Linear Conjugated Systems Bearing Aromatic Terminal Groups. VIII. Syntheses and Electronic Spectra of Bis(4-biphenylyl)- and 2,2′-Difluorenylpoly-ynes

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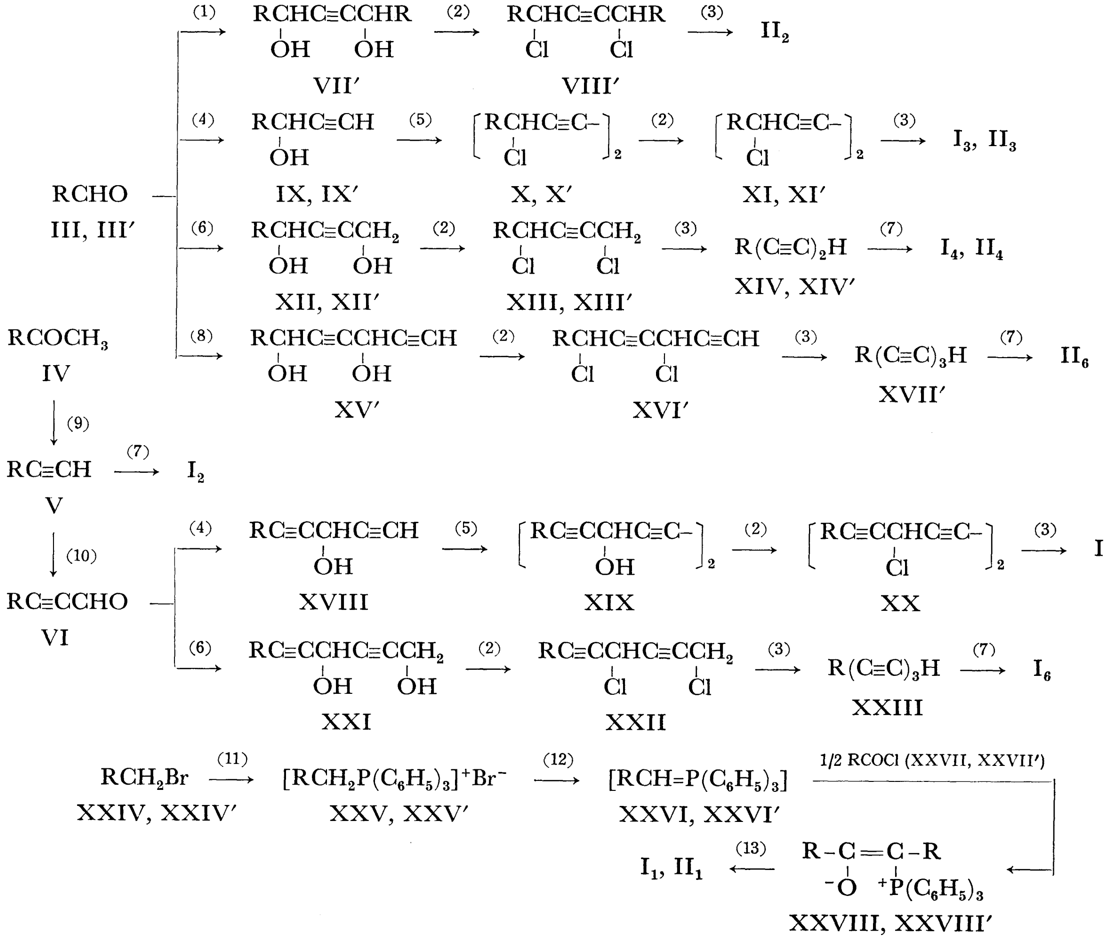
In order to get further information on the effect of terminal groups on the spectral regularity of diarylpoly-ynes, we carried out the syntheses of bis(4-biphenylyl)poly-ynes (I_n, $n=1$—6) and 2,2′-difluorenylpoly-ynes (II_n, $n=1$—4 and 6). The bathochromic shift of the longest-wavelength absorption maxima (λ_L) along with the increase in n was found to be expressed by the following empirical formulas:

$$I_n:\ \lambda_L = 24.0n^{1.1} + 304 \quad \text{(nm in tetrahydrofuran)}$$

$$II_n:\ \lambda_L = 9.0n^{1.5} + 350 \quad \text{(nm in tetrahydrofuran)}$$

The spectral behavior of bis(4-biphenylyl)poly-ynes (I_n) strongly supported the relationship $\lambda_L \propto n$ in diphenylpoly-ynes.

The syntheses and electronic spectral behavior of various diarylpoly-ynes [$Ar(C{\equiv}C)_nAr$] bearing condensed aromatic nuclei as terminal groups have been reported.[1] It was found that the bathochromic shift of the longest-wavelength absorption maxima (λ_L) can



Scheme 1. Syntheses of I_n and II_n

Roman numerals bearing prime indicate the fluorenyl series.
(1) $BrMgC{\equiv}CMgBr$/THF, (2) $SOCl_2$-pyridine/THF, (3) $NaNH_2$/liq. NH_3, (4) $HC{\equiv}CMgBr$/THF or $LiC{\equiv}CH$/liq. NH_3, (5) $CuCl$-NH_4Cl-O_2/CH_3OH, (6) $BrMgC{\equiv}CCH_2OMgBr$/THF, (7) $Cu(OCOCH_3)_2$/pyridine, (8) $BrMgC{\equiv}CCH(OMgBr)C{\equiv}CH$/THF, (9) i) PCl_5, ii) $NaNH_2$/liq. NH_3, (10) i) C_2H_5MgBr/THF, ii) DMF/THF, iii) dil. H_2SO_4, (11) $P(C_6H_5)_3$/benzene, (12) C_6H_5Li/toluene, (13) thermolysis. THF = tetrahydrofuran, DMF = dimethylformamide.

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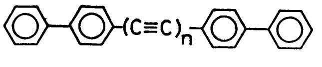
[1] K. Nakasuji, S. Akiyama, and M. Nakagawa, This Bulletin, **45**, 875 (1972) and references cited therein.

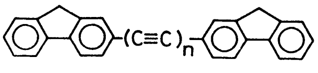
be expressed by the empirical formula

$$\lambda_L = An^x + B.$$

The value of x was found to depend on the nature of terminal group as well as on the position of linking of acetylenic chain. In view of the gradual change of the value of x, it was desirable to synthesize diarylpoly-ynes bearing non-condensed aromatic terminal groups to get further information on the effect of terminal groups on the electronic spectra of diarylpoly-ynes. In this paper, we will describe the syntheses and electronic spectral regularity of bis(4-biphenylyl)poly-ynes (I_n, n=1—6) and 2,2′-difluorenylpoly-ynes (II_n, n=1—4 and 6).



I_n



II_n

Syntheses. The reaction sequence used in the syntheses of I_n and II_n are shown in Scheme 1.

