[Chem. Pharm. Bull.
16(7)1235—1239(1968)]

UDC 547.551.58.03 : 543.422.6

# Correlation of the Electronic Absorption Spectra of *para*-Disubstituted Benzene Series with Some Physical Constants

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(Received September 7, 1967)

The ultraviolet absorption spectra of *para*-disubstituted benzene series with two substituent groups of opposite electrical property are measured in *n*-heptane, ethanol and water. The transition energies of three bands, namely shifted one of 200 mμ band ($A_{1g} \rightarrow B_{1U}$ transition), intramolecular chargetransfer band and 250 mμ band ($A_{1g} \rightarrow B_{2U}$ transition) are discussed with respect to substituent constants and molecular dipole moment.

The results are as follows: (1) The chargetransfer band is more sensitive than other band to the character of substituent groups, polarity of solvent and molecular dipole moment.

(2) The sum of *para*-substituent constants, $|\sigma_{p1}| + |\sigma_{p2}|$ and molecular dipole moment correlate well with the absorption maxima of this series.

There have been many theoretical and experimental studies concerning the effect of substituent groups upon the ultraviolet absorption spectra of benzene.[2–6] Most works carried out hitherto in order to obtain empirical regularity of this effect have dealt with so-called primary band corresponding to 200 mμ band ($A_{1g} \rightarrow B_{1U}$ transition[7]) of benzene.[8,9] In those works, all absorption maxima appearing in the wavelength region longer than 200 mμ have been interpreted as shifted one of 200 mμ band of benzene. But it has been recently examined in the theoretical and experimental studies[2–4,10] that substituted benzenes show new band caused by chargetransfer interaction between substituent groups and benzene ring in addition to three bands pertinent to benzene molecule, namely $E_{1U}$ band (180 mμ), $B_{1U}$ band (200 mμ) and $B_{2U}$ band (240—260 mμ).

In addition, it has been suggested that the energy level of new band called intramolecular chargetransfer band[11] lies at lower than that of $B_{1U}$ band in such cases as nitrobenzene, benzoic acid and aniline which has strong interaction between substituent groups and benzene ring, on the other hand it lies at upper than that of $B_{1U}$ band, in the vacuum ultraviolet region, in such cases as phenol, anisole and toluene which has weak substituent groups.[12] According to the theoretical and experimental results mentioned above, it turns out that empirical regularities discussed hitherto have some confusions in assignments of spectra concerning $B_{1U}$ band and CT-band. Moreover it is expected that the effect of substituent groups appears on CT-band primarily, not on $B_{1U}$ band or $B_{2U}$ band perinent to benzene. In this paper,

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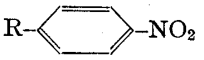
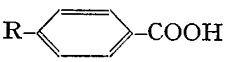
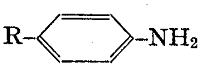
[1] Location: *Toneyama, Toyonaka, Osaka.*
[2] S. Nagakura, M. Kojima, and Y. Maruyama, *J. Mol. Spectry.*, **13**, 174 (1964).
[3] K. Kimura, H. Tubomura, and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 1336 (1964).
[4] J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 833 (1963).
[5] J.N. Murrell and H.C. Longuet-Higgins, *Proc. Phys. Soc.* (London), A, **68**, 969 (1955).
[6] R. Pariser, R.G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1963).
[7] "200 mμ band ($A_{1g} \rightarrow B_{1U}$ transition)" is abbreviated as "$B_{1U}$ band".
[8] L. Doub, J.M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947), **71**, 2414 (1949).
[9] C.N. Rao, *Chem. & Ind.* (London), 666 (1956).
[10] H. Labhart, *Tetrahedron*, **19**, Suppl. 2 (1963).
[11] "chargetransfer band" is abbreviated as CT-band.
[12] S. Nagakura and K. Kimura, *Nippon Kagaku Zasshi*, **86**, 1 (1956).

therefore *para*-substituted nitrobenzene, *para*-substituted benzoic acid and *para*-substituted aniline series with two substituent groups of opposite electrical property will be treated to discuss the correlation of transition energy of $B_{1U}$ band, CT-band and $B_{2U}$ band with substituent constants, polarity of solvent and molecular dipole moment from following reasons. One of them is that assignments of spectra of these series can be done with respect to nitrobenzene, benzoic acid and aniline, respectively. Another reason is that CT-bands of which are recognized intuitively in the ultraviolet region, thus the effect of methoxy, hydroxy and alkyl group on TC-band can be observed as perturbation on CT-bands of nitrobenzene and benzoic acid without extending measurements to the vacuum ultraviolet region.

