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Intramolecular Cyclization of Thiophene-Based [7]Helicenes to Quasi-[8]Circulenes

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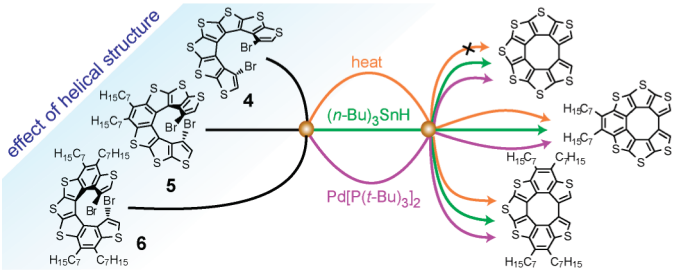

Intramolecular cyclization in a series of thiophene-based dibromo[7]helicenes (**4**−**6**) with different helix structures is investigated by vacuum pyrolysis, tin- and palladium-mediated C−C bond forming reactions. The product with the cyclic structure of the annelated aromatic rings, which resembles [8]circulene devoid of an atom linkage, is referred to as quasi-[8]circulene. Vacuum pyrolysis of **4** gives insoluble, unidentified products, while **5** and **6** yield the corresponding quasi-[8]circulenes under similar conditions. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses for **4** indicate complex reaction pathways, while those for **5** and **6** show a single process corresponding to a loss of 1 equiv of Br_2 at about 330 °C. Pd-mediated reductive cyclization provides quasi-[8]circulenes for all three [7]helicenes, though only **4** gives a good isolated yield. Tributyltin hydride-mediated radical cyclization of **4**−**6** provides quasi-[8]circulenes in excellent yields, and it is practically insensitive to the helix structure. Experimental and calculated UV−vis absorption spectra for quasi-[8]circulenes and [8]circulenes are reported. The results suggest that the lack of atom linkage in quasi-[8]circulene does not significantly affect properties and conformation, compared to those for the corresponding [8]circulenes.

Introduction

Oligomers of [*n*]helicenes that are connected through C−C bonds at their inner rims are predicted to provide rigid helices with extraordinary preference for helical folding.[1] For example, carbon−sulfur bis[7]helicene **1**, in which the two [7]helicene moieties have the same configuration, adopts rigid, helically locked conformation both in the solid state and in solution (Figure 1).[1]

The convergent synthetic route to "helically-locked" oligomers of [*n*]helicenes could rely on intermolecular C−C bond homocoupling reactions of functionalized [*n*]helicenes with adequate solubility. However, we find that such an approach is hindered by the competing intramolecular cyclization, as illustrated by the C−C bond formation at the inner helical termini of dibromo[7]helicene **2** to product **3** (Scheme 1).

The cyclic structure of the annelated aromatic rings such as **3** is an intriguing oligothiophene with a planar, cross-conjugated π-system,[2,3] and it appears to resemble the Nenajdenko's "sulflower", carbon−sulfur [8]circulene $(C_2S)_8$,[4−6] a

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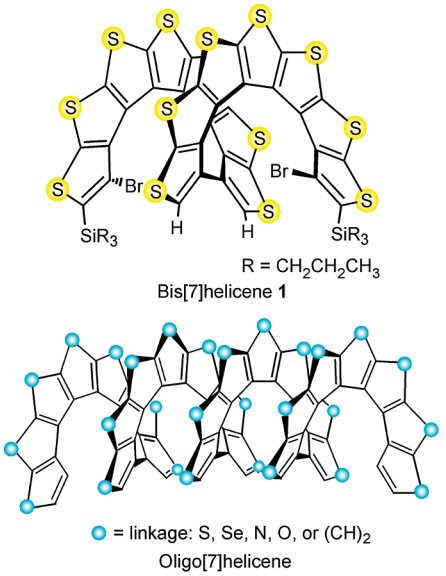
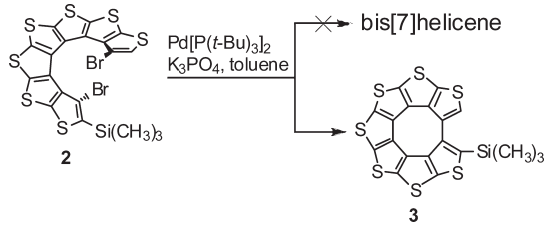


FIGURE 1. Bis[7]helicene and oligo[7]helicene.

SCHEME 1



beautiful molecule with potentially important materials properties but with very limited solubility (Figure 2).[7,8] We note that the α-CH positions of thiophenes in **3** would enable functionalization, which is not possible in the carbon−sulfur [8]circulene, thus providing an avenue to the cyclic structure of annelated aromatic rings with improved solubility and/or as building blocks for extended macromolecular structures and assemblies.