The formyl- (III, III′) and the propargylaldehyde derivatives (VI) are used as starting materials. In 4-biphenylyl series, the tri- and tetraacetylenes (I_3 and I_4) were obtained from formyl derivative (III), and propargylaldehyde (VI) was used in the preparation of penta- and hexaacetylenes (I_5 and I_6). 2,2′-Difluorenylpoly-ynes (II_n, n=1—4 and 6) were prepared from 2-formylfluorene (III′). Dehydrochlorination of intermediate chloro-compounds by means of sodium amide in liquid ammonia successfully applied to biphenylyl series resulted in the formation of decomposition products in fluorenyl series, presumably owing to the presence of acidic methylene group. The elimination reactions of fluorenyl series were achieved by means of sodium or potassium ethoxide in ethanol. An attempt to prepare 2,2′-difluorenylpentaacetylene (II_5) according to the following reaction sequence gave fruitless results in the final step: $RCHO \rightarrow RCH(OH)(C{\equiv}C)_2H \rightarrow RCH(OH)(C{\equiv}C)_4(HO)CHR \rightarrow RCHCl(C{\equiv}C)_4ClCHR \rightarrow R(C{\equiv}C)_5R$.

Monoacetylenes (I_1 and II_1) were prepared by the intramolecular Wittig reaction,[2] *i.e.*, by thermolysis of betaines (XXVIII and XXVIII′).

TABLE 1. PHYSICAL PROPERTIES OF I_n

n	Color of crystals	Mp (°C)	$\nu_{C\equiv C}$
1	colorless	253—254	—
2	colorless	232—233	2140
3	pale yellow	(*ca.* 250)	2185
4	yellow	(*ca.* 240)	2200
5	yellow	(*ca.* 200)	2180
6	orange yellow	(*ca.* 160)	2145

Numbers in parentheses indicate decomposition points.

TABLE 2. PHYSICAL PROPERTIES OF II_n

n	Color of crystals	Decomposition point (°C)	$\nu_{C\equiv C}$
1	colorless	*ca.* 295	—
2	pale yellow	*ca.* 280	—
3	yellowish brown	*ca.* 250	2190
4	orange yellow	*ca.* 210	2180
6	orange	*ca.* 150	2140

The physical properties of I_n and II_n are given in Tables 1 and 2.

The IR spectra of I_n and II_n exhibit the same characteristics observed in the other diarylpoly-ynes, *viz.*, the highest wave number of stretching vibration of acetylenic bond ($\nu_{C\equiv C}$) was observed in the cases of I_4 and II_3 and as illustrated in Fig. 1 the absorption intensity of $\nu_{C\equiv C}$ increased with the increase of n.

Electronic Spectra. The absorption curves and spectral data of I_n and II_n are summarized in Figs. 2 and 3, and Tables 3 and 4.

The marked difference in location of absorption maximum between biphenyl and fluorene has been

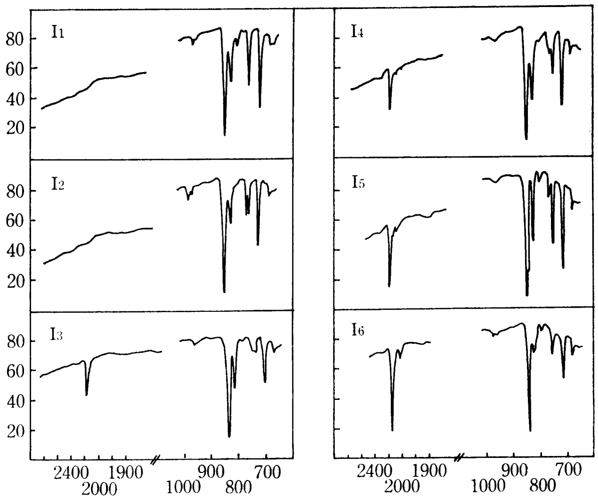


Fig. 1. The IR spectra of bis(4-biphenylyl)poly-ynes (I_n).

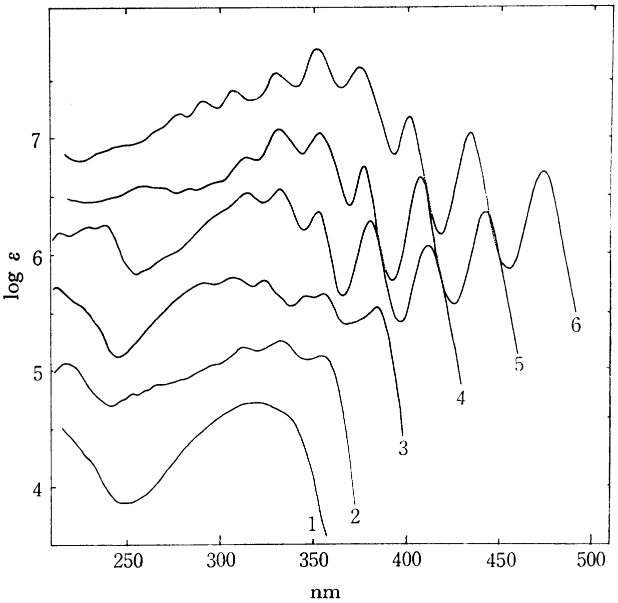


Fig. 2. The absorption curves of bis(4-biphenylyl)poly-ynes (I_n). The curves, with the exception of monoacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below (in tetrahydrofuran).

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[2] S. Akiyama, K. Nakasuji, and M. Nakagawa, This Bulletin, **44**, 2231 (1971).

Table 3. Electronic spectral data of I_n

n	λ_{max} (log ε) in nm in tetrahydrofuran										
1	319										
	(4.62)										
2	217	296*	313	332	355						
	(4.58)	(4.56)	(4.71)	(4.76)	(4.63)						
3	212	292	307	324	345	356	385				
	(4.75)	(4.74)	(4.83)	(4.81)	(4.67)	(4.69)	(4.57)				
4	214	230	240	314.5	332.5	353	381	413			
	(4.71)	(4.75)	(4.77)	(5.05)	(5.07)	(4.88)	(4.79)	(4.57)			
5	244	262	270	283	298	314.5	332	353	379	409	445
	(4.59)	(4.68)	(4.67)	(4.66)	(4.72)	(4.92)	(5.16)	(5.12)	(4.83)	(4.72)	(4.44)
6	210	278	291.5	306.5	330	353	375	401	434	474	
	(4.61)	(4.73)	(4.84)	(4.92)	(5.06)	(5.27)	(5.11)	(4.69)	(4.55)	(4.21)	

* indicates shoulder.

