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Mutual Correlation between Nonaqueous Oxidation–Reduction Potentials and Electronic Spectra, and Its Extension to describe the Substituent Effect on Electronic Spectra by Means of Substituent Constants

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In order to confirm and to extend the scope of the equation $(E^{\mathrm{oxd}}_{1/2}-E^{\mathrm{red}}_{1/2})=k_1$[1,3] $E^{\mathrm{UV}}_{\mathrm{ho-lu}}+k_2$, presented previously by us, the polarographic half-wave reduction ($E^{\mathrm{red}}_{1/2}$) and oxidation ($E^{\mathrm{oxd}}_{1/2}$) potentials in nonaqueous media and the electronic spectra of 4,4′-disubstituted stilbenes have been measured and analyzed by means of the equation with reasonable results. The substituent effect on $E^{\mathrm{oxd}}_{1/2}$ and $E^{\mathrm{red}}_{1/2}$ values has been well described by using the Hammett-type substituent constants. This result has been combined with the above equation, and thus a general equation describing the substituent effect on electronic spectra in terms of substituent constants has been derived as $E^{\mathrm{UV}}_{\mathrm{ho-lu}}=aF+bR+c$, F and R being Swain and Lupton's substituent constants. This equation has been experimentally examined using the strong longest-wavelength π-π^* bands of 4,4′-disubstituted stilbenes and azoxybenzenes. The results were quite reasonable. Finally, the description of the substituent effect on electronic spectra in terms of substituent constants is discussed on the basis of molecular orbital theory.

Keywords——nonaqueous polarography; half-wave reduction potential; half wave oxidation potential; substituent effect on electronic spectra; substituent effect on half-wave potential; substituent constant; PPP-SCFMO-CI calculation; CNDO/S; 4,4′-disubstituted stilbene; 4,4′-disubstituted azoxybenzene

So far, substituent effects on polarographic oxidation and reduction potentials have been well studied by applying the Hammett-type substituent constants[1-4] and also molecular orbital (MO) theory.[2,4-6] For the case of substituent effects on electronic spectra, however, various kinds of MO theories have been successfully applied so far,[7-10] but the reports on the systematic application of the Hammett-type substituent constants[11-15] are not so many as compared with those on MO studies. In addition, the theoretical background of the latter studies is not always clear. The mutual relation between polarographic half-wave potentials and electronic spectra has been discussed by several authors,[16-24] and in the foregoing papers we derived the following equation:[16-19]

$$(E^{\mathrm{oxd}}_{1/2}-E^{\mathrm{red}}_{1/2})=k_1E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}}+k_2 \qquad (1)$$

which in general can explain the interrelation between the half- wave potentials and electronic spectra. The value $E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}}$ corresponds to the singlet or triplet absorption band derived mainly from the HOMO→LUMO transition. In order to confirm and to develop this relation we have studied in this work the substituent effect on nonaqueous polarographic half-wave reduction ($E^{\text{red}}_{1/2}$) and oxidation ($E^{\text{oxd}}_{1/2}$) potentials and electronic spectra of 4,4′-disubstituted stilbenes and 4,4′-disubstituted azoxybenzenes, which seemed suitable for the present study. The extension and modification of Eq. 1 may also lead to equations which describe the substituent effect on the electronic spectra in terms of the Hammett-type substituent constants, and should provide a reasonable theoretical basis for further work. Here we will discuss these problems in detail from the experimental and theoretical viewpoints.

Experimental

Polarographic and Spectral Measurements——The direct current (DC) polarograms were measured with a Yanagimoto polarograph, Model P-1000 (three-electrode system), a saturated calomel electrode (SCE) being used as the reference electrode. The capillary constants used for the dropping mercury electrode to yield the $E^{\text{red}}_{1/2}$ are: $m=1.355$ mg/s, $t=5.82$ s, and $h=70$ cm in distilled water at open circuit. Alternatively the $E^{\text{oxd}}_{1/2}$ values were obtained using a rotating platinum electrode (600 rpm), which has a platinum rod, 1 mm in diameter, sealed in a soft glass tube with a diameter of ~6 mm.[19] Just before the use of this electrode, we polished the plane head of the rotating platinum electrode with a polishing powder commercially available from the USA as Royal Diamond Compound. All the experiments were carried out at 25±0.1 °C in *N, N*-dimethylformamide (DMF) or CH_3CN containing 0.1 mol dm^{-3} tetrapropylammonium perchlorate (TPAP). The methods used in the purification of DMF, CH_3CN, and TPAP were the same as reported previously.[16-19]

The absorption spectra were recorded in the usual manner with a Hitachi spectrophotometer, Model 323, at room temperature. The organic solvents used were *n*-heptane, CH_3CN, and CH_3OH, all of which were of spectrograde purity. They were dried sufficiently over CaH_2, and then carefully rectified.

Samples——The substances used in this report are 4,4′-disubstituted stilbenes and 4,4′-disubstituted azoxybenzenes. The former substances were synthesized and purified according to the literature,[25-34] but all of the data on the latter products are cited from our foregoing paper.[16] The stilbene derivatives used are listed in the Table I along with the methods of synthesis and purification. The structure and purity of the samples were checked by means of thin-layer chromatography (TLC), infrared (IR), ultraviolet (UV), and elemental analyses. A good agreement was obtained between the calculated and the experimental values in the elemental analyses. The structure of the stilbenes synthesized here and the azoxybenzenes reported before[16] are well known to be the *trans*-in-plane form, just like (I) and (II), where the coordinates employed for MO calculation are given.