Other conjugated cyclic structures similar to **3** are known in the synthetic pathways to [*n*]circulenes. In Yamamoto's photosynthesis of [7]circulene, the Reiss' "hexa[7]circulenes" were used as key synthetic precursors.[9,10] Wynberg and coworkers reported synthesis of heterocirculenes from "dehydrohelicenes", compounds in which the two termini of a

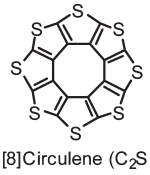


FIGURE 2. Carbon−sulfur [8]circulene $(C_2S)_8$.

helicene are connected by a σ bond, formed by dehydrogenation of [5]helicenes and [6]helicenes, using a Scholl-type reaction.[11] Notably, all these examples are limited to the cyclic structures of 5 and 6 annelated aromatic rings devoid of solubilizing groups, and thus they possess exceedingly low solubility. As it appears, the nomenclature for these conjugated cyclic structures is not established, we refer to **3** as carbon−sulfur quasi-[8]circulene.[12]

In addition to the appeal as direct precursors to [*n*]circulenes and building blocks for extended structures and assemblies, the structure of these quasi-[*n*]circulenes poses an interesting question, whether the lack of an atom linkage would significantly affect electronic structure and conformation, compared to those for the corresponding [*n*]circulenes. For comparison, chirooptical properties of bis[7]helicene **1** are similar to those calculated for the corresponding [15]helicene, suggesting that the absence of sulfur linkage in **1** has only a minor effect on the chirooptical properties and on the conformation, compared to the [15]helicene.[1]

We have recently prepared a series of dibromo[7]helicenes (**4**−**6**) and their trimethylsilyl derivatives, both as racemic and enantiomerically pure products, and obtained their X-ray single crystal structures.[13−16] Thus, we have an avenue to examine intramolecular cyclization of dibromo[7]helicenes to quasi-[8]circulenes. The helix structure of [7]helicenes **4**−**6** dictates the proximity of the two helical termini and the relative orientation of the C−Br bonds. Therefore, the C−C bond formation at the two helical termini of the [7]helicenes may presumably be more efficient when the C···C distance (*r*) is shorter or the Br−C−C−Br torsion angle (*ϕ*) is approximately within the coplanar arrangement ($\phi \approx 180°$). We note that the average *ϕ* values determined from the X-ray structures of **4**, **5**, and **6** are 176°, 153°, and 146°, respectively; in the same series, the C···C distances decrease from about 4 Å to 3.3 Å (Figure 3).[17]

We consider vacuum pyrolysis, tin- and palladium-mediated C−C bond forming reactions. There are a plethora of precedents for cyclization of bromoaryls and dibromoaryls, forming C−C bonds, using flash vacuum pyrolysis and

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(12) [*m*]Circulene is commonly defined as a circulene constructed out of *m* aromatic rings. Quasi is a prefix meaning "resembling" or "in some manner" and it is usually hyphenated to a noun. Therefore, we propose to refer to cyclic compounds analogous to [*m*]circulenes, but composed of only $m - 1$ aromatic rings, as quasi-[*m*]circulenes.

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(17) The X-ray crystallographically determined helical shapes are similar to those calculated at the B3LYP/6-31G(d,p) level of theory (Table S1, SI).

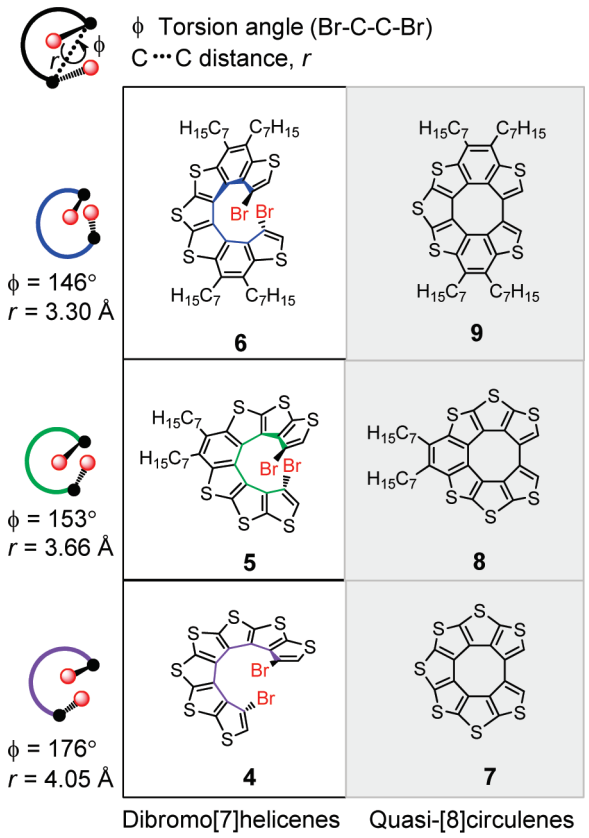

FIGURE 3. Dibromo[7]helicenes and the corresponding quasi-[8]circulenes.

vacuum pyrolysis to provide both planar and curved polycyclic aromatic compounds.[18−21] Tin- and palladium-mediated cyclization of dibromo[7]helicenes **4**−**6** could provide an advantage of much lower reaction temperatures than vacuum pyrolysis.[22] In particular, the bis(tri-*tert*-butylphosphine)palladium/K_3PO_4 catalytic system[23] was shown to be effective for typically difficult C−C bond formation between the β-positions of the sterically hindered bromo-thiophene derivatives.[24−26]

Here we report the intramolecular cyclization in a series of [7]helicences, for which we optimize the cyclization reactions in **4**−**6** to provide a synthetic pathway to quasi-[8]circulenes **7**−**9** (Figure 3).

