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Syntheses and Physical Properties of Several Octiphenyls Containing Mixed Linkages[1]

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Eight new linear octiphenyls containing two or three kinds of linkage were synthesized by the Ullmann homo-coupling reaction of iodoquaterphenyl. Among them, five compounds were alternatively synthesized by the Kharash-type Grignard cross-coupling of biphenylylmagnesium bromide and diiodoquaterphenyl or of terphenylylmagnesium iodide and diiodobiphenyl in the presence of bis(acetylacetonato)nickel(II). Spectral studies proved that the octiphenyls thus prepared displayed highly characteristic infrared, ultraviolet, and nuclear magnetic resonance spectra. Empirical Hückel molecular orbital calculations of the longest wavelength absorption bands of the octiphenyls were also performed. The calculated and observed wavelengths were in rather good agreement, except for the cases of two compounds.

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

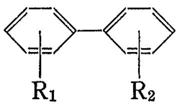
Previous papers[2] from our laboratory have described the synthesis of a series of linear quinque- to octiphenyls and the relationship between the structures and the physical properties, including the infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectral characteristics. The correlations between the structures and properties of several octiphenyls were found to be very similar to those observed in the quinque- and sexiphenyls.

In the present work, eight new symmetrical linear octiphenyls (**1**—**8**) containing two or three kinds of linkage were synthesized, in order to investigate the spectral characteristics of polyphenyls having more complicated structures. The Ullmann homo-coupling and Kharash-type Grignard cross-coupling reactions[3] were utilized for the syntheses. The IR, UV, and NMR spectra were measured, and the relationship between the number and arrangement of the benzene rings and the physical properties is discussed. In addition, we performed empirical Hückel molecular orbital (HMO) calculations of the longest wavelength absorption bands of these octiphenyls. The calculated results are compared with the observed values.

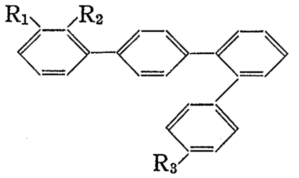
In a manner similar to that used for the syntheses of simple octiphenyls,[2d] the Ullmann homo-coupling reaction of appropriate iodoquaterphenyls (**15c**—**22c**) was employed for the preparation of eight octiphenyls (**1**—**8**). The key intermediate iodoquaterphenyls (**15c**—**22c**) were prepared *via* the Ullmann cross-coupling of iodobiphenyls (**9**—**11**) and iodonitrobiphenyls (**12**—**14**) to nitroquaterphenyls (**15a**—**22a**), and reduction of the latter to the corresponding amines (**15b**—**22b**) followed by diazotization and iodine substitution. The octiphenyls and by-products[4] thus obtained are listed in Table I.

Five octiphenyls (**1**, **2**, **4**, **6**, and **7**) were also prepared by means of two types of Kharash-type Grignard cross-coupling reactions (catalyst: bis(acetylacetonato)nickel(II)) involving firstly the coupling of biphenylylmagnesium bromide and diiodoquaterphenyls, and secondly the coupling of terphenylylmagnesium iodide and diiodobiphenyl. The intermediate diiodoquaterphenyls (**23c** and **24c**) were prepared from the corresponding dinitroquaterphenyls (**23a** and **24a**) obtained by the Ullmann homo-coupling of iodonitrobiphenyls (**14** and **12**, respectively). Four octiphenyls (**1**, **2**, **6**, and **7**) were synthesized by the first method, the cross-coupling of **23c** or **24c** with the Grignard reagent derived from **25** or **26**, respectively. The remaining octiphenyl (**4**) was successfully prepared by the second method, the cross-coupling of **27** with the Grignard reagent derived from **28**. The octiphenyls[5)] and by-products[4)] thus obtained are also listed in Table I.

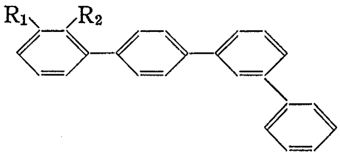
The hitherto-unknown octiphenyls (**1**—**8**) thus prepared gave satisfactory analytical results and spectral (IR and MS) data consistent with their structures. In all of the Ullmann



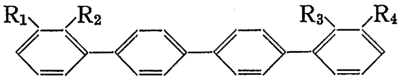
9: R_1=2-I, R_2=H
10: R_1=3-I, R_2=H
11: R_1=4-I, R_2=H
12: R_1=4-I, R_2=2′-NO_2
13: R_1=4-I, R_2=3′-NO_2
14: R_1=2-I, R_2=4′-NO_2
25: R_1=2-Br, R_2=H
26: R_1=3-Br, R_2=H
27: R_1=3-I, R_2=3′-I
28: R_1=4-I, R_2=2′-C_6H_5
30: R_1=3-C_6H_5, R_2=3′-C_6H_5
31: R_1=2-C_6H_5, R_2=H
35: $R_1=R_2$=H



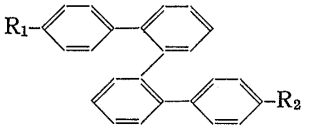
1: $R_1=R_3$=H, R_2=}-
4: R_1=}-, $R_2=R_3$=H
8: $R_1=R_2$=H, R_3=}-
15a: $R_1=R_3$=H, $R_2=NO_2$
15b: $R_1=R_3$=H, $R_2=NH_2$
15c: $R_1=R_3$=H, R_2=I
18a: $R_1=NO_2$, $R_2=R_3$=H
18b: $R_1=NH_2$, $R_2=R_3$=H
18c: R_1=I, $R_2=R_3$=H
22a: $R_1=R_2$=H, $R_3=NO_2$
22b: $R_1=R_2$=H, $R_3=NH_2$
22c: $R_1=R_2$=H, R_3=I
34: $R_1=R_2=R_3$=H



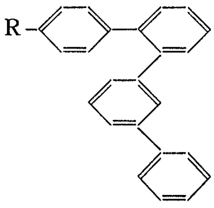
2: R_1=H, R_2=}-
5: R_1=}-, R_2=H
16a: R_1=H, $R_2=NO_2$
16b: R_1=H, $R_2=NH_2$
16c: R_1=H, R_2=I
19a: $R_1=NO_2$, R_2=H
19b: $R_1=NH_2$, R_2=H
19c: R_1=I, R_2=H
32: $R_1=R_2$=H



3: $R_1=R_3=R_4$=H, R_2=}-
17a: $R_1=R_3=R_4$=H, $R_2=NO_2$
17b: $R_1=R_3=R_4$=H, $R_2=NH_2$
17c: $R_1=R_3=R_4$=H, R_2=I
24a: $R_1=R_4$=H, $R_2=R_3=NO_2$
24b: $R_1=R_4$=H, $R_2=R_3=NH_2$
24c: $R_1=R_4$=H, $R_2=R_3$=I
29: $R_1=R_4$=H, $R_2=R_3=C_6H_5$
33: $R_1=R_2=R_3=R_4$=H
37: $R_1=R_4=NO_2$, $R_2=R_3$=H



6: R_1=}-, R_2=H
20a: $R_1=NO_2$, R_2=H
20b: $R_1=NH_2$, R_2=H
20c: R_1=I, R_2=H
23a: $R_1=R_2=NO_2$
23b: $R_1=R_2=NH_2$
23c: $R_1=R_2$=I
36: $R_1=R_2$=H



7: R=}-
21a: R=NO_2
21b: R=NH_2
21c: R=I
38: R=H

Chart

TABLE I. Syntheses of Octiphenyls

Reactant	Procedure[a)]	Octiphenyl (Yield/%)	Other products
15c	A	**1** (67)	**34**
25+**23c**	B-1	**1** (85)	**35**, **36**
16c	A	**2** (63)	**32**
26+**23c**	B-1	**2** (87)	**35**, **30**
17c	A	**3** (53)	**33**
18c	A	**4** (64)	**34**
28+**27**	B-2	**4** (35)	**31**, **29**
19c	A	**5** (50)	**32**
20c	A	**6** (61)	**36**
25+**24c**	B-1	**6** (36)	**35**, **36**
21c	A	**7** (57)	**38**
26+**24c**	B-1	**7** (37)	**35**, **30**
22c	A	**8** (73)	**34**

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

reactions, the octiphenyls were obtained in fairly good yields (50—73%) and at high levels of purity. In the Grignard reaction, the yields of two octiphenyls (**1** and **2**) were excellent (85 and 87%), whereas those of three (**4**, **6**, and **7**) were rather low (35—37%). The low yields of **6** and **7** are probably due to poor solubility in ethereal solution and steric factors related to **24c**, whereas that of **4** may arise from the difficulty of formation of the Grignard reagent from **28**. These results suggest that the Kharash-type Grignard cross-coupling reaction is also applicable for the syntheses of higher polyphenyls in some cases.

