Alternant Conjugate Systems. I. Syntheses and Properties of Polytolans

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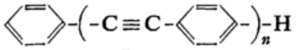
(Received March 7, 1961)

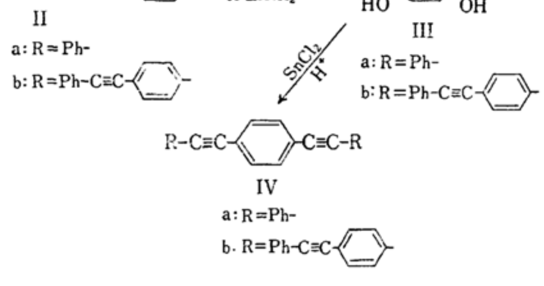
Alternative insertion of benzene nuclei between the triple bonds of the polyacetylenic chain of α,ω-diphenylpolyyne constitutes an interesting conjugate system, polytolan (I). The present author has investigated the syntheses of a series of polytolans (I; $n=2, 3, 4$) to compare their ultraviolet spectroscopic properties with those of polyphenylpolyene[1] and diphenylpolyacetylene.



I

The several methods[2-4] proposed for the synthesis of tolan all seem to be inadequate to the syntheses of the higher homologues owing to the poor solubility or the difficulty in the syntheses of the intermediates.

During the course of a study concerning the reaction of quinones with acetylenes, the author has found that polytolans having an even number of n can be synthesized according to the following series of reactions. For example, the reaction of sodium phenylacetylide(IIa) in



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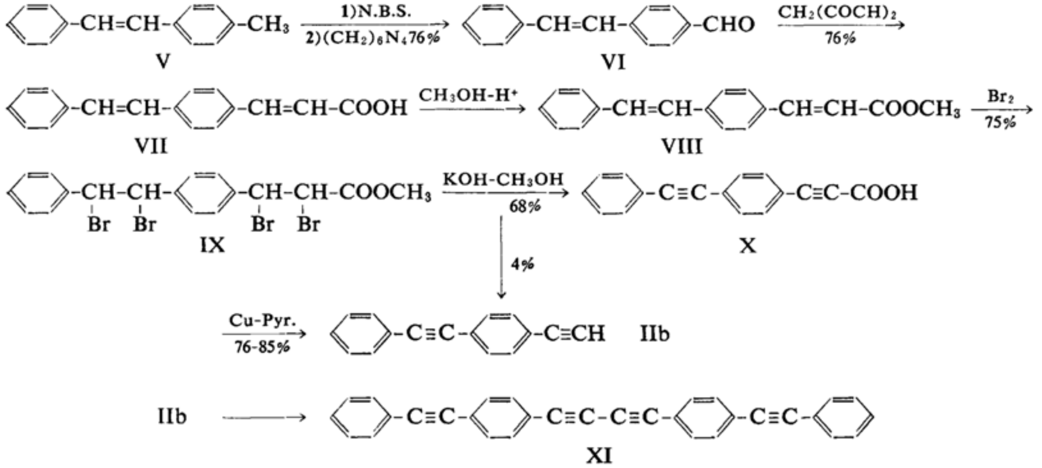
liquid ammonia with *p*-benzoquinone afforded the diacetylenic glycol (IIIa) in a yield of 31%. The reductive aromatization of IIIa with phosphorus diiodide or stannous chloride[5] resulted in the formation of distolan(IVa)[6]. Independently, IVa was synthesized by Ried according to essentially the same procedure[7]. The generalization of the reductive aromatization was achieved by his employing several kinds of quinones[7].

The present author has employed this method for the synthesis of tetrakistolan (I; $n=4$). The reaction of *p*-benzoquinone with the sodium salt of *p*-ethynyltolan (IIb) in liquid ammonia, in which IIb and its sodium salt are sparingly soluble, resulted in a recovery of the starting materials. As it was known that a lithium salt of an ethynyl compound has a larger solubility than a salt of other alkali metal[8], the reaction of the lithium salt of IIb with *p*-benzoquinone was carried out in dioxane, yielding tetra-acetylenic glycol(IIIb) in a yield of 13%. The reductive aromatization of IIIb afforded tetrakistolan (IVb) as light yellow needles with a green fluorescence. The solutions of IVb in various organic solvents exhibit an intense and characteristic violet fluorescence.

