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I hereby recommend that the thesis prepared under my supervision by Elizabeth Kreiser Weisburger

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Approved by:

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THE STEREOCHEMISTRY OF FLUORENE

A dissertation submitted to the

Graduate School
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requirements for the degree
of

DOCTOR OF PHILOSOPHY

1947

by
Elizabeth Kreiser

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ACKNOWLEDGMENT

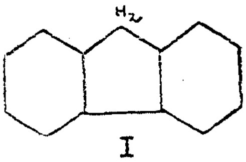
The author wishes to express her deepest gratitude to Dr. Francis E. Ray under whose guidance this work was undertaken.

Part I

INTRODUCTION

A. Reported Position Isomerism of Fluorene

Although the structure of fluorene, I, would appear to be straightforward, there have been a number of conflicting opinions with regard to the stereochemistry of this hydrocarbon.

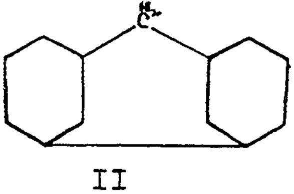


I

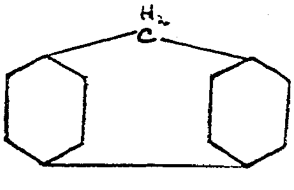
Fluorene was first prepared in 1867 by Berthelot (1) who isolated it from the fraction of coal tar boiling at 300-340° and reported that it melted at 113°. Fittig (2) obtained fluorene by reduction of diphenylene ketone. Graebe (3) prepared fluorene by heating diphenylmethane while Barbier (4) repeated Berthelot's work, obtaining fluorene by fractionation of coal tar. All reported one form (M.P. 113°).

1. Isomers of fluorene

Later Carnelley (5) claimed that he had isolated isomeric forms of fluorene, obtained by heating a mixture of benzene and toluene and fractionally distilling the mixture. Carnelley claimed his gamma fluorene (M.P. 118°), II, had a di-meta structure and his delta fluorene (M.P. 205°), III, had a di-para structure.



II
gamma fluorene

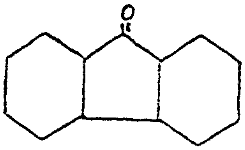


III
delta fluorene

This work has not been confirmed and it is probable that Carnelley's isomers were molecular addition products resulting from the tendency of fluorene to form complexes with similar compounds (6).

2. Isomers of fluorenone

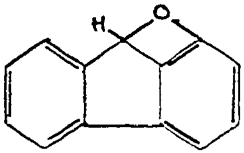
In 1873 Fittig (7) obtained fluorenone (M.P. 83-84°), IV, by distillation of diphenic acid with lime and reported



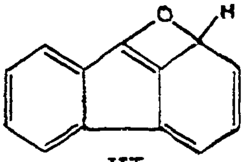
IV

that besides the yellow fluorenone some red material was formed in the mass of fluorenone.

Fittig did not report on the composition of this red material. In 1896 Kerp (8) reported a red form (M.P. 85°) in addition to the normal form of fluorenone formed when the calcium salt of diphenic acid was distilled. He reported that the red form had the same empirical formula as the yellow form, the same oxime, and the same reduction product. The red form kept its color in solution, indicating a rather stable substance. Kerp thought that his red form of fluorenone could have two possible forms, V, VI, and called this red form pseudodiphenylene ketone.

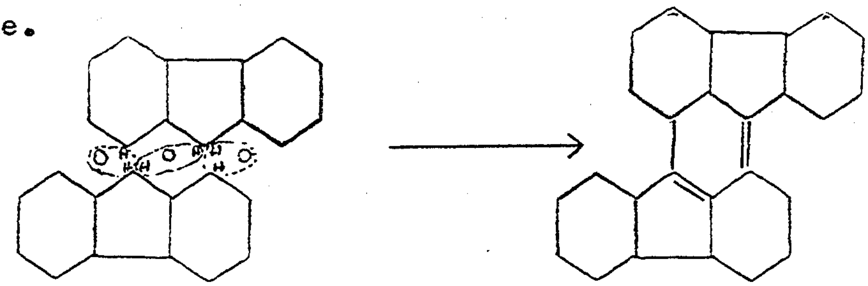


V



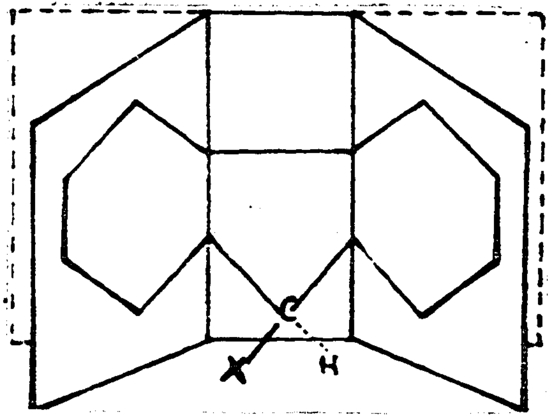
VI

This work was reinvestigated by Stobbe (9) and apparently confirmed by him. However, later investigation showed that this red substance was rubicene (10) also a coal tar hydrocarbon. A small amount of rubicene is formed, probably according to the reactions shown below, when diphenic acid is distilled with alkali or when fluorene is oxidized to fluorenone.

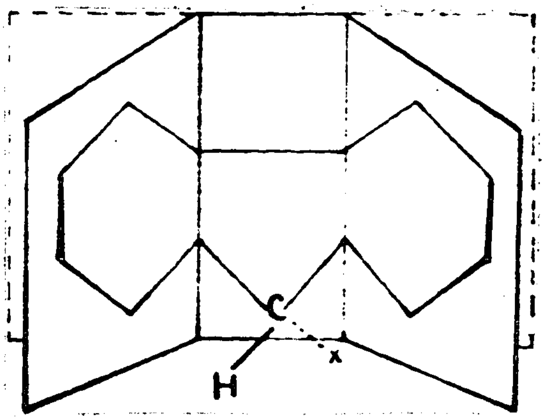


B. Reported Stereoisomerism of Fluorene

According to present day theories there are two structures which may be assigned to fluorene. One is a uniplanar structure; the other is a folded ring structure with the planes of the six-membered rings inclined to the plane of the five-membered ring. If this latter be the case, the substitution of the 9-carbon atom will produce two possible isomers, depending on the whether the substituent group is cis, VII, or trans, VIII, to the inclined six-membered rings.



VII

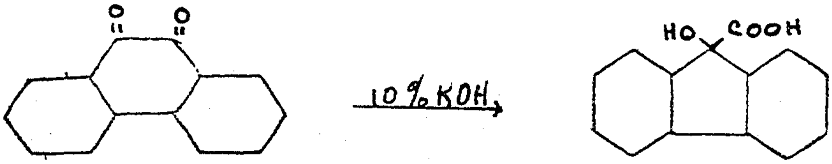


VIII

The isolation of isomers of 9-substituted fluorenes would furnish conclusive evidence for the nonplanar form of fluorene. This question was first brought up in 1905 by Schmidt and Bauer (11) who claimed that they had isolated two forms of diphenyleneglycolic acid.

1. Diphenyleneglycolic acid

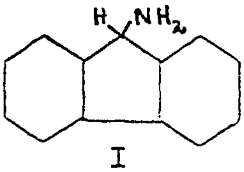
Baeyer, Friedlander, and Caro (12) were the first to prepare diphenyleneglycolic acid (M.P. 162°) by the benzilic acid rearrangement of phenanthrenequinone.



Schmidt and Bauer claimed the isolation of an isomer which melted at 212°. Their isomer was obtained by heating the previously known form with acetic anhydride, adding alcohol, and distilling off the ester formed; the oil which remained was crystallized and purified. Twenty years later Kliegl, Wunsch, and Weigele (13) proved that the alleged isomer was the acetylated diphenyleneglycolic acid.

2. 9-Aminofluorene

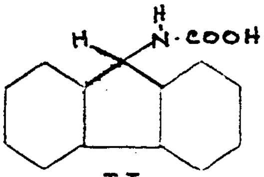
Probably the most discussed case of isomerism was that of 9-aminofluorene, I.



I

This compound was first prepared by Wegerhoff(14) who reported a melting point of 64°. Schmidt and Stutzel (15) reported that they had obtained isomers, an alpha form (M.P. 53-55°) and a beta form (M.P. 123°). In addition Kerp, loc.cit., reported a form melting at 161°. Kuhn and Jacob (16) also isolated Schmidt and Stutzel's alpha form and the form reported by Wegerhoff melting at 64°.

However, Kliegl, loc.cit., showed that in reality Kerp's compound (M.P. 161°) was the acetate of 9-aminofluorene. He, as well as Kuhn and Jacob, proved that Schmidt and Stutzel's beta form (M.P. 123°), was the carbamate of 9-aminofluorene, II, formed by reaction of 9-aminofluorene with the carbon dioxide of the air.



