BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3561—3566 (1970)

Linear Conjugated Systems Bearing Aromatic Terminal Groups. II. The Synthesis and the Electronic Spectra of 9,9′-Dianthrylpoly-ynes

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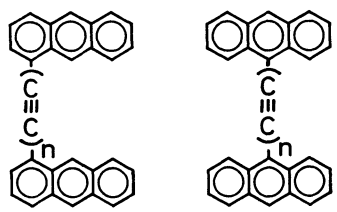
(Received June 15, 1970)

A series of 9,9′-dianthrylpoly-ynes (II_1–II_6) were prepared, and their electronic spectra were measured. It was found that the novel linear relation between λ_{max} and the square of the number of the triple bond (n^2) which has been found in the spectra of 1,1′-dianthrylpoly-ynes (I_1–I_6) also held in the 9,9′-series.

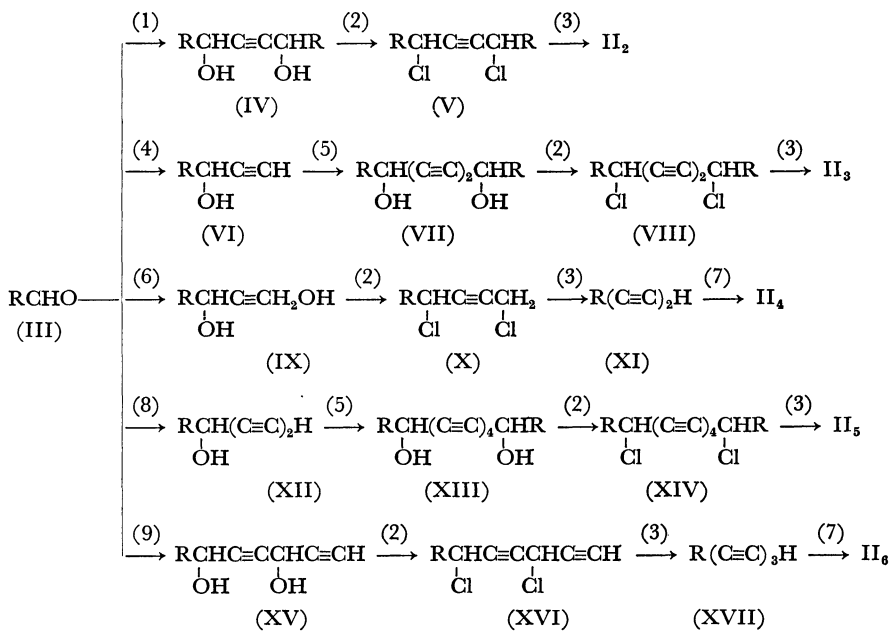
The present authors have pointed out in previous papers that the plot of the λ_{max} of the electronic spectra of 1,1′-dianthrylpoly-ynes (I_n) against the square of the number of the triple bond (n^2) gave a straight-line relationship;[1] this novel relationship has been explained in terms of HMO, applying a modified bond-alternation approximation.[2]

This interesting spectral behavior prompted the authors to the synthesis of 9,9′-dianthrylpoly-ynes (II_1–II_6) in order to get further information on



I_n II_n

n=1, 2, 3, 4, 5, 6



Scheme 1. Synthesis of 9,9′-Dianthrylpoly-ynes (II_2–II_6)

R=9-Anthryl. (1) BrMgC≡CMgBr in benzene–THF; (2) $SOCl_2$-pyridine in THF; (3) $NaNH_2$ in liq. NH_3; (4) LiC≡CH in liq. NH_3; (5) CuCl-NH_4Cl-O_2 in CH_3OH; (6) $BrMgC{\equiv}CCH_2OMgBr$ in THF; (7) $Cu(OAc)_2$ in pyridine; (8) $Li(C{\equiv}C)_2H$ in liq. NH_3; (9) BrMgC≡CCH(OMgBr)C≡CH in THF. THF=tetrahydrofuran.

1) S. Akiyama and M. Nakagawa, This Bulletin, **40**, 340 (1967). The paper is to be regarded as Part I of this series. For a preliminary report, see *Tetrahedron Lett.*, **1968**, 1121.

