# Rotational Isomerism in Fluorene Derivatives. IX. Restricted Rotation about the C(9)-C(9′) Bonds in 9(or 9′)-Substituted 2-Methyl-9,9′-bifluorenyls[1]

Shoji KAJIGAESHI,* Akiko NISHIDA, and Shizuo FUJISAKI
*Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755*
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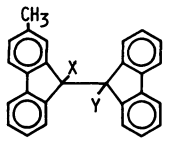
Several 9(or 9′)-substituted 2-methyl-9,9′-bifluorenyls were prepared and the restricted rotation about the $C_{sp^3}$–$C_{sp^3}$ bonds in these compounds were investigated by DNMR. In these cases, nonequivalent gauche conformers were observed at low temperatures. Barriers ($\Delta G^*$) for the forward and backward interconversions were slightly increased in agreement with the bulkiness of the 9(or 9′)-substitutents.

Previously, we have discussed the conformations of 9-(9-fluorenyl)-9-(2-substituted 9-fluorenyl)fluorene derivatives[2] (**1**) and 9-aryl-9-(2-methyl-9-fluorenyl)-fluorene derivatives[3] (**2**) concerning the restricted rotation about the $C_{sp^3}$–$C_{sp^3}$ bonds on the basis of their DNMR behavior.

This work was undertaken to examine the restricted rotation about the $C_{sp^3}$–$C_{sp^3}$ bonds in 9(or 9′)-substituted 2-methyl-9,9′-bifluorenyl derivatives (**3**). These compounds have a simpler skeleton than **1** or **2**, such as 9,9′-unsubstituted[4] (**3a**), 9-bromo-[4] (**3b**), 9′-hydroxy-[4] (**3c**), 9-methoxy-[4] (**3d**), 9′-methoxy- (**3e**), 9-ethoxy-[4] (**3f**), 9′-ethoxy[4] (**3g**), 9-propoxy- (**3h**) and 9-isopropoxy-2-methyl-9,9′-bifluorenyl (**3i**).



**3**

| | X | Y | | X | Y |
|---|---|---|---|---|---|
| **3a**: | H | H | **3f**: | $OC_2H_5$ | H |
| **3b**: | Br | H | **3g**: | H | $OC_2H_5$ |
| **3c**: | H | OH | **3h**: | $O(CH_2)_2CH_3$ | H |
| **3d**: | $OCH_3$ | H | **3i**: | $OCH(CH_3)_2$ | H |
| **3e**: | H | $OCH_3$ | | | |

## Results and Discussion

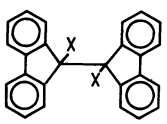
The compounds **3h** and **3i** were prepared by refluxing **3b** with 1-propanol and 2-propanol, respectively. The $^1$H-NMR data of **3** at room temperature are shown in Table 1.

It has been noted that bifluorenyl has a gauche geometry in the solid state, and the same gauche conformation prevails in solution judging from the magnitude of the H(9)–H(9′) vicinal coupling constant in its $^1$H-NMR spectrum.[5] We have also reported that rotational isomerization in **1** or **2** may occur by interconversion between two stable gauche conformers of these compounds.[2,3]

TABLE 1. $^1$H-NMR DATA OF **3** IN $CDCl_3$: $\delta$

| Compd | 2-$CH_3$ | 9- or 9′-H | 9- or 9′-Substituent | Aromatic proton |
|---|---|---|---|---|
| **3a** | 2.26$^s$ | 4.76$^s$ | | 6.60—7.68$^m$ |
| **3b** | 2.28$^s$ | 5.11$^s$ | | 6.96—7.68$^m$ |
| **3c** | 2.21$^s$ | 4.69$^s$ | 2.45$^s$ | 6.80—7.48$^m$ |
| **3d** | 2.24$^s$ | 4.70$^s$ | 2.85$^s$ | 6.60—7.54$^m$ |
| **3e** | 2.22$^s$ | 4.62$^s$ | 2.87$^s$ | 6.59—7.53$^m$ |
| **3f** | 2.26$^s$ | 4.76$^s$ | 1.16$^t$ 2.98$^q$ | 6.78—7.64$^m$ |
| **3g** | 2.26$^s$ | 4.77$^s$ | 1.16$^t$ 2.97$^q$ | 6.72—7.68$^m$ |
| **3h** | 2.31$^s$ | 4.78$^s$ | 0.91$^t$, 1.41—1.79$^m$, 2.88$^t$ 2.90$^t$ | 6.67—7.63$^m$ |
| **3i** | 2.22$^s$ | 4.64$^s$ | 0.94$^d$ 0.96$^d$, 3.10$^m$ | 6.62—7.50$^m$ |

