Linear Conjugated Systems Bearing Aromatic Terminal Groups. IX. Syntheses and Elctronic Spectra of α,ω-Di-1-anthrylpolyenes*

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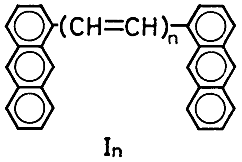
(Received May 12, 1972)

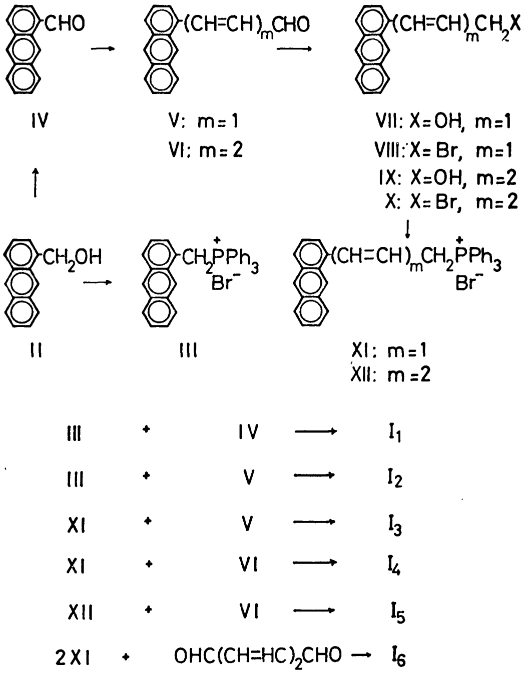
Syntheses of α,ω-di-1-anthrylpolyenes have been carried out by the Wittig reaction for information on the role of aromatic terminal groups on the electronic spectral regularity of α,ω-diarylpolyenes. The reaction of phosphoranes derived from 1-anthrylmethyl-, 3-(1-anthryl)propenyl-, and 5-(1-anthryl)-pentadienyltriphenylphosphonium bromides with 1-formylanthracene, 3-(1-anthyrl)propenal, 5-(1-anthryl)pentadienal, and muconic aldehyde afforded a series of di-1-anthrylpolyenes (I_{1-6}) by a proper combination of the phosphorane and the aldehyde moiety. Owing to the broading of absorption bands in the long wavelength region, no discussion could be made on the electronic spectral regularity.

It has been generally accepted that the square of wavelength of the longest wavelength absorption maxima ($\lambda^2_{\max}$) of a series of all-*trans* linear polyenes varies linearly with the number of double bond (n) [$\lambda^2_{\max} \propto n$].1) However, the linear relationship between the longest wavelength absorption maxima ($\lambda_{\max}$) and the xth power of the number of acetylenic bond (n) [$\lambda_{\max} \propto n^x$, $1 \leqq x \leqq 2$] observed in various kinds of diarylpoly-ynes2–13) clearly indicates the marked influence of terminal groups on the electronic excitation of polyacetylene chromophore. This suggests that the aromatic terminal groups in α,ω-diarylpolyenes also exert a similar effect on the spectral regularity of linear polyenes. In order to clarify the effect, we have carried out the synthesis of α,ω-di-1-anthrylpolyenes (I_n) first, because anthryl groups have been found to exert the most prominent effect in polyyne series.2,4)



I_n

Syntheses. The reaction sequence of the syntheses of α,ω-di-1-anthrylpolyenes (I_n) is outlined in the Scheme. The starting material of syntheses of I_n is 1-hydroxymethylanthracene (II).14) 1-Anthrylmethyltriphenylphosphonium bromide (III) was prepared from II *via* 1-bromomethylanthracene.8) 1-Formylanthracene (IV) which was obtained from II was converted into 3-(1-anthryl)-2-propen-1-al (V) according to a modified J. F. Arens and van Dorp method.15) 5-(1-Anthryl)-2,4-pentadien-1-al (VI) was synthesized from IV by the reaction of Grignard derivative of methoxybutenyne.16) Reduction of V and VI with sodium borohydride afforded allyl alcohol derivatives, VII and IX, respectively. The bromides (VIII and X) obtained from VII and IX were treated with triphenylphosphine to give phosphonium bromides (IX and XII). The reaction of aldehyde (IV, V, or VI) with phosphorane derived from phosphonium bromide (III, XI, or XII) according to the combination shown in the Scheme afforded α,ω-di-1-anthrylpolyenes



Scheme. Syntheses of Di(1-anthryl)polyenes (I_n)

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* For Part VIII of this series, see Ref. 13.