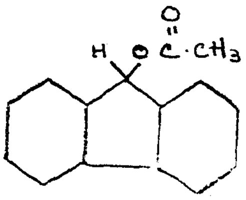
II

Kliegl, Wunsch, and Weigele could find only one form of 9-aminofluorene (M.P. 61.5-62.5°). Ingold and Wilson (17) in a later investigation also obtained the form melting at 62-63°.

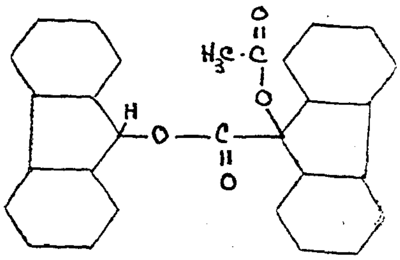
The alpha form obtained by Schmidt and Stutzel with a melting point lower than that of the pure 9-aminofluorene was probably an impure form. By proving that the other forms claimed as isomers were in reality entirely different compounds, the case for isomers of 9-aminofluorene and for a cis-trans type of isomerism was undermined.

3. Derivatives of 9-hydroxyfluorene

a. 9-Acetoxyfluorene: Schmidt and Mezger (18) reported that they had found isomers of 9-acetoxyfluorene, one melting at 208-209°, the other melting at 69-70°. Their lower melting form corresponded to the form (M.P. 75°) previously obtained by Barbier (19) by action of acetic anhydride on 9-fluorenol. Kliegl and his co-workers proved that this isomer was in reality not an isomer of 9-acetoxyfluorene, I, but was the 9-fluorenyl ester of O-acetyldiphenyleneglycolic acid, II.



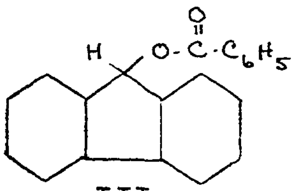
I



II

The percentage compositions of these compounds are so nearly alike that the analyses did not differentiate sharply between them.

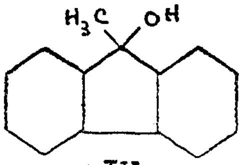
b. 9-Fluorenyl benzoate: By the reaction of fluorenol and benzoyl chloride, Schmidt and Stutzel (20) obtained 9-fluorenyl benzoate, III, which melted at 161°.



III

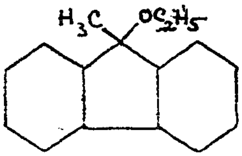
Staudinger and Gaule (21) who obtained the compound from benzoic acid and diphenylenediazomethane reported a melting point of 100°. They thought this a case of isomerism. Upon reinvestigation of Schmidt and Stutzel's method, Kliegl obtained only the form reported by Staudinger and Gaule, M.P. 100°.

c. 9-Methylfluorenol: By reacting methylmagnesium bromide and fluorenone, Ullmann and Wurstemberger (22) obtained 9-methylfluorenol (M.P. 175°), IV.



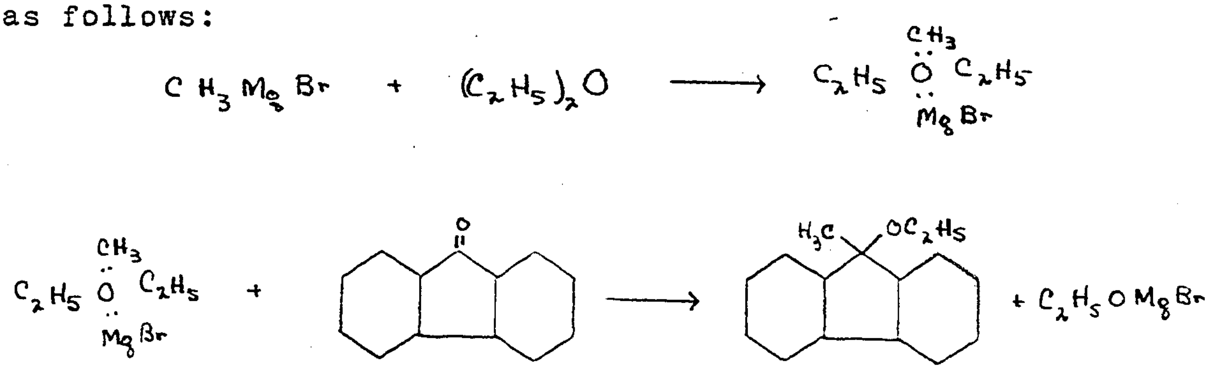
IV

Then Wieland and Krause (23) reported that they found an isomeric form (M.P. 84°) of 9-methylfluorenol, obtained from the reaction mixture of the methylmagnesium bromide and fluorenone. They later found that their isomeric carbinol was the ethyl ether, V, derived from 9-methylfluorenol (24).



V

Wieland and Cerezo offer no satisfactory explanation of how the ether was formed. A possible mechanism is as follows:



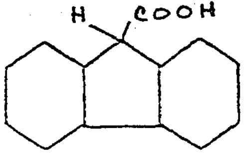
$$CH_3MgBr + (C_2H_5)_2O \longrightarrow C_2H_5\overset{\overset{CH_3}{\cdot\cdot}}{\underset{\underset{MgBr}{\cdot\cdot}}{O}}C_2H_5$$

It was thus shown (25) that all the cases of isomerism which had been reported up to 1925 were incorrect.

4. The Schlenk and Bergmann Isomers

In a series of papers Schlenk and Bergmann (26) claimed they had prepared isomers of several fluorene compounds.

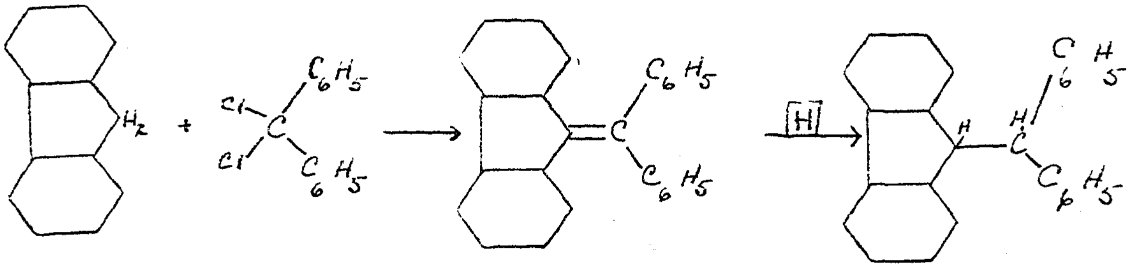
a. Fluorene-9-carboxylic acid, I: This compound was first prepared by Weissgerber (27) who reported a melting point of 222-223°.



I

Schlenk and Bergmann reported two forms of this acid; one form melting at 226°, the other at 232°. Kliegl (28) took up the problem and found only one form. Jeanes and Adams (29) found that the lower melting form of the fluorene-9-carboxylic acid probably resulted from imperfect crystals. They found that slow crystallization produced harder and brighter crystals which melted at 232°; rapid crystallization resulted in a lower melting form (M.P. 224°), which changed crystal form and melted at 232° after several months.

b. Diphenylenediphenylethane: By reacting diphenyldichloromethane and fluorene, Kaufmann (30) obtained diphenylenediphenylethylene, II, which on reduction produced diphenylenediphenylethane (M.P. 217°), III.

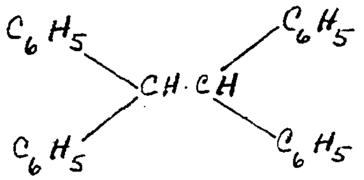


II III

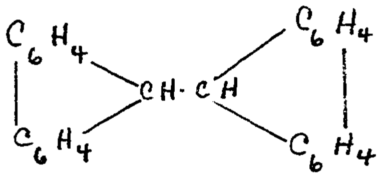
Kaufmann reported that several products were possible, depending on the relative proportions of the reactants.

Schlenk and Bergmann claimed that by action of diphenylbromomethane on fluorene-9-lithium, they obtained the form of diphenylenediphenylethane melting at 217°; by action of diphenylmethylsodium on 9-chlorofluorene an isomer (M.P. 187°) was obtained.

Kliegl showed that this supposed isomer was a trimolecular addition compound of tetraphenylethane (M.P. 209°), IV, a small amount of difluorenyl (M.P. 240°), V, and the previously known form of diphenylenediphenylethane, III.

