Charge-transfer Complexes, Gas-liquid Chromatographic and Photochemical Characteristics, and Solvent Adducts of Polyphenylenes and Related Linear Polyphenyls[1)]

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The absorption spectra of the charge-transfer (CT) complexes formed by two acceptors (tetracyanoethylene and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone) with thirteen macrocyclic polyphenylenes and with thirty-eight linear polyphenyls were measured in dichloromethane. A linear relationship existing between the first transitions of the CT-complexes and those of the uncomplexed donor hydrocarbons made it possible to predict the CT-bands of new polyphenylenes and polyphenyls. By the gas-liquid chromatography using a glass capillary column, forty-nine polyphenyls and polyphenylenes, containing a large number of isomers, were successfully analyzed. The relationship between the retention times and the structure of linear polyphenyls was expressed by means of a simple empirical equation, and the equation was also applicable to the polyphenylenes by adding a correction factor. These equations are extremely useful for the estimation of the retention time and elution order and the structure of unknown polyphenyls and polyphenylenes. The reductive irradiation of *m,m,o,p,o*-pentaphenylene provided the bridged annulene compound. For six polyphenylenes and the related compounds, the criteria for the occurrence of the intramolecular photocoupling reaction were discussed. Among the examined polyphenylenes, *m,o,o,m,o,o*-hexaphenylene and *o,p,p,o,p,p,o,p,p*-nonaphenylene formed the adducts with several solvents.

In the preceding paper[2)] fourteen macrocyclic polyphenylenes have been synthesized to elucidate the relationship between the structures (the number and arrangement of the phenylene rings) and the physical properties such as infrared (IR), ultraviolet (UV), proton magnetic resonance (^{1}H NMR), and mass (MS) spectra on a series of linear and branched polyphenyls.[3)] The polyphenylenes have been characterized by the structure, in which both terminal rings of polyphenyls were linked to each other so that the rotation of pivot bonds was restricted significantly due to their rigid geometry. The results have indicated that the ^{1}H NMR and UV spectral studies provided useful conformational information, and the Hückel molecular orbital (HMO) calculations of the longest-wavelength absorption bands of polyphenylenes also gave additional grounds for their conformation deduced from their spectral data and Dreiding stereomodels.

The present study was undertaken to investigate several chemical behaviors of thirteen polyphenylenes {*m,m,o,p,o*-pentaphenylene (**1**); *m,m,o,m,m,o*- (**2**), *m,o,o,m,o,o*- (**3**), *o,o,p,o,o,p*- (**4**), *m,o,p,m,o,p*-(**5**), *o,p,o,p,o,p*- (**6**), *m,o,p,o,p,o*- (**7**), *m,o,m,o,m,o*- (**8**), *m,m,m,o,m,o*- (**9**), and *m*-hexaphenylene (**10**); *m,o,p,p,o,m,p*- (**11**) and *m,m,m,m,p,o,p*-heptaphenylene (**12**); and *o,p,p,o,p,p,o,p,p*-nonaphenylene (**13**)} as well as those of the closely related linear polyphenyls (**14—53**). So far, several studies have been reported on the charge-transfer (CT) complexes of biphenyl and three terphenyls,[4)] on the photodehydrocyclization of several *o*-terphenyl-type compounds,[5)] and further on the gas chromatographic analysis of linear and branched polyphenyls,[6)] but none on those of polyphenylenes. On the gas-liquid chromatography (GLC) of aliphatic or monocyclic compounds, it has been known that the "retention index" by Kovâts serves to estimate their structure.[7)] Karger *et al.*[8)] and Ono[9)] have reported the applicability of the Hammet Equation for GLC using the series of isomers of phenols and anilines and of alkyl benzenes, respectively. In a programmed-temperature gas chromatography Solomon has suggested a relationship between elution temperatures and structures of polyphenyls, but their analytical conditions and the complex additive terms are to be improved.[6a)]

The CT-complexes have been formed by the donor hydrocarbons with two acceptors (tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)) in dichloromethane, and the relationship between the longest-wavelength absorption bands of the CT-complexes and those of the uncomplexed donors has been discussed. The gas-liquid chromatographic analysis of the polyphenylenes and polyphenyls has been performed and the relationship between the structures (the number and arrangement of the benzene rings) and the retention time has been formulated. In addition, the intramolecular photocoupling reactions and solvent adduct formations of polyphenylenes have also been discussed.

Results and Discussion

Charge-transfer Complexes. The CT-complexes between the donors (thirteen polyphenylenes (**1—13**) and thirty-eight related polyphenyls (**14—34**, **36—41**, and **43—53**)) and two acceptors (TCNE and DDQ) were prepared in dichloromethane[10)] and their absorption spectra were determined. The CT-complexes, which were characterized by the intensely colored solutions (orange to greenish blue), showed generally plural absorption bands for TCNE[12)] and only one band for DDQ. Tables 1 and 2 list the longest-wavelength absorption (first) CT-bands of the polyphenylenes and polyphenyls, respectively, and also the first bands of each uncomplexed hydrocarbon. Now the observed first transition energies (E_{ct}) for the CT-complexes are plotted against the observed first π-π* transition ener-

Table 1. Longest-wavelength absorption bands of TCNE- and DDQ-polyphenylene CT-complexes^a) and of the donors^b) (λ_{max}/nm)

Compound No.	TCNE-complex	DDQ-complex	Donor
1	510	588	256 sh
2	485	565 sh	248 sh
3	540 sh	600 sh	242 sh
4	597	693	288 sh
5	547	630	264 sh
6	545 sh	630 sh	276 sh
7	525 sh	605 sh	237
8	505 sh	580 sh	254 sh
9	505 sh	590	252 sh
10	490 sh	—	247
11	590	687	312 sh
12	515 sh	610 sh	284 infl
13	625	703	320 sh

a) In dichloromethane. b) In cyclohexane (*cf.* Ref. 2).