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

Table 1. The colors and the melting points of II_n and I_n

n	II_n		I_n	
	Color	Mp (°C)	Color	Mp (°C)
1	orange	*ca.* 310 (dec.)	yellow	272—273
2	orange	290—292 (dec.)	bright yellow	289—291 (dec.)
3	deep orange	*ca.* 295 (dec.)	deep yellow	*ca.* 270 (dec.)
4	orange red	*ca.* 265 (dec.)	golden yellow	*ca.* 245 (dec.)
5	red	*ca.* 250 (dec.)	orange	*ca.* 220 (dec.)
6	dark red	*ca.* 200 (dec.)	red	*ca.* 210 (dec.)

the role of the terminal groups on the electronic spectra of diarylpoly-yne compounds.

Synthesis. The synthesis of 9,9′-dianthrylacetylene (II_1) by means of an intramolecular Wittig reaction will be reported in the following paper, together with the synthesis of other diarylacetylenes. The higher members (II_2–II_6) have been synthesized according to the sequence depicted in the following scheme, starting from the common precursor, 9-formylanthracene (III).[3]

The color of the crystals and the melting points of 9,9′-dianthrylpoly-ynes (II_1–II_6) are compared with those of 1,1′-analogs in Table 1.

Infrared Spectra. Just as in the case of the 1,1′-series,[1] a remarkable intensification of the absorption ($A=1-I/I_0$) due to $\nu_{C\equiv C}$ with an increase in the number of n was also observed in the case of II_n, as is illustrated in Fig. 1. The absorption intensity of the $\nu_{C\equiv C}$-band relative to the intensity of the 880 cm^{-1}-band (ν_{C-H} of the isolated hydrogen atom in the anthryl groups) and to the 730 cm^{-1}-band (ν_{C-H} of the adjacent four hydrogen atoms in the terminal groups) is summarized in Table 2. It seems to be noteworthy that the $\nu_{C\equiv C}$-band of the tetraacetylene (II_4) exhibited the highest wavenumber, as in the cases of diphenyl-, dimethyl-,[4] and 1,1′-dianthrylpoly-ynes.[1]

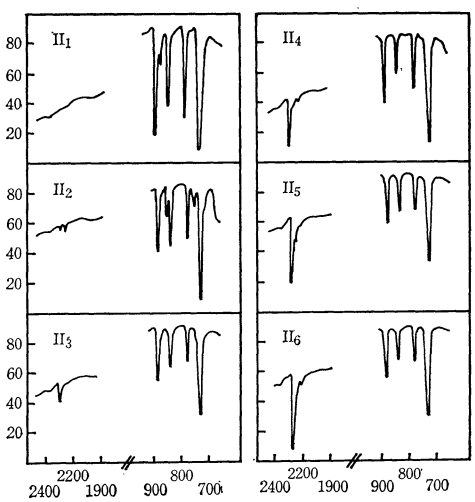


Fig. 1. Infrared spectra of 9,9′-dianthrylpoly-ynes (II_1–II_6) in the 1900—2400 cm^{-1} and 700—900 cm^{-1} region.

Table 2. The wave numbers and the relative absorption intensities of $\nu_{C\equiv C}$ -band of II_n (KBr-disk)

II_n	$\nu_{C\equiv C}$-band	Relative absorption intensities	
		Ratio to the 880 cm^{-1} -band	Ratio to the 730 cm^{-1} -band
II_1	—	—	—
II_2	2180†, 2115	0.07	0.04
II_3	2185†, 2150*	0.52	0.32
II_4	2200†, 2060	1.26	0.76
II_5	2150†, 2100, 2040*	1.95	1.09
II_6	2120†, 2010	2.30	1.29

The daggers indicate the absorption bands used in the calculation.
The asterisks denote the shoulders.

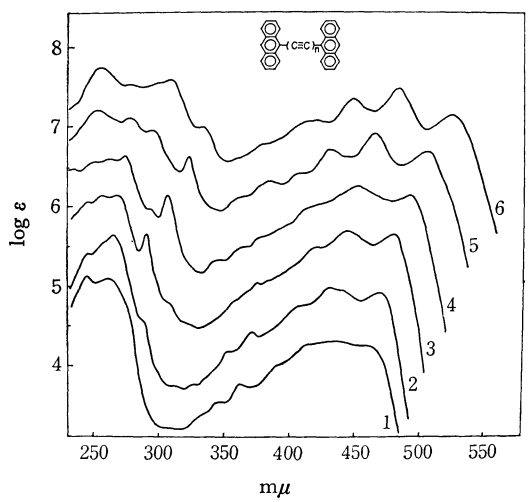


Fig. 2. The absorption curves of 9,9′-dianthrylpoly-ynes (II_1–II_6) . The curves, with the exception of the monoacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below (in tetrahydrofuran).