The IR spectra of the octiphenyls were measured by the KBr-disk method. The characteristic bands in the region of 680—920 cm^{-1} are shown in Table II. These bands are consistent with the substitution patterns of benzene rings constituting each octiphenyl.

Table II. Positions and Tentative Assignments of Characteristic Bands in the IR Spectra (680—920 cm^{-1}) of Octiphenyls[a)]

1			**3**			**5**			**7**		
686	m	$\gamma_{\text{C-C}}$	693	s	$\gamma_{\text{C-C}}$	698	s	$\gamma_{\text{C-C}}$	693	s	$\gamma_{\text{C-C}}$
699	s		717	w		719	vw		699	s	
720	vw		733	s	$\gamma_{\text{C-H}}$ (M, *o*)	737	w		706	s	
728	vw		740	s		755	sh, s	$\gamma_{\text{C-H}}$ (M)	714	sh, w	
748	s	$\gamma_{\text{C-H}}$ (M, *o*)	755	s		758	s		729	w	
758	sh, s		768	s		762	sh, s		745	s	$\gamma_{\text{C-H}}$ (M, *o*)
766	m		779		$\gamma_{\text{C-H}}$ (*o*)	779	s	$\gamma_{\text{C-H}}$ (*m*)	752	s	
772	sh, m	$\gamma_{\text{C-H}}$ (*o*)	822	s	$\gamma_{\text{C-H}}$ (*p*)	787	sh, m		769	s	
776	s		826	sh, s		797	m		807	s	$\gamma_{\text{C-H}}$ (*m*)
833	m	$\gamma_{\text{C-H}}$ (*p*)	855	m		845	s	$\gamma_{\text{C-H}}$ (*p*)	827	s	$\gamma_{\text{C-H}}$ (*p*)
840	s		876	vw		855	w		839	w	
876	m		890	vw		877	w	$\gamma_{\text{C-H}}$ (*m*)	857	m	
878	m		909	w		887	m		876	w	
910	w		**4**			920	vw		901	m	$\gamma_{\text{C-H}}$ (*m*)
			693	m	$\gamma_{\text{C-C}}$				911	w	
2			703	s		**6**			918	w	
690	sh, m	$\gamma_{\text{C-C}}$	719	vw		699	s	$\gamma_{\text{C-C}}$			
699	s		735	sh, w		715	vw		**8**		
704	sh, s		746	s	$\gamma_{\text{C-H}}$ (M, *o*)	743	s	$\gamma_{\text{C-H}}$ (M, *o*)	684	m	$\gamma_{\text{C-C}}$
720	vw		756	s		753	s		695	s	
731	m		762	sh, s		759	s		708	w	
734	m		779	s	$\gamma_{\text{C-H}}$ (*m*, *o*)	775	s	$\gamma_{\text{C-H}}$ (*o*)	729	m	
741	m	$\gamma_{\text{C-H}}$ (M, *o*)	787	sh, m	$\gamma_{\text{C-H}}$ (*m*)	779	sh, m		742	s	$\gamma_{\text{C-H}}$ (M, *o*)
754	s		804	vw		820	sh, m	$\gamma_{\text{C-H}}$ (*p*)	755	s	
765	s		839	s	$\gamma_{\text{C-H}}$ (*p*)	825	m		760	sh, s	
778	m	$\gamma_{\text{C-H}}$ (*o*)	872	vw		832	s		764	sh, s	
799	s	$\gamma_{\text{C-H}}$ (*m*)	885	w	$\gamma_{\text{C-H}}$ (*m*)	840	w		776	sh, m	$\gamma_{\text{C-H}}$ (*o*)
840	m	$\gamma_{\text{C-H}}$ (*p*)	898	vw		853	vw		826	s	$\gamma_{\text{C-H}}$ (*p*)
845	m		922	w		874	w		832	s	
876	w					877	w		845	s	
895	w	$\gamma_{\text{C-H}}$ (*m*)				914	w		876	vw	
916	vw								914	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-, *ortho*-, *meta*-, and *para*-substituted rings.

In the spectra of **1**, **2**, **4**, and **5**, which contain two isolated *p*-phenylene rings, the strong or medium C–H out-of-plane bending vibration bands of two adjacent hydrogens of *p*-phenylene rings are observed in the 833—845 cm^{-1} region. The spectra of **3**, **6**, and **7**, which have two consecutive *p*-phenylene rings, displayed bands in the 820—832 cm^{-1} region. Furthermore, the spectrum of **8**, which contains both types of *p*-phenylene rings, showed reasonably assignable bands in both regions. A significant shift of the characteristic band to lower frequencies in the spectra of **3** and **6**—**8** has been observed previously in the spectra of polyphenyls containing *p*-linkage(s) by us[2b)] and other groups.[6)]

These results indicate that the positions of strong or medium bands of the octiphenyls in the 820—845 cm^{-1} region, regardless of the presence of *o*- and/or *m*-phenylene rings in the molecules, are an indication of the presence of isolated or consecutive *p*-phenylene rings.

The mass spectra (MS) of the octiphenyls showed a molecular ion corresponding to the molecular weight of 610 as the most abundant ion.

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

TABLE III. NMR Spectral Data for Octiphenyls and a Related Compound in $CDCl_3$[a]

