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Aromaticity

Synthesis and Structural Data of Tetrabenzo[8]circulene

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Abstract: In 1976, the first attempted synthesis of the saddle-shaped molecule [8]circulene was reported. The next 37 years produced no advancement towards the construction of this complicated molecule. But remarkably, over the last six months, a flurry of progress has been made with two groups reporting independent and strikingly different strategies for the synthesis of [8]circulene derivatives. Herein, we present a third synthetic method, in which we target tetrabenzo[8]circulene. Our approach employs a Diels–Alder reaction and a palladium-catalyzed arylation reaction as the key steps. Despite calculations describing the instability of [8]circulene, coupled with the reported instability of synthesized derivatives of the parent molecule, the addition of four fused benzenoid rings around the periphery of the molecule provides a highly stable structure. This increased stability over the parent [8]circulene was predicted by using Clar's theory of aromatic sextets and is a result of the compound becoming fully benzenoid upon incorporation of these additional rings. The synthesized compound exhibits remarkable stability under ambient conditions—even at elevated temperatures—with no signs of decomposition over several months. The solid-state structure of this compound is significantly twisted compared to the calculated structure primarily as a result of crystal-packing forces in the solid state. Despite this contortion from the lowest-energy structure, a range of structural data is presented confirming the presence of localized aromaticity in this large polycyclic aromatic hydrocarbon.

Introduction

Since the discovery and isolation of benzene by Faraday in 1825, the concept of aromaticity has been prevalent in the scientific literature.[1] For nearly two centuries, significant efforts have been made to understand the unique stability and reactivity that are inherent to cyclic species possessing conjugation. The generally accepted model of aromaticity proposes that electrons located in the p_z orbitals of rings, Kekulé structures of which are composed of alternating single and double bonds are free to move throughout the entire π system of the molecule.[2] Although this model typically holds true for systems composed of single rings, it is not an accurate description of the aromaticity in polycyclic aromatic hydrocarbons (PAHs).[3] A more accurate representation, as was described by Clar,[4] depicts these π electrons as localized to individual rings known as aromatic sextets, which are represented as circles in Clar structures (Figure 1). The most stable structures, according to this theory, are those in which hexagons can be represented as either isolated sextets or shown as "empty", that is, no double bonds exist outside of sextets (i.e., **2**). These are known as fully benzenoid structures. Compounds that display double bonds that are not incorporated into sextets (i.e., **1**) are considered to be less stable, and these double bonds are typically the sites of reactivity within a PAH.

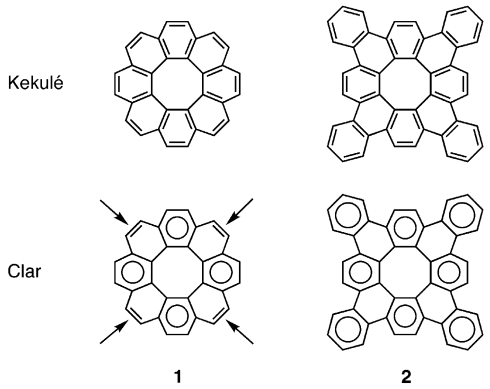

Figure 1. Kekulé and Clar structures of [8]circulene **1** and tetrabenzo[8]circulene **2**. The nonaromatic double bonds, and likely sites of instability in **1** are indicated. These double bonds are incorporated into aromatic sextets in **2** resulting in a fully benzenoid, and therefore more stable structure.

With Clar's theory in mind, we set our sights on the synthesis of a stable [8]circulene derivative. [8]Circulene belongs to the [*n*]circulene family of molecules, in which a central *n*-mem-