Table 2. Longest-wavelength absorption bands of TCNE- and DDQ-polyphenyl CT-complexes^a) and of the donors^b) (λ_{max}/nm)

Compound^c) No.	TCNE-complex	DDQ-complex	Donor
ϕϕ (**14**)	496	563	248
ϕoϕ (**15**)	500 sh	560 sh	251 sh
ϕmϕ (**16**)	496	563	247
ϕpϕ (**17**)	555	637	276
ϕooϕ (**18**)	490 sh	560 sh	245 sh
ϕomϕ (**19**)	502	570 sh	251 sh
ϕopϕ (**20**)	552	639	278
ϕmmϕ (**21**)	495	562	248
ϕmpϕ (**22**)	537	613	268
ϕppϕ (**23**)	590	680	294
ϕoooϕ (**24**)	475 sh	545 sh	237
ϕomoϕ (**25**)	500 sh	575 sh	250 sh
ϕopoϕ (**26**)	535	625 sh	280
ϕmomϕ (**27**)	498	573	249 sh
ϕpopϕ (**28**)	563	648	284 sh
ϕopmϕ (**29**)	493	575	275 sh
ϕoppϕ (**30**)	585	680	295
ϕmmmϕ (**31**)	494	560	249
ϕmpm (**32**)	505	590 sh	280 sh
ϕpmpϕ (**33**)	558	640	280
ϕmppϕ (**34**)	572	672	296
ϕooooϕ (**36**)	465 sh	—	231
ϕoomoϕ (**37**)	500 sh	570 sh	250 sh
ϕoopoϕ (**38**)	495 sh	565	275 sh
ϕmoomϕ (**39**)	510	570	245
ϕommoϕ (**40**)	495 sh	580 sh	252 sh
ϕpoopϕ (**41**)	560	650	272
ϕompoϕ (**43**)	500 sh	625	272 sh
ϕoppoϕ (**44**)	575	690	297
ϕmommϕ (**45**)	493	562	250 sh
ϕmopmϕ (**46**)	498	575 sh	249
ϕpompϕ (**47**)	560	643	275
ϕopmmϕ (**48**)	493	575	277 sh
ϕopppϕ (**49**)	605	705	306
ϕmmmmϕ (**50**)	492	565	249
ϕmmpmϕ (**51**)	505	590	286 sh
ϕpmmpϕ (**52**)	550	630	273
ϕmppmϕ (**53**)	590	665 sh	296

a) In dichloromethane. b) In cyclohexane (*cf.* Ref. 3a-d and 3f). c) ϕ, o, m, and p refer to phenyl and to *o*-, *m*-, and *p*-phenylene rings.

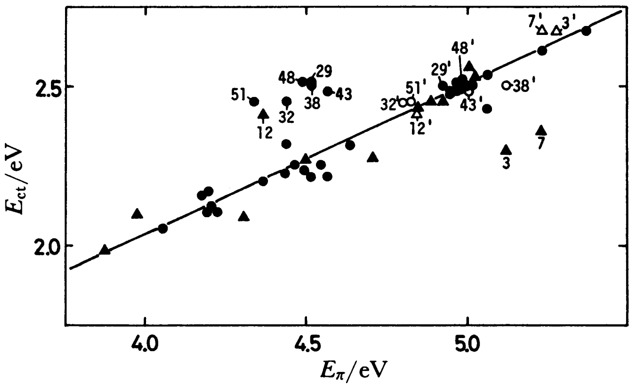


Fig. 1. Plot of the transition energy (E_{ct}) for the first CT-band of TCNE-donor complex *vs.* the energy (E_π) for the first π-π^* transition of the donor; the points are numbered according to the compound number in Tables 1 and 2; ●: Linear polyphenyls, ▲: polyphenylenes.

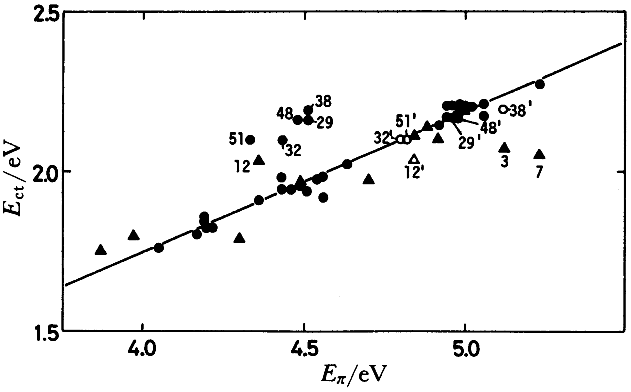


Fig. 2. Plot of the transition energy (E_{ct}) for the first CT-band of DDQ-donor complex *vs.* the energy (E_π) for the first π-π^* transition of the donor; the points are numbered according to the compound No. in Tables 1 and 2; ●: Linear polyphenyls, ▲: polyphenylenes.

gies (E_π) for the donor hydrocarbons (Figs. 1 and 2).

In Fig. 1, all but nine of the points lie approximately on a straight line (slope=0.47).[13] This linear relationship between E_{ct} and E_π is similar to that found previously for the CT-complexes between polycyclic aromatic hydrocarbons and trinitrofluorenone and defined by the following Eq. 1.[14]

$$E_{ct} = (1/2)E_\pi + C, \qquad (1)$$

where C is a constant for the acceptor such as TCNE or DDQ.

