Cyclic Acetylenes. XIII. The Syntheses and Properties of *p,p'*-Bridged Cyclic Diphenyldiacetylenes

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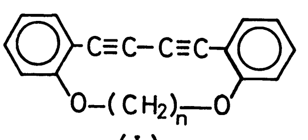
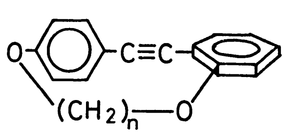
Concerning the studies on the effect of ring strain on the electronic spectra of cylcic acetylenes, a series of polymethylene ether derivatives of *p,p'*-dihydroxydiphenyldiacetylene (VI_n, $n=13$, 14, 15, and 18) has been prepared by the oxidative coupling of *p*-hydroxyphenylacetylene polymethylene ethers (V_n, $n=13$, 14, 15, and 18) under a high dilution condition. A slight bathochromic shift accompanied by hypochromism was observed in the electronic spectra of VI_n resulting from the increase of the ring strain. The same trend has been observed in the *p,p'*-bridged cyclic tolans.[1] However, the bathochromic shift observed in the *p,p'*-series makes a contrast with the hypsochromic shift in the strained *o,o'*-bridged cyclic diphenyldiacetylene (I)[2] and *o,p'*-bridged cyclic tolans (II).[3] The NMR and IR spectra of VI_n were discussed.

As has been pointed out in previous papers, the increase of strain in the cyclic polymethylene ether derivatives of *o,o'*-dihydroxydiphenyldiacetylene (I)[2] and *o,p'*-dihydroxytolan (II)[3] brought about hypsochromic shift of their electronic spectra. In contrast, bathochromic shift was observed in the spectra of strained cyclic polymethylene ether derivatives of *p,p'*-dihydroxytolan.[1] We hoped to synthesize another series of *p,p'*-bridged cyclic acetylenes to get further insight into the effect of the ring strain on the electronic spectra of cyclic acetylenes. The present paper deals with the syntheses and the properties of *p,p'*-bridged cyclic diphenyldiacetylenes (VI_n).


(I)


(II)

Syntheses. Alkylation of methyl 4-hydroxycinnamate with polymethylene dibromide gave the bis-cinnamic ester (III_n). Ester (III_n) was converted into bis-phenylpropiolic acid (IV_n) *via* bromination followed by dehydrobromination. Propiolic acid (IV_n) was decarboxylated without isolation to give *p*-hydroxyphenylacetylene polymethylene ether (V_n). α,ω-Diethynyl compounds (V_n) thus obtained was purified by means of chromatography on alumina. It is to be noted that a minor amount of hydration product, 1,14-bis(*p*-acetylphenoxy)tetradecane and 1-(*p*-ethynylphenoxy)-13-(*p*-acetylphenoxy)tridecane are obtained from the fractions eluted with benzene-ether in the case of $n=14$ and 13, respectively. The oxidative coupling of V_n according to the method of Eglinton under a high dilution condition using ether as an entraining agent afforded *p,p'*-bridged diphenyldiacetylene (VI_n) as colorless crystals. A solution of V_n in pyridine-ether (6:1) was added slowly into a refluxing solvent (pyridine-ether, 6:1) containing cupric acetate monohydrate. The temperature of the refluxing solvent was 83—84°C. The reaction conditions, the yields and the melting points of VI_n are summarized in Table 1. The monomeric nature of VI_n was confirmed by elemental analyses and molecular weight determination.

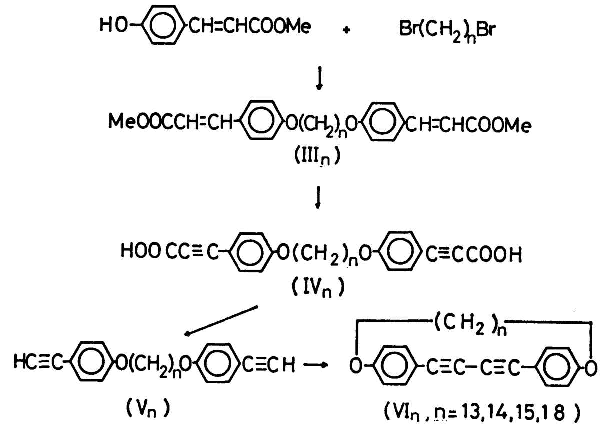


TABLE 1. THE REACTION CONDITIONS, YIELDS AND MELTING POINTS OF VI_n

n	Amount of V_n (mmol)	Amount of solvent (m*l*)	Period of addition of V_n (hr)	Yield of VI_n (%)	Mp of VI_n (°C)
18	1.52	280	7.5	60	138.8—140.0
15	1.70	350	7.5	53	168.8—169.2[a)] 174.7—176.0
14	1.19	210	6.0	37	167.2—169.2
13	1.72	400	5.5	0.8	151.2—153.0
	2.03	2500	8.0	2.0	

a) Dimorphism.