Table 4. Electronic spectral data of II_n

n	λ_{max} (log ε) in nm in tetrahydrofuran										
1	229*	239*	255	335	341	358	383				
	(4.43)	(4.24)	(3.89)	(4.77)	(4.76)	(4.83)	(4.16)				
2	220	255	331	347	374						
	(4.69)	(4.24)	(4.81)	(4.89)	(4.84)						
3	220	240	260*	273	298.5	312	322	333	352	368	397
	(4.78)	(4.44)	(4.23)	(4.45)	(4.67)	(4.73)	(4.73)	(4.96)	(4.87)	(4.86)	(4.79)
4	241	304*	324	339	360	389	422				
	(4.84)	(4.71)	(4.90)	(5.03)	(5.08)	(4.88)	(4.68)				
6	280	295	308	322	340	363	383	407	441	481	
	(4.83)	(4.93)	(4.87)	(4.84)	(5.05)	(5.27)	(5.11)	(5.01)	(4.76)	(4.42)	

* indicates shoulder

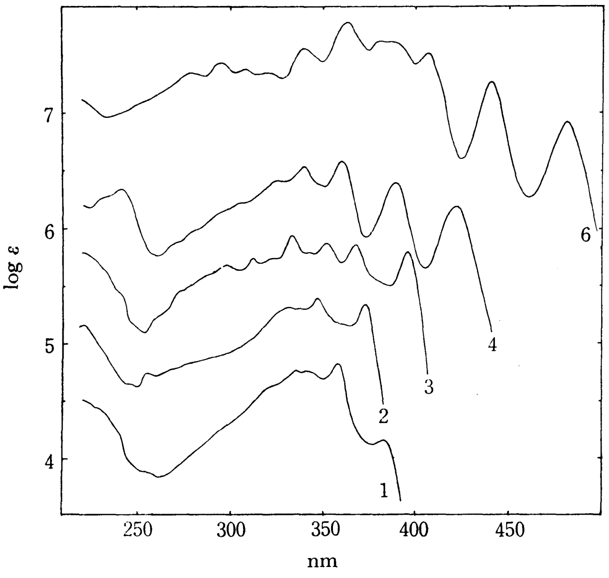

Fig. 3. The absorption cruves of 2,2'-difluorenylpoly-ynes (II_n). The cruves, with the exception of monoacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below (in tetrahydrofuran.)

attributed to the strained planar structure of the latter.[3] The same characteristic difference was observed between I_n and II_n. Bis(4-biphenylyl)acetylene (I_1) displays a broad and structureless band in the long-wavelength region, while 2,2'-difluorenylacetylene (II_1) exhibits a band with vibrational structure, and an absorption maximum which might be related to ^1L_b band of fluorene can be observed in the longest-wavelength region. However, the members of biphenylyl series higher than diacetylene (I_2—I_6) exhibit vibrational fine structure. As with other diarylpoly-ynes, the fine structure in the spectra of I_n and II_n becomes progressively distinct with the increase of length of the acetylenic chain.

As shown in Table 5, the spacing between the longest-wavelength vibrational sub-band and the next longest-wavelength sub-band was found to be 1900—200 cm^{-1}. Detailed discussion on the spacing and $\nu_{C\equiv C}$ of diarylpoly-ynes is presented elsewhere.[4]

Table 5. Spacing of vibrational fine structure of I_n and II_n

n	2	3	4	5	6
I_n	1950	2120	2030	1980	1940
II_n	2080	1990	2010	—	1890

The plots of the longest-wavelength absorption maxima (λ_L) of I_n and II_n against $n^{1.1}$ and $n^{1.5}$ gave straight lines, as illustrated in Figs. 4 and 5. The linear relationships can be expressed by the following empirical formulas:

$$I_n:\ \lambda_L = 24.0n^{1.1} + 304 \quad \text{(nm in tetrahydrofuran)}$$

$$II_n:\ \lambda_L = 9.0n^{1.5} + 350 \quad \text{(nm in tetrahydrofuran)}$$

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[3] H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press Inc., New York (1967), p. 261.

[4] M. Nakagawa, S. Akiyama, K. Nakasuji, and K. Nishimoto, *Tetrahedron*, **27**, 5401 (1971).

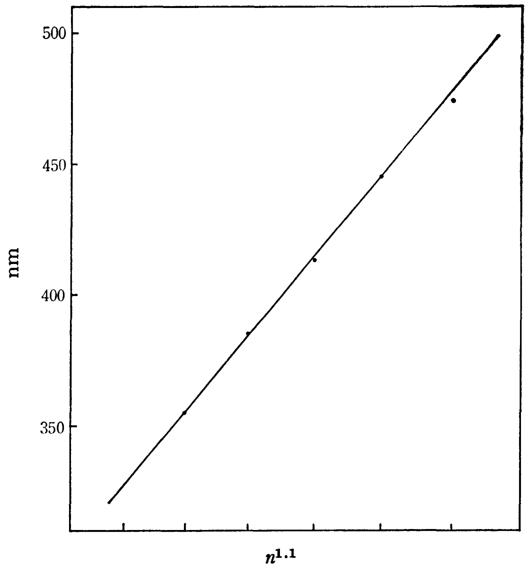

Fig. 4. Plot of λ_L against $n^{1.1}$ for bis(4-biphenylyl)poly-ynes (I_n).

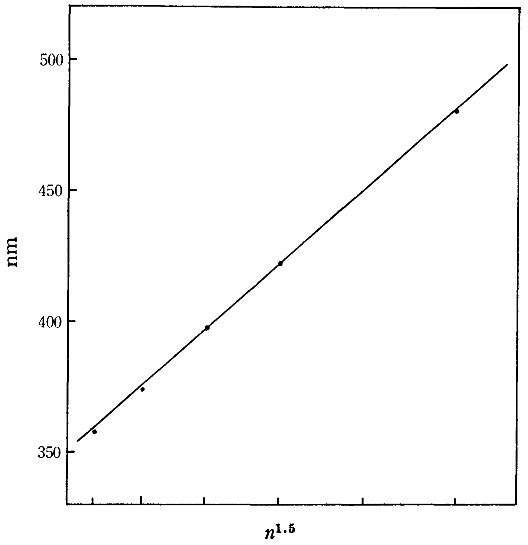

Fig. 5. Plot of λ_L against $n^{1.5}$ for 2,2′-difluorenylpoly-ynes (II_n).

Table 6. Observed and calculated λ_L of I_n and II_n

n		1	2	3	4	5	6
I_n	Obsd	—	355	385	413	445	474
	Calcd	328	355	384	414	445	476
	λ		0	1	−1	0	−2
II_n	Obsd	358	374	397	422	—	481
	Calcd	359	375	397	422	451	482
	λ	−1	−1	0	0		−1

As is shown in Table 6, the agreement between observed and calculated values was found to be satisfactory.

It is to be noted that the linear relationship of 1,1′-dinaphthylpoly-ynes[5] could be expressed by the same empirical formula which is valid for 2,2′-difluorenylpoly-ynes (II_n).

We pointed out[6] that the spectral shift of diphenylpoly-ynes should be expressed by the relation $\lambda_L \propto n^{1.0}$ instead of the widely accepted $\lambda_L^2 \propto n$.[7] The spectral behavior of bis(4-biphenylyl)poly-ynes (I_n) seems to afford an additional strong support for the relation $\lambda_L \propto n^{1.0}$ in diphenylpoly-ynes.