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(I_{1-5}). 1,12-Di-1-anthryldodecahexene (I_6) was obtained by the reaction of XI with muconic aldehyde.[17] The Wittig reaction was performed under shielding from light in anhydrous benzene or xylene. An ethereal solution of phenyllithium was used as a base for the conversion of phosphonium bromides to phosphoranes. The reaction product was extracted with hot benzene or toluene and percolated through a column of alumina. The first crop of crystals obtained from the concentrated filtrate was recrystallized from benzene or toluene. The pure specimen of I_n thus prepared was subjected to measurement of the electronic spectrum. 1,4-Di-1-anthryl-1,3-butadiene (I_2) was also prepared from di-1-anthryldiacetylene[18] by reduction with sodium in liquid ammonia and proved to be identical with I_2 obtained by the Wittig reaction.

The color of the crystals, melting points, and wave numbers of IR absorption due to CH out-of-plane deformation (δ) of *trans*-double bonds of I_n are summarized in Table 1. The polyenes (I_n) were found to be stable and exhibited definite melting points in contrast to the fact that almost all diarylpoly-ynes showed decomposition points. Regular increase in melting point with the increase in the number of ethylenic bonds reported in α,ω-diphenylpolyenes[19] could not be observed in I_n. The solubility of I_n in organic solvents decreases markedly with the increase of n. Shift of δ due to C–H out-of-plane deformation of the *trans*-double bond to a higher wave number and an increase in the absorption intensity with the increase of n were observed (Table 1).

Table 1. Physical properties of α,ω-di(1-anthryl)polyenes (I_n)

n	Color of crystals	Mp (°C)	δ (cm^{-1})
1	greenish yellow	277—279	967
2	yellow	273—275	990
3	yellowish orange	304—305	1001
4	bright yellow	289.5—290	1004
5	orange	290—292	975, 1010
6	orange red	279—280	995, 1010

Electronic Spectra. Absorption curves and numerical data of the electronic spectra of I_n are shown in Fig. 1 and Table 2. The intense and broad bands in the long wavelength region which presumably arise from an interaction of L_a band of anthracene nucleus with the polyene chromophore shift to a longer wavelength with the increase in the length of polyene chain. On the other hand, the length of polyene chain exerts no effect on the location of short wavelength bands. The bands with moderate intensity at medium wavelength region shift to longer wavelength with an increase in n. Owing to disappearance of the vibrational fine structure, exact estimation of wavelength of the maxima of long wavelength bands was difficult. However, the plots of the square of approximate wavelength of long wavelength absorption maxima (λ^2) against the number of double bonds (n) gave no straight line (Fig. 2). The fact that the widely accepted linear relationship ($\lambda^2 \propto n$) does not hold for di-1-anthrylpolyenes (I_n) indicates an appreciable effect of terminal groups on polyene chromophore. Disappearance of

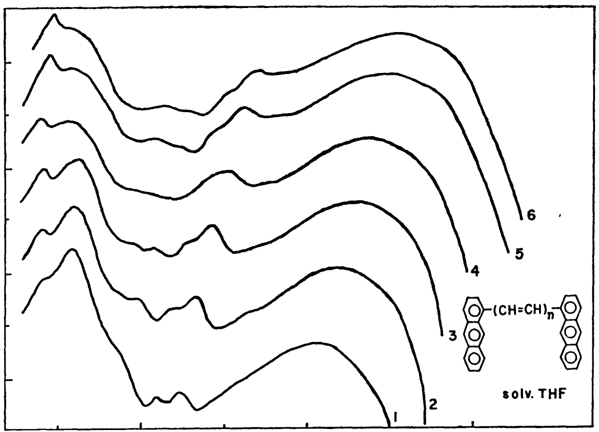

Fig. 1. The absorption curves of di(1-anthryl)polyenes (I_n). The curves, with the exception of I_1 at the bottom have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below.

