Linear Conjugated Systems Bearing Aromatic Terminal Groups. V. Syntheses and Electronic Spectra of 2,2′-, 3,3′-, and 9,9′-Diphenanthrylpoly-ynes

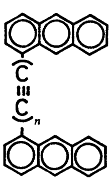
Shuzo Akiyama and Masazumi Nakagawa
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received March 8, 1971)

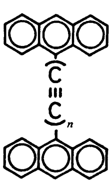
2,2′-, 3,3′-, and 9,9′-Diphenanthrylpoly-ynes (V_n, VI_n, and VII_n, n= 1—6) were synthesized and their electronic spectra were measured. It was found that the longest-wavelength absorption maxima ($\lambda_{\max}$) in the spectra of each series of the diphenanthrylpoly-ynes (V_n, VI_n and VII_n) shift linearly with the xth power of the number of acetylenic bond (n), [$\lambda_{\max} \propto n^x$], being x= 1.3 for V_n and x= 1.4 for VI_n and VII_n.

In previous papers of this series,[1-4] it was shown that the shifts of the absorption maxima ($\lambda_{\max}$) of the long-wavelength bands of diarylpoly-ynes, such as 1,1′-dianthryl-(I_n), 9,9′-dianthryl-(II_n), 1,1′-dinaphthyl-(III_n) and 2,2′-dinaphthylpoly-ynes (IV_n) with the increase of the number of acetylenic bonds (n) can be expressed by the empirical formula:

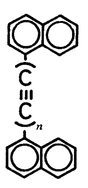
$$\lambda_{\max} = An^x + B$$



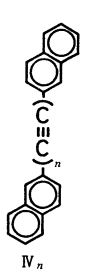
I_n
(x=2)



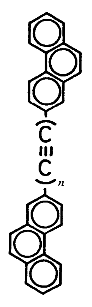
II_n
(x=2)



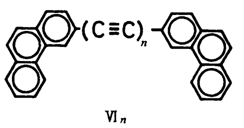
III_n
(x=1.5)



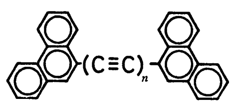
IV_n
(x=1.3)



V_n
(x=1.3)



VI_n
(x=1.4)



VII_n
(x=1.4)

It is interesting that the values of x, given below the formulas, vary with the change of the nature of the terminal groups and the position of the linking of the polyacetylenic chain.

This paper deals with the syntheses and the electronic spectral characteristics of 2,2′-, 3,3′- and 9,9′-diphenanthrylpoly-ynes (V_n, VI_n, and VII_n, n=1—6).

Syntheses. Syntheses of diphenanthrylpoly-ynes (V_n, VI_n, and VII_n) were performed according to the analogous reaction sequence which had been employed in the syntheses of dianthryl-(I_n and II_n)[1,3] and dinaphthylpoly-ynes(III_n and IV_n).[4] Formyl and acetyl derivatives(VIII and IX) were used as starting materials. Preparation of diphenanthrylacetylenes (V_1, VI_1, and VII_1) by means of an intramolecular Wittig reaction has been reported.[5]

Application of mild conditions to the conversion of the acetylenic hydroxy compounds to the corresponding chloro-derivatives was essential. Chloro-compounds(XI, XIV, XVI, XX, XXII, and XXVIII) were subjected to the following dehydrochlorination without isolation and purification owing to their intractable nature.

Elemental analyses of phenanthryldi-(XVII) and triacetylenes (XXIII) could not be performed due to their high instability. Diphenanthrylpoly-ynes (V_{1-5}, VI_{1-5}, and VII_{1-5}) were found to be fairly stable compounds. However, hexaacetylenes (V_6, VI_6 and VII_6) were unstable, and decomposed at room temperature in a few days. It was observed that the solubility of V_n, VI_n and VII_n in organic solvents remarkably decreased with the increase of the length of poly-yne chain. The color of crystals, melting points and IR absorption due to $\nu_{C\equiv C}$ are summarized in Table 1. The most intense peaks of the $\nu_{C\equiv C}$ bands of the diarylpoly-ynes (V_n, VI_n and VII_n) showed remarkable intensification and shift to lower wave number with the increase of the length of the poly-yne chain. The same trend has been observed in the IR spectra of the other series of diarylpoly-ynes.[1,3,4] The IR spectra of V_n are shown in Fig. 1 as a represen-

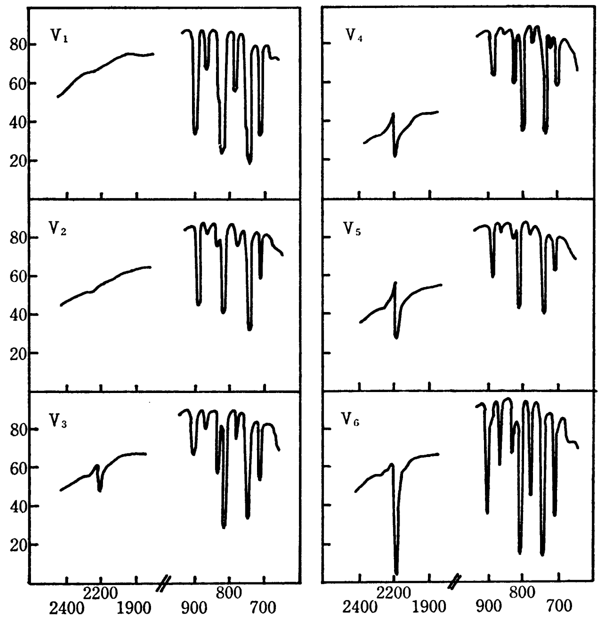


Fig. 1. Infrared spectra of 2,2′-diphenanthrylpoly-ynes (V_1—V_6) in the 1900—2400 cm^{-1} and 700—900 cm^{-1} region.

---

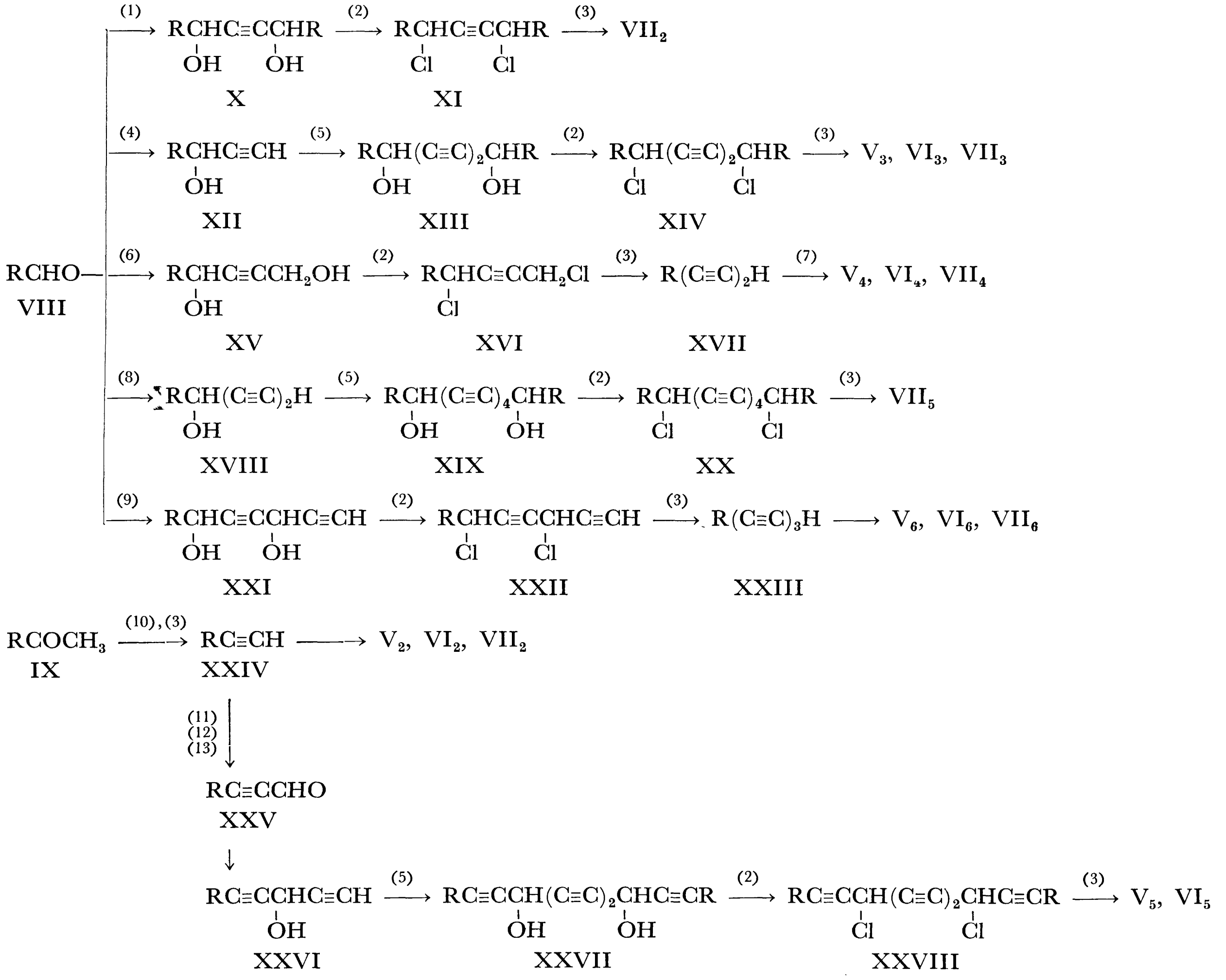
[1] S. Akiyama and M. Nakagawa, This Bulletin, **40**, 340 (1967).

