# Convenient Synthesis and Photophysical Properties of Tetrabenzopentakisdehydro[12]annuleno[12]annulene

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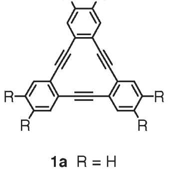
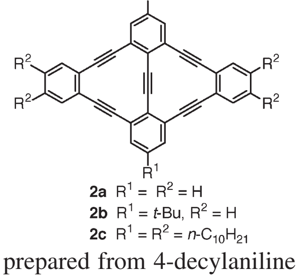
A convenient synthesis of tetrabenzopentakisdehydro-[12]annuleno[12]annulene **2c** with substantial solubility was achieved by double cyclization of tetrabromotolan **3** with *o*-diethynylbenzene **4**.

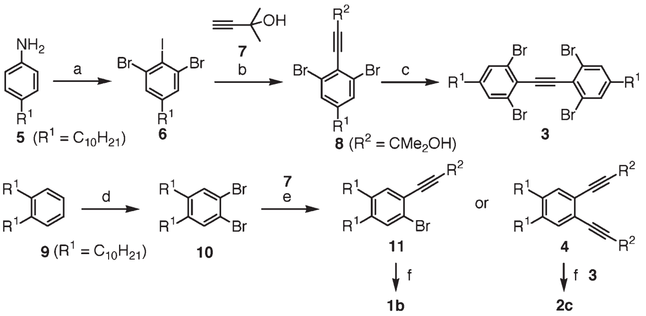
Much attention has been focused in recent years on the dehydrobenzoannulene derivatives because of their potential as functional materials such as nonlinear optical,[1] conductive,[2] and ferromagnetic materials[3] and building blocks for the hitherto unknown two-dimensional carbon networks,[4] e.g., graphyne. The ultimate carbon network was predicted to be moderately stable and to exhibit semiconductive as well as nonlinear optical properties.[5] Recently, Zhou and Feng reported that the ladder oligomers of trisdehydrotribenzo[12]annulene, [12]DBA (**1a**), would exhibit increasing second hyperpolarizabilities with increasing number of the DBA unit based on the semi-empirical molecular orbital calculations.[6] Since the absorption ends of a series of ladder oligomers would not exceed 350 nm, they predicted that these compounds would be promising as third-order nonlinear optical materials. Although the parent [12]DBA **1a** and a number of its derivatives have been known for almost four decades,[7] a derivative of its dimer **2b** has been prepared only recently by Haley and co-workers.[8,9] Despite the first synthesis of **2b** utilizing protection/masking protocols was highly selective, it required 13 steps and its solubility might not be enough to determine its second hyperpolarizability. In this connection, we planned to prepare tetrabenzopentakisdehydro[12]annuleno-[12]annulene **2c** having six alkyl chains, which would make it soluble enough for the measurement of its photophysical properties. At the same time, we also planned to develop short and convenient method of the preparation of **2c** that would also be applicable to the synthesis of ladder oligomers. Namely, we envisioned that **2c** would be formed convergently from tetrabromotolan **3** and the protected *o*-diethynylbenzene **4** by the in-situ deprotection Pd(0)-catalyzed coupling protocol developed by Linstrumelle.[10]



**1a** R = H
**1b** R = $n$-$C_{10}H_{21}$



**2a** $R^1 = R^2 = H$
**2b** $R^1 = t$-Bu, $R^2 = H$
**2c** $R^1 = R^2 = n$-$C_{10}H_{21}$



**Scheme 1.** (a) (i) BTMABr$_3$, $K_2CO_3$, $CH_2Cl_2$, rt, 87%; (ii) $(CH_3)_2CHCH_2ONO$, $I_2$, $C_6H_6$, reflux, 70%. (b) $Pd(PPh_3)_4$, CuI, $Et_3N$, reflux, 62%. (c) (i) KOH, $C_6H_6$, reflux, 92%; (ii) **6**, $Pd(PPh_3)_4$, CuI, $Et_3N$, reflux, 64%. (d) $Br_2$, $I_2$, Fe, $CCl_4$, 0 °C to rt. (e) $Pd(PPh_3)_4$, CuI, piperidine, reflux, 65% for **4**, 34% for **11** (2 steps from **9**). (f) $Pd(PPh_3)_4$, CuI, $PPh_3$, KOH, $C_6H_6$, $CH_3N[(CH_2)_7CH_3]_3Cl$, reflux, 9% for **2c**, 5% for **1b**.

