Literature Cited

(1) Auwers, K. V., Mauss, H., *Justus Liebigs Ann. Chem.*, **452**, 204 (1927).
(2) Browne, E. J., Polya, J. B., *J. Chem. Soc.*, 575 (1962).
(3) Burawoy, A., Salem, A. G., Thompson, A. R., *J. Chem. Soc.*, 4793 (1952).
(4) *Chem. Abstr.*, **59**, 6413*c* (1963), and *ibid.*, **68**, 87 286*g* (1968).
(5) Cum, G., Lo Vecchio, G., Aversa, M. C., Crisafulli, M., *Gazz. Chim. Ital.*, **97** (3), 346 (1967).
(6) Cum, G., Lo Vecchio, G., Aversa, M. C., *Atti Accad. Peloritana Pericolanti, Cl. Sci. Fis., Mat. Nat.*, **49**, 151 (1966); *Chem. Abstr.*, **69**, 43 836 (1968).
(7) Dieckmann, W., *Ber.*, **47**, 1435 (1914).
(8) Gardner, E. W., Lee, J., *J. Org. Chem.*, **26**, 1514 (1961).
(9) Gillam, A. E., Stern, E. S., "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, London, 1957, p 302.
(10) Hickinbottom, W. J., "Reactions of Organic Compounds", Wiley, New York, N.Y., 1962, p 336.
(11) Jones, R., Ryan, A. J., Sternhall, S., Wright, S. E., *Tetrahedron*, **19**, 1497 (1963).
(12) Kletz, L., Lapworth, A., *J. Chem. Soc.*, 1262 (1915).
(13) Knorr, L., *Ber.*, **29**, 249 (1896).
(14) Korte, F., Wusten, F., *Chem. Ber.*, **96**, 2841 (1963).
(15) Mustafa, A., Khattab, S., Asker, W., *Can. J. Chem.*, **41**, 1813 (1963).
(16) Rothenburg, R. V., *Ber.*, **26**, 1722 (1893).
(17) Sakurai, K., Hiroichi, M., Jun, A., *Yakugaku Zasshi*, **88** (7), 919 (1968); *Chem. Abstr.*, **69**, 94792*j* (1968).
(18) Sawdey, G. W., *J. Am. Chem. Soc.*, **79**, 1955 (1957).
(19) Snavely, F. A., Trahanovesky, W. S., Suydam, F. H., *J. Org. Chem.*, **27**, 994 (1962).
(20) Summers, L. A., Freeman, P. F. H., Shieldes, D. J., *J. Chem. Soc.*, 3312 (1965).
(21) Thiele, J., Salzberger, N., *Justus Liebigs Ann. Chem.*, **319**, 196 (1901).
(22) Toda, S., *J. Chem. Soc. Jpn.*, **80**, 402 (1959).
(23) Wiley, P. F., Weaver, O., *J. Am. Chem. Soc.*, **78**, 808 (1956).
(24) Yao, H. C., Resnick, P., *J. Am. Chem. Soc.*, **84**, 3514 (1962).
(25) Zollinger, H., "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds", Interscience, New York, N.Y., 1961, pp 153, 231.
(26) Zsolnai, T., *Biochem. Pharmacol.*, **14**, (9), 1325 (1965); *Chem. Abstr.*, **63**, 15467d (1965).

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Synthesis and Electronic Spectra of Substituted Bis(hexaphenylbenzenes)

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The syntheses of 5 disubstituted hexaphenylbenzenes and 27 tetrasubstituted bis(hexaphenylbenzenes) are reported, and their ultraviolet spectra are discussed.

In two previous papers (*10, 11*) the synthesis and electronic spectra of a number of bis(hexaphenylbenzenes) (BHPB) were reported and discussed in terms of existing information. The conclusions reached were that the main contributor to the electronic spectra for this class of compounds was either the angle between the outer rings and the central ring, the ridigity of the molecule's structure, or a combination of the two (*11*). In an effort to more fully interpret the electronic spectra for these compounds a series of substituted BHPB has been synthesized and their electronic spectra observed.

