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Linear Conjugated Systems Bearing Aromatic Terminal Groups. VI. Syntheses and Electronic Spectra of 6,6′-Dichrysenylpoly-ynes

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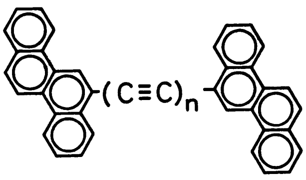
6,6′-Dichrysenylpoly-ynes (I_n, $n=1$—6) have been synthesized and their electronic spectra were measured. It was found that the bathochromic shifts of the longest-wavelength absorption peaks (λ_{max}) along with an increase in the number of acetylenic bond (n) were proportional to $n^{1.6}$ ($\lambda_{max}=5.8\,n^{1.6}+394$ nm).

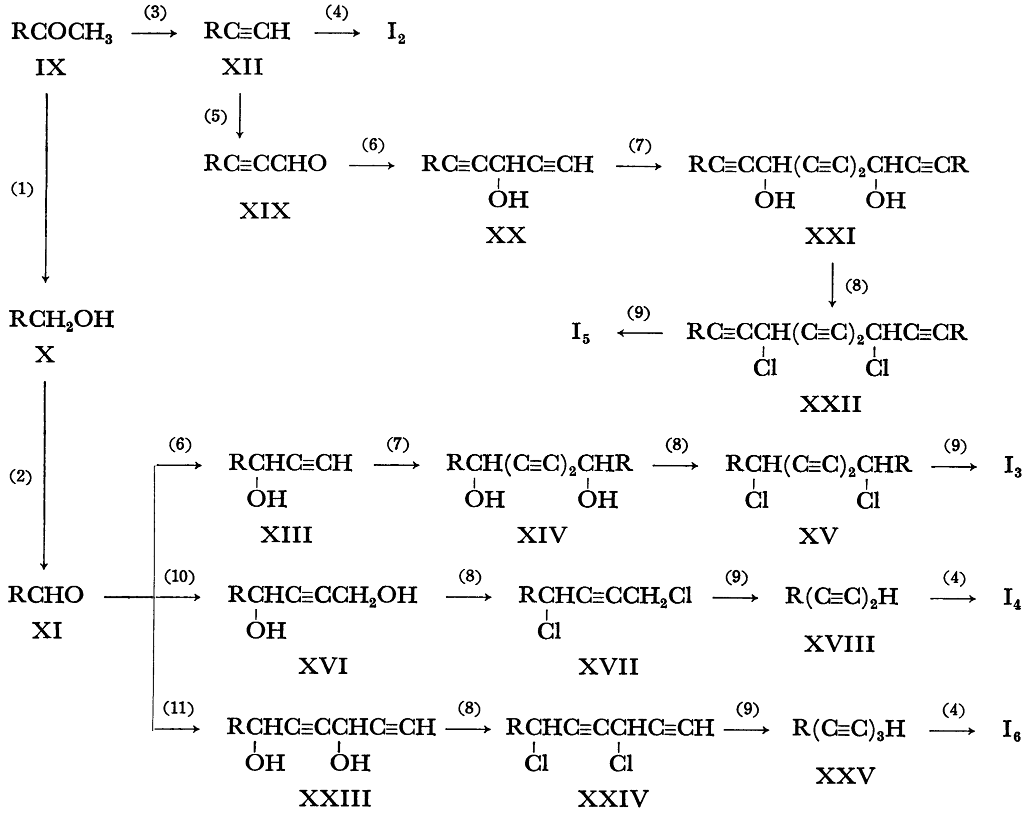
In previous papers we reported that new linear relationships between the longest-wavelength absorption maxima (λ_{max}) and the xth power of the number of acetylenic bond (n) [$\lambda_{max} \propto n^x$] hold in various kinds of diarylpoly-ynes (II_n[1], III_n[2], IV_n[3], V_n[3], VI_n[4], VII_n[4], and $VIII_n$[4]) (Fig. 1). It was shown that the value of x is dependent on the nature of terminal groups as well as on the position of linking of polyacetylene chain.

