Rotational Isomerism in Fluorene Derivatives. III.[1] The Conformation of 9-(9-Fluorenyl)-9-(2-substituted 9-fluorenyl)fluorene Derivatives

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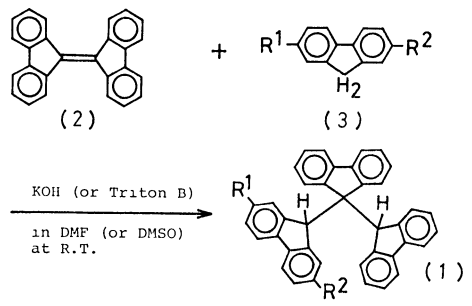
The conformations of 9,9-di(9-fluorenyl)fluorene derivatives (**1**) with substituents at the 2- or 2,7-positions in a terminal fluorene ring were illustrated by the *gauche-gauche* forms at room temperature. DNMR studies of **1** gave the values of about 85—88 kJ/mol for the free energy of activation ($\Delta G^{\ddagger}$) for the restricted rotation around the C(9)–C(9) bonds. The conformation of 9,9-di(9-fluorenyl)fluorene, the parent compound of **1**, was also shown to the only *gauche-gauche* ($+sc$, $+sc$ or $-sc$, $-sc$) form at room temperature.

We have recently reported[2] that the NMR signal of 9-(9-fluorenyl)-9-(2-methyl-9-fluorenyl)fluorene (**1a**) at room temperature showed the existence of two conformers which were caused by restricted rotation around the C(9)–C(9) bonds, and that both the conformations were illustrated by the more stable form, the *gauche-gauche* form. In this paper, we would like to describe the conformations of 9,9-di(9-fluorenyl)fluorene derivatives (**1**) with methyl, ethyl, methoxy, acetyl, and bromo substituents at the 2- or 2,7-positions in a terminal fluorene ring, and also the conformation of the parent 9,9-di(9-fluorenyl)fluorene (**4**).

The derivatives **1** were prepared from the Michael reactions[3] of 9,9′-bifluorenylidene (**2**) with 2(or 2,7-di)-substituted fluorene derivatives **3**, catalyzed by a base in DMF or DMSO at room temperature. The ^{1}H-NMR data of **1** are shown in Table 1.



The NMR spectra for the 2-substituents in **1** have shown the set of signals illustrated in Table 1, suggesting that the rotation around the C(9)–C(9) bonds in **1b**—**1g**, as well as in **1a**,[2] is frozen at room temperature on the NMR time scale. The restricted rotation around the C(9)–C(9) bonds of **1** was investigated by temperature-dependent NMR spectroscopy: some typical DNMR spectra of **1b** are shown in Fig. 1. The values of the free energy of activation ($\Delta G^{\ddagger}$) for the rotation around the bonds in **1** were obtained by means of the usual line-shape analysis[4] on their DNMR spectra of

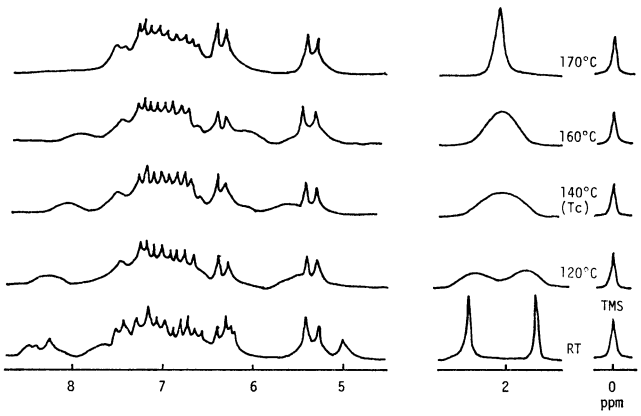


Fig. 1. Temperature dependence of ^{1}H-NMR spectra of **1b** (solvent: HCB).

