

THE CONDENSATION OF 9-FORMYLFLUORENE AND
AMMONIA. STRUCTURE OF THE PRODUCT AS
INDICATED BY ULTRAVIOLET SPECTRA¹

FRANKLYN D. MILLER² AND E. C. WAGNER

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This study supplements the findings reported earlier (1) as to the structure of the compound formed when formylfluorene condenses with dry ammonia, represented by Wislicenus and Russ (2) to be one or a mixture of the tautomers 9-(aminomethylene)fluorene (I) and 9-(iminomethyl)fluorene (II). Von and Wagner (1) found compound I *alter* II to give chemical reactions clearly attributable to structure I but none attributable to structure II.³ Similar findings for other compounds of analogous structures and similarly capable of enamine-ketimine tautomerism were reported by von Auwers and Süssmühl (3) and by Krabbe and Schmidt (4), who found evidence for only the enamine forms. There is reason to believe that form I may be stabilized owing jointly to the lability of hydrogen attached to carbon 9 of fluorene, to conjugation of the 9, α -double bond with the unsaturation of the fluorene system, and to the proton-binding character of nitrogen, and that as a consequence of these influences the tendency of I to isomerize to II may be depressed.⁴ Since the chemical evidence at best is indecisive with respect to the presence of II, the examination of this system was continued by physical means, *viz.*, ultraviolet spectroscopy. There were compared

¹ Constructed from the Ph.D. dissertation of Franklyn D. Miller, University of Pennsylvania, 1950.

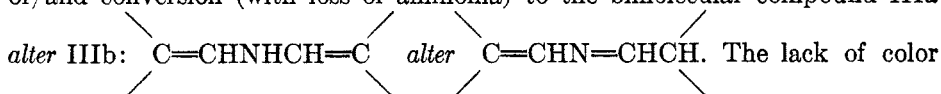
² Present address: National Distillers Products Corporation, Research Division, Cincinnati, Ohio.

³ Results of ozonolysis were decisive in showing structure I, but this treatment would not reveal II if present. Bromination occurred by addition, and hydrolysis of the product yielded 9-bromo-9-formylfluorene and ammonium bromide (this over-all result indicating structure I), but it is unlikely that by this test the presence of II in small amount could be detected. The fact that I *alter* II yields no ammonia on heating with aqueous alkali is not decisive in excluding II, since a ketimine would not necessarily be cleaved in this way. The conventional cleavage by acid is here inapplicable, for this treatment of I-II causes loss of ammonia and formation of the bimolecular condensation product IIIa-IIIb.

⁴ In systems of the type $RCH_2CH=NH \rightleftharpoons RCH=CHNH_2$ there may be some stabilization of the enamine owing to the proton-fixing character of nitrogen (3). In systems of the type $RCH=CHCH_2CH=NH \rightleftharpoons RCH=CHCH=CHNH_2$ there is added to this influence the effect of conjugation in the righthand member. In β,β -diphenylvinylamine (*alter* β,β -diphenylacetaldehyde imine) these combined influences stabilize the enamine form to such an extent that the ketimine form cannot be detected (4). It may be supposed that in 9-(aminomethylene)fluorene the effect of conjugation is even stronger. Certain allylic-type rearrangements are unidirectional if one form presents a structure that is the more extensively conjugated. Thus the Hofmann deamination of piperidine yields pentadiene-1,3 and not the expected pentadiene-1,4; compounds of the type $ArCH_2CH=CH_2$ are isomerized to $ArCH=CHCH_3$ by alkali; vinylacetic acid is readily isomerized to crotonic acid, etc.

the ultraviolet absorption spectra of compound I *alter* II and of synthetically prepared and structurally similar reference compounds in each of which the external double bond is locked in one of the two positions 9, α or α, β as in I and II respectively.⁵