3) E. Campaigne and W. L. Archer, *J. Amer. Chem. Soc.*, **75**, 989 (1953).

4) C. L. Cook, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1952**, 2883.

Table 3. The spectral data of 9,9′-dianthrylpoly-ynes (II_1–II_6)

n	λ_{max} in mμ and log ε (in parentheses) in tetrahydrofuran									
1	245.5 (5.14)	262 (5.10)	346 (3.59)	362 (3.81)	416* (4.30)	436 (4.34)	457* (4.27)			
2	224.5 (4.60)	246.5 (4.94)	265.5 (5.18)	287* (4.14)	345 (3.76)	372 (4.00)	410 (4.33)	431 (4.55)	470 (4.50)	
3	246 (5.06)	256 (5.14)	269 (5.15)	290 (4.66)	308* (3.78)	356* (3.81)	374 (4.04)	422* (4.51)	443 (4.69)	479 (4.66)
4	235 (5.00)	262 (5.12)	273.5 (5.15)	294 (4.47)	306 (4.65)	366* (4.00)	376* (4.12)	451 (4.77)	491 (4.65)	
5	254.5 (5.20)	277 (5.11)		294.5 (4.96)	322.5 (4.63)	386 (4.32)	412 (4.45)	431 (4.73)	466 (4.93)	505 (4.71)
6	256.5 (5.19)	278.5 (4.98)		308.5 (5.06)	333 (4.50)	376* (4.28)	417 (4.57)	447 (4.84)	482 (4.95)	523 (4.65)

The asterisks indicate the shoulders.

Electronic Spectra. The absorption curves and the numerical data of the electronic spectra of II_n are shown in Fig. 2 and Table 3. Similarly to the case of 1,1′-dianthrylpoly-ynes (I_n),[1] the electronic spectra of II_n could be divided into three groups, *i. e.*, the short-wavelength band (240—280 mμ), the medium-wavelength band (280—330 mμ), and the long-wavelength band (330—500 mμ). The appearance of the medium-wavelength band and the distinct vibrational fine structure of the long-wavelength maxima are characteristics of the spectra of the poly-ynes (I_n and II_n). However, the long-wavelength band of II_1 was found to be rather broad, and the peak corresponding to the longest-wavelength sub-bands in II_2–II_6 could not be observed. The bathochromic shift of the longest-wavelength maximum (λ_L) caused by the addition of an acetylenic linkage becomes progressively greater as the length of the polyacetylenic chain is increased. The shifts were found to be 9, 12, 14, and 18 mμ respectively in the II_2–II_6 series. Just as in the case of I_n, the ratios of λ_L to the wavelength of the medium-wavelength maxima (λ_M) were found to be almost constant, regardless of the length of the poly-yne chain (n) and the nature of the solvent (Table 4).

A good correlation between the λ_L of II_2–II_6 and the square of the number of the acetylenic bond (n^2) has also been observed. A plot of this relation is shown in Fig. 3, together with that of the I_n-series.*1 The linear relationship could be expressed by the following empirical formulae, which shows excellent agreement with the observed values, as is summarized in Table 5. As is clearly shown in Fig. 3, II_n absorbs at a longer wavelength

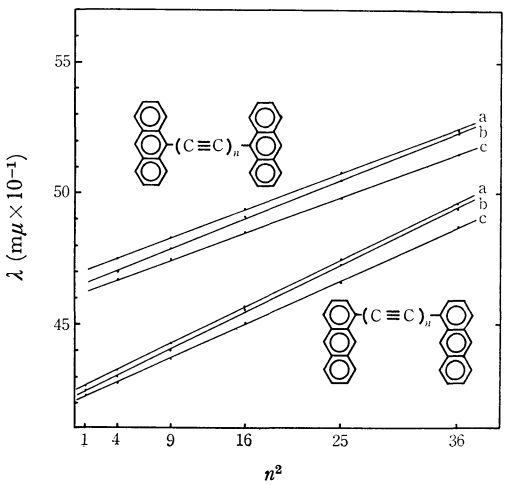


Fig. 3. Plot of λ_{max} *versus* n^2 for 9,9′-dianthrylpoly-ynes (II_1–II_6) and 1,1′-dianthrylpoly-ynes (I_1–I_6).
a: benzene; b: tetrahydrofuran; c: cyclohexane

