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The Synthesis and the Electronic Spectra of 1, 1'-Dianthrylpoly-ynes

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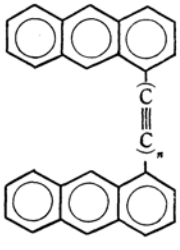
The synthesis of 1, 1'-dianthryldi- and tetra-acetylenes has been reported previously by the present authors. Now, 1, 1'-dianthryltri-, penta- and hexa-acetylenes have been synthesized in order to complete the series of 1, 1'-dianthrylpoly-ynes. It is well known that the square of the wavelength of the longest absorption maxima, λ_{max}, in the electronic spectra of some series of poly-enes and poly-ynes varies linearly with the number of the multiple bonds, n ($\lambda^2_{max} \propto n$). It was anticipated that the dianthrylpoly-ynes would exhibit analogous spectral behavior. Unexpectedly, however, it was observed that the λ_{max} of the dianthrylpolyacetylenes varied linearly with the square of the number of the triple bonds, n ($\lambda_{max} \propto n^2$).

Previously, the present authors have reported the synthesis of 1, 1'-dianthryldi-[1] and tetra-acetylenes[2] (Ia and Ib) as open-chain models of the macrocyclic tetra-[3] and octa-acetylenes[4] containing two anthracene nuclei.



Ia: (n=2) Ib: (n=3) Ic: (n=4)
Id: (n=5) Ie: (n=6)

It is of interest to compare the electronic spectra of the disubstituted poly-ynes (I) with those of the other series of linearly conjugated systems, such as diphenylpoly-enes and diphenylpoly-ynes. Now, the corresponding tri- (Ib), penta- (Id) and hexa-acetylenes (Ie) have been synthesized to complete the series of the polyacetylenes. The present paper will deal with the synthesis of the poly-ynes (Ib, Id and Ie) and with the novel linear relationship observed in the electronic spectra of the series (Ia—Ie).[5]

Synthesis. The sequence of reactions used in the synthesis of 1, 1'-dianthryltri-, penta- and hexa-acetylenes (Ib, Id and Ie) is outlined in Chart 1. The tetra-acetylenic glycol (IV, n'=2), the tetra-acetylenic dichloride (V, n'=2), and the triacetylene (VIII) were found to be extremely unstable and were used without further purification in the subsequent reaction.

Infrared Spectra. As the infrared absorption curves of 1, 1'-dianthrylpoly-ynes (Ia—Ie) are included in the IRDC Cards,[*1] only the most characteristic features of the spectra will be pointed out here. An unusual intensification of the absorption ($A=1-I/I_0$) due to $\nu_{C\equiv C}$ was observed in the spectra of Ia—Ie. The ratio of the absorption of the $\nu_{C\equiv C}$-band to those of the 880 cm^{-1}-band (δ_{C-H} of the isolated hydrogen atoms in the anthryl groups) and the 725 cm^{-1}-band (δ_{C-H} of the four adjacent hydrogen atoms in the terminal groups) is summarized in Table 1.

TABLE 1. THE WAVE NUMBERS AND THE RELATIVE ABSORPTION OF $\nu_{C\equiv C}$-BAND OF Ia—Ie (KBr-disk)

I	n	Wave number cm^{-1}	Relative absorption: Ratio to the 880 cm^{-1}-band	Relative absorption: Ratio to the 725 cm^{-1}-band
Ia	2	2200†, 2140	0.06	0.06
Ib	3	2190†	0.26	0.27
Ic	4	2205†	0.75	0.78
Id	5	2178†, 2120, 2070	0.98	0.91
Ie	6	2140†, 2010	1.30	1.23

The daggers indicate the absorption bands used in the calculation.

It was also remarkable that the absorption band of the tetra-acetylene (Ic) exhibited the highest wave number, just as in the case of diphenyl- and dimethylpoly-ynes.[6]

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[1] S. Akiyama and M. Nakagawa, This Bulletin, **33**, 1291 (1960).

[2] S. Akiyama and M. Nakagawa, *ibid.*, **35**, 1826 (1962).

[3] S. Akiyama, S. Misumi and M. Nakagawa, *ibid.*, **33**, 1293 (1960).

