

Department of Chemistry
University of New Mexico

Biomedical Research Group
Los Alamos Scientific Laboratory
University of California

Liquid Scintillators. XIII.

Steric Inhibition of Resonance in Liquid Scintillators

Richard L. Taber (1), Guido H. Daub (2),
F. Newton Hayes, and Donald G. Ott (3)

2'',3'-Dimethyl-*p*-quaterphenyl (I), 2'',3',5',6''-tetramethyl-*p*-quaterphenyl (II), 6,7-dihydro-6-methyl-3,9-diphenyl-5*H*-dibenz[*c,e*]azepine (III), 5,7-dihydro-3,9-diphenyl-dibenzo[*c,e*]thiepin (IV), 5,7-dihydro-3,9-diphenyldibenzo[*c,e*]selenepin (V), and 6,6-dicarbethoxy-6,7-dihydro-3,9-diphenyl-5*H*-dibenzo[*a,c*]cycloheptene (VI) have been synthesized and screened as potential primary liquid scintillation solutes. The scintillation properties of I, II, III, IV, V, and VI have been compared with 2,7-diphenylfluorene (VII) (4), 9,10-dihydro-2,7-diphenylphenanthrene (VIII) (5), and 5,7-dihydro-3,9-diphenyldibenz[*c,e*]oxepin (IX) (5). The relative pulse-heights of I, VI, VII, VIII, and IX at 3 *mM* in toluene gave a linear relationship when plotted against the \cos^2 of the respective estimated angles of torsion about the 1'',4'-bond in the *p*-quaterphenyl system. The azepine III, thiepin IV, selenepin V, and tetramethyl-*p*-quaterphenyl II were very poor scintillators in toluene solution.

In previous communications (4,5,6) it was shown that 2,7-diphenylfluorene (VII), 9,10-dihydro-2,7-diphenylphenanthrene (VIII), and 5,7-dihydro-3,9-diphenyldibenz[*c,e*]oxepin (IX) were excellent liquid scintillation solutes. Molecular models of VIII indicate that the $-\text{CH}_2-\text{CH}_2-$ bridge in this compound causes the bridged benzene rings to be twisted at an angle of about 31° with respect to one another, while the $-\text{CH}_2-\text{O}-\text{CH}_2-$ bridge in IX causes the benzene rings to be twisted at an angle of about 47° (Figure 1). The $-\text{CH}_2-$ bridge in the fluorene VII causes the two benzene rings to be essentially coplanar but not colinear. The resonance interaction between the benzene rings should be greatest in VII and least in IX, since the *p*-orbital overlap between the directly bonded carbon atoms of the bridged benzene rings should decrease in the order VII >

VIII > IX. The high I-max values obtained for VIII and IX (1.15 and 1.14, respectively (7)) as compared to 0.97 for VII could not be rationalized on the basis of coplanarity of the *p*-quaterphenyl system since the bridged rings in VIII and IX were twisted considerably from a common plane.

Studies carried out on biphenyl systems in which free rotation about the 1,1'-biphenyl bond is hindered by bulky groups in the 2,2'-positions indicate that the covalent bond order of the 1,1'-bond will be at a maximum when the two benzene rings lie in the same plane (8-11). Accordingly, the synthesis of a number of 2'',3'-substituted *p*-quaterphenyls was carried out in an effort to study the effect of steric inhibition of resonance across the 1'',4'-*p*-quater-

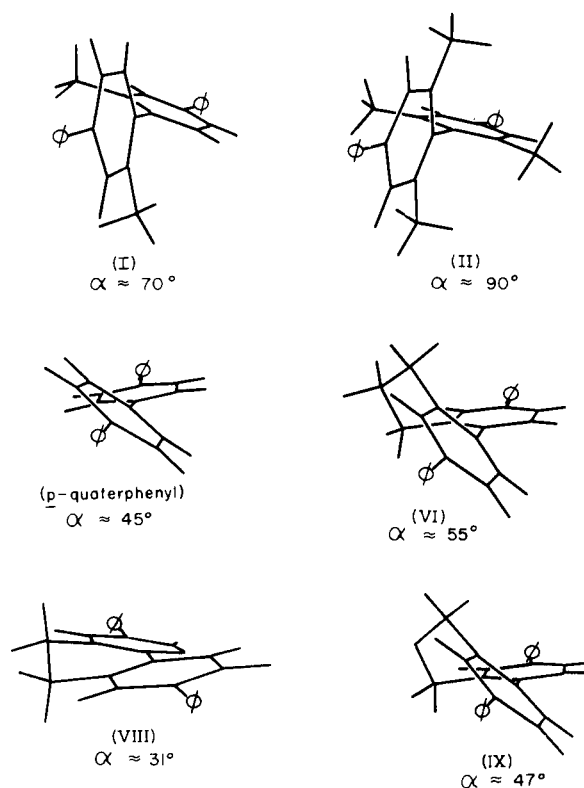
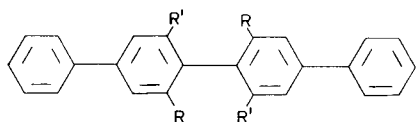
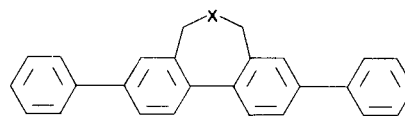
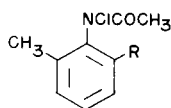


Figure 1. Perspective Drawings of *p*-Quaterphenyl Derivatives Showing Estimated Angle of Twist.

