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New π-Conjugated System with a Rigid Framework of 1,8-Anthrylene–Ethynylene Cyclic Dimer and Its Monoanthraquinone Analogue[1]

Shinji Toyota,* Megumi Kurokawa, Mai Araki, Kazuya Nakamura, and Tetsuo Iwanaga

Department of Chemistry, Faculty of Science, Okayama University of Science,
1-1 Ridaicho, Okayama 700-0005, Japan

stoyo@chem.ous.ac.jp

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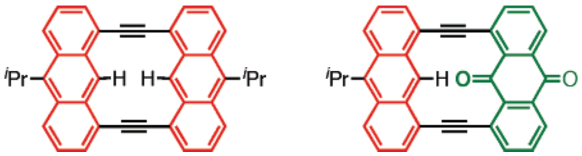
ABSTRACT



Two types of π-conjugated compounds were synthesized by Sonogashira coupling, and their structures and properties were investigated by X-ray analysis and spectroscopic measurements. The monoanthraquinone compound features an out-of-plane deformation of the inner carbonyl moiety and dimer formation in crystals and solution.

We have previously reported that the molecular design based on 1,8-anthrylene units and linear acetylene linkers is a simple yet versatile approach to building a variety of oligomeric structures[2,3] as new types of arylene−ethynylene compounds.[4] For example, the tetrameric structures of **1** were readily constructed from these building units, which adopted a unique diamond prism structure (Figure 1).[2] We also synthesized cyclic trimers **2** even though the molecules suffer from deformation for geometric reasons.[3] During the course of these studies, we learned that the molecular system of the smallest cyclic analogue, namely, 1,8-anthrylene−

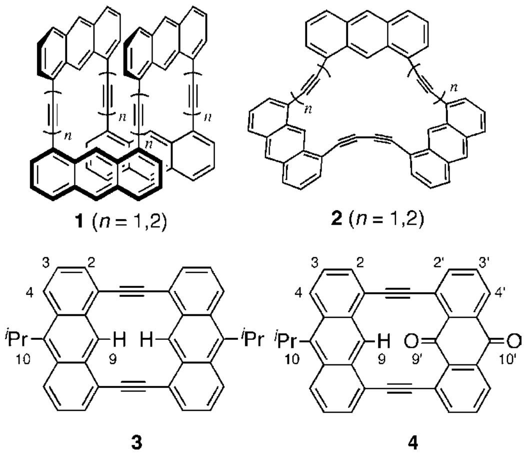


Figure 1. 1,8-Anthrylene−alkynylene cyclic systems.

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[1] Part 7 of Chemistry of Anthracene−Acetylene Oligomers. For Part 6 see: Goichi, M.; Yamasaki, S.; Miyahara, H.; Wakamatsu, K.; Akashi, H.; Toyota, S. *Chem. Lett.* **2007**, *36*, 404.

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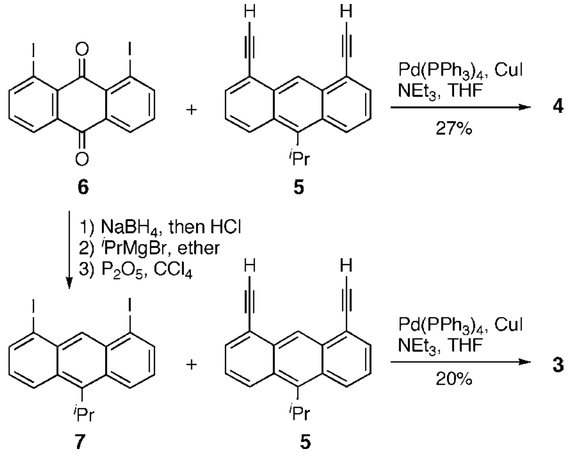
ethynylene dimer **3**, is still unknown while the corresponding ethenylene[5] and butadiynylene analogues[6] are known as novel fused annulenes. In the molecular model of **3**, the inner H atoms collide with each other in the rigid framework, and this steric situation is the reason why its synthesis is difficult to perform. Despite such difficulties, we managed to synthesize compound **3** with two alkyl groups at the 10-positions by the cross-coupling reaction. Moreover, a similar coupling reaction afforded anthraquinone analogue **4** even though one of the carbonyl-oxygen atoms pointed inside the central ring. Hence, we studied the structures and properties of these new π-conjugated compounds, particularly steric hindrance in the rigid ring system, photophysical properties, and self-aggregation, a phenomenon often observed in shape-persistent aromatic compounds.[7]

