New Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants, II.\textsuperscript{1,2)} n–π* and π–π* Transitions

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(Received September 12, 1983)

In order to confirm and to extend the scope of the equation \(1.3E_{\text{UV}}^{\text{homo}} = aF + bR + c\), presented by us in the foregoing paper, the polarographic half-wave reduction (\(E_{1/2}^{\text{red}}\)) and oxidation (\(E_{1/2}^{\text{ox}}\)) potentials in nonaqueous media and the electronic spectra of 4-substituted azobenzenes have been analyzed. Although the equation was originally derived for π–π* type HOMO→LUMO transitions with the same character in a series of substances, in this paper we have theoretically verified that the equation is also applicable to the n–π* bands of conjugated systems. The singlet n–π* and π–π* bands of 4-substituted azobenzenes and the triplet n–π* bands of 4,4'-disubstituted benzophenones were employed to examine the above equation. The results were reasonable, and are discussed from the viewpoint of molecular orbital theory.

Keywords—nonaqueous polarography; half-wave reduction potential; half-wave oxidation potential; substituent effect on electronic spectra; substituent constant; n–π* transition; π–π* transition; CNDO/S-CI calculation; 4-substituted azobenzene; 4,4'-disubstituted benzophenone

Although the substituent effect on electronic spectra has been extensively studied on the basis of the molecular orbital (MO) theory, the basic principles of the application of the Hammett-type substituent constants for describing the substituent effect on electronic spectra have not so far been well established.\textsuperscript{4)} The reason seems to be mainly that the electronic transition between two different electronic states, each of which may be controlled by different substituent constants, produces an absorption or an emission band. In a foregoing paper\textsuperscript{2)} we have discussed this problem in detail, and derived the following general equation:

\[\text{1.3}E_{\text{homo}}^{\text{UV}} = aF + bR + c\]  

where \(E_{\text{homo}}^{\text{UV}}\) means the singlet or triplet absorption band resulting mainly from the HOMO→LUMO transition, and \(F\) and \(R\) are the field and resonance substituent constants derived by Swain and Lupton,\textsuperscript{5)} respectively.

Equation 1 was obtained as an extension of Eq. 2 derived by us,\textsuperscript{6)} where the polarographic half-wave oxidation and reduction potentials obtained in nonaqueous medium are expressed by \(E_{1/2}^{\text{red}}\) and \(E_{1/2}^{\text{ox}}\), respectively.

\[(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}) = k_1 \text{1.3}E_{\text{homo}}^{\text{UV}} + k_2\]  

An experimental examination of Eqs. 1 and 2 was described in a foregoing paper. The results for the strong π–π* absorption bands of substituted stilbenes and azoxybenzenes were quite reasonable.\textsuperscript{2)} In this paper the application of Eq. 1 to n–π* bands, as well as π–π* bands, is discussed from both experimental and theoretical viewpoints.

Experimental

Polarographic and Spectral Measurements—The techniques used for these measurements were almost the same
as in the preceding paper. The direct current (DC) polarograms were recorded with a Yanagimoto polarograph (model P-1000), a saturated calomel electrode (SCE) being used as the reference electrode. The capillary constants employed for the dropping mercury electrode are: \( m = 1.355 \text{ mg s}^{-1} \), \( t = 5.82 \text{ s} \), and \( h = 70 \text{ cm} \) in distilled water at open circuit. Alternatively the oxidation wave was recorded by using a rotating platinum electrode (600 rpm). The details are given in ref. 2. The apparatus for cyclic voltammetric (CV) measurement was constructed in our laboratory, as already reported. All the experiments were carried out at 25.0 ± 0.1 °C in \( N,N \)-dimethylformamide (DMF) or \( \text{CH}_3\text{CN} \) containing 0.1 mol dm\(^{-3}\) tetrabutylammonium perchlorate (TBAP). The purification methods for DMF, \( \text{CH}_3\text{CN} \), and TPAP were the same as reported previously.  