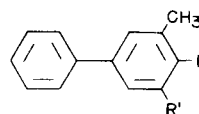
I, R' = CH₃, R = HII, R' = R = CH₃XV, R = H, R' = CH₂BrIII, X = NCH₃

IV, X = S

V, X = Se

VI, X = C(COOC₂H₅)₂

XI, R = H

XVII, R = CH₃XII, R = NHCOCH₃, R' = HXIII, R = NH₂·HCl, R' = H

XIV, R = I, R' = H

XVIII, R = NHCOCH₃, R' = CH₃XIX, R = NH₂, R' = CH₃XX, R = I, R' = CH₃

phenyl bond on the scintillation properties of the molecule.

2'',3'-Dimethyl-*p*-quaterphenyl (I) was prepared via the Ullmann coupling of 4-iodo-3-methylbiphenyl (XIV), which was available in four steps from *o*-acetotoluidide (X). The amide X was converted to N-chloro-*o*-acetotoluidide (XI) in 85% yield by a modification of a procedure previously described by Barnett (4). The chloramide XI was allowed to react with benzene in the presence of anhydrous aluminum chloride to give 4-acetamido-3-methylbiphenyl (XII), which upon hydrolysis with 20% hydrochloric acid gave 4-amino-3-methylbiphenyl hydrochloride (XIII). The diazonium salt of XIII was allowed to react with potassium iodide to give the iodo compound XIV.

The synthesis of the 3-atom bridged compounds III, IV, V, and VI was accomplished from 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV). This compound was prepared in 83% yield by the reaction of N-bromosuccinimide with the hydrocarbon I in the presence of catalytic amounts of benzoyl peroxide (12). 6,7-Dihydro-6-methyl-3,9-diphenyl-5H-dibenzo[*c,e*]azepine (III) was prepared in 69% yield from the dibromide XV by reaction with methylamine in absolute benzene according to the method described by Wenner (13). The preparation of 5,7-dihydro-3,9-diphenyldibenzo[*c,e*]thiepin (IV) was accomplished in 52% yield by refluxing XV with sodium sulfide monohydrate in a mixture of water, methanol, and dioxane. 5,7-Dihydro-3,9-diphenyldibenzo[*c,e*]-

selenepin (V) was obtained in 51% yield by a reaction of XV with potassium selenide in a manner as described by Truce and Emrick (11). The preparation of 6,6-dicarbethoxy-6,7-dihydro-3,9-diphenyl-5H-dibenzo[*a,c*]cycloheptene (VI) was accomplished by the reaction of XV with ethyl 2,2-disodiummalonate in a mixture of anhydrous methanol and dioxane.

The preparation of 2'',3',5',6''-tetramethyl-*p*-quaterphenyl (II) was accomplished by a route similar to that one employed in the synthesis of I. 2,6-Dimethylacetanilide (XVI) was prepared in 87% yield from 2,6-dimethylaniline. Conversion of XVI to N-chloro-2,6-dimethylacetanilide (XVII) was accomplished via the procedure described for the preparation of XI. The chloramide XVII was then converted to 4-acetamido-3,5-dimethylbiphenyl (XVIII) which was hydrolyzed with 100% phosphoric acid to 4-amino-3,5-dimethylbiphenyl (XIX). Diazotization of XIX, followed by treatment with potassium iodide, gave 4-iodo-3,5-dimethylbiphenyl (XX). The iodide XX was converted to the Grignard reagent, which in the presence of anhydrous cobaltous chloride gave the hydrocarbon II in 21% yield. An attempt to prepare II from the iodo compound XX via the Ullmann reaction gave only a trace of the desired product.