Preparation of VI_{14} by means of the alkylation of *p*-hydroxyphenylacetylene with 1,14-dibromotetradecane was found to be less satisfactory as compared with the above method presumably owing to the instability of the hydroxyacetylene.

Electronic Spectra. The electronic spectral data of *p,p'*-bridged diphenyldiacetylene (VI_n) measured in *n*-hexane and the absorption curves are recorded in Table 2 and Fig. 1 together with those of the open chain analog, *p,p'*-di-*n*-butoxydiphenyldiacetylene.

The absorption band at long-wavelength region consists of four distinct vibrational peaks (A~D) which are considered to arise from the stretching vibration of poly-yne linkage. All of these vibrational sub-

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1) T. Ando and M. Nakagawa, This Bulletin, **44**, 172 (1971).

2) F. Toda and M. Nakagawa, *ibid.*, **34**, 862 (1961).

3) M. Kataoka, T. Ando, and M. Nakagawa, *ibid.*, **44**, 177 (1971).

TABLE 2. ELECTRONIC SPECTRA OF VI_n

λ_{max} in mμ ($\varepsilon \times 10^{-2}$)

n				A	B	C	D
18	203.5 (673)	240 (219)	268 (174)	283 (206)	300.5 (332)	320 (518)	342.5 (465)
15	204 (706)	240.5 (222)	269 (111)	284.5 (168)	301.5 (332)	321 (543)	343.5 (514)
14	204 (565)	241.5 (219)	269 (115)	285.5 (162)	302.5 (288)	321.5 (436)	344 (425)
13	204 (572)	241.5 (242)	269.5 (95)	287 (141)	303.5 (252)	323 (408)	345.5 (367)
n-Bu	203.5 (673)	238.5 (223)	267.5 (308)	281 (310)	298.5 (365)	318 (485)	340.5 (407)

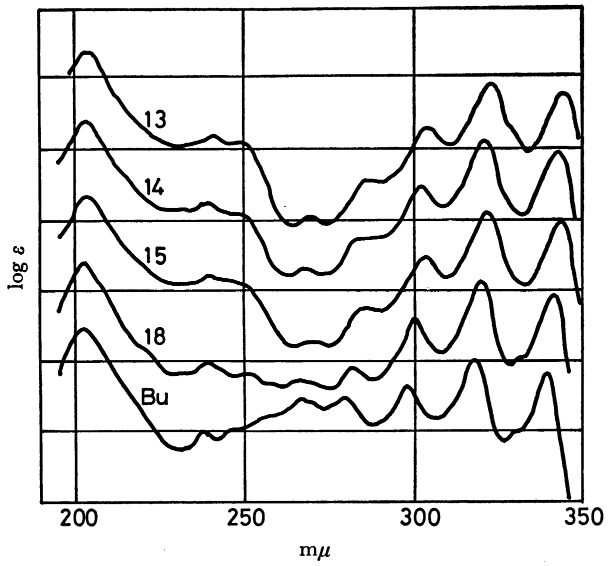

Fig. 1. The absorption curves of VI_n and p,p'-di-n-butoxydiphenyldiacetylene. The curves, with the exception of the di-butoxydiphenyldiacetylene at the bottom, are displaced upward on the ordinate axis by 1/3 log ε unit increments from the curve immediately below, and each horizontal line corresponds to log ε=4. (in n-hexane)

peaks exhibit bathochromic shift due to the decrease in the ring size making a sharp contrast with the hypsochromic shift observed in the strained o,o'-bridged diphenyldiacetylene (I)[1]

An inspection of molecular model of compound VI_n reveals that a chain of fifteen methylene groups is of the minimum length to link p,p'-position of dihydroxydiphenyldiacetylene without ring strain and the two phenyl groups are held almost in a coplanar fashion owing to the restricted rotation.