Table 4. The ratios of the wavelength of the absorption maxima

II_n	λ_M			λ_L			λ_L/λ_M		
	a	b	c	a	b	c	a	b	c
II_2	287*	287*	289*	467	470	475	1.63	1.64	1.65
II_3	289	290	292	475	479	483	1.64	1.65	1.65
II_4	305	306	309	485	491	494	1.59	1.61	1.60
II_5	320	322.5	324	498	505	508	1.56	1.57	1.58
II_6	332	333	336	515	523	524	1.55	1.58	1.56

a: cyclohexane; b: tetrahydrofuran; c: benzene.
The asterisks indicate the shoulders.

*1 The synthesis of 1,1′-dianthrylacetylene (I_1) will be reported in the following paper.

Table 5. The longest wavelength absorption maxima (mμ)

II_n	Benzene		Tetrahydrofuran		Cyclohexane	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
II_2	475	475	470	471	467	467
II_3	483	483	479	479	475	475
II_4	494	494	491	490	485	485
II_5	508	508	505	505	498	499
II_6	524	525	523	523	515	515

$\lambda_{max} = 1.50\,n^2 + 461$ mμ (cyclohexane)

$\lambda_{max} = 1.65\,n^2 + 464$ mμ (tetrahydrofuran)

$\lambda_{max} = 1.55\,n^2 + 469$ mμ (benzene)

than the corresponding I_n. However, the slopes of the straight lines of the 1,1′-series (I_n) are steeper than those of the 9,9′-series (II_n). Accordingly, the difference in the wavelength between the corresponding members of these two series diminishes with the increase in the length of the poly-yne chain (n=2, 42; n=3, 40; n=4, 37; n=5, 30 and n=6, 28 mμ) in tetrahydrofuran. The solvent effect is found to be more pronounced in the case of II_n, even in the lower members.

It seems to be important to obtain the knowledge regarding electronic spectra of 2,2′-dianthrylpoly-ynes, as the polyacetylenic chromophore extends in the direction of the polarization of the ^1B_b-band of the anthracene nucleus, whereas in the cases of 1,1′- and 9,9′-dianthrylpoly-ynes (I_n and II_n) the direction of the polyacetylenic chromophore is parallel with the direction of the polarization of the ^1L_a-band of the aromatic nucleus.[5] Unfortunately, all attempts to prepare 2,2′-dianthrylpoly-ynes impeded by the extremely poor solubilities of the 2-substituted anthracene derivatives.

The studies of the synthesis and the spectral properties of dinaphthylpoly-ynes will be reported in the following paper.

Experimental

All the melting points are uncorrected. The electronic spectra were obtained on a Hitachi EPS-3T spectrophotometer at room temperature using a well-matched pair of 1-cm cells. A Hitachi EPI-2 spectrophotometer was used for the infrared spectroscopy.

1,4-Di(9-anthryl)-1,4-dihydroxy-2-butyne (IV). 9-Anthraldehyde (III[3], 6.18 g, 0.03 mol) in tetrahydrofuran (100 m*l*) was added to an ice-cooled solution of acetylene dimagnesium bromide [from excess acetylene, magnesium (1.75 g, 0.073 g atom), and ethyl bromide (9.70 g, 0.088 mol)] in benzene - tetrahydrofuran (50m*l*). The mixture was stirred overnight at room temperature, and then the strongly cooled mixture (ice-salt bath) was treated with a saturated aqueous solution of ammonium chloride. After the separation of the organic layer, the aqueous layer was extracted with benzene. The combined organic layer was dried (magnesium sulfate). The orange-red viscous liquid obtained by evaporating the solvent under reduced pressure was dissolved in benzene (40 m*l*). The solution was filtered through a short column of alumina (8 g). The filtrate was concentrated under reduced pressure, and a small amount of benzene - cyclohexane (1 : 1) was added to the residue. The mixture was warmed on a water bath, resulting in crystallization (4.7 g, 71%). The crystals were recrystallized twice from benzene, yielding IV, mp 204—207°C (dec.), as pale yellow needles.