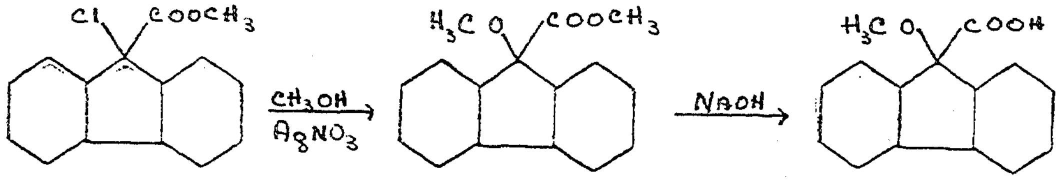


IV



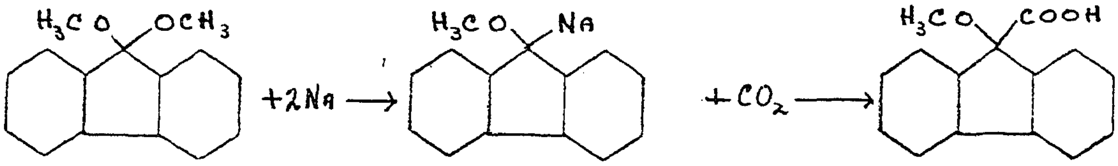
V

c. 9-Methoxyfluorene-9-carboxylic acid, VI: Klinger (31) obtained this compound by hydrolysis of the methyl ester, which was in turn produced by heating a methanol solution of diphenylenechloroacetic acid in the presence of silver nitrate, and reported a melting point of 181°.



VI

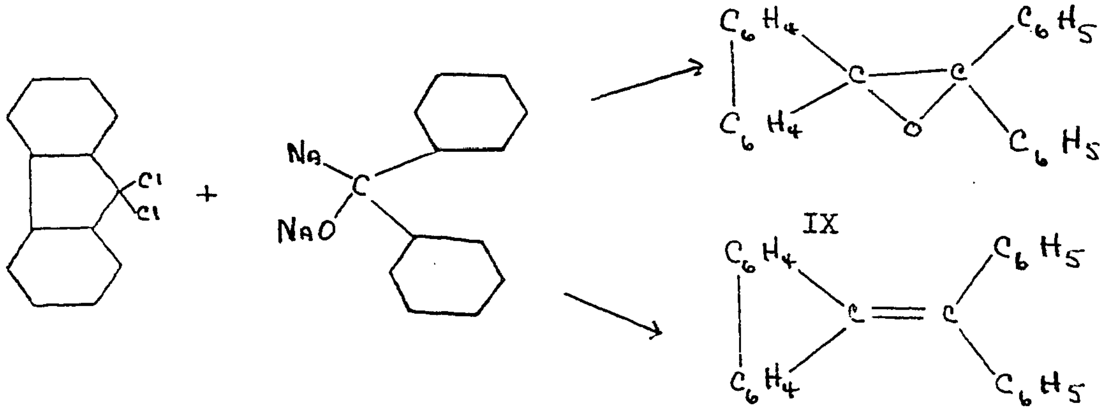
Schlenk and Bergmann reported an isomeric form (M.P. 172-173°) prepared by the action of sodium on fluorenedimethylacetal, VII, followed by the action of carbon dioxide on the fluorenemethoxysodium, VIII.



VII VIII

Kliegl was unable to confirm this; all the methods used yielded only one product (M.P. 184°).

d. Diphenylenediphenylethylene: Kaufmann (30) had prepared this compound by the action of diphenyldichloromethane and fluorene and reported a melting point of 224-225°. Schlenk and Bergmann claimed that the reaction of the sodium addition product of benzophenone with 9,9-dichlorofluorene produced a mixture of the oxide (M.P. 228°), IX, the previously known form, X, and an isomer which melted at 213°.

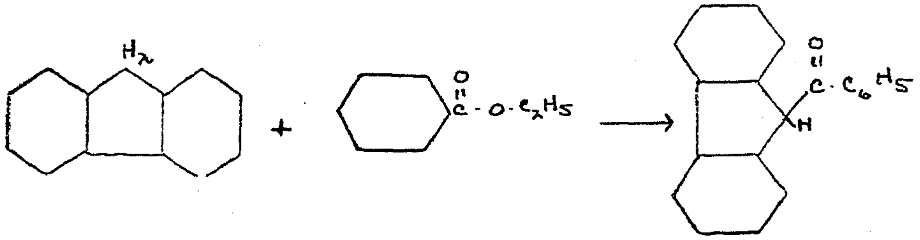


IX

X

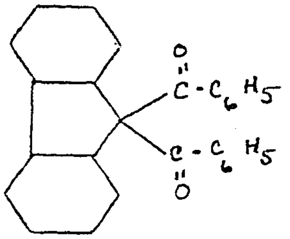
Kliegl proved that this so-called isomer was an isomorphous mixture of the oxide, IX, and the hydrocarbon, X, which he was able to separate by careful fractional crystallization.

e. 9-Benzoylfluorene, XI: By means of a Clais~~s~~en condensation between fluorene and ethyl benzoate, Werner (32) obtained 9-benzoylfluorene (M.P. 138°).



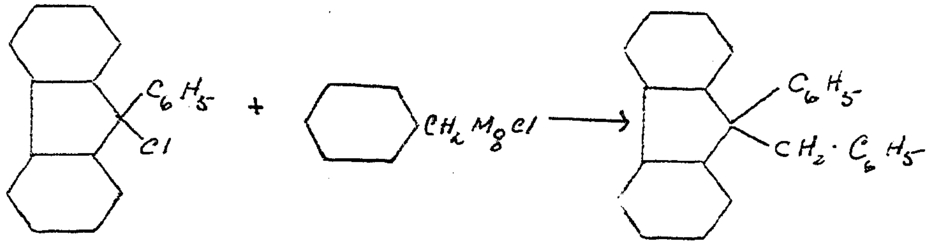
XI

Schlenk and Bergmann (33) reported that by reacting benzoyl chloride and fluorene lithium they obtained an isomeric form melting at 180°. Pfeiffer and Lubbe (34) later discovered that in this case the condensation had continued and the reported isomer was 9-9-dibenzoylfluorene, I.



I

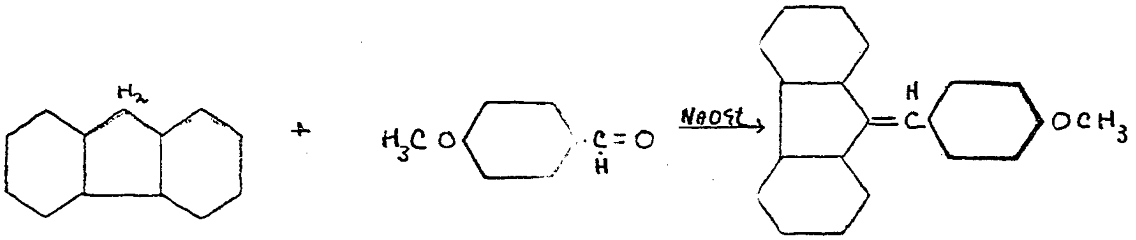
b. 9-Phenyl-9-benzylfluorene, II: Gomberg and Cone (35) prepared this compound by reacting 9-phenyl-9-chlorofluorene with benzylmagnesium chloride and reported a melting point of 139°.



II

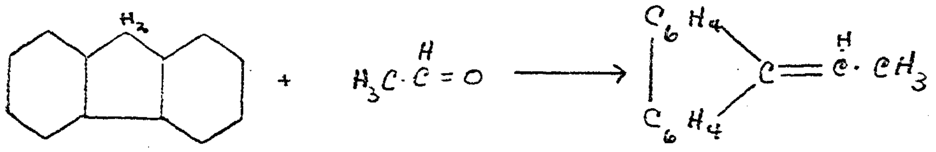
Schlenk and Bergmann reported that by using 9-phenylfluorene-sodium and benzyl chloride an isomer melting at 125° was obtained. Schmidt, Stein, and Bamberger (36), following Schlenk and Bergmann's method, were unable to confirm their results. Bachmann (37) repeated the work and was also unable to obtain the isomer.

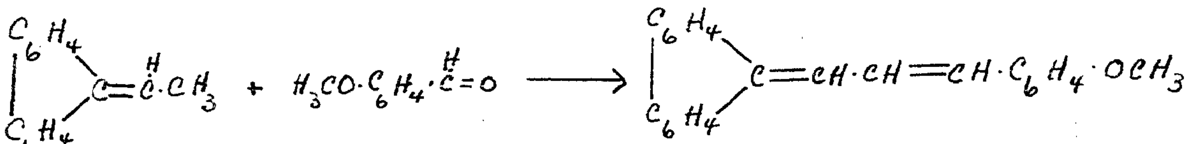
g. 9-Anisalfluorene, III: Fluorene condenses with anisaldehyde in the presence of sodium ethylate to form 9-anisalfluorene (M.P. 120°) (38).



III

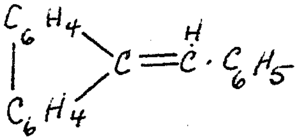
Schlenk and Bergmann reported an isomer which melted at 145°. Kliegl, Weng, and Wiest (39) found, however, that the isomer was in reality 9-(p-methoxycinnamylidene)-fluorene, IV. In this case part of the ethanol used as a solvent was oxidized to acetaldehyde which also condensed with the fluorene.





