Studies of Polyphenyls and Polyphenylenes. I. The Syntheses and Infrared and Electronic Spectra of Several Sexiphenyls

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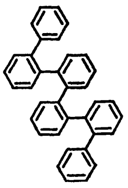
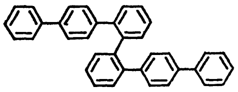
Seven linear sexiphenyls were synthesized by the Ullmann reaction of iodobiphenyl and diiodobiphenyl. Infrared studies indicated that the fine structure in the 780—810 cm^{-1} region suggests the presence of consecutive *m*-phenylene units, and that the positions of the strong or medium bands in the 820—840 cm^{-1} region indicate approximately the number of continuous *p*-phenylene units. The electronic spectra commonly displayed a prominent E-band in the narrow region of 192—207 nm. The intense K-band above 260 nm was considered to be an indication of the presence of one or more *p*-phenylene units.

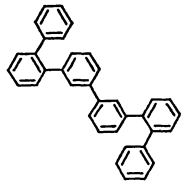
It has been known that a twist of the pivot bond in a conjugated system of polyphenyls influences the interaction of π-electrons across the pivot bond and also the conjugation of the system, and consequently affects the spectral features.1—3) In order to investigate the relationship between the number and arrangement of the benzene rings and the physical properties of polyphenyls and polyphenylenes, a series of symmetrical linear sexiphenyls, with closely related structures, have been prepared and their infrared and electronic spectra have been measured.



X



XIII



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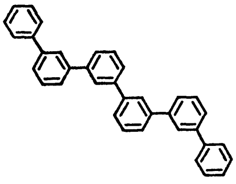
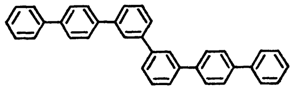
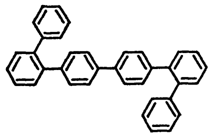


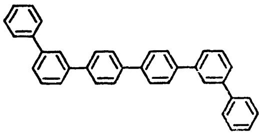
XVIII



XX



XXI



XXII

The convenient route generally used for the preparation of polyphenyls is based on the reaction of arylcyclohexenone or arylcyclohexanone with an appropriate Grignard reagent or a corresponding lithium compound, followed by dehydration and dehydrogenation.4,5) The resultant polyphenyl, however, is liable to be contaminated with a partially hydrogenated product.6)

To avoid this disadvantage, the Ullmann coupling of aryl halides has been used in the present work. There are two forms of coupling in the syntheses of a series of symmetrical sexiphenyls: a) the coupling of iodoterphenyl, and b) the coupling of iodobiphenyl and diiodobiphenyl. In this work, the b method has been adopted in spite of the troublesome separation of polyphenyl from the reaction products, because the b method has the advantage of synthesizing both iodo compounds with ease from commercially available materials. Thus, iodobiphenyls (2- [I], 3- [II], and 4-iodobiphenyl[III]) and diiodobiphenyls (2,2′- [IV], 3,3′- [V], and 4,4′-diiodobiphenyl[VI]) were prepared from commercial aminonitrobenzene, chloronitrobenzene, aminobiphenyls, and benzidine. Then a mixture of mono- and diiodo compounds in the molar ratio of 2 to 1 was subjected to the Ullmann reaction at 260—270 °C with copper powder. The sexiphenyls and by-products thus obtained are shown in Table 1.

Table 1. Ullmann syntheses of sexiphenyls

Iodides	Sexiphenyls (Yield, %)	By-products
I+IV	X (5.4)	VII VIII IX XI
II+IV	—	VII VIII XI XIV XVII
III+IV	XIII (1.6)	VII VIII XII XIV XV
I+V	XVI (5.5)	VII IX
II+V	XVIII (8.6)	VII XVII
III+V	XX (9.7)	VII XV XIX
I+VI	XXI (9.0)	VII IX XV
II+VI	XXII (14.0)	VII XVII XIX

Four sexiphenyls, X, XIII, XVI, and XXI, were found by the mixed-melting-point method and the IR spectra to be identical with authentic samples synthesized by the Ullmann coupling of the corresponding iodoterphenyls. An alternative synthesis of six sexiphenyls (X, XIII, XVIII, XX, XXI, XXII) has been reported earlier by other workers. Whereas the melting points of XIII and XX7) do not coincide with those of the previous authors, those of the four remaining sexiphenyls fall within 1—2 °C of those of the other authors (X, XVIII,8) XXI,9) XXII10,11)).