Found: C, 88.06; H, 5.32%. Calcd for $C_{17}H_{12}O$: C, 87.64; H, 5.06%. IR (KBr-disk): 3400 (O–H), 1040 (C–O) cm^{-1}. *Cf.* IRDC Cards No. 3642.

9,9′-Dianthryldiacetylene (II_2). *The Preparation of the Dichloride (V).* A mixture of thionyl chloride (0.36 g, 3 mmol), pyridine (0.24 g, 3 mmol), and ether (5 m*l*) was added, drop by drop over a 30-min period to a cooled solution (−20°C) of IV (0.440 g, 1 mmol) in tetrahydrofuran (10 m*l*) under vigorous shaking. The immediate deposition of a yellow crystalline solid was observed. Shaking was then continued for an additional hour.

The Dehydrochlorination of V. The above-mentioned reaction mixture was added, in one portion, to a stirred suspension of sodium amide [from sodium 0.40 g (0.017 g atom)] in liquid ammonia (50 m*l*) at −70°C. After 1 hr, ammonium chloride (2.0 g) was added to the mixture and the ammonia was allowed to evaporate. The residue, after the organic solvent had been removed under reduced pressure, was mixed with water. The insoluble material was washed with small amounts of ethanol and benzene successively, resulting in a yellowish brown powder. This was dissolved in benzene (100 m*l*) and passed through a short column of alumina (8 g). Yellowish brown crystals obtained by evaporating the filtrate were recrystallized from benzene, yielding II_2, as orange cubes; 0.160 g (40%). An analytical specimen was obtained by recrystallizing the crystals twice from benzene; mp 290—292°C (dec.).

Found: C, 95.64; H, 4.58%. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%. IR: *Cf.* IRDC Cards No. 3717.

9-Anthryl-2-propyn-1-ol (VI). A solution of 9-anthraldehyde (III, 16.0 g, 0.078 mol) in tetrahydrofuran (300 m*l*) was added to a suspension of lithium acetylide [from lithium 1.6 g (0.24 g atom)] at −70°C over a 1-hr period. The mixture was stirred a further 5.5 hr at −50°C, and then ammonium chloride (8.0 g) was added. After the evaporation of the ammonia, a saturated aqueous solution of ammonium chloride was added to the residue. The aqueous layer was extracted with benzene and combined with the organic layer. The combined organic layer was dried (magnesium sulfate) and concentrated under reduced pressure. The residue was dissolved in hot benzene (40 m*l*) to yield crude crystals of VI (14.4 g, 72%). The second crop of VI (1.3 g, 7%) was obtained from the mother liquor. Recrystallization of the crude material from tetrahydrofuran-benzene yielded pure VI as pale yellow plates; mp 124—125°C.

Found: C, 87.73; H, 5.30%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR (KBr-disk): 3570 (O–H), 1022, 1013 (C–O), 3280 (≡CH) and 2130 (C≡C) cm^{-1}. *Cf.* IRDC Cards, No. 4161.

1,6-Di(9-anthryl)-1,6-dihydroxy-2,4-hexadiyne

5) *Cf.* R. N. Jones, *Chem. Rev.*, **41**, 365 (1947).

(VII). A mixture of the anthrylpropynol (VI, 2.32 g, 0.01 mol), cuprous chloride (0.10 g, 1 mmol), ammonium chloride (0.07 g), and methanol (40 m*l*) was vigorously stirred at room temperature under an atmosphere of oxygen at a slight elevated pressure. After 30 min, a minor amount of the cuprous acetylide which deposited was dissolved, two drops of concentrated hydrochloric acid were added, and the stirring was continued overnight. The coupling product thus deposited was collected by filtration, washed with methanol, and dissolved in acetone (40 m*l*) to remove any inorganic material. The oily residue obtained by concentrating the acetone solution was triturated with hot benzene, resulting in crystallization (1.79 g, 78%; mp *ca.* 220°C (dec.)). This was recrystallized three times from acetone - benzene to yield pure VII as pale yellow cubes; mp *ca.* 220°C (dec.).

Found: C, 88.40; H, 4.93%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%. IR (Nujol): 3350 (OH), 1009 (C–O), 2130 (C≡C) cm^{-1}. *Cf.* IRDC Cards, No. 3270.

