Aromatic Systems

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A Nonaromatic Thiophene-Fused Heptalene and Its Aromatic Dianion**

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Abstract: *Heptalene, a nonaromatic, bicyclic 12 π-electron system with a twisted structure, is of great interest with regard to its potential Hückel aromaticity in the two-electron oxidized or reduced forms. The synthesis of thiophene-fused heptalene* **5** *from the reductive transannular cyclization of bisdehydro[12]annulene* **4***, and its solid-state structure, which was confirmed by X-ray crystallographic analysis, is presented. Chemical reduction of* **5** *readily generated the corresponding dianion, which was successfully isolated as* $[(K\text{-}[2.2.2]cryptand)^+]_2\mathbf{5}^{2-}$*. The X-ray crystallographic analysis of the dianion revealed a shallower saddle structure for the heptalene moiety and a lesser degree of bond alternation relative to* **5**. ^1H *NMR spectroscopy exposed the effect of a diamagnetic ring current on dianion* $\mathbf{5}^{2-}$*, which was corroborated by nucleus-independent chemical shift (NICS) calculations. These results demonstrate that the heptalene dianion, containing 14 π-electrons, does indeed exhibit pronounced degrees of Hückel aromaticity.*

Non-alternant hydrocarbons, such as pentalene,[1] azulene,[2] and *s*-indacene,[3] not only exhibit intriguing properties and reactivity patterns, but also allow an extended interpretation of the context of aromaticity.[4] Recently, their use as core skeletons in optoelectronic materials has also sparked considerable interest.[5] Among these non-alternant hydrocarbons, heptalene is an especially fascinating entity that consists of two fused seven-membered rings with 12 π-electrons.[4] In comparison to other non-alternant hydrocarbons, the most notable feature of the heptalene skeleton is its twisted geometry with negative curvature, giving rise to a nonaromatic character. Most importantly, a two-electron oxidation or reduction of heptalene, potentially generating the corresponding aromatic dication or dianion with 10 or 14π electrons, respectively, should be accompanied by a drastic structural change to give a planarized structure. Even though Vogel and co-workers previously reported a heptalene dianion, which was characterized by NMR spectroscopy and cyclic voltammetry,[6] structural evidence, for example from X-ray crystallography, confirming the aromaticity of the heptalene dianion or dication remains to be presented.

One of the main reasons for the lack of progress in this area is most likely the high reactivity of heptalene. In 1961, parent heptalene **1** was first reported as a thermally unstable compound, which decomposed by self-polymerization at the reactive double bonds.[7] However, it was later demonstrated that the thermal stability of the heptalene skeleton could be significantly increased by the introduction of electron-withdrawing groups[8] or fused aromatic rings (Figure 1 a).[9,10] In particular, benzannulation is widely recognized as a powerful method for the thermodynamic and kinetic stabilization of reactive annulene derivatives to avoid polymerization.[7] Nevertheless, benzoheptalene **2** still remains thermally unstable.[9] On the other hand, circulene derivative **3**[10] is an example of a stable heptalene, but unfortunately its heptalene character is substantially compromised on account of the fully benzene-fused structure. To investigate the aromatic character of a heptalene dianion or dication, the design of an

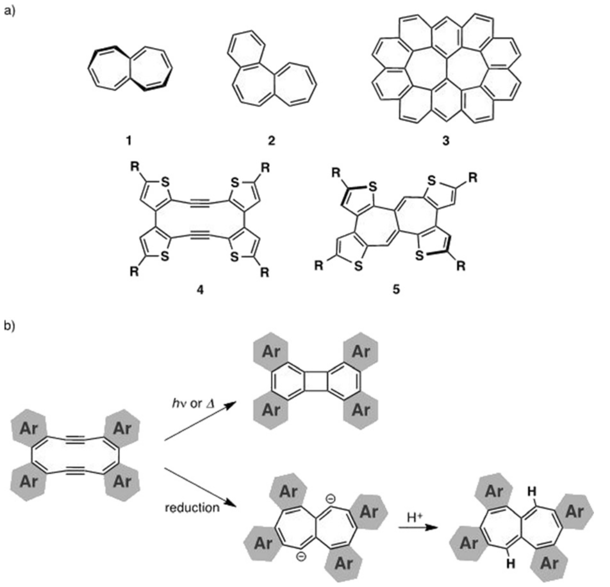

Figure 1. a) Heptalene-based π-electron systems **1**–**3**, **5**, and key precursor **4** (R = *tert*-butyldimethylsilyl); b) transannular cyclization of an arene-fused bisdehydro[12]annulene.