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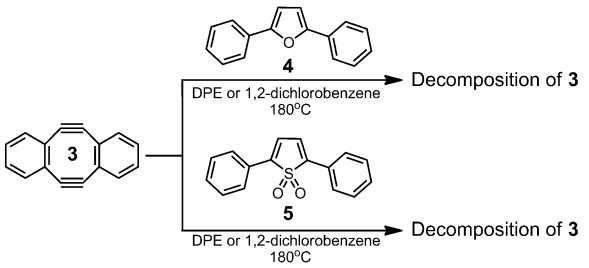
bered ring is surrounded by *n*-fused benzene rings. These molecules are particularly interesting, because the shape of the structures changes considerably with a changing value of *n*.[5] This *n*-dependent conformation of the [*n*]circulene is revealed in the crystal structures of bowl-shaped quadrannulene[6] ([4]circulene) and corannulene[7] ([5]circulene), planar coronene[8] ([6]circulene) and saddle-shaped pleiadannulene ([7]circulene).[9] Although [8]circulene is the next largest synthetic target in this family, the compound has remained quite elusive. The first attempted synthesis was reported in 1976 by Wennerström and co-workers, but the reversible nature of the photoreaction used in the final step of their synthetic strategy was not conducive to retaining the strain formed in the final bond closures.[10] Calculations following this report indicated that **1** is unstable as a result of concentric aromatic currents between the inner and outer rings of the molecule.[11] Nevertheless, Wu and co-workers recently reported the first synthesis of a number of highly substituted [8]circulene derivatives.[12] Unfortunately, these compounds—as calculations predicted—appear to lack stability under ambient conditions. This instability could also be explained with Clar's theory of aromatic sextets. Consider the Clar structure of **1** (Figure 1): there are four double bonds present that are external to the four sextets in the molecule. Although such bonds also exist in smaller circulene analogues, the greater strain inherent to [8]circulene has the potential to make these bonds more reactive and therefore a source of instability. If this is the case, the reactivity of these bonds could be masked by incorporating them into sextets through the installation of additional benzenoid rings around the periphery of the molecule. This results in a fully benzenoid, and therefore a theoretically highly stable derivative of [8]circulene.

Following the submission of this manuscript, an elegant synthesis of this very molecule, tetrabenzo[8]circulene, was reported by Suzuki and co-workers[13] utilizing a Scholl reaction on a cyclic octaphenylene precursor as the final bond forming step. Surprisingly, there is little discussion of the remarkable stability of this compound despite the low stability of the parent compound predicted by calculations[11] and confirmed from Wu's syntheses.[12] Herein, we describe an alternative strategy for the preparation of tetrabenzo[8]circulene and report on the innate structural features that support the concept of localized aromaticity and the inherent stability that goes along with it.

Results and Discussion

Synthesis

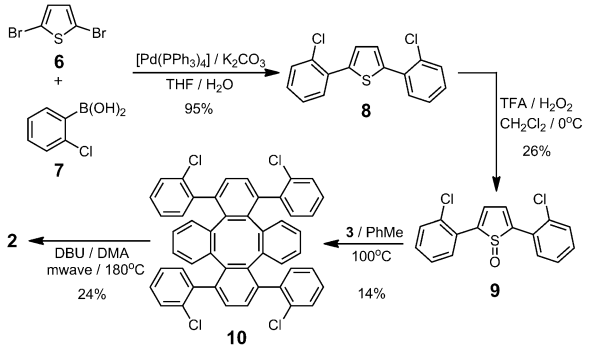
In contrast to the previous report by Sakamoto and Suzuki, in which the requisite eight-membered ring was formed in the final step of the synthetic sequence,[13] we chose to initiate our synthesis with this ring already assembled. With this in mind, we envisioned that dibenzocyclooctadiyne[14] (**3**) would be the ideal starting material, because it possesses the central eight-membered ring and has been demonstrated to be an efficient dienophile in Diels–Alder reactions with a number of dienes.[15]



Scheme 1. Attempted Diels–Alder reactions between diyne, **3**, and either furan **4** or sulfone **5**. As a result of the high reaction temperatures required for these reactions, only decomposition of **3** was observed and no desired product was recovered from the cycloaddition reaction.

Although the Diels–Alder reaction of **3** with a 3,4-disubstituted furan derivative has been reported,[15b] extension of this methodology to incorporate 2,5-diphenylfuran (**4**), as displayed in Scheme 1, was unsuccessful. This failure is likely a result of the higher temperature required to overcome the increased steric bulk installed at the reactive carbons of the diene coupled with the relatively low decomposition temperature of dienophile, **3** (ca. 110 °C).[16] The incorporation of a 2,5-diphenylthiophene dioxide (**5**) as the diene gave similar results again due to the decomposition of **3** at the high temperature required for the reaction. Attempts to expedite the reaction by using microwave irradiation were also unsuccessful.