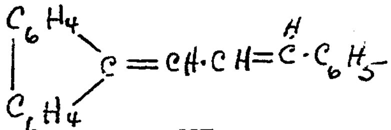
IV

h. 9-Benzalfluorene, V: Similarly, fluorene condenses with benzaldehyde to form 9-benzalfluorene (M.P. 76°) (38).



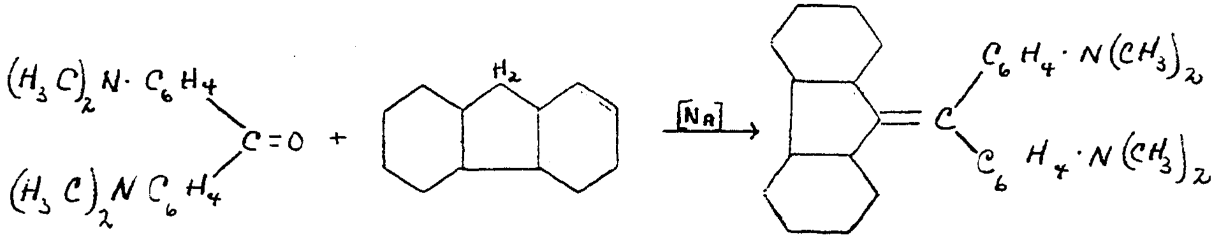
V

In this case Schlenk and Bergmann reported an isomer melting at 153°. Kliegl, Weng, and Wiest proved the supposed isomer was 9-cinnamylidenefluorene, VI, formed similarly to the 9-(p-methoxycinnamylidene)-fluorene.



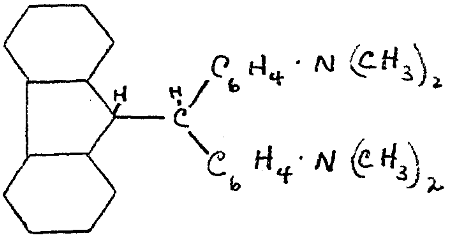
VI

i. 9-(Tetramethyldiaminodiphenylmethylene)-fluorene, VII: By the action of sodium on a mixture of fluorene and Michler's ketone in dry benzene, Rodd and Lench (40) obtained what they thought was 9-(tetramethyldiaminodiphenylmethylene)-fluorene (M.P. 239-240°).



VII

Schlenk and Bergmann described an isomer which melted at 237-238°, produced by the method of Rodd and Lench. Bergmann (41) subsequently proved that the compound prepared by Rodd and Lench was in reality 9-(tetramethyldiaminodiphenylmethyl)-fluorene, VIII.



VIII

The Schlenk and Bergmann isomer was actually the ethylenic compound which on reduction was shown to be identical with that prepared by Rodd and Lench. The saturated product obtained by the latter probably resulted from the reducing action of sodium on the water formed during the condensation.

Thus it may be seen that the supposed isomers were impure, or were molecular addition compounds caused by the tendency of the fluorenes to form complexes with similar compounds, or were in reality not isomers but entirely different substances (41). Thus the case for the existence of non-planar fluorene collapsed through lack of evidence.

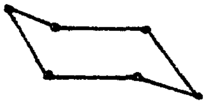
C. Stereochemistry of Fluorene

Although it was found that the isomers which had been advanced as proof for the folded ring structure of fluorene did not exist, it does not necessarily follow that fluorene could not exist in a non-planar form.

1. Physical Evidence

a. X-Ray studies: It might be expected that X-ray examination would furnish the clue to the structure of fluorene. This is not, however, the case for there are several interpretations of the available data.

Hengstenberg and Mark (42) on the basis of crystal lattice studies came to the conclusion that the six-membered rings in fluorene possessed a puckered structure and isomers were not due to the inclination of the rings but to their puckered structure. A puckered six-membered ring may possess one of two possible forms, a "boat" or a "chair" form.



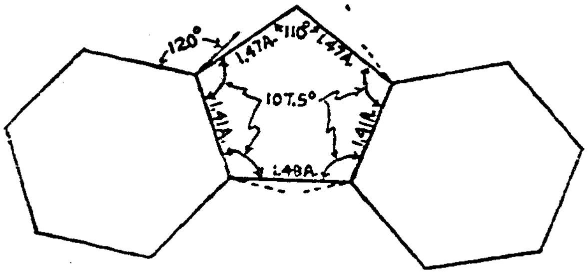
On the basis of puckered six-membered rings in fluorene, if the 9-carbon atom were monosubstituted, there should be three possible isomers, i.e., one isomer in which both rings had the "boat" form, a second isomer in which both rings had the "chair" form, and a third isomer in which one ring had the "boat" form while the other ring had the "chair" form.

Bergmann and Mark (43) explained the Schlenk and Bergmann isomers on the basis of this puckered structure.

Despite the fact that these investigators interpreted the data as proof for the puckered six-membered rings, the six-membered rings in fluorene are in reality benzene rings and are usually considered planar. Therefore a puckered ring would appear somewhat far-fetched. In harmony with this view, Stuart (44) later interpreted Hengstenberg and Mark's data as evidence for the uniplanar configuration.

Sundararajan (45) obtained data from optical studies which he thought indicated a planar structure for fluorene. Krishnan and Banerjee's (46) magnetic anisotropy studies led them to the same conclusion. Cook and Iball (47), however, interpreted the data of these investigators, together with Iball's (48) X-ray data, as evidence for a non-planar structure in which the planes of the six-membered rings were inclined at 20° to the plane of the five-membered ring and at 40° to each other. They suggested that the molecule may possess sufficient elasticity to undergo oscillation between two non-planar forms and thus prevent the isolation of isomers.

On the other hand, Pinck and Hilbert (49) from X-ray and electron diffraction data obtained by Robertson and Hendricks (50) proposed a planar model, I, for fluorene.



I

In the normal tetrahedral carbon atom, the four valence forces are directed from the center of the atom to the corners of a regular tetrahedron and therefore form an angle of 109° 28' with each other. Robertson's data were considered evidence that in the benzene ring the carbon atoms appear to be trivalent with an angle of 120° between the valence forces. Therefore, in the planar model proposed by Pinck and Hilbert, from a consideration of the valency angles and interatomic distances, there is a considerable strain, the normal benzenoid valence angles being distorted 12-13°. As the linkages in the benzene rings are quite rigid the five-membered ring must therefore be strained.

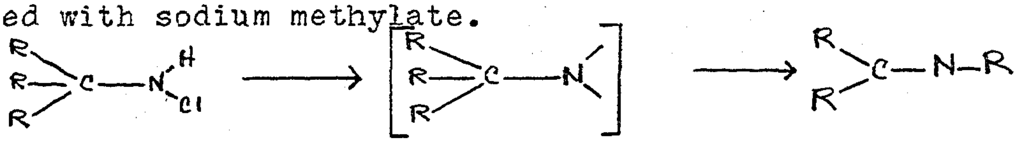
b. Measurements of dipole moments: Bergmann, Engel, and Hoffmann (51) obtained measurememts of dipole moments of fluorene compounds in inert solvents which indicated a uniplanar structure for fluorene. The dipole moment of a molecule is the product of the electronic charge and the relative displacement of the positive and negative electrical centers. A molecule which is perfectly symmetrical electrically has no dipole moment.

Hughes, LeFevre, and LeFevre (52) maintained that their measurements of dipole moments supported the planar configuration theory. They pointed out that their results did not necessarily contradict those of Cook and Iball since their own measurements were carried out on compounds in solution while Cook and Iball's results were based on solid forms. This would imply that in the solid state the fluorene molecule is held in a non-planar configuration due to the rigidity of the crystal lattice. In a subsequent investigation, Hughes, LeFevre and LeFevre (53) were unable to obtain results for one specific configuration.

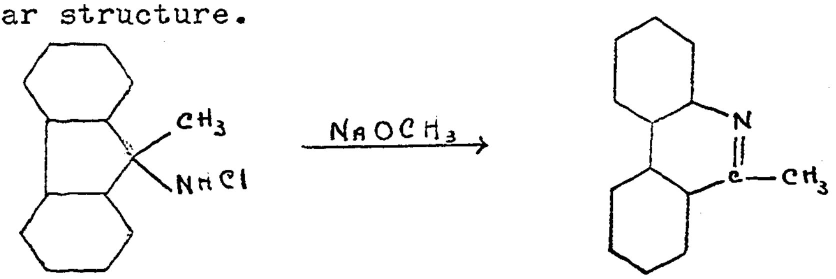
It is thus seen that the use of X-ray examination and the measurement of dipole moments has not solved the problem of the structure of the fluorene molecule. There is evidence for both forms.

