Construction of Strained Frameworks with 1,8-Anthrylene Units and Acetylene Linkers: Synthesis and Structures of Cyclic Trimers[1]

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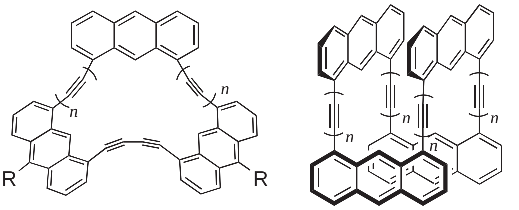
Two 1,8-anthrylene cyclic trimers with acetylene or diacetylene linkers were synthesized by macrocyclization with the Eglinton coupling. These compounds have nonplanar and strained cyclic structures with significant bending deformations of acetylene carbons as revealed by X-ray analysis and DFT calculation. The effects of the molecular structures on the ^{13}C NMR chemical shifts and the electronic spectra are discussed.

We recently reported the synthesis of several oligomeric macrocycles consisting of 1,8-anthrylene units and linear acetylene linkers, which may potentially serve as tools to create new types of π-conjugated compounds with fascinating structures and properties.[2,3] Examples of such oligomers are cyclic tetramers **3** and **4** (Figure 1), which possess diamond prism structures without severe bending deformations in the linker moieties. Oligomeric structures with an odd number of 1,8-anthrylene units suffer from strain due to geometrical reasons. Therefore, we were interested in whether the smallest analogue of this series of oligomers, namely, cyclic trimers, could be constructed regardless of the expected molecular strain, since cyclic arylene–ethynylene structures have been extensively applied to the design of functionalized molecules.[4,5] We herein report the synthesis, structures, and properties of 1,8-anthrylene cyclic trimers **1** and **2** with ethynylene and butadiynylene linkers, as strained macrocycles.

We synthesized two kinds of cyclic trimers, **1** with three diacetylene linkers and **2** with one diacetylene and two acetylene linkers, the latter having two isopropyl groups to improve solubility. Linear precursor **7** was prepared by the Eglinton coupling[6] between **5**[3] and **6**[2b] under statistical conditions followed by chromatographic separation (Scheme 1). After the desilylation of **7**, the Eglinton coupling afforded cyclized product **1** in 34% yield. Compound **8** was prepared with a modified procedure of a known method,[2b] and the macrocyclization afforded desired product **2** in 22% yield.[7] These macrocycles were obtained as yellow crystals and reasonably characterized by NMR and mass spectroscopies.[8]

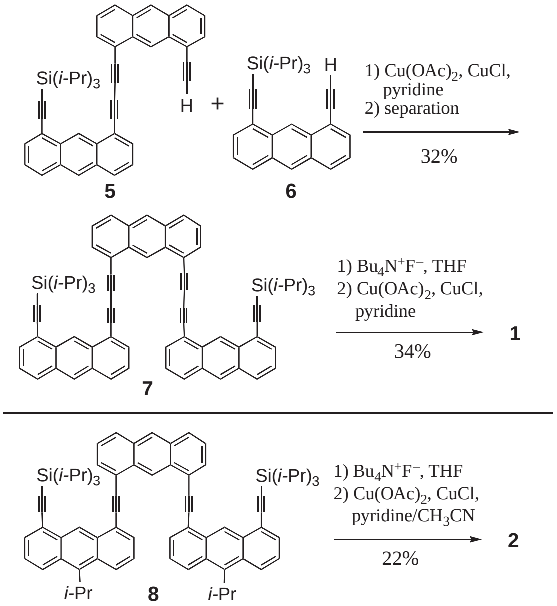
The molecular structure of **1** was investigated by X-ray analysis.[9] The ORTEP drawing in Figure 2 indicates a nearly C_2 symmetric structure, where the axis of rotation passes through the 9,10-carbon atoms in anthracene A and the middle of the linker at the opposite side.[10] The sp carbons are distorted from the linear geometry (bond angle 165.6–174.3°),[11] and each linker moiety is curved to connect the two anthracene moieties in a



1 (n = 2, R = H)
2 (n = 1, R = i-Pr)

3 (n = 2)
4 (n = 1)

Figure 1. 1,8-Anthrylene cyclic trimers and tetramers with acetylene linkers.



Scheme 1. Synthesis of cyclic trimers **1** and **2**.

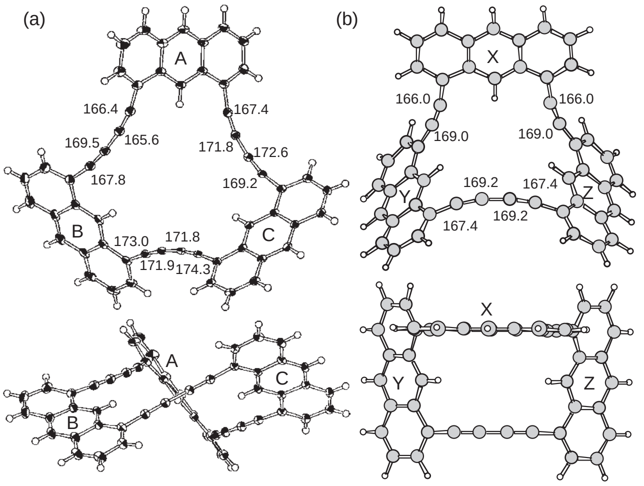


Figure 2. Two views of molecular structures of cyclic trimers. (a) X-ray structure of **1**. (b) Calculated structure of **2′** (R = H) at the B3LYP/6-31G* level. Numbers are bond angles (°) at sp carbons.

