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Syntheses and Physical Properties of Several Octiphenyls and a Septiphenyl[1]

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Six symmetrical linear octiphenyls were synthesized by the Ullmann homo-coupling reaction of iodoquaterphenyl. Another satisfactory method for synthesizing octiphenyls is also described, *i.e.*, a Kharash-type Grignard cross-coupling of biphenylylmagnesium bromide and diiodoquaterphenyl in the presence of bis(acetylacetonato)nickel(II). Moreover, *m*-septiphenyl was successfully synthesized by deamination of the corresponding amino compound. Infrared studies of the polyphenyls indicated that the fine-structure bands in the regions of 770—810 and 870—915 cm^{-1} may be considered as indicators of the presence of consecutive *m*-phenylene rings, regardless of the existence of *o*- or *p*-phenylene rings. The ultraviolet spectra of the octiphenyls, which contain two kinds of linkages, showed absorption curves closely related to those of quaterphenyls corresponding to the structural units of the former compounds. The nuclear magnetic resonance spectra of the polyphenyls without an *o*-phenylene ring showed multiplet peaks due to the resonances of an isolated *m*-phenylene proton at the lowest field within a narrow region (δ 7.81—7.95). Hückel molecular orbital calculations of the longest wavelength absorption bands of ten polyphenyls were carried out. The calculated and observed wavelengths were in rather good agreement except for the cases of three compounds.

Keywords——Ullmann reaction; Ni-complex-catalyzed cross-coupling; octiphenyls; septiphenyl; IR; UV; NMR; MO; quaterphenyl derivatives; polyphenyls

In previous studies,[3] in order to investigate the relationship between the structure and the physical properties of polyphenyls, we synthesized a series of linear quinque- and sexiphenyls and investigated their infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectral characteristics.

In the present work, six symmetrical linear octiphenyls (**1**—**6**) and one septiphenyl (**7**) were synthesized to investigate the spectral characteristics of polyphenyls larger than sexiphenyls. The Ullmann homo-coupling, a new Grignard cross-coupling reaction, and the arylamine deamination reaction were used for the syntheses of these polyphenyls. The IR, UV, and NMR spectra of the polyphenyls were measured, and the relationship between the number and arrangement of the benzene rings and their spectral properties was analyzed. In addition, HMO calculations of the longest wavelength absorption bands of these polyphenyls and closely related sexiphenyls were performed. The calculated results were compared with the observed values.

On the basis of the previous work,[3a,c] the Ullmann homo-coupling of appropriate iodoquaterphenyls was adopted to synthesize the six octiphenyls (**1**—**6**). Thus, the intermediate nitroquaterphenyls (**13a**—**18a**) were prepared by the Ullmann cross-coupling of iodobiphenyls (**8**—**10**) and iodonitrobiphenyls (**11** and **12**). The nitro compounds thus prepared were converted into the iodo compounds (**13c**—**18c**) *via* the corresponding amines (**13b**—**18b**), and then each of the iodoquaterphenyls was subjected to the Ullmann homo-coupling reaction. The

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[1] This paper forms Part IV of "Studies of Polyphenyls and Polyphenylenes." The preceding paper, Part III: E. Ibuki, S. Ozasa, Y. Fujioka, and H. Kitamura, *Chem. Pharm. Bull.*, **28**, 1468 (1980).

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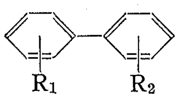
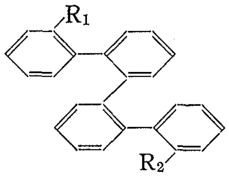
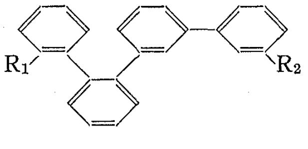
[3] *a*) E. Ibuki, S. Ozasa, and K. Murai, *Bull. Chem. Soc. Jpn.*, **48**, 1868 (1975); *b*) S. Ozasa, N. Hatada, Y. Fujioka, and E. Ibuki, *ibid.*, **53**, 2610 (1980); *c*) E. Ibuki, S. Ozasa, Y. Fujioka, and H. Kitamura, *Chem. Pharm. Bull.*, **28**, 1468 (1980).



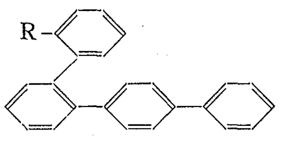
8: $R_1=2\text{-I}, R_2=H$
9: $R_1=3\text{-I}, R_2=H$
10: $R_1=4\text{-I}, R_2=H$
11: $R_1=2\text{-I}, R_2=2'\text{-}NO_2$
12: $R_1=3\text{-I}, R_2=3'\text{-}NO_2$
22: $R_1=2\text{-Br}, R_2=H$
23: $R_1=3\text{-Br}, R_2=H$
27a: $R_1=3\text{-}NO_2, R_2=3'\text{-}C_6H_5$
27b: $R_1=3\text{-}NH_2, R_2=3'\text{-}C_6H_5$
27c: $R_1=3\text{-I}, R_2=3'\text{-}C_6H_5$
31: $R_1=4\text{-}C_6H_5, R_2=4'\text{-}C_6H_5$
34: $R_1=R_2=H$



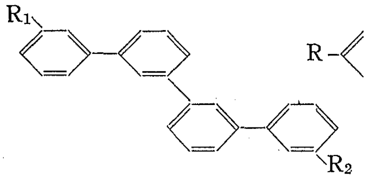
1: $R_1=$ ┬, $R_2=H$
13a: $R_1=NO_2, R_2=H$
13b: $R_1=NH_2, R_2=H$
13c: $R_1=I, R_2=H$
35: $R_1=R_2=H$
36: $R_1=R_2=NO_2$



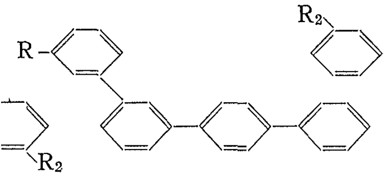
2: $R_1=$ ┬, $R_2=H$
14a: $R_1=NO_2, R_2=H$
14b: $R_1=NH_2, R_2=H$
14c: $R_1=I, R_2=H$
4: $R_1=H, R_2=$ ┬
16a: $R_1=H, R_2=NO_2$
16b: $R_1=H, R_2=NH_2$
16c: $R_1=H, R_2=I$
37: $R_1=R_2=H$



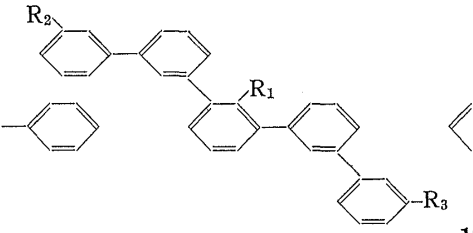
3: $R=$ ┬
15a: $R=NO_2$
15b: $R=NH_2$
15c: $R=I$
32: $R=H$



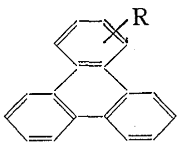
5: $R_1=$ ┬, $R_2=H$
17a: $R_1=NO_2, R_2=H$
17b: $R_1=NH_2, R_2=H$
17c: $R_1=I, R_2=H$
21a: $R_1=R_2=NO_2$
21b: $R_1=R_2=NH_2$
21c: $R_1=R_2=I$
30: $R_1=R_2=H$



6: $R=$ ┬
18a: $R=NO_2$
18b: $R=NH_2$
18c: $R=I$
33: $R=H$



7: $R_1=H, R_2=R_3=C_6H_5$
28a: $R_1=NO_2, R_2=R_3=C_6H_5$
28b: $R_1=NH_2, R_2=R_3=C_6H_5$
26: $R_1=R_2=R_3=H$
25a: $R_1=NO_2, R_2=R_3=H$
25b: $R_1=NH_2, R_2=R_3=H$
29: $R_1=R_3=H, R_2=C_6H_5$



19: $R=1\text{-}C_6H_5$
20: $R=2\text{-}C_6H_5$

TABLE I. Syntheses of Octiphenyls

Reactant	Procedure[a]	Octiphenyl (Yield, %)	Other products
13c	A	**1**(3)	**19**, **35**
14c	A	**2**(23)	**19**, **20**, **37**
15c	A	**3**(12)	**20**, **32**
16c	A	**4**(60)	**37**
22+**21c**	B	**4**(79)	**34**, **35**
17c	A	**5**(54)	**30**
23+**21c**	B	**5**(70)	**30**, **34**
18c	A	**6**(63)	**33**

a) A: Ullmann reaction, B: Grignard reaction.

octiphenyls and by-products[4] thus obtained are shown in Table I.