The deviation of the values for compounds (**12**, **29**, **32**, **38**, **43**, **48**, and **51**) from the straight line is probably due to the obscurity of their real first CT-bands, because their first CT-bands were broad at the longer-wavelength side, and their E_{ct} were correlated to the energies of the second bands for the uncomplexed donors, in which all the first bands were observed as a shoulder or an inflection (the points with primed numbers in Fig. 1). For compounds, **3** and **7**, the deviation cannot be explained, even though the energies of the second CT-bands (465 and 460 nm, respectively) were correlated to the energies of the second (235 nm) and first (237 nm) bands of the donors.[2]

An analogous correlation was observed between the CT-bands of DDQ-complexes and the first bands of the uncomplexed donors (Fig. 2; the slope of the fitted straight line=0.43).[15]

The foregoing results indicated that the polyphenylenes (containing 5—9 benzene rings) and polyphenyls (containing 2—6 benzene rings) formed the weak CT-complexes with TCNE or DDQ in solution, and an approximately linear relationship with a slope of one-half existed between the first transitions of the CT-complexes and those of the uncomplexed donors. Consequently, these results made it possible to predict the CT-bands of new polyphenylenes and polyphenyls.

Gas-liquid Chromatographic Characteristics. The retention times (t_R) of nine polyphenylenes (**1**—**9**) and a series of polyphenyls (**14**—**53**), having high boiling points and a large number of isomers, were determined at 5—15 different column temperatures (70—340 °C) using a glass capillary column (Dexsil 300GC as liquid phase).[16] For comparison the t_R at the same column temperature were calculated using Eq. 2

$$\log t_R = A \times 1/T + B \qquad (2)$$

and the least squares method.[17] The log t_R at 250 °C thus determined are shown in Tables 3 and 4.

To investigate the structure-retention time correlation of the polyphenyls and polyphenylenes, the retention indexes (R_I) were firstly obtained as a simple difference between the log t_R of each polyphenyl and biphenyl (**14**) as a standard. Then, the comparison between the R_I-values of three terphenyls (**15**—**17**) and that of **14** gave the following estimated values for each phenylene unit: *o*- (0.74), *m*- (1.17), and *p*-phenylene (1.23). Further, by introduction of the correction factor

TABLE 3. RETENTION TIMES AND INDEXES OF THE LINEAR POLYPHENYLS

Compound[a)] No.	$\log t_R = A \times 1/T + B$ A	B	$\log t_R$[b)] (250 °C)	R_I	R'_I
$\phi\phi$ (**14**)	2968	−7.307	−1.632	0	
ϕoϕ (**15**)	3515	−7.613	−0.892	0.74	0.74
ϕmϕ (**16**)	3784	−7.694	−0.459	1.17	1.17
ϕpϕ (**17**)	3822	−7.713	−0.405	1.23	1.23
ϕooϕ (**18**)	3957	−7.767	−0.201	1.43	1.40
ϕmoϕ (**19**)	4310	−8.158	0.083	1.72	1.72
ϕopϕ (**20**)	4383	−8.220	0.161	1.79	1.79
ϕmmϕ (**21**)	4746	−8.518	0.558	2.19	2.25
ϕmpϕ (**22**)	4802	−8.541	0.644	2.28	2.31
ϕppϕ (**23**)	4846	−8.574	0.694	2.33	2.38
ϕoooϕ (**24**)	4536	−8.238	0.438	2.07	2.02
ϕomoϕ (**25**)	4915	−8.767	0.633	2.27	2.33
ϕopoϕ (**26**)	5027	−8.861	0.753	2.39	2.40
ϕmomϕ (**27**)	5209	−9.043	0.916	2.55	2.62
ϕpopϕ (**28**)	5424	−9.282	1.087	2.72	2.75
ϕmpoϕ (**29**)	5528	−9.349	1.210	2.84	2.80
ϕoppϕ (**30**)	5584	−9.427	1.248	2.88	2.87
ϕmmmϕ (**31**)	5927	−9.795	1.537	3.17	3.23
ϕmpmϕ (**32**)	6024	−9.797	1.721	3.35	3.31
ϕpmpϕ (**33**)	6041	−9.824	1.726	3.36	3.35
ϕmppϕ (**34**)	6062	−9.856	1.735	3.37	3.37
ϕpppϕ (**35**)	6096	−9.874	1.782	3.41	3.43
ϕooooϕ (**36**)	5178	−8.874	1.023	2.66	2.58
ϕomooϕ (**37**)	5396	−9.188	1.127	2.76	2.88
ϕoopoϕ (**38**)	5567	−9.414	1.244	2.88	2.94
ϕmoomϕ (**39**)	5729	−9.511	1.445	3.08	3.15
ϕommoϕ (**40**)	5779	−9.596	1.455	3.09	3.17
ϕpoopϕ (**41**)	5896	−9.637	1.639	3.27	3.27
ϕopopϕ (**42**)	5900	−9.640	1.643	3.28	3.29
ϕompoϕ (**43**)	5905	−9.648	1.649	3.28	3.24
ϕoppoϕ (**44**)	5927	−9.696	1.666	3.30	3.31
ϕmmomϕ (**45**)	6237	−10.117	1.808	3.44	3.55
ϕmopmϕ (**46**)	6379	−10.247	1.950	3.58	3.62
ϕpmopϕ (**47**)	6410	−10.243	2.013	3.65	3.67
ϕmmpoϕ (**48**)	6453	−10.234	2.104	3.74	3.72
ϕopppϕ (**49**)	6496	−10.138	2.282	3.91	3.85
ϕmmmmϕ (**50**)	6750	−10.455	2.451	4.08	4.14
ϕmmpmϕ (**51**)	6758	−10.318	2.603	4.24	4.21
ϕpmmpϕ (**52**)	6779	−10.309	2.652	4.28	4.26
ϕmppmϕ (**53**)	6811	−10.345	2.678	4.31	4.28

a) Refer to the footnote c) to Table2. b) Observed values: $-0.30 < \log t_R < 1.70$; inserted values: $\log t_R < -0.30$ and $\log t_R > 1.70$.