The building block **3** was prepared from 4-decylaniline (**5**) as shown in Scheme 1. Dibromination of **5** using BTMABr$_3$[11] followed by deaminative iodination using isoamyl nitrite and $I_2$[12] gave dibromoiodobenzene **6**. Selective Sonogashira coupling of **6** with 2-methyl-3-butyn-2-ol (**7**) occurred at the position of iodo substituent, yielding ethynyldibromobenzene **8**. Deprotection of the ethynyl end of **8** followed by the Sonogashira coupling with **6** gave tetrabromotolan **3** in 22% overall yield for 5 steps. Another building block **4** was prepared from 1,2-dichlorobenzene. 1,2-Didecylbenzene (**9**) was prepared from 1,2-dichlorobenzene by the Tamao–Kumada–Corriu coupling[13] using a Ni catalyst and *n*-decylmagnesium bromide. 4,5-Dibromo-1,2-didecylbenzene (**10**),[14] which was derived by bromination of **9**, was reacted with excess **7** (9 equiv.) under the Sonogashira coupling conditions to give diethynylbenzene **4** in 40% overall yield for 3 steps. The double cyclization of tetrabromotolan **3** with diethynylbenzene **4** using a palladium complex and a copper salt in the presence of a phase-transfer catalyst[10] gave the desired annulene **2c** in 9% yield. Though the yield of the final step is not good, each macrocyclization was estimated to proceed in about 30% yield. Moreover, by this method a few hundred milligrams of **2c** was readily prepared in several steps.

As a reference compound we also prepared [12]DBA derivative **1b**. Thus, cyclotrimerization[10] of bromoethynylbenzene **11**, derived by coupling of **10** with 1.6 equiv. of acetylene **7**, gave **1b** in 5% yield.

In the $^1$H NMR spectrum, it shows only two singlets for aromatic protons at $\delta$ 7.07 and 6.93 ppm.[15] In the $^{13}$C NMR spectrum, seven aromatic and three acetylenic carbon peaks are observed. These spectral data are consistent with the highly symmetrical structure of **2c**.[16] Attempts to obtain X-ray quality crystals of **2c** have been unsuccessful.

The electronic absorption spectra of **1b** and **2c** are shown in Figure 1a. While the absorption spectrum of **1b** is similar to that of **1a**,[7a] it exhibits a bathochromic shift (ca. 10 nm) relative to that of **1a**.[17] The absorption of **2c** shows further bathochromic shift with an absorption maximum at 312 nm ($\mathcal{E} = 4.5 \times 10^5$). Absorption bands of **2c** in the low energy region exhibit vibrational fine structures ($\lambda_{\max} = 433$, 461 nm). Figure 1b shows the fluorescence emission spectra of **1b** and **2c**. Like the absorption spectrum, the fluorescence emission spectrum of **2c** exhibits well resolved vibrational structures, reflecting the rigidity of the macrocyclic framework. The quantum yields of the fluorescence of **1b** and **2c** were determined to be 0.08 and 0.06, respectively, which are slightly smaller than that of **1a** ($\Phi = 0.15$).[18]

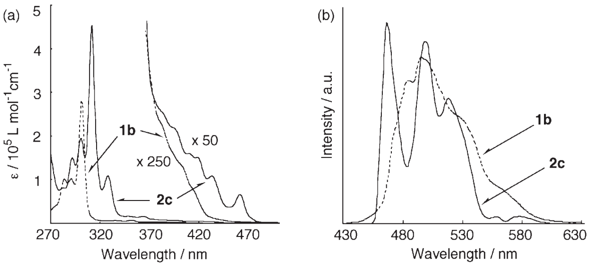


**Figure 1.** (a) Electronic absorption spectra of **1b** (dashed line) and **2c** (solid line) in $CH_2Cl_2$. (b) Fluorescence emission spectra of **1b** (dashed line) and **2c** (solid line) in $CH_2Cl_2$ ($5 \times 10^{-6}$ M).