p-Ethynyltolan (IIb), which was used as a starting material for the synthesis of IVb, was synthesized according to the following series of reactions. A quantitative yield of the ester (VIII) was obtained by refluxing the suspension of *p*-styrylcinnamic acid (VII)[9] in methanol containing a catalytic amount of sulfuric acid. The dehydrobromination of the tetrabromide (IX) resulted in *p*-phenylethynyl-phenylpropiolic acid (X), together with a small amount of decarboxylated product (IIb). Several methods have been proposed for the decarboxylation of substituted phenylpropiolic acids[10-11], but the author has found that the acid (X) in pyridine or quinoline was smoothly decarboxylated to IIb in the presence of copper powder. Extension of the synthetic route of phenylacetylene[12] from cinnamic acid to styrylcinnamic acid (VII) was found to be unsuccessful owing to the poor solubility of the intermediate tetrabromide in various solvents.

p-Ethynyltolan (IIb) crystallizes in the form of colorless needles and gives amorphous yellow cuprous salt. Its mercuric acetylide was obtained in well-defined fine silky needles. As illustrated in Fig. 1, the ultraviolet spectrum of IIb was found to be closely related to tolan rather than to phenylacetylene, with a red-shift of ca. 15 mμ. The oxidative coupling of IIb according to Eglinton's method[13] afforded bis(*p*-phenylethynyl-phenyl)diacetylene (XI) as colorless plates. The disappearance of fine structure in the ultraviolet spectrum of XI as compared with that of diphenyldiacetylene is remarkable (Fig. 1).

Tristolan (I; $n=3$) was synthesized from



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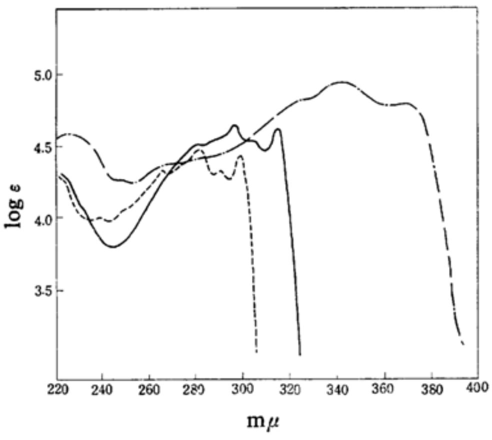

Fig. 1. The ultraviolet spectra of *p*-ethynyltolan (IIb, ——) and tolan (----) in *n*-hexane and bis(*p*-phenylethynylphenyl)-diacetylene (XI, —·—) in ethanol.

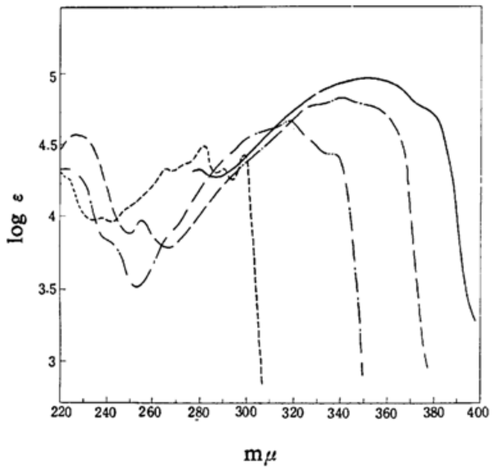

Fig. 2. The ultraviolet spectra of polytolans (I)
$n=4$, ——; $n=3$, —·—; $n=2$, —··—; $n=1$, ----

p,p'-distyrylstilbene[14] according to the procedure of Drefahl[2].

The ultraviolet spectra and the physical properties of these polytolans are presented in Fig. 2 and Table I. An examination of the ultraviolet spectra of polytolans indicates that an increase in the length of the conjugate system causes a displacement of the strongest absorption band towards a longer wavelength; this bathochromic displacement, however, becomes smaller for each additional $-C_6H_4-C\equiv C-$ grouping. Two empirical formulae ($\lambda=kn+\lambda_0$ or $\lambda=k\sqrt{n}+\lambda_0$) have been proposed to relate the number of double bonds in a conjugated chromophore group (n) with the wavelength of the absorption maximum (λ)[15], but the absorption maxima of polytolans could not be expressed by either of these empirical formulae, because the plot of the wavelength of the absorption maxima against n or the square root of n does not give a straight line, as is illustrated in Fig. 3.

