Some 9-Arylfluorenes. Ring-Current Effects on Nuclear Magnetic Resonance Spectra, Carbonium Ions, and the 9-Mesitylfluorenyl Radical

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Received January 25, 1968

Abstract: The nmr spectra of various 9-arylfluoren-9-ols and derived carbonium ions are reported. 9-Mesitylfluoren-9-ol exhibits three methyl resonance lines because of the magnetic anisotropy of the fluorene nucleus; similarly 9-durylfluoren-9-ol exhibits four methyl lines. These spectra are independent of temperature. 9-Chloro-9-mesitylfluorene has a temperature-dependent nmr spectrum in which the *o*-methyl lines are sharp at −10° and broad at 40° while the sharp line of the *p*-methyl is unaffected by temperature. This behavior is explained on the basis of the interconversion of mirror image forms of the chloride *via* reversible ionization. Other explanations involving either rotation of the 9-aryl substituent or simple equilibration with the 9-mesitylfluorenyl-9 cation are shown to be inconsistent with the experimental data. Similar behavior is observed for 9-chloro-9-durylfluorene. The nmr and optical spectra of various 9-arylfluorenyl-9 cations are reported and discussed briefly. The preparation and the optical and esr spectra of the stable, monomeric 9-mesitylfluorenyl radical are reported.

The studies of the unusual nmr spectra of various 9-arylfluorenes described in this paper originated during an attempt to synthesize a reasonable stable arylfluorenyl radical. Such radicals appeared to be intermediates in the chemiluminescent reductions of various fluorene derivatives, and we wished to examine a simple stable fluorenyl radical to see if its behavior was consistent with the proposed mechanistic scheme.

The only derivative of the fluorenyl radical previously reported to be monomeric is 9-tritylfluorenyl.[1] It did not appear to be suitable for our purposes because of the method of preparation and its low solubility. Further the structure assigned to the radical was reasonable but was not established unambiguously even though the synthesis is not necessarily straightforward. The 9-phenyfluorenyl radical is related to the triphenylmethyl radical but, apparently because of a decrease in steric hindrance, associates completely to a dimer at room temperature.[2]

We attempted to prepare the 9-*t*-butylfluorenyl radical by reduction of the 9-chloro compound, analogous to the well-known reaction of trityl chloride, but we were unable to detect any radical in the product (esr). We then turned to the 9-mesitylfluorenyl system. An examination of space-filling molecular models indicated that the desired intermediates could probably be prepared and that dimerization of the radical, at C-9, would be essentially impossible.

The nmr spectrum of 9-mesitylfluoren-9-ol (**1**) is unusual as are the spectra of most of the related compounds. The spectrum of 9-chloro-9-mesitylfluorene (**2**) is temperature dependent, and the explanation for this behavior involves the interconversion of mirror image isomers by ionization and recombination.

Experimental Section

The 9-*t*-butyl and 9-arylfluoren-9-ols and aryldiphenylcarbinols were synthesized using standard literature preparations of the requisite Grignard or organolithium reagents for reaction with the appropriate ketone. All reactions were run in ether under dry nitrogen or argon. The aryl-substituted carbinols, which tended to form oils, were all recrystallized from hexane at 0°. The results are given in Table I. 9-*t*-Butylfluoren-9-ol was not purified but was converted directly to the chloride as described by Fuson, *et al.*[3a] Elemental analyses, performed by Midwest Microlab, Inc., are reported for new compounds. The yields are of purified product and are based on the amount of fluorenone or benzophenone used in the given reaction. Melting points are corrected.

The carbinols were converted to the corresponding chlorides by reaction with 2 equiv of thionyl chloride in methylene chloride solution at room temperature. The crude products were purified by crystallizing each three times from hexane by dissolving the product in boiling solvent and then cooling immediately to 0° in a refrigerator. The results are given in Table II.

The carbinols were converted to their corresponding carbonium ions by solution in either concentrated (96%) sulfuric acid or trifluoroacetic acid. Optical spectra were measured using the former solvent and nmr spectra using the latter solvent, with the solute present in about 10% concentration. The nmr spectra were not concentration dependent and, apart from some slight line broadening, sulfuric acid gave the same spectra as trifluoroacetic acid. The chemical shifts of carbonium ions were measured relative to tetramethylammonium fluoroborate internal standard.[4]

The nmr spectra of the previously described carbinols and chlorides were determined in deuteriochloroform solution at 42°, the ambient-probe temperature, unless otherwise specified, with tetramethylsilane as internal standard. All nmr spectra were taken with a Varian A-60 spectrometer equipped with a variable-temperature probe. The low-temperature measurements were calibrated using the temperature-dependent chemical shift curve of methanol.[5] All nmr spectra were integrated, and the relative fractions of protons were consistent with the structure assigned to each compound.

9-Mesitylfluorene. 9-Chloro-9-mesitylfluorene (1.7 g, 5.4 mmol) was stirred for 30 min with zinc dust (1.1 g, 17 mg-atom) in glacial acetic acid (35 ml). The resulting clear light green solution was filtered into ice water and the precipitated white solid dissolved in ether (50 ml), washed with 5% $NaHCO_3$ solution, dried, and evaporated. Chromatography of the resulting gummy brown solid on silica gel (Davison Chemical) with 3:1 hexane–chloroform eluent and crystallization from hexane yielded 9-mesitylfluorene (0.80 g, 54%), mp 85–88°.

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[1] W. Schlenk and H. Mark, *Ber.*, **55**, 2285 (1922).

[2] S. G. Cohen, F. Cohen, and C. H. Wang, *J. Org. Chem.*, **28**, 1479 (1963).

[3] (a) R. C. Fuson, *et al.*, *ibid.*, **15**, 1155 (1950). (b) *t*-Butylmagnesium chloride was prepared by the method of S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 524; (c) R. Weiss and E. Knapp, *Monatsh.*, **61**, 61 (1932); (d) durylmagnesium bromide is ether insoluble and was obtained in only *ca.* 50% conversion from bromodurene; *cf.* R. C. Fuson, *et al.*, *J. Org. Chem.*, **11**, 60 (1946); (e) R. Adams, *J. Am. Chem. Soc.*, **74**, 5588 (1952).

[4] D. G. Farnum, *ibid.*, **86**, 934 (1964).

[5] Varian Associates, Palo Alto, Calif., publication no. 87-100-110.

Table I

Carbinol	Organometallic reagent	Mp, °C	Yield, %	Calcd, %		Found, %	
				C	H	C	H
9-*t*-Butylfluoren-9-ol	Grignard[3b]	. . .	. .	. . .	. . .	. . .	. . .
9-Mesitylfluoren-9-ol (**1**)	Lithium[3a]	108–111	31	87.96[d]	6.71	87.90	7.05
9-*o*-Tolylfluoren-9-ol	Lithium	121–122[a]	64				
9-(2,4-Dimethylphenyl)-fluoren-9-ol	Grignard	97–99	49	88.08[e]	6.34	88.02	6.58
9-(2,6-Dimethylphenyl)-fluoren-9-ol	Grignard	90–93	29	88.08[e]	6.34	88.05	6.46
9-Durylfluoren-9-ol [9-(2,3,5,6-tetramethylphenyl)-fluoren-9-ol]	Grignard[3d]	141–142	33	87.86[f]	7.05	88.03	7.22
Diphenyl-*o*-tolylcarbinol	Grignard	99–100[b]	54	. . .	. . .	. . .	. . .
Diphenylmesitylcarbinol	Lithium	86–88[c]	43	. . .	. . .	. . .	. . .