The condensation of formylfluorene and ammonia or diethylamine. At the outset it is necessary to correct a misapprehension as to the identity of the initial condensation product of formylfluorene and ammonia, and as to certain of the properties of compound I *alter* II. As reported by Wislicenus and Russ (2) and corroborated by Von and Wagner (1), the compound as first obtained is colorless and melts at 146–149° after sintering near 110°; during storage or more rapidly upon heating it becomes yellow, a change hitherto attributed to deterioration or/and conversion (with loss of ammonia) to the bimolecular compound IIIa



of the condensation product is inconsistent with the conclusion, forced by the chemical evidence, that the compound previously investigated has structure I or that I is present, for compounds in which a 9, α -double bond is cross-conjugated with the unsaturation of fluorene are distinctly colored, *e.g.*, fluorenone and its oxime, hydrazone, semicarbazone, anil, etc.; 9-(N-piperidinomethylene) fluorene, 9-ethylidene fluorene, etc. Acceptance of structure I–II for the colorless condensation product has rested apparently upon the fact that Wislicenus and Russ reported for it analytical values sufficiently close to the requirements of the formula $\text{C}_{14}\text{H}_{11}\text{N}$ to satisfy later workers. By working rapidly with this compound there was confirmed the suspicion that it is the unstable addition product (IV) of formylfluorene and ammonia, *viz.*, the aldehyde-ammonia

$\begin{array}{c} \diagdown \\ \text{CHCH}(\text{OH})\text{NH}_2 \\ \diagup \end{array}$. The nitrogen content corresponded to the requirement of the formula $\text{C}_{14}\text{H}_{13}\text{NO}$, and the compound was readily transformed into I–II, which when pure is bright yellow in color and melts without previous sintering.

The condensation of formylfluorene and diethylamine appears to proceed similarly, yielding a colorless product (m.p. 78°) which rapidly becomes yellow; after some hours the odor of diethylamine is pronounced, and the only compound isolable is fluorenone. To test the supposition that the colorless product is the addition compound it was heated in a stream of dry air in an apparatus that permitted selective absorption and semiquantitative determination of any water and any diethylamine disengaged. The amount of water was 77.5% of that calculated for the conversion of 9-(diethylaminomethylolyl)fluorene to 9-(diethylaminomethylene)fluorene, allowing for the extent of cleavage of the condensation product indicated by the amount of diethylamine recovered.

The condensation of 9-formyl-2,7-dibromofluorene and ammonia was reported

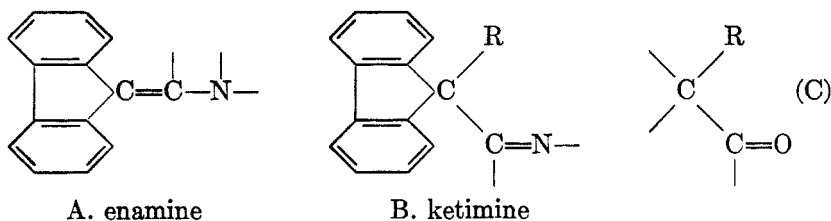
⁵ Comparative application of the refractometric method was judged to be unpromising when tests indicated that the requisite accuracy would be unobtainable owing to the slight solubilities of the compound in nonpolar solvents (0.001 M in isoöctane), and to the probable complications if polar solvents were used.

by Von and Wagner (1) to yield a colorless product which rapidly became yellow on standing, and which was designated as 9-aminomethylene-2,7-dibromofluorene. In the present study the condensation yielded at once a yellow product, indicated by analysis to be the compound named.

It is concluded that if condensation products of 9-acylfluorenes and ammonia or amines are colorless they may be addition compounds of aminoalkylol type, which appear to be unstable, losing water more or less rapidly to yield the 9-aminoalkylidene fluorenes which are colored.

STUDY OF THE STRUCTURE OF COMPOUND I-II BY ULTRAVIOLET
SPECTRAL EXAMINATION

Reference compounds. The lack of recorded ultraviolet absorption data for fluorene derivatives containing unambiguously the structural conditions needed for comparison with compound I *alter* II, *viz.*, A and B,



made necessary the preparation of appropriate compounds with external attachments such as to exclude tautomeric shift and to introduce no complicating absorptive effects. There was used successfully also a reference compound containing the system C which is isosteric with B. As a compound with locked structure A there was prepared 9-(N-piperidinomethylene)fluorene (VI) by condensation of piperidine and formylfluorene (2); the effect of the piperidine ring proved to be not disturbing. Repeated attempts to prepare the presumably more suitable compound 9-(diethylaminomethylene)fluorene (V), either by condensation of formylfluorene and diethylamine or of fluorene and diethylformamide, were unsuccessful, as mentioned above and explained in the experimental section. As a compound with locked structure of type C there was used 9-methyl-9-acetylfluorene (VII), the oxime of which (VIII) served as a compound of type B. Compound VII, not obtainable by ester condensation owing to its instability under alkaline conditions, was made from phenanthrene *via* phenanthraquinone by an ingenious and elegant sequence due in part to Meerwein (5). The main steps are (a) ring-contraction of phenanthraquinone by internal rearrangement of the benzylic acid type, (b) esterification of the resulting 9-hydroxyfluorene-9-carboxylic acid, (c) conversion to the pinacol by action of methylmagnesium iodide, and (d) conversion to VII by pinacolone rearrangement. Compound VII could not be converted to the imino-compound (type B) by action of ammonia. Compound VII (type C), though less obviously suitable than the imine, was used instead of it;