In order to get further information on the role of aromatic terminal groups in the photoexcitation of diarylpoly-ynes, 6,6′-dichrysenylpoly-ynes (I_n) have been synthesized. The present paper deals with the syntheses and spectral regularity of I_n.



I_n
$n=1, 2, 3, 4, 5, 6.$

Syntheses. The synthesis of 6,6′-dichrysenylacet-



R = 6-chrysenyl

(1) i. NaOCl, ii. methanol-H_2SO_4, iii. $LiAlH_4$; (2) pyridine-CrO_3; (3) i. PCl_5, ii. $NaNH_2$/liq. NH_3;
(4) $Cu(OAc)_2 \cdot H_2O$/pyridine; (5) i. *iso*-C_3H_7MgBr/THF, ii. DMF, iii. *dil.* H_2SO_4; (6) $HC{\equiv}CMgBr$/THF;
(7) CuCl-NH_4Cl-O_2; (8) $SOCl_2$-pyridine/THF; (9) $NaNH_2$/liq. NH_3; (10) $BrMgC{\equiv}CCH_2OMgBr$;
(11) $BrMgC{\equiv}CCH(OMgBr)C{\equiv}CH$/THF.
DMF = dimethylformamide. THF = tetrahydrofuran.

Scheme 1. Syntheses of 6,6-dichrysenylpoly-ynes (I_n)

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[1] S. Akiyama and M. Nakagawa, This Bulletin, **40**, 340 (1967).

[2] S. Akiyama and M. Nakagawa, *ibid.*, **43**, 3561 (1970).

[3] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, *ibid.*, **43**, 3576 (1970).

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

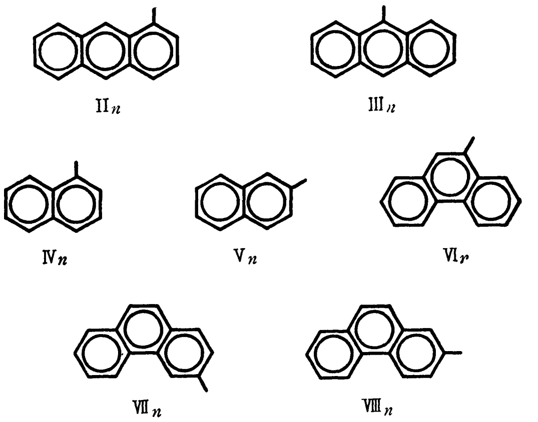

Fig. 1. The terminal groups (R) of diarylpoly-ynes [R(C≡C)$_n$R].

ylene (I_1) by means of an intramolecular Wittig reaction has been reported[5] together with other diarylacetylenes.

Acetyl-[6] and formyl derivatives (IX and XI) were used as starting materials for the syntheses of 6,6′-dichrysenylpoly-ynes (I_n, n=2—6). 6-Chrysenecarboxaldehyde (XI) was obtained in a good yield by chromium trioxide-pyridine oxidation of hydroxymethyl derivative (X).[7] The reaction sequence adapted for the preparation of I_n is a general method which had been established to be useful for the syntheses of various types of diarylpoly-ynes.[1-4]

6,6′-Dichrysenylpoly-ynes (I_1—I_6) were found to be fairly stable. It was observed that I_n is less soluble in common organic solvents as compared with other diarylpoly-ynes. I_2 and I_6 in particular were found to be the least soluble materials. Upon recrystallization from toluene, the solvent persistently incorporated into the crystals of diacetylene (I_2) and tetraacetylene (I_4), and the solvent of crystallization of I_4 (1 mol) could not be removed *in vacuo* even at elevated temperature.

TABLE 1. PHYSICAL PROPERTIES OF I_n

n	Color of crystals	Decomposition point (°C)	$\nu_{C\equiv C}$ (cm^{-1})
1	light yellow	>330	—
2	yellow	>330	—
3	deep yellow	*ca.* 295	2185
4	deep yellow	*ca.* 250	2190
5	orange	*ca.* 230	2170
6	orange red	*ca.* 150	2150

a) The crystals (I_4) contain 1 mol of toluene as solvent of crystallization.