In all of the Ullmann coupling experiments, biphenyl and one or two kinds of quaterphenyls were isolated as by-products. Beside these substances, biphenylene and 1-phenyltriphenylene were separated from the product of I+IV, and biphenylene and 2-phenyltriphenylene, from III+IV.12)

The yields of all the pure sexiphenyls except XIII were 5—14%. In the coupling reactions using IV

Table 2. Positions and tentative assignments of the characteristic bands of the infrared spectra (675—910 cm^{-1}) of sexiphenyls[a)]

X			
698	s	γ_{C-C}	
734	s	γ_{C-H}	(M, *o*)
743	s		
753	s		
776	s	γ_{C-H}	(*o*)
XIII			
698	s	γ_{C-C}	
726	w		
744	sh, m	γ_{C-H}	(M, *o*)
754	s		
778	m	γ_{C-H}	(*o*)
834	sh, m	γ_{C-H}	(*p*)
842	s		
XVI			
702	s	γ_{C-C}	
709	sh, s		
744	s	γ_{C-H}	(M, *o*)
759	s		
776	m	γ_{C-H}	(*o*)
796	m	γ_{C-H}	(*m*)
901	w	γ_{C-H}	(*m*)
907	w		
XVIII			
690	sh, m	γ_{C-C}	
699	s		
754	s	γ_{C-H}	(M)
776	m	γ_{C-H}	(*m*)
786	m		
803	w		
817	vw		
873	m	γ_{C-H}	(*m*)
883	m		
897	w		
907	vw		
XX			
687	s	γ_{C-C}	
698	sh, s		
707	m		
723	w		
759	s	γ_{C-H}	(M)
781	m	γ_{C-H}	(*m*)
800	vw		
839	s	γ_{C-H}	(*p*)
880	w	γ_{C-H}	(M, *m*)
912	w		
XXI			
703	s	γ_{C-C}	
709	s		
747	s	γ_{C-H}	(M, *o*)
761	s		
773	vw	γ_{C-H}	(*o*)
786	m		
821	sh, m	γ_{C-H}	(*p*)
832	s		
XXII			
699	s	γ_{C-C}	
724	vw		
755	s	γ_{C-H}	(M)
761	s		
793	s	γ_{C-H}	(*m*)
826	m	γ_{C-H}	(*p*)
833	m		
837	m		
888	m	γ_{C-H}	(*m*)

a) v: very, s: strong, m: medium, w: weak, sh: shoulder. γ_{C-C} and γ_{C-H} refer to vibrations which are primarily out-of-plane C–C, and out-of-plane C–H bending motions. M, *o*, *m*, *p* in parentheses refer to mono-, *ortho*-, *meta*-, and *para*-substituted rings.

as one of the iodo compounds (I+IV, and III+IV), the sexiphenyls were obtained only in low yields; furthermore, in the case of II+IV, no corresponding sexiphenyl was isolated, but biphenylene, 1- and 2-phenyltriphenylene were obtained. Hence, the Ullmann coupling of appropriate iodoterphenyl is preferable for these three sexiphenyls with an *o*-quaterphenyl unit in the middle of their structure.

For the separation of polyphenyl from a mixture of several products, liquid column chromatography, using alumina as the adsorbent and a cyclohexane or cyclohexane–benzene mixture as the eluent, was found to be a satisfactory technique.[13)]

The IR spectra of the sexiphenyls were measured by the KBr-disk method. All the sexiphenyls commonly show the following absorptions: a group of prominent bands due to C–H out-of-plane deformation vibrations in the 675—910 cm^{-1} region; intense bands due to C–C out-of-plane deformation vibrations in the fairly narrow region of 685—710 cm^{-1};[14)] medium bands due to C–C in-plane deformation vibrations near 1000 cm^{-1}, and weak bands due to C–H in-plane deformation vibrations in the 975—1350 cm^{-1} region. In addition, groups of medium bands due to C–C stretching vibrations and a weak band due to aromatic C–H stretching vibrations in the 1350—1600 cm^{-1} and 3000—3100 cm^{-1} regions respectively were observed.

The most characteristic bands of sexiphenyls in the 675—910 cm^{-1} region are shown in Table 2; the table indicates that these bands are consistent with the kinds of phenylene rings in each sexiphenyl.

Let us now discuss the assignment of the strong bands in the 734—761 cm^{-1} region of X, XIII, XVI, and XXI, in all of which one or more *o*-phenylene rings are present. Stewart and Hellman[16)] have pointed out that the bands at 733—757 cm^{-1} of *o*-quaterphenyl must be due to C–H out-of-plane deformation vibrations of terminal rings; Sandroni and Geiss[17)] have proposed a similar assignment for the intense bands in the 753±10 cm^{-1} region of polyphenyls. However, the strong bands near 745—755 cm^{-1} were also observed in the spectra of some polyphenylenes, which contain no terminal rings. Thus, tetraphenylene, *o*-hexaphenylene, *o*-octaphenylene,[20)] and *o*,*p*,*o*,*p*,*o*,*p*-hexaphenylene[21)] showed strong bands at 745—755 cm^{-1}. Consequently, in the case of polyphenyls containing *o*-phenylene rings, the intense bands in the 734—761 cm^{-1} region should be assigned not only to the C–H out-of-plane bending bands of terminal rings, but also to those of *o*-phenylene rings.