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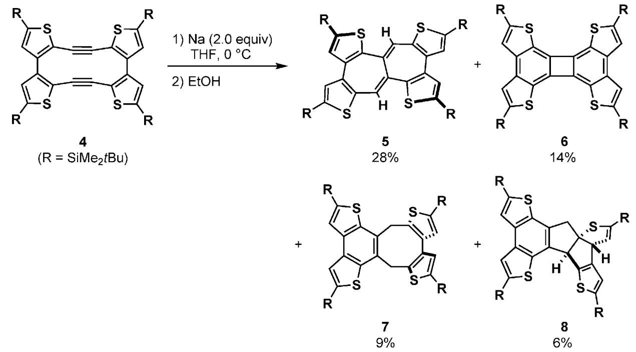
appropriately ring-fused heptalene and the development of a synthetically facile access route are therefore required.

Based on these considerations, we chose thiophene-fused heptalene **5** as a ring-fused target skeleton. Recently, we reported a gram-scale synthesis of bisdehydro[12]annulene **4**, which contains a highly twisted twelve-membered ring with two alkyne moieties in close spatial proximity.[11] Under photochemical or thermal conditions, this compound is able to undergo a transannular cyclization affording tetrathienobiphenylene **6**, which is the formal [2+2]-type cycloadduct (Figure 1 b). We then envisioned that it should be possible to convert **4** into a heptalene framework by inducing a different transannular cyclization mode. To test this hypothesis, we conducted the reductive transannular cyclization of **4** with alkali metals, which afforded tetrathienoheptalene **5**. The obtained product was subsequently converted into heptalene dianion $\mathbf{5}^{2-}$. The aromaticity of **5** and $\mathbf{5}^{2-}$ was then examined on the basis of their structural analysis.

Initially, thiophene-fused bisdehydro[12]annulene **4** was treated with two equivalents of Na metal in THF at 0 °C, which smoothly produced a brown solution. A treatment of the mixture with EtOH afforded tetrathienoheptalene **5** as the major product, together with **6**, **7**, and **8** as minor products (Scheme 1). These products were isolated in pure form in 28 % (**5**), 14 % (**6**), 9 % (**7**), and 6 % yield (**8**).[12] The molecular structures of new compounds **5**, **7**, and **8** were unambiguously determined by single-crystal X-ray crystallographic analysis (see below; see also the Supporting Information, Figures S1 and S2).[13] The results suggested that an initially generated one electron-reduced intermediate with a radical anion character in the alkyne moieties undergoes the transannular cyclization, preferably in an *endo-exo* mode.[14] A similar reaction mode has been reported for the reductive cyclization of cyclic triynes.[15,16] The use of Li metal instead of Na as a reducing agent also produced heptalene **5** as the major product (see the Supporting Information).



Scheme 1. Reductive transannular cyclization of bisdehydro[12]annulene **4** (R = *tert*-butyldimethylsilyl).

Tetrathienoheptalene **5** thus obtained exhibited substantial thermal stability, and no decomposition was observed upon heating to 290 °C under atmospheric conditions. This is in stark contrast to the behavior of benzoheptalene **2**, which decomposes in air even at room temperature.[9] These results clearly demonstrated that the fused structure of tetrathienoheptalene **5**, involving four thiophene rings, is able to effectively stabilize the inherently reactive heptalene skeleton. According to the comparison of HOMO/LUMO energy levels as well as the bond lengths in the heptalene frameworks of a model compound **5′** (where $\mathrm{R = SiMe_3}$) and relevant previously reported heptalene derivatives, neither the electronic effect nor the structural effect, but thermodynamic stabilization by fused aromatic rings is likely responsible for the high stability of **5** (see the Supporting Information). The bulky $t\mathrm{BuMe_2Si}$ groups might also contribute to suppression of the undesirable decomposition reactions.

