_2Cl_2 from a mixture of CH_2Cl_2/ethanol (1:1) giving small pale-yellow needles. The presence of four *tert*-butyl groups on the diazadioxa[8]circulenes prevents π-stacking to dominate the crystal packing. Both diazadioxa[8]circulene possess cyclic 8π-electron conjugation at the central cyclooctatetraene (COT) and the structure is almost completely planar,



Scheme 3. Synthesis of diazadioxa[8]circulene (**3**). R = propyl (**3**$_{\mathbf{Pro}}$) or benzyl (**3**$_{\mathbf{Bn}}$). Conditions: oxidant (chloranil or DDQ), Lewis acid ($BF_3{\cdot}OEt_2$, $FeCl_3$, or $AlCl_3$), CH_2Cl_2, yield: 71–85 %.

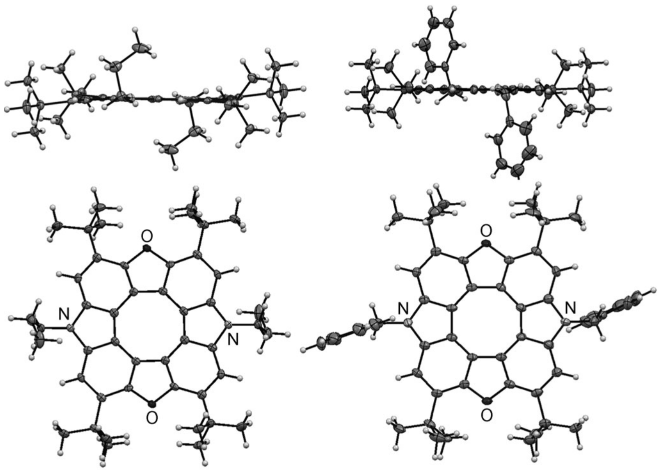


Figure 2. Single-crystal X-ray structure of **3**$_{\mathbf{Pro}}$ (left) and **3**$_{\mathbf{Bn}}$ (right). The top pictures show a side-view illustrating the planarity of the diazadioxa[8]circulenes and the bottom images show the front view of the structures.

and only minor bond-length alterations are observed in the eight-membered ring. These bond length alterations are similar to those observed in tetraoxa[8]circulene (between 1.40 and 1.44 Å).[7]

The UV/Vis and fluorescence spectra of tetraoxa[8]circulene (**1**), azatrioxa[8]circulene, (**2**$_{\mathbf{Pro}}$) and diazadioxa[8]circulene (**3**$_{\mathbf{Pro}}$) are shown in Figure 3. Three common electronic transitions are centered at ≈260 (≈4.8 eV), ≈360 (≈3.4 eV), and ≈425 nm (≈2.9 eV) with varying intensities. The oscillator strength and Franck-Condon factors for each transition are not identical when comparing the transitions at, for example, ≈425 nm. The transition at ≈425 nm is weak in intensity in the spectrum of **1** (extinction coefficient of ≈5000 $\text{M}^{-1}\text{cm}^{-1}$) when comparing to the spectra of **2**$_{\mathbf{Pro}}$ and **3**$_{\mathbf{Pro}}$ (extinction coefficients of ≈18000–25000 $\text{M}^{-1}\text{cm}^{-1}$). The S_1 energies were deduced from the UV/Vis and fluorescence spectra to be ≈2.9 eV for all three heterocyclic [8]circulenes.

To investigate the effect of symmetry and selection rules for the individual electronic transitions in the heterocyclic [8]circulenes, the completely unsubstituted compounds were investigated computationally (**1**$_{\mathbf{model}}$, **2**$_{\mathbf{model}}$, and **3**$_{\mathbf{model}}$). Calculations of the electronic transitions were carried out at the B3LYP/6-31G(d), B3LYP/cc-pVDZ, and CAM-B3LYP/cc-pVDZ level by using the response methodology as implemented in the Dalton quantum chemistry program. Additional calculations were carried out using the TD-DFT method implemented in Gaussian 03 on **1**, **2**, and **3**$_{\mathbf{Pro}}$ at the B3LYP/6-31G(d) level of theory. The CAM-B3LYP functional is known to describe excited states better than other density functionals mainly due the increased flexibility in the exchange functional caused by the "switching on" and increasing the "exact" Hartree–Fock exchange into the Kohn–Sham orbitals as the interelectronic distance increases.[17] This functional has been shown to provide accurate descriptions of two-photon absorption cross sections.[18–19]