Then the prominent bands observed commonly in the spectra of X, XIII, XVI, and XXI at 776—786 cm^{-1} should be assigned to the C–H out-of-plane bending vibrations of *o*-phenylene rings, as has been suggested by Stewart and Hellman[16] and Sandroni and Geiss,[17] because the medium or weak bands at 766—773 cm^{-1} were found commonly in the spectra of four polyphenylenes.

The four bands at 776, 786, 803, and 817 cm^{-1} in the spectra of XVIII were assigned to the C–H out-of-plane bending vibrations of *m*-phenylene rings. Stewart and Hellman[16] have pointed out that the characteristic C–H bands of some *m*-polyphenyls in the 780—810 cm^{-1} region are observed as a multiplet with an increase in the complexity, in accordance with the progression of *m*-phenylene rings, and have concluded that the fine structure can be attributed to the interaction bands between a ring and its nearest neighbors. The spectrum of XVIII supports strongly their opinion.

In the spectra of XIII, XX, XXI, and XXII, strong C–H out-of-plane bending vibration bands of two adjacent hydrogen atoms of *p*-phenylene rings were clearly observed at 842; at 839; at 832, and at 826, 833, and 837 cm^{-1} respectively. While XIII and XX have two *p*-linkages separated, respectively, by *o*- and *m*-phenylene groups, XXI and XXII have two consecutive *p*-linkages. A red shift of the characteristic bands was observed in the spectra of the latter two compounds. A similar red shift has been reported by Doss[19] and others[17] in the spectra of compounds with consecutive *p*-phenylene units.

These results show that the fine structure in the 780—810 cm^{-1} region suggests the presence of consecutive *m*-phenylene units, and that the positions of strong or medium bands in the 820—840 cm^{-1} region serve as an indication of the number of continuous *p*-phenylene units.

The electronic spectra of the seven sexiphenyls were measured in a cyclohexane solution. The absorption curves are shown in Figs. 1—4. The absorption maxima above 220 nm coincide within 1—2 nm for XIII, XVIII, XX, and XXI, and within 3—4 nm for X and XXII, with those of other workers.[8–10,22]

Gillam[1] has reported that the first intense band of the first four *p*-polyphenyls is shifted progressively toward a longer wavelength and increases in intensity with an increase in the number of rings. In the *m*-series, terphenyl and compounds containing 9—16 benzene rings absorb at substantially the same wavelength and with an intensity which is approximately proportional to the number of ring units.[1] In the case of *o*-polyphenyls, however, Dale[2] and others[20] have observed a blue shift and a weakening of the conjugate band as compared with those of the corresponding *m*-polyphenyls; these are results of reduced π-π interaction across the pivot bond.

In the present study, all seven sexiphenyls displayed two groups of intense bands: one in the fairly narrow region of 192—207 nm (ε=72800—98700) and another in the broad region of 230—300 nm with a high intensity. While the band position for the former was found to be rather independent of the structure, that for the latter was substantially affected by the nature and number of linkages formed between benzene rings. The first one, corresponding to the band at 203 nm (ε=49600) of biphenyl, is considered to be the E-band (the notation is according to Braude[23]), which is presumably due to the transitions between localized π-orbitals within each benzene ring.[2,3] The other one, corresponding to the band at 248 nm (ε=18500) of biphenyl, is regarded as the K-band (Burawoy's notation[23]), which should originate from

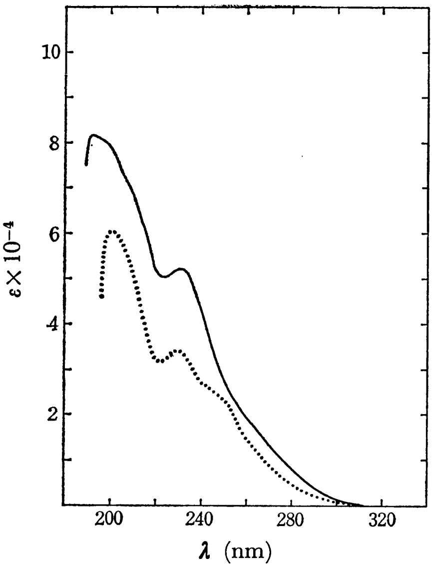


Fig. 1. Electronic spectra of quaterphenyl and sexiphenyl in cyclohexane.
……: *o*-Quaterphenyl (IX),
——: *o*-Sexiphenyl (X).

