

## New description of the substituent effect on electronic spectra by means of substituent constants—VI. Ultraviolet spectra of 4-substituted pyridine *N*-oxides and blue shifted iodine bands of their EDA complexes with iodine\*

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(Received 17 September 1988; in final form 14 March 1989; accepted 15 March 1989)

**Abstract**—Electronic spectra of 4-substituted pyridine *N*-oxides and their EDA complexes with iodine were studied. The substituent effect on the near u.v.  ${}^1A_1$  intramolecular CT bands of the *N*-oxides and on the blue shifted iodine bands caused by CT complex formation are discussed in terms of a general equation, theoretically derived in order to describe the substituent effect on electronic spectra by means of substituent constants. The results are quite successful and supported by semi-empirical SCFMO-CI calculations. Based on the results mentioned above, the character of *n*- $\sigma$  type *N*-oxide—iodine CT complexes is also examined. The complex formation constants (log *K*) and *pK<sub>a</sub>* values of the *N*-oxides correlate especially well, indicating that the CT interaction mechanism cannot be neglected in proton addition reactions such as hydrogen bonding and *pK<sub>a</sub>* values.

### INTRODUCTION

In previous studies [1–5] we have proposed the application of substituent constants of SWAIN *et al.* [6] or SAWADA *et al.* [7] for describing the substituent effect on electronic spectra, since the theoretical treatment of this kind of study has not been previously attempted. Keeping in mind that the substituent effect on electronic ground and excited states is very different [8], we have derived Eqns (1) and (2)

$${}^{1,3}E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}} = aF + bR + c \quad (1)$$

$${}^{1,3}E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}} = \alpha\sigma_i + \beta\sigma_x^+ + \gamma\sigma_x^- + C. \quad (2)$$

Here, *F* and *R* are SWAIN's substituent constants, and SAWADA's constants are given by  $\sigma_i$ ,  $\sigma_x^+$ , and  $\sigma_x^-$ . Singlet or triplet energy contribution mainly from the HOMO  $\rightarrow$  LUMO transition is expressed by  ${}^{1,3}E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}}$ . Based on the theoretical background discussed in the foregoing papers, Eqn (1) would be safely applied to various kinds of electronic transitions, such as  $\pi$ - $\pi^*$  bands, *n*- $\pi^*$  bands, *n*- $\sigma^*$  bands,  $\pi$ - $\pi$  type or *n*- $\sigma$  type charge transfer bands, etc.; however, Eqn (2) is suitable for the electronic spectra of  $\pi$ -electron systems. The derivation of Eqns (1) and (2) was already given in detail in the previous papers [1–5], but it is necessary to point out that the above equations are obtained as an extension of Eqn (3) [9–11],

$$(E_{1/2}^{\text{oxd}} - E_{1/2}^{\text{red}}) = k_1 {}^{1,3}E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}} + k_2 \quad (3)$$

where  $E_{1/2}^{\text{oxd}}$  and  $E_{1/2}^{\text{red}}$  stand for, in principle, the half-wave oxidation and reduction potentials of the cation and anion radical formation in nonaqueous solvents, respectively.

In this paper we report the analysis of substituent effects on the strong near u.v. band of 4-substituted pyridine *N*-oxides by Eqns (1) and (2), because the character of this u.v. band has already been studied experimentally and theoretically [8, 12, 13], indicating that the band has the nature of intramolecular charge transfer (ICT) (see below), so these bands seem to be quite good for testing Eqns (1) and (2). In addition, we will apply Eqn (1) to the blue shifted iodine visible band caused by *n*- $\sigma$  type EDA (electron-donor-acceptor) complex formation of iodine with the above 4-substituted pyridine *N*-oxides. Since the extent of blue shift was hitherto reported to be well correlated with CT complex stability [8, 14], this visible band would be suitable to check the applicability of Eqn (1). Also, this is the first case for testing the equations for spectral change of an electron acceptor itself brought about by CT complex formation.

### EXPERIMENTAL

#### Spectral measurements

All the u.v. spectra of the 4-substituted pyridine *N*-oxides studied were recorded in the usual manner with a Hitachi spectrophotometer, Model 323, at room temperature, 1 cm or 10 cm matched quartz cells being used. Solvents employed were  $\text{CCl}_4$ , *n*-heptane,  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  of spectrograde purity, dried over  $\text{CaH}_2$  and then carefully distilled. Preparation of sample solutions was always carried out in a dry box filled with  $\text{N}_2$  gas, because pyridine *N*-oxides are generally hygroscopic.