The ring system was constructed by the Sonogashira coupling of appropriate iodides and terminal alkynes. Because we failed to synthesize the parent compound without substituents, isopropyl groups were introduced at the 10-positions to improve solubility. The cross-coupling reactions of **5**[3] and **6**[8] afforded cyclic product **4** in 27% yield after chromatographic purification (Scheme 1). Compound **7** was prepared from **6** in three steps, and this diiodide was coupled with **5** to give **3** in 20% yield.[9] Compounds **3** and **4** were obtained as stable orange crystals that melted at high temperature with decomposition. These compounds were reasonably characterized by NMR and mass spectroscopy.[10]

Scheme 1. Synthesis of Compounds **3** and **4**



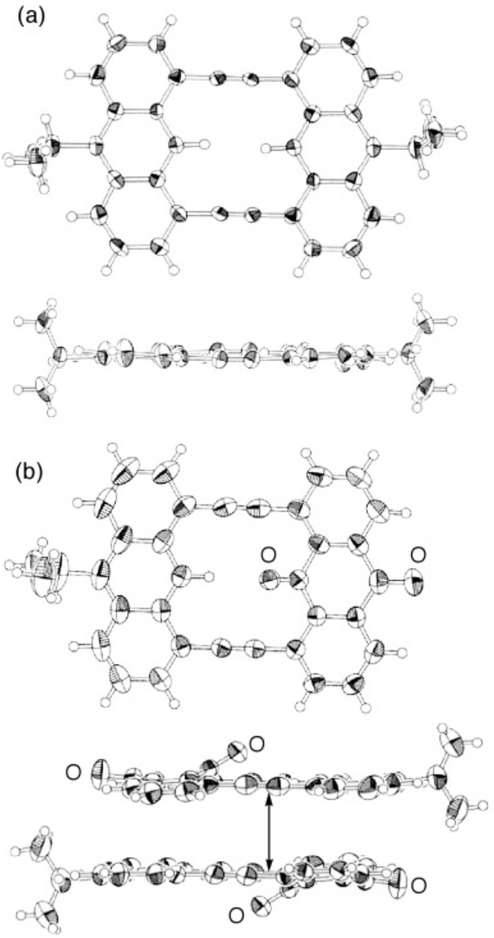


Figure 2. Two views of X-ray structures of **3** (a) and **4** (b: side view of a dimeric pair).

The X-ray structures of **3** and **4** are shown in Figure 2.[11] **3** is an almost planar molecule having two anthracene planes and linear sp carbons (bond angles 176.7−178.3°). The interatomic distance between the inner H atoms is 2.19 Å, which is smaller than the sum of van der Waals radii. For **4**, some atoms, especially the inner carbonyl oxygen atom O9′ (for numbering, see Figure 1), are positioned outside the average plane of the framework to avoid severe steric interactions with the inner H atom in the anthracene moiety (O9′⋯H9 2.41 Å). This structural feature is a result of deformation of the benzoquinone six-membered ring into a shallow boat form (folding angle is 29° for O9′) rather than

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(9) For the synthesis of **3**, the coupling of 1-ethynyl-8-iodo-10-isopropylanthracene afforded a trace amount of the desired product.