Three octiphenyls (**4**—**6**) were obtained in good yields (54—63%) without any significant by-product formation. In the cases of the remaining three octiphenyls (**1**[5]—**3**), however, the yields (3—23%) were unsatisfactory due to the competitive formation of 1- (**19**) and/or 2-phenyltriphenylene (**20**), apparently *via* intramolecular elimination of hydrogen iodide.

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4) These by-products were identified by mixed-melting-point determination and comparison of the IR and UV spectra with those of authentic samples (Ref. 3).

5) Wittig and Klar reported the low-yield formation of *o*-octiphenyl (1.8%) by the reaction of 2,2'-dilithiumbiphenyl with cuprous chloride (Ref. 6).

In 1972, Corriu and Masse[7] reported that the reaction of phenylmagnesium bromide and *p*-dibromobenzene, with bis(acetylacetonato)nickel (II) as a catalyst, gave *p*-terphenyl in 80% yield. Thus, the Kharash-type Grignard cross-coupling reaction in the presence of the Ni-complex was tested and found to be a new and effective synthetic procedure for octiphenyls (**4** and **5**). The intermediate diiodoquaterphenyl (**21c**) was obtained from the corresponding dinitroquaterphenyl (**21a**) prepared by the Ullmann homo-coupling of **12**. The reaction of **21c** with Grignard reagent derived from **22** in the presence of the Ni-complex provided **4** (79%). Analogously, the octiphenyl **5** was obtained in 70% yield[8] by the reaction of **21c** with 3-biphenylylmagnesium bromide (Table I). These results suggest that the Kharash-type reaction in the presence of the Ni-complex catalyst is an excellent method for octiphenyl synthesis.

An alternative synthetic method for polyphenyls, the method involving the deamination of arylamines, was also attempted. The nitroquinquephenyl (**25a**), obtained by the Ullmann cross-coupling of **9** and 1,3-dibromo-2-nitrobenzene (**24**), gave **26** in 60% yield *via* reduction to the corresponding amine (**25b**) followed by deamination. Therefore, the deamination reaction was utilized for the synthesis of **7**. The nitroseptiphenyl (**28a**), obtained by the Ullmann reaction of **27c** and **24**, was converted into the corresponding amine (**28b**), and then deamination of **28b** gave **7** (17%). The low yield of **7** compared with that of **26** may be ascribed to the poor solubility of **28b** in an acidic solution. These results, however, suggest that the deamination reaction is efficient for the preparation of odd-numbered symmetrical linear polyphenyls having an *m*-phenylene ring located in the middle of their structures.

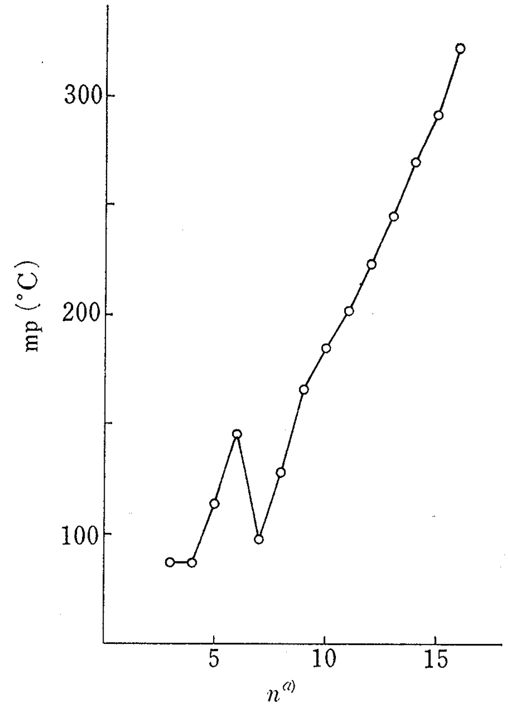

Fig. 1. Melting Points of *m*-Polyphenyls

a) *n*: Number of benzene rings. For compounds with *n*=9 to 16, refer to ref. 13.

The polyphenyls (**1**—**7**), thus prepared, gave satisfactory analytical results and spectral (IR and MS) data consistent with their proposed structures. Alternative syntheses of two of the octiphenyls have been reported earlier by other workers (**1**[6,9] and **5**[10]). Though the melting point of **1** does not coincide with that reported by the previous authors,[11] that of **5** falls within about 2° of the reported values.[10] The melting points of *m*-polyphenyls containing 3—16 benzene rings are shown in Fig. 1. The lower melting point of *m*-octiphenyl compared with *m*-sexiphenyl has already been pointed out.[12] The present synthesis of the hitherto unknown *m*-septiphenyl (**7**) to led us discover that the melting point of **7** is lower than those of *m*-octi- and *m*-sexiphenyls, though the reason for this is not clear at present. However, it

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[6] G. Wittig and G. Klar, *Ann. Chem.*, **704**, 91 (1967).

[7] R.J.P. Corriu and J.P. Masse, *J. Chem. Soc.*, *Chem. Commun.*, **1972**, 144.

[8] These octiphenyls (**4** and **5**) were identified by mixed-melting-point determination and comparison of the IR and UV spectra with those of the samples prepared by Ullmann homo-coupling.

[9] G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).

[10] *a)* R.L. Alexander, Jr., *J. Org. Chem.*, **21**, 1464 (1956); *b)* M. Bennette, N.B. Sunshine, and G.F. Woods, *ibid.*, **28**, 2514 (1963).

[11] Wittig *et al.* have reported different melting points for **1** (287—290° and 312—320°) (Refs. 6 and 9).

[12] W. Ried and D. Freitag, *Angew. Chem. Int. Ed. Engl.*, **7**, 835 (1968).

[13] M. Busch and W. Weber, *J. prakt. Chem.*, **146**, 1 (1936).

Table II. Positions and Tentative Assignments of Characteristic Bands in the IR Spectra (680—915 cm^{-1}) of Septi- and Octiphenyls[a)]

2	698 sh, s	$\gamma_{\text{C-C}}$
	703 s	
	716 w	
	737 sh, m	$\gamma_{\text{C-H}}$ (M, *o*)
	747 s	
	752 sh, s	
	765 m	
	775 m	$\gamma_{\text{C-H}}$ (*o*)
	805 m	$\gamma_{\text{C-H}}$ (*m*)
	821 vw	
	843 vw	
	876 w	
	898 m	$\gamma_{\text{C-H}}$ (*m*)
	901 m	
3	686 m	$\gamma_{\text{C-C}}$
	698 s	
	712 w	
	727 m	
	739 sh, m	$\gamma_{\text{C-H}}$ (M, *o*)
	749 s	
	759 sh, s	
	770 sh, s	$\gamma_{\text{C-H}}$ (*o*)
	773 s	
	839 s	$\gamma_{\text{C-H}}$ (*p*)
	873 w	
4	699 s	$\gamma_{\text{C-C}}$
	708 s	
	728 vw	
	743 sh, s	$\gamma_{\text{C-H}}$ (M, *o*)
	746 s	
	749 s	
	758 sh, s	
	761 s	
	779 s	$\gamma_{\text{C-H}}$ (*o*)
	786 s	$\gamma_{\text{C-H}}$ (*m*)
	799 w	
	805 m	
	810 m	
	821 w	
	841 w	
	849 vw	
	877 vw	$\gamma_{\text{C-H}}$ (*m*)
	899 m	
	908 m	
6	692 sh, s	$\gamma_{\text{C-C}}$
	697 s	
	705 sh, m	
	728 m	
	752 m	$\gamma_{\text{C-H}}$ (M)
	767 s	
	784 sh, m	$\gamma_{\text{C-H}}$ (*m*)
	788 m	
	796 sh, w	
	808 w	
	841 m	$\gamma_{\text{C-H}}$ (*p*)
	870 w	$\gamma_{\text{C-H}}$ (*m*)
	886 sh, w	
	891 w	
	905 vw	
7	693 sh, s	$\gamma_{\text{C-C}}$
	698 s	
	703 s	
	740 sh, w	$\gamma_{\text{C-H}}$ (M)
	752 sh, s	
	755 s	
	773 s	$\gamma_{\text{C-H}}$ (*m*)
	785 m	
	791 sh, m	
	805 m	
	808 sh, m	
	845 m	
	875 m	$\gamma_{\text{C-H}}$ (*m*)
	886 m	
	894 m	
	912 w	

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

may be ascribed to the presence of rotational stereoisomers in *o*-octiphenyl, as noted by Ried and Freitag.[12)]

The IR spectra of the seven polyphenyls were measured by the KBr-disk method. The characteristic bands of five polyphenyls (**2**—**4**, **6**, and **7**) in the 680—915 cm^{-1} region are listed in Table II. These bands are consistent with the kinds of benzene rings constituting each of the polyphenyls.

