high S_s/S_w values especially for benzophenone suggest some loose interaction of the substrates with the head group. Coupled with relatively small $a_{CH_3(CH_2)_n}$ values, these data make solubilization close to the micelle surface quite reasonable.

The markedly higher (S_s/S_w) values for DDAPS indicate interactions with the substrates to be unique among the surfactants considered. One explanation is to evoke a sort of "double association" with the -C=O hydrogen bonding near the surface, while the phenyl groups interact with the ammonium ion as well as the methylene groups at a greater distance from the surface. This type of interaction would be expected to provide more stability to the system than the simple hydrophobic association normally encountered in the micelle interior.

References and Notes

(1) (a) Supported in part by the U.S. Atomic Energy Commission and the National Science Foundation; E.J.F. is a Research Career Development Awardee of The National Institutes of Health; (b) Texas A&M University; (c) Carnegie-Mellon University.

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Hindered Rotation in 9-Arylfluorenes. Resolution of the Mechanistic Question

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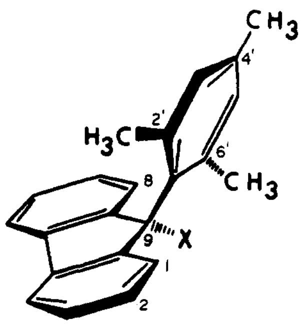
Received July 17, 1974

Abstract: Conclusive evidence is presented to rule out ionization as the process responsible for the dynamic nmr behavior of 9-arylfluorenes, in which rotation about the aryl-C_9 bond is hindered. The observation of separate resonances for the diastereotopic isopropyl methyl groups of 2-(2-propyl)-9-mesityl-9-fluorenol (**6b**) and 2-(2-propyl)-9-mesityl-9-chlorofluorene (**6c**) under conditions of rapid exchange of the mesityl methyl groups excludes any mechanism which requires loss of chirality of C_9. The possibility that intramolecular hydrogen shifts are responsible for equilibration of the diastereomers of 1-methyl-9-(2-methyl-1-naphthyl)fluorene (**4a** and **5a**) is discounted because of the absence of such shifts in fluorene-*9,9-d*$_2$. All the evidence presented is consistent with simple hindered rotation around the aryl-C_9 bond.

The pmr spectra of a number of 9-arylfluorenes in which the aryl group is a substituted phenyl or naphthyl moiety show marked temperature dependence indicative of an exchange process on the nmr time scale.[1-7] This process is illustrated by 9-mesityl-9-chlorofluorene (**1c**). Rotation of the mesityl group around the bond linking it to the fluorene ring is hindered because of steric interactions of the 2′- and 6′-methyls with H_1 and H_8 of the fluorene ring. As a result, the 2′- and 6′-methyls are nonequivalent at ambient temperature. The singlet for the 2′-methyl, which (as shown) is in the shielding zone of the aromatic fluorene ring, appears at δ 1.10,[2] considerably upfield from the normal chemical shift demonstrated by the 4′-methyl at δ 2.15. The 6′-methyl, in the deshielding zone of the fluorene ring, appears at δ 3.0. When **1c** is heated in a variety of solvents, the two sharp singlets for the 2′- and 6′-methyls broaden and coalesce at about 60° and presumably would emerge at higher temperature as one sharp singlet if the thermal instability of the compound did not prevent higher temperature spectra from being obtained.[2] Similar behavior is exhibited by the aromatic protons $H_{3'}$ and $H_{5'}$, which appear upfield from the rest of the aromatic protons. This indicates that the two edges of the mesityl ring of **1** exchange environments by some process, the activation energy of which was calculated by Rieker and Kessler[4] to be about 16 kcal/mol. Table I gives several examples of exchange barriers in 9-arylfluorenes, along with two representative 9-arylxanthenes which show similar behavior.[8]



1a, X = H
b, X = OH
c, X = Cl

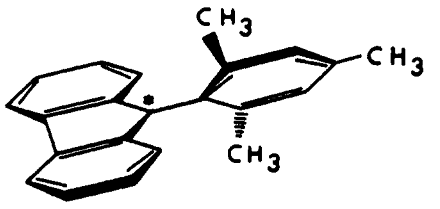
Three distinct mechanisms can be envisioned to account for the observed nmr behavior. (1) Rotation around the aryl–fluorene bond may become facile enough as the tem-

Table I. Activation Energies for Rotation in Selected 9-Aryl-9-X-fluorenes

Compd	Aryl	X	Solvent	ΔG^*, kcal/mol (T, °C)	Ref
1a	Mesityl	H	C_4Cl_6	>26 (200)	3c
1b	Mesityl	OH	1,2,4-$C_6H_3Cl_3$	20.2 (145)	4
			C_4Cl_6 or $C_{10}H_{10}$	20.8 (133)[b]	*a*
				20.8 (157)[c]	*a*
1c	Mesityl	Cl	1,2,4-$C_6H_3Cl_3$	16.2 (66)	4
6b	Mesityl	OH	Dioxane	20.8 (131)[d]	*a*
				20.9 (142)[e]	*a*
6c	Mesityl	Cl	CCl_4	15–17[f]	*a*
7	α-Bromomesityl	H	C_4Cl_6	~30 (200)[g]	5
8a	2,6-Dimethoxyphenyl	H	1,2,4-$C_6H_3Cl_3$	20.6 (145)	4
8b	2,6-Dimethoxyphenyl	OH	$CDCl_3$	14.4 (24)	4
8c	2,6-Dimethoxyphenyl	Cl	CH_2Cl_2	9.2 (−81)	4
9a[h]	Mesityl	H	CH_2Cl_2	17.6 (25)	8
9b[h]	2,6-Dimethylphenyl	OH	CH_2Cl_2	10.9 (25)	8
12	1-Naphthyl	H	C_2Cl_4	18.7 (116)	3c
			DMSO	17.8 (60)	7
3	2-Methyl-1-naphthyl	H	C_2Cl_4	29.2 (116)	3c
4a	2-Methyl-1-naphthyl	H	C_4Cl_6	33.3 (166)	*a*
			C_4Cl_6–TsOH	33.8 (172)	*a*
4b	2-Methyl-1-naphthyl	OH	C_4Cl_6	>26 (170)[i]	*a*