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 (14) with a ten-channel pulse-height analyzer deriving its input

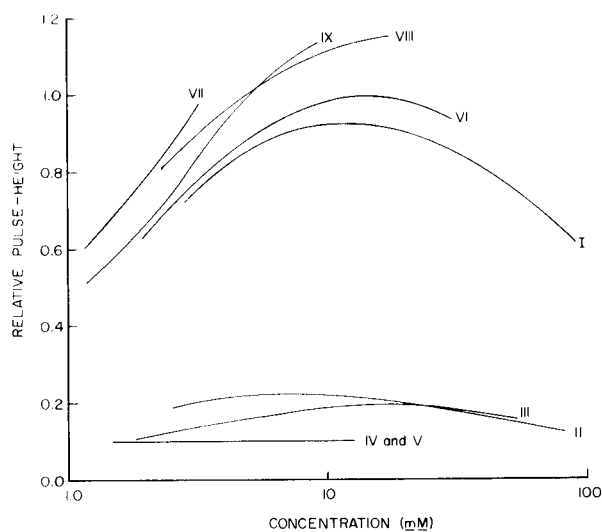


Figure 2. Relative pulse-height curves for some methyl substituted and 2'',3'-bridged *p*-quaterphenyls: 5,7-Dihydro-3,9-diphenyldibenz[*c,e*]oxepin (IX); 6,7-Dihydro-6-methyl-3,9-diphenyl-5*H*-dibenz[*c,e*]azepine (III); 5,7-Dihydro-3,9-diphenyldibenzo[*c,e*]thiepin (IV); 5,7-Dihydro-3,9-diphenyldibenzo[*c,e*]selenepin (V); 6,6-Dicarbethoxy-6,7-dihydro-3,9-diphenyl-5*H*-dibenzo[*a,c*]cycloheptene (VI); 2,7-Diphenylfluorene (VII); 9,10-Dihydro-3,9-diphenylphenanthrene (VIII); 2'',3'-Dimethyl-*p*-quaterphenyl (I); and 2'',3',5',6''-Tetramethyl-*p*-quaterphenyl (II).

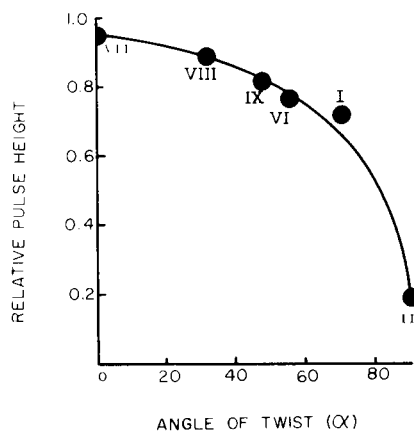


Figure 3. Relative pulse-height versus angle of twist (α) for some 2'',3'-disubstituted *p*-quaterphenyls at 3 *mM*: 9,10-Dihydro-2,7-diphenylphenanthrene (VIII); 2,7-Diphenylfluorene (VII); 5,7-Dihydro-3,9-diphenyldibenz[*c,e*]oxepin (IX); 2'',3'-Dimethyl-*p*-quaterphenyl (I); 2'',3',5',6''-Tetramethyl-*p*-quaterphenyl (II); and 6,6-Dicarbethoxy-6,7-dihydro-3,9-diphenyldibenzo-5*H*-[*a,c*]cycloheptene (VI).

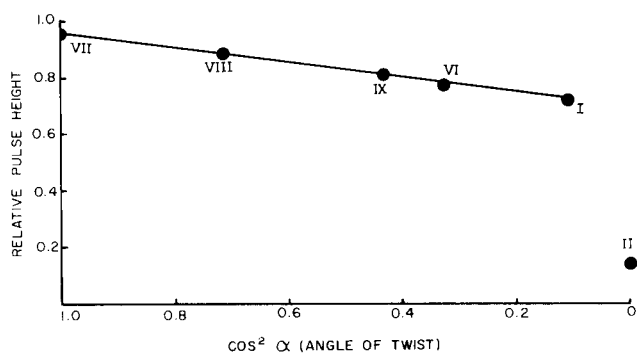


Figure 4. Relative pulse-height at 3 *mM* in toluene versus $\cos^2 \alpha$ (angle of twist) for some 2'',3'-disubstituted *p*-quaterphenyls: 9,10-Dihydro-2,7-diphenylphenanthrene (VIII); 2,7-Diphenylfluorene (VII); 5,7-Dihydro-3,9-diphenyldibenz[*c,e*]oxepin (IX); 2'',3'-Dimethyl-*p*-quaterphenyl (I); 2'',3',5',6''-Tetramethyl-*p*-quaterphenyl (II); and 6,6-Dicarbethoxy-6,7-dihydro-3,9-diphenyl-5*H*-dibenzo[*a,c*]cycloheptene (VI).

signals from an RCA 6903 quartz-face photomultiplier tube having average S-13 spectral characteristics. The ultraviolet-excited fluorescence spectra (15) were obtained by irradiation of toluene solutions (approximately 1 g./l.) contained in a triangular quartz cuvette and analysis of the spectrum with an Aminco-Bowman spectrophotofluorometer. The mean fluorescence wave lengths ($\bar{\lambda}$) were determined as previously described by Ott (15). All of the compounds were evaluated as primary solutes, and the relative pulse-height values at various concentrations in toluene are presented graphically in Figure 2, along with the values for VII, VIII, and IX. 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.

