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Preparation of *syn* and *anti* cyclophanes having oligothiophene units and their spectral properties

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ABSTRACT

Syn and *anti* cyclophanes consisting of oligothiophene units as a component have been synthesized for the first time. Correlation between the cyclophane structure and fluorescence spectral properties has been examined. Emission from intramolecular excimer-formation is confirmed for the *syn* cyclophanes and the mobile cyclophanes, but not for the *anti* cyclophanes.

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Recently there has been a considerable increase in interest in thiophene-based π-conjugated oligomers as advanced molecular electronic materials, including, for example, organic field effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic solar cells[1] because of the feasibility in manipulation of their chemical structures. In this regard, in order to improve electronic and optical properties of oligothiophenes, introduction of end-capping groups,[2] insertion of various functional groups,[3] and changing oligomer lengths[4] have been carried out. It is obvious that these strategies are closely related to creation of novel π systems. From this point of view cyclophane structure could be a unique candidate to build the characteristic π systems. Some oligothiophenes consisting of a [2.2]metacyclophane skeleton have been investigated.[2a,5] Cyclophane-type compounds in which two oligothiophene units are bridged with alkylene chains have also been reported.[6] Meanwhile, we have been interested in small-sized cyclophanes in terms of unique π systems owing to strong transannular π-electronic interactions between aromatic components in proximity.[7] We have focused on the dithia[3.3]metacyclophanes into which the oligothiophene units were introduced.[8] Correlation between the cyclophane structure and their fluorescence spectral properties has been clarified. These cyclophanes described above are characterized by their conformational flexibility meaning conversion between the *syn* and the *anti* conformers. On the other hand, by employing the rigid [3.3]metacyclophane skeleton it could be possible to fix two π conjugated units in some particular orientation. We believe such a fixation of two oligothiophene chains could provide information of the π systems involving oligothiophenes.

Thus, we describe the syntheses of the *syn* and the *anti* metacyclophanes having two oligothiophene units and their spectral properties.

It is known that the inner substituent of the dithia[3.3]metacyclophanes has a great effect on their conformational mobility.[9] In the previous related paper,[8] we have focused on the dithia[3.3]metacyclophanes carrying no substituent at the inner position showing conformational flexibility. In order to obtain the fixed dithia[3.3]-metacyclophane skeleton a bulky substituent has to be introduced at the inner position since an inner bulky group hampers rotation of the aromatic rings. Here the methoxy group has been employed as the inner substituent.

The bromomethyl compound **1** and the sulfanylmethyl compound **2** were coupled using Cs_2CO_3 as a base under a highly diluted condition to give the corresponding *syn* dithiacyclophane **3** and *anti* dithiacyclophane **4** as the mixture. Careful separation using a column chromatography eventually afforded **3** and **4** in 49% and 5% yields, respectively. No more than 5% yield of **4** has been achieved in any trials. This might be attributable to a stable intermediate of the *syn* structure due to π–π interaction. Treatment of **3** with *n*-butyllithium followed by quenching with hydrochloric acid gave the cyclophane **5a** in 45% yield. The cyclophane having two thiophene units **5b** was obtained from **3** and tributylstannylthiophene **6a** in 62% yield. Similarly the cyclophane having three thiophene units **5c** was synthesized by the coupling of **3** and the corresponding tributylstannylthiophene **6b** in 42% yield. Considering the solubility, two alkyl chains seem to be necessary for the cyclophanes consisting of more than four thiophene units. Thus, the cyclophane **5d** having the hexyl chain at the β position was prepared by the reaction of **3** and boronic ester **6c**. Bromination of **5d**, followed by the coupling with **6b** afforded the cyclophane **5e** in 28% yield. After **5b** was brominated, the coupling with **6c** was carried out to give the cyclophane **5f** in 75% yield. The cyclophane **5g** consisting of five thiophene units was obtained by the bromination of **5f**, followed by the coupling with **6b** in 62% yield (Scheme 1).