Iodine molecular complexes with 4-substituted pyridine *N*-oxides were studied in  $\text{CH}_2\text{Cl}_2$ , their spectral measurements being performed using 1 cm matched quartz cells equipped with stoppers, regulated to  $25 \pm 0.5^\circ\text{C}$  by circulating constant temperature water throughout the cell compartment by the use of a Taiyo thermoleader, Model EZL-80. In order to prevent moisture contamination, the EDA complex solutions were prepared in a dry box, because the side formation of  $\text{I}_3^-$  ion in the complex solution is quite sensitive to moisture, and the strong absorption due to  $\text{I}_3^-$  brings

\*Presented in part at the Symposium of Structure Chemistry and the Electronic State of Molecules, Kanazawa, Japan, October (1987), abstract p. 628.

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about an error in the spectral measurements of EDA complexes.

### Samples

Substances employed here were the 4-substituted pyridine *N*-oxides known in the literature. Pyridine *N*-oxide (PNO) and 4-methylpyridine *N*-oxide (MPNO), commercially available from Tokyo Chemical Industry for PNO and Wako Pure Chemical for MPNO, were purified by a repeated distillation under reduced pressure for PNO, but by vacuum sublimation and then the recrystallization from benzene (m.p. 190°C) for MPNO. 4-Nitropyridine *N*-oxide (NPNO: m.p. 173–175°C) and 4-carboxypyridine *N*-oxide (CBPNO: m.p. 295–298°C) purchased from Tokyo Chemical Industry for NPNO, and Aldrich Chemical for CBPNO, were recrystallized from acetone and dioxane–ethanol mixtures for the former and the latter, respectively. Pyridine *N*-oxides substituted with 4-ethyl (EPNO), 4-*tert*-butyl (TBPNO), 4-acetyl (APNO), and 4-acetylamino (AAPNO) groups were synthesized by the oxidation of the corresponding pyridines with hydrogen peroxide [15]. EPNO was purified by vacuum sublimation and recrystallization from ethylacetate (m.p. 110–112.5°C). Crude TBPNO and APNO were recrystallized from ethylacetate (m.p. 92–94°C for TBPNO, and 144–145°C for APNO). AAPNO was recrystallized from an ethanol–benzene mixture after vacuum sublimation (m.p. 294–296°C). NPNO was used to synthesize pyridine *N*-oxides substituted with 4-chloro (CPNO), 4-bromo (BPNO), 4-methoxy (MOPNO), and 4-ethoxy (EOPNO) groups [15]. The halogenation, employing  $\text{CH}_3\text{COCl}$  and  $\text{CH}_3\text{COBr}$ , was applied to NPNO to derive CPNO and BPNO, respectively, but the reaction of NPNO with sodium methylate or sodium ethylate was used to obtain MOPNO or EOPNO, respectively. CPNO (m.p. 181.5–183°C) and BPNO (m.p. 149°C [dec.]) were repeatedly recrystallized from acetone, alternatively the solvents for recrystallizing MOPNO (m.p. 86–87°C) and EOPNO (m.p. 137–138°C) being ethylacetate and benzene, respectively. 4-Aminopyridine *N*-oxide (AMPNO) was obtained by the catalytic reduction of NPNO with  $\text{H}_2$  in the presence of 5% palladium on carbon [16], and recrystallized from an ethanol–ethylacetate mixture (m.p. 247–248°C). 4-Dimethylaminopyridine *N*-oxide (DAPNO) was prepared by heating the sealed tube containing CPNO and dimethylamine aqueous solution, at 140°C for 18 h [17]. It was recrystallized from ethanol–ethylacetate (m.p. 232–234°C). Pure samples of 4-CN (CNPNO: m.p. 232°C) and 4-COOC<sub>2</sub>H<sub>5</sub> (ECPNO: m.p. 62.5°C) derivatives of pyridine *N*-oxide were kindly supplied by Dr M. YAMAKAWA of the Shionogi Research Laboratory, and used as received.

Iodine commercially available from Wako Pure Chemical was repeatedly sublimed under nitrogen atmosphere, and once again just before use. The purity of all the samples was checked by elemental analysis and such spectral methods as u.v., i.r. and MS.