Results and Discussion

Synthesis. The route chosen to prepare the substituted BHPB is the same as that previously reported (*11*) for the preparation of the unsubstituted BHPB, namely Diels–Alder addition of a series of bis(tetracyclones) with substituted diphenylacetylenes followed by the evolution of carbon monoxide. The substituted diphenylacetylene dienophiles used were all prepared by literature procedures. Preparation of the substituted BHPB was accomplished by allowing the bis(tetracyclones) to react with an excess of the substituted diphenylacetylene at 270–280 °C in a Carius tube sealed under an atmosphere of nitrogen and placed in a Woods' metal bath. All reactions gave good yields of the desired substituted BHPB products, except for the reactions using 4,4'-dinitrodiphenylacetylene (**2**, R = NO_2) with methylene (**6**, Y = CH_2), ether (**6**, Y = O), and sulfide (**6**, Y = S) bis(tetracyclones) which afforded only low melting solids and intractable tars.

The initial product isolated from the reaction of 4,4'-dichlorodiphenylacetylene (**2**, R = Cl) with the sulfur bis(tetracyclone) (**6**, Y = S) was a white solid which softened at 200 °C and appeared to melt from 300 to 310 °C. Heating this solid at 375 °C for 3 min afforded the desired product, bis[2',5',6'-triphenyl-3,4'-di(*p*-dichlorophenyl)biphenylyl] sulfide (**7**, R = Cl, Y = S). Although no attempts were made to isolate either the mono- or dicarbonyl adducts from the Diels–Alder addition of the substituted diphenylacetylenes with the bis(tetracyclones), it appears that inadvertently one or both of these carbonyl adducts were isolated in the case of the above reaction. This adduct upon heating completely eliminated the carbon monoxide bridge to afford **7** (R = CL, Y = S).

The possibility that the tetrasubstituted octaphenylquinquephenyls (**3** and **5**) may exist as cis,trans rotamers, effectively

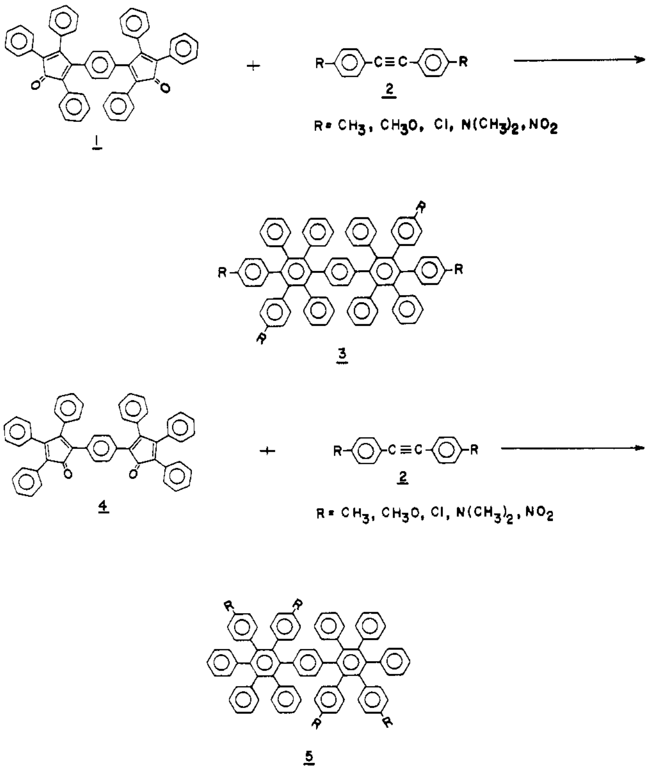
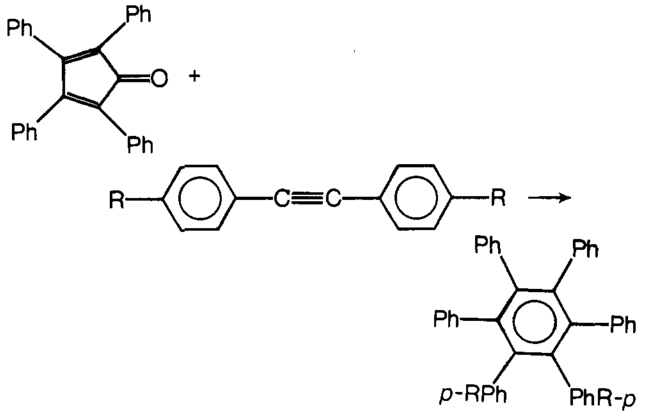


