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Linear Conjugated Systems Bearing Aromatic Terminal Groups. VII. Syntheses and Electronic Spectra of 1,1'- and 2,2'-Dipyrenylpoly-ynes

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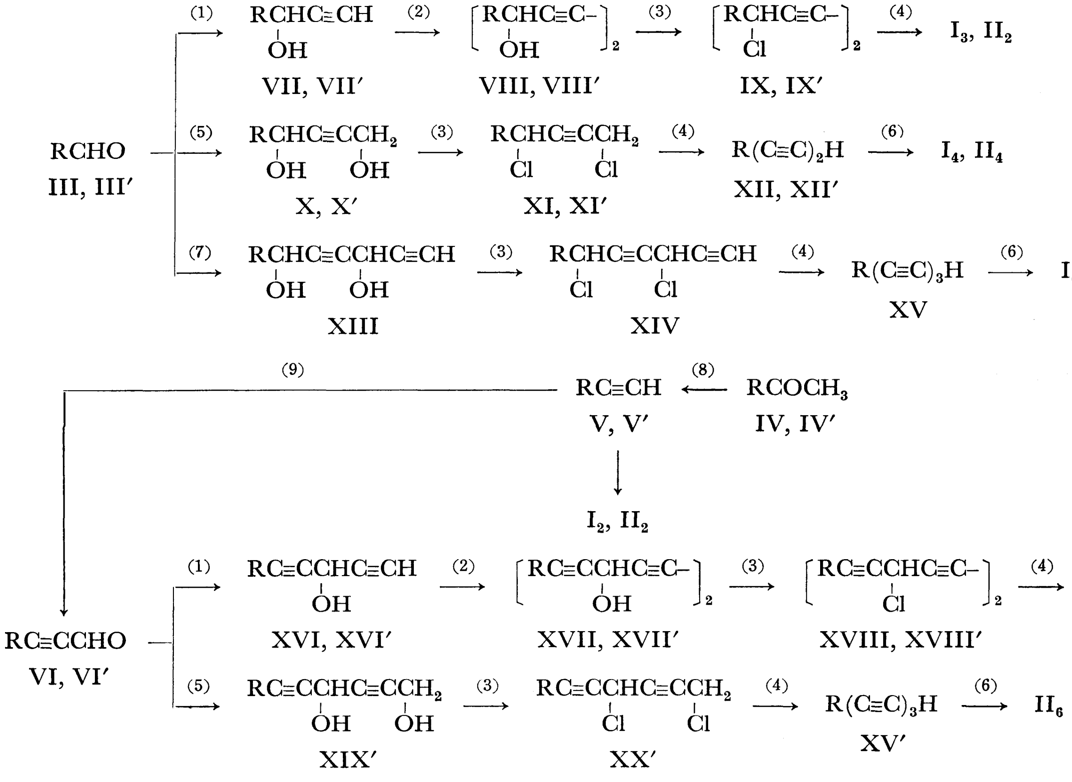
1,1'- and 2,2'-Dipyrenylpoly-ynes (I_n and II_n, $n=1$—6) have been synthesized. It was found that the bathochromic shift of the longest-wavelength absorption maxima (λ_L) according to the increase in the number of acetylenic bond (n) can be well expressed by the following formulas:

$$I_n:\ \lambda_L = 3.7n^{1.7} + 430 \quad \text{(nm in toluene)}$$
$$II_n:\ \lambda_L = 12.6n^{1.4} + 327 \quad \text{(nm in toluene)}$$

New linear relationships between the longest-wavelength absorption maxima (λ_L) and the xth power of the number of acetylenic bond (n)[$\lambda_L \propto n^x$] observed in various kinds of diarylpoly-ynes have been reported in previous papers.[1-9] Since the value of x is dependent on the nature of terminal groups and the position of linking of polyacetylene chain, we were interested in the behavior of pyrene as the terminal groups of poly-yne system. The present paper deals with the syntheses and electronic spectral properties of 1,1'- and 2,2'-dipyrenylpoly-ynes (I_n and II_n, $n=1$—6).

Syntheses. The syntheses of monoacetylenes (I_1



Scheme 1. Syntheses of dipyrenylpoly-ynes (I_n, II_n)

Roman numerals with prime indicate 2-pyrenyl series.
(1) HC≡CMgBr/THF, (2) CuCl-NH_4Cl-O_2/CH_3OH or CH_3OH-acetone, (3) $SOCl_2$-pyridine/THF, (4) $NaNH_2$/liq. NH_3, (5) BrMgC≡CCH_2OMgBr/THF, (6) $Cu(OCOCH_3)_2$/pyridine, (7) BrMgC≡C-CH(OMgBr)C≡CH/THF, (8) i) PCl_5, ii) $NaNH_2$/liq. NH_3, (9) i) i-C_3H_7MgBr, ii) DMF/THF, iii) dil. H_2SO_4.
THF = tetrahydrofuran; DMF = dimethylformamide.

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[1] S. Akiyama and M. Nakagawa, *Tetrahedron Lett.*, **1964**, 719.

[2] K. Nishimoto, R. Fujishiro, S. Akiyama, and M. Nakagawa, This Bulletin, **39**, 2320 (1966).

[3] S. Akiyama and M. Nakagawa, *ibid.*, **40**, 340 (1967).

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

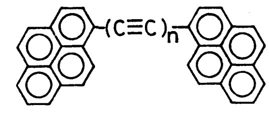
[5] S. Akiyama and M. Nakagawa, This Bulletin, **43**, 3561 (1970).

[6] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, *ibid.*, **43**, 3567 (1970).

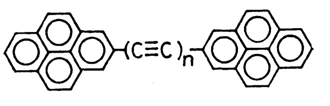
[7] S. Akiyama, K. Nakasuji, and M. Nakagawa, *ibid.*, **44**, 2231 (1971).

[8] S. Akiyama and M. Nakagawa, *ibid.*, **44**, 2237 (1971).

[9] S. Akiyama and M. Nakagawa, *ibid.*, **45**, 259 (1972).



I_n



II_n

and II_1) by means of an intramolecular Wittig reaction have been reported.[8] As illustrated in Scheme 1, the reaction sequence used in the syntheses of I_n and II_n is a general method which has been successfully adapted for the preparation of various kinds of diarylpoly-ynes.[6,8,9] 2,2′-Dipyrenylhexaacetylene (II_6) was found to be an unstable, scarcely soluble substance, and gave an unsatisfactory elemental analysis. However, the compound gave a satisfactory electronic spectrum for the present purpose.

Some physical properties of 1,1′- and 2,2′-dipyrenylpoly-ynes (I_n and II_n) are summarized in Tables 1 and 2.