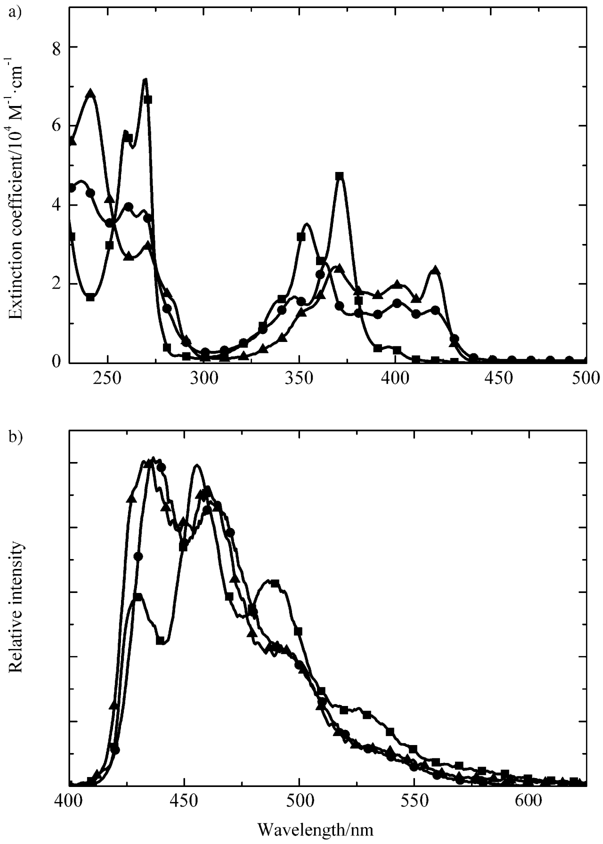


Figure 3. a) UV/Vis and b) fluorescence spectra of **1** (■; 0N), **2**$_{\mathbf{Pro}}$ (●; 1N), and **3**$_{\mathbf{Pro}}$ (▲; 2N) recorded in CH_2Cl_2.

Previous calculations on comparatively large aromatic systems have indicated that the cc-pVDZ basis set is sufficient to describe the excitation energies and it was also shown that augmented functions and even larger basis sets such as the cc-pVTZ basis set do not alter the calculated values for the excitation energies.[7,20] Excitation energies and oscillator strengths for the different molecules are presented in Table S1 (see the Supporting Information) along with designations or relevant symmetries.

In validating the performance of the theoretical levels it was noted that the B3LYP/cc-pVDZ and B3LYP/6-31G(d) level of theories adequately predicted the observed UV/Vis spectra. For example, compound **1** has a band centered around 3.61 eV/≈360 nm, which corresponds well to the calculated excitation energy of 3.45 eV for $\mathbf{1}_{\mathbf{model}}$. The calculations on the model compound ($\mathbf{1}_{\mathbf{model}}$) predicted that this energy state was degenerate resulting in total oscillator strength of 0.48. The oscillator strengths for the corresponding transitions of $\mathbf{2}_{\mathbf{model}}$ and $\mathbf{3}_{\mathbf{model}}$ both are 0.23, in accordance with the UV/Vis spectra. Calculations carried out at the CAM-B3LYP level (see the Supporting Information) consistently overestimate the excitation energies leading to suggest that the ground state may not be very well described with this functional.