9,9′-Dianthryltriacetylene (II_3). *The Preparation of the Dichloride (VIII).* A mixture of thionyl chloride (0.24 g, 2 mmol), and pyridine (0.16 g, 2 mmol) in ether (5 m*l*) was added, drop by drop, a cooled solution (−20°C) of the glycol (VII, 0.308 g, 0.67 mmol) in tetrahydrofuran (15 m*l*) over a 15 min-period, and then the mixture was shaken for an additional hour. The orange-yellow reaction mixture containing a yellow precipitate was directly subjected to the following dehydrochlorination reaction.

Dehydrochlorination of VIII. To a vigorously-stirred suspension of sodium amide [from sodium 0.35 g (0.016 g atom)] in liquid ammonia (60 m*l*) the above-mentioned solution of the dichloride (VIII) was added in one portion at −70°C. After 1 hr, ammonium chloride (2.0 g) was added and the ammonia was allowed to evaporate. The organic solvent which remained was removed under reduced pressure. The residue was mixed with water, and the resulting insoluble material was washed with a small amount of methanol and benzene, affording a yellowish brown, crystalline mass (0.255 g, 90%; mp *ca.* 280°C (dec.)). The crude material was recrystallized from toluene to give pure II_3, as deep orange needles; mp 295°C (dec.); 0.203 g (71%).

Found: C, 95.72; H, 4.17%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%. IR: *Cf.* IRDC Cards, No. 3719.

1-(9-Anthryl)-2-butyne-1,4-diol (IX). To a stirred and ice-cooled solution of the Grignard derivative of propargyl alcohol in tetrahydrofuran (170 m*l*), which had been prepared from magnesium (8.65 g (0.36 g atom)), ethyl bromide (32.2 g (0.36 mol)), and propargyl alcohol (10.1 g (0.18 mol)), there was added a solution of 9-anthraldehyde (III, 12.4 g, 0.06 mol) in tetrahydrofuran (180 m*l*) over a 30 min-period. The mixture was stirred a further 30 min, refluxed for 3 hr, and allowed to stand overnight. A saturated aqueous solution of ammonium chloride was added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted 4 times with tetrahydrofuran - benzene (total 400 m*l*). The combined organic layer was dried (magnesium sulfate) and concentrated under reduced pressure. The residue was treated with hot benzene (10 m*l*), affording fine, pale yellow crystals; 6.9 g (44%); mp 224—228°C (dec.). A second crop of crystals (1.1 g (7%)) was obtained from the mother liquor. The crystals were recrystallized from tetrahydrofuran to yield pure IX as tiny, pale yellow cubes; mp 227—229°C (dec.).

Found: C, 82.27; H, 5.41%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. IR (KBr-disk): 3220 (OH), 1019 (C–O) cm^{-1}. *Cf.* IRDC Cards, No. 3640.

9-Butadiynylanthracene (XI). *The Preparation of the Dichloride (X).* A solution of thionyl chloride (6.0 g, 0.05 mol) in tetrahydrofuran (10 m*l*) was added to a stirred and ice-cooled solution of the anthrylbutyne diol (IX, 2.60 g, 0.01 mol), and pyridine (3.0 g, 0.04 mol) in tetrahydrofuran (20 m*l*) over a period of 50 min. The stirring was continued for 30 min at room temperature, and then the mixture was gradually heated to the boiling point. After refluxing for 1 hr, cracked ice was added to the chilled reaction mixture (ice-salt bath) and it was extracted with benzene (70 m*l*). The extract was washed with water, a sodium hydrogen carbonate solution, and water successively, dried (sodium sulfate), and concentrated under reduced pressure. The resulting dark red oil (crude X) was subjected to the subsequent reaction without further purification.

The Dehydrochlorination of X. The above-mentioned crude X in tetrahydrofuran (25 m*l*) was added to a stirred suspension of sodamide [from sodium (4.6 g (0.2 g atom))] in liquid ammonia (150 m*l*) at −70°C over a 30-min period and then stirred for 1.5 hr. Ammonium chloride (10 g) was added to the mixture, and the ammonia was allowed to evaporate. The residue was repeatedly digested with *n*-hexane (total, 1000 m*l*). The hexane solution was concentrated to 350 m*l* and percolated through a short column of alumina (13 g). The resulting pale yellow solution, with a strong lavender fluorescence, was concentrated under reduced pressure thus affording XI as yellow cubes (0.36 g (16% based on the glycol, IX)). The diacetylene, XI, was found to be a fairly unstable substance, and an explosive decomposition at *ca.* 130°C was observed. Also, the crystals rapidly turned black at room temperature.