The color of crystals, decomposition points and IR absorptions due to $\nu_{C\equiv C}$ are summarized in Table 1. The highest wave number of $\nu_{C\equiv C}$ was observed in the spectrum of tetraacetylene (I_4), as in the case of II_n[1], diphenyl- and dimethylpoly-ynes.[8] Like other series

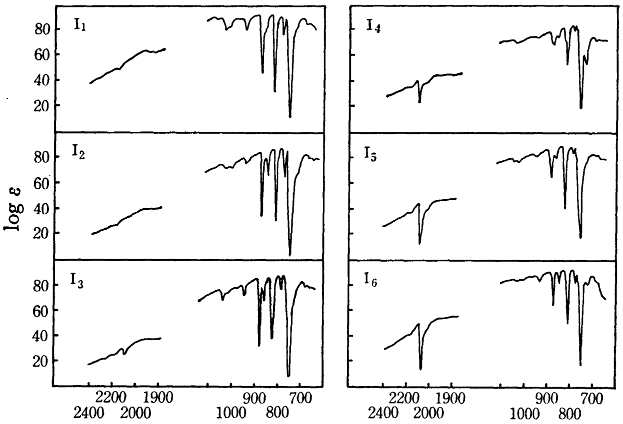

Fig. 2. IR spectra of 6,6′-dichrysenylpoly-ynes (I_n). Measurements were performed by KBr-disk method except for I_6. The spectrum of I_6 was obtained by Nujol-mull method. The sample of I_4 contains 1 mol of toluene as a solvent of crystallization.

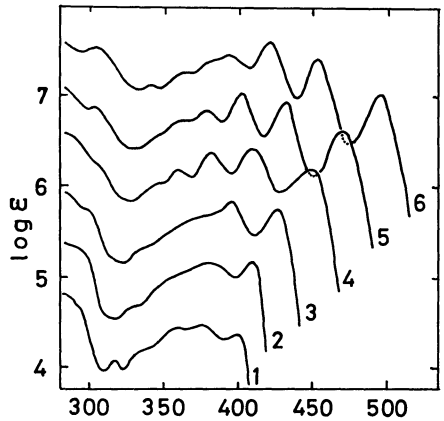

Fig. 3. Absorption curves of 6,6′-dichrysenylpoly-ynes (I_n) in toluene. The curves, with the exception of I_1 at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below.

TABLE 2. ELECTRONIC SPECTRAL DATA OF 6,6-DICHRYSENYLPOLY-YNES (I_n)

n	Absorption maxima, λ (in nm) and log ε (in parentheses) in toluene							
1	284.5 (4.911)	316 (4.159)	357 (4.508)	377 (4.535)	400 (4.452)			
2	283.5 (4.885)	379 (4.670)	411 (4.668)					
3	284 (4.925)	297.5 (4.776)	377 (4.677)	396 (4.834)	428 (4.759)			
4	283.5 (5.119)	358 (4.705)	381 (4.889)	407 (4.927)	449 (4.696)			
5	283 (5.064)	305 (4.952)	362 (4.715)	378 (4.854)	402 (4.869)	431 (4.955)	471 (4.631)	
6	283.5 (5.039)	302.5 (5.067)	340 (4.626)	363 (4.767)	392 (4.938)	421 (5.087)	453 (4.903)	495 (4.530)

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

[6] W. Carruthers, *J. Chem. Soc.*, **1953**, 3486.

[7] M. J. S. Dewar and R. J. Sampson, *ibid.*, **1957**, 2946.

[8] C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem, Soc.*, **1952**, 2883; M. Yamaguchi and Y. Hayashi, "Infrared Spectroscopy, No. 9" (Special issue of Kagaku no Ryoiki, No. 40), Nankodo Tokyo (1960).

of diarylpoly-ynes, the absorption intensities of the most intense peaks in $\nu_{C\equiv C}$ bands seem to increase with the increase in the length of poly-yne chain. The IR spectra of I_n are shown in Fig. 2.

Electronic Spectra. The absorption curves and electronic spectral data of I_n are shown in Fig. 3 and Table 2. The L_b band of chrysene could not be observed in the spectra of I_n, due presumably to its coalescence with the L_a band which is shifted to a longer wavelength by interaction with polyacetylenic chromophore.