[a] Lit.[3c] 121–122°. [b] Lit.[3e] 98–99°. [c] Lit.[3a] 90–91°. [d] Calculated for $C_{22}H_{20}O$. [e] Calculated for $C_{21}H_{18}O$. [f] Calculated for $C_{23}H_{22}O$.

Table II

Chloride	Mp, °C	Yield, %	Calcd, %			Found, %		
			C	H	Cl	C	H	Cl
9-*t*-Butyl-9-chlorofluorene	100.5–103.5[a]	35						
9-Chloro-9-mesitylfluorene (**2**)	120–123	68	82.91[d]	6.00	11.12	82.51	6.23	11.06
9-Chloro-9-*o*-tolylfluorene	113–115[b]	72						
9-Chloro-9-(2,4-dimethylphenyl)-fluorene	121–122.5	68	82.76[e]	5.58	11.66	82.73	5.68	11.58
9-Chloro-9-(2,6-dimethylphenyl)-fluorene	100–103 dec	63						
9-Chloro-9-durylfluorene (**5**)	124[c]	73	83.01[f]	6.61	10.66	83.05	6.56	19.56

[a] R. C. Fuson, *et al.*, *J. Org. Chem.*, **16**, 21 (1951), report 104–105°. [b] R. Boltman, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1855 (1964). [c] The melting point sample evolved gas at 105–108°, changed from yellow to green to dark blue but did not melt until 124°. [d] Calculated for $C_{22}H_{19}Cl$. [e] Calculated for $C_{21}H_{17}Cl$. [f] Calculated for $C_{23}H_{21}Cl$.

Anal. Calcd for $C_{22}H_{20}$: C, 93.00; H, 7.00. Found: C, 93.01; H, 7.11.

9-Mesitylfluorenyl Free Radical. A solution of 9-chloro-9-mesitylfluorene (0.040 g, 0.13 mmol) in dry, degassed tetrafuran (20 ml) was treated with powdered copper (*ca.* 30 mg) in a conventional vacuum line windmill apparatus. The apparatus was fitted with a quartz cell to determine the optical absorption spectrum of the free radical and a side arm to determine the fluorescence spectrum. The reaction of the chloride with Cu was rapid; the yellow-green color of the radical was apparent after about 5 min. The solution was stirred overnight with a magnetic stirrer. The deep yellow-green solution of the radical was filtered through a medium glass frit contained in the apparatus, and the reaction vessel was removed from the apparatus. It was possible to crystallize the product as medium green needles.

Results and Discussion

9-Mesitylfluoren-9-ol (**1**) was originally synthesized as an intermediate in a synthetic sequence leading to 9-mesitylfluorenyl free radical. The unusual and unexpected nmr spectrum of the carbinol **1** (Figure 1) shows *three* distinct methyl resonance lines at τ 8.83, 7.75, and 7.1. If the mesitylene methyl resonance line at τ 7.75 is taken as a standard toluene methyl, two methyls of the mesityl substituent in **1** are shifted quite far from their normal positions. The line at τ 8.05 is assigned to the hydroxyl group. The methyl group resonances of the various 9-arylfluoren-9-ols studied are given in Table III.

Table III. Nmr Spectra of Methyl Groups in 9-Arylfluoren-9-ols

Carbinol	CH$_3$ at position, τ				
	2′	3′	4′	5′	6′
9-Mesitylfluoren-9-ol	8.83		7.75		7.1
9-*o*-Tolylfluoren-9-ol	8.75				
9-(2,4-Dimethylphenyl)fluoren-9-ol	8.80		7.80		
9-(2,6-Dimethylphenyl)fluoren-9-ol	8.85				7.1
9-Durylfluoren-9-ol	8.90	8.0		7.70	7.20
Diphenyl-*o*-tolylcarbinol[12b]	7.90				
Diphenylmesitylcarbinol[12b]	8.15		7.75		8.15

Molecular models of the 9-arylfluoren-9-ol system show that the substituent is held at an angle of approximately 55° above the plane of the fluorene ring and that any *ortho* (2′ or 6′) substituents on the aryl group will restrict rotation of this group severely (Figure 2). Space-filling Courtauld molecular models of **1** are so crowded that the fluorene ring itself may not be constructed so as to accommodate the mesityl group without omission of the restraining rings which prevent severe bond deformation.

For the sake of the present discussion, the aryl and mesityl rings are numbered separately as shown in Figure 2. Assuming a planar nuclear geometry, the fluorene group is taken as lying in the "ring plane" and the plane perpendicular of this through C-9, the only nontrivial symmetry plane in fluorene, is defined as the "π plane."

Attempted rotation of the mesityl group about the sp^2–sp^3 carbon–carbon bond results in considerable steric interaction between the 2′- and 6′-methyls and the 1- and 8-protons of fluorene which lie in the ring plane. Thus carbinol **1** is subject to hindered rotation in the same sense as *o,o*′-substituted biphenyls.[6,7]

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(6) The models indicate that the interaction between *ortho* substituents in the aryl group and the C-9 substituent will tend to twist the plane of the aryl group about 10° out of the π plane and further that there will be no appreciable barrier to motion across the π plane.

(7) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p 15 ff.

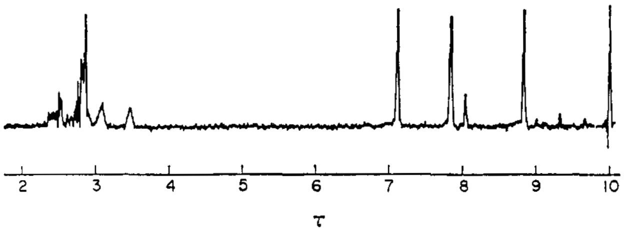

Figure 1. The nmr spectrum of 9-mesitylfluoren-9-ol in $CDCl_3$ with TMS standard.

The nmr spectrum of **1** may now be explained in terms of this hindered rotation which, at temperatures below at least 150°, effectively fixes the geometry. The 2′-methyl is held over the ring plane whereas the 6′-methyl is held approximately in this plane. The two methyls will then be influenced unequally by the magnetic anisotropy[8] of the fluorene system, which, for this purpose, is considered as a pair of adjacent but independent benzene rings.

The model and calculations of Johnson and Bovey[9] show that if the 2′-methyl is held over an aromatic ring, it is subject to a shielding effect which shifts the nmr line of that group to higher fields. The 6′-methyl, held in the ring plane, is influenced by a deshielding effect which shifts its resonance line to lower fields. The 4′-methyl is sufficiently removed from the fluorene ring-current area to remain unaffected and thus serves as a convenient standard by which to measure the chemical shifts of the other methyl groups. Approximate measurements of the horizontal and vertical distances of the 2′- and 6′-methyls from the center of one phenyl ring of fluorene were taken from Courtauld models of **1**. The use of these approximate values in tables of nuclear shielding values[9] yields calculated shifts of 0.66 ppm upfield for the 2′-methyl (*vs.* 1.08 ppm observed) and 0.86 ppm downfield for the 6′-methyl (*vs.* 0.60 ppm observed). The fair agreement of the calculated values with experiment is not surprising since the calculations were based on the effect of only one phenyl ring of fluorene, not two. The influence of the second ring on the field of the first is not easy to determine. We do not know if the effects of the two benzene rings are simply additive or how their ring currents may be influenced by that in the mesityl ring which may not be exactly perpendicular to the fluorene ring.

