Preparation and Structural Properties of Novel Fluorenophanes

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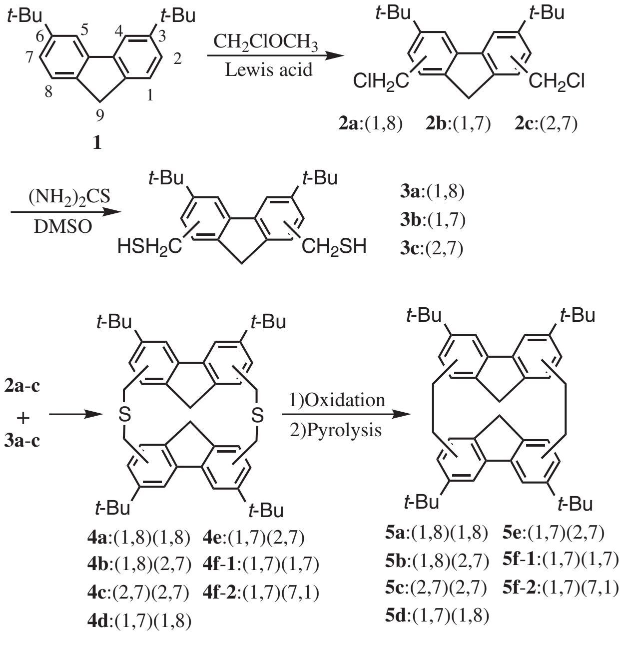
All kinds of fluorenophanes with bridging at 1,7-, 1,8-, and 2,7-positions of each fluorene unit have been successfully prepared. Dynamic structural properties clearly depend on the positions of the bridges. It has been found out that one (2,7)-bridged fluorene ring in the [2.2](1,8)(2,7)fluorenophane is bent to result in formation of the π-cavity.

Recently the fluorene unit has enjoyed various applications as a key component in stable blue-emitting materials,[1] π-conjugated polymer[2] or dendric matrix.[3] On the other hand, cyclophanes,[4] which are bridged aromatic molecules, have been considerably expanding their interests in many fields. Regarding the fluorenophanes, which are cyclic molecules containing the fluorene units, however, [2.2](2,7) fluorenophane is the only example[5] to have been investigated so far. After we successfully prepared 1,8-bis(chloromethyl)fluorene, our work[6,7] concerning fluorene compounds has focused on 1,8-bridged fluorenophanes consisting of one fluorene unit and another aromatic component. Further development of the method to introduce chloromethyl groups into 1,7-, 1,8-, or 2,7-positions of the fluorene encouraged us to employ these chloromethylated fluorenes for the construction of a new class of fluorenophanes.

Thus, we describe here the synthesis of a series of (1,7), (1,8), and (2,7)fluorenophanes and their structural properties.

Treatment of **1**[8] with chloromethyl methyl ether in the presence of $TiCl_4$ gave the mixture of **2a** and **2b** (3:1 by the ^{1}H NMR spectrum) from which **2a** was isolated in 63% yield. Similarly the mixture of **2a** and **2b** (1:1 by the ^{1}H NMR spectrum) was obtained when $SnCl_4$ as a catalyst was utilized in this reaction. On the other hand in the reaction using $ZnCl_2$ as a catalyst **2c** was isolated from the mixture of **2b** and **2c** (1:3 by the ^{1}H NMR spectrum) in 56% yield. In any cases unfortunately it has been unsuccessful to obtain **2b** as a pure form. **2a** and **2c** were reacted with thiourea in DMSO to afford **3a** and **3c** in 80 and 72% yields, respectively. The mixture of **2a** and **2b** was likewise treated to yield the mixture of **3a** and **3b**.



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2a:(1,8) **2b**:(1,7) **2c**:(2,7)

3a:(1,8)
3b:(1,7)
3c:(2,7)

4a:(1,8)(1,8) **4e**:(1,7)(2,7)
4b:(1,8)(2,7) **4f-1**:(1,7)(1,7)
4c:(2,7)(2,7) **4f-2**:(1,7)(7,1)
4d:(1,7)(1,8)

5a:(1,8)(1,8) **5e**:(1,7)(2,7)
5b:(1,8)(2,7) **5f-1**:(1,7)(1,7)
5c:(2,7)(2,7) **5f-2**:(1,7)(7,1)
5d:(1,7)(1,8)

Scheme 1.