## Experimental

*para*-Disubstituted benzene series measured in this work are shown in Table I.

Table I

| |  |  |  |
|---|---|---|---|
| R | $-H$ | $-H$ | $-H$ |
| | $-CH_3$ | $-CH_3$ | $-Cl$ |
| | $-OH$ | $-OH$ | $-COOH$ |
| | $-OCH_3$ | $-OCH_3$ | $-COOCH_3$ |
| | $-NH_2$ | $-NH_2$ | $-COCH_3$ |
| | | | $-NO_2$ |

Absorption spectra of these derivatives (*ca.* $10^{-4}$ M) in the wavelength region from 200 mμ to 400 mμ were measured with a Hitachi Recording Spectrometer Model EPS-2 in *n*-heptane, ethanol and water with quartz cell of 1 cm path length.

Absorption spectra of *para*-substituted nitrobenzene, *para*-substituted benzoic acid and *para*-substituted aniline series are shown in Fig. 1, 2, and 3, respectively.

Assignments of the spectra of *para*-substituted compounds of nitrobenzene, benzoic acid and aniline were made with respect to nitrobenzene, benzoic acid and aniline, respectively.

In *para*-substituted nitrobenzene series, as are shown in Fig. 1 both shoulders of $B_{1U}$ band (208 mμ and 213 mμ band ) and CT-band (250 mμ) of nitrobenzene show red-shift, consequantly $B_{2U}$ band (280 mμ) is masked with CT-band displaced to longer wavelength than 280 mμ by electronreleasing substituent group in *para*-position.

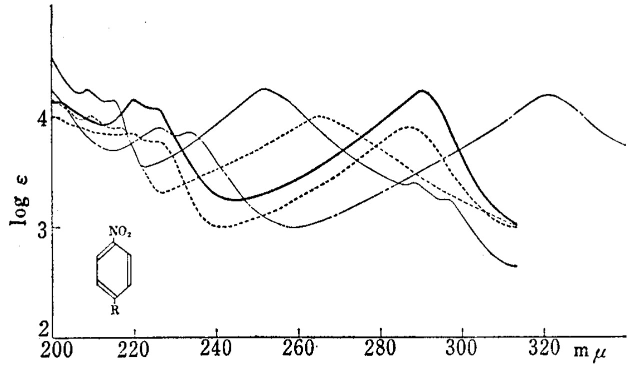


Fig. 1. Ultraviolet Absorption Spectra of *para*-Substituted Nitrobenzene Series in *n*-Heptane

——— R=H ⋯⋯ R=OH
—·—·— $R=NH_2$ - - - - - - $R=CH_3$
▬▬▬ $R=OCH_3$

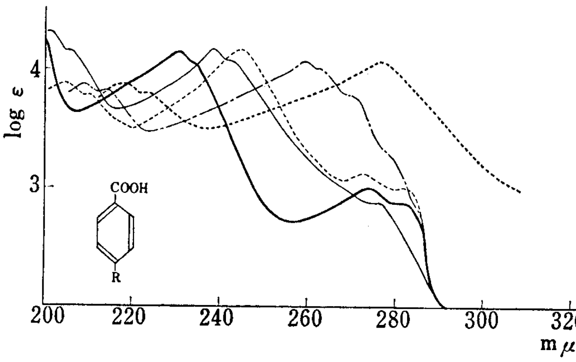


Fig. 2. Ultraviolet Absorption Spectra of *para*-Substituted Benzoic Acid Series in *n*-Heptane

▬▬▬ R=H ——— $R=CH_3$
- - - - - - R=OH —·—·— R=OCH
⋯⋯ $R=NH_2$

It is also observed that CT–band shows greater displacement than $B_{1U}$ band.