Table I. Spectral Features of Tetrasubstituted Bis(hexaphenylbenzenes)

Substituent R =	λ_1, Å	$10^{-3}\epsilon_1$	Point of inflection	λ_{sh}, Å	$10^{-3}\epsilon_2$
		Octaphenylquinquephenyls (3)			
CH_3	2550	84.3	2790	2840	48.1
CH_3O	2580	78.6	2780	2860	58.3
Cl	2540	86.9	3060	2850	48.1
$N(CH_3)_2$	2540	95.0	[a]	2990	62.6
NO_2	2550	81.9	2810	2830	58.0
		Octaphenylquinquephenyls (5)			
CH_3	2540	51.9	2720	2850	30.9
CH_3O	2540	72.6	2770	2900	49.3
Cl	2520	69.5	2740	2840	32.7
$N(CH_3)_2$	2560	76.3	2730	2830	59.7
NO_2	2475	79.0	2620	2875	21.6
		Octaphenylsexiphenyls (7, Y = nil)			
CH_3	2530	55.3	2685	2820	43.5
CH_3O	2550	68.2	2710	2870	58.7
Cl	2555	83.8	2760	2880	73.6
$N(CH_3)_2$	2540	89.4	2750	2960	69.8
NO_2	2560	62.4	2765	3040	59.1
		Bis(2′,3′,5′,6′-tetraphenylterphenylyl)methanes (7, Y = CH_2)			
CH_3	2505	97.2	2680	2820	39.9
CH_3O	2515	77.2	2690	2855	39.7
Cl	2500	99.0	2680	2805	39.8
$N(CH_3)_2$	2480	89.6	2680	2855	38.5
NO_2[b]					
		Bis(2′,3′,5′,6′-tetraphenylterphenylyl) ethers (7, Y = O)			
CH_3	2505	79.9	2650	2805	37.5
CH_3O	2535	89.6	2700	2830	54.7
Cl	2505	103.2	2680	2820	48.2
$N(CH_3)_2$	2490	83.9	2670	2840	56.3
NO_2[b]					
		Bis(2′,3′,5′,6′-tetraphenylterphenylyl) sulfides (7, Y = S)			
CH_3	2460	90.0	2685	2830	45.2
CH_3O	2540	80.9	2700	2850	53.1
Cl	2510	92.9	2705	2840	44.0
$N(CH_3)_2$	2475	86.9	2680	2890	54.5
NO_2[b]					

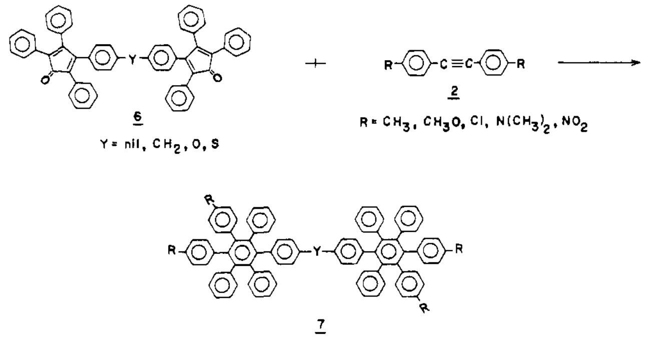
[a] Peaks distinctively separated. [b] No pure product obtained.

Table II. Spectral Features of Disubstituted Hexaphenylbenzenes



Substituent R =	λ_1, Å	$10^{-3}\epsilon_1$	Point of inflection	λ_{sh}, Å	$10^{-3}\epsilon_2$
CH_3	2480	46.6	2680	2770	18.8
CH_3O	2500	44.1	2690	2845	19.4
Cl	2480	54.2	2670	2800	19.2
$N(CH_3)_2$	2470	49.8	2690	2795	21.3
NO_2	2450	44.5	2690	3035	21.7

frozen in their conformations because of steric crowding, was considered when these compounds were isolated, and it was expected that these products would exhibit somewhat different melting points if they could be isolated. However, based upon differential thermal analysis (DTA) performed on all the tetrasubstituted octaphenylquinquephenyls (**3** and **5**) prepared, the possibility that this type of isomer actually was formed is unlikely since exotherms for these compounds were observed at only one narrow range up to 455 °C. If the difference in either melting or decomposition points for the possible rotamers was small, however, the thermal analyzer may not have been sensitive enough to differentiate these differences. There is no possibility of cis,trans rotamers existing in the tetrasubstituted bis(2′,3′,5′,6′-tetraphenylterphenylyl)methanes (**7**, Y = CH_2), ethers (**7**, Y = O), and sulfides (**7**, Y = S) because free rotation is possible about the bond connecting each disubstituted hexaphenylbenzene moiety to the linking group.



