The Ultraviolet Spectra of Monohalo-, Mononitro- and Monoamino-p-terphenyls

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The molecule of *p*-terphenyl has a system of eighteen π-electrons and shows ultraviolet absorption with the peak at 276 mμ. When *p*-terphenyl is monosubstituted, the absorption peak shifts to red or blue and sometimes splits into two or three peaks according to the nature and the position of the substituent. These phenomena are due to the perturbation of the π-electronic system caused by the substitution. The perturbation consists principally of the following two factors: (1) interaction between the molecular orbital of *p*-terphenyl and the substituent orbital, and (2) the steric effect caused by the substituent. The ultraviolet absorption spectrum will give useful information concerning these factors.

The ultraviolet spectra of all isomers of monochloro-, monobromo-, monoiodo-, mononitro- and monoamino-*p*-terphenyl were measured, and the wavelength for maximum absorbance, the half-width of the absorption peak, the oscillator strength and the molar extinction coefficient were determined. For halo-*p*-terphenyls, the shift of the absorption peak was qualitatively treated theoretically by a molecular orbital method, which gave rather a good result considering its simplicity.

Experimental

The preparation of the compounds has been reported[1] previously, together with some of their properties. A weighed amount (ca. 1 mg.) of the sample was dissolved in purified *n*-heptane (10 ml.); then a definite volume (ca. 0.3 ml.) of the solution was withdrawn and added to the same solvent (10 ml.) in an absorption cell. The spectrum was measured at room temperature with a Shimadzu SV-50 A spectrophotometer in the range of 210～340 mμ. The oscillator strength (f) was determined by the use of Mulliken and Rieke's formula[2]:

$$f=\frac{mC^2}{\pi e^2 n}\int \gamma k_\nu \mathrm{d}\tilde{\nu}=\frac{4.318\times 10^{-9}}{\text{mol. density}}\int D\mathrm{d}\tilde{\nu} \qquad (1)$$

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[1] T. Nozaki and Y. Harada, This Bulletin, 35, 1783 (1962).

[2] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, 8, 231 (1941).

where n is the number of molecules in 1 ml. of solution; γ, the correction constant (here taken as unity); k_ν, the extinction coefficient, and D, the optical density ($\log_{10} I_0/I$). The integration was performed graphically by means of a planimeter.

Results and Discussion

The Absorption Peak and Oscillator Strength. —The measured spectra are shown in Figs. 1–5, while the numerical results are given in Tables I–V. The wavelength for the absorption peak depends strongly on the position of the substituent but only slightly on its nature. A similar tendency is also seen in the case of the melting point and the solubility[1], though the ultraviolet spectrum of the solution depends principally on the intramolecular state, while

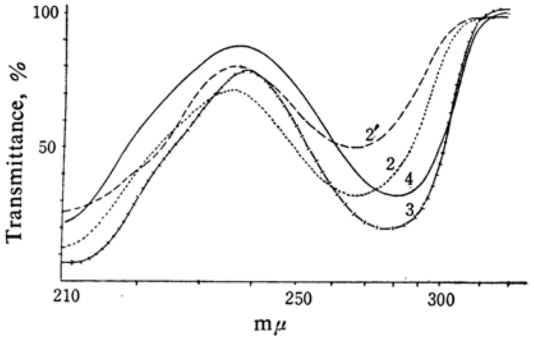

Fig. 1. Absorption spectra of chloro-*p*-terphenyls.
Curve 4 (position of substitution);
$C=1.386\times10^{-5}$
3; $C=1.228\times10^{-5}$
2; $C=1.383\times10^{-5}$
2′; $C=1.042\times10^{-5}$ mol./l.
(C=Conc. of solution)