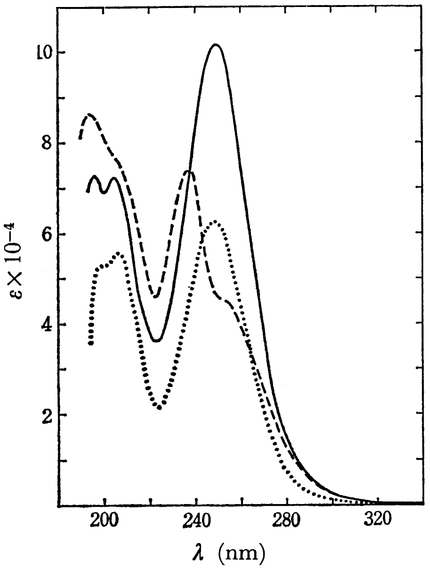


Fig. 2. Electronic spectra of quaterphenyl and sexiphenyls in cyclohexane.
……: *m*-Quaterphenyl (XVII),
——: *m*-Sexiphenyl (XVIII),
----: 3,3′-Di(2-biphenylyl)biphenyl (XVI).

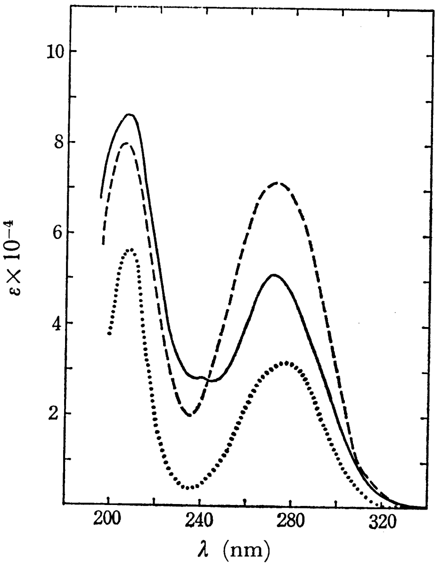


Fig. 3. Electronic spectra of terphenyl and sexiphenyls in cyclohexane.
······: *p*-Terphenyl,
——: 2,2′-Di(4-biphenylyl)biphenyl (XIII),
----: 3,3′-Di(4-biphenylyl)biphenyl (XX).

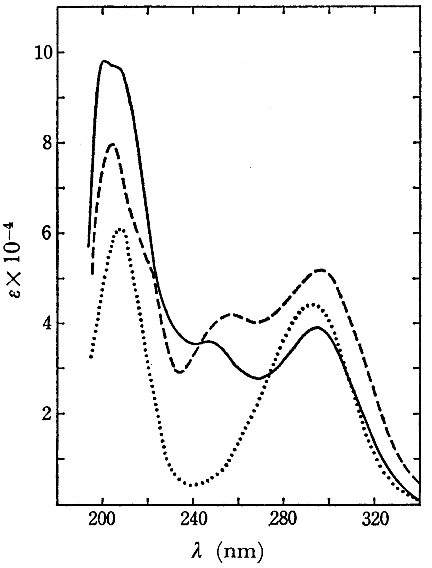


Fig. 4. Electronic spectra of quaterphenyl and sexiphenyls in cyclohexane.
······: *p*-Quaterphenyl (XV),
——: 4,4′-Di(2-biphenylyl)biphenyl (XXI),
----: 4,4′-Di(3-biphenylyl)biphenyl (XXII).

transitions between whole-molecular π-orbitals made up of ring orbitals with no longitudinal node.[2,3)]

Thus, the spectrum of X has the K-band with $\lambda_{\max}$ at 231 nm and an $\varepsilon_{\max}$ value of 52200, slightly stronger in its intensity than, but very similar in its location to, *o*-quaterphenyl (230; 34100) (Fig. 1). The spectra of XVIII and XVII (*m*-quaterphenyl) revealed intense bands at substantially the same wavelength, 248± 1 nm, with intensities about five times and three times respectively those of the biphenyl band. Therefore, the intensity of the K-band in the *m*-series may be correlated with the maximum number of biphenyl units in each compound (Fig. 2). In the case of XVI, in which *o*- and *m*-linkages are present, the spectrum revealed a strong K-band at 237 nm (ε=74100) which may correspond to the band near 230 nm of *o*-polyphenyls, but the characteristic band of *m*-polyphenyls near 250 nm was observed only as a shoulder.

Then in the spectra of XIII, XX, XXI, and XXII, all of which have *p*-linkage, a remarkable red shift of the K-band as compared with that in biphenyl was distinctly observed, as is shown in Figs. 3 and 4. Thus, XIII and XX have two *p*-terphenyl units in each structure and show a distinct band at about 270 nm, while XXI and XXII each have one *p*-quaterphenyl unit and both reveal a strong band near 300 nm. It may be considered that the arrangement of the *p*-phenylene units in the four sexiphenyls, even in the presence of *o*- or *m*-phenylene units, has a tendency to maintain a coplanarity of the rings; a distinct bathochromic shift of K-band results because of the elongation of the conjugated system.

On the basis of these results, the intense K-band above 260 nm in the spectra of sexiphenyl may be considered to be an indication of the presence of one or more *p*-phenylene units.