In a recent publication[10] describing the temperature-dependent (40–174°) nmr spectrum of di-*t*-butyl-*p*-methoxyphenylcarbinol, the authors claim the first direct evidence for a high-energy barrier to rotation about a carbon–carbon sp^3–sp^2 bond. The nmr spectrum of **1** indicates that it also exhibits precisely the same type of hindered rotation. The published nmr spectra[10] of the above carbinol indicate that rotation about the hindered bond has begun to occur in the range 100–120°. In contrast, the nmr spectrum of **1**, in *m*-dibromobenzene, gave no indication that rotation had begun to occur at temperatures up to 150°. The 2′- and 6′-methyls, which should see an average ring-current field upon rapid revolution[11] of the mesityl group about the sp^2–sp^3 band, are still as sharp and distinct at this temperature as at 42°, indicating a high-energy barrier to rotation.

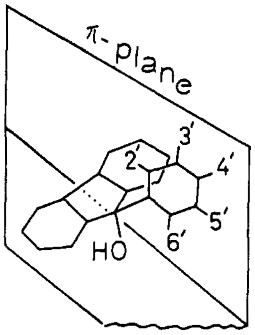

Figure 2.

In the course of this investigation, other 9-arylfluoren-9-ols, as well as two aryldiphenylcarbinols (Table I, Experimental Section), were prepared for comparison with carbinol **1** and to provide experimental verification of the nmr methyl proton assignments for **1**. The nmr spectral results for the methyl groups in these carbinols, using the numbering system of Figure 2 to designate a given methyl, are given in Table III.

Examination of Courtauld models of 9-*o*-tolylfluoren-9-ol suggests that the conformation which places the *o*-methyl at position 2′, approximately in the π plane (Figure 2) and well above the ring plane, is the sterically favored one. This is in agreement with the nmr spectrum, given in Table III, which indicates that this methyl is strongly shielded by an aromatic ring current. The other possible rotamer, which places the *o*-methyl at position 6′, approximately in the ring plane (the deshielding area), would result in steric crowding between the methyl and hydroxyl groups.

The nmr results obtained for 9-(2,4-dimethylphenyl)-fluoren-9-ol corroborate the original assignment of the τ 7.75 line to the 4′-methyl of **1**. Similarly, the spectrum of 9-(2,6-dimethylphenyl)fluoren-9-ol confirms the assignment of the τ 8.83 and 7.1 peaks to the 2′- and 6′-methyls, respectively.

The nmr spectrum of 9-durylfluoren-9-ol (Figure 3) is interesting because all four duryl methyls appear as sharp singlets, at τ 8.90, 8.00, 7.70, and 7.20. The assignments given in Table III to the 3′-methyl and 5′-methyl are based on the proximity of these groups to the *o*-methyls which are assigned to shielding and deshielding zones, respectively.

The unusual ring-current effects observed in the 9-arylfluoren-9-ol series provoked some curiosity concerning comparable effects in the nmr spectra of some related aryldiphenylcarbinols. It appeared that the latter series would probably be magnetically comparable to the former, if the fluorene ring may be considered as a pair of bound phenyls. These substituted triphenylcarbinols would differ sterically, however, since these two phenyls are now free to twist out of the ring plane of Figure 2 in order to avoid interaction between the new pair of *o*-hydrogens (Figure 4).

The contrast between the 2′-methyl proton resonance lines of 9-*o*-tolylfluoren-9-ol and diphenyl-*o*-tolyl-

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[8] For a recent discussion of the anisotropic magnetic effects of aromatic rings as they affect methyl groups see T. H. Regan and J. B. Miller, *J. Org. Chem.*, 32, 502 (1967), as well as references therein.

[9] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, 29, 1012 (1958).

[10] G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 2539 (1967).

[11] Appreciable blurring of the sharp lines of these two methyl groups would require an exchange rate of *ca.* 150 sec^{-1}.

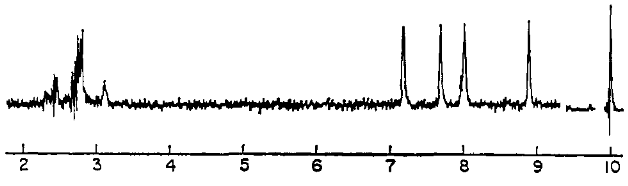

Figure 3. The nmr spectrum of 9-durylfluoren-9-ol in $CDCl_3$ with TMS standard.

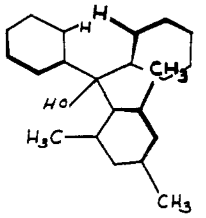

Figure 4.

carbinol (Table III) shows this configurational change clearly. In the former, the 2′-methyl is held over the ring plane and there is a large shielding effect. In the latter open form the shielding effect, though present, is considerably smaller. Molecular models show that the two phenyl rings are twisted so that if the 2′-methyl is in the shielding zone of one, it is about equally well in the deshielding zone of the other.

Similar results are obtained for the nmr spectrum of diphenylmesitylcarbinol. However, the added 6-methyl appears to have induced a small steric change in the molecule, as reflected in the shift of the *o*-methyl proton resonance lines to slightly higher field. It should be noted that, in contrast to the nmr spectrum of **1**, the 2- and 6-methyl protons of diphenylmesitylcarbinol occur at the same field (τ 8.15).

9-Chloro-9-mesitylfluorene and Its Temperature-Dependent Nmr Spectrum. 9-Mesitylfluoren-9-ol reacts with thionyl chloride to give a good yield of 9-chloro-9-mesitylfluorene (**2**). The structure assigned to this compound is in accord with its ultraviolet spectrum which is the same as that of 9-mesitylfluoren-9-ol, a typical fluorene spectrum. After the reaction of **1** with thionyl chloride is over the solution is deep blue, as are solutions of the 9-mesitylfluorenyl-9 cation (*vide infra*). When the solution is concentrated on a rotary evaporator the color changes rapidly to pale yellow. It appears that the HCl present in the solution is necessary for appreciable ionization to occur in a solvent of low dielectric constant. The chloride is highly reactive and reacts rapidly with silver tosylate in methylene chloride to give a blue solution of the carbonium ion. The corresponding reaction with 9-chloro-9-phenylfluorene is much slower.

The nmr spectrum of chloride **2** at 42° was initially quite puzzling. A single methyl group appeared as a sharp singlet at τ 7.85 and aromatic protons occurred as a well-defined multiplet centered at τ 2.8. However, the other two groups of methyl protons occurred as broad bands, about 25 Hz wide, centered at τ 8.95 and 7.05 (Figure 5).

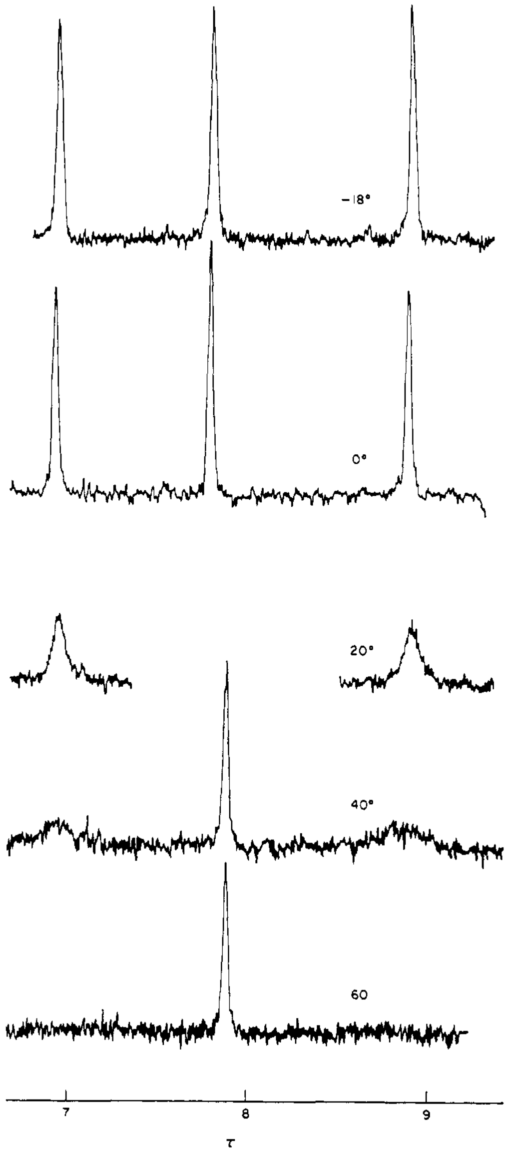

Figure 5. The nmr spectrum of 9-chloro-9-mesitylfluorene in $CDCl_3$ in various temperatures.

