Rotational Isomerism in Fluorene Derivatives XXII[1)] Syntheses of 1-Substituted 2'-methyl-9, 9'-bifluorenyl Derivatives and Structures of Their Stereoisomers

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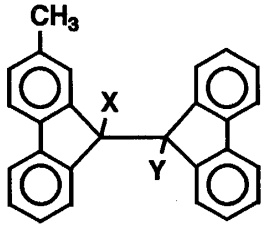
Abstract

Several 1-substituted 2'-methyl-9-hydroxy-9,9'-bifluorenyl derivatives (**2**) and 1-substituted 2'-methyl-9,9'-bifluorenyl derivatives (**3**) (1-substituents: CH_3, F, Cl, Br, I, and OCH_3) were prepared. These derivatives were confirmed as the mixture of *erythro*- and *threo*-isomers by their ^{1}H-NMR spectra. Restricted rotation about the C(9)- C(9') bonds was not observed owing to their considerably stable structures.

1. Introduction

We have previously prepared several 9(or 9')-substituted 2-methyl-9, 9'-bifluorenyls (**1**)[2)] and investigated the restricted rotation about the C(9)-C(9') bonds in these compounds on the basis of their DNMR behavior.[3)] In these cases, 2-methyl groups of **1** did not directly hinder the rotation around their C(9)-C(9') bonds.

In this paper, we wish to describe the preparation and determination of structures of the title derivatives **2** and **3** having 1-substituents which should affect the steric hindrance for the rotation about the C(9)-C(9') bonds.



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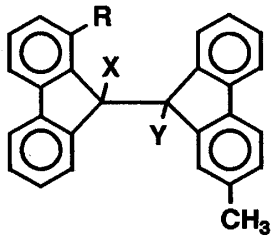

2 : X= OH, Y= H
3 : X= Y= H

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2. Results and Discussion

2.1 Syntheses of 1-Substituted 2'-methyl-9-hydroxy-9,9'-bifluorenyls (2) and 1-Substituted 2'-methyl-9, 9'-bifluorenyls (3)

The derivatives **2** were prepared from the reactions of 1-substituted fluorenones (**4**) with 2-methyl-9-fluorenyllithium (**5**)[1] in dry benzene under nitrogen atmosphere and the subsequent decomposition reactions. In these cases, we chose 1-substituents of **4** such as methyl-[4], fluoro-[5], chloro-[6], bromo-[7], iodo-[6], and methoxyl-group[8]. The reduction of **2** with hydroiodic acid in acetic acid gave **3**. Mp, yield and partial NMR data of the obtained **2** and **3** are shown in Table 1, and their analytical data are shown in Table 2.