TABLE 1. ^{1}H-NMR DATA OF **1** IN $CDCl_3$ (ppm)

Compd	R^1	R^2	R^1 and/or R^2		K[c]	9-H	Aromatic protons
			A[a]	**C**[b]			
1a[2]	CH_3	H	1.76s	2.55s	0.9/1	5.32s 5.38s	5.00—8.60 m
1b[2]	CH_3	CH_3	1.76s	2.55s	1/1	5.28s 5.40s	5.00—8.60m
1c[2]	C_2H_5	H	0.68t($CH_2\underline{CH_3}$) 2.03q($C\underline{H_2}CH_3$)	1.32t($CH_2\underline{CH_3}$) 2.83q($C\underline{H_2}CH_3$)	0.8/1	5.34s 5.38s	5.10—8.50m
1d	OCH_3	H	3.08s	3.88s	0.4/1	5.32s 5.37s	5.00—8.60m
1e	$COCH_3$	H	1.90s	2.68s	0.3/1	5.34s 5.40s	5.20—8.60m
1f	OCH_3	$COCH_3$	2.71s($COCH_3$) 3.15s(OCH_3)	1.91s($COCH_3$) 3.98s(OCH_3)	1.6/1	5.36s 5.41s	5.00—9.00m
1g	OCH_3	Br	3.20s	3.80s	0.9/1	5.18s 5.25s	4.80—8.50m

a) **A**: Conformation **A**. b) **C**: Conformation **C**. c) K: Equilibrium constants for the **A**⇌**C** systems in **1**, $K=N_C/N_A$.

TABLE 2. FREE ENERGIES OF ACTIVATION FOR THE ROTATION AROUND THE C(9)–C(9) BONDS IN **1**

Compd	Solvent[b]	$\Delta G^{\ddagger}$[a]/kJ mol^{-1}(T/°C)
1a[2]	*o*-DCB	85.4 (145)
1b	HCB	84.5 (140)
1c	*o*-DCB	84.5 (135)
1d	*o*-DCB	86.2 (140)
1e	*o*-DCB	85.4 (120)
1f	HCB	87.9 (120)
1g	HCB	84.5 (140)

a) The estimated errors of $\Delta G^{\ddagger}$ are $\pm$1.3—1.7 kJ/mol.
b) *o*-DCB: *o*-dichlorobenzene. HCB: hexachlorobutadiene.

2-substituents, which did not directly hinder the rotation around the C(9)–C(9) bonds, as shown in Table 2.

Figure 2 shows two conformations, (**A**) (*ap*, +*sc*) and (**C**) (+*sc*, −*sc*), both of them *gauche-gauche* forms, and their interconversion process. The conformation **C** is derived from **A** *via* an unstable intermediate (**B**) (+*ac*, *sp*) by the rotation of the two C(9)–C(9) bonds in a conrotatory manner. In the conformation **A**, the substituent R^1 at the 2-position in the terminal fluorene ring **b** is located in a shielding zone of the central fluorene ring **a**. Thus, it is reasonable to assume that the R^1 gives the ^{1}H-NMR signal at a higher field than the R^2 at the 7-position, which is located in a deshielding zone of the two fluorene rings **a** and **c**. The same thing can also be said for the ^{1}H-NMR signals of R^1 and R^2 in the conformation **C** or **D** (enantiomer of **C**). Table 1 illustrates the assignments of the conformations **A** and **C** based on these ^{1}H-NMR signals, and also shows the equilibrium constants K (N_C/N_A) for the equilibria **A**⇌**C** of **1**.

Recently, Suzuki and Minabe reported that 9,9-di(9-fluorenyl)fluorene (**4**), the parent compound of **1**, has two conformational isomers occuring as a result of the restricted rotation around the C(9)–C(9) single bonds, and proposed, on the basis of the ^{1}H-NMR data at room temperature, that the two rotamers can exist in the *s-cis*, *s-cis* form (mp 291—293 °C) (corresponding to our *gauche-gauche* form) and the *s-cis*, *s-trans* form (mp 256—257 °C).[5] However, we could not confirm any isomers of the above *s-cis*, *s-trans* type from **1**. Actually, the reaction of **2** with fluorene catalyzed by potassium hydroxide in DMF gave the sole product **4** (mp 291—293 °C).[3] The DNMR spectra of **4** in HCB are shown in Fig. 3.

The spectrum of **4** is almost analogous to that of **1** (Fig. 1) except for the region of the substituents, supporting the *gauche-gauche* form as the stable conformation of **4** by analogy with **1**. The isomerization process between the +*sc*, +*sc* and −*sc*, −*sc* (enantiomer of +*sc*, +*sc*) forms of **4** can be well demonstrated in a manner similar to that described in the case of **1**. The $\Delta G^{\ddagger}$ value for the restricted rotation around the C(9)–C(9) bonds in **4** may also be about 85—88 kJ/mol, by analogy with that of **1**. Unfortunately, we could not find the *s-cis*, *s-trans* isomer[6] which was reported by Suzuki and Minabe in these DNMR process.