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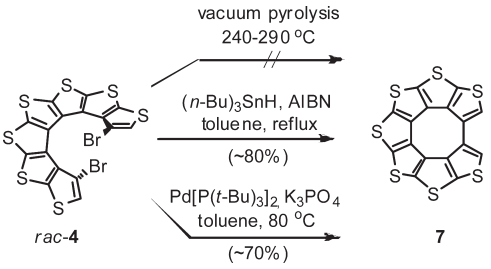
SCHEME 2. Carbon−Sulfur Quasi-[8]Circulene 7



Results and Discussion

Quasi-[8]circulene 7. When dibromo[7]helicene *rac*-**4** is heated to ~240 °C under vacuum in a sealed capillary, the color of the sample gradually darkens without melting, and after several hours at ~240 °C a black solid is obtained. The solid is only partially soluble in organic solvents. In chloroform-*d*, the ^{1}H NMR spectrum shows a weak singlet at the chemical shift corresponding to the starting material *rac*-**4**, with no evidence for quasi-[8]circulene **7** (Scheme 2). A significant increase in the temperature of pyrolysis (50 °C) leads to complete conversion of starting material *rac*-**4**, to give a black, insoluble solid for which high-field ^{1}H NMR spectra in organic solvents such as chloroform-*d* or benzene-d_6 could not be obtained even with the aid of a cryoprobe.

Pyrolysis of dibromo[7]helicene *rac*-**4** was monitored by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). The DSC plot shows no intense peaks, and three processes associated with mass loss at 200, 270, and 400 °C are observed in the TG plot (Figure S12, SI), suggesting complex reaction pathways.[27]

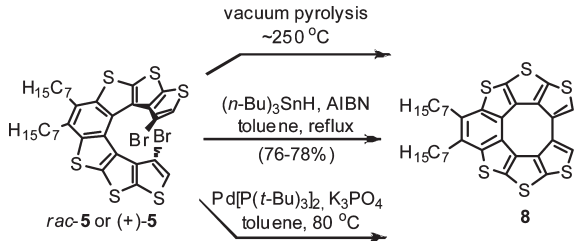
Tributyltin hydride-mediated radical cyclization of *rac*-**4** provides a relatively clean crude reaction mixture, as indicated by ^{1}H NMR spectra (Figures S18 and S21, SI); upon washing with methanol and acetone, a poorly soluble colorless quasi-[8]circulene **7** is obtained in 80% yield. The solubility of **7** is markedly decreased after purification to the extent that the signature singlet ^{1}H-resonance at δ 7.95 ppm for **7** is difficult to detect even with the aid of a cryoprobe. The mass spectrum (EI) of **7** shows the peak corresponding to M^+ that has dominant intensity in the m/z 150−440 range and exact mass of 417.8204 that is within less than 1 ppm of the calculated value for $C_{16}H_2S_7$. In the IR spectrum, the stretching mode for the α-C−H is found at 3105 cm^{-1}.

Pd-mediated reductive cyclization of *rac*-**4** gives crude reaction mixtures containing quasi-[8]circulene **7**, as indicated by the singlet at δ 7.95 ppm in the ^{1}H NMR spectra and by the molecular ion (M^+) at m/z 417.8197 in the FABMS; however, the aromatic region of the ^{1}H NMR spectra also shows doublets, which are tentatively assigned to other debrominated byproduct (Figures S22 and S23, SI). Quasi-[8]circulene **7** is isolated in 70% yield (Figure S24, SI). Bis[7]helicene products, corresponding to intermolecular homocoupling of [7]helicene **4**, are not detected.

Diheptyl Quasi-[8]Circulene 8. Vacuum pyrolysis of dibromo[7]helicene *rac*-**5** at 180−250 °C provides quasi-[8]-circulene **8**, with optimum conditions at 250 °C and recycling

(27) The mass loss near and above a temperature of 200 °C is consistent with the onset of decomposition of [7]helicene *rac*-**4** observed as a color change in the melting point apparatus (ref 13).

SCHEME 3. Diheptyl Quasi-[8]Circulene 8



of the deposited *rac*-**5** (Scheme 3). ^{1}H NMR spectra of the crude reaction mixtures show **8** as the major product, with negligible content of *rac*-**5** (Figures S25 and S26, SI).

Pyrolysis of dibromo[7]helicene (+)-**5** was also monitored by DSC, for which the sample is encapsulated inside a crimped aluminum pan, the most widely used standard sample preparation. Dibromo[7]helicene (+)-**5** shows melting behavior (endothermic peak) with the onset temperature of 138 ± 2 °C, as reported previously.[14] To explore pyrolysis of (+)-**5**, we increased the upper temperature limit of the DSC scan to 180 °C, and after the experiment we collected the sample for ^{1}H NMR analysis. The ^{1}H NMR spectrum of the DSC samples shows the presence of [7]helicene (+)-**5** (δ 7.107) and a very small admixture of quasi-[8]circulene **8** (δ 7.989) (Figure S7, SI).[28,29] Further extension of the upper temperature limit to 200 °C reveals an additional exothermic peak at about 182 °C (onset at 181 °C); after 1 min at 200 °C, the return scan is flat without significant changes in the heat flow (Figure 4).

^{1}H NMR and FABMS analyses of the recovered DSC samples indicate clean formation of quasi-[8]circulene **8**, with a melting point at 320−322 °C that is significantly above 200 °C (Figures S8 and S9, SI). Therefore, the exothermic peak at about 182 °C is assigned to a cyclization reaction in which dibromo[7]helicene (+)-**5** is debrominated to produce quasi-[8]circulene **8**.