In the spectra of **5**—**7**, which contain no *o*-phenylene rings, the strong or medium bands in the range 740—767 cm^{-1} were assigned to the C-H out-of-plane deformation vibrations of the terminal rings. The strong bands observed in the spectra of **1** (at 769 and 776 cm^{-1}), **2** (at 775 cm^{-1}), **3** (at 770 and 773 cm^{-1}), and **4** (at 779 cm^{-1}) can be assigned to the C–H out-of-plane bending vibrations of *o*-phenylene rings, as suggested by Sandroni and others.[14)] The prominent bands of **1**—**4** in the region of 733—765 cm^{-1} should be due not only to the C–H out-of-plane bending vibrations of the terminal rings, but also to those of their *o*-phenylene rings, as discussed in the previous paper.[3a)]

In the spectra of **3** and **6**, strong or medium C–H out-of-plane bending vibration bands of two adjacent ring hydrogens were observed at 839 and 841 cm^{-1}, respectively.

In the spectrum of **2**, medium C–H out-of-plane bending vibration bands of three adjacent hydrogens and an isolated hydrogen of *m*-phenylene rings were observed at 805, and at 898 and 901 cm^{-1}, respectively. In the case of **4**—**7**, which contain four to six consecutive *m*-phenylene rings, characteristic fine-structure C–H bands were observed in the 771—810 cm^{-1} region, as pointed out by Stewart and others.[14)] In addition, fine structures were also

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[14)] S. Sandroni and F. Geiss, *Z. Anal. Chem.*, **220**, 321 (1966); J.E. Stewart and M. Hellmann, *J. Res. Natl. Bur. Stand.*, **60**, 125 (1958).

observed in the 870—915 cm^{-1} region. The results indicated that fine-structure bands which increase in complexity in accordance with the number of *m*-phenylene rings appear in both regions (770—810 and 870—915 cm^{-1}) in the spectra of polyphenyls containing consecutive *m*-phenylene rings, regardless of the presence of *o*- or *p*-phenylene rings in them.

The MS spectra of the septiphenyl and the six octiphenyls invariably showed a molecular ion corresponding to a molecular weight of 534 or 610 as the most abundant ion.

The NMR spectra of the polyphenyls and closely related compounds were measured at 80 MHz in $CDCl_3$ solution, and the chemical shifts are summarized in Table III.

TABLE III. NMR Spectral Data for **1**—**7** and Related Compounds in $CDCl_3$[a]

26	7.84—7.93 (3H, m, *m*-C_6H), 7.32—7.75 (19H, m, *m*-C_6H_3 and C_6H_5)
29	7.83—7.93 (4H, m, *m*-C_6H), 7.31—7.76 (22H, m, *m*-C_6H_3 and C_6H_5)
7	7.83—7.95 (5H, m, *m*-C_6H), 7.31—7.76 (25H, m, *m*-C_6H_3 and C_6H_5)
5	7.84—7.95 (6H, m, *m*-C_6H), 7.32—7.76 (28H, m, *m*-C_6H_3 and C_6H_5)
ϕpmmpϕ[b,c]	7.89—7.94 (2H, m, *m*-C_6H), 7.73 (8H, s, *p*-C_6H_4), 7.33—7.77 (16H, m, *m*-C_6H_3 and C_6H_5)
ϕmppmϕ[c]	7.83—7.90 (2H, m, *m*-C_6H), 7.76 (8H, s, *p*-C_6H_4), 7.33—7.72 (16H, m, *m*-C_6H_3 and C_6H_5)
6	7.88—7.94 (4H, m, *m*-C_6H), 7.71 (8H, s, *p*-C_6H_4), 7.33—7.77 (22H, m, *m*-C_6H_3 and C_6H_5)
4	7.16 (10H, s, C_6H_5), 7.05—7.59 (24H, m, *o*-C_6H_4 and *m*-C_6H_4)
ϕoooϕ[d]	5.93—7.43 (22H, m, all protons)
ϕooooϕ	5.62—7.31 (26H, m, all protons)[e]
1	5.61—7.35 (34H, m, all protons)
2	5.74—7.46 (34H, m, all protons)
3	5.73—7.72 (34H, m, all protons)

a) δ (ppm) from internal standard TMS.
b) ϕ, p, m, and o refer to phenyl and to *p*-, *m*-, and *o*-phenylene rings, respectively.
c), *d*), and *e*) refer to refs. 3*a*, 16, and 3*c*.

The lowest field multiplet peaks (δ 7.83—7.95) found commonly in the spectra of **5**—**7**, **26**, **29**, and closely related sexiphenyls, 3,3'-di(4-biphenylyl)biphenyl[3a] and 4,4'-di(3-biphenylyl)biphenyl,[3a] may be assigned to isolated *m*-phenylene protons by comparison with the signals of *m*-quaterphenyl (**30**) (δ 7.81—7.88, 2H, m, *m*-C_6H).[3b]

The spectrum of **4** shows one singlet peak at δ 7.16, which can be assigned to the protons of phenyl groups adjacent to *o*-phenylene rings by comparison with the phenyl proton signal of *o*-terphenyl (δ 7.17, 10H, s, C_6H_5)[3b] and 3,3'-di(2-biphenylyl)biphenyl (δ 7.18, 10H, s, C_6H_5).[3c]

The spectra of **6**, 3,3'-di(4-biphenylyl)biphenyl,[3a] and 4,4'-di(3-biphenylyl)biphenyl,[3a] which contain two *p*-phenylene rings, each display one singlet peak near δ 7.73 assignable to *p*-phenylene protons by comparison with the signals of *p*-terphenyl (δ 7.68, 4H, s, *p*-C_6H_4)[3b] and *p*-quaterphenyl (**31**) (δ 7.71, 8H, s, *p*-C_6H_4).[3b]

The remaining multiplet peaks in all spectra are difficult to assign. Among them, the proton signals of five polyphenyls (**1**—**3**, *o*-quinque-[15] and *o*-sexiphenyl[3c]), however, are extended to the high field side compared with those of other polyphenyls. These marked high field shifts may reflect the ring current effects caused by benzene rings spatially close to one another, because the compounds containing consecutive *o*-phenylene rings exist in crowded conformations.

These and previous results[3b] show that an isolated *m*-phenylene proton in compounds which contain no *o*-phenylene ring appears as a multiplet peak in a narrow region at the lowest field (δ 7.81—7.95).

The UV spectra of the seven polyphenyls were measured in cyclohexane solution. The absorption curves are shown in Figs. 2—5. All of the polyphenyls displayed the E-band in the fairly narrow region of 191—205 nm and the K-band in the broad region of 225—276 nm.

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15) E. Ibuki, S. Ozasa, Y. Fujioka, M. Okada, and Y. Yanagihara, unpublished work.

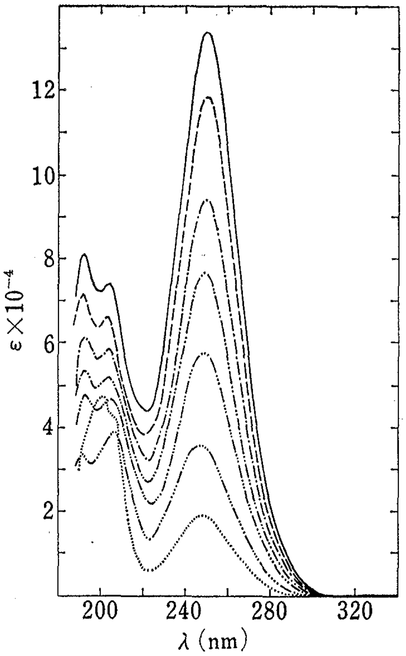

Fig. 2. UV Spectra of Biphenyl and *m*-Polyphenyls in Cyclohexane

———: *m*-Octiphenyl (**5**),
-------: *m*-septiphenyl (**7**),
—·—·—: *m*-sexiphenyl (**29**),
—··—··: *m*-quinquephenyl (**26**),
— ··· —: *m*-quaterphenyl (**30**),
—···—: *m*-terphenyl,
········: biphenyl (**34**).

