The Ultraviolet Absorption Spectra of Some Chlorinated Biphenyls

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Abstract

The UV spectra of 29 chlorobiphenyls have been examined. With increasing chloro substitution in which there are less than two chlorine groups ortho to the Ph-Ph bond the λ_{max} values for the κ band (attributed to conjugation between the two phenyl rings) are shifted to longer wavelengths and for the more highly substituted chlorobiphenyls there is also a bathochromic shift of the main band (due to the benzenoid skeleton). Introduction of two or more chlorine atoms ortho to the Ph-Ph bond results in a hipsochromic shift of κ band and diminished ε value due to steric inhibition of resonance between the two phenyl rings. The sterically hindered chlorobiphenyls and the more highly chlorinated Aroclors also exhibit a series of low-intensity fine-structured absorption maxima between 268-302 nm.

The UV spectra of chlorobiphenyls are particularly diagnostic with respect to the degree of substitution at the 2,2',6 and 6' positions and can be used in the structural analysis of separated chlorobiphenyls. The data may also aid in correlating the photochemical reactivities.

Introduction

Several groups (PICKETT et al. 1936; BURAWOY and THOMPSON 1956; BEAVEN and HALL 1956; HALL and MINHAJ 1957; BEAVEN 1958) have studied the ultraviolet (UV) absorption spectra of chlorobiphenyls and other closely related aromatic systems (BALLESTER and CASTANER 1960; BROCKLEHURST et al. 1960). More recently the major UV absorption maxima of some chlorobiphenyls have been reported (SAEKI et al. 1971; DREESKAMP et al. 1972; SUNDSTRÖM 1973) and UV spectra have actually been used as aid in the structural assignment of separated chlorobiphenyls. (SAEKI et al. 1971; DREESKAMP et al. 1972; SUNDSTRÖM 1973). In addition Zitko has also observed that some of the more highly chlorinated commercial Aroclor mixtures exhibited a series of weak absorption maxima at 280-290 nm. (ZITKO 1970a, ZITKO 1970b). Since these bands may be related to the photochemical activity of chlorobiphenyls, it was therefore of interest to closely examine the UV spectra of a number of structurally different compounds of this series and to examine the effects of the

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degree of chlorine substitution and the location of the substituents on the UV absorption bands.

Experimental.

Standard solutions (conc. 1.0×10^{-5} M) of the compounds listed in Table I were prepared in spectral grade cyclohexane. The chlorobiphenyls were all pure standards prepared in the laboratory or obtained from Analabs, Inc. Commercial samples of Aroclor^{R} 1232 and 1260 were used.

Spectra were measuring using a Beckman DK-2A spectrophotometer with a deuterium lamp. Silica cells with 1 cm-pathlength were used for all measurements.

Results and Discussion.

A number of factors have been shown to effect the UV absorption bands and these can be summarized as follows: (a) the nature of the substituent, (b) the location of the substituent, (c) the number of substituents present in the biphenyl nucleus and particularly the degree of substitution at the positions ortho to the Ph-Ph bond (i.e. 2,2'6 and 6' positions). The UV spectrum of biphenyl shows two important absorption maxima; one at λ_{max} 202 nm (ε, 44,000) and a second at λ_{max} 242 nm (ε, 17,000). The former band is generally referred to as the "main band" and the latter is generally known as the κ band which is attributed to the conjugated biphenyl system with the contributions of both phenyl rings. The effects of chlorine substitution on the UV spectrum of biphenyl are summarized in the data shown in Tables I and II. The results given in these Tables will be discussed according to degree of ortho chloro substitution since this factor markedly affects the UV spectral features.

(A) Chlorinated biphenyls with less than two chlorine atoms ortho to the Ph-Ph bond.

The data shown in Table I indicated that both the number and position of the Cl substituent caused some significant variations in the position and intensity of both the main absorption band and the κ band in the UV spectra.