A yellow to orange THF solution of **5** showed a strong absorption band with a maximum at $\lambda_{\mathrm{abs}} = 399$ nm ($\varepsilon = 1.6 \times 10^4$) and a broad tail at approximately 500 nm in its absorption spectrum (Supporting Information, Figure S3). These absorption bands are significantly red-shifted compared to those of benzoheptalene **2** ($\lambda_{\mathrm{abs}} \approx 260$ nm, 345 nm) and dimethyl heptalene-4,5-dicarboxylate ($\lambda_{\mathrm{abs}} \approx 265$ nm, 340 nm).[9] TD-DFT calculations for **5** at the B3LYP/6-31G(d) level of theory showed that both the HOMO and the LUMO are delocalized over the entire π skeleton. They also suggested that the longest-wavelength absorption band should be assigned to a symmetry-forbidden HOMO→LUMO transition with an oscillator strength of 0.0082 (Supporting Information, Figure S4 and Table S3).

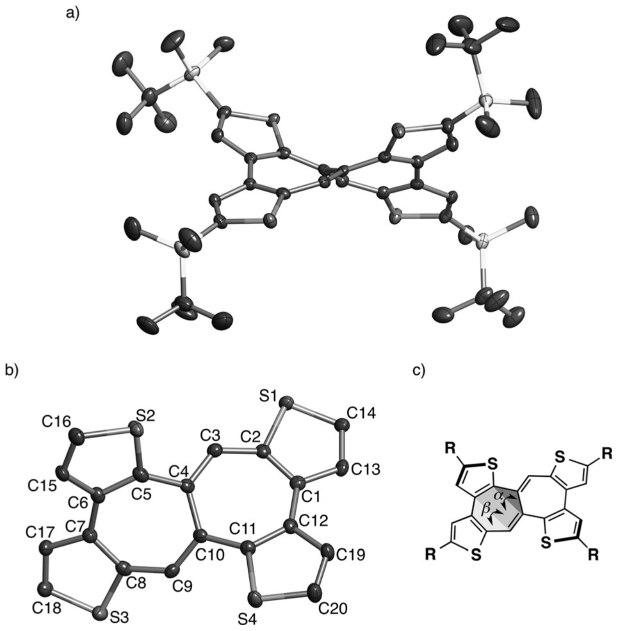


Figure 2. a) Crystal structure of **5** with ellipsoids set at 50 % probability, b) core geometry of the thiophene-fused heptalene moiety with atom labels, and c) definition of the dihedral angles in the heptalene. Hydrogen atoms are omitted for clarity, and only one of the enantiomers is shown.

The molecular structure of **5** was obtained from single-crystal X-ray analysis (Figure 2),[13] and revealed that the heptalene moiety adopts a highly twisted saddle structure, and that the unit cell contains a pair of enantiomers. While the dihedral angles between the thiophene mean planes in the

3,3′-bithiophene substructure are 17.56(27)° and 25.61(20)°, those in the di(2-thienyl)ethene substructure are 59.73(12)° and 64.79(13)°. This structural feature results from a highly twisted geometry of the heptalene skeleton itself. The dihedral angles α and β, defined in Figure 2c, are 31.76/33.80° and 18.12/21.32° (see the Supporting Information), which are comparable to those in previously reported heptalene derivatives.[17] Moreover, the peripheral twelve-membered ring of the heptalene framework shows substantial bond alternation. The four thiophene-fused C−C bonds (C1−C2 1.387(6), C5−C6 1.379(6), C7−C8 1.390(6), C11−C12 1.385(6) Å) and two ethene C−C bonds (C3−C4 1.345(5), C9−C10 1.344(6) Å) are much shorter than the remaining C−C bonds (C2−C3 1.442(5), C4−C5 1.492(6), C6−C7 1.467(5), C8−C9 1.444(6), C10−C11 1.485(5), C12−C1 1.458(6) Å). The harmonic oscillator model of aromaticity (HOMA),[18] obtained from the geometry of the X-ray crystal structure of **5**, provided a value of 0.113, which is consistent with a nonaromatic character of the charge-neutral heptalene framework.