Cyclization of **2a** and **3a** using CsOH as a base under a highly dilute condition gave dithiafluorenophanes **4a** in 80% yield. Similar couplings of **2c** with **3a** and **3c** were carried out to obtain **4b** and **4c** in 37 and 46% yields, respectively. The reaction of impure **2b** containing **2a** with **3a** afforded the mixture of **4a** and **4d**, which was separated by the column chromatography to give **4d** in 10% yield. Similarly **4e** was obtained from the coupling of impure **2b** and **3c** in 28% yield. After the coupling of impure **2b** and impure **3b**, careful chromatography enabled us to separate **4f** from other potential isomers. The yield was 32%. Furthermore two kinds of isomers of **4f**, which are (1,7)(1,7) and (1,7)(7,1) isomers, could be also isolated by recrystallization.

After oxidation of **4a–f** with MCPBA, the pyrolyses were carried out to give the corresponding [2.2]fluorenophanes **5a–f** in 10–45% yields. Two kinds of isomers of **4f** gave similar NMR spectra from which one cannot tell which isomer corresponds to which NMR patterns. However, the compounds obtained from each isomer after the pylolysis exhibit quite different NMR patterns; one is characterized by two sets of doublets for the bridge protons indicating the symmetrical structure and the other one shows multiplet resonances. From these results these isomers can be assigned to their structure as shown in Scheme 1. *Trans-tert*-butylation of **5c** using $AlCl_3$ in toluene was carried out to give [2.2](2,7)fluorenophane in 63% yield, which was found out to be identical to the authentic compound,[5] indicating that the present fluorenophanes possibly assume the *anti* structure due to a bulky *tert*-butyl group.

The dynamic structure of the fluorenophanes was examined by the VT-NMR technique as summarized in Table 1. At room temperature the bridge protons in **4a**, **4d**, **4f–1**, and **4f–2** appear as singlets suggesting that these fluorenophanes are a flexible structure. As the temperature was lowered, the singlet peak passed through a coalescence point (shown in Table 1) to freezing the conformation. On the contrary **4b**, **4c**, and **4e** are rigid at room temperature as indicated by two sets of doublets for the bridge protons. For these compounds no obvious changes were observed when the temperature was raised up to 150 °C. Taking account of the coalescence temperatures, evidently the order of flexibility in this fluorenophane system is found as follows, that is, 1,8- > 1,7- > 2,7-component. [2.2]fluorenophanes **5a–f** seem to have a rigid fixed conformation.

Signals of the protons at 9-position in the ^{1}H NMR spectra

Table 1. Chemical shifts[a] of bridge protons and dynamic process of **4a–f**

Compd.	Chemical shift(δ)	[*T*c / °C $\Delta G^\ddagger$ / kJ mol^{-1}][b]
4a	3.91(8H,s)	[$Tc = -75$, $\Delta G^\ddagger = 36.8$]
4b	2.19(2H,d,$J = 17$ Hz) 3.22(2H,d,$J = 17$ Hz) 3.93(2H,d,$J = 13$ Hz) 4.31(2H,d,$J = 13$ Hz)	
4c	3.77(4H,d,$J = 16$ Hz) 4.75(4H,d,$J = 16$ Hz)	
4d	3.23(2H,s) 3.27(2H,s) 3.74(2H,s) 4.11(2H,s)	[$Tc = -60$, $\Delta G^\ddagger = 41.8$]
4e	2.92(1H,d,$J = 12$ Hz) 3.48(1H,d,$J = 14$ Hz) 3.82(1H,d,$J = 14$ Hz) 3.84(1H,d,$J = 12$ Hz) 3.86(1H,d,$J = 15$ Hz) 4.49(1H,d,$J = 14$ Hz) 4.63(1H,d,$J = 14$ Hz) 4.81(1H,d,$J = 15$ Hz)	
4f-1	3.68(4H,s) 4.01(4H,s)	[$Tc = -20$, $\Delta G^\ddagger = 49.0$]
4f-2	3.61(4H,s) 4.19(4H,s)	[$Tc = -30$, $\Delta G^\ddagger = 47.1$]

[a]In $CDCl_3$ at 27 °C. [b]400 MHz.