the absorptive effect of the isosteric groups —C=O and —C=NH is somewhat similar and is exerted in the region in which fluorene itself absorbs strongly (6). Compound VIII appears to introduce no irregularities caused by isomerization

of the oxime group, as indicated both by the results presented below and by the observation of Ramart-Lucas, *et al.* (7) that the absorptive effects of ketoximes of similar structure are those of the normal form —C=NOH . The colors of the reference compounds are as follows: 9-(piperidinomethylene)fluorene (VI), bright orange-yellow; 9-methy-9-acetylfluorene (VII), colorless; its oxime (VIII), colorless. Since fluorene is colorless⁶ (6) it thus appears that the presence of a cross-

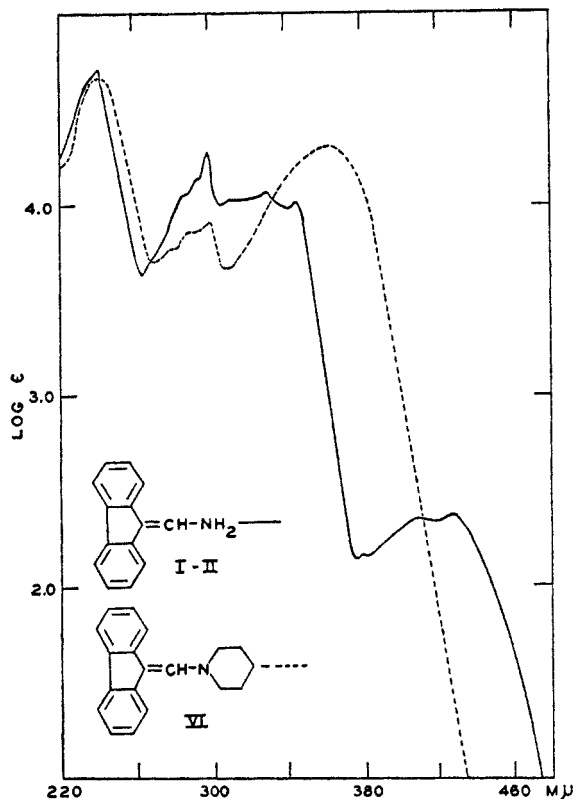


FIGURE 1. ULTRAVIOLET ABSORPTION SPECTRA OF COMPOUNDS I *alter* II AND VI.

conjugated $9, \alpha$ -double bond, as in VI, fluorenone, etc., confers visible color, but that interposition of a carbon atom between the external double bond and the fluorene system (as in VII and VIII) excludes this effect. It is an obvious inference that the condensation product of formylfluorene and ammonia, which is bright yellow in color, is probably wholly or largely I, since a compound of structure II would probably be colorless.

ULTRAVIOLET ABSORPTION OF COMPOUNDS I-II, VI, VII, AND VIII

Absorptions of I-II and of the several reference compounds are plotted in Figures 1-3. Interpretation of the absorption curves is relatively simple, since

⁶ Highly purified fluorene (6), freed from impurities such as acenaphthene and anthracene, lacks the fluorescence exhibited by many specimens not rigorously purified.

the significant comparisons are clearly shown, and for this reason the discussion is brief.

Figure 1, showing absorptions of aminomethylenefluorene (I-II) and piperidinomethylenefluorene (VI), discloses marked similarity of structure, with similar and striking narrow band maxima at 240–242 $m\mu$. A second and broader band (with some fine structure), centered around 300 $m\mu$, is similar for the two compounds. A third broad band overlaps the visible region and accounts for the visible colors of the compounds.

