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McMURRY COUPLING OF DIFORMYLDITHIENYLACETYLENE: SYNTHESIS OF [24]-, [36]-, AND [48]ANNULENES COMPOSED OF THIOPHENE, ACETYLENE, AND ETHYLENE UNITS

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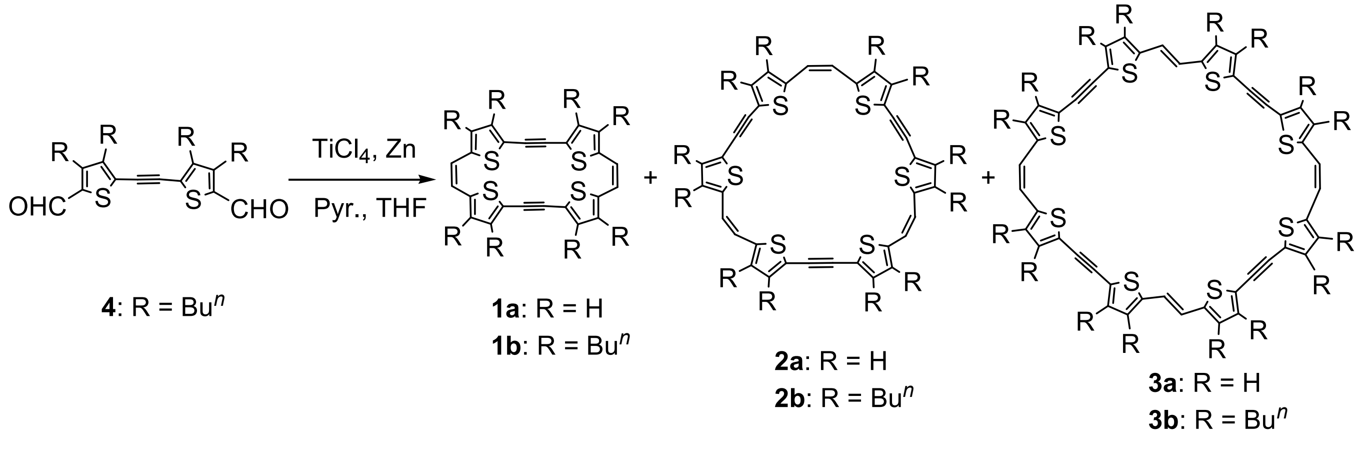
Abstract – The reaction of diformyldithienylacetylene **4** with a McMurry reagent prepared from $TiCl_4$, Zn, and pyridine in THF afforded 24π-dimer **1b** (15%), 36π-trimer **2b** (13%), and 48π-tetramer **3b** (6%). From X-ray analysis, **1b** adopts a twisted conformation, although the ^{1}H NMR spectrum of **1b** shows a symmetrical structure owing to a rapid conformational change in solution. Absorption and emission spectra, redox properties, and electric conductivities of **1b**–**3b** were measured in order to study the structure–property relationship of these macrocyclic systems.

Fully conjugated macrocycles with well-defined shapes have attracted considerable attention owing to their potential applications in organic electronic and photovoltaic devices, field effect transistors, and chemical sensors.[1] In this regard, π-expanded porphyrins and cyclic oligothiophenes have been extensively studied as candidates for novel electronic materials.[2,3] Kawase and Oda reported the synthesis and X-ray structure of 5,6,17,18-tetradehydrotetrathia[24]annulene[2.2.2.2] (**1a**) using a double Fritsch-Buttenberg-Wiechell rearrangement reaction.[4] In the same communication, they also reported that the McMurry coupling reaction of 5,5′-diformyl-2,2′-dithienylacetylene with $TiCl_3(DME)_{1.5}$ and Zn(Cu) in DME affords only a trace amount of **1a** with macrocyclic oligothiophene **2a**. Recently, we have reported the synthesis of giant macrocycles using McMurry coupling with $TiCl_4$, Zn, and pyridine in THF.[5,6] We synthesized octabutyl derivative **1b** using the same reaction conditions. The latter McMurry coupling sometimes yields macrocycles in better yields than the former one can (Scheme 1).[7] We report here the synthesis of tetradehydrotetrathia[24]annulene **1b**, hexadehydrohexathia[36]annulene **2b**, and octadehydrooctathia[48]annulene **3c** together with their structure–property relationship.