Found: C, 95.32; H, 4.54%. Calcd for $C_{18}H_{10}$: C, 95.54; H, 4.46%. IR (KBr-disk): 3280 (≡CH), 2190 (C≡C) cm^{-1}. UV (in *n*-hexane): λ_{max} (mμ) (log ε): 226 (3.47), 260.5 (5.11), 283 (4.09), 355 (3.70), 371 (4.04), 392 (4.28), 414.5 (4.29).

9,9′-Dianthryltetraacetylene (II_4). Cupric acetate monohydrate (5.3 g) was added to a stirred solution of the diacetylene (XI, 0.27 g, 0.013 mol) in pyridine (35 ml);[6] the mixture was then stirred for 45 min at 23°C, and for 2 hr at 40°C. Further stirring was continued overnight at room temperature, after which insoluble material was collected by filtration, and washed with water. This yielded fine, orange-brown crystals; 0.23 g (79%); mp 255°C (dec.). The mother liquor was concentrated under reduced pressure and mixed with water to afford crude II_4 (0.05 g, 17%). The combined crystals were recrystallized from benzene and toluene successively to give pure II_4, as orange-red needles; mp 265°C (dec.).

Found: C, 95.86; H, 4.00%. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%. IR: *Cf.* IRDC Cards, No. 4164.

9,9′-Dianthrylpentaacetylene (II_5). *The Preparation of 9-Anthrylbutadiynyl Carbinol (XII).* 9-Anthraldehyde (III, 3.05 g, 0.015 mol) in tetrahydrofuran (50 m*l*) was added to a suspension of lithium diacetylide in liquid ammonia at −70°C, which was prepared by the reaction

6) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

of 1,4-dichloro-2-butyne (2.40 g, 0.059 mol) in ether (5 ml) with lithium amide [from lithium 1.24 g (0.177 g atom)] in liquid ammonia (80 ml). The temperature of the reaction mixture was raised to −45°C, and the mixture was stirred for a further 2 hr at the temperature. Ammonium chloride (2 g) was then added, and the ammonia was allowed to evaporate. The residue was digested with benzene (50 ml). The extract was washed with water and dried (magnesium sulfate). The solvent was removed under reduced pressure, resulting in an unstable, viscous, light brown oil. The absence of carbonyl and the presence of hydroxyl and ethynyl groups were revealed by the IR sepectroscopy of the crude material (XII). This was used without further purification in the subsequent oxidative coupling.

The Oxidative Coupling of XII. A mixture of the above-mentioned crude XII, cuprous chloride (0.30 g), ammonium chloride (0.20 g), and methanol (50 ml) was vigorously stirred in an atmosphere of oxygen at room temperature. Two drops of concentrated hydrochloric acid was added to prevent the precipitation of the cuprous acetylide, and then the stirring was continued overnight. The crystalline material thus deposited was collected by filtration, washed with a small amount of methanol, and dissolved in tetrahydrofuran (15 ml). The insoluble material was removed by filtration. The filtrate was passed through a short column of alumina (5 g) and concentrated under reduced pressure. The tarry residue was triturated with benzene, resulting in light brown needles; 1.37 g (36%); mp *ca.* 160°C (dec.). A second crop of the crystals (0.22 g (6%)) was obtained from the mother liquor. The tetraacetylene glycol (XIII) thus obtained was found to be a rather unstable substance, and repeated recrystallizations from acetone - benzene gave only a somewhat impure material whose IR spectrum was in accord with that expected for XIII.

The Preparation of the Dichloride (XIV). To a stirred solution of the crude glycol (XIII, 0.130 g, 0.23 mol) in tetrahydrofuran (20 ml), there was added a mixture of thionyl chloride (0.090 g, 0.76 mmol), pyridine (0.055 g, 0.76 mmol), and ether (5 ml) over a period of 30 min at −20°C. The mixture was stirred for a further 2 hr and then directly subjected to the subsequent reaction.