Table 2. Electronic spectral data of I_n

n	$\lambda_{\max}$ nm (log ε)					
1			259.5 (5.20)	310.5 (3.81)	324.5 (3.87)	406 (4.31)
2	241.5 (4.79)	261.5 (5.15)	299.5 (4.26)	321.5 (4.16)	334 (4.27)	423 (4.51)
3	243 (4.66)	265 (4.85)	3.3 (4.23)		344.5 (4.44)	433 (4.65)
4*					352 (4.43)	440 (4.73)
5	246.5 (5.08)	259 (4.95)			364 (4.56)	452 (4.87)
6*				314 (4.16)	374 (4.41)	456 (4.76)

Solvent: tetrahydrofuran. * Measured in glass cells.

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the vibrational fine structure is attributed to a steric interference between hydrogen atoms at ethylenic linkage and those at *peri*- and *o*-positions of anthracene nuclei.

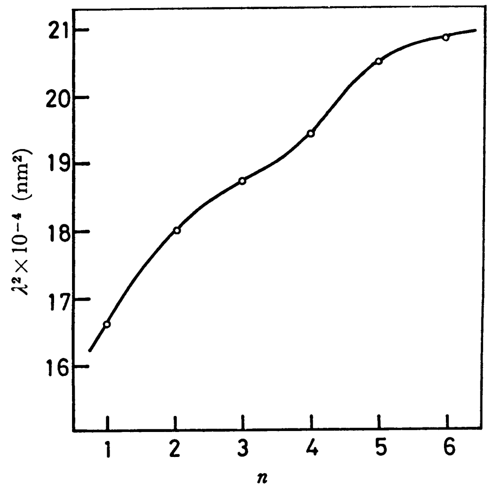

Fig. 2. Plot of λ^2_{max} agaist n for I_n

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, unless otherwise stated. The IR spectra were determined with a Hitachi EPI-2 infrared spectrophotometer by KBr-disk method.

3-(1-Anthryl)-2-propen-1-al (V). To a solution of lithium salt of ethoxyacetylene (prepared from 2-chlorovinyl ethyl ether (35.3 g, 0.33 mol) and lithium amide (lithium, 4.55 g, 0.66 g-atom)) in liquid ammonia (500 m*l*) was added a solution of 1-formylanthracene (IV, 13.6 g, 0.066 mol) in tetrahydrofuran (120 m*l*) over a period of 15 min. After the mixture had been stirred for 12 hr at the boiling point of liquid ammonia, a saturated solution of ammonium chloride (50 g) was added and the ammonia was allowed to evaporate. The organic layer was separated and combined with the benzene extract of aqueous layer. After washing and drying, the solvent was removed under reduced pressure. A benzene solution of the residue was passed through a thin layer of alumina. Dark red liquid (IR: 2260 ($C \equiv CH$), 3400 cm^{-1} (OH)) obtained by concentration of the filtrate *in vacuo* was dissolved in ether (110 m*l*). The ethereal solution was added under stirring to a suspension of lithium aluminum hydride (5.7 g, 0.15 mol) in ether (200 m*l*). After 4 hr, ethyl acetate (20 m*l*) and then 4 N sulfuric acid were added to the stirred mixture. After 30 min, the mixture was extracted with ether and the extract was washed with water and dried. The residue obtained by evaporating the solvent under reduced pressure was dissolved in benzene. The solution was percolated through a short column of alumina. The dark brown liquid obtained from the filtrate was triturated with a small amount of benzene-cyclohexane to yield yellow crystals (4.95 g). The crystals were recrystallized from cyclohexane to give pure V, yellow plates. V showed double melting point, mp 98—99°C and mp 119—120°C, IR: 2815 (CHO), 1690 (C=O), 965 (C=CH) cm^{-1}.

Found: C, 87.73; H, 5.22%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%.