This paper is dedicated to Professor Dr. Albert Eschenmoser on his 85th birthday.



Scheme 1. McMurry reaction of **4**

Dialdehyde **4** was prepared via a four-step reaction starting from 3,4-dibutylthiophene in 37% overall yield.[8,9] As reported previously, the McMurry coupling reagent, which is a low-valent titanium reagent prepared from the reaction of $TiCl_4$ (excess amounts) with Zn in the presence of pyridine in THF, is an effective catalyst to produce cyclooligomerization products.[5] Thus, cyclooligomerization of **4** under modified McMurry conditions (low-valent titanium reagent (5 equiv.), pyridine (7.5 equiv.), THF, 65 ºC, 3 h) resulted in the formation of dimer **1b**, trimer **2b**, and tetramer **3b** in 15%, 13%, and 6.0% yields, respectively.[10] The low yield of **1b** as compared to that by using the previously reported cyclooligomerization may be due to the strained acetylene bonds in **1b**. A similar reaction of **4** with 10 equiv. of a low-valent titanium reagent for a longer time resulted in a marked decrease in the yield of **1b** owing to the reduction of the strained acetylene bonds in **1b** to produce **5**.[11] Although **1b** formed yellow crystals from hexane, **2b** and **3b** precipitated as gummy orange solids. All of the compounds are stable and can be stored at room temperature.

The structure of **1b** was determined by using X-ray structural analysis (Figure 1).[12] Single crystals of **1b** were prepared from ether–methanol. As shown in Figure 1, **1b** has a crystallographic C_2 symmetry axis passing through the midpoints of the two acetylene bonds (C5-C5* and C11-C11*). The sulfur atom S1 is located in the center of the neighboring thiophene ring, and the S1···S2 distance is 3.262(1) Å, which is 12% shorter than the sum of van der Waals radii (3.7 Å). Although the X-ray structure of **1a** has been reported to be planar, **1b** has an extremely twisted structure. The ^{1}H NMR spectrum of **1b** at room temperature was consistent with a symmetrical structure having two different butyl groups and an olefinic singlet (δ 6.61). In other words, **1b** undergoes a rapid conformational change in solution. Furthermore, the ^{1}H NMR spectra of *all-Z*-**2b** (two different butyl groups and an olefinic singlet (δ 6.57)) exhibited no conformational change in solution, whereas and *E,Z,E,Z*-**3b** (two different butyl groups and two different olefinic singlet (δ 6.90 and 6.61)) showed a rapid rotation of the two *E*-olefins at room temperature.[13]

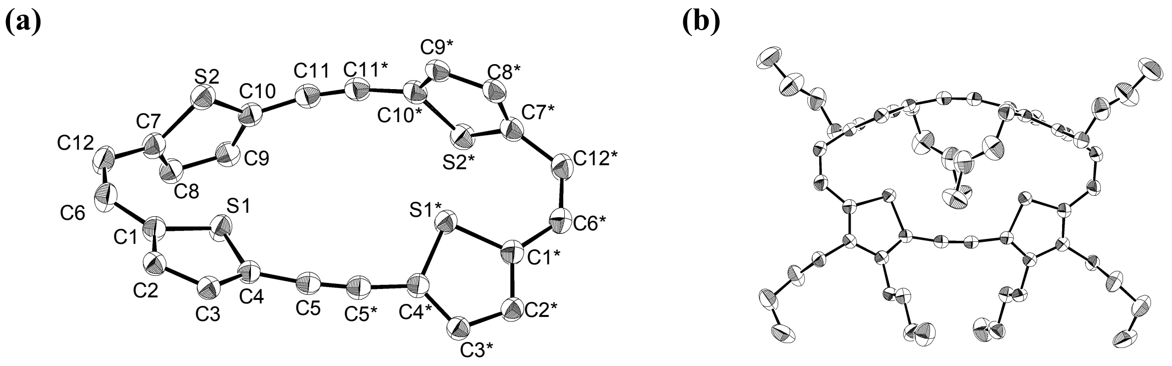


Figure 1. ORTEP drawing of **1b** at the 50% probability level. (a) Side view with butyl groups and hydrogen atoms omitted for clarity. (b) Top view with hydrogen atoms omitted for clarity

As shown in Figure 2, the absorption maxima of **1b**–**3b** (λ_{max}: **1b**, 355 nm; **2b**, 369 nm; **3b**, 436 nm) were red-shifted in relation to the size of the π system, whereas in the fluorescence spectra of **1b**–**3b**, no red shift was observed (λ_{em}: **1b**, 582 nm, $\Phi_F = 0.0003$; **2b**, 587 nm, $\Phi_F = 0.001$; **3b**, 589 nm, $\Phi_F = 0.03$).[14] The low quantum yield of **1b** may be due to the rapid conformational change in solution.