The maximum extinction coefficient for **2** and $\mathbf{3}_{\mathbf{Pro}}$ of the band centered at ≈425 nm is approximately half the extinction coefficient of the corresponding band for **1**. The band observed at ≈2.9 eV/≈425 nm in the spectra of **2** and $\mathbf{3}_{\mathbf{Pro}}$ has higher oscillator strengths than what is observed in the spectrum of **1**. This finding was also confirmed by the calculations in which the lowest symmetry allowed transitions for $\mathbf{1}_{\mathbf{model}}$ is at 3.45 eV, whereas the lowest symmetry allowed transitions for $\mathbf{2}_{\mathbf{model}}$ and $\mathbf{3}_{\mathbf{model}}$ are at 3.16 eV. The highest symmetry groups possible for $\mathbf{1}_{\mathbf{model}}$, $\mathbf{2}_{\mathbf{model}}$, and $\mathbf{3}_{\mathbf{model}}$ are *D4h*, *D2h* and *C2v*, respectively, whereas the symmetry is lowered when alkyl groups are considered, for example, the highest symmetry group for **1**, **2**, and $\mathbf{3}_{\mathbf{Pro}}$ is *Cs*. Calculations carried out on **1**, $\mathbf{2}_{\mathbf{Pro}}$, and $\mathbf{3}_{\mathbf{Pro}}$ are presented in the Supporting Information. Some transitions rendered forbidden by symmetry are now allowed. The lowest transitions for **2** and $\mathbf{3}_{\mathbf{Pro}}$ are 3.00 and 2.92 eV, respectively, which corresponds well with the S_1 energies deduced from the UV/Vis and fluorescence spectra. However, the transitions moments are weak, which also explains the comparatively lower quantum yields observed (0.3 for **2** and **3**). We observed the same phenomenon for **1**, in which calculations on $\mathbf{1}_{\mathbf{model}}$ give a value for the energy of S_1 to 2.95 eV. According to the calculations, this transition is symmetry forbidden explaining the low quantum of 0.1 for **1**. In previous work, two fluorescence lifetimes were found for tetra-*tert*-butyl-tetraoxa[8]circulene, which can be ascribed the symmetry forbidden nature of the S_1 state for this compound making decay from the S2 to the ground state viable. Solvent effects were probed by computations using a PCM model and dielectric constants for dichloromethane. A negligible shift in excitation energies was observed compared to the values found from the calculations in vacuo (see the Supporting Information).

We have previously observed that the first oxidation potentials of a series of π-extended tetraoxa[8]circulenes decrease almost exponentially with the number of benzene rings in the molecules.[10] At the same time, the first reduction potentials for this series of molecules have identical values. This trend is not observed for the series studied here. The reduction potentials for **2** (−2.52 V) and $\mathbf{3}_{\mathbf{Pro}}$ (−1.55 V) clearly differs from the reduction potential of −2.40 V for **1**. The first oxidation potential for **2** and $\mathbf{3}_{\mathbf{Pro}}$ are identical (0.67 V), whereas the second potential is sensitive to the number of nitrogen atoms in the ring system.

Aromaticity/antiaromaticity of the different rings in the diazadioxa[8]circulene was evaluated by using NICS calculations (Figure 4). Both NICS(0) and $\mathrm{NICS(1)}_{zz}$ values were calculated at the B3LYP/6-311+G(d,p) level of theory by using geometries obtained from B3LYP/6-31+G(d) calculations.[7,20] The results suggest that in the neutral form, the planarized COTs of **1**, **2** and **3** are antiaromatic (positive values). Meanwhile the benzene, the furan and pyrrole rings are aromatic, which is in accordance with our previous work. In the case of the doubly oxidized (2+) **1**–**3** our calculations indicate that the COTs retain their antiaromaticity, whereas in the doubly reduced (2−) species the COTs are aromatic (large negative values). In all oxidation states studied, the benzene, furan, and pyrrole rings appear to retain their aromaticity.

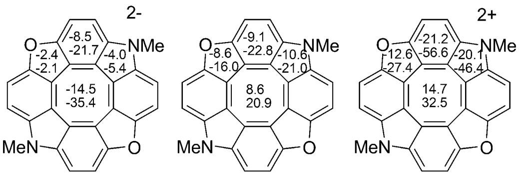


Figure 4. NICS(0) and $\mathrm{NICS(1)}_{zz}$ (lower numbers) values calculated for diazadioxa[8]circulene ($\mathbf{3}_{\mathbf{Me}}$). For comparison, the same values for tetraoxa[8]circulene (**1**) and azatrioxa[8]circulene (**2**) are given in the Supporting Information.