[a] This work. ΔG^* is considered accurate to ±0.5 kcal/mol. [b] Calculated from coalescence of $H_{3'}$ and $H_{5'}$. [c] Calculated from coalescence of 2′- and 6′-methyl groups. [d] 60 MHz. [e] 100 MHz. [f] Estimated from behavior qualitatively similar to **1c**. [g] Calculated from reported values for E_a and log A. [h] Xanthene system rather than fluorene. [i] Calculated from line width = 3.2 Hz compared with 2.0 Hz for reference samples.

perature increases to average the environment of the diastereomeric methyl positions. (2) Cleavage of the C_9–X bond might lead to a cation, radical, or anion with the structure **2**, in which the 2′- and 6′-methyls are equivalent. Return to tetrahedral C_9 could then occur equally well with retention or inversion of the original configuration. This is the mechanism favored by Chandross[2,9] for the compounds in which X = Cl, based on their ready ionizability and thermal instability, and on the much higher activation energies for exchange of the corresponding hydrocarbons (X = H). Because of the lack of a solvent effect, Chandross postulates formation of a tight ion pair, which can collapse with either retention or inversion of configuration. (3) At least when X = H, a series of orbital symmetry-allowed intramolecular [1,5] and [1,9] sigmatropic hydrogen shifts from C_9 into the other fluorene rings and back again to C_9 could invert configuration at C_9. This mechanism has not been considered previously. In this paper we present evidence which very strongly favors rotation about the aryl-fluorene bond as the only mechanism necessary to account for the temperature-dependent behavior of all these compounds.



2, * = +, −, or •

Results

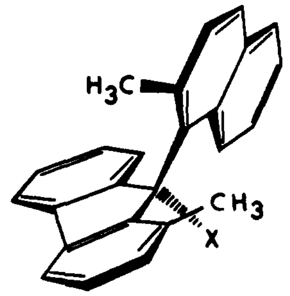
Syntheses of the new compounds employed in this study are detailed in the Experimental Section. The key features of the pmr spectra considered here appear in Table II.

9-(2-Methyl-1-naphthyl)fluorenes. The rotational barrier in 9-(2-methyl-1-naphthyl)fluorene (**3**) is so high that Siddall and Stewart[3c] were able to separate its rotational isomers by fractional crystallization. Reequilibration of the isomers at 116° gave a barrier ΔG^*_{116} = 29.2 kcal/mol. In order to test the possibility that hindered 9-arylfluorenes and 9-arylfluoren-9-ols might isomerize by an ionic mechanism, we synthesized compounds **4** and **5** on the assumption that the 1-methyl group would prevent equilibration of diastereomers by rotation. A mixture of the carbinols **4b** and **5b** was synthesized from 2-methyl-1-naphthyllithium and 1-methyl-9-fluorenone. Because it proved to be somewhat unstable, turning brown over a number of days, and resisted crystallization, we were unable to separate diastereomers **4b** and **5b**. However, the pmr spectrum of the mixture showed

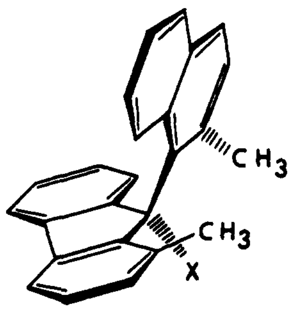
Table II. Proton Nmr Chemical Shifts[a]

Compd[b]	2′-CH_3	4′-CH_3	6′-CH_3	$H_{3'}$	$H_{5'}$	Isopropyl CH_3 (d, 6 H)	Other
1b	1.15	2.20	2.91	6.45	6.82		1.97 (OH)[c]
6a[d]	1.04	2.16	2.57	6.52	6.85	1.17, 1.18,[e] J = 6.9 Hz	2.81 (septet, 1 H, J = 6.9 Hz), 5.32 (s, H_9), 6.95 (s, H_1), 7.0–7.3 (m, 4 H), 7.5–7.7 (m, $H_{4,5}$)
6b[f]	1.15	2.13	2.91	6.50	6.89	1.16, 1.18,[g] J = 6.9 Hz	
6c[h]	1.11	2.18	3.08	6.56	6.98	1.21, J = 7.0 Hz	
4a	1.33						6.10 (H_9), 1.75 (1-CH_3), 8.53 ($H_{8'}$)
5a	2.88						5.70 (H_9), 1.77 (1-CH_3)
4b	1.46						1.66 (1-CH_3),[i] 9.75 ($H_{8'}$)
5b	3.10						1.82 (1-CH_3)[i]

[a] In parts per million downfield from internal TMS; spectra recorded in $CDCl_3$ or CCl_4 at 60 MHz, ambient probe temperature (28–44°) except where noted. [b] See structures in text. [c] Variable with temperature and concentration. [d] 100 MHz. [e] Diastereotopic splitting, $\Delta\nu$ = 1.0 Hz at 28°. [f] 100 MHz in dioxane. [g] $\Delta\nu$ = 1.6 Hz at 28°. [h] 100 MHz at 1° in dioxane–$CFCl_3$ (1:1 by volume). [i] These two could be reversed.