A general view of the spectral behavior of various kinds of diarylpoly-ynes and a HMO explanation based on a modified bond-alternation approximation for the novel linear relationship are given elsewhere.[4]

Experimental

All the melting points are uncorrected. The electronic and IR (KBr-disk method) spectra were obtained on Hitachi EPS-3T and EPI-2 spectrophotometers, respectively. Evaporation of solvent or concentration of solution was carried out under reduced pressure throughout this work.

Bis(4-biphenylyl)diacetylene (I_2). Diacetylene (I_2) was prepared by modifying the reported method. Oxidative coupling of 4-ethynylbiphenyl (V)[8,9] by means of the Eglinton method gave I_2 in a 90% yield as colorless needles, mp 232—233°C (lit, mp 232°C,[8] mp 235—236°C[9]).

1-(4-Biphenylyl)-2-propyn-1-ol (IX). A solution of 4-formylbiphenyl[10] (III, 7.3 g, 0.04 mol) in tetrahydrofuran (50 m*l*) was added over a period of 15 min to a stirred solution of lithium acetylide [from lithium, 0.83 g, 0.12 g-atom] in liquid ammonia (200 m*l*) at −60°C. The reaction mixture was stirred for 1 hr at this temperature, then for 17.5 hr at −50——55°C and finally for 3 hr at the boiling point of ammonia. Ammonium chloride (4 g) was added to the reaction mixture at −70°C, and the ammonia was allowed to evaporate. The residue was mixed with a saturated solution of ammonium chloride, and the aqueous layer was extracted with ether. The extract was combined with organic layer and dried. The residue obtained by evaporation of the solvent was crystallized from benzene - cyclohexane to yield brown crystals, 6.7 g (80%). Recrystallization of the crude crystals three times from the same solvent gave pure IX as colorless tiny crystals, mp 114—116°C.

Found: C, 86.31; H, 5.83%. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81%. IR: 3400—3300 (OH), 3290 (≡CH), 2090 (C≡C), 1015 (C–O) cm^{-1}.

1,6-Bis(4-biphenylyl)-2,4-hexadiyn-1,6-diol (X). A mixture of ethynylcarbinol (IX, 3.1 g, 0.015 mol), cuprous chloride (0.3 g, 3 mmol), ammonium chloride (0.23 g, 4.2 mmol) and methanol containing 1 drop of concentrated hydrochloric acid (20 m*l*) was vigorously stirred for 2 hr at room temperature under a slight excess of oxygen pressure. Five drops of concentrated hydrochloric acid was then added to the reaction mixture, and stirring was continued for further 2 hr. Inorganic materials were removed by filtration and washed with methanol. The residue obtained by evaporation of the combined organic layer was dissolved in ether

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[5] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, This Bulletin, **43**, 3567 (1970).

[6] S. Akiyama, K. Nakasuji, K. Akashi, and M. Nakagawa, *Tetrahedron Lett.*, **1968**, 1121.

[7] H. H. Schlubach and V. Franzen, *Ann.*, **503**, 110 (1951); C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, **1952**, 2883; J. B. Armitage, N. Entwistle, E. R. H. Jones, and M. C. Whiting, *ibid.*, **1954**, 147.

[8] H. Tani, F. Toda, and K. Matsumiya, This Bulletin, **36**, 391 (1963).

[9] W. Ried and V. Saxena, *Ann.*, **739**, 159 (1970).

[10] D. H. Hey, *J. Chem. Soc.*, **1931**, 2476.

containing tetrahydrofuran and washed with 2N hydrochloric acid. The crude material obtained after washing, drying and evaporation was crystallized from benzene - ethanol, giving crude X, 2.1 g (66%). Recrystallization of the crude X three times from the same solvent yielded pure X as light brown plates, mp 215—217°C.

Found: C, 86.73; H, 5.40%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%. IR: 3450—3350 (OH), 1005 (C–O) cm^{-1}.

Bis(4-biphenylyl)triacetylene (I_3). Preparation of Dichloride (XI). A solution of thionyl chloride (0.72 g, 6 mmol) in tetrahydrofuran (5 m*l*) was added to a stirred solution of the glycol (X, 0.83 g, 2 mmol) and pyridine (0.48 g, 6 mmol) in tetrahydrofuran (10 m*l*) under cooling on an ice-salt bath. Stirring was continued for 1 hr at the same temperature. The reaction mixture was subjected to the subsequent reaction without isolation of XI.

Dehydrochlorination of XI. The solution of XI was added to a stirred suspension of sodium amide [from sodium, 0.4 g, 0.018 g-atom] in liquid ammonia (50 m*l*) at −70°C. After the mixture had been stirred for 2 hr, ammonium chloride (3 g) was added and the ammonia was allowed to evaporate. The residue was mixed with water and the insoluble material was washed with a small amount of ethanol and benzene. The brown crystals thus obtained were dissolved in benzene, and the solution was percolated through a thin layer of alumina (6 g). The filtrate was concentrated to yield yellow crystals, 190 mg (25%). The product was recrystallized twice from benzene to give pure I_3 as pale yellow tiny crystals which decomposed at *ca.* 250°C.

Found: C, 94.74; H, 4.83%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%.

1-(4-Biphenylyl)-2-butyn-1,4-diol (XII). To an ice-cooled solution of the Grignard derivative of propargyl alcohol [from magnesium, 4.6 g (0.192 g-atom)], ethyl bromide, 25 g (0.23 mol) and propargyl alcohol, 5.4 g (0.096 mol)] in tetrahydrofuran (120 m*l*), was added under stirring a solution of 4-formylbiphenyl[10] (III, 10 g, 0.055 mol) in the same solvent (30 m*l*). The stirred mixture was allowed to warm to room temperature and stirring was continued overnight. 4N Sulfuric acid was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with benzene. The combined organic layer was washed successively with saturated solutions of sodium chloride, sodium hydrogen carbonate and water, and dried. The brown crystals obtained by evaporation of the solvent were dissolved in ethanol and treated with active charcoal and evaporated under reduced pressure. The crude crystals were recrystallized from benzene - ethanol, yielding brown crystals, 9.4 g (72%). The product was recrystallized 3 times from the same solvent to afford pure XII as colorless needles, mp 133—134°C.

Found: C, 80.85; H, 6.04%. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92%. IR: 3300—3200 (OH), 1015 (C–O) cm^{-1}.

4-Butadiynylbiphenyl (XIV). Preparation of Dichloride (XIII). A solution of thionyl chloride (14 g, 0.114 mol) in tetrahydrofuran (20 m*l*) was added over a period of 30 min to an ice-cooled mixture of butynediol (XII, 8.8 g, 0.037 mol), pyridine (9.0 g, 0.114 mol) and tetrahydrofuran (80 m*l*) and the reaction mixture was stirred for 1 hr. After the mixture had been stirred for further 40 min at 40°C, crushed ice was added to the mixture under ice-cooling. The aqueous layer was extracted with ether and combined with the organic layer, and washed with water and sodium hydrogen carbonate solution. It was dried and evaporated. Crude XIII thus prepared was used immediately in the following reaction.

