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Synthesis and Properties of 1,4-Dimethoxynaphtho[2,3]-annelated Dehydroannulenes

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Abstract: Synthesis and characterization of dehydroannulenes which consist of 1,4-dimethoxynaphthalene units connected at the 2,3-positions by acetylene and butadiyne linkages are described. The ^{1}H NMR spectra indicated neither significant diatropicity nor paratropicity in all of these annulenes. The electronic absorption maximum of the planar annulenes was shifted bathochromically compared with the absorption of 1,4-dimethoxy-2,3-bis[(trimethylsilyl)ethynyl)]naphthalene as a reference, whereas not much bathochromic shift was observed for annulenes with non-planar π-systems.

Keywords: Annulenes; Enynes; Naphthalenes; X-Ray crystal structures

The chemistry of dehydroannulenes is currently attracting renewed interest not only as basic models of the cyclic π-conjugated system but from the aspects of dynamic behaviors or molecular functionality. For example, some dehydroannulenes give rise to ordered carbon layers of tube- and onion-type structures upon explosive thermolysis [1], and other derivatives are reported to show non-linear optical properties [2]. These dehydroannulenes mostly consist of benzene rings and alkyne linkages. In comparison, there are rather few studies which are concerned with annulenes fused with naphthalene or other condensed aromatics [3]. Recently, we demonstrated that the annelation with rigid bicyclic frameworks is effective to rigidly hold the π-system and to decrease the oxidation potentials of the π-system [4]. Being interested in the properties of the naphtho-annelated dehydroannulenes in comparison with those having bicyclic frameworks and also intrigued by the possibility of transforming them into derivatives having highly redox-active naphthoquinone units, we were prompted to synthesize a series of the titled dehydroannulenes.

For the synthesis of dehydroannulene with the naphthalene units connected by acetylene linkage, the 2-propynyl-3-bromonaphthalene **2** was subjected to one-pot *in-situ* deprotection and Pd-catalyzed cross-coupling [5] to give **3**[1] as the only cyclized product (Scheme 1a). On the other hand, the oxidative coupling of diethynyl derivative **5** [6] under standard Eglinton conditions [7] afforded the cyclic dimer to pentamer **6–9**.[1] (Scheme 1b). This is in contrast to

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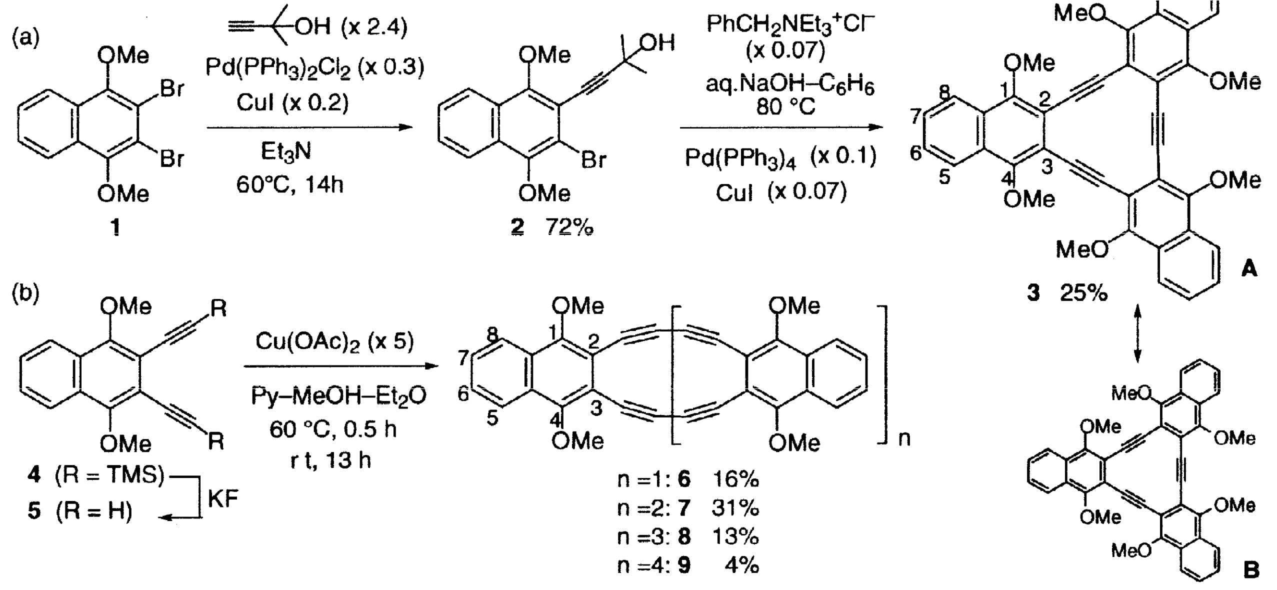
the coupling of 1,2-diethynylbenzene which gave only the cyclic dimer [7,8]. Dimer **6** was hardly soluble in common organic solvents (e.g., 0.07 mg / 1 ml of $CHCl_3$) and precipitated from the reaction mixture while the other products were separated by preparative gel permeation chromatography.