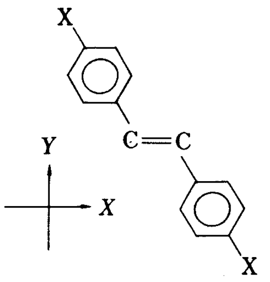
TABLE I. Substituted Stilbenes investigated, with the Methods of Synthesis and Purification and Melting Points

Substituent	mp[a] (°C)	Synthesis[b]	Purification[c]
H(stilbene)	124.3—125.0(124)		R
4,4′-$(CH_3)_2$	179.0—180.0(177—178)[25]	25	R
4,4′-Cl_2	172.0(172)[33]	26	R
4,4′-Br_2	210.5—211.0(210—211)[33]	26	R
4,4′-$(OCH_3)_2$	211.0—212.0(211)[34]		R
4,4′-$(NH_2)_2$	228.0—229.0(227—228)[27]	27	R
4,4′-$[N(CH_3)_2]_2$	254.0—255.0(253—254)[28]	28	R
4,4′-$(COOCH_3)_2$	228.0—229.0(227—228)[29]	29	TR
4,4′-$(COCH_3)_2$	212.5—213.0(210—211)[30]	30	R
4,4′-$(CN)_2$	278.0—280.0(275—280)[31]	31	SR
4,4′-$(NO_2)_2$	284.0—287.0(280—285)[32]	32	R

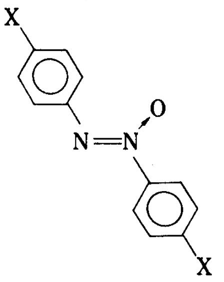
a) The melting points are uncorrected. The values in parentheses were taken from the references given in the text.

b) The compounds were synthesized according to the references given in the text. The others were purchased from Wako Pure Chemical Industries, Ltd. and Aldrich Chemical Co.

c) R: recrystallized from ethanol, except for 4,4′-$[N(CH_3)_2]_2$, 4,4′-$(COOCH_3)_2$ and 4,4′-$(NO_2)_2$, where benzene, ethanol (1)-chloroform (1) mixture, and acetic acid were used as the solvents, respectively.
TR: purified by preparative thin-layer chromatography (PTLC) and recrystallized from nitrobenzene.
SR: purified by repeated sublimation and recrystallized from nitrobenzene.



[I]



[II]

Calculation of Electronic Spectra and Electronic States——In order to interpret the electronic spectra and their correlation with $E_{1/2}^{\mathrm{red}}$, $E_{1/2}^{\mathrm{oxd}}$, and the Hammett-type substituent constants, the calculations of the electronic spectra and electronic states of stilbenes have been made using the PPP-SCFMO-CI and CNDO/S methods.[35,36] The substituents employed in the PPP calculations are the CH_3, Cl, $OCH_3(OH)$, NH_2, $N(CH_3)_2$, $COCH_3$, CN, and NO_2 groups. In the case of PPP calculation, valence state ionization potential (I_P) and electron affinity (E_A), and core resonance energy ($\beta_{XY}^{\mathrm{core}}$) for π-electrons were taken from our previous papers[16,35,37-39] in which the details of these evaluations are given together with the dimensions pertinent to the substituents. The values (eV) for I_P and E_A are (in this order): 25.07, 13.80 for Cl; 32.90, 10.00 for OH; 27.30, 9.30 for NH_2; 25.46, 8.11 for $N(CH_3)_2$; 17.28, 2.01 for O in $CO{\cdot}CH_3$; 14.47, 1.21 for N in CN; 11.24, 0.68 for C in CN; 17.58, 2.62 for O in NO_2; 28.81, 12.21 for N in NO_2. The values of $\beta_{XY}^{\mathrm{core}}$ (eV) and the X-Y distance (Å) are (in this order): 0.948, 1.73 for C-Cl; 1.00, 1.356 for C-OH; 1.896, 1.431 for C-NH_2 ; 2.43, 1.386[40] for C-$N(CH_3)_2$; 2.29, 1.43 for C-$CO{\cdot}CH_3$; 3.00, 1.22 for $O{=}C(CH_3)$; 2.216, 1.455 for C-CN; 3.500, 1.159 for C≡N; 2.00, 1.472 for C-NO_2; 3.00, 1.185 for N=O in NO_2. The hyperconjugation effect of CH_3 was taken into account by decreasing the I_p value of the atom bonded to the CH_3 group by 1 eV.[37,41] A regular hexagon with 1.395 Å dimension was assumed for a benzene ring, the π-electrons in which have the I_p and E_A values of 11.22 eV and 0.62 eV, respectively.[35] The $\beta_{CC}^{\mathrm{core}}$ is 2.37 eV[35] except for the carbon atoms of the bridge part in stilbene. The values for the latter are 2.230 eV and 2.570 eV for the bonds (C_1-C_7)=($C_{1'}$-C_8) and C_7-C_8 in [I], respectively.[42] The bond lengths 1.45 Å for C_1-C_7 and 1.33 Å for C_7-C_8 were adopted.[43] All the bond angles were taken as 120° (sp^2 hybridization) for convenience.

The parameters necessary for CNDO/S calculations were taken mainly from the papers by Jaffé and his colleague.[36,44] The values of Slater exponent (μ), bonding parameter ($-\beta_X^0$), one-center repulsion integral (γ_{XX}), ($I_p^s+E_A^s$), and ($I_p^p+E_A^p$) are (in this order) as follows: 1.2, 12.0, 12.85, 14.35, 0 for H; 1.625, 17.5, 10.93, 29.92, 11.61 for C; 1.95, 26.0, 13.10, 40.98, 16.96 for N; 2.275, 30.0,[45] 15.27, 54.51, 21.93 for O; 2.033, 15.0, 11.30, 35.0, 18.76 for Cl. The calculation was done on all the substituents except for CN and $N(CH_3)_2$ groups. The N atom in the NH_2 group was put at the 0.204 Å out-of-plane position[40] from the plane connecting the two NH_2 group hydrogen atoms and the benzene ring carbon atom which bonds to the NH_2 group. The angles of ∠HNH and the two ∠CNH's around the NH_2 group are all 115°.[40]

Two-center repulsion integrals were evaluated using Nishimoto—Mataga's equation[46] throughout the PPP and CNDO/S calculations. In the UV spectral calculation, one-electron transitions alone were taken into account. All the calculations were carried out with a FACOM M-200 computer in the Nagoya University Computation Center.

Results and Discussion

Nonaqueous Polarograms and Half-wave Reduction and Oxidation Potentials

The reduction polarograms were recorded in DMF and CH_3CN with a dropping mercury electrode. All the compounds exhibitd two waves in DMF, since the polarograms can be recorded toward more negative potentials in DMF than in CH_3CN. The first wave is clearly due to the anion radical formation as verified by a cyclic voltammogram typical of a redox couple.[47] Also, experiments on the mercury pressure effect, temperature effect, and concentration dependence showed that the first wave is diffusion-controlled. In addition, the so-called log plot indicated the first wave to be a one-electron reduction process. As an example, the reduction polarogram and CV curve of 4,4'- dimethoxystilbene are illustrated in Fig. 1.