In Table II are reported the RPH values for compounds I, II, VI, VII, VIII, and IX at 3 *mM* in toluene and α , the estimated angle of torsion about the 1'',4'-*p*-quaterphenyl bond. These RPH values are plotted against the angle, α , in Figure 3 and against the $\cos^2 \alpha$ in Figure 4.

As can be seen from Table II and Figures 3 and 4, the RPH values for the compounds decrease as the angle of torsion increases. Dewar (16) has emphasized that resonance does not require perfect planarity of the conjugated system, but that the effect of conjugation between two directly bonded benzene rings is greatest when the rings are coplanar. The resonance energy of the system RS relative to (R + S) varies as the \cos^2 of α , where α is the angle through which \mathcal{E} is twisted out of

TABLE I

Scintillation and Fluorescence Spectral Data for Primary Solutes

Compound	I-max (a)	C-max (b)	λ max (m μ)	$\bar{\lambda}$ (m μ)
I	0.92	11.25	345	352
II	0.21	5.18	325	339
III	0.19	13.30	370	430
IV	< 0.10	-	360	369
V	< 0.10	-	355	369
VI	1.00	14.75	368	370

(a) Relative to 3 g./l. of 2,5-diphenyloxazole (PPO) in toluene. (b) Concentration in millimoles/liter at I-max.

TABLE II

The Relative Pulse-Heights and Angles of Torsion for Some 2'',3'-Disubstituted *p*-Quaterphenyl Derivatives at 3*m*.M in Toluene

2'',3'- <i>p</i> -Quaterphenyl Derivative	α	RPH	$\text{Cos}^2\alpha$
-CH ₂ - VII	~ 0° (a)	0.96	1.00
-CH ₂ CH ₂ - VIII	~ 31° (b)	0.89	0.735
-CH ₂ OCH ₂ - IX	~ 47° (b)	0.82	0.465
-CH ₂ C(COOEt) ₂ CH ₂ - VI	~ 55° (a)	0.77	0.330
-CH ₃ , CH ₃ - I	~ 70° (b)	0.72	0.117
2'',3',5',6''-tetramethyl- II	~ 90° (a)	0.19	0.00

(a) Estimated from molecular models. (b) Estimated by Suzuki for analogous biphenyls (8).

TABLE III

Ultraviolet Absorption Maxima and Log ϵ Values for Some 2'',3'-Disubstituted *p*-Quaterphenyl Derivatives

2'',3'- <i>p</i> -Quaterphenyl Derivative	Max (m μ)	Log ϵ	α
-CH ₂ - VII	310	4.72	strained
	323	4.76	planar
-CH ₂ CH ₂ - VIII	323	4.60	31°
-CH ₂ -O-CH ₂ - IX	298	4.64	47°
-CH ₂ C(COOEt) ₂ CH ₂ - VI	296	4.65	55°
-CH ₂ N(CH ₃)CH ₂ - III	290	4.55	--
-CH ₂ SeCH ₂ - V	288	4.55	--
-CH ₂ SCH ₂ - IV	286	4.51	--
-CH ₃ , CH ₃ - I	265	4.63	70°
2'',3',5',6''-Tetramethyl II	264	4.94	90°

coplanarity with R. It is interesting to note from Figure 4 that a plot of RPH at 3 mM for the compounds listed in Table II versus the \cos^2 of the estimated angle of twist (α) gives essentially a straight line. The notable exception is 2'',3',5',6''-tetramethyl-*p*-quaterphenyl (II), which does not show the scintillation properties of a *p*-quaterphenyl system but of a biphenyl system. The results of this investigation indicate that there is an appreciable amount of *p*-orbital overlap across the 1'',4'-bond in *p*-quaterphenyl derivatives even though the biphenyl portions of the molecule may be twisted as much as 70° out of a common plane.

A tabulation of the ultraviolet absorption maxima for the compounds evaluated as primary scintillation solutes, as given in Table III, shows that a definite hypsochromic shift of the maximum occurs as the angle of twist increases. The maxima for 2'',3'-dimethyl-*p*-quaterphenyl (I) and 2'',3',5',6''-tetramethyl-*p*-quaterphenyl (II) are close to the maxima exhibited by biphenyl systems. The value of 264 μ for II should probably be corrected for the presence of two additional methyl groups for the purposes of comparison with the dimethyl compound I. Truce and Emrick (11) have suggested that about 8 μ should be subtracted for the addition of the two methyl groups. This would give a value of 256 μ for the maximum of II, which is close to the maximum of 3,5-dimethylbiphenyl (252 μ) (17).

As seen from Table I and Figure 2, 6,7-dihydro-6-methyl-3,9-diphenyl-5*H*-dibenz[*c,e*]azepine (III) (maximum RPH = 0.19), 5,7-dihydro-3,9-diphenyl-dibenzo[*c,e*]selenepin (V) (maximum RPH < 0.1), and 3,9-diphenyl-5,7-dibenzo[*c,e*]thiepin (IV) (maximum RPH < 0.1) are very poor liquid scintillation solutes.

