Oligomers and Polymers Containing Triple Bonds. II.
Derivatives of Ethynylazobenzene

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Previous studies[1,2] have shown that various diethynyl compounds react with cupric or cuprous salts to produce linear and stable polymers containing triple bonds. In the present paper, the preparation of 4-ethynyl- and 4, 4′-diethynylazobenzene and the polymerization of the latter will be described.

The treatment of 4-acetylazobenzene[3] (II), prepared from *p*-aminoacetophenone (I) and nitrosobenzene, with phosphorus pentachloride and then with a large excess of sodium amide in liquid ammonia, resulted in the formation of *trans*-4-ethynylazobenzene (IIIa), together with a small amount of cis-isomer (IIIb). When a nearly theoretical amount of sodium amide was employed, however, 4-(chloroethynyl)-*trans*-azobenzene (IVa) and IIIa were obtained in almost equal yields.

Confirmatory evidence for the configurations of IIIa and IIIb was found in the following experimental results: the relationship between the electronic absorption properties of IIIa and IIIb resembled that between those of *cis*- and *trans*-azobenzene (Fig. 1), and IIIa (m. p. 81∼82°C) was eluted with carbon tetrachloride faster than was IIIb (m. p. 183.5°C) during the course of chromatography on alumina. It has previously been well known that cis-derivatives of azobenzene are more strongly adsorbed on

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[1] H. Tani, F. Toda and K. Matsumiya, This Bulletin, 36, 391 (1963).

[2] H. Tani, K. Murayama and F. Toda, *Chem. & Ind.*, 1962, 1980.

[3] F. Kunckell, *Ber.*, 33, 2641 (1900).

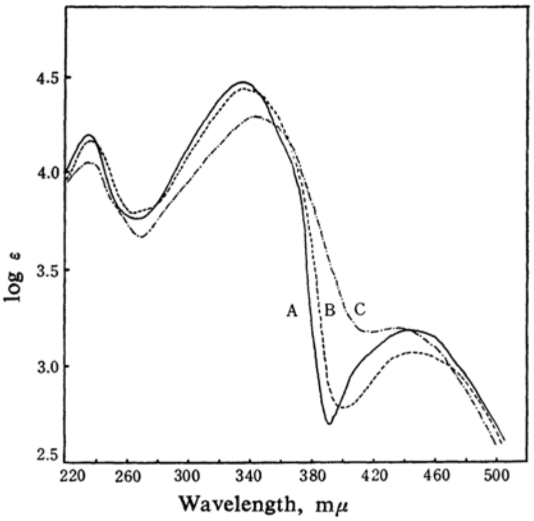
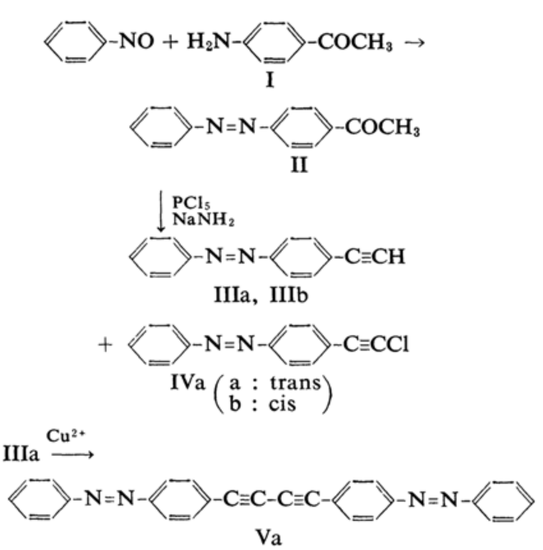


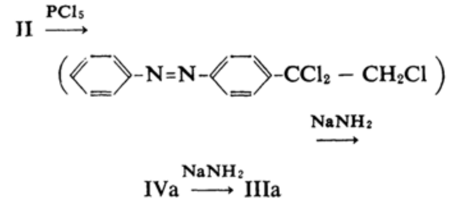
Fig. 1. Electronic absorption spectra.
A 4-Ethynyl-*trans*-azobenzene (III_a)
B 4-(Chloroethynyl)-*trans*-azobenzene (IV_a)
C 4-Ethynyl-*cis*-azobenzene (III_b)
all in dioxane.