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

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

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

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



Scheme. Syntheses of diarypoly-ynes

R = 2-, 3- or 9-phenanthryl

(1) $BrMgC{\equiv}CMgBr$ in benzene-tetrahydrofuran; (2) $SOCl_2$-pyridine in tetrahydrofuran; (3) $NaNH_2$ in liq. NH_3; (4) $LiC{\equiv}CH$ in liq. NH_3 or $BrMgC{\equiv}CH$ in tetrahydrofuran; (5) O_2-CuCl-NH_4Cl in methanol; (6) $BrMgC{\equiv}CCH_2OMgBr$ in tetrahydrofuran; (7) $Cu(OAc)_2H_2O$ in pyridine; (8) $Li(C{\equiv}C)_2H$ in liq. NH_3; (9) $BrMgC{\equiv}CCH(OMgBr)C{\equiv}CH$ in tetrahydrofuran; (10) PCl_5 in benzene; (11) C_2H_5MgBr in tetrahydrofuran; (12) *N*,*N*-dimethylformamide in tetrahydrofuran; (13) H_2SO_4.

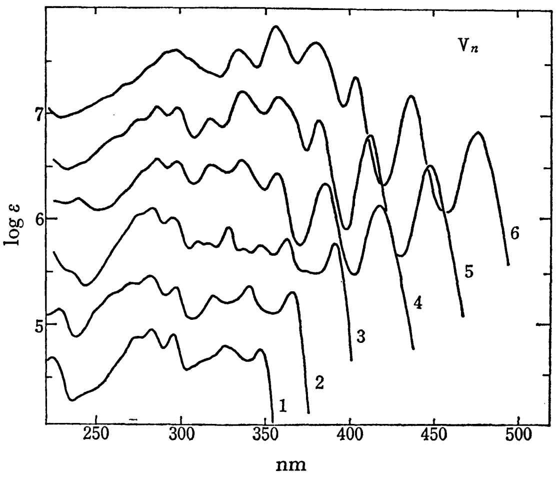


Fig. 2. Absorption curves of 2,2′-diphenanthrylpoly-ynes (V_1—V_6). Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

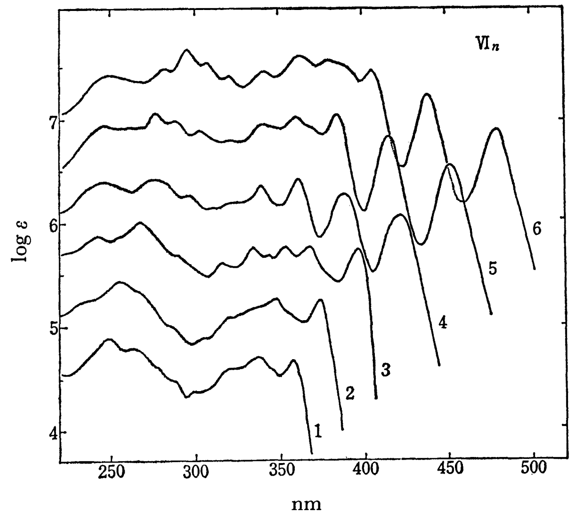


Fig. 3. Absorption curves of 3,3′-diphenanthrylpoly-ynes (VI_1—VI_6). Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

Table 1. Physical properties of diphenanthrylpoly-ynes

n	V_n			VI_n			VII_n		
	color	Mp (°C)	$\nu_{C\equiv C}$	color	Mp (°C)	$\nu_{C\equiv C}$	color	Mp (°C)	$\nu_{C\equiv C}$
1	colorless	261—262		colorless	266—267		colorless	243—244	
2	colorless	243—244		pale yellow	280—282	2125 (vw)	pale yellow	256—257	2135 (vw) 2210 (vw)
3	pale yellow	*ca.* 270 (dec.)	2200 (s)	light yellow	*ca.* 260 (dec.)	2195 (s)	light yellow	285—286 (dec.)	2195 (s)
4	yellow	*ca.* 220 (dec.)	2195 (s)	yellow	*ca.* 200 (dec.)	2055 (w) 2110 (w) 2190 (s)	yellow	*ca.* 255 (dec.)	2060 (vw) 2115 (m) 2195 (s)
5	bright yellow	*ca.* 200 (dec.)	2175 (s)	orange yellow	*ca.* 190 (dec.)	2180 (s)	orange yellow	*ca.* 200 (dec.)	2070 (vw) 2130 (m) 2175 (s)
6	light orange	*ca.* 180 (dec.)	2025 (vw) 2145 (s)	light orange	*ca.* 100 (dec.)	2140 (s)	orange	*ca.* 130 (dec.)	2150 (s)

vw=very weak; m=medium; s=strong.
a) As hexaacetylene decomposed under pressure in the preparation of the KBr-disk, the spectrum was obtained by the Nujol mull method.

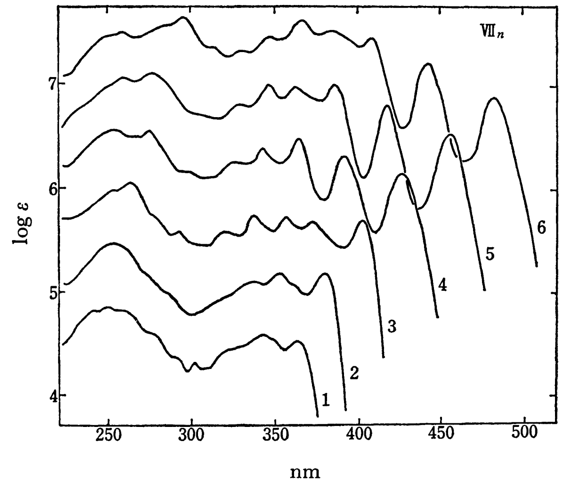


Fig. 4. Absorption curves of 9,9'-diphenanthrylpoly-ynes (VII_1—VII_6). Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

tative of the diphenanthrylpoly-ynes.

Electronic Spectra. The absorption curves and electronic spectral data of the three series of diphenanthrylpoly-ynes (V_n, VI_n and VII_n) are given in Figs. 2, 3, and 4, and Tables 2, 3, and 4.

Usually, the electronic spectra of the lower members of diarylpoly-ynes retain the characteristic of the spectra of the parent aromatic hydrocarbons corresponding to the respective terminal groups. However, in the case of the diphenanthryl derivatives (V_n, VI_n, and VII_n), the characteristic feature of the spectrum of phenanthrene can not be observed even in the spectra of diphenanthrylacetylenes (V_1, VI_1, and VII_1).

On the basis of free electron model (FEM),[6] the x-axis polarized transitions were assigned to ^1L_b and ^1C_b bands, and the y-axis polarized transitions were assigned to ^1L_a and ^1B_a bands for the electronic spectrum of phenanthrene (Fig. 5). The short-wavelength bands of diphenanthrylpoly-ynes (V_n, VI_n and VII_n) seem to be associated with the ^1C_b and the ^1B_a bands of phenanthrene.

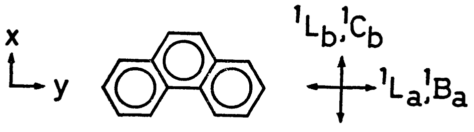


Fig. 5. Polarization diagram of phenanthrene.

The spectral feature of 3,3'-derivatives (VI_n) was found to be closely related to that of 9,9'-derivatives (VII_n). This indicates that the poly-yne chains extending in the same direction with regard to the molecular axis exert the same effect on the electronic spectra. On the other hand, 2,2'-derivatives (V_n) exhibit quite a different spectral feature as compared with 3,3'- and 9,9'-derivatives (VI_n and VII_n). The poly-yne chain attached to 2-position should exert a minor effect on the x-axis-polarized ^1C_b band, since the substituent at 2-position is parallel to the y-axis and can not contribute to the x-axis polarization. Consequently, the appearance of an absorption minimum at *ca.* 230—240 nm region in the spectrum of the lower member of 2,2'-derivative (V_n) might be ascribed to the separation of ^1C_b band and ^1B_a band due to the profound bathochromic shift of the y-axis-polarized ^1B_a band.

The long-wavelength bands of diphenanthrylpoly-ynes (V_n, VI_n, and VII_n) can be considered to arise from the interaction of poly-yne chromophore with ^1L_a band of the terminal group. ^1L_b band disappeared in the spectra of diphenanthrylpoly-ynes (V_n, VI_n, and VII_n) except for 2,2'-diphenanthrylacetylene(V_1), probably because of the large bathochromic shift of ^1L_a band. The remarkable enhancement of the vibrational fine structure and the regular bathochromic

---

[6] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949); J. R. Platt, *ibid.*, **17**, 489 (1949); N. S. Ham and K. Ruedenberg, *ibid.*, **25**, 13 (1956).

TABLE 2. SPECTRAL DATA OF 2,2′-DIPHENANTHRYLPOLY-YNES (V_1—V_6)

n	λ_{max} in nm and log ε (in parentheses) in tetrahydrofuran									
1	224 (4.67)	273 (4.88)	282.5 (4.95)	295.5 (4.90)	326 (4.80)	346.5 (4.68)	356 (3.32)			
2	227.5 (4.63)	271 (4.90)	282 (4.96)	296.5 (4.82)	318 (4.77)	340 (4.87)	366 (4.81)			
3	275.5[a] (5.08)	282.5 (5.12)	294.5 (5.02)	309 (4.80)	316 (4.77)	326.5 (4.93)	336.5 (4.72)	346 (4.77)	362 (4.83)	391 (4.78)
4	239.5 (4.69)	286 (5.09)	297 (5.07)	317 (5.02)	335 (5.08)	355.5 (4.95)	384 (4.85)	417 (4.65)		
5	264[a] (4.80)	275 (4.96)	288.5 (5.10)	297.5 (5.08)	316.5 (4.98)	335 (5.23)	357 (5.17)	381 (4.96)	411 (4.82)	447 (4.55)
6	297 (5.12)	333.5 (5.12)	355.5 (5.34)	378 (5.19)	403 (4.86)	436 (4.69)	476 (4.35)			

[a] Shoulders.