At this point, we turned our focus to 2,5-disubstituted sulfoxide, **9**. Sulfoxides derived from thiophenes have been identified as intermediates in the formation of thiophene dioxides as a result of the self-dimerization products of the sulfoxide being present following the oxidation reactions. Surprisingly, despite the fact that methods to synthesize these compounds[17] have been known for nearly two decades, they have been significantly underutilized as dienes in Diels–Alder reactions. We were surprised to find that sulfoxides are much more reactive dienes than their dioxide counterparts and typically require lower reaction temperatures. This makes them an ideal candidate for reactions incorporating temperature sensitive dienophiles. Synthetically, our target diene could be readily synthesized from the Suzuki coupling of 2,5-dibromothiophene (**6**) and *o*-chlorophenylboronic acid (**7**) to produce 2,5-diarylthiophene (**8**) as shown in Scheme 2. The oxidation of **8** was car-



Scheme 2. Preparation of tetrabenzo[8]circulene (**2**); DBU = 1,8-diaza-bicycloundec-7-ene; DMA = *N*,*N*-dimethylacetamide; and Cy = cyclohexyl.

ried out through the dropwise addition of 30% H_2O_2 (aq.) into a TFA/CH_2Cl_2 (1:2) mixture at 0 °C to produce **9** in 26% yield. It is important to note that this reaction is highly time dependent, and extended reaction times led to increased production of the undesired dioxide. To avoid over-oxidation, shorter reaction times, typically 3 h, were utilized. Although this resulted in low yields of the desired product, a near-quantitative recovery of unreacted starting material was possible. Compound **9** can be stored for extended periods of time at 0 °C, but decomposes quickly at approximately 120 °C to thiophene precursor, **8**.

The double Diels–Alder reaction between diyne **3** and sulfoxide **9** proceeded smoothly in PhMe at 100 °C. However, the ^{1}H NMR spectrum of product **10** (Figure S5 in the Supporting Information) exhibited an unexpectedly large number of broad peaks in the aromatic region, indicating that there is hindered rotation of the chlorinated phenyl rings. As a result, this compound likely exists as a mixture of atropisomers. Variable-temperature ^{1}H NMR of **10** in [D_6]DMSO at 100 °C provided no resolution of these broad peaks indicating a significantly high barrier to rotation within the molecule. The high steric congestion responsible for this rotational barrier also provides some insight into the low yields of the Diels–Alder reaction.

Compound **10** was exposed to microwave-assisted arylation conditions by using [$Pd(PCy_3)_2Cl_2$] as the catalyst and 1,8-diazabicycloundec-7-ene (DBU) as the base. These coupling conditions have been used to produce a number of contorted PAHs, and this method has proven to be extremely powerful at generating strained molecules.[18] Surprisingly, by using standard reaction times and temperatures under microwave irradiation, we observed only starting material with no formation of the desired compound. We believe this result can also be attributed to the high rotational barrier of the pendant aryl rings and the fact that these rings must be provided with enough energy to allow them to overcome this barrier and rotate into a reactive position. As a result, it was required that we heat our reaction to 180 °C to provide the necessary energy to perform the transformation, and **2** was isolated in an impressive 24% (70% per coupling) yield.

Despite the significant differences between our synthetic strategy and the one employed by Sakamoto and Suzuki,[13] the overall yields of our sequences from known materials are quite similar. However, we believe that our method provides a significant advantage. For the final strain-inducing bond formation, we employed the reliable palladium-catalyzed arylation reaction, whereas the method developed by Sakamoto and Suzuki utilizes an oxidative coupling commonly referred to as the Scholl reaction. Although the Scholl reaction has the benefit of not requiring the installation of halides to accomplish bond formation, it suffers from the fact that the reaction can be extremely temperamental. The success of the transformation is typically highly dependent on the substrate, and electron-donating groups are often required to promote the oxidative coupling.[19] Additionally, Scholl reactions are historically used for ring closures on planar species,[20] most notably in the final bond formation of hexa-*peri*-hexabenzocoronene,[21] and aside from the synthesis of **2** by Suzuki, there are few examples of strained nonplanar PAHs that are formed through such conditions.[22] Although this fact makes the methodology developed by Sakamoto and Suzuki even more impressive, we believe that the implementation of the Scholl reaction will present limitations on the functionality that can be introduced onto the periphery of compound **2**. As a result of this limitation, we believe that the method reported herein provides greater potential to incorporate a range of functional groups onto **2**, thereby allowing greater control over its optoelectronic properties. Studies to accomplish this task are currently underway in our laboratory.