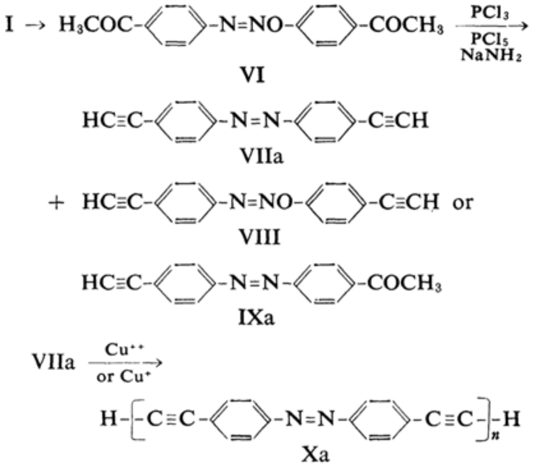
alumina and have higher melting points than do trans-derivatives. The configurations assigned to all the remaining compounds obtained in the present work were similarly confirmed.

IIIa gave, on oxidative coupling with cupric acetate in pyridine, the normal product Va in a good yield.

The formation of IVa in the course of the conversion of II to III may offer valuable evidence for the initial formation of 4-(1, 2, 2-trichloroethyl)azobenzene, from which IVa and further IIIa were produced by the action of sodium amide.



4, 4′-Diethynyl-*trans*-azobenzene (VIIa) was prepared from 4, 4′-diacetylazoxybenzene (VI), which had been obtained by the oxidation of I with neutralized Caro's acid[4] or with perboric acid,[5] by the reduction of azoxy group with phosphorus trichloride, followed by treatment with the same method as was employed for II. When phosphorus oxychloride and chloroform were used as solvents in the reduction process, 4, 4′-diethynylazoxybenzene (VIII) and 4-ethynyl-4′-acetyl-*trans*-azobenzene (IXa) were formed as the respective by-products. The electronic spectra of VIIa, VIII and IXa, indicating valuable evidence for their configuration, are shown in Fig. 2.



The polymerizations of VIIa with copper salt catalysts in pyridine or in dimethylformamide, as summarized in Table I, resulted in the formation of insoluble and infusible reddish brown or dark brown solids. The infrared and electronic absorption spectra indicated that these products were conjugated linear polymers. When polymerizations were carried out in pyridine, the linear dimer of VIIa ($Xa, _{n=2}$) was obtained. This is because of the low solubility of the initially-formed dimer in the solvent used for the polymerization. When the polymerization was carried out in dimethylformamide, linear hexamer ($Xa, _{n=6}$) was obtained. It is not clear whether the

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[4] J. C. E. Simpson, *J. Chem. Soc.*, **1952**, **2606**.
[5] S. Mehta and M. V. Vakilwala, *J. Am. Chem. Soc.*, **74**, 563 (1952).