For the monochlorobiphenyls the main absorption band was only slightly changed in comparison to biphenyl however the 4- -and 3-chloro groups induced a marked bathochromic shift of κ band with this shift greater for the para substituent (ca 11 nm) than for the meta substituent (ca 6 nm). The κ band for 2-chlorobiphenyl is shifted to slightly lower wavelengths (ca 2 nm) with a diminished ε value. This effect is undoubtedly due to some steric inhibition of resonance between the two phenyl groups with the resultant hipsochromic shift and diminished intensity of the absorption maxima of the conjugation κ band. This effect will be discussed in detail for the more highly hindered isomers given in Table II.

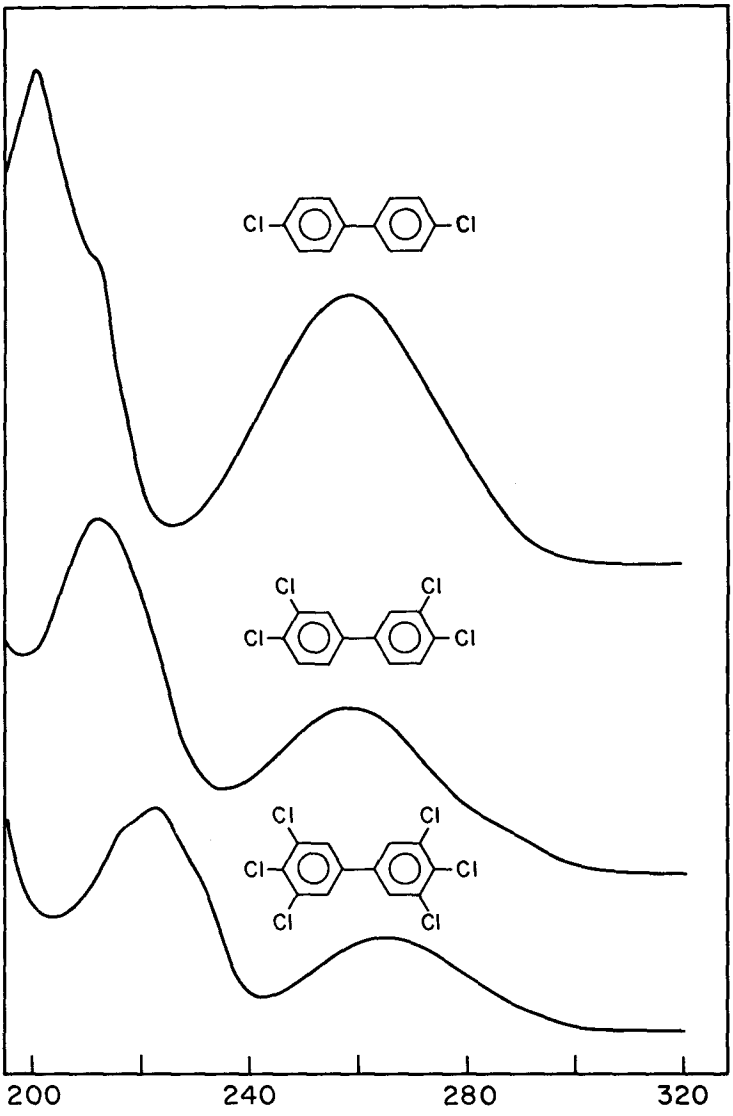

Fig.1. U.V. spectra of three chlorobiphenyls without ortho chlorine substitution.