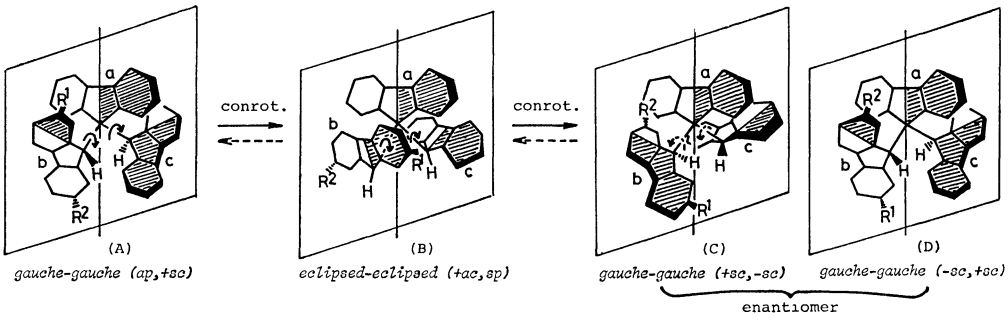


Fig. 2. The process for isomerization of **1** by rotation around the C(9)–C(9) bonds.

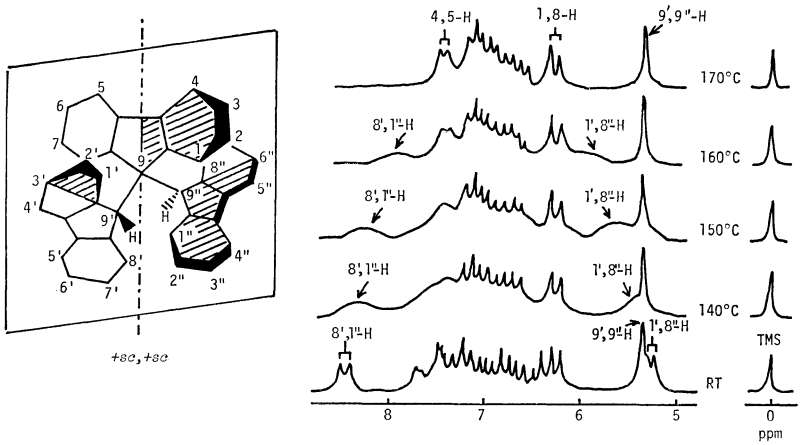


Fig. 3. Temperature dependence of ^{1}H-NMR spectra of **4** (solvent: HCB).

From the behavior of the DNMR spectra of **4**, the doublets of $\delta=5.22$ ($J=8$ Hz) and $\delta=8.40$ ($J=8$ Hz) at room temperature were identified as protons at the 1′,8″- and 8′,1″-positions, respectively. These two doublets are broadened, and are observed to approach each other gradually with an increase in the temperature, and are then hidden in the region of other aromatic protons at 165 °C. On the other hand, the doublets of $\delta=6.22$ ($J=8$ Hz) and $\delta=7.44$ ($J=8$ Hz) which are observed clearly at high temperatures are identified as protons at the 1,8- and 4,5-positions in the central fluorene ring, respectively. Then, 9,9-di(9-fluorenyl)-fluorene was prepared by the Michael addition of fluorene to **2** with sodium ethoxide in ethyl alcohol by the same method as that described by Suzuki and Minabe.[5] The two products, **4** (mp 291—293 °C) and **5** (mp 255—257 °C), were obtained just as has been described in the literature.

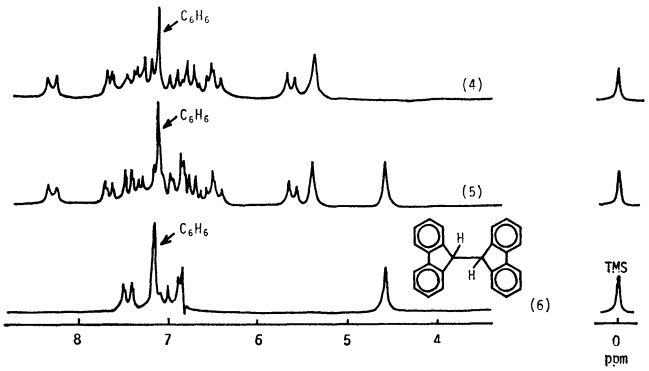


Fig. 4. ^{1}H-NMR spectra of **4**, **5**, and **6** at room temperature (solvent: C_6D_6).