Chrysene can be regarded as benzophenanthrene. Thus, the 6-position in chrysene corresponds to either 3- or 9-position of phenanthrene. Actually, 6,6′-dichrysenylpoly-ynes (I_n) exhibit closely related electronic spectra with those of 3,3′- and 9,9′-diphenanthrylpoly-ynes.[4] The characteristic of the spectrum of chrysene could not be observed even in the spectra of a lower member of I_n just as in the case of diphenanthrylpoly-ynes. Like the spectra of other diarylpoly-ynes, the pronounced vibrational fine structure in the long-wavelength absorption band exhibits characteristic features of the spectra of I_n. The magnitude of red shift of the longest-wavelength maximum (λ_{max}) increases gradually with an increase in the number of n (11, 17, 21, 22, and 24 nm).

TABLE 3. SPACING OF VIBRATIONAL FINE STRUCTURE

n	1	2	3	4	5	6
Spacing (cm^{-1})	—	2050	1890	2300	1970	1870

As is shown in Table 3, the highest wave number of spacing between the longest-wavelength vibrational sub-band and the next longest-wavelength one was observed in the spectrum of tetraacetylene (I_4), which corresponds to the fact that the highest wave number of $\nu_{C\equiv C}$ is also observed in I_4.[9]

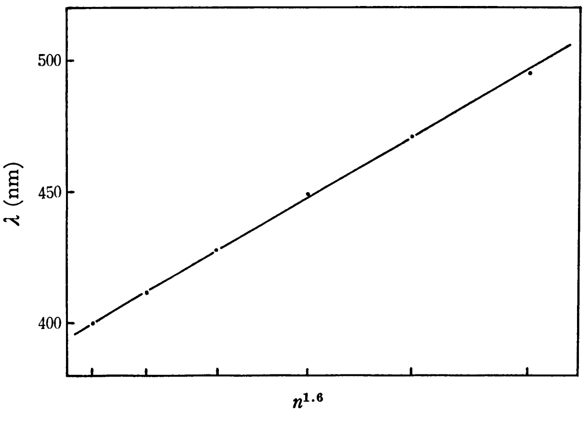

Fig. 4. Linear relationship between λ and $n^{1.6}$.

The plots of longest-wavelength absorption maxima (λ_{max}) against $n^{1.6}$ gave an excellent straight line as illustrated in Fig. 4. The linear relationship could be expressed by the following empirical formula:[10]

$$\lambda_{max} = 5.8n^{1.6} + 394 \text{ nm (in toluene).}$$

The observed and calculated values of λ_{max} are listed in Table 4.

TABLE 4. OBSERVED AND CALCULATED VALUES OF λ_{max} (nm)

n	1	2	3	4	5	6
Found	400	411	428	449	471	495
Calcd	400	412	428	447	470	496
$\Delta\lambda$	0	−1	0	+2	+1	−1

Experimental

All melting points are uncorrected. The electronic spectra were obtained on a Hitachi EPS-3T Spectrophotometer at room temperature. The infrared spectra were measured with a Hitachi EPI-2 Infrared Spectrophotometer by KBr-disk method. Evaporation of solvent and concentration of solution were performed under reduced pressure.

6-Chrysenecarboxaldehyde (XI). A solution of X (14.30 g, 0.056 mol)[7] in pyridine (120 m*l*) was added to a chilled solution of chromium trioxide (18.0 g, 0.18 mol) in pyridine (250 m*l*). The mixture was shaken in an ice-salt bath for 30 min, and then for 45 min at room temperature. The reaction mixture was poured into water (2 *l*). The resulting precipitate was filtered, washed with water and dried to give a brown powder. The powder was extracted with benzene (500 m*l*) using a Soxhlet type extractor. The extract was passed through a short column of alumina (15 g). Concentration of the filtrate (up to *ca.* 30 m*l*) gave faint yellow cubes (12.30 g, 86%, mp 164—166°C). Recrystallization of this material three times from benzene gave analytical sample with mp 165—166°C.

Found: C, 88.91; H, 4.66%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%. IR: 1690 (C=O) cm^{-1}.