Recently, Olah *et al.*[6] have determined the energy barriers for the interconversion of the equivalent gauche conformers of the symmetrical 9,9′-disubstituted 9,9′-bifluorenyl derivatives (**4**) by complete line-shape analysis of the DNMR spectra of the protons in aromatic regions. We have now obtained the energy barriers for the rotation about the $C_{sp^3}$–$C_{sp^3}$ bonds in **3** from the line-shape analysis of their DNMR spectra due to the protons of the 2-methyl group; this does not directly hinder rotation about the central bonds. The observed and simulated $^1$H-NMR spectra of **3c** are shown in Fig. 1 as a typical example.



X=H, Me, Cl, Br

**4**

In Fig. 1, the 2-methyl signal ($\delta$=2.21) which is observed as a singlet at room temperature gradually broadens when the temperature is lowered, and is completely split into two nonequivalent singlets ($\delta$=2.56 and 1.84) at −75 °C. That is, two different conformers which are caused by restricted rotation about the C(9)–C(9′) bond can be observed at low

temperature.

Figure 2 shows the conformations concerned with rotation about the C(9)–C(9′) bond in **3c**, and their interconversion processes by Newman projection formulas. The conformation B (+*ac*), D(*sp*), and F(−*ac*) should be unstable forms because of their eclipsed geometries. An examination of the molecular model suggests that anti conformation E(−*sc*) is also unstable on account of the steric interaction between the 1- and 1′-protons as well as the 8- and 8′-protons in the two fluorene moieties. Consequently, the observed conformations at low temperature are attributed to the gauche forms A(*ap*) and C(+*sc*). In this case, it is reasonable to assume that the methyl group in conformation A which is located in a shielding zone of the other

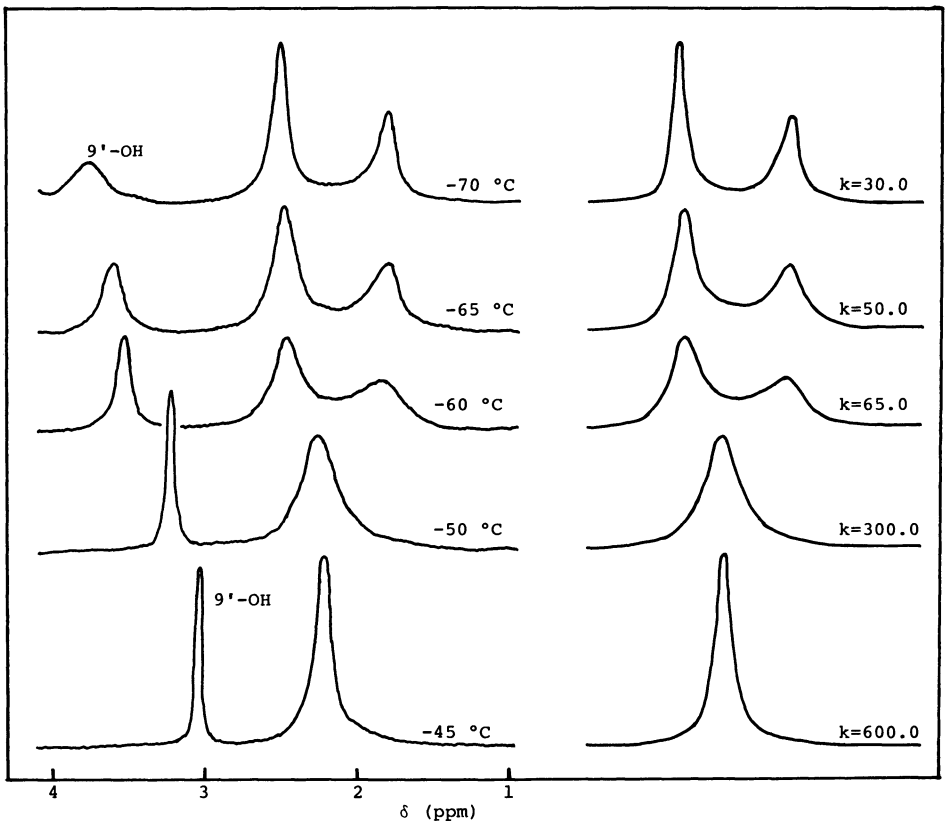



Fig. 1. Obserbed (left) and calculated (right) spectra of 2-$CH_3$ in **3c** at various temperature.

