Nonplanar and Dynamic Structures of 1,8-Anthrylene–Ethenylene Cyclic Dimers

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The title cyclic compounds, synthesized by cross-coupling reactions, have nonplanar frameworks, as revealed by X-ray analysis and DFT calculations. The barrier to exchange between the nonplanar structures of the mesityl derivative was determined to be $34 \text{ kJ} \text{ mol}^{-1}$ by a dynamic NMR method.

In the molecular design of π -conjugated oligomers, several arene units are alternately connected to unsaturated linkers to extend the π system. These compounds are attractive for applications in material chemistry because of their interesting electrical and optical properties.¹ As examples of such compounds, we have studied anthracene-acetylene cyclic oligomers by adopting 1,8-anthrylene units and ethynylene (or butadiynylene) linkers.²⁻⁴ Their structures, dynamic behavior, and spectroscopic properties are influenced by the number of anthracene units, as revealed by the experimental and theoretical results for dimers to dodecamers. Dimers 1^5 and 2^6 , the smallest analogs, have planar rigid frameworks and show characteristic electronic properties (Figure 1). This structural feature has been applied to the generation of new stereoisomers by introducing intraannular substituents.⁷ 1,2-Ethenylene (or vinylene, hereafter ethenylene) linkers are also commonly used in the π -conjugated system,¹ and anthrylene-ethenylene oligomers and polymers have been studied by many researchers for potential use of functional materials.⁸ In contrast to linear ethynylene linkers, ethenylene linkers have a nonlinear zigzag shape, and the conformation about single bonds considerably influences the chain shape and the extent of conjugation. As regards anthracene cyclic dimers, ethenylene derivative $3a^9$ was reported as a [14]annulene analog by Akiyama and Nakagawa in 1971.¹⁰ Although the authors focused on the nonplanar structure, no further details were disclosed because of the low solubility of the compound. Hence, we synthesized soluble substituted derivatives 3b with a phenyl group and 3c with a mesityl group to solve the structural problem. We expected that the mesityl group in 3c would enable conformational analysis, as in the case of anthracene-acetylene macrocyclic oligomers.¹¹

In the original procedure, compound **3a** was synthesized by the Wittig reaction.¹⁰ We adopted cross-coupling reactions to connect the aromatic and ethenylene moieties according to the protocol reported by Itami et al. (Scheme 1).¹² Ethenyl groups were introduced by the Mizoroki–Heck reaction of 1,8-diiodoanthracene (**4a**)¹³ and ethenylboronate **5** to give **6** in 86% yield. Cyclization of **6** and **4a** by the Suzuki–Miyaura coupling under high-dilution conditions (ca. $1 \times 10^{-4} \text{ mol L}^{-1}$) afforded **3a** in 32% yield. Compound **6** was similarly cyclized with substituted 1,8-diiodoanthracenes **4b** and **4c**, and cyclic products **3b** and **3c** were obtained in 30% and 33% yields, respectively. In each cyclization reaction, the mass spectrum of the crude product showed peaks due to the corresponding cyclic tetramer



Figure 1. 1,8-Anthrylene cyclic dimers with various linkers.



Scheme 1. Synthesis of cyclic dimers 3.

and other oligomers. Compounds **3b** and **3c** were much more soluble in organic solvents than was **3a**. Even though the yields were not high, this synthetic route offered rapid access to the cyclic compounds. The compounds were obtained as yellow crystals and reasonably characterized by NMR spectroscopy and mass spectrometry.¹⁴ In the ¹H NMR spectra, alkene proton signals were observed at δ ca. 7.8 as a singlet for **3a** and **3c**¹⁵ and as an AB quartet with J = 16.8 Hz for **3b**. This large coupling constant supports the trans junction at the ethenylene moieties. Hereafter, we mainly describe the results of mesityl derivative **3c**.

