  Bull. Chem. Soc. Jpn., 57, 1970—1975 (1984) [Vol. 57, No. 7

Restricted Rotation Involving the Tetrahedral Carbon. LIV. The Effects of 1-Substituents on the Barriers to Rotation in 9-(2-Methyl-1-naphthyl)fluorenes[1,2]

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(Received December 20, 1983)

A series of 1-substituted 9-(2-methyl-1-naphthyl)fluorenes, where the substituent is fluoro, chloro, bromo, or methyl, has been prepared and barriers to rotation in these compounds have been examined to investigate the substituent effects. The barrier is enhanced generally, if we go from the 1-substituent of a small size to that of a large size with an exception of the fluorine case: the 1-fluoro compound exhibits a lower barrier to rotation than the unsubstituted compound by *ca.* 0.5 kcal mol^{-1}. X-Ray crystallographic analysis suggests that, in the fluoro compound, the C_9(fluorene)-to-C_1(naphthalene) bond is abnormally long, although other compounds possess bonds of normal lengths. The low barrier to rotation in the fluoro compound relative to the unsubstituted is thus attributed to the raise of the ground state energy and insufficient raise of the transition state energy in the former compound.

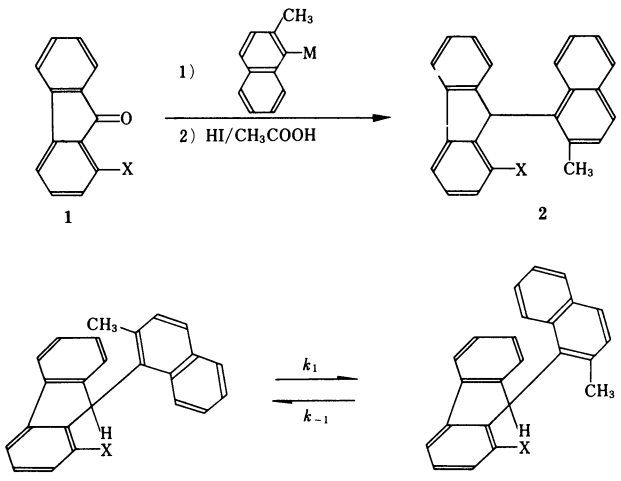
Although various stable rotamers of 9-arylfluorenes are isolated at room temperature, their barriers to rotation are usually less than 30 kcal mol^{-1} (1 cal=4.184 J).[3,4] The only exceptions to these are the reports by Ford *et al.*[5] and by Kajigaeshi and associates.[6] The former authors pointed out that the barrier to rotation in 1-methyl-9-(2-methyl-1-naphthyl)-fluorene (**2b**) was 33.3±0.3 kcal/mol at 166 °C, and the latters that of 32.8 kcal mol^{-1} at 170 °C in 1,2-benzo-annelated 9-(2-methyl-1-naphthyl)fluorene. These reports certainly suggest that the transition state for rotation about the C_9(fluorene)-to-C_1(naphthalene) bond is raised relative to the ground state because the substituent in the 1-position of the fluorene ring interacts strongly with the 2-methyl-1-naphthyl group in the transition state for rotation.

In this context, it will be of interest to see the effect of the 1-substituent in the fluorene ring on the barrier to rotation. At the outset, we prepared 1-fluoro-9-(1-naphthyl)fluorene and surprisingly found that the introduction of the fluoro substituent into the 1-position of the fluorene moiety reduced the barrier to rotation. This finding prompted us to reexamine the barriers to rotation in the parent compound, 9-(1-naphthyl)fluorene. The results shown in Table 1 clearly indicate that the barriers reported by others[7,8] were reproducible and confirm that the introduction of a fluorine atom to the 1-position of fluorene reduces the barrier height in the system of 9-(1-naphthyl)-fluorene.

In order to find generality of the trend in the barrier heights, we examined the barrier to rotation in 1-fluoro-9-(2-methyl-1-naphthyl)fluorene (**2c**). The barrier to rotation in **2c** was again lower than that reported for the parent compound.[7] Thus the reduction of the barrier height on introduction of a fluorine atom to the 1-position of fluorene seems to be a general practice.

Then it became of interest to examine the barriers in a series of 1-substituted 9-(2-methyl-1-naphthyl)fluorenes (**2**): what is the general tendency in affecting the barrier heights due to the presence of a 1-substituent in these compounds? This paper reports the results of the investigation and discusses the origin of the anomalous barrier heights in the fluoro compounds from the X-ray crystallographic data of **2c** and two related compounds.

