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A Study on the Electronic Spectra of 1-(*p*-Substituted phenyl)pyrroles*[1]

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The longest wavelength electronic absorption band of 1-(*p*-substituted phenyl)pyrrole has been found to show a regular bathochromic shift as the electronegativity of the substituent on the phenyl group increases. The substituent effect is closely related to that for the intramolecular charge-transfer bands of *p*-substituted anilines. Therefore, the longest wavelength absorption band of 1-(*p*-substituted phenyl)pyrroles have been suggested to be originated from an electron transfer from the pyrryl group to the phenyl group. Only one exception is the spectra of 1-(*N,N*-dimethyl-*p*-aminophenyl)pyrrole. In this case, the longest wavelength electronic absorption band is suggested to be due to an electron-transfer from the *N,N*-dimethylamino group to the phenyl group.

A large number of experimental studies have been reported on the electronic spectra of pyrrole derivatives.[1] The present status of the theoretical interpretation, however, is far from satisfactory except for the case of pyrrole itself.[1g,2] The situation may be improved by making a systematic study of the spectra of a series of related pyrrole derivatives. In the present paper, the nature of the longest wavelength absorption bands of 1-(*p*-substituted phenyl)pyrroles are described and the origin of the electronic transitions is discussed.

Results and Discussion

The longest wavelength electronic absorption bands of 1-(*p*-substituted phenyl)pyrroles are invariably strong and appear in the region between 250 mμ and 350 mμ. The wave numbers and the extinction coefficients for the absorption maxima are summarized in Table 1. It is clearly observed there that the absorption band shows a regular bathochromic shift, except for the case of *N,N*-dimethylamino group, as the electronegativity of the *p*-substituent increases. The trend may be taken to indicate that the absorption bands arise from intramolecular charge-transfer as has been suggested in the cases of mono-substituted benzenes.[3,4] Since pyrryl group is a very strong π-electron donor in the formation of charge-transfer complexes,[5] it is very likely that the pyrryl group in 1-phenylpyrrole donates its electrons to the phenyl group. The substituent effect on

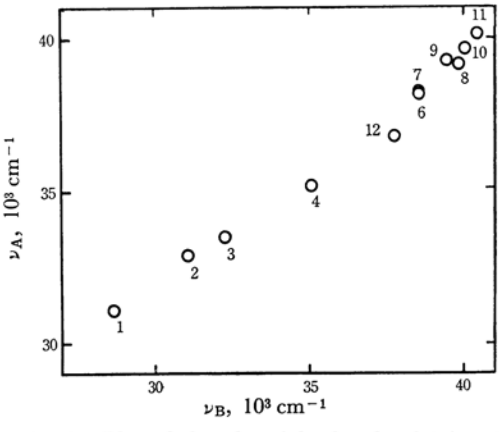

Fig. 1. Plot of the ultraviolet bands of 1-(*p*-substituted phenyl)pyrroles (ν_A) *vs.* those of *p*-substituted *N,N*-dimethylanilines (ν_B) in *n*-hexane. The numbers correspond to the numbering of the compounds listed in Tables 1 and 2.

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*[1] Contribution No. 154 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

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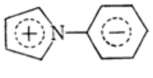
TABLE 1. THE LONGEST WAVELENGTH ELECTRONIC ABSORPTION BANDS OF 1-(*p*-SUBSTITUTED PHENYL)PYRROLES

No.	Compound	The *n*-hexane solution		The ethanol solution	
		ν[a)]	ε[b)]	ν[a)]	ε[b)]
1	1-*p*-Nitrophenylpyrrole	31.1	17.4	30.3	16.4
2	1-*p*-Formylphenylpyrrole	33.4	27.5	32.6	22.8
		32.3	26.3		
3	1-*p*-Acetylphenylpyrrole	34.1	25.1	33.4	24.0
		32.8[c)]	19.6		
4	1-*p*-Cyanophenylpyrrole	35.2	22.0	34.8	22.8
5	1-*p*-Carbomethoxyphenylpyrrole	35.0	23.3	34.5	22.2
6	1-*p*-Bromophenylpyrrole	38.2	18.7	38.1	18.2
7	1-*p*-Chlorophenylpyrrole	38.3	17.9	38.4	17.2
8	1-Phenylpyrrole	39.2	13.5	39.4	13.2
9	1-*p*-Tolylpyrrole	39.3	14.7	39.3	14.5
10	1-*p*-Anisylpyrrole	39.7	15.7	39.8	15.1
		34.1[c,d)]	2.0	34.1[c,d)]	1.9
11	1-*p*-Hydroxyphenylpyrrole	40.2	e)	40.0	26.9
		33.9[c,d)]	e)	33.8[c,d)]	3.3
12	1-(*N,N*-Dimethyl-*p*-amino-phenyl)pyrrole	36.8	21.0	36.6	18.6
		31.1[c,d)]	2.0	31.2[c,d)]	2.1