### Calculation of electronic spectra and electronic states

In order to interpret the electronic spectra and electronic states of 4-substituted pyridine *N*-oxides, semi-empirical PPP-SCFMO-CI and CNDO/S calculations were carried out. In the case of PPP calculations the valence state ionization potential and electron affinity, and the core resonance energy necessary for the calculation were taken from our previous papers [1, 12, 18], in which the details of these evaluations were given, together with the bond length and bond angle for the pyridine *N*-oxide moiety and substituents. Also, such parameter values of CNDO/S calculations as the Slater exponent ( $\mu$ ), bonding constant ( $-\beta_x^0$ ) one-centre repulsion integral ( $\gamma_{xx}$ ), ( $I_p^0 + E_x^0$ ) and ( $I_p^0 + E_x^0$ ) are the same as those used in our foregoing paper [1–5]. The NISHIMOTO–MATAGA (NM) approximation was employed for two-centre repulsion integrals [19]. The PPP calculations were carried out with an NEC PC-9801 personal computer in

our laboratory, but the CNDO/S calculations were done with a FACOM M-382 computer in the Nagoya University Computation Center.

## RESULTS AND DISCUSSION

### Substituent effect on the strong near u.v. band of pyridine *N*-oxide

The electronic structures and electronic spectra of heterocyclic amine *N*-oxides have been extensively studied by us and other workers from theoretical and experimental viewpoints [8, 11–13, 15, 18]. In the case of PNOs the electronic spectra were particularly analysed, indicating that the strong  $\pi$ - $\pi^*$  band of PNO appearing near 280 nm in aprotic solvents has  $^1A_1$  symmetry and has by far the largest contribution of ICT configuration due to an electron transition (HOMO  $\rightarrow$  LUMO transition) from an *N*-oxide group oxygen atom to a ring  $\pi$ -system. In Fig. 1 is illustrated the u.v. spectra of 4-substituted PNOs in  $\text{CH}_3\text{CN}$  (a relatively polar solvent) where we see that the above  $^1A_1$  ICT band of PNO is quite sensitive to the substituents and moves to longer wavelengths. The spectral data in  $\text{CCl}_4$ , *n*-heptane and  $\text{CH}_3\text{CN}$  are compiled in Table 1, in which we have also listed the  $^1A_1$  transition energies calculated by PPP and CNDO/S methods and the contribution of main configuration interaction terms. Both the u.v. calculation results seem to reproduce the substituent effect on the strong  $^1A_1$  band of pyridine *N*-oxide. Also, CI terms are predominantly (more than 90%) localized on  $\pi$ -HOMO ( $b_2$ )  $\rightarrow$   $\pi$ -LUMO ( $b_2$ ) transition.\* The values of  $E_{1/2}^{\text{oxd}}$  and  $E_{1/2}^{\text{red}}$  of 4-substituted PNOs in non-aqueous solvents were previously reported by us [9, 20], so we have examined the linear relation of Eqn (3). The result is  $(E_{1/2}^{\text{oxd}} - E_{1/2}^{\text{red}}) = 1.360^1 E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}} - 1.917$  with  $n=8$ ,  $r$  (correlation coefficient) = 0.959,  $^1E_{\text{ho} \rightarrow \text{lu}}^{\text{u.v.}}$  being the data in  $\text{CCl}_4$  (see below). The correlation is quite good, and therefore we would naturally expect an accurate result

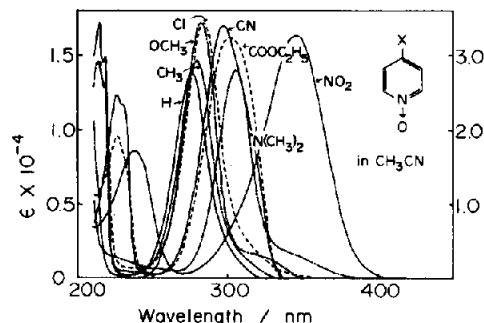


Fig. 1. Electronic spectra of pyridine *N*-oxides with the representative substituents at 4-position. The solvent is  $\text{CH}_3\text{CN}$  (see footnote \* in Table 1), and refer to the right ordinate scale for the  $\text{N}(\text{CH}_3)_2$  substituent.

\*The coordinate is as follows: the molecular axis is  $z$ , and the molecular plane is put in a  $xz$  plane. The MO is treated under  $C_{2v}$ .