2. Chemical evidence

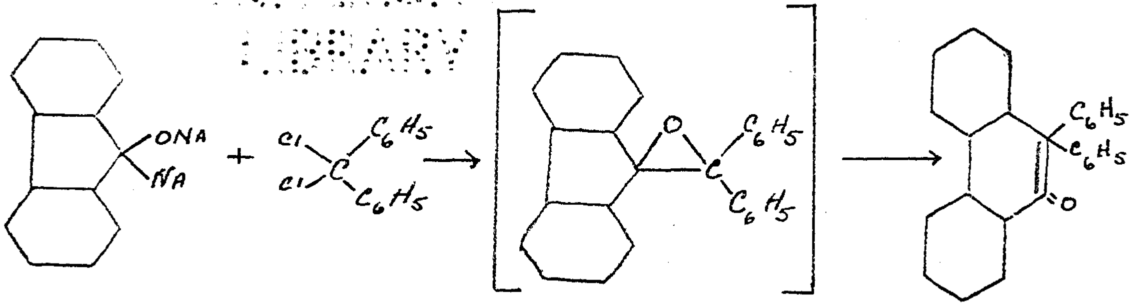
If a planar model is assumed for fluorene, then the strain should be evident in the chemical properties of fluorene compounds. In harmony with this view, the five-membered fluorene ring shows a tendency to expand during the Stieglitz rearrangement (49) in which an aryl group migrates from a triarylmethyl radical to nitrogen when a haloamine is treated with sodium methylate.



The expansion of the five-membered fluorene ring during this rearrangement seems to indicate a strained condition and thus implies a planar structure.

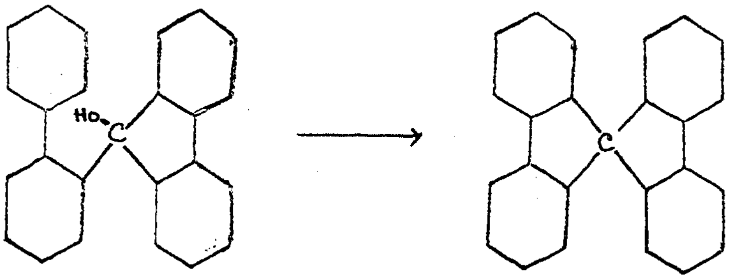


Schlenk and Bergmann (54) also found that the five-membered ring tended to expand when the addition product of fluorenone and sodium, fluorenone-disodium, was reacted with diphenyldichloromethane. 9,9-Diphenylphenanthrone resulted.

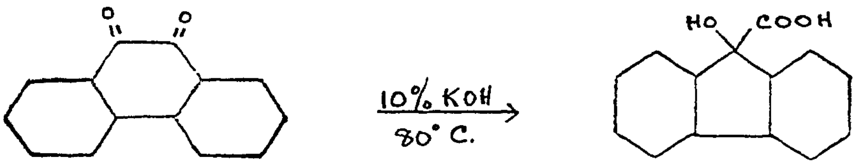


On the other hand, the ready formation of spirofluorenes (55) seems to indicate that the resulting five-membered ring has little strain.

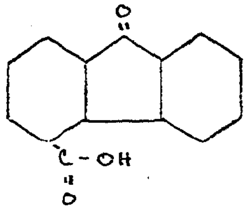
For example 9,9-spirobifluorene is made by addition of <u>one drop</u> of hydrochloric acid to five grams of 9-(2-biphenyl)-9-fluorenol.

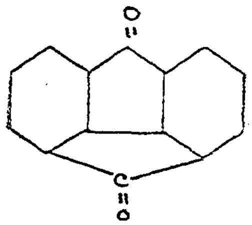


Phenanthrenequinone, when treated with alkali, undergoes the benzilic acid rearrangement and becomes diphenyleneglycolic acid. This indicates the latter is the more stable structure with less strain and implies a non-planar configuration.



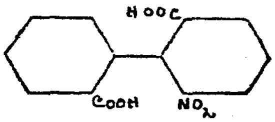
This viewpoint is also advanced by Mills, Palmer, and Tomkinson (56) who pointed out that fluorenone-4-carboxylic acid does not condense further to a diketone or difluorenone.





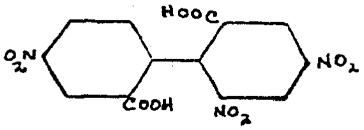
They claim that this is evidence for the nonplanar structure since the distance between the 4- and 5-positions must be increased so that further reaction cannot take place. Rieveschl and Ray (57) are of the opinion that in the planar formula the bond joining the six-membered rings is necessarily bent, thus increasing the distance between the 4- and 5-positions and preventing formation of a difluorenone.

Bell and Robinson (58) found that 5-nitrodiphenic acid, I,



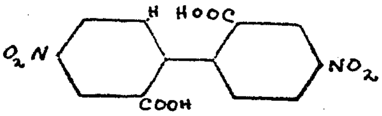
I

forms a fluorenone when heated with sulfuric acid although 4, 4', 6'-Trinitrodiphenic acid, II, does not.



II

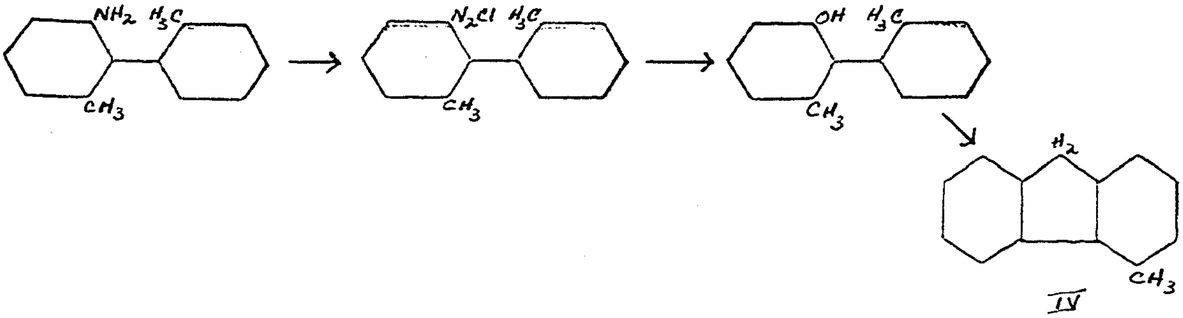
The latter compound has been resolved into optical antipodes because of the interference of the ortho groups which makes it impossible for both rings to lie in the same plane. The failure of this compound to react suggests that fluorene requires coplanar rings. This conclusion was questioned by Underwood and Kochmann (59) who reported that 4,4'-dinitrodiphenic acid, III, which had no interfering ortho groups, did not form a fluorenone.



III

Underwood and Kochmann's opinion was that the failure of 4,4'-dinitrodiphenic acid to react was caused by an induced strengthening of the bonds holding the ring hydrogen and the carboxyl group, because of the presence of the nitro groups.

Mascarelli (60) was able to obtain a fluorene from a diphenyl in which three of the four ortho positions were substituted. On diazotizing 2,6'-dimethyl-2'-aminodiphenyl and then heating the reaction mixture, he obtained a small amount of 4-methylfluorene, IV. He regarded this as casting doubt on the steric hindrance theory.



IV

It is obvious, however, that one of his ortho groups disappears in the process of ring closure. This destroys the validity of his argument.

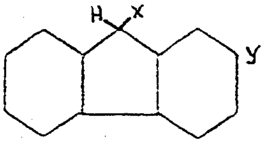
In the substituted diphenyls, the ring hydrogen and part of the carboxyl group may meet, but they may not be in a suitable position to eliminate the elements of water, regardless of the planar or non-planar structure of the diphenyl. Thus the mere failure of a diphenyl to form a fluorene cannot be regarded too highly as evidence for a planar configuration.

We see that both the chemical and physical evidence have failed to render a decision as to the spatial configuration of fluorene. Despite the considerable amount of work done, the question is still undecided.

Part II

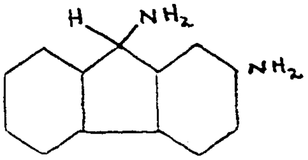
PROCEDURE AND DISCUSSION

Previous attempts to prepare stereoisomers of fluorene compounds were based on the assumption that fluorene has a non-planar structure. Resolution of a fluorene substituted on the 9-carbon would be conclusive evidence for the non-planar form. However, even such expected optical antipodes of the classical form,



in which the 9-carbon atom is asymmetric have not been resolved up to the present.

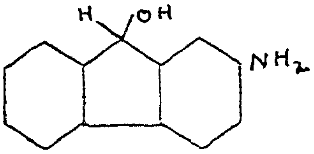
Bader (61) attempted to resolve 2,9-diaminofluorene, I,



I

with d-tartaric acid and also by the aldehyde condensation with d-helicin and failed. He explained his failure by a novel theory that optical isomers do not exist in this case because of a mutual repulsion between the two amino groups that destroys the tetrahedral arrangement of the 9-carbon atom by forcing the substituents on the 9-carbon into the same plane.

