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Rotational Isomerism in Fluorene Derivatives. X.[1] The Conformational Equilibria of 9-Substituted 9-(2-Methylthiophenyl)- and 9-Substituted 9-(2-Methylsulfinylphenyl)fluorene Derivatives

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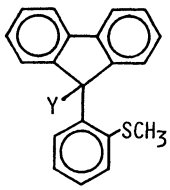
Several 9-substituted 9-(2-methylthiophenyl)fluorene derivatives and their oxidation products, 9-substituted 9-(2-methylsulfinylphenyl)fluorene derivatives were prepared. Each equilibrium constant was investigated and the conformational equilibria *ap* ⇄ *sp* of these compounds were discussed on the basis of nonbonding intramolecular interactions (attraction or repulsion) between 2-substituents in phenyl moieties (methylthio or methylsulfinyl) and fluorene ring or 9-substituents. It was found that the conformational equilibria were effected by the electronic properties of methylthio and methylsulfinyl groups. Kinetic data for internal rotation of a few compounds were shown.

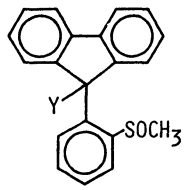
9-(2-Substituted phenyl)fluorene derivatives have been the subject of recent interest because of their high barriers to rotation about the C(9)-C(Ar) bond; many important stereochemical effects have been found in these systems.[2,3] We have also investigated the restricted rotation about the C(9)-C(Ar) bonds in 9-substituted 9-(2-methylphenyl)fluorene derivatives[4] and 9-(2-methoxyphenyl)fluorene derivatives.[5] In the present paper, we wish to report on the syntheses of some 9-substituted 9-(2-methylthiophenyl)fluorene derivatives and their oxidation products, 9-substituted 9-(2-methylsulfinylphenyl)fluorene derivatives, and to discuss the conformational equilibria of these compounds on the basis of nonbonding intramolecular interactions between 9-substituents and the 2-methylthio or 2-methylsulfinyl group.

Results and Discussion

Preparation of 9-Substituted 9-(2-Methylthiophenyl)-fluorene Derivatives. The treatment of fluorenone with 2-methylthiophenyllithium, which was prepared by the reaction of 2-methylthiobromobenzene[6] and butyllithium in ether, followed by hydrolysis, afforded 9-(2-methylthiophenyl)-9-fluorenol (**1**). Bubbling hydrogen bromide into a solution of **1** in acetic acid gave 9-bromo-9-(2-methylthiophenyl)fluorene (**2**); then, **2** was refluxed in methanol or ethanol to give 9-methoxy- (**3a**) or 9-ethoxy-9-(2-methylthiophenyl)-fluorene (**3b**), respectively. The reduction of **1** with hydriodic acid gave 9-(2-methylthiophenyl)fluorene (**4**). 9-Lithio compound **5** was obtained from **4** and butyllithium, and then converted directly to 9-methyl- (**6a**) or 9-ethyl-9-(2-methylthiophenyl)fluorene (**6b**) by treating with methyl iodide or ethyl iodide, respectively. 9-(2-Methylthiophenyl)-9-fluorenecarboxylic acid (**7**) was prepared by the treatment of **5** with Dry Ice in ether. After heating **7** with thionyl chloride at 50 °C, methanol was added to afford 9-methoxycarbonyl-9-(2-methylthiophenyl)fluorene (**8**). Upon continuous heating of **7** with thionyl chloride at 80 °C, a ring compound, spiro[benzo[*b*]thiophene-3(2*H*),9′-fluoren]- 2-one (**10**) was obtained. 9-Acetyl- (**9a**) and 9-benzoyl-9-(2-methylthiophenyl)fluorene (**9b**) were obtained by the treatment of **5** with acetic anhydride and benzoyl chloride in ether, respectively. 9-Substituted 9-(2-methylthiophenyl)fluorene derivatives **1**—**9** are shown in Scheme 1.



	Y
1	OH
2	Br
3a	OCH_3
3b	OC_2H_5
4	H
6a	CH_3
6b	C_2H_5
7	COOH
8	$COOCH_3$
9a	$COCH_3$
9b	COPh



	Y
11	OH
12a	OCH_3
12b	OC_2H_5
13	H
14	CH_3
15a	$COCH_3$
15b	COPh

Scheme. 1.