Table 1. Observed spectral data of the near u.v.  ${}^1A_1$  band of 4-substituted pyridine *N*-oxides and their calculated values by semi-empirical SCFMO-CI methods

Substituents	CH <sub>3</sub> CN	$\lambda_{\max}$ (nm)			PPP-SCFMO-CI		CNDO/S-CI	
		$\epsilon_{\max}$ *	<i>n</i> -heptane	CCl <sub>4</sub> †	E(eV)	CI(%) <sup>‡</sup>	E(eV)	CI(%) <sup>‡</sup>
H	275.3	13 800	283.0	284.5(4.358)	4.543	96.2(4/5)	4.208	95.1(18/19)
CH <sub>3</sub>	278.6	14 600	285.1	287.2(4.317)	4.518	96.3(4/5)	4.160	94.7(21/22)
C <sub>2</sub> H <sub>5</sub>	278.5	16 900	284.8	287.6(4.311)				
<i>tert</i> -C <sub>4</sub> H <sub>9</sub>	278.6	16 500	285.9	287.6(4.311)				
Cl	283.8	17 200	290.0	291.1(4.259)	4.530	96.2(5/6)	4.161	94.7(21/22)
Br	285.0	19 700	289.0	292.8(4.234)	4.514	96.1(5/6)	4.152	94.4(24/25)
OCH <sub>3</sub>	282.2	17 200	290.0	292.0(4.246)				
OC <sub>2</sub> H <sub>5</sub>	282.5	20 700	290.7	292.0(4.246)				
NHCOCH <sub>3</sub>	297.6	21 300	—	—				
NH <sub>2</sub>	295.0	—	—	302.3(4.101)	4.340	95.9(5/6)	4.097	95.0(21/22)
N(CH <sub>3</sub> ) <sub>2</sub>	305.2	28 100	308.2	312.5(3.968)	4.300	94.8(5/7)	4.052	94.9(27/28)
COOH	300.1	—	—	310.0(4.000)	4.268	96.1(6/7)	3.976	92.8(26/27)
COOC <sub>2</sub> H <sub>5</sub>	301.3	16 200	—	309.0(4.012)				
COCH <sub>3</sub>	315.5	18 800	320.2	326.0(3.803)	4.276	96.1(5/6)	4.002	89.1(26/27)
CN	296.6	17 000	300.2	301.3(4.115)	4.351	96.2(5/6)		
NO <sub>2</sub>	345.4	16 400	347.5	348.0(3.563)	3.749	92.4(6/7)	3.543	96.2(26/27)

\* Values in CH<sub>3</sub>CN. The solubility of the samples is very small in *n*-heptane and CCl<sub>4</sub>, so accurate  $\epsilon_{\max}$  values in these solvents could not be determined.

† Values in parentheses are those in eV units.

‡ Per cent contribution of the main configuration interaction term, which is originated from the  $\pi$ -HOMO  $\rightarrow$   $\pi$ -LUMO transition for the two methods and all the samples.

from the examination of Eqns (1) and (2).<sup>\*</sup> Spectral data recorded in the nonpolar solvent  $\text{CCl}_4$  were employed to analyse Eqns (1) and (2), since good spectral data throughout all the substituents except  $\text{NH-CO-CH}_3$  were obtained (see Table 1). In principle, however, the same result as in  $\text{CCl}_4$  solvent was obtained for the spectral data measured in the other solvents (see Table 1). In Fig. 2 is illustrated the correlation of  ${}^1A_1$  ICT  $\pi-\pi^*$  band energies with those estimated using Eqn (2). We see a good agreement of observed and calculated values, the equation being written as  ${}^1E_{\text{ICT}}^{\text{u.v.}} = -0.163\sigma_i + 0.566\sigma_\pi^+ - 2.064\sigma_\pi^- + 4.352$  with  $n = 11$  and  $r = 0.988$ . Here, a CN group is ruled out in the plotting of Fig. 2, because KIMURA and NAGAKURA suggested [22] that the substituent ability (red shift) of a CN group on electronic spectra is weaker than that estimated from the other substituents. In fact, the estimated energy for a CN group using the equation given above falls way off the observed value in a red shifted direction. In the case of application of Eqn (1), the substituents should be divided into two groups, i.e. electron donating and accepting substituents. The reason is given in our foregoing papers [1-5], but in summary we can say that the two groups behave in a different way for the substituent constants  $F$  and  $R$ . In SAWADA's case, the constant  $\sigma_\pi^- = 0.000$  for electron donating substituents but  $\sigma_\pi^+ = 0.000$  for electron attracting groups, so that it is clear that both the substituent groups are expressed in Eqn (2). The mutual relation of the observed  ${}^1A_1$