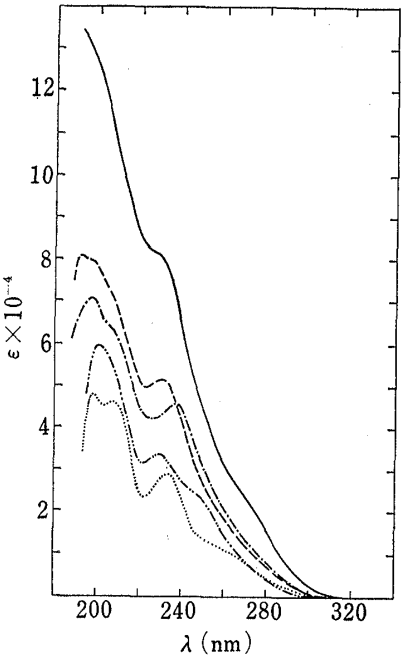

Fig. 3. UV Spectra of *o*-Polyphenyls in Cyclohexane

———: *o*-Octiphenyl (**1**),
-------: *o*-sexiphenyl,
—·—·—: *o*-quinquephenyl,
—··—··: *o*-quaterphenyl (**35**),
········: *o*-terphenyl.

The spectra of **5** and **7** displayed very intense K-bands at 249 nm. Jaffé and Orchin[16] have pointed out that the *m*-polyphenyls absorb at substantially the same wavelength but with an intensity which is approximately proportional to the maximum number of separate biphenyl groupings possible. This has been demonstrated by the near constancy (21000) of $\varepsilon/(n-1)$, except in the case of compounds containing 4—8 benzene rings. In the present study, the $\varepsilon/(n-1)$ values of the six *m*-polyphenyls (ter- to octiphenyl) were *ca.* 19000 (Table IV and Fig. 2).

In the spectrum of **1**, the K-band was only observed as a shoulder at 225 nm ($\varepsilon=82700$). The *o*-polyphenyls absorb at a similar wavelength (near 230 nm) and their intensity increases with the number of rings (Fig. 3).

The spectrum of **2**, in which both terminals of four consecutive *o*-phenylene rings are linked to *m*-phenylene rings, displayed a slight red shift and an increase of the intensity of the K-band (235 nm, $\varepsilon=80100$) as compared with *o*-sexiphenyl (231, 52200), because of the additional two *m*-phenylene rings. In the spectrum of **4**, a blue shift and a slight increase in the intensity of the K-band (238, 107700) as compared with **29** (249, 95200) were observed, presumably because two *o*-phenylene rings are linked to each terminal of the four consecutive *m*-phenylene rings. In addition, in both spectra, the characteristic bands of *m*-polyphenyls near 250 nm were observed only as a shoulder. Furthermore, these spectra showed absorption curves closely related to that of **37** (237 and 251 (sh) nm; $\varepsilon=49500$ and 32400), which has *o*- and *m*-linkages (Fig. 4).

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[16] H.H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, 1962, p. 273.

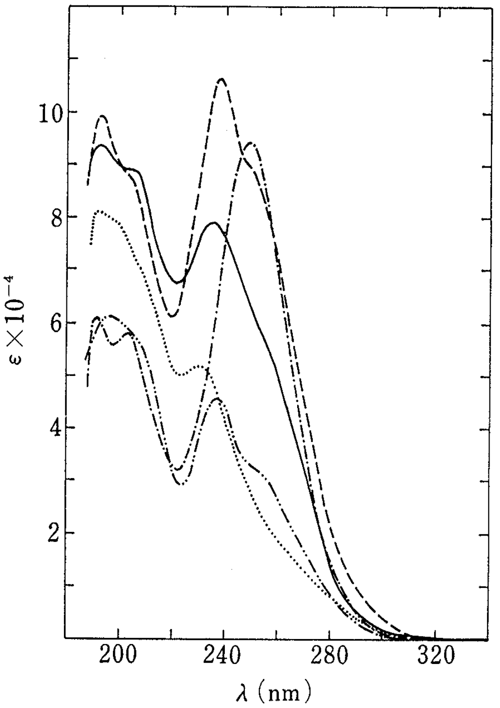

Fig. 4. UV Spectra of Quaterphenyl, Sexiphenyls and Octiphenyls in Cyclohexane

——— : 2,2'''-Di(3-biphenylyl)-*o*-quaterphenyl (**2**),
– – – – : 3,3'''-di(2-biphenylyl)-*m*-quaterphenyl (**4**),
········ : *o*-sexiphenyl,
—·—·— : *m*-sexiphenyl (**29**),
—··—·· : 2,3'-diphenylbiphenyl (**37**).

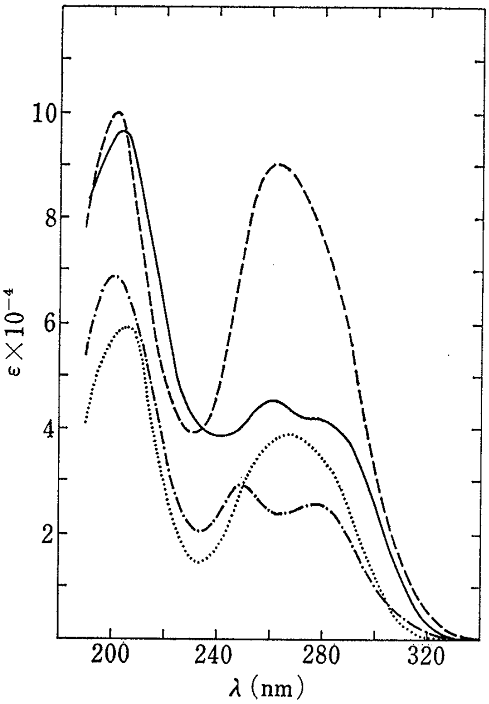

Fig. 5. UV Spectra of Quaterphenyls and Octiphenyls in Cyclohexane

——— : 2,2'''-Di(4-biphenylyl)-*o*-quaterphenyl (**3**),
– – – – : 3,3'''-di(4-biphenylyl)-*m*-quaterphenyl (**6**),
—·—·— : 2,4'-diphenylbiphenyl (**32**),
········ : 3,4'-diphenylbiphenyl (**33**).

TABLE IV. UV Spectra of Biphenyl and *m*-Polyphenyls in Cyclohexane

$n^{a)}$	λ_{max} (nm)	ε	ε/n-1
2	248	18500	18500
3	247	36100	18100
4	248	57400	19100
5	249	77600	19400
6	249	95200	19000
7	249	118200	19700
8	249	135100	19300

a) *n*: Number of benzene rings.

The spectra of **3** (*o*- and *p*-linkages) and **6** (*m*- and *p*-linkages) showed absorption curves closely related to those of **32** (249 and 277; 27100 and 23000) and **33** (268, 37700), which correspond to the structural units of **3** and **6**, respectively (Fig. 5).

These results suggest that the spectra of the octiphenyls in which two kinds of linkages are present show absorption curves closely related to those of quaterphenyls corresponding to their structural units.

The calculated and observed longest wavelength bands of the polyphenyls and closely related compounds are compared in Table V. The HMO calculations were performed by assuming the dihedral angle of the pivot bond to be as follows: 50° for phenyl—*o*- and *o*—*o*-

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17) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957); H. Suzuki, *Bull. Chem. Soc. Jpn.*, 32, 1340 (1959); 33, 109 (1960).