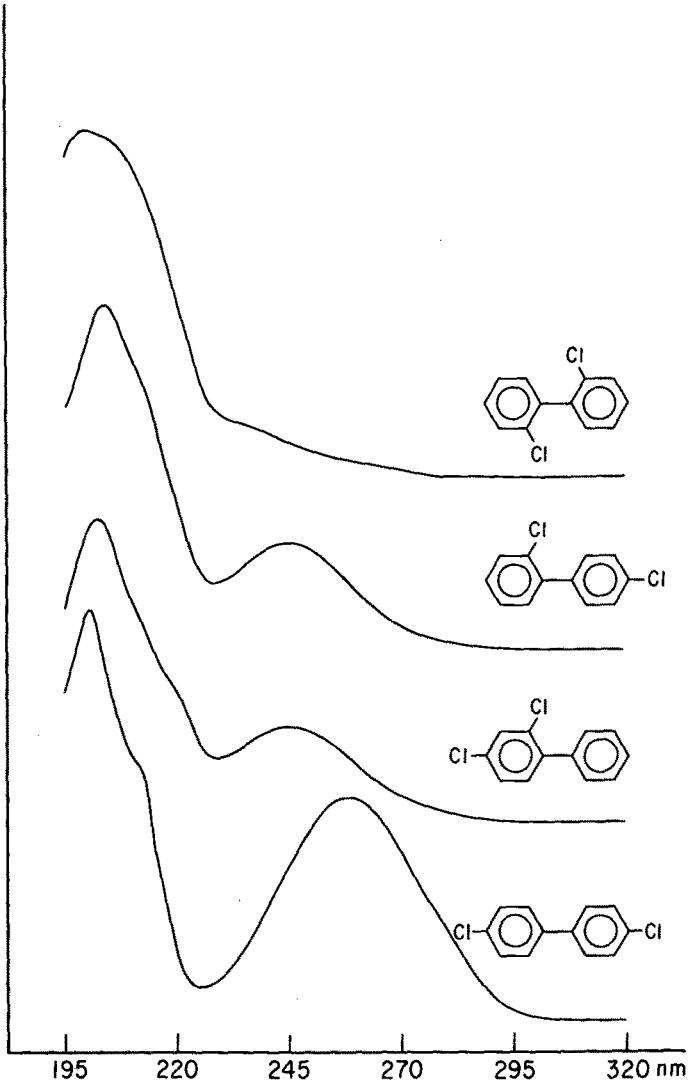

Fig. 2. U.V. spectra of four isomeric dichlorobiphenyls.

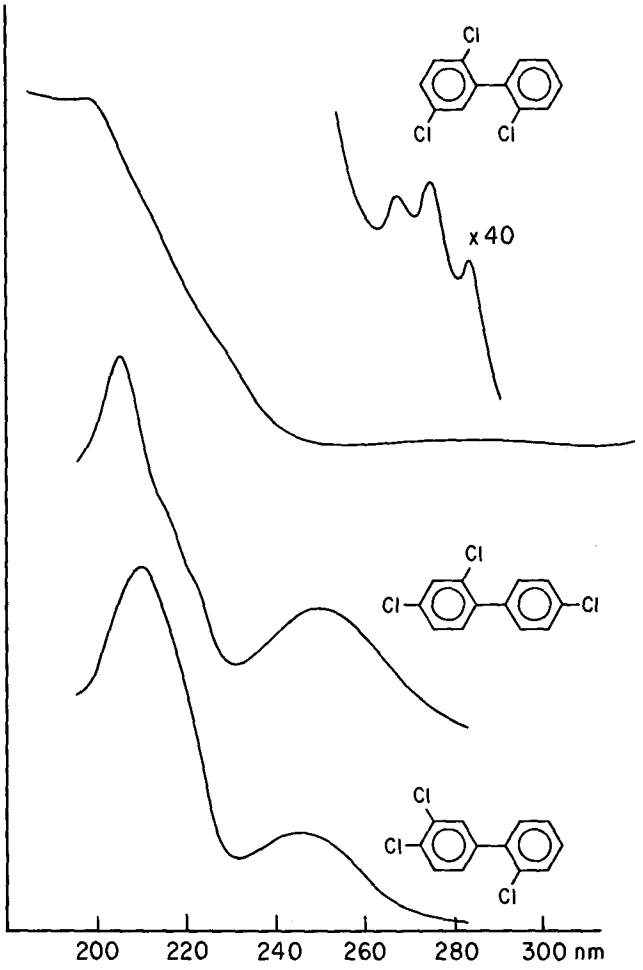

Fig. 3. U.V. spectra of three isomeric trichlorobiphenyls.