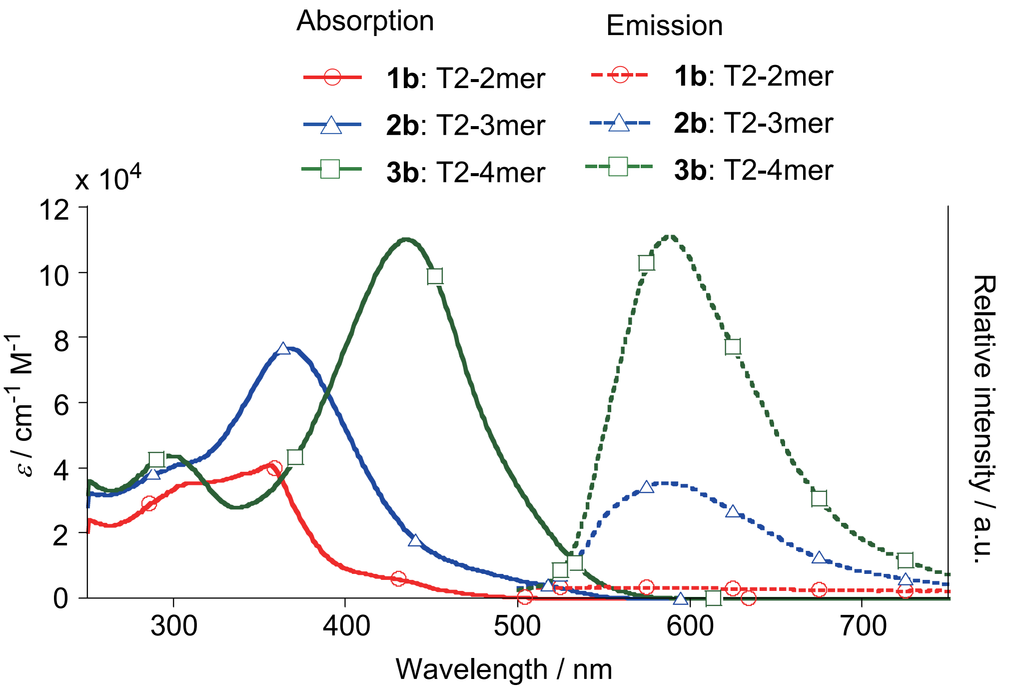
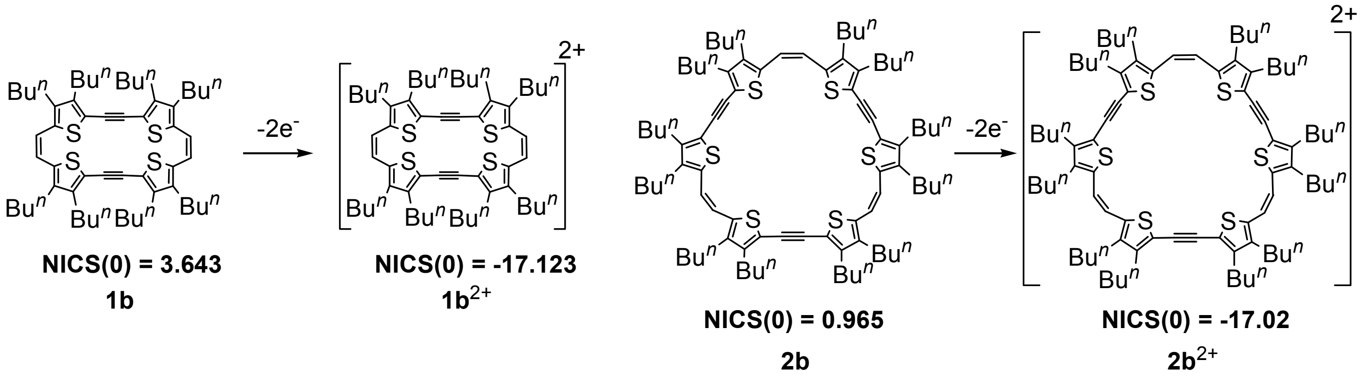