The syntheses of the compounds in question were straightforward. 1-Substituted 9-fluorenones (**1**) were treated with 2-methyl-1-naphthyllithium or the corresponding Grignard reagent and the products were reduced to the desired compound (**2**). The rotational isomers of **2** were separated by chromatography. The stereochemistry of each rotamer was assigned by considering the chemical shifts of the methyl protons which is



X=H	*sp*-**2a**	*ap*-**2a**
X=CH_3	*ac**(*R**)-**2b**	*sc**(*S**)-**2b**
X=F	*ac**(*S**)-**2c**	*sc**(*R**)-**2c**
X=Cl	*ac**(*S**)-**2d**	*sc**(*R**)-**2d**
X=Br	*ac**(*S**)-**2e**	*sc**(*R**)-**2e**

TABLE 1. BARRIERS TO ROTATION IN 1-SUBSTITUTED 9-(1-NAPHTHYL)FLUORENES

1-substituent	T_c/°C	ΔG_c^*/kcal mol^{-1} a)	K b)
H	96	19.0	0.50
F	84	18.5	0.45

a) For the process from the more populated isomer to the less populated. b) Equilibrium constants at coalescence temperature: *ap*/*sp* for the unsubstituted compound and *sc*/*ac* for the fluoro compound.

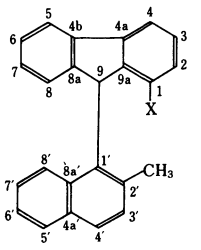
attached to the naphthalene nucleus in ^{1}H NMR spectra as are customarily done in other cases.

The rates of rotation in **2** together with equilibrium constants at various temperatures are summarized in Table 2 and activation parameters with relative rates of rotation in Table 3.

The equilibrium constants are very close to unity when **2** is a hydrocarbon irrespective of the substituent (H or methyl) in the 1-position of the fluorene ring. In contrast, if the 1-substituent is a halogen, a rotamer in which the 2-methyl group (in naphthalene) is over the fluorene ring is disfavored to some extent. This tendency is the largest when X is fluorine and equilibrium constants become closer to unity as the halogens become larger. The reason for this phenomenon is not well understood at the moment but could be a repulsive interaction between the 2-methyl (in naphthalene) and the fluorene groups and consequently the large deformation, as discussed in the crystal structure section.

The barriers to rotation about the C_9(fluorene)-to-C_1(naphthalene) bond indicate that they are enhanced as the bulkiness of the 1-substituent in the fluorene ring increases, except the case of fluorine. Therefore, the series of X=H, Cl, Br, and CH_3 is quite normal in the sense that the bulkier 1-substituent in the fluorene ring affects more the transition state of rotation than the ground state.

To shed light to the reason for the anomaly in the fluorine compound (**2c**), X-ray crystallography of *ac**(*S**)-**2c**[9] was carried out. The X-ray structures of **2a** and **2b** were also examined for comparison. Unfortunately, however, only *sc**(*S**) form of **2b** gave suitable crystals for the X-ray investigation, whereas *sp*-**2a** and *ac**(*S**)-**2c**, in which the 2-methyl groups are over the fluorene moiety, gave suitable crystals. Therefore, we may have to discuss with some reservations if we really compare the structures. The results are given in Tables 4 through 7. The nonhydrogen atoms are numbered or designated as shown below.



The first feature in the structures which we wish to discuss is the dihedral angles made by the naphthyl group and the C_9–H bond. Since we neglect the positions of hydrogens, the dihedral angles are given by the C–C–C planes in Table 6. The most apparent feature is that the naphthyl group does not bisect the C(8a)–C(9)–C(9a) angle, thus does not eclipse the C_9–H. This is interesting because, in solution chemistry, the eclipsing conformation about a C_{ar}–C_{aliph} bond is supposed to be often the energy minimum due to the fact that two equivalent groups in the geminal position give equivalent ^{1}H NMR chemical shifts when the internal rotation is frozen.[10] Although we have to discuss the difference carefully, because the conformation in the solid state is not nec-

Table 2. Rate constants of rotation and equilibrium constants in 1-substituted 9-(2-methyl-1-naphthyl)-fluorenes (**2**) in *o*-dichlorobenzene

1-substituent	Temp/°C	k_1/s^{-1}	K[a]
H	69.6	1.48×10^{-6}	1.14±0.02
	81.3	5.47×10^{-6}	
	102.0	4.15×10^{-5}	
	111.8	1.01×10^{-4}	
F	69.5	2.88×10^{-6}	1.52±0.04
	81.0	1.06×10^{-5}	
	102.0	7.76×10^{-5}	
	111.9	1.83×10^{-4}	
Cl	102.0	2.49×10^{-6}	1.43±0.03
	111.9	7.36×10^{-6}	
	132.6	2.82×10^{-5}	
	144.7	1.29×10^{-4}	
Br	111.6	3.68×10^{-6}	1.37±0.02
	132.6	2.82×10^{-5}	
	144.8	8.01×10^{-5}	
	156.4	1.86×10^{-4}	
CH_3	111.9	1.95×10^{-6}	1.12±0.02
	132.7	1.53×10^{-5}	
	144.7	4.31×10^{-5}	
	155.9	9.22×10^{-5}	

a) The equilibrium constants were constant within the error limit shown in the temperature range examined. K is *ap*/*sp*, *ac**(*R**)/*sc**(*S**), and *ac**(*S**)/*sc**(*R**), for **2a**, **2b**, and **2c**—**2e**, respectively.