Conclusion

We have presented the first synthetic protocol for a diazadioxa[8]circulene (**3**) and have compared its properties with those of its isoelectronic tetraoxa[8]circulene (**1**) and azatrioxa[8]circulene (**2**).

Experimental Section

General experimental procedures: Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). Dry column vacuum chromatography was carried out using silica gel 60 (Merck 9385, 0.015–0.040 mm). Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H- (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker instrument. Samples were prepared by using deuterated solvents ($CDCl_3$, [D$_6$]DMSO, CD_2Cl_2) purchased from Cambridge Isotope Labs. Fast atom bombardment (FAB) spectra were obtained on a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode using 3-nitrobenzyl alcohol (NBA) as matrix. EI-MS spectra were recorded on a ZAB-EQ (VG-Analytical) instrument. Microanalyses were performed by Mrs Birgitta Kegel at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen. UV/Vis spectra were recorded on a Cary 5E (Varian Inc.) with pure solvent as 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 $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods (SHELXS97) and refined using the SHELXL97 software package. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in the difference Fourier map and refined isotropically as constraint riding their parent atom in a fixed geometry. The molecular structure diagrams were made with the Ortep-3 and Mercury 3.0.1 programs.

Crystal-structure data

Compound 3_{Bn}. $C_{54}H_{54}N_2O_2$; $M_r=762.99$; monoclinic; $a=23.778(8)$, $b=15.476(4)$, $c=11.484(4)$ Å, $\alpha=90$, $\beta=98.82(2)$, $\gamma=90°$; $V=4176(2)$ Å^3; $T=122$ K; space group Cc; $Z=4$; $\mu(\mathrm{Mo_{K\alpha}})=0.07$ mm^{-1}; 38033 reflections measured, 7318 independent reflections ($R_{int}=0.120$). The final $R1$ values were 0.062 $[F^2>2\sigma(F^2)]$. The final $R1$ values were 0.079 (all data). The final w$R(F^2)$ (all data) values were 0.127. The goodness of fit on F^2 was 1.11. CCDC-945390 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 3_{Pro}: $C_{46}H_{54}N_2O_2$; $M_r=666.91$; triclinic; $a=10.951(2)$, $b=14.036(2)$, $c=14.394(3)$ Å; $\alpha=110.48(2)$, $\beta=103.361(14)$, $\gamma=105.763(16)°$; $V=1859.6(8)$ Å^3; $T=122$ K; space group $P\bar{1}$; $Z=2$; $\mu(\mathrm{Mo_{K\alpha}})=0.07$ mm^{-1}; 42204 reflections measured, 6539 independent reflections ($R_{int}=0.113$). The final $R1$ values were 0.064 $[F^2>2\sigma(F^2)]$. The final $R1$ values were 0.1018 (all data). The final w$R(F^2)$ (all data) values were 0.123. The goodness of fit on F^2 was 1.12. CCDC-945393 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations: The Gaussian 03 suite of programs was used for the DFT calculations. Initially, geometry optimizations were carried out at the B3LYP/6–31G(d) level of theory, in which all the structures were constrained to $C2v$ symmetry. Frequency calculations were then carried out to assure that the structures were indeed minima on the potential energy surface (no imaginary frequencies). TD-DFT calculations and single-point calculations on the anion radicals were then carried out at the B3LYP/6–31G(d) level of theory on these optimized 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, Bu_4NBF_4 (Aldrich, 98%) and acetonitrile, MeCN (Lab-Scan, HPLC grade) were used as received. The cell was a cylindrical vial equipped with a Teflon top with holes to accommodate the Pt working electrode, the Pt counter electrode and the Fc/Fc$^+$. The electrochemical equipment was 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 volume of the resulting solutions was typically between 5 and 10 mL. The solutions were purged with nitrogen saturated with MeCN for at least 10 min prior to the measurements.