Cyclic voltammograms of **5** were recorded in dichloromethane or THF for the oxidation and reduction processes, respectively. While compound **5** showed an irreversible wave with an anodic peak potential at $E_{pa} = 0.56$ V (vs Fc/Fc$^+$), corresponding to a one-electron oxidation, a two-step pseudo-reversible redox wave was observed for the reduction (Figure 3a). Differential pulse voltammograms revealed that the reduction waves should correspond to two-step one-electron reduction processes with cathodic peak potentials of −2.41 V and −2.55 V (vs Fc/Fc$^+$; Figure 3b), respectively. The observed reversibility of the reduction process thereby suggested that no decomposition of the dianionic species occurred under the electrochemical conditions applied.

In light of the encouraging results obtained from cyclic voltammetry, we subsequently set out to reduce **5** chemically. Treatment of **5** with a slight excess (2.6 equiv) of K in THF at room temperature resulted in a dramatic color change from yellowish orange to deep red. Slow diffusion of a heptane solution of [2.2.2]cryptand into the THF solution of the reaction mixture induced the deposition of single crystals of $[(K[2.2.2]cryptand)^+]_2$**5**$^{2-}$. X-ray crystallographic analysis[14] revealed that the dianion **5**$^{2-}$ is located between two [K([2.2.2]cryptand)]$^+$ ions (Figure 4a). The closest distance between the potassium ion and the heptalene skeleton is 6.64 Å, implying no significant interaction between the two fragments. Most importantly, dianion **5**$^{2-}$ adopts a shallower saddle structure compared to charge-neutral **5**, which is reflected in the dihedral angles between the mean planes of the thiophene rings in the 3,3′-bithiophene substructure (13.25(35)/7.83(18)°), and those in the di(2-thienyl)ethene substructure (42.36(20)/35.18(26)°; Figure 4b).

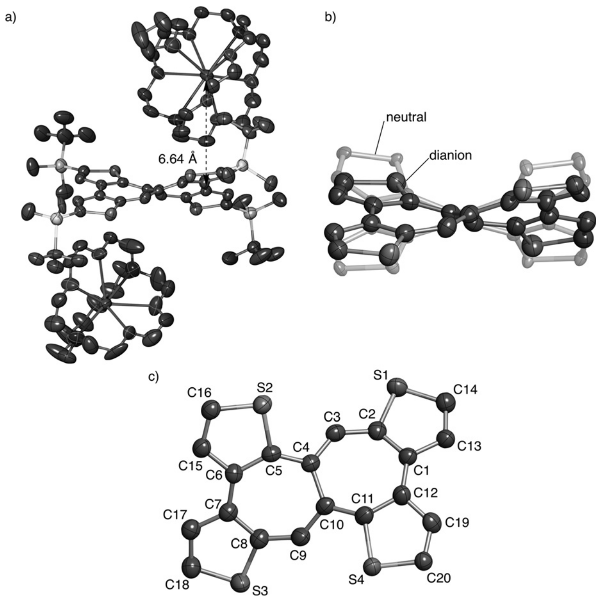


Figure 4. a) Crystal structure of **5**$^{2-}$ drawn with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity and only one of the enantiomers is shown; b) Superimposed structure of the central thiophene-fused heptalene moiety of **5**$^{2-}$ with that of charge-neutral **5**. c) Geometry of the thiophene-fused heptalene moiety in **5**$^{2-}$ with atom labels. Hydrogen atoms and peripheral *t*BuMe$_2$Si groups are omitted for clarity.

