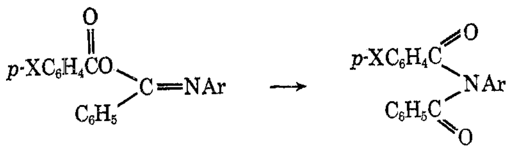
TABLE II

Compd no.	Substituent	Formula	Mp,[a] °C	Ir maxima in carbonyl region, cm^{-1}	Uv and visible maxima, mμ (ε)	Calcd, %			Found, %		
						C	H	N	C	H	N
IVb	Br	$C_{27}H_{19}O_2N_2Br$	148.5–149[b]	1740	251 (4.14×10^4) 346–350 (2.31×10^4) 450–458 (4.83×10^2)	67.09	3.96		67.25	4.11	
Vb	Br		177–179	1675 1660 (sh)	251–255 (2.66×10^4)	67.09	3.96		66.84	3.93	
IVc	NO_2	$C_{27}H_{19}O_4N_3$	164–165[b]	1755	255 (3.08×10^4) 343–351 (1.98×10^4) 450 (4.76×10^2)	72.15	4.26	9.35	72.22	4.32	9.59
Vc	NO_2		167.5–168	1690 (sh) 1670	257–260 (3.02×10^4)	72.15	4.26	9.35	72.91	4.28	9.33
IVd	OCH_3	$C_{28}H_{22}O_3N_2$	143–146[b]	1740	259–260 (2.70×10^4) 347–352 (2.01×10^4) 446–458 (4.96×10^2)	77.40	5.14	6.46	77.08	5.02	
Vd	OCH_3		163–164	1680 1670 (sh)	255–257 (2.80×10^4)	77.40	5.14	6.46	76.87	5.07	6.56

[a] Melting points of the azo esters were obtained by placing a sample into the Mel-Temp apparatus at about 120° and heating at 2 deg/min. [b] These compounds crystallize as red nuggets and yellow needles. The yellow needles showed a fuzzier melting point. However, both kinds of crystals melted to a red melt which decolorized to the rearranged product. Both kinds of crystals move as one spot on Chromagram sheet. Their infrared spectra appeared identical.

effect on the stability of the singlet whose formation is rate determining.[3] The isomerization mechanism is also strengthened and the single step postulate weakened by the finding of a marked substituent effect in the benzimidoyl benzoate rearrangement[1c] where aroyl migration is rate determining. Work with enol benzoates (IV) in which substituents are placed on the stilbene phenyl groups is in progress. Preliminary work suggests that *p*-nitro substituents on the stilbene phenyl groups have a retarding effect on the rate of reaction 4.



The rearrangement is particularly intriguing in the solid state. It can be followed under the microscope by changes in color from the red enol benzoate (IV) to the colorless hydrazone V. V forms whiskers on the surface of the crystal and at defect points. The red crystal becomes opaque but retains its shape. V sublimes appreciably at about 105° for the several days which the solid state rearrangement requires. This escape of some of the product from the crystal undoubtedly produces many holes which act as new defects to initiate reaction. A "shrinking" in the crystal at the reaction locus would provide enough space for rotation and reorientation of groups in the molecule. A sample of IVb is in the hands of an X-ray crystallographer for further study.

Experimental Section

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were measured in a Perkin-Elmer Model 137 spectrophotometer and ultraviolet spectra in a Beckman DU spectrophotometer and in a Perkin-Elmer Model 202 spectrophotometer.

Rates of Rearrangement of α-Phenylazo-β-(*p*-X-benzoyloxy)-stilbenes (IV).—The rates of rearrangement in decalin were studied at two temperatures by following changes in absorption at 350 mμ as previously described.[2] The expression for first-order constants was

$$\ln \frac{OD_0^{350} - C_0(\epsilon_V^{350})}{OD_t^{350} - C_0(\epsilon_V^{350})}/t$$

where OD_0^{350} is optical density at 350 mμ at 0 time, OD_t^{350} is optical density at 350 mμ at time t, C_0 is concentration of IV at time 0, and ϵ_V^{350} is the extinction coefficient of V at 350 mμ.