***N*-Benzyl-9*H*-carbazole (6)**: The 9*H*-carbazole (95%, 50.0 g, 280 mmol) was suspended in toluene (350 mL) and 12 M NaOH (400 mL) was added to the solution. After stirring for 10 min, tetrabutylammonium iodide (11.2 g, 30 mmol) was added to the orange reaction mixture under constant stirring at room temperature. Benzylbromide (40 mL, 336 mmol) was added at once, which resulted in a yellow reaction mixture after one hour. The reaction mixture was left stirring at room temperature for two hours. The conversion was determined by TLC on silica. The phases were separated and the aqueous phase was extracted with dichloromethane (3×150 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 recrystallized from 96% ethanol (200 mL). The crystals were washed with cold 96% ethanol (≈80 mL) until white needle-shaped crystals of *N*-benzyl-9*H*-carbazole were achieved. Yield: 70.1 g, 96%. M.p. 114–116°C. TLC: $R_f=0.67$ (*n*-heptane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=5.53$ (s, 2H), 7.15 (d, 2H, $J=7.5$ Hz), 7.23–7.29 (m, 5H), 7.37 (d, 2H, $J=7.5$ Hz), 7.44 (t, 2H, $J=7.5$ Hz), 8.15 ppm (dt, 2H, $J=7.5$, 0.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=46.58$, 108.91, 119.22, 120.41, 123.05, 125.86, 126.43, 127.46, 128.79, 137.20, 140.69 ppm; GC-MS: $t_R=25.874$ min ($m/z=257.2$ [M^+]); elemental analysis calcd (%) for $C_{19}H_{15}NC$: C 88.68, H 5.88, N 5.44; found: C 88.58, H 5.53, N 5.59;.

***N*-Benzyl-3,6-dibromo-9*H*-carbazole (7)**: The *N*-benzyl-9*H*-carbazole (64.73 g, 251.5 mmol) was suspended in glacial acetic acid (500 mL) followed by a drop-wise addition of bromine (13.5 mL, 41.85 g, 523 mmol) in glacial acetic acid (500 mL) over the course of one hour at RT. After addition of half the bromine, the solution turned clear, followed by the formation of a white precipitate. More glacial AcOH (300 mL) was added. After stirring for two hours, the reaction product was filtered and the crystals washed with H_2O (200 mL). The mother-liquor was treated with water (ca. 400 mL) until no more product precipitated. It was again filtered and washed with H_2O (100 mL). The crude product was crystallized from glacial AcOH (800 mL) and washed several times with cold 96% EtOH to yield a white solid. Yield: 102.73 g, 98%. M.p. 151–152°C; TLC: R_f =0.38 (*n*-heptane/EtOAc, 5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=5.68$ (s, 2H), 7.12 (d, 2H, $J=7.5$ Hz), 7.20–7.28 (m, 3H), 7.59 (d, 2H, $J=8.5$ Hz), 7.64 (d, 2H, $J=8.5$ Hz), 8.51 ppm (s, 2H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta=45.76$, 111.62, 111.92, 123.11, 123.52, 126.62, 127.38, 128.62, 128.99, 137.16, 139.23 ppm; GC-MS: $t_R=30.159$ min ($m/z=415.0$ [M^+]); elemental analysis calcd (%) for $C_{19}H_{13}Br_2N$: C 54.97, H 3.16, N 3.37; found: C 55.04, H 2.92, N 3.34.