Experimental

All the melting points and boiling points are uncorrected. The IR spectra were recorded with a Leitz IIIG spectrophotometer. The electronic spectra were measured on a Shimadzu QV-50 spectrometer and a Hitachi EPS-2 spectrophotometer, using spectral-grade cyclohexane as the solvent. In the measurement in the short-wavelength region, 2-mm silica cells were used. The molecular weights were determined with a Mechrolab 301A vapor-pressure osmometer unless otherwise noted.

2-Iodobiphenyl (I). Commercial 2-aminobiphenyl (20 g, 0.12 mol) dissolved in sulfuric acid was diazotized with sodium nitrite. The suspension of the diazonium salt thus formed was treated with a potassium iodide solution. The product was purified by distillation *in vacuo* to give a pale yellow liquid; bp 130—134 °C/4 mmHg (lit,[24)] bp 158 °C/ 6 mmHg); yield, 26.3 g (79.8%). (Found: C, 51.51; H, 3.26%.)

3-Iodobiphenyl (II). 3-Nitroaniline (69 g, 0.50 mol) in sulfuric acid (33 ml) and water (500 ml) were treated with sodium nitrite (36 g) in water (76 ml) at 0—5 °C with stirring. To the cold suspension of diazonium salt thus formed, benzene (1000 ml) and sodium acetate (160 g) in water (330 ml) were added in portions, after which the mixture was stirred at an ambient temperature for 7 hr and then at 30—35 °C for 40 hr. The benzene layer was separated, washed with water, and then dried. After the removal of the benzene, the residue was distilled *in vacuo* to afford a pale yellow oil; bp 166—170 °C/8 mmHg. Recrystallization from methanol gave 3-nitrobiphenyl as pale yellow needles; mp 59—60 °C (lit,[25)] mp 61 °C); yield, 50.0 g (50.3%).

3-Nitrobiphenyl (20 g, 0.10 mol) was dissolved in hot benzene (800 ml) and treated with activated iron by a method similar to that of Hazlet and Dornfeld.[26)] After filtration, hydrogen chloride was passed into the filtrate. The precipitate was separated off, washed with benzene, and dried. Then the salt was treated in the usual manner with 20% aqueous alkali. The benzene extract was washed with water and dried. The evaporation of the solvent, followed by distillation *in vacuo*, yielded 3-aminobiphenyl as a colorless oil; mp 30 °C; bp 175—177 °C/13 mmHg (lit,[27] mp 31—31.5 °C; bp 177—178 °C/18 mmHg); yield, 12.3 g (72.4%).

3-Iodobiphenyl was prepared by the method described for the preparation of I to give a pale yellow oil; mp 25—26 °C; bp 175—178 °C/15 mmHg (lit,[27] bp 149—152 °C/1 mmHg); yield, 78.6%. (Found: C, 51.58; H, 3.48%.)

4-Iodobiphenyl (III). 4-Iodobiphenyl was prepared from 4-aminobiphenyl in the manner described above. Colorless plates from ethanol; mp 112.5—113.5 °C (lit,[28] mp 112 °C); yield, 70.8%. (Found: C, 51.51; H, 3.41%.)

2,2′-Diiodobiphenyl (IV). 2-Chloronitrobenzene (40 g, 0.25 mol) was heated with copper powder (80 g, 1.26 g-atom) at 215—225 °C and then at 225 °C for 1 hr. The subsequent extraction of the cooled mass with hot benzene, followed by evaporation, and the recrystallization of the residue from ethanol gave 2,2′-dinitrobiphenyl as pale yellow prisms; mp 122.5—124.5 °C (lit,[29] mp 123.5—124.5 °C); yield, 18.8 g (60.7%).

2,2′-Dinitrobiphenyl was reduced with activated iron in hot benzene in a manner previously described. Recrystallization from petroleum benzine afforded colorless prisms; mp 79—80 °C; yield, 73.0%.

The 2,2′-diaminobiphenyl (10 g, 0.054 mol) thus obtained was subjected to tetrazotization, followed by treatment with potassium iodide. The product was purified by distillation *in vacuo*; the subsequent recrystallization of the distillate (bp 130—170 °C/4 mmHg) from methanol gave 2,2′-diiodobiphenyl as pale yellow needles; mp 107.5—108.5 °C; yield, 8.8 g (40.0%). (Found: C, 35.63; H, 2.28%.)

3,3′-Diiodobiphenyl (V). 3-Iodonitrobenzene was prepared from 3-aminonitrobenzene by a method similar to that of Daines and Eberly;[30] mp 35.5—36.5 °C; yield, 55.4%. 3,3′-Diiodobiphenyl was obtained by the Ullmann reaction of 3-iodonitrobenzene, followed by reduction with tin and hydrochloric acid, and the Gries reaction of the product. Colorless needles from petroleum benzine; mp 71—72 °C (lit,[31] mp 72 °C); yield, 23.2% (based on 3-iodonitrobenzene). (Found: C, 35.59; H, 2.09%.)