TABLE V. Calculated and Observed Longest Wavelenght Absorption Bands of Polyphenyls and Related Compounds

Compound	Calcd trans. energy β[a]	Absorption band		
		Calcd	Obsd	
		λ_{max} (nm)	λ_{max} (nm)	ε
ϕoϕ[b]	−1.4810	226[c]	251 sh	13300
35	−1.4192	236[c]	245	25600
ϕoooϕ[d]	−1.3834	242	237	45900
ϕooooϕ[e]	−1.3610	246	231	52200
1	−1.3354	251	225 sh	82700
2	−1.2932	259	254 sh	58300
3	−1.1968	280	276 sh	41900
ϕmϕ	−1.3564	247[c]	247	36100
30	−1.3222	253[c]	248	57400
26	−1.3048	257[c]	249	77600
29	−1.2948	259	249	95200
7	−1.2886	260	249	118200
5	−1.2844	261	249	135100
4	−1.2945	259	249 sh	90300
6	−1.2018	279	262	89100

a) A mean value of −3.70 eV for β was calculated from the absorption bands of biphenyl and the first four *p*-polyphenyls.
b) ϕ, o, and m refer to phenyl and to *o*-, and *m*-phenylene rings, respectively.
c), *d*), and *e*) refer to refs. 3*b*, 16, and 3*a*.

phenylene linkages, 35° for *o*—*p*- and *m*—*p*-phenylene linkages, and 20° for other linkages.[3b,17] The resonance integrals (π—π) were used the values of cos θ of these dihedral angles, respectively. The table shows rather good agreement between the calculated and observed wavelengths, except in the cases of *o*-terphenyl, *o*-sexiphenyl, **1**, and **6**.

Experimental

All melting points and boiling points are uncorrected. UV spectra were measured on a Shimadzu MPS-50L spectrophotometer, IR spectra on a Leitz III-G spectrometer, and NMR spectra on a Varian CFT-20 spectrometer at 80 MHz using tetramethylsilane as an internal standard. MS spectra were recorded on a Hitachi RMU-6E mass spectrometer.

2- (**8**), 3- (**9**), and 4-Iodobiphenyl (**10**) were prepared as reported previously.[3a] 2- (**22**) and 3-Bromobiphenyl (**23**) were prepared by the Sandmeyer reaction of the corresponding aminobiphenyls;[3a] **22**, bp 123—125° (2 mmHg) (lit.[18] bp 160° (11 mmHg)); **23**, bp 127—130° (3 mmHg) (lit.[19] bp 158—167° (11 mmHg)).

2-Iodo-2′-nitrobiphenyl (**11**)——2,2′-Dinitrobiphenyl[3a] was partially reduced with sodium polysulfide in ethanol by a method similar to that of Purdie[20] to give 2-amino-2′-nitrobiphenyl; mp 64—65° (lit.[21] mp 64—64.5°); yield, 50%. The aminonitro compound was converted into **11** in the usual manner; pale yellow plates from ethanol; mp 81.5—82.5° (lit.[22] mp 81—82°); yield, 51%. *Anal.* Calcd for $C_{12}H_8NO_2I$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.28; H, 2.68; N, 4.54.

3-Iodo-3′-nitrobiphenyl (**12**)——3-Amino-3′-nitrobiphenyl (bp 224—226° (2 mmHg)) was obtained from 3,3′-dinitrobiphenyl[3a] by partial reduction[23] with sodium disulfide in benzene. The amine was transformed into **12** in the usual manner; pale yellow needles from ethanol; mp 95—96.5° (lit.[24] mp 96—97°); yield, 21% (based on 3,3′-dinitrobiphenyl). *Anal.* Calcd for $C_{12}H_8NO_2I$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.59; H, 2.61; N, 4.46.

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18) S.H. Zaheer and S.A. Faseeh, *J. Indian Chem. Soc.*, **21**, 27 (1944).
19) W.F. Huber, N. Renoll, A.G. Rossow, and D.T. Mowry, *J. Am. Chem. Soc.*, **68**, 1109 (1946).
20) D. Purdie, *J. Am. Chem. Soc.*, **63**, 2276 (1941).
21) G.M. Badger and W.F.H. Sasse, *J. Chem. Soc.*, **1957**, 4.
22) L. Mascarelli, D. Gatti, and M. Piroma, *Gazz. Chim. Ital.*, **61**, 782 (1931).
23) E. Ibuki, S. Ozasa, and H. Kitamura, *Nippon Kagaku Zasshi*, **92**, 361 (1971).
24) L. Mascarelli and D. Gatti, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.*, **65**, 143 (1930) [*C.A.*, **24**, 4777 (1930)].

3-Nitro-*m*-terphenyl (27a)——Copper powder (10.2 g, 160 mg-atom) was added in portions to a mixture of **9** (5.6 g, 20 mmol) and *m*-iodonitrobenzene (5.0 g, 20 mmol) in a reaction tube (ϕ 3.5 × 21 cm) with stirring at 220° over a 3-hr period, then the mixture was heated at 225° for 1 hr. The hot benzene extract of the product (4.5 g) was subjected to chromatography on alumina (200 g), with a cyclohexane–benzene (5: 2, v/v) mixture (C-B(5: 2)) as the eluent to give two fractions. Fraction (Fr.) 1 provided *m*-quaterphenyl (**30**) as colorless needles from ethanol; mp 86.5—87.7° (lit.[25] mp 85.5—86°); 0.59 g. Fr. 2 afforded **27a** as pale yellow needles from ethanol; mp 114—115°; yield, 1.23 g (22%). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.77; H, 4.84; N, 4.82. Subsequent elution with benzene gave 3,3'-dinitrobiphenyl (0.30 g).

3-Amino-*m*-terphenyl (27b)——A solution of **27a** (10.0 g) in hot benzene (400 ml) was treated with activated iron by a method similar to that of Hazlet and Dornfeld.[26] After filtration, hydrogen chloride was passed into the filtrate, then the precipitate was collected, washed with benzene, and dried; yield, 10.0 g (97%). A portion of the salt was treated in the usual manner with aqueous alkali. The free base **27b** was obtained as a pale yellow oil. Acetate: mp 103—104°. *Anal.* Calcd for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.50; H, 5.91; N, 4.91.

3-Iodo-*m*-terphenyl (27c)——A suspension of **27b**·HCl (8.3 g) in concentrated sulfuric acid (7 ml) and water (180 ml) was diazotized with sodium nitrite (2.5 g) in water (5 ml) at 0—5° with stirring for 1.5 hr. The cold suspension of diazonium salt formed was added to a solution of potassium iodide (6.5 g) in water (7 ml) with stirring, and the mixture was heated slowly up to *ca.* 80°, then cooled. The chloroform extract was washed with water, sodium thiosulfate solution, sodium hydroxide solution, and then water. After removal of the solvent, the residue was dissolved in cyclohexane and subjected to chromatography on alumina with the same solvent as the eluent to provide **27c**; colorless plates from petroleum benzine; mp 61—62° (lit.[27] an oil); yield, 5.0 g (48%). *Anal.* Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68. Found: C, 60.94; H, 3.74.

3,3'''-Dinitro-*m*-quaterphenyl (21a)——Copper powder (38.1 g, 600 mg-atom) was added in portions to **12** (32.5 g, 100 mmol) in a reaction tube with stirring at 225—230° over a 3-hr period, then the mixture was heated at 230—235° for 1 hr. The hot benzene extract was chromatographed on alumina with a C-B (1: 1) mixture and benzene as eluents to afford **21a**; yellow needles from benzene; mp 185—186.5°; 12.3 g (62%). *Anal.* Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.93; H, 3.91; N, 6.87.

3,3'''-Diamino-*m*-quaterphenyl (21b)——A solution of **21a** (17.1 g) in benzene was reduced in the manner described for **27b** to give **21b**; pale brown needles from ethanol; mp 119—120°; 12.0 g (83%). *Anal.* Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.78; H, 6.25; N, 8.50.

3,3'''-Diiodo-*m*-quaterphenyl (21c)——A suspension of **21b** (12.0 g) in concentrated hydrochloric acid (53 ml) and water (260 ml) was worked up as described for **27c**. The crude product (18.1 g) was purified by chromatography on alumina with a C-B (1: 1) mixture to provide **21c**: colorless needles from cyclohexane; mp 124—126°; 10.0 g (50%). *Anal.* Calcd for $C_{24}H_{16}I_2$: C, 51.64; H, 2.89. Found: C, 51.91; H, 2.69.