4a, X = H
b, X = OH



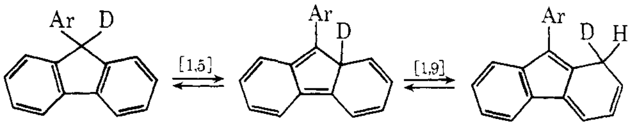
5a, X = H
b, X = OH

no significant exchange broadening of the methyl resonances up to 170°. Even with more than 0.5 equiv of added trichloroacetic acid at 119°, there was no evidence of exchange between **4b** and **5b** on the nmr time scale. This lack of acid catalysis suggests, but does not prove, that ionization to a carbonium ion is not part of the exchange process.

A mixture of the hydrocarbons **4a** and **5a** was prepared from **4b** and **5b** by reduction with lithium aluminum hydride and aluminum chloride, and the diastereomers were separated by column chromatography. Isomer **4a** is distinguished by the upfield chemical shift of the 2′-methyl and the downfield shift of H$_9$ relative to isomer **5a** (Table II). Reequilibration of the isomers was followed at 166° in the nmr probe by starting with **4a** and measuring the relative areas of the 2′-methyl signal for each isomer,[10] yielding an activation energy $\Delta G^*_{166} = 33.3 \pm 0.3$ kcal/mol. The most likely ionization mechanism available for isomerization of **4a** is loss of H$_9$ to give a fluorenyl carbanion, but a similar equilibration experiment at 172° in the presence of 0.5 equiv of *p*-toluenesulfonic acid gave $\Delta G^*_{172} = 33.8 \pm 0.3$ kcal/mol, within experimental error of the value in the absence of acid. This rules against an ionization mechanism for equilibration of **4a** and **5a.**

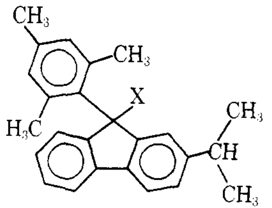
Another mechanism that could account for equilibration of **4a** and **5a** is a series of orbital symmetry allowed suprafacial [1,5] and [1,9] sigmatropic hydrogen shifts (Scheme I). In order to determine the likelihood of such a process, fluorene-*9,9-d*$_2$ was heated without solvent in a sealed tube. There was no detectable increase in the area of its residual H$_9$ resonance after 13 hr at 350° or after 5.5 hr at 390°.

Scheme I



9-Mesitylfluorenes. The dynamic pmr behavior of 9-mesityl-9-fluorenol (**1b**) has been examined in two other laboratories. Rieker and Kessler[4] reported $T_c = 145°$ for its 2′- and 6′-methyl resonances in 1,2,4-trichlorobenzene. Chandross and Sheley[2] reported no observable broadening of the 2′- and 6′-methyl resonances up to 200° in *m*-dibromobenzene. We have reexamined this problem and found, as shown in Table I, coalescence of the H$_{3'}$ and H$_{5'}$ resonances at 133°, and of the 2′- and 6′-methyl resonances at 157°. These data correspond to a barrier $\Delta G^* = 20.8$ kcal/mol at both temperatures, in good agreement with the results reported by Rieker and Kessler.[4,11] Identical results were obtained with either hexachlorobutadiene or naphthalene as the solvent. Washing the nmr tube with base to eliminate acid impurities from the glass did not change either coalescence temperature.

The rotation mechanism is indicated unequivocally by the dynamic nmr behavior of 2-(2-propyl)-9-mesityl-9-fluorenol (**6b**), which differs structurally from **1b** only by a remote diastereotopic probe.[12] The two methyls of the isopropyl group are nonequivalent (diastereotopic) because of the chiral center at C$_9$. At 100 MHz in 1,4-dioxane[13] (28°), the nonequivalence amounts to 1.6 Hz so that this region appears as two slightly separated doublets, further complicated by overlap of one of the peaks with the 2′-methyl singlet from the mesityl group (Figure 1b). At the same time, H$_{3'}$ and H$_{5'}$ appears as two singlets (broadened by long range coupling) well upfield from the rest of the aromatic protons (Figure 1a). As the temperature is raised (Figures 1c,d), H$_{3'}$ and H$_{5'}$ broaden and begin to coalesce, and the 2′-methyl broadens into a lump beneath the isopropyl methyl signals, which still exhibit diastereotopic splitting. At 150°, H$_{3'}$ and H$_{5'}$ have clearly coalesced ($T_c = 142°$), and yet the diastereotopic splitting of 1.1 Hz[14] is still exhibited in the isopropyl methyl signals (Figure 1e,f). This result unambiguously eliminates any exchange mechanism which involves inversion at C$_9$, because such a mechanism requires that the rate of exchange of the isopropyl methyl groups be equal to the rate of exchange of H$_{3'}$ and H$_{5'}$. Since the exchange rate at the coalescence temperature T_c can be approximated by $k_c = \pi\Delta\nu/\sqrt{2}$, where $\Delta\nu$ is the separation of the coalescing peaks in hertz,[15] the diastereotopic isopropyl methyl resonances ($\Delta\nu = 1.6$ Hz) would coalesce at a considerably lower temperature than those of the aromatic protons H$_{3'}$ and H$_{5'}$ ($\Delta\nu = 39$ Hz) if the exchange occurred by an ionization mechanism.



6a, X = H
b, X = OH
c, X = Cl

The rotational barrier of **6b** in dioxane was determined from coalescence temperatures of the two aromatic protons H$_{3'}$ and H$_{5'}$ in both 60-MHz and 100-MHz spectra. Its value, $\Delta G^* = 20.8$ kcal/mol, reported in Table I, is in close agreement with the barrier found for the prototype compound **1b.** Coalescence data from the 2′- and 6′-methyls were not used to calculate the barrier in **6b** because of interference from solvent sidebands and the difficulty of determining a precise coalescence temperature for the peaks, which disappear into the baseline.