The absorption spectra were recorded with a Hitachi spectrophotometer (model 323) at room temperature. The solvents, \( n \)-heptane and \( \text{CH}_3\text{CN} \), were of spectrograde purity and were dried sufficiently over CaH\(_2\), then carefully rectified.  

**Samples**—The substances used here are 4-substituted azobenzenes having the trans-in-plane form as in [I], where the coordinate axes employed for the MO calculation are also given. These compounds seem to be suitable for the present study, since azobenzenes exhibit a well-separated \( n-\pi^* \) band and \( \pi-\pi^* \) type HOMO→LUMO transition band in the near UV region as described later. Azobenzenes with the substituents \( \text{X} = \text{H}, \text{OH}, \text{OCH}_3, \text{NH}_2, \text{and} \ N(\text{CH}_3)_2 \) were purchased from Wako Pure Chemical Industries Ltd. or Tokyo Kasei Co., Ltd. They were repeatedly recrystallized from ethanol (1)–water (1) mixture. On the other hand, 4-Cl and 4-CN substituted azobenzenes were synthesized according to the literature. The former was recrystallized from ethanol (2)–water (1) mixture after removal of impurities by alumina column chromatography (mp 89.0 °C). The purification of the latter was done by repeated sublimation and preparative thin-layer chromatography (TLC), then the product was recrystallized from ethanol (mp 121.5 °C). The structure and purity of all the samples were checked by means of TLC, infrared (IR), ultraviolet (UV), and elemental analyses. A good agreement was obtained between experimental and calculated values in the elemental analyses.  

**Calculation of Electronic Spectra and Electronic States**—Although the electronic states of azobenzene derivatives have already been discussed on the basis of several kinds of MO approximation, the calculation of the electronic spectra and electronic states was newly carried out here by CNDO/S semiempirical method in order to interpret the spectra and their correlations with the \( E_{11}^{\text{HOMO}} \) and \( E_{12}^{\text{LUMO}} \) values. The parameters necessary for the calculation and the molecular dimensions pertinent to the substituents are the same as those previously reported for the CNDO/S calculation of substituted stilbenes. The molecular dimensions of the azobenzene skeleton are taken from an X-ray crystal analysis, but it was assumed that the bond lengths and bond angles of H atoms attached to the benzene ring are 1.08 Å and 120° (sp\(^2\) hybridization), respectively. Two-center repulsion integrals were evaluated by using Nishimoto–Mataga’s equation. Only the one-electron transition was taken into account for the calculation of electronic spectra. All the calculations were done with a FACOM M-200 computer at Nagoya University Computation Center.  

**Results and Discussion**

**n–\( \pi^* \) and \( \pi–\pi^* \) Transitions and Nonaqueous Oxidation–Reduction Potentials of Substituted Azobenzenes**  

Tables I and II list the experimental data on \( n–\pi^* \) and \( \pi–\pi^* \) transitions of 4-substituted azobenzenes in \( n \)-heptane and \( \text{CH}_3\text{CN} \), respectively, along with the CNDO/S calculated values. The \( n–\pi^* \) and \( \pi–\pi^* \) absorption spectra of the azobenzenes are also shown in Fig. 1. It is clear from these data that the \( n–\pi^* \) band of azobenzene is blue-shifted by introducing electron-donating substituents, but the \( \pi–\pi^* \) band is red-shifted. However, in the case of the
TABLE I. CNDO/S-CI Calculated Values of the $n$-$\pi^*$ Transition Energies, Oscillator Strengths, Symmetries under $C_s$, and Main Singly Excited Configurations of 4-Substituted Azobenzenes, with the Experimental Data