a) The values are given in units of 10^3 cm^{-1}, and the uncertainty is within 100 cm^{-1} unless otherwise specified.
b) The values are given in units of 10^3 l/mol·cm, and the uncertainty is within 100 l/mol·cm.
c) The position of a shoulder (±200 cm^{-1}).
d) The absorption band may be mainly due to the locally excited B_{2u} configuration of the phenyl group.
e) No reliable value has been obtained because the solubility of the sample is extremely low.

the charge-transfer band of *N,N*-dimethylaniline[*2] was also investigated for the comparison (Table 2). In Fig. 1, the positions of absorption maxima of the 1-phenylpyrrole analogues are plotted against those of the corresponding *N,N*-dimethylanilines. A very close resemblance is observed between the substituent effects in the two series. Analogously to the case of aniline, the absorption spectra of the 1-phenylpyrrole analogues are suggested then to be related to the charge-transter conffgurations of the following type:



In agreement with this suggestion, the absorption band shows both hypsochromic shift and hypochromic effect when the conjugation between the pyrryl and phenyl groups is hindered by the presence of methyl group at either the 2- or the 2′-position[*3] (Table 3, Fig. 2). Similar observation was reported also by several investigators.[1b,1g)]

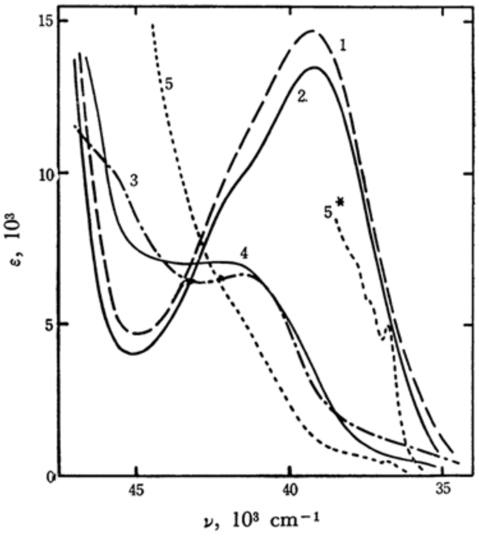


Fig. 2. The ultraviolet spectra of 1-phenylpyrrole and its methyl-substituted analogues in *n*-hexane. The numbers correspond to the numbering of the compounds listed in Table 3. * The real molecular extinction coefficient is one tenth of the value shown in this figure.

When an electronegative group is attached to the *p*-position of the phenyl group, the energy of the charge-transfer configuration should be lowered.

[*2] The charge-transfer nature of this band has been well established by Nagakura and his associates.[4b)]

[*3] If one uses Braude and Sondheimers' relationship (Eq. (1))[7)] to estimate the angle of twist, θ, between the two groups;

$$\varepsilon/\varepsilon_0 = \cos^2\theta \tag{1}$$

he gets 50° for 1-(*o*-tolyl)pyrrole. On the basis of a three dimensional molecular model with appropriate van der Waals radii, θ for the same compound is estimated to be approximately 60°.