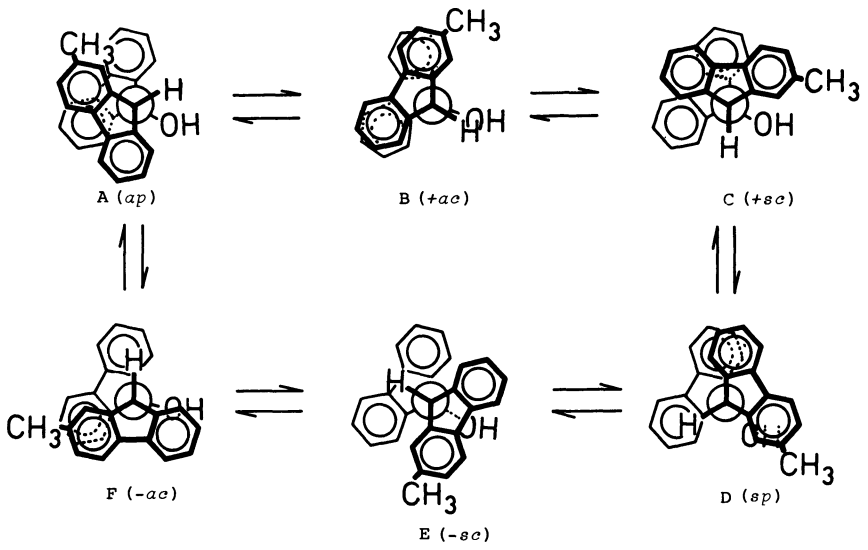



Fig. 2. Stereoisomerization process of **3c** by rotation about the C(9)–C(9′) bond.

fluorene moiety gives $^1$H-NMR signal at a high field, and the methyl group in C located in a deshielding zone of the other's gives the signal at low field. Thus, the singlet at $\delta$=1.82 is assigned to the methyl signal of A and the singlet at $\delta$=2.52 is assigned to that of C. Furthermore, the equilibrium constant $K(N_A/N_C)$ for the equilibria C$\rightleftarrows$A was found to be 0.54—0.73 from the intensity ratio of the two methyl signals.

Interconversion between the two gauche conformers, A and C, can occur by two different pathways, *via* the fully eclipsed form B, or *via* the anti form E. But irrespective of the pathways, the observed dynamic behavior can be viewed as a rocking motion from one gauche form to the other. The rotational energy profile for **3c** is illustrated graphically in Fig. 3. The same convincing argument is applicable to the other deirvatives in the series of **3**.

In the $^1$H-NMR spectra of the derivatives **3** at low temperature, signal intensities of the methyl groups observed at the higher magnetic field were always smaller than that observed at the lower magnetic field. As shown in Fig. 2, it turned out that the conformer A in which the 2-methyl group of **3** is located above the other fluorene moiety is less stable than the conformer C, and the conformational equilibrium between A and C favors C. Therefore, it can be expected that there would be appreciable $\pi$-$\pi$ repulsive interaction between the phenyl moiety with an electron-donating methyl group and the other fluorene moiety.

The activation parameters for internal rotation in **3** obtained from the line-shape analysis of their DNMR spectra due to the methyl groups are listed in Table 2, together with the equilibrium constants between the two rotamers at low temperature.

Steric interactions are obviously responsible for the observed barriers. In fact, as shown in Table 2, the free energies of activation ($\Delta G^{\ddagger}$) for rotation about the C(9)–C(9′) bonds in **3** were slightly increased as the size of 9- or 9′-substituents (X or Y) increased, except for the OH in **3c**. Particularly, 9-alkoxy-2-methyl 9,9′-bifluorenyls gave the magnitudes of the rotational barriers (A→C and/or C→A) in the following order, $\Delta G^{\ddagger}_{3i} > \Delta G^{\ddagger}_{3h} \approx \Delta G^{\ddagger}_{3f} > \Delta G^{\ddagger}_{3d}$.