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\bar{\nu}_{obs}^{a)}$ (10$^3$ cm$^{-1}$)</th>
<th>$\varepsilon_{max}^{obs}$</th>
<th>$\bar{\nu}_{calcd}^{b)}$ (10$^3$ cm$^{-1}$)</th>
<th>$f_{calcd}$</th>
<th>Sym</th>
<th>Main configuration (%)$^{b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (Azobenzene)</td>
<td>22.55</td>
<td>428</td>
<td>19.79</td>
<td>0.000</td>
<td>A'</td>
<td>67.5 (30/35), 18.9 (30/39)</td>
</tr>
<tr>
<td>4-CH$_3$</td>
<td>22.61</td>
<td>607</td>
<td>21.30</td>
<td>0.000</td>
<td>A'</td>
<td>67.8 (33/38), 18.8 (33/42)</td>
</tr>
<tr>
<td>4-Cl</td>
<td>22.95</td>
<td>741$^{(c)}$</td>
<td>20.00</td>
<td>0.000</td>
<td>A'</td>
<td>68.3 (33/38), 18.9 (33/42)</td>
</tr>
<tr>
<td>4-OCH$_3$</td>
<td>23.05</td>
<td>729$^{(d)}$</td>
<td>20.02</td>
<td>0.000</td>
<td>A'</td>
<td>67.1 (33/38), 18.8 (33/42)</td>
</tr>
<tr>
<td>4-OH</td>
<td>23.26</td>
<td>739$^{(e)}$</td>
<td>21.30</td>
<td>0.000</td>
<td>A'</td>
<td>67.9 (33/38), 19.1 (33/42)</td>
</tr>
<tr>
<td>4-NH$_2$</td>
<td>22.08</td>
<td>532</td>
<td>20.02</td>
<td>0.000</td>
<td>A'</td>
<td>67.5 (36/41), 19.7 (36/45)</td>
</tr>
</tbody>
</table>

$^{a)}$ These are the values at the maximum intensity in n-heptane.
$^{b)}$ For example, (30/35) means a singly excited configuration from non-bonding orbital $\psi_{30}$, localized mainly in the N=N bond, to the 35th unoccupied $\pi^*$-orbital $\psi_{35}$.
$^{c)}$ These $n$-$\pi^*$ absorption bands overlap with the longer wavelength tail of the next $\pi$-$\pi^*$ strong bands, particularly in the case of 4-NH$_2$ substituent (see Fig. 1), so that the $\varepsilon_{max}^{obs}$ values are larger than those of the other substances.

TABLE II. CNDO/S-CI Calculated Values of the $\pi$-$\pi^*$ Transition Energies, Oscillator Strengths, Symmetries under $C_s$, and Main Singly Excited Configurations of 4-Substituted Azobenzenes, with the Experimental Data

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\bar{\nu}_{obs}^{a)}$ (10$^3$ cm$^{-1}$)</th>
<th>$\varepsilon_{max}^{obs}$</th>
<th>$\bar{\nu}_{calcd}^{b)}$ (10$^3$ cm$^{-1}$)</th>
<th>$f_{calcd}$</th>
<th>Sym</th>
<th>Main configuration (%)$^{b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (Azobenzene)</td>
<td>31.65</td>
<td>21400</td>
<td>33.96</td>
<td>0.964</td>
<td>A'</td>
<td>97.0 (34/35)</td>
</tr>
<tr>
<td>4-CH$_3$</td>
<td>31.06</td>
<td>17900</td>
<td>33.35</td>
<td>0.988</td>
<td>A'</td>
<td>97.1 (37/38), 1.0 (34/41)</td>
</tr>
<tr>
<td>4-Cl</td>
<td>29.07</td>
<td>23900</td>
<td>33.77</td>
<td>0.988</td>
<td>A'</td>
<td>96.9 (37/38)</td>
</tr>
<tr>
<td>4-OCH$_3$</td>
<td>29.07</td>
<td>25300</td>
<td>33.43</td>
<td>0.995</td>
<td>A'</td>
<td>97.1 (37/38), 1.1 (34/41)</td>
</tr>
<tr>
<td>4-OH</td>
<td>26.18</td>
<td>27800</td>
<td>32.76</td>
<td>1.003</td>
<td>A'</td>
<td>96.6 (37/38), 1.1 (34/41)</td>
</tr>
<tr>
<td>4-NH$_2$</td>
<td>24.50</td>
<td>28000</td>
<td>32.76</td>
<td>1.003</td>
<td>A'</td>
<td>96.6 (37/38), 1.1 (34/41)</td>
</tr>
<tr>
<td>4-CN</td>
<td>31.15</td>
<td>24000</td>
<td>33.61</td>
<td>1.011</td>
<td>A'</td>
<td>96.8 (40/41), 1.1 (37/44)</td>
</tr>
</tbody>
</table>