As is shown in Fig. 2 *para*–substituted benzoic acid series show similar displacement as in the case of *para*–substituted nitrobenzene series except that $B_{2U}$, band of the former is not masked by CT–band, because CT–bands of this series appear considerably shorter wavelength region than that of $B_{2U}$ band, therefore three bands ($B_{1U}$, CT and $B_{2U}$ band) can be obserbed except for *para*–amino benzoic acid.

In *para*–substituted aniline series, both $B_{1U}$ band (180 mμ), unobservable in *n*–heptane, and CT–band (235 mμ) in aniline show red–shift, therefore $B_{1U}$ band can be observed and $B_{2U}$ band (275—300 mμ with vibrational structure) comes to be masked with increasing electronattracting ability of substituent group in *para*–position.

Also in this series, CT–band shows greater red–shift compared with $B_{1U}$ band.

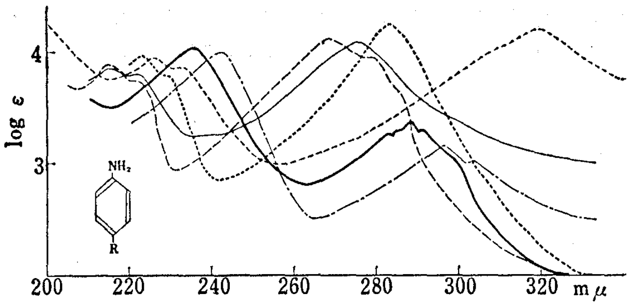


Fig. 3. Ultraviolet Absorption Spectra of *para*–Substituted Aniline Series in *n*–Heptane

—— R=H
—·—·— R=Cl
– – – R=COOCH₃
—— R=COOH
········ R=COCH₃
- - - - R=NO₂

## Results and Discussion

### 1. Correlation of Absorption Spectra with Substituent Constants

Fig. 4 shows plots of transition energy (eV) of absorption band *vs.* $|\sigma_{p1}|+|\sigma_{p2}|$.[13] $|\sigma_{p1}|+|\sigma_{p2}|$ represents a sum of the absolute value of *para*–substituent constants for invariant ($p_1$) and varying group ($p_2$).

The plots in Fig. 4 show that energy level of CT–band is more sensitive to character of *para*–substituent group than other bands and shows an approximately linear relationship for almost all substituent groups. It may be concluded that energy level of $B_{2U}$ band is scarcely affected by *para*–substituent group as is shown in the case of *para*–substituted benzoic acid series. Contrary to the expectation based upon $|\sigma_{p1}|+|\sigma_{p2}|$ value, methoxy group shows greater red–shift than hydroxy group in *n*–heptane

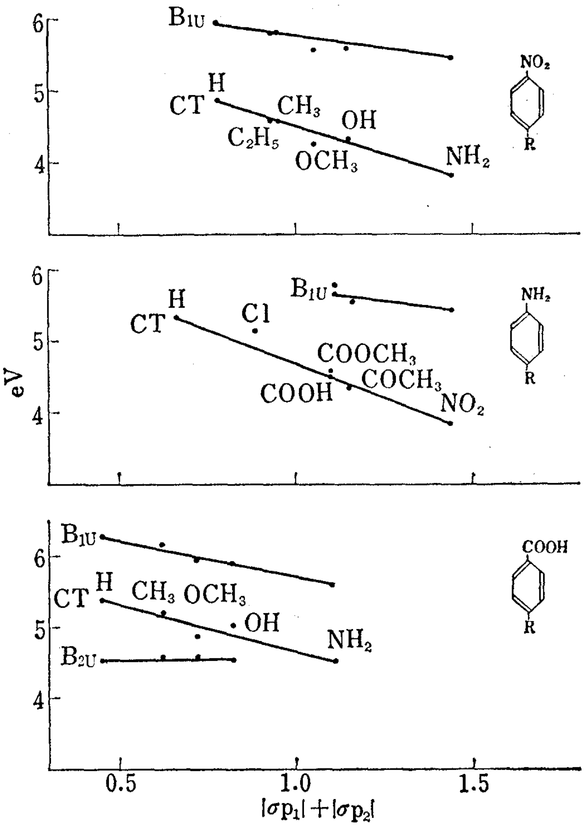


Fig. 4. Correlation of the Absorption Maxima of *para*–Disubstituted Benzene Derivatives with Substituent Constants