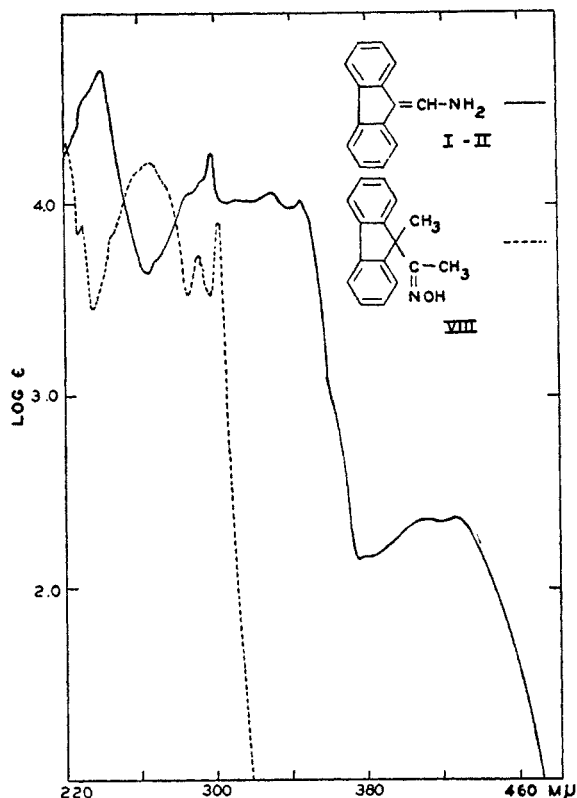


FIGURE 2. ULTRAVIOLET ABSORPTION SPECTRA OF COMPOUNDS I *alter* II AND VIII.

Figure 2 reveals unmistakable dissimilarities in the absorptions of aminomethylenefluorene (I-II) and 9-(9-methylfluorenyl)methyl ketoxime (VIII). The curve for VIII shows less fine structure than that of I-II, and discloses a minimum at 240 $m\mu$, where I-II shows a strong maximum. The spectrum of VIII is in fact very like that of fluorene; the absorption maxima are respectively 301 $m\mu$ and 303 $m\mu$. Since it is known (8, 9) that 9-phenylfluorene, 9-hydroxy-9-ethylfluorene, and fluorene show very similar ultraviolet absorptions, with maxima and extinction values nearly identical, it appears that simple substituents in position 9 of fluorene, and the presence of an α,β -double bond, do not greatly alter the absorption of the fluorene system. The inference that compounds such

as VII and VIII should show absorptions which are alike and which resemble the absorption of fluorene is supported by Figure 3, which indicates also that both VIII and VII qualify as reference compounds, and that structures B and C are, for present purposes, equivalent. When an external double bond is at 9, α the resulting augmented conjugation leads to absorption unlike that of fluorene.⁷ This has been observed for fluorenone and 9-ethylidene fluorene (8, 9), both of which show (in addition to some fine structure attributable to strains involved in the 9, α -double bond) absorptions that overlap the visible region (maximum

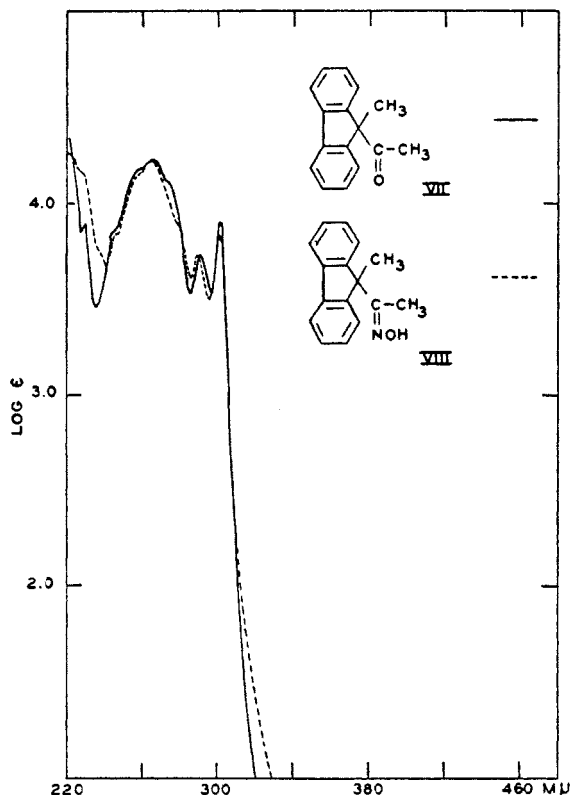


FIGURE 3. ULTRAVIOLET ABSORPTION SPECTRA OF COMPOUNDS VII AND VIII.