α-Phenylazo-β-(*p*-X-benzoyloxy)stilbenes (IV) were prepared as described previously[2] for IVa. They could be purified on Eastman chromatogram sheet as previously described,[2] or by column chromatography on Florisil packed in hexane with benzene as eluent. The properties of these compounds and their rearranged products are described in Table II.

Registry No.—IVb, 18153-62-3; IVc, 18153-63-4; IVd, 18153-64-5; Vb, 18181-27-6; Vc, 18153-65-6; Vd, 18153-66-7.

Acknowledgment.—This work was supported in part by a Faculty Research Grant from the City University of New York.

Proton Magnetic Resonance Studies of Slow Rotation in 9-Arylfluorenes[1]

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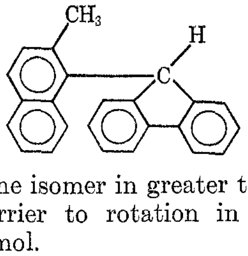
Received July 1, 1968

Slow rotation around the bond between the aryl group and the central carbon atom is reported for five 9-arylfluorenes. Kinetic quantities were determined for two of these by pmr signal shape analysis. One was isolated as one isomer in greater than 90% isomer purity. The barrier to rotation in this compound (E_a) is 29.8 kcal/mol.



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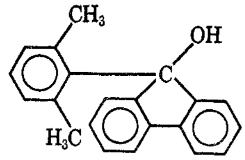
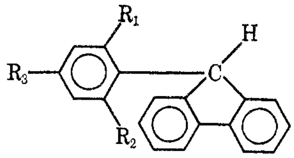
[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

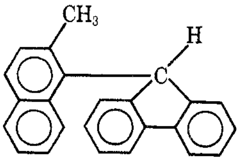
The observation of slow site exchange for the two methyl groups in carbinols[2] such as



suggested the possibility of observing the same type of phenomenon in the hydrocarbons of analogous structure. This paper (a) reports the observation of slow site exchange in five 9-arylfluorenes of the general type



(b) reports the kinetic quantities for the internal motion responsible for the exchange; (c) discusses the exchange mechanism; and (d) reports the isolation of one of these (III) in one isomer form (>90% isomer purity).



III

Experimental Section

The 9-arylfluorenes were prepared by treating the corresponding carbinols with a large excess of hydriodic acid at reflux for 2–3 hr in glacial acetic acid. The carbinols were prepared as described by Adams and Campbell.[3] Compound III was obtained without isolating the carbinol. The crude reaction mixture of the carbinol preparation was stripped under high vacuum at 120° and then treated directly with HI. All of the 9-arylfluorenes were distilled under high vacuum and then were crystallized until crystals were pure white. Identification of the compounds was made primarily by proton magnetic resonance spectroscopy (pmr) and infrared spectroscopy. However, satisfactory elemental analyses were also obtained.

Compound III was obtained as an equilibrium mixture (50/50) after distillation at about 180° (1×10^{-3} mm). Complete crystallization from hexane always yielded a near-equilibrium mixture of isomers. However, when the mixture was dissolved, in large volumes of hexane (roughly 50/1) and evaporated rapidly, the first fraction of crystals (about 10%) was obtained with an isomer purity of >90%. This isomer is identified by its methyl signal at lower field and is referred to as isomer A in the following discussion. (See the discussion section for assignment of signals to isomers.) When samples of III were crystallized out as several fractions, the last fraction was enriched in isomer B up to a ratio of about 7/5—not a sufficient enrichment to allow useful reequilibration experiments.

Samples for signal shape analysis (100–200 mg/500 μl of solvent) were sealed under vacuum or nitrogen. All pmr measurements were made with a Varian A-60 spectrometer equipped with the variable temperature assembly.