Treatment of **4** using *n*-butyllithium gave the cyclophane **7a** in 40% yield. The coupling of **4** with **6a** afforded the cyclophane **7b** having two thiophene units in 42% yield. The similar coupling of

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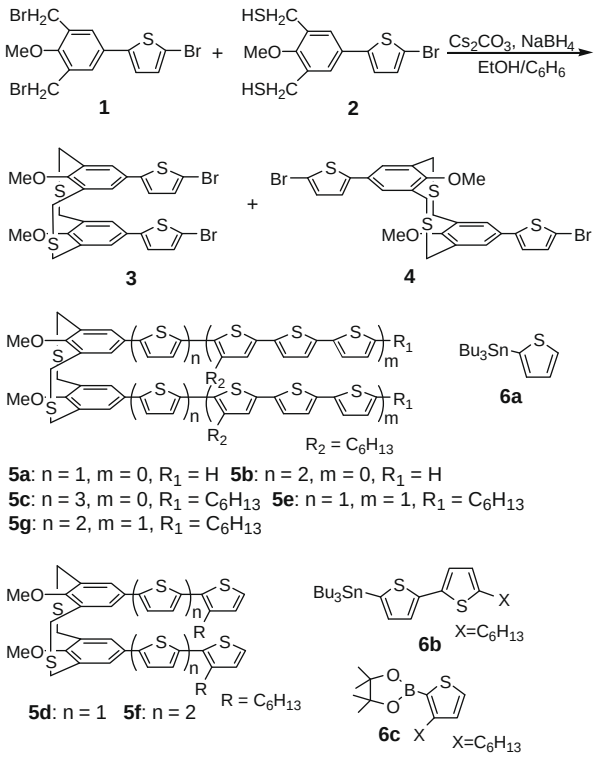
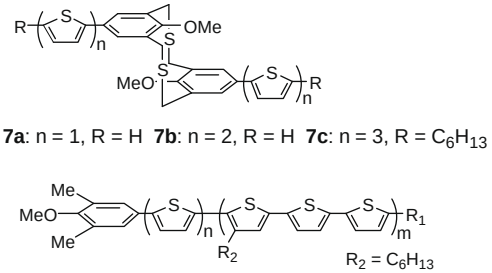


Scheme 1. Preparation of *syn* cyclophanes **5a**–**g**.

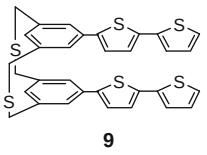
4 and **6b** was carried out to give the cyclophane **7c** having three thiophene units in 35% yield.

The referential oligothiophenes **8a**–**e** were also prepared according to the methods described in Scheme 1 (Scheme 2). All compounds were identified by their ^{1}H NMR spectra, mass spectrometric measurement, and/or elemental analyses.

The protons of the bridges in the cyclophanes prepared here appear as two sets of doublets. For example, the *syn* cyclophane **5c** shows the doublets at δ 3.42 and 4.44 with the coupling constant of 14.9 Hz. The similar doublets at δ 3.47 and 3.86 were observed for the *anti* cyclophane **7c**, however, one of them is more shielded than the corresponding peak in **5c**. This upfield shift can probably be ascribed to the opposite aromatic ring in the *anti* structure. From these results it can be indicated that these cyclophanes are a rigid structure, meaning no flipping of their aromatic rings. For these cyclophanes no obvious signal changes were observed when the temperature was raised up to 150 °C. On the contrary the cyclophane **9** (Scheme 3) exhibited the protons of the bridges as the singlet at δ 3.84, indicating that **9** is a flexible structure. These



Scheme 2. Structure of *anti* cyclophanes **7a**–**c** and **8a**–**e**.



Scheme 3.

results suggest that the inner methoxy group is crucial for mobility of these cyclophanes. The signal of the inner methoxy group in the *anti* cyclophanes **7a**–**c** shows ca. 0.3 ppm upfield shift compared with the corresponding signal in the *syn* cyclophanes **5a**–**g**. This upfield shift is due to a shielding effect of the opposite benzene ring. Such a NMR characteristic based on the conformational structure can be seen for the protons of the oligothiophene units. The protons of the thiophene units in the *syn* cyclophanes appear between 6.6 and 6.9 ppm, on the contrary the corresponding signals in the *anti* cyclophanes are observed between 7.0 and 7.3 ppm. These upfield shifts in the *syn* cyclophanes obviously stems from two oligothiophene chains being located in the close proximity.