A variable-temperature nmr study of chloride **2** shows the high- and low-field methyl protons beginning to emerge as well-defined peaks at 10°. At 0° or at −10°, these signals are as sharply defined as the τ 7.85 methyl peak (Figure 5). This temperature dependence of the spectrum appears to be essentially independent of the polarity of the solvent: CS_2, CCl_4, $CDCl_3$, and 85% CD_3COCD_3–15% $CDCl_3$ gave identical results. Attempts to use more polar solvents such as acetonitrile or benzonitrile were frustrated by their inability to dissolve the chloride. The nmr spectra of the various 9-aryl-9-chlorofluorenes are given in Table IV.[12a]

Three hypotheses were considered to explain these experimental results: (1) rotation of the mesityl group; (2) a rapid, reversible homolytic cleavage of the carbon–chlorine bond to give free radicals; (3) ionization of the carbon–chlorine bond. These possibilities are considered in this order.

Molecular models indicate that the aryl group at C-9 in all of these compounds will lie slightly out of the π plane but that there will be no substantial barrier to placing it in this plane. If the mesityl group of the

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(12) (a) All areas have the correct number of protons relative to the aryl proton area. (b) The aryldiphenylcarbinols are given the same numbering system as the substituted fluorenols of Figure 2.

Table IV. Nmr Spectra of Methyl Groups in 9-Aryl-9-chlorofluorenes

	CH$_3$ at position, τ					
Chloride	2′	3′	4′	5′	6′	Temp, °C
9-Chloro-9-mesityl-fluorene	7.0		7.85		8.90	0
9-Chloro-9-*o*-tolyl-fluorene	8.75 8.71					42 180[18]
9-Chloro-9-(2,4-dimethyl-phenyl)fluorene	8.85		7.75			42
9-Chloro-9-(2,6-dimethyl-phenyl)fluorene	8.90				7.05	0
9-Chloro-9-durylfluorene	9.00	8.10		7.75	7.15	−4

chloride is rotated 10 or 20° about the sp^2–sp^3 bond to either side of the π plane, the 2′- and 6′-methyl groups have been exchanged between equivalent positions (reflection in the π plane) and no change in their nmr signals will be seen. However, if the mesityl group can undergo a 180° rotation whose frequency is about several hundred to 10^3 sec^{-1}, the 2′- and 6′-methyls will be exchanged between nonequivalent magnetic positions. This exchange could then explain the blurring of the methyl proton signals at 42° and the low-temperature sharpening of these lines.

The following objections may be raised against this hypothesis. No similar rotation was observed in the case of the carbinol, even at 150°. The substitution of chlorine for hydroxyl would not be expected to lessen the rotational barrier for the mesityl group since chlorine has a larger van der Waals radius than oxygen (1.80 *vs.* 1.40 Å). Molecular models show that the primary barrier to rotation comes as a result of steric interactions between the 2′- and 6′-methyls and the 1 and 8 ring protons of fluorene rather than because of any substituent on the C-9 carbon of fluorene.

If, for some other presumably steric reason, substitution of chlorine for hydroxyl has lowered the rotational barrier for the mesityl group, the substitution of hydrogen for chlorine should lower the barrier even more. Accordingly, 9-mesitylfluorene (**3**) was synthesized, and its nmr spectrum was examined. The spectrum of hydrocarbon **3**[13] at 42° shows methyl proton peaks as sharp singlets at τ 8.9, 7.85, and 7.4, indicating, at least, that no rapid rotational exchange of the 2′- and 6′-methyls is occurring. A variable-temperature spectrum of hydrocarbon **3**, examined at 20° intervals up to 200°, shows no change in methyl proton peak position or shape, indicating highly restricted rotation of the mesityl group. Thus the unusual spectrum of chloride **2** cannot be attributed to rotation about the bond joining the mesityl group to the fluorene system.

A homolytic dissociation of the carbon–chlorine bond could conceivably yield a small equilibrium concentration of the 9-mesitylfluorenyl free radical. The blurring of the *o*-methyls would then have to be explained in terms of a fairly rapid equilibrium between singlet and doublet species, but it would be expected that the *p*-methyl would be affected by the odd electron as well. Under any circumstances, the aromatic protons of the fluorene ring, which have the major fraction of spin splittings in the esr spectrum of the radical, would be even more strongly affected. However, these proton lines are sharp and are unaffected by changes in temperature.

The third explanation for the unusual nmr spectrum of the chloride, which we believe to be the only tenable one, involves heterolytic cleavage of the carbon–chlorine bond. Qualitative chemical tests indicate that the chloromesityl compound **2** is much more reactive than its less hindered relatives which are discussed below. It reacts instantly with silver tosylate in methylene chloride or with methanolic silver nitrate.[14] In common with many of the other chlorides it dissolves in trifluoroacetic acid to give deep blue solutions of the carbonium ion. It reacts very rapidly with copper metal to give the related free radical. Courtauld models of 9-chloro-9-mesitylfluorene show that the 6′-methyl of the mesityl is forced quite close to the chlorine and should provide considerable steric acceleration to cleavage of the C–Cl bond. In the related *o*-tolyl compound the solitary methyl is fixed on the other side of the fluorene ring and cannot provide any such assistance. Accordingly the *o*-tolyl chloride reacts relatively slowly with silver salts even though the chlorine atom is more accessible. Such solvolyses are expected to be first order in any case.[15]

Solutions of the stable 9-mesitylfluorenyl-9 cation (**4**) are easily obtained by dissolving either the alcohol or the chloride in sulfuric acid or in trifluoroacetic acid. Presumably in this ion the C-9 of fluorene has become trigonal. This conformation, with the mesityl group in the π plane or nearly so, provides the greatest relief of steric interactions. The 2′- and 6′-methyls are now symmetrically disposed about the fluorene nucleus and both have the same magnetic environment. The nmr spectrum of carbonium ion **4** has only two methyl lines: the *o*-methyls at 7.70 and the *p*- at 7.75 (*vide infra*).

The optical absorption spectrum of a solution of 9-chloro-9-mesitylfluorene in methylene chloride at room temperature shows a weak visible absorption essentially identical with that of the carbonium ion and indicates that ionization has ooccurred to the extent of *ca.* 0.1%. This experiment does not distinguish between intimate and separated ion pairs because we do not expect substantial differences in the visible absorption which is broad in the case of the free ion. The ultraviolet spectrum of chloride **2** is that of a simple, covalent fluorene derivative and resembles that of carbinol **1** ($\lambda_{\max}$ 270, 280, 290, 300, and 310 nm).

The behavior of the nmr spectrum of **2** is the same in CS$_2$, CCl$_4$, CH$_2$Cl$_2$, and 85% CD$_3$COCD$_3$–15% CH$_2$Cl$_2$. The dielectric constants for the first three solvents are 2.6, 2.2, and 8.7. That for the fourth is estimated as 18. It seems reasonable to conclude that we are dealing only with tight ion pairs in which the components are not separated appreciably by the interposition of solvent molecules.