5-(1-Anthryl)-2,4-pentadien-1-al (VI). A solution of 1-methoxy-1-buten-3-yne (12.5 g, 0.152 mol) in tetrahydrofuran (20 m*l*) was added to a stirred solution of ethylmagnesium bromide (prepared from ethyl bromide, 8.8 g and magnesium, 1.5 g) in the same solvent (38 m*l*) at 40°C. The mixture was stirred under nitrogen atmosphere for 30 min at 40°C and then 1 hr at room temperature. A solution of 1-formylanthracene (8.2 g, 0.04 mol) in tetrahydrofuran (90 m*l*) was added to the ice-cooled solution of Grignard derivative of methoxybutenyne over a period of 1 hr. After the mixture had been stirred overnight at room temperature, a saturated solution of ammonium chloride (90 m*l*) was added. The organic layer was separated, washed with water and dried. Brown liquid obtained by evaporation of the solvent *in vacuo* was dissolved in ether (100 m*l*) and added to a suspension of lithium aluminum hydride (4.5 g, 0.12 mol) in ether (65 m*l*). The mixture was stirred at room temperature for 2 hr and then ethyl acetate (18 m*l*), water (5 m*l*) and 4 N sulfuric acid (135 m*l*) were added successively. After the mixture had been stirred for 30 min at room temperature, the organic layer was separated and washed with water and dried. Fine orange crystals obtained by evaporation of the solvent under reduced pressure were dissolved in methanol and mixed with a saturated solution of sodium hydrogen sulfite. The adduct precipitated was filtered, washed successively with methanol and hot benzene. The adduct was decomposed with a solution of sodium carbonate, and the mixture was extracted with benzene. The extract was worked up according to the usual manner to yield orange yellow fine crystals (6.4 g, 63%). This material was recrystallized from cyclohexane to give pure VI as yellow plates, mp 147.5—149°C, IR: 1685 (C=O), 985 (C=CH) cm^{-1}.

Found: C, 87.90; H, 5.43%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46%.

3-(1-Anthryl)-2-propen-1-ol (VII). A solution of sodium borohydride (0.23 g, 6.0 mmol) in methanol (22 m*l*) was added to a stirred solution of anthrylpropenal (V, 0.23 g, 1.0 mmol) in tetrahydrofuran (10 m*l*) and methanol (40 m*l*). Stirring was continued for 1.5 hr at room temperature. Dilute hydrochloric acid was then added to the reaction mixture. Pale yellow crystals (0.22 g, 92%, mp 138—140°C) obtained from the organic layer were recrystallized from benzene to afford pure VII as yellow needles, mp 141.0—141.5°C, IR: 3300 (OH), 995 (C–O), 980, 970 (C=CH) cm^{-1}.

Found: C, 87.38; H, 6.16%. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

5-(1-Anthryl)-2,4-pentadien-1-ol (IX). A solution of sodium borohydride (0.40 g, 10 mmol) in methanol (20 m*l*) was added at room temperature to a stirred solution of anthrylpentadienal (VI, 0.90 g, 3.5 mmol) in tetrahydrofuran (13 m*l*) and methanol (20 m*l*). After 2 hr, dilute hydrochloric acid was added to the reaction mixture and the organic solvent was removed under reduced pressure. The solid deposited was filtered, washed and dried to give yellow fine crystals (1.0 g, mp 140—147°C). The crude alcohol (IX) thus obtained was recrystallized from benzene-cyclohexane, yielding pure IX as yellow plates, mp 159—160.5°C, IR: 3350 (OH), 1015 (C–O), 995, 980, 972 (C=CH) cm^{-1}.

Found: C, 87.44; H, 6.12%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

3-(1-Anthryl)-2-propen-1-yltriphenylphosphonium Bromide (XI). To a solution of anthrylpropenol (VII, 1.5 g, 6.4 mmol) in chloroform (60 m*l*) containing 2 drops of pyridine which was chilled on an ice-salt bath was added a solution of phosphorus tribromide (1.7 g, 6.5 mmol) in the same solvent (10 m*l*) and the mixture was stirred for 1 hr at room temperature. The reaction mixture was poured onto ice-water and the organic layer was separated, washed and dried. Crude bromide (VIII) obtained as yellow fine crystals by evaporation of the solvent under reduced pressure was mixed with triphenylphosphine (1.9 g, 7.2 mmol) in benzene (26 m*l*). The mixture was refluxed overnight, and the crystals deposited were filtered and washed with benzene, yielding pale yellow crude phosphonium bromide (XI, 3.2 g, 89.5%, mp 256—260°C). Recrystallization of crude XI from ethanol afforded pure XI as yellow crystals, mp 260—262°C.

Found: C, 73.14; H, 5.45%. Calcd for $C_{35}H_{28}PBr \cdot C_2H_5OH$: C, 73.40; H, 5.62%.