[4] S. Akiyama, S. Misumi and M. Nakagawa, *ibid.*, **35**, 1829 (1962).

[5] For a preliminary report, see *Tetrahedron Letters*, **1964**, 719.

[*1] Nos. 3639, 3716, 3718, 3723 and 3724.

[6] 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).

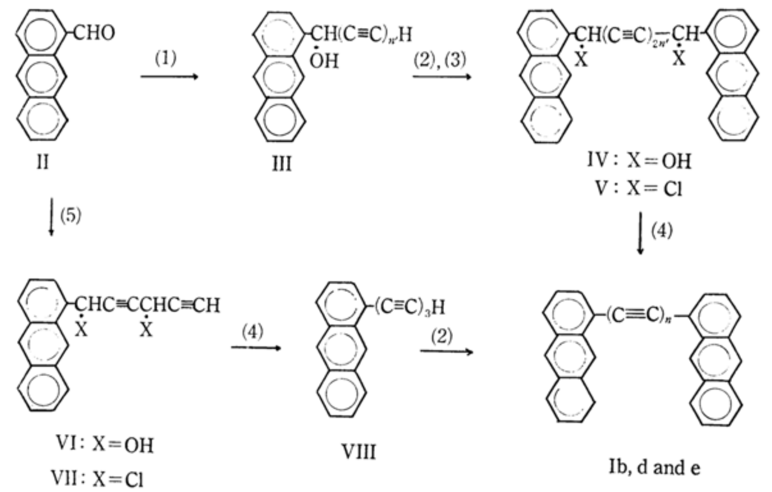

Chart 1. The synthesis of 1,1'-dianthrylpoly-ynes (Ib, Id and Ie).

(1) LiC≡CH ($n'=1$) and Li(C≡C)$_2$H ($n'=2$) (2) oxidative coupling
(3) $SOCl_2$ in tetrahydrofuran and pyridine (4) $NaNH_2$ in liq. NH_3
(5) BrMgC≡CCH(OMgBr)C≡CH

Electronic Spectra. The electronic spectral data of Ia—Ie are summarized in Table 2, while the absorption curves are illustrated in Fig. 1.

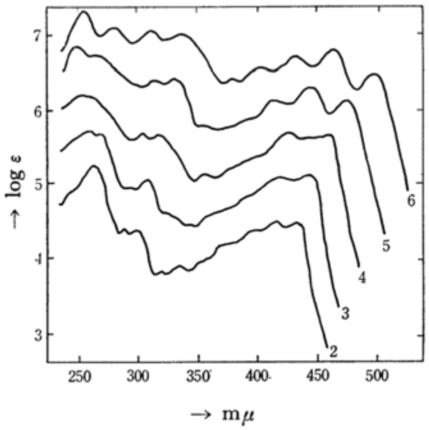

Fig. 1. The absorption curves of 1,1'-dianthryl-poly-ynes (Ia—Ie). The curves, with the exception of the diacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below. (in tetrahydrofurn)

The electronic sectra of the speries of 1,1'-dianthrylpoly-ynes (Ia—Ie) consist of three groups of absorption maxima, *i.e.*, the maxima in the short wave length region (270 mμ), the maxima in the medium wavelength region (270—320 mμ), and the maxima in the long wavelength region (320—500 mμ). As the electronic spectrum of anthracene exhibits only two groups of absorption bands, lacking the medium wavelength maxima, the presence of medium wavelength maxima confers a characteristic feature on the spectra of the dianthrylpolyacetylenes. The width of the absorption band in the long wavelength region increases with the increasing number of the acetylenic linkage. Also, it seems to be noteworthy that the vibrational fine structure of the absorption band in the long wavelength region, which is distinctly observed in the spectra of Ia, Id and Ie, disappears in those of Ib and Ic. An interesting relation was observed in the ratio of the wavelength of the longest-wavelength maximum (λ_L) to the wavelengths of the two maxima of the medium-wavelength absorption bands (λ_1 and λ_2). As is summarized in Table 3, the ratios, $\lambda_L/\lambda_1=1.51$—1.54 and $\lambda_L/\lambda_2=1.43$—1.45, are found to be constant independent of the number of the acetylenic bond (n) and of the nature of the solvent.

