8-oxa-3-azabicyclo[3.2.1]octane (XXIV), $n^{25}D$ 1.4848, was obtained. Distillation under reduced pressure through a semi-micro column gave 1.35 g. (75%) of XXIV, b.p. 54–59° (0.05–0.08 mm.), $n^{25}D$ 1.4901–1.4903; reported[4] b.p. 94° (1 mm.), $n^{25}D$ 1.4894. The picrate was obtained in 87% yield, m.p. 169.8–171.0°, by treating an ethereal solution of XXIV with an ethereal solution of picric acid. After recrystallization from ethanol it had m.p. 169.2–171.0°, and was found to be identical (mixed m.p.) to an authentic sample.[4]

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, THE UNIVERSITY OF NEW MEXICO, AND BIOMEDICAL RESEARCH GROUP,[3] LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Liquid Scintillators. VI. 2-Aryl- and 2,7-Diarylfluorenes[1]

BY MARTIN D. BARNETT,[2] GUIDO H. DAUB, F. NEWTON HAYES AND DONALD G. OTT

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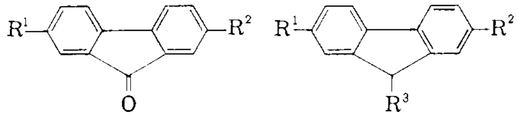
2-Phenylfluorene (II), 2-(4-biphenylyl)-fluorene (IX), 9-methyl-2-(4-biphenylyl)-fluorene (X), 2,7-diphenylfluorene (XVI) and 2,2′-bifluorene (VI) have been synthesized and screened as potential primary liquid scintillation solutes. Although the scintillation properties of II were inferior to those of *p*-terphenyl, the pulse-height values for VI, IX, X and XVI were greater than *p*-quaterphenyl at comparable concentrations. In addition, VI, IX and XVI were evaluated as secondary solutes and found to possess excellent scintillation characteristics.

In connection with work being carried out, in part, by the Biomedical Research Group of the Los Alamos Scientific Laboratory on the evaluation of organic compounds as solutes in liquid scintillation detector systems, it seemed of interest to investigate the liquid scintillation properties of fluorene analogs of *p*-terphenyl and *p*-quaterphenyl. These latter compounds have been shown to possess remarkable scintillation properties; however, the use of *p*-quaterphenyl has been severely curtailed by its low solubility in toluene. Accordingly, the synthesis of a number of 2-aryl- and 2,7-diaryl-substituted fluorenes was carried out in an effort to obtain a more soluble, completely conjugated aromatic system and to learn what effect, if any, the presence of a methylene bridge would have on the scintillation properties of the molecule.

The synthesis of 2-aryl-substituted fluorenes is complicated by the fact that the halogen atoms in 2-bromofluorene and 2-iodofluorene are relatively inert toward the usual reactions with magnesium or lithium metal. Thus, Miller and Bachman[4] report that 2-bromofluorene did not react with either magnesium or lithium in ether or boiling xylene, while Korczynski[5] was unable to couple two molecules of 2-iodofluorene using copper powder in a sealed tube at 300°. Another factor limiting the use of 2-fluorenylmetallic derivatives is the acidity of the methylene hydrogens in fluorene.

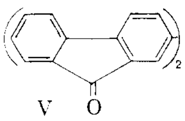
2-Phenylfluorenone (I) was prepared in four steps from 1,4-diphenylbutadiene[6] essentially according to the procedure described by Weizmann.[7] Reduction of I with hydrazine in a modified Wolff–Kishner reduction without alkali[8] afforded 2-phenylfluorene (II) in 76% yield.



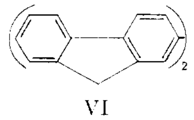
I, $R^1 = C_6H_5$, $R^2 = H$
IV, $R^1 = I$, $R^2 = H$
VIII, $R^1 = 4\text{-}C_6H_5C_6H_4$, $R^2 = H$
XV, $R^1 = R^2 = C_6H_5$
II, $R^1 = C_6H_5$, $R^2 = R^3 = H$
III, $R^1 = I$, $R^2 = R^3 = H$
IX, $R^1 = 4\text{-}C_6H_5C_6H_4$, $R^2 = R^3 = H$
X, $R^1 = 4\text{-}C_6H_5C_6H_4$, $R^2 = H$, $R^3 = CH_3$
XVI, $R^1 = R^2 = C_6H_5$, $R^3 = H$

Although 2-iodofluorene (III) is reported[5] to be inert in the Ullmann reaction, there is ample evidence[9] to indicate that the presence of an electron-withdrawing group in the molecule may enhance the reactivity of the iodine to coupling. Hence, 2-iodofluorene (III), prepared in 32% yield by the reaction of 2-fluorenediazonium chloride[10] with potassium iodide, was oxidized with sodium dichromate in glacial acetic acid to 2-iodofluorenone (IV) in 75% yield.