Compound	*p*-C_6H_4	Other protons
1	6.39 and 6.74 (8H, AA′BB′-q, $J=8.4$ Hz, C_2, C_6–H and C_3, C_5–H)	7.36 (8H, s, $C_6H_5\cdot o\text{-}C_6\underline{H}_4$) 7.02—7.42 (18H, m, *o*-C_6H_4 and C_6H_5)
2	6.70 and 7.30 (8H, AA′BB′-q, $J=8.6$ Hz, C_2, C_6–H and C_3, C_5–H)	7.75—7.80 (2H, m, *m*-C_6H) 7.11—7.71 (24H, m, *m*-C_6H_3, *o*-C_6H_4, and C_6H_5)
3	7.66 (8H, s, $C_6H_5\cdot p\text{-}C_6\underline{H}_4$) 6.69 and 7.30 (8H, AA′BB′-q, $J=8.5$ Hz, C_2, C_6–H and C_3, C_5–H)	7.02—7.42 (18H, m, *o*-C_6H_4 and C_6H_5)
4	7.24 and 7.50 (8H, AA′BB′-q, $J=8.5$ Hz, C_3, C_5–H and C_2, C_6–H)	7.80—7.85 (2H, m, *m*-C_6H) 7.40—7.62 (6H, m, *m*-C_6H_3) 7.45 (8H, s, *o*-C_6H_4) 7.21 (10H, s, C_6H_5)
5	7.77 (8H, s)	7.83—7.89 (2H, m, $C_6H_5\cdot m\text{-}C_6\underline{H}$) 7.91—7.96 (2H, m, $m\text{-}C_6H\cdot m\text{-}C_6H$) 7.32—7.80 (22H, m, *m*-C_6H_3 and C_6H_5)
6	6.66 and 7.19 (8H, AA′BB′-q, $J=8.5$ Hz, $C_{2'}$, $C_{6'}$–H and $C_{3'}$, $C_{5'}$–H)	6.53—7.50 (26H, m, *o*-C_6H_4 and C_6H_5)
7	7.25 and 7.49 (8H, AA′BB′-q, $J=8.5$ Hz, $C_{2'}$, $C_{6'}$–H and $C_{3'}$, $C_{5'}$–H)	7.25 (10H, s, C_6H_5) 7.19—7.61 (16H, m, *o*-C_6H_4 and *m*-C_6H_4)
8		7.10—7.62 (26H, m, *p*-C_6H_4 and C_6H_5) 7.46 (8H, s, *o*-C_6H_4)
ϕopooϕ[b,c]	6.45 and 6.79 (4H, AA′BB′-q, $J=8.6$ Hz, $C_{2'}$, $C_{6'}$–H and $C_{3'}$, $C_{5'}$–H)	7.38 (4H, s, $C_6H_5\cdot o\text{-}C_6\underline{H}_4\cdot p\text{-}C_6H_4$) 6.53—7.45 (18H, m, $o\text{-}C_6H_4\cdot o\text{-}C_6H_4$ and C_6H_5)

a) δ (ppm) from internal standard TMS.
b) ϕ, *o*, and *p* refer to phenyl, *o*-, and *p*-phenylene rings.
c) 2,4′-Di(2-biphenylyl)biphenyl (S. Ozasa, Y. Fujioka, and E. Ibuki, unpublished).

The protons of *p*-phenylene rings in **3** and **5** (outer rings in **3**) exhibited a sharp singlet near δ 7.72 in each case, as in the spectra of 2-phenyl-*p*-quaterphenyl (δ 7.66, 4H, s, $p\text{-}C_6H_4\cdot C_6H_5$) and 3,3″-diphenyl-*p*-terphenyl (δ 7.75, 4H, s, *p*-C_6H_4).[2b]

On the other hand, the protons of the *p*-phenylene rings linked by *o*-phenylene ring(s) in **1**—**4**, **6**, and **7** resonated in an apparent AA′BB′-q pattern. Thus, AA′BB′-q patterns were observed near δ 7.25 and 7.50 in the spectra of **4** and **7**, each of which has a *p*-phenylene ring linked to one *o*-phenylene ring,[7] near δ 6.68 and 7.26 in the spectra of **2**, **3**, and **6**, each of which has a *p*-phenylene ring linked to consecutive *o*-phenylene rings,[8] and at δ 6.39 and 6.74 in the spectrum of **1**, which has a *p*-phenylene ring linked to both consecutive *o*-phenylene rings and a single *o*-phenylene ring.[9]

In other words, the *p*-phenylene proton signals of these octiphenyls were observed at higher field in the order of **4** and **7** (0.44 and 0.18 ppm), **2**, **3**, and **6** (1.00 and 0.42 ppm), and **1** (1.29 and 0.94 ppm), as compared with *p*-terphenyl (δ 7.68, s).[2b]

These significant high field shifts presumably reflect the increasing ring current effects caused by the presence of *o*-C_6H_4, $o\text{-}C_6H_4\cdot o\text{-}C_6H_4$, or both *o*-$C_6H_4$ and $o\text{-}C_6H_4\cdot o\text{-}C_6H_4$ groups adjacent to the *p*-phenylene ring.

In addition, the magnitude of the high field shift of the *p*-phenylene proton signal caused per one *o*-phenylene ring was estimated to be approximately 0.5 and 0.2 ppm for the *o,o'*- and *m,m'*-protons, respectively.

The isolated proton signals of the *m*-phenylene ring in **2**, **4**, and **5**, in each of which the *m*-phenylene ring is not linked to an *o*-phenylene ring, were observed as a multiplet within a narrow region at the most downfield position (δ 7.75—7.90), as has already been pointed out by us in the preceding paper.[2d)]

The UV spectra of the eight octiphenyls were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—3. All of the octiphenyls displayed the E-band in the fairly narrow region of 196—206 nm and the K-band in the broad region of 232—300 nm.

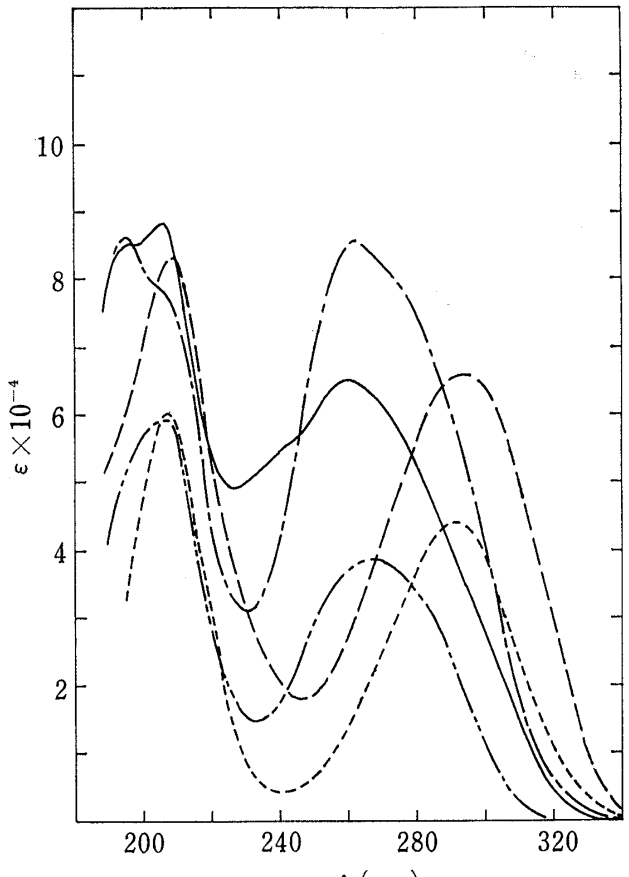


Fig. 1. UV Spectra of Octiphenyls and Quaterphenyls in Cyclohexane

———: 4,4‴-di(3-biphenylyl)-*o*-quaterphenyl (**2**),
— — —: 4,4‴-di(4-biphenylyl)-*o*-quaterphenyl (**3**),
— - — -: 4,4‴-di(3-biphenylyl)-*m*-quaterphenyl (**5**),
— – —: 3,4'-diphenylbiphenyl (**32**),
--------: *p*-quaterphenyl (**33**).