6-Ethynylchrysene (XII). Chlorination of 6-Acetylchrysene (XI): A mixture of 6-acetylchrysene (XI, 27.0 g, 0.1 mol),[6] phosphorus pentachloride (22.9 g, 0.11 mol) and benzene (150 m*l*) was refluxed for 75 min. The volatile material was removed under reduced pressure and the residue was placed for several hours in an evacuated desiccator containing potassium hydroxide. Light brown crystalline mass obtained was subjected to the subsequent reaction.

Dehydrochlorination of the Chloride: The crude chloride in tetrahydrofuran (100 m*l*) was added over a period of 20 min at −70°C to a suspension of sodium amide (from sodium, 9.2 g, 0.4 g-atom) in liquid ammonia (500 m*l*). After 3 hr the ammonia was allowed to evaporate, and then a saturated solution of ammonium chloride was added to the reaction mixture. The organic solvent was distilled off and the residue was collected by filtration and washed with water. The benzene extract of the residue (800 m*l*) was passed through a short column of alumina (80 g). Concentration of the filtrate resulted in yellow cubes, mp 176—178°C (dec.), 24.0 g (96%). A solution of the crude crystals in petroleum ether (bp 60—80°C) was passed through a thin layer of alumina. Crystals obtained by concentrating the filtrate were recrystallized from methanol to afford colorless cubes (mp 182°C (dec.)), which gave yellow silver and yellow cuprous acetylides.

Found: C, 94.89; H, 4.79%. Calcd for $C_{20}H_{12}$: C, 95.21; H, 4.79%. UV: $\lambda_{max}^{benzene}$ (log ε) 282 (4.97), 301.5 (3.93), 315 (4.10), 329 (4.33), 344 (4.35) nm. IR: 3280 (≡CH) cm^{-1}.

6,6′-Dichrysenyldiacetylene (I_2). A mixture of 6-ethynyl-

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[9] Detailed discussion on the spacing and the $\nu_{C\equiv C}$ will be given elsewhere.

[10] The linear relationship between λ_{max} and n^x in various diaryl-poly-ynes could be explained in terms of HMO based on a modified bond-alternation approximation.

chrysene (XII, 0.070 g, 0.28 mmol), cupric acetate monohydrate (0.70 g), pyridine (20 m*l*) and methanol (5 m*l*) was stirred for 2 hr at 50°C. The reaction mixture was cooled. The insoluble material was collected by filtration and washed with methanol and water successively, yielding light yeollw fine crystals in a quantitative yield (dec. p>330°C). This was recrystallized from toluene to give yellow cubes (dec. p>330°C). Elemental analysis of the cryatals revealed that the substance contained solvent of crystallization, which could be removed by heating the crystals at 100°C for several hr under reduced pressure (2×10^{-3} mmHg).

Found: C, 95.35; H, 4.52%. Calcd for $C_{40}H_{22}$: C, 95.59; H, 4.41%.

6-Chrysenyl-2-propyn-1-ol (XIII). A solution of 6-formylchrysene (XI, 6.15 g, 0.024 mol) in tetrahydrofuran (200 m*l*) was added to an ice-cooled solution of ethynylmagnesium bromide (from magnesium, 1.80 g, 0.075 g-atom and ethyl bromide, 8.20 g, 0.075 mol) in tetrahydrofuran (35 m*l*). After having been stirred overnight at room temperature, the reaction mixture was decomposed by adding a saturated ammonium chloride solution. The organic layer was separated, and dried. Concentration of the solution (up to *ca.* 10 m*l*) gave an oily material, which was mixed with benzene (20 m*l*). Crystals deposited on warming the mixture were washed with a small amount of benzene to yield light brown fine crystals, mp 170—173°C, 5.98 g (88%).

Found: 89.15; H, 5.03%. Calcd for $C_{21}H_{14}O$: C, 89.33; H, 5.00%. IR: 3100—3400 (O–H), 3290 (≡CH), 1060 (C–O) cm^{-1}.