Heating the ketone IV in a sealed tube with copper bronze gave a 31% yield of 2,2′-bifluorenone (V) from which 2,2′-bifluorene (VI) was prepared in 82% yield by a modified Wolff–Kishner reduction without alkali. 2,2′-Bifluorene (VI) has been reported previously[11] as a possible product in the reduction of 2,7-dibromofluorene with hydrazine over palladium–calcium carbonate; however, no physical constants were given.



V



VI

The availability of *p*-quaterphenyl-2,2′-dicarboxylic acid (VII), prepared by the oxidation of

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[1] From the dissertation presented by Martin D. Barnett to the graduate faculty of The University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Graduate Research Assistant under Los Alamos Contract SC-5 with The University of New Mexico.

[3] Work done in part under the auspices of the U. S. Atomic Energy Commission.

[4] H. F. Miller and G. B. Bachman, THIS JOURNAL, **57**, 766 (1935).

[5] A. Korczynski, G. Karlowska and L. Kierzek, *Bull. soc. chim.*, [4] **41**, 65 (1927).

[6] B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 229.

[7] Ch. Weizmann, E. D. Bergmann and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).

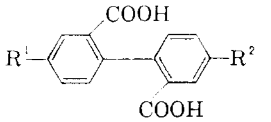
[8] A. S. Harris, E. N. White and D. McNeil, *ibid.*, 4216 (1955).

[9] P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946).

[10] E. D. Bergmann, H. Hoffmann and D. Winter, *Ber.*, **66B**, 46 (1933).

[11] M. Busch, W. Weber and H. Zink, *J. prakt. Chem.*, **155**, 163 (1940).

2-(4-biphenylyl)-phenanthrene,[12] afforded a convenient route to 2-(4-biphenylyl)-fluorene (IX). Pyrolysis of the diacid (VII) at 360° as suggested by the work of Huntress[13] provided a 60% yield of 2-(4-biphenylyl)-fluorenone (VIII) which was readily reduced in 61% yield to the fluorene (IX).



VII, $R^1 = 4\text{-}C_6H_5C_6H_4$, $R^2 = H$
XIV, $R^1 = R^2 = C_6H_5$

The relatively low solubility of IX in toluene (1.5 g./l.) would limit its use as a primary scintillation solute, and in an attempt to increase the solubility of the 2-(4-biphenylyl)-fluorenyl moiety, the 9-methyl derivative of IX was prepared. The ketone VIII was allowed to react with methylmagnesium iodide, and the resulting methyl carbinol dehydrated by refluxing with glacial acetic acid. The product was hydrogenated directly at atmospheric pressure in the presence of Adams catalyst[14] affording 2-(4-biphenylyl)-9-methylfluorene (X) in 33% over-all yield from VIII.

N-Chloro-*o*-acetotoluidide, prepared in 52% yield by the reaction of potassium hypochlorite with *o*-acetotoluidide,[15] was allowed to react with benzene in the presence of anhydrous aluminum chloride[16] to give a 54% yield of 4-acetamido-3-methylbiphenyl (XI). Permanganate oxidation of XI in the presence of magnesium sulfate gave an excellent yield of a mixture of N-acetyl-5-phenylanthranilic acid (XII) and 5-phenylanthranilic acid (XIII), which was converted readily to the amino acid XIII by refluxing with dilute hydrochloric acid. When 5-phenylanthranilic acid (XIII) was diazotized and the resulting diazonium salt treated with an ammoniacal reducing solution of cuprous ion,[17] there was obtained a 44% yield of *p*-quarterphenyl-2″,3′-dicarboxylic acid (XIV). Heating XIV at 375° afforded 2,7-diphenylfluorenone (XV) in 56% yield. A modified Wolff-Kishner reduction of XV without alkali produced a 56% yield of 2,7-diphenylfluorene (XVI).