Signal shape analysis was done by matching experimental spectra with spectra calculated from the computer program given by Nakagawa.[4] Reequilibration experiments to obtain rate constants were performed, and the results treated as described previously.[5,6]

The effect of the ring current of the fluorene nucleus on the chemical shifts of protons in the other aromatic ring were calculated using the dipole approximation.[7,8] Distances and angles were measured using Dreiding models.

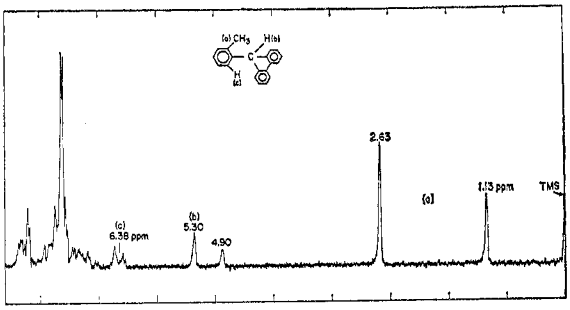


Figure 1.—Pmr spectrum of I at 0°, 100 mg/500 μl of $CDCl_3$.

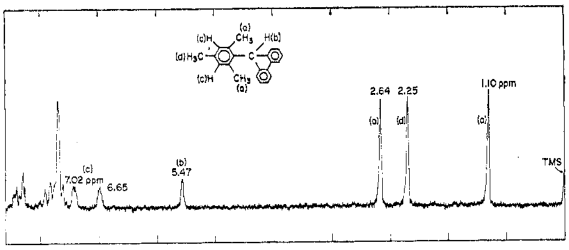


Figure 2.—Pmr spectrum of IV at 0°, 100 mg/500 μl of $CDCl_3$.

Results

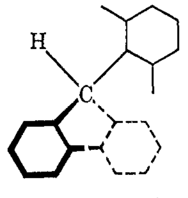
Pmr spectra of two of the compounds in $CDCl_3$ are given in Figures 1 and 2. Pmr spectra in $CDCl_3$ at 0° are summarized in Table I. Kinetic data are given in Table II. Data for the reequilibration of III are $k = 6.2 \times 10^{-7}$, 2.3×10^{-6}, 2.3×10^{-5}, and 1.9×10^{-4} $\sec^{-1}$ at 67, 80, 100, and 116°.

For compounds IV and V, the *two* separate signal sets remained sharp and clean even when the temperature was raised to 200° and only a *lower* limit can be set for ΔF^*. Exchange is slow on the nmr time scale even at 200°. An exchange rate as high as 10 $\sec^{-1}$ would noticeably broaden the signals. On the basis of an exchange rate of 10 or less, $\Delta F^* \geq 26$ kcal/mol.

The other extreme is encountered with VI and only an *upper* limit can be set for ΔF^*. Exchange is so rapid that a *single* set of sharp signals was obtained even at −85° in CH_2Cl_2. With a chemical shift of 10 cps and a rate as low as 100 $\sec^{-1}$, the single sharp set would be noticeably broadened. On that basis the rate is so rapid that $\Delta F^* \leq 9$ kcal/mol.

Discussion

Ground-State Conformation.—It is very probable that the ground state for these 9-arylfluorenes is with the aryl group in a plane approximately perpendicular to the plane of the fluorene nucleus. The hydrogen atom on the central carbon atom would force the aryl



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[2] T. H. Siddall, III and W. E. Stewart, *Tetrahedron Lett.*, in press.

[3] R. Adams and J. Campbell, *J. Amer. Chem. Soc.*, **72**, 153 (1950).

[4] T. Nakagawa, *Bull. Chem. Soc. Jap.*, **39**, 1006 (1966).

[5] T. H. Siddall, III, *Inorg. Nucl. Chem. Lett.*, **1**, 155 (1965).