TABLE 3. SPECTRAL DATA OF 3,3′-DIPHENANTHRYLPOLY-YNES (VI_1—VI_6)

n	λ_{max} in nm and log ε (in parentheses) in tetrahydrofuran											
1	248.5 (4.88)	263.5 (4.78)	299 (4.38)	323 (4.59)	337 (4.69)	358 (4.67)						
2	256 (4.93)	285[a] (4.72)	306 (4.40)	321[a] (4.58)	348 (4.76)	374 (4.75)						
3	243.5 (4.87)	267.5 (5.00)	289.5 (4.68)	316 (4.60)	322[a] (4.57)	334 (4.76)	343 (4.67)	353 (4.77)	368 (4.77)	397 (4.74)		
4	245 (4.91)	275.5 (4.92)	296.5 (4.77)	321 (4.69)	339 (4.86)	361 (4.92)	388 (4.78)	422 (4.58)				
5	247 (4.95)	261 (4.92)	277 (5.06)	288.5 (4.98)	303 (4.88)	321.5 (4.79)	340 (4.94)	359 (5.02)	384 (5.03)	414 (4.83)	451 (4.55)	
6	249 (4.92)	270[a] (4.87)	282 (4.98)	296 (5.16)	307.5 (5.03)	321 (4.90)	341 (4.96)	363 (5.10)	379 (5.06)	405 (4.96)	438 (4.72)	479 (4.39)

[a] Shoulders.

TABLE 4. SPECTRAL DATA OF 9,9′-DIPHENANTHRYLPOLY-YNES (VII_1—VII_6)

n	λ_{max} in nm and log ε (in parentheses) in tetrahydrofuran											
1	240 (4.82)	250 (4.86)	257.5 (4.83)	277.5[a] (4.50)	290 (4.37)	302 (4.31)	341 (4.56)	363 (4.51)				
2	253 (4.97)	287[a] (4.46)	334 (4.58)	252 (4.69)	379 (4.67)							
3	250[a] (4.96)	263.5 (5.07)	291 (4.59)	303.5 (4.45)	319 (4.59)	337 (4.73)	357 (4.71)	372 (4.68)	402 (4.81)			
4	254 (5.04)	264 (4.98)	273.5 (5.06)	296.5 (4.66)	324.5 (4.74)	342 (4.89)	364 (4.97)	392 (4.79)	425 (4.59)			
5	258 (5.06)	275.5 (5.12)	327 (4.97)	345 (5.00)	363 (4.99)	387 (5.00)	416 (4.80)	453 (4.53)				
6	250[a] (4.94)	258 (4.98)	284.5 (5.04)	295 (5.13)	311[a] (4.84)	328 (4.81)	345 (4.95)	366 (5.11)	383 (5.00)	408 (4.93)	440 (4.68)	481 (4.35)

[a] Shoulders.

shifts in the longest-wavelength bands with the increase of n are also observed in the three series of diphenanthrylpoly-ynes. The same trend has been observed in other series of diarylpoly-ynes.[1-4] The sequence of the bathochromic displacement of the longest-wavelength bands was found to be $V_n < VI_n < VII_n$ in apparent contradiction to what we expected from FEM. The same apparent discrepancy was also observed in the spectra of ethynyl- (XXIV), butadiynyl- (XVIII) and hexatriynylphenanthrenes. The apparent contradictions have been explained in terms of a configuration interaction.[7] As shown in Table 5, the spacings between the longest-wavelength vibrational sub-bands (λ_I) and the next longest-wavelength sub-bands (λ_{II}) are found to be 1900—2000 cm^{-1} except those of diphenanthrylacetylenes (V_1, VI_1, and VII_1). The spacings, as in the other diarylpoly-ynes, correspond to the stretching vibrations of acetylenic linkage in their IR spectra (*cf.* Table 1.)

The plots of the sub-peaks, λ_I and λ_{II} of the 2,2′-series (V_n) *versus* $n^{1.3}$ gave excellent straight lines as is shown in Fig. 6. (The plot of λ_{II} of V_1 is omitted.) In the cases of 3,3′- and 9,9′-diphenanthrylpoly-ynes (VI_n and VII_n), good linear correlations between λ_I, λ_{II} and $n^{1.4}$ were obtained (Figs. 7 and 8). It is interesting that the value x is dependent on the posi-

---

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

Table 5. Spacings between the longest-wavelength maxima (λ_I) and the next longest-wavelength maxima (λ_{II}) (cm^{-1})

n	V_n	VI_n	VII_n
1	(1710)	(1740)	(1780)
2	2090	2000	2020
3	2040	1980	2000
4	1990	2070	1980
5	1960	1980	1960
6	1930	1910	1940

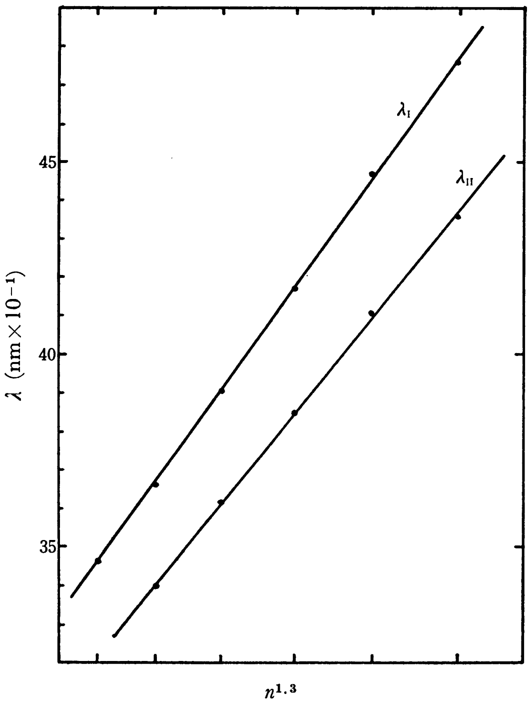


Fig. 6. Plot of λ_{max} *vs.* $n^{1.3}$ for 2,2′-diphenanthrylpoly-ynes (V_1—V_6).
λ_I: longest-wavelength maxima
λ_{II}: second-longest-wavelength maxima

tion of substitution as in the case of 1,1′- and 2,2′-dinaphthylpoly-ynes.[4]

The spectral reguralities are expressed by the following empirical formulas, and the agreement with the observed values is found to be excellent.

$$\lambda = An^x + B \quad \text{(in tetrahydrofuran)}$$

2,2′-series (V_n): $\lambda_I = 13.9\,n^{1.3} + 333$ nm
$\lambda_{II} = 12.3\,n^{1.3} + 310$

3,3′-series (VI_n): $\lambda_I = 10.8\,n^{1.4} + 347$
$\lambda_{II} = 9.4\,n^{1.4} + 324$

9,9′-series (VII_n): $\lambda_I = 10.5\,n^{1.4} + 352$
$\lambda_{II} = 9.0\,n^{1.4} + 329$

The spectral regularities in benzene and cyclohexane solution can be expressed by similar empirical formulas with about the same A and the same x as in the case of tetrahydrofuran solution, but with slightly modified B values.

The syntheses and electronic spectral properties of poly-ynes bearing other types of terminal groups will be reported in the near future.

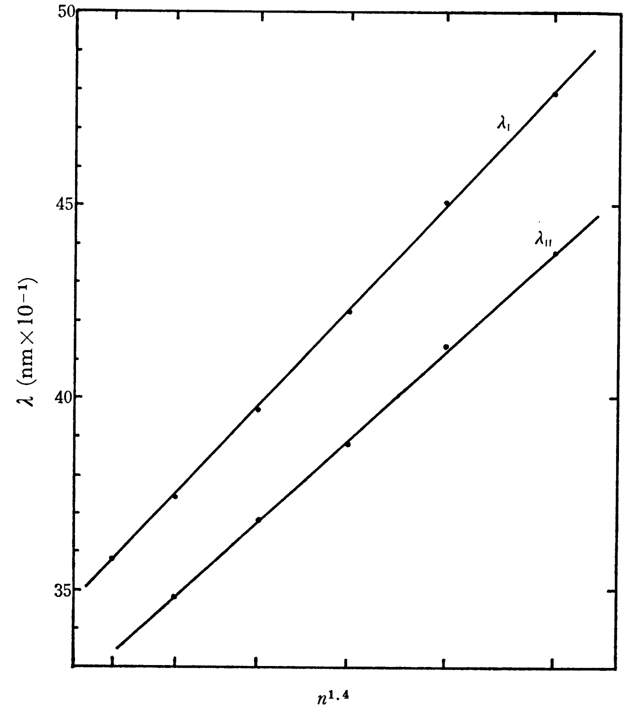


Fig. 7. Plot of λ_{max} *vs.* $n^{1.4}$ for 3,3′-diphenanthrylpoly-ynes (VI_1—VI_6).
λ_I: longest-wavelength maxima
λ_{II}: second-longest-wavelength maxima