5-(1-Anthryl)-2,4-pentadien-1-yltriphenylphosphonium Bromide (XII). A solution of phosphorus tribromide (0.97 g, 3.8 mmol) in chloroform (20 m*l*) was added to a strongly chilled (ice-salt bath) solution of anthrylpentadienol (IX, 0.465 g, 1.8 mmol) in chloroform (70 m*l*) containing 2 drops of pyridine. After stirring for 30 min at the same temperature, the reaction mixture was poured onto ice-water and the organic layer was separated. After washing and drying the organic layer was treated with active charcoal. Greenish yellow crystals obtained by evaporation of the solvent under reduced pressure were mixed with benzene (40 m*l*) and triphenylphosphine (0.54 g, 2.2 mmol) and the mixture was allowed to stand overnight at room temperature. Evaporation of the solvent under reduced pressure gave fine greenish yellow crystals. The crystals were washed with a small amount of benzene-cyclohexane (1 : 1) to give slightly crude XII, mp 140—143°C, 0.45 g (44%). The crude XII was used in the subsequent reaction without further purification.

1,2-Di(1-anthryl)ethylene (I_1). To a suspension of 1-anthrylmethyltriphenylphosphonium bromide[8] (III, 0.533 g, 1.0 mmol) in benzene (15 m*l*) was added 0.22 N ethereal solution of phenyllithium (4.6 m*l*) under nitrogen atmosphere. After stirring for 15 min, a solution of 1-formylanthracene[14] (IV, 0.206 g, 1 mmol) in benzene (10 m*l*) was added to the resulting red solution of phosphorane and the mixture was stirred overnight at room temperature. The crystals deposited were filtered and digested with boiling benzene. Yellow crystals (0.108 g, 28.5%, mp 267—279°C) obtained by concentration of the extract were recrystallized from benzene, yielding pure I_1 as greenish yellow crystals, mp 277—279°C, IR: 1615, 1540, 1455, 1430, 1325, 975, 967, 875, 795, 734 cm^{-1}.

Found: C, 94.38; H, 5.29%. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%.

1,4-Di(1-anthryl)-1,3-butadiene (I_2). *(a) By the Wittig Reaction*: An ethereal solution of phenyllithium (0.84 N, 1.6 m*l*) was added to a suspension of 1-anthrylmethyltriphenylphosphonium bromide (III, 0.69 g, 1.3 mmol) in xylene (70 m*l*) under nitrogen atmosphere and the mixture was stirred for 30 min at 50—60°C resulting in a dark red solution of phosphorane. To this was added under shielding from light a solution of 3-(1-anthryl)-2-propen-1-al (V, 0.30 g, 1.3 mmol) in xylene (50 m*l*) and the mixture was stirred for 19 hr at room temperature. The crystals deposited were filtered and digested with hot toluene. The yellow crystals (0.256 g, 48%, mp 266—270°C) obtained by concentration of the extract were recrystallized from toluene to yield pure I_2 as yellow leaflets, mp 273—275°C, IR: 1613, 1538, 1455, 1300, 990, 874, 784, 728 cm^{-1}.

Found: C, 94.41; H, 5.46%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%.

(b) Reduction of Di-(1-anthryl)diacetylene: Sodium (0.4 g) was added to a solution of di-(1-anthryl)diacetylene[18] (0.603 g) in liquid ammonia (120 m*l*). After the mixture had been stirred for 5 hr, ammonium nitrate and then water were added. The insoluble material was collected by filtration, washed successively with water and ethanol and dried. The crude material was dissolved in benzene (90 m*l*). The crystals obtained by concentration of the solution up to 70 m*l* were recrystallized from benzene, yielding yellow leaflets, mp 273—275°C.

Found: C, 94.10; H, 5.65%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%.

The butadiene (I_2) thus prepared was found to be identical with that prepared by the Wittig reaction.