TABLE 4. RETENTION TIMES AND INDEXES OF THE POLYPHENYLENES (**1**—**9**)

Compound[a)]	$\log t_R = \mathrm{A}\times 1/T + \mathrm{B}$		$\log t_R$[b)]	R_I	R'_I
No.	A	B	(250 °C)		
1	5232	−8.819	1.181	2.81	2.79
3	5629	−9.277	1.488	3.12	2.89
8	5705	−9.367	1.548	3.18	3.17
7	5762	−9.368	1.644	3.28	3.29
6	5789	−9.400	1.663	3.30	3.35
2	5878	−9.443	1.796	3.42	3.43
5	5953	−9.445	1.937	3.57	3.55
4	5957	−9.449	1.941	3.57	3.01
9	6276	−9.741	2.259	3.89	3.53

a) Refer to the footnote b) to Table 3.

for the number of the phenylene ring, $(0.96)^{n-1}$ (n: the total number of phenylene rings), following empirical Eq. 3 was obtained.

$$R'_I = (0.96)^{n-1} \times (0.74x + 1.17y + 1.23z + \alpha), \quad (3)$$

where x, y, and z are the number of *o*-, *m*-, and *p*-phenylene rings constituting each polyphenyl, respectively, and α is the correction factor for the substitution pattern of the phenylene rings. The values are estimated as follows: −0.01, −0.12, and −0.11 for an *o*-, *m*-, and *p*-phenylene rings adjacent to the *o*-phenylene ring, respectively, and +0.11 for a *m*- or *p*-phenylene ring adjacent to the *p*-phenylene ring.

The R'_I-values calculated by Eq. 3 are in good agreement with the experimental R_I-values (Table 3). The results are also confirmed by the approximate linear relation of the $\log t_R$ values to the R'_I-values (Fig. 3).[18)] Care must be taken in appling indiscriminately a variety of analytical conditions. However, when unknown polyphenyls were bracketed with polyphenyls of known retention indexes, empirical Eq. 3 is useful for the estimation of the retention time, the elution order and the presumption of their structures.

Meanwhile the data of nine polyphenylenes (penta- and hexaphenylenes) are also listed in Table 4, which differ from the linear polyphenyls in not having both terminal rings. Empirical Eq. 4 for the polyphenylenes was derived from Eq. 3 by adding a new correction factor ($\beta = -1.20$).

$$R''_I = (0.96)^{n-1} \times (0.74x + 1.17y + 1.23z + \alpha) + \beta \quad (4)$$

The R''_I-values calculated by Eq. 4 are in fair agreement with R_I- or $\log t_R$-values obtained from the experimental values except for compounds **3**, **4**, and **9** (Table 4 and Fig. 3). These results can be explained by the fact that compounds **1**, **2**, and **5**—**8**, showing a good agreement with experimental values, are nonplanar due to a spacial overcrowded conformation, while other compounds **3**, **4**, and **9** are more planar in the vapor phase.

Furthermore, when the R_I-values of the polyphenylenes were compared with those of the corresponding linear analogues (Table 5), the former gave approximately the same or somewhat larger R_I-values than the latter, except for **4** and **9** which showed clearly larger values. That is to say, by the cyclization of the linear polyphenyls to the macrocyclic analogues the retention times were hardly affected or slightly delayed.

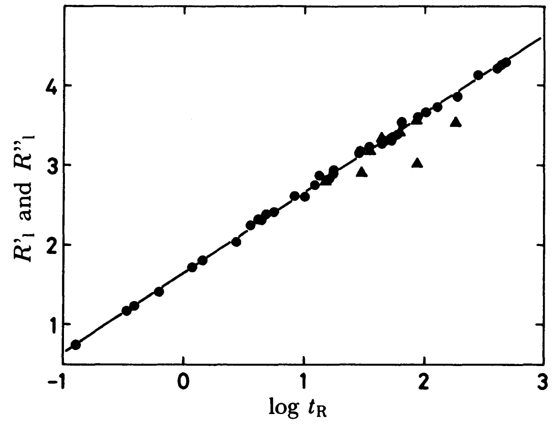


Fig. 3. Plot of the log of the retention time ($\log t_R$) *vs.* the calculated retention index (R'_I and R''_I); ●: Linear polyphenyls, ▲: polyphenylenes.

Foregoing results indicated that the relationship between the number and arrangement of benzene rings and the retention times of polyphenyls and polyphenylenes could be expressed by simple empirical equations, respectively. Both equations are very useful for the prediction of the retention time, elution order and the presumption of structures of unknown polyphenylenes and polyphenyls.