When simultaneous TG/DSC is carried out in a ceramic open sample pan, only the peak for melting of (+)-**5** has a significant intensity in the DSC plot. In contrast to *rac*-**4**, the TG plot for (+)-**5** shows only one process with a mass decrease corresponding to the loss of 1 equiv of Br_2 at about 330 °C (Figure S10, SI). The ^{1}H NMR spectrum of the recovered TG/DSC sample indicates formation of quasi-[8]circulene **8** (Figure S11, SI).

The tributyltin hydride-mediated cyclization of (+)-**5** provides quasi-[8]circulene **8** at much milder conditions compared to those for pyrolysis. Analyses of the aromatic region of the ^{1}H NMR spectra for crude reaction mixtures indicate complete conversion of (+)-**5** to quasi-[8]circulene **8**. Diheptyl quasi-[8]circulene **8** is readily isolated as a pale yellow solid by washing with organic solvents. Pd-mediated C−C bond forming reactions provide reaction mixtures containing **8** (NMR yield of 10%) and unreacted *rac*-**5**; no

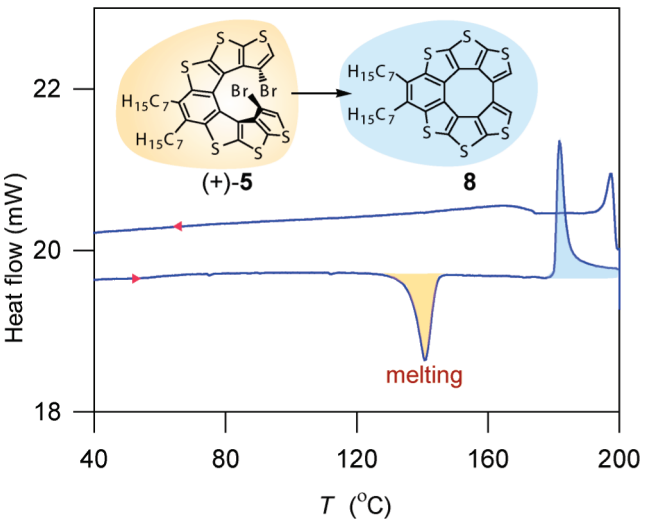
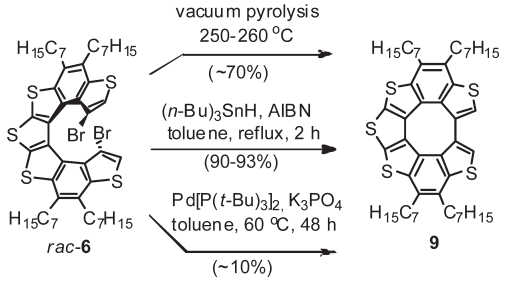


FIGURE 4. Differential scanning calorimetry for [7]helicene (+)-**5**. Scan rate 20 deg/min.

SCHEME 4. Tetraheptyl Quasi-[8]Circulene 9



evidence for products corresponding to intermolecular homocoupling of [7]helicene **5** is found.[30]

Tetraheptyl Quasi-[8]Circulene 9. Following the same procedure for pyrolysis of dibromo[7]helicenes *rac*-**5** and (+)-**5**, pyrolysis of dibromo[7]helicene *rac*-**6** at 250−260 °C provides the corresponding quasi-[8]circulene **9** as a pale yellow solid in 70% isolated yields (Scheme 4).[31]

Simultaneous TG/DSC of *rac*-**6** gives similar results to that for (+)-**5**. In particular, TG indicates a single process with a mass decrease corresponding to the loss of 1 equiv of Br_2 at about 330 °C, which is the same temperature as observed for (+)-**5**. The corresponding DSC plot shows the expected melting behavior (endothermic peak) at about 100 °C, and more importantly, another broad, exothermic peak at about 330 °C, which coincides with the loss of Br_2 observed in the TG plot (Figure 5).[32,33]

Tributyltin hydride-mediated cyclization of *rac*-**6** gives quasi-[8]circulene **9** in excellent (~90%) isolated yields. In contrast, Pd-mediated C−C bond forming reactions of dibromo[7]helicene *rac*-**6** (and (+)-**6**) give complex reaction

(28) Vacuum pyrolysis of dibromo[7]helicene *rac*-**5** at 180 °C leads to a low conversion to diheptyl quasi-[8]circulene **8** (Table S8, SI).

(29) In FABMS of dibromo[7]helicenes **4** and **5**, and bis(trimethylsilyl)-substituted derivatives of **4**−**6**, the $[M - 2Br]^+$ fragment ions have low relative amplitude (15% or less) compared to that of the $[M]^+$ or $[M + 2]^+$ ions; however, for dibromo[7]helicene **6**, the $[M - 2Br]^+$ fragment ion is dominant (Table S4 and Figure S15, SI).

(30) Bis(trimethylsilyl)-substituted quasi-[8]circulene **8**, designated as **8**-$(TMS)_2$, is also isolated in low yield from the McMurry reaction of the corresponding dibromo[7]helicene (SI).

(31) Quasi-[8]circulene **9** was isolated in low yields from acid-mediated deprotections of bis(trimethylsilyl)-substituted derivatives of [7]helicene *rac*-**6** (ref 15).