TABLE 2. THE LONGEST WAVELENGTH INTRAMOLECULAR CHARGE-TRANSFER BANDS OF *p*-SUBSTITUTED *N,N*-DIMETHYLANILINES[a]

No.[b]	Compound	ν[c]	ε[d]
1	*N,N*-Dimethyl-*p*-nitroaniline[e]	28.7	
2	*N,N*-Dimethyl-*p*-amino-	31.4	29.9
	benzaldehyde	30.8	29.6
3	*N,N*-Dimethyl-*p*-amino-	32.8[f]	24.1
	acetophenone	31.8	27.5
4	*N,N*-Dimethyl-*p*-cyanoaniline	35.6	29.0
		34.6[f]	23.5
6	*N,N*-Dimethyl-*p*-bromoaniline	38.6	19.5
7	*N,N*-Dimethyl-*p*-chloroaniline	38.6	19.6
8	*N,N*-Dimethylaniline	39.9	15.1
9	*N,N*-Dimethyl-*p*-toluidine	39.5	15.2
10	*N,N*-Dimethyl-*p*-anisidine	40.1	13.3
11	*N,N*-Dimethyl-*p*-aminophenol[g]	40.5	11.0
12	*N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine	37.8	16.4

a) Solvent: *n*-hexane.
b) The numbering of the compounds is made so that the substituent on the para position of the phenyl group in this table is the same to that of the corresponding number in Table 1.
c) The values are given in units of $10^3\,\text{cm}^{-1}$, and the uncertainty is within $100\,\text{cm}^{-1}$ unless otherwise specified.
d) The values are given in units of $10^3\,l/\text{mol}\cdot\text{cm}$, and the uncertainty is within $100\,l/\text{mol}\cdot\text{cm}$.
e) K. Semba, This Bulletin, **34**, 722 (1961).
f) The position of a shoulder ($\pm 200\,\text{cm}^{-1}$).
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TABLE 3. THE ULTRAVIOLET ABSORPTION BANDS OF METHYL SUBSTITUTED 1-PHENYLPYRROLES[a]

No.	Compound	ν[b]	ε[c]
1	1-*p*-Tolylpyrrole	42.2 ± 0.2[d]	9.80 ± 0.03
		39.3 ± 0.1	14.7 ± 0.1
2	1-Phenylpyrrole	42.2 ± 0.2[d]	9.00 ± 0.03
		39.2 ± 0.1	13.5 ± 0.1
3	1-Phenyl-2,5-dimethylpyrrole	45.7 ± 0.2[d]	10.1 ± 0.1
		41.4 ± 0.1	6.66 ± 0.02
4	1-*o*-Tolylpyrrole	41.2 ± 0.2[d]	6.70 ± 0.02
5	1-(2′,6′-Xylyl)pyrrole	41.3 ± 0.2[d]	4.80 ± 0.02

a) Solvent: *n*-hexane.
b) The values are given in units of $10^3\,\text{cm}^{-1}$.
c) The values are given in units of $10^3\,l/\text{mol}\cdot\text{cm}$.
d) The position of a shoulder.

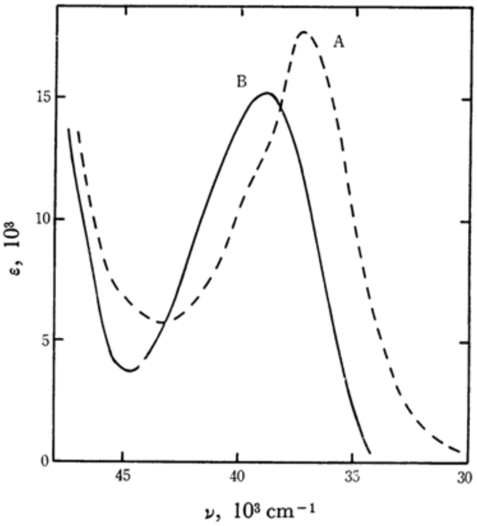

Fig. 3. The ultraviolet spectra of 1-(*N,N*-dimethyl-*p*-aminophenyl)pyrrole in 10% (vol/vol) ethanol-water solution; A, the neutral solution; B, the 10^{-2} N hydrochloric acid solution.