These results may be rationalized either by the supposition that the angles of twist in III, IV, and V are much greater than in IX and VI, therefore greatly decreasing the *p*-orbital overlap across the 1'',4'-bond, or more reasonably, that the scintillation is being quenched due to the presence of the respective hetero atom. The latter hypothesis was substantiated in the case of the azepine by an experiment in which a sample of a good scintillator, 2'',3'-dimethyl-*p*-quaterphenyl (I), had a relative pulse-height of 0.72, but with an equimolar concentration of triethylamine present the solution had a relative pulse-height of less than 0.1. An earlier study of the role of solvents in liquid scintillators (18) has shown that the addition of aliphatic amines or thiophene to the scintillation solution causes an abrupt decrease in the relative pulse-height. This would indicate that the low RPH for IV may be due to the presence of the aliphatic sulfur atom.

EXPERIMENTAL (19)

N-Chloro-*o*-acetotoluidide (XI).

To a stirred solution of 183 g. (1.23 moles) of *o*-acetotoluidide (Eastman Kodak Co. 405) and 216 g. (2.16 moles) of potassium bi-

carbonate in 2 l. of ethanol and 8 l. of water cooled to 5° was added a solution of potassium hypochlorite prepared from 148.5 g. of "H. T. H.," 109 g. of potassium carbonate, and 29.1 g. of potassium hydroxide. The temperature was not allowed to rise above 5° during the addition. After approximately three-fourths of the hypochlorite had been added, the mixture suddenly became milky in appearance. Stirring was continued for 1.0 hr. after addition was complete. The nearly colorless solid was filtered, washed with a small amount of ice-cold water, and dried overnight in a vacuum desiccator. The yield was 192 g. (85%), m.p. 41-43°; reported (4) m.p. 44-45°. The material is sufficiently pure for the next step, and recrystallization is not recommended because of decomposition at elevated temperatures.

4-Acetamido-3-methylbiphenyl (XII).

Treatment of 139 g. (0.757 mole) of N-chloro-*o*-acetotoluidide (XI), m.p. 41-43°, with anhydrous C. P. benzene and aluminum chloride in the manner described by Barnett (4) gave 92 g. (54%) of tan 4-acetamido-3-methylbiphenyl (XII), m.p. 165-167°; reported (4) m.p. 168-171°.

4-Amino-3-methylbiphenyl Hydrochloride (XIII).

One hundred and fifty grams (0.667 mole) of 4-acetamido-3-methylbiphenyl (XII), m.p. 165-168°, in 3700 ml. of dilute (1:1) hydrochloric acid was refluxed with stirring for 24 hr., after which the mixture was cooled in ice. The solid hydrochloride was filtered, washed with a small amount of ice-cold water, and air-dried overnight to give 140 g. (96%) of 4-amino-3-methylbiphenyl hydrochloride (XIII), m.p. 230-235°.

4-Iodo-3-methylbiphenyl (XIV).

A mixture of 290 g. (1.32 moles) of 4-amino-3-methylbiphenyl hydrochloride (XIII), 1550 ml. of water, and 580 ml. of concentrated hydrochloric acid was cooled to 0° and a solution of 91.8 g. (1.33 moles) of sodium nitrite in 625 ml. of water was added dropwise over a period of 1.0 hr. with the temperature being maintained at 0-2°. After stirring for 1.0 hr. at 0-2°, 3.0 g. of urea was added, and stirring was continued for 15 min. The diazonium salt was decomposed by the dropwise addition of a solution of 766 g. (4.62 moles) of potassium iodide in 1 l. of water. After stirring for 3.0 hr., the pasty mixture was warmed to expel nitrogen, and 25 g. of solid sodium bisulfite was added to reduce any free iodine. The mixture was extracted with benzene; the benzene layer was washed with 10% sodium bisulfite and then with water. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed to afford 288 g. of a red oil. The product decomposed when distillation was attempted, but purification was accomplished by chromatographing a cyclohexane solution through an alumina column. Concentration of the eluates yielded 276 g. (71%) of a pale yellow oil. A sample of the oil was crystallized from ethanol to give colorless crystals, m.p. 35-36.5°.

Anal. Calcd. for C₁₃H₁₁I: C, 53.08; H, 3.77. Found: C, 53.23; H, 3.76.

2'',3'-Dimethyl-*p*-quaterphenyl (I). (a) Via the Ullmann Reaction.