***N*-Benzyl-3,6-dimethoxy-9*H*-carbazole (8)**: The *N*-benzyl-3,6-dibromo-9*H*-carbazole (35.0 g, 84 mmol) was dissolved in dry DMF (500 mL) under a nitrogen atmosphere. Cu^{I}I (20 mol%, 3.21 g, 17 mmol) and NaOMe in methanol (840 mL, 25% in MeOH) were added at once, respectively. The reaction mixture was kept under nitrogen and heated at reflux overnight. The resulting suspension was treated with aqueous ammonia (ca. 180 mL, 24% in H_2O) to give a brown suspension, which turned blue after the addition of water (300 mL). The suspension was extracted with dichloromethane (3×150 mL) and the combined organic extracts were washed with brine (2×80 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was crystallized from methanol (ca. 250 mL) to give a white crystalline solid. Yield: 25 g, 94%. M.p. 134–135°C; TLC: $R_f=0.38$ (*n*-heptane/EtOAc, 5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=3.85$ (s, 6H), 5.56 (s, 2H), 7.03 (dd, 2H, $J=9$, 2 Hz), 7.11 (d, 2H, $J=7.5$ Hz), 7.18–7.25 (m, 3H), 7.47 (d, 2H, $J=9$ Hz), 7.75 ppm (d, 2H, $J=2$ Hz). ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta=45.68$, 55.60, 103.22, 110.26, 114.94, 122.48, 126.61, 127.10, 128.46, 135.61, 138.12, 152.98 ppm; GC-MS: $t_R=28.669$ min ($m/z=317.2$ [M^+]); elemental analysis calcd (%) for $C_{21}H_{19}NO_2$: C 79.47, H 6.03, N 4.41; found: C 79.55, H 5.78, N 4.59.

***N*-Benzyl-3,6-dimethoxy-2,7-di-*tert*-butyl-9*H*-carbazole (9)**: Under a nitrogen atmosphere, the *N*-benzyl-3,6-dimethoxy-9*H*-carbazole (1.00 g, 3.2 mmol) was dissolved in dry dichloromethane (15 mL). Iron(III) chloride (anhydrous, 0.40 g, 2.5 mmol) was added to the solution. The reaction mixture was cooled to 0°C followed by a very slow drop-wise (four hours) addition of 2-chloro-2-methylpropane (20 mL, 181.5 mmol) at 0°C. After stirring overnight, another portion of iron(III) chloride (anhydrous, 0.40 g, 2.5 mmol) was added. The reaction was left to stir under a nitrogen atmosphere for another two hours and the conversion was determined by GC-MS. The reaction mixture was quenched with 2 M HCl (30 mL) and the phases where separated. The aqueous phase was extracted with dichloromethane (3×30 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and filtered. Thick purple/black oil was obtained after removal of the solvent under reduced pressure. The crude product was crystallized in 96% ethanol (ca. 25 mL) and the resulting off-white solid was washed several times with cold 96% ethanol (ca. 15 mL). Yield: 0.98 g, 73%. M.p. 168–169°C; TLC: $R_f=0.64$ (*n*-heptane/EtOAc, 5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=1.39$ (s, 18H), 3.92 (s, 6H), 5.56 (s, 2H), 7.18–7.23 (m, 3H), 7.28 (t, 2H, $J=7$ Hz), 7.34 (s, 2H), 7.70 (s, 2H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta=30.01$, 35.10, 45.64, 55.79, 103.03, 107.00, 120.00, 126.90, 127.11, 128.94, 135.06, 136.29, 138.41, 152.40 ppm; GC-MS: $t_R=31.058$ min ($m/z=429.3$ [M^+]); elemental analysis calcd (%) for $C_{29}H_{35}NO_2$: C: 81.08, H 8.21, N 3.26; found: C 81.14, H 8.43, N 3.22.