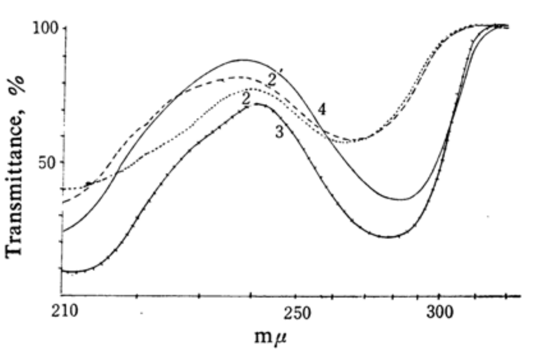

Fig. 2. Absorption spectra of bromo-*p*-terphenyls.
Curve 4; $C=0.922\times10^{-5}$
3; $C=1.236\times10^{-5}$
2; $C=0.927\times10^{-5}$
2′; $C=0.967\times10^{-5}$ mol./l.
(C=Conc. of solution)

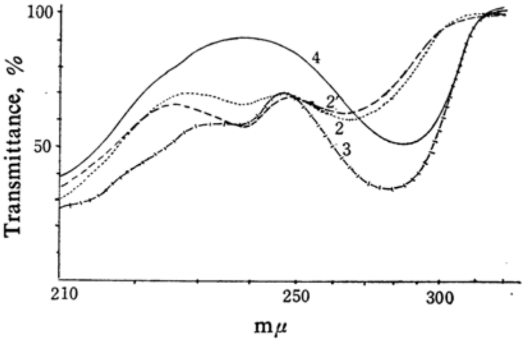

Fig. 3. Absorption spectra of iodo-*p*-terphenyls.
Curve 4; $C=0.707\times10^{-5}$
3; $C=1.317\times10^{-5}$
2; $C=0.736\times10^{-5}$
2′; $C=0.866\times10^{-5}$ mol./l.
(C=Conc. of solution)

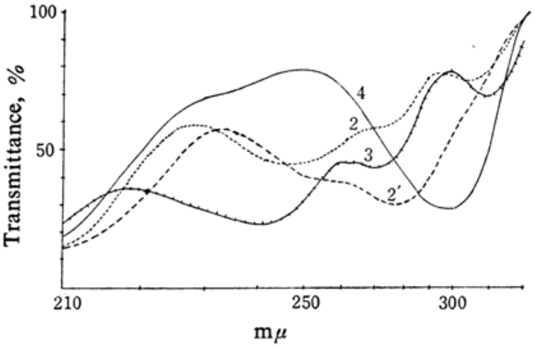

Fig. 4. Absorption spectra of amino-*p*-terphenyls.
Curve 4; $C=1.515\times10^{-5}$
3; $C=1.354\times10^{-5}$
2; $C=1.274\times10^{-5}$
2′; $C=1.667\times10^{-5}$ mol./l.
(C=Conc. of solution)

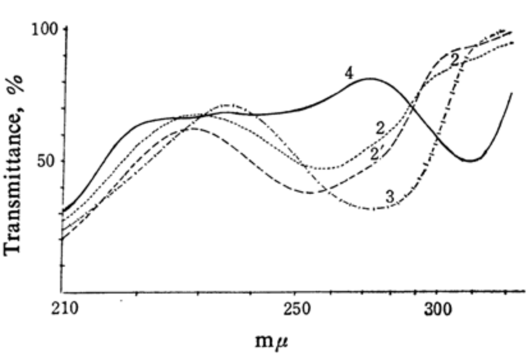

Fig. 5. Absorption spectra of nitro-*p*-terphenyls.
Curve 4; $C=0.992\times10^{-5}$
3; $C=1.424\times10^{-5}$
2; $C=1.233\times10^{-5}$
2′; $C=1.404\times10^{-5}$ mol./l.
(C=Conc. of solution)

TABLE I. CHLORO-*p*-TERPHENYLS

Position of substitution	4	3	2	2′
λ_m mμ	281	278	266	266
$\tilde{\nu}_m$ 10^4 cm^{-1}	3.56	3.60	3.76	3.76
Half width 10^4 cm^{-1}	0.57_5	0.58_5	0.61	0.58
f	0.929	1.256	0.920	0.733
ε 10^4 mol^{-1} l. cm^{-1}	3.50	5.81	3.49	2.87