The $E_{1/2}^{\mathrm{red}}$ values measured here are listed in Table II.[48] It should be noted that the $E_{1/2}^{\mathrm{red}}$ values obtained in CH_3CN are more negative than in DMF by about 30—40 mV, except for some substituents such as NO_2, NH_2, and $N(CH_3)_2$.

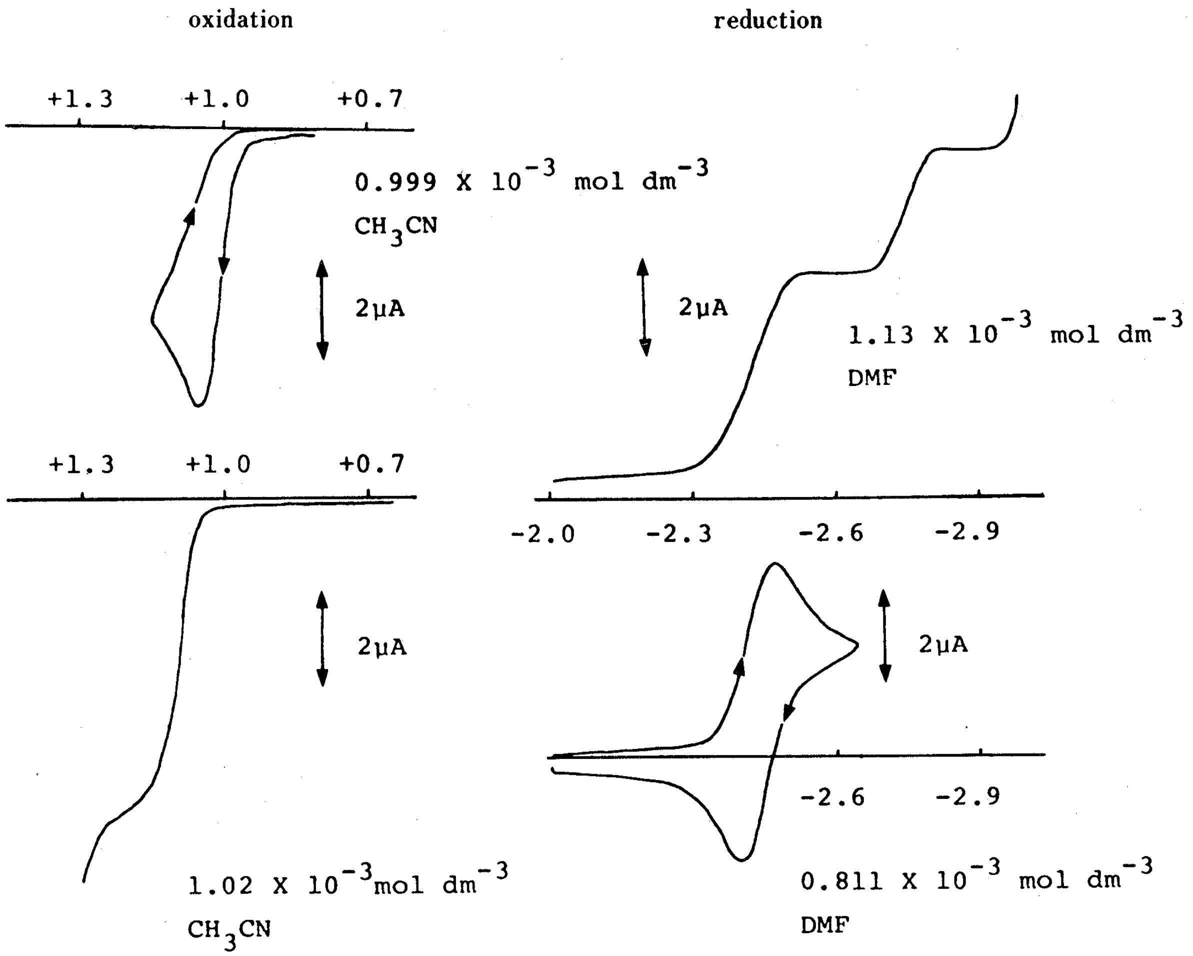


Fig. 1. Reduction Polarogram in DMF and Oxidation Voltammogram in CH_3CN of 4,4'-Dimethoxystilbene with the Cyclic Voltammograms (0.5 V/s) for the First Wave

For details, see the text.

TABLE II. Half-wave Reduction and Oxidation Potentials and Substituent Constants on 4,4'-Disubstituted Stilbenes

Substituent	$E_{1/2}^{red}$ (V)[a]		$E_{1/2}^{oxd}$ (V)[a]	Substituent constant[c]			
	CH_3CN[b,e]	DMF[b,e]	CH_3CN[b]	$\sigma_p(\sigma^-)$[d]	$\sigma^+(\sigma_p)$[f]	F	R
Stilbene	−2.240	−2.200	1.476	0.00	0.00	0.00	0.00
4,4'-$(CH_3)_2$	−2.341	−2.315	1.225	−0.170	−0.311	−0.04	−0.13
4,4'-Cl_2	−1.962	−1.933	1.547	0.227	0.114	0.41	−0.15
4,4'-Br_2	−1.846	−1.810	1.605	0.232	0.150	0.44	−0.17
4,4'-$(OCH_3)_2$	−2.436	−2.408	0.996	−0.268	−0.778	0.26	−0.51
4,4'-$(NH_2)_2$	−2.588	−2.635	0.396	−0.660	−1.36	0.02	−0.68
4,4'-$[N(CH_3)_2]_2$	−2.530	−2.530	0.420	−0.83	−1.78	0.10	−0.92
4,4'-$(COOCH_3)_2$	−1.619	−1.583	1.793	(0.70)	(0.45)	0.33	0.15
4,4'-$(COCH_3)_2$	−1.555	−1.517	1.743	(0.86)	(0.50)	0.32	0.20
4,4'-$(CN)_2$	−1.520	−1.495	1.825	(0.96)	(0.660)	0.51	0.19
4,4'-$(NO_2)_2$	−0.953	−0.971	1.940	(1.24)	(0.778)	0.67	0.16

a) Data *vs.* S.C.E.
b) Measured in the solvents designated.
c) Taken from refs. 54, 55, 61, 62, and 63.
d) The values in parentheses are σ^-.
e) The first reduction potential alone is shown in this table (see the text).
f) The values in parentheses are the usual σ_p ones.