Dehydrochlorination of XIII. A solution of the crude XIII in a mixture of tetrahydrofuran (15 m*l*) and ether (5 m*l*) was added in a stirred suspension of sodium amide [from sodium, 6 g (0.26 g-atom)] in liquid ammonia (450 m*l*) at −70°C and the mixture was stirred for a further 2 hr. Ammonium chloride (20 g) was then added and the ammonia was allowed to evaporate. The residue obtained by evaporation of the organic solvent was repeatedly digested with petroleum benzine (total 600 m*l*). The benzine solution was concentrated to *ca.* 200 m*l* and passed through a column of alumina (10 g). Diacetylene (XIV) was obtained as colorless needles, 1.9 g (26%) on concentration of the filtrate. The product was recrystallized from petroleum benzine to give pure XIV, colorless needles, mp 105°C (dec.). XIV was found to be unstable and turned to black insoluble material on standing.

Found: C, 94.57; H, 4.87%. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98%. UV: $\lambda_{\max}^{n\text{-hexane}}$ ($\log \varepsilon$) 302* (4.52), 292 (4.56), 245 (3.99) nm. The asterisk indicates shoulder.

Bis(4-biphenylyl)tetraacetylene (I_4). A solution of 4-butadiynylbiphenyl (XIV, 0.8 g, 4 mmol) in petroleum benzine (20 m*l*) was added to a mixture of cupric acetate monohydrate (4 g) and pyridine (20 m*l*) and the mixture was stirred for 2 hr at room temperature. After benzine had been removed under reduced pressure, stirring was continued for a further 3 hr at 50°C. The reaction mixture was chilled on an ice-salt bath. The solid deposited was filtered and washed with a small amount of methanol and water, successively. The yellowish brown crystals, 620 mg (77%) thus obtained were dissolved in benzene and treated with active charcoal. Recrystallization twice from the same solvent afforded pure I_4 as yellow rods which decomposed at *ca.* 240°C.

Found: C, 95.90; H, 4.48%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

3-(4-Biphenylyl)-prop-2-ynal (VI). To an ice-cooled and stirred solution of ethynylmagnesium bromide [from magnesium, 2.92 g (0.12 g-atom), ethyl bromide, 15.8 g (0.15 mol) and an excess of acetylene] in tetrahydrofuran (70 m*l*) was added over a period of 20 min a solution of 4-ethynylbiphenyl[8,9] (V, 17.8 g, 0.1 mol) in the same solvent (40 m*l*). After 1 hr, the mixture was refluxed for 30 min and then cooled on an ice-salt bath. A solution of dimethylformamide (23 m*l*) in tetrahydrofuran (40 m*l*) was added in one portion to the chilled mixture. The reaction mixture was left to reach room temperature. After stirring for 6 hr, the reaction mixture was poured into cold 5% sulfuric acid (700 m*l*) under vigorous agitation, after which the stirring was continued overnight. The mixture was then extracted with benzene. The extract was washed successively with water and sodium hydrogen carbonate solution and dried. The crude yellow crystals obtained by evaporation of the solvent were recrystallized from benzene - petroleum ether to give colorless needles, 12.3 g (60%), mp 75—78°C. This substance was recrystallized 3 times from benzene - cyclohexane to give pure VI as colorless needles, mp 76—78°C.

Found: C, 87.54; H, 4.89%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR: 2180 (C≡C), 1652 (C=O) cm^{-1}.

1-(4-Biphenylyl)-1,4-pentadiyn-3-ol (XVIII). A solution of the aldehyde (VI, 7.22 g, 0.035 mol) in tetrahydrofuran (50 m*l*) was added to an ice-cooled solution of ethynylmagnesium bromide [from magnesium, 2.13 g (0.088 g-atom), ethyl bromide, 11.43 g (0.105 mol) and an excess of acetylene] in tetrahydrofuran (100 m*l*), after which the mixture was stirred for 1 hr at the same temperature. The cooling bath was then removed and stirring continued overnight at room temperature. The reaction mixture was chilled again on an ice-salt bath and a saturated solution of ammonium chloride was added, extracted with benzene. The extract was dried and evaporated, resulting in crude crystals. The crude material was dissolved in ethanol and treated with charcoal. The crystals obtained from the filtrate were recrystallized from benzene - petroleum benzine to give slightly crude XVIII, 5.6 g (69%), mp 100—103°C. Recrystallization of this substance twice from the same solvent gave pure XVIII, mp 107—109°C.

Found: C, 87.85; H, 5.19%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: 3320—3180 (OH, ≡CH), 2220, 2105 (C≡C) cm^{-1}.

1,10-Bis(4-biphenylyl)-1,4,6,9-decatetrayn-3,8-diol (XIX). A mixture of diacetylene alcohol (XVIII, 4.64 g, 0.02 mol), cuprous chloride (0.40 g, 0.004 mol), ammonium chloride (0.30 g, 0.0056 mol), methanol (30 m*l*) and a drop of concentrated hydrochloric acid was vigorously stirred overnight at room temperature under a slight excess pressure of oxygen. The inorganic materials deposited were removed by filtration. The filtrate was evaporated and the residue was dissolved in ether, washed successively with 2N hydrochloric acid, water, sodium hydrogen carbonate solution and water, and dried. The crystals obtained by evaporation of the solvent were dissolved in ethanol and treated with active charcoal. Slightly impure XIX, 2.8 g (56%), thus prepared, was used in the subsequent reaction without further purification.

Bis(4-biphenylyl)pentaacetylene (I_5). Preparation of the Dichloride (XX). A solution of thionyl chloride (0.54 g, 4.5 mmol) and pyridine (0.36 g, 4.5 mmol) in ether (5 m*l*) was added over a period of 20 min to a stirred solution of the glycol (XIX, 0.69 g, 1.5 mmol) in tetrahydrofuran (10 m*l*) at −58°C and the mixture was stirred for a further 30 min at the same temperature. The reaction mixture was used immediately in the following reaction without isolation of XX.

Dehydrochlorination of XX. The reaction mixture containing XX was added into a stirred suspension of sodium amide [from sodium, 0.6 g (0.26 g atom)] in liquid ammonia (60 m*l*) maintained at −70°C. After stirring for an additional 1 hr at the same temperature, ammonium chloride (3 g) was added and the ammonia was allowed to evaporate. The residue obtained by evaporating the organic solvent was mixed with water. The insoluble material was filtered, washed with ethanol and a small amount of benzene. The deep brown solid thus obtained was dissolved in benzene and the solution was percolated through a short column of alumina (10 g). Yellowish crystals, 345 mg (54%) obtained by evaporation of the filtrate were recrystallized twice from benzene to yield pure I_5 as yellow needles. I_5 decomposed at *ca.* 200°C.