The nmr spectrum (Table II) of the analogous chloride **6c**, prepared by treatment of **6b** with thionyl chloride, is very similar to that reported for the prototype compound **1c**[2] and demonstrates a lower exchange barrier than **6b**, as expected. The singlets for the 2′- and 6′-methyls of **6c** are noticeably broadened at 44° at 60 MHz in CCl$_4$. Exchange is slow enough at 1° that all peaks appear sharp at 100 MHz, but no diastereotopic splitting of the isopropyl methyl doublet can be resolved down to −16° in CCl$_4$, CDCl$_3$, or dioxane–CFCl$_3$ (1:1 by volume). Assuming that this difficulty is a reflection of the small magnitude of the diastereotopic nonequivalence rather than a result of rapid inversion at C$_9$, we turned to ^{13}C nmr.

Proton decoupled ^{13}C nmr spectra of **6c** are shown in Figure 2. Peak assignments are made on the basis of comparison with known chemical shifts of mesitylene, cumene, and fluorene[16] and on the basis of the temperature dependence of certain peaks. All 25 carbons in **6c** are resolved as

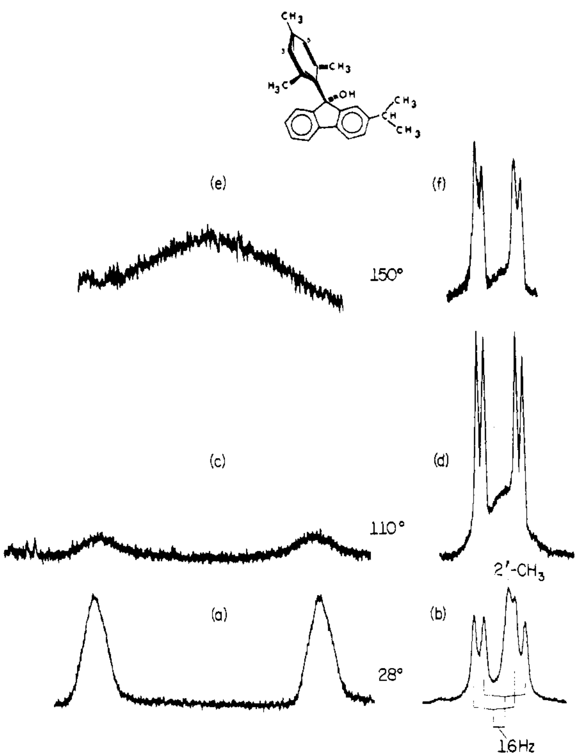


Figure 1. Proton nmr spectra of **6b** in dioxane (100 MHz): (a) aromatic region, showing signals for $H_{3'}$ and $H_{5'}$, 28°; (b) isopropyl methyl region with overlapping 2′-methyl from mesityl group, 28°; (c) aromatic region showing exchange-broadened signals for $H_{3'}$ and $H_{5'}$ at 110°; (d) isopropyl methyl signals, with severely broadened 2′-methyl peak, 110°; (e) aromatic region showing coalesced signals for $H_{3'}$ and $H_{5'}$ at 150°; and (f) isopropyl methyl signal, two overlapping doublets from the two diastereotopic methyls, 150°.

separate singlets, including each of the diastereotopic isopropyl methyl resonances, which are separated by 5.7 Hz. At −10°, all the peaks are sharp (Figure 2a), but at 45° an exchange process causes dramatic broadening of the signals from carbons b, d, g, h, i, and j (Figure 2b), and the aromatic carbons g and h are close to coalescence. At the same temperature, though, the two isopropyl methyl resonances are still clearly resolved ($\Delta\nu$ = 3.6 Hz), and their peak widths are identical with their peak widths at −10°. At 56°, the signals for carbons i and j disappear into the baseline, those for g and h coalesce into a single broad peak, and the isopropyl methyl resonances are still separated by about 2 Hz. The changes observed in the cmr spectrum of **6c** by warming from −10 to 45° are completely reversible. Thus the process which exchanges the mesityl carbons does not invert C_9. The ionization mechanism proposed by Chandross[2] for the prototype compound **1c** is therefore rigorously excluded for the specific case of compound **6c** and by extrapolation for **1c** also. Thermal decomposition of chloride **6c** over the time necessary for data acquisition has so far prevented any reliable measurement of its rotational barrier, but the qualitative behavior of its pmr spectrum is so similar to that of **1c** that we estimate the barrier as 15-17 kcal/mol.

Discussion

Other results in the literature support the rotation mechanism for the temperature-dependent nmr spectra of 9-arylfluorenes. The activation energies for exchange in pmr spectra of **1c** vary little in such widely different solvents as carbon disulfide, chloroform, and acetone.[2] Although ionization to a tight ion pair that interacts little with solvent might possibly explain this lack of solvent effect, it is better explained by the rotation mechanism.

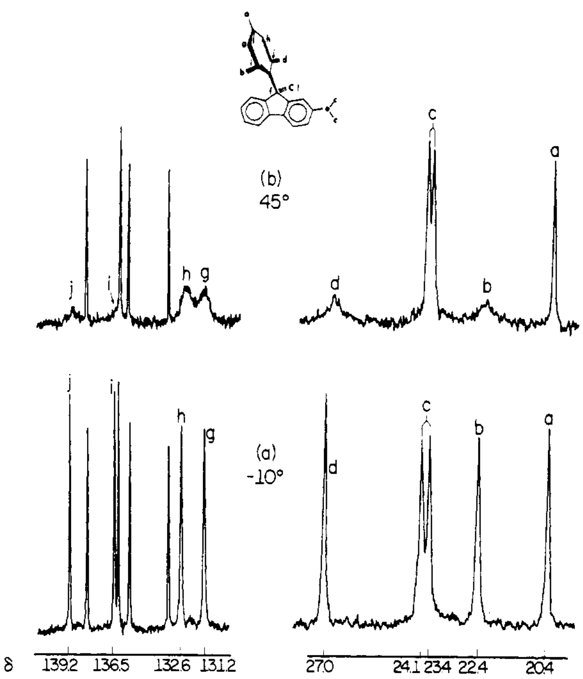
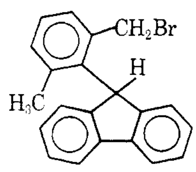
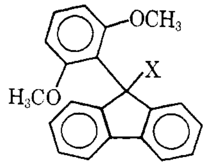