TABLE II. BROMO-*p*-TERPHENYLS

Position of substitution	4	3	2	2′
λ_m mμ	282.5	278	265	266
$\tilde{\nu}_m$ 10^4 cm^{-1}	3.54	3.60	3.78	3.76
Half width 10^4 cm^{-1}	0.58	0.56	0.57	0.59_5
f	1.253	1.351	0.645	0.626
ε 10^4 mol^{-1} l. cm^{-1}	2.10	5.26	2.62	2.41

TABLE III. IODO-*p*-TERPHENYLS

Position of substitution	4		3		2		2′	
λ_m mμ	284.5	237.5	279	237	265	238	264	238
$\tilde{\nu}_m$ 10^4 cm^{-1}	3.51_5	4.21	3.59	4.20	3.78	4.20	3.79	4.20
Half with 10^4 cm^{-1}	0.58	0.28_5	0.57	0.25	0.61	0.66	0.60	0.67
f	1.135	0.032	0.858	0.095	0.782	0.201	0.645	0.195
ε 10^4 mol^{-1} l. cm^{-1}	4.19	0.26	3.43	0.80	3.01	1.71	2.33	1.66

TABLE IV. AMINO-*p*-TERPHENYLS

Position of substitution	4		3		
λ_m mμ	239	297.5	240	270	317.5
$\tilde{\nu}_m$ 10^4 cm^{-1}	4.18	3.36	4.17	3.70	3.15
Half width 10^4 cm^{-1}	0.39	0.56	0.55	0.38	0.12
f	0.091	0.932	1.095	0.338	0.185
ε 10^4 mol^{-1} l. cm^{-1}	0.53	3.70	4.73	2.67	1.17

Position of substitution	2			2′		
λ_m mμ	245	269	308	245	277	314.5
$\tilde{\nu}_m$ 10^4 cm^{-1}	4.07	3.71_5	3.25	4.07	3.61	3.18
Half width 10^4 cm^{-1}	0.41	0.42	0.38	0.37	0.54	0.34
f	0.459	0.282	0.123	0.260	0.764	0.076
ε 10^4 mol^{-1} l. cm^{-1}	2.77	1.93	1.02	1.66	3.17	0.51

TABLE V. NITRO-*p*-TERPHENYLS

Position of substitution	4		3	2			2′		
λ_m mμ	243	316	272	257	278	323	254	276	319.5
$\tilde{\nu}_m$ 10^4 cm^{-1}	4.12	3.16_5	3.67_5	3.89	3.60	3.10	3.94	3.62	3.13
Half width 10^4 cm^{-1}	0.62	0.63	1.28	0.72	0.15	0.40	0.72	0.33	0.31
f	0.478	0.824	1.425	0.849	0.004	0.571	1.247	0.035	0.043
ε 10^4 mol^{-1} l. cm^{-1}	1.76	3.09	3.50	2.65	0.07	0.18	2.76	0.23	0.29

TABLE VI. LOWEST TRANSITION ENERGIES OF MONOHALO-*p*-TERPHENYLS, ΔE†

Position of substitution	
4	$1.185+0.088\times\left(\frac{1}{\alpha+0.593}-\frac{1}{\alpha-0.593}\right)\gamma^2$
3	$1.185+0.008\times\left(\frac{1}{\alpha+0.593}-\frac{1}{\alpha-0.593}\right)\gamma^2$
2	$1.185+0.060\times\left(\frac{1}{\alpha+0.593}-\frac{1}{\alpha-0.593}\right)\gamma^2-0.328\times(\delta\beta)$
2′	$1.185+0.049\times\left(\frac{1}{\alpha+0.593}-\frac{1}{\alpha-0.593}\right)\gamma^2-0.328\times(\delta\beta)$

† in units of $(-\beta)$

The values of $C^i{}_r$ in Eq. 2 are obtained from the following reference: A. and B. Pullman, *J. chim. phys.*, **46**, 212 (1949).

the melting point and solubility should relate strongly to the intermolecular forces.