The equilibrium between the covalent chloride **2** and the carbonium ion **4** would exchange the different *o*-methyl resonances (τ 7.0 and 8.90) of the former with

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[13] The C-9 proton of 9-mesitylfluorene occurs as a singlet at τ 4.6. In comparison, the same proton of 9-phenylfluorene occurs at τ 4.95. This shift in position may reflect the greater restriction of mesityl to a position nearer the π plane, as compared with phenyl, and therefore greater average deshielding of this proton.

[14] Ionization of the chloride is assumed to be a first-order process by analogy with the solvolysis of other 9-aryl-9-chlorofluorenes studied by Boltman, Chapman, and Shorter, Table II, footnote *b*.

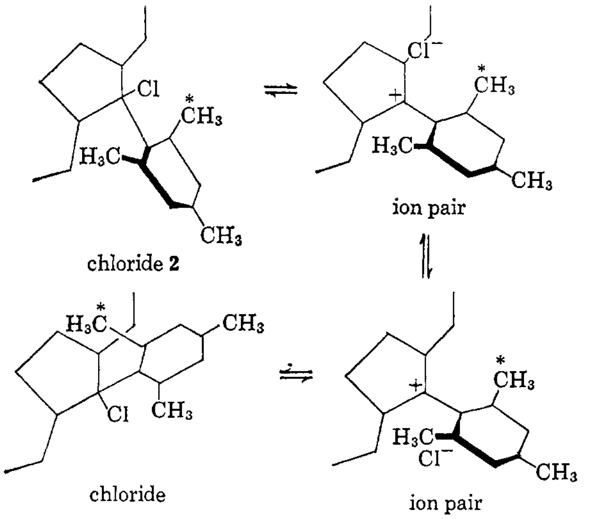
[15] See Boltmann, *et al.*, Table II, footnote *b*.

the common position (τ 7.70) of the o-methyls in the latter. However this simple hypothesis is not sufficient to explain the observed line broadening. We would expect to see strong lines for the methyls in covalent chloride **2** and a weak line for those in ion **4** which might be present at low concentration. The situation may be considered for the exchange of one of the o-methyls in **2** with the corresponding group in **4**. The broadening is then due to exchange between protons in a dominant line and those in a weak line and may be estimated in this case even though we cannot see the weak line because it would fall under the p-methyl line. Meiboom[16] has discussed this type of exchange and, for our case, the equation he derives becomes

$$\Delta = \tau\frac{p\delta^2}{1 + \tau^2\delta^2}$$

where Δ is the line broadening in hertz, p is the fraction of protons in the minor species, τ is the exchange lifetime (seconds), and δ is the frequency separation, in radians sec^{-1}, between the two lines. If this equation is rearranged to $\Delta/p\delta = \tau[\delta/(1 + \tau^2\delta^2)]$ the left side contains only experimental quantities which we know or can estimate fairly well. The maximum broadening will occur when $\tau\delta = 1$ and $\Delta/p\delta = 0.5$. Since $\delta = 72$ Hz for the τ 8.9 line and $p = 0.1\%$, the exchange of this methyl between the covalent chloride and the ion will lead to a broadening of less than 1 Hz which is far too small to account for the observed result.

The temperature dependence of the nmr spectrum of 9-chloro-9-mesitylfluorene can be explained in terms of rapid ionization and recombination. Consider the equilibria



The large temperature-dependent broadening can be accounted for on the basis of the second equilibrium which requires the facile transfer of the chloride ion from one side of the ring plane to the other, a process which converts the original ion pair into its mirror image. The subsequent collapse of this ion pair, which must occur at the same rate as that of the original one because the two are mirror images, will then form the mirror image of the original covalent chloride (assuming that the barrier to motion of the mesityl group across the π plane in the covalent form is low as discussed above). This change in molecular conformation exchanges the 2′- and 6′-methyls.

The case of exchange of protons between two different sites is discussed by Pople, Bernstein, and Schneider,[17a] and our experimental results are similar to the theoretical behavior they discuss. The p-methyl is too far away from the fluorene nucleus to be influenced by its magnetic anisotropy and it is therefore not affected by the exchange process. The o-methyls are exchanging between two sites, each with 50% of the population and separated by 120 Hz, and this leads to the conclusion that the average lifetime between exchanges is about 3 msec at room temperature.[17b]

There is another explanation to be considered for the nmr behavior of the chloride which is a variation of that given above. If the mesityl group were free to rotate in the carbonium ion and/or ion pair the 2′- and 6′-methyls could be exchanged without requiring that the chloride ion migrate from one side of the ring plane to the other. A Courtauld model of the 9-mesitylfluorenyl-9 cation demonstrates that this rotation would be extremely difficult to accomplish and we do not consider this alternative mechanism to be a reasonable possibility; *cf.* the hindered rotation in 9-mesitylfluorene discussed above. It seems certain that the chloride ion must be able to migrate to the other side of the fluorenyl ring.

Higher temperature experiments[18] with the chloride were unsatisfactory because the compound decomposes rapidly in the range 90–100°. The only noteworthy result of the experiment was that the broad bands at τ 8.95 and 7.05 disappear into the base line of the spectrum completely at 60–80°, while the τ 7.85 methyl signal remains unaffected.

There is a reasonable possibility that the ionization of the chloride is accelerated by traces of moisture in the solvents employed. For example, the concentration of water in Fisher methylene chloride is said to be 0.02% which is about 0.2 *M*. The nmr spectra were determined at *ca.* 1 *M* chloride. The observation that the temperature dependence of the nmr spectrum was the same in the four different solvents used makes this possibility seem unimportant because it depends upon a coincidence of effects.

9-Chloro-9-durylfluorene (5). The explanation proposed for the nmr spectrum of the mesityl compound **2** is substantiated by the similar behavior of the duryl compound (Figure 6). The greater thermal stability of the latter made it possible to examine the nmr spectrum at temperatures up to 80°. We had anticipated that the additional m-methyls would assist the ionization of chloride **5** *via* a buttressing effect. This effect does appear to be present because the temperature required to sharpen the methyl resonances is some 5 to 7° lower than that required for the mesityl compound. The most interesting feature of the nmr spectrum is that all four methyls show broadening of *ca.* 20 Hz at 42°. This contrasts with the case of the mesityl compound **2** in which the p-methyl was always a narrow line. The 5′-methyl, in both the durylfluorene and in chloride **5** below −10°, has an nmr line at τ 7.75 which is essen-

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[16] S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1964); see also M. Cocivera, *J. Am. Chem. Soc.*, **88**, 672 (1966).

[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, Ed., "High Resolution NMR," McGraw-Hill Book Co., Inc., New York, N. Y., 1959: (a) Chapter 10; (b) see p 223.

[18] m-Dibromobenzene was used as the solvent for spectra run above the ambient magnet temperature.

tially that of an ordinary toluene methyl. The resonance of this methyl group occurs at essentially the same position in the carbonium ion as well. Because of the coincidence of line positions the broadening of the 5′-methyl peak cannot be due to exchanging it between its position in one mirror image of the chloride and the corresponding position in the ion pair. However, the other *m*-methyl (3′) shows a resonance at τ 8.0–8.1 and is exchanged with the 5′-methyl in the interconversion of mirror image forms of the chloride. Thus, the latter type of exchange is the only kind which can explain the experimental observation.

The spectrum of the duryl compound **5** also shows the anticipated behavior as the temperature is raised above room temperature.[18] The two *m*-methyl peaks which are separated by 24 Hz move toward each other and at 80° begin to coalesce in a single line. The *o*-methyls which are separated by 87 Hz should coalesce at a higher temperature but the compound began to decompose rapidly above 100°, and the second coalescence could not be observed.