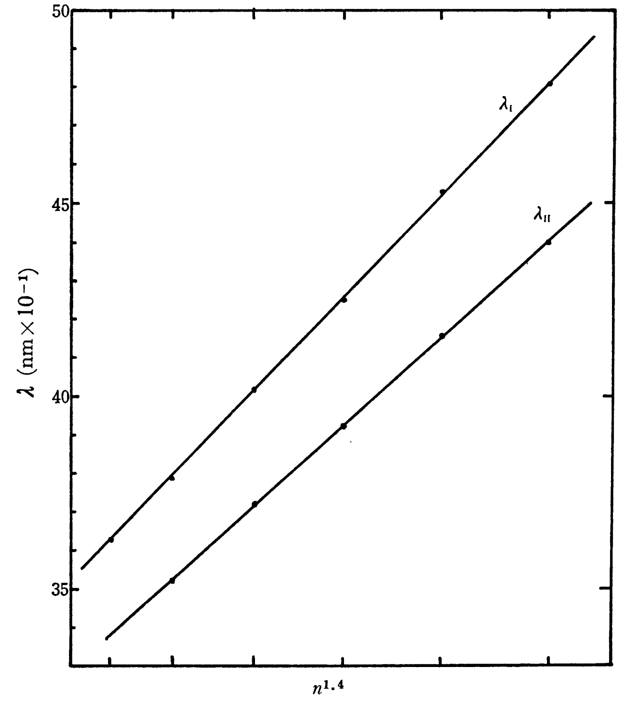


Fig. 8. Plot of λ_{max} *vs.* $n^{1.4}$ for 9,9′-diphenanthrylpoly-ynes (VII_1—VII_6).
λ_I: longest-wavelength maxima
λ_{II}: second-longest-wavelength maxima

Experimental

All the melting points are uncorrected. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer at room temperature employing a well-matched pair of 1-cm quartz cells. The IR spectra were obtained on a Hitachi EPI-2 infrared spectrophotometer by KBr-disk method.

Acetylphenanthrenes(IX). *2- and 3-Acetylphenanthrenes.* The acetylphenanthrenes were prepared according to the method of Mosettig and van de Kamp.[8]

9-Acetylphenanthrene. Diethyl ethoxymagnesiomalonate was prepared from magnesium (1.20 g, 0.05 g atom), diethyl malonate (8.0 g, 0.05 mol), anhydrous ethanol (5.05 g, 0.11 mol) and toluene (50 m*l*) and excess ethanol was removed. A solution of the acid chloride of 9-carboxyphenanthrene (6.03 g, 0.025 mol) in toluene (30 m*l*) was added to the toluene solution of ethoxymagnesiomalonate, and the mixture was heated for 2 hr at 80°C. 6 N Sulfuric acid was added to the ice-cooled reaction mixture. The organic layer was washed with water and a solution of sodium hydrogen carbonate, successively, and dried. The oily material obtained by the evaporation of the solvent under reduced pressure was mixed with acetic acid (40 m*l*) and 4 drops of concentrated sulfuric acid. The mixture was refluxed for 2.5 hr under evolution of carbon dioxide, then 4 N sulfuric acid (20 m*l*) was added to the reaction mixture. After having been refluxed for additional 3 hr, the reaction mixture was cooled. The solid deposited was collected and washed thoroughly with water and then dissolved in benzene (60 m*l*). The benzene solution was washed with sodium hydrogen carbonate solution and dried. The cubic crystals obtained by the evaporation of the solvent were re-dissolved in benzene and the solution was passed through a thin layer of alumina (6 g). The filtrate gave the acetyl compound, mp 73—74°C (lit. value, 74°C),[9] 5.14 g (94%). This material was recrystallized twice from ethanol to give an analytical specimen, mp 74°C, colorless needles.

Found: C, 87.43; H, 5.52%. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49%. IR: 1670 (C=O) cm^{-1}.

Formylphenanthrenes VIII. *2-Formylphenanthrene (2-VIII).* 2-acetylphenanthrene was treated with alkaline sodium hypochlorite solution to give 2-carboxyphenanthrene. Lithium aluminum hydride reduction of the ester of the carboxyphenanthrene afforded 2-hydroxymethylphenanthrene. A solution of the hydroxymethyl compound (24.8 g, 0.12 mol) in pyridine (150 m*l*) was added to a chilled solution of chromium trioxide (36.0 g, 0.36 mol) in pyridine (500 m*l*).

The mixture was shaken in an ice-bath for 30 min, and then for 45 min at room temperature. The reaction mixture was poured into water (2.5 *l*) and was extracted with ether. The extract was washed successively with water, cold diluted hydrochloric acid, water, cold sodium hydroxide solution and water. The crude crystals (23.4 g, 97%) obtained on the evaporation of the solvent were converted into a sodium hydrogen sulfite adduct. Decomposition of the adduct gave 2-formylphenanthrene as colorless cubes, mp 55—58°C. The material was recrystallized twice from methanol-water to give pure specimen, mp 56—57°C. (lit. value, 59—59.5°C).[10]

Found: C, 87.48; H, 4.90%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR: 2820, 2730 (CHO), 1695 (C=O) cm^{-1}.

3-Formylphenanthrene(3-VIII). According to the procedure for the preparation of the 2-formyl compound, the 3-hydroxymethyl compound was oxidized to give 3-formylphenanthrene in yield of 86%, colorless needles, mp 77—79°C (lit. value, 79.5—80°C).[10] The material was recrystallized twice from methanol to yield pure aldehyde, colorless needles, mp 79—80°C.

Found: C, 87.38; H, 4.89%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR: 2835, 2740 (CHO), 1698 (C=O) cm^{-1}.

9-Formylphenanthrene(9-VIII). Dimethylformamide (4.4 g, 0.06 mol) was added dropwise to a stirred solution of 9-phenanthrylmagnesium bromide (prepared from 9-bromophenanthrene, 5.14 g, 0.02 mol and magnesium 0.504 g, 0.021 g atom)[11] in tetrahydrofuran under cooling in an ice-salt bath. After the addition had been completed, the cooling bath was removed and stirring was continued overnight. Diluted sulfuric acid was added to the reaction mixture, and then the mixture was extracted with benzene (50 m*l*). The extract was washed with a saturated solution of sodium chloride. A mixture of the extract and a saturated solution of sodium hydrogen sulfite was shaken overnight, and the deposited sulfite adduct was collected, washed with benzene, acetone, methanol, and water, successively. Treatment of the adduct with a saturated sodium hydrogen carbonate solution afforded 9-formylphenanthrene, mp 93—98°C, 2.46 g (62%). Recrystallization from benzene yielded pure 9-aldehyde, colorless fine needles, mp 100-102°C (lit. value. 100—101°C).[11]

Found: C, 87.28; H, 4.94%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR: 2850, 2745 (CHO), 1690 (C=O) cm^{-1}.

1,4-Di(9-phenanthryl)-1,4-dihydroxy-2-butyne (X). To an ice-cooled solution of bis-Grignard derivative of acetylene (prepared from magnesium 1.75 g, 0.073 g atom and ethylbromide 9.70 g, 0.088 mol) in benzene-tetrahydrofuran (50 m*l*), was added a solution of 9-formylphenanthrene (6.18 g, 0.03 mol) in tetrahydrofuran (80 m*l*). After the mixture had been stirred at room temperature overnight, a saturated solution of ammonium chloride was added. The aqueous layer was removed, and was extracted with benzene. The organic layer was combined with the extract and dried (magnesium sulfate). It was concentrated under reduced pressure to yield colorless needles, mp 225—229°C, 5.41 g (83%), which was recrystallized from tetrahydrofuran-benzene, and then from tetrahydrofuran-toluene to afford pure butynediol, colorless needles, mp 230—235°C.

Found: C, 87.43; H, 4.97%. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06%. IR: 3430 (OH), 1070 (C–O) cm^{-1}.

Ethynylphenanthrenes(XXIV). *9-Ethynylphenanthrene (9-XXIV).* A mixture of 9-acetylphenanthrene (2.20 g, 0.01 mol), phosphorus pentachloride (2.08 g, 0.01 mol) and benzene (25 m*l*) was refluxed for 1.5 hr. The viscous oily material obtained by the evaporation of the solvent *in vacuo* was kept in an evacuated desiccator containing potassium hydroxide for several hours. The crude chloride thus obtained was dissolved in tetrahydrofuran (10 m*l*), and the solution was added over a period of 10 min to a suspension of sodium amide (prepared from sodium 1.8 g, 0.08 g atom) in liquid ammonia (90 m*l*). After 1.5 hr, ammonia was allowed to evaporate, and ether (50 m*l*) and a saturated solution of ammonium chloride were added to the reaction mixture. The mixture was extracted with ether (200 m*l*). The residue obtained by evaporating the solvent was repeatedly digested with petroleum benzene (bp 60—80°C, 120 m*l*), and the benzine solution was passed through a short column of alumina (5 g). Concentration of the filtrate gave colorless cubes, mp 60—62°C, 1.71 g (85%). A solution of the crude crystals in petroleum ether (bp 40—60°C) was passed through a thin layer of alumina. The filtrate was concentrated to give pure material, color-

---

8) E. Mosettig and J. van de Kamp, *J. Amer. Chem. Soc.*, **52**, 3704 (1930).

9) E. Mosettig and J. van de Kamp, *ibid.*, **55**, 3445 (1933).

10) E. Mosettig and J. van de Kamp, *ibid.*, **55**, 2995 (1933).

11) C. A. Dornfeld and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, p. 701 (1955).

less needless, mp 62.5—63°C. The ethynyl compound gave pale yellow silver and yellow cuprous acetylides.