6
Y = nil, CH_2, O, S

2
R = CH_3, CH_3O, Cl, $N(CH_3)_2$, NO_2

7

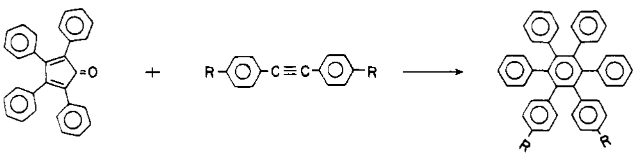
Ultraviolet Spectra. The principal spectral characteristics of the tetrasubstituted BHPB are reported in Table I. All compounds exhibited one clearly defined absorption band in the 2450–2580 Å region. Utilizing the interpretation (*10, 11*) of the electronic spectra of hexaphenylbenzene and the BHPB as our model for the interpretation of the electronic spectra for the tetrasubstituted BHPB, we find many similarities and a few noticeable differences. In the case of the BHPB, it was observed that their electronic spectra showed the λ_{max} of these compounds to be similar to that of hexaphenylbenzene, and also that the molar extinction coefficient of the BHPB, which possessed a linking group such as CH_2, O, or S between the two hexaphenylbenzene chromophores, was approximately twice the molar coefficient of hexaphenylbenzene itself. In the case where there was no linking group between the two hexaphenylbenzene moieties, such as for 2′,3′,5′,6′,2′′′′,3′′′′,5′′′′,6′′′′-octaphenylsexiphenyl (**7**, Y = nil, R = H) it was found that the λ_{max} appeared in the same vicinity as the λ_{max} for hexaphenylbenzene, but that the molar extinction coefficient was only 1.38 as large as that of hexaphenylbenzene. In this case it appeared that the absence of a linking group was preventing each hexaphenylbenzene moiety from acting as individual chromophores.

If we examine the tetrasubstituted BHPB in the same light, it is necessary to use the appropriate disubstituted hexaphenylbenzene chromophore as our model. Interestingly a search of the literature revealed that only the 1,2-di(*p*-chlorophenyl)-3,4,5,6-tetraphenylbenzene had been reported (*4*) but not it's electronic spectra. This compound and the other required model disubstituted hexaphenylbenzenes were thus prepared by Diels–Alder reaction of 2,3,4,5-tetraphenylcyclo-2,4-pentadien-1-one (tetracyclone) with the appropriately disubstituted diphenylacetylenes (**2**, R = CH_3, CH_3O, Cl, $N(CH_3)_2$, and NO_2). The electronic spectral characteristics of these compounds are reported in Table II.

Table III. Physical Data For Disubstituted Hexaphenylbenzenes and Tetrasubstituted Bis(hexaphenylbenzenes)[a]

Substituent, **2**, R =	Recrystallization solvent	Yield, %	Mp,[b] °C	Formula
2,3,4,5-tetraphenylcyclo-2,4-pentadien-1-one + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → 1,2-di(*p*-substituted phenyl)-3,4,5,6-tetraphenylbenzene				
CH_3	Acetic acid	50	357–358	$C_{44}H_{34}$
CH_3O	Acetic acid	46	292–293	$C_{44}H_{34}O_2$
Cl	Benzene	40	337–339[c]	$C_{42}H_{28}Cl_2$
$N(CH_3)_2$	Benzene	77	308–310[d]	$C_{46}H_{40}N_2$
NO_2	Benzene	60	231–233	$C_{42}H_{28}N_2O_4$
3,3′-(1,4-phenylene)bis(2,4,5-triphenylcyclo-2,4-pentadien-1-one) (**1**) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → 3,4,3″,4″-tetra(*p*-substituted phenyl)-2,5,6,2″,5″,6″-sexiphenylterphenyl (**3**)				
CH_3	Benzene	64	456–458[d]	$C_{82}H_{62}$
CH_3O	Benzene	57	427–429[d]	$C_{82}H_{62}O_4$
Cl	Benzene	67	460–462	$C_{78}H_{50}Cl_4$
$N(CH_3)_2$	Benzene	60	436–438[d]	$C_{86}H_{74}N_4$
NO_2	Benzene	30	428–430[d]	$C_{78}H_{50}N_4O_8$
2,2′-(1,4-phenylene)bis(3,4,5-triphenylcyclo-2,4-pentadien-1-one) (**4**) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → 2,3,2″,3″-tetra(*p*-substituted phenyl)-4,5,6,4″,5″,6″-sexiphenylterphenyl (**5**)				
CH_3	Nitrobenzene, benzene	65	479–481[d]	$C_{82}H_{62}$
CH_3O	Nitrobenzene, benzene	65	424–426[d]	$C_{82}H_{62}O_4$
Cl	Benzene, pentane	67	465–467	$C_{78}H_{50}Cl_4$
$N(CH_3)_2$	Benzene	54	430–432[d]	$C_{86}H_{74}N_4$
NO_2	Benzene, pentane	20	427–430[d]	$C_{78}H_{59}N_4O_8$
3,3′-(4,4′-biphenylene)bis(2,4,5-triphenylcyclo-2,4-pentadien-1-one) (**6**, Y = nil) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → 3,4,3⁗,4⁗-tetra(*p*-substituted phenyl)-2,5,6,2⁗,5⁗,6⁗-sexiphenylquaterphenyl (7, Y = nil)				
CH_3	Nitrobenzene, benzene	51	>500	$C_{88}H_{68}$
CH_3O	Nitrobenzene, benzene	54	478–480[d]	$C_{88}H_{68}O_4$
Cl	Benzene	57	490–492	$C_{84}H_{54}Cl_4$
$N(CH_3)_2$	Benzene	65	460–462[d]	$C_{92}H_{78}N_4$
NO_2	Benzene, pentane	31	>500[d]	$C_{84}H_{54}N_4O_8$
4,4′-methylenedi(*p*-phenylene)bis(2,4,5-triphenyl-3-cyclo-2,4-pentadien-1-one) (**6**, Y = CH_2) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → bis(3′,4′-di(*p*-substituted phenyl)biphenyl-2′,5′,6′-triphenyl)methane (7, Y = CH_2)				
CH_3	Nitrobenzene, benzene	56	375–379[d]	$C_{89}H_{68}$
CH_3O	Nitrobenzene, benzene	58	376–378[d]	$C_{89}H_{68}O_4$
Cl	Benzene	68	350–352	$C_{85}H_{46}Cl_4$
$N(CH_3)_2$	Benzene	56	387–390[d]	$C_{93}H_{80}N_4$
NO_2[e]				
3,3′-oxydi(*p*-phenylene)bis(2,4,5-triphenylcyclo-2,4-pentadien-1-one) (**6**, Y = O) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → bis(3′,4′-di(*p*-substituted phenyl)biphenylyl-2′,5′,6′-triphenyl) ether (7, Y = O)				
CH_3	Nitrobenzene, benzene	61	382–384	$C_{88}H_{66}O$
CH_3O	Nitrobenzene, benzene	56	378–380[d]	$C_{88}H_{66}O_5$
Cl	Nitrobenzene, benzene	57	354–356	$C_{88}H_{54}Cl_4O$
$N(CH_3)_2$	Benzene	62	411–413[d]	$C_{92}H_{74}N_4O$
NO_2[e]				
3,3′-thiodi(*p*-phenylene)bis(2,4,5-triphenycyclo-2,4-pentadien-1-one) (**6**, Y = S) + 4,4′-di(*p*-substituted)diphenylacetylene (**2**) → bis(3′,4′-di(*p*-substituted phenyl)biphenyl-2′,5′,6′-triphenyl) sulfide (**7**, Y = S)				
CH_3	Nitrobenzene, benzene	65	372–374	$C_{88}H_{66}S$
CH_3O	Nitrobenzene, benzene	68	373–375	$C_{88}H_{66}O_4S$
Cl	Benzene	36	336–338	$C_{84}H_{54}Cl_4S$
$N(CH_3)_2$	Benzene	65	360–362	$C_{92}H_{78}N_4S$
NO_2[e]				

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] All melting points were checked by DTA. [c] Reported (*4*) mp 327–328 °C. [d] Decomposed. [e] None isolated.