Preparation of 9-Substituted 9-(2-Methylsulfinylphenyl)fluorene Derivatives. Some of the 9-substituted 9-(2-methylthiophenyl)fluorene derivatives were converted to 9-substituted 9-(2-methylsulfinylphenyl)-fluorene derivatives by oxidation with nitric acid (d=1.38). That is, 9-(2-methylsulfinylphenyl)-9-fluorenol (**11**) was prepared by the reaction of **1** with nitric acid in acetic acid at 10—20 °C. In this case, when the reaction temperature was raised to 50 °C, a ring closed compound, spiro[3*H*-2,1-benzoxathiole-3,9′-fluorene] 1-oxide (**16**), was obtained. The reactions of **3a** and **3b** with nitric acid in acetic acid at 10—20 °C afforded 9-methoxy- (**12a**) and 9-ethoxy-9-(2-methylsulfinylphenyl)fluorene (**12b**), respectively. Then, **4** was treated with nitric acid under the same reaction conditions to give 9-(2-methylsulfinylphenyl)fluorene (**13**). Furthermore, the oxidation of **6a** by nitric acid was

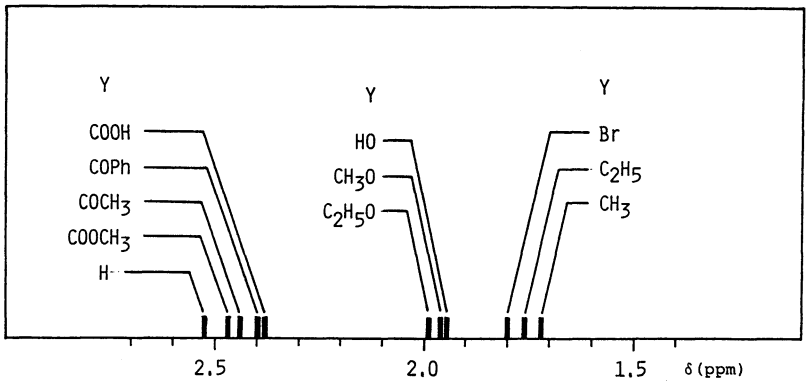


Fig. 1. The δ values for 2-SCH_3 of 9-substituted 9-(2-methylthiophenyl)fluorenes in $CDCl_3$ at room temperature.

Table 1. Oxidation of 9-Substituted 9-(2-Methylthiophenyl)fluorenes by Nitric Acid (d=1.38)

Material (2.0 mmol)	Reaction condition		Solvent (10 ml)	Product	Yield
	Time/h	Temp/°C			%
1	3	10—20	AcOH	**11**	75
1	1	150	AcOH	**16**	40
3a	5	10—20	AcOH	**12a**	93
3b	3	10—20	AcOH	**12b**	33
4	7	10—20	AcOH	**13**	82
6a	5	35—45	AcOH	**14**	78
9a	8	35—40	AcOH	**15a**	21
9b	24	40	AcOH	**15b**	12

carried out at 35—45 °C in acetic acid to afford 9-methyl-9-(2-methylsulfinylphenyl)fluorene (**14**). Reactions of **9a** and **9b** with nitric acid in acetic acid were carried out at 35—45 °C to give 9-acetyl-(**15a**) and 9-benzoyl-9-(2-methylsulfinylphenyl)fluorene (**15b**), respectively. These results are shown in Table 1.

Conformational Equilibria of 9-Substituted 9-(2-Methylthiophenyl)fluorene Derivatives. Previously, we discussed the conformations of 9-substituted 9-(2-methylphenyl)- and 9-substituted 9-(2-methoxyphenyl)fluorene derivatives on the basis of their 2-methyl and 2-methoxyl signals in ^1H NMR at low or room temperature.