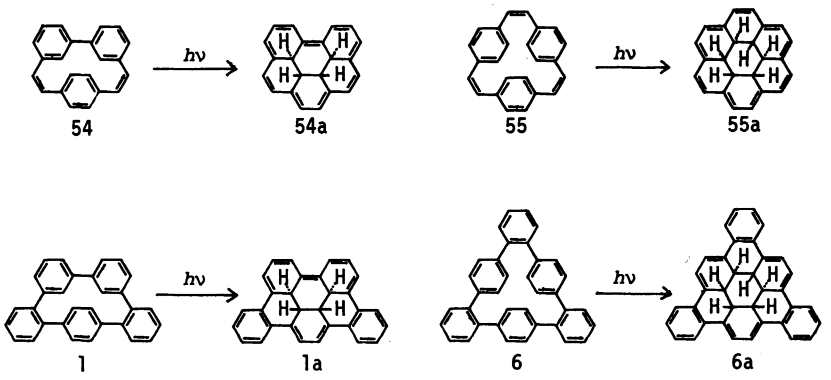
Photo-aryl Coupling Reaction. The bridged-annulene formation and photodehydrocyclization were examined by UV irradiation under degassed and oxidative conditions for compounds **1**, **5**, **6**, **9**, and **11**—**13** (except for **12** and **13** under the former conditions). Of these polyphenylenes, **1** and **6** correspond respectively to the di- and tribenzo analogues of the cyclophanes (**54** and **55**), for which the formation of the bridged annulenes (**54a** and **55a**) have been reported by Boekelheide *et al.*[19)] (Scheme 1). In these attempts, the reductive coupling of **1** and the oxidative coupling of **1** and **6** gave the desired products, but other coupling reactions examined were unsuccessful.

When the degassed solution of **1** was irradiated, its color became immediately reddish orange (new absorption bands appeared at 372 (sh), 386, 468, and 498 nm) and then reddish orange needles (**1a**)

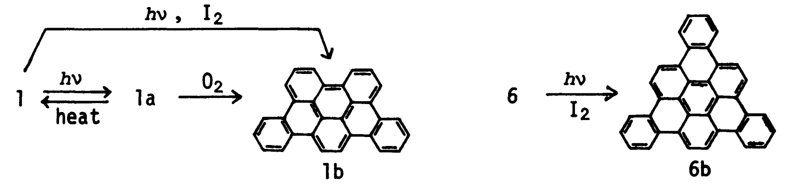
Table 5. Comparison of R_I of the polyphenylenes (**1**—**9**) with those of related linear polyphenyls

Polyphenylene		Polyphenyl			
Compound[a]	R_I	Compound[a]	R_I[b]	Compound[a]	R_I
1 [m,m,o,p,o]	2.81	ϕopoϕ	2.39		
		ϕmopϕ	(2.68)	*cf.* ϕopmϕ	2.84
		ϕommϕ	(2.73)	*cf.* ϕmomϕ	2.55
3 [m,o,o,m,o,o]	3.12	ϕmoomϕ	3.08		
		ϕoomoϕ	2.76		
8 [m,o,m,o,m,o]	3.18	ϕmomoϕ	(3.17)	*cf.* ϕmoomϕ	3.08
				ϕommoϕ	3.09
7 [m,o,p,o,p,o]	3.28	ϕopopϕ	3.28		
		ϕomopϕ	(3.23)	*cf.* ϕompoϕ	3.28
		ϕopomϕ	(3.23)		
6 [o,p,o,p,o,p]	3.30	ϕopopϕ	3.28		
2 [m,m,o,m,m,o]	3.43	ϕommoϕ	3.09		
		ϕmommϕ	3.44		
5 [m,o,p,m,o,p]	3.57	ϕompoϕ	3.28		
		ϕmopmϕ	3.58		
		ϕpompϕ	3.65		
4 [o,o,p,o,o,p]	3.57	ϕpoopϕ	3.27		
		ϕoopoϕ	2.88		
9 [m,m,m,o,m,o]	3.89	ϕmommϕ	3.44		
		ϕommmϕ	(3.65)		
		ϕomomϕ	(3.17)	*cf.* ϕmoomϕ	3.08
				ϕommoϕ	3.09

a) Refer to the footnote c) to Table 2. b) The values in parentheses were calculated using Eq. 3.



Scheme 1.



Scheme 2.

precipitated on prolonged irradiation.[20] On heating the colored solution or after standing it overnight at room temperature, it returned to the original colorless solution with the disappearance of the crystals. The reversible change was also confirmed by their absorption spectra.[21] On the other hand, in the presence of oxygen the irradiation yielded stable yellow needles (**1b**) *via* a reddish orange solution. The dehydrocyclized compound **1b** was also obtained by the photocoupling in the presence of iodine, and the absorption spectrum (λ_{max}: 228 (sh), 234, 256 (sh), 289, 300, 333, 349, 362, 368, 385, and 397 nm) was clearly distinguishable from those of **1** and **1a**.[22] The foregoing conversions can be reasonably summarized as shown in Scheme 2.

The irradiation of **6** gave dehydrocyclized compound **6b** in the presence of iodine, but not bridged annulene **6a** under the degassed conditions (Scheme 2).[24]

In connection with the photocoupling reactions of stilbene- and *o*-terphenyl-type compounds, the principal reasons for the occurrence of the coupling are summarized as follows: 1) the electron density on the carbon atoms undergoing coupling,[26] 2) the steric factors,[5a,c] 3) the nonexistence of the intermediate dihydro structures,[27] 4) the sum of the free valence numbers in the first excited state ($\sum Fr^*$) obtained for the atoms undergoing coupling and the localization energy (L^*).

The latter is the difference between the π-electron energy in the first excited state of the starting compound and that in the ground state of the intermediate dihydro derivative of the end product.[5c,27,28] Laarhoven *et al.*[5c], and Sato and Morita[28b] have independently carried out the calculation of the $\sum Fr^*$- and L^*-values by the HMO-method, and presented the critical values for the occurrence of the photocoupling: $\sum Fr^*>1$ and $L^*<3.45$, and $\sum Fr^*>0.95$ and $L^*<3.54$, respectively.