TABLE 1. PHYSICAL PROPERTIES OF 1,1′-DIPYRENYLPOLY-YNES (I_n)

n	Color of crystals	Melting point (°C)	$\nu_{C\equiv C}$(cm^{-1})
1	yellow	266	—
2	yellow	(297—298)	2125
3	yellow	(*ca.* 300)	2185
4	orange yellow	(*ca.* 260)	2190
5	orange	(*ca.* 215)	2175
6	red	(*ca.* 200)	2145

Figures in parentheses indicate decomposition points.

TABLE 2. PHYSICAL PROPERTIES OF 2,2′-DIPYRENYLPOLY-YNES (II_n)

n	Color of crystals	Melting point (°C)	$\nu_{C\equiv C}$(cm^{-1})
1	pale yellow	>330	—
2	light yellow	>330	—
3	yellow	(*ca.* 260—270)	2190
4	yellow	(*ca.* 180)	2195
5	orange yellow	(*ca.* 140)	2185
6	orange		

Figures in parentheses indicate decomposition points.

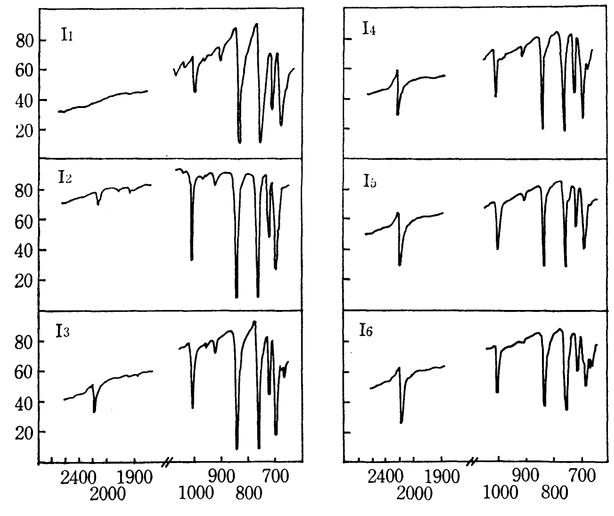


Fig. 1. IR spectra of 1,1′-dipyrenylpoly-ynes (I_n).

The IR spectra of I_n are shown in Fig. 1 as representative of dipyrenylpoly-ynes. The most intense peak in $\nu_{C\equiv C}$ band showed appreciable intensification with increasing number of n. The highest wave number of $\nu_{C\equiv C}$ was observed in the spectra of the tetraacetylenes (I_4 and II_4). The same trend has been observed in the other series of diarylpoly-ynes.[3,4,6,8,9]

Electronic Spectra. The absorption curves and numerical data of the electronic spectra of I_n and II_n are shown in Figs. 2 and 3, and Tables 3 and 4, respectively. In the electronic spectrum of pyrene, there is a low intensity band in the 350—370 nm region (^1L_b) and a strong band in the 290—340 nm region (^1L_a). Both bands exhibit considerable fine structure. The longest-wavelength bands in I_n and II_n seem to arise from the interaction of ^1L_a band of pyrene with polyacetylenic chromophore. The difference in wave-

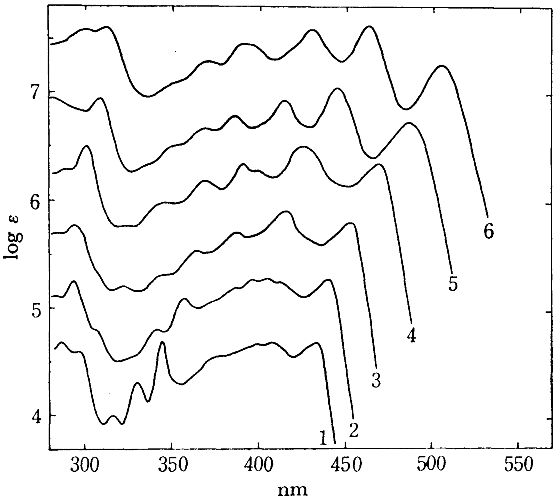


Fig. 2. Absorption curves of 1,1′-dipyrenylpoly-ynes (I_n). With the exception of the monoacetylene at the bottom, the curves are shifted upward along the ordinate by 0.5 log ε unit increments from the curve immediately below (in toluene).

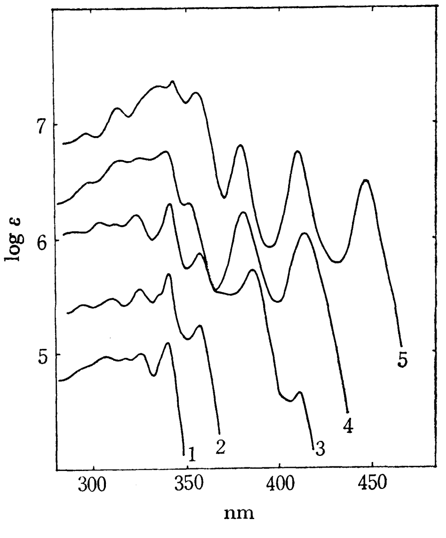


Fig. 3. Absorption curves of 2,2′-dipyrenylpoly-ynes (II_n). With the exception of the monoacetylene at the bottom, the curves are shifted upward along the ordinate by 0.5 log ε unit increments from the curve immediately below (in toluene).

TABLE 3. ELECTRONIC SPECTRAL DATA OF I_n

n	λ in nm (log ε) in toluene						
1	287.5 (4.68)	297.5 (4.60)	315.5 (3.99)	330.5 (4.31)	345 (4.68)	401 (4.66)	408 (4.68)
	434 (4.68)						
2	283.5 (4.62)	294 (4.75)	341 (4.29)	367 (4.58)	387 (4.68)	396 (4.74)	405 (4.77)
	413 (4.73)	442 (4.76)					
3	294.5 (4.77)	322.5 (4.20)	345* (4.31)	364 (4.53)	387 (4.70)	417 (4.89)	454 (4.79)
4	289 (4.78)	301.5 (5.00)	325 (4.27)	346 (4.46)	370 (4.67)	392 (4.83)	400 (4.77)
	427 (4.98)	470 (4.83)					
5	282.5 (4.95)	309 (4.94)	352* (4.50)	370 (4.66)	386 (4.78)	415 (4.92)	446 (5.04)
	487 (4.72)						
6	301.5 (5.08)	313 (5.09)	373 (4.78)	393 (4.94)	432 (5.08)	465 (5.10)	507 (4.73)

Asterisks indicate shoulders.

TABLE 4. ELECTRONIC SPECTRAL DATA OF II_n

n	in nm (log ε) in toluene							
1	306 (4.99)	317 (4.97)	324 (5.00)	340 (5.10)	373 (a)	380 (a)	394 (a)	403 (a)
2	294 (4.94)	310 (5.00)	325 (5.07)	335 (5.03)	341 (5.21)	358 (4.75)	385 (a)	407 (a)
3	304 (5.05)	313 (5.02)	324 (5.12)	342 (5.21)	359 (4.78)	387 (4.64)	413 (3.52)	
4	297 (5.01)	315 (5.20)	327 (5.21)	340 (5.27)	351 (4.86)	382 (4.78)	415 (4.60)	
5	296 (4.87)	314 (5.12)	336 (5.29)	343 (5.35)	355 (5.28)	379 (4.82)	410 (4.77)	447 (4.51)
6[b)]				355	379	404	437	478

a) Accurate ε-values could not be obtained owing to poor solubility.
b) On account of the purity of II_6, only the locations of the long-wavelength bands are shown.