Found: C, 94.98; H, 4.95%. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98%. IR: 3295 (≡CH) cm^{-1}. UV (in *n*-hexane): $\lambda_{\max}$ (nm)(log ε): 213 (4.51), 234 (4.53), 256.5 (4.72), 260 (4.73), 237.5 (4.36), 287.5 (4.08), 259 (4.31), 312 (4.42), 331.5 (2.47), 339.5 (2.48), 347 (2.33), 355.5 (1.93).

2-Ethynylphenanthrene (2-XXIV). According to the procedure used in the preparation of 9-ethynyl compound, 2-acetylphenanthrene gave 2-ethynyl compound as colorless cubes in a yield of 72%, mp 72—76°C. A petroleum ether solution of this material was passed through a short column of alumina. Pure 2-ethynyl compound was obtained from the filtrate as colorless tiny cubes, mp 77—78°C. The 2-ethynyl derivative gave white silver and yellow cuprous acetylides.

Found: C, 95.00: H, 5.03%. Calcd for $C_{16}H_{10}$: C, C, 95.02; H, 4.98%. IR: 3295 (≡CH) cm^{-1}.
UV (in *n*-hexene): $\lambda_{\max}$ (nm) (log ε) 256 (4.78), 264 (5.00), 280 (4.38), 291 (4.50), 297.5 (4.09), 309 (2.36), 320 (2.30), 326 (2.48), 334 (2.50), 341.5 (2.71), 350.5 (2.51), 358.5 (2.78).

3-Ethynylphenanthrene(3-XXIV). The 3-ethynyl compound was prepared according to the above-stated procedure. Pale yellow needles, mp 100—106°C (62%) obtained were recrystallized three times from petroleum benzine to give pure material, colorless needles, mp 110—111°C. The ethynyl compound gave yellow silver and bright yellow cuprous acetylides.

Found: C, 94.69; H, 4.90%. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98%. IR: 3290 (≡CH), 2090 (C≡C) cm^{-1}. UV (in *n*-hexane): $\lambda_{\max}$ (nm) (log ε) 219.5 (4.47), 237 (4.61), 251 (4.71), 258.5 (4.81), 274 (4.21), 278.5 (4.27), 296 (4.37), 309 (4.46), 330.5 (2.50), 338 (2.49), 346.5 (2.36), 355 (1.98).

2,2′-Diphenanthryldiacetylene (V_2). A solution of 2-ethynylphenanthrene (0.940 g, 4.7×10^{-3} mol) and cupric acetate monohydrate (10.0 g) in pyridine (50 ml) and methanol (5 ml) was stirred at 50°C for 3 hr.[12] The reaction mixture was cooled, and the insoluble material was collected by filtration, and washed with water, thus affording V_2 as colorless fine needles, mp 241—245°C, 0.794 g (84%). A second crop of V_2, 0.083 g (9%) was obtained by concentrating the filtrate. The combined crystals were dissolved in toluene, and the solution was passed through a short column of alumina to yield pure V_2, colorless needles, mp 243—244°C.

Found: C, 95.31; H, 4.48%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

3,3′-Diphenanthryldiacetylene (VI_2). According to the procedure used in the preparation of V_2, 3-ethynylphenanthrene was converted into VI_2 as pale yellow needles in a yield of 86%. This material was recrystallized from toluene to give pure VI_2, pale yellow needles mp 280—282°C.

Found: C, 95.33; H, 4.53%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

9,9′-Diphenanthryldiacetylene(VII_2). *a) Oxidative Coupling of 9-Ethynylphenanthrene(9-XXIV).* 9-Ethynylphenanthrene was oxidatively coupled according to the above procedure to give VII_2, pale yellow cubes, mp 256—257°C (97%). The crystals were recrystallized to yield pure VII_2, mp 256—257°C.

Found: C, 95.30; H, 4.57%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

b) The Dehydrochlorination of 1,4-Bis-(9-phenanthryl)-1,4-dichloro-2-butyne(XI). A solution of thionyl chloride 0.43 g, 3.6 mmol) and pyridine (0.28 g, 3.6 mmol) in ether (5 ml) was added dropwise to a solution glycol (X, 0.562 g, 1.2 mmol) in tetrahydrofuran (15 ml) at −20°C over a period of 10 min. After being shaken for 1 hr at this temperature, the mixture was added to a stirred suspension of sodium amide (prepared from sodium 0.42 g, 18 mg atom) in liquid ammonia (60 ml). After 1 hr, ammonium chloride (2 g) was added to the mixture and the ammonia was allowed to evaporate. The solvent was then removed under reduced pressure. The residue was mixed with water, and the insoluble material was collected by filtration, washed with water and methanol, successively. The brown solid thus obtained was dissolved in toluene (150 ml) and the solution was passed through a short column of alumina (15 g). Concentration of the yellow filtrate gave VII_2 as yellow fine needles, mp 253—255°C, 0.394 g (81%). This material was recrystallized twice from toluene to give pure VII_2, mp 256—257°C.

Found: C, 95.47; H, 4.57%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%. The hydrocarbons prepared by the two different methods gave identical electronic and IR spectra.

Phenanthryl-2-propyn-1-ols(XII). *9-Phenanthryl Derivative(9-XII).* A solution of 9-phenanthaldehyde (8.00 g, 0.039 mol) in tetrahydrofuran (80 ml) was added over a period of 15 min to a suspension of lithium acetylide (prepared from lithium 0.83 g, 0.12 g atom) in liquid ammonia (200 ml) at −50—−55°C. After being stirred for 3 hr at this temperature, stirring was continued for further 3 hr at the temperature of the boiling point of ammonia. Then, ammonium chloride (3 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. A saturated solution of ammonium chloride was added to the residue and the mixture was extracted with benzene. The extract was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure gave an oily material. This material was mixed with benzene (20 ml) and was warmed to promote crystallization. The crystals were collected by filtration and were washed with a small amount of benzene to afford light brown tiny cubes, mp 129—133°C, 6.40 g (69%). Concentration of the filtrate gave the second crop, mp 119—124°C, 1.33 g (14%). The material was recrystallized from benzene 5 times to give pure sample, colorless needles, mp 134—135°C.

Found: C, 87.70; H, 5.20%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: 3380 (OH), 3300 (≡CH), 2100 (C≡C), 1067 (C–O) cm^{-1}.

2-Phenanthryl Derivative(2-XII). To an ice-cooled solution of ethynylmagnesium bromide (prepared from magnesium, 1.80 g, 0.075 g atom, ethylbromide, 8.20 g, 0.075 mol) in tetrahydrofuran (50 ml), was slowly added a solution of 2-formylphenanthrene (6.18 g, 0.03 mol) in the same solvent (60 ml). The cooling bath was removed then and the mixture was stirred overnight at room temperature. A saturated solution of ammonium chloride was added to the reaction mixture. The aqueous layer was extracted with benzene. The extract was combined with the organic layer, and dried. The oily material obtained by evaporation of the solvent under reduced pressure was mixed with benzene and was warmed to promote crystallization. The crystals thus obtained were washed with benzene-cyclohexane to give light brown fine crystals, 6.50 g (93%). A solution of the crystals in ethyl acetate was passed through a short column of alumina. The crystals obtained by concentrating the filtrate was recrystallized from benzene to afford pure 2-XII, pale yellow tiny cubes, mp 134.5—135°C.

Found: C, 87.92; H, 5.18%. Calcd for $C_{17}H_{12}O$: C,

---

[12] *Cf.* G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

87.90; H, 5.21%. IR: 3400 (OH). 3290 (≡CH), 2110 (C≡C), 1017 (C–O) cm^{-1}.

3-Phenanthryl Derivative(3-XII). According to the procedure for the preparation of 2-isomer, 3-formylphenanthrene gave 3-carbinol, light brown needles, mp 80—85°C in a yield of 82%. The crude material was recrystallized from benzene-cyclohexane to give pure material, pale yellow needles, mp 82—84°C.

Found: C, 87.37; H, 5.21%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: 3100—3600 (OH), 3295 (≡CH), 2100 (C≡C), 1056 (C–O) cm^{-1}.

1,6-Di(phenanthryl)-1,6-dihydroxy-2,4-hexadiynes(XIII). *9-Phenanthryl Derivative(9-XIII).* Cuprous chloride (0.02 g, 2 mmol), ammonium chloride (0.14 g, 2 mmol) and 2 drops of concentrated hydrochloric acid were added to a solution of the 9-ethynyl carbinol (9-XII, 4.64 g, 0.02 mol) in methanol (80 m*l*). The mixture was vigorously stirred in oxygen atmosphere at a slightly elevated pressure. Deposition of pale yellow precipitate was observed after 1.5 hr. After being stirred overnight, the precipitate was collected by filtration. The precipitate was washed with methanol, diluted hydrochloric acid, and water, successively, and dried. The pale yellow powder, 3.51 g (76%), mp 210—215°C (dec.) thus obtained was recrystallized 5 times from tetrahydrofuran-benzene to give pure glycol (9-XIII) as colorless fine needles. mp 252—254°C (dec.).

Found: C, 87.99; H, 4.78%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%. IR: 3400 (OH), 1067 (C–O), 2140, 2250 (C≡C) cm^{-1}.

3-Phenanthryl Derivative(3-XIII). The Glaser oxidative coupling of 3-ethynyl carbinol(3-XII) under the reaction conditions used in the case of 9-isomer afforded 3-XIII as colorless powder in a yield of 66%. The material was recrystallized 3 times from acetone-benzene to yield pure 3-XIII, mp 208—210°C.

Found: C, 87.90; H, 4.78%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%. IR: 3600—3100 (OH), 2130 (C≡C), 1010 (C–O) cm^{-1}.