(32) TG/DSC of *rac*-**6**, contained in a ceramic open sample pan that was covered with aluminum foil, is qualitatively similar to that in Figure 5. However, in TG, the loss of Br_2 is observed at a much lower temperature of about 265 °C and in the narrower temperature range; in DSC, the exothermic peak at about 265 °C is narrower and more intense (Figure S13, SI).

(33) ^{1}H NMR spectrum of the recovered TG/DSC sample indicates formation of quasi-[8]circulene **9** (Figure S14, SI).

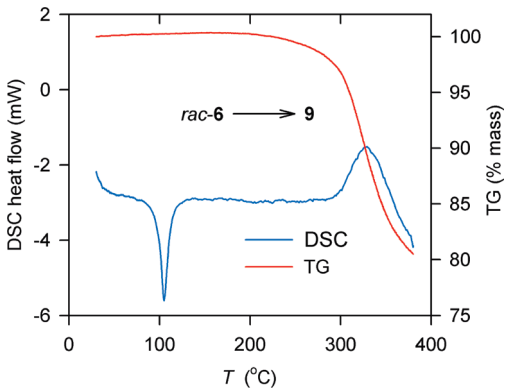


FIGURE 5. Simultaneous thermogravimetry and differential scanning calorimetry for [7]helicene *rac*-**6**. Scan rate 20 deg/min.

mixtures, as indicated by ^{1}H NMR (chloroform-*d*) spectra; quasi-[8]circulene **9** is isolated in ~10% yield. The major product is isolated in ~50% yield. In the mass spectrum (FAB) of this product, the peak with dominant intensity in the *m*/*z* 200−2000 range has an exact mass of 798.3442, which is within 1.6 ppm of the calculated value for $C_{48}H_{62}S_5$. Although this molecular formula is identical to that of quasi-[8]circulene **9**, ^{1}H and ^{13}C NMR spectra are consistent with the C_1 point group, thus indicating that this product is an isomer of **9**. Attempts to identify this product by X-ray crystallography were not successful.[34]

Crystal Structure of Tetraheptyl Quasi-[8]Circulene 9. The X-ray structure of **9** was determined by synchrotron radiation, using a small colorless plate-shaped crystal (Figure 6).

The π-system of **9** adopts an approximately planar conformation as indicated by a small value (0.0650 Å) of mean deviation from a calculated least-squares plane including all benzene and thiophene rings (S1−S5, C1−C20). In the bay area, the C1−C2−C19−C20 torsion angle of 8.7(15)° suggests a small out-of-plane distortion.

The π-systems of **9** slip-stack with the distance between least-squares planes of about 3.52 Å, forming columns along the crystallographic *a*-axis. Short intermolecular S···S contacts are observed within the columns and between neighboring columns varying between 3.53 and 3.64 Å (Figure 7).

Experimental and Calculated UV−Vis Absorption Spectra for Quasi-[8]Circulenes and [8]Circulenes. UV−vis absorption spectra for quasi-[8]circulenes **7**−**9** (Figure 8) show similar spectral patterns and are slightly blue-shifted compared to the corresponding [7]helicenes **4**−**6**.[15] The spectra are progressively more red-shifted from **7** to **8** to **9** (Table S2, SI), which is similar to the trend found in the corresponding [7]helicenes.[15] This result corroborates the increased electron delocalization from **7** to **8** to **9**, due to replacement of cross-conjugated thiophene rings in **7** with conjugated benzene rings.

Computational modeling is carried out to investigate whether the lack of atom linkage in quasi-[8]circulenes **7**−**9** would significantly affect the conformation and electronic structure, compared to those for the corresponding [8]circulenes. Quasi-[8]circulene **7** and [8]circulene $(C_2S)_8$, as well as simplified structures corresponding to **8** and **9**, in which the heptyl chains are replaced with methyl groups (Chart 1), are studied.

(34) One of the reviewers suggested the possibility of cyclization between the α- and β-positions of thiophenes.

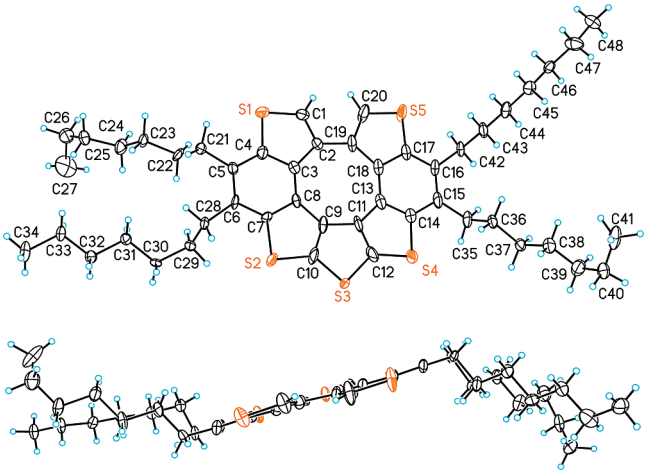
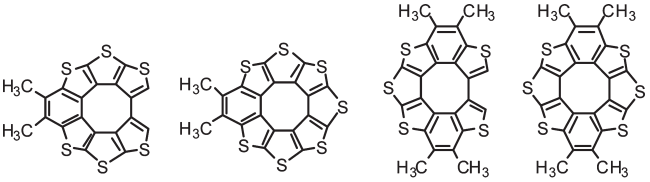


FIGURE 6. Molecular structure of tetraheptyl quasi-[8]circulene **9**. Carbon and sulfur atoms are depicted with thermal ellipsoids set at the 50% probability level. Disorder in two heptyl groups and in S3/S3d (60:40) are omitted for clarity. Disorder is illustrated in Figure S1, SI.