Figure 2. Partial 25.2-MHz ^{13}C nmr spectra of 2-(2-propyl)-9-mesityl-9-chlorofluorene (**6c**), 1 *M* in $CDCl_3$ (a) at −10°, and (b) at 45°. In addition to the assigned peaks in (a), aromatic carbon resonances appeared at 120.2, 120.4, 122.7, 124.5, 126.8, 127.9, 128.8, 133.3, 135.6, 136.3, 138.1, 149.6, 149.8, and 150.7 ppm, and aliphatic carbon resonances appeared at 34.2 (e) and 76.6 (f) ppm, relative to internal TMS.

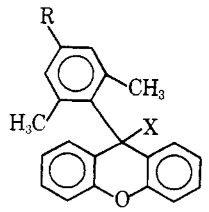
Data in Table I show that the free energies of activation for exchange in **1a–c** increase in the order Cl < OH < H as the size of the substituent X decreases. Although the barrier reported for **1a** is a lower limit, its magnitude is probably similar to that of **7**, the isomers of which have been isolated and reequilibrated on a laboratory time scale.[5] The same qualitative dependence of rotational barriers on X is observed in compounds **8a–c** and in the related xanthenes **9a,b**. The observed dependence of ΔG^* on X has been explained for the xanthenes in terms of a steric effect.[8] The same explanation applies to compounds **1a–c** and **8a–c**. In the ground state of **1** there is a steric interaction between the 6′-methyl and the substituent X. The larger X is, the more this interaction will destabilize the ground state. How-



7

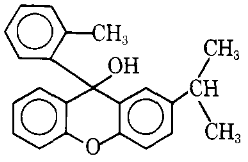


8a, X = H
b, X = OH
c, X = Cl



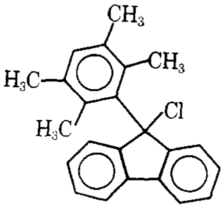
9a, R = CH_3; X = H
b, R = H; X = OH

ever, in the transition state for rotation there is less interaction of X with the aryl substituent, so the energy of the transition state will be less affected by the size of X. Thus a larger X such as Cl will narrow the energy difference between ground state and transition state by elevating the ground state, reducing the activation energy for exchange. The barriers for xanthenes **9a,b** are about 10 kcal/mol lower than the barriers for the analogous fluorenes, probably because of the greater flexibility of the xanthene ring. The observation of two doublets for the diastereotopic isopropyl methyls ($\Delta\nu$ = 1.5 Hz in dioxane at 100 MHz) of **10** under conditions which give a single peak for the tolyl methyl rules out an ionization mechanism for the xanthenes.[8]



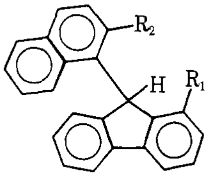
10

Behnke, Chandross, and Marquardt[9] have claimed that the entropy of activation for exchange in 9-duryl-9-chlorofluorene (**11**) supports an ionization mechanism. A two-point Arrhenius plot based on the coalescence temperatures for the two sets of nonequivalent methyls in **11** gave a large positive value of ΔS^* (11-46 eu). However, we seriously question the reliability of this approach, in view of the well-known[17,18] inaccuracies of such approximate dynamic nmr methods and the dramatic magnification of these inaccuracies in ΔS^*.



11

The 9-(1-naphthyl)fluorenes **12**, **3**, and **4a** (**5a**) form a series with increasing steric hindrance to bond rotation according to the ΔG^* values in Table I, which are consistent with a rotational mechanism for exchange. A carbanionic mechanism for exchange in the pmr spectra of these compounds is discounted on other grounds. When a solution of **12** in DMSO was observed at 100° in the presence of 5% D_2O, constant intensity of the H_9 signal indicated no deuterium incorporation even though rotation about the naphthyl-C_9 bond was rapid on the nmr time scale.[7] The barrier for **4a** was essentially the same in the presence or absence of *p*-toluenesulfonic acid, which would be expected to suppress a base-catalyzed exchange mechanism.



12, $R_1 = R_2 = H$
3, $R_1 = H$; $R_2 = CH_3$
4a (**5a**), $R_1 = R_2 = CH_3$

From the fact that no deuterium scrambling was detected in fluorene-*9,9-d*$_2$ after 5.5 hr at 390°, we can calculate a lower limit for the activation energy required for a first-order process. Assuming that 10% loss of D at the 9 position could have easily been detected, $\Delta G^* \geq 56$ kcal/mol. The possibility which stimulated study of fluorene-*9,9-d*$_2$ was a sigmatropic hydrogen shift mechanism for equilibration of the isomeric naphthylfluorenes **4a** and **5a**, for which the observed ΔG^* = 33.8 kcal/mol. Although the lower limit of 56 kcal/mol for fluorene is clearly much higher, it might be argued that the 9-aryl substituent lowers the barrier enough for such a mechanism to become important. A comparison with substituted indenes argues against this. For the [1,5] sigmatropic hydrogen shift in 1-phenylindene,[19] ΔG^*_{150} = 33 kcal/mol, just 6 kcal/mol lower than that in indene,[20] ΔG^*_{220} = 39 kcal/mol. By analogy it is highly unlikely that a 9-aryl group would lower the barrier to sigmatropic hydrogen shifts in fluorene by as much as 22 kcal/mol. Therefore we conclude that, in **4a** in particular and in fluorenes in general, intramolecular sigmatropic hydrogen shifts are not important at the temperatures employed in the hindered rotation studies of 9-arylfluorenes.

