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# Furan-Containing Oligoaryl Cyclophanene

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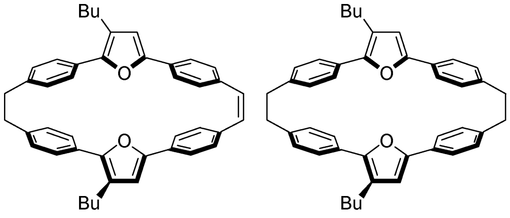
## ABSTRACT



**1**

**2**

**Furan-containing oligoaryl cyclophanene 1 and the corresponding cyclophane 2 were synthesized from propargylic dithioacetal 3. The electrochemical and photophysical properties and the fluxional behavior of these molecules have been examined. The emission of 1 appeared at 499 nm whereas that of 2 appeared at 389 nm.**

Cyclophanes have provided useful models for the investigation of through-space interactions between chromophores.[1−5] Several factors are known to dictate the nature of such interactions. Recently, Bazan and co-workers have shown that the conjugation length and the orientation of the chromophores in paracyclophanes may play an important role in this respect.[1] Five-membered heteroaromatic ring(s) in cyclophanes are well documented.[2] These compounds may demonstrate a unique structural feature because the stereochemistry of these molecules is very different from those constituted of only para-substituted benzene derivatives.[2−4] It is noteworthy that oligoaryl cyclophanes whose backbone contains five-membered heteroaromatic ring(s) have been sporadically studied.[2] Incorporation of double bond(s) in the tethering aliphatic chain(s) such as cyclophanenes may alter the geometry of the molecules.[5] An extreme case can be seen in planar and annulene-like porphycenes and related analogues, although they can be considered structurally as cyclophanes.[4] Other than porphycene and related compounds, study on the influence of the double bond in nonplanar cyclophanenes on the photophysical properties of these molecules has been rare.

We recently reported a new annulation procedure for the synthesis of trisubstituted furans from the corresponding propargylic dithioacetals.[6] The strategy has been employed for the iterative construction of a variety of soluble furan- and pyrrole-containing oligoaryls leading to molecular wires. We now wish to report the synthesis and unusual properties

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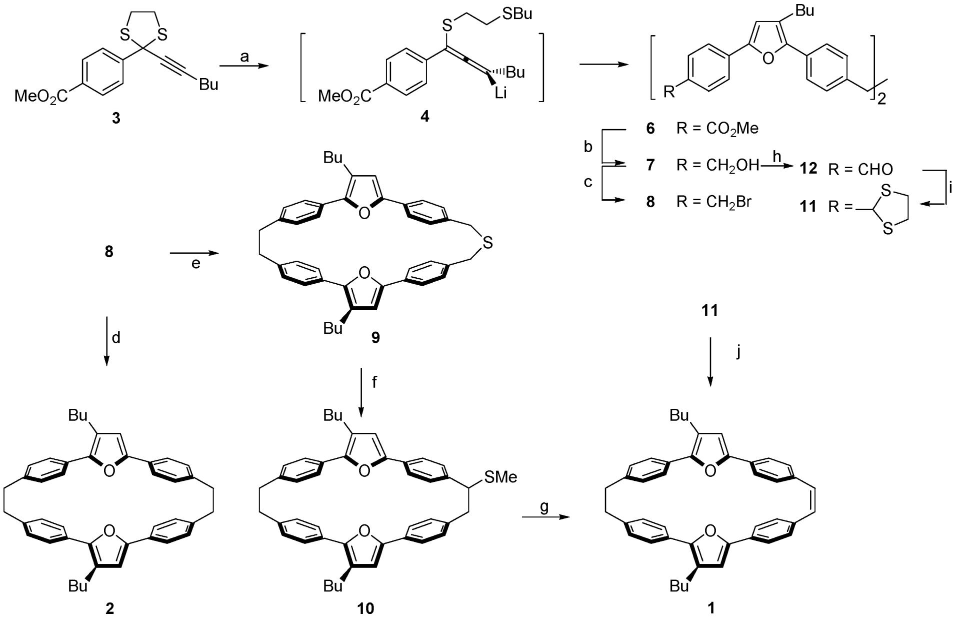
**Scheme 1**[a]