Next, the $E^{\mathrm{oxd}}_{1/2}$ values were determined from the oxidation voltammogram obtained in CH_3CN using a rotating platinum electrode. Typical voltammograms are illustrated in Fig. 1 for 4,4′-dimethoxystilbene, and we see that the cyclic voltammogram pertinent to the oxidation wave does not show a backward sweep wave at the rate of 0.5 V/s, indicating an overall irreversible system at this rate. The oxidation voltammograms of the other substituents were quite similar to those shown in Fig. 1, the Lingane constant (μA/mol m^{-3}) being about 6—9. Assuming that the potential $E^{\mathrm{oxd}}_{1/2}$ is mainly controlled at the step of cation radical formation caused by a one-electron oxidation,[49] these values were employed in the discussions in this paper (*vide infra*: see also reference 47), and are listed in Table II.

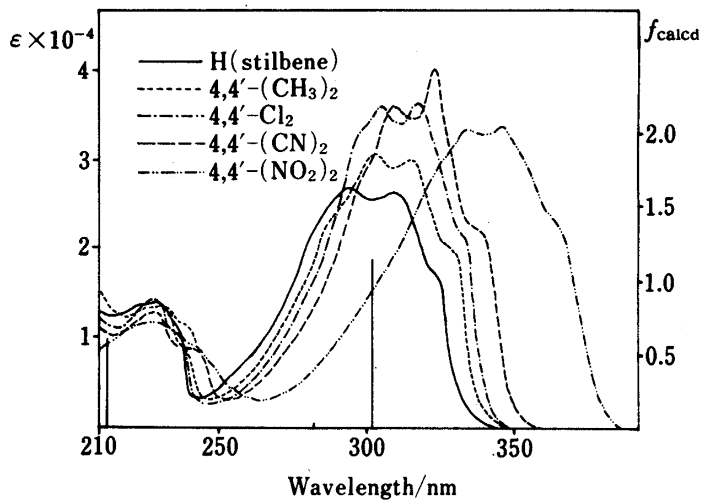


Fig. 2. Electronic Spectra of 4,4′-Disubstituted Stilbenes in *n*-Heptane

The intensity (left ordinate scale) for CN and NO_2 substituents is less accurate than that for the other substituents because of the low solubility. The stick diagram indicates the CNDO/S calculation results for stilbene. See the right ordinate for the oscillator strength.

Electronic Spectra of Substituted Stilbenes and Azoxybenzenes

The UV spectra of some of the 4,4′-disubstituted stilbenes are shown in Fig. 2, where we see that the strong π-π^* band of stilbene appearing in the longer-wavelength region shows a red shift with increasing substituent effect, though the spectral pattern are almost the same.

The electronic structures and spectra of stilbenes were hitherto studied mainly by Suzuki,[50] Jaffé,[8] and Nagakura[51,52] *et al.* in relation to the steric effect on the spectra and also the photochemical *trans–cis* isomerization reaction. The above calculaions were mainly made at the HMO level.[8,50] Here, the characters of the excited states of 4,4′-disubstituted stilbenes were newly examined from the viewpoint of PPP-SCFMO-CI and CNDO/S calcula-

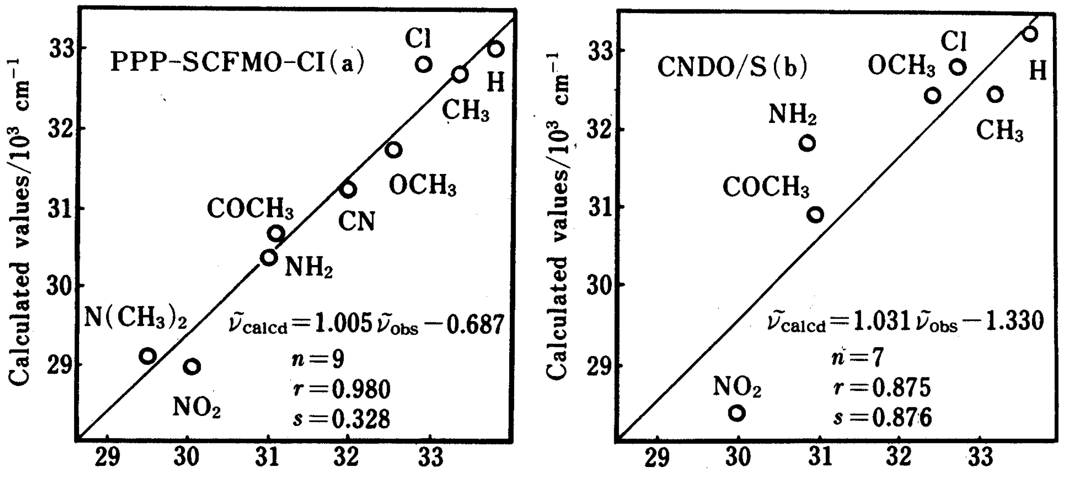


Fig. 3. The Correlation of Observed and Calculated Values of the UV Spectra of 4,4′-Disubstituted Stilbenes

The results obtained by the PPP-SCFMO-CI and CNDO/S methods are shown in (a) and (b), respectively.