It is well-known that the square of the wavelength of the absorption maxima (λ_{max}) varies linearly with the number of the conjugated multiple bond (n) in serveral series of poly-enes[7] and poly-acetylenes[8] ($\lambda^2_{max} \propto n$). On the other hand, a linear relation between the λ_{max} and the n ($\lambda_{max} \propto n$) in some charge-resonance systems, such

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[7] L. N. Ferguson, *Chem. Revs.*, **43**, 408 (1948) and the references cited therein; L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall Englewood Cliffs, N. J. (1963), Chap. 5; F. Sondheimer, D. A. Ben-Efraim and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961); J. H. C. Nayler and M. C. Whiting, *J. Chem. Soc.*, **1955**, 3037; F. Bohlmann and M. Manhardt, *Chem. Ber.*, **89**, 1307 (1956).

[8] H. H. Schlubach and V. Franzen, *Ann.*, **573**, 110 (1951); J. B. Armitage, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1954**, 147; C. L. Cook, E. R. H. Jones and M. C. Whiting, *ibid.*, **1952**, 2883.

TABLE 2. THE SPECTRAL DATA OF 1,1′-DIANTHRYLPOLY-YENS (Ia—Ie)

n	λ_{max} in mμ and log ε (in parentheses) in tetrahydrofuran										
2	260 (5.27)		285 (4.39)	297 (4.42)	317 (3.80)	332 (3.89)	349* (3.90)	367 (4.14)	391 (4.36)	410 (4.50)	430 (4.46)
3	256 (5.20)	263 (5.17)	287 (4.45)	304 (4.55)	320* (4.10)	380* (4.24)	406* (4.50)	420 (4.53)	440 (4.62)		
4	250 (5.20)		299 (4.67)	315 (4.71)	352 (4.09)	370* (4.12)	390* (4.34)	422 (4.62)	456 (4.61)		
5	252 (5.30)	265 (5.16)	312 (4.86)	328 (4.88)	354 (4.26)	380* (4.30)	410 (4.60)	440 (4.79)	473 (4.61)		
6	254 (5.29)	273 (5.05)	307 (5.00)	325 (4.96)	373 (4.38)	397 (4.53)	425 (4.75)	457 (4.81)	494 (4.50)		

Asterisk indicates the shoulder.

TABLE 3. THE RATIOS OF THE WAVELENGTH OF THE ABSORPTION MAXMA

n	λ_1, mμ			λ_2, mμ			λ_L, mμ			λ_L/λ_1			λ_L/λ_2		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
2	283	285	286	295	297	298	428	430	433	1.51	1.51	1.51	1.45	1.45	1.45
3	285	287	287	303	304	306	437	440	443	1.53	1.53	1.54	1.44	1.45	1.45
4	298	299	299	315	315	316	450	456	457	1.51	1.53	1.53	1.43	1.45	1.45
5	309	312	313	327	328	330	466	473	475	1.51	1.52	1.52	1.43	1.44	1.44
6	*	325	325	*	*	*	487	494	496	—	1.52	1.53	—	—	—

* In the case of n=6, no distinct peaks were observed in λ_1 (a) and λ_2.
a: cyclohexane, b: tetrahydrofuran, c: benzene

as cyanine dyes and polyene-Lewis acid complexes, has also been well recognized.[7,9]

It was anticipated that the plots of λ^2_{max} of the poly-ynes (Ia—Ie) *versus* n might give a straight line, as in the other series of poly-yne compounds. In fact, however, the plots of λ^2_{max} against n gave distinct concave curves, as is illustrated in Fig. 2. Unexpectedly, good straight lines were obtained by plotting the λ_{max} of the longest-wavelength peaks in various solvents against n^2 (Fig. 3). The variation in λ_{max} with an increasing number of triple bonds, n, is expressed by the following empirical formulae with an excellent agreement with the observed values. The observed and calculated wavelengths of the maxima are given in Table 4;