Experimental Section

Pmr spectra were run on a Varian Associates Model A-60A or HA-100 spectrometer with a Varian Model 6040 variable-temperature controller. Probe temperature was measured both with a thermocouple and by the peak separation of a calibrated ethylene glycol sample and is considered accurate to ±2°. All proton decoupled ^{13}C nmr spectra were obtained at 25.2 MHz on a Varian XL-100-15 spectrometer equipped with a Digilab Model FTS-NMR-3 Fourier transform accessory. Computer-limited resolution was 0.7 Hz. Data were collected with 25-μsec pulse and 1.39-sec acquisition times. All samples for pmr kinetic experiments were degassed by several freeze-thaw cycles and sealed under vacuum. Hexachlorobutadiene was purified by filtration through a column of alumina followed by vacuum distillation. Naphthalene was purified by sublimation. Dioxane from a newly opened bottle was used without further purification. Exchange barriers ΔG^* determined by dynamic nmr at coalescence temperatures were calculated according to the approximate formula $k_c = \pi\Delta\nu/\sqrt{2}$.[15] Melting points are uncorrected. Mass spectra at 70 eV were obtained with a Varian-MAT CH-5 instrument.

1-Methyl-9-fluorenone. Air oxidation of 1-methylfluorene[21] with *ca.* 1% *N*-benzyltrimethylammonium hydroxide[23] in pyridine at 25° for 1.5 hr gave the ketone in 81% yield: mp 99.5-101° (lit.[24] 98-99°); ir (KBr) 1691 cm^{-1}.

1-Methyl-9-(2-methyl-1-naphthyl)-9-fluorenol (4b,5b). A solution of 2-methyl-1-naphthyllithium was generated by stirring 1-bromo-2-methylnaphthalene (8.83 g, 40 mmol, Aldrich) with lithium wire clippings (0.70 g, 100 mg-atoms) in 45 ml of dry ether at 25° for 1 hr under argon. The solution was filtered, and to it was added a solution of 1-methyl-9-fluorenone (5.19 g, 26.7 mmol) in 75 ml of ether. The mixture was quenched with water, extracted with ether, dried ($MgSO_4$), and chromatographed over silica gel with 2% acetone in pentane (v/v) to yield 8.55 g (89%) of **4b** and **5b** as a colorless oil or white flakes. The mixture turned yellow slowly and resisted crystallization. Pmr data for **4b** and **5b** taken with the mixture are in Table II.

1-Methyl-9-(2-methyl-1-naphthyl)fluorene (4a, 5a). By the method of Nystrom and Berger,[25] $LiAlH_4$ (2.85 g, 75 mmol) was stirred with 75 ml of dry ether to which $AlCl_3$ (9.96 g, 75 mmol) in 50 ml of ether was added over 1 hr. To this mixture was added a solution of **4b** and **5b** (1.68 g, 5.0 mmol) over 1 hr, and the mixture was allowed to stir for 1 hr. The mixture was quenched by careful addition of water, extracted with ether, dried, and chromatographed on silica gel with 2% acetone in pentane (v/v). Two fractions of hydrocarbon were obtained, and each was separately crystallized from acetone to give isomers **4a** and **5a** (in order of elution) in a total yield of 15%: **4a**, mp 152-153.5°; **5a**, mp 189-191°; pmr, see Table II. The rate of conversion of **4a** to an equilibrium mixture of **4a** and **5a** was determined by heating a sealed sample in hexachlorobutadiene in the nmr probe for several hours and periodically measuring the relative areas of the 2′-methyl signals for each isomer. Each barrier ΔG^* reported in Table I represents a single experiment. The equilibrium constant K = 1.0 for **4a** $\rightleftarrows$ **5a**

was established by several experiments starting from both of the pure isomers.

Fluorene-9,9-d_2[26] contained 1.94 atoms of D per molecule at the 9 position by pmr analysis and 1.93 atoms of excess D by combustion and falling drop analysis.[27]

9-Mesityl-9-fluorenol (1b). 2-Bromomesitylene (2.45 g, 12.3 mmol, Aldrich) and a few drops of 1,2-dibromoethane were added to magnesium turnings (0.84 g, 35 mg-atoms) in 20 ml of dry ether. The mixture was stirred and gently heated until the reaction started, and then an additional 2.64 g (13.2 mmol) of 2-bromomesitylene was added. After 2 hr at reflux a solution of 9-fluorenone (4.50 g, 25 mmol, Aldrich) in 20 ml of dry THF was added dropwise. The mixture was quenched in 10% sulfuric acid, extracted with ether, dried ($MgSO_4$), and concentrated. Chromatography on silica gel with dichloromethane followed by four recrystallizations from hexane gave **1b**: mp 115.0-115.5° (lit.[2] 108-111°); pmr, see Table II.

Dimethyl-(2-fluorenyl)carbinol (13). Addition of a solution of 2-acetylfluorene[28] (37.5 g, 180 mmol, mp 131-132°) in 500 ml of dry THF-ether (1:1, v/v) to 3 *M* CH_3MgBr in ether (360 mmol, Ventron), followed by the usual isolation and two recrystallizations from hexane, yielded 25.6 g (64%) of **13**: mp 125.5-127° (lit.[29] 125.5-126.5°); pmr ($CDCl_3$) δ 1.58 (s, 6 H), 2.02 (s, 1 H, exchangeable with D_2O), 3.77 (s, 2 H), 7.1-7.9 (m, 7 H).