(10) Compound **3**: mp 320−330 °C dec; ^{1}H NMR (400 MHz, CDCl$_3$, δ) 1.81 (d, $J = 7.3$ Hz, 12H), 4.63 (septet, $J = 7.3$ Hz, 2H), 7.52 (dd, $J = 7.3$, 8.8 Hz, 4H), 7.94 (d, $J = 7.3$ Hz, 4H), 8.53 (d, $J = 8.8$ Hz, 4H), 10.04 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, δ) 23.3, 28.8, 94.1, and 8 aromatic signals. Compound **4**: mp 361−364 °C dec; ^{1}H NMR (400 MHz, CDCl$_3$, δ) 1.79 (d, $J = 7.3$ Hz, 6H), 4.61 (septet, $J = 7.3$ Hz, 1H), 7.49 (dd, $J = 6.8$, 8.8 Hz, 2H), 7.64 (t, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 6.8$ Hz, 2H), 7.89 (d, $J = 7.8$ Hz, 2H), 8.12 (d, $J = 7.8$ Hz, 2H), 8.53 (d, $J = 8.8$ Hz, 2H), 9.84 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, δ) 23.4, 28.7, 92.4, 93.8, 182.5, 184.6 and 14 aromatic signals.

(11) X-ray data. **3**: formula $C_{38}H_{28}$, FW 484.64, monoclinic, space group $P2_1/a$ (no. 14), $a = 15.538(1)$ Å, $b = 9.8645(9)$ Å, $c = 17.735(1)$ Å, $\beta = 108.639(2)°$, $V = 2575.7(4)$ Å^3, $Z = 4$, $D_{calc} = 1.25$ g/cm^3, μ(Mo Kα) $= 0.71$ cm^{-1}, $T = 273$ K, number of data 5324, $R1 = 0.086$, $wR2 = 0.228$, GOF 0.970, CCDC 654615. **4**: formula $C_{35}H_{20}O_2\cdot{}^1/_2(C_6H_6)$, FW 511.59, orthorhombic, space group *Pbcn* (no. 60), $a = 13.4503(4)$ Å, $b = 11.4759(4)$ Å, $c = 33.377(1)$ Å, $V = 5151.9(3)$ Å^3, $Z = 8$, $D_{calc} = 1.32$ g/cm^3, μ(Mo Kα) $= 0.80$ cm^{-1}, $T = 273$ K, number of data 5818, number of data used 5008 ($I > 2.0\sigma(I)$), $R1 = 0.052$, $wR2 = 0.131$, GOF 0.976, CCDC 654616.

the pyramidalization of carbonyl carbon atoms.[12] The IR spectrum of **4** gave two $\tilde{\nu}_{max}$ (C=O) bands at 1670 and 1679 cm^{-1}, and showed no significant effects of the deformation (cf. anthraquinone 1680 cm^{-1}). In the crystal of **4**, anthracene and anthraquinone moieties partially face each other to form a dimer. The interlayer separation (3.46 Å) indicates the presence of attractive $\pi-\pi$ interactions between electron-rich and electron-deficient aromatic groups in the crystal as often observed in other systems.[13] This is in contrast to the herringbone-like crystal packing of **3**, which is dominated by edge-to-face interactions.

In the ^{1}H NMR spectrum, signals due to the inner protons were observed at δ 10.0 and 9.8 for **3** and **4**, respectively, and these were shifted by ca. 0.5 ppm to the lower field upon cyclization. The ^{13}C chemical shifts of sp carbons (δ 92.4−94.0) are typical of similar oligomers without significant deformation.[2,3,14] Some aromatic proton signals of **4**, especially those due to H9, H2′, H3′, and H4′ protons, were shifted to the higher magnetic field with increasing concentration (Figure 3). Since these protons are located in the shielding region of the facing aromatic system in the X-ray structure, this observation indicates that the molecules form similar dimers in solution. Analysis of chemical shift changes assuming the monomer−dimer equilibrium model afforded the association constant of K_a of 9 (mol/L)$^{-1}$ at 22 °C in CDCl$_3$,[15] suggesting weak but significant self-association. The small association constant compared with those of other shape-persistent macrocyclic compounds[7] is partly attributed to steric hindrance of the 10-substituents and the absence of substituents enhancing solvophobic interactions. Compound **3** did not show chemical shift dependence on concentration. Therefore, the incorporation of an anthraquinone moiety is essential for the associative property of this molecular system.