Table 1. ^{13}C NMR and UV data of cyclic trimers **1** and **2** and the related compounds[a]

	^{13}C NMR/δ[b]		UV $\lambda_{\max}$/nm[c]
	–C≡C–C≡C–	–C≡C–	
1	81.4, 86.2	—	443
2	82.4, 89.1	94.8, 96.1	458
3	80.1, 81.1[d]	—	446
4	—	93.1	439

[a]Data of cyclic tetramers **3** and **4** from Refs. 3 and 2b, respectively. [b]Chemical shifts of alkynic carbons measured in $CDCl_3$ at rt. [c]Absorptions at the longest wavelengths, measured in CH_2Cl_2 or $CHCl_3$. [d]Data for **3** with four octadecyl groups at 10-position.

three-dimensional fashion. The anthracene moieties are slightly twisted from the planar structure: some torsion angles around 1,8-carbon atoms deviate by more than 6° from the planar structure. The symmetric ^{1}H NMR signal pattern, two singlets and an ABC system, was retained even at $-60\,°C$, suggesting that the inversion or pseudorotation averaging the anthracene moieties under different environments took place rapidly at the low temperature. The structure of **2′** (R = H) was optimized at the B3LYP/6-31G* level to give a saddle-like structure of C_s symmetry. All bond angles at sp carbons are smaller than 170°, and there are significant out-of-plane deformations in the anthracene rings. The framework of **2** appears to be so rigid that the ring inversion is unlikely under ordinary conditions.

The ^{13}C NMR chemical shifts of sp carbons for **1** and **2** are compared with those of the reference compounds in Table 1. Generally, the alkynic carbon atoms are deshielded with increasing bending deformation because of the change in hybridization from sp to sp^2.[12,13] This effect is notable in one of the signals due to butadiynylene carbons,[14] and the shifts are ca. 5 and 8 ppm for **1** and **2**, respectively, relative to **3**. This tendency is consistent with the molecular structures in Figure 2, where the alkynic carbons in **2** are more distorted than those in **1**. A similar effect was observed for the carbon signals due to the ethynylene carbons in **2** (shift ca. 3 ppm).

Trimers **1** and **2** showed structured absorption bands in the range of 380–460 nm in the UV spectra. The $\lambda_{\max}$ values at the longest wavelength are only slightly influenced by the structures among the trimers and tetramers (Table 1). Since the wavelengths are influenced by several factors including ring size, substituents on the anthracene rings, and so on, it is difficult to estimate the effect of deformations at the linker and aromatic moieties from available data. Compounds **1** and **2** gave emission bands at 471 and 459 nm, respectively, with moderate intensities (Φ_f ca. 0.25).

In summary, strained macrocyclic structures with three anthracene units were successfully constructed by the Eglinton coupling of the acyclic precursors. The molecular strains spread over the linker moieties and the aromatic rings as structural deformations. These compounds will serve as a guide to attempts of synthesizing cyclic trimers with three ethynylene linkers to determine the limitation of the molecular strains. Further studies on the properties and functions of these macrocycles are in progress.

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References and Notes

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8 Selected data. **1**: mp 298–301 °C (dec); ^{1}H NMR ($CDCl_3$, rt) δ 7.48 (6H, t, $J = 7.3$ Hz), 7.97 (6H, d, $J = 6.8$ Hz), 8.01 (6H, d, $J = 8.8$ Hz), 8.45 (3H, s), 9.24 (3H, s); HR-MS (FAB) Found m/z 673.1920. Calcd for $C_{54}H_{25}$: $[M + H]^+$, 673.1956. **2**: mp 298–300 °C (dec); ^{1}H NMR ($CDCl_3$, rt) δ 1.70 (12H, d, $J = 7.3$ Hz), 4.47 (2H, septet, $J = 7.3$ Hz), 7.32 (2H, dd, $J = 6.8$, 9.3 Hz), 7.40 (2H, dd, $J = 7.3$, 8.8 Hz), 7.44 (2H, dd, $J = 6.8$, 9.3 Hz), 7.65 (2H, d, $J = 7.1$ Hz), 7.74 (2H, d, $J = 7.8$ Hz), 7.83 (2H, d, $J = 6.3$ Hz), 8.03 (2H, d, $J = 8.8$ Hz), 8.34 (2H, d, $J = 9.3$ Hz), 8.38 (2H, d, $J = 9.3$ Hz), 8.53 (1H, s), 9.36 (2H, s), 9.55 (1H, s); HR-MS (FAB) Found m/z 708.2827. Calcd for $C_{56}H_{36}$: M^+, 708.2817.

9 Crystal data for **1**: $C_{54}H_{24}\cdot C_6H_5Cl$, $M_r = 785.34$, monoclinic, space group $C2/c$ (#15), $a = 40.8092(8)$, $b = 14.5730(2)$, $c = 13.7874(2)$ Å, $\beta = 102.0447(8)°$, $V = 8019.1(2)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 1.30\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo}\,K\alpha) = 1.38\ \mathrm{cm^{-1}}$, $T = 123$ K, 8800 reflections, $R1 = 0.038$, $R\mathrm{w} = 0.085$. CCDC deposition number: 611249.

10 The structure of **1** was approximately reproduced by DFT calculations at the B3LYP/6-31G* level.

11 Bond angles at alkynic carbons are 178.5–180.0° for **3** (AM1) and 171.8–177.5° for **4** (X-ray). See Refs. 2b and 3.

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14 These signals are assignable to the 1,4-carbon atoms in the butadiynylene moiety, which usually give signals at a lower field than the 2,3-carbon atoms, see Ref. 12a.