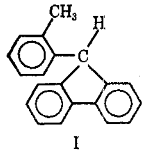
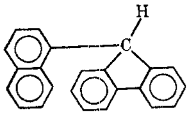
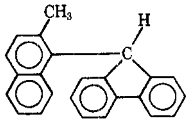
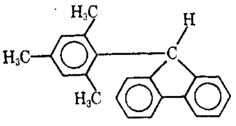
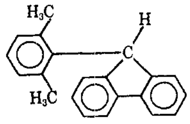
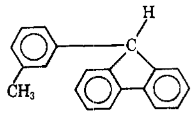
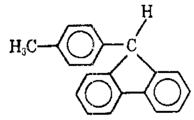
[6] T. H. Siddall, III, *Tetrahedron Lett.*, 4515 (1965).

[7] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

[8] R. A. Hoffman, P. O. Kinell, and G. Bergström, *Arkiv Kemi*, **15**, 533 (1960).

TABLE I

CHEMICAL SHIFTS[a] FROM TMS, 0°

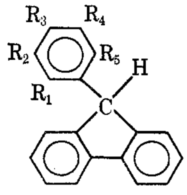
Compd[b]	CH₃		H		*ortho* H[d]	Other	Isomer ratio
 I	1.13	*2.63*	4.90	*5.30*	*6.38*		1.6 at 10° (major isomer signals underlined)
 II			5.22	*5.93*	*7.75*		2.0 at 30°
 III	1.32	2.84[c]	5.83[c]	6.22	6.49[c]		1.0 as distilled; also at 100° in CCl_2CCl_2
 IV	1.10	2.64	5.47			*para* CH_3 = 2.25 *meta* H = 7.02, 6.65	
 V	1.13	2.69	5.50				
 VI	2.21		4.97				
 VIII	2.27		4.98				

[a] In parts per million. [b] 100 mg/500 μl of $CDCl_3$. [c] Isomer A. [d] Of rotating aromatic moiety (not fluorene).

ring slightly out of the perpendicular plane. As a consequence the ground state might possess two mirror-image minima with a small potential and rapid torsional motion between them. In this ground state, otherwise equivalent substituents in the 2,6 (or 3,5) positions in the aryl ring are nonequivalent.

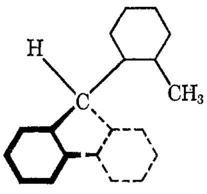
The alternative ground state, with the aryl ring rotated through about 90°, does not permit the 2 and 6 positions to be nonequivalent. This alternative can be dismissed on that basis alone. However, additional quantitative support for the perpendicular ground state is available from calculations of chemical shifts.

The pmr spectrum at 0° of

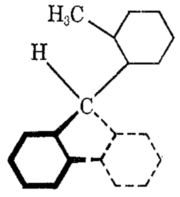


I

in $CDCl_3$ with $R_1 = CH_3$, $R_2 = R_3 = R_4 = R_5 = H$, showed two methyl absorptions separated by 92 cps (see Figure 1 and Table I). In dimethyl sulfoxide and dimethyl formamide, the separation is slightly larger, ~95 cps (solvent peak partly obscures methyl signal at low field). Ring current calculations of the differences in chemical shift of the methyl group in the two structures Ia and Ib gave a predicted value of 86 cps. In compound IV, with $R_1 = R_3 = R_5 = CH_3$, $R_2 = R_4 = H$, the *meta* protons gave two absorptions separated by 22 cps. Ring current calculations based on the

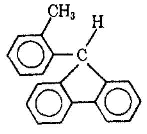
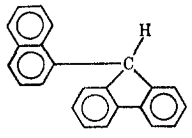
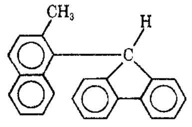
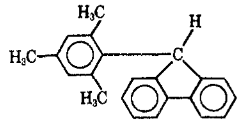
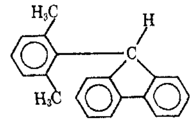
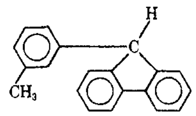
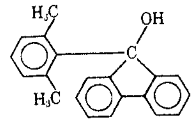