The absorption intensities of the four vibrational peaks exhibited an interesting change with that of the length of polymethylene bridge. As illustrated in Fig. 2, ε-values of the peaks A and B diminish monotonously with the decrease of the number of n. On the other hand, the absorption intensities of C and D attain maximum in the case of n=15, and then rapidly fall with the increase of ring strain. The nature of the transition corresponding to each of the vibrational peaks has not been clarified yet, and it is difficult to deduce a precise correlation between the ring strain and the above-mentioned intensity change. However, the spectral behavior of VI_n seems to be the result of the effects of coplanarity of the benzene rings (hyperchromism of C and D observed in VI_{15} and VI_{18}), the strain of the diacetylenic linkage caused by the short bridging chain (hypochromism of C and D observed in VI_{13} and VI_{14}) and the diminish of population of molecules in high vibrational sub-levels according to the decrease of the ring size (hypochromism of A and B according to the decrease of the number of n).

Nuclear Magnetic Resonance Spectra. As illustrated in Fig. 3, the protons on the benzene rings exhibit two AB pattern doublets at τ 2—3. The down field

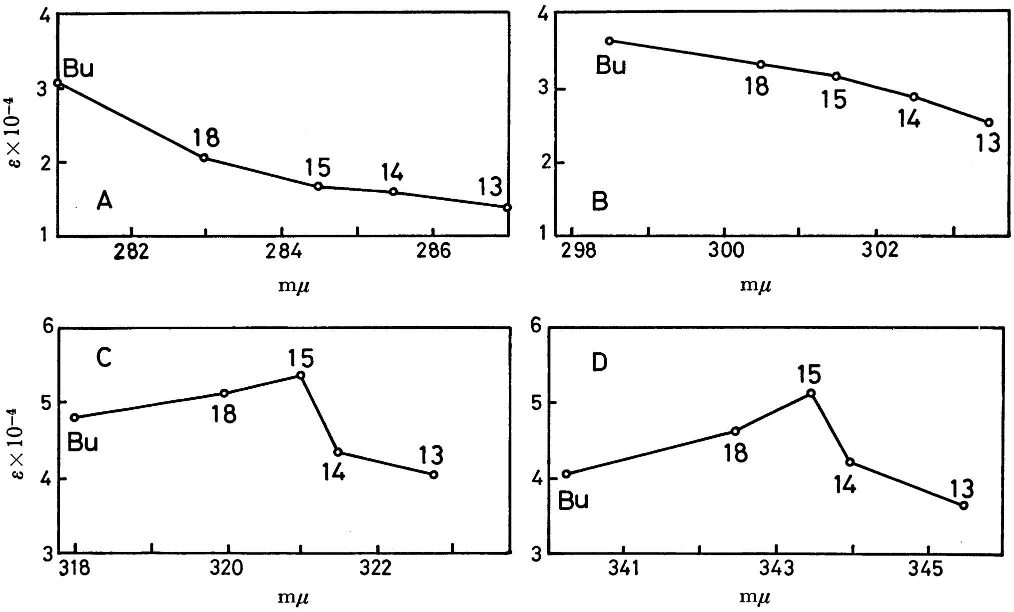

Fig. 2. Change in absorption intensities of the long-wavelength bands of VI_n.

TABLE 3. ASSIGNMENT OF NMR SPECTRA OF VI_n, 60 MHz in $CDCl_3$ (τ-value)

VI_n	Aromatic	α-Methylenes	β-Methylenes	Other methylenes
18	2.53 (4H), 3.08 (4H)	5.72 (4H)	8.37 (5H)[a]	8.84, 9.10 (27H)[a]
15	2.57 (4H), 3.06 (4H)	5.73 (4H)	8.42 (4H)	9.01 (22H)
13[b]	2.54 (4H), 3.04 (4H)	5.72 (4H)	8.47 (7H)[a]	9.04 (16H)
n-BuO	2.54 (4H), 3.14 (4H)	6.02 (4H)	8.0—8.3 (8H)	9.03 (6H)

a) Accurate intensity was not obtained owing to the poor resolution.
b) Measured on a 100 MHz spectrometer.