TABLE 5. DIFFERENCE OF WAVELENGTH OF λ_L BETWEEN I_n AND II_n

n	1	2	3	4	5	6
I_n	434	442	454	470	487	502
II_n	340	358	387	415	447	478
$\Delta\lambda$	94	84	67	55	40	29

length of the longest-wavelength absorption maxima (λ_L) between I_n and II_n is shown in Table 5. The marked difference ($\Delta\lambda$) between I_n and II_n was found to be the largest ever observed, *i.e.*, the difference between 1,1'- and 2,2'-dinaphthylacetylenes is 23 nm,[6)] and that between 2,2'- and 3,3'-, and between 3,3'- and 9,9'-diphenanthrylacetylenes 11.5 and 16.5 nm,[8)] respectively. Since the transition associated with ${}^1L_a$ band of pyrene is considered to be polarized in the direction of the long axis,[10)] the remarkable hypsochromic shift of λ_L of II_n as compared with that of I_n indicates that we do not get what we expect intuitively for dipyrenylpoly-ynes. A similar phenomenon has been observed in phenanthrene derivatives and explained in terms of configuration interaction.[11)] Thus, it seems to be pertinent to ascribe the hypsochromism of II_n to configuration interaction.

The absorption band associated with ${}^1L_b$ band of pyrene could not be observed in the spectra of I_n. However, II_1, II_2, and II_3 showed low intensity bands at long-wavelength region. The same phenomena were observed in the lower member of 2,2'-dinaphthylpoly-ynes[6)] and in that of 2,2'-difluorenylpoly-ynes.[12)]

As has been observed in various series of diarylpoly-ynes, increase in the length of poly-yne chain results in a progessive enhancement of the vibrational fine structure. Thus the spectra of higher members of I_n and II_n exhibit a characteristic feature of polyacetylene chromophore. The spacing, *i.e.*, the difference of wavelength between the longest-wavelength sub-band and the next longest-wavelength sub-band, was found to be 1800—2150 cm^{-1} in the case of $n=3$—6 (*cf.* Table 6). The spacing can be considered to correspond to the stretching vibration of acetylenic linkage at excited state. The unusual value of spacing of the diacetylenes (I_2 and II_2) can be attributed to the superposition of vibration of acetylene bond with that inherent to the terminal groups. The same unusual spacing has been observed in the electronic spectra of dianthrylpoly-ynes.[5)] The correlation of spacing and $\nu_{C\equiv C}$ with the electronic spectral behavior of diarylpoly-

TABLE 6. SPACING OF ELECTRONIC SPECTRA OF I_n AND II_n (cm^{-1})

n	2	3	4	5	6
I_n	(1590)	1950	2140	1890	1790
II_n	(1390)	2030	2080	1990	1960

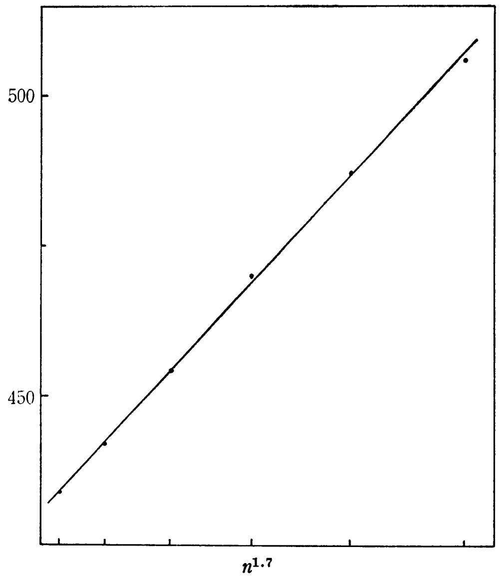


Fig. 4. Plot of λ_L *versus* $n^{1.7}$ for 1,1'-dipyrenylpoly-ynes (I_n).

[10)] R. S. Becker, I. S. Singh, and E. A. Jackson, *J. Chem. Phys.*, **38**, 2144 (1963) and the references cited therein.

[11)] S. Akiyama, M. Nakagawa, and K. Nishimoto, This Bulletin, **44**, 1054 (1971).

[12)] K. Nakasuji, S. Akiyama, and M. Nakagawa, *ibid.*, **45**, 883 (1972).

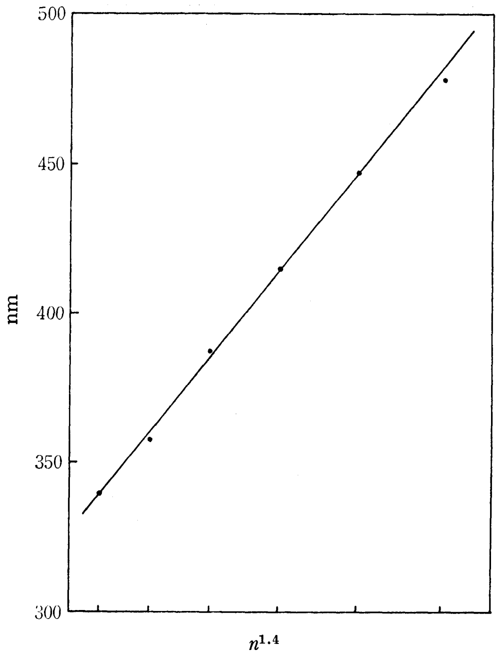


Fig. 5. Plot of λ_L *versus* $n^{1.4}$ for 2,2′-dipyrenylpoly-ynes (II_n).

ynes was discussed elsewhere.[13]

The plots of λ_L of I_n against $n^{1.7}$ and those of II_n *versus* $n^{1.4}$ gave good straight lines as illustrated in Figs. 4 and 5. The linear relationships can be expressed by the following empirical formulas. Agreement of calculated values with observed data was found to be excellent (*cf.* Table 7).

I_n: $\lambda_L = 3.7n^{1.7} + 430$ (nm in toluene)

II_n: $\lambda_L = 12.6n^{1.4} + 327$ (nm in toluene)

TABLE 7. OBSERVED AND CALCULATED λ_L (nm)

	n	1	2	3	4	5	6
I_n	Obs.	434	442	454	470	487	507
	Calcd	434	442	454	469	487	508
	$\varDelta$	0	0	0	1	0	−1
II_n	Obs.	340	358	387	415	447	478
	Calcd	340	360	386	415	447	482
	$\varDelta$	0	−2	1	0	0	−4

In the above-mentioned dipyrenyl series, the difference in position of linking of polyacetylenic chain exerts a prominent effect on the location of λ_L. This tendency seems to be reflected in the marked difference of the value of x between 1,1′-series (I_n, $x=1.7$) and 2,2′-series (II_n, $x=1.4$).