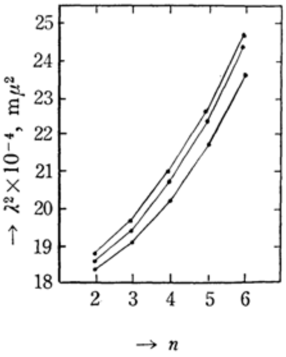

Fig. 2. Plot of λ^2_{max} *versus* n for 1,1′-dianthryl-poly-ynes (Ia—Ie).
a: benzene; b: tetrahydrofuran; c: cyclohexane

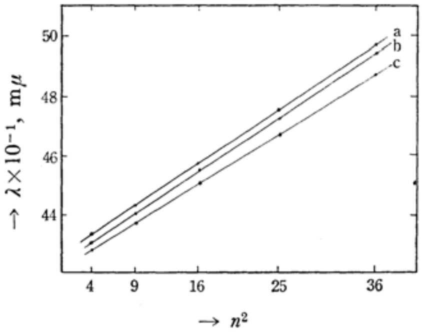

Fig. 3. Plot of λ_{max} *versus* n^2 for 1,1′-dianthryl-poly-ynes (Ia—Ie).
a: benzene; b: Tetrahydrofuran; c: cyclohexane

$$\lambda_{max} = 2.0\,n^2 + 425\ \text{m}\mu\ \ \text{(benzene)}$$

$$\lambda_{max} = 2.0\,n^2 + 422\ \text{m}\mu\ \ \text{(tetrahydrofuran)}$$

$$\lambda_{max} = 1.85\,n^2 + 420.5\ \text{m}\mu\ \ \text{(cyclohexane)}$$

As one can anticipate from the above-mentioned constant ratios of λ_1 or λ_2 to λ_L, the plots of λ_1 or λ_2 *versus* n^2 gave also straight lines.

The novel linear relationship ($\lambda_{max} \propto n^2$) seems

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[9] *Inter alia,* K. Hafner and H. Pelster, *Angew. Chem.*, **73**, 342 (1961); K. Hafner and K. Goliasch, *ibid.*, **74**, 118 (1962); J. F. Thomas and G. Branch, *J. Am. Chem. Soc.*, **75**, 4793 (1953); S. S. Malhotra and M. C. Whiting, *J. Chem. Soc.*, **1960**, 3812.

TABLE 4. THE LONGEST-WAVELENGTH ABSORPTION MAXIMA

	λ_{max}, mμ					
n	Benzene		Tetrahydrofuran		Cyclohexane	
	obs.	calcd.	obs.	calcd.	obs.	calcd.
2	433	433	430	430	428	428
3	443	443	440	440	437	437
4	457	457	456	454	450	450
5	475	475	473	472	466	467
6	496	497	494	494	487	487

to indicate the pronounced contribution of the 1-anthryl terminal groups to the electronic excitation of the polyacetylenic chromophore.*2

Further studies of the synthesis and spectral properties of 9,9'-dianthryl-, 1,1'- and 2,2'-dinaphthylpoly-ynes are now in progress in order to get further information on the role of the end-groups in the electronic excitation of the poly-yne system.

Experimental

All melting points are uncorrected. The electronic spectra were measured on a Hitachi EPS-2 autorecording spectrophotometer using a 1-cm cell at room temperature. The infrared spectra were obtained on a Hitachi EPI-2 infrared spectrophotometer.

1-Anthryl-2-propyn-1-ol (III, $n'=1$). To a solution of lithium acetylide (from lithium, (1.6 g); 0.24 g atom) in liquid ammonia (400 m*l*), there was added a solution of 1-anthraldehyde (II; 16 g; 0.08 mol) in tetrahydrofuran (320 m*l*) at −70°C during 1-hr period. The mixture was then stirred for 10 hr at −40°C. After the evaporation of the ammonia, a saturated, aqueous solution of ammonium chloride was introduced into the residue and then extracted with ether (150 m*l*). The extract was washed with water and dried over sodium sulfate. The oily material obtained by the evaporation of the solvent under reduced pressure solidified on standing. The solid was dissolved in benzene (350 m*l*), and the solution was passed through a short column of alumina (25 g). The effluent was concentrated under reduced pressure, yielding III ($n'=1$) as pale yellow needles (12.7 g (74%)); mp 119—120°C. The crystals were then recrystallized twice from petroleum benzine - benzene, affording an analytical specimen, mp 120°C.