4,4′-Diiodobiphenyl (VI). Commercial benzidine (18.4 g, 0.10 mol) was tetrazotized and then treated with potassium iodide in the manner described above to give VI as colorless leaves from benzene; mp 202—203 °C (lit,[32] mp 202 °C); yield, 35.0 g (86.3%). (Found: C, 35.78; H, 2.19%.)

Preparation of o-Sexiphenyl (X). A mixture of I (5.6 g, 20.0 mmol) and IV (4.0 g, 9.9 mmol) in a test tube (ϕ 2.5 × 20 cm) was heated in an oil bath at 265—270 °C, and then copper powder (28 g, 440 mg-atom) was stirred in in portions over a 1.5-hr period, after which the mixture was heated at 270 °C for an additional 1.5 hr. After cooling, the mixture was extracted with hot benzene, and the solvent was distilled off. The resulting solid (4.98 g) was subjected to chromatography on alumina, with cyclohexane and then with a cyclohexane-benzene (5 : 1 v/v) mixture (C–B (5 : 1)) as the eluents. The cyclohexane eluted three fractions, which, upon the evaporation of the solvent and recrystallization from ethanol, afforded VII, VIII, and IX. The mixture eluted two fractions, which, upon treatment as above, yielded X and XI. The properties of these compounds are as follows.

i) Biphenyl (VII): colorless leaves; mp 70—71 °C; yield, 11 mg.

ii) Biphenylene (VIII): pale yellow needles; mp 110—111 °C (lit,[33] mp 111—112 °C); yield, 322 mg.

Found: C, 94.45; H, 5.56%. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30%. Picrate: 121—122 °C. (Found: C, 56.67; H, 3.11; N, 10.83%.) Styphnate: 160—162 °C. (Found: C, 54.43; H, 3.01; N, 10.60%.)

iii) *o*-Quaterphenyl (IX): colorless cubes; mp 118—119 °C (lit,[15] mp 118 °C); yield, 1880 mg.

Found: C, 93.87; H, 6.18%; mol wt (Rast), 324. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%; mol wt, 306.

iv) *o*-Sexiphenyl (X): colorless cubes from ethanol; mp 217—217.5 °C (lit,[8] mp 216—217 °C); yield, 249 mg (5.4%). UV: $\lambda_{\max}$ (ε) 192(82100), 231 nm (52200).

Found: C, 94.14; H, 5.98%; mol wt, 451. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

v) 1-Phenyltriphenylene (XI): colorless needles from ethanol; mp 160—161 °C (lit,[34] mp 162 °C); yield, 245 mg.

Found: C, 94.46; H, 5.47%; mol wt, 298. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%; mol wt, 304.

Reaction of II and IV. A mixture of II (8.4 g, 30.0 mmol) and IV (6.0 g, 14.8 mmol) was treated with copper powder (27.0 g, 430 mg-atom) at 270—280 °C for 1 hr. The hot benzene extract of the mixture was then chromatographed on an alumina column in a manner previously described. The three fractions which were eluted with a C–B (5 : 1) mixture gave VII (876 mg), VIII (545 mg), and XVII; the one fraction which was eluted with C–B (5 : 2) afforded XI (158 mg), and a last fraction which was eluted with benzene yielded XIV.

i) *m*-Quaterphenyl (XVII): colorless needles from ethanol; mp 86—87 °C (lit,[6] mp 85.5—86 °C); yield, 1250 mg.

Found: C, 93.80; H, 6.06%; mol wt (Rast), 314. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%; mol wt, 306.

ii) 2-Phenyltriphenylene (XIV): colorless needles from the C–B (5 : 2) mixture; mp 183—183.5 °C (lit,[34] mp 185 °C); yield, 200 mg.

Found: C, 94.74; H, 5.53%; mol wt, 306. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%; mol wt, 304.

Preparation of 2,2′-Di(4-biphenylyl)biphenyl (XIII). A mixture of III (9.8 g, 35 mmol) and IV (7.0 g, 17.5 mmol) was treated with copper powder (32 g, 500 mg-atom) at 265—270 °C for 1 hr and then at 270—280 °C for 1.5 hr. The hot benzene extract of the mixture was treated with the C–B (5 : 2) mixture to separate it into soluble and insoluble parts. Filtration and several crystallizations of the latter from benzene provided XV. The former, after the removal of the solvent, was dissolved in cyclohexane and subjected to chromatography on alumina. The cyclohexane eluted two fractions, which, upon recrystallization from ethanol, afforded VII (406 mg) and VIII (1357 mg). A mixture of C–B (5 : 1) eluted three fractions, which, after recrystallization, provided XII, XIII, and XIV (640 mg).

i) 2,4′-Diphenylbiphenyl (XII): colorless prisms from cyclohexane; mp 116—118 °C (lit,[35] mp 119—119.5 °C); yield, 50 mg.