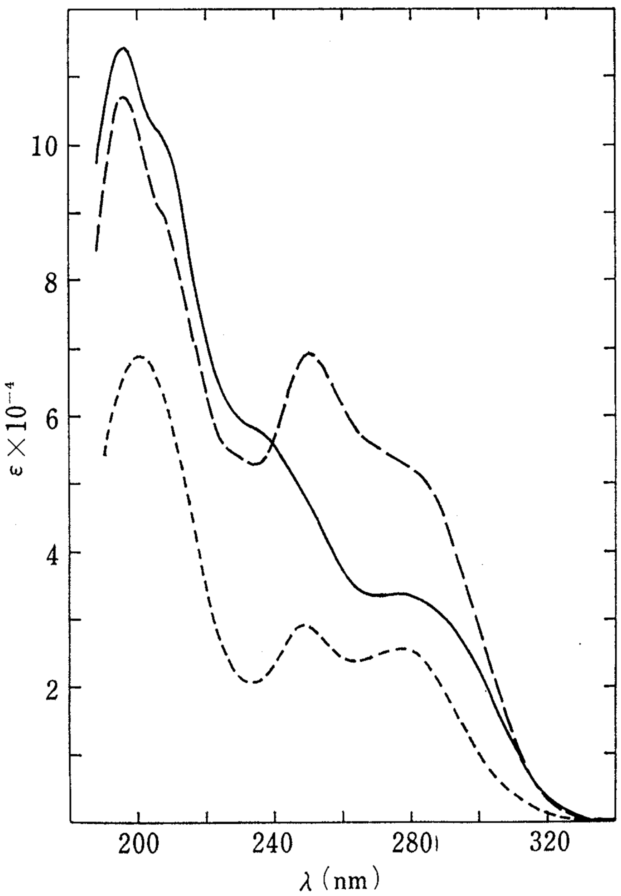


Fig. 2. UV Spectra of Octiphenyls and Quaterphenyl in Cyclohexane

———: 4,4‴-di(2-biphenylyl)-*o*-quaterphenyl (**1**),
— — —: 4,4‴-di(2-biphenylyl)-*m*-quaterphenyl (**4**),
--------: 2,4'-diphenylbiphenyl (**34**).

The spectrum of **3**, which has two *p*-quaterphenyl units linked by an *o*-linkage, showed the K-band (294 nm, ε=66900) at substantially the same wavelength but with an increase in intensity, compared with that (294, 44600) of **33**, corresponding to the half structural unit of **3**. Analogously, the absorption curves of **2** (260, 65300) and **5** (263, 85300) were related closely to that of **32** (268, 38400), corresponding to the half structural unit (Fig. 1). Furthermore, in the cases of **1** (232 (sh) and 276 nm; ε=58700 and 33800) and **4** (250 and 274 (sh); 69100 and 54000), the absorption curves were also closely related (but accompanied by a slight blue shift of the band (249 nm) in **1**) to that of **34** (249 and 278; 29100 and 25100), corresponding to the half structural unit (Fig. 2).

On the other hand, in the cases of **6** (248 (sh) and 298; 31000 and 31500), **7** (247 and 294 (sh); 74200 and 29300), and **8** (269 and 300 (sh); 62600 and 35800), which have identical half structural units linked by a *p*-linkage, the absorption curves were rather related to that of **29** (250 and 297; 35700 and 38900), corresponding to the interior structural unit. Moreover, additional effects attributable to the terminal *o*-, *m*-, and *p*-phenylene groups in **6**, **7**, and **8**, respectively, were also observed in their spectra (Fig. 3).

The UV absorption curves of the octiphenyls containing mixed linkages were related to those of the quaterphenyls or sexiphenyl corresponding to their half or interior structural units, respectively. In addition, the spectral data (Figs. 1—3) suggest that the K-band above *ca.* 260 nm of the octiphenyls, regardless of the presence of *o*- and/or *m*-phenylene ring(s), may be an indication of the presence of isolated or consecutive *p*-phenylene rings.[2b]

The HMO calculations of the longest wavelength absorption bands of the octiphenyls were carried out by assuming the dihedral angles of the pivot bonds to be as follows: 50° for phenyl—*o*- and *o*-—*o*-phenylene linkages, 35° for *o*-—*p*- and *m*-—*p*-phenylene linkages, and 20° for other linkages.[2b,10] The resonance integrals (π–π) were used with the values of $\cos\theta$ of the appropriate dihedral angles. Table IV summarizes the calculated and observed longest wavelengths of the octiphenyls, showing rather good agreement of the values except in the cases of **2** and **5**. The marked deviations in the cases of **2** and **5** may be due to inappropriate

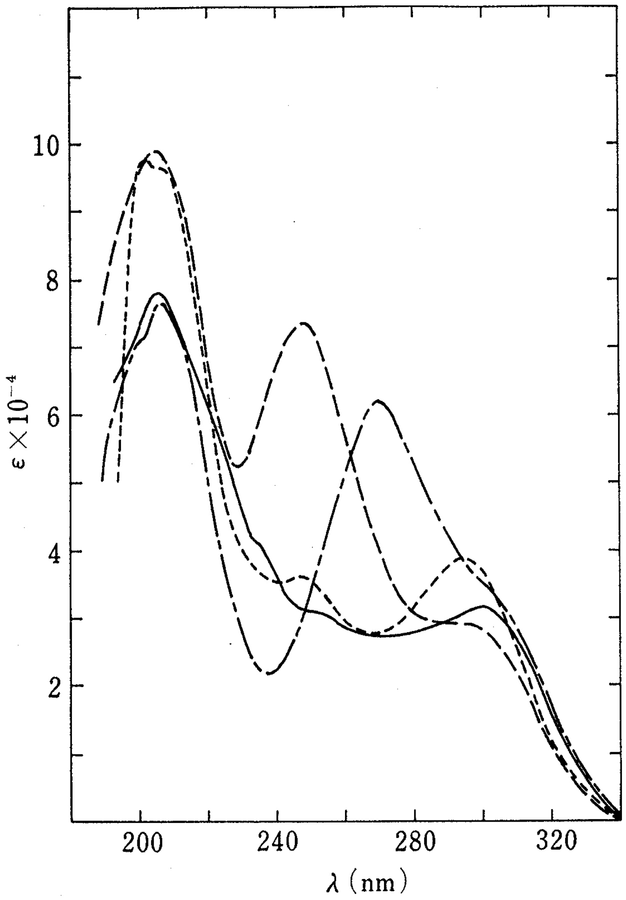


Fig. 3. UV Spectra of Octiphenyls and Sexiphenyl in Cyclohexane

———: 2,2'''-di(2-biphenylyl)-*p*-quaterphenyl (**6**),
— — — : 2,2'''-di(3-biphenylyl)-*p*-quaterphenyl (**7**),
- - - - : 2,2'''-di(4-biphenylyl)-*p*-quaterphenyl (**8**),
--------: 4,4'-di(2-biphenylyl)biphenyl (**29**).

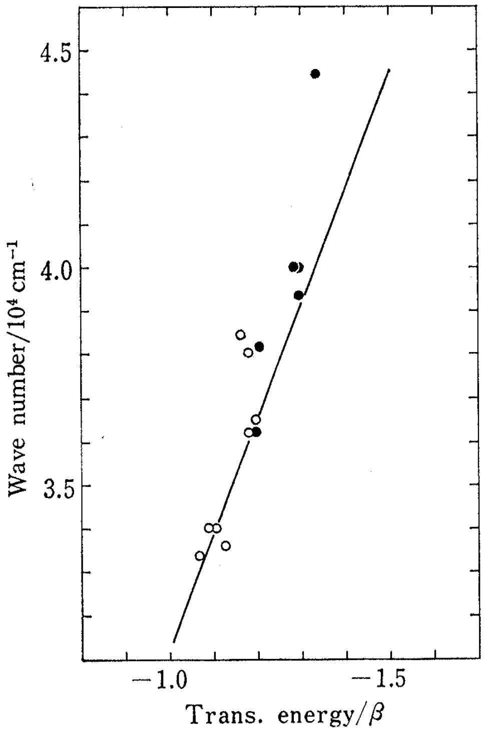


Fig. 4. Plots of the Wave Numbers of the Longest Wavelength Absorption Bands *vs.* Calculated Longest Wavelength Transition Energies of the Octiphenyls, together with Data Reported Previously[2d]

○: octiphenyls (**1**—**8**),
●: octiphenyls (preceding work).