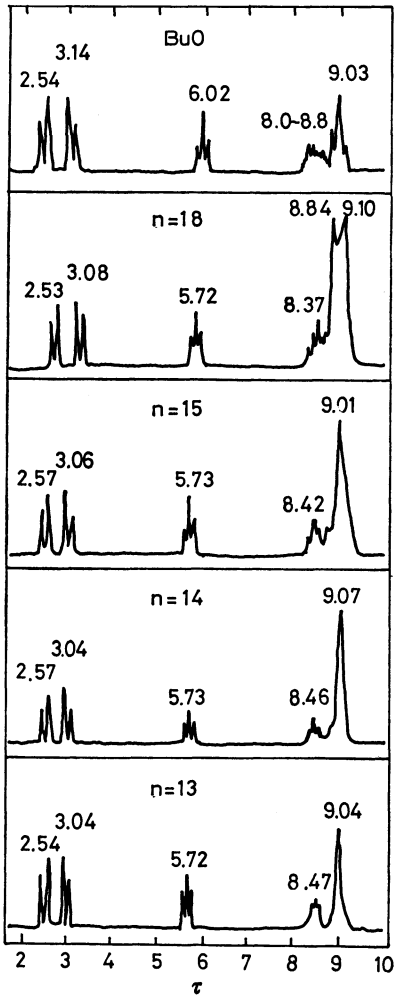

Fig. 3. NMR spectra of VI_n and *p*,*p*′-di-*n*-butoxydiphenyldiacetylene. The spectrum of VI_{13} was obtained on a 100 MHz spectrometer and the others were measured with a 60 MHz spectrometer (in $CDCl_3$).
(I_n) n=3,4,5,6 (III_n) n=13,14,15,16
(II_n) n=7,8,9,10,11,12 (IV_n) n=11,12,13,14,18

doublet was assigned to the ortho protons to the ethereal oxygen. The protons on the α-methylene groups adjacent to the ethereal oxygen exhibit distinct triplet at τ *ca.* 5.7. Another triplet was observed at around τ 8.4. A decoupling technique was applied for VI_{14} in which the centers of the two triplets were found at τ 5.73 and τ 8.46. The high field triplet was assigned to the methylene protons at the β-position to the ethereal oxygen, because the triplet at τ 5.73 was changed to a sharp singlet by the irradiation at τ 8.46. Therefore, the broad and intense peaks at τ *ca.* 9 should be assigned to the protons on other methylene groups. This indicates that an almost uniform magnetic environment is formed in the vicinity of the *p*,*p*′-bridged diphenyldiacetylene system as in the case of *p*,*p*′-bridged cyclic tolans.[1] The assignments are summarized in Table 3 together with that of *p*,*p*′-di-*n*-butoxydiphenyldiacetylene. The NMR spectroscopic feature of VI_n was found to be closely related to those of *p*,*p*′-bridged cyclic tolans, however, the slight down field shift of the τ-values of VI_n as compared with those of *p*,*p*′-bridged tolans seems to indicate that the diacetylenic unit in VI_n exerts more enhanced effect than the acetylenic linkage in the cyclic tolans.

TABLE 4. IR SPECTRA OF VI_n KBr-disk (cm^{-1})

VI_n	$\nu_{C=O}$	$\nu_{C=C}$ (arom.)	δ_{C-H} (arom.)
18	2120 (w)	1600 (s)	835 (s)
15	2120 (w)	1595 (s)	840 (m)
14	2130 (w)	1595 (s)	845 (m)
13	2120 (w), 2200 (w)	1600 (m)	835 (s)
n-BuO	2120 (w)	1959 (s)	830 (s)

(w): weak, (m): medium, (s): strong

Infrared Spectra. The characteristic peaks in the IR spectra of VI_n are tabulated in Table 4 with that of the open-chain analog, *p*,*p*′-di-*n*-butoxydiphenyldiacetylene. A decrease of intensity of the absorption band due to skeletal in-plane vibration of aromatic ring conjugated with the lone pair electrons in the substituent was observed in the spectra of VI_n as compared with that of the open-chain analog. The same trend has been observed in the IR spectra of *p*,*p*′-bridged tolans.[1] This seems to be attributable to a resonance inhibition of the oxygen with the benzene owing to a fixation of conformation by the spanning of the bridging chain. The splitting of $\gamma_{C\equiv C}$ band into two peaks (2120 and 2200 cm^{-1}) in the spectra of the strained VI_{13} may be pertinently attributed to some restriction of stretching vibration mode due to the ring strain. The same phenomenon has been observed in the spectrum of 2,4-hexadiynylene ether of 1,5-bishydroxymethylnaphthalene.[4]

Experimental

All melting points are uncorrected. The IR spectra were obtained with a Hitachi EPI-2 spectrophotometer by KBr-disk method, the electronic spectra with a Hitachi EPS-2 spectrophotometer and the NMR spectra with Varian A60 and Jeol JMN-4H-100 spectrophotometers. The molecular weights were measured on a Hitachi Perkin-Elmer 115 vapor osmometer.