Figure 2. Absorption and emission spectra of **1b**, **2b**, and **3b** in dichloromethane

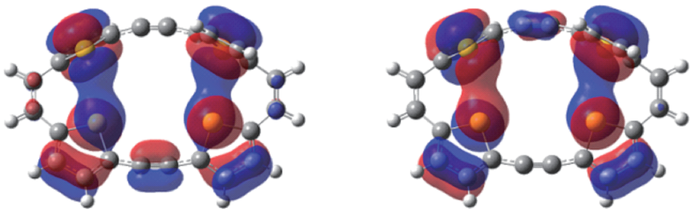
All of the compounds had relatively low oxidation potentials, which were determined by using cyclic voltammetry: **1b**, $E^{ox}_{1/2} = 0.37$ V (2e); **2b**, $E^{ox}_{1/2} = 0.33$ V (2e); **3b**, $E^{ox1}_{1/2} = 0.28$ V (1e); and $E^{ox2}_{1/2}$ =

0.56 V(1e) vs. Fc/Fc$^+$.[15] These macrocycles can be oxidized to produce aromatic 22π and 34π dications (NICS(0) = –17.123 and –17.02, respectively). However, **1b**$^{2+}$ and **2b**$^{2+}$ were not stable enough to observe via ^{1}H NMR spectroscopy, and we could only acquire their UV-vis-NIR spectra.



Scheme 2. Oxidation of paratropic **1b** and **2b** to produce diatropic **1b**$^{2+}$ and **2b**$^{2+}$

The most interesting feature in these 24π, 36π, and 48π annulenes is the structure of **1b**. Although Kawase and Oda have reported that **1a** has a planar π-π stacked structure, MO calculations indicate that **1a** should have a twisted conformation like the crystal structure of **1b**. As shown in Figure 3, there is strong S···S overlap in HOMO-6 and HOMO-7.[4,16] In other words, the S atoms interact favorably.



HOMO-6 (7.17 eV) HOMO-7 (7.18 eV)

Figure 3. HOMO-6 and HOMO-7 of **1a**[17]

In summary, we synthesized octabutyltetradehydrotetrathia[24]annulene[2.2.2.2] (**1b**) and the higher homologues **2b** and **3b** by using a modified McMurry coupling reaction. From X-ray analysis, **1b** adopts a twisted conformation with a C_2 axis passing through the midpoints of the two acetylene bonds. On the basis of the spectroscopic characterization of **1b** and the MO calculations on tetradehydrotetrathia[24]annulene[2.2.2.2] (**1a**), a twisted structure appears to be the most stable conformation of **1a**.