Table 3. Activation parameters and relative rates of internal rotation in 1-substituted 9-(2-methyl-1-naphthyl)fluorenes (**2**) in *o*-dichlorobenzene

Substituent	ΔH^* / kcal mol^{-1}	ΔS^* / e.u.	ΔG^*(383 K) / kcal mol^{-1}	k(383 K) / s^{-1}	k_{rel}(383 K)
H	25.5±0.2	−11.2±0.6	29.7	8.53×10^{-5}	1.0
F	24.8±0.5	−11.6±1.5	29.3	1.54×10^{-4}	1.8
Cl	27.9±0.8	−10.3±0.8	31.8	5.70×10^{-6}	0.067
Br	28.1±0.9	−10.8±0.9	32.2	3.24×10^{-6}	0.038
CH_3[a]	28.2±1.5	−11.7±3.8	32.7	1.66×10^{-6}	0.019

a) These data give a free energy of activation which is in good agreement with that given by Ford *et al.* at 166 °C.[5]

Table 4. Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses and equivalent isotropic thermal parameters of 1-substituted 9-(2-methyl-1-naphthyl)fluorenes (**2**)

Atom	x	y	z	B_{eq}/Å^2
		***sp*-2a** (X=H)		
C(1)	11106(5)	3176(5)	4806(2)	4.6
C(2)	12107(6)	3553(5)	5282(2)	5.5
C(3)	13166(5)	2502(6)	5485(2)	5.1
C(4)	13238(5)	1034(5)	5209(2)	4.5
C(4a)	12226(4)	642(4)	4733(2)	3.6
C(4b)	11996(4)	-802(4)	4380(2)	3.6
C(5)	12754(5)	-2203(5)	4403(2)	4.4
C(6)	12259(6)	-3408(5)	4014(2)	5.2
C(7)	11086(6)	-3235(5)	3609(2)	5.5
C(8)	10317(5)	-1817(5)	3578(2)	4.0
C(8a)	10809(4)	-621(4)	3966(2)	3.6
C(9)	10145(4)	988(4)	4045(2)	3.4
C(9a)	11159(4)	1701(4)	4542(2)	3.4
C(1')	9799(4)	1989(4)	3748(2)	3.6
C(2')	10823(5)	2259(5)	3021(2)	4.2
C(3')	10459(6)	3212(5)	2484(2)	5.2
C(4')	9164(6)	3944(5)	2426(2)	5.1
C(4a')	8118(5)	3741(5)	2890(2)	4.3
C(5')	6777(6)	5741(5)	2845(2)	4.5
C(6')	5727(6)	4306(6)	3218(3)	6.0
C(7')	5992(5)	3298(6)	3793(2)	5.6
C(8')	7295(5)	2531(5)	3857(2)	4.4
C(8a')	8420(4)	2745(4)	3416(3)	3.5
CH_3	12326(6)	1586(6)	3064(3)	6.0
		***sc**(*S**)-2b** (X=CH_3)		
X	613(2)	6780(6)	393(2)	7.4
C(1)	1059(2)	5090(6)	420(1)	5.5
C(2)	1416(2)	4373(7)	-8(1)	7.3
C(3)	1855(2)	2840(7)	24(2)	7.8
C(4)	1972(2)	1973(6)	475(2)	6.7
C(4a)	1625(2)	2636(5)	903(1)	4.6
C(4b)	1649(2)	2003(4)	1426(1)	4.3
C(5)	2037(2)	592(5)	1654(2)	5.6
C(6)	1959(2)	319(5)	2165(2)	6.0
C(7)	1508(2)	1404(5)	2453(1)	5.5
C(8)	1111(2)	2814(4)	2233(1)	4.3
C(8a)	1194(2)	3102(4)	1719(1)	3.7
C(9)	875(2)	4618(4)	1395(1)	3.5
C(9a)	1165(2)	4165(5)	872(1)	4.1
C(1')	52(2)	4944(4)	1464(1)	3.4
C(2')	-185(2)	6524(4)	1685(1)	4.2
C(3')	-947(2)	6815(5)	1759(1)	5.1
C(4')	-1453(2)	5588(5)	1611(1)	5.2
C(4a')	-1234(2)	3978(5)	1373(1)	4.2
C(5')	-1758(2)	2703(5)	1201(1)	5.5
C(6')	-1549(2)	1162(5)	970(1)	5.8
C(7')	-794(2)	772(5)	907(1)	5.1
C(8')	-276(2)	1976(4)	1069(1)	4.2
C(8a')	-470(2)	3631(4)	1303(1)	3.4
CH_3	341(2)	8003(5)	1853(1)	5.7
		***ac**(*S**)-2c** (X=F)		
X	7949(2)	5816(2)	1602(2)	7.3
C(1)	6481(4)	6045(2)	1266(3)	4.4
C(2)	6081(4)	6827(2)	705(3)	5.3
C(3)	4592(4)	7059(2)	365(3)	5.3
C(4)	3527(4)	6523(2)	560(3)	4.7
C(4a)	3973(4)	5740(2)	1118(3)	4.1
C(4b)	3111(4)	5046(2)	1427(3)	4.3
C(5)	1593(4)	4978(2)	1272(3)	5.3
C(6)	1071(4)	4234(3)	1642(3)	6.4
C(7)	2040(5)	3563(3)	2158(3)	6.3
C(8)	3560(4)	3638(2)	2334(3)	5.5
C(8a)	4083(4)	4385(2)	1973(3)	4.3
C(9)	5676(4)	4612(2)	2053(3)	4.1
C(9a)	5477(4)	5501(2)	1496(3)	4.0
C(1')	6790(4)	4528(2)	3286(3)	4.2
C(2')	6795(4)	5098(2)	4163(3)	4.9
C(3')	7848(4)	4990(3)	5292(3)	5.9
C(4')	8855(4)	4343(3)	5515(3)	5.8
C(4a')	8870(4)	3734(2)	4663(3)	5.0
C(5')	9901(4)	3044(3)	4892(4)	6.3
C(6')	9877(4)	2437(3)	4080(5)	7.3
C(7')	8836(5)	2497(3)	2967(4)	7.3
C(8')	7838(4)	3172(2)	2701(3)	5.7
C(8a')	7815(4)	3814(2)	3515(3)	4.4
CH_3	5729(5)	5842(3)	4040(3)	6.3