[a] Key: (a) (1) BuLi, THF, −78 °C, 50 min, (2) 4,4′-diformylbibenzyl (**5**), THF, −78 °C, 1 h; rt, 30 min, (3) $CF_3CO_2H$, rt, 12 h, 65%; (b) *i*-$Bu_2AlH$, THF, 0 °C, 3 h, 94%; (c) $PBr_3$, $C_6H_6$, rt, 6 h, 97%; (d) PhLi, THF, −78 °C, 2 h, 76%; (e) $Na_2S \cdot 9H_2O$, EtOH, reflux, 12 h, 61%; (f) (1) *i*-$Pr_2NLi$, THF, 0 °C, 1 h, (2) MeI, rt, 1 h, 94%; (g) (1) $Me_3O \cdot BF_4$, $CH_2Cl_2$, 0 °C, 2 h; rt, 12 h, (2) *t*-BuOK, THF, rt, 12 h, 51%; (h) $MnO_2$, $CH_2Cl_2$, rt, 6 h, 95%; (i) 1,2-ethanedithiol, $BF_3 \cdot OEt_2$, $CH_2Cl_2$, rt, 12 h, 92%; (j) $W(CO)_6$, PhCl, reflux, 48 h, 25%.

of the first furan-containing teraryl cyclophanene **1** and its saturated analogue **2**.

Treatment of allenyllithium **4**, prepared from propargylic dithioacetal **3** and BuLi, with dialdehyde **5** followed by trifluoroacetic acid afforded **6** in 65% yield. Reduction of **6** with *i*-$Bu_2AlH$ gave **7** in 94% yield, which was further converted into bromide **8** ($PBr_3$) in 97% yield. Intramolecular cyclization of **8** with $Na_2S \cdot 9H_2O$ was achieved in refluxing EtOH under dilute conditions to give **9** in 61% yield. Exposure of **9** to *i*-$Pr_2NLi$ at 0 °C followed by trapping the intermediate with MeI afforded **10** in 94% yield.[7] The formation of the double bond was obtained by treating **10**