The nmr spectrum of 9-chloro-9-(2,6-dimethylphenyl)fluorene was examined briefly and was found to be quite similar in temperature dependence to the mesityl compound at temperatures up to room temperature. It was not studied further.

The unusual and unexpected results encountered in the nmr spectrum of 9-chloro-9-mesitylfluorene prompted a similar investigation of other 9-aryl-9-chlorofluorenes. The nmr spectral results for all chlorides investigated are given in Table IV; the numbering system of Figure 2 is retained. The spectra of 9-chloro-9-*o*-tolylfluorene and 9-chloro-9-(2,4-dimethylphenyl)fluorene, in contrast to that of 9-chloro-9-mesitylfluorene, show no temperature-dependent line broadening. This observation effectively eliminates any unusual inductive or quadrupole effects of chlorine which might explain the spectrum of the latter chloride. The spectrum of 9-chloro-9-*o*-tolylfluorene remains essentially unchanged at 180°, indicating that one *o*-methyl suffices to block rotation of the aryl substituent.

The variable-temperature spectrum of 9-chloro-9-(2,6-dimethylphenyl)fluorene shows the same temperature dependence as that of the mesityl derivative, suggesting that the *p*-methyl of the latter plays no important role in the line broadening. Solvolysis data for 9-chloro-9-(substituted phenyl)fluorenes[15] show that a *p*-methyl substituent at 25° accelerates the rate of solvolysis by a factor of 10. In this latter system, however, the phenyl substituent may more easily attain coplanarity, thereby increasing the influence of the inductive effect of the methyl group.

9-Aryl- and 9-*t*-Butylfluorenyl-9 Cations. All of the 9-chlorofluorenes and 9-fluorenols described above dissolved in sulfuric acid or trifluoroacetic acid to give stable carbonium ions whose nmr spectra are given in Table V.

The isolation of salts of various 9-arylfluorenyl-9 cations has been reported,[19] and the destabilization of the 9-phenylfluorenylcarbonium ion relative to the triphenylcarbonium ion has been discussed by Breslow.[20] We have not made detailed studies of these ions and we report briefly the nmr and optical spectra.

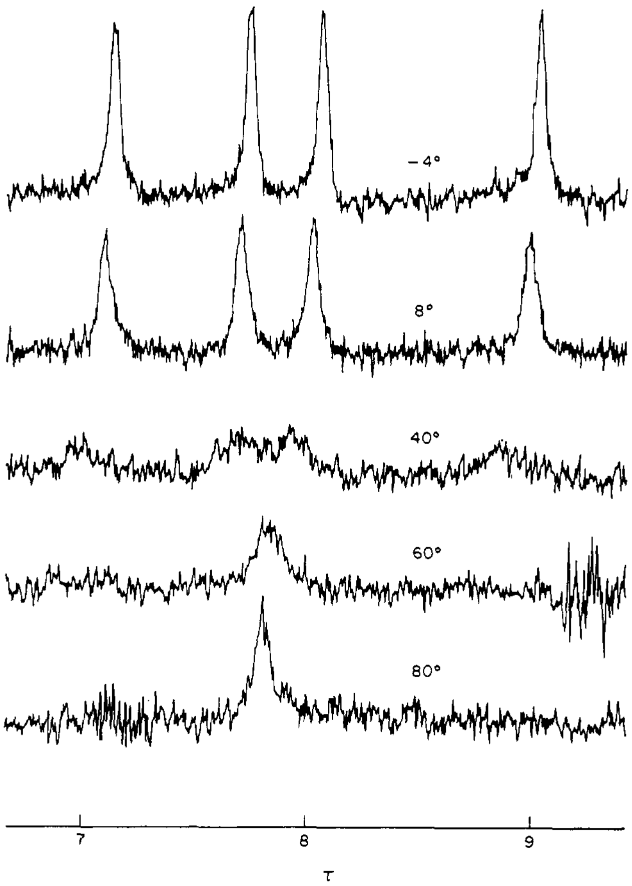

Figure 6. The nmr spectrum of 9-chloro-9-durylfluorene at various temperatures. Spectra at or below 40° were determined in $CDCl_3$, those at 60 and 80° were determined in *m*-dibromobenzene.

The nmr spectrum of the 9-mesitylfluorenyl-9 cation (Figure 7) shows that the two *o*-methyls have become equivalent, with a common resonance line at τ 7.70. It is of interest to note that these methyls are quite close to the position of the *p*-methyl at τ 7.75 and that all methyls are close to the chemical shift of the usual aromatic methyl (τ 7.65–7.75). The nearly complete orthogonality of the mesityl and fluorene rings, due to the steric situation, prohibits any sizable resonance effect which might alter the chemical shift of the methyls. Apparently the inductive effect is negligible as well. There is a possibility of a new peripheral ring current in the fluorenyl carbonium ion, but the interpretation

Table V. Nmr Spectra of Methyl Groups in 9-Arylfluorenyl-9 Cations and Related Carbonium Ions in Trifluoroacetic Acid

Ion	CH_3 at position, τ (relative area) 2′,6′	3′,5′	4′
9-*o*-Tolyl	7.70 (1)		
9-(2,4-Dimethylphenyl)	7.60 (1)		7.62 (1)[a]
9-(2,6-Dimethylphenyl)	7.70 (2)		
9-Mesityl	7.70 (2)		7.75 (1)
9-Duryl	7.75 (2)	7.82 (2)	
Diphenyl-*o*-tolylcarbonium ion	8.12		
Diphenylmesityl	8.34 (2)	7.65	
9-*t*-Butylfluorenyl	$-C_4H_9$ at 7.5 in H_2SO_4		

[a] Split peak, 1–2-Hz separation.

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(19) H. Volz, *Tetrahedron Letters*, 1965 (1963).

(20) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 3737 (1961).

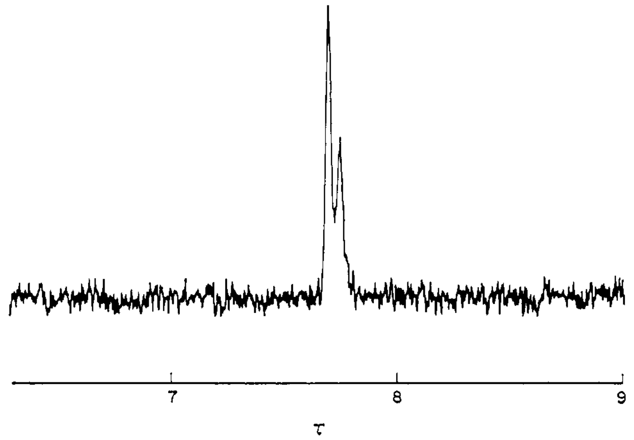

Figure 7. The nmr spectrum of 9-mesitylfluorenyl-9 cation in CF_3CO_2H.

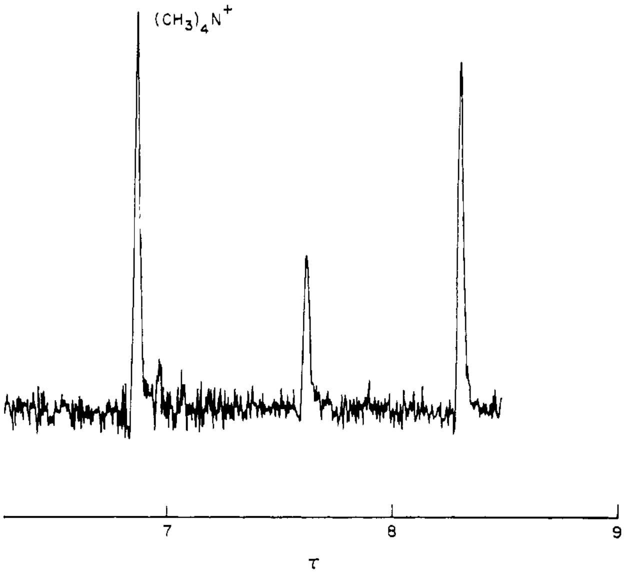

Figure 8. The nmr spectrum of diphenylmesitylcarbonium ion in CF_3CO_2H.