2-(2-Propyl)fluorene (14). Carbinol **13** (40.2 g, 180 mmol) and 700 ml of acetic anhydride were refluxed for 2 hr, and then the solution was poured into water. The resulting crude solid 2-(2-propenyl)fluorene was filtered, washed, and dried at 100° under vacuum and was used without further purification: mp 153-156° (lit.[30] 156-157°); pmr ($CDCl_3$) δ 2.20 (d of d, 3 H), 3.82 (s, 2 H), 5.07 (m, 1 H, $J \leq 2$ Hz), 5.4 (m, 1 H, $J \leq 1$ Hz), 7.0-7.9 (m, 7 H). Hydrogenation in 400 ml of ethanol over 7.0 g of 5% Pd/C at 45 psig of hydrogen for 2 hr, followed by evaporation at 100° (0.05 Torr) onto a cold finger and recrystallization from methanol-water, gave **14** in 82% yield from **13**: mp 83-84° (lit.[30] 81-82°); ir identical with literature;[31] pmr ($CDCl_3$) δ 1.25 (d, 6 H, $J = 7$ Hz), 2.88 (m, 1 H, $J = 7$ Hz), 3.73 (s, 2 H), 6.9-7.8 (m, 7 H); mass spectrum, major fragments at *m/e* 208, 193, 178, and 165.

2-(2-Propyl)-9-fluorenone (15). 2-(2-Propyl)fluorene (12.0 g, 57.7 mmol) was dissolved in 3 l. of dry pyridine (distilled from barium oxide), and a solution of *N*-benzyltrimethylammonium hydroxide in pyridine (15.0 ml, 40%, Aldrich) was added.[32] The solution instantly turned deep green. Oxygen was bubbled through for 20 min, and the reaction was quenched by adding 20 ml of glacial acetic acid, followed by 125 ml of water. The solvent was removed on a rotary evaporator, and the residue was taken up in ether and extracted in turn with 3 *M* HCl, 2 *M* NaOH, and saturated NaCl solution. The ether phase was dried ($MgSO_4$), concentrated to an oil, and distilled in a molecular still at 130° (0.03 Torr) to give 11.5 g (89%) of **15**. At room temperature, **15** is a bright yellow liquid, but it is solid at −10°: pmr ($CDCl_3$) δ 1.17 (d, 6 H, $J = 6.7$ Hz), 2.82 (septet, 1 H, $J = 6.7$ Hz), 6.92-7.62 (m, 7 H); mass spectrum, major fragments at *m/e* 222, 207, 193, 179, 165, and 152; ir (neat) 1715, 1605, 1382, 1360, 730 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.24; H, 6.29.

2-(2-Propyl)-9-mesityl-9-fluorenol (6b). To a stirred mixture of magnesium turnings (5.35 g, 220 mg-atoms) in 50 ml of dry ether was added a solution of 2-bromomesitylene (21.9 g, 110 mmol, Aldrich) and 1,2-dibromoethane (20.7 g, 110 mmol, Aldrich) in 50 ml of dry ether at a rate that maintained reflux. After another 2 hr at reflux, 1.5 ml more of 1,2-dibromoethane was added to consume the remaining magnesium. A solution of **15** (11.48 g, 51.6 mmol), diluted to 25 ml in ether, was added over 20 min, and the reaction was heated at reflux for 1 hr. The mixture was quenched in 10% sulfuric acid. Crude **6b** was isolated and chromatographed on 800 g of silica gel with 2% ether in hexane (v/v) to give **6b** (13.6 g, 77%) as a clear, colorless gum which was pure by pmr (see Table II): ir (CS_2) 3520 (O-H), 2940, 1613, 1443, 1385, 1368, 1332, 1135, 1006, 760, 740 cm^{-1}; mass spectrum, major peaks at *m/e* 342, 341, and 325. The product was low melting (49-52°) and difficult to crystallize. It could be crystallized with patience from 80% methanol-water but could not be completely dried without melting. It discolored slowly at room temperature but did not discolor over 6 months when stored at −10°. Since no change in its pmr spectrum resulted from recrystallization, the gum obtained from chromatography was used for pmr experiments without further purification. The stability of **6b** in dioxane over the time required for the higher temperature pmr studies was tested by heating a sample at 165° for 25 min. Its pmr spectra before and after heating were identical.

2-(2-Propyl)-9-mesityl-9-chlorofluorene (6c). A solution of **6b** (2.0 g, 6 mmol) in 10 ml of dichloromethane was added dropwise to a stirred solution of thionyl chloride (2.5 g, 21 mmol) in 10 ml of dichloromethane. After stirring at room temperature for 2 hr, the solvent and excess thionyl chloride were removed by azeotropic distillation with dry benzene on a rotary evaporator. The resulting green-brown oil was stored at −10° overnight and then dissolved in $CDCl_3$ for the ^{13}C nmr studies. This solution showed no impurities by pmr and was used without further purification. The oily **6c** was unstable above 60°. Exposure to the moisture in the air destroyed **6c** in 2 days, and attempts to purify it by column chromatography, even at −6° over stringently dried silica gel or alumina, resulted in complete decomposition on the column. After four recrystallizations from pentane at −78° (crystals have not been obtained at room temperature), the pmr spectrum was identical with that of the mother liquor, and neither showed any impurity other than pentane. Spectra clearly showed that the reaction product was different from the carbinol **6b** and was not contaminated with **6b**: pmr, see Table II; ir (CS_2) 2950, 1700-2000 (aromatic substitution pattern, almost identical with **6b**), 1613, 1369, 1352, 742 cm^{-1}. Notably absent in the ir were peaks corresponding to the carbinol bands at 3520, 1332, 1135, 1006, 760 cm^{-1}.