The ^{1}H-NMR spectra of **4** and **5** in C_6D_6 at room temperature are shown in Fig. 4, together with that of 9,9′-bifluorenyl (**6**).[5] In this case, the shape of spectrum of **5** was in fair agreement with the overlapped shape of the spectrum of **4** with **6**. The chemical shift (4.60 ppm) in **5** is the same as that of methine protons in **6**, and the signal is amplified by the addition of **6**. The equimolar mixture of **4** and **6** was recrystallized from ethyl acetate to give crystals with the melting point of 255—257 °C; its ^{1}H-NMR spectrum was identical with that of **5**. Furthermore, the product **5** was confirmed to be an equimolar mixture of **4** and **6** by high-speed liquid-chromatographic analysis.

On the Michael reaction of **2** with fluorene, if alkoxide is used as a catalyst, **5** is obtained as the product. In this case, **6** should be produced along with **4** in the reaction mixture. That is, the alkoxide should act on **2** as a reductant. The reaction of **2** with fluorene using other bases (*e.g.*, KOH in DMF,[3] Triton B in DMSO, and KOH in pyridine[5]) instead of alkoxide gave **4** as the sole product. Actually, the reaction of **2** with sodium ethoxide in ethyl alcohol in a sealed tube gave **6** in a substantial yield.

It is known that, in the case of $\Delta G^{\ddagger}<96$ kJ/mol rotamers are unstable at room temperature.[7] If the $\Delta G^{\ddagger}$ value for **4** is estimated as 85—88 kJ/mol as in the case of **1**, we should not be able to isolate the *s-cis*, *s-trans* rotamer of **4** stably at room temperature.

Experimental

All the melting points are uncorrected. The NMR spectra were run on a JEOL-MH-100 spectrometer with a JEOL model JES-VT-3 variable-temperature controller. The chemical shifts are expressed in ppm, with tetramethylsilane as the internal standard. Signal-shape-analysis was done by matching the experimental spectra with the spectra calculated from the computer program given by Nakagawa.[8] High-speed liquid-chromatographic analysis was carried out on a Tōyō Sōda TSK-HLC-803 apparatus equipped with a UV monitor using an LS-410K (4 mm i.d. × 30 cm) column, with acetonitrile as the mobile phase, at room temperature.

Syntheses of **1**. *A Typical Synthetic Procedure for* **1**: The starting material, 2-acetyl-7-methoxyfluorene (**3f**), was prepared by the reaction of 2-methoxyfluorene with acetyl chloride, using $AlCl_3$ as the catalyst, by the procedure reported by Gray *et al.*;[9] mp 131—132 °C (lit, 134.5 °C); IR (KBr) 1670 cm^{-1} (C=O); NMR ($CDCl_3$) $\delta=2.60$ (3H, s, $COCH_3$), 3.83 (2H, s, 9-methylene), 3.84 (3H, s, OCH_3), 6.70—8.20 (6H, m, aromatic protons).

To a mixture of **2** (1.6 g, 0.005 mol) and **3f** (1.2 g, 0.005 mol) in DMF (2 ml), we added Triton B (0.1 ml) at room temperature. The solution was stirred for 5 min, during which the color changed from red to dark brown, and was then poured into dil hydrochloric acid (10 ml). The precipitate thus obtained was filtered, washed with water, and recrystallized from acetone to give colorless crystals **1f**; 2.0 g (70%); mp 244—248 °C. Found: C, 89.43; H, 5.07%. Calcd for $C_{42}H_{30}O_2$: C, 89.02; H, 5.34%.

1d, mp 237—242 °C; Found: C, 91.82; H, 5.36%. Calcd for $C_{40}H_{28}O$: C, 91.57; H, 5.38%.

1e, mp 251—255 °C; Found: C, 91.51; H, 5.15%. Calcd for $C_{41}H_{28}O$: C, 91.76; H, 5.26%.

1g, mp 260—263 °C; Found: C, 79.24; H, 4.48%. Calcd for $C_{40}H_{27}OBr$: C, 79.60; H, 4.51%.

Reaction of **2** *with Sodium Ethoxide.* Metallic sodium (0.23 g, 0.01 g-atom) was treated with 20 ml of absolute ethanol, and then there was added 0.33 g (0.001 mol) of **2**. The mixture was heated in a sealed tube at 95—98 °C for 14 h. After cooling, the precipitate was filtered off and dissolved in benzene. The benzene solution was chromatographed on alumina. The eluent was evaporated to dryness under reduced pressure, and the residue was recrystallized from benzene–ethanol (1: 1) to afford **6**: 0.20 g (61%); mp 246—247 °C. This compound was confirmed by direct comparison with an authentic sample. On the other hand, **2** was recovered unchanged from the red ethanolic solution; 0.05 g (15%).

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