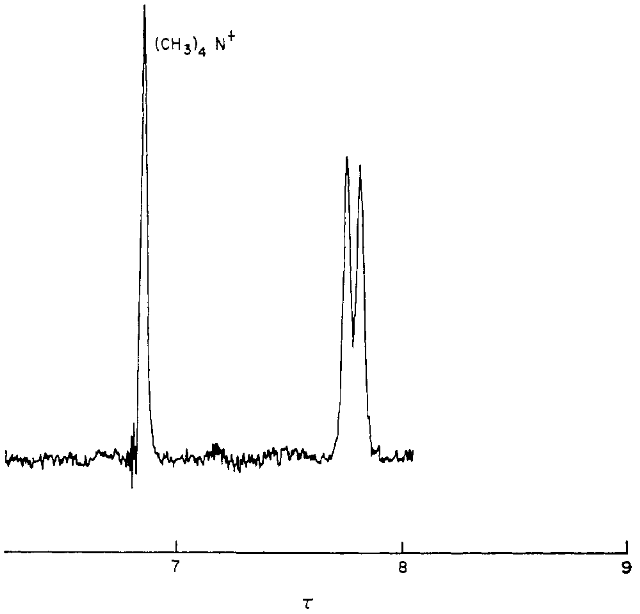

Figure 9. The nmr spectrum of 9-durylfluorenyl-9 cation in CF_3CO_2H.

of the data presented does not require it to have any appreciable effect.

The nmr spectrum of diphenyl-*o*-tolylcarbonium ion exhibits an upfield (to τ 8.12) shift for the *o*-methyl, relative to the methyl resonance signal of the corresponding carbinol. Calculations on neighboring ring-current anisotropies of tritylcarbonium ions give a reasonable correlation between observed and calculated *o*-proton chemical shifts using a 45° twist angle between the phenyls.[21] In this instance, the *o*-protons are found to be in a shielding zone of the aromatic rings. Courtauld models of diphenyl-*o*-tolylcarbonium ion, in which the phenyls are rotated 45°, indicate that the *o*-methyl is held more in the shielding zone of one ring than in the deshielding zone of the other. Whatever inductive or resonance effects the carbonium ion center exerts are apparently outweighed by concomitant ring-current effects.

The nmr spectrum (Figure 8) of the diphenylmesitylcarbonium ion shows a chemical shift of τ 8.34 for the two *o*-methyls while the *p*-methyl protons are found at τ 7.65. This larger upfield shift probably reflects a greater twist angle of the two phenyl groups which in turn leads to increased shielding of these methyls.

The nmr spectrum of 9-durylfluorenyl-9 cation (Figure 9) is similar to that of the corresponding mesityl ion. The *o*-methyls are assigned to the lower field line on the basis of the anticipated relative inductive effects of the carbonium ion at the *ortho* and *meta* positions of the duryl group, assuming that there is no appreciable shielding effect of the fluorene system on the *o*-methyl groups.

The optical spectra of several fluorenyl-9 cations are given in Table VI. The 9-arylfluorenyl-9 cations fall into a consistent pattern which is similar to the spectra of the 9-methyl, 9-hydroxy, and 9-chloro ions. The latter three solutions were prepared by solution of each of the precursors (9-methylfluoren-9-ol, fluorenone, and 9,9-dichlorofluorene) in acetic acid followed by dilution with sulfuric acid. One might expect that the dichloride would be converted to fluorenone in sulfuric acid, but the spectra are sufficiently different in the ultraviolet that the hydrolysis must not have occurred rapidly. The solutions of the aryl ions appeared to be stable for some days but the 9-methyl cation was appreciably decomposed after 20 hr. Fluorenol gave a deep blue solution in sulfuric acid, after prior solution in acetic acid, but the spectrum of this solution measured within a few minutes after preparation was appreciably different from the others. It showed bands at 650 (ϵ 1100), 480 (640), 310 (11,000), and 281 nm (15,000, broad). Further the long-wavelength band increased in intensity on standing. We believe that this spectrum should be discounted because of decomposition of the solution and that the pK_{R^+} for fluorenol,[22] measured spectrophotometrically at the long-wavelength band, should also be discounted. The 9-methylfluorenyl-9 cation appears to be considerably more stable and,

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(21) D. G. Farnum, *J. Am. Chem. Soc.*, **89**, 2970 (1967).

(22) N. C. Deno, J. J. Jaruzelski, and D. Schriescheim, *ibid.*, **77**, 3044 (1955).

Table VI. Optical Spectra of 9-Fluorenyl-9 Cations in H_2SO_4

9 Substituent	λ_{max}, nm (ϵ)			
Phenyl		492 (36,000)	373 (4300)	278 (23,000), 269 (21,000)
o-Tolyl		493 (30,000)	315 sh (3700) 375 (2800)	273 (29,000)
2,4-Xylyl	545 (sh) (17,000)	482 (23,200)	314 (2400) 372 (2000)	271 (25,000)
2,6-Xylyl	550–570 (9000) (broad)	500 (29,000) 472 sh (15,000)	331 (4000)	270 (32,000)
Mesityl	610 (8700)	498 (23,000)	331 (4000) *Ca.* 370 sh (*ca.* 700)	271 (28,000)
Duryl	600 (6800)	500 (23,000) 465 sh (9600)	332 (5200) *Ca.* 370 (*ca.* 500)	270 (30,000)
Methyl		488 (21,000) 458 (9300)	329 (6250) 319 sh (5900)	271 (28,000)
OH (fluorenone)		405 (12,000) 390 sh (10,000)	295 (7800)	267 (53,000)
Cl	500 (1000), very broad	405 (12,000) 390 sh (9,000)	295 (6700)	258 (43,000)
t-Butyl		530 (6200)	332 (9000)	265 (25,000)

further, decomposition leads to a *decrease* in the visible absorption.

The spectra of the stable fluorenyl-9 cations resemble the spectrum of the diphenylcarbonium ion[23] which has bands at 442 (ϵ 53,000) and 300 nm (3000). The additional strong band at *ca.* 270 nm is similar to that found for fluorene and biphenyl. The aryl groups at C-9 apparently do not interact appreciably with the fluorenyl system because they are substantially out of the fluorene ring plane. Thus the 329-nm band in the methyl ion is moved to *ca.* 375 nm in the phenyl and *o*-tolyl ions, where some conjugation is possible, but is essentially unchanged when two *ortho* substituents are placed in the aryl ring and conjugation would be expected to be diminished substantially.

The unusual feature of these spectra is the longest wavelength band which is split into two bands in the ions which have a 2′,6′-disubstituted group at C-9. In these compounds molecular models indicate that the aryl substituent is forced to be virtually orthogonal to the ring plane and we expected no appreciable difference between these spectra and that of the 9-methylfluorenyl-9 cation. The new longest wavelength band (610 nm in the mesityl ion) may possibly be a charge-transfer band. It does seem to depend on the number of methyl groups on the substituent ring which would lower its ionization potential and the energy of the transition. There are not sufficient data to say anything further; it would be necessary to have model compounds in which the geometry is also altered by substituents in the fluorene nucleus, *e.g.*, derivatives of 1-methylfluoren-9-ol.