Seventy-seven grams (0.262 mole) of 4-iodo-3-methylbiphenyl (XIV) was warmed to 200° and three 5 g. portions of copper bronze (O. Hommel Co., Pittsburgh, Pa., 5347) were added with stirring. The temperature was slowly raised to 270°, and 85 g. of copper bronze was added over a period of 5.0 hr. The reaction mixture was allowed to cool and was extracted with large amounts of benzene. The benzene solution was filtered, the solvent was removed, and the residue was dissolved in cyclohexane. The cyclohexane solution was chromatographed through an alumina column, the eluates were concentrated, and upon cooling 19.64 g. (45%) of 2'',3'-dimethyl-*p*-quaterphenyl (I), m.p. 173-175°, crystallized. Repeated crystallizations from cyclohexane gave colorless crystals, m.p. 176-176.5°; reported (20) m.p. 176°.

(b) Via the Grignard Reaction.

About one-fourth of a solution of 71.0 g. (0.241 mole) of 3-methyl-4-iodobiphenyl (XIV) in 250 ml. of anhydrous ether was added to 32.0 g. (0.245 g.-atom) of magnesium turnings in 50 ml. of anhydrous ether under a stream of dry nitrogen. The reaction started immediately, and the remaining solution was added at such a rate as to maintain gentle refluxing. The reaction mixture was refluxed for 8.0 hr., during which time the magnesium had completely disappeared. A suspension of 31.4 g. (0.242 mole) of anhydrous cobaltous chloride in anhydrous ether was then added in portions over a period of 1.0 hr. The reaction mixture was refluxed for 3.0 hr., allowed to cool, and hydrolyzed with 10% hydrochloric acid. The mixture was extracted with benzene and dried, and the solvent was removed to yield a brown solid. Recrystallization of the residue from cyclohexane gave 12.26 g. (30%) of 2'',3'-dimethyl-*p*-quaterphenyl (I), m.p. 173-175°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 265 μ

(4.63). The fluorescence spectrum of I was determined using an activating wavelength of 295 μ , and λ max (fluorescence) was 345 μ .

2'',3'-Bis(bromomethyl)-*p*-quaterphenyl (XV).

The preparation of XV was accomplished by the addition of 13.9 g. (0.0782 mole) of *N*-bromosuccinimide (Arapahoe Chemicals, Inc., 401) to 12.3 g. (0.0368 mole) of 2'',3'-dimethyl-*p*-quaterphenyl (I), m.p. 175-176°, and 0.13 g. of benzoyl peroxide dissolved in 250 ml. of anhydrous carbon tetrachloride. The mixture was gently refluxed with stirring for 1.0 hr. before the reaction began. After refluxing for 24 hr., the reaction mixture was allowed to cool and then filtered, and the filtrate was concentrated on a steam bath. The oily residue was crystallized from benzene to give 13.85 g. (76%) of 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV) as a pale yellow solid, m.p. 164-167°. Repeated crystallizations from benzene gave colorless crystals, m.p. 172-173°; reported (5) m.p. 172-173°.

6,7-Dihydro-6-methyl-3,9-diphenyl-5*H*-dibenzo[*c,e*]azepine (III).

A solution of 1.35 g. (0.0027 mole) of 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV), m.p. 168-170°, in 40 ml. of anhydrous benzene was added dropwise to a stirred solution of 0.372 g. (0.012 mole) of methylamine in 10 ml. of dry benzene. The temperature was kept below 30° during the addition. Shortly after the beginning of the addition, methylammonium bromide began to precipitate. Stirring was continued at 30° for 3.0 hr., and then the mixture was slowly warmed to 70° and kept at this temperature for 1.0 hr. The reaction mixture was allowed to cool and stand overnight. The mixture was filtered, the precipitate was washed with benzene, and the filtrate was repeatedly extracted with water. The benzene layer was extracted with 10% hydrochloric acid, and the acidic layers were made alkaline. The liberated base was extracted with ether, and the solvent was removed on a steam bath to yield 0.75 g. (69%) of nearly colorless solid, m.p. 214-216°. Repeated crystallizations from benzene gave an analytical sample of III as a colorless solid, m.p. 215-216°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 290 μ (4.55). The fluorescence spectrum of III was determined using an activating wavelength of 311 μ , and λ max (fluorescence) was 370 μ .

Anal. Calcd. for $C_{27}H_{23}N$: C, 89.71; H, 6.41. Found: C, 89.76; H, 6.27.

5,6-Dihydro-3,9-diphenyldibenzo[*c,e*]thiepin (IV).

A mixture of 75 ml. of methanol, 100 ml. of dioxane, 10 ml. of water, 1.67 g. (0.0034 mole) of 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV), m.p. 168-170°, and 2.76 g. (0.0115 mole) of sodium sulfide nonahydrate was refluxed with vigorous stirring for 24 hr. The solvent was removed by distillation, the residue was treated with ice-water, and the crude solid was collected and crystallized from benzene to yield 0.7 g. (56%) of 5,7-dihydro-3,9-diphenyldibenzo[*c,e*]thiepin (IV), m.p. 272-276°. Repeated crystallizations from ethanol gave an analytical sample, m.p. 273.5-274.5°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 286 μ (4.51). The fluorescence spectrum of IV was determined using an activating wavelength of 310 μ , and λ max (fluorescence) was 360 μ .