Experimental

All melting points are uncorrected. The electronic spectra were measured on a Hitachi EPS-3T Spectrophotometer. The IR spectra were obtained on a Hitachi EPI-2 Spectrophotometer by KBr-disk method. Evaporation of solvent or concentration of solution was carried out under reduced pressure.

1-Ethynylpyrene (V). *Chlorination of 1-Acetylpyrene (IV)*: 1-Acetylpyrene (IV, mp 89°C, 4.88 g, 0.02 mol) prepared by the reported method[14] was mixed with phosphorus pentachloride (4.58 g, 0.022 mol) in benzene (20 m*l*). After the mixture had been refluxed for 1 hr, volatile materials were removed under reduced pressure. The residue was placed in an evacuated desiccator containing potassium hydroxide, thus yielding greenish yellow crystals. This material was used in the subsequent reaction without purification.

Dehydrochlorination. To a stirred suspension of sodium amide [from sodium, 1.80 g (0.08 g-atom)] in liquid ammonia (100 m*l*) was added a solution of the crude chloride in tetrahydrofuran (10 m*l*) over a period of 20 min. After stirring for 3 hr, ammonia was allowed to evaporate. Ether (200 m*l*) was added to the residue and a saturated ammonium chloride solution was added under cooling on an ice-salt bath. The organic layer was washed with water and dried. The residue obtained by evaporation of the solvent was dissolved in benzene (30 m*l*), and the solution was passed through a short column of alumina (15 g). Concentration of the filtrate yielded the ethynyl derivative (V) as pale yellow needles (3.92 g, 87%, mp 112—114°C). Percolation of crude V in petroleum benzine through a column of alumina gave pure V as colorless needles, mp 113—114°C. 1-Ethynylpyrene (V) gave orange cuprous and yellow silver acetylides.

Found: C, 95.45; H, 4.44%. Calcd for $C_{18}H_{10}$: C, 95.54; H, 4.46%. IR: 3310 (≡CH), 2090 (C≡C), 1027 (C–O) cm^{-1}. UV: $\lambda_{\text{max}}^{n\text{-hexane}}$ (log ε): 218 (4.10), 236 (4.59), 246.5 (4.78), 261 (4.09), 270.5 (4.47), 281.5 (4.76), 311.5 (3.74), 324 (4.19), 338.5 (4.57), 356.5 (4.80), 373.5 (3.04), 381.5 (3.23) nm.

2-Acetylpyrene (IV′). Acid chloride prepared from 2-carboxypyrene[15] (24.6 g, 0.1 mol) and thionyl chloride (16 m*l*) was dissolved in hot tetrahydrofuran (200 m*l*). The hot solution was added to an ice-cooled solution of diethyl magnesiomalonate [from magnesium, 2.4 g (0.1 g-atom), diethyl malonate, 16.0 g (0.1 mol), anhydrous ethanol, 10.1 g (0.2 mol) and anhydrous toluene (100 m*l*). The excess of ethanol had been removed by an azeotropic distillation with toluene] in toluene. After the addition had been completed, the mixture was stirred for 3 hr at 80°C. 4N Sulfuric acid (40 m*l*) was then added to the reaction mixture. The organic layer was washed with water and dried. The crude ketomalonate obtained by evaporating the solvent was mixed with acetic acid (80 m*l*) and concentrated sulfuric acid (0.5 m*l*). After the mixture had been refluxed for 2.5 hr, 4N sulfuric acid (40 m*l*) was added to the mixture and the reflux was continued for further 2 hr. The reaction mixture was put to stand overnight. The crude crystals deposited were collected by filtration and washed with water and then dissolved in ethyl acetate. After treatment with active charcoal, the solvent was removed to give yellow crystals (16.2 g, 66%). The crude material was recrystallized twice from ethyl acetate to give pure IV′, pale yellow leaflets, mp 145—147°C.

Found: C, 88.27; H, 4.87%. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95%.

2-Hydroxymethylpyrene. Reduction of 2-carbethoxypyrene[15] by means of lithium aluminum hydride afforded 2-hydroxymethylpyrene in a good yield. Recrystallization from ethanol gave pure material as colorless needles, mp 168—169°C.

Found: C, 87.61; H, 5.17%. Calcd for $C_{17}H_{12}O$: C,

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

[14] W. E. Bachmann and M. Carmack, *J. Amer. Chem. Soc.*, **63**, 2494 (1941).

[15] H. Vollmann, H. Becker, M. Correll, and H. Streek, *Ann.*, **531**, 1 (1937).

87.90; H, 5.21%.

2-Formylpyrene (III′). A solution of 2-hydroxymethylpyrene (8.68 g, 0.04 mol) in pyridine (60 m*l*) was added to a mixture of chromium trioxide (12.4 g, 0.124 mol) in pyridine (140 m*l*) under ice-cooling. After shaking for 30 min, the cooling bath was removed and the mixture was kept at room temperature for 1 hr. The reaction mixture was then poured into water (1 *l*) and extracted with ether (1.8 *l*). The extract was washed several times successively with 10% hydrochloric acid, a saturated solution of sodium carbonate and water. The residue obtained by evaporating the solvent was recrystallized from ethyl acetate to yield III′ (6.2 g, 68%). This material was recrystallized 3 times from the same solvent to give pure III′, yellow rods, mp 153—154°C.

Found: C, 88.63; H, 4.36%. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38%.

2-Ethynylpyrene (V′). A mixture of 2-acetylpyrene (IV′, 15.9 g, 0.065 mol), phosphorus pentachloride (14.0 g, 0.067 mol) and benzene (200 m*l*) was refluxed for 2 hr, and the volatile materials were removed under reduced pressure. The residue which had been kept in an evacuated desiccator over potassium hydroxide was dissolved in tetrahydrofuran (100 m*l*). The solution was added to a suspension of sodium amide [from sodium, 9.2 g (0.4 g-atom)] in liquid ammonia (500 m*l*) at −70°C. After stirring for 3 hr, the ammonia was allowed to evaporate. A saturated solution of ammonium chloride was added to the residue at −30°C. The aqueous layer was extracted with ether and combined with the organic layer and dried. The residue obtained by evaporating the solvent was dissolved in hot ligroin containing a small amount of benzene. The filtrate obtained by passing the hot solution through a column of alumina (30 g) was concentrated to yield V′ as colorless needles, 11.0 g (75%). Recrystallization twice from ethanol gave pure specimen, mp 125—127°C.

Found: C, 95.53; H, 4.41%. Calcd for $C_{18}H_{10}$: C, 95.54; H, 4.46%.