Scheme 1



A single crystal was obtained only for trimer **3**. The X-ray crystallography demonstrated that **3**[2] has a planar structure (Fig. 1(a)). The PM3 calculations showed that the annulene ring of **3** as well as **6** and **7** is planar while that of **8** and **9** has bent structures (Fig. 1(b)). Another feature in the X-ray structure of **3** is the considerable bond alternation in the naphthalene ring. Thus, among the canonical structures **A** and **B**, the contribution of structure **B** should be much smaller. Particularly, the bond length of C2–C3 (1.439(4) Å) was found to be longer than the observed length of unsubstituted naphthalene (1.412 Å) [9]. This is more pronounced than the elongation of the corresponding bond in trisdehydrotribenzo[12]annulene (1.408(1) Å) [10] in comparison with benzene (1.399 Å) [9]. This elongation in the C2-C3 bond is attributed to the decrease in the π-bond order due to the conjugation with the acetylene moiety because a gradual elongation was observed for the corresponding bond in the calculated structure (PM3) of unsubstituted- (1.415 Å), 2-ethynyl- (1.422 Å), and 2,3-diethynylnaphthalenes (1.430 Å). For reference, the calculated C2-C3 bond lengths for **3** (1.430 Å) and **7** (1.431 Å) were almost identical to that of the corresponding bond in 2,3-diethynylnaphthalene.

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1. The other data for **3** and **6**–**9** not shown in Table 1 are as follows. **3**; brown crystals, mp 270–271 °C(dec.), IR (KBr) 2197 cm^{-1} (C≡C), EI MS m/z 630(M^+). **6**; yellow solid, mp >250 °C(dec.), IR (KBr) 2183, 2118 cm^{-1} (C≡C), EI MS m/z 468(M^+). **7**; yellow solid, mp >250 °C(dec.), IR (KBr) 2200, 2132 cm^{-1} (C≡C), FAB MS m/z 702(M^+). **8**; brown solid, mp >250 °C(dec.), IR (KBr) 2200, 2129 cm^{-1} (C≡C), FAB MS m/z 936(M^+). **9**; brown solid, mp >250 °C(dec.), IR (KBr) 2197 cm^{-1} (C≡C), FAB MS m/z 1171(M^++1). 2. Crystal data for **3**: space group $P4_12_12$; a = 10.971(2) Å, c = 26.099(2) Å; V = 3141(1) Å^3; Z = 4; D_{calc} = 1.334 g/cm^3; total of 1464 reflections within 2θ = 120.1° and $I > 3.00\sigma(I)$; the final R factor = 3.7% (R_w = 5.2%).

Table 1. ^{1}H NMR, UV-vis, and Fluorescence Spectra in $CDCl_3$ or $CHCl_3$ of Monomer **4** and Dehydroannulenes **3**, **6**–**9**.

Compd. [n]annulene	^{1}H NMR / ppm C5-H	C6-H	MeO	UV-vis λ_{max} / nm (log ε)	λ_{edge} / nm	Fluorescence Emission maximum /nm	Φ^b
4	8.09	7.51	4.08	275 (5.1)	380	379^a	0.32
3 [12]	8.16	7.57	4.32	330 (5.1)	430	427	0.82
6 [12]	8.05	7.52	4.19	342 (5.0)	460	460	0.44
7 [18]	8.16	7.60	4.22	347 (5.1)	440	431	0.52
8 [24]	8.11	7.56	4.16	287 (5.3)	415	427	0.14
9 [30]	7.95	7.44	4.11	282 (5.2)	445	—	—

^{a} In cyclohexane. ^{b} The quantum yields, estimated by the use of 9,10-diphenylanthracene (Φ = 0.90).