Structural characterization

Compound **2** has limited solubility in common organic solvents, although it will readily dissolve in 1,2-dichlorobenzene (ca. 10 mg mL^{-1}) upon heating. Unlike the [8]circulene derivatives synthesized by Wu and co-workers,[12] the compound is highly stable and no decomposition was observed after five months of storage under ambient conditions. Furthermore, heating **2** in an aerobic solution of [D_6]DMSO at 100 °C for 24 h revealed no observable decomposition products.

The ^{1}H NMR spectrum of **2** matches the previously reported data,[13] and is composed of three peaks of equal integration at $\delta = 8.09$, 7.69, and 7.56 ppm. Similarly, the ^{13}C NMR spectrum displays only six different chemical environments for the 48 carbon atoms in the structure. This indicates that **2** is highly symmetric, and the experimental data agrees with the saddle-shaped structure (Figure 2A and B) of D_{2d} symmetry derived from gas-phase DFT calculations (B3LYP/6-31G** and M06-2X/6-31G** produced nearly identical structures).

Yellow block-like crystals of **2** were grown from the slow evaporation of 1,2-dichlorobenzene, and the structure confirmed by X-ray crystallography[23] is identical to the reported structure obtained from crystals grown from toluene.[13] As has been observed previously, the solid-state structure deviates significantly from the DFT predictions and two symmetry independent molecules of **2** (residue I is displayed in Figure 2C and D) that belong to an S_4 point group are present in the crystal. These residues are not significantly different from each other (the mean comparable bond lengths between the two residues is 0.01 Å with a maximum deviation of 0.04 Å and a root-mean square deviation in atomic positions of 0.196 Å, an image overlaying these two residues is displayed in Figure S8 in the Supporting Information), and for our purposes, the structure of only one of these residues will be discussed.

DFT calculations are typically accurate at predicting the structure of contorted PAHs, and as a result of the high symmetry indicated by ^{1}H NMR and ^{13}C NMR spectroscopy, we believe the DFT structure is an accurate representation of the molecule as it exists in solution (the solid-state structures with S_4 symmetry would display six unique proton signals in the ^{1}H NMR spectrum) and that crystal-packing forces in the solid state are responsible for the distortion in the X-ray structure. To identify which arrangement is more stable, single-point calculations (M06-2X/6-311G**++//M06-2X/6-31G**) were performed and demonstrated that the DFT structure is lower in