1,1′-Dipyrenyldiacetylene (I_2). Cupric acetate monohydrate (5.0 g) was added to a stirred solution of 1-ethynylpyrene (V, 0.510 g, 2.3 mmol) in pyridine (20 m*l*). The mixture was stirred for 3 hr at 55°C. The insoluble material deposited on cooling the reaction mixture was collected by filtration and washed successively with methanol and water to yield tiny yellow cubes, 0.504 g (98%), mp 297—298°C (dec.). The crude material was dissolved in hot toluene and passed through a short column of alumina. The crystals obtained from the filtrate were recrystallized from toluene, yielding pure I_2, yellow cubes, mp 298°C (dec.).

Found: C, 95.93; H, 4.07%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

2,2′-Dipyrenyldiacetylene (II_2). According to the procedure used in the synthesis of I_2, 2-ethynylpyrene (V′) gave II_2, pale yellow needles (from toluene) in a 96% yield. The crystals showed no melting point, but began to decompose at 330°C.

Found: C, 95.91; H, 3.97%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

1-(1-Pyrenyl)-2-propyn-1-ol (VII). A solution of 1-formylpyrene[16] (III, 6.90 g, 0.03 mol) in tetrahydrofuran (60 m*l*) was added to an ice-cooled solution of ethynylmagnesium bromide [from ethyl bromide, 8.20 g (0.075 mol), magnesium, 1.80 g (0.075 g atom) and an excess of acetylene] in the same solvent (85 m*l*). After the mixture had been stirred overnight at room temperature, a saturated solution of ammonium chloride was added to the reaction mixture. The organic layer was dried and the crystals obtained by evaporating the solvent were dissolved in acetone. The insoluble material was removed by filtration. The crystals (6.95 g, 91%, mp 145—150°C) obtained from the filtrate were redissolved in acetone and passed through a short column of alumina. The filtrate was concentrated, and the crystals deposited were recrystallized from ethanol - benzene, yielding pure VII as colorless rods, mp 159—160°C.

Found: C, 88.90; H, 4.67%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%. IR: 3600—3100 (OH), 3300 (≡CH), 2100 (C≡C) cm^{-1}.

1-(2-Pyrenyl)-2-propyn-1-ol (VII′). According to the procedure used for VII, 2-formylpyrene (III′) gave crude VII′ in a 96% yield. The crude material was recrystallized 3 times from carbon tetrachloride - ethanol to give pure VII as colorless needles, mp 132—135°C.

Found: C, 89.06; H, 4.71%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%. IR: 3350—3200 (OH), 3250 (≡CH), 1035 (C–O) cm^{-1}.

1,6-Di-(1-pyrenyl)-2,4-hexadiyn-2,6-diol (VIII). A mixture of ethynylcarbinol (VII, 3.98 g, 0.0156 mol), acetone (50 m*l*), methanol (50 m*l*), ammonium chloride (0.30 g), and cuprous chloride (0.40 g) was vigorously stirred at room temperature under a slight excess pressure of oxygen for 48 hr. The crystalline material deposited was collected by filtration and washed with methanol containing hydrochloric acid. The light brown crystals thus obtained (2.02 g, 51%, decomposed at *ca.* 220°C) were dissolved in tetrahydrofuran and passed 4 times through a thin layer of alumina. Concentration of the filtrate gave pure VIII as fine colorless needles. The crystals turned pink at *ca.* 160°C and decomposed at *ca.* 225—260°C.

Found: C, 88.96; H, 4.42%. Calcd for $C_{38}H_{22}O_2$: C, 89.39; H, 4.34%. IR: 3400—3100 (OH), 2250 (C≡C), 1015 (C–O) cm^{-1}.

1,6-Di-(2-pyrenyl)-2,4-hexadiyn-1,6-diol (VIII′). According to the procedure for VIII, the oxidative coupling of ethynylcarbinol (VII′) afforded a crude VIII′ in a 47% yield which decomposed at *ca.* 245°C. Owing to its poor solubility, the crude material was subjected to the following reaction without purification.

1,1′-Dipyrenyltriacetylene (I_3). Preparation of Dichloride (IX). A mixture of thionyl chloride (0.144 g, 1.2 mmol), pyridine (0.096 g, 1.2 mmol) and tetrahydrofuran (5 m*l*) was added over a period of 30 min to a solution of diacetylenic glycol (VIII, 0.244 g, 0.4 mmol) in tetrahydrofuran (15 m*l*) at −10°C. When the addition had been completed, the mixture was shaken for 10 min at the same temperature and immediately used for the following reaction.

Dehydrochlorination. To a stirred suspension of sodium amide [from sodium, 0.14 g (6 mg-atom)] in liquid ammonia (90 m*l*) maintained at −60°C was added a solution of dichloride (IX). After 30 min, ammonium chloride (1 g) was added and the ammonia was allowed to evaporate. After the organic solvent had been removed, a small amount of water was added to the residue. The insoluble material was collected by filtration, washed with a small amount of methanol and benzene. The solid thus obtained was dissolved in boiling toluene and the hot solution was percolated through a short column of alumina. Concentration of the filtrate afforded fine yellow needles, 0.080 g (42%) which decomposed at *ca.* 295°C. The crystals were redissolved in boiling toluene and passed through a thin layer of alumina, yielding pure I_3 as yellow needles which decomposed at *ca.* 300°C.

Found: C, 96.18; H, 3.85%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

2,2′-Dipyrenyltriacetylene (II_3). The procedure used in the preparation of I_3 was followed. Chlorination of crude

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[16] A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).

VIII′ followed by dehydrochlorination gave crude II_3 in a 27% yield. Purification of this material gave II_3 as yellow needles (decomp. 260—270°C).

Found: C, 95.93; H, 3.81%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

1-(1-Pyrenyl)-2-butyn-1,4-diol (X). A solution of 1-formylpyrene (II, 6.00 g, 0.026 mol) in tetrahydrofuran (60 m*l*) was added dropwise to an ice-cooled solution of the Grignard derivative of propargyl alcohol [from magnesium, 3.74 g (0.156 g-atom), ethyl bromide, 17 g (0.156 mol), and propargyl alcohol, 4.37 g (0.078 mol)]. The mixture was stirred overnight and then a saturated solution of ammonium chloride was added. The dried organic layer was concentrated. The residue was triturated with benzene and washed with the same solvent, thus yielding pale yellow crystalline powder, 7.20 g (97%), mp 141—145°C. Recrystallization of the crystals from ethanol and from ethanol - benzene afforded pure X as colorless needles, mp 150—151°C.

Found: C, 83.56; H, 4.95%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR: 3600—3100 (OH), 1055, 1012 (C–O) cm^{-1}.

1-(2-Pyrenyl)-2-butyn-1,4-diol (X′). According to the procedure for X, 2-formylpyrene (III′) gave crude X′ in 82% yield. Recrystallization three times of this material from ethanol yielded pure X′, colorless leaflets, mp 183—185°C.