In order to consider the occurrence of the photocoupling reactions, the $\sum Fr^*$- and L^*-values of the polyphenylenes (**1**, **5**, **6**, **9**, **11**, and **12**), as well as those of the closely related compounds (**54**—**62**)[19,29] were calculated by the HMO-method (Table 6).

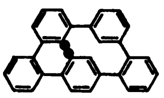
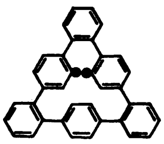
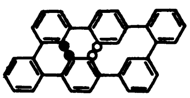
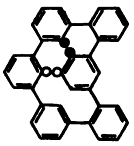
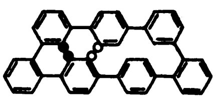
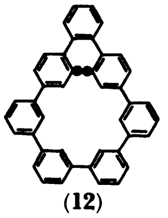
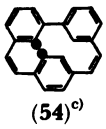
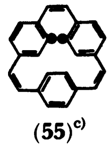
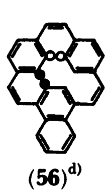
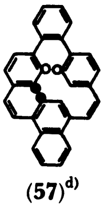
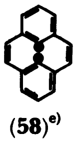
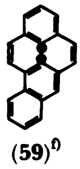
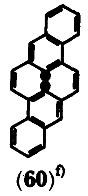
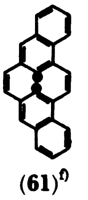
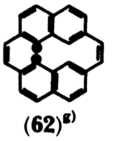
These values ($\sum Fr^*$ and L^*) indicate that the results of the photocoupling of the polyphenylenes and the related compounds may be explained on the basis of the criteria proposed by Sato and Morita, except for **6**, **9** and **55**. The photocoupling exceptions (**6** and **55**) may be correlated to the structures, in which three *p*-phenylene rings are fixed by three coplanar linkage. Meanwhile the uncoupled exception (**9**) is reasonably explained by the steric hindrance.

The foregoing results have indicated that the reaction indices ($\sum Fr^*$ and L^*) are useful as a measure for the occurrence of the photocoupling of macrocyclic polyphenylenes and cyclophanes with the coupling position on the macroring.

Formation of the Solvent Adducts. As described above, all the investigated aromatics formed the CT-complexes based on the weak affinity between the π-electrons of the donor and acceptor. Rapson *et al.* have previously reported the adduct-formation between *o*-tetraphenylene and a few solvents.[30] In the present study the formation of solvent adducts of the polyphenylenes was examined for several solvents, which is presumably due to the dipole-dipole interaction.

Among seven polyphenylenes (**1**—**6** and **13**) investigated, two compounds (**3** and **13**) formed successfully the adducts with several solvents, except for **3**-*m*-xylene and **13**-aniline. The thermogravimetric data are given in Table 7. The molar ratios of **3**-solvent adducts were 1:1 except for **3**-benzene (1:2), while those of **13**-solvent adducts were 1:2 except for **13**-*p*-xylene and **13**-pyridine (1:1). When some adducts (*e.g.*, **3**-benzene and **13**-*m*-xylene) were allowed to stand overnight in air at room temperature, the transparent

Table 6. Free valence numbers ($\sum Fr^*$) and localization energies ($L^*/-\beta$) for polyphenylenes and related cyclophanes

Compound No.						
		(**1**)	(**6**)	(**5**)	(**9**)	(**11**)
$\sum Fr^*$	●[a]	0.957	0.911	0.937	1.062	0.943
	○			0.896	0.867	0.900
L^*	●	2.627	3.523	3.411	3.231	3.469
	○			—[b]	—[b]	—[b]
Compound No.						
		(**12**)	(**54**)[c]	(**55**)[c]	(**56**)[d]	(**57**)[d]
$\sum Fr^*$	●[a]	0.946	0.979	0.932	0.957	0.953
	○				0.885	0.865
L^*	●	3.544	3.436	3.451	3.506	3.545
	○				3.626	3.920
Compound No.						
		(**58**)[e]	(**59**)[f]	(**60**)[f]	(**61**)[f]	(**62**)[g]
$\sum Fr^*$	●[a]	1.001	1.028	1.026	1.046	1.248
L^*	●	2.889	3.024	3.135	3.079	2.894

a) Coupling position. b) Nonexistence of intermediate dihydro structure. c), d), e), f), and g) refer to Refs. 19a, 19b, 29a, 29b, and 29c, respectively.

Table 7. Solvent adducts of polyphenylenes (**3** and **13**)

Solvent	**3**			**13**		
	Solvent release			Solvent release		
	Temp$^{a)}$/°C	%	mol	Temp$^{a)}$/°C	%	mol
benzene	110	25.2	2.0	151	18.3	2.0
toluene	101	14.9	0.9	107	19.3	1.8
o-xylene	87	17.1	0.9$^{b)}$	110	23.4	2.0
m-xylene		0		69	23.7	2.0
p-xylene	135	17.0	0.9	130	13.2	1.0
pyridine	110	13.9	0.9	159	10.2	1.0
aniline	109	16.9	1.0		0	

a) Temperature at which the maximum weight decrease in the DTG curve is observed. b) Adduct-formation temperature (%, mol): >60 °C (0.22, 0.01); >50 °C (0.41, 0.02); >40 °C (2.54, 0.11); >30 °C (15.76, 0.80); <30 °C (17.10, 0.90).

crystals became opaque, and after a longer time disintegrated gradually to powder with the release of solvents. However, the adducts such as **3**-*p*-xylene and **13**-benzene were appreciably stable, especially in a tightly stoppered tube. The facts may be correlated to the solvent release temperatures of the adducts. Furthermore, for the **3**-*o*-xylene adduct the experimental results shown in Table 7 (footnote b) were obtained. Thus, **3** and *o*-xylene gave the approximately 1:1 adduct at temperatures under 30 °C, but no adduct above 60 °C. Consequently the formation of the adduct is obviously related with the solvent release.