Ethyl p-n-*butoxycinnamate.* To a refluxing mixture of methyl *p*-hydroxycinnamate (6.98 g, 39 mmol), *n*-butyl

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[4] T. Ando and M. Nakagawa, This Bulletin, **40**, 363 (1967).

bromide (11 g, 80 mmol), and anhydrous ethanol (120 m*l*) was added 56 m*l* of 0.70 M solution of potassium hydroxide in anhydrous ethanol over a period of 100 min. After further stirring for 2.5 hr, the reaction mixture was poured into water and extracted with ether. The extract was washed successively with a dilute sodium hydroxide and water, and dried. Evaporation of the solvent gave colorless crystals (7.48 g, 98%). This was recrystallized twice from *n*-hexane to give pure ethyl *p*-*n*-butoxycinnamate, mp 35.3—38.0°C.

Ethyl p-n-*butoxycinnamate dibromide.* Thirty six m*l* of 0.902 M solution of bromine in carbon tetrachloride was added under stirring over a period of 50 min to an ice-cooled solution of slightly crude ethyl *p*-*n*-butoxycinnamate (7.48 g, 31 mmol) in the same solvent (70 m*l*). Stirring was continued for 40 min at room temperature and then for 40 min at 50°C. The reaction mixture was washed with dilute sodium hydroxide and water successively and dried. The crystals (9.46 g, 74%) obtained by evaporation of the solvent were recrystallized twice from *n*-hexane to give pure dibromide, colorless prisms, mp 105.3—106.3°C. Found: C, 43.95; H, 4.94; Br, 39.47%. Calcd for $C_{15}H_{20}O_3Br_2$: C, 44.14; H, 4.94; Br, 39.16%.

p-n-*Butoxyphenylacetylene.* Anhydrous methanol (95 m*l*) was added to an ice-cooled intimate mixture of ethyl *p*-*n*-butoxycinnamate dibromide (5.44 g, 14 mmol) and powdered potassium hydroxide (21.4 g).5) After a vigorous exothermic reaction had subsided, the mixture was refluxed for 4 hr. The reaction mixture was mixed with 6N hydrochloric acid (40 m*l*) and extracted with ether. The extract was washed with a saturated aqueous solution of sodium chloride and dried. The violet amorphous solid (2.84 g) obtained by the evaporation of the solvent was dissolved in anhydrous pyridine (28 m*l*). The pyridine solution was refluxed for 50 min in the presence of copper powder (280 mg). Petroleum benzine (100 m*l*) was added to the reaction mixture and washed thoroughly with 2N hydrochloric acid. After the usual washing and drying procedures, distillation of the solvent furnished a dark brown oily material (1.77 g). The IR spectrum of this substance indicates the presence of carbonyl function (1670 cm^{-1}) presumably owing to the formation of a minor amount of *p*-butoxyacetophenone. The crude material was chromatographed on alumina (15 g). The fractions eluted with petroleum benzine gave crude *p*-*n*-butoxyphenylacetylene (light brown liquid, 1.26 g, 53%) free from carbonyl compound. This was used without further purification for the following reaction.

p,p′-*Di*-n-*butoxydiphenyldiacetylene.* To a stirred mixture of cupric acetate monohydrate (1 g) and anhydrous pyridine (80 m*l*), was added a solution of *p*-*n*-butoxyphenylacetylene (2.26 g, 13 mmol) in pyridine (20 m*l*) over a period of 10 min at 50—55°C.6) Stirring was continued for 4 hr at the same temperature. Benzene (100 m*l*) was added to the reaction mixture and washed thoroughly with 2N hydrochloric acid. The crude diacetylene (yellow crystals, 1.06 g, 47%), obtained by the usual washing, drying and evaporating procedures, was recrystallized twice from benzene to afford pure *p*,*p*′-di-*n*-butoxydiphenyldiacetylene, mp 154.7—155°C, colorless prisms. Found: C, 83.29; H, 7.64%. Calcd for $C_{14}H_{26}O_2$: C, 83.20; H, 7.56%.