In this case, the conformations of 9-(2-methylthiophenyl)fluorene derivatives were investigated on the basis of 2-methylthio signals in ^1H NMR at 50—40 °C. The NMR data for these signals are illustrated in Fig. 1. These compounds can be clearly classified into three groups: The first group includes compounds **2**, **6a**, and **6b** in which the signals for methylthio groups appear at a high field; the second includes compounds, **4**, **7**, **8**, **9a**, and **9b** in which the signals for methylthio groups are observed in a low field; the third contains the compounds, **1**, **3a**, and **3b** in which the signals for methylthio groups are found in a middle field.

The compounds that belong to the third group (9-substituents: OH, OCH_3, OC_2H_5) showed a broad singlet for methylthio protons at room temperature. As

ap-form *sp*-form

Y: OH, OCH_3, OC_2H_5

Fig. 2. Isomerization processes between *sp* and *ap* forms in **1**, **3a**, and **3b**.

the temperature was lowered, these signals gradually changed to broad two singlets; then, the signal of **1** showed two sharp singlets at δ 1.88 and 2.55 (2.0 : 1) at −30 °C, whereas that of **3a** showed two sharp singlets at δ 1.89 and 2.51 ppm (2.3 : 1) at −30 °C. The methylthio signal at the higher field corresponds to a conformation of the *ap*-form and the other at a lower field to that of the *sp*-form. It is known that the 2-substituent of the *ap* conformation is located in a shielding zone of the fluorene ring. Thus, the substituent gives an ^1H NMR signal at a higher field than that of the *sp* conformation, which is located in a deshielding zone of the fluorene ring. We have already reported that in 9-(2-methoxyphenyl)-9-fluorenol the *sp*-form was only observed because of its high stabilization, which was caused by an intramolecular hydrogen bond between the oxygen atom of the 2-methoxyl group and the hydrogen atom of the 9-hydroxyl group. However, in compound **1**, the hydrogen bond between the sulfur atom of the 2-methylthio group and the hydrogen atom of the 9-hydroxyl group could not be recognized by its IR spectra in several solvents. This may be due to the weakness of the electronegativity of the sulfur atom compared with that of the oxygen atom. The steric repulsion between the methylthio group and the hydroxyl group may unstabilize the *sp*-form of **1**. After all, third-group compounds predominantly existed as the *ap*-form (Fig. 2).

Furthermore, the rotational barriers about the C(9)–C(Ar) bonds in **1** and **3a** were obtained by line-shape analyses of methylthio signals in their DNMR spec-

Table 2. Activation Free Energies for Rotation about C(9)-(Ar) Bonds and *ap*/*sp* Ratios of the Compounds **1**—**15**

9-Substituent	2-SCH_3				2-$SOCH_3$			
	Compd.	$\Delta G^{\neq}_{sp\to ap}$[a] kcal mol^{-1}	$\Delta G^{\neq}_{ap\to sp}$[a] kcal mol^{-1}	$K(ap/sp)$	Compd.	$\Delta G^{\neq}_{sp\to ap}$[a] kcal mol^{-1}	$\Delta G^{\neq}_{ap\to sp}$[a] kcal mol^{-1}	$K(ap/sp)$
OH	**1**	14.0	14.3	2.0/1	**11**	14.3	13.5	1/4.0
OCH_3	**3a**	13.6	14.1	2.3/1	**12a**	14.5	12.9	1/15
H	**4**			*sp*[b]	**13**	15.5	15.3	1/1.5
Br	**2**			*ap*[c]	—			
R	**6**[d]			*ap*[c]	**14**[e]			*ap*[c]
COR	**7**—**9**[f]			*sp*[b]	**15**[g]			*sp*[b]

a) 1 cal=4.18 J. b) *sp*-Form was predominant. c) *ap*-Form was predominant. d) R=CH_3, C_2H_5. e) R=CH_3. f) R=OH, OCH_3, CH_3, Ph. g) R=CH_3, Ph.

Table 3. NMR Spectral Data of 9-Substituted 9-(2-Methylsulfinylphenyl)fluorene Derivatives **11**—**15** at Room Temperature

Compd.	NMR ($CDCl_3$): δ/ppm			
	$SOCH_3$	6-H	9-Substituent	Aromatic proton
11	2.52br.s		4.10br.s	6.22—8.18m
12a	2.93br.s	6.45br.d	2.93s	7.00—8.20m
12b	3.00br.s	6.74br.s	1.14t 3.18q	7.04—8.03m 8.42d
13	1.79br.s 3.00br.s	6.62br.d	5.35br.s	7.02—7.94m 8.24d
14	1.60s		1.82s	7.00—8.10m
15a	2.85s	6.66d	1.73s	7.0—8.01m 8.23d
15b	2.98s	6.62d		6.90—8.04m 8.24d

tra.[7] The results are tabulated together with those of compounds in which the equilibria were onesided, in Table 2.

In first-group compounds (Y: Br, CH_3, C_2H_5), the chemical shifts for these methylthio protons appeared at δ 1.72—1.80. These chemical shifts have been approximated to those for the *ap*-methylthio proton (roughly δ=1.9) in third-group compounds; these methylthio signals do not split, even at −50 °C. These results indicate that a steric repulsion between the 9-substituents and the 2-methylthio group in first-group compounds makes the equilibria *ap*⇄*sp* incline to the *ap*-form, exclusively.

The chemical shifts (δ 2.28—2.53) for methylthio protons in the compounds (Y: H, CO_2CH_3, $COCH_3$, COPh, and CO_2H) that belong to the second group, have been approximated to those for *sp*-methylthio group in third-group compounds (roughly δ=2.5); no split of these signals occured until −50 °C. It is then shown that the equilibria *ap*⇄*sp* lies very far to the *sp* side, contrary to the case of the first group.

We have described that in the 9-substituted 9-(2-methoxyphenyl)- and 9-substituted 9-(2-methylphenyl)fluorene derivatives, the compounds in which 9-substituents bear carbonyl groups have an intramolecular attractive interaction between the carbonyl group and the methoxyl or methyl group. Furthermore, Ōki and his coworkers have proposed that the same interaction existed in several 1,4-dimethyl-9-(carbonylmethyl)triptycene.[8] It is reasonable that in compounds **7**—**9** a dipole-electric charge interaction between the carbonyl and methylthio group makes the *sp*-conformation more predominant (Fig. 3).

ap-form *sp*-form

Fig. 3. Isomerization processes between *sp* and *ap* forms in 9-carbonyl compounds **7**—**9**.

Conformational Equilibria of 9-Substituted 9-(2-Methylsulfinylphenyl)fluorene Derivatives. Regarding 9-(2-methylsulfinylphenyl)fluorene derivatives, their conformations are discussed in terms of the chemical shifts for the 2-methylsulfinyl proton in their ^1H NMR.

These NMR data are listed in Table 3. The equilibrium constants, or predominant conformers, are tabulated in Table 2. Regarding compound **13**, two signals (δ 1.72 and 3.00) appeared at room temperature, the former being assigned to methylsulfinyl protons of the *ap*-form; the latter was assigned to those of the *sp*-form (*ap*/*sp*=1/1.5). On the contrary, only the *sp*-form was observed in **4**. The *sp*-form was fairly unstabilized by means of a steric repulsion between the 9-

hydrogen and methylsulfinyl group; then, two conformers existed in equilibria. Table 3 also shows that the signals for methylsulfinyl protons in most compounds, except **14**, can be approximated to that for methylsulfinyl protons in the *sp*-form of **13** (δ 3.0). It is suggested that the *sp*-form exists predominantly in these compounds.

When **11** was measured in the NMR spectra at low temperatures, the signal of methylsulfinyl protons split into two singlets at δ 1.24 (*ap*-form) and 2.64 (*sp*-form), and its ratio was 1/4. The conformational equilibria of **11** was different from that of **1**. The *sp*-form was predominant due to a dipole-electric charge interaction between the methylsulfinyl and hydroxyl groups rather than hydrogen bond. An attempt to measure the FT-IR spectra of **11** in CCl_4 failed because of the insolubility of **11** in the solvent.

In compound **12a**, with a methoxyl group at the 9-position, the signal for the methylsulfinyl proton appeared as a broad singlet at room temperature, and split into two singlets at δ 1.66 and 3.18 (*ap*/*sp*=1/15) at −33 °C. Accordingly, the *sp*-form must be exclusively predominant. The favorable conformation has also been reversed compared with the case of sulfides, **3a** and **3b**. It can be considered that an attractive (dipole-electric charge) interaction operates between the methylsulfinyl and alkoxyl groups.

The chemical shifts for the methylsulfinyl proton in **15a** and **15b** have approximated to that for the methylsulfinyl proton of the *sp*-form in **13**. The signal in **15a** appeared as a sharp singlet in the temperature range −50 to 30 °C. The predominance of the *sp*-conformation stemmed from an attractive interaction between the methylsulfinyl and carbonyl group.

The signal for the methylsulfinyl group in **14** was observed as a sharp singlet at δ 1.56 near to the value of the *ap*-form of **13**. The steric strain between the methylsulfinyl and methyl groups results in a predominance of the *ap*-from.

The activation free energies of the internal rotation (*ap*⇄*sp*) of **11**, **12a**, and **13** are shown in Table 2. The higher barrier of **13**, compared to that of **11**, may be attributed to a lowering of the ground state of **13**.

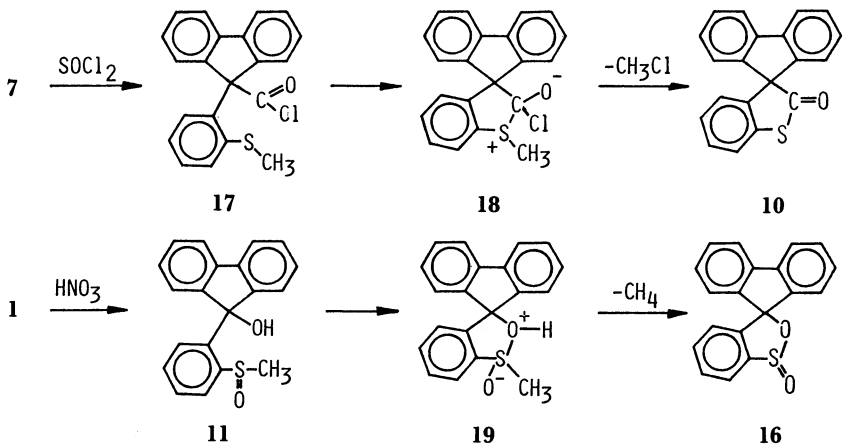
Formation of Ring-Closed Compounds 10 and 16. As described above, an attempted esterification of **7** and an oxidation of **1** under severe conditions gave ring closed compounds **10** and **16**, respectively. These mechanisms are considered to be as follows. Acid chloride **17** was obtained by the reaction of **7** with thionyl chloride and converted to cyclic sulfonium salt **18** at a higher temperature (80 °C); then **10** should have been obtained by the elimination of methyl chloride from this unstable intermediate **18**. The oxidation of **1** by nitric acid afforded **11**, which is ring closed to intermediate **19**; then **19** eliminates methane to give **16**. These reactions are shown in Scheme 2.

Experimental

All melting points are uncorrected. 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 an internal standard. Dynamic NMR spectra were analyzed by using a modified version of the computer program DNMR3. The IR spectra were measured on a IRA-1 spectrometer as potassium bromide pellets.

9-(2-Methylthiophenyl)-9-fluorenol (1). To a solution of *o*-bromophenyl methyl sulfide (27.4 g, 0.14 mol) in dry ether (80 ml) was added a solution of commercial butyllithium in hexane (82.2 ml) at −40 °C. After the reaction mixture was stirred for 1.5 h, a solution of fluorenone (24.3 g, 0.14 mol) in dry benzene was added dropwise. The reaction mixture was stirred for 15 min and allowed to warm at room temperature. The mixture was hydrolyzed by dil. hydrochloric acid, extracted with benzene, washed with water, dried ($MgSO_4$) and concentrated in vacuo to give a solid which was recrystallized first from benzene and then ethanol to give **1** as colorless needles; yield: 25.2 g (61%); mp 141 °C. ^{1}H NMR ($CDCl_3$) δ=1.95 (3H, br. s, SCH_3), 2.52 (1H, br.s, OH), and 6.92—8.36 (12H, m, H_{arom}). Found: C, 79.05; H, 5.26%. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30%.

9-Bromo-9-(2-methylthiophenyl)fluorene (2). Into a solution of **1** (1.83 g, 6 mmol) in acetic acid (20 ml) was



Scheme 2.

bubbled hydrogen bromide gas generated from tetralin and bromine for 30 min. After being stirred for 1 h, the precipitated solid was filtered and washed with water. The crude product was recrystallized from hexane-benzene (1 : 4) to give **2** as slight yellow prisms; yield: 2.03 g (92%); mp 167 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s, SCH_3), 6.92—7.69 (11H, m, H_{arom}), and 8.46—8.62 (1H, m, 6′-H). Found: C, 65.58; H, 4.10%. Calcd for $C_{20}H_{15}BrS$: C, 65.40; H, 4.12%.

2-Methoxy-9-(2-methylthiophenyl)fluorene (3a). A solution of **2** (0.55 g, 1.5 mmol) in methanol (5 ml) was refluxed for 1.5 h. After cooled, the product **3a** was filtered and pure enough for analysis; colorless prisms; yield: 0.46 g (97%; mp 96—97 °C. ^{1}H NMR ($CDCl_3$) δ=1.96 (3H, br. s, SCH_3), 2.78 (3H, s, OCH_3), and 7.00—8.12 (12H, m, H_{arom}). Found: C, 78.86; H, 5.68%. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70%.

2-Ethoxy-9-(2-methylthiophenyl)fluorene (3b). Compound **2** (0.55 g, 1.5 mmol) was treated with ethanol instead of methanol and the reaction mixture was worked up as described for the preparation of **3a** to give **3b** as colorless crystals; yield: 0.38 g (76%); mp 127—128 °C. ^{1}H NMR ($CDCl_3$) δ=1.04 (3H, t, $CH_2C\underline{H}_3$), 1.99 (3H, br.s, SCH_3), 2.89 (2H, q, CH_2), and 7.0—8.0 (12H, m, H_{arom}). Found: C, 79.44; H, 6.08%. Calcd for $C_{22}H_{20}OS$: C, 79.48; H, 6.06%.

9-(2-Methylthiophenyl)fluorene (4). Hydriodic acid (57%, 15 g, 70 mmol) was added dropwise to a solution of **1** (6.08 g, 20 mmol) in acetic acid (150 ml), and refluxed for 1.5 h. The reaction mixture was poured into water and $NaHSO_3$ powder was added to the above mixture. The solution was extracted with benzene. The benzene solution was washed with Na_2CO_3 solution and water, and then dried with $MgSO_4$. The solution was evaporated in vacuo, leaving a residue which was recrystallized from benzene-acetone (1 : 2) to give **4** as colorless needles; yield: 4.54 g (79%); mp 118—119 °C. ^{1}H NMR ($CDCl_3$) δ=2.53 (3H, s, SCH_3), 5.74 (1H, s, 9-H), 6.32 (1H, d, 6′-H), and 6.64—7.78 (11H, m, H_{arom}). Found: C, 83.40; H, 5.61%. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59%.

9-Methyl-9-(2-methylthiophenyl)fluorene (6a). 9-Lithio-(2-methylthiophenyl)fluorene (**5**) was prepared from the reaction of **4** (0.5 g, 1.73 mmol) in dry ether (50 ml) and a solution of commercial butyllithium in hexane (1.7 ml) under a N_2 atmosphere.

To the above solution was added methyl iodide (0.22 ml, 3.46 mmol) dropwise, stirred for 30 min. The reaction mixture was poured into water, extracted with benzene, and dried with $MgSO_4$. The solution was evaporated in vacuo, leaving a residue which was column-chromatograhed on alumina using benzene as an eluent to give **6a**; yield: 0.38 g (73%); colorless needles; mp 149—151 °C (from hexane). ^{1}H NMR ($CDCl_3$) δ=1.72 (3H, s, SCH_3), 1.76 (3H, s, CH_3), and 6.87—7.84 (12H, m, H_{arom}). Found: C, 83.66; H, 5.99%. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00%.

9-Ethyl-9-(2-methylthiophenyl)fluorene (6b). Compound **5** prepared for **1** (0.5 g, 1.7 mmol) was treated with ethyl iodide (1.0 ml, 12.5 mmol) instead of methyl iodide and the reaction mixture was worked up as described for the preparation of **6a**, to give **6b** as colorless crystals; yield: 0.38 g (76%); mp 69—73 °C. ^{1}H NMR $CDCl_3$) δ=0.30 (3H, t, $CH_2C\underline{H}_3$), 1.76 (3H, s, SCH_3), 2.32 (2H, q, CH_2), and 6.80—7.86 (12H, m, H_{arom}). Found: C, 83.35; H, 6.35%. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37%.

9-(2-Methylthiophenyl)-9-fluorenecarboxylic Acid (7). A solution of compound **5** from **1** (2.6 g, 9 mmol) in ether was poured into crushed Dry Ice and stirred for 30 min. The reaction mixture was poured into a ice-water. The precipitated solid was filtered and recrystallized from ethyl acetate to give **7** as colorless crystals; yield: 1.93 g (64%); mp 180 °C (decomp). IR (KBr): 1680 cm^{-1} (CO), 3070 (OH); ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s, SCH_3), and 6.43—7.81 (12H, m, H_{arom}). Found: C, 75.54; H, 4.91%. Calcd for $C_{21}H_{16}O_2S$: C, 75.87; H, 4.85%.

9-Carboxymethyl-9-(2-methylthiophenyl)fluorene (8). A mixture of **7** (0.2 g, 0.6 mmol), thionyl chloride (5 ml), and *N,N*-dimethylformamide (3 drops) were heated at 50—60 °C for 1 h. To the reaction mixture was added methanol (10 ml); the precipitated solid was then extracted with benzene. The benzene solution was washed with $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated in vacuo. The crude product was recrystallized from acetone to give **8** as colorless prisms; yield: 0.05 g (24%); mp 132—135 °C. IR (KBr): 1700 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=2.47 (3H, s, SCH_3), 3.59 (3H, s, $COOCH_3$), 6.42 (1H, d, 6′-H), and 6.53—7.75 (11H, m, H_{arom}). Found: C, 75.98; H, 5.33%. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24%.

9-Acetyl-9-(2-methylthiophenyl)fluorene (9a). To a solution of **5** prepared from **1** (0.6 g, 2 mmol) in ether was added a solution of acetic acid anhydride (0.3 ml) in ether (1 ml) dropwise at room temperature. After being stirred for 1 h, the reaction mixture was poured into water, extracted with benzene, washed with water, and dried with $MgSO_4$. The solvent was distilled off in vacuo, leaving a residue which was recrystallized from benzene to give **9a** as colorless plates; yield: 0.25 g (36%); mp 174—175 °C. IR (KBr): 1680 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=1.88 (3H, s, $COCH_3$), 2.44 (3H, s, SCH_3), 6.55 (1H, d, 6′-H), and 6.72—7.85 (11H, m, H_{arom}). Found: C, 80.04; H, 5.51%. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49%.

9-Benzoyl-9-(2-methylthiophenyl)fluorene (9b). Compound **5** prepared from **1** (1.0 g, 3.5 mmol) was reacted with benzoyl chloride (0.74 g, 5 mmol) instead of acetic anhydride; the reaction mixture was worked up as described for the preparation of **9a**, to give **9b** as colorless prisms; yield: 1.27 g (92%); mp 181—182 °C (from acetone). IR (KBr): 1645 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=2.39 (3H, s, SCH_3), 6.51 (1H, d, 6′-H), and 6.63—7.86 (16H, m, H_{arom}). Found: C, 82.25; H, 5.09%. Calcd for $C_{27}H_{20}OS$: C, 82.62; H, 5.14%.