2-Phenanthryl Derivative(2-XIII). 2-ethynyl carbinol (2-XII) was converted to di-(2-phenanthryl)-diol(2-XIII) under the reaction conditions used in 3- and 2-isomers. Almost colorless powder (77%) thus obtained was recrystallized thrice from acetone-benzene to yield pure 2-XIII as colorless fine needles, mp 204—206°C (dec.).

Found: C, 88.36; H, 4.84%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%. IR: 3450—3100 (OH), 1000 (C–O) cm^{-1}.

9,9'-Diphenanthryltriacetylene(VIII$_3$). *Formation of the Dichloride (9-XIV).* A solution of thionyl chloride (0.36 g, 3 mmol) in pyridine (0.24 g, 3 mmol) was added to a solution of 9-glycol (9-XIII, 0.462 g, 1 mmol) in tetrahydrofuran (15 m*l*) over a period of 30 min at −20°C, and the mixture was shaken for 30 min.

Dehydrochlorination of 9-XIV. The above-mentioned reaction mixture was added to a suspension of sodium amide (prepared from sodium, 0.40 g, 0.017 g atom) in liquid ammonia (100 m*l*) under vigorous stirring at −70°C. After 30 min, ammonium chloride (2.0 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. After the solvent had been removed under reduced pressure, a small amount of water was added to the residue. The insoluble material was successively washed with water, methanol, acetone, and benzene, and was dissolved in hot toluene (200 m*l*). The hot solution was passed through a thin layer of alumina (15 g). The light orange-yellow filtrate was concentrated under reduced pressure to yield VII$_3$ as yellow fine needles, 0.134 g (31%) mp 284—287°C (dec.). This substance was recrystallized from toluene to give pure VII$_3$, mp 285—286°C (dec.).

Found: C, 95.80; H, 4.24%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

3,3'-Diphenanthryltriacetylene (VI$_3$). The procedure used for the preparation of VII$_3$ was applied to the 3-glycol (3-XIII) to give pale yellow fine needles in a yield of 39%, which decomposed at *ca.* 260°C. The material was recrystallized to afford pure VI$_3$, which decomposed at *ca.* 260°C without fusion.

Found: C, 95.71; H, 4.22%. Calcd for $C_{34}H_{18}$; C, 95.75; H, 4.25%.

2,2'-Diphenanthryltriacetylene (V$_3$) Chlorination of 2-glycol(2-XIII) followed by dehydrochlorination according to the reaction conditions used in the preparation of VII$_3$ and VI$_3$ gave pale yellow needles, dec. p *ca.* 270°C in a yield of 11%. This was recrystallized from toluene to give pure V$_3$, pale yellow needles, which decomposed, at *ca.* 270°C without fusion.

Found: C, 95.58; H, 4.22%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

1-(Phenanthryl)-2-butyn-1,4-diol(XV). *9-Phenanthryl Derivative(9-XV).* A solution of propargyl alcohol (5.04 g, 0.09 mol) in tetrahydrofuran (20 m*l*) was added dropwise in an ice-cooled solution of ethylmagnesium bromide in the same solvent (prepared from magnesium, 4.32 g, 0.18 g atom and ethyl bromide 20.0 g, 0.183 mol). After the mixture had been refluxed for 1 hr, it was cooled again with an ice-bath and a solution of 9-formylphenanthrene (9-VIII, 6.18 g, 0.03 mol) in tetrahydrofuran (90 m*l*) was added under stirring. The reaction mixture was stirred overnight at room temperature. A saturated solution of ammonium chloride was added to the mixture, and the organic layer was separated. The aqueous layer was extracted with benzene. The organic layer was combined with the extract and dried. After evaporation of the solvent, there remained an oily material which was mixed with a small amount of benzene. The crystals deposited on warming the mixture were washed with a small amount of benzene to yield light brown crystals, mp 133—135°C, 7.35 g (93%). The crystals were recrystallized three times from ethanol-cyclohexane to give pure diol, colorless needles, mp 138—139°C.

Found: C, 83.59; H, 5.70%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. IR: 3350 (OH), 1017 (C–O) cm^{-1}. Recrystallization of the crude crystals three times from benzene afforded colorless needles, mp 104—106°C which contained half mole of benzene as a solvent of crystallization.

Found: C, 83.59; H, 5.70%. Calcd for $C_{18}H_{14}O_2 \cdot 1/2\ C_6H_6$: C, 82.69; H, 5.69%.

3-Phenanthryl Derivative(3-XV). The above-mentioned procedure was adapted to 3-formylphenanthrene(3-VIII). The yield of crude crystals, light brown leaflets, mp 115—119°C was found to be 89%. The crude material was recrystallized four times from ethanol-benzene to give pure 3-XV, colorless leaflets, mp 122—124°C.

Found: C, 82.62; H, 5.40%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. IR: 3600—3100 (OH), 1008 (C–O) cm^{-1}.

2-Phenanthryl Derivative(2-XV). According to the same procedure, a slightly impure 2-XV, mp 123—125°C was obtained from 2-formylphenanthrene(2-VIII). The crude material was recrystallized twice from acetone-benzene to afford pure 2-XV, colorless leaflets, mp 126—127°C.

Found: C, 82.37; H, 5.42%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. IR: 3500—3100 (OH), 1000 (C–O) cm^{-1}.

9-Butadiynylphenanthrene(9-XVII). Formation of Dichloride (9-XVI). A solution of thionyl chloride (5.00 g, 0.042 mol) and pyridine (3.31 g, 0.042 mol) in ether (10 m*l*) was added over a period of 1 hr in a solution of 9-XV (4.200 g, 0.016 mol) in tetrahydrofuran (50 m*l*) under cooling with an ice-salt bath. After the mixture has been stirred for further 1 hr at room temperature, cracked ice was added, and the mixture was extracted with benzene. The extract was washed with water and an aqueous solution of sodium hydrogen carbonate, successively, and dried. The extract was concentrated to *ca.* 20 m*l* under reduced pressure, and the solution was subjected to the following reaction.

Dehydrochlorination of 9-XVI. The above-stated benzene solution of 9-XVI was added over a period of 15 min to a suspension of sodium amide (prepared from sodium 2.3 g, 0.1 g atom) in liquid ammonia (100 m*l*) at −70°C. After the mixture had been stirred for 30 min, ammonium chloride (10 g) was added, and the ammonia was allowed to evaporation. The residue obtained by evaporation of the solvent under reduced pressure was repeatedly digested with petroleum benzine (bp 60—80°C, total 500 m*l*). The benzine solution was percolated through a thin layer of alumina (5 g). Concentration of the colorless filtrate under reduced pressure afforded diacetylene (9-XVII) as colorless fine needles, mp *ca.* 110°C (dec.), 1.664 g (47%). Diacetylene (9-XVII) was found to be extremely unstable substance. The colorless crystals readily turned from blue to violet and then deep brown insoluble material. However, the solution of 9-XVII in benzine could be kept without decomposition in a refrigerator. Diacetylene (9-XVII) gave orange-yellow cuprous and yellow silver acetylides. UV (petroleum ether): $\lambda_{\max}$ (nm): 328.5 (L_a), 360 (L_b).

2-Butadiynylphenanthrene (2-XVII). Hexadiynediol (2-XV) was converted to diacetylene (2-XVII) according to the same reaction sequence under the conditions employed for the preparation of 9-XVII. Extremely unstable diacetylene (2-XVII) was obtained as colorless needles, mp *ca.* 110°C (dec.) in a yield of 50%. The substance gave yellow cuprous and light yellow silver acetylides. UV (petroleum ether): $\lambda_{\max}$ (nm): 314.5 (L_a), 365 (L_b).

3-Butadiynylphenanthrene(3-XVII). This substance was also prepared according to the method used for 9- and 2-isomer. The diacetylene(3-XVII) was obtained as colorless cubes in a yield of 15%. This substance was found to be highly unstable. It began to decompose at *ca.* 60°C and completely decomposed at 98—100°C. Diacetylene (3-XVII) gave orange cuprous and yellow silver acetylides. UV (petroleum ether): $\lambda_{\max}$ (nm): 326.5 (L_a), 362 (L_b).

9,9′-Diphenanthryltetraacetylene(VII$_4$). A mixture of the butadiynyl compound (9-XVII, 1.050 g, 4.65 mmol), cupric acetate monohydrate (10.0 g) and pyridine (50 m*l*) was stirred for 6 hr at 40°C.[12] The insoluble material was collected by filtration, and was washed thoroughly with water, then with a small amount of methanol and acetone. The yellow crystals, 1.018 g (97%). dec. p *ca.* 250°C were recrystallized four times from toluene to give pure tetraacetylene (VII$_4$), which decomposed at *ca.* 255°C without fusion.

Found: C, 95.69; H, 4.41%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

3,3′-Diphenanthryltetraacetylene(VI$_4$). The oxidative coupling of 3-butadiynylphenanthrene(3-XVII) according to the above described procedure afforded yellow needles. dec. p *ca.* 190°C in a yield of 78%. The substance was recrystallized twice from toluene to give pure VI$_4$, yellow needles, which decomposed at *ca.* 200°C without fusion.

Found: C, 95.92; H, 4.02%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

2,2′-Diphenanthryltetraacetylene(V$_4$). According to the procedure used in the cases of 3- and 9-isomers, diacetylene (2-XVII) was converted into tetrayne (V$_4$), yellow needles, 82%, dec. p *ca.* 220°C. The crude crystals in hot toluene were percolated through a thin layer of alumina. Pure V$_4$, yellow needles, which decomposed at *ca.* 220°C without fusion was obtained by concentration of the filtrate.