$^{a)}$ Data at the absorption maximum in CH$_3$CN.
$^{b)}$ For example, the notation (34/35) means a singly excited configuration from the 34th filled $\pi$-orbital ($\psi_{34}$) to the 35th unoccupied $\pi^*$-orbital ($\psi_{35}$).

CN derivative (electron-accepting substituent) both the $n$-$\pi^*$ and $\pi$-$\pi^*$ bands are red-shifted. These phenomena are well known and can be reasonably explained by using molecular orbital theory. Here we wish to apply the substituent constants $F$ and $R$ to describe the behavior of the above $n$-$\pi^*$ and $\pi$-$\pi^*$ transition energies. The values of the $E_{1/2}^{red}$ and $E_{1/2}^{red}$ for the first wave of azobenzenes are listed in Table III. These are useful to interpretation of the substituent effects on the orbital energies and electronic spectra. CV measurement at the pen-and-ink recording speeds indicated that the first reduction wave of the azobenzenes used is due to a reversible redox couple between neutral species and their anion radicals except for amino and dimethylamino substituents, for which reversibilities are not good. However, it was verified that each of these amino compounds shows a reversible electrode reaction at scanning rates higher than the above rate. On the other hand, the NH$_2$- and N(CH$_3$)$_2$-
substituents alone among the azobenzenes show a reversible oxidation wave resulting from formation of the corresponding cation radicals; the other substituents gave an irreversible oxidation wave. Assuming that the potential due to the irreversible oxidation wave is mainly controlled at the step of cation radical formation caused by a one-electron oxidation, these half-wave oxidation potentials were employed here.

**Description of the Substituent Effect on the n-π* Band by Means of the Substituent Constants F and R**

As was stated in the introduction, Eq. 1 has been proposed by us and experimentally verified as regards the HOMO→LUMO π-π* transitions of substituted stilbenes and azoxybenzenes. However, Table I indicates that the observed n-π* transition of substituted azobenzenes consists mainly of two configurations i.e. n-π1* and n-π2*, where each of the orbital natures of n, π1*, and π2* in the azobenzene skeleton part is almost unchanged.

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**Table III. Half-wave Reduction and Oxidation Potentials of 4-Substituted Azobenzenes**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>CH₃CN&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DMF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CH₃CN&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (Azobenzene)</td>
<td>-1.317</td>
<td>-1.318</td>
<td>1.825</td>
</tr>
<tr>
<td>4-Cl</td>
<td>-1.252</td>
<td>-1.252</td>
<td>1.845</td>
</tr>
<tr>
<td>4-OCH₃</td>
<td>-1.432</td>
<td>-1.455</td>
<td>1.605</td>
</tr>
<tr>
<td>4-OH</td>
<td>&lt;i&gt;d&lt;/i&gt;</td>
<td>-1.357</td>
<td>1.483</td>
</tr>
<tr>
<td>4-NH₂</td>
<td>-1.511</td>
<td>-1.589</td>
<td>0.950</td>
</tr>
<tr>
<td>4-N(CH₃)₂</td>
<td>-1.524</td>
<td>-1.533</td>
<td>0.884</td>
</tr>
<tr>
<td>4-CN</td>
<td>-1.030</td>
<td>-1.024</td>
<td>1.989</td>
</tr>
</tbody>
</table>

<a> The reversibility of the polarographic waves corresponding to the reduction and oxidation potentials listed in this table is discussed in detail in the text.

b> Data vs. SCE.

c> Measured in the solvents designated.