Found: C, 83.90; H, 4.86%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR: 3350—3200 (OH), 1000, 1007 (C–O) cm^{-1}.

1-Butadiynylpyrene (XII). Preparation of the Dichloride (XI). A solution of thionyl chloride (4.65 g, 0.039 mol) in tetrahydrofuran (10 m*l*) was added over a period of 1 hr to a mixture of acetylene glycol (X, 4.30 g, 0.015 mol), pyridine (3.08 g, 0.039 mol), and tetrahydrofuran (10 m*l*) kept at −10°C. The temperature of the reaction mixture was gradually raised to room temperature and stirring was continued for 1 hr and then for 1 hr at 30°C. Cracked ice was then added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with benzene (100 m*l*). The combined organic layer was dried, and concentrated to *ca.* 5 m*l*. The solution of dichloride (XI) thus prepared was used in the subsequent reaction.

Dehydrochlorination. The solution of XI was added over a period of 20 min to a stirred suspension of sodium amide [from sodium, 2.5 g (0.11 g-atom)] in liquid ammonia (100 m*l*) at a temperature of −70°C. After 3 hr ammonium chloride (7 g) was added to the reaction mixture and the ammonia was allowed to evaporate. After the organic solvent had been removed, the residue was extracted with petroleum ether (bp 60—80°C, total 450 m*l*). The extract was passed through a thin layer of alumina (12 g). Concentration of the filtrate afforded extremely unstable XII as fine needles, 1.33 g (36%), mp *ca.* 105°C (dec.). XII gave orange yellow, silver and orange cuprous acetylides.

UV: $\lambda_{max}^{petroleum\ ether}$ 377 nm.

1,1′-Dipyrenyltetraacetylene (I_4). A mixture of 1-butadiynylpyrene (XII, 0.050 g, 0.2 mmol), cupric acetate monohydrate (0.50 g), pyridine (3 m*l*) and methanol (0.5 m*l*) was stirred at room temperature for 12 hr. The insoluble material was collected by filtration and washed successively with water, a small amount of methanol and benzene, yielding fine yellow needles, 0.038 g (76%), which decomposed at *ca.* 255°C. This material was dissolved in hot toluene and percolated through a thin layer of alumina. Concentration of the filtrate gave pure I_4 as fine orange yellow needles, which decomposed at *ca.* 260°C.

Found: C, 96.06; H, 3.64%. Calcd for $C_{40}H_{18}$: C, 96.36; H, 3.64%.

2-Butadiynylpyrene (XII′). Preparation of the Dichloride (XI′). A solution of thionyl chloride (2.33 g, 19.5 mmol) in tetrahydrofuran (10 m*l*) was added to a stirred mixture of the acetylene glycol (X′, 2.15 g, 7.5 mmol), pyridine (1.54 g, 19.5 mmol), and tetrahydrofuran (40 m*l*) under cooling on an ice-salt bath. The temperature of the reaction mixture was allowed to rise gradually to room temperature, and stirring was continued at 30°C for 1 hr. Cracked ice was added to the reaction mixture under external cooling with ice-water. The organic layer was washed successively with water and sodium hydroxide solution, and dried. The concentrated solution of XI′ (*ca.* 10 m*l*) was subjected to the following reaction.

Dehydrochlorination. To a stirred suspension of sodium amide [from sodium, 1.3 g (0.055 g-atom)] in liquid ammonia (50 m*l*) was added the solution of XI′ at −70°C, and stirring was continued for 3 hr. After ammonium chloride (4 g) had been added tothe reaction mixture, ammonia was allowed to evaporate and the organic solvent was removed. The residue was extracted with petroleum benzine (1 *l*). The extract was concentrated to *ca.* 500 m*l* and passed through a short column of alumina, yielding colorless filtrate. It was impossible to isolate diacetylene (XII′) in solid state owing to the unstable nature of the compound. The petroleum benzine solution of XII′ was thus used in the subsequent reaction.

UV: $\lambda_{max}^{benzine}$ 336, 321, 306, 300, 288 nm.

2,2′-Dipyrenyltetraacetylene (II_4). To a stirred solution of cupric acetate monohydrate (4.0 g) in pyridine (20 m*l*) was added a small portion of the solution of diacetylene (XII′), and petroleum benzine was removed under reduced pressure at room temperature. A second portion of the solution was then added, benzine being again removed *in vacuo*. The entire benzine solution was added, portion by portion to the oxidizing reagent, repeating the above procedure. After addition of the solution and removal of the benzine had been completed, additional pyridine (20 m*l*) and methanol (5 m*l*) were added to the solution, and the mixture was stirred overnight at room temperature. After the solvent had been removed, water was added to the residue and the insoluble material was collected by filtration, washed thoroughly with water and then ethanol and benzene. The yellow crystals thus obtained [140 mg, 15% based on the glycol (X′)] were dissolved in hot toluene. The filtrate obtained by percolating the hot solution through a short column of alumina was put to stand to deposit pure II_4 as fine yellow needles. II_4 decomposed at *ca.* 180°C accompanying decoloration.

Found: C, 96.51; H, 3.62%. Calcd for $C_{40}H_{18}$: C, 96.36; H, 3.64%.

3-(1-Pyrenyl)-prop-2-ynal (VI). A solution of 1-ethynylpyrene (V, 10.08 g, 0.045 mol) in tetrahydrofuran (50 m*l*) was added under stirring over a period of 20 min to an ice-cooled solution of isopropylmagnesium bromide [from magnesium, 2.16 g (0.09 g-atom) and isopropyl bromide, 12.18 g (0.099 mol)] in tetrahydrofuran (60 m*l*). The mixture had been refluxed for 1 hr, and then chilled on an ice-salt bath. Dimethylformamide (16 m*l*) was added in one portion to the chilled mixture and stirred for 20 min. Stirring was continued for further 4 hr at room temperature. The reaction mixture was then poured into vigorously stirred 5% sulfuric acid (600 m*l*) and stirred overnight. The mixture was extracted with benzene (1 *l*) and the extract was washed successively with water and a solution of sodium hydrogen carbonate. The organic layer was shaken with a saturated solution of sodium hydrogen sulfite. The adduct deposited was washed with ether, tetrahydrofuran and ether, successively, and decomposed with a saturated solution of sodium hydrogen carbonate. The crude propynal (VI) thus obtained was extracted with hot benzene (100 m*l*) using a Soxhlet extractor. Orange cubes, 9.19 g (81%), mp 145—147°C, obtained from the extract were recrystallized several times from benzene - cyclohexane. Aldehyde (VI) showed dimorphism, *viz.*, rapid cooling of the benzene - cyclohexane solution gave orange needles, mp 141—142°C. On the other hand, orange cubes, mp 148—149°C were obtained on slow cooling of the solution.