Table IV. Calculated and Observed Longest Wavelength Absorption Bands of the Octiphenyls

Compound	Calcd trans. energy $\beta^{a)}$	Absorption band Calcd λ_{max}/nm	Obsd λ_{max}/nm	ε
1	−1.1785	284	276	33800
2	−1.1604	289	260	65300
3	−1.0844	309	294	66900
4	−1.1956	280	274 sh	54200
5	−1.1780	284	263	85300
6	−1.1244	298	298	31500
7	−1.1036	304	294 sh	29300
8	−1.0634	315	300 sh	35800

a) For β, −3.70 eV was used as a mean value calculated from the absorption bands of biphenyl and the first four *p*-polyphenyls.

selection of λ_{max} 260 nm in **2** and 263 nm in **5**, instead of hardly discernible shoulders near 275 nm, as the longest wavelength absorption bands. The results in Table IV are also confirmed by the approximately linear relation of the wave numbers of the longest wavelength absorption bands to the calculated longest wavelength transition energies, as shown in Fig. 4. In addition, the same parameters (cosθ and β) as those used previously for calculation of the wavelengths of twenty-four bi- to quinquephenyls,[2b)] were proved to be applicable to linear octiphenyls containing mixed linkages.

Experimental

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

2- (**9**), 3- (**10**), and 4-Iodobiphenyl (**11**), and 2- (**25**) and 3-bromobiphenyl (**26**), and 3,3′-diiodobiphenyl (**27**), and 4-iodo-*o*-terphenyl (**28**) were prepared as reported previously.[2)]

4-Iodo-2′-nitrobiphenyl (12)——Commercial 2-nitrobiphenyl was subjected to direct iodination[11)] to give **12**; pale yellow leaves from ethanol; mp 92—93° (lit.[11)] mp 93°); yield, 63%. *Anal.* Calcd for $C_{12}H_8I$-NO_2: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.12; H, 2.46; N, 4.40.

4-Iodo-3′-nitrobiphenyl (13)——3-Nitrobiphenyl[2a)] prepared from *m*-nitroaniline was subjected to direct iodination[11)] to provide **13**; colorless needles from ethanol; mp 113—113.5° (lit.[11)] mp 114°); yield, 76%. *Anal.* Calcd for $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.61; H, 2.45; N, 4.36.

2-Iodo-4′-nitrobiphenyl (14)——2-Aminobiphenyl was subjected to nitration[12)] to afford 2-amino-4′-nitrobiphenyl; orange needles from ethanol; mp 156—157.5° (lit.[12)] mp 156—158.5°). The aminonitro compound was converted into **14** in the usual manner; pale yellow needles from ethanol; mp 98—100° (lit.[13)] mp 100—101.5°); yield, 32% (based on 2-aminobiphenyl). *Anal.* Calcd for $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.50; H, 2.59; N, 4.36.

4,4‴-Dinitro-*o*-quaterphenyl (23a)——Copper powder (36.2 g, 570 mg-atom) was added in portions to **14** (30.8 g, 95 mmol) in a reaction tube (ϕ 3.5×21 cm) 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 subjected to chromatography on alumina with a cyclohexane–benzene (1 : 2, v/v) mixture (C–B (1 : 2)) as the eluent to give **23a**; yellow needles from benzene; mp 297—299° (lit.[13)] mp 290°); yield, 9.6 g (51%). *Anal.* Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07. Found: C, 73.00; H, 4.21; N, 7.04.

4,4‴-Diamino-*o*-quaterphenyl (23b)——A solution of **23a** (7.2 g) in hot benzene (300 ml) was treated with activated iron by a method similar to that of Hazlet and Dornfeld.[14)] After filtration, the filtrate was evaporated to dryness. The residue was purified by recrystallization from cyclohexane to give **23b**; colorless needles; mp 161—162° (lit.[13)] mp 163—164°); 5.8 g (95%). *Anal.* Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.92; H, 5.92; N, 8.38.

4,4‴-Diiodo-*o*-quaterphenyl (23c)——A suspension of **23b** (3.9 g) in concentrated hydrochloric acid (18 ml) and water (100 ml) was tetrazotized with sodium nitrite (5.6 g) in water (8 ml) at 0—5° with stirring for

2 hr. The cold suspension of tetrazonium salt formed was added to a solution of potassium iodide (17.5 g) in water (30 ml) with stirring, and the mixture was heated slowly up to *ca.* 80°, then cooled. The benzene extract was washed with water, sodium thiosulfate solution, sodium hydroxide solution, and then water. After removal of the solvent, the residue (6.2 g) was dissolved in a C–B (4: 1) mixture and subjected to chromatography on alumina with the same solvent as the eluent to provide **23c**; colorless needles from cyclohexane; mp 209—210° (lit.[13] mp 205—206°); 3.8 g (59%). *Anal.* Calcd for $C_{24}H_{16}I_2$: C, 51.64; H, 2.89. Found: C, 51.90; H, 3.16.

2,2‴-Dinitro-*p*-quaterphenyl (24a)——The iodonitro compound **12** (65.0 g) was treated with copper powder (76.2 g) as described for **23a**. The hot benzene extract was chromatographed on alumina with benzene to afford **24a**; yellow plates from ethanol–benzene; mp 236.5—237° (lit.[11] mp 233°); 16.6 g (42%). *Anal.* Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.97; H, 3.91; N, 6.87.

2,2‴-Diamino-*p*-quaterphenyl (24b)——A solution of **24a** (13.1 g) in hot benzene (1300 ml) was worked up in the manner described for **23b** to give **24b**; colorless cubes from benzene; mp 235—236°; 10.7 g (96%). *Anal.* Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.69; H, 6.12; N, 8.52.

2,2‴-Diiodo-*p*-quaterphenyl (24c)——A suspension of **24b** (29.0 g) in concentrated sulfuric acid (50 ml) and water (500 ml) was worked up as described for **23c**. The crude product was purified by chromatography on alumina with a C–B (1: 1) mixture to provide **24c**; colorless needles from benzene–ethanol; mp 178—178.5°; 18.0 g (37%). *Anal.* Calcd for $C_{24}H_{16}I_2$: C, 51.64; H, 2.89. Found: C, 51.88; H, 3.03.

4-(2-Biphenylyl)-2′-nitrobiphenyl (15a)——Copper powder (20.0 g, 315 mg-atom) was added in portions to a mixture of **9** (5.6 g, 20 mmol) and **12** (6.5 g, 20 mmol) in a reaction tube with stirring at 230—235° over a 3-hr period, then the mixture was heated at 240° for 1 hr. The hot benzene extract of the product (6.0 g) was treated with 150 ml of C–B (5: 2) to separate it into soluble and insoluble parts. Recrystallization of the latter (1.0 g) from ethanol afforded **24a** (0.90 g). The former, after removal of the solvent, was dissolved in C–B (5: 1) and then separated into three fractions by chromatography on alumina. Fraction (Fr.) 1, eluted with C–B (5: 1), afforded *o*-quaterphenyl (**36**) as colorless cubes from ethanol; mp 117.5—118° (lit.[15] mp 118°); 0.93 g. Fr. 2, eluted with C–B (5: 2), gave **15a** as pale yellow prisms from ethanol; mp 126—127.5°; 1.5 g (21%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.12; H, 4.80; N, 4.25. Fr. 3, eluted with benzene, provided additional **24a** (0.15 g).

2-Amino-4′-(2-biphenylyl)biphenyl (15b)——The nitroquaterphenyl **15a** (5.9 g) was reduced in the manner described for **23b** to give **15b** as colorless needles from petroleum benzin; mp 112—113°; 5.0 g (93%). *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.76; H, 5.70; N, 4.36.

4-(2-Biphenylyl)-2′-iodobiphenyl (15c)——A suspension of **15b** (4.7 g) in concentrated sulfuric acid (3 ml) and water (55 ml) was diazotized with sodium nitrite (1.3 g) in water (4 ml) at 0—5°. The cold suspension of diazonium salt formed was treated with a solution of potassium iodide (2.9 g) in water (5 ml). The crude product was purified by chromatography on alumina with C–B (5: 1) to afford **15c** as a colorless oil; 4.6 g (73%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.43; H, 3.89.