Finally we comment on the spectrum of 9-*t*-butyl-9-chlorofluorene in sulfuric acid. The spectrum of this solution was unchanged on standing for several days. The nmr spectrum of the chloride in sulfuric acid indicated that the *t*-butyl group remained intact. The ultraviolet portion of the spectrum compares favorably with the other ions but the visible absorption is quite different. This could be due to the fact that the *t*-butyl substituent distorts the planarity of the ion and changes appreciably the band associated with the carbonium ion center. Alternatively we may not have a fluorenyl ion at all and the unusual spectrum may be due to a decomposition product. We do not know which of these possibilities is correct, but we do not think that a decomposition reaction in this case should be so very different from the 9-fluorenyl and 9-methylfluorenyl products.

9-Mesitylfluorenyl Free Radical. The relationship between inherent stabilities and steric factors of triphenylmethyl *vs.* phenylfluorenyl radicals was discussed recently.[2] As mentioned earlier we originally began this work in order to prepare a monomeric 9-phenylfluorenyl radical. The evidence available for the unsubstituted radical demonstrates that it is dimerized completely at room temperature. Lewis, Lipkin, and Magel[24] were able to obtain the spectrum of the radical by heating a toluene solution of the dimer to 93°. The only 9-substituted fluorenyl radical which appeared to be completely dissociated at 25° is 9-tritylfluorenyl. However its mode of preparation, with attendant difficulty in purification and separation from by-products due to a very low solubility in most solvents, made this compound unattractive to us.

A comparison of the Courtauld models of 9-phenyl-, 9-*t*-butyl-, and 9-mesitylfluorenyl systems indicated that the *t*-butyl substituent would interfere more with dimerization than would the phenyl group and also that dimerization of the mesityl compound, at C-9, would be virtually impossible. We found that 9-*t*-butyl-9-chlorofluorene reacted with powdered zinc or copper but that the resulting solutions had no esr spectrum. We then turned to 9-chloro-9-mesitylfluorene whose preparation was described above. It reacted readily with powdered copper in tetrahydrofuran solution to give a dark yellow-green solution containing the desired radical. The optical spectrum of this solution is given in Figure 10. It is essentially identical with that reported for 9-phenylfluorenyl. We were unable to observe any fluorescence, either at 25 or −196°.

The esr spectrum of the radical is quite complex and did not lend itself readily to analysis. Overmodulation produced a five-line spectrum which can be attributed to splitting by the four essentially equivalent *o*- and *p*-

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[23] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 457 ff.

[24] G. N. Lewis, D. Lipkin, and T. Magel, *J. Am. Chem. Soc.*, 66, 1579 (1944).

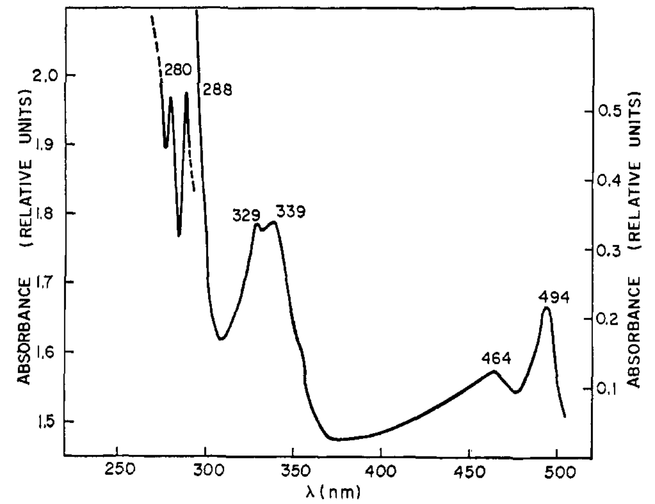

Figure 10. The optical spectrum of 9-mesitylfluorenyl free radical.

hydrogens of the fluorenyl system. The splitting is *ca.* 2 G. The major conclusion drawn from the complex spectrum obtained under high resolution is that there is no line at the center of the spectrum. This requires that there be one group which causes a splitting into an even number of lines and this group must have an odd number of protons. All protons in the 9-mesitylfluorenyl radical occur in pairs or in even multiples with the sole exception of the *p*-methyl group. There must be some spin density in the mesityl ring but it is probably not large.

The radical is quite stable in solution and the esr spectrum did not change in intensity upon cooling below room temperature, which indicates that dimerization does not occur. It reacts with oxygen but much more slowly than triphenylmethyl reacts. When a degassed solution of the radical was aerated thoroughly for a few minutes the only noticeable change in the esr spectrum was line broadening attributable to dissolved oxygen. Longer exposure to air caused decomposition with the formation of a red solution whose composition was not studied.[25]

Acknowledgments. We thank Dr. S. H. Glarum and J. H. Marshall for determining the esr spectra and for discussions of them. We are especially grateful to Dr. M. Cocivera for informative discussions of exchange in nmr spectroscopy.

(25) NOTE ADDED IN PROOF. Professor H. Volz of the University of Karlsruhe has informed us (May 1968) that he and Miss B. Schelberger have made related studies of various 9-arylfluorene-9 cations which will be published shortly in *Chemische Berichte*. Professor Volz also called our attention to a previous report of the 9-mesitylfluorenyl radical (W. Theilacker, *et al.*, *Angew. Chem.*, **69**, 322 (1957)) which, unfortunately, is not indexed in *Chemical Abstracts*.

Electron Paramagnetic Resonance and Electron–Nuclear Double Resonance Studies of Phenoxyl Radicals Derived from Substituted Diphenylmethanes

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Abstract: A series of five oxidized diphenylmethane derivatives related to the free radical galvinoxyl has been prepared. The four *t*-butyl groups are replaced by several combinations of methyl, methoxyl, and *t*-butyl groups. Two of these compounds are new and their syntheses involved some interesting reactions and side products; a quinone methide intermediate is proposed to account for these. Electron–nuclear double resonance (endor) and electron paramagnetic resonance (epr) spectra of these compounds in solution have been obtained with the following results. (a) All proton hyperfine couplings have been determined and a previously published assignment for the compound with all *t*-butyls replaced by methoxyls has been corrected. (b) In order to interpret the spectra, molecular orbital calculations have been carried out treating the methyl, *t*-butyl, and methoxyl groups by the "heteroatom model." The parameters to describe the methyl and *t*-butyl groups are found to be nearly identical ($h_X = 2.0$, $k_{C-X} = 0.7$), but the methoxyl group is best treated by $h_X = 2.2$ and $k_{C-X} = 0.6$. (c) When the two *t*-butyl groups on one of the rings are replaced by methyl groups, the methyls are inequivalent. This molecular asymmetry results in a splitting of the methyl proton endor line. If a perturbation is introduced into molecular orbital calculations for the various molecules which is sufficient to cause the observed splitting in this molecule, the resulting splittings of all of the other endor lines of this series are calculated to be below detectability. (d) If one *t*-butyl of each ring is replaced by a methyl, two isomers yielding separate endor spectra exist in solution, and an approximate activation energy of 1 kcal/mol has been obtained describing the interconversion of the isomers.

The free radical galvinoxyl (I) (sometimes referred to as Coppinger's radical) was prepared by Coppinger[2] and Kharasch[3] in 1957. This radical possesses remarkable stability, both in the solid state and when dissolved in various organic solvents. It has been the subject of several electron paramagnetic resonance

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(1) (a) University of Arizona; (b) Varian Associates Postdoctoral Fellow; (c) Varian Associates.

(2) G. M. Coppinger, *J. Amer. Chem. Soc.*, **79**, 501 (1957).

(3) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).