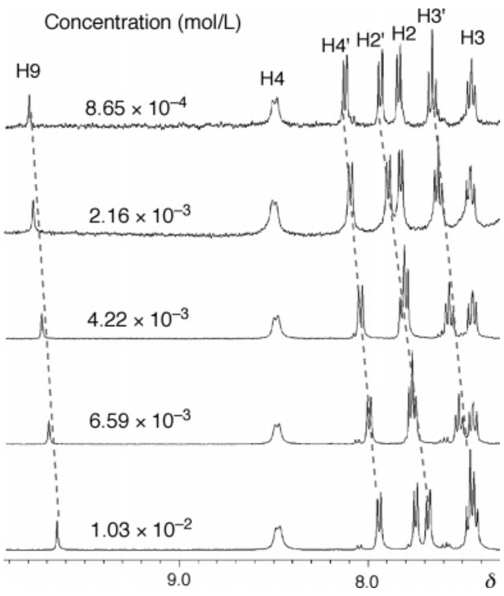

Figure 3. ^{1}H NMR of **4** in CDCl$_3$ at variable concentrations at 22 °C (400 MHz).

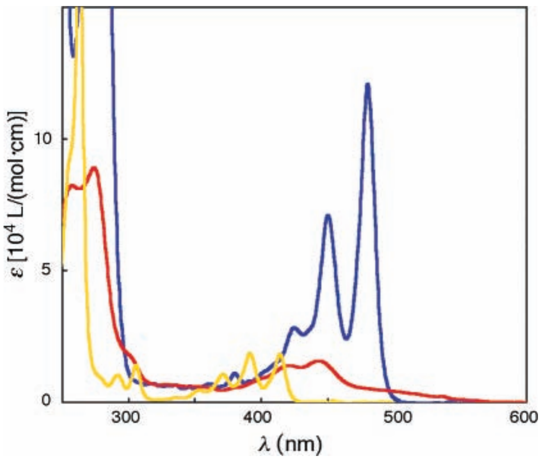

Figure 4. UV−vis spectra of **3** (blue), **4** (red), and 1,8-bis(trimethylsilylethynyl)anthracene (yellow) in CHCl$_3$.

The absorption spectra of **3** and **4** are shown in Figure 4. Compound **3** gave intense structured absorption bands in the *p*-band region peaking at 480 nm (ϵ 121 000). This large bathochromic and hyperchromic effect compared with the reference compound, 1,8-bis(trimethylsilylethynyl)anthracene,[2b] is attributed to the formation of planar macrocyclic structure with two anthracene chromophores. Compound **4** showed broad absorption bands with a weak shoulder extending to 550 nm. This spectral feature is also evidence of the self-association in solution. A strong emission band was observed at 488 nm (Φ_f 0.39) for **3** in the fluorescence spectra. In contrast, the emission was very weak for **4**. The above data indicate that the core structure of **3** can serve as a new type of dye or fluorophore for various purposes.

In summary, we constructed the new π-conjugated structures with two anthracene groups and two ethynylene linkers regardless of the expected severe congestion within the central ring. These compounds are interesting not only from a structural aspect but also from aspects of electronic spectra and aggregation properties. Further studies are in progress to reveal other properties and reactivities.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research (C) No. 19550054 from

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(12) The same type of deformations were reported for some anthraquinone derivatives. For example, the folding angle was 14.1° for O9 in 1,8-dinitroanthraquinone. Becker, H.-D.; Becker, H.-Ch.; Langer, V. *Z. Kristallogr.* **1996**, *211*, 319.

(13) Selected data of interlayer distances for anthracene−arene complexes. 2,3,5,6-Tetrachloro-1,4-dicyanobenzene 3.43 Å: Britton, D. *Acta Crystallogr.* **2005**, *E61*, o1707. 2,7-Dinitroanthraquinone 3.42 Å and 1,8-dinitroanthraquinone 3.48 Å: ref 12.

(14) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: New York, 1990; Chapter 4.3.

(15) Connors, K. A. *Binding Constants*; John Wiley & Sons: New York, 1987; Chapter 5. Higher order association is unlikely in this case because the deformed carbonyl oxygen blocks the other side of the plane.

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Supporting Information Available: Experimental procedures, compound characterization data, ^{1}H NMR, ^{13}C NMR, and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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