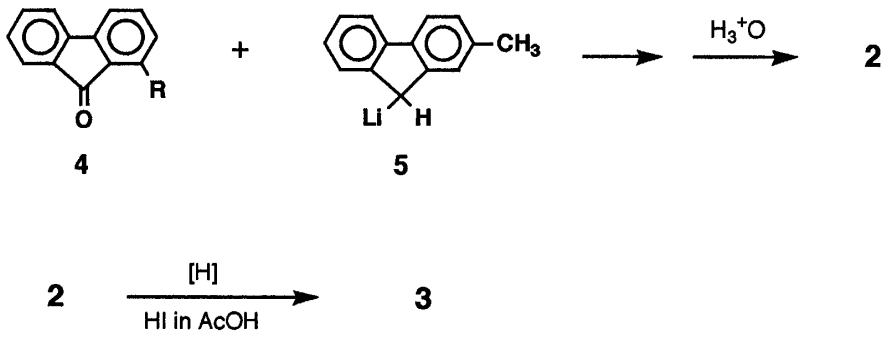
Table 1. Syntheses of **2** and **3**

Compd.	R	Yield (%)	mp (℃)	NMR: δ (ppm) in $CDCl_3$ at room temperature 2'-CH3	9-H	9'-H	1'-H	8-H	8'-H	1-CH_3	Form
2a	CH_3	83	191-193[a]	1.96		5.17s	5.75s	6.16d	8.31d	2.90	A
			200-202[b]	2.56		5.17s	8.26s	6.20d	5.99d	2.90	B
2b	F	51	139-143[c]	1.98		5.06s	6.00s	6.18d	8.10d		A
				2.47		5.31s	8.05s	6.24d	6.16d		B
2c	Cl	84	150-158[c]	1.78		5.34s	5.63s	6.00d	8.16d		A
				2.40		5.31s	8.05s	6.06d	5.88d		B
2d	Br	61	165-170[c]	1.94		5.54s	5.70s	6.18d	8.46d		A
				2.54		5.50s	8.29s	6.17d	6.00d		B
2e	I	73	145-156[c]	1.96		5.59s	5.69s	6.15d	8.43d		A
				2.54		5.63s	8.29s	6.21d	5.86d		B
2f	OCH_3	83	155-158[c]	1.90		5.12s	5.75s	5.98d	8.12d		A
				2.42		5.16s	8.06s	6.12d	6.10d		B
3a	CH_3	88	224-227[c]	2.00	4.98d	5.02d	5.90s	6.16d	-	2.82	A
				2.61	4.98d	5.02d	-	6.16d	6.10d	2.79	B
3b	F	80	173-175[c]	2.02	5.12s	5.12s	6.12s	6.24d	-		A
				2.56	5.12s	5.12s	-	6.18d	6.28d		B
3c	Cl	61	197-200[c]	1.96	5.12d	5.49d	5.87s	6.11d	7.97d		A
				2.59	5.12d	5.49d	7.85s	6.09d	6.13d		B
3d	Br	65	188-194[c]	1.92	4.83d	5.40d	5.64s	5.98d	7.84d		A
				2.59	4.83d	5.40d	7.08s	5.96d	6.00d		B
3e	I	48	178-186[c]	1.98	4.68d	5.40d	5.78s	5.84d	7.76d		A
				2.64	4.68d	5.40d	7.92s	5.88d	5.92d		B

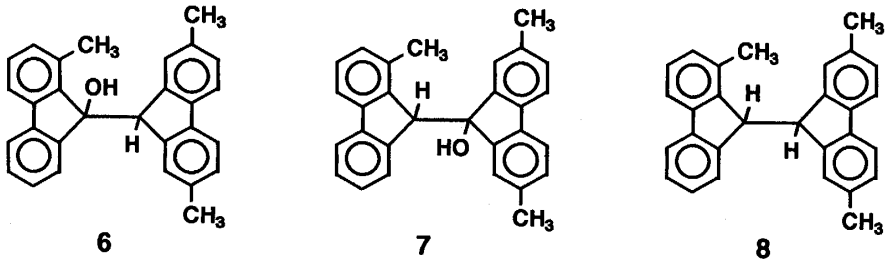
a) Mp of isolated **A**-form. b) Mp of isolated **B**-form. c) Mp of a mixture of **A**- and **B**-form.

Table 2. Analytical data for **2** and **3**

compd.	Empirilal formula	Calcd. C(%)	Calcd. H(%)	Found C(%)	Found H(%)
2a	$C_{28}H_{22}O$	89.81	5.92	89.77	5.90
2b	$C_{27}H_{19}OF$	85.70	5.06	85.44	5.00
2c	$C_{27}H_{19}OCl$	82.13	4.85	82.01	4.79
2d	$C_{27}H_{19}OBr$	73.82	4.36	73.55	4.35
2e	$C_{27}H_{19}OI$	66.68	3.94	-	-
2f	$C_{28}H_{22}O2$	86.13	5.68	86.42	5.76
3a	$C_{28}H_{22}$	93.81	6.19	93.56	6.16
3b	$C_{27}H_{19}F$	89.48	5.28	89.42	5.13
3c	$C_{27}H_{19}Cl$	85.59	5.06	85.36	5.01
3d	$C_{27}H_{19}Br$	76.60	4.52	76.39	4.63
3e	$C_{27}H_{19}I$	68.95	4.07	68.72	4.20



As shown in Table 1, these compounds were generally obtained as a mixture of A- and B- form, which resulting A/B proportions did not appreciably differ. It turned out that A- and B- form were isomeric with each other, because their A/B ratios changed by recrystallization. Particularly, compound **2a** could be separated A-(mp 191-193 ℃) and B-isomer (mp 200-202 ℃) upon recrystallization the crude product from methanol. On the other hand, we prepared 1,2',7'-trimethyl-9-hydroxy-9, 9'-bifluorenyl (**6**), 1,2',7'-trimethyl-9'-hydroxy-9,9'-bifluorenyl (**7**), and 1,2',7'-trimethyl-9,9'-bifluorenyl (**8**) according to the same method showed above. However, these compounds were obtained as a single product.