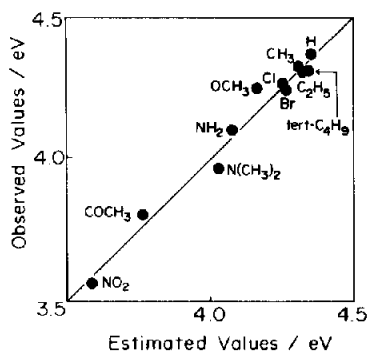


Fig. 2. The correlation of observed (solvent  $\text{CCl}_4$ ) and estimated [Eqn (2)] values of near u.v.  ${}^1A_1$  band energies of 4-substituted pyridine  $N$ -oxides. See the text for details.

<sup>\*</sup>Many examples satisfying Eqn (3) have already been published by us [1-5, 9-11], however there is no example of the singlet ( $S$ )-triplet ( $T$ )  $\pi-\pi^*$  transitions. In previous studies we reported the  $S \rightarrow T$   ${}^3L_a$  absorption bands as well as the values of  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  in the series: PNO (2.973, 1.802, -2.302), quinoline  $N$ -oxide (2.311, 1.537, -1.840), isoquinoline  $N$ -oxide (2.607, 1.600, -1.948), and acridine  $N$ -oxide (1.620, 1.280, -1.358) [9, 21]. The values in parentheses are  ${}^3L_a$  (eV),  $E_{1/2}^{\text{ox}}$  (V vs SCE), and  $E_{1/2}^{\text{red}}$  in the above order. We have now examined the application of Eqn (3) to the  ${}^3L_a$  bands, the regression equation being  $(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}) = 1.05{}^3L_a + 0.927$  with  $n = 4$  and  $r = 0.992$ . The result is very accurate, and this is the first case of an application of Eqn (3) to triplet  $\pi-\pi^*$  energies.

energies to those evaluated by Eqn (1) is depicted in Figs 3 and 4 for electron donating and accepting substituents, respectively. In Fig. 4 the CN substituent was also deleted for the same reason mentioned in Fig. 2. If we include it, the  $r$  value falls to 0.903. As a conclusion we would say that the substituent effect on the near u.v.  ${}^1A_1$   $\pi-\pi^*$  (ICT) band of PNO is also described reasonably by the use of Eqns (1) and (2), and that in the present case, Eqn (2) gave the best (the largest  $r$  value) interpretation of the spectral data.

#### Substituent effect on the blue shifted iodine band of iodine EDA complexes with 4-substituted PNOs

KUBOTA and co-workers [23, 24] previously reported in detail that some typical aromatic and aliphatic amine  $N$ -oxides form  $n-\sigma$  type EDA complexes with iodine in a 1:1 molar ratio, where the active centre for complex formation is an  $N$ -oxide group oxygen atom, and a clear explanation of the spectral and thermodynamic characteristics was given there. Although the CT spectra of  $\pi-\pi$  and  $n-\sigma$  type EDA complexes were hitherto known to be well described by Eqns (1) and (2) [3, 4], there is no precedent for

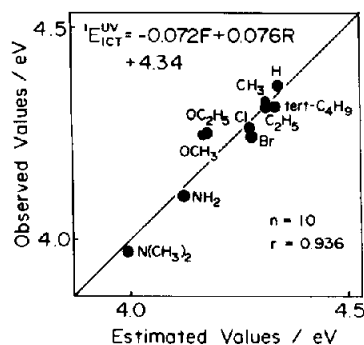


Fig. 3. The correlation of observed (solvent  $\text{CCl}_4$ ) and estimated [Eqn (1)] values of near u.v.  ${}^1A_1$  band energies of pyridine  $N$ -oxides with  $\pi$ -electron donating substituents at the 4-position.

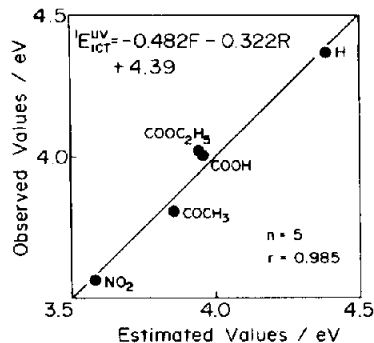


Fig. 4. The correlation of observed (solvent  $\text{CCl}_4$ ) and estimated [Eqn (1)] values of near u.v.  ${}^1A_1$  band energies of pyridine  $N$ -oxides with  $\pi$ -electron accepting substituents at 4-position.