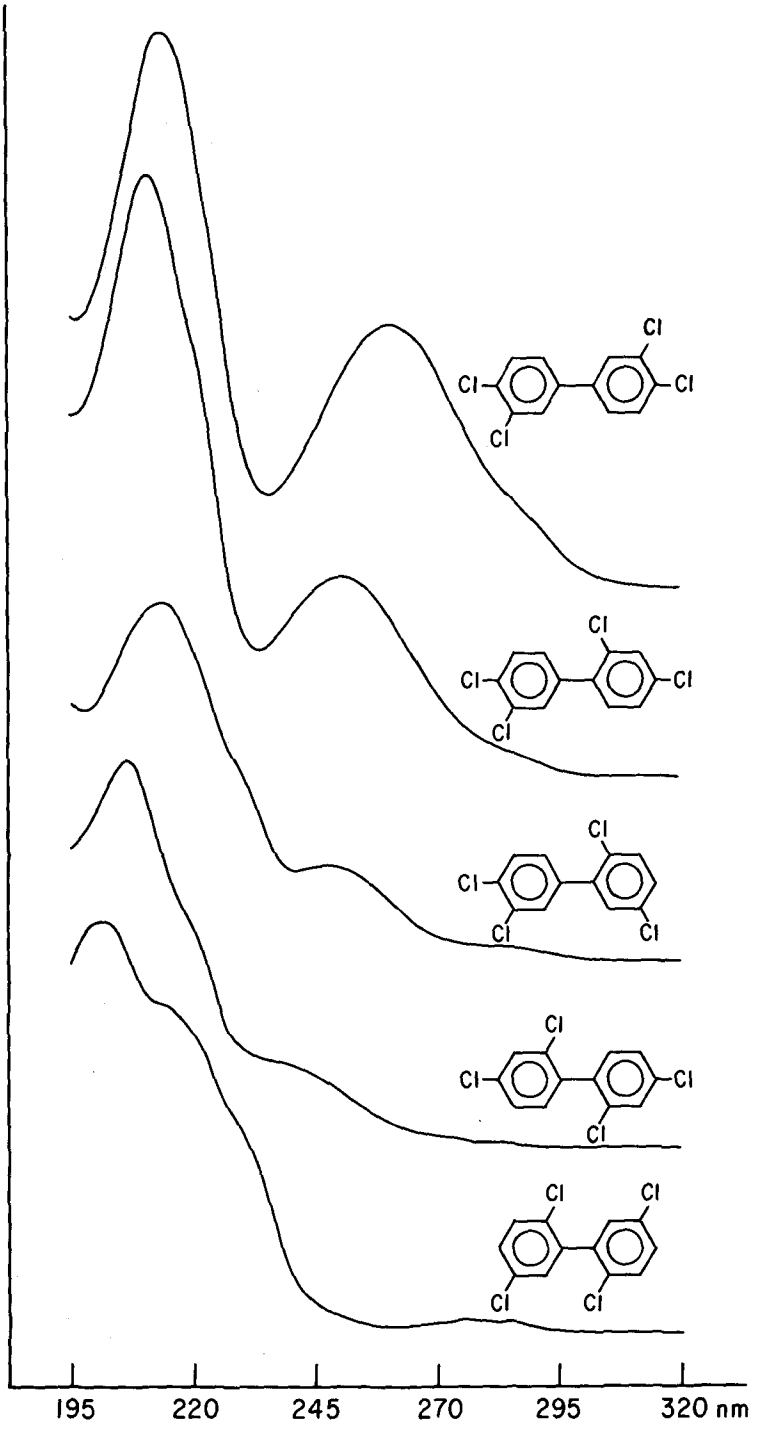

Fig. 4. U.V. spectra of five isomeric tetrachlorobiphenyls.