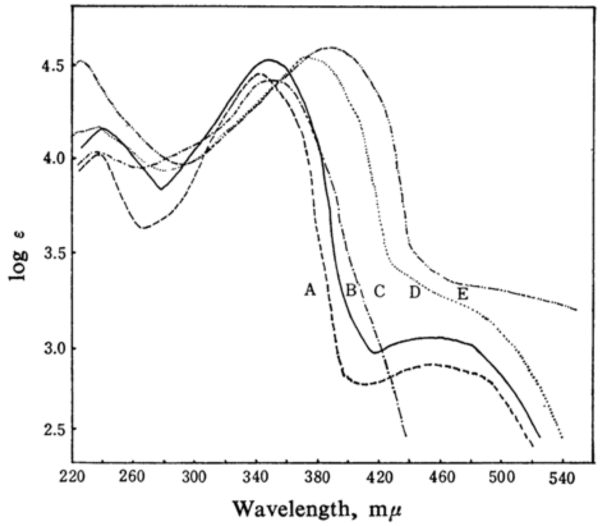

Fig. 2. Electronic absorption spectra.
A 4-Ethynyl-4′-acetyl-*trans*-azobenzene (IXa)
B 4, 4′-Diethynyl-*trans*-azobenzene (VIIa)
C 4, 4′-Diethynylazoxybenzene (VIII)
D 4, 4′-Bis(phenyl-*trans*-azo)diphenyldiacetylene (Va)
E 4, 4′-Bis(*p*-ethynylphenyl-*trans*-azo)diphenyldiacetylene (Xa, $_{n=2}$) ; all in dioxane.

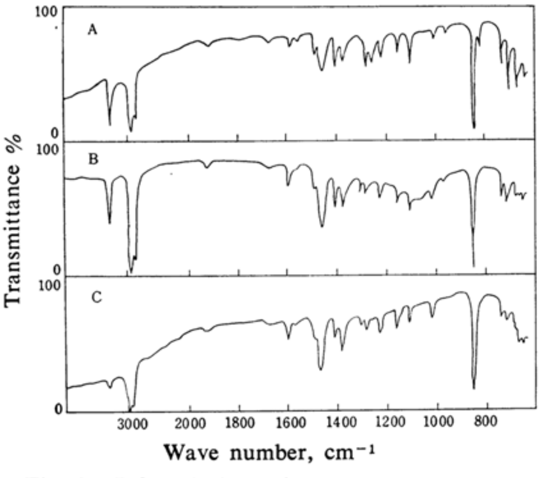

Fig. 3. Infrared absorption spectra.
A 4, 4′-Diethynyl-*trans*-azobenzene (VIIIa)
B 4, 4′-Bis(*p*-ethynylphenyl-*trans*-azo)diphenyldiacetylene (Xa, $_{n=2}$)
C Polymer (Xa, $_{n=6}$)
all in Nujol mull.

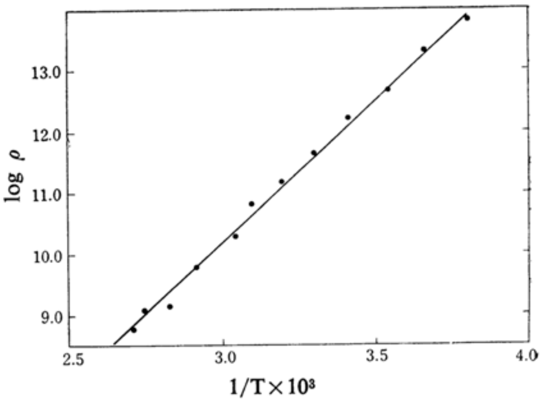

Fig. 4. Resistance-temperature characteristic for Xa, $_{n=6}$.

difference in the degree of polymerization is due to the basicity of the solvent or to the solubility of the oligomer in the solvent.

The degree of polymerization of all the polymers thus obtained was estimated by comparing the intensity at the ethynyl maximum (3300 cm^{-1}) in the infrared spectra of these polymers with that of VIIa, used as a reference standard (Fig. 3). This estimation was based on the assumption that the absorbancy of the ethynyl band is not affected by the length of the conjugation system. This assumption was justified by comparing the electronic spectra of Xa, $_{n=2}$ with that of Va, as shown in Fig. 2; these spectra show that Xa, $_{n=2}$ absorbs at wave lengths longer by ca. 11 mμ than does Va. It is most reasonable to consider that this bathochromic shift is attributable to the two additional ethynyl substituents. On the other hand, the shift exhibited when one more ethynyl group was introduced in to IIIa is 14 mμ (Figs. 1 and 2), which is comparable to the value (11 mμ) of the shift due to the conversion of Va to Xa, $_{n=2}$.