Found: C, 96.03; H, 4.42%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

1-(4-Biphenylyl)-1,4-hexadiyn-3,6-diol (XXI). A solution of biphenylylpropynal (VI, 8.24 g, 0.04 mol) in tetrahydrofuran (20 m*l*) was added to a stirred solution of the Grignard derivative of propargyl alcohol [from magnesium, 2.88 g (0.12 g-atom), ethyl bromide, 15.7 g (0.144 mol) and propargyl alcohol, 3.66 g (0.06 mol)] in tetrahydrofuran (75 m*l*) under cooling on an ice-salt bath, after which the cooling bath was removed and the mixture was stirred overnight at room temperature. To the ice-cooled reaction mixture was added a saturated solution of ammonium chloride and the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was washed with sodium chloride solution and dried. The light yellow crystals, 9.0 g (85%) obtained by the evaporation of the solvent were recrystallized twice from benzene to give pure XXI as colorless needles, mp 115—117°C.

Found: C, 82.40; H, 5.51%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. IR: 3300—3200 (OH), 2220 (C≡C), 1020 (C–O) cm^{-1}.

1-(4-Biphenylyl)-1,3,5-hexatriyne (XXIII). Preparation of the Dichloride (XXII). To a stirred solution of glycol (XXI) 2.36 g, 9 mmol) in tetrahydrofuran (15 m*l*) maintained at −40°C, was added over a period of 30 min a solution of thionyl chloride (3.12 g, 27 mmol) and pyridine (2.13 g, 27 mmol) in ether (7 m*l*). The mixture was stirred for a further 30 min at the same temperature and then for 1 hr at room temperature. The reaction mixture containing XII was subjected immediately to the following reaction.

4-Biphenylyltriacetylene (XXIII). The solution containing XII was added to a suspension of sodium amide [from sodium, 2.0 g (0.09 g-atom)] in liquid ammonia (150 m*l*) at −70°C. After the mixture had been stirred for 1 hr at the same temperature, ammonium chloride (7 g) was added and ammonia was allowed to evaporate. The residue obtained by removing the organic solvent was digested with petroleum benzine (total 800 m*l*) and the extract was concentrated to *ca.* 200 m*l*. The extract was passed through a short column of alumina (15 g). The filtrate containing extremely unstable XXIII was used in the following reaction.

UV: $\lambda_{\text{max}}^{\text{benzine}}$ 338, 317, 300 nm.

Bis(4-biphenylyl)hexaacetylene (I_6). The benzine solution of XXIII was evaporated *in vacuo* under continuous addition of ethanol. The ethanol solution of XXIII thus prepared was mixed with a solution of cupric acetate monohydrate (15 g) in pyridine (100 m*l*), and ethanol was removed under reduced pressure. After the reaction mixture had been stirred for 2 hr at 50°C, pyridine was evaporated. The residue was mixed with benzene, and benzene was evaporated to remove the remaining pyridine. The resulting deep brown crystalline mass was dissolved in benzene and percolated through a thin layer of alumina (10 g). Concentration of the filtrate afforded yellowish brown crystals, 180 mg (9%). The procedure of percolation of the benzene solution was rapidly repeated 2 times to give pure I_6, orange yellow needles, which decomposed at *ca.* 160°C.

Found: C, 95.68; H, 4.50%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

1,4-Bis(2-fluorenyl)-2-butyn-1,4-diol (VII′). A solution of 2-formylfluorene[11] (III′, 5.4 g, 0.028 mol) in tetrahydrofuran (30 m*l*) was added to an ice-cooled solution of acetylenedimagnesium bromide [from magnesium, 1.9 g (0.08 g-atom), ethyl bromide, 10.7 g (0.096 mol)] in benzene - tetrahydrofuran (1: 1, 100 m*l*). The reaction mixture was stirred overnight at room temperature, and was then chilled on an ice-salt bath. A saturated solution of ammonium chloride was added to the chilled reaction mixture and the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was dried, and evaporated, thus yielding a solid contaminated with a reddish brown oily material. Recrystallization of this material from benzene - ethanol yielded light brown crystalline powder, 3.5 g (60%). The crude material was recrystallized twice from tetrahydrofuran to yield pure VII′ as light yellow leaflets, mp 236—238°C.

Found: C, 86.58; H, 5.33%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.32%. IR: 3350—3250 (OH), 1005, 980 (C–O) cm^{-1}.

2,2′-Difluorenyldiacetylene (II_2). Preparation of the Dichloride (VIII′). A solution of thionyl chloride (360 mg, 3 mmol) in tetrahydrofuran (5 m*l*) was added to a stirred solution of glycol (VII′, 310 mg, 0.75 mmol) and pyridine (240 mg, 3 mmol) in tetrahydrofuran (5 m*l*) under cooling on an ice-salt bath. After the mixture had been stirred for 1 hr at the same temperature and for 2 hr at room temperature,

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[11] R. Rieche, H. Gross, and E. Hoft, *Chem. Ber.*, **93**, 88 (1960).

crushed ice was added to the reaction mixture under cooling with ice-water. The mixture was extracted with benzene. The extract was washed with water and a solution of sodium hydrogen carbonate and dried. The residue obtained by evaporation of the solvent was used in the following reaction without further purification.

Dehydrochlorination of VIII′. A solution of the crude VIII′ in tetrahydrofuran (60 m*l*) and ethanol (20 m*l*) was added dropwise into an ice-cooled solution of potassium ethoxide [from potassium, 0.15 g (3.8 mg-atom)] in ethanol (10 m*l*). After the reaction mixture had been stirred for 2 hr at room temperature, the solvent was evaporated. The residue was extracted with benzene and the extract was passed through a short column of alumina (15 g). The yellow filtrate was evaporated to yield yellowish brown crystals, 180 mg. This material was recrystallized from benzene to yield yellow crystals, 120 mg (42%). The crystals were redissolved in benzene and percolated through a thin layer of alumina (5 g). The crystals obtained from the filtrate were recrystallized twice from benzene to yield pure II_2 as pale yellow needles, mp 280—282°C (dec.). [lit[8]) mp 278°C (dec.)].

Found: C, 95.08; H, 4.80%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%.

1-(2-Fluorenyl)-2-propyn-1-ol (IX′). To an ice-cooled solution of ethynylmagnesium bromide [from magnesium, 1.80 g (0.075 g-atom), ethyl bromide, 8.20 g (0.075 mol) and an excess of acetylene] in tetrahydrofuran (150 m*l*) was added a solution of 2-formylfluorene (III′, 5.82 g, 0.03 mol) in tetrahydrofuran (30 m*l*). The reaction mixture was left to reach room temperature and stirring was continued overnight. The mixture was then chilled on an ice-salt bath and a saturated solution of ammonium chloride was added. The organic layer was dried, and evaporated to give crude brown crystals. After recrystallization from benzene, the crystals were dissolved in ethanol and treated with charcoal, giving brown crystals, 5.3 g (80%). A solution of the crystals in ethyl acetate was passed through a thin layer of alumina (10 g). A slightly crude material obtained from the filtrate was recrystallized 3 times from petroleum benzine-benzene to yield pure IX′ as pale yellow needles, mp 147—149°C.

Found: C, 87.37; H, 5.50%. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49%. IR: 3450—3300 (OH), 3260 (≡CH), 2120 (C≡C), 1010 (C–O) cm^{-1}.