<i>d</i> A well-resolved polarogram was not obtained in this solvent.
throughout all the substituents on the basis of the CNDO/S calculation, the n–π*$ configuration contributing dominantly to the observed n–π* transition. In addition, the contribution ratio of the n–π* configuration to the n–π* one is constant throughout all the samples. Thus, we may say that the character of the observed n–π* transition is the same among the samples used here. The n–π* transition energy is now written as Eq. 3, where $E_{CI}$ is the configuration interaction energy and arises predominantly according to Eq. 4 in the present case.

$$E_{CI}^{UV} = \varepsilon_{n-\pi*} + E_{CI}$$

$$E_{CI} = \langle \chi_{n-\pi^*} | H | \chi_{n-\pi^*} \rangle$$

$$= \varepsilon_{n-\pi^*} - \langle n\pi^* | G | n\pi^* \rangle + 2 \langle n\pi^* | G | \pi n \rangle$$

It should be noted that the term $\varepsilon_{n-\pi^*}$ turns out to be zero under the SCFMO employed in the present calculations. Since the character of the MO's n, $\pi^*$, and $\pi^*$ is almost the same for all the samples employed here, as mentioned above, the value of $[2 \langle n\pi^* | G | \pi n \rangle - \langle n\pi^* | G | n\pi^* \rangle]$ seems to be almost constant, that is, the energy terms $E_{CI}$ in Eq. 3 may be put as a constant. As a result, the contribution of n–π* and n–π* configurations to the excited state wave function $\Psi_{n-\pi^*}$ corresponding to the observable n–π* transition is almost the same among all the substituents (Table I). We can write Eq. 5 for the $E_{CI}^{UV}$ transition under such conditions, since the change of orbital energies $\varepsilon_n$ and $\varepsilon_{\pi^*}$ with substituents, or the change of physical quantities, such as half-wave potentials corresponding to the orbital energies, with substituents should be describable by using substituent constants.

$$E_{CI}^{UV} = aF + bR + c$$

That the term $E_{CI}$ in Eq. 3 is also involved in the constant term “c” of the right-hand side of Eq. 5 should be noted here. The results of a linear plot of $E_{CI}^{red}$ against the substituent constant $\sigma_p$ is depicted in Fig. 2, where $\sigma^-$ value is employed for the CN group as discussed elsewhere. Figure 3 also shows the substituent dependence of CNDO/S $\varepsilon_n$ orbital energy in terms of substituent constants F and R. The linearity seen in Figs. 2 and 3 seems to be
quite good, so that Eq. 5 can be safely applied to predict the \( n-\pi^* \) band observed here for azobenzenes. This kinds of plot is depicted in Fig. 4, where we can see a good linear relation between observed and estimated \( E_{n-\pi^*}^{\text{UV}} \) values, the relation being written as \( E_{n-\pi^*}^{\text{UV}} = -0.0570F - 0.128R + 2.796 \) with \( n \) (sample number) = 6, \( s \) (standard deviation) = 0.010, \( r \) (correlation coefficient) = 0.994.

As expected theoretically, we can now say that the substituent effect on the \( E_{n-\pi^*}^{\text{UV}} \) band of azobenzenes is well described by means of Swain and Lupton’s \( F \) and \( R \) substituent constants. The fact that electron-donating substituents such as \( \text{OCH}_3 \), \( \text{N(CH}_3)_2 \), etc. bring about a blue shift of the \( n-\pi^* \) band is already well understood on the basis of MO theories.\(^{14,15}\) In addition, we see that the regression equation (\textit{vide supra}) for the linear relation in Fig. 4 is heavily dependent on the term \( R \). Because the substituent effect on the \( \pi^*_1 \) orbital of azobenzene is of course larger than that on the \( n \)-orbital, the above result seems to be reasonable.