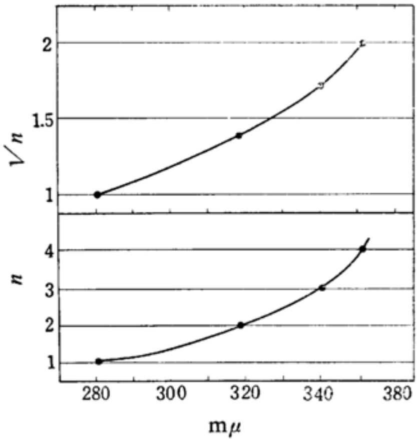

Fig. 3. Wavelength positions of the main absoption maxima plotted against number or n $\sqrt{n}$ of polytolans (I).

The spectra of tristolan (I; $n=3$) and tetrakistolan (I; $n=4$) showed absorption maxima at 256 and 279 mμ respectively. Similar maxima are also observed in the spectra of the corresponding ethylenic analogues. The occurrence of these bands can presumably be attributed to a higher order transition of the total chromophore, as is pointed out by Dale[16] and Zechmeister et al.[17].

The ultraviolet spectra of diphenylpolyacetylenes exhibit a regular bathochromic shift in accordance with the increase of the number of acetylenic linkage, also, the fine structure of the spectra becomes more and more distinct with the increase in the length of the conjugate system[18]. The same trend is also recognized in the case of diphenylpolyenes[19]. Kortüm attributed the increase in the fine structure of the spectra of diphenyl-polyyne and -polyene to the increase of the double bond character of single bonds in these conjugate systems. The increase in double bond character results

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[14] The synthesis of this substance will be reported on the following paper.

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TABLE I. PROPERTIES OF POLYTOLANS AND RELATED COMPOUNDS

	M.p., °C	Fluorescence		UV spectrum	
		Solid	Solution	λ_{max}, mμ	Solvent
Distolan(I : n=2)	181.5～182	—	Light violet	222, 318, 337	a
Tristolan(I : n=3)	283 ～285	Light green	Violet	226, 256, 325*, 340	c
Tetrakistolan(I : n=4)	307 ～312	Light green	Intense violet	279, 351, 378*	b
p-Ethynyltolan(IIb)	90.5～91	—	—	279, 288*, 295, 303, 314	a
(XI)	229 ～229.5	—	Violet	225, 268*, 326*, 342, 368	d

* inflexion ; a : n-hexane, b : benzene, c : chloroform, d : 95% alcohol

in a fixation of the molecule in a uniplanar conformation and necessarily retards the torsional vibration of the molecule[20].

On the contrary, the fine structure in the spectra of polytolans gradually becomes obscure with the increase in the length of the alternant conjugate system. The distinct fine structure observed in the spectrum of tolan can be traced in that of distolan (IVa), but the spectra of tris- and tetrakis-tolan show only a weak inflection at the corresponding positions, as is illustrated in Fig. 2. The single bond length of the C_6H_5–C≡ grouping has been reported to be almost identical in the series of diphenylpolyyne, whereas a distinct contraction of the single bond length inserted between two acetylenic linkages was observed in the same series, as is summarized in Table II. These results indicate that the single bond in the C_6H_5–C≡ grouping has a minor degree of multiple bond character as compared with the single bond in ≡C–C≡ grouping. Consequently, an insertion of the p-phenylene group in a position of single bond in a conjugate polyyne chain may cause an increase of torsional vibration about the single bond of the ≡C–C_6H_4–C≡ grouping. Also, the increase in the number of single bond with a minor multiple bond character may increase the transition energy of photo-ecxitation. The disappearance of the fine structure and the hypsochromic shift of absoption maxima in the spectra of polytolans as compared with those of diphenylpolyynes seem to be attributable to the above-mentioned two reasons. This inference is also cosistent with the fact that p-ethynyltolan and tolan show quite similar absorption curves (Fig. 1) and the fact that the fine structure which is observed in the spectrum of diphenyldiacetylene is almost lost in the absorption curve of bis(p-phenylethynyl-phenyl)diacetylene (XI) (Fig. 1).