1,6-Di(6-chrysenyl)-1,6-dihydroxy-2,4-hexadiyne (XIV). A mixture of 6-chrysenyl-2-propyn-1-ol (XIII, 3.00 g, 0.011 mol), cuprous chloride (1.4 g), ammonium chloride (1.0 g) and acetone-methanol (1: 1, 80 m*l*) was vigorously stirred at room temperature under an atmosphere of oxygen at a slightly elevated pressure. After being stirred overnight, the precipitate deposited was collected by filtration and dissolved in tetrahydrofuran. Insoluble material was removed by filtration and the filtrate was passed through a short column of alumina (8 g). The crystals, 1.62 g (54%), obtained by evaporating the solvent were recrystallized from dioxane to give faint yellow needles (dec. p *ca.* 160°C). Elemental analysis indicates that the crystals contain 1 mol of dioxane as a solvent of crystallization.

Found: C, 84.96; H, 5.14%. Calcd for $C_{42}H_{26}O_2\cdot C_4H_8O_2$: C, 84.90; H, 5.27%. IR: 3600—3100 (O–H), 1065 (C–O) cm^{-1}.

6,6′-Dichrysenyltriacetylene (I_3). *Formation of XV*: A solution of thionyl chloride (0.21 g, 1.8 mmol) and pyridine (0.14 g, 1.8 mmol) in tetrahydrofuran (5 m*l*) was added to a solution of glycol (XIV, 0.337 g, 0.6 mmol) in tetrahydrofuran (15 m*l*) over a period of 15 min at −20°C, and the mixture was then shaken for 30 min. The reaction mixture containing chloride (XV) was subjected to the following reaction without isolation.

Dehydrochlorination of dichloride (XV): To a vigorously stirred suspension of sodium amide (from sodium, 0.46 g, 0.02 g-atom) in liquid ammonia (90 m*l*), the solution of dichloride (XV) was added in one portion at −70°C. After 30 min, ammonium chloride (2.5 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 and washed successively with water, a small amount of ethanol and benzene, and then dissolved in hot toluene (350 m*l*). The hot solution was passed through a short column of alumina (13 g). On cooling the filtrate to room temperature, I_3 crystallized out as yellow needles (dec. p *ca.* 295°C, 0.147 g, 47%). Analytical specimen was prepared by recrystallization from toluene.

Found: C, 95.94; H, 4.20%. Calcd for $C_{42}H_{22}$: C, 95.79; H, 4.21%.

1-(6-Chrysenyl)-2-butyn-1,4-diol (XVI). A solution of aldehyde (XI, 5.1 g, 0.02 mol) in tetrahydrofuran (200 m*l*) was added to an ice-cooled solution of Grignard derivative of propargyl alcohol in tetrahydrofuran (70 m*l*), which had been prepared from magnesium, 2.88 g, 0.12 g-atom, ethyl bromide, 13.1 g, 0.12 mol and propargyl alcohol, 3.36 g, 0.06 mol. The mixture was allowed to stand overnight, then a saturated aqueous solution of ammonium chloride was added to the reaction mixture. The organic layer separated was dried and concentrated. The residue was treated with a small amount of hot benzene to cause crystallization. The crystals (mp 193—197°C, 5.54 g, 89%) were recrystallized from ethanol-benzene to give colorless fine crystals (mp 197—198°C).

Found: C, 84.27; H, 5.19%. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16%. IR: 3600—3100 (O–H), 1040—1000 (C–O) cm^{-1}.

6-Butadiynylchrysene (XVIII). *Preparation of XVII*: A solution of thionyl chloride (3.22 g, 0.027 mol) in tetrahydrofuran (10 m*l*) was added over a period of 15 min to a solution of glycol (XIV, 2.00 g, 6.4 mmol) and pyridine (2.13 g, 0.027 mol) in tetrahydrofuran (40 m*l*) at −10°C. After the mixture had been stirred for further 2 hr at room temperature, crushed ice was added, and extraction was carried out with benzene (100 m*l*). The extract was washed with an aqueous solution of sodium hydrogen carbonate, and dried. The solvent was removed to yield an oily material which solidified on standing.