Found: C, 87.54; H, 5.24. Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: (in Nujol) 3100—3200 (OH), 3280 (≡CH), 2090 (C≡C) and 1053 cm^{-1} (C–O).

1, 6-Di(1-anthryl) - 1, 6 - dihydroxy-2, 4 -hexadiyne (IV, $n'=1$). A solution of III ($n'=1$; 2.00 g; 0.008 mol) in pyridine (50 m*l*) was added, dropwise to a stirred suspension of cupric acetate (20.0 g) in pyridine (50 m*l*).9) The mixture was stirred for 2.5 hr at 50°C, and then the solvent was removed under reduced pressure. Water was added to the residue, and the insoluble material was collected by filtration and washed with water, yielding brown amorphous powder containing a tarry material. A solution of the crude product in tetrahydrofuran (20 m*l*) was filtered through a short column of alumina (5 g). The tarry material obtained by evaporating the solvent from the filtrate under reduced pressure was triturated with a small amount of benzene, resulting in crystallization. The tiny white crystals (0.95 g; 45%) were recrystallized 5 times from tetrahydrofuran to give pure IV ($n'=1$) as tiny, pale yellow cubes, mp 135—140°C.

Found: C, 88.02; H, 5.07. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%. IR: (in Nujol) 3220 (OH), 2140 (C≡C) and 1059 cm^{-1} (C–O).

1, 6-Di(1-anthryl)-1, 6-dichloro-2, 4-hexadiyne (V, $n'=1$). To an ice-cooled solution of IV ($n'=1$, 0.46 g; 0.001 mol) in tetrahydrofuran (5 m*l*) containing a drop of pyridine, there was added a solution of thionyl chloride (0.48 g; 0.004 mol) in tetrahydrofuran (2 m*l*). The orange-colored mixture was then shaken for 2 hr without external cooling. The fine yellow needles deposited were collected by filtration (0.4 g (82%); mp 140°C (decomp.)). The crude V ($n'=1$) thus obtained was recrystallized three times from tetrahydrofuran-benzene to give an analytical specimen, mp 165—170°C (decomp.).

Found: C, 82.03; H, 4.40; Cl, 14.05%. Calcd for $C_{34}H_{20}Cl_2$: C, 81.76; H, 4.04; Cl, 14.20%. IR: (KBr-disk) 2140 cm^{-1} (C≡C).

1, 1'-Dianthryltriacetylene (Ib). The diacetylenic glycol (IV, $n'=1$; 0.46 g) was converted to V ($n=1'$) according to the same procedure described above, and the resulting suspension of V ($n'=1$) in tetrahydrofuran was directly subjected to the subsequent reaction. The suspension of V ($n'=1$) was introduced, drop by drop, into a stirred solution of sodium amide (from sodium 0.50 g) in liquid ammonia (50 m*l*). After 5.3 hr, ammonium chloride (1.0 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was repeatedly digested with boiling benzene (400 m*l*). Crude triacetylene (Ib); yellow leaflets; 0.17 g (40%), mp 265—270°C (decomp.), was obtained on cooling the benzene solution. An analytical specimen was obtained by recrystallizing the crude material three times from benzene and twice from toluene, yellow leaflets; mp 270°C (decomp.).

Found: C, 95.63; H, 4.27%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

Partially-evaporated mother liquor was chilled to yield the second crop of Ib (0.08 g). The recrystallization of this material afforded Ib (0.03 g (13%)), mp 270°C (decomp.).

1-(1-Anthryl)-2, 4-pentadiyn-1-ol (III, $n'=2$). To a suspension of lithium amide (from lithium, (0.82 g); 0.117 g atom) in liquid ammonia (150 m*l*) there was added dropwise a solution of 1, 4-dichloro-2-butyne (4.8 g; 0.039 mol) in tetrahydrofuran (10 m*l*) over a 20-min period. After 5 min, a solution of the aldehyde (II, 6.1 g, 0.03 mol) in the same solvent (100 m*l*) was introduced into the solution of lithium diacetylide over a period of 15 min; this mixture was then stirred at −40°C for 60 hr. Ammonium chloride (3.0 g) was added to the reaction mixture, and the ammonia was

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*2 For a theoretical treatment of this spectral property, see K. Nishimoto, R. Fujishiro *et al.*, This Bulletin, **39**, 2320 (1966).