The electronic absorption and fluorescence spectral data of the cyclophanes, together with referential compounds, are summarized in Table 1. The absorption maxima of the *syn* cyclophanes are red-shifted with increasing number of thiophene units as observed for the referential oligothiophenes. Such a red shift is also confirmed for a series of the *anti* cyclophanes. Examining the absorption maxima among the compounds having the same oligothiophene units (for example; **5c**, **7c**, **8c**, and **9**) the *syn* cyclophanes tend to exhibit blue-shifted peaks in comparison with those of the corresponding non-cyclic oligothiophenes. However, the absorption maxima of the *anti* cyclophanes show red-shifted peaks. These results can be explained by orientation of two oligothiophene units, since a head-to-head type stacking of two oligothiophene units is likely formed in the *syn* cyclophanes which is known to cause a blue shift in the absorption spectra. On the other hand the red-shifted peak of the *anti* cyclophanes is probably due to a head-to-tail type orientation. The cyclophane **9** shows the same absorption maximum as **5c**, implying that the *syn* conformation is a dominant one in **9**.

No blue shift is observed for the *syn* cyclophanes having more than four thiophene units compared with the corresponding referential compounds, which indicates that elongation of thiophene units having a β-hexyl chain could possibly hamper a head-to-head stacking.

Table 1
Maximum wavelength (2max/nm)[a] of absorption and fluorescence spectra for **5a**–g, **7a**–**c**, **8a**–**e**, and **9**

Compound	Absorption	Fluorescence[b]
5a	280	335 (357)
5b	340	(478)
5c	388	470 (557)
5e	410	505
5g	427	528
7a	296	360
7b	354	423
7c	400	456
8a	289	346
8b	346	418
8c	392	453
8d	409	491
8e	426	514
9[8]	341	418 (482)

[a] In cyclohexane, T = 295 K.
[b] Values in parentheses indicate excimer fluorescence.

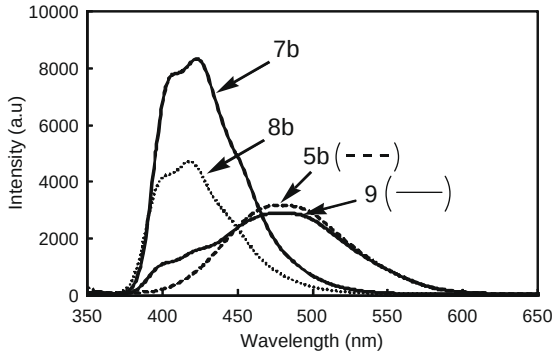


Figure 1. Fluorescence spectra for **5b**, **7b**, **8b**, and **9**.

The *syn* cyclophane **5a** exhibited a weak excimer fluorescence band accompanied with a locally excited fluorescence band. For **5b** and **5c**, an intense excimer fluorescence band was observed. Unexpectedly no such excimer bands were obtained for **5e** and **5g** having four and five oligothiophene units. On the contrary the *anti* cyclophanes **7a**, **7b**, and **7c** showed fluorescence spectra with vibronic structures. These observations indicate that the fluorescence of these compounds is not excimeric, but from the corresponding monomer moieties. That can be reasonably explained by the *anti* conformation leading to no overlap of the oligothiophene units. It has been reported[8] by us that the flexible cyclophanes having the oligothiophene units exhibit characteristic fluorescence depending on the length of oligothiophene chains.

Fluorescence spectra of three kinds of analogous cyclophanes carrying three thiophene units together with the referential thiophene trimer are shown in Figure 1.

These profiles reflect conformational properties of the cyclophane compounds. As described the *anti* cyclophane **7c** shows the fluorescence band similar to the referential compound **8c**, which can be ascribed to the emission from the monomeric species. The *syn* cyclophane **5c** and the flexible cyclophane **9** gave similar spectra, probably due to excimeric species. Interestingly the shoulder peak was observed for the cyclophane **9**. This peak corresponds to a monomeric emission. Furthermore a slight decrease in intensity for an excimer bond is observed as compared with that in **5c**. These facts strongly suggest that there exists conformational change between the *syn* and *anti* conformers in **9**. Such a conformational flexibility of **9** is also supported by the singlet signal for its bridge protons in the NMR spectrum at the room temperature.[8] The spectral profile of **9** with a relative strong excimer band is due to its dominant *syn* conformer, which is consistent with the *syn* conformer in the solid state indicated by the X-ray analysis.[8] It should be noted that conformational properties of these kinds of small-sized cyclophanes can be characterized by the emission spectra from the monomeric species and the excimer one for the first time.

Supplementary data

Supplementary data (characterization data for all new compounds and UV spectral data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.05.070.

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