Table 5. Bond lengths and bond angles

	***sp*-2a**	***sc**(*S**)-2b**	***ac**(*S**)-2c**
Bond length l/Å			
C(1)-X	——	1.494(6)	1.367(9)
C(1)-C(2)	1.416(6)	1.407(5)	1.383(9)
C(1)-C(9a)	1.385(8)	1.392(5)	1.358(6)
C(2)-C(3)	1.372(15)	1.392(7)	1.386(10)
C(3)-C(4)	1.394(8)	1.370(6)	1.379(6)
C(4)-C(4a)	1.397(6)	1.385(5)	1.389(6)
C(4a)-C(4b)	1.463(6)	1.460(5)	1.464(6)
C(4a)-C(9a)	1.395(15)	1.411(5)	1.402(10)
C(4b)-C(5)	1.397(15)	1.399(5)	1.391(6)
C(4b)-C(8a)	1.397(8)	1.395(4)	1.400(10)
C(5)-C(6)	1.395(6)	1.374(6)	1.380(7)
C(6)-C(7)	1.394(9)	1.376(5)	1.400(10)
C(7)-C(8)	1.386(15)	1.396(4)	1.390(7)
C(8)-C(8a)	1.389(6)	1.385(4)	1.381(6)
C(8a)-C(9)	1.505(13)	1.527(4)	1.518(5)
C(9)-C(9a)	1.531(7)	1.517(4)	1.520(5)
C(9)-C(1')	1.518(7)	1.516(4)	1.539(20)
C(1')-C(2')	1.390(1)	1.381(4)	1.377(5)
C(1')-C(8a')	1.437(6)	1.431(4)	1.441(6)
C(2')-C(3')	1.432(8)	1.415(5)	1.427(19)
C(2')-CH_3	1.509(7)	1.520(5)	1.508(6)
C(3')-C(4')	1.358(7)	1.352(5)	1.352(7)
C(4')-C(4a')	1.406(15)	1.407(5)	1.397(6)
C(4a')-C(5')	1.432(7)	1.417(5)	1.416(6)
C(4a')-C(8a')	1.423(7)	1.423(4)	1.440(20)
C(5')-C(6')	1.371(15)	1.350(5)	1.352(7)
C(6')-C(7')	1.403(8)	1.410(5)	1.405(20)
C(7')-C(8')	1.380(7)	1.366(5)	1.379(7)
C(8')-C(8a')	1.428(15)	1.419(4)	1.402(5)
Bond angle ϕ/°			
C(2)-C(1)-X	——	121.9(3)	118.2(6)
C(2)-C(1)-C(9a)	117.3(7)	116.2(4)	122.8(5)
C(9a)-C(1)-X	——	121.9(3)	119.0(3)
C(1)-C(2)-C(3)	120.8(4)	121.5(4)	118.2(6)
C(2)-C(3)-C(4)	121.9(6)	121.7(4)	121.3(3)
C(3)-C(4)-C(4a)	117.8(7)	118.2(4)	118.7(5)
C(4)-C(4a)-C(4b)	130.7(6)	130.2(3)	130.9(4)
C(4)-C(4a)-C(9a)	120.4(4)	120.6(3)	121.0(6)
C(4b)-C(4a)-C(9a)	109.0(5)	109.2(3)	108.0(3)
C(4a)-C(4b)-C(5)	131.1(4)	131.6(3)	130.7(4)
C(4a)-C(4b)-C(8a)	108.5(7)	108.7(3)	108.8(3)
C(5)-C(4b)-C(8a)	120.3(6)	119.7(3)	120.5(6)
C(4b)-C(5)-C(6)	118.7(4)	118.8(3)	118.4(5)
C(5)-C(6)-C(7)	120.2(6)	121.3(4)	121.1(4)
C(6)-C(7)-C(8)	121.5(6)	121.0(3)	120.6(6)
C(7)-C(8)-C(8a)	118.2(4)	117.9(3)	118.3(5)
C(4b)-C(8a)-C(8)	121.1(6)	121.3(3)	121.2(3)
C(4b)-C(8a)-C(9)	110.7(6)	110.1(2)	110.7(5)