CHART 1. Structures of Simplified Quasi-[8]Circulenes and [8]Circulenes



Conformations for **7**, $(C_2S)_8$, **10**-$(CH_3)_2$, **11**-$(CH_3)_2$, **12**-$(CH_3)_4$, and **13**-$(CH_3)_4$ are assessed by full geometry optimizations and vibrational frequency calculations within the respective point groups of symmetry, using the B3LYP/6-31G(d,p) method (Table S13, SI).[35] We found that all of the three [8]circulenes, $(C_2S)_8$, **11**-$(CH_3)_2$, and **13**-$(CH_3)_4$, possess planar π-systems.[36] For quasi-[8]circulenes, the planar geometries are either shallow minima with very small, positive vibrational frequency (6 cm^{-1} for **7**) or structures with one imaginary frequency (*i*21 cm^{-1} for **10**-$(CH_3)_2$ and *i*101 cm^{-1} for **12**-$(CH_3)_4$). These very small, positive vibrational frequencies and imaginary frequencies correspond to the out-of-plane distortion of the π-system with the disrotatory movement of the CH bonds in the bay area of quasi-[8]circulene. The corresponding nonplanar geometries for **10**-$(CH_3)_2$ and **12**-$(CH_3)_4$ with the C_2 point groups of symmetry are minima; however, their energy is practically identical and only 4.7 kcal mol^{-1} lower than the planar C_{2v}-symmetric structures, respectively.[37] For C_2-symmetric quasi-[8]circulenes **10**-$(CH_3)_2$ and **12**-$(CH_3)_4$, the C(H)−C−C−

(35) Frisch, M. J.; et al. *Gaussian 03*, Revision E.01; Gaussian, Wallingford, CT, 2004.

(36) This result is in agreement with the previously reported X-ray structure and calculations for [8]circulene $(C_2S)_8$: ref 6.

(37) (a) For quasi-[8]circulene **10**-$(CH_3)_2$, the C_2-symmetric minimum and the C_{2v}-symmetric transition state possess similar energies; the C_2-symmetric structure is lower in energy by 0.04 kcal mol^{-1}, but after zero-point vibrational energy (ZPVE) correction, the C_{2v}-symmetric structure is lower in energy by 0.04 kcal mol^{-1}. (b) For quasi-[8]circulene **12**-$(CH_3)_4$, the C_2-symmetric minimum is lower in energy by 5.00 kcal mol^{-1} before ZPVE correction and by 4.69 kcal mol^{-1} after ZPVE, compared to that of the C_{2v}-symmetric transition state.

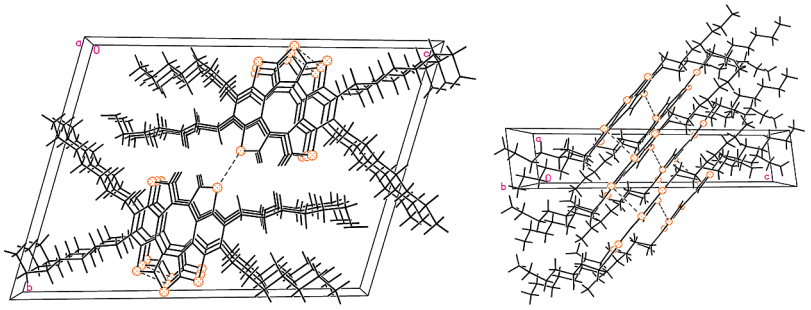


FIGURE 7. Crystal packing plots of tetraheptyl quasi-[8]circulene **9**. Left plot: View along the *a*-axis. Right plot: View along the *b*-axis. Sulfur atoms and short S···S contacts are indicated with yellow-orange circles and dashed lines, respectively.

C(H) torsion angles, analogous to the C1−C2−C19−C20 torsion angle of 8.7(15)° in the X-ray structure of **9**, are 7.8° and 28.6°, respectively. These results suggest that the preference for nonplanar geometry of the π-system is increasing, with the greater number of benzene rings, but overall the potential energy surfaces for all three quasi-[8]circulenes are rather shallow with nearly planar geometries.[38]

The UV−vis absorption spectra for **7**, $(C_2S)_8$, **10**-$(CH_3)_2$, **11**-$(CH_3)_2$, **12**-$(CH_3)_4$, and **13**-$(CH_3)_4$ are calculated by using the TD-B3LYP/6-31G(d,p) method with the IEF-PCM-UAHF solvent model for cyclohexane.[35] The calculated spectra for quasi-[8]circulenes **7**, **10**-$(CH_3)_2$, and **12**-$(CH_3)_4$ show an excellent agreement with experimental spectra for the corresponding quasi-[8]circulenes **7**, **8**, and **9**; in particular, the UV−vis spectra are progressively more red-shifted with the increasing number of benzene rings (Figure 8). Most importantly, the calculated spectra of [8]circulenes and the corresponding quasi-[8]circulenes possess similar spectral patterns. Overlapping onsets of absorption are observed, with the exception of quasi-[8]circulene **7** and the corresponding D_{8h}-symmetric [8]circulene $(C_2S)_8$, in which the lowest energy transitions are symmetry-forbidden.[39] Thus, we conclude that both conformations and electronic structures for the studied quasi-[8]circulenes are similar to those for the corresponding [8]circulenes.