TABLE III. Calculated Values of the Longest-wavelength π-π^* Transition Energies Oscillator Strengths, Symmetries under C_{2h}, and Main singly Excited Configurations of 4,4′-Disubstituted Stilbenes, with the Experimental Data

Substituent	$\tilde{\nu}_{obs}$[b] (10^3 cm^{-1})	ε_{max}^{obs}[b]	PPP SCFMO-CI[a]				CNOD/S[a]			
			$\tilde{\nu}_{calcd}$ (10^3 cm^{-1})	f_{calcd}	Sym	Main configuration (%)[d]	$\tilde{\nu}_{calcd}$ (10^3 cm^{-1})	f_{calcd}	Sym	Main configuration (%)[d,e]
H(stilbene)	32.55	26700	33.01	1.245	^1B_u	98.2(7/8)	33.19	1.168	^1B_u	97.3(34/35), 1.1(31/38)
			36.63	0.000	^1B_u	40.6(7/9), 40.6(6/8)	35.73	0.019	^1B_u	50.6(34/36), 25.3(33/35), 11.2(32/38)
	43.76	15200	46.95	0.816	^1B_u	48.6(6/8), 48.6(7/9)	47.11	0.620	^1B_u	51.8(33/35), 38.9(34/36), 3.1(34/39)
4,4′-$(CH_3)_2$	31.83	30300	32.70	1.253	^1B_u	98.1(7/8)	32.40	1.202	^1B_u	96.7(40/41), 1.3(39/44)
4,4′-Cl_2	31.55	34800	32.84	1.267	^1B_u	98.2(9/10), 1.2(6/13)	32.74	1.511	^1B_u	97.1(40/41), 1.3(37/44)
4,4′-Br_2	31.38	39600								
4,4′-$(OCH_3)_2$	30.82	35300	31.74	1.312	^1B_u	96.6(9/10), 2.9(8/13)	32.39[g]	1.503[g]	^1B_u	96.7(40/41), 1.4(39/44)
4,4′-$(NH_2)_2$	29.41	29000[c]	30.36	1.471	^1B_u	96.2(9/10), 2.5(8/13)	31.80	1.238	^1B_u	96.0(40/41), 1.8(39/44)
4,4′-$[N(CH_3)_2]_2$	27.89	>30000[c]	29.12	1.542	^1B_u	95.2(9/10), 2.9(8/13)				
4,4′-$(COOCH_3)_2$	30.53	>30000								
4,4′-$(COCH_3)_2$							28.05[f]	0.000	^1A_u	32.8(45/52), 26.1(46/51), 19.1(46/55), 10.8(45/56)
							28.29[f]	0.000	^1B_g	33.5(46/52), 25.7(45/51), 18.9(45/55), 11.2(46/56)
	29.93	>30000	30.69	1.591	^1B_u	96.4(9/10), 2.3(6/11)	30.92	1.601	^1B_u	95.5(50/51), 2.6(47/52)
			35.55	0.025	^1B_u	50.3(8/10), 28.3(9/12), 13.4(7/11)	35.28	0.016	^1B_u	38.1(48/51), 35.8(50/53), 13.5(49/52), 9.3(47/54)
	43.48	>8000	45.86	0.762	^1B_u	54.0(9/12), 34.9(8/10), 5.3(9/14)	45.16	0.376	^1B_u	39.7(50/53), 25.2(50/55), 24.9(48/51), 5.1(47/52)
4,4′-$(CN)_2$	30.72	45000[c]	31.24	1.577	^1B_u	97.0(9/10), 2.0(6/11)				
4,4′-$(NO_2)_2$							24.60[f]	0.000	^1A_u	37.0(38/52), 35.9(39/51) 10.8(39/53), 9.7(40/52)
							24.61[f]	0.000	^1B_g	42.9(39/52), 30.8(38/51), 9.2(38/53)
							25.40[f]	0.000	^1B_g	40.2(41/52), 29.7(40/51), 8.7(40/53)
							25.44[f]	0.000	^1A_u	35.8(40/52), 34.1(41/51), 9.7(41/53)
	29.03	33800[c]	28.97	1.462	^1B_u	91.9(11/12), 5.8(8/13)	28.31	1.782	^1B_u	90.0(50/51), 7.2(47/52)
			35.21	0.100	^1B_u	60.6(10/12), 28.9(9/13), 9.6(11/15)	33.75	0.042	^1B_u	49.0(49/51), 23.1(48/52), 17.0(50/54), 5.7(47/55)
			39.60	0.056	^1B_u	79.7(11/14), 15.6(8/13)	38.47	0.105	^1B_u	84.8(50/53), 9.7(47/52), 1.7(47/56)
			43.28	0.040	^1B_u	39.5(11/15), 30.2(10/14), 27.2(9/13)	40.79	0.069	^1B_u	34.2(50/54), 23.2(49/53), 7.1(48/56), 4.3(47/55)
	44.44	17500[c]	46.07	0.061	^1B_u	36.9(11/15), 21.0(10/12), 12.9(9/13)	46.14	0.059	^1B_u	21.6(49/51), 21.5(50/54), 21.1(49/53), 16.3(48/52)
			46.94	0.163	^1B_u	50.3(8/13) ,25.4(5/12), 16.6(11/14)	47.67	0.102	^1B_u	65.3(47/52), 12.2(42/51), 9.3(50/53), 8.7(50/51)

[a] See the text for details of the calculation methods.
[b] These are the values at the maximum intensity in *n*-heptane.
[c] The values in CH_3CN.
[d] For example, (7/8) means a singly excited configuration from ψ_7 to ψ_8.
[e] MO'S entering into main configurations are π-orbitals unless otherwise noted.
[f] These are σ-π transitions with n-π^* characters. The filled MO'S corresponding to these transitions are σ-orbitals localized mainly on the oxygen atoms.
[g] Calculated values for 4,4′-dihydroxystilbene.

tions, especially to clarify the nature of the longest-wavelength strong π-π^* band. The calculation results for various 4,4′-disubstituted stilbenes are collected in Table III, from which we can understand that the above-mentioned π-π^* band is largely derived from the HOMO →LUMO transition in all these substances. The orbital characters of HOMO and LUMO under CNDO/S were the same as those obtained by PPP-SCFMO, as were the π-orbitals. In addition the accuracy of the theoretical calculation results is quite good. Figure 3 shows a linear plot of experimental values against theoretical ones for the longest-wavelength π-π^* bands, whose maximum values were taken into consideration.[53] The linearity seems to be good, particularly for the case of PPP-SCFMO-CI calculation. Electronic spectra of 4,4′-disubstituted azoxybenzenes and their interpretation were reported in the foregoing paper.[16] The character of their longest-wavelength π-π^* band is almost the same as that of the 4,4′-disubstituted stilbenes discussed hitherto and is largely derived from the HOMO→ LUMO π-π^* transition.[16]

Correlation between Electronic Spectra and Non-aqueous Oxidation–Reduction Potentials