Examination of the tetrasubstituted BHPB which have a linking group between the two hexaphenylbenzene units (7, Y = CH_2, O, and S) shows their λ_{max} to be in the same region as the λ_{max} of the appropriate disubstituted hexaphenylbenzene, and further, their molar coefficient is approximately twice as large as those observed for the model compounds. Thus, the tetrasubstituted BHPB which have a linking group between the two hexaphenylbenzene units behave as if they are composed of two individual disubstituted hexaphenylbenzene chromophores and, surprisingly, the varied electronic effects of the substituents do not cause vast differences in the electronic transitions observed when the tetrasubstituted BHPB are compared to each other or to the unsubstituted BHPB of similar structure.

The tetrasubstituted BHPB which have no linking group, the tetrasubstituted octaphenylsexiphenyls (**7**, Y = nil), also show the same tendency as observed above, i.e., the region of the λ_{max} for compounds **5** is the same and the ratio of their molar coefficient is less than two, as for their unsubstituted counterparts, with the substituent offering no observable effect on the electronic transitions involved.

Examination of the tetrasubstituted octaphenylquinquephenyls (**3** and **5**) shows that the λ_{max} for these compounds has been shifted to higher wavelengths in comparison with the other tetrasubstituted polyphenylated compounds indicating that neither hexaphenylbenzene nor the disubstituted hexaphenylbenzenes are good models for the basic chromophore of these compounds. This trend is internally consistent and again shows no deviation being caused by the substituents.

In conclusion, if we compare hexaphenylbenzene with the disubstituted hexaphenylbenzenes, and the BHPB with the tetrasubstituted BHPB, we observe that the electronic spectra of the compounds containing substituents are shifted to slightly higher wavelengths and the molar extinction coefficients are slightly less than the corresponding unsubstituted compounds. It is thus obvious that the substituents exert a negligible to very small effect on the overall spectral features of these compounds and that this effect must be confined to a change in the ground state and excited states of the molecules but no new observable electronic transitions are created by the presence of the substituents. It should also be noted that no shift in position of the major peaks was observed for both solid and liquid state electronic spectra for any of these compounds.

Experimental Section

The melting points of all compounds melting below 250 °C were obtained on a Thomas-Hoover melting point apparatus and are corrected, while those compounds melting above 250 °C were obtained on a Mel-Temp melting point apparatus and are also corrected. In addition, all melting points were checked by differential thermal analysis (DTA) using a Stone differential thermal analyzer and alumina as the standard. The ultraviolet spectra were obtained and checked on three different recording spectrophotometers, a Beckman DK-2, a Beckman ACTA-C III, and a Cary 14 instrument, using a set of matched 1.0-cm quartz cells. In each case, duplicate samples were analyzed and all spectral values obtained agreeded within ±0.01% for the wavelength determinations and ±1.00% for the molar extinction coefficient determinations. All spectra were taken in freshly distilled 1,2-dichloroethane and because these compounds afforded a solubility problem, solution was effected by refluxing the sample with care being exercised to guarantee complete solution of the weighed solid.

Disubstituted Diphenylacetylenes. 4,4′-Dimethyldiphenylacetylene (*9*) and 4,4′-dimethoxydiphenylacetylene (*13*) were prepared by mercuric oxide oxidation of their respective benzil bishydrazones (*1, 5, 13*). 4,4′-Bis(dimethylamino)diphenylacetylene (*7*) and 4,4′-dichlorodiphenylacetylene (*6, 9*) were prepared by reaction of their respective benzils (*8, 14, 15*) with triethyl phosphite (*9*). 4,4′-Dinitrodiphenylacetylene (*12*) was prepared by dehydrohalogenation of 4,4′-dinitrostilbene dibromide (*12*).