for fluorenone at about 380 mμ). Compound I-II shows a similar absorption that extends into the visible region, with a maximum at somewhat longer wavelengths than that of fluorenone; the displacement can be regarded as a bathochromic shift caused by the auxochromic amino group of I. The intense absorption of I-II at 240-250 mμ corresponds to the like absorption of fluorenone and

⁷ The pronounced effect of an external double bond conjugated with aromatic unsaturation is shown (10) by the isomeric compounds 1-propenylbenzene and allylbenzene. The former shows a band at 293 mμ which is about 600 times as intense as the benzene band nearest the visible (286 mμ), and a second band at 249 mμ which is about 700 times as intense as the strongest line of benzene and more than 650 times as strong as the strongest band shown by allylbenzene.

9-ethylidene fluorene. Results for compound VI (9-piperidinomethylene fluorene) are similar. The maximum near the visible region (361 m μ) seems to represent a hyperchromic shift due to the mass of the piperidine unit (as compared with the amino group of I), the character of which also decreases the strain in the 9, α -double bond, with resulting loss of fine structure in the spectrum. The hypsochromic shift for VI as compared with I, associated with the replacement of the hydrogen atoms of the amino group by the pentamethylene group, may be attributed to the constraints imposed upon the electrons binding nitrogen and carbon in the rigid azine ring, as compared with their great lability in $-\text{NH}_2$.

Consideration of the evidence available justifies small doubt that structure I should be assigned to the colored compound formed from formylfluorene and ammonia followed by loss of water, and that this compound may be designated as 9-(aminomethylene)fluorene. It is probable that the analogous colored products obtained from 2,7-dibromo-9-formylfluorene and 9-acetylfluorene are likewise the Δ^9,α -compounds. No direct evidence now exists for the reality of the ketimine form II.⁸ It appears that the stabilizing effect of the augmented conjugation in I suffices virtually or wholly to exclude prototropy.

EXPERIMENTAL

Formylfluorene was made by the method of Von and Wagner (1) with modifications. The dry potassium methoxide (3.5 g. of potassium; 0.09 mole) was treated with 60–70 ml. of dry ether and 15 g. (0.09 mole) of fluorene (Eastman T598 twice recrystallized from ethanol), and the mixture was heated under reflux about 30 minutes, to form in quantity the potassium salt of fluorene as indicated by the appearance of a tan color. Ethyl formate (6.7 g.; 0.09 mole) was introduced and heating was continued until the potassium methoxide had disappeared, and then 15 minutes longer. The reaction time was thus decreased by nearly three hours. It seems necessary to work up the reaction mixture immediately. The yield is about 70%, but depends upon the purity of the materials and upon the care taken to exclude moisture.

9-(Aminomethanolyl)fluorene (IV) and *9-(Aminomethylene)fluorene* (I *alter* II). The method of Von and Wagner (1) was only slightly changed. Dry ammonia was bubbled for four hours into a 40% solution of freshly distilled formylfluorene in ether, chilled in an ice-bath. The ether was evaporated from the red mixture and the residue was extracted with hot benzene; on chilling the extract a voluminous colorless solid separated, and was washed with *n*-hexane. Material for analysis was recrystallized rapidly from benzene, then suspended in hot *n*-hexane, washed on the filter with *n*-pentane, and there dried. Samples for Kjeldahl analysis were weighed out and handled rapidly.

*Anal.*⁹ Calc'd for $\text{C}_{14}\text{H}_{11}\text{N}$ (I *alter* II): N, 7.25.

Calc'd for $\text{C}_{14}\text{H}_{13}\text{NO}$ (IV): N, 6.63. Found: N, 6.67, 6.52.

After standing for three days the compound was yellow, and it crystallized from cyclohexane in a yellow gelatinous form. Several recrystallizations from cyclohexane yielded material of m.p. 144.6–147.1° (corr.) without previous sintering. In all preparations of this compound (I *alter* II) some of the yellow bimolecular compound IIIa–IIIb was obtained.

