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[8]Circulenes

Synthesis, Structural Analysis, and Properties of [8]Circulenes**

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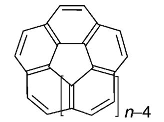
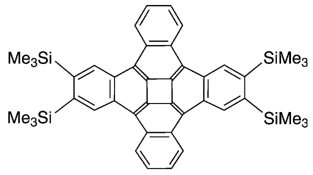
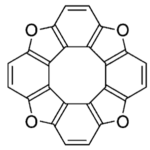
[*n*]Circulene is a macrocyclic arene in which a central *n*-sided polygon is completely surrounded and fused by benzenoids.[1] Only three members of this family, [5]circulene (or corannulene),[2] [6]circulene (or coronene),[3] and [7]circulene (or pleiadannulene)[4] have been prepared to date. The shapes of these circulenes change from a bowl ([5]circulene) through a plane ([6]circulene) to a saddle ([7]circulene). Although investigations of [4]circulene remain theoretical, tetrabenzo[4]circulene has recently been synthesized and determined to be a bowl-shaped molecule.[5] [8]Circulene (**1**) has not yet been synthesized in the laboratory, presumably because of its highly strained structure and instability. In contrast, its various planar analogues, such as tetraoxo[8]circulene,[6] octathio[8]circulene,[7] and tetracyclopenta[*def*,*jkl*,*pqr*,*vwx*]-tetraphenylene (TCT),[8] have been successfully generated. [8]Circulene has been predicted to have a saddle-shaped structure[9] with a higher strain than [7]circulene.[10] Moreover, a harmonic oscillator model of aromaticity (HOMA)[11] analysis showed that the central, eight-membered ring and the peripheral benzenoids of **1** all have significant aromatic character, and the thus generated concentric aromatic current causes **1** to be unstable.[12] Despite the interesting geometry and unusual aromaticity of [8]circulene derivatives, this study is the first to elucidate their synthesis, structural analysis, and properties.[13]



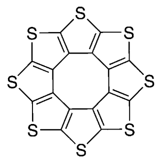
[5]circulene (*n* = 5)
[6]circulene (*n* = 6)
[7]circulene (*n* = 7)
[8]circulene (*n* = 8, **1**)



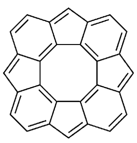
tetrabenzo[4]circulene



tetraoxo[8]circulene



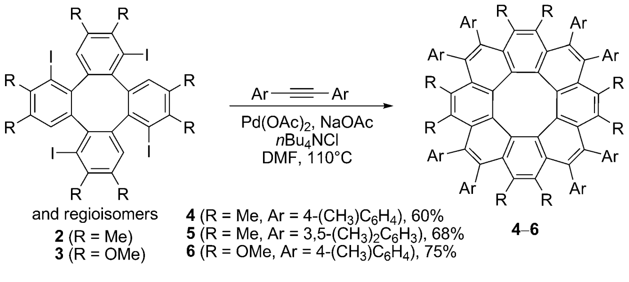
octathio[8]circulene



TCT

Attempts to obtain [8]circulene through the oxidative photochemical cyclization of [2.2](3,6)phenanthrenophanediene have been unsuccessful.[14] This domino reaction was supposed to form the central eight-membered ring and two peripheral benzenoids from a planar starting material in one synthetic step, but it is unsuitable for the synthesis of a highly strained molecule. In light of this information, the synthetic strategy presented herein is to first construct the central eight-membered ring, and then to generate the peripheral benzenoids. Tetraphenylene should be an ideal starting material, because the target molecule could be accessed by annulation of each "bay region" with a C$_2$ building block, thus forming a phenanthrenyl moiety from a biphenyl moiety. We previously summarized synthetic methods for the preparation of phenanthrene,[15] and the most effective protocol is the palladium-catalyzed annulation of a 2-iodobiphenyl with an alkyne.[16] Scheme 1 shows the synthetic method toward substituted [8]circulenes. The key precursors, tetraiodo-substituted tetraphenylenes **2** and their iodo-substituted regioisomers, can be easily prepared by the Cu$^{\text{II}}$-mediated cyclodimerization of 2,2′-diiodo-4,4′,5,5′-tetramethylbiphenyl[17] and subsequent iodination (see the Supporting Information). Although the latter reaction is not regioselective, each "bay region" contains only one iodo substituent and the regioisomeric mixture was directly used in the following step. The palladium-catalyzed annulations of tetraiodo-substituted tetraphenylenes with symmetric diarylethynes gave *peri*-substituted [8]circulenes **4** and **5** in moderate yields on a scale of several hundred milligrams. Although the stability of both products was not closely examined, they were stable for a few days at room temperature in aerobic solutions. Octamethoxy-substituted [8]circulene **6** was similarly obtained, but its degassed solution was relatively unstable and decomposed within 24 hours.