Found: C, 95.68; H, 3.95%. Calcd for $C_{36}H_{18}$; C, 95.97; H, 4.03%.

Phenanthrypropynals (XXV). 3-Phenanthrylpropynal (3-XXV). To a solution of ethylmagnesium bromide (prepared form magnesium, 2.30 g, 0.09 g atom, ethyl bromide, 13.0 g, 0.12 mol) in tetrahydrofuran (170 m*l*), was added over a period of 20 min a solution of 3-ethynylphenanthrene (3-XXIV, 12.25 g, 0.061 mol) in the same solvent (40 m*l*). After the mixture had been refluxed for 30 min, a solution of dimethylformamide (23.0 m*l*) in the same solvent (40 m*l*) was added under cooling with an ice-salt bath. The reaction mixture turned yellow, and then deposition of colorless crystals took place. The mixture was stirred for 2 hr at room temperature and then for 2.5 hr at 30°C. The mixture was poured into cold 5% sulfuric acid (600 m*l*) and benzene (150 m*l*). The mixture was stirred overnight, and extracted with ether. The extract was washed successively with water and sodium hydrogen carbonate solution, and dried. The oily material obtained by evaporation of the solvent, upon trituration with benzene-cyclohexane (1 : 1, 20 m*l*), gave yellow cubes, mp 130-133°C, 12.23 g (88%). The pure material was obtained by recrystallization of the crude crystals three times from benzene, and once from benzene-cyclohexane as yellow prisms, mp 132—134°C.

Found: C, 88.79; H, 4.43%. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38%. IR: 2840, 2740 (-CHO), 2210, 2180 (C≡C), 1658 (C=O) cm^{-1}.

2-Phenanthrylpropynal (2-XXV). The procedure described in the preparation of 3-aldehyde (3-XXV) was successfully adapted in the preparation of 2-aldehyde (2-XXV). The yellow fine needles, mp 104—108°C obtained in a yield of 62% were recrystallized four times from benzene-cyclohexane to give the pure material, yellow fine needles, mp 109—111°C.

Found: C, 88.62; H, 4.38%. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38%. IR: 2180 (C≡C), 1658 (C=O) cm^{-1}.

1-(Phenanthryl)-1,4-pentadiyn-3-ols (XXVI). 2-Phenanthryl Derivative (2-XXVI). To an ice-cooled solution of ethynylmagnesium bromide (prepared form magnesium, 1.44 g, 0.06 g atom and ethyl bromide, 7.20 g, 0.066 mol) in tetrahydrofuran (70 m*l*), was added a solution of 2-phenanthrylpropynal (2-XXV, 6.45 g, 0.028 mol) in tetrahydrofuran (60 m*l*). The temperature of the reaction mixture was gradually raised to room temperature and stirring was continued overnight. The mixture was hydrolyzed by the addition of a saturated ammonium chloride solution. The organic layer was then separated, and the aqueous layer was extracted with benzene. The extract was combined with the organic layer and was worked up in the usual manner to yield a dark-red oil. On being warmed with benzene (20 m*l*) it gave light brown needles, mp 120—122°C, 5.88 g (82%). The substance as recrystallized three times to give pure alcohol (2-XXVI), colorless needles, mp 121°C.

Found: C, 88.79; H, 4.71% Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%. IR: 3100—3450 (OH), 3295 (≡CH), 2330, 2110 (C≡C) cm^{-1}.

3-Phenanthryl Derivative (3-XXVI). The crude crystals, mp 114—117°C (74%) which were obtained by the procedure described above were recrystallized three times from benzene and once from benzene - methanol to afford pure 3-XXVI as colorless tiny plates, mp 117—118°C.

Found: C, 88.87; H, 4.72%. Calcd for $C_{19}H_{12}O$; C, 89.04; H, 4.72%. IR: 3600—3100 (OH), 3280 (≡CH), 2210, 2110 (C≡C), 1012 (C–O) cm^{-1}.

1,10-Di(Phenanthryl)-1,4,6,9-decatetrayn-3,8-diols (XXVII). 2-Phenanthryl Derivative (2-XXVII). A mixture of 2-phenanthrylpentadiynol (2-XXVI, 2.80 g, 0.011 mol), cuprous chloride (0.35 g), ammonium chloride (0.30 g) and methanol (60 m*l*) was vigorously stirred under oxygen atmosphere at a slightly elevated pressure. After the mixture had been stirred for 48 hr, the solid deposited was collected by filtration. The solid was washed with a small amount of methanol, and then was dissolved in tetrahydrofuran-acetone (1 : 1;20 m*l*). The solution was passed through a short column of silica gel (5 g), and the filtrate was concentrated under reduced pressure to afford crude crystals, 2.40 g (84%), dec. p *ca.* 120°C. The substance was recrystallized from tetrahydrofuran-acetone to yield colorless needles, dec. p *ca.* 125°C. The unstable tetraacetylene glycol turned yellow in a short time.

Found: C, 89.21; H, 4.25%. Calcd for $C_{38}H_{22}O_2$: C, 89.39; H, 4.34%. IR: 3100—3400 (OH), 2235 (C≡C), 1008 (C–O) cm^{-1}.

3-Phenanthryl Derivative (3-XXVI). According to the above procedure, the 3-phenanthrylpentadiynol (3-XXVII) gave light brown crystals, dec. p *ca.* 110°C in a yield of 70%. Recrystallization of this material from acetone-ethanol and then from acetone-benzene afforded rather unstable colorless fine needles, dec. p *ca.* 140°C.

Found: C, 89.47; H, 4.34%. Calcd for $C_{38}H_{22}O_2$: C, 89.39; H, 4.34%. IR: 3600—3100 (OH), 2230 (C≡C), 1010 (C–O) cm^{-1}.

1,10-Di(9-Phenanthryl)-3,4,6,8-decatetrayn-1,10-diol (XIX). Formation of 1-(9-Phenanthryl)-2,4-pentadiyn-1-ol (XVIII). A solution of 1,4-dichloro-2-butyne(7.20 g, 0.059 mol) in ether (10 m*l*) was added over a period of 20 min to a suspension of lithium amide (prepared from lithium, 1.24 g, 0.179 atom) in liquid ammonia (250 m*l*) at −60°C. After having been stirred for 5 min, a solution of 9-formylphenanthrene (9.27 g, 0.045 mol) in tetrahydrofuran (150 m*l*) was added, and the mixture was stirred at −55°C for 1 hr, at −50°C for 1 hr and additional 1.5 hr at −40°C. Ammonium chloride (9 g) was then added to the reaction mixture at −60°C. After ammonia had been allowed to evaporate, water was added to the residue, and was extracted with benzene. Evaporation of the solvent from the dried extract gave a deep brown tarry material, which was re-dissolved in benzene, and then passed through a short column of alumina (7 g). However, no crystalline material could be obtained from the filtrate. The IR spectrum of the crude material indicated the presence of –C≡CH and OH groups. The absorption of C=O was found to be very weak. Owing to the unstable nature of diacetylene carbinol (XVIII), the crude material was subjected to the subsequent reaction.

Oxidative Coupling of Diacetylene Carbinol (XVIII). Cuprous chloride (0.30 g, 3 mmol) and ammonium chloride (0.20 g) were added to a solution of the above-mentioned crude carbinol (XVIII) in methanol (120 m*l*). The mixture was vigorously stirred under oxygen atmosphere at slightly elevated pressure. After having been stirred for 2 hr at room temperature, 2 drops of concentrated hydrochloric acid was added to the reaction mixture to dissolve the deposited cuprous acetylide. Stirring was continued overnight. The insoluble material deposited was washed with a small amount of methanol. The greenish-brown powder thus obtained was dissolved in tetrahydrofuran (60 m*l*) and the insoluble material was removed. The solution was percolated through a thin layer of alumina (10 g). The filtrate was concentrated under reduced pressure, and the tarry residue was mixed with a small amount of benzene. The mixture was warmed to promote crystallization. The crystals were dissolved in acetone and were precipitated by the addition of benzene to give fairly pure crystals, 2.25 g (20% based on 9-formylphenanthrene). The crystals decomposed at *ca.* 175°C without fusion. Owing to the instability of tetraacetylene glycol(XIX), the crude crystals were used in the following reaction.

IR: 3400 (OH), 2200, 2150, 2070 (C≡C), 1063 (C–O) cm^{-1}.

9,9′-Diphenanthrylpentaacetylene(VII$_5$). Formation of Dichloride(XX). A mixture of thionyl chloride (0.36 g; 3 mmol), pyridine (0.24 g, 3 mmol) and ether (5 m*l*) was added over a period of 20 min to a solution of the crude tetraacetylene glycol (XIX, 0.510 g, 1.0 mmol) in tetrahydrofuran (20 m*l*) at −20°C. The mixture was shaken for 30 min, and was immediately subjected to the following reaction.

Dehydrochlorination of Dichloride(XX). The mixture containing dichloride(XX) was added to a suspension of sodium amide (prepared from sodium, 0.40 g, 0.017 g atom) in liquid ammonia (100 m*l*) at −60°C under vigorous stirring. After 30 min, ammonium chloride (2 g) was added, and ammonia was allowed to evaporate. The residue obtained on removal of the solvent under reduced pressure was mixed with water. The insoluble material was washed successively with water, a small amount of acetone and benzene, and was dissolved in toluene (400 m*l*). The solution was passed through a short column of alumina (15 g). The yellow filtrate was concentrated under reduced pressure to yield orange-yellow needles, 0.213 g (45%). The substance was recrystallized twice from toluene to give pure VII$_5$, orange-yellow needles. The crystals decomposed at *ca.* at 200°C without fusion.