Solutions of the compounds prepared in this study were subjected to conventional scintillation and spectral tests. The scintillation measurements were carried out as described previously[18] with a ten-channel pulse-height analyzer deriving its input signals from a photomultiplier tube having average S-11 spectral characteristics. The ultraviolet-excited fluorescence spectra[19] were obtained by irradiation of the toluene solutions (approximately 1 g./l.) by the 314-mμ excitation isolated from a mercury arc by passage through a Beckman DU monochromator unit. The mean fluorescence wave lengths ($\bar{\lambda}$) were determined as previously described by Ott.[19] All of the compounds were evaluated as primary solutes, and the relative pulse-height values at various concentrations in toluene are presented graphically in Fig. 1, along with those values for *p*-quaterphenyl, biphenyl and fluorene. In Table I are reported the values for I_{max} (maximum relative pulse-height), C_{max} (concentration of solute at I_{max}), λ_{max}, and $\bar{\lambda}$ for the ultraviolet-excited fluorescence spectra, and TiO_2/Al reflector ratios.[18]

Table I

Scintillation and Fluorescence Spectral Data for Primary Solutes

Compound	I_{max}[a]	C_{max}[b]	λ_{max}, mμ	$\bar{\lambda}$, mμ	TiO_2/ Al[c]
II	0.68	3.6	354	368	0.88
VI	.54	0.4[d]	378	386	1.00
IX	.99	1.5[d]	375	381	1.00
X	.91	2.4	377	389	1.01
XVI	.97	1.0[d]	372	382	0.97
p-Quaterphenyl	.37	0.36[d]	357	374	0.94

[a] Relative to 3 g./l. 2,5-diphenyloxazole (PPO) in toluene. [b] Concentration in g./l. at I_{max}. [c] Ratio of relative pulse height using titanium dioxide reflector to relative pulse height using aluminum reflector[18] at 3 g./l. or saturated solution. [d] Saturated solution.

Within their limited solubility ranges, 2,2′-bifluorene (VI), 2,7-diphenylfluorene (XVI), 2-(4-biphenylyl)-fluorene (IX) and 9-methyl-2-(4-biphenylyl)-fluorene (X) have scintillation properties better than *p*-quaterphenyl; however, 2-phenylfluorene (II) is a poorer scintillation solute than *p*-terphenyl.

In addition, 2,2′-bifluorene (VI), 2,7-diphenylfluorene (XVI) and 2-(4-biphenylyl)-fluorene (IX) were evaluated as secondary solutes.[20] These data are presented in Table II and show the three hydrocarbons to be good secondary solutes.

Table II

Scintillation Data for Secondary Solutes[a]

Compound	I[b]	TiO_2/Al
VI	1.20	0.98
IX	1.18	.92
XVI	1.22	.94

[a] Evaluated at 0.1 g./l. in toluene containing 4 g./l. *p*-terphenyl. [b] Pulse height relative to a toluene solution containing 3 g./l. 2,5-diphenyloxazole (PPO).

Experimental[21]

2-Phenylfluorene (II).—A mixture of 1.0 g. (0.0039 mole) of 2-phenylfluorenone (I),[7] 5 ml. of 95% hydrazine (Eastman Kodak Co. 902), and 30 ml. of diethylene glycol (Eastman Kodak Co. 2041) was refluxed for 5.0 hr., cooled, and poured into dilute hydrochloric acid. The dried, colorless solid (0.90 g., m.p. 185–190°) was dissolved in benzene and chromatographed over alumina. Removal of the solvent left 0.82 g. of colorless solid, m.p. 190–194°, which was sublimed at 175–185° at 0.1 mm. to yield 0.72 g. (76%) of colorless **2-phenylfluorene** (II), m.p. 193.5–194°.[22] Maxima

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[12] S. P. Birkeland and G. H. Daub, unpublished work.

[13] E. H. Huntress, E. B. Hershberg and I. S. Cliff, This Journal, **53**, 2720 (1931).

[14] G. M. Badger, *J. Chem. Soc.*, 535 (1941).

[15] C. D. Barnes and C. W. Porter, This Journal, **52**, 1721 (1930).

[16] G. Kranzlein, P. Ochwat and K. Moldaenke, U. S. Patent 2,012,569 (1935); *C. A.*, **29**, 6905 (1935).