Table 5. Continued

	sp-**2a**	*sc**(*S**)-**2b**	*ac**(*S**)-**2c**
Bond angle ϕ/°			
C(8)-C(8a)-C(9)	128.2(3)	128.5(3)	128.1(5)
C(8a)-C(9)-C(9a)	102.0(4)	102.4(2)	101.4(6)
C(8a)-C(9)-C(1')	115.4(6)	115.0(2)	114.4(9)
C(9a)-C(9)-C(1')	119.5(4)	119.0(2)	117.3(3)
C(9)-C(1')-C(2')	121.1(5)	119.9(3)	121.7(4)
C(9)-C(1')-C(8a')	120.0(9)	120.8(3)	118.1(6)
C(2')-C(1')-C(8a')	118.8(6)	119.3(3)	120.2(8)
C(1')-C(2')-C(3')	119.6(5)	120.0(3)	119.5(4)
C(1')-C(2')-CH_3	122.7(6)	122.4(3)	124.8(8)
C(3')-C(2')-CH_3	117.7(9)	117.6(3)	115.6(6)
C(2')-C(3')-C(4')	121.8(9)	121.5(3)	121.2(6)
C(3')-C(4')-C(4a')	120.2(6)	120.5(3)	121.4(8)
C(4')-C(4a')-C(5')	120.7(6)	121.3(3)	121.9(8)
C(4')-C(4a')-C(8a')	119.5(5)	119.2(3)	119.1(4)
C(5')-C(4a')-C(8a')	119.9(9)	119.5(3)	118.9(6)
C(4a')-C(5')-C(6')	121.2(6)	121.4(3)	121.8(9)
C(5')-C(6')-C(7')	119.7(6)	120.0(3)	119.8(4)
C(6')-C(7')-C(8')	120.5(9)	120.0(3)	119.9(7)
C(7')-C(8')-C(8a')	121.7(6)	122.0(3)	122.3(8)
C(1')-C(8a')-C(8')	122.9(5)	123.5(3)	124.4(8)
C(1')-C(8a')-C(4a')	120.1(9)	119.4(3)	118.5(6)
C(8')-C(8a')-C(4a')	117.0(5)	117.1(3)	117.1(4)

essarily retained in solution, it is possible that, by ^{1}H NMR, the rapid exchange $+ap \rightleftharpoons -ap$ *or* $+sp \rightleftharpoons -sp$ cannot be detected.[11] Another common feature of interest in the structures is concerned with C(9) and its vicinity: the C(8a)–C(9) and C(9)–C(9a) distances are very long and the C(8a)–C(9)–C(9a) bond angle is very small relative to those in fluorene.[12] These must be the results of steric strain which is eased by lengthening the bonds and by sharpening the angle.