2-Nitro-*o*-quaterphenyl (13a)——Copper powder (16.5 g, 260 mg-atom) was added in portions to a mixture of **8** (4.7 g, 17 mmol) and **11** (5.4 g, 17 mmol) in a reaction tube with stirring at 230—235° over a 3-hr period. The mixture was then heated at 240° for 1 hr. The hot benzene extract of the product (5.4 g) was separated into four fractions by chromatography on alumina. Elution with a C-B (5: 1) mixture gave two fractions, which afforded biphenyl (**34**) as colorless leaves from methanol, mp 68—69°, 0.07 g, and *o*-quaterphenyl (**35**) as colorless cubes from ethanol, mp 118—119° (lit.[28] mp 118°), 0.80 g. Subsequent elutions with C-B (5: 1) and C-B (5: 2) mixtures gave **13a** as pale yellow prisms from ethanol; mp 135.5—136.5°; .14 g (20%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.26; H, 4.75; N, 4.26. Finally, elution with benzene gave one more fraction which provided 2,2'''-dinitro-*o*-quaterphenyl (**36**); yellow plates from ethanol; mp 187—188°; 0.48 g. *Anal.* Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.90; H, 3.96; N, 7.11.

2-Amino-*o*-quaterphenyl (13b)——A solution of **13a** (5.6 g) in benzene was reduced in the manner described for **27b** to give **13b**·HCl as a white powder; mp 195—198°; 5.6 g (98%). *Anal.* Calcd for $C_{24}H_{20}NCl$: C, 80.55; H, 5.63; N, 3.91. Found: C, 80.83; H, 5.87; N, 3.96.

2-Iodo-*o*-quaterphenyl (13c)——A suspension of **13b**·HCl (5.3 g) in concentrated sulfuric acid (7 ml) and water (50 ml) was worked up as described for **27c**. The crude product (4.9 g) was chromatographed on alumina with C-B (5: 1) to provide two fractions. Fr. 1 afforded **13c** as a pale yellow oil; 1.5 g (23%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.55; H, 3.98. Fr. 2 gave 1-phenyltriphenylene (**19**) as a by-product; colorless needles from ethanol; mp 161—162° (lit.[29] mp 162°); 0.95 g.

***o*-Octiphenyl (1)**——The iodoquaterphenyl **13c** (1.36 g, 3.1 mmol) was heated with copper powder (1.6 g, 25 mg-atom) at 255—260° for 1 hr, then at 265° for an additional 1 hr. The hot benzene extract (1.12 g)

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[25] G.F. Woods and F.T. Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).
[26] S.E. Hazlet and C.A. Dornfeld, *J. Am. Chem. Soc.*, **66**, 1781 (1944).
[27] J.A. Cade and A. Pilbeam, *J. Chem. Soc.*, **1964**, 114.
[28] J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).
[29] P.G. Copeland, R.E. Dean, and D. McNen, *J. Chem. Soc.*, **1960**, 4522.

was subjected to chromatography on alumina with cyclohexane to afford **35** (88 mg). Subsequent elutions with C-B (9: 1) and then C-B (5: 1) afforded **19** (275 mg) and **1**, respectively.

1: Colorless needles from ethanol–benzene; mp 301—303° (lit.[6] mp 312—320°); 30 mg (3%). IR (KBr) cm^{-1}: 695 s, 698 sh s ($\gamma_{\mathrm{C-C}}$); 712 vw, 723 w; 733 s, 741 s, 750 s ($\gamma_{\mathrm{C-H}}$, M, *o*); 769 s, 776 m ($\gamma_{\mathrm{C-H}}$, *o*). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 225 (sh) (82700). MS *m/e*: 610 (M^+).

2-(3-Biphenylyl)-2′-nitrobiphenyl (14a)——A mixture of **9** (4.2 g, 15 mmol) and **11** (4.9 g, 15 mmol) was treated with copper powder (15.2 g, 240 mg-atom) as described for **13a**. The benzene extract (4.5 g) was chromatographed on alumina with C-B (5: 1) to provide **34** (0.08 g) and **30** (0.46 g). Subsequent elutions with C-B (5: 2) and C-B (1: 1), and then benzene afforded two fractions. Fr. 1 provided **14a**; pale yellow plates from ethanol; mp 110—111°; 1.05 g (20%). *Anal.* Calcd for $\mathrm{C_{24}H_{17}NO_2}$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.04; H, 4.64; N, 4.14. Fr. 2 gave **36** (0.75 g).

2-Amino-2′-(3-biphenylyl)biphenyl (14b)——A solution of **14a** (2.5 g) in benzene was worked up in the manner described for **27b** to give **14b**·HCl; 2.5 g (98%). A portion of the salt was converted into the free base, which provided **14b** as a colorless oil. *Anal.* Calcd for $\mathrm{C_{24}H_{19}N}$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.48; H, 6.24; N, 4.50.

2-(3-Biphenylyl)-2′-iodobiphenyl (14c)——A suspension of **14b**·HCl (3.0 g) in sulfuric acid was worked up in the usual manner. The crude product was purified by chromatography on alumina with C-B (5: 1) to afford **14c**; colorless plates from ethanol; mp 103—104°; 0.76 g (21%). *Anal.* Calcd for $\mathrm{C_{24}H_{17}I}$: C, 66.68; H, 3.96. Found: C, 66.97; H, 4.13. Subsequent elutions with C-B (5: 1) and C-B (1: 1) gave **19** (0.62 g) and 2-phenyltriphenylene (**20**), respectively. **20**: Colorless needles from ethanol; mp 186—187° (lit.[29] mp 183—183.5°); 0.55 g.

2,2‴-Di(3-biphenylyl)-*o*-quaterphenyl (2)——The iodoquaterphenyl **14c** (0.47 g, 1.1 mmol) was heated with copper powder (1.10 g, 17 mg-atom) at 275—280° for 2 hr, then at 280—285° for 1 hr. The benzene extract of the product was separated into four fractions by chromatography on alumina. Fr. 1, eluted with cyclohexane, gave 2,3′-diphenylbiphenyl (**37**) as colorless needles from ethanol; mp 91—92° (lit.[30] mp 90.5—91°); 68 mg. *Anal.* Calcd for $\mathrm{C_{24}H_{18}}$: C, 94.08; H, 5.92. Found: C, 94.35; H, 5.81. Fr. 2, 3, and 4, eluted with C-B (9: 1), afforded **19** (35 mg), **2**, and **20** (40 mg), respectively.

2: Colorless plates from ethanol; mp 177.8°; 76 mg (23%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 192 (95400), 202 (sh) (90500), 235 (80100), 254 (sh) (58300). *Anal.* Calcd for $\mathrm{C_{48}H_{34}}$: C, 94.39; H, 5.61. Found: C, 94.10; H, 5.86. MS *m/e*: 610 (M^+).

2-(4-Biphenylyl)-2′-nitrobiphenyl (15a)——A mixture of **10** (16.8 g, 60 mmol) and **11** (13.0 g, 40 mmol) was heated with copper powder at 235—240°. After cooling, the product was extracted with hot benzene followed by hot toluene. The benzene extract (13.9 g) was separated into three fractions by chromatography on alumina. Fr. 1, eluted with C-B (5: 1), afforded **34** (0.57 g). Fr. 2, eluted with C-B (1: 1), gave **15a** as pale yellow needles from ethanol; mp 138—139°; 3.2 g (23%). *Anal.* Calcd for $\mathrm{C_{24}H_{17}NO_2}$: C, 82.03; H, 4.88; N, 3.99. Found: C, 81.77; H, 4.99; N, 3.98. Fr. 3, eluted with benzene, provided **36** (0.34 g). The toluene extract (1.3 g) was recrystallized from toluene to give *p*-quaterphenyl (**31**) as colorless leaves; mp 316.5—318° (lit.[31] mp 317.7—318.7°); 1.13 g.

2-Amino-2′-(4-biphenylyl)biphenyl (15b)——A solution of **15a** (1.6 g) in benzene was reduced in the manner described above to give **15b**·HCl; 1.5 g (92%). Free base **15b**: Colorless cubes from ethanol; mp 138.5—139.5°. *Anal.* Calcd for $\mathrm{C_{24}H_{19}N}$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.63; H, 5.97; N, 4.52.