[17] E. R. Atkinson and J. J. Lawler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 222.

[18] F. N. Hayes, D. G. Ott, V. N. Kerr and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955).

[19] D. G. Ott, F. N. Hayes, E. Hansbury and V. N. Kerr, This Journal, **79**, 5448 (1957).

[20] F. N. Hayes, D. G. Ott and V. N. Kerr, *Nucleonics*, **14**, No. 1, 42 (1956).

[21] Melting points are uncorrected. Ultraviolet absorption spectra were determined in cyclohexane at concentrations of *ca.* 3×10^{-6} *M* in 1-cm. silica cells using a Beckman DK-1 recording spectrophotometer.

[22] This compound has just recently been synthesized from

and (log ε) values for the ultraviolet absorption spectra are 288 (4.52) and 309 mμ (4.42).

Anal. Calcd. for $C_{19}H_{14}$: C, 94.17; H, 5.83. Found: C, 94.55; H, 5.96.

2-Iodofluorene (III).—A solution of 3.8 g. (0.02 mole) of 2-aminofluorene (Eastman Kodak Co. 4682) in 300 ml. of hot 2 *N* hydrochloric acid was cooled rapidly to 50° and a solution of 1.45 g. (0.021 mole) of sodium nitrite in 10 ml. of water added. After 5 min., 1.0 g. of urea was added and the reaction mixture poured with stirring into a solution of 16.6 g. (0.10 mole) of potassium iodide in 25 ml. of water. The evolution of gases ceased after warming on a steam-bath for 1.0 hr. The cooled mixture was filtered and the solid washed with 10% sodium bisulfite solution, hot 10% sodium hydroxide, and water until neutral. The air-dried solid (4.7 g.) was dissolved in anhydrous ether, filtered, and the filtrate saturated with anhydrous hydrogen chloride to remove unreacted amine. After removal of the amine salt by filtration, the filtrate was evaporated to dryness and the residue dissolved in benzene and chromatographed on alumina to yield, after crystallization from ethanol, 1.85 g. (32%) of colorless 2-iodofluorene (III), m.p. 127–129°, reported[5] m.p. 129°. Attempts to prepare 2-iodofluorene according to Diels[23] or Bachmann[24] consistently gave poorer yields.

2-Iodofluorenone (IV).—To a hot, stirred solution of 7.4 g. (0.025 mole) of III in 80 ml. of glacial acetic acid was added 24.4 g. (0.083 mole) of technical sodium dichromate dihydrate portionwise. The reaction mixture was refluxed and stirred for 1.25 hr. and poured onto ice. The precipitate was filtered, washed with water, and air-dried to yield 6.7 g. of yellow solid, m.p. 143–151°. A benzene solution of the solid was chromatographed through a short alumina column, elution being accomplished with 1:20 methanol-benzene. Crystallization of the eluted solid from ethanol gave 5.7 g. (75%) of the ketone IV as bright yellow needles, m.p. 151–153°, reported[25] m.p. 152°.

2,2′-Bifluorenone (V).—A mixture of 3.0 g. (0.0098 mole) of IV and 6.0 g. of copper bronze (O. Hommel Co., Pittsburgh, Pa., 5347) was heated in a sealed tube with shaking at 225–230° for 18.0 hr. The solid was extracted with several portions of boiling toluene which upon cooling deposited 0.80 g. of orange plates, m.p. 287–300°. Crystallization from toluene yielded 0.55 g. (31%) of **2,2′-bifluorenone (V)** as golden yellow plates, m.p. 294–297°. The analytical sample, after sublimation at 230–245° (0.005 mm.) and recrystallization from toluene, melted at 295–297°.

Anal. Calcd. for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found: C, 87.24; H, 4.05.

2,2′-Bifluorene (VI).—A mixture of 0.55 g. (0.0015 mole) of V, 2 ml. of 95% hydrazine (Eastman Kodak Co. 902) and 10 ml. of diethylene glycol (Eastman Kodak Co. 2041) was heated under an air condenser at 185–190° for 0.5 hr. The condenser was removed and the temperature raised to 205–210° for 10 min. after which the mixture was refluxed for 3.5 hr. After cooling, the reaction mixture was poured into dilute hydrochloric acid, filtered, and the colorless plates washed with water. One crystallization from toluene yielded 0.41 g. (82%) of **2,2′-bifluorene (VI)** as colorless, highly fluorescent plates, m.p. 316–318°. The analytical sample, m.p. 316.5–318°, was crystallized from toluene. Maximum and (log ε) values for the ultraviolet absorption spectrum are 324 mμ (4.84).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.32; H, 5.60.