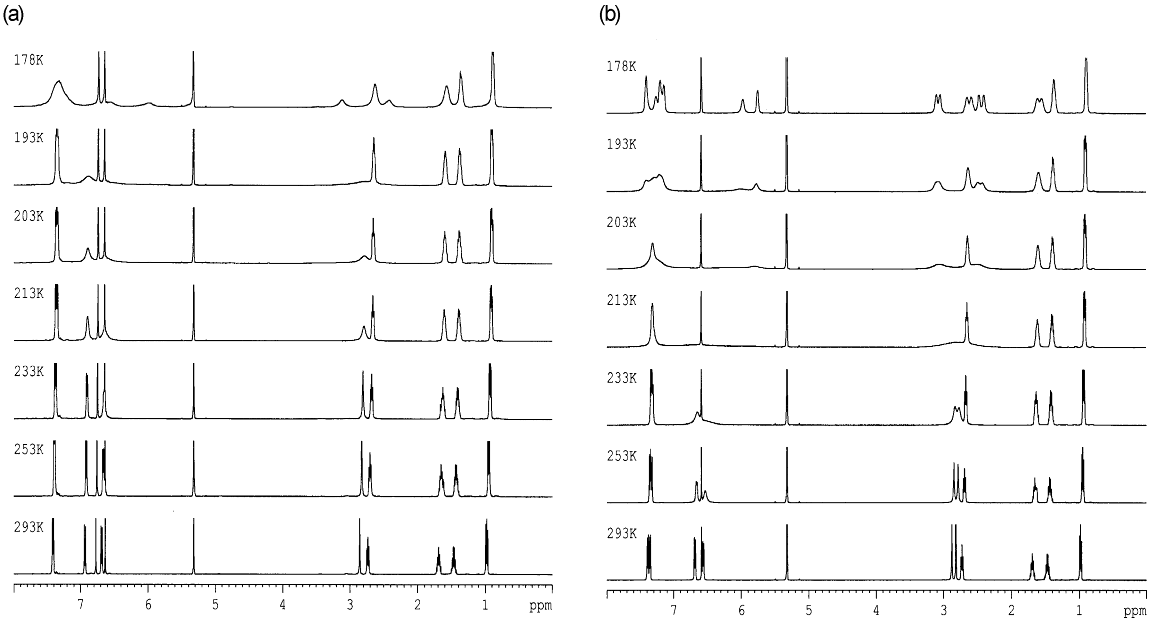


**Figure 1.** Variable-temperature $^1H$ NMR spectra of (a) **1** and (b) **2** in $CD_2Cl_2$.

with Meerwein reagent followed by *t*-BuOK, to give **1** in 51% yield (Scheme 1). Alternatively, **1** was obtained in 25% yield from the $W(CO)_6$-mediated intramolecular desulfurdimerization of bisdithioacetal **11** (Scheme 1).[8] Compound **11** was synthesized in two steps in 87% yield from **7** by $MnO_2$ oxidation (giving **12**) followed by 1,2-ethanedithiol in the presence of $BF_3{\cdot}Et_2O$. A dilute THF solution of **8** (0.001 M) was allowed to react with PhLi at −78 °C to afford **2** in 76% yield (Scheme 1).

Dynamic $^1H$ NMR spectra for **1** and **2** were examined, coalescence of the signals attributed to the protons on the benzene rings being observed (Figure 1). The chemical shifts were assigned based on COSY and NOESY experiments at ambient temperature and at −95 °C. It is noteworthy that certain signals of fluxional protons in **1** and **2** were not completely resolved even at −95 °C, and the signal due to the absorption of the furan protons in **1** and **2** remained a sharp singlet at −95 °C. For **1**, the signal at $\delta$ 6.69 coalesced at ca. −60 °C and appeared as two broad peaks at ca. $\delta$ 6.0 and 7.2. The fluxional barrier for **1** was thus estimated to be 9 kcal/mol.[9] In a similar manner, the signal at $\delta$ 6.68 for **2** coalesced at ca −50 °C and appeared as two broad peaks at ca. $\delta$ 6.0 and 7.2. The barrier was calculated to be 9.7 kcal/mol.[9]

Cyclophane **2** exhibited reversible two-electron redox process electrochemically and the oxidation potential for **2** appeared at 0.614 V with reference to the ferrocene/ferrocenium ion (Figure 2).[10] The two oligoaryl moieties in **2** were oxidized independently and appeared at the same potential. Two sequential oxidation potentials at 0.540 and 0.665 V were observed for **1**, one at lower potential than that of **2** whereas the other at higher potential. The presence of the double bond might contribute to the interaction of the two oligoaryl moieties in **1**. It is noteworthy that the reference compound teraryl **13** exhibited lower oxidation potential (0.593 V) than that of **2**. Presumably, the coplanarity of the teraryl moiety in **13** may account for this observation.

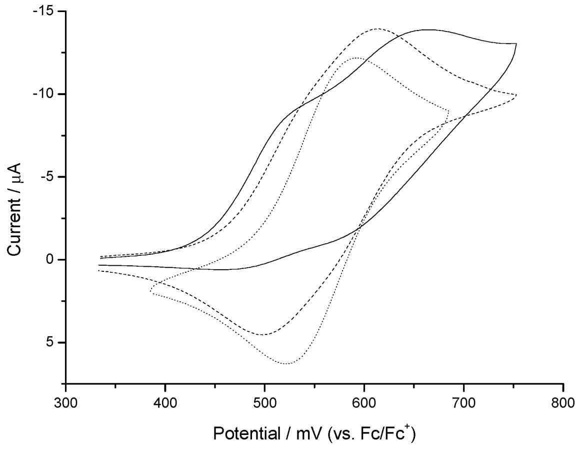
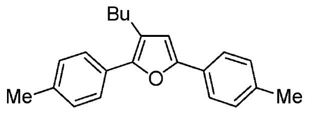


**Figure 2.** Cyclic voltammograms of **1** (solid line), **2** (dash line), and **13** (dotted line) in $CH_2Cl_2$ with 0.1 M $Bu_4NPF_6$ as supporting electrolyte. A glassy carbon electrode, a Pt wire, and a Ag/Ag$^+$ (0.1 M $AgNO_3$) electrode were used as the working, counter, and reference electrodes, respectively. The scan rate was 20 mV/s.