TABLE I. POLYMERIZATION OF 4, 4'-DIETHYNYL-*trans*-AZOBENZENE (VIIa)

VIIa mg.	Catalyst mg.		Solvent* ml.	Reaction temp., °C	Reaction time, min.	Atmosphere	Color	Product mg.	Degree of polymerization
65.75	CuCl	50.0	P 30	40∼ 45	30	O_2	Brown	61.0	2
16.25	CuCl	14.2	P 10	95∼100	90	O_2	Reddish Brown	14.63	2
10.75	CuCl	19.2	D 7	61∼ 62	60	O_2	Dark Brown	2.90	6
13.02	CuCl	11.7	D 7.5	95∼ 98	30	O_2	Dark Brown	2.96	3
20.30	$Cu(OAc)_2$	35.3	P 10	60	90	air	Brown	16.8	2
11.74	$Cu(OAc)_2$	20.86	D 8	62	35	air	Reddish Brown	5.84	2

* P, Pyridine D, Dimethylformamide

The resistivities of $\mathrm{Xa}_{n=6}$ at 25° and at 0°C were found to be 3.8×10^{12} and 3.9×10^{-4} ohm. cm. respectively. The temperature dependence of the resistivity obeyed the following relation:

$\rho=\rho_0\mathrm{exp.}\ \Delta\varepsilon/2kT$ where $\Delta\varepsilon=1.85$eV. (Fig. 4)

From the above data, it is apparent that this polymer has the typical characteristics of an organo-semiconductor.

Experimental*

4-Ethynyl-*trans*-azobenzene (IIIa) and 4-Ethynyl-*cis*-azobenzene (IIIb).—A mixture of 4-acetylazobenzene (2.2 g., 0.01 mol.), phosphorus pentachloride (2.4 g., 0.011 mol.), and phosphorus oxychloride (20 ml.) was heated at 60°C for 1 hr. The crude chloride obtained by the evaporation of phosphorus oxychloride under reduced pressure was dissolved in dry ether, and the solution was then added to sodium amide in liquid ammonia (sodium 1.0 g., 0.044 g. atom, liquid ammonia 100 ml.). After the evaporation of the ammonia, the crude product was extracted with ether. The ethereal layer was washed with water and dried over sodium sulfate. The residue obtained by the evaporation of the ether was chromatographed on alumina.

The orange crystals obtained from the fraction eluted with carbon tetrachloride were recrystallized from *n*-hexane to give 4-ethynyl-*trans*-azobenzene (IIIa); 160 mg. as orange leaflets; m. p. 81∼82°C. IR: KBr disk, 3270 (ethynyl), 1414 (azobenzene), 843 (*p*-disubstituted benzene) and 769, 675 cm^{-1} (monosubstituted benzene). UV: $\lambda_{\max}^{\text{Dioxane}}$: 234 m$\mu$ (ε, 15500), 334 (28200), 442 (1400).

Found: C, 81.36; H, 4.88; N, 13.38. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58%.

Elution with benzene, followed by recrystallization from *n*-hexane, yielded a small amount of 4-ethynyl-*cis*-azobenzene (IIIb) as orange needles; m. p. 183.5°C. IR: KBr disk, 1400 (azobenzene), 845 (*p*-disubstituted benzene), and 773, 685 cm^{-1} (monosubstituted benzene). UV: $\lambda_{\max}^{\text{Dioxane}}$: 234 m$\mu$ (ε, 11800), 344 (20000), 415 (1500), 432 (1500).

Found: N, 13.37. Calcd. for $C_{14}H_{10}N_2$: N, 13.58%.

The mercury salt of IIIb (orange) did not melt, but turned black at ca. 245°C. IR: KBr disk, 2130 (acetylene), 1410 (azobenzene), 850 (*p*-disubstituted benzene) and 770, 685 cm^{-1} (monosubstituted benzene).

4-(Chloroethynyl)-*trans*-azobenzene (IVa). — 4-Acetylazobenzene (5.1 g., 0.023 mol.) was treated with phosphorus pentachloride (5.0 g., 0.024 mol.) in phosphorus oxychloride (30 ml.) and then with sodium amide in liquid ammonia (sodium 1.5 g., 0.065 g. atom, liquid ammonia 150 ml.) in the manner described above. The ammonia was removed, and the residue was extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the crude material remaining was chromatographed on alumina from carbon tetrachloride.