The NMR spectra of [8]circulenes **4**–**6** are very simple, each showing one distinct structure (see below). For example, the ^{1}H NMR spectrum of a solution of **4** in CDCl$_3$ at room



Scheme 1. Preparation of [8]circulenes. DMF = *N*,*N*′-dimethylformamide.

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temperature shows four doublets with equal integrations in the aromatic region and two sharp singlets, which correspond to methyl groups. The ^{13}C NMR spectra and DEPT (distortions enhancement by polarization transfer) experiments show two signals associated with the carbon atoms of the methyl groups, and six signals of quaternary carbon atoms (C_{quat}) and four signals of CH groups in the aromatic region. The information suggests that the [8]circulenyl core contains only four types of carbon atoms. *p*-Tolyl substituents have more signals than would be expected for a planar environment, thus showing that [8]circulene is nonplanar at room temperature on the NMR timescale. Notably, the methyl and methoxy groups that are directly attached to the backbones of **4**/**5** and **6**, respectively, cause a high-field shift in the ^{1}H NMR spectra. This shielding effect is probably caused by the ring current of the pendant aryl substituents. For instance, the methyl protons in **4** resonate at 1.45 ppm, whereas the chemical shift of the benzylic hydrogen atoms in toluene is 2.36 ppm in $CDCl_3$.

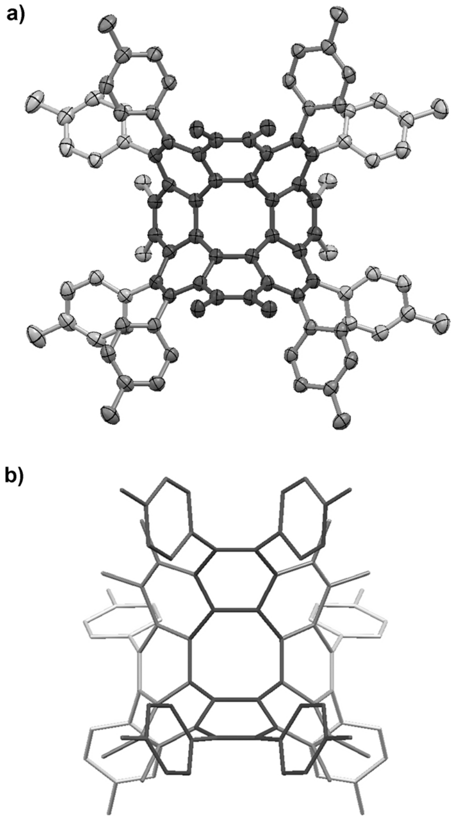
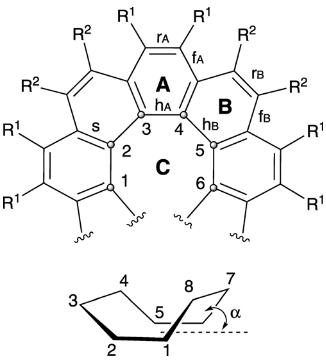


Figure 1. a) Crystallographic structure of **4**. Only carbon atoms are shown for clarity, the thermal ellipsoids are set at 30% probability. b) Calculated geometry of **4′**.