Tetracyclone and Bis(tetracyclones). Tetracyclone (*2*) and the bis(tetracyclones) (*10, 11*) were prepared from literature references, except for 2,2′-(*p*-phenylene)bis(3,4,5-triphenylcyclo-2,4-pentadien-1-one) which was prepared according to the procedure of Higgins and Jones (*3*).

p,p′-1,2-Disubstituted Hexaphenylbenzenes and p,p′-5,6,5′′,6′′-Tetrasubstituted Bishexaphenylbenzenes. Into a Carius tube was placed 9.7 mmol of the appropriate 4,4′-disubstituted diphenylacetylene and 2.0 g (5.2 mmol) of tetracyclone or 1.5 mmol of the appropriate bis(tetracyclone), the tube sealed under nitrogen and heated for 2 h in a Woods' metal bath at 270 °C. After this time the tube was removed from the bath, cooled, and opened. (Caution! Pressure is built up from the carbon monoxide given off.) The mixture was slurried with 100 ml of acetone, the solid filtered and recrystallized two or three times from the solvent indicated in Table III.

Bis(2′,5′,6′-triphenyl-3′,4′-di(p-dichlorophenyl)biphenylyl) Sulfide (7, R = Cl, Y = S). The reaction conditions are essentially those given above starting with 2.39 g (9.7 mmol) of 4,4′-dichlorodiphenylacetylene and 1.20 g (1.5 mmol) of 3,3′-[thio(*p*-phenylene)]bis(2,4,5-triphenylcyclo-2,4-pentadien-1-one). The residue was slurried with 100 ml of acetone and filtered, affording 1.38 g of pinkish white solid. After four recrystallizations from 40-ml portions of benzene, 1.31 g of white powder was obtained which softened at 200 °C and appeared to melt at 300–310 °C. The remaining solid was placed in a 50-ml Erlenmeyer flask and heated for 3 min at 375 °C. The resulting residue was slurried with acetone, filtered, and recrystallized three times from 20-ml portions of benzene to afford 0.68 g (0.55 mmol, 36% overall) of white solid, mp 336–338 °C.

Reaction of 4,4′-Dinitrodiphenylacetylene with 4,4′-Methylenedi(p-phenylene)bis(2,4,5-triphenyl-3-cyclo-2,4-pentadien-1-one), 3,3′-Oxydi(p-phenylene)bis(2,4,5-triphenyl-3-cyclo-2,4-pentadien-1-one), and 3,3′-(Thiodi(p-phenylene))bis(2,4,5-triphenyl-3-cyclo-2,4-pentadien-1-one). These condensations were performed exactly as described above; however, whether the reaction mixture was heated for 2 h, 1 h, or less, workup did not afford any polyphenylated derivatives of the respective bis(tetracyclones). Various attempts (chromatography, crystallization, distillation, and sublimation) to purify the resulting semisolids all resulted in affording low melting solids and intractable tars.

Literature Cited

(1) Cope, A. C., Smith, D. S., Cotter, D. J., "Organic Synthesis", Coll. Vol. IV, Wiley, New York, N.Y., 1963, p 377.
(2) Grummitt, O., Johnson, J. R., "Organic Synthesis", Coll. Vol. III, Wiley, New York, N.Y., 1955, p 806.
(3) Higgins, J., Jones, J. F., *Ann. Ill. Acad. Sci.*, 97 (1971).
(4) Hubel, W., Hoogzand, C., *Chem. Ber.*, **93**, 103 (1963).
(5) Kastner, R., Curtius, T., *J. Prakt. Chem.*, **83**, 215 (1911).
(6) Kenner, J., Witham, E. W., *J. Chem. Soc.*, 1960 (1910).
(7) Kurreck, H., private communication.
(8) Montagne, P. T., *Recl. Trav. Chim. Pays-Bas*, **21**, 6 (1902).
(9) Mukaiyama, T., Wambu, H., Kumamoto, T., *J. Org. Chem.*, **29**, 2243 (1964).
(10) Ogliaruso, M. A., Shadoff, L. A., Becker, E. I., *J. Org. Chem.*, **28**, 2725 (1963).
(11) Ogliaruso, M. A., Becker, E. I., *J. Org. Chem.*, **30**, 3354 (1965).
(12) Ruggli, P., Lang, F., *Helv. Chim. Acta*, **19**, 996 (1936); **21**, 38 (1938).
(13) Schlenk, W. S., Bergmann, E., *Justus Liebigs Ann. Chem.*, **463**, 76 (1928).
(14) Thaller, F. J., Trucker, D. E., Becker, E. I., *J. Am. Chem. Soc.*, **73**, 228 (1951).
(15) Tuzun, C., Ogliaruso, M. A., Becker, E. I., "Organic Synthesis", Coll. Vol. V, Wiley, New York, N.Y., 1973, p 111.

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