Effect of Helix Structure on the Intramolecular Cyclization Reaction of [7]Helicenes to Quasi-[8]Circulenes. The helix structure dictates the geometry at the two C−Br termini of the inner helix in [7]helicene (Table S1, SI), and therefore it may affect the cyclization reaction forming the C−C bond between the termini carbons.

We postulate that shorter C···C distances between the termini of the inner helix in [7]helicenes facilitate cyclization by pyrolysis, i.e., [7]helicene **6**, with the shortest C···C distance of 3.30 Å, is most efficiently converted to the corresponding quasi-[8]circulene. Notably, tributyltin hydride-mediated radical cyclization of **4**−**6**, which is carried out in solution under relatively milder conditions, appears to be practically insensitive to the C···C distances, and thus provides a general method for the synthesis of quasi-[8]circulenes from dibromo[7]helicenes.

Pd-mediated reductive cyclization to quasi-[8]circulene is most efficient for [7]helicene **4**. This result may be rationalized by considering the palladium complex prior to the reductive elimination.[40,41] Formation of such a complex would require distortion of the helix so both termini are oriented in the same direction to accommodate the C−Pd−C bond angle of about 90°. This distortion of the helix, which may be analogous to that calculated for the C_s-symmetric transition state for racemization of a typical [*n*]helicene ($n < 9$),[42] will be most facile when the termini are the least overlapping as in the helix of **4**.

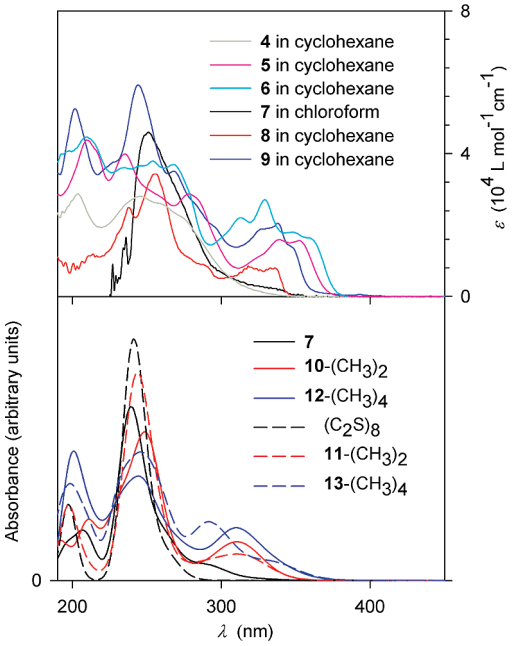


FIGURE 8. UV−vis absorption spectra. Top plots: Experimental spectra for quasi-[8]circulenes **7**−**9**. Bottom plots: Calculated spectra for quasi-[8]circulenes **7** (C_{2v}), **10**-$(CH_3)_2$ (C_2), and **12**-$(CH_3)_4$ (C_2) (solid lines), and the corresponding [8]circulenes $(C_2S)_8$, **11**-$(CH_3)_2$, and **13**-$(CH_3)_4$ (dashed lines). All spectra are calculated at the TD-B3LYP/6-31G(d,p) level with the IEF-PCM-UAHF solvent model for cyclohexane; the ground state geometries are optimized at the B3LYP/6-31G(d,p) level in the gas phase. Because of low solubility of **7** and **8** in cyclohexane, their experimental spectra are only qualitative.

Conclusion

Intramolecular cyclization at the two bromine-substituted termini of the inner helix in [7]helicene provides a pathway to

(38) Increasing preference for nonplanarity is expected as, already with seven annelated benzene rings, [7]circulene adopts saddle-shape geometry: ref 10a.
(39) Calculated onsets for the lowest energy electronic transitions (λ_{onset} in Table S13, SI) are similar, with small red shifts for quasi-[8]circulenes.
(40) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398–3416.
(41) Altman, R. A.; Hyde, A. M.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 9613–9620.
(42) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031–6035.

a quasi-[8]circulene, a cyclic structure of the annelated aromatic rings that closely resembles [8]circulene. Tributyltin hydride-mediated radical cyclization gives quasi-[8]circulenes in excellent yields, and this cyclization reaction is practically insensitive to the geometry of the termini of inner helix in [7]helicenes. We found that the lack of atom linkage in thiophene-rich quasi-[8]circulenes does not significantly affect conformation and electronic structure, compared to those for the corresponding [8]circulenes.

Experimental Section

General Procedures for Cyclization of [7]Helicenes 4−6 to Quasi-[8]Circulenes 7−9: Vacuum Pyrolysis. [7]Helicene was pyrolyzed at 180−290 °C, with the vacuum ($p \gg 0.1$ mTorr) adjusted for each [7]helicene for optimum trade-off between rate of sublimation/evaporation and of quasi-[8]circulene formation. After several hours, the sublimed material (primarily unreacted [7]helicene) was recycled to the pyrolysis vessel with solvent, and the pyrolysis was resumed. This process was repeated until the starting [7]helicene was consumed. From pyrolysis of *rac*-**4**, quasi-[8]circulene **7** could not be isolated. From pyrolysis of **5** at ∼250 °C, quasi-[8]circulene **8** could only be obtained as a brown solid and in low yield either from the residue at the bottom of the pyrolysis vessel or following rapid filtration through silica plug with benzene. From pyrolysis of **6** at 250−260 °C (65.0 mg, 0.0678 mmol), quasi-[8]circulene **9** (39.1 mg, 72%) was isolated as a pale yellow solid after column chromatography (silica, hexane). Residual impurities in the aliphatic region of the NMR spectra were removed by washing with methanol and pentane.