4,4‴-Di(2-biphenylyl)-*o*-quaterphenyl (1)——Procedure A: The iodoquaterphenyl **15c** (1.80 g, 4.2 mmol) was heated with copper powder (2.1 g, 33 mg-atom) at 265—270° for 2 hr, then at 270—275° for an additional 0.5 hr. The hot benzene extract (1.32 g) was subjected to chromatography on alumina with cyclohexane and then C–B (5: 1) to provide 2,4′-diphenylbiphenyl (**34**) as colorless prisms from ethanol; mp 118.5—119.5° (lit.[16] mp 119—119.5°); 206 mg. Subsequent elution with C–B (2: 1) gave **1** as colorless cubes from ethanol; mp 203.0°; 851 mg (67%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 196 (114700), 204 (sh) (104100), 232 (sh) (58700), 276 (33800). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.25; H, 5.45. MS *m/e*: 610 (M^+).

Procedure B-1: An ethereal solution of 2-biphenylylmagnesium bromide was prepared from **25** (2.80 g, 12 mmol), magnesium turnings (0.30 g, 12 mg-atom), and absolute ether (25 ml) under nitrogen in the usual manner. To the Grignard reagent thus prepared, a mixture of **23c** (1.67 g, 3 mmol) and bis(acetylacetonato)-nickel(II) (15 mg, 0.06 mmol) in benzene (30 ml) was added all at once. The mixture was stirred for 1 hr, refluxed for 3 hr, then hydrolyzed with dilute hydrochloric acid. The benzene extract was washed with water, and then dried. After removal of the solvent, the residue was chromatographed on alumina with C–B (5: 1) to afford biphenyl (**35**) (colorless leaves from methanol; mp 68—69°; 860 mg) and **36** (163 mg). Subsequent elution with C–B (7: 3) provided **1**; 1550 mg (85%).

4-(3-Biphenylyl)-2′-nitrobiphenyl (16a)——A mixture of **10** (22.4 g) and **12** (13.0 g) was treated with copper powder (61.0 g) as described for **15a**. The hot benzene extract (16.9 g) was separated into three fractions by chromatography on alumina. Fr. 1, eluted with C–B (5: 1), gave *m*-quaterphenyl (**30**) as colorless needles from ethanol; mp 86—87° (lit.[17] mp 85.5—86°); 5.2 g. Fr. 2, eluted with C–B (5: 2) and C–B (3: 2), afforded **16a** as pale yellow leaves from ethanol; mp 98—99°; 2.8 g (20%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 81.83; H, 4.67; N, 3.97. Fr. 3, eluted with benzene, gave **24a** (0.75 g).

2-Amino-4′-(3-biphenylyl)biphenyl (16b)——The nitroquaterphenyl **16a** (5.0 g) was reduced with activated iron in hot benzene. After filtration, hydrogen chloride was passed into the filtrate, then the precipitate was collected, washed with benzene, and dried; 4.8 g (94%). A portion of the salt was treated in the usual manner with aqueous alkali. The free base **16b** was obtained as pale yellow needles from petroleum benzin; mp 105—106°. *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.79; H, 5.90; N, 4.32.

4-(3-Biphenylyl)-2′-iodobiphenyl (16c)——The amine salt **16b**·HCl (4.4 g) in sulfuric acid was worked up as described for **15c**. The crude product (4.5 g) was purified by chromatography on alumina with C–B (5: 1) to provide **16c** as colorless needles from petroleum ether; mp 64.5—66°; 1.6 g (31%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.89; H, 4.12.

4,4‴-Di(3-biphenylyl)-*o*-quaterphenyl (2)——Procedure A: The iodoquaterphenyl **16c** (1.56 g) was heated with copper powder (1.8 g) in the manner described for **1** (procedure A). The benzene extract (1.08 g) was chromatographed on alumina with C–B (5: 1) to give 3,4′-diphenylbiphenyl (**32**) as colorless needles from ethanol; mp 165—166° (lit.[18] mp 166—167°); 150 mg. Subsequent elutions with C–B (5:1) and C–B (5: 2) provided **2** as colorless needles from ethanol; mp 144.3°; 697 mg (63%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 196 (sh) (85800), 206 (88400), 260 (65300). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.26; H, 5.79. MS *m/e*: 610 (M^+).

Procedure B-1: A mixture of **23c** (1.67 g) and bis(acetylacetonato)nickel(II) (15 mg) in benzene was added to an ethereal solution of 3-biphenylylmagnesium bromide, prepared from **26** (2.80 g) and magnesium turnings (0.30 g). The mixture was worked up as described for **1** (procedure B-1). The benzene extract was chromatographed on alumina with C–B (5: 1) to give **35** (843 mg). Subsequent elution with C–B (7: 3) afforded **30** (292 mg) and **2** (1595 mg, 87%).

2-Nitro-*p*-quaterphenyl (17a)——A mixture of **11** (16.8 g) and **12** (13.0 g) was heated with copper powder (50.8 g) as described for **15a**. After cooling, the product was extracted with hot benzene followed by hot toluene. The benzene extract (13.9 g) was treated with 300 ml of C–B (5: 2) to separate it into soluble [B_1] (10.8 g) and insoluble [B_2] (3.1 g) parts. The [B_2] part was treated with 500 ml of hot cyclohexane to separate it into soluble [C_1] (1.7 g) and insoluble [C_2] (1.4 g) parts. The [C_2] part and the toluene extract (1.7 g) were combined and recrystallized from benzene to provide *p*-quaterphenyl (**33**) as colorless plates; mp 317—319° (lit.[19] mp 317.7—318.7°); 2.9 g. The [B_1] and [C_1] parts were separated into three fractions by chromatography on alumina. Fr. 1, eluted with C–B (5: 2), provided **35** (0.23 g). Fr. 2, eluted with C–B (1: 1) and C–B (1: 2), gave **17a** as pale yellow needles from benzene; mp 210—211.5°; 3.1 g (22%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.05; H, 4.85; N, 4.04. Fr. 3, eluted with C–B (1: 2) and benzene, afforded **24a** (0.92 g).

2-Amino-*p*-quaterphenyl (17b)——The nitroquaterphenyl **17a** (5.6 g) was reduced in the manner described for **16b** to give **17b**·HCl; 5.5 g (96%). Free base **17b**: colorless needles from ethanol–benzene; mp 223.5—225.5°. *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.62; H, 5.88; N, 4.16.

2-Iodo-*p*-quaterphenyl (17c)——The amine salt **17b**·HCl (5.3 g) was converted into **17c** as described above. The crude product (5.4 g) was purified by chromatography on alumina with C–B (1: 3) to afford **17c** as colorless plates from C–B (2: 1); mp 180.5—181.5°; 2.9 g (46%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.83; H, 3.93.

4,4‴-Di(4-biphenylyl)-*o*-quaterphenyl (3)——The iodoquaterphenyl **17c** (2.55 g) was heated with copper powder (3.1 g) in the manner described for **1**. The benzene extract (1.69 g) was chromatographed on alumina with C–B (1: 1) to give **3** as colorless plates from C–B (1: 1); mp 253.1°; 962 mg (53%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 207 (83900), 294 (66900). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.50; H, 5.56. MS *m/e*: 610 (M^+). Subsequent elutions with C–B (1: 3) and benzene provided **33** (293 mg).