2-(2-Propyl)-9-mesitylfluorene (6a). To further establish the identity of the chloride **6a**, it was converted to the hydrocarbon **6a** by reduction with zinc in acetic acid:[2] pmr, see Table II; mass spectrum, major peaks at *m/e* 326, 311, 283, 268, and 253; ir (neat) 3100-2850, 1620, 1490-1425, 1385, 1368 cm^{-1}.

Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 92.13; H, 7.97.

Acknowledgments. We thank E. I. duPont de Nemours & Company for partial support of this research and the National Science Foundation for a predoctoral fellowship (T.B.T.). The ^{13}C nmr equipment was funded in part by the National Science Foundation. S. K. Silber ran some of the variable-temperature nmr spectra.

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Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. II.[1] Anisylation of Thianthrene Cation Radical

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Received February 20, 1974

Abstract: The thianthrene cation radical ($Th\cdot^+$) reacts with anisole (AnH) to give a complex which reacts further by one of two pathways depending upon the concentration of the cation radical. At low cation radical concentration ($\sim 10^{-5}$ *M*), a pseudo-first-order rate law is followed. Electrochemical techniques indicate that the reduction of $Th\cdot^+$ to thianthrene (Th) is a quantitative reaction under these conditions. At higher cation radical concentration the reaction becomes more complex obeying the rate law $-d[Th\cdot^+]/dt = 2k_3K_1K_2[Th\cdot^+]^2[AnH]/(k_3/k_{-2} + [Th])$, where the K's and k's are equilibrium constants and rate constants for the following equations. Dibenzo-*p*-dioxin cation radical ($DBO\cdot^+$) was found to accelerate

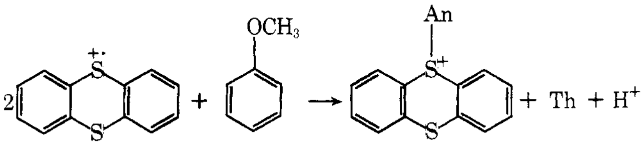
$$Th^{\cdot+} + AnH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Th-AnH)^{\cdot+};\ (Th-AnH)^{\cdot+} + Th^{\cdot+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (Th-AnH)^{2+} + Th;\ (Th-AnH)^{2+} \xrightarrow{k_3} (Th-An)^+ + H^+.$$

the rate of anisylation of $Th\cdot^+$ by a factor of 200 which was attributed to $DBO\cdot^+$, a better oxidant than $Th\cdot^+$, participating in equilibrium 2. A disproportionation mechanism was ruled out, because the observed rate constants were found to be as much as 5×10^4 times higher than predicted for diffusion-controlled reaction of Th^{2+}.

During the past few years, the mechanisms of the reactions of aromatic cation radicals have been under vigorous discussion in the literature. At about the same time, two different mechanisms for electrophilic reactions of cation radicals were published. Shine and Murata[2,3] proposed that the hydroxylation of the thianthrene cation radical ($Th\cdot^+$) involved a disproportionation to the reactive dication, while Manning, Parker, and Adams[4] proposed that the pyridination of the 9,10-diphenylanthracene cation radical involved a direct electrophilic reaction of the radical ion. A cross refutation of the two mechanisms appeared shortly afterward: Parker and Eberson[5] presented evidence that the hydroxylation of $Th\cdot^+$ involved a direct electrophilic reaction of the radical ion, while Marcoux[6] proposed that the pyridination of the 9,10-diphenylanthracene cation radical followed the disproportionation mechanism. More recently, the observation of reversible cation radical-dication redox couples in acetonitrile has given a reliable equilibrium constant for the disproportionation of $Th\cdot^+$ and has indicated that disproportionation reactions are very unlikely for the radical ion.[7] Furthermore, a homogeneous kinetic study of the pyridination of the 9,10-diphenylanthracene cation radical has confirmed that the radical ion reacts directly with pyridine.[8]

The initial reaction of a cation radical with a nucleophile produces a radical more easily oxidized than the substrate from which the radical ion is derived. A further one-electron oxidation of the radical is necessary to obtain stable products. When the reaction takes place at an electrode, electron transfer to the electrode can take place. However, in homogeneous solution the oxidant is usually a second equivalent of cation radical which is thereby reduced to substrate. This reaction has been called the half-regeneration mechanism and has been demonstrated in several cases.[9] However, it should be pointed out that this terminology only describes the stoichiometry of the reaction and says little about the mechanism since it does not define the reactive species, *i.e.*, cation radical, dication, etc.

Recently, Silber and Shine[10] have reported the reaction of $Th\cdot^+$ with anisole (AnH) to give a sulfonium salt (eq 1).



$Th\cdot^+$ AnH $(Th\text{-}An)^+$ (1)

The reaction was found to be second order in cation radical and inhibited by unoxidized substrate, conditions expected for the disproportionation mechanism. Since the more recent work has cast serious doubt on disproportionation mechanisms for $Th\cdot^+$,[7] the anisylation reaction was reinvestigated in order to establish the mechanism.

Results

Voltammetric Anisylation of the Thianthrene Dication. In "nucleophile-free" acetonitrile,[7] the reversible first and second charge transfers from Th appear at +1.26 and +1.77 V.[11] In the same medium, AnH is oxidized irreversibly with a peak potential of +1.71 V. The cyclic voltammogram of Th (1.0 m*M*) in acetonitrile containing n-Bu_4NBF_4 (0.2 *M*) over neutral alumina is shown in Figure 1a which shows the two reversible couples. The addition of AnH (0.2 m*M*) had no effect upon the first charge transfer, but a pre-peak