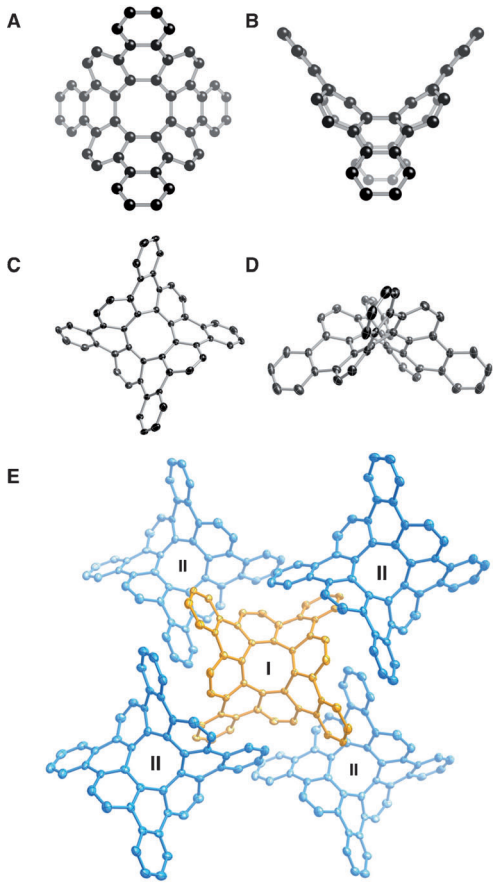


Figure 2. A) Top and B) side views of the DFT-minimized structure (B3LYP/6-31G**) of **2**. C) Top and D) side views of residue I of the X-ray structure of **2**. E) Illustration of the crystal packing between residue I (orange) and residue II (blue) in the crystal structure of **2**. In the 3-dimensional structure, the peripheral benzenoid rings of each residue form π-stacking interactions with the analogous rings of four molecules of the opposite residue (two on each face) creating a 3-dimensional π-stacking network. The thermal ellipsoids are displayed at 50% probability, and the hydrogen atoms have been removed for clarity. Disordered solvent was SQUEEZED during refinement.

energy by approximately 1.8 kcal mol^{-1} compared to the x-ray structures.[24]

The two pinwheel-like residues present in the crystal structure of **2** and a representation of the crystal packing of these residues are displayed in Figure 2E. As a result of the highly contorted nature of **2**, we initially predicted that these structures would form self-complementary linear stacks much like the contorted derivatives of hexa-*cata*-hexabenzocoronene developed by Nuckolls and co-workers.[22,25] Therefore, we were surprised to find the unique packing structure inherent to these molecules. Rather than a herringbone or slip-stacked packing typical of PAHs, we found that the structure instead forms a complex 3-dimensional arrangement, in which each of the four peripheral benzenoid rings on each molecule of residue I forms a π-stacking interaction with the analogous rings on a molecule of residue II (these rings are offset with a minimum intermolecular C–C distance of 3.25 Å; see Figure S9 in the Supporting Information). Likewise, each molecule of residue II forms equivalent interactions with four molecules of residue I providing an uninterrupted 3-dimensional π-stacking network. Experiments to determine if this packing motif can be exploited for molecular electronics applications are currently underway.

The experimental structure is higher in energy than the DFT structure, and the manner in which this tension is distributed throughout the molecule is particularly interesting. To analyze the strain, π-orbital axis vector (POAV)[26] pyramidalization angles (defined as $\theta_{\sigma\pi}-90^{\circ}$) were calculated for the relevant carbon atoms in the X-ray and DFT structures (Figure 3A and

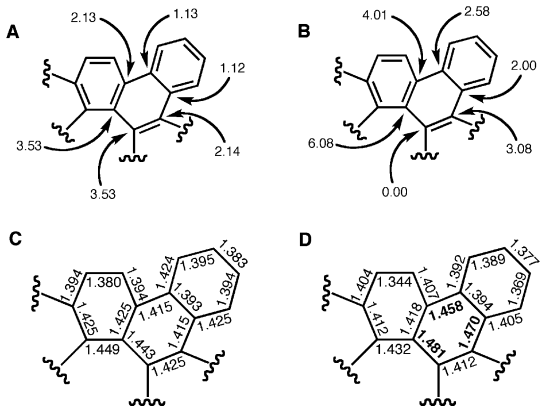
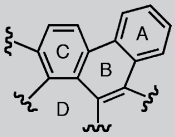


Figure 3. POAV angles [°] of A) DFT-minimized structure and B) the solid-state structure of tetrabenzo[8]circulene (**2**). Selected bond lengths [Å] of C) DFT-minimized structure and D) solid-state structure. Quasi-single bonds identified in the solid-state structure are indicated by bold values. A complete list of bond lengths and their associated errors can be found in Table S1 in the Supporting Information.

B). The most noteworthy angles arise from the eight-membered ring. In the DFT structure, strain is evenly distributed throughout the ring with each carbon atom displaying a POAV angle of 3.53° (Figure 3A). However, in the X-ray structure, the strain is distributed on alternating carbon atoms. For example, half of the carbon atoms (Figure 3B) have POAV angles of 6.08°, and the remaining carbon atoms are completely planar, that is, exhibit POAV angles of 0°. If we move away from the central ring, the DFT structure exhibits symmetrical strain with decreasing POAV angles when we approach the peripheral benzenoid rings. The corresponding POAV angles in the experimental structure are larger and continue to lack the symmetrical distribution of strain observed in the DFT structure.