Dehydrochlorination of dichloride (XVII): The crude XVII in tetrahydrofuran (15 m*l*) was treated with sodium amide (from sodium, 1.0 g, 0.44 g-atom) in liquid ammonia (100 m*l*) for 1 hr at −70°C. The reaction mixture was worked up as usual. The product was repeatedly digested with petroleum ether (bp 60—80°C, total 600 m*l*). The filtrate obtained by passing the extract through a thin layer of alumina (3.5 g) was concentrated to yield XVIII as faint yellow crystals, 1.138 g (34%). The butadiynyl compound (XVIII) was found to be extremely unstable, and readily turned into an insoluble deep green substance. XVIII gave orange-yellow silver and deep yellow cuprous acetylides.

UV: $\lambda_{max}^{petroleum\ ether}$ 357 (L_a), 375 (L_b) nm.

6,6′-Dichrysenyltetraacetylene (I_4). The yellow crystalline powder (0.180 g, 50%) obtained by the cupric acetate oxidation [cupric acetate monohydrate (2.5 g), methanol (5 m*l*) and pyridine (50 m*l*), 1 hr at 50°C] of XVIII (0.360 g, 1.3 mmol) was digested with boiling toluene (350 m*l*). The hot extract was percolated through a short column of alumina (10 g). On standing the filtrate, I_4 containing 1 mol of solvent of crystallization was obtained as deep yellow fine needles (dec. p *ca.* 250°C, 0.096 g, 27%). It was found that the solvent could not be removed upon heating to 60°C for 24 hr under reduced pressure (2×10^{-3} mmHg).

Found: C, 95.38; H, 4.62%. Calcd for $C_{44}H_{22}\cdot C_7H_8$: C, 95.30; H, 4.70%.

3-(6-Chrysenyl)-prop-2-ynal (XIX). To an ice-cooled solution of isopropylmagnesium bromide (from magnesium, 1.92 g, 0.08 g-atom and isopropyl bromide, 10.8 g, 0.088 mol) in tetrahydrofuran (50 m*l*) was added, over a period of 15 min, a solution of 6-ethynylchrysene (XII, 10.08 g, 0.04 mol) in the same solvent (250 m*l*) under stirring. The mixture was refluxed for 1 hr, and dimethylformamide (18 m*l*) was added under cooling with an ice-salt bath. After the mixture had been stirred for 4 hr at 30°C, 5% sulfuric acid (600 m*l*) was added under vigorous agitation, after which benzene (500 m*l*) was added and then stirring was continued overnight. The mixture was extracted with benzene (500 m*l*). The extract was washed with a saturated solution of sodium hydrogen carbonate, and dried. The solvent was removed to afford yellow crystals. The crystals were washed with a small amount of benzene-cyclohexane (1: 1), thus yielding light orange-yellow needles (8.11 g, 72%). This was recrystallized twice from benzene-cyclohexane (1: 1) to yield XIX as orange-yellow needles, mp 160—161°C (dec.).

Found: C, 89.70; H, 4.36%. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.32%. IR: 2830, 2730 (CHO), 2175 (C≡C), 1655 (C=O) cm^{-1}.

1-(6-Chrysenyl)-1,4-pentadiyn-3-ol (XX). The reaction of ethynylmagnesium bromide with XIX (5.60 g, 0.02 mol) according to the procedure used for XIII afforded XX as yellow fine crystals, mp *ca.* 140°C (dec.), 3.51 g (62%). This substance was recrystallized twice from ethyl acetate to yield pure XX, mp 152—154°C (dec.).

Found: C, 89.68; H, 4.56%. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61%. IR: 3600—3100 (OH), 3300 (≡CH), 2220, 2100 (C≡C), 1023 (C–O) cm^{-1}.

6,6′-Dichrysenylpentaacetylene (I_5). Oxidative Coupling of Chrysenylpentadiynol (XX): The product obtained by the Glaser reaction [cuprous chloride (1.00 g), ammonium chloride (0.90 g), methanol (80 m*l*) and oxygen] of XX (2.50 g, 8.2 mmol) was dissolved in tetrahydrofuran (100 m*l*). The solution was percolated through a thin layer of alumina (3 g). Concentration of the filtrate afforded a viscous brown oil which crystallized on treatment with a small amount of benzene (0.90 g, 36%). Repeated recrystallization of this substance from tetrahydrofuran or dioxane gave slightly impure material whose IR spectrum was in accord with that expected for XXI.