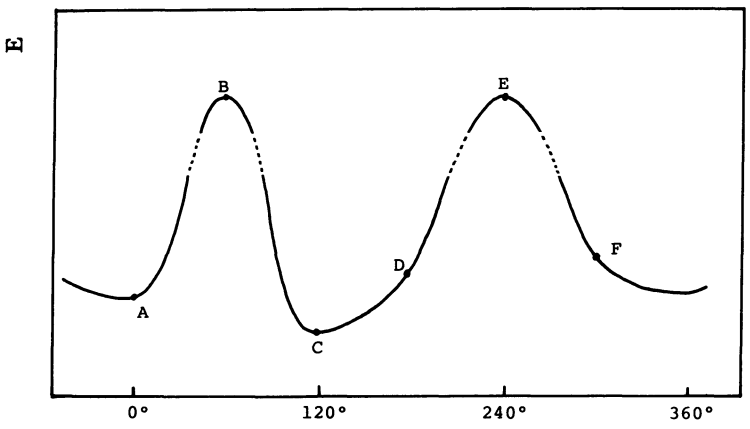



Fig. 3. Rotational energy profile for **3c**.

Table 2. Equilibrium constants and activation parameters of the A$\rightleftarrows$C systems of **3** at 25 °C

| | | A⟶C | | | C⟶A | | |
|---|---|---|---|---|---|---|---|
| | | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}$ |
| Compd | $K(N_A/N_C)$ | kcal/mol[a] | e.u.[b] | kcal/mol[a] | kcal/mol[a] | e.u.[b] | kcal/mol[a] |
| **3a** | 0.54 | 9.4 | −4.5 | 10.4 | 9.4 | −5.8 | 10.8[c] |
| **3b** | 0.60 | 9.3 | −4.5 | 10.7 | 9.3 | −5.5 | 11.0 |
| **3c** | 0.73 | 10.6 | 1.6 | 10.1 | 10.6 | 0.9 | 10.3 |
| **3d** | 0.60 | 10.0 | −3.1 | 10.9 | 10.0 | −4.1 | 11.2 |
| **3e** | 0.73 | 11.3 | 2.2 | 10.6 | 11.3 | 1.6 | 10.8 |
| **3f** | 0.60 | 10.2 | −5.2 | 11.7 | 10.2 | −6.2 | 12.0 |
| **3g** | 0.60 | 10.7 | −3.4 | 11.7 | 10.7 | −4.4 | 12.0 |
| **3h** | 0.60 | 10.8 | −2.5 | 11.6 | 10.8 | −3.5 | 11.9 |
| **3i** | 0.66 | 9.2 | −11.2 | 12.5 | 9.2 | −12.0 | 12.7 |

a) 1 cal=4.18 J. b) 1 e.u.=4.18 JK$^{-1}$·mol$^{-1}$. c) $\Delta G^{\ddagger}_{240°C}$ of **3a** was obtained as 9.9 kcal/mol in Ref. 6.

## Experimental

The $^1$H-NMR spectra were recorded 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. Dynamic NMR spectra were analyzed by using a modified version of the computer program DNMR3.[7] The melting points of the compounds obtained are uncorrected.

*2-Methyl-9-propoxy-9,9'-bifluorenyl (**3h**).* A solution of **3b** (0.21 g, 0.5 mmol) in 1-propanol (3 ml) was refluxed for 30 min. Solvent was distilled off and the residue was chromatographed on alumina using benzene as eluent. The crude product was recrystallized from acetone to give **3h** (0.16 g, 80%) as slight yellow crystals; mp 135—136 °C. $^1$H-NMR ($CDCl_3$) $\delta$=0.91 (3H, t, $J$=7 Hz, $(CH_2)_2C\underline{H}_3$), 1.4—1.79 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.31 (3H, s, $CH_3$), 2.88, 2.90 (2H, two t, $J$=7 Hz, $C\underline{H}_2CH_2CH_3$), 4.78 (1H, s, CH), 6.67—7.63 (15H, m, aromatic protons).

Found: C, 89.69; H, 6.63%. Cacld for $C_{30}H_{26}O$: C, 89.51; H, 6.51%.

*9-Isopropoxy-2-methyl-9,9'-bifluorenyl (**3i**).* A solution of **3b** (0.21 g, 0.5 mmol) in 2-propanol (3 ml) was refluxed for 30 min. After the same procedure as above, **3i** (0.15 g, 75%) was obtained as slight yellow crystals; mp 141—142 °C. $^1$H-NMR ($CDCl_3$) $\delta$=0.94, 0.96 (6H, two d, $J$=6 Hz, $CH(C\underline{H}_3)_2$), 2.22 (3H, s, $CH_3$), 3.10 (1H, m, $J$=6 Hz, $C\underline{H}(CH_3)_2$), 4.64 (1H, s, CH), 6.62—7.50 (15H, m, aromatic protons).

Found: C, 89.54; H, 6.52%. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51%.

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