2.2 Determination of Structure of Derivatives 2 and 3

In order to determine the structure of **2** and **3**, we considered an interconversion of these compounds showed in Fig.1. That is, the figure shows the conformations concerned with rotation about the C(9)-C(9') bond in **2** or **3**, and their interconversion processes by Newman projection formulas. In these cases, we struck unstable eclipsed form off the Figure. An examination of the molecular model suggests that *anti* conformations C_3 and D_3 are unstable on account of the steric interaction between the 1- and 1'-substituent as well as the 8- and 8'-substituent in the two fluorene moieties. Furthermore, *gauche* forms C_1 and D_2 are also unstable because of the steric interaction between 1-substituent and other fluorene nucleus. Concequently, we presumed that the most stable conformations are *gauche* forms C_2 and D_1. Thus, NMR behaviors for **2** and **3** should be explained by the forms of C_2 (*erythro*) and D_1 (*threo*).

As an example, we wish to discuss the structures of **2a** on the basis of its NMR data. NMR spectra of isolated A- and B- forms of **2a** are shown in Fig. 2.

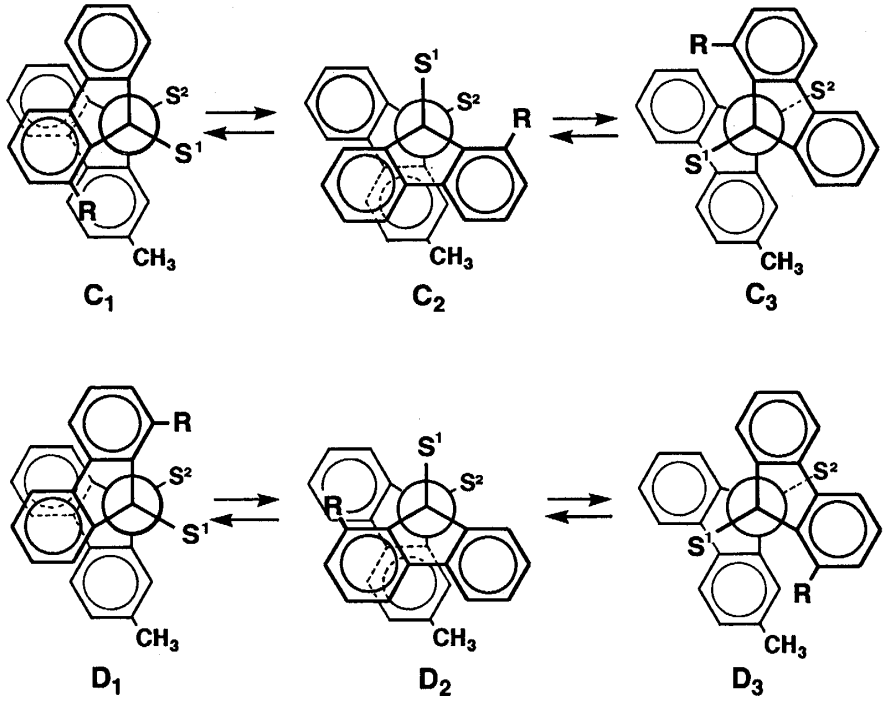


Fig. 1 Interconversion of **2** (or **3**)