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8. Dialdehyde **4** was prepared in 75% yield by successive treatments of bis(3,4-dibutyl-2-thienyl)acetylene[9] with *n*-BuLi (2.75 equiv.) at 0 ºC and DMF (2.9 equiv.) in the temperature range from 0 ºC to room temperature.
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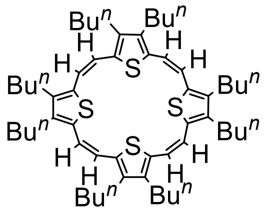
10. Spectral data of new compounds: **1b**, yellow crystal, mp 116 ºC (DSC), ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ 6.61 (s, 4H), 2.61 (t, J = 7.8 Hz, 8H), 2.47 (t, J = 7.8 Hz, 8H), 1.33–1.58 (m, 32H), 0.87–0.94 (m, 24H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 144.80, 141.4, 134.6, 123.6, 120.7, 92.5, 32.9, 32.7, 28.4, 27.3, 22.8, 22.7, 13.9; MS (EI) *m/z* 877 ($\mathrm{M^+}$); **2b**, red amorphous waxy solid, ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ 6.57 (s, 6H), 2.64 (t, J = 7.8 Hz, 12H), 2.49 (t, J = 7.8 Hz, 12H), 1.34–1.59 (m, 48H), 0.90–0.94 (m, 36H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 146.3, 141.2, 134.0, 122.6, 119.3, 89.7, 32.8, 32.5, 28.3, 27.3, 22.7, 22.7, 14.0, 13.8; LDI-TOF-MS *m/z* 1314.70 ($\mathrm{M^+}$); **3b**, red amorphous waxy solid, ^{1}H NMR ($\mathrm{CDCl_3}$) δ 6.90 (s, 4H), 6.61 (s, 4H), 2.67 (t, J = 7.8 Hz, 8H), 2.63 (t, J = 7.8 Hz, 8H), 2.56 (t, J = 7.8 Hz, 8H), 2.51 (t, J = 7.8 Hz, 8H), 1.35–1.61 (m, 64H), 0.94 (m, 48H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 147.7, 146.2, 141.6, 140.1, 137.7, 134.2 , 122.7, 120.2, 119.3, 117.1, 90.5, 90.2, 33.2, 33.0, 32.64, 32.56, 28.41, 28.36, 27.4, 27.1, 22.81, 22.78, 22.75, 22.73, 14.1, 14.03, 13.95, 13.93; LDI-TOF-MS *m/z* 1753.10 ($\mathrm{M^+}$); **4**, red viscous oil, ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ 10.00 (s, 2H), 2.89 (t, J = 8.0 Hz, 4H), 2.71 (t, J = 7.8 Hz, 4H), 1.56–1.62 (m, 8H), 1.40–1.46 (m, 8H), 0.98-0.95 (m, 12H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 180.9, 150.0, 148.0, 137.6, 125.8, 90.9, 33.3, 31.5, 26.8, 26.0, 21.7 (2C), 13.0, 12.8; MS (EI) *m/z* 470 ($\mathrm{M^+}$).
11. **5** was obtained in 10% yield based on **4**. Yellow viscous oil, ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ 6.46 (s, 8H), 2.46 (t, J = 7.8 Hz, 16H), 1.27–1.43 (m, 32H), 0.89 (t, J = 7.8 Hz, 24H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 144.80, 141.4, 134.6, 123.6, 120.7, 92.5, 32.9, 32.7, 28.4, 27.3, 22.8, 22.7, 13.9; MS (EI) *m/z* 880 ($\mathrm{M^+}$).



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12. X-Ray analysis of **1b**: $\mathrm{C_{56}H_{76}S_4}$, *Mw* 877.41, monoclinic, space group *C2/c* (#15), a = 24.271(6) Å, b = 10.824(3) Å, c = 22.530(6) Å, β = 118.543(5)º, V = 5200(2) Å^3, Z = 4, Dc = 1.121 g cm^{-3}, R_1 = 0.0796, Rw = 0.1854, GOF = 1.060. Among a total of 11150 reflections measured, 3752 were unique, and the observed ($I > 2.00\sigma(I)$) 2948 reflections were used for the refinement. The crystal structure was solved by using the SHELXS-97 program and refined by using the full matrix least-squares method in the SHELXS-97 software package. Cambridge Crystallographic Data Centre deposition No. CCDC–752997.
13. The most stable diastereomers of **2b** and **3b** are *all-Z-* and *E,Z,E,Z*-isomers, respectively, on the basis of MO calculations at the B3LYP/6-31G(d) level.
14. Fluorescence quantum yields (Φ_F) were determined via a comparison with quinine sulfate in 0.5 M $\mathrm{H_2SO_4}$ (Φ_F = 0.546).
15. CV analyses were carried out using 0.5 M solutions of the compounds in $\mathrm{CH_2Cl_2}$ at 23 °C using Pt working and counter electrodes, Ag/Ag$^+$ as a reference electrode, and $\mathrm{Bu^n{}_4NPF_6}$ as a supporting electrolyte.

16. Kawase and Oda have reported a planar X-ray structure for **1a**.[4] Since the S···S interatomic distances are 3.014 and 3.024 Å, which are 18.3% and 18.5% shorter than the sum of van der Waals radii (3.7 Å) respectively, the distances are too short to stabilize the structure. However, the π-π stacking interactions in the crystal may stabilize the planar structure.

17. HOMOs of **1a** on the basis of MO calculations at the B3LYP/6-31G(d) level are as follows: