Reactivities of Stable Rotamers. IX. Ionizing Reactions of 9-(2-Bromomethyl-6-methylphenyl)fluorene Rotamers[1]

Shigeru Murata, Seiichiro Kanno, Yo Tanabe, Mikio Nakamura, and Michinori Ōki*

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

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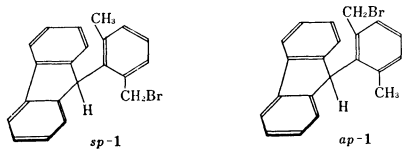
Ionizing reactions of *ap*-9-(2-bromomethyl-6-methylphenyl)fluorene in ionizing solvents afforded 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene and its dehydrogenated compound, whereas the *sp* isomer remained intact. Forced ionization of the *sp* isomer with silver salts afforded products originated from the corresponding cation and either the anion of the salt or the solvent, whereas the *ap* isomer gave cyclized product under the same conditions, if the nucleophilicity of the solvent was poor. The reaction of the *sp* isomer was faster than the *ap* in nucleophilic solvents, whereas the reverse was true for poorly nucleophilic solvents. Solvolysis of the rotamers in formic acid yielded the corresponding formates, the *sp* isomer reacting faster than the *ap*. The results are discussed on the basis that the solvation shell in the *ap* form is completed by the participation of the fluorene ring whereas in the *sp* form the shell is completed by the solvent molecules.

Some years ago successful isolation of *sp*- and *ap*-rotamers of 9-(2-bromomethyl-6-methylphenyl)fluorene (**1**) was reported from this laboratory.[2] Since then, reactivities of stable rotamers both in 9-arylfluorenes[3] and 9-substituted triptycenes[1,4] have been investigated. Some of the rotamers show striking differences in reactivities, although some showed differences by only small factors. These findings aroused our interests in investigating the differences in reactivities of *sp*-**1** and *ap*-**1**. Preliminary experiments of heating the isomers of **1** in trifluoroacetic acid revealed that the *ap* form reacted with a measurable rate at 62 °C whereas the *sp* remained intact.[5] In order to get into further insight, we have carried out a series of ionizing reactions of rotamers of **1**. This paper reports and discusses the results of such investigations, which show dramatic changes according to solvents used, in addition to the rotational barrier in **1**.



Experimental

9-(2-Bromomethyl-6-methylphenyl)fluorene Rotamers (1). To a boiling solution of 2.5 g (9.3 mmol) of 9-(2,6-dimethylphenyl)fluorene[6] in 100 mL of benzene was added 2.5 g (14 mmol) of *N*-bromosuccinimide and 170 mg of benzoyl peroxide in small portions during a period of 17 h. After filtration, the solvent was removed by evaporation and the residue was submitted to chromatography on silica gel, which used hexane as an eluent. The *sp* form was eluted first and the *ap* form followed. The separation of the isomers was more conveniently performed by using a Waters System 500 preparative liquid chromatographic apparatus, μ-porasil and hexane. In a typical run, 17% of *sp* and 6% of *ap* forms were obtained with 40% of the recovered starting material. The *sp* form, mp 115.0—115.5 °C. Found: C, 72.37; H, 4.76; Br, 23.06%. Calcd for $C_{21}H_{17}Br$: C, 72.22; H, 4.91; Br, 22.88%. ^{1}H NMR ($CDCl_3$, δ): 1.12 (3H, s), 4.83 (2H, s), 5.60 (1H, s), 6.8—7.9 (11H, m). The *ap* form, mp 125.0—126.0 °C. Found: C, 72.40; H, 4.74; Br, 23.06%. Calcd for $C_{21}H_{17}Br$: C, 72.22; H, 4.91; Br, 22.88%. ^{1}H NMR ($CDCl_3$, δ): 2.70 (3H, s), 3.37 (2H, s), 5.52 (1H, s), 7.0—8.0 (11H, m).

9-[2,6-Bis(bromomethyl)phenyl]fluorene, mp 143—144 °C, was obtained as a byproduct which was eluted later than the monobromo compounds in the chromatography. Found: C, 58.83; H, 3.54; Br, 37.65%. Calcd for $C_{21}H_{16}Br_2$: C, 58.91; H, 3.77; Br, 37.32%. ^{1}H NMR (CCl_4, δ): 3.22 (2H, s), 4.72 (2H, s), 5.50 (1H, s), 7.0—8.0 (11H, m).

Rates of Rotation. Either one of pure *sp* and *ap* isomers was dissolved in hexachlorobutadiene and the solution was heated by immersing it in an appropriate boiling solvent bath. The decrease in the amount of the starting material and/or the increase in the amount of the other isomer was monitored by ^{1}H NMR spectroscopy. Equilibrium constants were obtained at the temperature by heating the solution for a long enough time and were found to be invariant at $sp/ap = 3.6 \pm 0.2$ throughout the temperature range examined. The same equilibrium constants were obtained by starting from either of the isomers. The rate constants were obtained by utilizing the following equation (1), where K is now known, a is the initial amount and x the amount at time t, by assuming the first order reaction. The plot gave very good straight lines.

$$\ln\left\{1-\left(1+\frac{1}{K}\right)\frac{a}{x}\right\} = -k\left(1+\frac{1}{K}\right)t \qquad (1)$$

Putting these k's into the Arrhenius and the Eyring equations, we obtained the activation parameters.

Reaction of 1 with Silver Nitrate in Acetonitrile. To a solution of 22 mg (0.06 mmol) of *sp*-**1** in 2 mL of acetonitrile, 10 mg (0.06 mmol) of silver nitrate in 1.0 mL of acetonitrile was added. The whole was allowed to react for 30 min at 50 °C. The reaction mixture was filtered and the filtrate was evaporated. Recrystallization of the residue from ethanol afforded 20 mg (90%) of *sp*-2-(9-fluorenyl)-3-methylbenzyl nitrate, mp 104 °C. Found: C, 76.19; H, 5.03; N, 4.18%. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23%. ^{1}H NMR ($CDCl_3$, δ): 1.16 (3H, s), 5.32 (1H, s), 5.80 (2H, s), 7.0—7.9 (11H, m). IR (KBr disk): 1628, 1278, 842 cm^{-1}.

ap-**1** similarly gave *ap*-2-(9-fluorenyl)-3-methylbenzyl nitrate, mp 128 °C. Found: C, 75.97; H, 4.97; N, 4.30%. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23%. ^{1}H NMR ($CDCl_3$, δ): 2.75 (3H, s), 4.22 (2H, s), 5.56 (1H, s), 7.0—8.0 (11H, m). IR (KBr disk): 1617, 1280, 875 cm^{-1}.

Reaction of 1 with Silver Perchlorate in Acetonitrile. The reaction was carried out similarly as above except using silver perchlorate instead of silver nitrate and treating the reaction mixture as follows. The reaction mixture was

treated with 5% aqueous lithium chloride. Ether was added and the mixture was filtered to remove insoluble materials. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layer was washed, dried, and evaporated. The residue was recrystallized from hexane–ethanol.

sp-**1** gave *sp*-9-(2-acetamidomethyl-6-methylphenyl)-fluorene, mp 194 °C, in 70% yield. Found: C, 84.17; H, 6.31; N, 4.29%. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28%. ^{1}H NMR ($CDCl_3$, δ): 1.13 (3H, s), 1.96 (3H, s), 4.76 (2H, d, J=5.4 Hz), 5.37 (1H, s), 5.7 (1H, br s), 6.8—8.0 (11H, m). IR (KBr disk): 3240, 1635, 1550 cm^{-1}.

ap-**1** gave *ap*-9-(2-acetamidomethyl-6-methylphenyl)-fluoene, mp 188 °C, in 50% yield. Found: C, 84.23; H, 6.24; N, 4.37%. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28%. ^{1}H NMR ($CDCl_3$, δ): 1.46 (3H, s), 2.73 (3H, s), 3.23 (2H, d, J=6.3 Hz), 4.1 (1H, br s), 5.54 (1H, s), 7.0—8.0 (11H, m). IR (KBr disk): 3270, 1640, 1550 cm^{-1}.

Reaction of **1** *with Silver Perchlorate in Benzene.* The reaction was carried out similarly with that in acetonitrile except that benzene was used as a solvent and the reaction mixture was allowed to stand overnight at 22 °C.

sp-**1** afforded *sp*-9-(2-benzyl-6-methylphenyl)fluorene, mp 105 °C, as a sole product in 64% yield. Found: C, 93.50; H, 6.20%. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40%. ^{1}H NMR ($CDCl_3$, δ): 1.10 (3H, s), 4.37 (2H, s), 5.45 (1H, s), 6.8—7.9 (16H, m).

Formation of bis[*sp*-2-(9-fluorenyl)-3-methylbenzyl] ether (see below) was detected during the reaction but this compound subsequently reacted under the reaction conditions to afford *sp*-9-(2-benzyl-6-methylphenyl)fluorene.

ap-**1** afforded 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene, which was characterized in the section of the reaction in trifluoroacetic acid, and *ap*-9-(2-benzyl-6-methylphenyl)-fluorene, mp 143 °C, in 1:12 ratio. Found: C, 93.76; H, 6.22%. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40%. ^{1}H NMR ($CDCl_3$, δ): 2.67 (2H, s), 2.69 (3H, s), 5.54 (1H, s), 6.5—7.9 (16H, m).

Bis[sp-*2-(9-fluorenyl)-3-methylbenzyl*] *Ether.* A mixture of 15 mg of *sp*-**1** in 2.6 mL of benzene and 17.8 mg of silver perchlorate in 1.7 mL of benzene containing *ca.* 10 μL of water was stirred for 30 h at room temperature and then was heated at 50 °C for 30 min. To the cooled mixture, 3.5 mL of methanol and then 5% aqueous lithium chloride were added. Silver salts were removed by filtration and the organic products were collected. Preparative TLC on silica gel (3:1 hexane–benzene) afforded *ca.* 4 mg of the desired ether, which was recrystallized from benzene–ethanol, mp 192—193 °C, and small amounts each of *sp*-9-(2-methoxymethyl-6-methylphenyl)fluorene (see below) and *sp*-(2-benzyl-6-methylphenyl)fluorene. Found: C, 91.23; H, 5.88%. Calcd for $C_{42}H_{34}O$: C, 90.94; H, 6.18%. MS (M^+): 554. ^{1}H NMR ($CDCl_3$, δ): 1.12 (6H, s), 4.98 (4H, s), 5.64 (2H, s), 6.8—7.9 (22H, m).

9-(2-Hydroxymethyl-6-methylphenyl)fluorene. To a solution of 60 mg (0.17 mmol) of *sp*-**1** in 6 mL of acetone was added a solution of 106 mg (0.51 mmol) of silver perchlorate in 1 mL of water. The mixture was stirred for 10 min at room temperature in dark, and then warmed at 50 °C for 10 min. After silver bromide was removed by filtration, the reaction product was precipitated by addition of water and extracted with ether. The extract was washed with water, dried, and evaporated. The residue was developed on a preparative TLC plate (1:4 hexane–benzene) to give 40 mg (81%) of *sp*-9-(2-hydroxymethyl-6-methylphenyl)-fluorene, mp 74—75 °C, which was recrystallized from hexane. Found: C, 88.17; H, 6.21%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%. ^{1}H NMR ($CDCl_3$, δ): 1.12 (3H, s), 1.8 (1H, br s), 5.02 (2H, s), 5.59 (1H, s), 6.8—7.9 (11H, m).

Solvolysis of **1** *in Formic Acid.* A solution of 29 mg of *sp*-**1** in 3 mL of chloroform and 20 mL of formic acid was heated at 50—60 °C for 24 h and poured into water. The organic materials were extracted with ether and the ether extract was washed and dried. After evaporation of the solvent, the residue was developed on a preparative TLC plate (1:2 hexane–benzene) to give *ca.* 80% *sp*-2-(9-fluorenyl)-3-methylbenzyl formate, oil. High resolution MS (M^+): 314.1314. Calcd for $C_{22}H_{18}O_2$: 314.1307. ^{1}H NMR ($CDCl_3$, δ): 1.12 (3H, s), 5.37 (1H, s), 5.54 (2H, s), 6.8—8.0 (11H, m), 8.14 (1H, s). IR (neat): 1722, 1150 cm^{-1}.

Similarly, *ap*-**1** afforded *ca.* 80% *ap*-2-(9-fluorenyl)-3 methylbenzyl formate, mp 106 °C, which was recrystallized from pentane–ethanol. Found: C, 84.02; H, 5.50%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%. ^{1}H NMR ($CDCl_3$, δ): 2.75 (3H, s), 3.97 (2H, s), 5.53 (1H, s), 6.9—8.0 (12H, m). IR (KBr disk): 1716, 1178 cm^{-1}.

Reaction of **1** *Caused by Heating a Trifluoroacetic Acid (TFA) Solution.* A solution of 33 mg of *ap*-**1** in 1.5 mL of chloroform was added to 25 mL of TFA. The whole solution was heated at 60 °C for 6 h. The mixture was poured into water and then extracted with chloroform. After the usual treatment, the products were purified by silica gel TLC (hexane) to afford 8 mg (32%) of 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene, mp 180—181 °C, after recrystallization from benzene–ethanol. Found: C, 94.23; H, 5.78%. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%. ^{1}H NMR ($CDCl_3$, δ): 2.48 (3H, s), 3.99 (1H, d, J=16.4 Hz), 4.14 (1H, dd, J=16.4 and 2.3 Hz), 4.80 (1H, d, J=2.3 Hz), 6.9—8.1 (10H, m). MS (M^+): 268.

The product was always accompanied by 12-methylbenz[*a*]aceanthrylene which was eluted before the dihydro compound. Preparation of the dehydrogenated compound is described below. This dehydrogenation seemed to be effected by atmospheric oxygen, since careful exclusion of oxygen decreased the amount of this product, increasing the yield of the dihydro compound.

The concentration of *ap*-**1** in trifluoroacetic acid plays an important role in determining the yield of the cyclized product. Heating a solution of 80 mg of *ap*-**1** in 5 mL of chloroform and 15 mL of TFA gave at least 10 spots in TLC, although the cyclized product was main, and a more concentrated solution, which was convenient for the routine ^{1}H NMR measurement, than this afforded only polymers.

sp-**1** did not apparently react under the similar conditions. Heating a solution of 20 mg of *sp*-**1** in 0.1 mL of chloroform and 0.4 mL of TFA at 62 °C for 40 h gave only the recovered starting material.

12-Methylbenz[a]*aceanthrylene.* A solution of 6 mg of 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene in 1 mL of benzene was mixed with 6 mg of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in benzene. The mixture was stirred for 1 h at room temperature and then heated at 50 °C for 1 h. The hydroquinone produced in the reaction was removed by passing the solution through a column of 200 mg of silica gel. The filtrate and washings (1:1 hexane–benzene) were combined and evaporated to give the desired compound, orange oil, in an almost quantitative yield. High resolution MS (M^+): 266.1106. $C_{24}H_{14}$ requires M^+ 266.1095. ^{1}H NMR ($CDCl_3$, δ): 3.17 (3H, s), 7.2—8.5 (11H, m). UV (EtOH, λ_{max} in nm and log ε in parentheses): 430 (3.65), 366 (3.40), 260 (4.54).

Reaction of **1** *Caused by Heating a 1,1,1,3,3,3-Hexafluoro-2-propanol (HFP) Solution.* A solution of 10 mg of *ap*-**1**

in 0.3 mL of chloroform and 15.6 mL of HFP was heated at 50—55 °C for 4 h. The reaction product was similarly treated as above to give 65—75% 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene. The dehydrogenated product was detected only in a trace amount.

Under the similar conditions, *sp*-**1** was completely recovered.

Reaction of **1** *in HFP with Silver Perchlorate.* A heterogeneous mixture of 10 mg of *ap*-**1** in 0.6 mL of chloroform and 15.6 mL of HFP and *ca.* 3 equiv. of silver perchlorate was stirred at 20 °C for 5 h. The mixture was treated with methanol to decompose any of the possible perchlorate still present. After the usual treatment, 3 mg (40%) of 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene was obtained. No methoxy compound was detected.

Similar treatment of *sp*-**1** afforded 30% *sp*-(2-methoxymethyl-6-methylphenyl)fluorene (for the characterization, see below). No cyclized product was obtained.

Reaction of **1** *in TFA with Silver Perchlorate.* This reaction was performed similarly as above. The *ap* form gave the cyclized product, whereas the *sp* form afforded the methoxy compound only.

9-(2-Methoxymethyl-6-methylphenyl)fluorene Rotamers. To a solution of 25 mg (0.07 mmol) of *sp*-**1** in 0.4 mL of chloroform and 5 mL of methanol, was added a solution of 56 mg (0.27 mmol) of silver perchlorate in 2 mL of methanol. The mixture was allowed to stand for 10 min at room temperature in dark. Silver bromide was removed by filtration and the filtrate was poured into water. The mixture was extracted with dichloromethane. The extract was washed, dried, and evaporated to give a colorless oil. High resolution MS (M^+): 300.1497. $C_{22}H_{20}O$ requires 300.1512, ^{1}H NMR ($CDCl_3$, δ): 1.12 (3H, s), 3.44 (3H, s), 4.76 (2H. s), 5.56 (1H, s), 6.8—7.9 (11H, m).

Similarly, *ap*-9-(2-methoxymethyl-6-methylphenyl)fluorene (recrystallized from ethanol), mp 118 °C, was obtained from *ap*-**1**. Found: C, 88.11; H, 6.66%. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71%. ^{1}H NMR ($CDCl_3$, δ): 2.56 (3H, s), 2.71 (3H, s), 3.14 (2H, s), 5.48 (1H, s), 6.9—8.0 (11H, m).

Reaction of **1** *in TFA–CH_3OH–$CHCl_3$ or HFP–CH_3OH–$CHCl_3$.* The reaction was similarly carried out as for those without methanol, except 3 (v/v)% methanol was added to TFA or HFP prior to the mixing. *ap*-**1** afforded 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene and its dehydrogenated compound in both systems. *sp*-**1** was recovered unchanged in TFA, whereas it gave *sp*-9-(2-methoxymethyl-6-methylphenyl)fluorene in HFP. When *sp*-**1** in TFA–CH_3OH–$CHCl_3$ was heated, only polymers were obtained.

Competitive Reactions. A typical procedure follows. To a solution of 6.0 mg (17 μmol) of *sp*-**1**, the same amount of *ap*-**1** and 2.9 mg of fluorene in 1 mL of acetonitrile was added a solution of 3.0 mg (17 μmol) of silver nitrate. The mixture was stirred for 40 min at 25 °C. An excess amount of aqueous lithium chloride was added and the precipitate was removed by filtration. The amount of unreacted material was measured with the use of a Waters M-6000A high pressure liquid chromatograph which was equipped with a UV detecter. Fluorene which had been added to the original mixture served as an internal standard. The relative reactivity was calculated by applying the following equation (2).

$$k_{sp}/k_{ap} = \log\frac{[sp]}{[sp]_0}\Big/\log\frac{[ap]}{[ap]_0}, \quad (2)$$

where subscript 0 denotes the initial concentration.

In the cases of other competitive reactions, the solvent systems quoted in the independent reactions for the respective rotamers were used. The amount of the substrate and a silver salt was kept equimolar in every reaction. Solvolytic reactions were also carried out similarly.

Table 1. Rate constant for isomerization of 9-(2-bromomethyl-6-methylphenyl)fluorene rotamers in hexachlorobutadiene

Temperature/°C	$k_{sp\to ap}/10^{-6}$ s^{-1}	$k_{ap\to sp}/10^{-5}$ s^{-1}
80	1.0	0.36
100	6.4	2.3
111	19	6.9
121	57	21

Table 2. Activation parameters for internal rotation in 9-(2-bromomethyl-6-methylphenyl)-fluorene and in 9-(2-methyl-1-naphthyl)fluorene

	9-(2-Bromomethyl-6-methylphenyl)-fluorene[c]		9-(2-Methyl-1-naphthyl)-fluorene[d] (both direction same)
	sp→*ap*	*ap*→*sp*	
E_a/kcal mol^{-1} [a]	27.0	27.1	29.8
log A/s^{-1}	10.7	11.3	12.9
ΔH^*/kcal mol^{-1} [a]	26.2	26.3	29.9
ΔS^*/e. u.[b]	−12.2	−9.3	0.4
ΔG^*_{373}/kcal mol^{-1} [a]	30.7	29.8	29.8

a) 1 cal=4.18 J. b) 1 e. u.=4.18 J K^{-1} mol^{-1}. c) Hexachlorobutadiene solvent. d) Tetrachloroethylene solvent.

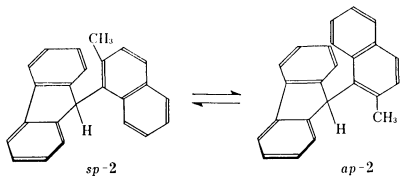
Spectral Measurements. ^{1}H NMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz or on a Varian EM390 spectrometer operating at 90 MHz. A detailed spectrum of 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene was obtained with a Bruker 270 MHz machine. IR and UV spectra were obtained with a Hitachi IR-260-30 spectrometer and a Hitachi UV-340 spectrometer, respectively. High resolution mass spectra were recorded on a JEOL D-300 machine.

Results and Discussion

Rotational Barriers and Rotamer Populations. Assignment of the stereochemistry of the rotamers were performed by taking the ring current effect of the fluorene ring in ^{1}H NMR spectra into account. In the *sp* conformation, the CH_2Br group is in the shielding zone of the benzene ring, whereas the methyl group is in the deshielding zone. In contrast, the CH_2Br group in the *ap* conformation is in the deshielding zone and the methyl group is in the shielding. Thus the methyl and the methylene protons in the *ap* form show a very large difference in chemical shifts, whereas those in the *sp* show a small chemical shift difference.

Results of the kinetic measurements are summarized in Table 1. Putting these rate constants into the Arrhenius equation, we obtain E_a and log A as shown in Table 2 which summarizes ΔH^* and ΔS^* obtained by putting the rate constants into the Eyring equation as well, together with the free energies of activation for rotation at 373 K. Table 2 also contains activation parameters for rotation in 9-(2-methyl-1-

naphthyl)fluorene (**2**) for comparison: the data by the Arrhenius plot were obtained by Siddall and Stewart[6b] and those by the Eyring plot were calculated by us, using the reported rate constants.[6b]



sp-2 *ap*-2

The barrier to rotation in 9-(2,6-dimethylphenyl)-fluorene was predicted to be over 25 kcal/mol on the basis of dynamic NMR study.[7] The present results conform with this expectation. Comparison of the rate constants of internal rotation in compound **2** with those in compound **1** shows interesting trends: At low temperatures, the rotation in compound **2** is relatively slow whereas that in compound **1** is definitely slower than that in the naphthyl compound (**2**) at higher temperatures. On close examination, one notices that the enthalpy of activation and Arrhenius activation energy are definitely larger for compound **2** than those for compound **1**. The slow rotation in compound **1** at the higher temperature is attributed to large negative entropy of activation. This point deserves further mention.

The steric effect of a methyl group given to its ortho position in a substituted phenyl system is often comparable with that of the peri-CH group given to the 1-position of a naphthalene system. As far as we discuss the enthalpy of activation and the Arrhenius activation energy, this general trend is not held here. We may have to admit that the rigidity of the molecule has a profound effect on the enthalpy of activation in 9-arylfluorene systems: Being more rigid than the 2,6-dimethylphenyl group, the 2-methyl-1-naphthyl group will give severer interactions in the transition state for rotation with the fluorene. The effect of the bromo group in **1** may be neglected in discussion, since substitution of a substituent for hydrogen in a methyl group is normally quoted as increasing the size of the whole substituent (however, *vide infra*).

The role of entropy of activation in realizing almost the same free energies of activation for rotation for both systems in the vicinity of 100 °C is thus important. Namely, the negative entropy of activation for rotation in compound **1** makes a contrast with the entropy of activation for **2** which is almost zero. On one hand, we may attribute this outcome to the effect of solvation: in the ground state, the solvation is more difficult than in the transition state for rotation in **1** because of the steric effect. Thus entropy is decreased in the transition state relative to the ground state due to the loss of freedom in the motion of solvent molecules.

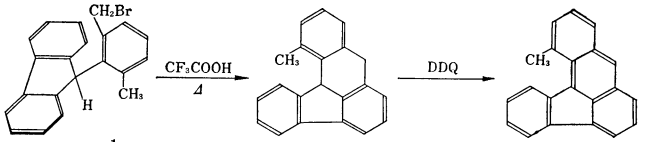
On the other hand, the freedom of internal rotation of the CH_2Br group must be considered. Entropy will be decreased when the *sp* form approaches the transition state for rotation from the ground state, because the conformation in the transition state is limited whereas the conformations in the ground state are not. But the decrease in entropy is not certain in the *ap* conformation, because, in its ground state, the possible conformations are also limited due to the steric interaction between the bromo group in the CH_2Br and the fluorene moiety: If the bromo group takes certain positions in possible conformations, the strain will be prohibitively strong.

Summation of these effects together with other unknown factors contributes to the observed entropy change. The results suggest therefore that comparison of the amount of free energies should be made carefully when hydrocarbons and their substituted derivatives are involved.

As for the distribution of *sp* and *ap* conformers at equilibrium, the *sp* form is favored by a factor of 3.6. This is usually attributed to the size of the substituent by saying that the bromomethyl group is larger than a methyl. However, if one compares the size of CH_2Br with CH_3 in the part of direct interactions, one notices that it is the CH_2 in both cases that is responsible because, in the CH_2Br group, the bromine atom is too large to direct toward the fluorene ring. We may attribute this difference in populations to the effect of entropy and/or the solvation effect. Entropy in the *ap* does decrease relative to the *sp* form because of the restriction of some rotamers. Formation of a solvation shell cannot be completed with the solvent molecules only in the *ap* conformation because of the steric effect. The invariance in the equilibrium constants throughout the temperature range suggests that the entropy factor controls equilibrium.

From the barriers to rotation, one calculates that the time necessary for conversion of 5% of the *sp* isomer to the *ap* at 80 °C is *ca.* 1×10^4 s: The limit of errors in NMR spectroscopy to detect a molecular species is considered to be at this level. The reaction conditions used in bromination exceed this limit, yet the reaction period is not long enough to reach equilibrium. Therefore the formation ratio (*sp*/*ap*=2.2—2.7) clearly shows that the *sp* methyl is kinetically favored in bromination. Since there is no apparent strong electronic effects which favor the bromination of the *sp*-methyl, we may attribute this result to the steric effects: the direction of attack on the *ap*-methyl is limited because, at least, one side of the methyl group is blocked by the fluorenyl group.

Products from ap-***1*** *Heated in Trifluoroacetic Acid (TFA).* When a solution of *ap*-**1** in TFA–$CHCl_3$ was heated at 62 °C, the products were dependent on the concentration. If the concentration was high, the products were polymer mixtures. If the concentration was lowered, however, a compound was obtained in a pure state. Its MS and elemental analyses were consistent with the formula in that a molecule of hydrogen bromide was lost from the starting material. The most probable structure of the product is 12-methyl-8,12b-dihydrobenz[*a*]aceanthrylene (**3**), of



ap-1 3 4

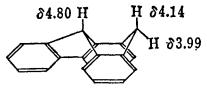
TABLE 3. DEPENDENCE OF DISTRIBUTION OF PRODUCTS IN THE REACTION OF *ap*-**1** WITH SILVER PERCHLORATE IN BENZENE

Reaction conditions		Products[a]			7/(3+4)
Temperature/°C	Duration/h	*ap*-**7**	**3**	**4**	
70	0.7	4.22	1.0	0.28	3.2
50	2.0	5.23	1.0	0.07	4.9
20	23	13.1	1.0	0.14	11.5

a) The product distribution is shown in relative amounts, taking the amount of **3** as reference.

which formation is rationalized by considering the ionization at the CH_2Br group followed by a Friedel-Crafts type cyclization.

^1H NMR spectral data are consistent with the structure. Long-range couplings in the 9,10-dihydroanthracene structure have been known,[8] and the coupling constants are in the order $J_{aa}>J_{ae}>J_{ee}$, where subscripts a and e denote axial and equatorial hydrogens, respectively. In the present compound, the hydrogen in the 12b position is fixed in the axial direction because of the ring structure. Therefore the proton signal which is located at a lower field and shows a coupling constant 2.3 Hz is assigned to the axial proton in the 8-position, as shown in the scheme.



a perspective of 3

When **3** was dehydrogenated with DDQ, a colored hydrocarbon was obtained. This latter compound (**4**) showed absorption maxima at 260, 366, and 430 nm in a UV-VIS spectrum which are very close to those of a known benz[*a*]aceanthrylene skeleton.[9] The UV-VIS data give further confirmation of the structure of the product in the TFA treatment.

Compound **3** was always accompanied by **4** in the reaction in TFA. However, the amount of **4** could be reduced appreciably when atmospheric oxygen was carefully purged.

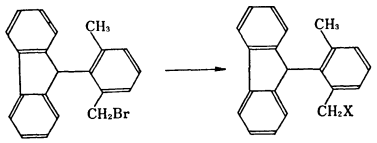
Reaction of ***1*** *with Silver Salts.* In the heating experiment of a TFA solution of *sp*-**1** no reaction was detected although the solution was heated at 62 °C for 40 h. If the ring system is rigid, there should be formed a diastereomer from the *sp* form by a similar ring closure. In order to explore the possibility, several reactions of *sp*-**1** and *ap*-**1** with silver salts were investigated.

Silver salts are often used for forced ionization of organic halides. Because of the complexity derived by the catalytic action of silver halide, the reaction machanism is not well understood: Pocker *et al.* found the reaction of silver nitrate to be of 2.5th order[10] and Kevill *et al.* carried out some detailed investigations on the reaction of allyl chlorides with silver nitrate.[11] These authors suggest that the reaction proceeds with the intermediacy of ion pairs. In spite of these difficulties, silver nitrate is the most handy reagent for the ionization of organic halides from the stand point of synthesis. We therefore used silver nitrate at the outset.

To our surprise, both isomers gave the corresponding nitrate esters (**5**) in good yields. It is especially interesting in that the *ap* isomer gave the nitrate instead of the cyclized product (**3**). Probably the nucleophilicity of the nitrate anion is so high[12] that the ion pair collapses before the internal rotation, which is necessary for the ring closure, takes place.

In order to lower the nucleophilicity of the anion present in the system, silver perchlorate was used, although we cannot avoid the complexity of the reaction mechanism by using the perchlorate salt.[13]

The reaction of *sp*-**1** and *ap*-**1** with silver perchlorate in acetonitrile gave, after treatment of the reaction mixture with water, the corresponding acetamido derivatives (**6**) which were expected if the Ritter type reaction[14] should take place. The results suggest that acetonitrile is nucleophilic enough to react with carbocations in this system. Since no cyclization product was found from *ap*-**1**, the reaction of the carbocation with acetonitrile is by far the more favored process than the cyclization to afford **3**.



The reaction of *ap*-**1** with silver perchlorate in benzene afforded *ap*-9-(2-benzyl-6-methylphenyl)fluorene (*ap*-**7**) and the cyclized product (**3**) in a 12:1 ratio; apparently the intermolecular Friedel-Crafts reaction is favored over the intramolecular reaction. The intermediacy of a common species is apparent from the temperature dependence of the product ratio. As shown in Table 3, the formation of the cyclized product (**3**) becomes relatively favored as the temperature is raised, though it does never become a main reaction.

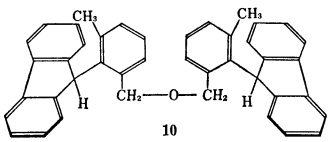
Although Pocker and Kevill[15] showed that organic perchlorate can survive for some time in a nonpolar solvent such as benzene, no trace of a product which might be derived from the perchlorate and water was detected under the conditions. However, the long lifetime of the perchlorate could be reproduced as follows. Whereas both *ap*-**1** and *sp*-**1** in benzene reacted very rapidly with silver perchlorate at room temperature to produce silver bromide precipitate, 9-(2-methoxymethyl-6-methylphenyl)fluorene (**8**) with retention of the stereochemistry was formed on addition of methanol after 2—3 h together with 9-(2-benzyl-6-methylphenyl)fluorene (**7**).

Table 4. Relative reactivity of *sp*-**1** and *ap*-**1** under ionizing conditions

Silver salt	Solvent	Concn/mM		Temp °C	Reaction period	k_{sp}/k_{ap}	k_{bz}/k_{sp}[c]
		Substrate	Silver salt				
$AgNO_3$	CH_3CN	9	9	25	40 min	5.9	0.36
$AgClO_4$	CH_3CN	9	9	60	20 h	1.3	0.21
$AgClO_4$	C_6H_6	10	20	22	2 h	1.6	*ca.* 34
$AgClO_4$	HFP[a]	0.8	b)	14	72 min	0.78	—
$AgClO_4$	TFA[a]	0.8	b)	25	13 min	0.94	—

a) These solvents contain *ca.* 5 (v/v)% chloroform. b) Heterogeneous reactions. c) k_{bz}/k_{sp} denotes the relative reactivity of benzyl bromide, taking the reactivity of *sp*-**1** as a reference.

Though not found after the reaction period of 23 h, bis[*sp*-2-(9-fluorenyl)-3-methylbenzyl] ether (**10**) was detected when the reaction mixture from *sp*-**1** and silver perchlorate was treated with methanol after a few hours. This product is derived from water which is present within the reaction system, because careful drying of the reagent and the solvent decreased the amount of the ether (**10**). No such ether was detected when *ap*-**1** was treated similarly. This difference, together with the unusuality discussed below, led us to believe that water or the benzyl alcohol (**9**) derived from *sp*-**1** and water is strongly adsorbed on the silver bromide surface where the formation reaction of **10** takes place.



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During the reaction of *sp*-**1** with silver perchlorate in benzene, the formation of the corresponding benzyl alcohol (**9**) was detected, if water was intentionally added. However, an attempted coupling of the benzyl alcohol (**9**) in the presence of concentrated sulfuric acid did not give any of **10** but led to the formation of polymers. Neither an attempted Williamson synthesis of **10** from *sp*-**1** and the *sp*-alcohol (**9**) in DMF in the presence of silver oxide succeeded. Feasibility of the reaction occurring on the surface of silver bromide is supported also if one considers the concentration of water or the benzyl alcohol (**9**) in the system: if the reaction is to occur in solution, the concentration of the substrate may be prohibitively low. The disappearance of the ether (**10**) in the reaction products after 23 h must be ascribed to the possibility that the ether (**10**) is cleaved by perchloric acid which is formed as a result of the Friedel-Crafts reaction.

TFA is known to be little nucleophilic[16] and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) is even less nucleophilic.[17] Therefore, in these solvents, the reaction with solvent molecules is practically prohibited. In order to explore further the feasibility of the ring closure of *sp*-**1**, the ionization of *sp*-**1** in these solvents were investigated with the aid of silver perchlorate. Silver perchlorate is not appreciably soluble in these solvents: the reaction had to be carried out in heterogeneous systems. If the reaction was carried out at room temperature, the corresponding perchlorate ester (or perchlorate ion pair or trifluoroacetate ion pair) survived until more nucleophilic reagent was added. Thus the *sp* isomer of the methoxy compound (**8**) was the sole product when methanol was added. When the reaction mixture was heated, only polymers resulted. *ap*-**1**, under the similar conditions, reacted to give the cyclic compound (**3**) in good yields. Thus it becomes apparent that the *ap* isomer cyclized easily whereas the *sp* isomer gave only polymers if the cation is forced to develop.

A rationale for the apparent difference in reactivity of *ap*-**1** and *sp*-**1** may be given in the following way. As has been pointed out, the internal rotation is necessary to form the cyclized product (**3**): The barrier to rotation is over 25 kcal/mol. This may be the reason why even poorly nucleophilic benzene can react with *ap*-**1** to produce *ap*-**7** in the presence of silver perchlorate, in competition with the benzene ring in the fluorene moiety, to consitute the main process at 20 °C. A precise estimation of the barriers to rotation in the *ap* cation (or the ion pair) is not possible at present, but the barrier should be lowered in the cation relative to the parent compound because the barrier to rotation in 9-(2-formyl-1-naphthyl)fluorene,[18] a model compound with an sp^2-carbon as a substituent, is known to be appreciably lower than that in 9-(2-methyl-1-naphthyl)fluorene,[6b] that has an sp^3-hybridized carbon as a substituent in the 2 position of the naphthalene ring: The substituent in the 2 position of the naphthalene ring is responsible in determining the barrier to rotation. Molecular models suggest that it is the substituent in the *ap* position, with respect to the 9-H, rather than the substituent in the *sp* that determines the sharpness of the rising of the potential curve at the early stage of rotation from the ground state. Then in *sp*-**1**, the ease of rotation may not be changed on ionization to an appreciable extent, whereas the ease of rotation is increased in *ap*-**1** on ionization. Thus the polymerization is the preferred process in *sp*-**1** under the conditions examined. At extreme dilution, the cyclization of *sp*-**1** may be possible in principle, but it is not practicable.

Competitive Reactions between sp-***1*** *and* ap-***1***. In order to see whether the large difference in reactivity of the diastereomers of **1** in TFA is peculiar in that solvent, competitive reactions of *sp*-**1** and *ap*-**1** with silver salts in various solvents were carried out. The results are summarized in Table 4 together with the relative reactivity of benzyl bromide used as a reference compound under the same conditions. We may compare the reactivity of *sp*-**1** and *ap*-**1**, although the

products are formed by different mechanisms after ionization, because the initial ionization can be considered as the rate determining step in both isomers.

Of silver nitrate and silver perchlorate, the former gave a larger k_{sp}/k_{ap} value than the latter in acetonitrile. As has been noticed, the corresponding perchlorate ester is formed, though its lifetime is short, in the reaction with silver perchlorate, which then reacts with the solvent molecule. This will be the main source of difference between the perchlorate and nitrate cases, in the latter of which the collapse of the ion pair gives directly the product. At any rate, the *sp* form is more reactive than the *ap*, making a contrast to the reactivity in TFA.

It is interesting to note that, while the relative reactivity of *sp*-**1** is larger than that of *ap*-**1** in acetonitrile and in benzene, the reverse is true in TFA and HFP. However, the reactivity ratio is not so large as that obtained by heating a TFA solution. The difference may again reflect that in silver perchlorate cases the rate of decomposition of the perchlorate ester is important, whereas the ionization in TFA occurs from the bromide.

In acetonitrile, benzyl bromide is less reactive than *sp*-**1**, while the former is more reactive by a large factor than the latter in benzene. We wish to attribute these phenomena tentatively to the steric effects within the substrates and to those in solvation. On one hand, because of the molecular shape and the fact that the molecule coordinates to a cation with its nitrogen, the steric effect in the solvation with acetonitrile may not play an important role for retardation in the ionization of the CH_2Br group in *sp*-**1**. On the other, the steric interaction in the ground state of *sp*-**1** is relieved to some extent on its ionization. Thus the steric acceleration is operative in the ionization of *sp*-**1** in acetonitrile. In contrast, the completion of the solvation shell for the cation derived from *sp*-**1** requires extra energy in benzene because of the space-demanding molecular shape of the solvent molecule. Therefore the cation derived from *sp*-**1** in benzene is much more unstable than that derived from benzyl bromide. This solvation effect rather than the steric acceleration seems to be a ruling factor in the reactions in benzene.

Solvolytic Reactions. In the foregoing section, the role of solvent is found to be important in determining the relative reactivity. To shed light further on this point, it may be necessary to keep the leaving group constant. Thus we have investigated the solvolytic reactions of *sp*-**1** and *ap*-**1** in various ionizing solvents.

The first choice was formic acid in which solvolytic reactions are close to S_N1.[19] Solvolysis of *sp*-**1** and *ap*-**1** in formic acid gave the corresponding formate to indicate that formic acid is nucleophilic enough to win the competition with cyclization in *ap*-**1**. The first order rate constants of the reaction of *sp*-**1** and *ap*-**1** in formic acid containing *ca.* 8 (v/v)% chloroform at 42 °C were obtained as 7.6×10^{-4} min^{-1} and 4.6×10^{-4} min^{-1}, respectively. Thus the relative rate k_{sp}/k_{ap} is 1.6: The *sp* form is more reactive than the *ap* under these conditions.

In a 1:1 (v/v) mixture of TFA and chloroform, the rate of disappearance of *ap*-**1** was determined at two concentrations. At 86 mM, the first order rate constant was 8.5×10^{-4} min^{-1} at 60 °C, whereas it was 5.6×10^{-4} min^{-1} at 48 mM at the same temperature. At this level of concentration, the products were polymers which were undoubtedly formed by intermolecular Friedel-Crafts reactions. The results suggest that the solute in TFA assists ionization in some ways. Under the similar conditions, *sp*-**1** was always recovered as well as benzyl bromide. The relative rate (k_{sp}/k_{ap}) is less than 0.05.

At 2 mM in TFA containing 3 (v/v)% chloroform, the half life of *ap*-**1** at 60 °C was 50—60 min. Heating a 2 mM HFP (containing 2 (v/v)% chloroform) solution of *ap*-**1** at 55 °C showed the disappearance of the solute with a half life of 30—40 min. Under the same conditions, *sp*-**1** was completely recovered, the relative reactivity (k_{sp}/k_{ap}) being less than 0.05. The main product in these reactions was **3**. The formation of **4** was diminished when HFP was used as a solvent and only a trace amount of **4** was usually detected.

Considering the ionizing ability of formic acid, TFA, and HFP,[20] one may wonder why the more ionizing solvents show no reaction of *sp*-**1** while the less ionizing solvent gives the solvolysis product. The key to solve this problem can be the fact that the more ionizing solvents are less nucleophilic. Namely, *sp*-**1** may ionize to contact ion pairs or to solvent separated ion pairs in TFA or HFP: It is more reasonable to assume so when one considers the ionizing power of these solvents. However, the nucleophilicity of TFA and HFP is so low that the ion pairs return to the covalent species rather than to give a reaction product. In contrast, formic acid is nucleophilic enough to give the formate if *sp*-**1** ionizes either to the contact ion pair or to the solvent separated ion pair.

If the above mentioned idea is correct, a TFA or HFP solution containing a nucleophile should show some reactivity of *sp*-**1**. Thus the reaction in HFP containing 5 (v/v)% chloroform and 3 (v/v)% methanol was investigated. As expected, *sp*-**1** afforded the corresponding methoxy compound (**8**) in a good yield, whereas *ap*-**1** afforded the cyclized products (**3** and **4**). The rates of decrease in the amount of *sp*-**1** and *ap*-**1** were treated as first order reactions. The rate constants were 1.5×10^{-3} and 8.4×10^{-3} min^{-1} for *sp*-**1** and *ap*-**1**, respectively, at 1.8 mM and at 40 °C. The rate constants may again be compared directly because in both cases the ionization is the rate determining step. Then the relative rate (k_{sp}/k_{ap}) is 0.18. It is striking to note that *ap*-**1** did not give *ap*-**8** to a measurable degree, because methanol is more nucleophilic than formic acid in which the solvolysis afforded the formate. We may have to assume that the ion pairs formed from *ap*-**1** in HFP are so tight that they react intramolecularly with the benzene ring of the fluorene rather than with external methanol.

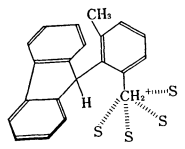
Under the same conditions in TFA (TFA–$CHCl_3$–CH_3OH, 40 °C, 18 mM) the rate constants of the reaction were 3.1×10^{-4} and 1.5×10^{-3} min^{-1}, respectively, for *sp*-**1** and *ap*-**1**, as measured by the decrease

in the amount of the substrates. The relative reactivity k_{sp}/k_{ap} is calculated to be 0.19. The TFA–$CHCl_3$–CH_3OH system did not give the corresponding methoxy compound (*sp*-**8**) from *sp*-**1**, however, although *ap*-**1** gave the cyclized products (**3** and **4**). The behaviors of the products from *sp*-**1** on a TLC plate were similar to those of the polymers obtained by heating a mixture of *sp*-**1** in TFA or HFP and silver perchlorate. We abandoned attempts to prepare the methoxy compound (*sp*-**8**) from *sp*-**1** under similar conditions for the following reasons. The apparent failure in affording *sp*-**8** in the TFA–$CHCl_3$–CH_3OH system must be attributed to the reduction in effective concentration of methanol in the system owing to protonation. Although we could have made *sp*-**8** by increasing the molar fraction of methanol in the system, the increase in the concentration of methanol also increases the reaction rate of *sp*-**1** with methanol in S_N2 fashion. It would become difficult to tell the extent of contributions of S_N1 and S_N2 reactions.

Role of Solvent Molecules in Ionization. At any rate, the above results suggest that in TFA and in HFP, ionization of *sp*-**1** is slower than that of *ap*-**1**. We have attributed this difference to π-participation of the fluorene system.[5] However, having additional experimental data in hand, we notice that the situation is not so simple as we have thought: Solvent plays an important role in controlling the rates of reaction.

The first we notice is that the ionization reaction of *sp*-**1** is faster than in *ap*-**1** in acetonitrile, in benzene, and in formic acid, whereas the reverse is true in TFA and in HFP. We wish to postulate, in summarizing the results described above, that the completion of the solvation shell is important in determining the ease of ionization.

Let us assume that free carbocations are formed by the ionization reaction. Then the cation must be surrounded by solvent molecules to form a solvation shell as depicted by **11** and **12**.[21] A main difference



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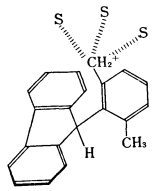

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here is that, while the solvent molecules form a solvation shell in the *sp* conformation, at least one of the solvent molecule cannot participate in the solvation of the cation derived from the *ap* form because of the steric effect of the fluorene ring. In other words, the benzene ring of the fluorene moiety participate in completing the solvation shell (This can be viewed as π-participation.). Mere consideration of this situation leads to a conclusion that if a solvent molecule is more basic than the benzene ring in fluorene, then *sp*-**1** can be more reactive than *ap*-**1**. Similarly *ap*-**1** can be more reactive than *sp*-**1**, if the basicity of the solvent molecule is lower than the benzene ring in fluorene.

The general tendency seen in the experimental results conform with this expectation: in more basic solvents, the *sp* form is more reactive, while the *ap* form is more reactive in poorly basic solvents. One might argue that if we admit the hypothesis we must consider that benzene and formic acid must be more basic than the benzene in fluorene, contrary to the common belief.[22] We consider that this result is derived because the relative arrangement, in space, of the fluorene ring and the cation derived from *ap*-**1** is limited and is not optimum for the interaction between them. Thus the benzene ring in the fluorene moiety is not as effective as it should be. Free benzene molecules can assume optimum arrangement to stabilize the cation. The case of formic acid can be understood similarly.

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