X-ray crystallography indicated that **4** is a saddle-shaped molecule (Figure 1 and Table 1).[18] The structure of **4** slightly deviates from the ideal point symmetry D_{2d}. The peripheral benzenoids are classified in two types: the curve-up/curve-down **A** ring and the "bridged" **B** ring, which are present in an alternating **ABAB** order. Only one conformer, which contains dimethyl-substituted **A** rings and ditolyl-substituted **B** rings, was observed. Similar to 1,3,5,7-cyclooctatetraene (COT), the central eight-membered ring is tub-shaped, but all bond lengths (approximately 1.45 Å) and bond angles (around 125°) are almost identical. The eight-membered ring is more puckered than that of COT,[19] as determined by comparing the bending angles (α; 47° vs. 43°) and the torsion angles for C1-C2-C3-C4 (62° vs. 56°; Table 1). The dihedral angle between two adjacent benzenoids **A**/**B** has a mean value of 33°, which exceeds the maximum value of 23° in [7]circulene.[4c] Although no significant distortion of bond angles in peripheral benzenoids (within 4°) is observed, the twisted conformations of these benzenoids with a torsion angle of about 30° reflect the strain. The mean length of the spoke bonds is approximately 1.41 Å. The substituents and their steric repulsions influence the lengths of the flank and rim bonds. The **A** ring has longer flank bonds than the **B** ring (fA: 1.452(1) vs. fB: 1.431(1) Å), but shorter rim bonds (rA: 1.352(1) vs. rB: 1.378(1) Å). According to the structural

Table 1: Selected structural data and HOMA analysis of **1** and **4**.[a]

			1 ($R^1 = R^2 = H$)	**4** (R^1 = Me, R^2 = 4-tol)	
			Calcd.	X-ray	Calcd.
	Bond length [Å]	hub hA; hB	1.442; 1.470	1.450(1); 1.447(1)	1.452; 1.447
		spoke s	1.417	1.414(1)	1.407
		flank fA; fB	1.417; 1.432	1.452(1); 1.431(1)	1.451; 1.432
		rim rA; rB	1.357; 1.349	1.352(1); 1.378(1)	1.362; 1.380
	Bond angle [°]	C1-C2-C3	125.9	124.7(1)	124.1
		C2-C3-C4	125.9	124.3(1)	124.1
	Torsion angle C1-C2-C3-C4 [°]		58.4	61.9	62.7
	Torsion angle C1-C2-C5-C6 [°]		0	0	0
	Dihedral angle **A**/**B** [°]		31.1	32.9	33.3
	Bent angle α [°]		43.7	46.8	47.4
	HOMA index [NICS(0) (ppm)]	**A**	0.689 [−8.9]	0.369 [−3.4]	0.418 [−4.0]
		B	0.407 [−4.5]	0.629 [−3.9]	0.650 [−4.1]
		C	−0.242 [9.8]	0.056 [12.9]	0.007 [12.2]

[a] The structural data are taken as the averages of symmetrical relevance. The geometric calculations were performed with density functional theory using Gaussian09 at the ωB97X-D/6-31G** level. The NICS(0) values were calculated using the GIAO/HF/6-31+G* level.

analysis, **4** is more similar to an [8]radialene,[20] in which double bonds emanate from all vertices of the cyclooctane, rather than a COT-based arene.

The structure of **4** was calculated with density functional theory using Gaussian 09[21] at the ωB97X-D/6-31G** level,[22] and the results correlate well with the experimental bond lengths and bond angles (Table 1). The maximum deviation was observed for the bond length of the rim bond rA (1.362 vs. 1.352(1) Å). Notably, this long-range corrected functional provides more accurate results than that at the B3LYP/6-31G** level (see the Supporting Information). The calculated geometries of **1** and **4** are similar, but the former has significant bond alternation in the eight-membered ring, and shorter flank and rim bonds. The parent [8]circulene also possesses an [8]radialene character.

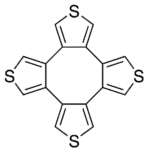
The aromaticities of **1** and **4** were analyzed with the HOMA index and the nucleus-independent chemical shift (NICS).[23] Table 1 shows the results of these calculations. HOMA values of 1 and 0 specify aromaticity and non-aromaticity, respectively. With respect to **4**, the eight-membered ring is non-aromatic and all six-membered rings have moderate to weak aromatic characteristics in the order **B** > **A**. The HOMA analysis also supports the fact that **4** is an [8]radialene. The HOMA indices in **1** and **4** are very similar, but the former has slight antiaromaticity in the **C** ring and the reverse aromatic sequence for peripheral six-membered rings (**A** > **B**). Notably, Salcedao et al. have suggested that the HOMA values for **A/B** and **C** in **1** are 0.803 and 0.953, respectively.[12] Their results differ significantly from those obtained herein because they utilized "uncommon" parameters.[24]