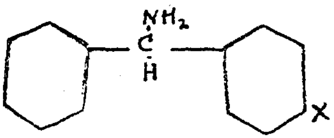
Later Bennett and Noyes (62) attempted to resolve 2,9-diaminofluorene using d-camphorsulfonic acid, d-phenylaminoacetic acid, and d-hydroxymethylenecamphor. These attempts, as well as an attempt to resolve 2-amino-9-hydroxyfluorene, II,



II

with d-camphorsulfonic acid, were unsuccessful. Their opinion was that failure to resolve these compounds was caused by lack of the proper experimental conditions rather than any inherent symmetry.

It is also of some interest to note here that Billon (63) was unable to resolve compounds of the type



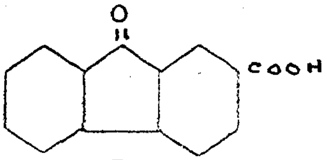
(p-$CH_3 \cdot C_6H_4 \cdot CHNH_2 \cdot C_6H_5$, p-$CH_3O \cdot C_6H_4 \cdot CHNH_2 \cdot C_6H_5$, o-$CH_3O \cdot C_6H_4 \cdot CHNH_2 \cdot C_6H_5$, and o-$HO \cdot C_6H_4 \cdot CHNH_2 \cdot C_6H_5$)

which are quite similar to the 9-aminofluorenes in structure.

If it is impossible to resolve a fluorene compound which should be asymmetric according to the classical laws of stereochemistry, there is even less hope of being able to resolve a fluorene compound which might exist in isomeric forms because of a non-planar structure. It was decided, therefore, to attempt resolution of fluorene compounds containing asymmetric 9-carbon atoms. Solution of this problem would increase the possibility of determining the spatial configuration of fluorene.

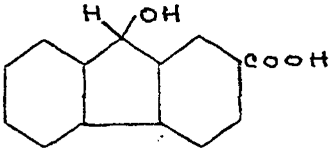
Bader's and Bennett's attempts were made using aminofluorenes. It was thought that using a compound which had an acid group as a substituent might produce favorable results. Moreover, if the fluorene compound is acidic, it is possible to use an optically active organic base as the resolving agent. A better selection of these bases of high molecular weight is available, thus increasing the probability of finding the proper conditions for separation of the diastereoisomeric salts.

Ray and Rieveschl (64) reported a method for preparing fluorenone-2-carboxylic acid, I.



I

By reduction of this keto acid, 9-hydroxyfluorene-2-carboxylic acid, II, can be prepared



II

This compound had been prepared by Ray and Rieveschl but had not been characterized. The hydroxy acid has a 9-asymmetric carbon atom and it should therefore be resolvable. It was found in the present work that zinc dust in alcoholic ammonia was the best reducing agent for preparation of 9-hydroxyfluorene-2-carboxylic acid, being more satisfactory than zinc in alcoholic potassium hydroxide.

Resolution was attempted using equivalent quantities of 9-hydroxyfluorene-2-carboxylic acid and brucine. No crystalline material, however, separated from the alcoholic solution, and on evaporation a sticky material appeared on the sides of the flask and then solidified to a glassy substance. Addition of ethyl ether to a portion of the solution precipitated a white gummy mass, which when worked thoroughly with ether, did appear to be crystalline. Solution of this material in other solvents resulted in a viscous solution as before so that no resolution was possible.

It was then decided to try strychnine as the resolving agent. Accordingly, equivalent quantities of the hydroxy acid and strychnine were dissolved in ethanol and chloroform respectively, and the same procedure was followed as with brucine. In this case white crystalline material in the form of rosettes, weighing almost half the total weight of the hydroxy acid and strychnine, separated from the solution. The acid was recovered by dissolving the salt in a slight excess of alcoholic sodium hydroxide and pouring this mixture into an excess of dilute hydrochloric acid. The free acid then precipitated,while the strychnine remained in solution as the hydrochloride. The acid thus obtained was pure white in color and melted at 263° (block), while the original acid melted at 240°. A solution of this acid in ethanol had a positive rotation, the rotation increasing as the wave length of light used decreased. This is shown in Table I.

Table I

9-Hydroxyfluorene-2-carboxylic acid

Actual and Specific Rotations of Isomers

Wave length of light	Actual Rotation		Specific Rotation	
	Dextro*	Levo*	Dextro	Levo
6563 Å	α^{27° 0.82°	α^{27° - 0.83°	$[\alpha]^{27^\circ}$ 29.3°	$[\alpha]^{27^\circ}$ - 27.6°
5893 Å	α^{27° 1.11°	α^{27° - 1.09°	$[\alpha]^{27^\circ}$ 39.6°	$[\alpha]^{27^\circ}$ - 36.3°
5463 Å	α^{27° 1.39°	α^{27° - 1.35°	$[\alpha]^{27^\circ}$ 49.6°	$[\alpha]^{27^\circ}$ - 45.0°

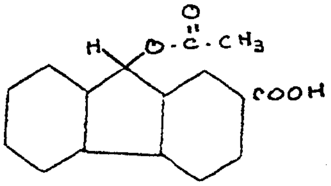
*The actual rotation for the dextro compound was found using 0.7000 grams of the acid in 50 cc. of ethanol in a 2-dm. tube. The actual rotation for the levo compound was found using 0.7500 grams of the acid in 50 cc. of ethanol in a 2-dm. tube.

An attempt to separate the more soluble strychnine salts of the hydroxy acid was not successful. Evaporation of the mother liquor resulted in a rather viscous solution with a small amount of sticky material on the sides of the evaporating dish. Addition of cinchonidine, cinchonine, or quinine to separate portions of the solution failed to precipitate the acid as the salts of these alkaloids.

The acid from the more soluble strychnine salt was therefore isolated directly from the solution. The free acid had a light yellow color and melted at 260° (black) as compared with 263° for the dextro form and 240° for the racemic form. A solution of this acid in ethanol had a negative rotation. Despite the fact that the strychnine salt could not be recrystallized, the specific rotation was almost equal in magnitude, although opposite in sign, to the specific rotation of the dextro form. This is also shown in Table I.

The impure levo form showed a greater tendency to racemize than the dextro form. After the solid acids had been standing for several weeks, the melting point of the dextro acid was still 263°, but the melting point of the levo form had decreased five degrees to 255° instead of 260°.

For the purpose of comparison the acetates, I, of the dextro, the levo, and the racemic 9-hydroxyfluorene-2-carboxylic acids were prepared by reaction of the acids with acetic anhydride.

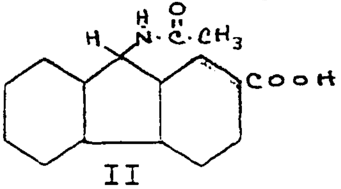


I

The melting points of these derivatives are given in Table II.

The resolution of this compound (65) increased the hope of being able to resolve an amino fluorene compound. A suitable compound seemed to be 9-aminofluorene-2-carboxylic acid prepared by reduction of the oxime of fluorenone-2-carboxylic acid. Since the amino group in 9-aminofluorene is oxidized very readily, it was acetylated to prevent oxidation.

An attempt was made to resolve the 9-acetylaminofluorene-2-carboxylic acid, II, with strychnine.



II

Table II

Properties of Various Forms of 9-Hydroxyfluorene-2-carboxylic Acid

Acid	Color	Form	Melting point (block)	Melting point of acetate (block)
Racemic	Creamy white	Small needles	240°	224-225°
Dextro	Pure white	Very fluffy needles	263°	228°
Levo	Light yellow	Small compact needles	260°	225°

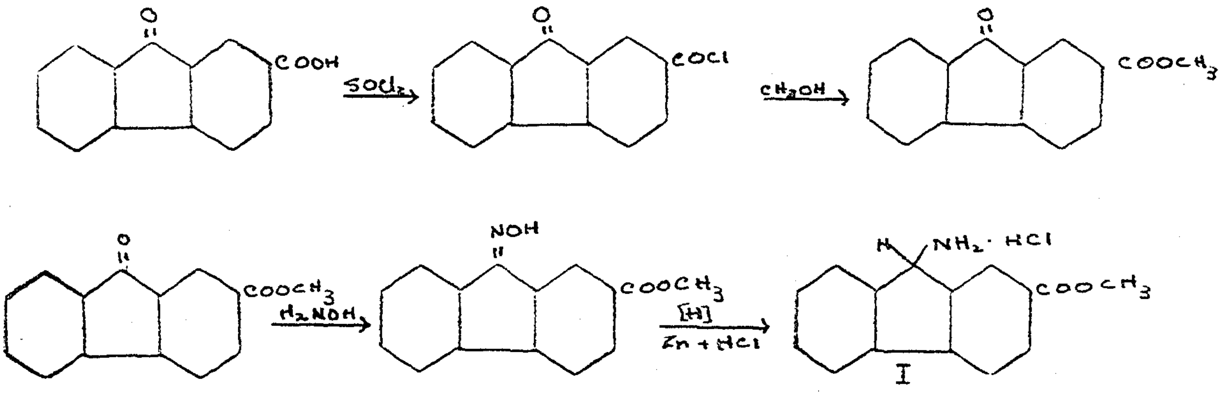
The free acid instead of the strychnine salt came out of solution, and no resolution was obtained.