4-(2-Biphenylyl)-3′-nitrobiphenyl (18a)——A mixture of **9** (22.4 g) and **13** (13.0 g) was heated with copper powder (61.0 g) as described for **15a**. The benzene extract (18.0 g) was separated into three fractions by chromatography on alumina. Fr. 1, eluted with C–B (4: 1), afforded **36** (4.8 g). Fr. 2, eluted with C–B (4: 1), C–B (2: 1), and C–B (5: 4), provided **18a** as pale yellow plates from C–B (1: 1); mp 154.5—155°; 3.2 g (23%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.26; H, 5.11; N, 3.92. Fr. 3, eluted with benzene, gave 3,3‴-dinitro-*p*-quaterphenyl (**37**) as orange needles from ethanol–benzene; mp 210.5—211.5° (lit.[11] mp 207°); 0.12 g. *Anal.* Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07. Found: C, 73.01; H, 4.01; N, 7.13.

3-Amino-4′-(2-biphenylyl)biphenyl (18b)——The nitroquaterphenyl **18a** (6.0 g) was reduced as described for **16b** to afford **18b**·HCl; 5.9 g (96%). Free base **18b**: pale yellow needles from ethanol; mp 128.5—130°. *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.94; H, 5.94; N, 4.24.

4-(2-Biphenylyl)-3′-iodobiphenyl (18c)——The amine salt **18b**·HCl (4.7 g) was converted into **18c** as described above. The crude product (5.1 g) was purified by chromatography on alumina with C–B (9: 1) and C–B (4: 1) to provide **18c** as colorless needles from petroleum ether; mp 90.5—91°; 2.9 g (51%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.44; H, 4.03.

4,4‴-Di(2-biphenylyl)-*m*-quaterphenyl (4)——Procedure A: The iodoquaterphenyl **18c** (2.49 g) was treated with copper powder (2.95 g) as described for **1**. The benzene extract (2.0 g) was chromatographed on alumina with C–B (9:1) to give **34** (313 mg). Subsequent elutions with C–B (4:1) and C–B (2:1) afforded **4** as colorless prisms from cyclohexane; mp 213.4°; 1120 mg (64%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 197 (107600), 205 (sh) (93300), 250 (69100), 274 (sh) (54200). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.16; H, 5.57. MS *m/e*: 610 (M^+).

Procedure B-2: An ethereal solution of 4-(*o*-terphenylyl)magnesium iodide was prepared from **28** (12.46 g, 35 mmol), magnesium turnings (0.85 g, 35 mg-atom), and an absolute ether–benzene (2: 1, v/v) mixture (45 ml) in the usual manner. To the Grignard reagent thus prepared, a mixture of **27** (2.03 g, 5 mmol) and bis(acetylacetonato)nickel(II) (85 mg, 0.35 mmol) in benzene (30 ml) was added all at once. The mixture was worked up as described for **1**. The benzene extract was chromatographed on alumina with cyclohexane to provide *o*-terphenyl (**31**) as colorless needles from methanol; mp 56—57°; 2825 mg. Subsequent elution with C–B (4: 1) gave 4,4′-di(2-biphenylyl)biphenyl (**29**) as colorless leaves from benzene–ethanol; mp 235.9° (lit.[20]) mp 237.9—238.1°); 1517 mg. Finally, elution with C–B (5: 2) gave one more fraction which afforded **4**; 1066 mg (35%).

4-(3-Biphenylyl)-3′-nitrobiphenyl (19a)——A mixture of **10** (22.4 g) and **13** (13.0 g) was treated with copper powder (61.0 g) as described for **15a**. The benzene extract (18.2 g) was chromatographed on alumina with C–B (5: 2), then C–B (3: 2) and C–B (2: 3), and finally with C–B (1: 4) and benzene to give one fraction in each case.

Fr. 2 gave **19a** as pale yellow leaves from ethanol–benzene; mp 134—135°; 3.1 g (22%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 81.88; H, 4.92; N, 4.00. Beside this, **30** (2.6 g) and **37** (0.09 g) were isolated as by-products from Frs. 1 and 3, respectively.

3-Amino-4′-(3-biphenylyl)biphenyl (19b)——The nitro compound **19a** (6.0 g) was reduced as described above to afford **19b** as colorless needles from ethanol; mp 140.5—141°; 5.4 g (98%). *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.41; H, 5.78; N, 4.19.

4-(3-Biphenylyl)-3′-iodobiphenyl (19c)——The amine **19b** (5.8 g) was converted into **19c** as described above. The crude product (3.3 g) was purified by chromatography on alumina with C–B (2: 1) and C–B (1: 1) to provide **19c** as colorless leaves from cyclohexane; mp 172—172.5°; 1.06 g (14%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.56; H, 4.01.

4,4‴-Di(3-biphenylyl)-*m*-quaterphenyl (5)——The iodo compound **19c** (0.80 g) was treated with copper powder (2.0 g) as described for **1**. The benzene extract (0.40 g) was chromatographed on alumina with C–B (1: 3) to give **32** (147 mg). Subsequent elutions with C–B (1: 3) and C–B (1: 9) provided **5** as colorless leaves from benzene–cyclohexane; mp 285.3°; 280 mg (50%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 195 (87200), 203 (80900), 263 (85300). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.62; H, 5.47. MS *m/e*: 610 (M^+).

4-Nitro-*o*-quaterphenyl (20a)——A mixture of **9** (16.8 g) and **14** (6.5 g) was heated with copper powder (40.6 g) as described for **15a**. The benzene extract (13.0 g) was chromatographed on alumina with C–B (4: 1), then C–B (2: 1) and C–B (1: 1), and finally with benzene to give one fraction in each case. Fr. 2 gave **20a** as pale yellow needles from cyclohexane; mp 135.5—137°; 1.5 g (21%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.23; H, 4.96; N, 4.01. Beside this, **36** (4.6 g) and **23a** (0.30 g) were isolated as by-products from Frs. 1 and 3, respectively.

4-Amino-*o*-quaterphenyl (20b)——The nitroquaterphenyl **20a** (6.0 g) was reduced as described above to afford **20b**·HCl; 6.0 g (98%). Free base **20b**: colorless needles from petroleum benzin; mp 120—121°. *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.98; H, 5.83; N, 4.47.

4-Iodo-*o*-quaterphenyl (20c)——The amine salt **20b**·HCl (5.6 g) was converted into **20c** as described above. The crude product (6.2 g) was purified by chromatography on alumina with C–B (9: 1) to provide **20c** as colorless needles from ethanol; mp 132—133°; 2.9 g (43%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.97; H, 3.87.

2,2‴-Di(2-biphenylyl)-*p*-quaterphenyl (6)——Procedure A: The iodoquaterphenyl **20c** (2.50 g) was treated with copper powder (2.9 g) as described for **1**. The benzene extract (1.9 g) was chromatographed on alumina with C–B (9: 1) to give **36** (376 mg). Subsequent elution with C–B (4: 1) afforded **6** as colorless leaves from benzene–ethanol; mp 235.1°; 1075 mg (61%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 207 (78200), 248 (sh) (31000), 298 (31500). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.24; H, 5.43. MS *m/e*: 610 (M^+).

Procedure B-1: A mixture of **24c** (1.67 g) and bis(acetylacetonato)nickel(II) (15 mg) in benzene was added to an ethereal solution of 2-biphenylylmagnesium bromide, and then the mixture was worked up as described for **1**. The benzene extract was chromatographed on alumina with C–B (9: 1) to afford **35** (385 mg) and **36** (488 mg). Subsequent elution with C–B (4: 1) provided **6** (656 mg, 36%).