Low mp isomer. Found: C, 89.27; H, 4.01%. High mp isomer. Found: C, 89.63; H, 3.99%. Calcd for $C_{19}H_{10}O$: C, 89.74; H, 3.96%. IR: 2840, 2735 (CHO), 2170 (C≡C), 1645 (C=O) cm^{-1}. Both isomers exhibited almost the same IR spectra, a slight difference being observed in the region 1200—650 cm^{-1}.

3-(2-Pyrenyl)-prop-2-ynal (VI′). To an ice-cooled and stirred solution of isopropylmagnesium bromide [from magnesium, 0.72 g (0.03 g-atom) and isopropyl bromide, 4.06 g (0.033 mol)] in tetrahydrofuran (20 m*l*) was added over a period of 15 min a solution of 2-ethynylpyrene (V′, 3.36 g, 0.015 mol) in tetrahydrofuran (20 m*l*). The mixture was stirred for 30 min at room temperature and then refluxed for 30 min. The mixture was then chilled on an ice-salt bath. After dimethylformamide (6 m*l*) had been added in one portion, the temperature of the reaction mixture was gradually raised to room temperature. Stirring was continued for 3 hr and then for 1 hr at 30°C. The reaction mixture was poured into vigorously agitated 5% sulfuric acid (200 m*l*) and stirring was continued overnight. The mixture was extracted with benzene (330 m*l*) and the extract was washed successively, with water, a saturated solution of sodium hydrogen carbonate and water, and dried. The crystalline residue obtained by evaporating the solvent was recrystallized from benzene to afford yellow crystals, 3.1 g (81%). The crystals dissolved in ethanol were treated with active charcoal and recrystallized 3 times from benzene - cyclohexane to yield pure VI′ as yellow cubes, mp 160—161°C.

Found: C, 89.60; H, 4.12%. Calcd for $C_{19}H_{10}O$: C, 89.74; H, 3.96%. IR: 2180 (C≡C), 1660 (C=O) cm^{-1}.

1-(1-Pyrenyl)-1,4-pentadiyn-3-ol (XVI). A solution of 1-pyrenylpropynal (VI, 5.09 g, 0.02 mol) in tetrahydrofuran (150 m*l*) was added over a period of 20 min into an ice-cooled and stirred solution of ethynylmagnesium bromide [from magnesium, 1.15 g (0.048 g-atom), ethyl bromide, 5.78 g (0.053 mol) and an excess of acetylene]. The cooling bath was removed after 3 hr, and stirring was continued overnight at room temperature. A saturated ammonium chloride solution was added to the reaction mixture under cooling with ice-salt bath. The organic layer was separated and the aqueous layer was extracted with benzene (100 m*l*). The combined organic layer was dried. A light brown oily material obtained by evaporation of the solvent was mixed with hot benzene (20 m*l*), thus yielding fine light brown needles, 4.07 g (73%), mp 114—119°C. The crystals were recrystallized 4 times from methanol-benzene to yield pure XVI as pale yellow needles, mp 122—123°C. XVI gave yellow cuprous acetylide.

Found: C, 89.69; H, 4.30%. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.32%. IR: 3400—3100 (OH), 3295 (≡CH), 2220, 2110 (C≡C), 1010 (C–O) cm^{-1}.

1-(2-Pyrenyl)-1,4-pentadiyn-3-ol (XVI′). Crude crystals of XVI′ obtained according to the procedure for the synthesis of XVI were dissolved in benzene - ethanol and treated with active charcoal, yielding light yellow crystals in a 73% yield. The material was recrystallized 3 times from ethanol to give pure XVI′ as colorless plates, mp 175—178°C.

Found: C, 89.98; H, 4.35%. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.32%. IR: 3500—3400 (OH), 3295 (≡CH), 1180 (C–O) cm^{-1}.

1,1′-Dipyrenylpentaacetylene (I_5). Oxidative Coupling of XVI. A mixture of pentadiynol (XVI, 2.10 g, 7.5 mmol), cuprous chloride (0.20 g), ammonium chloride (0.18 g) and methanol (50 m*l*) was vigorously stirred under a slight excess of oxygen pressure at room temperature for 48 hr. The residue obtained by evaporating the solvent was dissolved in acetone (50 m*l*) and the insoluble material was removed by filtration. The acetone solution was passed through a short column of alumina, and the filtrate was concentrated. The residue solidified on addition of a small amount of benzene. The solid was washed with a small amount of methanol to yield crude XVII as light brown unstable crystalline powder, 1.01 g (58%). The IR spectrum of this material indicates the absence of ethynyl group. The crude material was subjected to the subsequent reaction without purification because of its instability.

Chlorination of XVII. A solution of thionyl chloride (0.18 g, 1.5 mmol) and pyridine (0.12 g, 1.5 mmol) in tetrahydrofuran (5 m*l*) was added over a period of 15 min to a solution of the crude tetraacetylene glycol (XVI, 0.279 g, 0.5 mmol) in the same solvent (15 m*l*) at a temperature of −30°C. After shaking for 10 min, the reaction mixture was used immediately in the following reaction without isolation of XVIII.

Dehydrochlorination of XVIII. The reaction mixture containing XVIII was added to a suspension of sodium amide [from sodium, 0.20 g (8.7 mg-atom)] in liquid ammonia (70 m*l*) at −70°C. After the mixture had been stirred for 30 min, ammonium chloride (1.0 g) was added and the ammonia was allowed to evaporate. The organic solvent in the residue was removed. A small amount of water was added to the residue and the insoluble material was collected and washed successively with water, a small amount of acetone and benzene. A deep brown solid thus obtained was extracted with hot toluene (total 500 m*l*) and the hot extract was passed through a short column of alumina (15 g). I_5 (0.089 g, 34%) was obtained as fine orange needles on putting the orange yellow filtrate to stand. I_5 decomposed at *ca.* 215°C.

Found: C, 96.11; H, 3.55%. Calcd for $C_{42}H_{18}$: C, 96.53; H, 3.47%.

2,2′-Dipyrenylpentaacetylene (II_5). A mixture of diynol (XVI′, 1.05 g, 3.75 mmol), cuprous chloride (0.40 g), ammonium chloride (0.36 g), concentrated hydrochloric acid (1 drop) and methanol (80 m*l*) was vigorously stirred in an atmosphere of oxygen under slightly elevated pressure for 48 hr at room temperature. The precipitate collected by filtration was washed with methanol to give brown crystals. The crystals were dissolved in tetrahydrofuran and filtered. Concentration of the filtrate gave crude XVII′ as brown crystals, 500 mg (48%). Crude XVII′ was converted into dichloride (XVIII′) and then dehydrochlorinated to yield II_5 according to the method used in the preparation of I_5. Pentaacetylene (II_5) was obtained as orange yellow needles (13% based on XVII′) which decomposed at *ca.* 140°C.