Next we inspected the third-order nonlinear optical properties of annulenes **1b** and **2c** to examine the theoretical prediction of their second hyperpolarizabilities reported by Zhou and Feng.[6] They estimated that the static, orientationally averaged values $\langle\gamma\rangle$ of the second hyperpolarizability are $1.51 \times 10^5$ au (equiv. to $1.27 \times 10^{-35}$ esu)[19] for **1a** and $6.54 \times 10^5$ au ($5.49 \times 10^{-35}$ esu) for the parent **2a**. We measured the nonlinear refractive index change and nonlinear absorption of the annulenes in chloroform solutions (56 mM for **1b** and 27 mM for **2c**) by femto-second Z-scan method[20] at 1345 nm. However, the signals observed for both solutions agreed with that of the blank solvent within our experimental error (5% for nonlinear refractive, i.e. closed aperture, measurements and 1% for nonlinear refractive, i.e. open aperture, measurements). These results suggest that the off-resonant $\gamma$ values of **1b** and **2c** are not larger than $\approx 4 \times 10^{-35}$ esu.

In conclusion, a convenient synthesis of [12]annuleno[12]-annulene **2c** with substantial solubility was achieved by double cyclization of tetrabromodiphenyltolan **3** with *o*-diethynylbenzene **4**. The annulene **2c** and its parent annulene **1b** did not show obvious second hyperpolarizabilities contrary to the theoretical predictions for the hyperpolarizabilities of a series of ladder oligomers of annulenes.

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15 The $^1$H NMR chemical shift did not move in a concentration range of 3–20 mM, indicating the absence of self-association of **2c**.

16 **2c**: mp 110–111 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.07 (s, 4H), 6.93 (s, 4H), 2.53–2.40 (m, 12H), 1.53–1.28 (m, 96H), 0.88 (t, $J = 6.6$ Hz, 18H); $^{13}$C NMR ($CDCl_3$) $\delta$ 143.5, 141.7, 132.7, 131.5, 127.5, 127.1, 123.9, 95.9, 92.9, 91.5, 35.3, 32.3, 31.9, 30.7, 30.6, 29.7, 29.62, 29.58, 29.51, 29.4, 29.3, 29.2, 22.7, 14.1; UV ($CH_2Cl_2$, 25 °C) $\lambda_{\max}$ ($\log \mathcal{E}$) 328 (5.0), 312 (5.7), 301 (5.3), 292 (5.2) nm; fluorescence ($CH_2Cl_2$, 25 °C, $\lambda_{\mathrm{ex}} = 312$ nm) $\lambda_{\mathrm{em}} = 467$, 498, 518 nm; MS (MALDI (negative mode)) $m/z$ 1263 ($M^-$).

17 **1b**: UV ($CH_2Cl_2$, 25 °C) $\lambda_{\max}$ ($\log \mathcal{E}$) 301 (5.5), 291 (5.0), 284 (5.0) nm; fluorescence ($CH_2Cl_2$, 25 °C, $\lambda_{\mathrm{ex}} = 301$ nm) $\lambda_{\mathrm{em}} = 484$, 498, 524 (sh) nm.

18 The quantum yield of the fluorescence of **1a** normalized with quinine sulfate was reported to be 0.15 (in methylcyclohexane, at room temperature): K. Janecka-Styrcz, J. Lipinski, and Z. Ruziewicz, *J. Lumin.*, **17**, 83 (1978).

19 To convert second hyperpolarizability from in the atomic unit (au) system to in the esu-cgs system, the following relation is used: 1 au $= 5.0366 \times 10^{-40}$ esu. However, further conversion is needed because, in theoretical studies, $\gamma$ is preferably defined as $p = \alpha F + (1/2)\beta FF + (1/6)\gamma FFF\ldots$(Conversion I) while in many experimental researches, $p = \alpha F + \beta FF + \gamma FFF\ldots$(Conversion II) is preferred. Therefore, in the text, a factor of $(5.0366 \times 10^{-40}/6)$ was multiplied by the values in au in order to convert to the value in esu with Conversion II. See: K. Kamada, M. Ueda, T. Sakaguchi, K. Ohta, and T. Fukumi, *J. Opt. Soc. Am. B*, **15**, 838 (1998).

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