As was mentioned in the introduction, Eq. 1 applied well to a series of compounds, the electronic spectra of which have the same character and $E^{UV}_{ho\text{-}lu}$ nature (*vide supra*). Examination of the electronic spectra of stilbenes, discussed in the foregoing section, indicated that their longest-wavelength π-π^* bands should satisfy Eq. 1, and the linearity of the relation is actually shown in Fig. 4 using the data listed in Tables II and III. The linearity seems to be quite good. The equation obtained is $(E^{oxd}_{1/2}-E^{red}_{1/2})=1.532\,{}^1E^{UV}_{ho\text{-}lu}-2.469$ with $n=11$, s (standard deviation)$=0.0906$, r (correlation coefficient)$=0.950$. A similar result was also obtained in the case of 4,4′-disubstituted azoxybenzens.[16] However, the following points should be noted. Our calculations indicated that the longest-wavelength π-π^* band of 4,4′-disubstituted stilbenes and azoxybenzenes is divided into two bands in the case of 3,3′-disubstituents such as NH_2, NO_2, *etc*., the latter bands being mainly composed of several configuration interaction terms. Thus, application of Eq. 1 to these bands seems inappropriate. Also, the slope (1.532) of the above equation is rather large compared with the theoretical value of 1.[16-19] This would be due to the fact that the nature of the stilbenes used varies from nonpolar (stilbene, *etc.*) to very polar (NO_2 or NH_2 substituent), so that the solvent effect on $E^{oxd}_{1/2}$, $E^{red}_{1/2}$, and UV spectra may undergo a systematic change. This may cause the deviation from the theoretical slope value.

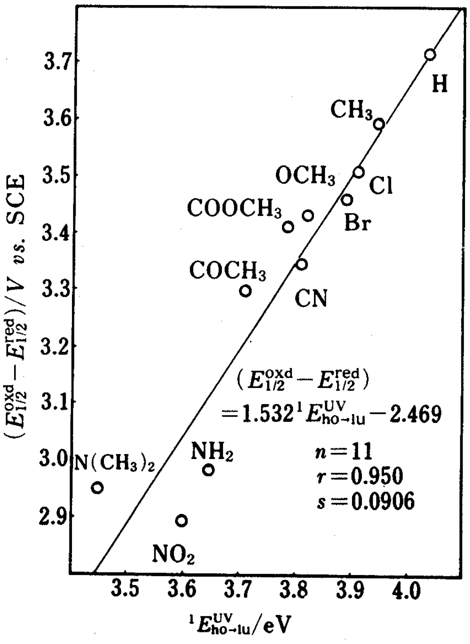


Fig. 4. The Relationship between $(E^{oxd}_{1/2}-E^{red}_{1/2})$ Values in CH_3CN and the First Strong π-π^* Band Energies for 4,4′-Disubstituted Stilbenes

See also Table II.

Substituent Effect on the $E^{oxd}_{1/2}$ and $E^{red}_{1/2}$ Values

The half-wave potential $E_{1/2}$ is expressed by $-\Delta F/F$ for a one-electron reversible system, F being the Faraday constant. Since the term ΔF is known to be correlated with the Hammett-type substituent constant, Eqs. 2 and 3 can be written, as reported in the literature.[1]

$$E^{oxd}_{1/2}=\rho_1\sigma_1+C_1 \qquad (2)$$

$$E^{red}_{1/2}=\rho_2\sigma_2+C_2 \qquad (3)$$

Study of the electrode reaction mechanism indicated that the σ^+ values are the best for σ_1 except in the cases of p-NO_2, p-CN, *etc*., where normal σ values are preferred, and that normal σ values are the most suitable as σ_2, except for strong electron-drawing groups at the *para*-position, for which σ^- values are the best.[2-4,19] These variations are due to the fact that the electron-donating ability or electron-accepting ability of substituents becomes large in the transition state of the electrode reaction of the compounds having σ^+ substituents for $E^{oxd}_{1/2}$ or σ^- substituents for $E^{red}_{1/2}$, respectively. The relations of Eqs. 2 and 3 are illustrated in Figs. 5 and 6; the linearity seems to be quite good, particularly in the case of Eq. 2. Results similar to the above were also reported in the previous paper for 4,4′-disubstituted azoxybenzenes.[16] These linear relations make it easy to predict the $E^{red}_{1/2}$ and $E^{oxd}_{1/2}$ values in a series of substances.

Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants

The combination of Eqs. 1, 2, and 3 would make it possible to derive a basis for the applicaion of substituent constants to explain the substituent effect on electronic spectra. As

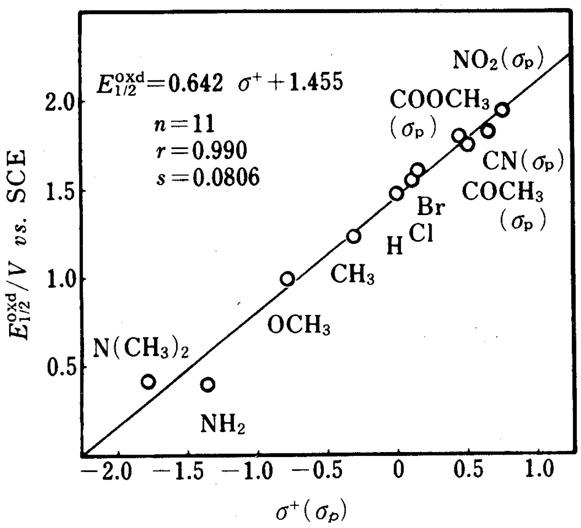


Fig. 5. Linear Relation between the $\sigma^+(\sigma_p)$ Values and the First $E^{oxd}_{1/2}$ Values in CH_3CN for 4,4′-Disubstituted Stildenes