1,13-Dibromotridecane, 1,14-Dibromotetradecane, and 1,18-Dibromooctadecane. The dibromoalkanes were prepared according to the method previously reported.3)

1,15-Dibromopentadecane. To a stirred and refluxing solution of diethyl sodiomalonate in ethanol [from sodium (7.8 g, 0.34 g atom), diethyl malonate (53 m*l*, 0.35 mol) and anhydrous ethanol (170 m*l*)], was added 1,11-dibromoundecane (50 g, 0.16 mol)3,7) over a period of 40 min. After stirring for further 2 hr, the solvent was removed under reduced pressure. The residue was mixed with ether, washed with water and dried. The crude reddish brown oily tetraethyl ester obtained by the evaporation of the solvent was added over 15 min-period to a stirred solution of potassium hydroxide (50 g) in water (100 m*l*). The mixture was refluxed for 13 hr under stirring. The reaction mixture was mixed with hot water (800 m*l*) and concentrated hydrochloric acid (200 m*l*). The oily material deposited crystallized on cooling under stirring. The tetracarboxylic acid thus obtained was heated to 160—180°C for 70 min to give 1,15-pentadecanedioic acid. The dioic acid in anhydrous methanol (160 m*l*) containing concentrated sulfuric acid (16 m*l*) was refluxed for 3 hr to give the dimethyl ester (bp 168—175°C/4 mmHg, 25.6 g, 53% based on dibromoundecane). The dimethyl ester was converted to 1,15-pentadecanediol by means of lithium aluminum hydride reduction.3) 1,15-Dibromopentadecane (bp 147—150°C/10^{-3} mmHg, 71%) was obtained from the diol according to the method previously reported.3)

α,ω-Bis-[p-(*2-methoxycarbonylvinyl*)*phenoxy*]*alkanes* (*III*n). As the alkylation of methyl *p*-hydroxycinnamate with α,ω-dibromoalkane was carried out under almost the same reaction conditions, the preparation of 1,15-bis[*p*-(2-methoxycarbonylvinyl)phenoxy]pentadecane (III_{15}) will be described as a representative example.

A solution of methyl *p*-hydroxycinnamate was mixed with a solution of sodium methoxide in methanol [prepared from sodium equivalent to the ester], and the solvent was removed under reduced pressure. The sodium salt of the ester (13.3 g, 67 mmol, yellow powder), thus obtained, was mixed with

Table 5. Results of the preparation of III_n

III_n	Reaction time (hr)	Yield (%)	Mp (°C)	Solv. of recryst.		Elemental analysis (%) C	H
18	19	39	130—134	B-M	Found	75.26	9.17
					Calcd	74.96	9.27
15	8	37	110—111	B	Found	74.40	8.54
					Calcd	74.43	8.57
14	4.5	21	134—137	B-H	Found	74.58	8.59
					Calcd	74.15	8.42
13	10	32	114—117	B	Found	73.47	8.24
					Calcd	73.85	8.26

B: benzene, M: methanol, H: *n*-hexane,

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5) *Cf.* S. Misumi, This Bulletin, **34**, 1827 (1961).

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

7) *Cf.* R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, 2nd Ed., p. 250 (1948).

TABLE 6. RESULTS OF THE PREPARATION OF V_n

V_n	Yield (%)	Mp (°C)	Crystal habit		Elemental analysis (%)		Solv. of recryst.
					C	H	
18	19	96.8—98.5	plates	Found	83.44	9.44	H
				Calcd	83.90	9.53	
15	16	72.2—73.0	prisms	Found	83.52	9.00	B-M
				Calcd	83.73	9.07	
14	25	93.0—94.2	leaflets	Found	83.66	8.84	H
				Calcd	83.67	8.90	
13	10	74.9—75.3	leaflets	Found	83.46	8.69	B-M
				Calcd	83.61	8.71	

H: *n*-hexane B: benzene, M: methanol

1,15-dibromopentadecane (11.6 g, 31 mmol). The mixture was heated on an oil-bath maintained at 165—170°C for 8 hr with occasional shaking. Benzene (100 m*l*) was then added to the reaction mixture and refluxed. The insoluble material was removed by filtration and filtrate was concentrated to *ca.* 50 m*l*. The yellow crystals deposited were recrystallized from benzene to afford pure III_{15} (6.71 g, 37%).