2-(4-Biphenylyl)-fluorenone (VIII).—Two grams (0.0051 mole) of *p*-quaterphenyl-2,2′-dicarboxylic acid (VII)[12] was heated slowly to 360° in a metal-bath and maintained at this temperature until bubbling had ceased (about 0.5 hr.).[13] The residue was extracted with several portions of boiling toluene, the extracts concentrated and chromatographed through an alumina column. Concentration of the eluates produced 1.13 g. of yellow solid, m.p. 240–248°, which was recrystallized from toluene to yield 1.0 g. (60%) of **2-(4-biphenylyl)-fluorenone (VIII)** as tiny, bright yellow needles, m.p. 246–248°. The analytical sample, recrystallized from toluene, melted at 247–249°.

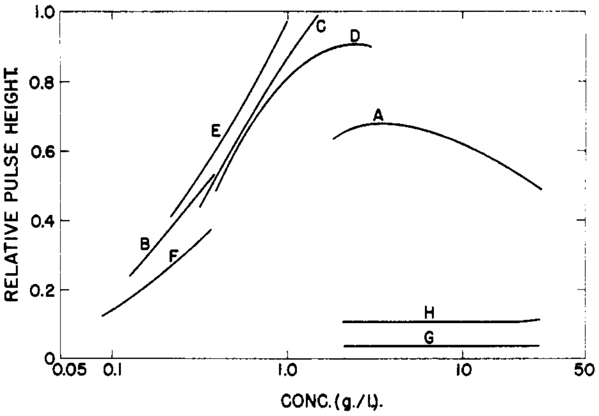

Fig. 1.—Relative pulse-height curves for some aryl-substituted fluorenes and related hydrocarbons as primary solutes: A, 2-phenylfluorene (II); B, 2,2′-bifluorene (VI); C, 2-(4-biphenylyl)-fluorene (IX); D, 9-methyl-2-(4-biphenylyl)-fluorene (X); E, 2,7-diphenylfluorene (XVI); F, *p*-quaterphenyl; G, biphenyl; H, fluorene.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.33; H, 4.85. Found: C, 90.21; H, 4.91.

2-(4-Biphenylyl)-fluorene (IX).—A mixture of 0.35 g. (0.0011 mole) of 2-(4-biphenylyl)-fluorenone (VIII), 2 ml. of 95% hydrazine (Eastman Kodak Co. 902) and 10 ml. of diethylene glycol (Eastman Kodak Co. 2041) was slowly heated to 185–190° and maintained at this temperature for 0.5 hr. After removing the air condenser for a few minutes, the reaction mixture was refluxed for an additional 1.25 hr. Upon cooling, dilute hydrochloric acid was added and the precipitated solid filtered, washed with water, and dried to yield 0.30 g. of nearly colorless material, m.p. 282–295°. Sublimation at 200–215° (0.02 mm.) and two recrystallizations from benzene provided 0.20 g. (61%) of **2-(4-biphenylyl)-fluorene (IX)** as colorless, highly fluorescent plates, m.p. 299–301°. Maximum and (log ε) values for the ultraviolet absorption spectrum are 313 mμ (4.64).

Anal. Calcd. for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.58; H, 5.91.

9-Methyl-2-(4-biphenylyl)-fluorene (X).—To a stirred ether solution of the Grignard reagent prepared from 4.55 g. (0.032 mole) of methyl iodide and 0.78 g. (0.032 g.-atom) of magnesium turnings was rapidly added a warm solution of 1.05 g. (0.0032 mole) of 2-(4-biphenylyl)-fluorenone (VIII) in 200 ml. of anhydrous C.P. benzene. The reaction mixture was refluxed for 2.0 hr., cooled, and decomposed by the addition of 50 ml. of saturated ammonium chloride solution. The organic layer was washed with water until neutral. After removal of the solvent under reduced pressure, the colorless residue (1.08 g.) was refluxed for 1.0 hr. with 40 ml. of glacial acetic acid during which time a granular yellow solid precipitated. The suspension was transferred to a hydrogenation flask with a small amount of glacial acetic acid and stirred at atmospheric pressure with 0.1 g. of Adams catalyst until hydrogen uptake had ceased (21.0 hr.). The reaction mixture was heated to boiling, filtered, and the filtrate concentrated to yield 0.60 g. of yellowish solid, m.p. 200–210°. Three crystallizations from toluene gave 0.35 g. (33%) of **9-methyl-2-(4-biphenylyl)-fluorene (X)** as a granular, faint yellow solid, m.p. 213–214°. Maximum and (log ε) values for the ultraviolet absorption spectrum are 312 mμ (4.67).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.07; H, 6.08.