The NICS(0) indices of **1** and **4** were calculated at the GIAO/HF/6-31+G* level. Similar to the results of the HOMA analysis, the NICS(0) values of peripheral rings **B** in **1** and both rings **A** and **B** in **4** indicate a moderate to weak aromatic character (around −4.0 ppm), whereas the aromaticity of rings **A** in **1** is remarkably high (−8.9 ppm vs. −9.7 ppm for benzene). The central ring **C** in both **1** (9.8 ppm) and **4** (12.2 ppm) cannot be clearly identified as either COT (1.9 ppm) or [8]radialene (−1.2 ppm). Tetrathiophene (**7**) is a saddle-shaped [8]radialene with structural data close to **1**.[25] The NICS(0) value of the central eight-membered ring in **7** was calculated to be 3.3 ppm. NICS(1) indicates the aromaticity at the position 1 Å above the center of the ring, in order to reduce interference from σ electrons and from other rings. However, NICS(1) was not investigated herein, because the result can be influenced by the two rings **A** rings that are concave. The distance between the test point for NICS(1) and the center of ring **A** is around 2.5 Å. Therefore, NICS cannot provide enough information to distinguish between an [8]radialene or a COT in [8]circulene.

[8]Circulenes **4–6** should have two saddle-shaped conformations, depending on the positions of the substituents. However, both NMR analysis and X-ray crystallography showed a single conformer. In contrast to **4**, the other conformer (**4′**) contains ditolyl-substituted **A** rings and dimethyl-substituted **B** rings (Figure 1). Attempts were made to study the interconversion between the two conformers **4** and **4′** in the temperature range 215–463 K by NMR spectroscopy (see below), but the ^{1}H NMR spectra did not show **4′**. The results demonstrate that either these two conformers cannot be distinguished in the ^{1}H NMR spectra or the conformer **4′** is thermodynamically much less stable.

The inversion dynamics of saddle-type circulenes are almost completely unknown. The barrier of the saddle-to-saddle inversion of [7]circulene was calculated to be approximately 8.5 kcal mol^{-1} via a planar transition structure, identified in theoretical studies,[26] and 12.2 kcal mol^{-1} from measurements of 1,2-dihydro[7]circulene.[4b] Owing to its higher strain, the inversion barrier of [8]circulene (**1**) should be higher than that of [7]circulene if the saddle-to-saddle inversion of the former also proceeds via a planar transition structure. Our preliminary investigations of the saddle-to-saddle inversion of **4** and interconversion between **4** and **4′** showed that the inversion mechanism and the transition structure are very complex, presumably because the molecule is in a sterically congested environment. Although computational work on the details of these dynamics is ongoing, some experimental results of variable-temperature NMR studies are presented here.

Variable-temperature ^{1}H NMR experiments were performed with a 500 MHz instrument. ^{1}H NMR spectra of **4** in $CDCl_3$ at 215 and 298 K are nearly identical, showing that the dynamic process is slower than the NMR timescale or does not occur in this temperature range. A solution of **4** in [D$_4$]-*o*-dichlorobenzene could not be used for measurements because the signals in the aromatic region overlap at room temperature. Fortunately, a solution of **5** in [D$_4$]-*o*-dichlorobenzene clearly gives well-resolved signals, each of which is a sharp singlet at 303 K (see the Supporting Information). When a solution of **5** in degassed [D$_4$]-*o*-dichlorobenzene was heated to 433 K, the two pairs of xylyl signals, which resonate at 1.89/2.39 and 6.16/6.86 ppm at 303 K, merged into two broad bands. In contrast, signals from methyl groups directly attached to the [8]circulenyl backbone and from 4-H at xylyl groups were slightly broadened without any significant change in chemical shift. Although the temperature specifications of the NMR instrument limited the determination of the dynamics, the coalescence temperature can be assumed to be slightly higher than 443 K, giving barrier values of 20.4 and 20.7 kcal mol^{-1}, based on aryl and methyl signals, respectively (see the Supporting Information). The coalescence of xylyl signals may arise from a structure that incorporates a planar central eight-membered ring and contains both C_2 rotation axes and mirror planes. Conformations **8** and **9** are two examples thereof: they could be transition structures for the saddle-to-saddle inversion, and accordingly, the inversion barrier for **5** is around 21 kcal mol^{-1}. When a solution of **5** in