2-(4-Biphenylyl)-2′-iodobiphenyl (15c)——The salt **15b**·HCl (5.3 g) was converted into **15c** in the usual manner. The crude product (4.6 g) was subjected to chromatography on alumina with C-B (5: 1) to afford **15c**; colorless prisms from ethanol; mp 136—137°; 0.96 g (15%). *Anal.* Calcd for $\mathrm{C_{24}H_{17}I}$: C, 66.68; H, 3.96. Found: C, 66.93; H, 4.05. Subsequent elutions with C-B (5: 1), C-B (1: 1), and C-B (1: 3) gave **20** (0.56 g).

2,2‴-Di(4-biphenylyl)-*o*-quaterphenyl (3)——The iodoquaterphenyl **15c** (0.77 g, 1.8 mmol) was heated with copper powder (1.8 g) in the manner described for **2**. The benzene extract (0.56 g) was separated into three fractions by chromatography on alumina. Fr. 1, eluted with C-B (5: 1), gave 2,4′-diphenylbiphenyl (**32**); colorless prisms from ethanol; mp 118—119° (lit.[32] mp 119—119.5°); 177 mg.

Fr. 2, eluted with C-B (2: 1), afforded **3** as colorless cubes from ethanol; mp 241.2°; 66 mg (12%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 204 (96200), 260 (45300), 276 (sh) (41900). *Anal.* Calcd for $\mathrm{C_{48}H_{34}}$: C, 94.39; H, 5.61. Found: C, 94.30; H, 5.37. MS *m/e*: 610 (M^+).

Subsequent elutions with C-B (2: 1) and C-B (1: 1) provided **20**, 168 mg.

3-(2-Biphenylyl)-3′-nitrobiphenyl (16a)——A mixture of **8** (8.4 g, 30 mmol) and **12** (5.0 g, 15 mmol) was treated with copper powder (30 g) as described for **13a**. The benzene extract (5.8 g) was separated into three fractions by chromatography on alumina. Fr. 2, eluted with C-B (3: 1), C-B (2: 1), and C-B (1: 1), provided **16a** as a pale yellow oil; 1.12 g (21%). *Anal.* Calcd for $\mathrm{C_{24}H_{17}NO_2}$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.32; H, 4.83; N, 4.14. Compounds **35** (1.8 g) and **21a** (0.43 g) were also obtained as by-products from Fr. 1

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30) G.F. Woods and A.L. Artsdale, *J. Am. Chem. Soc.*, **72**, 3221 (1950).

31) J.J.E. Schmidt and J.A. Krimmel, *J. Org. Chem.*, **25**, 252 (1960).

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

and 3 (eluted with C-B (4: 1) and benzene, respectively).

3-Amino-3′-(2-biphenylyl)biphenyl (16b)——The nitroquaterphenyl **16a** (4.0 g) was reduced as described above to give **16b**·HCl; a white powder; 3.5 g (86%). *Anal.* Calcd for $C_{24}H_{20}NCl$: C, 80.55; H, 5.63; N, 3.91. Found: C, 80.26; H, 5.74; N, 3.72.

3-(2-Biphenylyl)-3′-iodobiphenyl (16c)——A suspension of **16b**·HCl (3.3 g) in concentrated sulfuric acid (4 ml) and dioxane (100 ml) was diazotized by treatment with isoamyl nitrite (2.2 g) at 5—10° with stirring for 2 hr. The cold diazonium salt solution was treated with a solution of potassium iodide (2.9 g) in water (3 ml), then worked up as described above. The crude product (4.0 g) was chromatographed on alumina with C-B (3: 1) and C-B (1: 1). Several crystallizations of the eluate from ethanol gave **16c** as colorless needles; mp 123—124°; 0.93 g (23%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.93; H, 3.83.

3,3‴-Di(2-biphenylyl)-*m*-quaterphenyl (4)——Procedure A: The iodoquaterphenyl **16c** (0.83 g, 1.9 mmol) was treated with copper powder at 260—265°. The benzene extract (0.59 g) was separated into two fractions by chromatography on alumina. Fr. 1, eluted with C-B (9: 1) and C-B (7: 1), gave **37** (213 mg).

Fr. 2, eluted with C-B (2: 1), afforded **4** as colorless plates from ethanol-benzene; mp 157.7°; 351 mg (60%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 192 (100400), 203 (sh) (88900), 238 (107700), 249 (sh) (90300). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.13; H, 5.53. MS *m/e*: 610 (M^+).

Procedure B: An ethereal solution of 2-biphenylylmagnesium bromide was prepared from **22** (2.80 g, 12 mmol), magnesium turnings (0.30 g, 12 mg-atom), and absolute ether (25 ml) under nitrogen in the usual manner. A mixture of **21c** (1.67 g, 3 mmol) and bis(acetylacetonato)nickel(II) (15 mg, 0.06 mmol) in benzene (30 ml) was added as a single batch to the Grignard reagent thus prepared. The mixture was stirred for 1 hr, refluxed for 3 hr, and then hydrolyzed with dilute hydrochloric acid. The resulting mixture was extracted with benzene. The organic layer was separated, washed with water, and then dried. After removal of the solvent, the resulting material was chromatographed on alumina with C-B (9: 1) to give **34** (640 mg) and **35** (210 mg). Subsequent elution with C-B (1: 1) afforded **4** (1440 mg, 79%).

3-Nitro-*m*-quaterphenyl (17a)——A mixture of **9** (4.2 g, 15 mmol) and **12** (4.9 g, 15 mmol) was treated with copper powder (20.0 g) as described for **13a**. The benzene extract (5.0 g) was chromatographed on alumina with C-B (5: 2) to give **17a** as pale yellow needles from petroleum benzine; mp 81.5—82.5°; 0.95 g (18%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.19; H, 4.83; N, 4.21. Compounds **30** (0.61 g) and **21a** (0.51 g) were isolated as by-products from the fractions eluted with C-B (5: 2) and benzene, respectively.

3-Amino-*m*-quaterphenyl (17b)——The nitroquaterphenyl **17a** (3.3 g) was reduced as described above to give **17b**·HCl; 3.3 g (98%). Free base **17b**: a pale yellow oil. *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.60; H, 6.20; N, 4.47.

3-Iodo-*m*-quaterphenyl (17c)——The amine salt **17b**·HCl (3.0 g) was converted into **17c** as described above. The crude product (1.1 g) was purified by chromatography on alumina with C-B (5: 1) to afford **17c** as a colorless oil; 0.33 g (9%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.68; H, 4.24.

***m*-Octiphenyl** (5)——Procedure A: The iodoquaterphenyl **17c** (0.27 g) was treated with copper powder (0.44 g) as described for **2**. The benzene extract (0.20 g) was chromatographed on alumina (15 g) with cyclohexane and C-B (9: 1) to provide **30** (47 mg).

Subsequent elutions with C-B (9: 1) and C-B (2: 1) provided **5** as colorless plates after crystallization twice from ethanol–benzene followed by drying *in vacuo*; mp 127.7° (lit.[10a)] mp 127—129°; lit.[10b)] mp 129—131°); 103 mg (54%). IR (KBr) cm^{-1}: 682 m, 692 sh s, 702 s (γ_{C-C}); 727 vw; 752 s, 755 sh s (γ_{C-H}, M); 771 s, 782 s, 791 sh m, 804 m, 810 m (γ_{C-H}, *m*); 845 w; 874 m, 886 m, 898 w, 905 vw, 915 w (γ_{C-H}, *m*). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 192 (81600), 204 (74100), 249 (135100). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.30; H, 5.56. MS *m/e*: 610 (M^+).

Procedure B: A mixture of **21c** (1.67 g) and bis(acetylacetonato)nickel(II) (15 mg) in benzene was added to an ethereal solution of 3-biphenylylmagnesium bromide, prepared from **23** (2.80 g) and magnesium turnings (0.30 g). The mixture was worked up as described for **4** (procedure B). The benzene extract was chromatographed on alumina with C-B (9: 1), and with C-B (9: 1) and C-B (7: 3) to afford **34** (160 mg) and **30** (330 mg), respectively. Subsequent elutions with C-B (7: 3) and C-B (1: 1) gave **5** (1280 mg, 70%).