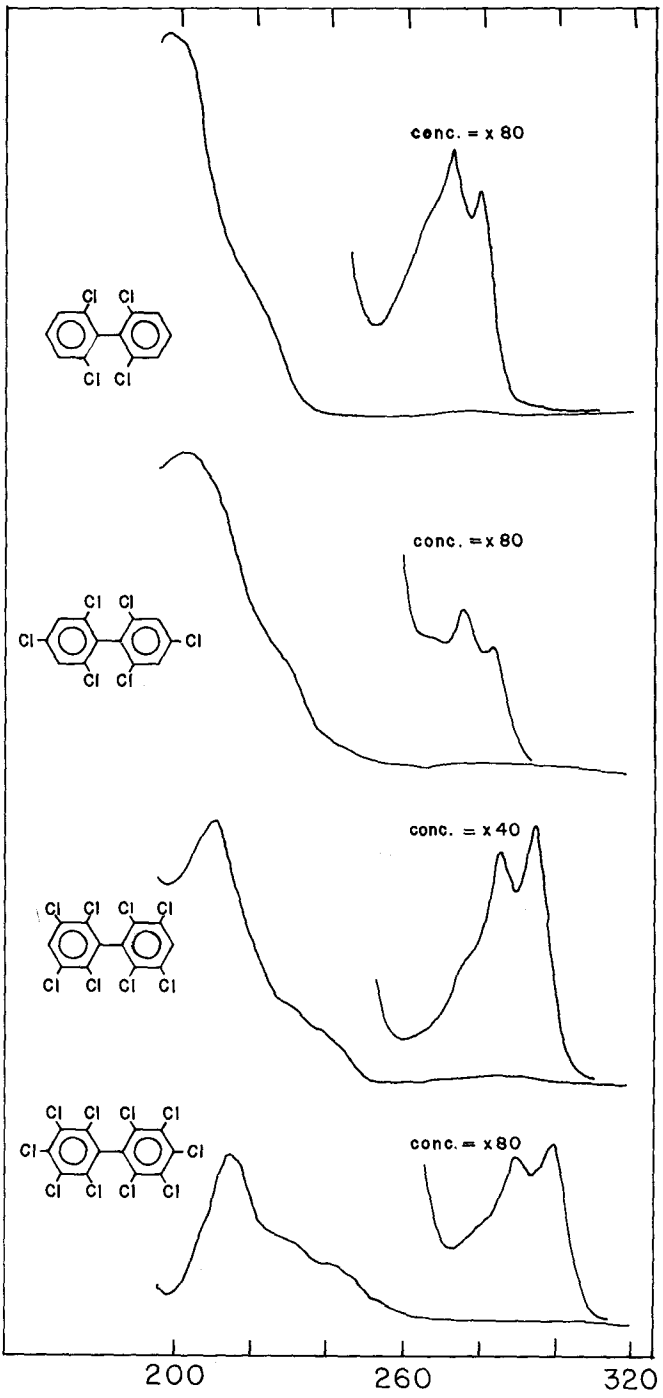

Fig. 5. U.V. spectra of four chlorobiphenyls with the 2,2',6,6'-positions substituted by chlorine.

Similarly for the 4,4'- and 3,3'-isomers the magnitude of the bathochromic shift for the κ absorption maximum is greater for the para disubstituted derivative. For the more highly substituted chlorinated biphenyls both the main absorption band and the κ band are shifted to longer wavelengths with increasing Cl substitution (see Figure 1).

(B) Chlorinated biphenyls with two or more chlorine atoms ortho to the Ph-Ph-bond.

The spectroscopic properties of the more highly hindered chlorobiphenyls are shown in Table II. It has previously been shown that introduction of substituents into the ortho positions (2,2', 6 and 6') of the biphenyl nucleus induces major changes in the UV absorption spectra (PICKETT et al. 1936; BEAVEN and HALL, 1956; HALL and MINHAJ 1957; BEAVEN 1958; SUNDSTRÖM 1973). It is generally accepted that in the highly hindered ortho-substituted biphenyls there is considerable hinderance to free rotation which results in the loss of coplanarity between the two phenyl rings. This results in a subsequent marked dimunition of the molar absorptivity of the conjugation band (κ band) with a shift of the absorption maxima to shorter wavelengths. Inspection of the UV spectra of the more highly substituted chlorinated biphenyl isomers (Table II) revealed a number of useful correlations.