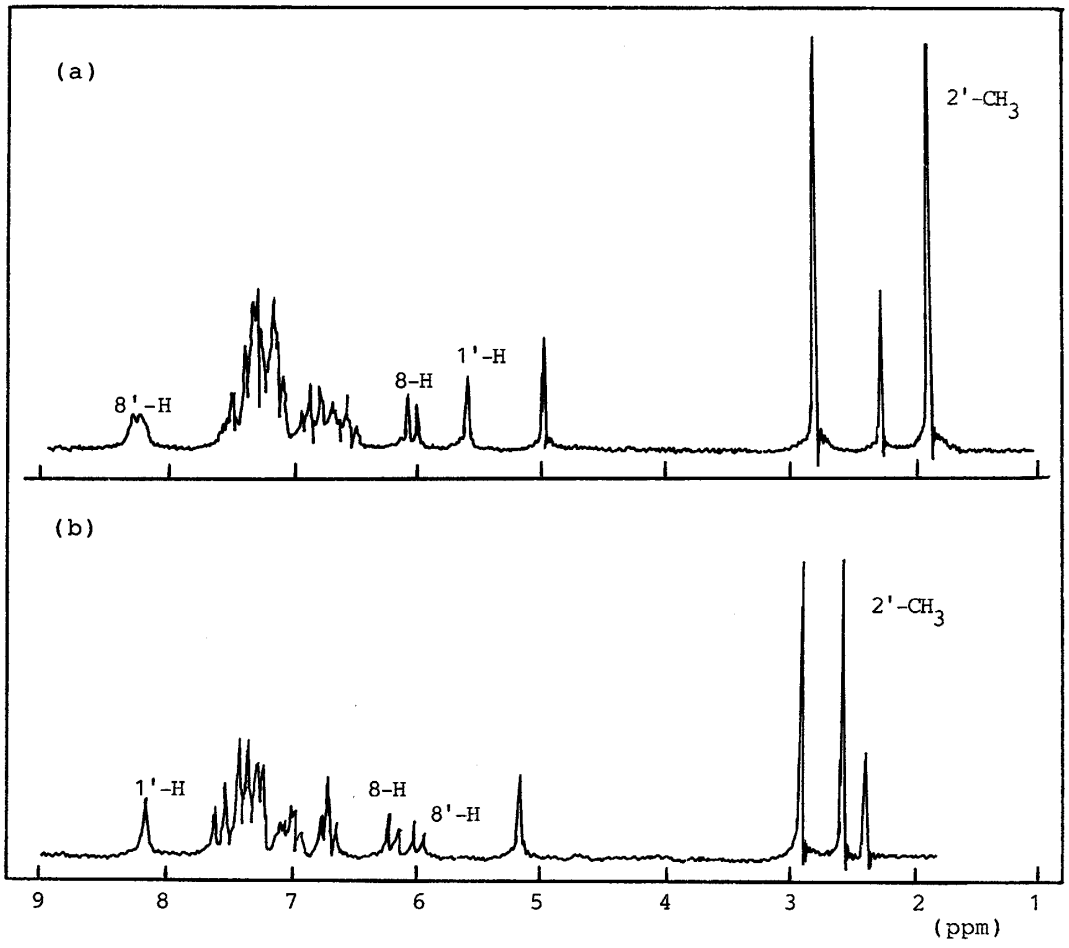


Fig. 2 ^{1}H-NMR spectra of **2a**-*erythro* isomer (a) and 2a-*threo* iomer (b) in $CDCl_3$

Now. we can show the C_2-form (*erythro*) of **2a** as follows (Fig.3). In the Fig. 3, the protons at 8- and 1'- positions are together located in a shielding zone of other fluorene ring. Thus, it is reasonable to assume that the two protons give the ^{1}H-NMR signals at the higher fields than usual aromatic protons. Similarly, CH_3-group at 2'- position may be given the NMR-signal at a higher field than usual aromatic methyl proton, because the CH_3-group is somewhat located in a shielding zone of the front fluorene ring. Whereas, the NMR-signals of 8'-proton and CH_3-group at 1-position may be given at the lower fields because the proton and the CH_3-group are together located in a deshielding zone of other fluorene ring.

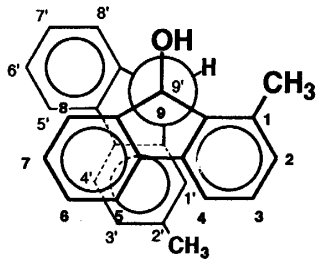


Fig. 3 C_2-form of **2a**

As shown in Fig. 2, **A**-form of **2a** gave the ^{1}H-NMR spectrum followed our above discussion. Thus, we concluded that **A**-form of **2a** was *erythro* form.

On the other hand, we could discuss the structure of D_1-form (*threo*) of **2a** in a similar manner as described above, and confirmed the structure of **B**- form of **2a** by its ^{1}H-NMR spectrum as shown in Fig.2. Thus, we concluded that **B**- form of **2a** was *threo* form. In Table 1, ^{1}H-NMR data of derivatives **2** and **3** have been illustrated as that of **A**- and **B**- form, individually.

Furthermore, we investigated the restricted rotation about the C(9)-C (9') bonds in these compounds by DNMR. However, any expected nonequivalent *gauche* conformers (C_1 for C_2, and D_2 for D_1) had never been observed in the range of about 150 ℃ to -60 ℃. That is, it turned out that the C_2- and D_1-conformers were considerably stable than the C_1- and D_2-conformers.

3. Experimental

All melting points are uncorrected. The ^{1}H- NMR spectra were recorded on a JEOL-MH-100 spectrometer. The chemical shifts are expressed in ppm, with TMS as an internal standard.

1,2'-Dimethyl-9-hydroxy-9,9'-bifluorenyl (2a). Typical Procedure for the Synthses of 2. A solution of 1-methylfluorenone (**4a**)[3] in dry ether was added into the 2-methyl-9-fluorenyllithium[1] which was prepared from phenyllithium and 2-methylfluorene in dry ether under nitrogen atmosphere. The mixture was refluxed for 20 min. After cooling, the solution was poured into dil. hydrochloric acid. Organic layer obtained was washed with water, dried with magnesium sulfate and distilled off in vacuo, leaving a residue was recrystallized from methanol to give **2a** as colorless prisms; yield 83 %, mp

190-197 ℃. Analytical data is shown in Table 2. By fractional recrystallization of **2a** with methanol, two isomers **2a-A** and **2a-B** were isolated; **2a-A**: mp 191-193 ℃, **2a-B**: mp 200-202 ℃ . ^{1}H-NMR data of these isomers are shown in Table 2.