Chlorination of XXI: According to the procedure used in the preparation of XV, glycol (XXI, 0.305 g, 0.5 mmol) was treated with a solution of thionyl chloride at −30°C. The reaction mixture containing XXII was immediately subjected to the following reaction.

Dehydrochlorination of XXII: Dehydrochlorination of XXII with sodium amide (from sodium, 0.20 g, 8.4 mg-atom) was performed according to the method used for I_3. I_5 was obtained as light orange fine needles (dec. p *ca.* 230°C, 31 mg, 11% based on crude XXI). The second crop of I_5 (15 mg, 5%) was obtained from the mother liquor.

Found: C, 96.05; H, 3.82%. Calcd for $C_{46}H_{22}$: C, 96.14; H, 3.86%.

1-(6-Chrysenyl)-2,5-hexadiyn-1,4-diol (XXIII). A solution of 6-formylchrysene (XI, 6.15 g, 0.024 mol) in tetrahydrofuran (200 m*l*) was added to a stirred and ice-cooled solution of the Grignard derivative of 2,4-pentadiyn-3-ol[11] (from alcohol, 2.65 g, 0.033 mol and ethylmagnesium bromide in tetrahydrofuran, 100 m*l*). The mixture was stirred overnight at room temperature. The reaction mixture was hydrolyzed by the addition of a saturated solution of ammonium chloride. The aqueous layer was extracted with benzene. Viscous oily material obtained by concentration of the combined organic layer was warmed with benzene (30 m*l*) to cause crystallization. The crude material was recrystallized from ethyl acetate-benzene to afford light brown powder (4.50 g, 56%). This was used without further purification in the subsequent reaction. A small portion of the crude material was dissolved in dioxane and passed through a thin layer of alumina. The crystals obtained by concentrating the filtrate were redissolved in ethyl acetate and chromatographed on alumina to result in pure XXIII as colorless needles, mp 197—199°C (dec.).

Found: C, 85.19; H, 4.75%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

The second crop obtained from the mother liquor was colorless needles, mp 165—170°C. (Found: C, 85.40; H, 4.83%). The two stereoisomeric kinds of crystal gave almost the same IR spectra. IR: 3600—3100 (O–H), 3300 (≡CH), 2100 (C≡C), 1035 (C–O) cm^{-1}.

6-Chrysenyltriacetylene (XXV). Chlorination of XXIII: According to the procedure used for XVII, XIII (2.02 g, 6 mmol) in a mixture of tetrahydrofuran (30 m*l*) and pyridine (1.42 g, 18 mmol) was converted into XXIV on treatment with thionyl chloride (2.14 g, 18 mmol) in tetrahydrofuran (5 m*l*) at −15°C. Crude XXIV obtained as a brown oily material was used without further purification in the subsequent reaction.

Dehydrochlorination of XXIV. The procedure used for XVII was applied to XXIV. Since the triacetylene (XXV, Faint yellow fine needles, UV: $\lambda_{\max}^{\text{petroleum ether}}$ 379 nm) was found to be extremely unstable, a petroleum ether solution was used in the following reaction.

6,6′-Dichrysenylhexaacetylene (I_6). A mixture of the solution of triacetylene (XXV), cupric acetate monohydrate (2.0 g) and pyridine (50 m*l*) was concentrated to *ca.* 30 m*l* *in vacuo* and pyridine (50 m*l*) and methanol (5 m*l*) were added. Stirring was continued overnight at room temperature. The insoluble material was collected and washed with ethanol and then with water. Crude hexaacetylene (I_6), thus obtained, brick red crystalline powder (0.440 g, 24% based on diol, XXIII), was digested with hot toluene (350 m*l*), and the hot extract was percolated through a short column of alumina (7 g). Pure I_6, orange-red needles, dec. p. *ca.* 150°C was obtained on standing the filtrate.

Found: C, 96.17; H, 3.77%. Calcd for $C_{48}H_{22}$: C, 96.30; H, 3.70%.

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[11] E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, **1956**, 4765.