Introduction of two or more ortho chloro substituents resulted in a marked dimunition of the ε value of the κ band which was also shifted to the shorter wavelengths. This is seen in the UV spectra of 2,2'-dichlorobiphenyl, 2,2',4,4'-tetrachlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl where the absorption maxima appears as a shoulder on the more intense band in the 197-216 nm region of the spectra. For the remaining compounds the κ band was not observed and was completely masked by the above mentioned absorption maxima. The effect of increasing ortho-chlorine substitution is illustrated in Figures 2, 3 and 4 with a series of di-, tri-, and tetrachlorobiphenyls.

It was also observed that the intensity of the 197-216 nm absorption maxima was also affected by increasing substitution at the ortho position. The molar absorptivity of this band for the 2,2',4,4'- and 2,2',5,5'-tetrachlorobiphenyl isomers was 51,200 and 43,300 respectively but the value for the 2,2',6,6' isomer was 88,900. This effect was also evident in comparing the 2,2',4,4',5,5'- and 2,2',4,4',6,6'-hexachlorobiphenyls and the 2,2',3,3',4,4',5,5'- and 2,2',3,3',5,5',6,6'-octachlorobiphenyls.

These highly ortho-substituted PCB isomers also exhibited a series of weak absorption maxima between 268-302 nm (e.g., Figure 5). These bands were reminiscent of the fine-structured B bands observed in the UV spectra of benzene and substituted benzenes. The absorptions are attributed to forbidden transitions to an excited state with increased contributions from homopolar structures (GILLAM and STERN 1957). Thus the maxima in the 268-302 nm region can be attributed to the individual contribution of the phenyl rings of the biphenyl nucleus. It was