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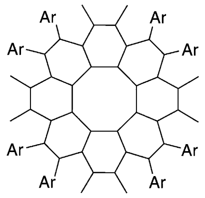

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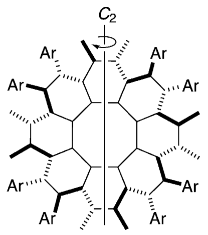

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[D$_4$]-*o*-dichlorobenzene was heated to 463 K, and then cooled to room temperature, its ^{1}H NMR spectrum was identical to that of an unheated sample. This information may suggest the conformer **5′** could not be observed at temperatures above that required to induce the coalescence of xylyl signals.

In conclusion, a simple method for the preparation of [8]circulenes **4–6**, which exhibit a unique saddle-shaped structure with an [8]radialenene character, is presented. Further investigations of their physical properties and chemical reactivity are under way. The synthetic approach is currently used to prepare higher circulenes.

Experimental Section

Procedure for the preparation of 1,2,5,6,9,10,13,14-octamethyl-3,4,7,8,11,12,15,16-octa(4-tolyl)[8]circulene (**4**): A mixture of tetraiodo-tetraphenylenes (**2** and its regioisomers; 276 mg, 0.30 mmol), 1,2-di(4-tolyl)ethyne (309 mg, 1.50 mmol), Pd(OAc)$_2$ (33.7 mg, 0.15 mmol), NaOAc (49.2 mg, 0.60 mmol), *n*Bu$_4$NCl (249 mg, 0.90 mmol), and DMF (2 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 110°C for 36 h. After cooling to room temperature, the suspension was diluted with hydrochloric acid (4N, 20 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3×20 mL). The combined organic layers were dried over anhydrous MgSO$_4$. The solvents of the filtrate were removed under reduced pressure. The residue was subjected to chromatography on silica gel, eluting with hexane/CH$_2$Cl$_2$ (10:1), to afford **4** (222 mg, 60%) as a dark red solid, m.p. > 300°C. Single crystals of **4** suitable for X-ray crystallographic analysis were grown by diffusion of MeOH into a solution of **4** in CHCl$_3$ at room temperature. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.45$ (s, 24H), 2.28 (s, 24H), 6.53 (d, $^3J = 7.7$ Hz, 8H), 6.73 (d, $^3J = 7.7$ Hz, 8H), 6.86 (d, $^3J = 7.7$ Hz, 8H), 7.08 ppm (d, $^3J = 7.7$ Hz, 8H). ^{13}C NMR (100 MHz, CDCl$_3$, plus DEPT): $\delta = 17.8$ (CH$_3$), 21.2 (CH$_3$), 127.3 (C$_{\text{quat}}$), 127.7 (CH), 128.1 (CH), 131.0 (CH), 131.6 (CH), 133.6 (C$_{\text{quat}}$), 134.9 (C$_{\text{quat}}$), 136.7 (C$_{\text{quat}}$), 138.8 ppm (C$_{\text{quat}}$). One quaternary carbon atom cannot be observed because of overlapping signals. HRMS (FAB) calcd for C$_{96}$H$_{80}$: 1232.6260; found: 1232.6281.

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Keywords: [8]circulenes · alkynes · annulation · palladium · tetraphenylenes

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[18] Single-crystal X-ray diffraction was performed on a Bruker APEX DUO [Cu-*K*α, ($\lambda = 1.54178$ Å)] at 100(2) K. Data were collected and processed by using APEX II 4K CCD detector. Crystal data for **4**: C$_{96}$H$_{80}$, orthorhombic, space group *Pnma*, unit cell dimensions: $a = 22.4352(7)$, $b = 25.3289(8)$, $c = 17.4665(6)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$. $V = 9925.5(6)$ Å^3, $Z = 4$. $R_1 = 0.0484$, $wR_2 = 0.1413$. CCDC 938414 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.

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