Found: C, 94.45; H, 5.76%; mol wt, 307. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%; mol wt, 306.

ii) 2,2′-Di(4-biphenylyl)biphenyl (XIII): colorless rhombs from benzene; mp 192—194 °C (lit,[8] mp 189—190 °C); yield, 125 mg (1.6%). UV: $\lambda_{\max}$ (ε) 207 (86700), 240 (sh) (28100), 272 nm (51200).

Found: C, 94.43; H, 5.60%; mol wt, 451. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

iii) *p*-Quaterphenyl (XV): colorless plates from benzene; mp 318—319 °C (lit,[36] mp 317.7—318.7 °C); yield, 2200 mg.

Found: C, 94.38; H, 6.02%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

Preparation of 3,3′-Di(2-biphenylyl)biphenyl (XVI). A mixture of I (3.5 g, 12.5 mmol) and V (2.5 g, 6.2 mmol) was heated with copper powder (13 g, 204 mg-atom) at 260—265 °C for 2 hr and at 270 °C for 1 hr. The hot benzene extract of the mixture was separated into three fractions by chromatography on alumina. A C–B (5 : 3) mixture eluted two fractions, which provided VII (17 mg) and IX (1950 mg). Benzene eluted the third fraction, which, upon recrystallization from methanol, gave XVI. The elution with benzene afforded a colorless oil which was unidentified (1210 mg).

3,3′-Di(2-biphenylyl)biphenyl (XVI): colorless needles; mp 151.5—152 °C; yield, 155 mg (5.5%). UV: $\lambda_{\max}$ (ε) 194 (86500), 237 (74100), 252 nm(sh)(45400).

Found: C, 94.43; H, 5.90%; mol wt, 458. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

Preparation of m-*Sexiphenyl (XVIII).* A mixture of II (2.8 g, 10 mmol) and V (2.0 g, 5 mmol) was treated with copper powder (10 g, 160 mg-atom) under conditions similar to those used in the preparation of XVI. The hot benzene extract of the reaction mixture was chromatographed on an alumina column in the manner previously described. The two fractions which were eluted with a C–B (5 : 2) mixture gave VII (159 mg) and XVII (440 mg) respectively, while the next fraction, which was eluted with C–B (5 : 3), afforded XVIII.

m-Sexiphenyl (XVIII): colorless needles from cyclohexane; mp 145—146 °C (lit,[8] mp 146—147 °C); yield, 195 mg (8.6%). UV: $\lambda_{\max}$ (ε) 196 (72800), 205 (72300), 249 nm (101700).

Found: C, 94.05; H, 5.78%; mol wt (Rast), 465. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

Preparation of 3,3′-Di(4-biphenylyl)biphenyl (XX). A mixture of III (3.7 g, 13 mmol) and V (2.7 g, 6.6 mmol) was treated with copper powder (9.5 g, 150 mg-atom) at 260 °C for 1 hr and then at 280 °C for an additional hour. The hot benzene extract of the reaction mixture was digested with 120 ml of the C–B (5 : 2) mixture to give soluble and insoluble parts. Upon filtration, the filtrate was chromatographed on alumina, with the same solvent as the eluent, to give VII (8 mg) and XIX. The insoluble part was dissolved in benzene and then subjected to chromatography on alumina with benzene. Several crystallizations of the eluate afforded XX and XV (57 mg).

i) 3,4′-Diphenylbiphenyl (XIX): colorless needles from ethanol; mp 164—165 °C (lit,[4] mp 166—167 °C); yield, 201 mg.

Found: C, 94.04; H, 6.12%; mol wt (Rast), 309. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%; mol wt, 306.

ii) 3,3′-Di(4-biphenylyl)biphenyl (XX): colorless small plates from benzene; mp 257—258 °C (lit,[8] mp 247.5 °C); yield, 295 mg (9.7%). UV: $\lambda_{\max}$ (ε) 206 (79800), 273 nm (71200).

Found: C, 94.34; H, 5.83%; mol wt (Rast), 461. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

Preparation of 4,4′-Di(2-biphenylyl)biphenyl (XXI). A mixture of I (4.2 g, 15 mmol) and VI (3.0 g, 7.4 mmol) was heated with copper powder (15 g, 236 mg-atom), as has been described in the preparation of XVIII. The benzene extract was chromatographed on alumina in a manner previously used. A C–B (5 : 2) mixture eluted three fractions, which, upon treatment as above, gave VII (47 mg), IX (1063 mg), and XXI. Benzene eluted one fraction, which, upon recrystallization from benzene, provided XV (164 mg).

4,4′-Di(2-biphenylyl)biphenyl (XXI): colorless plates from benzene; mp 233—236 °C (lit,[10] mp 237.9—238.1 °C); yield, 304 mg (9.0%). UV: $\lambda_{\max}$ (ε) 202 (98700), 205 (sh) (97000), 250 (35700), 297 nm (38900).