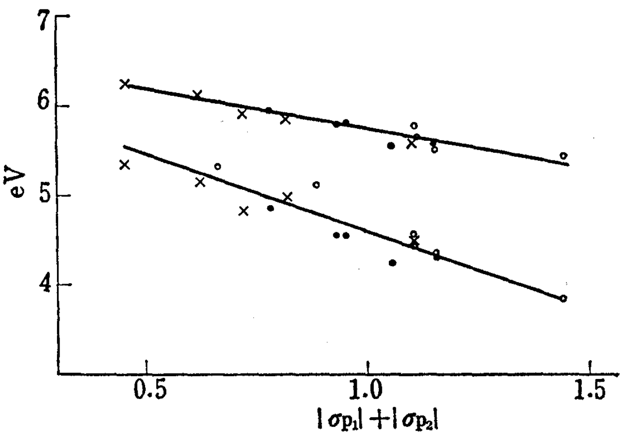


Fig. 5. Correlation of the Absorption Maxima of *para*–Disubstituted Benzene Derivatives

—●— nitrobenzene series
—×— bezoic acid series
—○— aniline series

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[13] D.H. McDaniel and H.C. Brown, *J. Org. Chem.*, 23, 420 (1958).

but shows red-shift almost similar magnitude in water. Roughly speaking, slope of line increases in the order of $B_{2U}<B_{1U}<CT$.

Fig. 5 shows the plots of transition energy against $|\sigma_{p1}|+|\sigma_{p2}|$, including the data for all three series.

As is shown in Fig. 5, there is satisfactory correlation of transition energy with a sum of *para*-substituent constants, $|\sigma_{p1}|+|\sigma_{p2}|$.

### 2. Solvent Effect on Absorption Maxima

Absorption maxima of these *para*-disubstituted benzene series were observed in *n*-heptane, ethanol and water in order to examine the solvent effect.

As is shown in Fig. 6 CT-band shows considerably larger red-shift compared with $B_{1U}$ band in proportion to the polarity of solvent. In *para*-substituted aniline series, however, both CT and $B_{2U}$ bands show smaller displacements in water compared with those in ethanol.

The probable explanation of this displacement may be that partial isolation of the $2pz$ electrons of nitrogen atom caused by the protonation on non-bonding electrons of nitrogen[14] reduces the interaction between $2pz$ electrons and benzene ring.