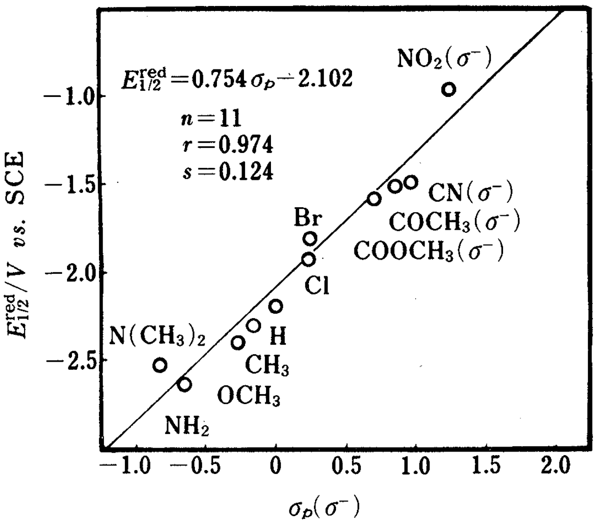


Fig. 6. Linear Relation between the $\sigma_p(\sigma^-)$ Values and the First $E^{red}_{1/2}$ Values in DMF for 4,4′-Disubstituted Stilbenes

mentioned in the preceding section, the σ_1 and σ_2 values are, in general, not equal. However, for substituents having equal or nearly equal σ_1 and σ_2 values we obtain

$$(E^{oxd}_{1/2}-E^{red}_{1/2})=\rho_3\sigma+C_3 \qquad (4)$$

where $\rho_3=(\rho_1-\rho_2)$ and $C_3=(C_1-C_2)$ are new constants. The combination of Eqs. 1 and 4, then, leads to

$$E^{UV}_{ho\rightarrow lu}=\rho_3'\sigma+C_3' \qquad (5)$$

Here ρ_3' and C_3' are also new constants. This equation means that UV spectra of the same character and derived mainly from HOMO→LUMO transition can correlate with σ under the above conditions. In general, however, σ_1 and σ_2 are not equal, as was discussed previously, so that Eq. 5 is not valid for all substituents. The substituent constants F (field effect) and R (resonance effect) derived by Swain and Lupton may be useful for the present purpose,[54,55] because the various kinds of σ values can be written as Eq. 6 using F and R values regardless of the characteristics of each σ value.

$$\sigma=fF+rR+C \qquad (6)$$

Moreover, as the F and R values are independent of the substituent position, Eqs. 7 and 8 are obtained.

$$\sigma_1=f_1F+r_1R+C_4 \qquad (7)$$

$$\sigma_2=f_2F+r_2R+C_5 \qquad (8)$$

From Eqs. 1, 2, 3, 7, and 8, we obtain Eq. 9,

$$(E^{oxd}_{1/2}-E^{red}_{1/2})=\alpha F+\beta R+\gamma \qquad (9)$$

in which α, β, and γ represent $(\rho_1f_1-\rho_2f_2)$, $(\rho_1r_1-\rho_2r_2)$, and $(C_1-C_2+\rho_1C_4-\rho_2C_5)$, respectively, and these terms would be constant for each series of substances studied. Thus, Eq. 10 was obtained from a combination of Eqs. 1 and 9.

$$E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}} = aF + bR + c \qquad (10)$$

The terms a, b, and c correspond to the values of (α/k_1), (β/k_1),and $(\gamma - k_2)/k_1$, respectively, which are constant independent of the substituents. Also, Eq. 10 can be employed instead of Eq. 5, because the σ value in Eq. 5 can be replaced by Eq. 6, so that Eq. 5 is easily rewritten in the form of Eq. 10. Thus, we may say that Eq. 10 is a general equation applicable to all cases of substituent effect on electronic spectra. Eq. 10 means that the electronic absorption bands with the same characteristics, derived mainly from the HOMO→LUMO transition in the series of compounds studied, are correlated with the substituent constants F and R. Note that Eqs. 1, 7, and 8 should be satisfied to derive Eq. 10. As mentioned hitherto, different σ values from normal are employed in Eqs. 2 and 3 for some substituents such as strong electron-withdrawing or electron-donating groups, and they may behave in different ways in Eqs. 7 and 8, *i.e.*, with different coefficients of F and R. These circumstances raise difficulties in applying Eq. 10 to overall substituents including the above exceptional ones. Separate application of Eq. 10 is necessary for those substituents. Substituent effect on electronic spectra has been extensively studied from the viewpoint of molecular orbital theory, and studies of this problem by applying the Hammett-type substituent constants were mainly made by Rao, Doub and Vandenbelt, Exner, and Hancock *et al.* before 1962.[11-15] At that time, however, the interpretation of electronic spectra of aromatic substances at the theoretical level of SCFMO-CI calculation was poorly understood, and the character of absorption bands which various authors utilized to study the substituent effect was not always the same.[56] Thus, it may be said that a clear theoretical background for applying the substituent constants in order to explain the substituent effect on electronic spectra has only now been provided, based on the above-mentioned treatment.

In order to verify Eq. 10, spectral and polarographic data for 4,4′-disubstituted [I] and [II] were used here. The data are listed in Tables II and III and in a foregoing paper[16] for the former and the latter, respectively. Discussions here and in a previous paper[16] lead to the conclusion that the spectral data for the above compounds can be applied to check Eq.

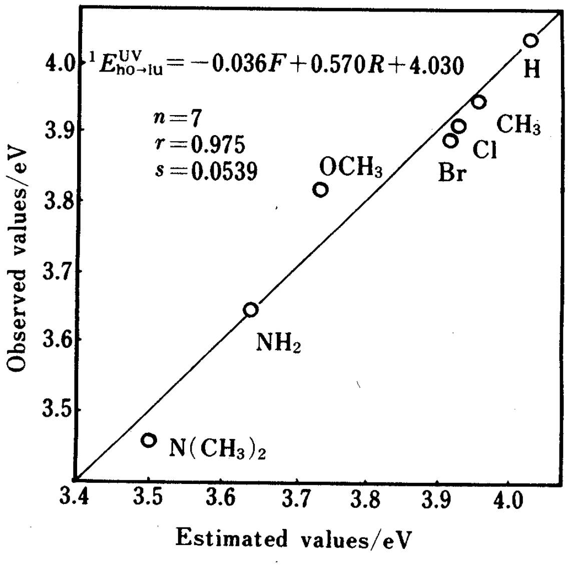


Fig. 7. Multiple Correlation of the First Strong π-π^* Band Energies and the Substituent Constants F and R for 4,4′-Disubstituted Stilbenes having the Groups shown in the Figure

See the text for details.