Table 2. Equilibrium constants ( $K$ ) and spectroscopic data of blue shifted iodine bands pertinent to the iodine CT complexes with 4-substituted pyridine  $N$ -oxides, and the  $pK_a$  values of the  $N$ -oxides

Substituents	$K^*$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	$\log K$	Blue shifted iodine band†			
			$\lambda_{\text{max}}(\text{nm})\ddagger$	$E(\text{eV})$	$\epsilon_{\text{max}}$	$pK_a\§$
H	39.7	1.60	426	2.91	1950	0.79
$\text{CH}_3$	103	2.01	421	2.95	2020	1.29
$\text{C}_2\text{H}_5$	99.0	2.00	422	2.94	2220	1.41
<i>tert</i> - $\text{C}_4\text{H}_9$	44.3	1.65	423	2.93	2450	1.37
Cl	13.0	1.11	429	2.89	2500	0.33
$\text{OCH}_3$	180	2.26	405	3.06	3540	2.05
$\text{OC}_2\text{H}_5$	260	2.41	405	3.06	3950	2.02
$\text{N}(\text{CH}_3)_2$	1500	3.18	362	3.43	6000	3.88
$\text{COOC}_2\text{H}_5$	10.2	1.01	448	2.77	1680	-0.41
$\text{COCH}_3$	5.18	0.714	450	2.75	1800	-0.47
$\text{NO}_2$	1.39	0.143	468	2.65	1630	-1.51

\* Values in  $\text{CH}_2\text{Cl}_2$  at  $25 \pm 0.5^\circ\text{C}$ .

† This is the value corresponding to the CT complex itself in  $\text{CH}_2\text{Cl}_2$ .

‡ The iodine visible band maximum without CT complex formation is 507 and 520 nm in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ , respectively. This is due to the difference of solvent polarity.

§ See the text and Ref. [28].

applying the equations to the above blue shifted iodine bands in the visible region, brought about by an iodine CT complex formation and attributed to the spectral change of an electron acceptor itself in CT complexes. Here we discuss this problem for the system of 4-substituted pyridine  $N$ -oxide-iodine complexes. A spectroscopic study of the  $N$ -oxide-iodine CT complex was made in  $\text{CH}_2\text{Cl}_2$  solvent, the complex formation constant ( $K [\text{dm}^3 \text{ mol}^{-1}] = C_{\text{DA}}/C_{\text{D}} \cdot C_{\text{A}}$ ) being evaluated using Eqn (4) [23]:\*

$$\epsilon = (1/K) [(\epsilon_{\text{A}} - \epsilon) / C_{\text{D}}^0] + \epsilon_{\text{DA}} \quad (4)$$

Here,  $\epsilon_{\text{A}}$ ,  $\epsilon_{\text{DA}}$  and  $\epsilon$  are the molar extinction coefficient ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) of free iodine (acceptor), the blue shifted iodine band of the EDA complex itself, and the apparent one calculated using an analytical iodine concentration  $C_{\text{A}}^0$ , respectively,  $C_{\text{D}}^0$  being the analytical donor ( $N$ -oxide) concentration. Equation (4) can be derived under the conditions that  $C_{\text{D}}^0 \gg C_{\text{DA}}$  and that the pyridine  $N$ -oxides (donors) employed do not show light absorption at a wavelength where evaluation of the  $K$  values occurs. These experimental conditions were well satisfied in the present systems, so that the  $K$  values were accurately determined. In Fig. 5 we illustrate the iodine spectral change with the addition of MPNO, where we can see a good isobestic point indicating a 1:1 complex formation. Alternatively the linear plot of  $\epsilon$  vs  $(\epsilon_{\text{A}} - \epsilon)/C_{\text{D}}^0$  is given in Fig. 6. The slope of the straight line is equal to  $1/K$ , but  $\epsilon_{\text{DA}}$  is obtained from  $\epsilon$  at  $[(\epsilon_{\text{A}} - \epsilon)/C_{\text{D}}^0] = 0$ . For the case of DAPNO the  $K$  value is quite large (see Table 2) compared with those of the other  $N$ -oxides, so experiments were done with the fixed  $\text{I}_2$  concentration of  $3.94 \times 10^{-5} \text{ mol dm}^{-3}$  but  $(1-31) \times 10^{-4}$  for DAPNO. The solubility of CNPNO and AMPNO in  $\text{CH}_2\text{Cl}_2$  is

\* If we put  $\epsilon_{\text{A}} = 0$ , Eqn (4) reduces to the BENESI-HILDEBRAND Eqn [25].