Found: C, 96.05; H, 3.85%. Calcd for $C_{38}H_{18}$; C, 96.18; H, 3.82%.

3,3′-Diphenanthrylpentaacetylene(VI$_5$). To a solution of di-(3-phenanthryl)-tetraacetylene glycol (3-XXVII; 0.510 g, 1 mmol) in tetrahydrofuran (15 m*l*), was added at −30°C a mixture of thionyl chloride (3.36 g, 3 mmol), pyridine (0.24 g, 3 mmol) and ether (5 m*l*) over a period of 15 min. The mixture was shaken for additional 5 min, and was added to a suspension of sodium amide (prepared from sodium, 0.40 g, 0.017 g atom) in liquid ammonia (90 m*l*) at −65°C. After having been stirred for 30 min, ammonium chloride (1 g) was added to the mixture, and ammonia was allowed to evaporate. The organic solvent was removed under reduced pressure, and the residue thus obtained was mixed with water. The insoluble material was washed successively with water, methanol, acetone and benzene, and was dissolved in hot toluene (400 m*l*). The hot solution was percolated through a thin layer of alumina (15 g). On cooling the yellow filtrate, orange-yellow needles, 0.276 g (58%) were obtained. The second crop of crystals, 0.029 g (6%) was obtained by the concentration of the mother liquor. The combined crystals were recrystallized from toluene to give pure VI$_5$, orange-yellow needles. It decomposed at *ca.* 190°C without fusion.

Found: C, 96.27; H, 3.74%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

2,2′-Diphenanthrylpentaacetylene (V$_5$). According to the procedure for the preparation of VI_5, the di-(2-phenanthryl)-tetraacetylene glycol(2-XXVII), were converted to V_5, silky yellow needles, in a yield of 22%. The crystals were recrystallized from toluene to afford pure V_5 as bright yellow fine needles. The crystals decomposed at *ca.* 200°C without fusion.

Found: C, 96.42: H, 3.78%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

1-(Phenanthryl)-2,5-hexadiyn-1,4-diols (XXI). 9-Phenanthryl Derivative(9-XXI). A solution of 2,4-pentadiyn-3-ol[13] (3.08 g, 0.039 mol) in tetrahydrofuran (65 m*l*) was added over a period of 20 min to a stirred solution of ethylmagnesium bromide (prepared from magnesium, 2.05 g, 0.086 g atom and ethyl bromide, 10.4 g, 0.095 mol) in tetrahydrofuran (55 m*l*) at a temperature of 20—25°C. After 30 min, a solution of 9-phenanthraldehyde (VIII, R=9-phenanthryl), (6.00 g, 0.029 mol) in tetrahydrofuran (60 m*l*) was added to the ice-cooled mixture, and the mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed by the addition of a saturated solution of ammonium chloride. The organic layer was combined with the benzene extract of the aqueous layer, and dried. Evaporation of the solvent gave a viscous oily material. The oily material was warmed with benzene (10 m*l*) to bring about crystallization. The light brown crystals, 6.10 g (74%) mp 135—140°C, obtained by washing with a small amount of cold benzene, were recrystallized three times from methanol-benzene. The colorless fine needles, mp 160—165°C, thus prepared, were re-dissolved in ethyl acetate, and the solution was passed through a short column of alumina to afford pure XXI (R=9-phenanthryl) as colorless fine needles, mp 169—171°C.

Found: C, 83.83; H, 4.90%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR: 3500—3200 (OH), 3295 (≡CH), 2110 (C≡C), 1074, 1030 (C–O) cm^{-1}.

3-Phenanthryl Derivative (3-XXI). The light brown crystalline powder obtained from 3-phenanthraldehyde (3-VIII) according to the procedure used for the preparation of 9-isomer in a yield of 79% was recrystallized from methanol-benzene to yield light brown needles, mp 127—135°C. This material was recrystallized three times from acetone-benzene to give pure 3-phenanthryl diol (3-XXI) as colorless fine needles mp 141—143°C.

Found: C, 83.69; H, 4.96%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR: 3600—3100 (OH), 3295 (≡CH), 2115 (C≡C), 1020 (C–O) cm^{-1}.

2-Phenanthryl Derivative (2-XXI). According to the procedure, 2-phenanthraldehyde (VIII, R=2-phenanthryl) was converted to slightly crude XXI (R=2-phenanthryl), light brown fine crystals, in a yield of 72%. The crystals were recrystallized three times from ethyl acetate-toluene to yield pure specimen as pale yellow leaflets, mp 151—153°C.

Found: C, 84.04; H, 4.92%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR: 3500—3100 (OH), 3280 (≡CH), 2115 (C≡C), 1020 (C–O) cm^{-1}.

9-Hexatriynylphenanthrene(9-XXIII). Chlorination of Hexadiynediol(9-XXI). To a solution of diol (9-XXI, 1.716 g, 6 mmol) in tetrahydrofuran (16 m*l*) was added over 30 min a mixture of thionyl chloride (2.14 g, 18 mmol), pyridine (1.42 g, 18 mmol) and ether (7 m*l*) at −20°C. The mixture was allowed to reach room temperature, after which it was shaken for 30 min, and was subjected directly to the subsequent reaction.

Dehydrochlorination of Dichloride (9-XXII). The reaction mixture containing dichloride(9-XXII) was added to a vigorously stirred suspension of sodium amide (prepared from sodium, 1.00 g, 0.044 g atom) in liquid ammonia (100 m*l*) at −70°C. After the mixture had been stirred for 45 min, ammonium chloride (4 g) was added, and ammonia was allowed to evaporate. The organic solvent was distilled off under reduced pressure and the residue was digested repeatedly with petroleum ether (bp 60—80°C, total 300 m*l*). The solution was passed through a thin layer of alumina (6 g). A small portion of the pale yellow filtrate was concentrated under reduced pressure to result in the deposition of pale yellow fine needles. Rapid decomposition of the crystals to form black tarry material was observed. Triacetylene (9-XXI, UV (petroleum ether): λ_{max} 352 nm) gave yellow silver and orange cuprous acetylides. Owing to the unstable nature of 9-XXI, the petroleum ether solution was used in the following reaction.

3-Hexatriynylphenanthrene (3-XXIII). A colorless petroleum ether solution of triacetylene (3-XXIII) was obtained from the 3-phenanthryl glycol (3-XXI, 0.860 g, 3 mmol) under the same reaction conditions. Concentration of a small portion of the solution gave extremely unstable colorless cubes, which decomposed immediately to a brown material. Triacetylene (3-XXIII), UV (petroleum ether): λ_{max} 350 nm, gave orange cuprous and yellow silver acetylides. The petrolum ether solution was used directly for the subsequent reaction.

2-Hexatriynylphenanthrene (2-XXIII). 2-Phenanthryl diynediol (2-XXI, 2.00 g, 7 mmol) was converted to a petroleum ether solution of triacetylene (2-XXIII) according to the same procedure. Colorless fine needles obtained by the concentration of a small portion of the solution decomposed to blue insoluble material. Triacetylene (2-XXII, UV (petroleum ether): λ_{max} 342 (L_a), 370 (L_b nm) gave orange cuprous and yellow silver acetylides. The petroleum ether solution was subjected to the following reaction without isolation of 2-XXIII.

9,9′-Diphenanthrylhexaacetylene (VII_6). The petroleum ether solution of 9-hexatriynylphenanthrene (9-XXIII) was mixed with cupric acetate monohydrate (4.0 g) and pyridine (50 m*l*), and the mixture was concentrated to *ca.* 40 m*l* under reduced pressure. After the concentrated mixture had been stirred overnight at room temperature, the mixture was again concentrated to *ca.* 20 m*l* *in vacuo*. The insoluble material was washed with a small amount of methanol and then with water. The crude hexaacetylene, brown powder, 0.101 g (7% based on the diol, 9-XXI), thus obtained, was digested with hot toluene (100 m*l*), and the hot solution was passed through a short column of alumina (5 g). On cooling the orange filtrate, it gave orange fine needles. The crystals were recrystallized twice from toluene to give pure VII_6 as orange fine needles. This substance decomposed without fusion at *ca.* 130°C.

Found: C, 96.30; H, 3.67%. Calcd for $C_{40}H_{18}$: C, 96.36; H, 3.64%.

3,3′-Diphenanthrylhexaacetylene (VI_6). According to the same procedure, the petroleum ether solution of 3-hexatriynylphenanthrene (3-XXIII) gave crude VI_6, as yellow fine leaflets, 0.094 g (13% based on the glycol, 3-XXI). A benzene solution (350 m*l*) of the crude material was percolated through a thin layer of alumina (5 g). The orange yellow filtrate gave 0.056 g of pure VI_6 as orange yellow tiny plates, which decomposed at *ca.* 100°C without fusion.

Found: C, 96.41; H, 3.67%. Calcd for $C_{40}H_{18}$: C, 96.36; H, 3.64%.

2,2′-Diphenanthrylhexaacetylene (V_6). Brown crystalline powder, 0.380 g (22% based on the glycol, 2-XXI),

---

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

obtained under similar conditions from the above-mentioned petroleum ether solution of 2-XXIII was dissolved in benzene (300 m*l*). The benzene solution was passed through a short column of alumina (12 g). The deep yellow filtrate was concentrated to *ca.* 100 m*l* *in vacuo* to yield pure V_6 as light orange fine crystals, 0.102 g (6% based on the glycol, 2-XXI), which decomposed without fusion at *ca.* 185°C.

Found: C, 96.15; H, 3.62%. Calcd for $C_{40}H_{18}$; C, 96.36; H, 3.64%.