1,2',7'-Trimethyl-9-hydroxy-9,9'-bifluorenyl (4a). Yield 80 %; colorless crystals; mp 201-202 ℃ (from methanol);
^{1}H NMR ($CDCl_3$) δ=1.96, 2.53 (6H, two s, 2'- and 7'-CH_3), 2.35(1H, s, 9-OH), 2.90(3H, s, 1-CH_3), 5.02(1H, s, 9'-H), 5.63(1H, s, 1'-H,) 6.12(1H, d, J=8Hz, 8-H), 6,5-7.3(10H, m, other arom. H), 8.18(1H, s, 8'-H). Found: C, 89.50; H, 6.25%. Calcd for $C_{29}H_{24}O$: C,89.66; H, 6.23%.

1,2',7'-Trimethyl-9'-hydroxy-9,9'-bifluorenyl (4b). Yield 71 %; colorless crystals; mp 210-211 ℃ (from methanol);
^{1}H-NMR($CDCl_3$) δ=2.00, 2.47 (6H, two s, 2'- and 7'-CH_3), 2. 17 (1H, s, 9'-OH), 2.66 (3H, s, 1-CH_3), 4.84(1H, s, 9-H), 5.88(1H. s, 1'-H), 6.08(1H, d, J=8Hz, 8-H), 6.5-7.5 (10H, m, other arom.H), 7.54(1H, s. 8'-H). Found: C, 89.45; H, 6.22 %. Calcd for $C_{29}H_{24}O$: C, 89.66; H, 6.23 %.

1,2',7'-Trimethyl-9,9'-bifluorenyl (5a). Yield 78 %; mp 211-213 ℃ (from methanol); ^{1}H- NMR($CDCl_3$) δ=1.96. 2.56(6H, two s, 2'- and 7'-CH_3), 2.75 (3H, s, 1-CH_3), 4.96 (1H, d, J=9Hz, 9-H), 5.00(1H, d, J=9Hz, 9'-H), 5.88(1H, s, 1'-H), 6.15 (1H, d, J=8Hz), 6.6-7.7(11H, m, other arom. H). Found: C, 93.26; H. 6.49 %. Calcd for $C_{29}.H_{24}$: C, 93.51 ; H. 6.49 %.

1,2'-Dimethyl-9,9'-bifluorenyl (3a). Typical Procedure for the Syntheses of 3. Hydroiodic acid (57 % , 1ml) was added into a solution of **2a** (0.5 g, 0.0013 mol) in acetic acid (20 mol), and the mixture was refluxed for 1 hr. After cooling, the solution was poured into water, and then free iodine was removed with sodium sulfite. Crude product obtained was extracted with benzene, washed with water, then with sodium carbonate solution. The organic layer was dried with magnesium sulfate and distilled off in vacuo. The residue was recrystallized from methanol to give **3a** as colorless crystals. Yield 88 %, mp 224-227 ℃ (a mixture of *erythro* and *threo* isomers). ^{1}H-NMR data of these isomers are shown in Table 1.

References

1) Part XXI of this series: A. Nishida, S. Nishiyama, S. Fujisaki and S. Kajigaeshi, *Mem. Fac. of Eng. Yamaguchi Univ.*, **43**, 265(1993).
2) S. Kajigaeshi, T. Akahoshi, Y. Tanaka, S. Fujisaki and M. Mashihara, *Nippon Kagaku Kaishi*, **1973**, 762.
3) S. Kajigaeshi, A. Nishida and S. Fujisaki, *Bull. Chem. Soc. Jpn.* **58**, 1967 (1985).
4) L. Chardonnens and R. Dousse, *Helv. Chim. Acta*, **50**, 321 (1967)
5) T. L. Fletcher, M. J. Namkung, Hsi- Lung Pan and W. H. Wetzel, *J. Org. Chem.*, **25**, 996 (1960).
6) N. Kharasch and T. C. Bruice, *J. Am. Chem. Soc.*, **73**, 3240 (1950).
7) K. Suzuki and S. Kajigaeshi, *Bull. Chem. Soc. Jpn.*, **35**, 408 (1962).
8) L. Horner and D. W. Baston, *Justus Liebigs Ann. der Chem.*, **1973**, 910.