⁸ In the serial dilutions incidental to the spectral work a slight deviation from Beer's law, not certainly beyond the error of observation, was noted. The possibility of detecting II in this way, or by means of methylmagnesium iodide, has not been tested.

⁹ Analyses reported in this paper were performed by Sarah Miles Woods.

From this there were isolated (mechanically) the two forms (yellow and blue-red) reported by Wislicenus and Russ (2).¹⁰

9-(Piperidinomethylene)fluorene (VI). Following the procedure of Wislicenus and Russ (2), 12.0 g. (0.06 mole) of freshly distilled formylfluorene in 30 ml. of 1:2 ethanol was treated with 8.8 g. (0.1 mole) of piperidine in 30 ml. of 1:2 ethanol, and the red solution was heated for five minutes on a steam-bath. The dilute alcohol was decanted from the oily red precipitate, which was treated with 95% ethanol and heated until the oil changed to a yellow solid. This was crystallized from alcohol; yield, 64%. Results were somewhat better when formylfluorene was used in larger proportion. Thus, from 17.1 g. (0.088 mole) of formylfluorene and 9.0 g. (0.106 mole) of piperidine there resulted a green reaction mixture and a green amorphous solid product in a yield (after crystallization from alcohol) of 73%. The products of the two procedures both melted at 110–111.7° (corr.) and were identical. Wislicenus and Russ reported satisfactory analyses but mentioned neither melting point nor yield. Three recrystallizations of the product failed to change the melting point, but almost entirely eliminated the original pronounced unpleasant odor. Material for spectroscopic examination was recrystallized twice more. The pure compound is bright orange-yellow.

9-Methyl-9-acetylfluorene (VII). Phenanthraquinone was made in small lots by a procedure based on that of Anschütz and Schultz (11). It is convenient to carry out the preparation in good-sized beakers; for the quantities specified hand-stirring suffices. To a solution of 28 g. of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) in 150 ml. of cold water was added 50 ml. (90 g.) of conc'd sulfuric acid, and into the hot solution was introduced, with rapid stirring, 10 g. of phenanthrene (Eastman T599 recrystallized from ethanol). Reaction was vigorous, with gas evolution, and a black oil appeared on the surface of the liquid; the mixture was kept near 100°, with occasional stirring, for about 30 minutes. (If the temperature falls below 80–90° the oil may solidify, trapping some unattacked phenanthrene; if the temperature is too high frothing occurs.) To complete the oxidation a hot solution of 28 g. of sodium dichromate in 50 ml. of water was added in small portions during 30 minutes with active stirring and while keeping the mixture hot. Addition of 400–500 ml. of cold water to the cooled mixture produced a yellow precipitate which was filtered on cotton, washed with 200 ml. of water acidified with sulfuric acid, and then with a liter of cold water. The crude product was extracted with 500 ml. of 2% sodium carbonate solution (diphenic acid) and then washed on the filter with a liter of cold water. The mass in the funnel (cotton included) was extracted with excess 20% sodium bisulfite solution at about 60° and the filtered extract (including a little cold water used to wash the undissolved residue) was treated with excess conc'd hydrochloric acid. The yellow precipitate was washed with cold water; the yield was 50–60%. The compound was again dissolved in sodium bisulfite and recovered, and was then recrystallized first from dioxane-water and then from benzene. This material was sufficiently pure for the next operation.

9-Hydroxyfluorene-9-carboxylic acid. Following the procedure of Schmidt and Bauer (12), 10 g. of phenanthraquinone was treated with 100 ml. of aqueous 10% potassium hydroxide at room temperature, and after several minutes the temperature was raised to

¹⁰ Consideration of the probable effects of the conjugated unsaturation of IIIa and that of IIIb leads to the conclusion that IIIa may be strongly yellow owing to the absorption of the >C=CH -system twice present, and that IIIb, containing the more extended conjugated system >C=CHN=CH- , should show a different absorption involving probably a bathochromic shift. This would reverse Wislicenus and Russ' assignment of structure IIIa to the red compound and of structure IIIb to the yellow compound. Examination of the two compounds in the ultraviolet spectrophotometer was blocked by their low solubilities in suitable solvents. Nitrobenzene is a satisfactory solvent for recrystallization but was judged to be not suitable for spectral work owing to its strong absorption in the near ultraviolet and to its polar character.