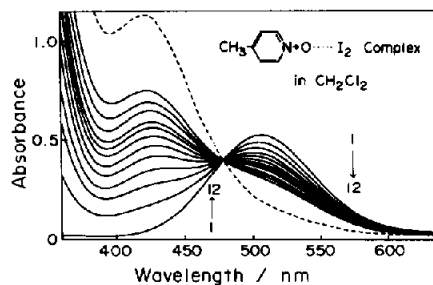


Fig. 5. The visible absorption spectra of iodine-4-methylpyridine  $N$ -oxide system in  $\text{CH}_2\text{Cl}_2$ . Curve 1 is for free iodine ( $5.62 \times 10^{-4} \text{ mol dm}^{-3}$ ); the concentrations of the  $N$ -oxide are 1.29, 2.57, 3.85, 5.14, 6.42, 7.71, 8.99, 10.3, 12.9, 15.4, 18.0 in  $10^{-3} \text{ mol dm}^{-3}$  units for the curves 2-12, respectively. The broken curve is for the absorption due solely to the complexed iodine molecule.

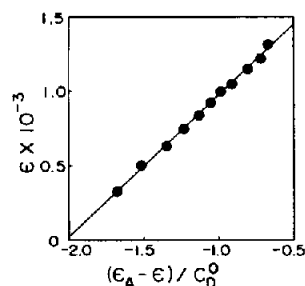


Fig. 6. The linear relationship between  $\epsilon$  and  $(\epsilon_{\text{A}} - \epsilon)/C_{\text{D}}^0$  in Eqn (4) at 430 nm for the system given in Fig. 5.

so small that the accurate  $K$  values could not be determined by the present spectroscopic method, and therefore these data are lacking in Table 2. Once the  $K$  value is evaluated, we can easily calculate the blue shifted iodine spectrum of the EDA complex itself, as is seen in Fig. 5, in order to determine the band

maximum and the band intensity. All the spectral data and  $K$  values are listed in Table 2. The iodine 507 nm band in  $\text{CH}_2\text{Cl}_2$  was assigned to a triplet  $\pi_g 5p$  (HOMO)  $\rightarrow \sigma_u 5p$  (LUMO) transition ( ${}^1\Sigma_g^+ \rightarrow {}^3\Pi_{0u}^+$ ) [14], which may borrow the intensity from an allowed strong iodine  $N \rightarrow V$  transition ( ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ ) as a result of strong spin-orbit coupling in heavy iodine atoms [14]. This iodine  $\sigma_u 5p$  orbital is a strongly antibonding MO and an important electron accepting orbital in the formation of the dative structure ( $\text{D}^+ - \text{A}^-$ ) of iodine CT complexes. Of course, this dative structure can mix with the above iodine locally excited state. Keeping in mind these circumstances MULLIKEN and PERSON [14] and NAGAKURA [26] discussed the origin (exchange repulsion effect, the interaction between electron donor and acceptor orbitals, and intensity borrowing from CT and  $NV$  transitions) of the blue shift and the intensification of the iodine visible band caused by CT complex formation, indicating that the degree of the blue shift and intensification is a good measure of iodine CT complex stability, especially for the former case. We have now tested the correlation of visible iodine band energies ( $E_{I_2}^{\text{vis}}$ ) to  $\log K$  values (Table 2) in a series of 4-substituted PNO- $\text{I}_2$  complexes, the result being

$$E_{I_2}^{\text{vis}} = 0.226 \log K + 2.57 \quad (n = 11, r = 0.946).$$

The correlation of both values is quite good and supports the discussion made hitherto. In other words this makes it possible to apply Eqn (1) to  $E_{I_2}^{\text{vis}}$ , because  $\log K$  is the value parallel to the free energy change of the complex formation. The mutual correlation between the observed and estimated  $E_{I_2}^{\text{vis}}$  values is given in Fig. 7. The result is very accurate, and we see that the observed  $E_{I_2}^{\text{vis}}$  values are well interpreted by Eqn (1). As discussed in the next section the iodine complexes investigated are of  $n-\sigma$  type [23], so that the application of Eqn (2) to the present problem is not justified. Needless to say, the  $\log K$  values are also written as  $\log K = -0.807F - 0.586R + 1.646$  with a high correlation coefficient  $r = 0.986$  ( $n = 11$ ) as would be expected.