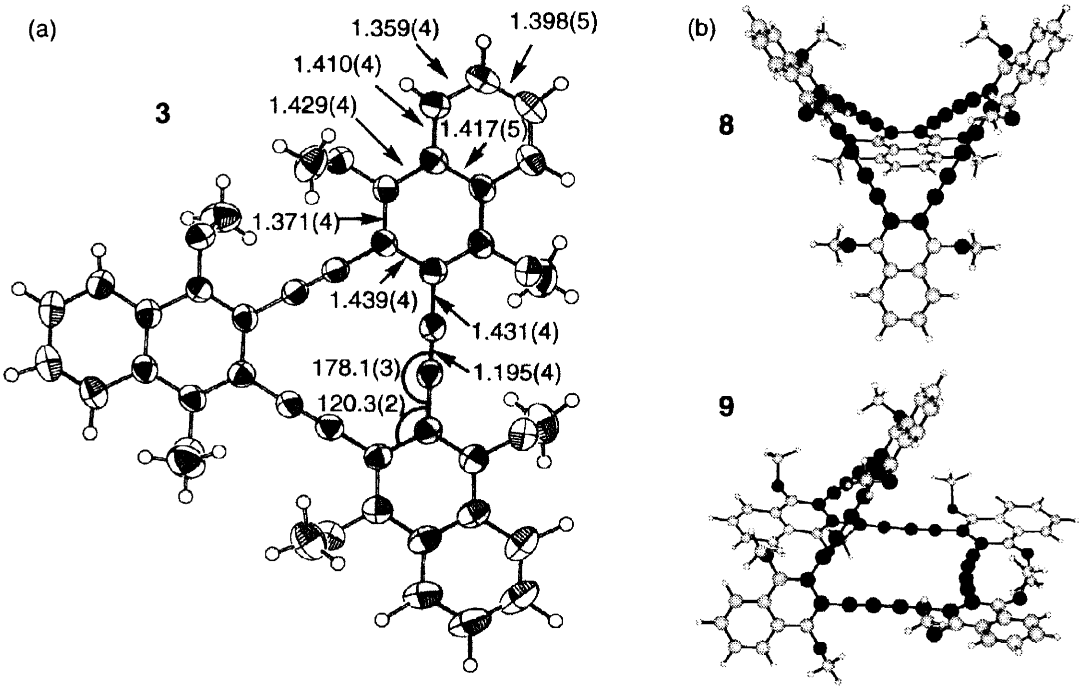

Figure 1. (a) X-ray structure of **3** with selected bond lengths (Å) and angles (°). (b) PM3 optimized structures for **8** and **9**.

As shown in Table 1, the ^{1}H NMR spectra for these dehydroannulenes were quite similar regardless of their planar or bent structures. Each naphthalene moiety in the bent annulene **9** is not differentiated, suggesting that the conformational change is sufficiently rapid within the NMR time scale. The signals for the methoxy group underwent downfield shift relative to **4** but did not correlate with the number of π electrons of the annulene ring. These results indicate that there is no appreciable effect of ring current on the central dehydroannulene ring in **3** and **6**–**9**. This atropicity can be attributed to the position of annelation within the naphthalene ring. Previous study has demonstrated that annelation at the 1,2-positions of naphthalene in dehydro[14]annulene is much more effective for the occurrence of diatropicity than that at the 2,3-positions [11].

On the other hand, the UV-vis absorption showed a difference between the annulenes having the planar and bent structures; the maximum absorption of planar annulenes **3**, **6**, and **7** was shifted bathochromically by 55–72 nm compared with monomer **4**, while the shift for the bent annulenes **8**, **9** was quite small. This is qualitatively in accord with the calculated result (PM3) that the HOMO-LUMO gap for planar annulenes **3** ($\Delta E_{H\text{-}L}$ 7.43 eV), **6** (7.41 eV), and **7** (7.44 eV) is smaller than that for bent annulenes **8** (7.62 eV), and **9** (7.48 eV). All these endiynes, except for highly bent annulene **9**, exhibited a blue-purple emission in solution. In the fluorescence spectra, the emission maximum of the strained annulene **6** was observed at the most long-wavelength region, and the quantum yield of annulene **3** linked by acetylene was found to be larger than that in other annulenes **6–8** linked by butadiyne.

The relatively higher HOMO and lower LUMO in annulenes **3**, **6**, and **7** should be reflected in the redox behaviors. Although the measurement of **6** was hampered by its extremely low solubility, the cyclic voltammetry in benzonitrile indicated the relevant redox potentials for **3** (E_{pa} = +0.91 V (irreversible) vs Fc/Fc^+, $E_{1/2}$ = –2.23 V (reversible)) and **7** (E_{pa} = +1.05 V (irreversible), $E_{1/2}$ = –2.11 V (reversible)) while no redox wave was observable in the region from +1.3 to –2.4 V for **8** and **9**. Upon comparison of the redox potentials of **3** and **7**, there was no such significant difference as observed for the bicyclo[2.2.2]octene-annelated derivatives, that is, the lower oxidation potential for the antiaromatic tridehydro[12]annulene system than for the aromatic hexadehydro[18]annulene system by 0.6 V [4].

In summary, it is concluded that the dehydroannulenes annelated at the 2,3-positions of naphthalene rings should be regarded more as the naphthalenes connected by acetylenic linkages rather than as *annulenes*. Studies are now under way to transform these π-systems into the naphthoquinone and hydroquinone derivatives and construct the supramolecular network via hydrogen bonds.

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