80–90°. The phenanthraquinone dissolved almost wholly to a deep red solution which was filtered through glass-wool. Upon acidifying the cooled filtrate with 1:1 sulfuric acid the product separated as an oily turbidity which crystallized on standing; the yield was 70% (12; cf. 13). The acid was purified by solution in hot water acidified with dilute hydrochloric acid, digestion with 2 g. of decolorizing carbon for each 400 ml. of solution, filtration, and chilling. This treatment was repeated once or twice until the product was colorless, m.p. 166–167° (corr.).

Ethyl 9-hydroxyfluorene-9-carboxylate. The esterification was based on the procedure of Schmidt and Meyger (14) using, for each 10 g. of 9-hydroxyfluorene-9-carboxylic acid, 150 ml. of 95% ethanol containing 0.8 ml. of conc'd sulfuric acid.¹¹ The solution was heated under reflux for four hours, and while hot was concentrated to half its volume with a stream of air.¹¹ The solution was adjusted to slight acidity with alkali and then acid. Concentration was continued without further heating, and the precipitate which formed was removed at intervals. The first two portions were usually colorless and fairly pure; the yield of crude product totalled about 75%. Purification to m.p. 96° was effected by solution in a little benzene and the addition of *n*-hexane to the chilled solution until the separation of crystals was complete.

9-Hydroxy-9-(α -hydroxyisopropyl)fluorene. This pinacol was prepared from the hydroxy-ester by the action of methylmagnesium iodide after the procedure of Meerwein (5) without significant change except in the purification, which was effected by several recrystallizations from 60% ethanol and then from ligroin (90–120°). The yield of crude material was nearly quantitative; the pure product was colorless, m.p. 101.2–102° (corr.).

9-Methyl-9-acetylfluorene (VII) was prepared from the preceding compound by pinacolone rearrangement substantially as described by Meerwein (5). The pinacol was added in small portions and with stirring to ten volumes of conc'd sulfuric acid chilled in an ice-bath, adding each fresh portion only after the preceding portion had dissolved. The deep red-brown solution was poured slowly onto cracked ice with steady stirring. The product, at first oily, crystallized on standing. These operations require care; in several runs, apparently improperly controlled, no product separated from the diluted reaction mixture. Two recrystallizations from pentane, by saturation at room temperature and then chilling in Dry Ice-acetone, followed by crystallization from isoöctane, proved more effective for purification than crystallization from 60% ethanol (3). The pure colorless ketone VII melted at 88.5–89° (corr.).

9-(9-Methylfluorenyl)methyl ketoxime (VIII; oxime of VII). A mixture of 0.52 g. of VII in 10 ml. of ethanol, 0.34 g. of hydroxylamine hydrochloride in 10 ml. of ethanol, and 0.66 g. of crystallized sodium acetate in 10 ml. of 50% ethanol was heated on a steam-bath for 30 minutes. Most of the product separated on chilling the mixture, and the rest was obtained by addition of water to the mother liquor; the yield was quantitative. After crystallization from ethanol-water and several crystallizations from pentane-hexane mixture the oxime was dissolved in hot isoöctane and the filtered solution was chilled. The pure oxime melted at 173.5–174.5 (corr.).

Anal. Calc'd for $C_{16}H_{15}NO$: C, 80.9; H, 6.37; N, 5.90.

Found: C, 80.8; H, 6.39; N, 5.90.

Condensation of formylfluorene and diethylamine. A slight excess of diethylamine was distilled into a solution of 1.84 g. of formylfluorene in 30 ml. of dry ether. The ether was decanted from the colorless crystalline product, which was washed by decantation with a little fresh ether. The product, now pale yellow in color, was extracted with boiling hexane and the extract was filtered and chilled, yielding colorless crystals which were washed with pentane and dried rapidly in the funnel. This material weighed 1.44 g. and melted

¹¹ The original procedure, with catalysis by (aqueous) hydrochloric acid and evaporation of alcohol by simple heating, yielded the crude product as a red oil, purification of which (60% alcohol) involved considerable loss, so that the final yield was smaller than by the modified procedure.

rather sharply at 78°. By the following day the product had changed into a red oil and smelled strongly of diethylamine. From this material efforts to isolate 9-(diethylamino-methylene)fluorene failed; the only compound isolated was some fluorenone, identified by analysis and absorption spectrum.