Anal. Calcd. for $C_{26}H_{20}S$: C, 85.68; H, 5.54. Found: C, 85.44; H, 5.61.

5,7-Dihydro-3,9-diphenyldibenzo[*c,e*]selenepin (V).

A potassium selenide solution was prepared by passing hydrogen selenide gas (21) into a solution containing 0.88 g. of potassium hydroxide in 10 ml. of water until saturated. To this solution was then added an additional 0.88 g. of potassium hydroxide in 5 ml. of water. The resulting potassium selenide solution (ca. 15 ml., ca. 0.015 mole) was added to 300 ml. of acetone and 1.75 g. (0.0036 mole) of 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV), and the resulting solution was refluxed with vigorous stirring for 24 hr., after which time about 275 ml. of the acetone was removed by distillation. Approximately 100 g. of ice was added to the residue, and the precipitated solid was removed by filtration. The gummy precipitate was extracted with benzene, dried over magnesium sulfate and filtered, and the solution was concentrated on a steam bath. Upon cooling, 0.81 g. (55%) of 5,7-dihydro-3,9-diphenyldibenzo[*c,e*]selenepin (V), m.p. 267-268°, crystallized as a brown solid. An analytical sample purified by recrystallization from benzene was obtained as a colorless powder, m.p. 267-268°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 288 μ (4.55). The fluorescence spectrum of V was determined using an activating wavelength of 318 μ , and λ max (fluorescence) was 355 μ .

Anal. Calcd. for $C_{26}H_{20}Se$: C, 75.90; H, 4.90. Found: C, 75.70; H, 4.96.

6,6-Dicarbethoxy-6,7-dihydro-3,9-diphenyl-5*H*-dibenzo[*a,c*]cycloheptene (VI).

To a solution of ethyl disodiummalonate prepared by the addition of 0.48 g. (0.003 mole) of ethyl malonate in 25 ml. of anhydrous ether to a sodium ethoxide solution [prepared by a reaction of 0.138 g. (0.006 g.-atom) of sodium with 10 ml. of absolute ethanol] was added 1.19 g. (0.0024 mole) of 2'',3'-bis(bromomethyl)-*p*-quaterphenyl (XV), m.p. 167-169°, in 75 ml. of anhydrous dioxane. After refluxing for 6 hr., the reaction mixture was filtered and extracted with benzene, and the solvent was removed on a steam bath to give a colorless solid residue. Crystallization from a 1:3 mixture of benzene-cyclohexane gave 1.07 g. (91%) of 6,6-dicarbethoxy-6,7-dihydro-3,9-diphenyl-5*H*-dibenzo[*a,c*]cycloheptene (VI), m.p. 185-190°. An analytical sample, m.p. 189-190°, was prepared by recrystallization from a 1:3 mixture of benzene and cyclohexane. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 296 μ (4.65). The fluorescence spectrum of VI was determined using an activating wavelength of 310 μ , and λ max (fluorescence) was 368 μ .

Anal. Calcd. for $C_{33}H_{30}O_4$: C, 80.79; H, 6.16. Found: C, 80.76; H, 6.26.

2,6-Dimethylacetanilide (XVI).

To a stirred solution of 100 g. (0.825 mole) of freshly distilled 2,6-dimethylaniline (Eastman Kodak Co., 1736), 690 ml. of concentrated hydrochloric acid, and 1.7 l. of water was added 97.5 ml. of acetic anhydride. As soon as the acetic anhydride went into solution, 101 g. (1.24 moles) of sodium acetate in 400 ml. of water was added. The reaction mixture was allowed to stir for 1.0 hr. and then was cooled to 5° and filtered. The crude product was recrystallized from benzene to yield 117 g. (87%) of 2,6-dimethylacetanilide (XVI), m.p. 179-180°; reported (22) m.p. 176°.

N-Chloro-2,6-dimethylacetanilide (XVII).

To a stirred solution of 49 g. (0.301 mole) of 2,6-dimethylacetanilide (XVI), m.p. 179-180°, and 50 g. (0.498 mole) of potassium bicarbonate in 9 l. of water cooled to 5° was added a solution of potassium hypochlorite prepared from 31.2 g. of "H. T. H.," 23.9 g. of potassium carbonate, and 6.82 g. of potassium hydroxide. The temperature was not allowed to rise above 5° during the addition. After all of the hypochlorite had been added, the mixture suddenly became milky in appearance. Stirring was continued for 1.0 hr. after addition was complete. The nearly colorless solid was filtered, washed with a small amount of ice-cold water, and dried overnight in a vacuum desiccator. The yield was 49 g. (82%), m.p. 110-112°; reported (23) m.p. 112-113°.