The results of the preparation of III_n are summarized in Table 5.

α,ω-Bis(p-*ethynylphenoxy*)*alkanes* (V_n). The bromination of III_n was carried out in chloroform at room temperature by the addition of a slight excess of 1N solution of bromine in the same solvent. Tetrabromides were obtained as viscous liquids and were subjected to the following reactions without purification. The procedures of dehydrobromination and decarboxylation used in the preparation of *p*-*n*-butoxyphenylacetylene were applied for the crude tetrabromides and the crude bis-phenylpropiolic acids (IV_n). After copper powder was removed by filtration, pyridine was distilled off under reduced pressure. The residue was mixed with ether and washed with dilute hydrochloric acid. The ether layer was dried over potassium carbonate. The crude material obtained by evaporation of the solvent was chromatographed on alumina. The fractions eluted with benzene afforded V_n as colorless crystals.

In the case of V_{14}, the fractions eluted with benzene-ether gave a minor amount of yellow crystals, mp 107—112°C (3% based on III_{14}). The substance was proved to be identical with bis(*p*-acetylphenoxy)tetradecane by comparison with an authentic sample which was prepared by the method described below. Also, in the case of $n=13$, a small amount of colorless solid (2% based on III_{13}, mp 86—92°C) was obtained from the fractions eluted with benzene-ether. This was recrystallized from *n*-hexane 5 times and from benzene-methanol 4 times to give colorless solid, mp 89—95°C. The structure of 1-*p*-ethynylphenoxy-13-*p*-acetylphenoxytridecane was assigned to this substance on the basis of NMR and IR spectroscopic evidences. Found: C, 80.34; H, 8.75%. Mol. wt. 438. Calcd for $C_{22}H_{38}O_3$: C, 80.14; H, 8.81%. Mol. wt. 435.

The results of the preparation of V_n are summarized in Table 6.

p,p′-*Dihydroxydiphenyldiacetylene Polymethylene Ether* (VI_n). The preparation of VI_{14} is described as a typical example. A solution of the diethynyl compound (V_{14}, 515 mg, 1.2 mmol) in pyridine-ether (6:1, 60 m*l*) was slowly added over a period of 6 hr to a vigorously stirred refluxing solution of cupric acetate monohydrate (2 g) in pyridine-ether (6:1, 210 m*l*) employing a high dilution apparatus. The change of color of the reaction mixture from blue to greenish brown was observed. After the addition had been completed, the mixture was stirred for 30 min under reflux. The solvent was removed under reduced pressure and the residue was dissolved in ether. The ether layer was successively washed with dilute hydrochloric acid, dilute sodium hydroxide, and a saturated sodium chloride solution, and dried. The reddish brown solid obtained by evaporation of the solvent was subjected to a chromatography on alumina (20 g). Recrystallization of the yellow crystals obtained from the fractions eluted with benzene furnished the cyclic diacetylene, (187 mg, 37%). The reaction conditions, yields and the melting points are given in Table 1, the analytical data and molecular weights are summarized in Table 7.

TABLE 7. ELEMENTAL ANALYSIS AND MOLECULAR WEIGHT OF VI_n

VI_n		Elemental analysis (%)[a]		MW
		C	H	
18	Found	84.09	9.17	503[b]
	Calcd	84.25	9.15	485
15	Found	84.31	8.69	484[b]
	Calcd	84.12	8.65	443
14	Found	83.78	8.47	409
	Calcd	84.07	8.47	429
13	Found	83.90	8.29	411
	Calcd	84.01	8.27	415

a) Recrytallized from benzene -*n*-hexane.
b) Measured by the Rast method.

The crystals of VI_n are colorless needles and development of brown color was observed at the temperature around its melting point.