Tributyltin Hydride-Mediated Cyclization. A solution of *n*-Bu_3SnH (2−6 equiv) and AIBN (2−4 equiv) in toluene was added dropwise to a refluxed solution of [7]helicene (2−25 mg, 1 equiv) in toluene. The total volume of toluene corresponded to about 6 mM concentration of [7]helicene in the resulting reaction mixture. After 2−4 h under reflux, the toluene was removed under vacuum, to provide a crude product as a sticky solid. Sequential washing with methanol and acetone or methanol and pentane provided quasi-[8]circulene as a white solid (**7**) or pale yellow solid (**8** and **9**) in good yield (76−93%).

Pd-Mediated Cyclization. [7]Helicene (1.9−51 mg, 1 equiv), $Pd[P(t\text{-}Bu)_3]_2$ (1−2.5 equiv), and K_3PO_4 (2−7 equiv) in toluene (0.5−4.5 mL) were stirred at 60−80 °C for 20−48 h. The reaction mixture, starting from *rac*-**4** (6.08 mg), was centrifuged, and then the insoluble part was treated with water, methanol, acetone, and ethyl acetate, to provide quasi-[8]circulene **7** as a brown solid (3.14 mg, 71%). The reaction mixture, starting from *rac*-**5** (1.6 mg), was filtered through Celite, and then concentrated in vacuo to provide the crude product; the ^{1}H NMR spectrum and FABMS showed quasi-[8]circulene **8**, starting material, and another byproduct. The reaction mixture, starting from *rac*-**6** (34.6 mg), was concentrated and worked up with chloroform/water; the chloroform layer was filtered through Celite and concentrated to provide the crude product. Reactions starting from (+)-**6** provided similar crude products (Figure S35, Supporting Information). Chromatography (deactivated silica, ethyl acetate, chloroform, hexane), followed by treatments with solvents, gave quasi-[8]circulene **9** as a yellow solid (2.9 mg, 10%) and another product (15.7 mg, Supporting Information).

Quasi-[8]circulene 7: Mp >400 °C (under vacuum). ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.95 (s, 2 H). LR/HR FABMS (ONPOE) *m*/*z* (ion type, %RA for *m*/*z* 200−2000, deviation from formula) 417.8197 ($[M]^+$, 100%, 1.2 ppm for $^{12}C_{16}{}^1H_2{}^{32}S_7$). LR/HR EIMS *m*/*z* (ion type, %RA for *m*/*z* 150−440, deviation for the formula) 417.8204 ($[M]^+$, 100%, 0.6 ppm for $^{12}C_{16}{}^1H_2{}^{32}S_7$). IR (ZnSe, cm^{-1}) 3105 (α-C−H of thiophene), 2961, 2918, 2850 (C−H).

Quasi-[8]circulene 8: Mp 320−322 °C (under nitrogen). ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.983 (s, 2 H), 3.062−3.029 (m, 4 H), 1.844−1.781 (m, 4 H), 1.556−1.489 (m, overlapped with H_2O, 4 H), 1.454−1.252 (m, 12 H), 0.912 (t, J = 7 Hz, 6 H). LR/HR FABMS (3-NBA) *m*/*z* (ion type, % RA for *m*/*z* 200−1500, deviation for the formula) 608.0839 ($[M]^+$, 100%, −1.7 ppm for $^{12}C_{32}{}^1H_{32}{}^{32}S_6$). IR (ZnSe, cm^{-1}) 3111 (α-C−H of thiophene), 2956, 2923, 2853, 1467.

Quasi-[8]circulene 9: R_f 0.56 (hexane). Mp 197−199 °C (lit.[15] mp 198−200 °C). ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.894 (s, 2 H), 3.086−3.035 (m, 8 H), 1.846−1.770 (m, 8 H), 1.435−1.422 (m, 8 H), 1.253−1.101 (m, 16 H), 0.914−0.766 (m, 12 H). ^{13}C NMR (125 MHz, chloroform-*d*) aromatic region, expected 10 resonances, found 10 resonances at δ 143.2, 140.2, 136.9, 135.06, 134.1, 131.0, 130.3, 127.9, 126.7, 125.4, aliphatic region, expected 14 resonances, found 11 resonances at δ 32.07, 32.05, 31.8, 30.20, 30.18, 29.96, 29.79, 29.70, 29.1, 22.7, 14.1. LR/HR FABMS (3-NBA) *m*/*z* (ion type, %RA for *m*/*z* 400−1200, deviation for the formula) 798.3448 ($[M]^+$, 100%, 0.8 ppm for $^{12}C_{48}{}^1H_{62}{}^{32}S_5$). IR (ZnSe, cm^{-1}) 3136 (weak), 2956, 2920, 2853, 1471, 1107, 802.

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Supporting Information Available: Complete ref 35 and description of experimental detail and product characterization, including X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.