Ia



Ib

TABLE II
KINETIC DATA

Compd	Solvent	E_a[a]	Log A_0	ΔF[a,b] (temp, °C)
 I	CDCl$_3$	Temperature range too limited for determination		16.4[c]
	CHCl$_2$CHCl$_2$	15.8	12.6	16.3
	CCl$_2$=CCl$_2$	14.3	11.3	16.5, 17.7[d]
	HC(O)N(CH$_3$)$_2$	12.4	10.3	16.5
	C$_6$D$_6$	14.8	11.8	16.3
	CH$_3$SOCH$_3$	14	11	16.3
	CD$_3$COCD$_3$			16.0[e] (52)
 II	CCl$_2$=CCl$_2$	14.8	10.8	18.0[f] 18.7 (116)
 III	CCl$_2$=CCl$_2$	29.8	12.9	29.2[g] (116)
 IV	Cl$_2$C=CClCCl=CCl$_2$			>26[h] (200)
 V	Cl$_2$=CClCCl=CCl$_2$			>26[h] (200)
 VI	CH$_2$Cl$_2$			>9[h] (−85)
 VII	Cl$_2$C=CClCCl=CCl$_2$			21.3[i] (200)

[a] Kilocalories per mole. [b] At 60° except as noted. [c] Isomer ratio = 1.4 at 60°, solvent independent. [d] At 116°. [e] Limited solubility prevented study over a temperature range. [f] Isomer ratio = 1.7 at 60°. [g] Isomer ratio = 1.0, temperature independent. [h] See results. [i] From ref 1.

structure analogous to I gave a predicted difference of 26 cps.

The fluorene C–H proton in I also appeared as a doublet (4.90 and 5.30 ppm). The relative intensities of the two components indicate that the low-field component arises from conformation Ib. When both *ortho* positions are occupied by methyl groups (V), a singlet at 5.50 ppm was observed. For the case with no *ortho* substitution (VI), a singlet at 4.97 ppm was observed. Ring current calculations indicate that the maximum separation to be expected for the C–H proton resonances as the plane of the tolyl group is rotated is 0.083 ppm. This result, plus the positions of the C–H proton shifts for the cases of no *ortho* substitution and di-*ortho* substitution suggests that the fluorene C–H is appreciably deshielded by the *ortho* methyl group in conformation Ib, because of van der Waals effects.

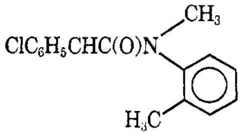
Still further support for the perpendicular ground state is obtained from observation of the decreased barrier in carbinol VII. The larger hydroxyl group as a replacement for the hydrogen atom should raise the energy level of the ground state of VII compared with the hydrocarbons.

Kinetics.—Two mechanisms of site exchange are available, in principle, for the *ortho* and *meta* substituents in the aryl group in these 9-arylfluorenes. Inversion allows the central carbon atom to either fall back into its original tetrahedral ground state or to fall back into the inverted tetrahedral ground state. Simple rotation around the aryl–central carbon bond accomplishes the same exchange. However, there is no obvious way that the activated state for inversion could be stabilized.

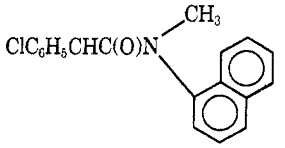
We interpret the experimental evidence in favor of rotation as the exchange mechanism. The data in Table II for I show that the exchange rate is essentially independent of solvent and dielectric constant. This solvent independence argues against an ionic activated state. On the other hand, this independence is consistent with rotation. These compounds may vary in their degree of association with solvent from solvent to solvent. However, it is difficult to imagine that the energy of this association varies more than a few hundred small calories. It is even less likely that a rotational activated state should associate with solvents very differently from the ground state.