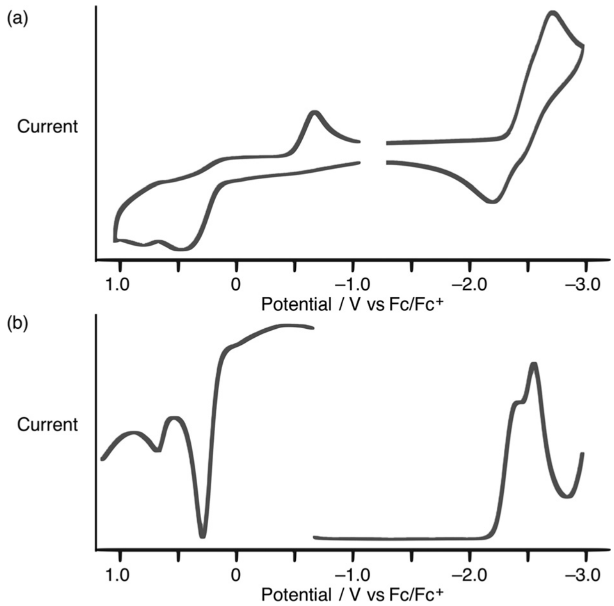


Figure 3. a) Cyclic voltammograms and b) differential pulse voltammograms of **5** at a scan rate of 100 mV s^{-1} in CH$_2$Cl$_2$ (oxidation) and THF (reduction) containing [Bu$_4$N$^+$][PF$_6^-$] (0.1 M).

Even more importantly, the dianionic heptalene skeleton in **5**$^{2-}$ shows a significantly lower degree of bond alternation compared to **5**: The four thiophene-fused C−C bonds (C1−C2 1.410(7), C5−C6 1.438(7), C7−C8 1.418(7), C11−C12 1.443(7) Å) and the two ethene C−C bonds (C3−C4 1.373(7), C9−C10 1.388(7) Å) in **5**$^{2-}$ are elongated compared to those in **5**. In contrast, the other C−C bonds (C2−C3 1.423(7), C4−C5 1.418(7), C6−C7 1.437(7), C8−C9 1.410(7), C10−C11 1.425(7), C12−C1 1.429(7) Å) in **5**$^{2-}$ are contracted relative to those in **5** (Figure 4c). HOMA of the peripheral twelve-membered ring of the heptalene moiety in **5**$^{2-}$ furnished a value of 0.674, which is significantly larger than that of charge-neutral **5** (0.113). These comparisons strongly support a significant degree of Hückel aromaticity in the dianionic heptalene skeleton in $\mathbf{5}^{2-}$.

To gain a better understanding of the aromaticity of $\mathbf{5}^{2-}$, we evaluated the aromaticity in terms of its magnetic character. Nucleus-independent chemical shift (NICS(0)) values of −11.68 ppm/−6.64 ppm were calculated at the HF/6-31+G(d,p) level of theory for two independent seven-membered rings in the crystal structure of heptalene dianion $\mathbf{5}^{2-}$, which are significantly lower than those in charge-neutral **5** (+4.86 ppm/+4.50 ppm). In the ^{1}H NMR spectrum of $\mathbf{5}^{2-}$ in [D$_8$]THF (Supporting Information, Figure S7), the resonance signal for the olefinic protons was detected at 7.96 ppm, which is more deshielded than that observed in **5** (6.68 ppm). This difference should be ascribed to the presence of a diamagnetic ring current in $\mathbf{5}^{2-}$. All these results clearly support a pronounced level of Hückel aromaticity in the dianionic heptalene skeleton with 14 π-electrons.

In summary, we have demonstrated that the alkali-metal-mediated reductive transannular cyclization of bisdehydro[12]annulene **4** allows straightforward synthetic access to a heptalene framework. The tetrathieno-fused heptalene **5** thus prepared can be successfully reduced with potassium metal to furnish the corresponding heptalene dianion, the crystal structure of which was unambiguously determined. A direct comparison of structural and magnetic characteristics between charge-neutral **5** and dianion $\mathbf{5}^{2-}$ delivered strong experimental evidence that even though the charge-neutral and nonplanar heptalene is nonaromatic, the dianionic heptalene, containing 14 π-electrons, exhibits substantial levels of aromaticity. Tetrathienoheptalene **5** may accordingly find applications in non-planar π-scaffolds for optoelectronic materials, and further investigations into this line of research are currently in progress.

Keywords: aromaticity · dehydroannulene · heptalene · π conjugation · transannular cyclization

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[12] Using 1,3,5-trimethoxybenzene as an internal standard, yields by NMR spectroscopy of 37, 23, 16, and 14% were established for **5**, **6**, **7**, and **8**, respectively. For details, see the Supporting Information.

[13] For crystal data of **5** and $[(\mathrm{K}[2.2.2]\mathrm{cryptand})^+]_2\mathbf{5}^{2-}$, see the Supporting Information. CCDC 1050780 (**5**), 1050783 ($\mathbf{5}^{2-}$), 1050781 (**7**), and 1050782 (**8**) contain 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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