2-(3-Biphenylyl)-4′-nitrobiphenyl (21a)——A mixture of **10** (22.4 g) and **14** (13.0 g) was heated with copper powder (61.0 g) as described for **15a**. The benzene extract (20.4 g) was treated with 300 ml of C–B (4: 1) to separate it into soluble and insoluble parts. The former was separated into three fractions by chromatography on alumina. Fr. 1, eluted with C–B (4: 1), afforded **30** (4.8 g). Fr. 2, eluted with C–B (4: 1) and C–B (2: 1), gave **21a** as pale yellow needles from ethanol; mp 144—145°; 3.5 g (25%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 81.82; H, 4.82; N, 4.00. Fr. 3, eluted with benzene, was combined with the insoluble part described above, and then recrystallized from benzene to give **23a** (0.83 g).

4-Amino-2′-(3-biphenylyl)biphenyl (21b)——The nitro compound **21a** (5.0 g) was reduced as described above to provide **21b** as pale yellow plates from ethanol; mp 122—123°; 4.3 g (94%). *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.85; H, 5.80; N, 4.36.

2-(3-Biphenylyl)-4′-iodobiphenyl (21c)——The amine **21b** (4.7 g) was converted into **21c** as described above. The crude product (5.0 g) was purified by chromatography on alumina with C–B (4: 1) and C–B (2: 1) to afford **21c** as colorless needles from ethanol; mp 98—99°; 3.7 g (59%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.42; H, 3.84.

2,2‴-Di(3-biphenylyl)-*p*-quaterphenyl (7)——Procedure A: The iodoquaterphenyl **21c** (3.03 g) was heated with copper powder (3.7 g) as described for **1**. The benzene extract (2.3 g) was chromatographed on alumina with C–B (9: 1) and C–B (4: 1) to give 2,3′-diphenylbiphenyl (**38**) as colorless needles from ethanol; mp 91—92° (lit.[21]) mp 90.5—91°); 257 mg. Subsequent elutions with C–B (4: 1) and C–B (2: 1) provided **7** as colorless plates from cyclohexane; mp 185.1°; 1223 mg (57%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 204 (99900), 247 (74200), 294 (sh) (29300). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.56; H, 5.86. MS *m/e*: 610 (M^+).

Procedure B-1: A mixture of **24c** (1.67 g) and bis(acetylacetonato)nickel(II) (15 mg) in benzene was added to an ethereal solution of 3-biphenylylmagnesium bromide, and then the mixture was worked up as described for **1**. The benzene extract was chromatographed on alumina with C–B (9: 1) to afford **35** (565 mg) and **30** (225 mg). Subsequent elution with C–B (4: 1) gave **7** (675 mg, 37%).

2-(4-Biphenylyl)-4′-nitrobiphenyl (22a)——A mixture of **11** (11.2 g) and **14** (6.5 g) was treated with copper powder (30.5 g) at 235—240°. After cooling, the product was extracted with hot benzene followed by hot toluene. The benzene extract (6.5 g) was treated with 60 ml of C–B (5: 2) to separate it into soluble and insoluble parts. Recrystallization of the latter together with the toluene extract (1.21 g) from benzene provided **33** (1.47 g). The former was chromatographed on alumina with the same solvent to give **22a** as pale yellow prisms from ethanol; mp 145—146°; 1.3 g (19%). *Anal.* Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.26; H, 4.82; N, 3.98. Beside this, **23a** (0.33 g) was isolated as a by-product from the fraction eluted with benzene.

4-Amino-2′-(4-biphenylyl)biphenyl (22b)——The nitro compound **22a** (6.0 g) was reduced as described above to provide **22b** as colorless needles from petroleum benzin; mp 152—153.5°; 5.2 g (95%). *Anal.* Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.66; H, 5.72; N, 4.42.

2-(4-Biphenylyl)-4′-iodobiphenyl (22c)——The amine **22b** (3.4 g) was converted into **22c** as described above. The crude product (4.9 g) was purified by chromatography on alumina with C–B (5: 1) to afford **22c** as colorless needles from ethanol-benzene; mp 152—153°; 3.4 g (74%). *Anal.* Calcd for $C_{24}H_{17}I$: C, 66.68; H, 3.96. Found: C, 66.86; H, 3.86.

2,2‴-Di(4-biphenylyl)-*p*-quaterphenyl (8)——The iodo compound **22c** (1.30 g) was treated with copper powder (1.9 g) as described for **1**. The benzene extract (0.94 g) was chromatographed on alumina with C–B (5: 2) to give **34** (154 mg). Subsequent elution with benzene provided **8** as colorless leaves from benzene; mp 302.5—304°; 670 mg (73%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 202 (sh) (72600), 205 (77400), 269 (62600), 300 (sh) (35800). *Anal.* Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.33; H, 5.43. MS *m/e*: 610 (M^+).

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References and Notes

1) This paper forms Part V of "Studies of Polyphenyls and Polyphenylenes." The preceding paper, Part IV: S. Ozasa, Y. Fujioka, M. Fujiwara, and E. Ibuki, *Chem. Pharm. Bull.*, **28**, 3210 (1980).
2) *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)~~; *d*) S. Ozasa, Y. Fujioka, M. Fujiwara, and E. Ibuki, *ibid.*, **28**, 3210 (1980).
3) R.J.P. Corriu and J.P. Masse, *J. Chem. Soc., Chem. Commun.*, **1972**, 144.
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. 2).
5) These octiphenyls (**1**, **2**, **4**, **6**, and **7**) were identified by mixed-melting-point determination and by comparison of the IR and UV spectra with those of the samples prepared by the Ullmann reaction.
6) S. Sandroni and F. Geiss, *Z. Anal. Chem.*, **220**, 321 (1966); J.E. Stewart and M. Hellmann, *J. Res. Natl. Bull. Stand.*, **60**, 125 (1958); R.C. Doss and P.W. Solomon, *J. Org. Chem.*, **29**, 1567 (1964).
7) Refer to 2,3″-diphenyl-*p*-terphenyl (δ 7.23 and 7.51, 4H, AA′BB′-q, $J=8.7$ Hz, $C_{2'},C_{6'}$–H and $C_{3'},C_{5'}$–H) and 2,2‴-diphenyl-*p*-quaterphenyl (δ 7.18 and 7.44, 8H, AA′BB′-q, $J=8.3$ Hz, $C_{2'},C_{6'}$–H and $C_{3'},C_{5'}$–H) (Ref. 2*b*).
8) Refer to 2,2′-di(4-biphenylyl)biphenyl (δ 6.66 and 7.23, 8H, AA′BB′-q, $J=8.5$ Hz, C_3,C_5–H and C_2,C_6–H) (Ref. 2*c*).
9) Refer to 2,4′-di(2-biphenylyl)biphenyl (δ 6.45 and 6.79) (Table III).
10) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957); H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340 (1959); **33**, 109 (1960).
11) H.O. Wirth, R. Müller, and W. Kern, *Makromol. Chem.*, **77**, 90 (1964).
12) G.D. Mendenhall and P.A.S. Smith, "Organic Syntheses," Coll. Vol. V, ed. by H.E. Baumgarten, John Wiley and Sons, Inc., New York·London·Sydney·Toronto, 1973, p. 829.
13) S. Sako, *Bull. Chem. Soc. Jpn.*, **10**, 585 (1935).

14) S.E. Hazlet and C.A. Dornfeld, *J. Am. Chem. Soc.*, **66**, 1781 (1944).
15) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).
16) G.F. Woods and F. Scotti, *J. Org. Chem.*, **26**, 312 (1961).
17) G.F. Woods and F.T. Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).
18) G.F. Woods and I.W. Tucker, *J. Am. Chem. Soc.*, **70**, 3340 (1948).
19) J.J.E. Schmidt and J.A. Krimmel, *J. Org. Chem.*, **25**, 252 (1960).
20) C. Beaudet, J. Horlait, A. Marcq, and G. Belpaire, *EUR* 31, f (1962).
21) G.F. Woods and A.L. Artsdale, *J. Am. Chem. Soc.*, **72**, 3221 (1950).