Another Preparation of 1,14-bis(p-*ethynylphenoxy*)*tetradecane* (V_{14}). p-*Hydroxyphenylacetylene.* A mixture of *p*-hydroxyacetophenone (5.0 g, 37 mmol), phosphorus pentachloride (8.5 g, 42 mmol) and benzene (7.5 m*l*) was stirred at 45°C for 10 min and then at 60°C for 20 min. Anhydrous ether (150 m*l*) was added to the reaction mixture. The ethereal solution was added over a period of 20 min to a solution of sodamide [from sodium 5.5 g, 0.24 g atom] in liquid ammonia (250 m*l*).[8] After stirring for 3.5 hr, ammonium chloride (17 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was mixed with water and extracted with ether. The extract was washed with a saturated aqueous solution of sodium chloride and dried. The reddish brown extract was passed through a short column of alumina (20 g). The yield of *p*-hydroxyphenylacetylene was estimated to be *ca.* 1.5 g (35%), since an

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[8] I. L. Kotlyarevskii and M. I. Bardamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1964**, 2073.

aliquot (6 m*l*) of pale yellow filtrate (250 m*l*) gave 35 mg of a liquid which changed immediately to violet materials. Owing to the instability of *p*-hydroxyphenylacetylene, the ethereal solution was used for the subsequent reaction without isolation of acetylene.

Alkylation of p-*hydroxyphenylacetylene with 1,14-dibromotetradecane.* The aforementioned ethereal solution was evaporated *in vacuo* under the addition of anhydrous ethanol. The resulting ethanol solution of *p*-hydroxyphenylacetylene was mixed with 1,14-dibromotetradecane (1.20 g, 3.4 mmol). The mixture was refluxed, and to it was added over a period of 25 min, with stirring, 1N solution of potassium hydroxide in anhydrous ethanol (8.0 m*l*). After refluxing for further 2 hr, water was added to the reaction mixture and extraction was carried out with ether. The extract was successively washed with dilute sodium hydroxide and a saturated sodium chloride solution and dried. The deep brown solid (1.77 g) obtained by evaporation of the solvent was chromatographed on alumina (50 g). The fractions eluted with petroleum benzine gave 1,14-dibromotetradecane (283 mg, 24%). The substance (148 mg) obtained from petroleum benzine-benzene (1:4—1:1) fractions gave positive Beilstein's test. The substance was recrystallized from *n*-hexane to yield colorless prisms, mp 78.5—79.5°C. The structure of *p*-*ω*-bromotetradecanoxyphenylacetylene was assigned to this substance on the basis of IR spectroscopy and analytical data. Found: C, 67.22; H, 8.50; Br, 20.14%. Calcd for $C_{22}H_{33}OBr$: C, 67.16; H, 8.45; Br, 20.32%.

The fractions eluted with benzene afforded 40 mg (3%) of V_{14}. This was recrystallized from *n*-hexane to give pure V_{14}, mp 93.0—94.2°C, colorless leaflets.

*α,ω-Bis(*p*-acetylphenoxy)alkanes.* The reaction of 1,14-dibromotetradecane with *p*-hydroxyacetophenone according to the procedure for the preparation of *α*,*ω*-bis[*p*-(2-methoxycarbonylvinyl)phenoxy]alkanes (III_n) gave bis(*p*-acetylphenoxy)tetradecane in a yield of 57%, colorless prisms, mp 112.0—113.2°C (from benzene-ethanol). Found: C, 77.43; H, 9.18%. Calcd for $C_{30}H_{42}O_4$: C, 77.21; H, 9.07%.

Similarly, the reaction of *p*-hydroxyacetophenone with 1,18-dibromooctadecane gave bis(*p*-acetylphenoxy)octadecane in a yield of 1.3% colorless leaflets, mp 115.4—117.0°C (from benzene-ethanol). Found: C, 78.19; H, 9.76%. Calcd for $C_{34}H_{50}O_4$: C, 78.12; H, 9.64%.

Hydrogenation of V_{15} and V_{18}. The cyclic diacetylene, V_{15} (127 mg) in benzene was hydrogenated over palladium-carbon. A theoretical amount of hydrogen was absorbed over a 70 min period. The reduction product was chromatographed on alumina (5 g). The fractions eluted with *n*-hexane-benzene (4:1) gave 95 mg (75%) of colorless prisms, mp 59.8—60.3°C. Found: C, 82.89; H, 10.31%. Calcd for $C_{31}H_{46}O_2$: C, 82.61; H, 10.29%.

The hydrogenation of V_{18} gave colorless prisms, mp 102.3—102.7°C (from benzene-methanol). Found: C, 82.50; H, 10.62%. Calcd for $C_{34}H_{52}O_2$: C 82.87; H 10.64%.