N-Chloro-*o*-acetotoluidide.—To a stirred solution of 50.0 g. (0.335 mole) of *o*-acetotoluidide (Eastman Kodak Co. 405) and 56.0 g. (0.555 mole) of potassium bicarbonate in 8 l. of water cooled to 7–8° was added dropwise a solution of potassium hypochlorite prepared from 38.0 g. of "H.T.H.," 26.6 g. of potassium carbonate and 7.6 g. of potassium hy-

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fluorene in two steps, m.p. 193–194°; N. G. Sidorova and G. Kh. Tyshchuk, *Zhur. Obshchei Khim.*, **28**, 2030 (1958); *C. A.*, **53**, 2179g (1959).

[23] O. Diels, *Ber.*, **34**, 1758 (1901).

[24] W. E. Bachmann and C. H. Boatner, This Journal, **58**, 2194 (1936).

[25] Ch. Courtot, *Ann. chim.*, [10] **14**, 5 (1930).

droxide.[26] The temperature was not allowed to rise above 8° during the addition. After approximately two-thirds of the hypochlorite solution had been added, the mixture suddenly became milky in appearance. Stirring was continued for 1.0 hr. after addition was complete, during which time the precipitated oil crystallized to a colorless solid which was filtered, washed with a small amount of ice-cold water, and dried overnight in a vacuum desiccator. The yield was 32.0 g. (52%), m.p. 44–45°, reported[27] m.p. 43°. The material is sufficiently pure for the next step and recrystallization is not recommended because of decomposition at elevated temperatures.

3-Methyl-4-acetamidobiphenyl (XI).—To an ice-cold (5–6°) slurry of 71.0 g. (0.532 mole) of anhydrous technical aluminum chloride in 700 ml. of anhydrous C.P. benzene was added with stirring 32.0 g. (0.174 mole) of N-chloro-*o*-acetotoluidide dissolved in 300 ml. of anhydrous C.P. benzene at such a rate as to maintain the temperature of the reaction mixture at 5–6°.[16] After addition was complete, the mixture was stirred at 4–5° for an additional 5.0 hr., then poured onto ice, and steam distilled to remove the benzene. The residue was cooled, filtered, washed with water, and air-dried to yield 30.0 g. of tan solid, m.p. 160–168°. Crystallization from ethanol (Norit) gave 21.0 g. (54%) of the amide XI as colorless needles, m.p. 168–170°. A small sample recrystallized from ethanol melted at 170–171°, reported m.p. 158°,[28] 166°.[16]

N-Acetyl-5-phenylanthranilic Acid (XII).—A mixture of 22.6 g. (0.10 mole) of 3-methyl-4-acetamidobiphenyl (XI), 48.2 g. (0.40 mole) of magnesium sulfate, 400 ml. of pyridine and 400 ml. of water was warmed to 60° with stirring and four 11.8-g. portions of potassium permanganate (total 0.30 mole) added at one-hour intervals with the temperature maintained at 60° throughout the reaction period. The mixture was stirred at 60° for an additional hour after addition was complete, then decolorized with solid sodium bisulfite, and filtered hot through Filter-cel. The residue was washed with hot portions of pyridine and water, the washings combined with the original filtrate, and the solution evaporated to dryness under reduced pressure. Two-hundred milliliters of 5% hydrochloric acid was added to the residue and the organic material extracted with two 200-ml. portions of warm benzene. The benzene extracts were shaken with two 100-ml. portions of 5% potassium hydroxide solution. Removal of the benzene under reduced pressure yielded 5.2 g. of unreacted XI, m.p. 163–168°.