The conformations about the C(9)–C(1′) bond in *ac**(*S**)-**2c** are interesting. The methyl group which is over the fluorene ring is close to C(1), which bears the 1-substituent, rather than to C(8a). The cause for this phenomenon is not clear at the moment.

The molecular structures of *sp*-**2a** and *sc**(*S**)-**2b** are quite normal, except the atomic positions close to C(9), as pointed out above. The bond distances and bond angles are very close to those reported for fluorene[12] and 1,5-dimethylnaphthalene[13] except some points discussed above and below. The abnormality is caused because of the presence of the 2′-methyl group over the fluorene ring and also because of the fact that the naphthyl group does not eclipse the C(9)–H bond. The steric congestion in *sp*-**2a** is relieved by lengthening the C(9)–C(9a) bond which is close to the 2′-methyl group. Thus the C(9)–C(9a) bond in *sp*-**2a** is longer than the C(8a)–C(9) (Table 5). This explanation is partially supported by the fact that the lengths of C(8a)–C(9) and C(9)–C(9a) bonds in *sc**(*S**)-**2b** are close to each other. Due to the small size of the π-system relative to the methyl, the congestion in *sc**(*S**)-**2b** must be small.

Table 7. Some distances (Å) between nonbonded atoms in proximity of steric crowding

Atom 1	Atom 2	*sp*-**2a**	*sc**(*S**)-**2b**	*ac**(*S**)-**2c**
X	C(1′)	—	3.299(5)	3.263(14)
CH_3[a]	C(8a)	3.328(21)	3.284(4)	3.369(23)
CH_3[a]	C(9a)	3.058(19)	3.123(4)	3.044(7)
CH_3[a]	C(1)	3.654(13)	3.762(5)	3.632(15)
CH_3[a]	C(8)	4.108(21)	4.026(5)	4.188(21)

a) Atom 1 is C(8a′) in the case of *sc**(*S**)-**2b**.

Some nonbonded distances between atoms in the congested sites are compiled in Table 7. The X–C(1′) distances in *sc**(*S**)-**2b** and *ac**(*S**)-**2c** are shorter than or very close to the sum of the van der Waals radii of the atom and/or the groups concerned. This strain seems to be distributed widely over the molecules. The small difference in distances CH_3–C(8a) and CH_3–C(9a) together with the same trend in the dihedral angle in *sc**(*S**)-**2b** relative to others is a reflection of the fact that a π-system is smaller in size than a methyl. As far as these nonbonded distances concern, *sp*-**2a** and *ac**(*S**)-**2c** take similar structures.

The structure of the fluoro compound, *ac**(*S**)-**2c**, shows some interesting features. The bond distance of C(1)–C(9a) is abnormally short, compared with those in other compounds, and that of C(9)–C(1′) abnormally long, although the latter involves a large error. It is tempting to consider that, due to the electronic effect of the fluorine substituent, the bond C(1)–C(9a) is shortened and this effect also restricts the lengthening of the C(9)–C(9a) bond: the latter bond is very long in *sp*-**2a** because of the steric effect but is almost normal in *ac**(*S**)-**2c**. The strain caused by these bond distances seems to be released by lengthening the C(9)–C(1′) bond together with widening the C(9)–C(1′)–C(2′) and C(1′)–C(2′)–CH_3 angles and contracting the C(9)–C(1′)–C(8a′) and C(3′)–C(2′)–CH_3 angles. We therefore conclude that the relatively low barrier to rotation in **2c** is caused by the strain in the ground state, whereas the transition state energy is not raised to a great extent.

Experimental

9-(2-Methyl-1-naphthyl)fluorene (2a). Rotamers were obtained as reported in a previous paper.[14]

1-Fluoro-9-(2-methyl-1-naphthyl)fluorene (2c). To a stirred solution of 2-methyl-1-naphthylmagnesium bromide, prepared from 1.3 g (5.9 mmol) of 1-bromo-2-methylnaphthalene, 0.14 g (5.8 mmol) of magnesium, and 9 mL of dry tetrahydrofuran under a nitrogen atmosphere, 0.97 g (4.9 mmol) of 1-fluoro-9-fluorenone (**1**:X=F)[15] was added at room temperature. The mixture was heated under reflux for 1.5 h with stirring, cooled and decomposed with

Table 6. Dihedral angles (degree) involving the naphthyl group in **2**

Plane 1	Plane 2	*sp*-**2a**	*sc**(*S**)-**2b**	*ac**(*S**)-**2c**
C(2′)-C(1′)-C(9)	C(1′)-C(9)-C(8a)	71.7	67.7	71.3
C(2′)-C(1′)-C(9)	C(1′)-C(9)-C(9a)	50.7	54.3	47.1

18 mL of 25% aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was submitted to chromatography on silica gel (3:1 hexane–benzene eluent). The product was dissolved in 35 mL of acetic acid and heated with 8.7 mL of 57% hydriodic acid for 3 h at 60 °C. The mixture was poured into a cold solution of sodium hydrogensulfite. The organic product was extracted with dichloromethane. The extract was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the product was separated by silica gel chromatography (hexane eluent). The *ac**(*S**) form was eluted first and then *sc**(*R**) form followed. The combined yield of the both forms was 0.91 g (57% based on the amount of 1-fluoro-9-fluorenone).