The increased exchange barrier for III, IV, and V as compared to I and II also is consistent with rotation. The free energy of exchange (ΔF^*) for III is about 80% of the sum of ΔF^*'s for I and II. It might have been supposed that $\Delta F^*_{\text{III}} = \Delta F^*_{\text{II}} + \Delta F^*_{\text{I}}$; however, there probably is sufficient distortion of the molecule to allow these groups to come into maximum steric conflict with the *ortho* hydrogen atoms of the fluorene nucleus one at a time rather than absolutely simultaneously. Bond distortion is accepted as the principal means of steric relief for rotation in biphenyls.[9]

The difference, $\Delta F^*_{\text{II}} - \Delta F^*_{\text{I}} \simeq 1.7$ kcal/mol, is very close to the similar difference (1.4 kcal/mol) noted for rotation around the aryl–nitrogen bond in the following compounds.[7] The larger "size" of the fused ring may be due in part to its increased rigidity over the methyl group.



and

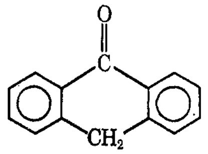


Substitution in the *meta* position may be too remote from the rotational axis to slow rotation down to the pmr time scale. Compound VI gave no evidence of slow rotation even at −85° (dissolved in CH_2Cl_2). The absence of detectable slow rotation in VI is consistent with the similar observation for rotation around the aryl–nitrogen bond in *meta*-substituted anilides.[10] There is a possibility that rotation is slow in VI but cannot be detected by pmr. If one isomer predominated over the other by a large factor, the minor isomer would not be observable, especially at low temperature where viscosity effects broaden signals.

The entropy of activation for site exchange is a small negative quantity for these compounds. The average of ΔS^* (calculated for transmission coefficient = 1) for I for all solvents is −6 eu. (We do not regard the apparent differences from solvent to solvent as real. ΔF^* from signal shape analysis is a much more accurate quantity than E_a.[11]) ΔS^* for III is +2 eu. Because the data for III depend on reequilibration experiments, this value is probably more significant than those obtained for I. Small negative entropies of activation were found for rotation around the aryl–nitrogen bond in *ortho*-substituted anilides.[10,12] It seems reasonable that small entropies of activation must be the rule for intramolecular processes. It is difficult to visualize any large restraint or lack of it in the activated state for rotation, for example, as compared to the ground state. Except where the activated state may be a triplet state, small entropies of activation are the rule for first-order gas reactions[13] and for isomerization of olefins in the liquid state.[14]

The Role of the Fluorene Nucleus in Slow Rotation.—We believe that, as Adams[3] supposed, the fluorene nucleus plays a vital role in making rotation slow in these molecules. As Adams pointed out, molecular models show that unjoined and unfixed aromatic rings are free to rotate in a synchronous manner. However, it seems likely that the work of Akkerman and Coops[15] with α-diarylcarboxylic acids can be extended to various triarylmethanes and derivatives and that sufficiently large *ortho* substituents alone will slow the rotation even for unfixed systems. However, the synthesis of such compounds may present some formidable problems.

Carbinols and triarylmethanes derived from anthrone



would represent an interesting intermediate state between the rigid, fixed fluorene nucleus, and a completely unfixed triaryl array. The extra flexibility permitted by the interposed CH_2 group should decrease the barrier to rotation as compared to the barrier in fluorene derivatives. We have, however, been unable to prepare the carbinols from anthrone by conventional Grignard syntheses.

Registry No.—I, 18181-25-4; II, 18153-38-3; III, 18153-39-4; IV, 18153-40-7; V, 18153-41-8; *meta* VI, 18153-42-9; *para* VI, 18153-43-0; VII, 18153-44-1.

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The Preparation of 3β-Acetoxy-17β-hydroxy-5α-androstane-16α-propionic Acid δ-Lactone

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In previous studies it was found that steroidal 17β-hydroxy-16β-acetic acids[1,2] and 17β-hydroxy-16β-propionic acids[3] were readily converted into the corresponding *cis*-fused γ- and δ-lactones, respectively. In contrast, the formation of the *trans*-fused γ-lac-

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