4-Acetamido-3,5-dimethylbiphenyl (XVIII).

To a stirred, cold solution of 91 g. (0.461 mole) of *N*-chloro-2,6-dimethylacetanilide (XVII), m.p. 110-112°, in 1870 ml. of anhydrous *C. P.* benzene was added, in portions, 186 g. (1.39 moles) of anhydrous aluminum chloride. After stirring for 5 hr. at 7°, the reaction mixture was poured over ice. The benzene was removed by steam distillation, and the resulting slurry was filtered. Crystallization of the brown solid from ethanol (Norit) gave 50.5 g. (46%) of 4-acetamido-3,5-dimethylbiphenyl (XVIII) as a colorless solid, m.p. 203-204°; reported (24) m.p. 203-204°.

4-Amino-3,5-dimethylbiphenyl (XIX).

To 55 g. (0.230 mole) of 4-acetamido-3,5-dimethylbiphenyl (XVIII), m.p. 200-202°, was added 150 ml. of 100% phosphoric acid prepared from 86 g. of phosphorus pentoxide and 200 g. of 85% phosphoric acid. The reaction mixture was stirred for 2.0 hr. at 200°, allowed to cool, neutralized with potassium hydroxide, and extracted with benzene. The benzene solution was dried over magnesium sulfate, and the solvent was removed on a steam bath to yield a brown oily residue which was dissolved in cyclohexane. The solution was chromatographed through an alumina column, and concentration of the eluates afforded 33 g. (72%) of pale yellow oil; reported as a brown oil (24). The product XIX was sufficiently pure for the next step.

4-Iodo-3,5-dimethylbiphenyl (XX).

A hot solution of 33 g. (0.168 mole) of 4-amino-3,5-dimethylbiphenyl (XIX) in 34.2 g. (0.349 mole) of sulfuric acid and 450 ml. of water was cooled to 0°, and a solution of 11.56 g. (0.169 mole) of sodium nitrite in 50 ml. of water was added over a period of 45 min. After stirring for 15 min., 2.0 g. of urea was added, and a solution of 74.6 g. (0.450 mole) of potassium iodide in 150 ml. of water was added dropwise over a period of 30 min. After stirring for 4.0 hr., the reaction mixture was warmed on a steam bath until the evolution of gases ceased. The reaction mixture was treated with sodium bisulfite and extracted with benzene, and the organic layer was dried over magnesium sulfate. The benzene solution was chromatographed through an alumina column, and the eluates were concentrated to afford a red oil. The viscous oil was distilled to give a colorless solid, b.p. 150-155° at 0.1 mm. Recrystallization from ethanol

(Norit) gave 24.7 g. (45%) of 4-iodo-3,5-dimethylbiphenyl (XX) as colorless needles, m.p. 69-70°. Repeated crystallization from ethanol gave an analytical sample, m.p. 69.5-70.5°.

Anal. Calcd. for $C_{14}H_{13}I$: C, 54.57; H, 4.25. Found: C, 54.55; H, 4.17.

2'', 3', 5', 6''-Tetramethyl-*p*-quaterphenyl (II).

About one-fourth of a solution of 5.0 g. (0.016 mole) of 4-iodo-3,5-dimethylbiphenyl (XX), m.p. 69-70°, in 25 ml. of anhydrous ether was added to 0.4 g. (0.0165 g.-atom) of magnesium turnings in 15 ml. of anhydrous ether under a stream of dry, oxygen-free nitrogen. The reaction started immediately upon warming, and the remaining solution was added rapidly enough to maintain gentle refluxing. After the addition was completed, the reaction mixture was refluxed for 4 hr., during which time the magnesium had completely reacted. A suspension of 2.3 g. (0.0175 mole) of anhydrous cobaltous chloride in anhydrous ether was then added in portions over a period of 15 min. The reaction mixture was then refluxed for 3 hr., allowed to cool, and hydrolyzed with 5% hydrochloric acid. The mixture was extracted with benzene, and the benzene solution was dried over magnesium sulfate, filtered, and rid of solvent on a steam bath to afford a brown solid residue. Recrystallization of the residue from ethanol (Norit) gave 0.61 g. (21%) of 2'', 3', 5', 6''-tetramethyl-*p*-quaterphenyl (II) as colorless needles, m.p. 175-176°. An analytical sample, m.p. 175.5-176°, was obtained by repeated crystallization from ethanol. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 264 $m\mu$ (4.94). The fluorescence spectrum of II was obtained using an activating wavelength of 280 $m\mu$, and λ max (fluorescence) was 325 $m\mu$.

Anal. Calcd. for $C_{28}H_{28}$: C, 92.77; H, 7.23. Found: C, 92.87; H, 7.44.

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Albuquerque, New Mexico
Los Alamos, New Mexico