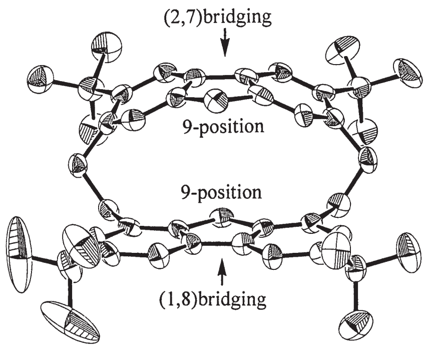

Figure 1. Perspective view of **5b**.

reflect the conformational properties, thus, these chemical shifts in the fluorenophanes are summarized together with 1,8- dimethylfluorene **6** in Table 2. The chemical shifts in flexible dithiafluorenophanes **4a**, **4d**, and **4f** reflect no decisive effect of the opposite fluorene ring. In the rigid dithiafluorenophanes **4b**, **4c**, and **4e** the chemical shifts are observed in somewhat upfield region as compared to δ 3.95 in **6**. For **5a–f** having two fluorene units with increasing proximity an interesting trend was recognized. Symmetrically substituted fluorenophanes such as **5a**, **5c**, and **5f** exhibit no significant large upfield shift in comparison with **6**. Similar shifts are seen in the fluorenophane **5d**, which dose not have the bridging at 2- and 7- positions. On the contrary a marked upfield shift was observed in 2,7-substituted fluorenophanes **5b**, **5e**.

Table 2. Chemical shifts[a] of 9-protons in **4a-f** and **5a-f**

Compd.	Chemical shift (δ)	Compd.	Chemical shift (δ)
4a	4.25(4H,s)	**5b**	0.99(1H,d,$J = 21$ Hz) 2.18(1H,d,$J = 19$ Hz) 2.58(1H,d,$J = 21$ Hz) 3.51(1H,d,$J = 19$ Hz)
4b	1.53(1H,d,$J = 21$ Hz) 1.87(1H,d,$J = 21$ Hz) 2.64(1H,d,$J = 22$ Hz) 2.98(1H,d,$J = 22$ Hz)	**5c**	2.21(2H,d,$J = 21$ Hz) 2.90(2H,d,$J = 21$ Hz)
4c	2.14(2H,d,$J = 22$ Hz) 3.00(2H,d,$J = 22$ Hz)	**5d**	2.67(1H,d,$J = 21$ Hz) 3.25(1H,d,$J = 21$ Hz) 3.95(1H,d,$J = 19$ Hz) 4.34(1H,d,$J = 19$ Hz)
4d	3.08(2H,s) 3.84(2H,s)	**5e**	0.44(1H,d,$J = 21$ Hz) 2.00(1H,d,$J = 20$ Hz) 2.46(1H,d,$J = 21$ Hz) 3.15(1H,d,$J = 20$ Hz)
4e	1.98(1H,d,$J = 22$ Hz) 2.34(1H,d,$J = 22$ Hz) 3.30(1H,d,$J = 21$ Hz) 3.69(1H,d,$J = 21$ Hz)	**5f-1**	2.33(2H,d,$J = 21$ Hz) 3.11(2H,d,$J = 21$ Hz)
4f-1	3.09(4H,s)	**5f-2**	1.61(2H,d,$J = 20$ Hz) 2.95(2H,d,$J = 20$ Hz)
4f-2	3.04(4H,s)	**6**	3.95(2H,s)
5a	3.40(2H,d,$J = 21$ Hz) 4.20(2H,d,$J = 21$ Hz)		

[a]In $CDCl_3$ at 27 °C.

Considering the molecular structure, the 9-protons is unlikely located in the shielding region of the opposite ring. The X-ray structure of **5b**[9] is shown in Figure 1. From the picture the fluorene ring with the bridging at 2- and 7- positions is obviously bent, implying that two benzene portions of the fluorene ring could direct toward the 9-position of the opposite fluorene ring to create a shielding cavity. Thus, the 9-proton on the opposite fluorene ring experiences a shielding effect. This assumption could be supported by the fact that more upfield shift was observed in **5e**, because more bent structure might be expected for the compound **5e** that has 1,7-connection instead of 1,8-connection in **5b**.

Details of fluorescence properties of fluorenophanes in terms of overlapping of their fluorene units are now being investigated.

This paper is dedicated to Emeritus Prof. Soichi Misumi on the occasion of his 77th birthday.

References and Notes

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9 Crystal data for **5b**: $C_{46}H_{56}$, M = 608.94, monoclinic, space group $P2_1/a$ (# 14), $a = 19.316(5)$, $b = 5.814(5)$, $c = 23.176(4)$ Å, $\alpha = 90°$, $\beta = 109.80(1)°$, $\gamma = 90°$, $V = 2449(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.108$ g/cm^3, μ(Mo Kα) = 4.59 cm^{-1}, Rigaku AFC7R diffractometer, 1890 reflections with $I > 3.0\sigma(I)$, $R_1 = 0.090$, $_wR_2 = 0.071$.

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