*ac**(*S**), mp 159—160 °C. Found: C, 89.02; H, 5.16%. Calcd for $C_{24}H_{17}F$: C, 88.86; H, 5.28%. ^{1}H NMR ($CDCl_3$) δ =1.38 (3H, s), 6.27 (1H, s), 6.9—7.9 (12H, m), 8.53 (1H, d, J=8 Hz). ^{19}F NMR ($CDCl_3$, ppm from C_6F_6): 44.2 (dd, J=9.3 and 4.5 Hz).

*sc**(*R**), mp 140—141 °C. Found: C, 89.15; H, 5.07%. Calcd for $C_{24}H_{17}F$: C, 88.86; H, 5.28%. ^{1}H NMR ($CDCl_3$), δ=2.86 (3H, s), 5.86 (1H, s), 6.44 (1H, d, J=9 Hz), 6.8—8.0 (12H, m). ^{19}F NMR ($CDCl_3$, ppm from C_6F_6): 42.7 (dd, J=9.3 and 4.5 Hz).

*1-Chloro-9-(2-methyl-1-naphthyl)fluorene (**2d**).* A solution of 2-methyl-1-naphthyllithium was prepared from 3.71 g (16.8 mmol) of 1-bromo-2-methylnaphthalene and 0.29 g of lithium in 16.8 mL of ether by stirring the mixture for 1 h at room temperature. To a 7.3 mL portion of the solution was added 1.25 g (5.8 mmol) of 1-chloro-9-fluorenone (**1**:X=Cl)[16] and the mixture was heated under reflux for 1 h with stirring. After the mixture was coold, it was treated similarly as above. The product was reduced with hydriodic acid by stirring a solution prepared as above for 15 h at room temperature. The total yield of **2d** was 57% based on the amount of 1-chloro-9-fluorenone used.

*ac**(*S**), mp 197—198 °C. Found: C, 84.29; H, 4.79; Cl, 10.49%. Calcd for $C_{24}H_{17}Cl$: C, 84.57; H, 5.03; Cl, 10.40%. ^{1}H NMR ($CDCl_3$) δ=1.35 (3H, s), 6.22 (1H, s), 7.0—7.9 (12H, m), 8.55 (1H, d, J=8 Hz).

*sc**(*R**), mp 186—187 °C. Found: C, 84.82; H, 4.79; Cl, 10.29%. Calcd for $C_{24}H_{17}Cl$: C, 84.57; H, 5.03; Cl, 10.40%. ^{1}H NMR ($CDCl_3$): δ=2.91 (3H, s), 5.80 (1H, s), 6.42 (1H, d, J=9 Hz), 6.8—8.0 (12H, m).

*1-Bromo-9-(2-methyl-1-naphthyl)fluorene (**2e**)* was prepared similarly as described in the preparation of the 1-chloro compound (**2d**). The yield was 32% based on the amount of 1-bromo-9-fluorenone (**1**:X=Br).[16]

*ac**(*S**), mp 192—193 °C. Found: C, 74.96; H, 4.39; Br, 21.06%. Calcd for $C_{24}H_{17}Br$: C, 74.82; H, 4.45; Br, 20.74%. ^{1}H NMR ($CDCl_3$) δ=1.34 (3H, s), 6.16 (1H, s), 6.9—8.0 (12H, m), 8.57 (1H, d, J=9 Hz).

*sc**(*R**), mp 189—190 °C. Found: C, 74.88; H, 4.36; Br, 21.02%. Calcd for $C_{24}H_{17}Br$: C, 74.82; H, 4.45; Br, 20.74%. ^{1}H NMR ($CDCl_3$) δ=2.74 (3H, s), 5.74 (1H, s), 6.42 (1H, d, J=9 Hz), 6.8—8.0 (12H, m).

*1-Methyl-9-(2-methyl-1-naphthyl)fluorene (**2b**)* rotamers were already prepared by Ford *et al.*[5] with a different method from that described above. These were also prepared as above in 56% yield based on 1-methyl-9-fluorenone (**1**:X=CH_3)[5,17] used.