1,6-Di(1-anthryl)-1,3,5-hexatriene (I_3). 3-(1-Anthryl)-2-propen-1-yltriphenylphosphonium bromide (XI, 0.839 g, 1.5 mmol) in xylene (80 m*l*) was mixed with phenyllithium (0.5 N ether solution, 3 m*l*) under nitrogen atmosphere and the mixture was stirred at 50—60°C for 30 min. A solution of 3-(1-anthryl)-2-propen-1-al (V, 0.348 g, 1.5 mmol) in xylene (50 m*l*) was added to the dark violet solution of phosphorane under shielding from light. Stirring was continued for 5 days at room temperature, and the yellow crystalline powder deposited (0.214 g, 33%) was digested with hot toluene and the hot extract was passed through a short column of alumina. Concentration of the filtrate under reduced pressure yielded pure I_3 as orange yellow plates, mp 304—305°C, IR: 1610, 1454, 1297, 1001, 877, 788, 728 cm^{-1}.

Found: C, 94.33; H, 5.64%. Calcd for $C_{34}H_{24}$: C, 94.41; H, 5.59%.

1,8-Di(1-anthryl)-1,3,5,7-octatetraene (I_4). A solution of 5-(1-anthryl)-2,4-pentadien-1-al (VI, 0.260 g, 1.0 mmol) in xylene (20 m*l*) was added under shielding from light to a dark violet solution of phosphorane [prepared by stirring a mixture of 3-(1-anthryl)-2-propen-1-yltriphenylphosphonium bromide (XI, 0.560 g, 1.0 mmol) in xylene (22 m*l*) and phenyllithium (0.06 N, ether solution, 16.6 m*l*) for 1 hr under nitrogen atmosphere]. After the reaction mixture had been stirred overnight at room temperature, the solvent was removed under diminished pressure. The residue was digested with hot toluene and the hot extract was percolated through a thin layer of alumina. Concentration of the filtrate yielded fine orange crystals (0.065 g, 14%), mp 286—290°C which were recrystallized from toluene to give pure I_4, bright yellow plates, mp 289.5—290.0°C, IR: 1610, 1537, 1428, 1010, 880, 787, 732 cm^{-1}.

Found: C, 93.79; H, 5.69%. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%.

1,10-Di(1-anthryl)-1,3,5,7,9-decapentaene (I_5). A solution of 5-(1-anthryl)-2,4-pentadien-1-al (VI, 0.130 g, 0.5 mmol) in benzene (20 m*l*) was added to a solution of phosphorane prepared from 5-(1-anthryl)-2,4-pentadien-1-yltriphenylphosphonium bromide (XII, 0.290 g, 0.5 mmol) in benzene (20 m*l*) and an ethereal solution of phenyllithium (0.12 N, 8.3 m*l*). After stirring overnight at room temperature, the solvent was removed under reduced pressure. The residue was extracted with hot toluene and the hot extract was passed through a short column of alumina. Orange crystalline powder (0.044 g, 18%, mp 282—292°C) deposited on cooling the filtrate was recrystallized from toluene to give pure I_5 as orange plates, mp 290—292°C, IR: 1610, 1535, 1428, 1010, 990, 975, 878, 865, 790, 730 cm^{-1}.

Found: C, 93.85; H, 5.87%. Calcd for $C_{38}H_{28}$: C, 94.18; H, 5.82%.

1,12-Di(1-anthryl)-1,3,5,7,9,11-dodecahexaene (I_6). To a suspension of 3-(1-anthryl)-2-propen-1-yltriphenylphosphonium bromide (XI, 0.670 g, 1.2 mmol) in benzene (20 m*l*) was added an ethereal solution of phenyllithium (0.33 N, 3.6 m*l*) under nitrogen atmosphere. After the mixture had been stirred for 20 min at room temperature, a solution of muconic aldehyde[17] (0.044 g, 0.4 mmol) in benzene (3 m*l*) was added and the mixture was stirred for 23 hr at room temperature. Crystalline orange powder deposited was digested with hot toluene. The extract was concentrated under reduced pressure to yield fine orange red crystals, 0.084 g, (41%), mp 273—280°C. The crude crystals were dissolved in hot toluene and the hot solution was passed through a short column of alumina, yielding pure $\mathbf{I}_6$ as orange red plates, mp 279—280°C, IR: 1612, 1535, 1455, 1428, 1010, 995, 876, 868, 788, 730 cm^{-1}.

Found: C, 93.71; H, 5.87%. Calcd for $C_{40}H_{30}$: C, 94.08; H, 5.92%.