1,6-Bis(2-fluorenyl)-2,4-hexadiyn-1,6-diol (X′). A mixture of ethynylcarbinol (IX′, 2.1 g, 10 mmol), cuprous chloride (200 mg, 3.0 mmol), ammonium chloride (150 mg, 2.8 mmol) and methanol (15 m*l*) containing 1 drop of concentrated hydrochloric acid was vigorously stirred overnight at room temperature under a slight excess of oxygen pressure. The reaction mixture was worked up according to the procedure used in the preparation of X, affording crystals, 1.36 g (63%). The crystals were recrystallized 3 times from benzene - ethanol to give colorless needles, mp 210—212°C (dec.).

Found: C, 87.80; H, 5.11%. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06%. IR: 3500—3200 (OH), 1000, 965 (C–O) cm^{-1}.

2,2′-Difluorenyltriacetylene (II_3). Preparation of the Dichloride (XI′). A solution of thionyl chloride (240 mg, 2.0 mmol) in tetrahydrofuran (10 m*l*) was added to a stirred solution of the glycol (X′, 220 mg, 0.5 mmol) and pyridine (160 mg, 2.0 mmol) in tetrahydrofuran (10 m*l*) under cooling on an ice-salt bath. The mixture was stirred for 30 min at the same temperature and for 2 hr at room temperature. The reaction mixture was chilled on an ice-salt bath and mixed with crushed ice, then extracted with ether. The extract was washed successively with water and a dilute solution of sodium hydroxide and dried. The brown crystals obtained by evaporating the solvent were dissolved in tetrahydrofuran (30 m*l*) and used in the subsequent reaction.

Dehydrochlorination of XI′. To a stirred and ice-cooled solution of sodium ethoxide [from sodium, 70 mg (3 mmol)] in ethanol (10 m*l*), was added the solution of crude XI′ in tetrahydrofuran. After the mixture had been stirred for 2 hr at room temperature, the solvent was removed and the residue was extracted with benzene. The extract was concentrated to *ca.* 80 m*l* and percolated through a short column of alumina (15 g). The brown solid obtained by evaporation of the filtrate was crystallized from benzene, yielding crude crystals, 120 mg (60%). The crude substance was dissolved in benzene and passed through a thin layer of alumina. The crystals obtained by evaporation of the filtrate were redissolved in the same solvent and passed again through a short alumina column. Pure II_3 was obtained from the filtrate as yellowish brown fine crystals, which decomposed at *ca.* 250°C.

Found: C, 95.34; H, 4.47%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

1-(2-Fluorenyl)-2-butyn-1,4-diol (XII′). The crude product obtained by the reaction of 2-formylfluorene[11]) (III′, 6.4 g, 0.033 mol) in tetrahydrofuran (20 m*l*) with the Grignard derivative of propargyl alcohol [from magnesium, 2.8 g (0.115 g-atom), ethyl bromide, 15 g (0.138 mol) and propargyl alcohol, 3.2 g (0.058 mol)] in the same solvent (75 m*l*) according to the procedure used for XII was recrystallized from benzene - ethanol to give light brown crystals, 6.4 g (82%). Recrystallization of this material 3 times from benzene containing a small amount of ethanol afforded pure XII′ as colorless plates, mp 133—135°C.

Found: C, 81.78; H, 5.54%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. IR: 3300—3100 (OH), 1105, 1000, 995 (C–O) cm^{-1}.

2-Butadiynylfluorene (XIV′). Preparation of Dichloride (XIII′). A solution of thionyl chloride (3.6 g, 0.03 mol) in tetrahydrofuran (20 m*l*) was added to a solution of butynediol (XII′, 2.2 g, 0.01 mol) and pyridine (2.4 g, 0.03 mol) in tetrahydrofuran (50 m*l*) under cooling on an ice-salt bath. The reaction mixture was stirred for 30 min at the same temperature, for 1 hr at room temperature and for 1 hr at 40°C. The reaction mixture was concentrated to *ca.* 30 m*l* and used in the following reaction.

Dehydrochlorination of XIII′. The solution of XII′ was added to a stirred solution of sodium ethoxide [from sodium, 2.1 g (0.09 g-atom)] in ethanol (80 m*l*) under cooling on an ice-salt bath. After the mixture had been stirred for 30 min at the same temperature and for 1 hr at room temperature, a saturated solution of ammonium chloride was added to the reaction mixture under ice-cooling. The aqueous layer was extracted with benzene. The combined organic layer was dried and evaporated. The residue was digested with petroleum benzine and the extract was passed through a thin layer of alumina (30 g). The resulting colorless filtrate was concentrated to *ca.* 200 m*l* and subjected to the subsequent reaction without isolation of XIV′.

UV: $\lambda_{\max}^{\text{benzine}}$ 324, 315, 303 nm.

2,2′-Difluorenyltetraacetylene (II_4). The oxidative coupling used in the synthesis of I_4 was applied to the benzine solution of XIV′ yielding crude II_4, 190 mg (9%). The crude material was recrystallized twice from benzene using active charcoal to yield pure II_4 as orange yellow rods which decomposed at *ca.* 210°C.

Found: C, 95.67; H, 4.32%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

1-(2-Fluorenyl)-2,5-hexadiyn-1,4-diol (XV′). A solution of 1,4-pentadiyn-3-ol (3.08 g, 0.039 mol) in tetrahydrofuran (65 m*l*) was added over a period of 20 min to a solution of ethylmagnesium bromide [from magnesium, 2.05 g (0.086 g-atom) and ethyl bromide, 10.4 g (0.095 mol)] in the same solvent (55 m*l*) under an atmosphere of nitrogen at 25°C. Stirring was continued for 30 min at the same temperature. A solution of 2-formylfluorene (III′, 5.82 g, 0.03 mol) in tetrahydrofuran (60 m*l*) was then added dropwise to the ice-cooled solution of the Grignard derivative of pentadiyneol. The reaction mixture was left to reach room temperature and stirring was continued overnight. After the reaction mixture had been stirred for 20 min at 40°C, a saturated solution of ammonium chloride was introduced to the mixture under cooling on an ice-salt bath. The organic layer was separated and the aqueous layer was extracted with benzene. The combined orgaic layer was washed, dried and evaporated. The resulting dark reddish brown oily material was mixed with a small amount of hot benzene to give crude crystals, 4.0 g (48%), mp *ca.* 120—140°C. The crude material was recrystallized twice from benzene to yield XV′ as light brown crystals, mp 153—173°C.

Found: C, 93.16; H, 5.11%. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%. IR: 3300—3250 (OH), 3260 (≡CH), 2120 (C≡C), 1025, 1010 (C–O) cm^{-1}.

1-(2-Fluorenyl)-1,3,5-hexatriyne (XVII′). Preparation of Dichloride (XVI′). A solution of thionyl chloride (720 mg, 6 mmol) in tetrahydrofuran (8 m*l*) was added to a stirred solution of glycol (XV′, 550 mg, 2 mmol) and pyridine (480 mg, 6 mmol) in tetrahydrofuran (10 m*l*) under cooling on an ice-salt bath. The reaction mixture was stirred for 1 hr at the same temperature and for 1 hr at 30°C. The reaction mixture was used in the following reaction without isolation of XVI′.