*ac**(*R**), mp 152—153 °C (lit,[5] 152—153.5 °C). Found: C, 93.63; H, 6.03%. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, s), 1.72 (3H, s), 6.12 (1H, s), 6.9—7.9 (12H, m), 8.58 (1H, d, J=9 Hz).

*sc**(*S**), mp 195—196 °C (lit,[5] 189—191 °C). Found: C, 93.77; H, 6.11%. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. ^{1}H NMR ($CDCl_3$) δ=1.71 (3H, s), 2.84 (3H, s), 5.70 (1H, s), 6.47 (1H, d, J=8 Hz), 6.8—8.0 (12H, m).

1-Fluoro-9-(1-naphthyl)fluorene, mp 109.0—110.5 °C, was prepared similarly as described in the preparation of **2c**. Found: C, 89.27; H, 4.71%. Calcd for $C_{23}H_{15}F$: C, 89.01; H, 4.87%. ^{1}H NMR ($CDCl_3$) δ=5.40 (2/3H, s), 6.06 (1/3H, s), 6.5—7.9 (13 1/3H, m), 8.43 (2/3H, br d).

9-(1-Naphthyl)fluorene was prepared according to the published method.[7]

Kinetic Measurement of Internal Rotation by Dynamic NMR. A sample was dissolved in hexachlorobutadiene to make up a *ca.* 5% solution. The temperature was read by the chemical shift differences of the ethylene glycol protons. The free energy of activation was calculated by the graphical method.[18]

Kinetic Measurement of Internal Rotation by Classical Method. Each pure rotamer (25—30 mg), *sp*-**2a** and other corresponding forms, was dissolved in 0.45 mL of *o*-dichlorobenzene. The solution was placed in an NMR sample tube and oxygen was purged from the solution by bubbling dry nitrogen gas for some time. The tube was sealed and was heated by immersing the tube in an appropriate boiling-solvent bath. The ratio of rotational isomers was determined by ^{1}H NMR spectroscopy at appropriate intervals and the equilibrium constant was obtained by heating the solution for a long enough time. The rate constants were calculated by assuming reversible first order kinetics. Activation parameters were obtained by putting these rate constants into the Eyring equation.

Spectral Measurement. ^{1}H NMR spectra were recorded either on a Hitachi R-20B, which operates at 60 MHz, or a Varian EM-390 spectrometer which operates at 90 MHz. ^{19}F NMR spectra were obtained with the Varian EM-390 spectrometer operating at 84.67 MHz.

X-Ray Crystallography. Crystals of *sp*-9-(2-methyl-1-naphthyl)fluorene (**2a**), *ac**(*S**)-1-fluoro-9-(2-methyl-1-naphthyl)fluorene (**2c**), and *sc**(*S**)-1-methyl-9-(2-methyl-1-naphthyl)fluorene (**2b**) were grown from hexane–benzene. The suitable crystals were mounted on a Rigaku AFC-M diffractometer and the intensity data of $|F_o| \geq 3\sigma|F_o|$ were collected using Cu $K\alpha$ radiation of 1.54180 Å wave length within the range of $2\theta \leq 57°$. Total reflections used for the analysis were 2011, 2335, and 2352 for *sp*-**2a**, *sc**(*S**)-**2b**, and *ac**(*S**)-**2c**, respectively.

The crystal data were as follows. *sp*-9-(2-Methyl-1-naphthyl)fluorene: $C_{24}H_{18}$, F. W. 306.41, monoclinic, space group $P2_1/N$, a=9.264(2) Å, b=8.621(2) Å, c=21.083(7) Å, β=91.53(2)°, z=4, D_C=1.21 g/cm^3.

*ac**(*S**)-1-Fluoro-9-(2-methyl-1-naphthyl)fluorene: $C_{24}H_{17}F$, F. W.=324.40, monoclinic, space group $P2_1/C$, a=9.438(4) Å, b=15.514(6) Å, c=12.032(6) Å, β=107.79(2)°, z=4, D_C= 1.28 g/cm^3.

*sc**(*S**)-1-Methyl-9-(2-methyl-1-naphthyl)fluorene: $C_{25}H_{20}$, F. W. 320.41, primitive orthorhombic, space group Pbcn, a=18.164(4) Å, b=7.414(2) Å, c=26.431(6) Å, z=8, D_C= 1.20 g/cm^3.

The structures were solved by the direct method. All the positional and thermal parameters were refined by the least-squares method. The final R values for *sp*-**2a**, *sc**(*S**)-**2b**, and *ac**(*S**)-**2c** were 7.6, 6.5, and 7.0%, respectively.

We wish to thank Rigaku Denki Company for the rent of an AFC-M machine which made this study possible. We also thank Mr. Toshihiko Hori and Miss Yukiko Takagi of the same company for the technical assistance.

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