TABLE II. SINGLE BOND LENGTHS IN DIPHENYLPOLYYNE Ph–(C≡C)$_n$–Ph

n	Bond length of Ph–C≡ Å	Bond length of ≡C–C≡ Å	Ref.
1	1.40	—	21
2	1.44	1.39	22
4	1.42	1.37, 1.33, 1.37	23
5	1.45	1.39, 1.33, 1.33, 1.39	23

The ultraviolet spectrum of distolan reported by Drefahl[2] showed a strong inflection at ca. 350 mμ which could not be observed in the spectrum of the compound prepared by the author. The presence of inflection at this wavelength seems to arise from a contamination with the starting material, p-distyrylbenzene (λ_{max} 350 mμ) or p-styryltolan (λ_{max} 333 ; $\lambda_{infl.}$ 352 mμ).

Experimental*

1, 4-Bisphenylethynyl-2, 5-cyclohexadien-1, 4-diol (IIIa).—To a solution of sodium amide (prepared from sodium, 3.8 g., 0.167 mol.) in liquid ammonia (100 ml.) was added dropwise phenylacetylene (17 g., 0.167 mol.) in dry ether (50 ml.). After stirring for 2 hr., p-benzoquinone (10 g., 0.093 mol.) in dry tetrahydrofuran (70 ml.) was dropped into the mixture over a period of 3 hr. A transient development of blue color was observed on the addition of the quinone, and the entire mixture gradually changed to a deep brown solution. Ammonia was evaporated after the addition of ammonium chloride, and the residual solid was extracted with ethyl acetate. The extract was thoroughly washed with water and dried. After removal of the solvent, the residue was dissolved in ethyl acetate-benzene and passed through a short column of alumina. The crude crystals obtained on concentrating the solvent were recrystallized from benzene to give IIIa, colorless leaflets, m. p. 176～177°C, yield 8.1 g. (31.2%). (Ried[7] reported a yield of 50～55% employing lithium amide.)

Found : C, 84.47 ; H, 5.04. Calcd. for $C_{22}H_{16}O_2$: C, 84.59 ; H,5.16%.

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* All melting points are uncorrected.

IR max(cm^{-1}) 3320, 3260(ν_{OH}), 2225($\nu_{C\equiv C}$), 1007(δ_{OH}).

***p*-Bis(phenylethynyl)benzene [Distolan] (I : n=2)**—A solution of stannous chloride dihydrate (1.0 g.) in concentrated hydrochloric acid (3.0 ml.) was added to a stirred solution of the glycol (IIIa, 388 mg.) in tetrahydrofuran (20 ml.), and the mixture was stirred for several hours at room temperature. After standing overnight, the reaction mixture was poured into water and extracted with benzene. The extract was washed with water and dried. After removal of the solvent, the residue was dissolved in light petroleum-benzene (1 : 1, 10 ml.). The solution was then chromatographed over alumina and eluted with the same solvent, resulting in crude crystals. This was recrystallized from dry ethanol, yielding IVa, m. p. 172∼175°C, 115 mg. (33.1%). Sublimation of this material in vacuo (160∼175°C/15 mmHg) afforded pure IVa, colorless needles.

Found : C, 95.12 ; H, 5.12. Calcd. for $C_{22}H_{14}$: C, 94.93 ; H, 5.07%.

IVa was also obtained in a yield of ca. 20% by a reductive aromatization of IIIa with phosphorus diiodide.

***p*-Bis(β-phenylethyl)benzene.**—IVa in dry tetrahydrofuran was catalytically reduced over palladium-charcoal (5%). After removal of the catalyst, the reduction product obtained by evaporating the solvent was recrystallized twice from ethanol to yield *p*-bis(β-phenylethyl)benzene, on colorless plates, m. p. 90.5∼91°C.

Found : C, 92.59 ; H, 7.67. Calcd. for $C_{22}H_{22}$: C, 92.26 ; H, 7.74%.

***p*-Stilbenealdehyde(VI).**—VI was prepared according to the procedure of Drefahl[9] with slight modifications, m. p. 113∼114°C., 76% yield (lit. value, m. p. 116∼117°C.).

IR max.(cm^{-1}) 1695($\nu_{C=O}$), 1205, 1165(-CHO), 968($\delta_{=CH-}$).

***p*-Styrylcinnamic Acid (VII).**—Stilbenealdehyde (VI, 30.2 g., 0.145 mol.) and malonic acid (31 g., 0.29 mol.) were dissolved in a mixture of pyridine (60 ml.) and piperidine (1.5 ml.). A vigorous evolution of carbon dioxide was observed when the solution was warmed to 60∼65°C. The solution was kept at 100°C for 3 hr. and then refluxed for 2 hr. The cooled reaction mixture was poured onto crashed ice (300 g.) containing hydrochloric acid (100 ml.). The precipitate was then filtered and washed with water. Recrystallization of this material from acetic acid yielded VII, on lustrous light yellow plates, m. p. 255∼256°C, 27.5 g. (76%) (lit. value, m. p. 256∼258°C, 70%)[9].