The photophysical properties of **1** and **2** are compared with those of **13** in Table 1. The absorption profiles for **1**, **2**, and **13** are similar (Figure 3). There was an additional weak absorption in the region of 350 to ca. 430 nm for cyclophanene **1**. As shown in Figure 3, the emission spectrum for **2** in EtOAc appeared at 389 nm with vibronic fine structure. Similarly, compound **13** exhibited fluorescence at 379 nm with vibronic splittings. It is striking to note that other than the weak emission in the same region, compound **1** showed a strong broad luminescence at 499 nm. In addition, the quantum yields for **1** and **2** were somewhat

**Table 1.** Photophysical Properties of **1**, **2**, and **13**



**13**

| compd | $\lambda_{max}$ | $10^{-4}\epsilon$ | $\lambda_{em}$ | $\phi$ |
|---|---|---|---|---|
| 1 | 321 | 5.3 | 372, 390, 416, 499 | 0.28 |
| 2 | 314 | 5.5 | 370, 389, 410 | 0.59 |
| 13 | 324 | 6.2 | 362, 379, 398 | 0.83 |

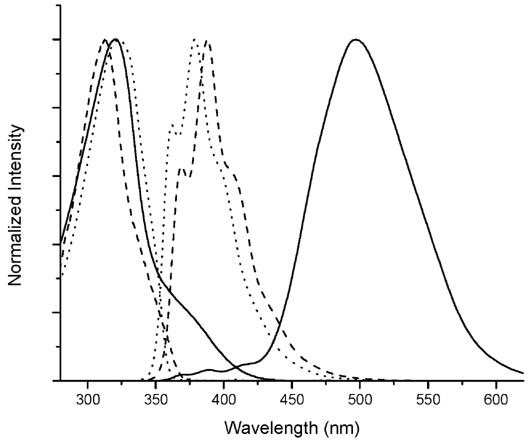


**Figure 3.** Absorption and emission spectra of **1** (solid line), **2** (dash line), and **13** (dotted line) in EtOAc.

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lower than that of the model compound **13**. Presumably, the small blue shift of the absorption peak and the small red shift of the emission peak of **2** relative to **13** can be rationalized in terms of exciton theory.[11] In other words, the cyclophane structure may cause intramoelcular interaction between the chromphores and the presence of a double bond in **1** may further influence the photophysical properties.

In summary, we have depicted the first synthesis of furan-containing oligoaryl cyclophanene **1** and cyclophane **2**. The double bond in **1** plays a critical role in dictating the photophysical properties of **1** which is very much different from those of the saturated counterpart **2**.

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**Supporting Information Available:** Experimental details of the synthesis of **1** and **2**, and COSY and NOESY of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Electron-transfer number, *n*, of **1** and **2** was determined by linear potential sweep chronoamperometry (Bard, A. J.; Faulkner, L. R.; *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; pp 228−231). With the peak potential, $E_p$, and the half-peak potential, $E_{p/2}$, determined by using a low scan rate (3 mV/s), the electron-transfer number was evaluated. For **2**, $E_p$ was 0.510 V (vs Fc/Fc$^+$) and $E_{p/2}$ was 0.483 V, and the calculated electron-transfer number was 2.06. For **1**, because there were two electron transfer steps in series, the current responses of each oxidation step were overlapped. Only the first electron-transfer number was estimated. The $E_p$ and $E_{p/2}$ were estimated to be 0.505 and 0.445 V (vs Fc/Fc$^+$), and the calculated electron-transfer number of **1** was 0.94.

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