The foregoing results suggested that the solvent adduct formation was limited to the particular polyphenylenes. Hence the adduct formation is different from the charge-transfer complex formation, and does not have an obvious correlation with the structures.

Experimental

Instruments. Melting points were determined with a Shimadzu DSC-30M differential scanning calorimeter. The absorption spectra were measured on a Shimadzu UV-240 spectrophotometer, and IR spectra on a Leitz III-G spectrophotometer. The molecular weights were determined with a Hitachi RMU-6MG mass spectrometer. The gas-chromatographic analyses were performed on a Shimadzu GC-7A gas chromatograph equipped with a flame ionization detector. The solvent releases of the adducts were measured by thermogravimetry using a Shimadzu TGA-30M thermogravimeter equipped with a Differentiator TD-30. The HMO calculations were carried out on Hewlett-Packard HP-85 or NEC PC-9801 personal computer.

Materials. The following polyphenylenes used were the authentic samples prepared previously[2]: *m,m,o,p,o*-pentaphenylene (**1**); *m,m,o,m,m,o*- (**2**), *m,o,o,m,o,o*- (**3**), *o,o,p,o,o,p*- (**4**), *m,o,p,m,o,p*- (**5**), *o,p,o,p,o,p*- (**6**), *m,o,p,o,p,o*- (**7**), *m,o,m,o,m,o*- (**8**), *m,m,m,o,m,o*- (**9**), and *m*-hexaphenylene (**10**); *m,o,p,p,o,m,p*- (**11**) and *m,m,m,m,p,o,p*-heptaphenylene (**12**); and *o,p,p,o,p,p,o,p,p*-nonaphenylene (**13**). Commercially available biphenyl (**14**) and terphenyls (**15**—**17**) were purified before use. Quater- to sexiphenyls (**18**—**53**) used were the authentic samples prepared previously.[3a—d,f] Commercially available tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were purified before use, and dichloromethane (spectral-grade) was used without further purification.

Electronic Spectroscopic Measurements of Charge-transfer Complexes. Solutions of the complexes were prepared by dissolving the donors (0.005—0.05 mmol) in the acceptor-solution (10 ml) of known concentration (TCNE or DDQ; 0.01—0.1 mol/l) in dichloromethane, except for several sparingly soluble donors, for which they were prepared by saturating in the similar acceptor solution. The absorption spectra were measured in a 1- or 10-cm cell for the range 350—900 nm. The most reliable absorption maxima were obtained by the several determinations using the different concentrations of the two components or by the differential spectra with the acceptor absorption in known concentration.

Determination of Retention Times on the Gas-chromatographic Analyses. The retention times of polyphenyls and polyphenylenes were determined for 5 to 15 appropriate column temperatures in the range of 70—340 °C and were corrected using methane gas. The samples were used as a benzene solution of approximately the same concentration except for a few less soluble compounds. The logarithm of retention time obtained (log t_R) was plotted against the reciprocal of the column temperature (T^{-1}, absolute temperature). All of the plots showed a linear relation[17] which was employed for the calculation of the t_R at 250 °C. Other analytical conditions were as follows. Column: Dexsil 300GC glass-SCOT 10 m$\times$0.3 mmϕ; acuracy of column temperature: ±0.1 °C; carrier gas: He; flow rate: 0.70 ml/min; inlet pressure: 0.4 kg/cm^2; sprit ratio: 60:1; make-up gas: 40 ml.

Irradiation of the Degassed m,m,o,p,o-*Pentaphenylene (1) Solution.* A cyclohexane solution of **1** (8.97×10^{-5} mol/l) in a quartz cell (12 mmϕ) was carefully degassed, sealed, and irradiated using a low-pressure mercury lamp (2537 Å). After a short time the colorless solution turned into a reddish orange one, and the absorption spectrum showed an intensity decrease of the characteristic band (at 237 nm) of **1**, with an appearance of the additional bands of **1a** at 372 (sh), 386, 468, and 498 nm. After two minutes irradiation the solution showed no further change. When the irradiated colored solution was heated or allowed to stand overnight at room temperature, the solution turned into the original colorless one showing identical absorption spectrum.

The similar 5 minutes irradiation of **1** in a cyclohexane solution in the presence of air gave a pale yellow solution with the characteristic bands of **1b** at 228 (sh), 234, 256 (sh), 300, 333, 349, 362, 368, 385, and 397 nm, *via* a reddish orange solution of **1a**.

Irradiation of m,m,o,p,o-*Pentaphenylene (1) in the Presence of Iodine.* A mixture of **1** (114 mg) and iodine (76 mg) in benzene (17 ml) was irradiated in a quartz cell under nitrogen atmosphere using a 500 W high-pressure mercury lamp for 20 h. The recrystallization of the product from xylene gave tribenzo[*b*,*n*,*pqr*]perylene (**1b**) as yellow needles; mp 390 °C (lit,[31] 380 °C); 107 mg (95%). IR: 697 w, 710 vw, 728 vw, 747 vs, 758 vs, 761 sh s, 799 s, 823 m, 833 vw, 838 vw, 857 w, 864 vw, 872 vw, 890 w, 899 cm^{-1} w. UV: $\lambda_{\text{max}}(\varepsilon)$ 228 (sh) (80700), 234 (103500), 256 (sh) (23100), 289 (74100), 300 (99500), 333 (15600), 349 (28400), 362 (27900), 368 (34200), 385 (2100), and 397 nm (600). (Found: C, 95.44; H, 4.50%; M$^+$, 376).