Recrystallization of the crystals obtained from the first fraction (eluted with carbon tetrachloride 700 ml.) from *n*-hexane afforded IVa (200 mg.), in the form of orange leaflets; m. p. 107.5°C. IR: KBr disk, 2210 (acetylene), 1410 (azobenzene), 838 (*p*-disubstituted benzene) and 763, 675 cm^{-1} (monosubstituted benzene). UV: $\lambda_{\max}^{\text{Dioxane}}$: 221 m$\mu$ (ε, 10900) 236 (14600) 338 (26800), 445 (1100).

Found: C, 69.27; H, 3.67; N, 11.56; Cl, 14.70.

Calcd. for $C_{14}H_9N_2Cl$: C, 69.86; H, 3.77; N, 11.64; Cl, 14.73%.

From the second fraction (eluted with carbon tetrachloride 800 ml.), there was obtained the crude solids, the recrystallization of which from *n*-hexane gave orange leaflets (200 mg.; m. p. 78∼79°C), identified as 4-ethynyl-*trans*-azobenzene (IIIa) by comparing their infrared spectrum and melting point with those of an authentic sample.

4, 4'-Bis(phenyl-*trans*-azo)diphenyldiacetylene (Va).—To a solution of IIIa (100 mg.) in pyridine (20 ml)., cupric acetate monohydrate (2.0 g.) was added; the mixture was then stirred at 60°C for 30 min. The solid precipitates which formed were collected by filtration and washed with a small amount of pyridine. The solid was dried and then recrystallized from chloroform to yield Va (95 mg.) (quantitative yield) as orange leaflets; m. p. 243∼234.5°C (decomp.). UV: $\lambda_{\max}^{\text{Dioxane}}$: 238 m$\mu$ (ε, 13800), 374 (33100), 448 (2200).

Found: C, 80.73; H, 4.42; N, 13.70. Calcd. for $C_{28}H_{18}N_4$: C, 81.93; H, 4.42; N, 13.65%.

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* All melting points are uncorrected.

4, 4′-Diacetylazoxybenzene (VI).—*Procedure (A).* —A mixture of *p*-aminoacetophenone (1, 2.7 g., 0.02 mol.), acetic acid (80 ml.), and sodium perborate (3.3 g., corresponding to 0.02 g. atom of oxygen) was heated at 60°C for 2hr. The precipitates which had separated after the addition of water were collected, washed with water, dried, and then recrystallized from alcohol to give VI, 700 mg. (25%) as yellow leaflets; m. p. 187∼190°C. IR: KBr disk, 1685 (ketone), 1462, 1360 (methyl), 1410 (azobenzene), 1260 (aromatic ketone) and 844 cm^{-1} (*p*-disubstituted benzene). UV: $\lambda_{\max}^{\text{Dioxane}}$: 274 m$\mu$ (ε, 10900), 338 (21900).

When the reaction was carried out at 52°C and 30°C, VI was obtained in a yield of 15 and 11% respectively.

Found: C, 67.96; H, 5.05; H, 9.63. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68,07; H, 5.00; N, 9.92%.

Procedure (B).—A solution of *p*-aminoacetophenone (1, 9.7 g., 0.072 mol.) in dioxane (10 ml.) was added to neutral Caro's acid (0.18 N, 900 ml.). After the solution had been shaken for 10 min. at room temperature, the precipitates which had formed were collected by filtration, washed with water, and dried. Recrystallization of the product from acetone afforded VI 3.2 g. (32%) as yellow needles (m. p. 195.5°C), which showed no depression of melting point upon being mixed with the sample prepared in procedure (A). When 0.07 N Caro's acid was used, the yield of VI was lowered to 14%.