Next, we examined the substituent effect on the triplet \( n-\pi^* \) band, \( E_{n-\pi^*}^{\text{UV}} \) of 4,4'-disubstituted benzophenones on the basis of Swain and Lupton’s substituent constants. The original spectral data were taken from the paper by Loutfy and Loutfy.\(^{22}\) The triplet state \( E_{n-\pi^*}^{\text{UV}} \) of benzophenones is due to the excitation of non-bonding electrons, localized in the carbonyl oxygen atom, to the \( \pi^* \) orbital, so that the nature of the excited state is expected to be similar to the \( E_{n-\pi^*}^{\text{UV}} \) of azobenzenes except for the spin multiplicity, and therefore the application of Eq. 5 to the \( E_{n-\pi^*}^{\text{UV}} \) band should be theoretically acceptable. The results are depicted in Fig. 5, in which we can find a good correlation between observed and estimated \( E_{n-\pi^*}^{\text{UV}} \) band energies. The contribution of the \( R \) term is also larger than that of the \( F \) term, although the excited state is in the triplet state and the benzophenones are not planar molecules.\(^{23}\)

**Description of the Substituent Effect on the \( \pi-\pi^* \) Band of Azobenzenes by Means of the Substituent Constants \( F \) and \( R \)**

Keeping in mind the fact that the characteristics of the \( \pi-\pi^* \) band of azobenzenes...
appearing in the longest-wavelength region are very similar to those of substituted stilbenes, as is apparent from their molecular structures and Fig. 1, the substituent constants $F$ and $R$ may be legitimately applied to explain the substituent effect on the $\pi-\pi^*$ band of azobenzenes. The relation of $E_{1/2}^{ox}$ values to the substituent constant $\sigma^+$ is shown in Fig. 6, where the data in Table III are adopted. The linearity seems to be quite good. The CNDO/S calculation results pertinent to the spectral data of $\pi-\pi^*$ band of azobenzenes are also included in Table II, from which it is easily understood that the dominant configuration contributing to the longest wavelength $\pi-\pi^*$ band is the HOMO$\rightarrow$LUMO transition. Together with the experimental data shown in Figs. 2 and 6, this indicates that the $\pi-\pi^*$ bands of azobenzenes should be well described by the $F$ and $R$ substituent constants. The result is illustrated in Fig. 7. The correlation seems to be quite good. In addition, a plot of $(E_{1/2}^{ox} - E_{1/2}^{red})$ vs. $1E_{\text{UV}}^{\text{uv}}$ was prepared using the data in Tables II and III for the azobenzenes; the result is as follows:\(27\)\( (E_{1/2}^{ox} - E_{1/2}^{red}) = 0.820 \times E_{\text{UV}}^{\text{uv}} - 0.0709 \) with $n = 7, r = 0.956, s = 0.0992$. The linearity seems to be satisfactory. Based on all the above results and discussions, we may finally say that the $n-\pi^*$ band as well as the longest-wavelength $\pi-\pi^*$ band of conjugated systems such as azobenzenes can be well expressed by means of Swain and Lupton's $F$ and $R$ substituent constants.