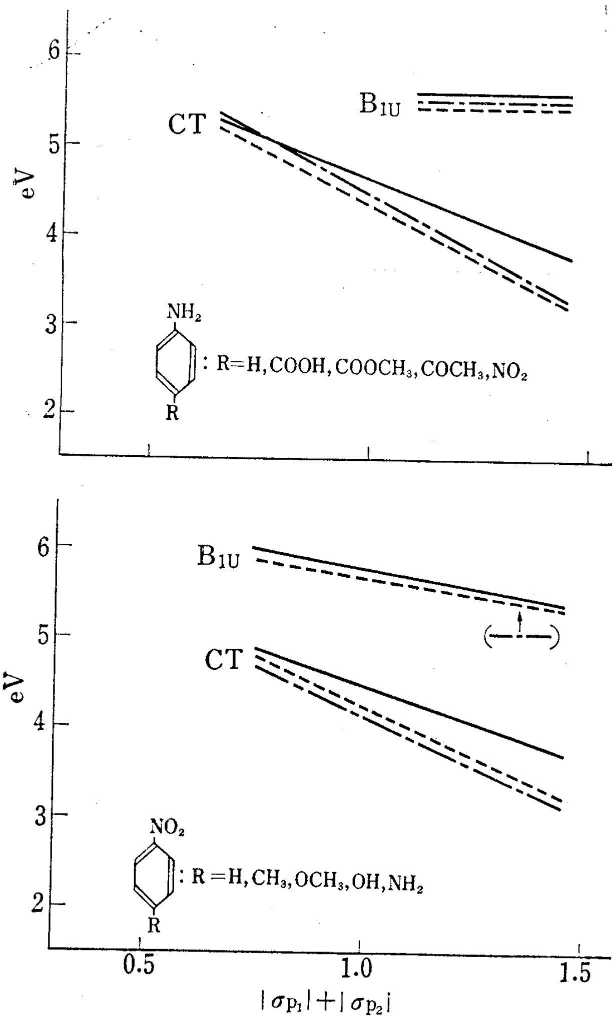

Fig. 6. Effect of Solvent on Absorption Maxima

——— in *n*-heptane ------- in ethanol
------ in water

On the basis of this experimental result which shows that energy level of CT-band is more stabilized than that of $B_{1U}$ band in the solvent of large polarity and the theoretical one obtained in nitrobenzene,[2] it is safely concluded that the CT-configuration generally has larger polarity than that of $B_{1U}$.

### 3. Correlation of Absorption Maxima with Molecule Dipole Moments

Correlations of transition energy of CT-band and $B_{1U}$ band with molecular dipole moment[15] in the cases of *para*-substituted compounds of nitrobenzene and aniline series are shown in Fig. 7.

The relationships illustrated in Fig. 7 suggest that molecule with large dipole moment at ground state have low energy in CT-configuration and CT-band is more sensitive than $B_{1U}$ band to molecular dipole moment.

These experimental results mentioned in the present study suggest that in these *para*-disubstituted benzene series CT-bands are more sensitive than $B_{1U}$ and $B_{2U}$ bands to the character of substituent group, polarity of solvent and molecular dipole moment and that $|\sigma_{p1}|+|\sigma_{p2}|$ can satisfactorily correlate the electronic absorptions maxima of these series. It is, however, necessary to extend measurements to the vacuum ultraviolet region for more

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[14] W.F. Forbes and I.R. Leckie, *Can. J. Chem.*, **36**, 1371 (1958).

[15] A.L. McClellan "Table of Experimental Dipole Moment," W.H. Freeman & Company, San Fransisco and London (1964).

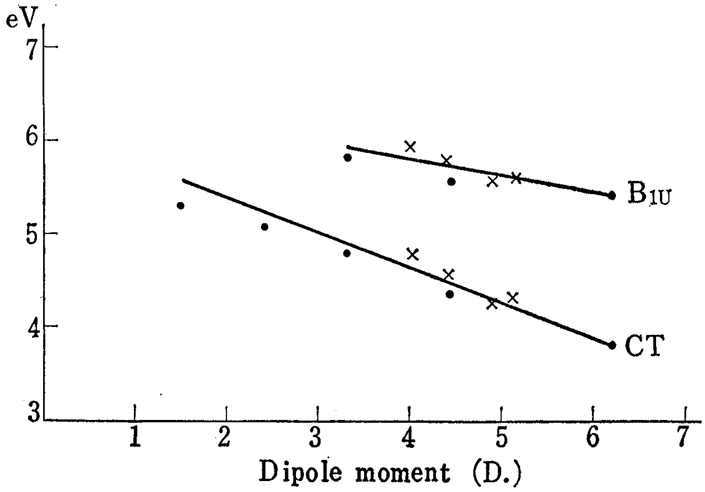
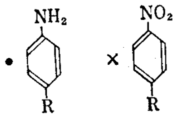


Fig. 7. Correlation of Absorption Maxima with Molecular Dipole moment



reliable relations of electronic absorption spectra with substituent constants or other physical constants.

**Acknowledgement** The author wishes to thank Associate Professor Y. Sasaki for his kind advices and encouragement.