Found: C, 96.43; H, 3.37%. Calcd for $C_{42}H_{18}$: C, 96.53; H, 3.47%.

1-(1-Pyrenyl)-2,5-hexadiyn-1,4-diol (XIII). A solution of 1-formylpyrene (III, 6.68 g, 0.029 mol) in tetrahydrofuran (60 m*l*) was added to a stirred solution of the Grignard derivative of 1,4-pentadiyn-3-ol [from 3.08 g of the alcohol] in tetrahydrofuran (15 m*l*) under cooling on an ice-salt bath. The temperature of the reaction mixture was gradually raised to room temperature, stirring was continued overnight and a saturated solution of ammonium chloride was then added. The aqueous layer was extracted with benzene (100 m*l*). The combined organic layer was dried and concentrated to give an oily material. The crystals formed by trituration with benzene were washed with a small amount of benzene and dissolved in acetone (50 m*l*). The acetone solution was passed through a short column of alumina (15 g) and the filtrate was concentrated. The oily residue was mixed with hot benzene (25 m*l*) to deposit fine light brown crystals, 6.55 g (73%), mp 115—125°C. Recrystallization of the crystals from ethyl acetate - benzene afforded pure XIII as pale yellow needles which decomposed at *ca.* 145—155°C.

Found: C, 84.88; H, 4.61%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%. IR: 3600—3100 (OH), 3290 (≡CH), 2110 (C≡C), 1027 (C–O) cm^{-1}.

1-Pyrenyltriacetylene (XV). Chlorination of XIII. To a solution of slightly crude XIII (0.310 g, 1 mmol) in tetrahydrofuran (5 m*l*) maintained at −30°C was added over a period of 15 min a solution of thionyl chloride (0.36 g, 3 mmol) and pyridine (0.24 g, 3 mmol) in the same solvent (5 m*l*). After the addition had been completed, the mixture was stirred for 2 hr at room temperature. Crushed ice was added to the reaction mixture and extraction was carried out with benzene (100 m*l*). The extract was washed successively with water and sodium hydrogen carbonate solution, and dried. The reddish brown oily material obtained by evaporation of the solvent was subjected to the following reaction.

Dehydrochlorination. A solution of crude dichloride (XIV) in tetrahydrofuran (5 m*l*) was added over a period of 10 min to a suspension of sodium amide [from sodium, 0.14 g (6 mg-atom)] in liquid ammonia (50 m*l*) at −70°C. After the mixture had been stirred for 30 min, ammonium chloride (0.7 g) was added and the ammonia was allowed to evaporate. The residue, after the organic solvent had been removed, was extracted with petroleum ether (bp 60—80°C, total 150 m*l*). The extract was passed through a thin layer of alumina (2 g) and the filtrate was used in the subsequent reaction. Extremely unstable yellow crystals (XV) were obtained by concentration of a small portion of the filtrate. The filtrate exhibiting UV maximum at 396 nm gave orange red cuprous acetylide.

1,1′-Dipyrenylhexaacetylene (I_6). The petroleum ether solution of XV was added to a mixture of cupric acetate monohydrate (1.5 g), methanol (5 m*l*), and pyridine (10 m*l*). Petroleum ether was removed under reduced pressure and additional pyridine (5 m*l*) was then added. The mixture was stirred for 2 hr at room temperature. The insoluble material was filtered, washed with water, a small amount of methanol and benzene to yield dark red fine crystals, 0.089 g (33% based on XIII). The crystals were digested with hot toluene (total 400 m*l*) and the extract was passed through a short column of alumina (10 g). On leaving the filtrate to stand, hexaacetylene (I_6) deposited as tiny red crystals which decomposed at *ca.* 200°C.

Found: C, 96.18; H, 3.24%. Calcd for $C_{44}H_{18}$: C, 96.68; H, 3.32%.

1-(2-Pyrenyl)-1,4-hexadiyn-3,6-diol (XIX′). To an ice-cooled and stirred solution of the Grignard derivative of propargyl alcohol [from propargyl alcohol, 1.86 g (0.033 mol)] in tetrahydrofuran (35 m*l*) was added a solution of the propiolaldehyde (VI′, 2.80 g, 0.017 mol) in tetrahydrofuran (30 m*l*). After the reaction mixture had been stirred overnight, a saturated solution of ammonium chloride was added. The aqueous layer was extracted with tetrahydrofuran and combined with the organic layer and dried. The combined organic layer was concentrated to yield light brown crystals, 2.9 g (85%). The crystals were recrystallized 3 times from ethanol to give pure XIX′ as tiny light brown leaflets, mp 200—203°C (dec.).

Found: C, 85.12; H, 4.58%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%. IR: 3350—3100 (OH), 2240 (C≡C), 1020, 1040 (C–O) cm^{-1}.

2-Pyrenyltriacetylene (XV′). Chlorination of XIX′. A solution of thionyl chloride (720 mg, 6 mmol) in tetrahydrofuran (10 m*l*) was added to a solution of XIX′ (620 mg, 2 mmol) and pyridine (480 mg, 6 mmol) in the same solvent (20 m*l*) at −30°C. The mixture was stirred for 30 min at room temperature and then for 40 min at 30°C. The mixture was chilled again on an ice-salt bath and crushed ice was added. The organic layer was washed with a solution of sodium hydrogen carbonate and dried. The residue obtained by evaporation of the solvent was redissolved in tetrahydrofuran (15 m*l*). The solution of XX′ thus prepared was subjected to the following dehydrochlorination.

Dehydrochlorination of XX′. The solution of XX′ was added to a suspension of sodium amide [from sodium, 1.3 g (0.055 mg-atom)] in liquid ammonia (100 m*l*) at −70°C. After the mixture had been stirred for 1 hr, ammonium chloride (5 g) was added and ammonia was allowed to evaporate. The residue obtained by evaporation of the organic solvent was extracted with petroleum ether (bp 60—80°C, total 500 m*l*). The extract was percolated through a thin layer of alumina (10 g) and the filtrate was used in the following oxidative coupling without isolation of triacetylene (XV′).

2,2′-Dipyrenylhexaacetylene (II_6). The petroleum ether solution of XV′ was mixed with a mixture of cupric acetate monohydrate (2 g) and pyridine (20 m*l*) and the petroleum ether was removed under reduced pressure. Pyridine (5 m*l*) and methanol (5 m*l*) were added to the residue and the resulting mixture was stirred for 2 hr at room temperature. The insoluble material was collected by filtration, washed successively with water, methanol and benzene. The yellowish brown solid thus obtained was digested with toluene and the hot extract was passed through a short column of alumina. The filtrate was allowed to cool to room temperature, yielding II_6 as tiny brownish orange yellow crystals. II_6 was found to be rather unstable and gave an unsatisfactory elemental analysis.

Found: C, 94.91; H, 3.90%. Calcd for $C_{44}H_{18}$: C, 96.68; H, 3.32%.