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

allowed to evaporate. A saturated solution of ammonium chloride (20 m*l*) was added to the residue, and the organic layer was separated. The aqueous layer was extracted with ether (100 m*l*). The extract was combined with the organic layer and dried over sodium sulfate. The solvent was removed under reduced pressure. The tarry material thus obtained was dissolved in benzene (50 m*l*) and filtered through a short column of alumina (15 g). A greenish-yellow substance (6.0 g (78%)) was obtained by concentrating the solvent under reduced pressure. The crude III ($n'=2$) thus obtained was recrystallized twice from cyclohexane and twice from cyclohexane-benzene to yield an analytical sample, mp 106—109°C.

Found: C, 89.07; H, 4.77%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%. IR: (KBr-disk) 3420 (OH), 3290 (≡CH) and 1043 cm^{-1} (C–O). III ($n'=2$) was found to be a fairly unstable substance. It changed rapidly to an insoluble material, developing a pink color on the surface of the crystals on exposure to the atmosphere.

1, 1′-Dianthrylpenta-acetylene (Id). *The Oxidative Coupling of III ($n'=2$).* A mixture of cuprous chloride (0.10 g; 0.001 mol), tetramethylethylenediamine (0.12 g; 0.001 mol), and acetone (10 m*l*) was vigorously stirred for 15 min in an atmosphere of oxygen. Then, a solution of III ($n'=2$; 2.0 g; 0.008 mol) in acetone (40 m*l*) was dropped into the stirred mixture.[10] After stirring for 1 hr at room temperature, the solvent was distilled under reduced pressure. The residue was dissolved in tetrahydrofuran (40 m*l*). The solution was then washed with a saturated solution of sodium chloride and dried over sodium sulfate. The residue obtained by evaporating the solvent *in vacuo* was triturated with benzene, resulting in the deposition of a brown, crystalline substance. This crude material was washed with benzene, giving 1.9 g of the crude IV ($n'=2$). As the purification of this substance proved to be difficult because of the instability, the crude IV ($n'=2$) was used without further purification in the subsequent reaction. The absence of terminal acetylene was proved by studying the infrared spectrum of the crude material.

The Formation of the Dichloride (V, $n'=2$). To an ice-cooled solution of the crude glycol (IV; $n'=2$; 1.0 g; 0.002 mol) in tetrahydrofuran (12 m*l*) containing a drop of pyridine, there was added a solution of thionyl chloride (0.7 g, 0.006 mol) in tetrahydrofuran (5 m*l*) over a 10-min period. After the addition had been completed, the cooling bath was removed and the mixture was shaken for 1 hr at room temperature. The development of a dark brown color and the deposition of a crystalline substance were observed during this period. The mixture was finally warmed to 40°C for 20 min in order to complete the reaction.

The Dehydrochlorination of V ($n'=2$). The above-mentioned suspension of V ($n'=2$) in tetrahydrofuran was added, over a period of 10 min, into a stirred solution of sodium amide (from sodium, (1.0 g); 0.04 g atom) in liquid ammonia (100 m*l*) at −70°C. After 1 hr, ammonium chloride (3.0 g) was added to the mixture and the ammonia was allowed to evaporate. The residue was repeatedly extracted with benzene (total amount: 400 m*l*). The extract was passed through a column of alumina (20 g). The orange yellow effluent was then concentrated *in vacuo*, resulting in Id, fine (orange needles; 0.09 g. (5% based on the crude IV, $n'=2$), mp 220°C (decomp.)). The crude Id was recrystallized from benzene to yield an analytical specimen, mp 220°C (decomp.).

Found: C, 95.81; H, 3.88%. Calcd for $C_{38}H_{18}$: C, 96.18; H, 3.82%. Id was found to be a highly stable substance with a poor solubility in common organic solvents.