Acidification of the potassium hydroxide extracts with concentrated hydrochloric acid produced 17.2 g. of nearly colorless acidic material, m.p. 190–200°, apparently a mixture of N-acetyl-5-phenylanthranilic acid (XII) and 5-phenylanthranilic acid (XIII). This mixture was hydrolyzed without further purification. A sample recrystallized several times from benzene–ethanol gave faintly yellow plates of N-acetyl-5-phenylanthranilic acid (XII), m.p. 208–209°, reported[16] m.p. 205–206°.

5-Phenylanthranilic Acid (XIII).—Sixteen grams of the crude mixture of XII and XIII and 400 ml. of dilute (1:1) hydrochloric acid were refluxed with stirring for 23.0 hr., after which the mixture was cooled in ice, filtered, and washed with a small amount of cold water. The damp solid was suspended in about 100 ml. of water, dissolved by the addition of concentrated ammonium hydroxide, filtered, and acidified with glacial acetic acid. The faint yellow solid, after being filtered, washed and air-dried, weighed 14.0 g., m.p. 200–205° dec. Crystallization from ethanol gave 12.0 g. of 5-phenylanthranilic acid (XIII) as nearly colorless needles, m.p. 203–205° dec., reported[16] m.p. 200–202°.

***p*-Quaterphenyl-2″,3′-dicarboxylic Acid (XIV).**—A mixture of 7.42 g. (0.0348 mole) of 5-phenylanthranilic acid (XIII), 8.75 ml. of concentrated hydrochloric acid and 150 ml. of water was heated on a steam-bath with occasional stirring for 1.0 hr., then cooled to 0–5°, and diazotized by the dropwise addition of 2.52 g. (0.0365 mole) of U.S.P. sodium nitrite dissolved in 25 ml. of water. The mixture was stirred at 0–5° for an additional 2.0 hr., then filtered through a chilled Büchner funnel, and added with vigorous stirring over a 15-min. period to a cold (10°) reducing solution.[17] This was prepared by adding a mixture of 3.43 g. (0.0493 mole) of C.P. hydroxylamine hydrochloride in 20 ml. of water and 8.05 ml. of 6 *N* sodium hydroxide to a mixture of 12.07 g. (0.0483 mole) of C.P. hydrated cupric sulfate in 250 ml. of water and 20.15 ml. of concentrated ammonium hydroxide. The foaming reaction mixture was heated to boiling and acidified with concentrated hydrochloric acid. The crude acid, after being filtered and washed with water, was dissolved in concentrated ammonium hydroxide, stirred at room temperature for 15 min. (Norit), and filtered through Filter-cel to yield, after acidification, 5.5 g. of tan acidic material, m.p. 295–310°. Two recrystallizations from ethanol (Norit) provided 3.0 g. (44%) of faintly tan ***p*-quaterphenyl-2″,3′-dicarboxylic acid (XIV)**, m.p. 333–336°. The analytical sample crystallized from ethanol as nearly colorless granules, m.p. 335–336°.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.10; H, 4.44.

2,7-Diphenylfluorenone (XV).—One gram (0.0025 mole) of *p*-quaterphenyl-2″,3′-dicarboxylic acid (XIV), was placed in a metal-bath previously heated to 330° and rapidly heated to 375°. This temperature was maintained for 2.0 hr., after which the residue was extracted with hot toluene, the extracts concentrated, and chromatographed over alumina. There was obtained, after concentration of the eluates, 0.47 g. (56%) of **2,7-diphenylfluorenone (XV)** as orange-yellow plates, m.p. 227–228°. The analytical sample crystallized from toluene melted at 228–229°.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.33; H, 4.85. Found: C, 90.13; H, 5.01.

2,7-Diphenylfluorene (XVI).—A mixture of 0.47 g. (0.0014 mole) of 2,7-diphenylfluorenone (XV), 2 ml. of 95% hydrazine (Eastman Kodak Co. 902) and 10 ml. of diethylene glycol (Eastman Kodak Co. 2041) was allowed to react as previously described in the preparation of 2-(4-biphenylyl)-fluorene (IX). The crude product (0.44 g., m.p. 278–283°) yielded, after three crystallizations from toluene, 0.25 g. (56%) of **2,7-diphenylfluorene (XVI)** as colorless plates, m.p. 292–294°. Maxima and (log ϵ) values for the ultraviolet absorption spectrum are 310(s) (4.72) and 323 mμ (4.76).

Anal. Calcd. for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.60; H, 5.80.

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LOS ALAMOS, N. M.

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