References and Notes

1) Presented at the Symposium on Structure Chemistry and the Electronic State of Molecules (Sendai, September 1983).
3) Present address: Chemical Development Laboratories, Central Research Division, Takeda Chemical Industries, Ltd., 17-85, Jusohonmacchi 2-chome, Yodogawa-ku, Osaka 532, Japan.
4) See reference 2 and the other papers cited therein.
7) Successful experimental and theoretical checks of Eq. 2 were reported by us\textsuperscript{80} and other workers.\textsuperscript{81}


14) C. J. Brown, \textit{Acta Cryst.}, \textbf{21}, 146 (1966). Although the molecular dimensions determined by the X-ray crystal analysis are somewhat different from those of the free molecule, the difference seems not to be large enough to affect the discussions in this paper. This is because the same dimensions were adopted for the azobenzene skeleton throughout all the substituents, and only the relative effect of the substituents on the electronic states of azobenzenes is discussed here at the CNDO/S calculation level.


17) a) When an MO is written as

\[ \psi_i = \sum_{r=1}^{n} c_{\nu r} \chi_r, \]

where \( \chi_r \) is the \( r \)-th atomic orbital, the orbital nature of \( \psi_i \) can be expressed by the orbital symmetry under group theory and also by the magnitude and the sign of the coefficient \( c_{\nu r} \) in \( \psi_i \); b) In Eq. 4 such terms as \( ^1\text{Xn}_r \) and \( \epsilon_{\nu_1 r} \) make a singly excited configuration from non-bonding orbital \( n \) to an unoccupied \( \pi^* \) orbital, \( \epsilon_{\nu_1 r} = \int \psi_{\nu_1 r}^* H \psi_{\nu r} d\tau \) (cross interaction energy between \( \psi_{\nu_1 r} \) and \( \psi_{\nu r} \)), and

\[ \langle n\pi^* | G | n\pi^* \rangle = \int \int \psi_{n\pi^*}(1)\psi_{n\pi^*}(2) \frac{e^2}{r_{12}} \psi_{n\pi^*}(1)\psi_{n\pi^*}(2)d\tau_1 d\tau_2 \]

(two-center repulsion integral), respectively. See refs. 12 and 13 for more details.

18) The CI energies calculated from \((E_{n-\pi^* r} - E_{n-\pi^* s})\) (see Eq. 3) are as follows: 1.525, 1.501, 1.384, 1.538, 1.511, and 1.416 eV for the substituents H (azobenzene), 4-CH\(_3\), 4-Cl, 4-OH, 4-NH\(_2\), and 4,4'-Cl\(_2\), respectively. Here the upper limit taken into account for CNDO/S-CI calculation is 10—12 eV. The CI values seem to be of almost the same order of magnitude.

19) A linear relation similar to that in Fig. 2 was also obtained using the data obtained in DMF solvent.

20) It appears likely that the \( E_{1/2}^{\text{red}} \) value given in Table III does not correspond to the \( \epsilon_r \) energy, but to the HOMO-π-orbital energy, since the \( \sigma \)-typecation radical resulting from electron removal from the non-bonding orbital is very unstable at usual temperatures. Many ESR studies of aromatic substances with N-heteroatoms indicate that the very free radicals produced electrochemically are of \( \pi \)-type and not \( \sigma \)-type at room temperature.\textsuperscript{21}


23) Two benzene rings of benzophenone are twisted with respect to each other with a dihedral angle of 56°.\textsuperscript{24}


25) The result in Fig. 7 is for spectral data in CH\(_2\)CN. Although a good correlation similar to that in Fig. 7 was also carried out using the data expressed in terms of weighted-mean wave number\textsuperscript{22} in \( n \)-heptane, the correlation coefficient was a little smaller (\( r = 0.945 \)). The main reason for this is as follows. Since the \( \pi-\pi^* \) type spectra in \( n \)-heptane are quite well resolved due to vibrational structures, and since their spectral patterns differ somewhat in every compound used here, some arbitrary error cannot be avoided in the determination of the absorption maximum\textsuperscript{22} even though the weighted-mean wave number is adopted.


27) Here, the \( E_{1/2}^{0} \) values are in DMF solvent, but the data in CH\(_2\)CN are used for the other constants \( E_{1/2}^{\text{red}} \) and \( E_{\text{UV}}^{\text{abs}} \).