Spiro[benzo[*b*]thiophene-3(2*H*),9′-fluorene]-2-one (10). A mixture of **7** (0.5 g, 1.5 mmol), thionyl chloride (3 ml), and *N,N*-dimethylformamide (3 drops) was refluxed for 2 h. Thionyl chloride was distilled off in vacuo and methanol (15 ml) was added to the above residue. The mixture was refluxed for another 1 h. The solution was concentrated in vacuo, leaving a crude product which was recrystallized from benzene to give **10** as colorless crystals; yield: 0.1 g (20%); mp 139—140 °C. IR (KBr): 1710 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=6.31—7.79 (12H, m, H_{arom}). Found: C, 80.26; H, 4.12%. Calcd for $C_{20}H_{12}OS$: C, 79.97; H, 4.03%.

9-Substituted 9-(2-Methylsulfinylphenyl)fluorenes (11—15). General Procedure: To a solution of **1** (0.61 g, 2.0 mmol) in acetic acid (10 ml) was added nitric acid (d=1.38, 1 ml) dropwise at 18 °C with stirring. After being stirred at 10—20 °C for 3 h, the reaction mixture was poured into water. The precipitated solid was extracted with benzene. The benzene solution was washed with a $NaHCO_3$ solution and water, and then dried with $MgSO_4$. The solvent was distilled off to obtain a residue which recrystallized from benzene and

then ethanol to give **11** as colorless needles; yield; 0.48 g (75%); mp 214—216 °C (decomp). IR (KBr): 1020 cm^{-1} (SO), 3080 (OH); ^1H NMR ($CDCl_3$) δ=2.52 (3H, br.s, $SOCH_3$), 4.10 (1H, br.s, OH), and 6.22—8.18 (12H, m, H_{arom}). Found: C, 74.82; H, 5.05%. Calcd for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03%.

9-Methoxy-9-(2-methylsulfinylphenyl)fluorene (12a). This compound was obtained as colorless crystals; yield: 93%; mp 222—223 °C (from methanol). IR (KBr): 1050 cm^{-1} (SO). Found: C, 75.49; H, 5.45%. Calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.43%.

9-Ethoxy-9-(2-methylsulfinylphenyl)fluorene (12b). This compound was obtained as colorless prisms; yield: 32%; mp 201—203 °C (from ethanol). IR (KBr): 1050 cm^{-1} (SO). Found: C, 76.08; H, 5.79%. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79%.

9-(2-Methylsulfinylphenyl)fluorene (13). This compound was obtained as colorless needles; yield: 82%; mp 233—235 °C (from benzene). IR (KBr): 1050 cm^{-1} (SO). Found: C, 79.25; H, 5.46%. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30%.

9-Methyl-9-(2-methylsulfinylphenyl)fluorene (14). This compound was obtained as colorless crystals (from benzene-hexane); yield: 78%; mp 177—178 °C. IR (KBr): 1050 cm^{-1} (SO). Found: C, 78.95; H, 6.03%. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70%.

9-Acetyl-9-(2-methylsulfinylphenyl)fluorene (15a). This compound was obtained as slight yellow prisms (from benzene-hexane); yield: 41%; mp 184—186 °C. IR (KBr): 1055 cm^{-1} (SO). Found: C, 76.32; H, 5.29%. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24%.

9-Benzoyl-9-(2-methylsulfinylphenyl)fluorene (15b). This compound was obtained as colorless crystals; yield: 12%; mp 186—189 °C (from benzene). IR (KBr): 1055 cm^{-1} (SO). Found: C, 79.15; H, 5.03%. Calcd for $C_{27}H_{20}O_2S$: C, 79.38; H, 4.94%.

Spiro[3*H*-2,1-benzoxathiole-3,9′-fluorene] 1-Oxide (16). To a solution of **1** (0.6 g, 2 mmol) in acetic acid (10 ml) was added nitric acid (d=1.38, 2 ml) dropwise. After being stirred at 50—60 °C for 30 min, the reaction mixture was poured into water. The mixture was extracted with benzene, and worked up as described for the preparation of **11** to give **16** as colorless prisms; yield: 0.23 g (38%); mp 161—162 °C (from acetone and then ethanol). IR (KBr): 1120 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=6.38—8.10 (12H, m, H_{arom}). Found: C, 74.99; H, 4.12%. Calcd for $C_{19}H_{12}O_2S$: C, 74.98; H, 3.97%.

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