The electronic spectra of **3c** were measured in chloroform (Figure 2). A broad absorption band was observed at 417 nm in the p-band region of the UV–vis spectrum. The wavelength was red-shifted by 19 nm compared with that of 1,8-diethenyl-anthracene (398 nm).^{10,16} The TDDFT calculations of **3a** supported that this absorption was assignable to the transition from the HOMO to the LUMO, and orbitals were delocalized over the molecules at those levels (see Supporting Information). The fluorescence spectrum gave an intense and broad emission band at 491 nm ($\Phi_f = 0.71$). The large Stokes shift (70 nm) was attributable to the large structural change after excitation.

The X-ray structure of 3c is shown in Figure 3. The macrocyclic framework is nonplanar, and the two double bond moieties are parallel and twisted by ca. 40° from the coplanar conformation to the same side of each anthracene unit (syn form). Accordingly, the two anthracene planes are also nearly parallel in a stair-like orientation. The mesityl-phenyl group is almost perpendicular to the attaching anthracene unit. The



Figure 2. UV-vis (solid line) and fluorescence (broken line) spectra of 3c in CHCl₃.



Figure 3. X-ray structure of 3c (one of the two independent molecules).



Figure 4. Calculated structures of **3a** at M05/6-31G(d) level. Values in brackets are relative free energies at 298 K in kJ mol⁻¹.



Figure 5. VT ${}^{1}HNMR$ spectra of methyl groups in 3c in $CD_{2}Cl_{2}$.



Scheme 2. Conformational interconversion of 3c (a) and mechanism of dynamic behavior of 3a (b).

structures of the macrocyclic framework were investigated by DFT calculations of **3a** at the M05/6-31G(d) level,¹⁷ which reasonably reproduced the observed structure of **3c** (Figure 4). We found two energy minimum structures: one was the *syn*-form, which was similar to the X-ray structure, and the other was the *anti*-form, in which the two double bond moieties were directed to the opposite sides of each anthracene unit. The latter *anti*-form was less stable by $8.8 \text{ kJ} \text{ mol}^{-1}$ than the *syn*-form, and this energy difference suggested that most of the molecules should exist in the *syn*-form under ordinary conditions.

Because the rotation of the mesityl group in 3c is highly restricted,¹⁸ its two *o*-Me groups can act as a convenient probe for the conformational analysis. The two Me groups in 3c are magnetically nonequivalent in the *syn*-form (Me^A and Me^B in Scheme 2a), whereas they are equivalent in the unstable C_2 symmetric *anti*-form. In the variable-temperature (VT) ¹H NMR spectra of 3c, the *o*-Me protons gave a sharp singlet at room temperature and even at -80 °C in CD₂Cl₂. This signal broadened at lower temperatures and decoalesced at -105 °C (Figure 5). The barrier to exchange between the two signals by line shape analysis was found to be 34 kJ mol^{-1} at 173 K. The observed line shape change is rationally explained by the inverconversion between the two *syn*-forms (Scheme 2a), which are topomers of each other and differ in the relative orientation of the two anthracene units.

The mechanism of this conformational exchange was analyzed by DFT calculations (Figure 4). A mechanism involving the concurrent rotation of the two linker moieties (the direct syn-to-syn conversion) is unlikely because this process should pass through the unstable planar structure having severe steric hindrance between the linker and the anthracene 9-H atoms in the inner region. We then searched for a mechanism involving stepwise rotation and finally obtained a transition-state structure for the conversion of the syn-form into the anti-form, where one linker was nearly coplanar to the two anthracene planes. This structure was less stable by 38 kJ mol^{-1} than the *syn*-form, and this energy was comparable to the observed barrier. These calculations supported the stepwise rotation mechanism for the conversion between the two syn-forms via the anti-form as an intermediate (Scheme 2b). The two zigzag linkers rapidly underwent rotation, leading to facile isomerization between the nonplanar structures.

In conclusion, anthrylene–ethenylene cyclic dimers were synthesized by cross-coupling reactions in short steps. The preference for the nonplanar *syn*-form was confirmed by X-ray analysis and DFT calculations. The introduction of a mesityl group not only increased solubility but also allowed us to observe the dynamic behavior by a dynamic NMR method. Synthesis of the soluble derivative will stimulate the application of this cyclic system to functional molecules such as fluorescent materials. Further studies on factors controlling the conformational stability and mobility as well as the improvement of the cyclization reactions are in progress.

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