The Dehydrochlorination of XIV. The above-mentioned solution of XIV was added in one portion to a vigorously-stirred suspension of sodium amide [from sodium (0.10 g) 4.4 mg atom) in liquid ammonia (80 ml)] at −70°C. After 2 hr, ammonium chloride (0.5 g) was introduced into the reaction mixture and the ammonia was allowed to evaporate. The organic solvent was removed under reduced pressure. The residue was mixed with water, and the insoluble material was collected by filtration and washed with small amounts of methanol and benzene. Recrystallization from toluene (400 ml) yielded fine, red needles; 0.046 g (38%); mp *ca.* 245°C (dec.). The second crop [0.33 g (27%); mp 245°C (dec.)] was obtained from the mother liquor. Recrystallization from the same solvent afforded the pure pentaacetylene, II_5, as fine, red needles; mp *ca.* 250°C (dec.).

Found: C, 96.21; H, 3.88%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%.

1-(9-Anthryl)-2,5-hexadiyn-1,4-diol (XV). A solution of 9-anthraldehyde (III, 6.10 g, 0.03 mol) in tetrahydrofuran (120 ml) was added to a stirred and ice-cooled solution of the Grignard derivative of 2,4-pentadiyn-3-ol, which had been prepared from 2.64 g (0.033 mol) of the alcohol according to a previously-reported method.[1] The mixture was stirred overnight at 17—18°C, and then a saturated aqueous solution of ammonium chloride was added. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried (sodium sulfate) and evaporated under reduced pressure; this yielded a dark red oil. This crystallized on standing; after treatment with hot benzene (20 ml), it was filtered and washed with benzene to afford a pale yellow crystalline powder; 3.60 g (45%); mp *ca.* 150°C (dec.). The crude material was recrystallized four times from benzene to give pure XV, as pale yellow leaflets; mp 195—198°C (dec.).

Found: C, 83.62; H, 4.88%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. IR (Nujol): 3300 (O–H, C≡CH), 2110 (C≡C), 1050, 1015, 1001 (C–O) cm^{-1}. *Cf.* IRDC Cards, No. 3715.

9-Anthryltriacetylene (XVII). *The Chlorination of XV.* A mixture of thionyl chloride (1.43 g, 0.012 mol), pyridine (0.95 g, 0.012 mol), and ether (7 ml) was added, over a period of 30 min, to a solution of the glycol (XV, 0.860 g, 3 mmol) in tetrahydrofuran (15 ml) at −15°C. The mixture was stirred for a further 30 min and then subjected to the dehydrochlorination reaction without the isolation of the dichloride (XVI).

The Dehydrochlorination of XVI. To a vigorously-stirred suspension of sodium amide [from sodium (0.30 g) (0.013 mol)] in liquid ammonia held at −70°C, there was added the above-mentioned solution of XVI in one portion. Stirring was continued for one more hour, and then ammonium chloride (2 g) was added. After the evaporation of the ammonia, the organic solvent was removed under reduced pressure. The residue was repeatedly digested with petroleum ether (bp 40—60°C; total 150 ml). The orange yellow solution was percolated through a short alumina column (5 g). The concentration of a small portion of the filtrate under reduced pressure gave XVII as yellow needles; this substance was found to extremely unstable, and the color of the crystals rapidly changed from green to a brownish grey, forming an entirely insoluble decomposition product. The petroleum ether solution was used directly for the subsequent reaction. The triacetylene (XVII) gave red cuprous and yellow silver acetylides. UV (petroleum ether): the longest wavelength absorption maximum, 429 mμ.

9,9′-Dianthrylhexaacetylene (II_6). A mixture of the above-mentioned solution of the triacetylene (XVII), cupric acetate monohydrate (2.0 g), and pyridine (15 ml) was concentrated to *ca.* 15 ml under reduced pressure. The concentrated solution was then stirred overnight at room temperature. After the addition of a small amount of water to the mixture, the insoluble material was collected and washed with water, acetone, and benzene successively, yielding a dark red powder (68 mg) [9% based on the glycol (XV)]. This was recrystallized twice from toluene to give the pure hexaacetylene (II_6), as fine, dark red needles; mp *ca.* 200°C (dec.). II_6 was found to have a poor solubility in common organic solvents.

Found: C, 96.19; H, 3.84%. Calcd for $C_{40}H_{18}$: C, 96.36; H, 3.64%.