The colorless condensation product was too unstable to permit satisfactory analysis. To test the possibility that it was the addition-product, 9-fluorenyldiethylaminocarinol, a weighed sample was warmed in an apparatus which included a weighed absorption tube charged with potassium hydroxide pellets, followed by an absorber charged with 2.5 *N* hydrochloric acid. During the test the train was flushed with a stream of air previously

TABLE I
PRINCIPAL ULTRAVIOLET ABSORPTION MAXIMA

COMPOUND	m μ	LOG ϵ
9-Methyl-9-acetylfluorene (VII).....	301	3.83
	290	3.72
	266	4.22
	230	4.14 ^a
	256	4.12 ^a
9-(9-Methylfluorenyl)methyl ketoxime (VIII).....	301	3.90
	290	3.73
	266	4.22
	230	3.90
	244	3.80 ^a
9-(N-Piperidinomethylene)fluorene (VI)..	360	4.30
	300	3.92
	290	3.88
	243-244	4.65
9-(Aminomethylene)fluorene (I-II).....	425	2.37
	410	2.36
	345	4.02
	328	4.06
	298	4.17
	240	4.70

^a Principal inflection points.

passed successively through cotton-wool, calcium chloride, solid potassium hydroxide, conc'd sulfuric acid, and Ascarite. The increase in weight of the potassium hydroxide receiver was calculated as water. Diethylamine, retained in the acid-charged receiver, was liberated with NaOH and titrated as in the Kjeldahl analysis. Decomposition was allowed to proceed first at room temperature for four hours, and after standing overnight (with air-stream discontinued) the test was continued an additional six hours with occasional warming; it was terminated when the gain in weight of the potassium hydroxide tube did not exceed the determined blank of 0.0001 g. per hour. In this way there were obtained from 0.8789 g. of compound 0.0405 g. of water and 0.0282 g. of diethylamine. After correcting for the latter (on the assumption that cleavage of diethylamine decomposed an equivalent amount of the original compound and excluded it from the water-eliminating reaction) the water recovered was 77.5% of that calculated for dehydration of 9-fluorenyldiethylaminocarinol.

Condensation of fluorene and diethylformamide. Attempts to prepare 9-(diethylamino-methylene)fluorene by heating these reactants in the presence of potassium methoxide were unsuccessful.

Condensation of 9-formyl-2,7-dibromofluorene and ammonia. Using the procedure of Von and Wagner (1) the products of a number of experiments were in no case colorless but were invariably yellow. Analysis showed the yellow compound to be 9-(aminomethylene)-2,7-dibromofluorene, the name originally assigned to the unstable and initially colorless product reported by Von and Wagner.

Anal. Calc'd for $C_{14}H_{11}Br_2NO$: C, 45.5; H, 3.01; N, 3.80.

Calc'd for $C_{14}H_9Br_2N$: C, 47.9; H, 2.58; N, 3.99.

Found, colorless compound (V. and W.): C, 48.7; H, 2.73; N, 3.63.

Found, yellow compound (M. and W.): C, 48.1; H, 2.39.

Ultraviolet spectral examination. A Beckman Model DU ultraviolet spectrophotometer was used for examination of compound I *alter* II, VI, VII, and VIII in solution in iso-octane (Phillips Petroleum Company "Spectrograde") and contained in 1.00-cm. quartz cells. Solutions were initially 0.01 *M*, except those of I *alter* II which, owing to the sparing solubility of this compound, were 0.001 *M*. Dilutions were made by the factor 0.1, ending with 10^{-5} *M*. Deviation from Beer's law was noted in the case of compound VII, and a small deviation, close to the error of observation, occurred with I-II.⁸ The molar extinction coefficients and wave-lengths for the principal maxima of the compounds examined are given in Table I. The spectral curves are shown in Figures 1-3.

SUMMARY

1. Unequivocal physical evidence obtained by ultraviolet absorption spectrometry is presented to establish as 9-aminomethylene-fluorene the compound formed by condensation of formylfluorene and ammonia followed by loss of water. The initial colorless product appears to be the unstable aldehyde-ammonia.

2. The observation that compounds of fluorene having a 9, α -double bond conjugated with the unsaturation of the nucleus are colored, while those with an unconjugated α,β -double bond are colorless, strengthens the conclusion that the compound studied, which is strongly colored, has the enamine structure.

PHILADELPHIA 4, PENNA.

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