Despite the relatively large POAV angles and the twisted nature of the solid-state structure, the hexagonal rings of **2** remain quite planar. For our purposes, we define planarity as the average distance of the carbon atoms in a ring from a generated best-fit plane. Using this method, a ring that has an average carbon–plane distance of 0 Å is considered to be completely planar, and an increase in this value is indicative of an increase in the distortion from planarity. The relatively planar nature of these rings indicates that a majority of the strain is built up at the sites of ring fusion rather than within the rings themselves. Notably, the carbon atoms in the ring that is "empty" in the Clar structure (Table 1, ring B) are displaced

Table 1. Structural data of the calculated and solid-state conformations.[a]



	Ring	DFT structure	X-ray structure
planarity [Å][b]	A	0.002	0.011
	B	0.116	0.130
	C	0.096	0.080
	D	0.397	0.375
average bond length [Å]	A	1.402	1.402
	B	1.420	1.438
	C	1.411	1.403
	D	1.446	1.457
HOMA index[c]	A	0.880	0.965
	B	0.689	0.064
	C	0.716	0.744
	D	0.131	−0.364

[a] The structural data is presented as symmetrical averages. [b] Planarity values were calculated by constructing a best-fit plane through the individual rings of **2** and measuring the average distance of the carbon atoms from this plane. [c] HOMA indices were calculated by using a normalization constant, α, of 257.7 and the optimal C–C bond length, $R_{opt,}$ of 1.338 Å.

from the plane significantly more than those in the rings containing aromatic sextets (Table 1, rings A and C); that is, the rings, which are expected to exhibit localized aromaticity, display less deviation from a planar structure than those that are not. This is strong evidence that the Clar representation is an accurate depiction of the aromaticity in this molecule. As expected, the central eight-membered ring distorts significantly to avoid the anti-aromaticity that would potentially result from it adopting a planar conformation (Table 1, ring D).

Further evidence supporting the Clar structure can be observed in the bond lengths of the calculated and experimental structures. Similar to the POAV angles, the bond lengths of the DFT structure are highly symmetrical, whereas those of the solid-state structure are not. Despite this dissymmetry, the bond lengths of the experimental structure correlate strongly with those expected from the Clar structure. Most notably is that three quasi-single bonds—that is, bonds that are significantly longer than all of the other bonds in the molecule (represented as bold values in Figure 3)—are present in the "empty" ring of the Clar structure. This is expected, because these bonds are not members of aromatic rings and serve only to connect the areas of localized aromaticity. As a direct consequence of these longer bonds, we observe that the rings containing aromatic sextets have a significantly shorter average bond length (1.402 and 1.403 Å) compared to the "empty" ring (1.438 Å).

The harmonic oscillator model of aromaticity (HOMA) was used to determine the aromaticity of the individual rings in the calculated and X-ray structure (Table 1).[27] HOMA values of −1, 0, and 1 indicate anti-aromaticity, nonaromaticy, and aromaticity, respectively. Although the calculated structure exhibits moderate to high levels of aromaticity for each of the hexagonal rings, the values calculated for the solid-state structure correlate strongly with the Clar structure. We observe values approaching 1 for the two rings represented as sextets in the Clar structure (Table 1) with values of 0.965 and 0.744 for rings A and C, respectively. Similarly, it is interesting to note that the ring that is represented as "empty" in the Clar structure (Table 1, ring B) exhibits a HOMA value of 0.064 indicating that this ring can be regarded as nonaromatic. These results are in agreement with the nucleus independent chemical shift (NICS)[28] data calculated by Sakamoto and Suzuki, in which the two sextet-containing rings exhibited aromatic character and the "empty" ring was only moderately aromatic.[13] Interestingly, the central eight-membered ring exhibits slight anti-aromaticity in the experimental structure. This is in contrast to the values calculated from the crystal structure of the [8]circulene derivatives synthesized by Wu and co-workers,[12] in which this ring exhibited nonaromatic character. Overall, this data provides further evidence that the Clar representation of the structure is accurate.