An attempt was then made with brucine. The free acid precipitated instead of the brucine salt and solutions of the acid did not possess any optical activity.

Since the free acid precipitated in each case, it was thought that the presence of water in the ethanol may have prevented the formation of the brucine and strychnine salts. The 9-acetylaminofluorene-2-carboxylic acid was therefore dissolved in absolute ethanol and a solution of strychnine in chloroform added. After addition of anhydrous benzene, the mixture was distilled so that any water present was removed in the ternary mixture of alcohol, water, and benzene. In this case also the salt failed to precipitate, only the free acid being obtained. Apparently, despite the acetylation of the amino group, the acid was too weak to form a salt, making a resolution impossible.

Since this compound which had an acid group could not be resolved, it was decided to attempt the resolution of an aminofluorene by means of an acid resolving agent.

The methyl ester of fluorenone-2-carboxylic acid was prepared by the method of Rieveschl (66). This compound was then converted into the oxime which was reduced by use of zinc dust and hydrochloric acid, producing the hydrochloride of methyl 9-aminofluorene-2-carboxylate, I, in fairly good yields.



I

An attempt was made to resolve this compound by use of the silver salt of d-camphor-sulfonic acid, but no resolution was obtained.

The amine hydrochloride was treated with dilute alkali to obtain the free amine. Molecular quantities of the amine and d-tartaric acid were dissolved separately in alcohol and the hot solutions poured together and boiled under reflux. Within a few minutes a white crystalline material began separating which was redissolved by adding more alcohol. Upon slow cooling and distilling off portions of the solvent, several fractions of crystalline material were obtained. Analysis of these fractions showed that although molecular quantities of the acid and amine had been used, they had not combined in these proportions. The first fraction had the proportions of two moles of amine to one of acid; the analysis for the second fraction indicated a material containing three moles of amine and two moles of acid, while the third fraction had a composition corresponding to one mole of amine to one mole of acid. From the first, less soluble fraction, the dextro form of the amine was obtained.

The free, optically active amines racemized readily, even on standing. Recrystallization was impossible without loss of activity. To determine the rotations, therefore, it was necessary to wash the free amine well, dry quickly, and dissolve without warming the solvent. The rotations obtained are shown in Table III.

The ready racemization of this amine may explain why previous attempts to resolve the aminofluorene compounds were not successful. It may also be interpreted as bearing out Cook and Iball's theory that the non-planar fluorene molecule oscillates rapidly between two non-planar forms, thus preventing the isolation of isomers. The inability to find isomers of 9-substituted fluorene compounds was explained by this theory. However, it could be applied to explain the ease of racemization of the fluorene compounds with asymmetric 9-carbon atoms. On the other hand, the ready racemization of the compounds may have been caused by the presence of impurities. Thus, it is apparent that the question of the spatial configuration of fluorene is still undecided, and further investigation of this problem would be worth-while.

Table III

Methyl 9-aminofluorene-2-carboxylate

ROTATIONS FROM VARIOUS FRACTIONS OF TARTRATE SALT

Wave length of light	First Fraction		Second Fraction		Third Fraction	
	0.3000g. in 50ml.ethanol		0.2000g. in 50ml.ethanol		.1500g. in 50 ml.ethanol	
	Actual Rotation	Specific Rotation	Actual Rotation	Specific Rotation	Actual Rotation	Specific Rotation
6563 Å	+ 0.08°	$[\alpha]^{27^\circ}$ +6.7°	+0.02°	$[\alpha]^{27^\circ}$ +3.75°	-0.03°	$[\alpha]^{27^\circ}$ -5.0°
5893 Å	+ 0.09°	$[\alpha]^{27^\circ}$ +7.5°	+0.08°	$[\alpha]^{27^\circ}$ +10.0°	-0.07°	$[\alpha]^{27^\circ}$ -11.7°
5463 Å	+ 0.11°	$[\alpha]^{27^\circ}$ +9.2°	+0.13°	$[\alpha]^{27^\circ}$ +16.3°	-0.09°	$[\alpha]^{27^\circ}$ -15.0°

The actual rotations were found using a 2-dm. tube.

Part III

EXPERIMENTAL DETAILS

A. Preparation of 9-hydroxyfluorene-2-carboxylic acid.- Seventy grams of fluorenone-2-carboxylic acid (0.312 moles)(64), 240 grams of zinc dust (3.67 moles) and 1500 cc. of ethanol were mixed in a 3 liter round bottom flask equipped with a reflux condenser and ammonia trap. Then 400 cc. concentrated ammonium hydroxide was added and the mixture boiled under reflux. Subsequent portions of 100 cc. and 150 cc. of concentrated ammonium hydroxide were added after one and three hours of refluxing, respectively. The total time of refluxing was five hours.

The hot mixture was filtered and the filtrate poured with stirring into 8 l. of water containing 600 cc. of concentrated hydrochloric acid. The 9-hydroxyfluorene-2-carboxylic acid precipitated as a fluffy white material which was filtered and washed with water. The crude product melted at 232-235° (block). After recrystallization from ethanol, the creamy white needles melted at 240°. The yield of purified material was 39 g. or 55% of theoretical.

Anal. Calcd. for $C_{14}H_{10}O_3$: mol. wt., 226.22. Found: neutral equivalent, 226, mol. wt. (pinene dibromide), 237.

The acetate of 9-hydroxyfluorene-2-carboxylic acid was prepared by boiling 6 cc. of acetic anhydride with 0.5 g. of the acid for several minutes, diluting with 10 cc. of water and boiling to decompose excess acetic anhydride. On cooling the acetate separated as a white crystalline material (M.P. 224-225°) which was recrystallized from ethanol.

B. Resolution of 9-hydroxyfluorene-2-carboxylic acid.- To 11.3 grams (0.05 moles) 9-hydroxyfluorene-2-carboxylic acid in 125 cc. of boiling ethanol there was added 16.7 grams (0.05 mole) strychnine in 125 cc. of hot chloroform. The solution was boiled for several minutes and then evaporated somewhat to remove the chloroform, filtered, and placed in a pan of hot water and the whole allowed to come to room temperature. The next day, crystals in the form of rosettes, weighing 13.2 grams, had crystallized from the solution.

This strychnine salt after recrystallization from 700 cc. of ethanol, sintered at 190° and melted at 203° (capillary tube). The salt was dissolved in a mixture of 100 cc. of ethanol and 100 cc. of 2% sodium hydroxide. This was poured into a liter of water containing 20 cc. of 6N hydrochloric acid. The white fluffy precipitate of dextro 9-hydroxyfluorene-2-carboxylic acid was recrystallized from 60 cc. of ethanol and fine needles melting at 263° (block) were obtained.

A solution of 0.7000 grams of this acid in 50 cc. of ethanol in a 2-dm. tube had the following rotations for red, yellow, and green light:

$\alpha^{27°}_{656.3}$ +0.82° $\qquad$ $[\alpha]^{27°}_{656.3}$ +29.3°

$\alpha_{589.3}^{27^\circ}$ $+1.11^\circ$ $[\alpha]_{589.3}^{27^\circ}$ $+39.6^\circ$

$\alpha_{546.3}^{27^\circ}$ $+1.39^\circ$ $[\alpha]_{546.3}^{27^\circ}$ $+49.6^\circ$

The mother liquor from the precipitation of the insoluble d-acid salt was boiled with 2 grams of Darco and filtered. The levo acid was isolated from this solution similarly to the dextro form and recrystallized from 75 cc. of ethanol. The recrystallized acid had a light yellow color which a second recrystallization did not remove. The purified acid melted at 260° (block).