The experimental facts are certainly in accordance with this expectation. The only one exception is *N,N*-dimethylamino group. In order to investigate the reason for the bathochromic effect of this group, the spectra were measured in acidic medium. Since the spectra of 1-(*N,N*-dimethyl-*p*-aminophenyl)pyrrole in acidic medium is very close to that of 1-phenylpyrrole in the neutral solution (Fig. 3), the former compound is concluded to be protonated on its *N,N*-dimethylamino group. This conclusion is in agreement with the fact that the basicity of pyrrole ($\text{p}K_a$, -4.4)[1g] is much lower than that of *N,N*-dimethylaniline ($\text{p}K_a$, 5.10).[6] In other words, *N,N*-dimethylamino group is more basic than pyrryl group. Therefore it is very important to take into account the contribution of the charge-transfer configurations where an electron is transferred from the *N,N*-dimethylamino group to the phenyl group. Such electronic configurations are of minor importance in the cases of other substituents in Table 1. Thus the nature of the longest wavelength absorption band of 1-(*N,N*-dimethyl-*p*-aminophenyl)pyrrole may be suggested to be different from those of the other 1-(*p*-substituted phenyl)pyrroles.

In order to understand the nature of electronic transitions of complex molecules, it is very useful to utilize the method of composite molecules.[3,4] In the present case, the constituent molecules are pyrrole (A) and substituted benzene (B). The presence of an electronegative group in the phenyl group will increase the electron affinity of B. Then the energy of local excitation in either A or B will be above that of the charge-transfei state (A^+B^-) where an electron is transferred from A to B. The situations is entirely different, if the substituent is *N,N*-dimethylamino group which is a highly electron-donating group. Since the electron affinity of B is considerably reduced, in this case, the energy of the charge-transfer state (A^+B^-)

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[6] N. F. Hall, *J. Am. Chem. Soc.*, **52**, 5115 (1930).

will be raised appreciably. The energy of the lowest excited state in B (*i. e.*, *N,N*-dimethylaniline), on the other hand, is known to be much less than that of unsubstituted benzene.[4b] Then it is quite likely that the local excitation in B may require less energy than an electron-transfer from A to B. If this is the case, the longest wavelength electronic absorption band of 1-(*N,N*-dimethyl-*p*-aminophenyl)pyrrole is considered to be due to an electron transfer from the *N,N*-dimethylamino group (rather than from the pyrryl group) to the phenyl group. The experimental facts are certainly in accordance with this view point. In order to testify the proposed explanation, a quantum mechanical calculation is being carried out to estimate the relative importance of various electronic configurations.

It may be adequate to mention here also that a weak absorption band corresponding to the B_{2u} state of benzene seems to be hidden under the longest wavelength absorption bands discussed above. The band appears only slightly at the tail of the absorption edge of 1-(2′,6′-xylyl)pyrrole (Fig. 2).

Experimental

Chemicals. The preparations of the materials other than described below have been reported elsewhere.[5] The following compounds were prepared according to the literatures as given in the parentheses: 1-*p*-nitrophenylpyrrole (Ref. 8, mp 180.2—181.2°C), 1-*p*-formylphenylpyrrole (Ref. 9,[*4] mp 94.5—95.5°C. Found: C, 77.31; H, 5.16; N, 8.12%. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.29; N, 8.18%), 1-*p*-cyanophenylpyrrole (Ref. 9,[*4] mp 104.5—105.5°C. Found: C, 78.58; H, 4.81; N, 16.50%. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.80; N, 16.65%), 1-*p*-carbomethoxyphenylpyrrole (Ref. 9,[*4] mp 127.7—128.7°C. Found: C, 71.58; H, 5.60; N, 7.17%. Calcd for $C_{12}H_{11}NO_2$: C, 71.68; H, 5.47; N, 6.96%), *N,N*-dimethyl-*p*-aminobenzaldehyde (Ref. 10, mp 74.0—75.0°C) and *N,N*-dimethyl-*p*-aminobenzonitrile (Ref. 11, mp 76.5—77.5°C). The prepared samples were identified by the nuclear magnetic resonance spectra and infrared spectra.

n-Hexane and ethanol were supplied by commercial sources as reagent grade chemicals. They were repeatedly purified by usual methods until they proved to be pure from spectroscopic points of view.

Spectroscopic Measurements. Spectra were measured at 17—19°C by a Baush & Lomb Spectronic Model 505 or Hitachi Model EPS-2 Recording Spectrophotometer. The concentration of the solutions were between 10^{-4} and 10^{-5} mol/*l*.

[*4] These compounds were synthesized by modifying the method for the preparations of similar compounds described in the references.

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10) H. H. Bosshard and Hch. Zollinger, *Helv. Chim. Acta*, **42**, 1659 (1959).

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