Found: C, 94.08; H, 5.70%; mol wt (Rast), 470. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

Preparation of 4,4′-Di(3-biphenylyl)biphenyl (XXII). A mixture of II (6.3 g, 22.5 mmol) and VI (4.5 g, 11 mmol) was treated with copper powder (22.5 g, 350 mg-atom) as has been described in the preparation of XX. The benzene extract of the mixture was digested with 150 ml of the C–B (5 : 2) mixture to separate it into soluble [A] and insoluble [B] parts. After filtration, the filtrate was chromatographed on alumina, with the same solvent as the eluent, to give VII (510 mg) and XVII (1470 mg); further elution with benzene gave XIX (410 mg) and XXII. The insoluble part [B] and the xylene extract of the reaction mixture also gave additional XXII after chromatography on alumina with benzene, followed by several recrystallizations.

4,4′-Di(3-biphenylyl)biphenyl (XXII): slender, colorless plates from benzene; mp 287—288 °C (lit,[9] mp 280—281 °C; lit,[10] mp 287—288 °C); yield, 710 mg (14.0%). UV: $\lambda_{\max}$ (ε) 204 (80000), 256 (41700), 296 nm (51900).

Found: C, 94.13; H, 5.84%; mol wt, 465. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%; mol wt, 458.

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References

1) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.
2) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).
3) H. Suzuki, This Bulletin, **32**, 1340 (1959).
4) G. F. Woods and I. W. Tucker, *J. Amer. Chem. Soc.*, **70**, 3340 (1948).
5) W. Ried and D. Freitag, *Angew. Chem. Int. Ed. Engl.*, **7**, 835 (1968).
6) G. F. Woods and F. T. Reed, *J. Amer. Chem. Soc.*, **71**, 1348 (1949).
7) Cade has reported lower melting points 189—190 °C for XIII and 247.5 °C for XX (Ref. 8).
8) J. A. Cade and A. Pilbeam, *J. Chem. Soc.*, **1964**, 114.
9) G. F. Woods, D. D. Centola, H. E. Ruskie, and C. D. Miller, *J. Amer. Chem. Soc.*, **82**, 5227 (1960).
10) C. Beaudet, J. Horlait, A. Marcq, and G. Belpaire, *EUR* 31. f (1962).
11) Woods has noted lower melting point 280—281 °C (Ref. 9).
12) These by-products VII, IX, XI, XV, XVII, and XIX were identified by means of the mixed melting point measurements with each of authentic samples.
13) Some close correlations between the structure of polyphenyls and the order of their elution were observed in the chromatographic separation of the products. The result will be reported later.
14) The assignment agrees with those of Dale, Stewart, and others (Ref. 15—17). It seems inadequate to assign them as C–H out-of-plane bending bands of terminal rings as noted by Doss and Solomon (Ref. 18, 19).
15) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).
16) J. E. Stewart and M. Hellmann, *J. Res. Natl. Bur. Stand.*, **60**, 125 (1958).
17) S. Sandroni and F. Geiss, *Z. Anal. Chem.*, **220**, 321 (1966).
18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y. (1954), p. 64.
19) R. C. Doss and P. W. Solomon, *J. Org. Chem.*, **29**, 1567 (1964).
20) G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).
21) E. Ibuki, S. Ozasa, Y. Fujioka, M. Maeda, and Y. Hayashi, presented at The 91st Annual Meeting of the Pharm. Soc. of Japan, Fukuoka, April 8, 1971.

22) R. L. Alexander, *J. Org. Chem.*, **21**, 1464 (1956).

23) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd Ed., John Wiley & Sons, Inc., New York·London·Sydney (1967), p. 152.

24) H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Amer. Chem. Soc.*, **51**, 2252 (1929).

25) J. Elks, J. W. Haworth, and D. H. Hey, *J. Chem. Soc.*, **1940**, 1284.

26) S. E. Hazlet and C. A. Dornfeld, *J. Amer. Chem. Soc.*, **66**, 1781 (1944).

27) E. Campaigne and Wm. B. Reid, *ibid.*, **68**, 1663 (1946).

28) W. Schlenk, *Ann. Chem.*, **368**, 295 (1909).

29) R. C. Fuson and E. A. Cleveland, "Organic Syntheses," Coll. Vol. III, p. 339 (1955).

30) F. B. Dains and F. Eberly, *ibid.*, Coll. Vol. II, p. 355 (1943).

31) L. Mascarelli and M. Piroma, *Gazz. Chim. Ital.*, **68**, 117 (1938).

32) C. Willgerodt and G. Hilgenberg, *Ber.*, **42**, 3826 (1909).

33) W. S. Rapson, R. G. Shuttleworth, and J. N. van Niekerk, *J. Chem. Soc.*, **1943**, 326.

34) P. G. Copeland, R. E. Dean, and D. McNen, *ibid.*, **1960**, 4522.

35) G. F. Woods and F. Scotti, *J. Org. Chem.*, **26**, 312 (1961).

36) J. J. E. Schmidt and J. A. Krimmel, *ibid.*, **25**, 252 (1960).