Dehydrochlorination of XVI′. The reaction mixture containing XVI′ was added dropwise to a stirred solution of potassium ethoxide [from potassium, 1.2 g (30 mg-atom)] in ethanol (40 m*l*) under cooling with an ice-salt mixture. After the mixture had been stirred for 30 min at the same temperature and then for 30 min at 30°C, a saturated solution of ammonium chloride (5 m*l*) was added to the ice-cooled reaction mixture and the volatile material was removed *in vacuo.* The residue was extracted with petroleum benzine, and the extract was concentrated to *ca.* 100 m*l*. Percolation of the concentrated extract through a short column of alumina (20 g) gave a light yellow filtrate. The filtrate was used in the following reaction without isolation of triacetylene (XVII′).

UV: $\lambda_{\max}^{\text{benzine}}$ 354, 325 nm.

2,2′-Difluorenylhexaacetylene (II$_6$). To a solution of cupric acetate monohydrate (2 g) in pyridine (10 m*l*) was added, portion by portion, the benzine solution of the triacetylene (XVII′) under reduced pressure. After addition of the solution and removal of benzine had been completed, the pyridine solution was stirred for 30 min at 35°C and then at room temperature overnight. The reaction mixture was concentrated, and benzene was added to the residue. The solvent was again evaporated to remove pyridine completely. The residue was triturated with cold benzene (10 m*l*) and the insoluble material was collected by filtration and washed thoroughly with water. The brown solid thus obtained was dissolved in hot benzene and the hot solution was passed through a short column of alumina (5 g). The resulting orange yellow filtrate gave orange yellow crystals, 70 mg (7%) on concentration. The crystals obtained by the recrystallization of this substance from benzene were redissolved in benzene and percolated through a short column of alumina. The crystals obtained from the filtrate were recrystallized again from benzene, yielding pure II$_6$ as orange yellow leaflets which decomposed at *ca.* 250°C.

Found: C, 95.75; H, 3.81%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

4-Biphenylylmethyl-triphenylphosphonium Bromide (XXV). A solution of 4-bromomethylbiphenyl[12] (XXIV, 3.9 g, 0.016 mol) and triphenylphosphine (5.8 g, 0.022 mol) in benzene (40 m*l*) was refluxed overnight. The solid deposited was collected by filtration and washed with benzene, yielding colorless crystalline powder, 7.4 g (92%). Recrystallization of this material from ethanol gave colorless leaflets, mp 283—287°C.

Found: C, 73.08; H, 5.21; Br, 15.69%. Calcd for $C_{31}H_{26}$-BrP: C, 73.10; H, 5.14; Br, 15.69%.

Preparation of the Betaine (XXVIII). To a suspension of the phosphonium bromide (XXV, 1.12 g, 2.2 mmol) in toluene (25 m*l*) was added an ethereal solution of phenyllithium (0.765N, 3.0 m*l*) under an atmosphere of nitrogen. Instanteneous deep red coloration took place. After the mixture had been stirred for 30 min at 60°C, a solution of acid chloride (XXVII) [from 4-biphenylcarboxylic acid,[13] 0.20 g (1 mmol) and thionyl chloride, 180 mg (1.5 mmol)] in toluene (20 m*l*) was added to the solution of phosphorane and stirred overnight. The insoluble material was collected by filtration and digested with boiling toluene (total 200 m*l*). The extract was concentrated and the residue dissolved in benzene - cyclohexane (1: 1, 5 m*l*). The crystals deposited, 510 mg (84%), were recrystallized from the same solvent to give pure XXVIII as light yellow rod which decomposed at 215—218°C (foaming was observed at *ca.* 200°C).

Found: C, 87.06; H, 5.53%. Calcd for $C_{44}H_{33}OP$: C, 86.83; H, 5.46%.

Bis(4-biphenylyl)acetylene (I$_1$). Betaine (XXVIII, 63 mg, 0.103 mmol) was gradually heated to 210°C under reduced pressure (20 mmHg) and kept at this temperature for 15 min. Foaming was observed at *ca.* 190°C. After cooling, the product was extracted with benzene. Evaporation of the solvent gave crude crystals, 32 mg (94%). The crude material was dissolved in benzene and passed through a thin layer of alumina. The crystals obtained by evaporating the filtrate were recrystallized from benzene to yield pure I$_1$ as colorless leaflets, mp 253—254°C (lit, mp 243—244°C[14]).

Found: C, 94.68; H, 5.44%. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49%.

2-Fluorenylmethyltriphenylphosphonium Bromide (XXV′). According to the same procedure as that for XXV, 2-bromomethylfluorene[15] (XXIV′, 3.5 g, 0.0134 mol) was converted into phosphonium bromide (XXV′, 6.0 g, 87%). The phosphonium bromide (XXV′) was recrystallized twice from ethanol - acetone (1:1). The crystals were dried at *ca.* 115°C for 48 hr under reduced pressure to give pure XXV′, mp 252—256°C.

Found: C, 73.31; H, 4.99; Br, 15.57%. Calcd for $C_{32}H_{26}$-BrP: C, 73.72; H, 5.03; Br, 15.32%.

Preparation of Betaine (XXVIII′). The same procedure as that used for XXVIII was employed. The reaction of phosphonium bromide (XXV′, 2.34 g) and acid chloride [from 2-fluorenylcarboxylic acid[16] (0.42 g)] gave the betaine

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12) H. Dahn and P. Zoller, *Helv. Chim. Acta,* **35**, 1438 (1952); L. Zervas and I. Dilaris, *J. Amer. Chem. Soc.,* **77**, 5354 (1955).

13) 4-Biphenylcarboxylic acid was prepared by the oxidation of 4-formylbiphenyl (III) by means of Tollens' reagent.

14) G. H. Coleman and R. D. Maxwell, *J. Amer. Chem. Soc.,* **56**, 132 (1934).

15) J. von Braun and H. Engel, *Ber.,* **57**, 191 (1924).

16) M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Amer. Chem. Soc.,* **82**, 2282 (1960).

(XXVIII′) in a yield of 87% (1.10 g). The material was recrystallized twice from benzene-cyclohexane to give pure XXVIII′ as pale yellow cubes, mp 268—270°C.

Found: C, 87.29; H, 5.45%. Calcd for $C_{46}H_{33}OP$: C, 87.33; H, 5.26%.

2,2′-Difluorenylacetylene (II_1). Pyrolysis of betaine (XXVIII′, 192 mg, 0.303 mmol) was performed at 230°C under reduced pressure (*ca.* 20 mmHg). Foaming was observed at *ca.* 220°C. The product was extracted with benzene. The extract was concentrated and passed through a short column of alumina. The crystals, 82 mg (77%) obtained by evaporating the filtrate were recrystallized from benzene affording pure II_1 as colorless rods which decomposed at *ca.* 295°C.

Found: C, 94.50; H, 5.17%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%.