IR max.(cm^{-1}) 1685($\nu_{C=O}$), 1427, 1278(-COOH), 959($\delta_{=CH-}$).

Methyl *p*-Styrylcinnamate (VIII).—A few milliliters of concentrated sulfuric acid was added to a suspension of styrylcinnamic acid (VII, 20 g.) in methanol (600 ml.), and the mixture was refluxed for 10 hr. The crystals of the acid gradually changed to pale greenish yellow plates. The cooled reaction mixture was then filtered. The crystals obtained by concentrating the filtrate were combined with the first crop and recrystallized from carbon tetrachloride, resulting in VIII, on light yellow plates, m. p. 185.5∼186°C, 20.4 g. (97%).

Found : C, 81.79 ; H, 6.18. Calcd. for $C_{18}H_{16}O_2$: C, 81.79 ; H, 6.10%.

UV max(mμ) 236(ε=8,000), 345(24,000) (in 95% ethanol)

IR max(cm^{-1}) 1717($\nu_{C=O}$), 1169, 1114(-COOCH$_3$), 980, 969, 961($\delta_{=CH-}$).

Methyl *p*-Styrylcinnamate Tetrabromide (IX).—Bromine (30.0 g., 0.19 mol.) in chloroform (30 ml.) was gradually added to a stirred solution of the ester (VIII, 20.4 g., 0.077 mol.) in chloroform (700 ml.) under cooling with running water. The large amount of crystals deposited made the agitation of the reaction mixture impossible after about two-thirds of bromine had been added. After all the bromine had been introduced, the mixture was warmed to 40°C to complete the reaction. The crystals were filtered and washed with a small amount of chloroform, yielding the tetrabromide, 33.8 g. (75%), m. p. 235∼238°C (decomp.). Further recrystallization from acetic acid afforded a pure material, colorless scale-like crystals, m. p. 242°C (decomp.).

Found : Br, 54.25. Calcd. for $C_{18}H_{16}O_2Br_4$: Br, 54.74%.

***p*-Phenylethynyl-phenylpropiolic Acid (X).**—The tetrabromide (IX, 34 g., 0.058 mol.) was intimately mixed with finely powdered potassium hydroxide (90 g., 0.6 mol.) and absolute methanol (400 ml.) was added in one portion to the mixture. After the vigorous reaction had ceased, the mixture was refluxed for 8 to 10 hr. The cooled reaction mixture was poured into water (600 ml.), and the potassium propiolate deposited was filtered and washed with a small amount of water. The combined filtrate and washing were extracted with ether. The ethereal extract was washed with water and dried. The residue obtained by removing the solvent was dissolved in light petroleum (b. p. 60∼70°C.) and passed through a short column of alumina. Recrystallization of the crude crystals which were obtained by concentrating the filtrate gave IIb, pale yellow needles, 0.5 g. (4.3 %), m. p. 87∼89.5°C.

The above-mentioned potassium salt was dissolved in hot methanol (400 ml.) and treated with active charcoal. On acidification of the methanolic solution with concentrated hydrochloric acid, crude *p*-phenylethynyl-phenylpropiolic acid (X) was obtained as crystals, m. p. 200∼203°C, 9.7 g. (68%). Further purification was carried out by repeating the precipitation of the acid (X) from the methanolic solution with the addition of water, while a decomposition was observed when a solution of the acid is heated, especially in the presence of active charcoal. The pure material melts at 206∼207°C.

Found : C, 82.67 ; H, 4.15. Calcd. for $C_{17}H_{10}O_2$: C, 82.91 ; H, 4.09%.

IR max. (cm^{-1}) 2205($\nu_{C\equiv C}$), 1667($\nu_{C=O}$), 1440, 1295(-COOH).