1-(1-Anthryl)-2, 5-hexadiyn-1, 4-diol (VI). A solution of 2, 4-pentadiyn-3-ol (2.64 g; 0.033 mol) in tetrahydrofuran (30 m*l*) was added to a stirred solution of ethylmagnesium bromide (from ethyl bromide (9.7 g), 0.088 mol, and magnesium (1.75 g), 0.073 g atom) in the same solvent (40 m*l*) at 20—25°C.[11] After 30 min, a solution of the aldehyde (II, 6.1 g, 0.03 mol) in tetrahydrofuran (100 m*l*) was added, drop by drop. The mixture was then stirred for a further 19 hr at room temperature. The ice-cooled reaction mixture was hydrolyzed with a saturated solution of ammonium chloride (60 m*l*). The organic layer was separated, and the aqueous layer was extracted with ether. The combined solution was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The viscous residue solidified after being kept in a refrigerator. The crystalline mass was triturated with a small amount of benzene and filtered. The light yellow, crystalline material was washed with benzene, yielding crude VI (4.85 g (56%)). The crude material was recrystallized twice from benzene to afford pure VI as light yellow leaflets, mp 160°C.

Found: C, 84.25; H, 4.98%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.95%. IR: (in Nujol) 3200—3400 (OH), 3300 (≡CH), 2110 (C≡C) and 1022 cm^{-1} (C–O).

1-Anthryltriacetylene (VIII). *The Chlorination of VI.* To an ice-cooled mixture of the glycol (VI; 2.90 g; 0.01 mol), pyridine (3.2 g; 0.04 mol), and tetrahydrofuran (20 m*l*), there was added a solution of thionyl chloride (4.75 g; 0.04 mol) in tetrahydrofuran (10 m*l*) over a 30-min period, after which the mixture was stirred for a further 2 hr at 35—40°C. Cracked ice was then added to the reaction mixture, and it was extracted with benzene. The extract was washed with water and an aqueous sodium hydrogen carbonate solution successively, and dried over sodium sulfate. The evaporation of the solvent under reduced pressure furnished partly-crystallized crude chloride (VII; 1.6 g; 50%). The infrared spectrum of the crude material showed the presence of an ethynyl group and the absence of a hydroxyl group. The crude VII was used in an following reaction without purification.

The Dehydrochlorination of VII. To a solution of sodium amide (from sodium, (3.0 g); 0.13 g atom) in liquid ammonia (150 m*l*), there was added, drop by drop, a solution of the crude VII (1.6 g) in tetrahydrofuran (5 m*l*). After being stirred for 1 hr at −70°C, the reaction mixture was decomposed with ammonium chloride (10.0 g). After all the ammonia had been evaporated off, the residue was digested repeatedly with petroleum ether (total 800 m*l*). The petroleum ether solution was then filtered through a short column of alumina (10 g). The filtrate (*ca* 800 m*l*) exhibited a beautiful lavender fluorescence. A part of the filtrate was concentrated under reduced pressure in a stream

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[10] A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962).

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

of nitrogen, resulting in the deposition of unstable yellow crystals of VIII. The immediate development of green color on the surface of the crystals was observed; then the crystals changed into an amorphous brown material. The triacetylene (VIII) gave orange cuprous and yellow silver acetylides. UV (uncertain concentration in *n*-hexane): λ_{max} (mμ) 232, 244, 249, 255, 261, 273, 284,5, 302, 323, 351, 369, 388.5, and 411.

1, 1′-Dianthrylhexa-acetylene (Ie). The abovementioned solution of VIII in pertroleum ether was concentrated to *ca.* 50 m*l* under nitrogen *in vacuo.* Pyridine (30 m*l*) was added to the concentrated solution, and then cupric acetate (3.0 g) was added under external cooling with ice.[9] The petroleum ether was removed under reduced pressure at room temperature, and the mixture was stirred for a further 2 hr. The insoluble material was collected by filtration and washed thoroughly with water to remove any inorganic material. The light brown crude hexa-acetylene (Ie, 0.21 g, 19% based on the crude V, $n=2$) thus obtained was recrystallized, once from benzene and again from toluene, affording pure Ie as stable, fine, red needles, mp *ca.* 210°C (decomp.).

Found: C, 96.18; H, 3.75%. Calcd for $C_{40}H_{18}$: C, 96.26; H, 3.64%.

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