The ultraviolet spectra of the halo-p-terphenyls have the following characteristics; (1) The wavelenthgs of the absorption peaks are in the order 4-halo$>$3-halo$>$$p$-terphenyl; (2) Halogenation at 2- or 2′-position, on the other hand, shows a blue shift probably because of the steric effect; (3) The wavelength for the main absorption peak depends only slightly on the nature of the halogen atom; (4) The oscillator strength of a 4- or 3-halo-p-terphenyl is usually larger than that of the 2- or 2′-compound. Similar phenomena have also been observed with substituted biphenyl[3] and in more general cases[4]. The 238 mμ peaks of the iodo-p-terphenyls may be attributed to the absorption by the iodine atom itself[3].

LCAO MO Perturbation Treatment.—Many authors have tried to elucidate theoretically the effect of a substituent on the ultraviolet spectrum. Matsen[5] gave general formulas for the wavelength and oscillator strength of ultraviolet absorption using the perturbation theory and then applied them to benzene derivatives. Longuet-Higgins and Sowden[6] successfully explained the ultraviolet spectrum of methylated hydrocarbons. I'haya[7] also developed the perturbation theory and treated benzene derivatives.

We intend to explain our experimental results on the basis of a simple LCAO MO perturbation treatment. The substitution has an effect on both the electronic structure and the steric configuration of the p-terphenyl molecule. The substitution at the 3- or 4-position has influence only on the electronic structure, while that at the 2- or 2′-position has the further effect of twisting the molecule. The variation in electronic structure is due to the change in the degree of resonance and inductive effects. In the present paper, however, only the resonance effect is considered on the assumption that the difference in the inductive effect is small among the halo-p-terphenyls. The steric effect is taken up in the form of a variation in the resonance integral of the carbon-carbon bond between two benzene rings.

For the perturbed system, the energy, λ'_i, is given as follows, with the higher terms being neglected[8];

$$\lambda'_i = \lambda_i + 2C^i_r C^i_s(\delta\beta) - \frac{(C^i_t)^2}{\alpha - \lambda_i}\gamma^2 \tag{2}$$

where λ_i is the energy and C^i_r, the coefficient of the r-th atom in i-th non-perturbed MO; the subscripts r and s denote the atoms binding the two benzene rings being considered, and t is the position of the substituent. Here, α designates the energy of the highest occupied orbital of the substituent, while γ is the resonance integral of the bond between the substituent and p-terphenyl, $\delta\beta$ is the change in the resonance integral caused by the twist of p-terphenyl and is negative. All these quantities are expressed in units of $(-\beta)$, the resonance integral of the benzene carbon-carbon bond.

The lowest transition of p-terphenyl in the simple LCAO MO treatment can be regarded as $A_{1g} \rightarrow B_{3u}$ on the assumption that p-terphenyl has a plane structure. The energy differences between the lowest vacant and the highest occupied orbitals, ΔE, are calculated and listed in Table VI. Since the biphenyl molecule twists slightly, the p-terphenyl molecule should twist too. Using the above assumptions, however, we probably have not committed any serious errors in drawing our conclusions.

Since the value of any α in Table VI is larger than unity, all the second terms in the formulas are negative. Hence, for 4- and 3-halo-p-terphenyls, ΔE becomes smaller and a red shift occurs. Further, it is apparent that 4-substitution gives a larger red-shift than 3-substitution. These results agree well with the experimental data. Substitution at the 2- or 2′-position causes a remarkable blue shift owing to the third term, which is positive and has a larger absolute value than the second. Moreover, the blue shift is of nearly the same degree for 2 and 2′ isomers, because the third terms are the same and the second terms differ only slightly between them. All these predictions are supported by the experimental data. The magnitude of the second term varies with the nature of the halogen. However, the change is too small to cause a shift of the peak, as may be seen in the experimental results. It is worth noticing that the all conclusions are derived independently of the values of the parameters in the formulas. In spite of the roughness in our treatment, the qualitative agreement with the experimental results is very good.

For the nitro- and amino-derivatives, however, the situation is too complicated to be treated by such a perturbation method; a more elaborate treatment is required.

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