3-(4-Biphenylyl)-3′-nitrobiphenyl (18a)——A solution of **10** (13.4 g, 48 mmol) and **12** (5.2 g, 16 mmol) in dimethylformamide (DMF) (100 ml) was brought to a reflux. Copper powder (20.4 g, 330 mg-atom) was added in three portions at intervals of 10 hr with stirring, and the mixture was refluxed for an additional 20 hr. The hot reaction mixture was filtered, and the solid material was washed several times with hot DMF and benzene. After cooling the filtrate, the resulting solid was collected and recrystallized from benzene to provide **31** (1.9 g). The filtrates, after removal of the solvents *in vacuo*, gave a solid which was treated with 100 ml of C-B (3: 1) to separate soluble and insoluble fractions. The latter fraction gave additional **31** (0.20 g) after several crystallizations from benzene. The former fraction was subjected to chromatography on alumina with C-B (3: 1), then with C-B (3: 1) and C-B (3: 2) to afford **34** (2.6 g) and **18a**, respectively. **18a**: Pale yellow needles from benzene–ethanol; mp 144.8°; 2.1 g (37%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.09; H, 4.78; N, 3.73. Subsequent elutions with C-B (1: 4) and benzene gave **21a** (0.28 g).

3-Amino-3′-(4-biphenylyl)biphenyl (18b)——The nitroquaterphenyl **18a** (5.3 g) was reduced as described above to give **18b** as colorless needles from benzene; mp 145.1°; 4.6 g (95%). *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.84; H, 5.79; N, 4.11.

3-(4-Biphenylyl)-3′-iodobiphenyl (18c)——A suspension of **18b** (4.3 g) in sulfuric acid was worked up in the usual manner. The crude product (3.2 g) was purified by chromatography on alumina with C-B (9: 1). After removal of the eluent, crystallization from cyclohexane afforded **18c** as colorless needles; mp 144.9°; 1.21 g (21%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.48; H, 3.90.

3,3‴-Di(4-biphenylyl)-*m*-quaterphenyl (6)——The iodo compound **18c** (1.9 g, 4.4 mmol) was heated with copper powder at 265—270°. The benzene extract (1.37 g) was chromatographed on alumina with C-B (3: 2) to provide two fractions. Fr. 1 gave 3,4′-diphenylbiphenyl (33); colorless needles from ethanol; mp 166.8° (lit.[33] mp 166—167°); 269 mg.

Fr. 2 afforded **6** as colorless needles from benzene; mp 216.3°; 845 mg (63%). UV $\lambda_{\mathrm{max}}^{\mathrm{cyclohexane}}$ nm (ε): 205 (100300), 262 (90100). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.29; H, 5.39. MS m/e: 610 (M^+).

1,3-Dibromo-2-nitrobenzene (24)——2,6-Dibromoaniline, mp 85—86° (lit.[34] mp 87—88°), was prepared by direct bromination of 4-aminobenzoic acid methyl ester and hydrolysis of the product with methanolic potassium hydroxide, followed by decarboxylation of the acid by refluxing it with 70% sulfuric acid for 8 hr. Yield, 67% (based on 4-aminobenzoic acid methyl ester). A pasty suspension of 2,6-dibromoaniline (12.6 g) in concentrated sulfuric acid (5.5 ml) and water (55 ml) was diazotized by treatment with sodium nitrite (4.2 g) in water (10 ml) with stirring at 0—5°. A solution of sodium borofluoride (7.7 g) in water (25 ml) was added in portions to the suspension of the diazonium salt, then the mixture was stirred at the same temperature for an additional hour. The crystals thus formed were separated by filtration, then added to ice-water (100 ml) to give the diazonium borofluoride solution. The salt solution was treated by a method similar to that of Hodgson,[35] and the product (13.5 g) was subjected to column chromatography on alumina to give **24** as pale yellowish needles from cyclohexane; mp 82—84° (lit.[36] mp 83°); 10.6 g (75%). *Anal.* Calcd for $C_6H_3NO_2Br_2$: C, 25.66; H, 1.08; N, 4.99. Found: C, 25.74; H, 0.99; N, 4.78.

2″-Nitro-*m*-quinquephenyl (25a)——Copper powder (63.5 g) was added to a mixture of **9** (22.4 g, 80 mmol) and **24** (5.6 g, 20 mmol) with stirring at 230—235° over a 2-hr period, then the mixture was heated at 235—240° for 1 hr. The benzene extract (15.5 g) was chromatographed on alumina with C-B (4: 1) and C-B (3: 2) to give **25a** as pale yellow needles from cyclohexane; mp 194—195°; 4.2 g (49%). *Anal.* Calcd for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.21; H, 5.13; N, 3.34. Elution with C-B (4: 1) also gave **30** (4.7 g) as a by-product.

2″-Amino-*m*-quinquephenyl (25b)——The nitroquinquephenyl **25a** (8.0 g) was reduced in the usual manner to afford **25b** as colorless needles from cyclohexane; mp 131—132°; 7.0 g (94%). *Anal.* Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.43; H, 6.06; N, 3.43.

***m*-Quinquephenyl (26)**——Isoamyl nitrite (0.70 g, 6 mmol) was added to a solution of **25b** (1.19 g, 3 mmol) and concentrated sulfuric acid (1 ml) in dioxane (40 ml) at 10—15°, then the mixture was stirred at the same temperature for 1 hr. The cold suspension of diazonium salt thus formed was added in portions to a dioxane suspension of Gattermann copper [freshly prepared from copper sulfate (4.5 g, 18 mmol)], and the resulting mixture was stirred at room temperature for 1 hr then heated at 70° for 0.5 hr. After cooling, the copper powder was filtered off, then water was added to the filtrate to give an insoluble solid. The benzene extract of the solid (1.6 g) was chromatographed on alumina with C-B (9: 1) and C-B (4: 1) to provide **26** as colorless needles from ethanol; mp 114.1° (lit.[3b] mp 114.0°); 690 mg (60%).

2‴-Nitro-*m*-septiphenyl (28a)——Copper powder (16.4 g) was added to a mixture of **27c** (7.9 g, 22 mmol) and **24** (2.8 g, 10 mmol) with stirring at 235—240° over a 3-hr period, then the mixture was heated at 240—245° for 1 hr. The benzene extract (4.5 g) was chromatographed on alumina with C-B (4: 1) and C-B (3: 1) to give *m*-sexiphenyl (29); colorless needles from cyclohexane; mp 145—146° (lit.[27] mp 146—147°); mixed mp 145.5—146.5°; 0.80 g. Subsequent elution with C-B (3: 2) afforded **28a** as pale yellowish needles from benzene–cyclohexane; mp 251—253°; 1.16 g (20%). *Anal.* Calcd for $C_{42}H_{29}NO_2$: C, 87.02; H, 5.04; N, 2.42. Found: C, 87.30; H, 5.04; N, 2.44.

2‴-Amino-*m*-septiphenyl (28b)——The nitro compound **28a** (1.23 g) was reduced in the usual manner to provide **28b** as a pale yellow oil; 1.11 g (95%). *Anal.* Calcd for $C_{42}H_{31}N$: C, 91.77; H, 5.68; N, 2.55. Found: C, 91.71; H, 5.66; N, 2.50.

***m*-Septiphenyl (7)**——Isoamyl nitrite (0.23 g, 2 mmol) was added as a single batch to a solution of **28b** (0.59 g, 1.1 mmol) and concentrated sulfuric acid (0.3 ml) in dioxane (20 ml) at 10—15°. The reaction

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33) G.F. Woods and I.W. Tucker, *J. Am. Chem. Soc.*, **70**, 3340 (1948).

34) M.K. Seikel, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horning, John Wiley and Sons, Inc., New York, 1955, p. 262.

35) H.H. Hodgson, A.P. Mahadevan, and E.R. Ward, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horning, John Wiley and Sons, Inc., New York, 1955, p. 341.

36) A.F. Hollemann, *Rec. Trav. Chim. Pays-Bas*, **25**, 183 (1906).

mixture was stirred at this temperature for 1 hr. The cold suspension of diazonium salt thus formed was worked up as described for **26**. The crude product (0.56 g) was purified by chromatography on alumina with C-B (9: 1) and C-B (4: 1) to give **7** as colorless needles from *n*-hexane; mp 97.8°; 93 mg (16%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 192 (71800), 204 (66300), 249 (118200). *Anal.* Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.56; H, 5.41. MS *m/e*: 534 (M^+).

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