N-Benzyl-3,6-dimethoxy-2,7-di-*tert*-butyl-9*H*-carbazole (4): Under a nitrogen atmosphere, the *N*-benzyl-3,6-dimethoxy-2,7-di-*tert*-butyl-9*H*-carbazole (500 mg, 1.13 mmol) and tetra-*n*-butylammonium iodide (838 mg, 2.27 mmol) were placed into a flame-dried round-bottomed flask. Boron trichloride (11 mL, 11.00 mmol, 1 M in CH_2Cl_2) was added over two minutes at room temperature. The reaction mixture was left stirring for 55 min and afterwards quenched with 1 M HCl (80 mL). The resulting two-phase system was extracted with dichloromethane (4×70 mL). After drying the combined organic phases over anhydrous Na_2SO_4 and filtration, the solvent was removed under reduced pressure and the off-white foam-like crude product was purified by using dry column chromatography (MeCN/toluene, 1:40) to yield a white powder. Yield: 0.400 g, 86 %. M.p. 209–212 °C; TLC: $R_f = 0.27$ (*n*-heptane/EtOAc, 3:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 1.40$ (s, 18 H), 5.47 (s, 2 H), 7.18–7.29 (m, 5 H), 7.23 (s, 2 H), 7.24 (s, 2 H), 8.87 ppm (s, 2 H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 29.69$, 34.94, 45.66, 105.56, 106.61, 119.66, 126.91, 127.03, 128.43, 134.60, 134.74, 138.62, 149.18 ppm; GC-MS: $t_R = 26.368$ min ($m/z = 401.4$ [M^+]); elemental analysis calcd (%) for $C_{27}H_{31}NO_2$: C 80.76, H 7.78, N 3.49; found: C 80.55, H 7.84, N 3.43.

Bis(*N*-benzyl)diazadioxatetra-*tert*-butyl[8]circulene (3_{Bn}): Under a nitrogen atmosphere, the *N*-benzyl-3,6-dihydroxy-2,7-di-*tert*-butyl-9*H*-carbazole (180 mg, 0.45 mmol) and 2,3,5,6-tetrachloro-1,4-benzoquinone (55 mg, 0.22 mmol) were dissolved in dichloromethane (20 mL) in a flame-dried round-bottomed flask. To the solution $BF_3 \cdot OEt_2$ (0.06 mL, 0.45 mmol) was added. After 45 min, 1.5, and 3.5 h, 2,3,5,6-tetrachloro-1,4-benzoquinone (55 mg, 0.22 mmol, 0.5 equiv) was added and also (after 1.5 h) a onetime portion of $BF_3 \cdot OEt_2$ (0.06 mL, 0.45 mmol). The reaction mixture was left stirring for another 30 min and was afterwards quenched with 1 M HCl (50 mL). The resulting two-phase system was extracted with dichloromethane (4×60 mL). After drying the combined organic phases over anhydrous Na_2SO_4 and filtration, the solvent was removed under reduced pressure and the crude product was boiled with KOH in toluene (10 mL, 100 equiv) and ethanol (10 mL) overnight. The reaction mixture was quenched with 1 M HCl (50 mL) and the separated aqueous phase was extracted with dichloromethane (3×50 mL). After drying the combined organic phases over anhydrous Na_2SO_4 and filtration, the solvent was removed under reduced pressure and the crude product was purified by dry column chromatography (toluene/*n*-heptane, 1:12) to yield a yellow solid. Yield: 0.121 g, 71 %. M.p. 301–303 °C (decomposition). TLC: $R_f = 0.61$ (*n*-heptane/toluene, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.73$ (s, 36 H), 5.80 (s, 4 H), 7.26–7.33 (m, 5 H), 7.43 ppm (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 30.43$, 35.08, 47.44, 104.95, 112.75, 116.80, 126.61, 127.39, 128.77, 133.35, 136.97, 138.02, 149.61 ppm; MALDI (method: TJS10de, polarity: positive): $m/z = 762.084$ [M^+]; elemental analysis calcd (%) for $C_{54}H_{54}N_2O_2$: C 85.00, H 7.13, N 3.67; found: C 84.83, H 7.83, N 3.11.

Bis(*N*-propyl)diazadioxatetra-*tert*-butyl[8]circulene (3_{Pro}): Procedure similar to that of 3_{Bn}. Yield: 0.82 g, 85 %. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.98$ (t, $J = 7.3$ Hz, 6 H), 1.92 (s, 36 H), 1.97–2.05 (hex, $J = 7.3$ Hz, 4 H), 4.44–4.54 (m, 4 H), 7.40 ppm (br s, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 12.13$, 23.23, 30.56, 35.09, 45.28, 104.63, 112.41, 116.75, 133.01, 136.81, 149.39 ppm; elemental analysis calcd (%) for $C_{46}H_{54}N_2O_2$: C 82.84, H 8.16, N 4.20; found: C 82.93, H 8.26, N 4.11.

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