***p*-Ethynyltolan (IIb).**—To a solution of the propiolic acid (X, 1 part) in pyridine (10 parts) was added copper powder (0.1 part). The evolution of carbon dioxide was observed immediately, and in a few minutes the reaction mixture began to froth vigorously. After the vigorous reaction had subsided, the mixture was refluxed for 40~60 min. To the cooled reaction mixture was added light petroleum (b. p. 60~70°C), and copper powder was removed by filtration. The filtrate was washed repeatedly with 2 N hydrochloric acid and then with aqueous sodium hydroxide and water successively. Concentration of the dried filtrate resulted in light brown needles, m. p. 78~83°C (yield, 76~85%). The crude ethynyltolan thus obtained was purified through chromatography over alumina, as the crude material was contaminated with a small amount of the propiolic ester. Recrystallization of the eluate from light petroleum gave pure IIb.

Found: C, 94.72; H, 4.98. Calcd. for $C_{16}H_{10}$: C, 95.02; H, 500%.

IR max.(cm^{-1}) 3260($\nu_{\equiv CH}$).

The mercuric acetylide which was prepared according to the method of Johnson[24] was recrystallized from ethanol-benzene, yielding silky long needles, m. p. 244~245°C.

IR max.(cm^{-1}) 2150 ($\nu_{C\equiv C}$).

Bis(*p*-phenylethynyl-phenyl)diacetylene (XI).—Cupric acetate monohydrate (7.5 g.) was added to a solution of *p*-ethynyltolan (IIb, 0.5 g.) in dry pyridine (50 ml.). The mixture was stirred for 8 hr. at 60~75°C. The reation mixture was diluted with benzene (200 ml.) and washed with 2 N hydrochloric acid, aqueous sodium hydroxide and water successively. The benzene solution was dried and the solvent removed, yielding a red solid. The crude material was washed twice with a small amount of light petroleum. The light yellow crystals thus obtained were recrystallized twice from benzene to give pure XI, on colorless plates.

Found: C, 95.04; H, 4.61. Calcd. for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

1, 4-Bis(*p*-phenylethynyl-phenylethynyl)-2, 5-cyclohexadien-1, 4-diol (IIIb).—Dry dioxane (50 ml.) was added to a solution of lithium amide (prepared from lithium, 0.1 g., 14.3 mmol.) in liquid ammonia, and the ammonia was evaporated, resulting in a light pink solution. Into this solution was stirred *p*-ethynyltolan (IIb, 3 g., 14.8 mmol.) in dry dioxane (10 ml.). The color of the solution gradually changed from yellow to a transparent dark brown. After warming to 50°C for 20 min., the mixture was refluxed for 10 min. to expel the remaining ammonia and then cooled to room temperature. Under vigorous stirring, a solution of *p*-benzoquinone (0.8 g., 7.5 mmol.) in dry dioxane (20 ml.) was slowly added to the mixture over a period of 4 hr. A transient development of blue color was observed, and the color of the mixture changed to brown, forming a large amount of precipitate. The reaction mixture was stirred for ca. 20 hr. at room temperature and then refluxed for 3 hr. The cooled reaction mixture was introduced into water (500 ml.) and extracted with ethyl acetate. The extract was washed with water, dried and chromatographed over alumina. The crystalline fractions were recrystallized from benzene, yielding the glycol (IIIb), in the form of fine, long silky needles, m. p. 248~250°C., 475 mg. (12.6%).

Found: C, 88.90; H, 4.72. Calcd. for $C_{38}H_{24}O_2$: C, 89.04; H, 4.72%.

IR max.(cm^{-1}) 3580, 3460(ν_{OH}), 2230($\nu_{C\equiv C}$), 1025, 1000 (δ_{OH}).

1, 4-Bis (*p*-phenylethynyl-phenylethynyl) benzene [Tetrakistolan] (IVb).—To a warm solution of the glycol (IIIb, 245 mg.) in ethyl acetate (30 ml.) was added a solution of stannous chloride dihydrate (1 g.) in acetic acid (2 ml.) and ethyl acetate (2 ml.). The immediate deposition of a light yellow precipitate was observed. The mixture was then refluxed for 4 hr. and cooled. The precipitate was filtered (172 mg.) and dissolved in ethyl acetate. The solution was passed through a short column of alumina, and the filtrate was dried by evaporation. The residue, after recrystallization from chlorobenzene, gave tetrakistolan (IVb), in the form of light greenish yellow needles with a green fluorescence.

Found: C, 95.06; H, 4.81. Calcd. for $C_{38}H_{22}$: C, 95.37; H, 4.63%.

The author wishes to express his hearty thanks to Professor Masazumi Nakagawa for his helpful guidance throughout this work. The cost of this research was partly defrayed from the Scientific Research Expenditure of the Ministry of Education, to which author's thanks are also due.

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