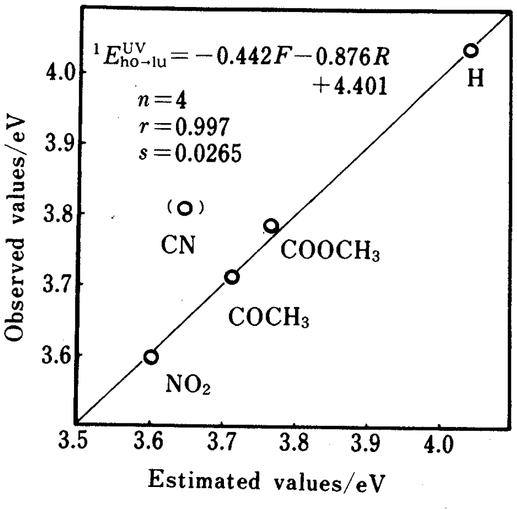


Fig. 8. Multiple Correlation of the First Strong π-π^* Band Energies and the Substituent Constants F and R for 4,4′-Disubstituted Stilbenes having the Groups shown in the Figure

See the text for details.

10. The results are illustrated in Figs. 7, 8, and 9 for 4,4′-disubstituted stilbenes and azoxybenzenes. These figures and the results of multiregression analyses based on Eq. 10, shown in the figures, indicate the agreement between observed and calculated values is quite good. Note here that the separate applicaion of Eq. 10 to such substituents as NO_2, $COCH_3$, $COOCH_3$, *etc.* was quite successful (see Fig.8), in accord with the foregoing discussions. However, the CN group is an exceptional substituent. Experimental studies and also ASMO-CI theory confirmed that the red shift effect of the C≡N group on the *p*-band of benzene UV spectra is not as strong[59] as is expected from the Hammett-type substituent constants derived from the ground electronic state. This seems to be the main reason why the CN group falls way off the straight line in Fig. 8.

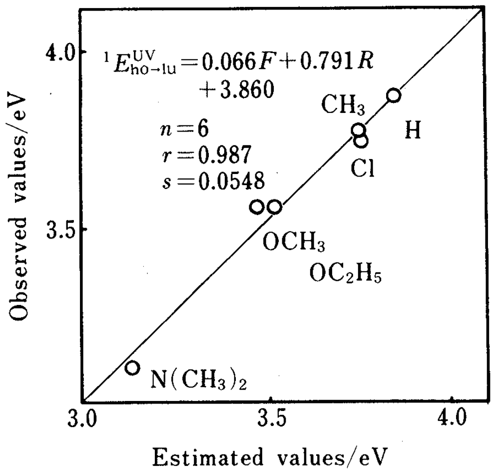


Fig. 9. Multiple Correlation of the First Strong π–π* Band Energies and the Substituent Constants *F* and *R* for 4,4′-Disubstituted Azoxybenzenes

See the text for details.

Finally, we conclude that electronic bands such as ${}^1E^{UV}_{ho\text{-}lu}$ or ${}^3E^{UV}_{ho\text{-}lu}$ can be correlated with the substituent constants *F* and *R* when the conditions given by Eqs. 1, 2, 3, 7, and 8 are satisfied. In addition, Eq. 10 can be regarded as a general equation describing the relation of UV spectra to substituent constants.

Appendix

As one approach to determine the number of electrons (n) participating in the polarographic reduction or oxidation wave, the so-called log-plotting method based on Eq. A1 is very popular.[60] Here we have modified this method, so that the estimation of the n values becomes easier compared to the usual method, while the accuracy is not much affected. The modification is as follows.

$$E=E_{1/2}-\frac{0.0591}{n}\log\frac{i}{i_d-i} \qquad \text{(A1)}$$

Here, 0.0591 is equal to 2.303 RT/F at 25°C. Differentiation of Eq. A1 with respect to i leads to Eq. A2.

$$n=-\frac{di}{dE}\cdot\frac{0.0591}{\ln 10}\cdot\frac{i_d}{i(i_d-i)} \qquad \text{(A2)}$$

At the point $i=i_d/2$, that is, at the half-wave potential, the term $i_d/i(i_d-i)$ becomes $4/i_d$, so Eq. A3 is easily obtained from Eq. A2.

$$n=-0.103\cdot\frac{1}{i_d}\cdot\frac{di}{dE} \qquad \text{(A3)}$$

where di/dE is the slope of the tangent at the point of half-wave potential on the current-potential curve. The tangent line should be drawn along the current-potential curve as reasonably as possible, this being illustrated in Fig. A1.

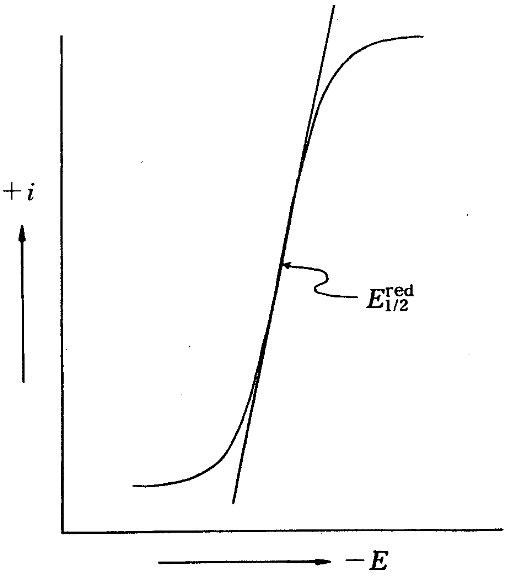


Fig. A1. Schematic Expression for Obtaining di/dE at the Half-wave Potential

See the text for details.

TABLE A-1. The Values of the Number of Electrons (n) participating in the First Reduction Wave of Some 4,4′-Disubstituted Stilbenes in Nonaqueous Solvent.[a] Comparison of the n_1 and n_2 Values evaluated from Eqs. A1 (log-Plotting Method) and A3, respectively

Substituent	n_1	n_2
H(stilbene)	1.028	0.991
4,4′-$(CH_3)_2$	0.907	0.936
4,4′-$(OCH_3)_2$	1.055	1.044
4,4′-$(NH_2)_2$	0.954	0.958
4,4′-$(CN)_2$	0.984	1.009
4,4′-$(NO_2)_2$	1.217	1.268

a) Solvent was DMF for all the samples except 4,4′-$(OCH_3)_2$, for which CH_3CN was used.

The present method based on Eq. A3 was compared with the usual log-plotting method. The results are listed in Table A1 for the stilbenes studied here. The n values determined by the two techniques seem to be in reasonably good agreement.

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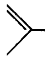
-$N(CH_3)_2$ and -NH_2.

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