A solution of 0.7500 grams in 50 cc. of ethanol in a 2-dm. tube had the following rotations:

$\alpha_{656.3}^{27^\circ}$ -0.83° $[\alpha]_{656.3}^{27^\circ}$ -27.6°

$\alpha_{589.3}^{27^\circ}$ -1.09° $[\alpha]_{589.3}^{27^\circ}$ -36.3°

$\alpha_{546.3}^{27^\circ}$ -1.35° $[\alpha]_{546.3}^{27^\circ}$ -45.0°

C. <u>Preparation of oxime of fluorenone-2-carboxylic acid</u>.- To a mixture of 50 grams (0.223 moles) fluorenone-2-carboxylic acid and 50 grams (0.595 moles) sodium acid carbonate in 750 cc. of 50% ethanol there was added 25 grams (0.36 moles) hydroxylamine hydrochloride. The mixture was refluxed for two hours, then 200 cc. of water was added and the solution allowed to stand for two hours longer. The solution was boiled with Darco, filtered and the filtrate acidified with dilute hydrochloric acid while the solution was stirred vigorously. The yellow, somewhat gelatinous precipitate, after standing overnight, became crystalline. It was filtered, washed, and dried in an oven at 70°. The yellow crystalline material melted at 284° (block). After recrystallizing from glacial acetic acid 41 g. or a 75% yield of pure material was obtained.

Anal. Calcd. for $C_{14}H_9O_3N$: N, 5.85. Found: N, 5.88.

D. Preparation of 9-acetylaminofluorene-2-carboxylic acid.- Ten grams (0.0417 moles) of the oxime of fluorenone-2-carboxylic acid was dissolved in 500 cc. of glacial acetic acid contained in a 1 l. three-necked flask equipped with a reflux condenser. 20 g. (0.3 moles) of zinc dust was added in portions to the boiling solution over a period of one-half hour. The color changed from yellow to gray-green and then to colorless. After refluxing for one hour, 30 cc. (0.3 mole) of acetic anhydride was added dropwise, and the mixture refluxed for another hour. It was then filtered and the filtrate cooled and diluted with 200 cc. of water. The 9-acetylaminofluorene-2-carboxylic acid precipitated as white, fluffy material which was filtered, washed and dried. The crude product, weight 8.5 g., sintered at 340° (block). After recrystallization from glacial acetic acid, it sintered at 345°. The yield was 70% of theoretical.

Anal. Calcd. for $C_{16}H_{13}O_3N$: N, 5.24. Found: N, 5.46.

E. Preparation of the oxime of methyl fluorenone-2-carboxylate. - To a mixture of 400 cc. of benzene and 100 cc. of ethanol, 45 g. (0.189 mole) of the methyl ester of fluorenone-2-carboxylic acid (66), 42 g. (0.213 moles) $BaCO_3$, and 30 g. (0.43 moles) hydroxylamine hydrochloride were added and the mixture boiled under reflux for three hours. The excess $BaCO_3$ and $BaCl_2$ were filtered and washed with ethanol. The filtrate was evaporated to one fourth of its volume whereupon the oxime crystallized out. Recrystallization from xylene resulted in light yellow needles melting at 206-208°. The yield was about 28 grams of pure oxime or 59% of theoretical.

Anal. Calcd. for $C_{15}H_{11}O_3N$: N, 5.53. Found: N, 5.41.

F. Preparation of the hydrochloride of methyl 9-aminofluorene-2-carboxylate.- Twenty-eight grams (0.11 mole) of the oxime of methyl fluorenone-2-carboxylate was dissolved in 1 l. of ethanol contained in a three-necked flask fitted with a reflux condenser and a dropping funnel. Over a period of 3/4 hour 100 cc. concentrated hydrochloric acid and 50 cc. of water were added dropwise while 80 g. (1.2 moles) of zinc dust was introduced in small portions. The solution turned from deep yellow to colorless. After refluxing for 1-1/2 hours, the solution was filtered to remove excess zinc and after cooling the hydrochloride of the methyl 9-aminofluorene-2-carboxylate crystallized out as a white fluffy material weighing 30 g. and sintering at 230° (capillary). It was recrystallized from ethanol.

Anal. Calcd. for $C_{15}H_{14}O_2NCl$: N, 5.07. Found: N, 4.68.

G. Preparation of methyl 9-aminofluorene-2-carboxylate.- A suspension of 25 g. of the hydrochloride of methyl 9-aminofluorene-2-carboxylate in 100 cc. of water was stirred mechanically for 10 minutes until a smooth suspension was formed. Then 600 cc. of a 3% sodium hydroxide solution was added and stirring continued for 1/2 hour. The free amine was filtered, washed, and dried. The yield of crude amine was about 20 grams. It was recrystallized from petroleum ether (B.P. 70-90°). The melting point was 98-100°. The yield of pure material was about 12 grams.

Anal. Calcd. for $C_{15}H_{13}O_2N$: N, 5.85. Found: N, 5.60, 5.52.

H. Resolution of methyl 9-aminofluorene-2-carboxylate.- Five grams (0.0209 mole) of methyl 9-aminofluorene-2-carboxylate and 3.1366 g. (0.0209 mole) of d-tartaric acid were dissolved separately in 50 cc. of ethanol. The hot solutions were poured together and boiled under reflux. After a few minutes a white crystalline material began separating from the solution. More ethanol was added in portions until the total volume was 750 cc., and the precipitate had dissolved. The solution was allowed to cool overnight on a disconnected hot plate.

The next day white crystals had formed. These were filtered, washed with ethanol, and dried. The weight of this material was 3.5 g. After recrystallizing twice from ethanol, it began decomposing at 195° and sintered at 210°.

<u>Anal</u>. Calcd. for $C_{15}H_{13}O_2N \cdot C_4H_6O_6$: N, 3.75. Calcd. for $C_{30}H_{26}O_4N_2 \cdot C_4H_6O_6$: N, 4.70. Found: N, 4.60.

This salt was stirred with 30 cc. of 3% NaOH solution for several minutes. The free amine (M.P. 95°) was filtered off, washed thoroughly and pressed dry. After drying for two hours it was weighed and dissolved in ethanol without warming the solvent. The actual and specific rotations for 0.3000 g. in 50 ml. of ethanol in a 2-dm. tube were:

$$\alpha^{27^\circ}_{656.3} \quad +0.08^\circ \qquad [\alpha]^{27^\circ}_{656.3} \quad +6.7^\circ$$

$$\alpha^{27^\circ}_{589.3} \quad +0.09^\circ \qquad [\alpha]^{27}_{589.3} \quad +7.5^\circ$$

$$\alpha^{27^\circ}_{546.3} \quad +0.11^\circ \qquad [\alpha]^{27^\circ}_{546.3} \quad +9.2^\circ$$

The mother liquor was evaporated to a volume of 650 cc. and allowed to stand. A second fraction of salt, weighing 2.5 g., M.P. 185-210° (with decomposition), was obtained.

<u>Anal</u>. Calcd. for $C_{45}H_{39}O_6N_3 \cdot C_8H_{12}O_{12}$: N, 4.33. Found: N, 4.02.

This salt was treated similarly to the first fraction. The amine (M.P. 98°) had the following rotations for a solution of 0.2000 g. in 50 ml. of ethanol in a 2-dm. tube:

$\alpha^{27^\circ}_{656.3}$ +0.02° $[\alpha]^{27^\circ}_{656.3}$ +3.75

$\alpha^{27^\circ}_{589.3}$ +0.08° $[\alpha]^{27^\circ}_{589.3}$ +10.0°

$\alpha^{27^\circ}_{546.3}$ +0.13° $[\alpha]^{27^\circ}_{546.3}$ +16.3°

The mother liquor was then evaporated to 100 cc. On standing, a third fraction of salt (M.P. 195-203°) weighing 2.0 grams was obtained.

Anal. Calcd. for $C_{15}H_{13}O_2N \cdot C_4H_6O_6$: N, 3.75. Found: N, 3.84.

This salt was treated in a similar fashion. The rotations of the amine (M.P. 92-95°) were as follows for a solution of 0.1500 g. in 50 ml. of ethanol using a 2-dm. tube:

$\alpha^{27^\circ}_{656.3}$ - 0.03° $[\alpha]^{27^\circ}_{656.3}$ - 5.0°

$\alpha^{27^\circ}_{589.3}$ - 0.07° $[\alpha]^{27^\circ}_{589.3}$ - 11.7°

$\alpha^{27^\circ}_{546.3}$ - 0.09° $[\alpha]^{27^\circ}_{546.3}$ - 15.0

Part IV

SUMMARY

Previous attempts to resolve aminofluorene compounds having asymmetric 9-carbon atoms were unsuccessful. In the present work two fluorene compounds having asymmetric 9-carbon atoms were resolved - 9-hydroxyfluorene-2-carboxylic acid and methyl 9-aminofluorene-2-carboxylate.

The resolution of the aminofluorene compound indicates that the failure of previous attempts was probably due to lack of the proper experimental conditions. In this work, it was fairly difficult to measure the rotations of the optically active isomers of methyl 9-aminofluorene-2-carboxylate because the active amines racemized readily.

Resolution of these compounds with asymmetric 9-carbon atoms does not indicate whether fluorene possesses a planar or non-planar structure, but it has removed the stumbling block to further study of the stereochemistry of fluorene. There is now no reason why the classical methods of stereochemistry should not be employed in further study of the spatial configuration of fluorene.

Part V

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