4, 4′-Diethynyl-*trans*-azobenzene (VIIa) and 4, 4′-Diethynylazoxybenzene (VIII).—A mixture of 4, 4′-diacetylazoxybenzene (2.8 g., 0.01 mol.), phosphorus oxychloride (40 ml.), and phosphorus trichloride (1.5 g., 0.01 mol.) was treated at 50°C for 30 min. To this warm mixture, phosphorus pentachloride (4.5 g., 0.02 mol.) was added, and the mixture was heated at 50°C for 1 hr. After removal of the phosphorus oxychloride and phosphorus trichloride by distillation in vacuo, the crude chloride which remained was suspended in dry ether (200 ml.), and the resulting suspension was added drop by drop to sodium amide in liquid ammonia (sodium 2.3 g., 0.1 g. atom, liquid ammonia 100 ml.), Stirring was continued for a further 30 min. The residue which remained after the evaporation of the ammonia was decomposed with water and extracted with ether. The ether layer was washed with water and dried over sodium sulfate. After evaporation of the solvent, the crude material was chromatographed on alumina. The crude crystals which were obtained from the first fraction, eluted with carbon tetrachloride, were recrystallized from *n*-hexane, giving VIIa (10 mg.) as orangered needles. Although VIIa did not show a melting point and turned black in the usual m. p. measurement, it melted at 201∼202°C with decomposition when immersed at 198°C. IR: Nujol mull, 3270 (ethynyl), 1925 (acetylene), 1419 (azobenzene) and 848 cm^{-1} (*p*-disubstituted benzene). UV $\lambda_{\max}^{\text{Dioxane}}$: 239 m$\mu$ (ε, 14100), 264 (shoulder) (7600), 348 (30200), 450 (1100).

Found: C, 83.52; H. 4.41; N, 12.46. Calcd. for $C_{16}H_{10}N_2$: C, 83.45; N, 4.38; N, 12.17%.

On the other hand, from the second fraction, eluted with benzene, orange yellow crystals were obtained. The crystals were recrystallized from *n*-hexane to yield VIII (10 mg.) as orange yellow leaflets; m. p. 141.5∼142.5°C. UV $\lambda_{\max}^{\text{Dioxane}}$: 230 m$\mu$ (ε, 11700), 349 (21400), 480 (shoulder) (100).

Found: C, 77.40; H, 4.29; N, 11.53. Calcd. for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.09; N, 11.38%.

4, 4′-Diethynyl-*trans*-azobenzene (VIIa) and 4-Acetyl-4′-ethynyl-*trans*-azobenzene (IXa).—A solution of 4, 4′-diacetylazoxybenzene (5.5 g., 0.02 mol.) in chloroform (80 ml.) with was treated phosphorus trichloride (2.7 g.) at 50°C for 1 hr. The resultant mixture was then heated with phosphors pentachloride (8.4 g., 0.04 mol.) at 50∼60°C for 1 hr. The crude chloride which remained after the evaporation of the chloroform and phosphorus trichloride was treated with sodium amide in liquid ammonia (sodium 3.5 g., 0.15 g. atom; liquid ammonia 150 ml.). After removal of the ammonia, the residue was decomposed with water and extracted with ether. The ether layer was washed with water and then evaporated to leave the crude product, which was chromatographed on alumina from benzene. The first fraction gave the desired compound (VIIa) as orange-red leaflets (96 mg.; m. p. 201∼202°C (decomp., immersed at 198°C) after recrystallization from *n*-hexane.

When the crystals which were obtained from the second fraction were recrystallized from aqueous ethanol, IXa (14 mg.) was obtained as orange leaflets; m. p. 163°C. IR: KBr disk, 3240 (ethynyl), 2090 (acetylene), 1660, 1264 (acetyl), 1414 (azo) and 850 cm^{-1} (*p*-disubstituted benzene). UV $\lambda_{\max}^{\text{Dioxane}}$: 236 m$\mu$ (ε, 10000), 344 (22400), 455 (600).

Found: C, 76.27; H, 4.99; N, 10.76. Calcd. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28%.

Electric Constants.—Electric constants were measured for the tablet of Xa, $_{n=6}$, on which indium had been sublimed in vacuo. The tablet was made by applying a pressure of 6000 kg./cm^2 on the powder of the polymer in a tube 13 mm. in diameter for a 30-min. period.

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