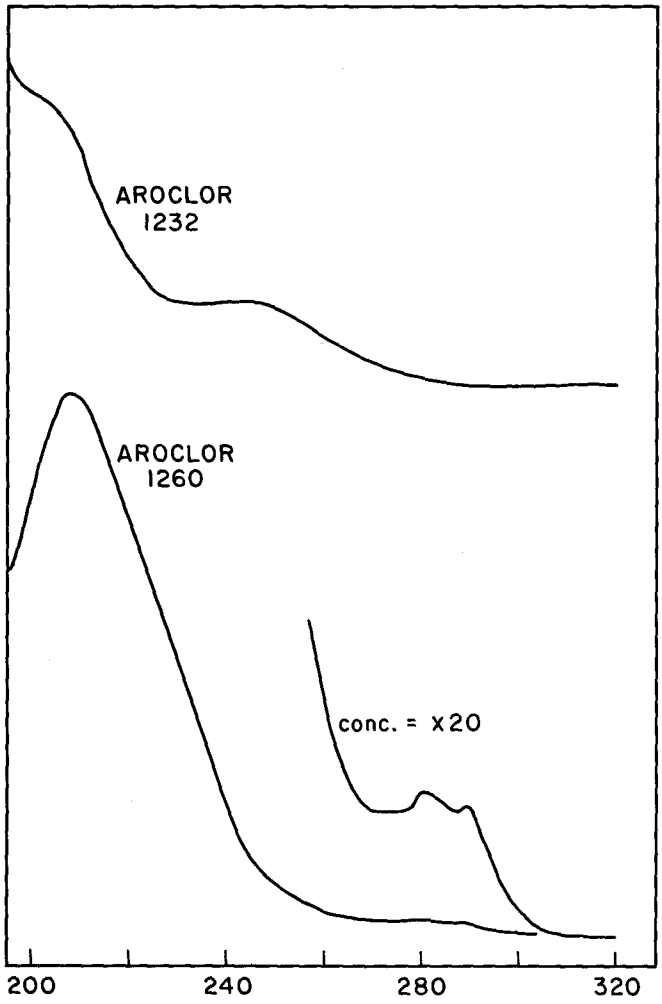

Fig. 6. U.V. spectra of Aroclor 1232 and Aroclor 1260

previously noted by Pickett and coworkers (PICKETT et al. 1936) that the "B band" absorption maxima of 2,2',4,4',6,6'-hexachlorobiphenyl were remarkably coincident with the B band maxima obtained for 1,3,5-trichlorobenzene. Moreover the extinction coefficients of the band maxima for the biphenyl derivative were two or three times greater than those observed for the trichlorobenzene isomer indicating that the absorption is approximately additive for the two benzene rings of the biphenyl derivative. Similar results have been obtained with highly hindered alkyl biphenyls. (BALLESTER and CASTANER 1960) have reported that the B bands for pentachlorobenzene were at λ_{max} 289 (ε, 390) and λ_{max} 298 (ε, 370). The position of these maxima were similar to those obtained for decachlorobiphenyl (Table II) with the molar absorptivity ca 2 - 2.5 times greater in the latter compound. The spectrum of the highly chlorinated Aroclor 1260 sample also shows the characteristic long wave length "B bands" which indicates a relatively high degree of ortho chlorosubstituted isomers in this mixture (Fig. 6).

Recently, considerable interest was shown in the photochemical reactivities of chlorobiphenyls (HUTZINGER et al 1974) since degradation of PCB under the influence of the UV portion of sunlight may be the main route of decomposition in the environment. The data presented in this paper are a necessary prerequisite for the study of the relation of structure to photochemical reactivity.

TABLE I

Ultraviolet Spectra of Chlorobiphenyls with less than two Chlorine Atoms ortho to the Ph-Ph bond.

Chlorobiphenyl	UV Maxima and Molar Absorptivity ($\times 10^{-3}$) "Main band" (nm)	κ band (nm)
-	202 (44.0)	242 (17.0)
4	199 (43.3)	253 (20.5)
3	205 (42.8)	248 (16.0)
2	204 (39.2)	240 (10.2)
4,4'	200 (41.9)	258 (22.9)
3,3'		248 (23.4)
2,4'	204 (42.4)	245 (12.8)
2,4,4'	205 (42.5)	250 (14.8)
2',3,4	210 (44.9)	246 (12.0)
2,3',4',5	214 (42.0)	248 (11.3)
3,3',4,4'		260 (22.9)
2,3',4,4'		253 (15.9)
2,4,4',5		257 (15.1)
2,3,4,4'		250 (12.6)
2,3',4,4',5		253 (2.5)
2,3,3',4,4'		253 (2.5)
3,3',4,4',5,5'	222 (51.7)	265 (27.7)

TABLE II

Ultraviolet Spectra of Chlorobiphenyls with two or more Chlorine Atoms ortho to the Ph-Ph bond

Chlorobiphenyl	UV Maxima and Molar Absorptivity ($\times 10^{-3}$) "Main band" (nm)	κ band (nm)	"B bands" (nm)
2,2'[+]	208 (36.0)	230 (6.6)	273 (.54) 266.5 (.74)
2,2',5	197 (62.5)		267 (1.10) 275 (1.17) 283 (0.82)
2,2',4,4'	207 (51.2)	220 (29.4)*	273 (1.49) 282 (0.82)
2,2',5,5'	204 (43.3)	214 (34.9)*	276 (1.32) 284 (1.25)
2,2',6,6'	197 (88.9)		272 (0.78) 280 (0.65)
2,2',3,4,5'	210 (43.0)		276 (0.91) 285 (0.78)
2,2',4,5,5'	211 (45.5)		282 (1.60) 290 (1.12)
2,2',4,4',5,5'	211 (45.5)		282 (1.60) 290 (1.12)
2,2',4,4',6,6'	202 (93.1)		267 (0.50) 275 (0.59) 288 (0.46)
2,2',3,4,5,5',6	214 (100)		268 (1.37) 277 (1.76) 286 (1.82) 297 (0.63)
2,2',3,3',4,4',5,5'	210 (57.5)		285 (0.69) 294 (0.59)
2,2',3,3',5,5',6,6'	210 (91.6)		285 (2.04) 295 (2.31)
2,2',3,3',4,4',5,5',6,6'	216 (108)		291.5 (1.10) 301.5 (1.22)

* Shoulder

[+] From reference 2

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