Irradiation of o,p,o,p,o,p-*Hexaphenylene (6) in the Presence of Iodine.* The irradiation of the solution of **6** (137 mg) and iodine (76 mg) in benzene (17 ml) was carried out in the same manner as **1**. The recrystallization of the product from dimethyl sulfoxide gave tribenzo[*a*,*g*,*m*]coronene (**6b**) as yellow needles; mp 550 °C; 130 mg (96%). IR: 686 w, 747 vs, 753 sh s, 790 w, 811 s, 822 w, 827 m, 833 w, 858 w, 880 cm^{-1} w. UV: λ_{max} 221, 242, 254, 260, 300 (sh), 310, 323, 339, 348, 355, 363 nm. Found: C, 95.89; H, 4.00%; M$^+$, 450. Calcd for $C_{36}H_{18}$: C, 95.97; H, 4.03%; M$^+$, 450.

Solvent Adduct Formations of m,o,o,m,o,o-*Hexaphenylene (3) and* o,p,p,o,p,p,o,p,p-*Nonaphenylene (13).* The polyphenylenes, **3** and **13**, were crystallized from the following solvents: benzene, toluene, *o*-, *m*-, and *p*-xylene, pyridine, and aniline. They were crystallized out as solvated forms from each of the solvents, except for **3** from *m*-xylene and **13** from aniline.

3-Benzene: one-to-two adduct, colorless transparent plates. Found: C, 94.13; H, 5.94%. Calcd for $C_{36}H_{24}\cdot 2C_6H_6$: C, 94.07; H, 5.93%.

3-Toluene: one-to-one adduct, colorless transparent cubes. Found: C, 94.15; H, 5.90%. Calcd for $C_{36}H_{24}\cdot C_7H_8$: C, 94.12; H, 5.88%.

3-*o*-Xylene: one-to-one adduct, colorless transparent cubes. Found: C, 94.01; H, 6.08%. Calcd for $C_{36}H_{24}\cdot C_8H_{10}$: C, 93.91; H, 6.09%.

3-*p*-Xylene: one-to-one adduct, colorless transparent plates. Found: C, 93.95; H, 6.15%. Calcd for $C_{36}H_{24}\cdot C_8H_{10}$: C, 93.91; H, 6.09%.

3-Pyridine: one-to-one adduct, colorless transparent plates. Found: C, 92.00; H, 5.55; N, 2.60%. Calcd for $C_{36}H_{24}\cdot C_5H_5N$: C, 91.93; H, 5.46; N, 2.61%.

3-Aniline: one-to-one adduct, colorless plates. Found: C, 91.85; H, 5.61; N, 2.51%. Calcd for $C_{36}H_{24}\cdot C_6H_7N$: C, 91.77; H, 5.68; N, 2.55%.

13-Benzene: one-to-two adduct, colorless transparent cubes. Found: C, 94.33; H, 5.80%. Calcd for $C_{54}H_{36}\cdot 2C_6H_6$: C, 94.25; H, 5.75%.

13-Toluene: one-to-two adduct, colorless transparent cubes. Found: C, 94.00; H, 6.10%. Calcd for $C_{54}H_{36}\cdot 2C_7H_8$: C, 93.97; H, 6.03%.

13-*o*-Xylene: one-to-two adduct, colorless transparent cubes. Found: C, 93.81; H, 6.29%. Calcd for $C_{54}H_{36}\cdot 2C_8H_{10}$: C, 93.71; H, 6.29%.

13-*m*-Xylene: one-to-two adduct, colorless transparent cubes. Found: C, 93.75; H, 6.36%. Calcd for $C_{54}H_{36}\cdot 2C_8H_{10}$: C, 93.71; H, 6.29%.

13-*p*-Xylene: one-to-one adduct, colorless transparent cubes. Found: C, 94.15; H, 5.79%. Calcd for $C_{54}H_{36}\cdot C_8H_{10}$: C, 94.14; H, 5.86%.

13-Pyridine: one-to-one adduct, colorless needles. Found: C, 92.86; H, 5.35; N, 1.85%. Calcd for $C_{54}H_{36}\cdot C_5H_5N$: C, 92.76; H, 5.41; N, 1.83%.

The solvent releases of the adducts were determined under the following conditions: heating rate, 10 °C/min; sample size, about 5 mg weighed accurately in a sealed cell with a pinhole; atmosphere, N_2 gas (40 ml/min).

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displayed commonly an absorption maximum or a shoulder near 400 nm as the second or the third CT-band. The energies of the CT-bands near 400 nm of polyphenyl- and polyphenylene–TCNE complexes are rather correlated with those of the E-bands near 200 nm of the respective donor hydrocarbons.

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15) Correlation coefficient: 0.95.

16) For polyphenyls and polyphenylenes, as well as for the series of alkylbenzenes (Ref. 9), the saturation vapor pressures of substituted components were assumed to be proportional to those of unsubstituted components.

17) Correlation coefficients: lager than 0.999 for all compounds.

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20) The crystals were not isolated due to the ready oxidative dehydrogenation.

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22) The radical anion (greenish blue) prepared from **1** with sodium in THF under nitrogen atmosphere showed the absorption maxima at 380 (sh), 415, 556, and 590 nm. In the presence of a trace of oxygen, however, the spectrum showed the bands at 363 (sh), 367, 384, 395 (sh), 421, 480, 534 (sh), 555, 676, 740, and 833 nm, and it was actually identical with that of the radical anion prepared from **1b**. This fact suggests that the radical anion undergoes an oxidative dehydrocyclization (*cf.* Ref. 23).

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