Conclusion

We have applied Clar's theory of aromaticity to transform the unstable [8]circulene molecule into a stable derivative simply by the installation of four benzenoid rings around the periphery of the molecule. The structure exhibits a deep saddle-shaped structure that is quite malleable and distorts significantly in the solid state to form a complex 3-dimensional π-stacking network. Despite the twisted nature of the solid-state structure measurements of ring planarity, bond lengths, and HOMA values all confirm the Clar representation of a fully benzenoid species, thereby offering an explanation for its high stability. The elaboration of this methodology to synthesize more functionalized derivatives and investigations of the electronic properties of these molecules are underway. Furthermore, the synthetic approach is currently being utilized to synthesize larger, fully benzenoid circulenes.

Experimental Section

General methods

Anhydrous and anaerobic solvents were obtained from purification columns (Pure Process Technology, Nashua, NH). All reagents were obtained from commercial sources and were used as received unless mentioned otherwise. All reactions were run under a nitrogen atmosphere and monitored by TLC by using silica-gel 60 F_{254} precoated plates (Silicycle). Column chromatography was performed on a CombiFlash R_f 200 system by using RediSep normal-phase silica columns (ISCO, Inc., Lincoln, NE). Microwave experiments were conducted in a CEM Discover model 909150 by using 10 mL microwave tubes (CEM Corporation, Matthews, NC). ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Ascend 500 MHz spectrometer at RT, and peaks were calibrated against an internal TMS standard. High-resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ Orbitrap Discovery. 3-Dimensional images were generated using Crystalmaker: a crystal and molecular structures program for Mac and Windows. Crystal-maker Software Ltd, Oxford, England (www.crystal-

maker.com). POAV angles were measured by using mol²mol (www.gunda.hu/mol2mol/index.html). Dibenzocyclooctadiyne (**3**) was synthesized according to a literature procedure.[14]

Syntheses

Synthesis of 2,5-bis(2-chlorophenyl)thiophene (8): In a 250 mL two-necked round-bottom flask equipped with a stir bar and reflux condenser, a mixture of deionized H_2O (62.5 mL) and THF (125 mL) was degassed by bubbling nitrogen for 15 min. 2,5-Dibromothiophene **6** (5.00 g, 20.7 mmol), 2-chlorophenylboronic acid **7** (6.93 g, 45.5 mmol), K_2CO_3 (17.13 g, 124.0 mmol), and $[Pd(PPh_3)_4]$ (1.19 g, 1.03 mmol, 5 mol%) were added, and the reaction mixture was vigorously stirred while heated at reflux over a period of 12 h. The reaction mixture was cooled to RT and quenched by the addition of saturated NH_4Cl (aq.; 50 mL). The crude reaction mixture was extracted with EtOAc (3× 30 mL). The combined extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, hexanes, $R_f = 0.51$) afforded pure 2,5-bis(2-chlorophenyl)thiophene **8** (6.27 g, 95%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.60$ (dd, $J = 7.5$, 1.5 Hz, 2H), 7.50 (dd, $J = 8.0$, 1.5 Hz, 2H), 7.39 (s, 2H), 7.32 (td, $J = 6.0$, 1.5 Hz, 2H), 7.27 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 140.9, 132.9, 132.2, 131.3, 130.6, 128.7, 127.7, 127.0 ppm; HRMS ESI $[M+1]$: calcd for $C_{16}H_{11}Cl_2S_1$: 304.9953, found: 304.9953.

Synthesis of 2,5-bis(2-chlorophenyl)thiophene-1-oxide (9): In a 25 mL round-bottom flask equipped with a stir bar, compound **8** (5.31 g, 17.39 mmol) was added to a solution of TFA (20 mL) and CH_2Cl_2 (40 mL). The mixture was cooled to 0 °C in an ice/water bath, and a 30% H_2O_2 (7.89 g, 69.6 mmol) solution was added dropwise over a period of 5 min. The temperature was maintained at 0 °C for 3 h before the reaction was quenched by the addition of saturated $NaHCO_3$ (aq.; 100 mL). The crude reaction mixture was extracted with CH_2Cl_2 (4×25 mL), the combined extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the crude material by column chromatography (SiO_2, hexanes/CH_2Cl_2 1:1; $R_f = 0.37$) afforded pure **9** (1.43 g, 26%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.78$ (dd, $J = 7.0$, 1.5 Hz, 2H), 7.53 (dd, $J = 6.5$, 0.5 Hz, 2H), 7.37 (m, 4H), 7.19 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 150.5$, 132.8, 131.5, 130.9, 130.2, 129.2, 128.8, 127.4 ppm; HRMS ESI $[M+1]$: calcd for $C_{16}H_{11}Cl_2O_1S_1$: 320.9902; found: 320.9905.

Synthesis of 1,4,9,12-tetrakis(2-chlorophenyl)tetraphenylene (10): In an oven-dried two-neck 25 mL round-bottom flask equipped with a reflux condenser and a stir bar, compound **9** (1.06 g, 3.29 mmol, 2.2 eq) and dibenzocyclooctyne **3** (300 mg, 1.50 mmol) were dissolved in anhydrous toluene (12 mL), and the reaction mixture was heated at 100 °C for 16 h. The crude reaction mixture was cooled to RT, and the solvent was removed under reduced pressure. Column chromatography (SiO_2, hexanes/CH_2Cl_2 4:1; $R_f = 0.26$) afforded pure **10** (161.10 mg, 14%) as an orange-red solid. ^{1}H NMR (500 MHz CD_2Cl_2) was very complex due to the presence of atropisomers, and therefore values are not reported. A spectrum is included in Figure S5 in the Supporting Information; HRMS ESI $[M+NH_4^+]$: calcd for $C_{48}H_{32}Cl_4N_1$: 764.1254; found: 764.1254.

Synthesis of tetrabenzo[8]circulene (2): In a 10 mL oven-dried microwave tube equipped with a stir bar, compound **10** (29.64 mg, 0.040 mmol) was dissolved in dimethylacetamide (1.4 mL), and the reaction mixture was degassed with bubbling nitrogen for 15 min. Subsequently, DBU (0.30 mg, 0.002 mmol) and $[Pd(PCy_3)_2Cl_2]$ (61.12 mg, 0.083 mmol, 40 mol%) were added, and the reaction mixture was heated in a microwave reactor (max. 200 W) at 180 °C for one hour and 15 min in a sealed microwave vial. After cooling, the reaction mixture was poured into H_2O (20 mL), extracted with CH_2Cl_2 (5×10 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the product by column chromatography (SiO_2, hexanes/CH_2Cl_2 4:1; $R_f = 0.20$) afforded the desired product and a small amount of the remaining palladium catalyst. Careful washing of this material with cold toluene gave pure **2** (5.76 mg, 24%) as a crystalline yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.11$ (dd, $J = 6.0$, 3.0 Hz, 8H), 7.68 (s, 8H), 7.57 ppm (dd, $J = 6.0$, 3.0 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 134.0, 129.7, 129.4, 127.3, 123.5, 122.9 ppm; HRMS ESI $[M^+]$: calcd for $C_{48}H_{24}$: 600.1873; found: 600.1872.

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[23] Single-crystal X-ray diffraction analysis was performed on a Bruker Apex II [$Mo_{K\alpha}$ ($\lambda = 0.71073$ Å)] at 125(2) K. Data were collected and processed by using a Bruker Kappa/Apex II CCD detector. Crystal data for **2**: $C_{48}H_{24}$; tetragonal; space group *I*4; unit-cell dimensions: $a = 17.1355(2)$, $b = 17.1355(2)$, $c = 10.7485(1)$ Å; $\alpha = 90$, $\beta = 90$, $\gamma = 90^\circ$; $V = 3156.0(6)$ Å^3; $Z = 2$; $R1 = 0.0409$; $wR2 = 0.0924$. Disordered solvent was SQUEEZED during refinement. CCDC-960537 contains 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.

[24] Relative energies were obtained by DFT calculations at the M06–2X/6–311G**++//M06–2X/6–31G** level, performed by using the Jaguar (see: Jaguar, Version 7.9; Schrödinger, LLC, New York, USA, **2012**) software package. The pseudospectral methodology (see: R. A. Friesner, *J. Phys. Chem.* **1988**, *92*, 3091–3096), which significantly speeds up the SCF iterations, was employed in all calculations. Default grids and SCF convergence criteria, as implemented in Jaguar, were used.

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