Next, let us consider the intensification of the blue shifted iodine  ${}^3\Pi_{0u}^+$  band brought about by the CT complex formation, since, as mentioned before, the intensification is a measure of the complex stability [14]. Figure 8 illustrates the mutual correlation between observed and estimated  $\epsilon_{I_2}^{\text{max}}$  values. In principle, the physically significant parameter is the integrated intensity, from which we can calculate the transition moment and oscillator strength. Unfortunately, an accurate estimate of the half-width at half-intensity ( $\Delta\bar{\nu}_{1/2}$ ) corresponding to the shifted iodine band was quite difficult to make in the present case because of a strong overlap with the CT band which continues to shorter wavelengths, originating in the iodine spectrum [23, 24]. Therefore the  $\epsilon_{I_2}^{\text{max}}$  value was employed instead of  $\Delta\bar{\nu}_{1/2} \epsilon_{I_2}^{\text{max}}$  in plotting Fig. 8. Never the less, we see that the observed  $\epsilon_{I_2}^{\text{max}}$  values are well

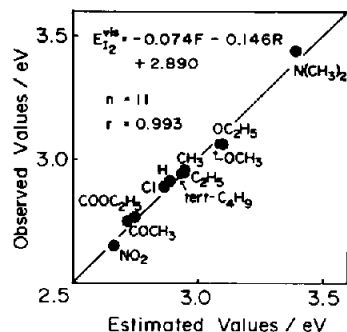


Fig. 7. The correlation of the observed (solvent  $\text{CH}_2\text{Cl}_2$ ) and estimated [Eqn (1)] values of blue shifted iodine band energies caused by the CT interaction with 4-substituted pyridine  $N$ -oxides.

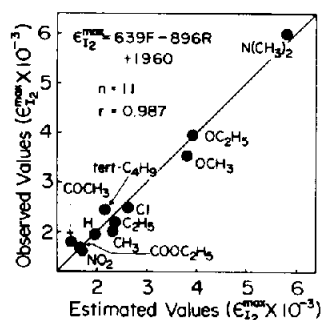


Fig. 8. The correlation of the observed (solvent  $\text{CH}_2\text{Cl}_2$ ) and estimated [Eqn (1)] values of blue shifted iodine band intensities caused by the CT interaction with 4-substituted pyridine  $N$ -oxides.

described by Eqn (1), this being in line with the prediction from CT theory.

#### The nature of 4-substituted PNO- $\text{I}_2$ EDA complexes

In previous papers the nature of the iodine complexes of aliphatic and aromatic amine  $N$ -oxides was extensively studied [8, 14, 23, 27], indicating that (i)  $N$ -oxide-iodine complexes are of  $n-\sigma$  type, corresponding to the charge transfer of an electron from the  $N$ -oxide group oxygen atom to a  $\sigma_u 5p$  antibonding MO of  $\text{I}_2$ , (ii) this kind of CT complex stability parallels the hydrogen bond formation ability of  $n$ -donors, a non-bonding electron of which would transfer to the antibonding  $X-H$   $\sigma$  orbital of  $X-H$  groups in the CT model of hydrogen bonding, and (iii)  $pK_a$  values may be considered as an extreme case of hydrogen bonding, and therefore  $n-\sigma$  type CT complex stability is also parallel to the  $pK_a$  values pertaining to the  $n$ -type electron donors. Mutual correlation between  $\log K$  values of 4-substituted PNO-iodine complexes and the  $pK_a$  values of the  $N$ -oxides is depicted in Fig. 9, and the  $pK_a$  values are listed in Table 2 and taken from

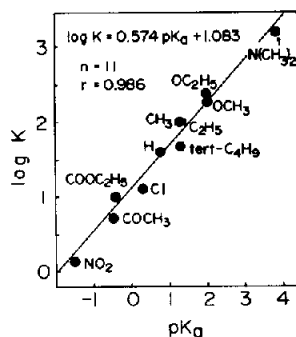


Fig. 9. The linear relationship of  $\log K$  (for the iodine complex formation with 4-substituted pyridine  $N$ -oxides) and the  $pK_a$  values of the  $N$ -oxides.

Ref. [28], except for  $X=C_2H_5$ ,  $tert-C_4H_9$ , and  $OC_2H_5$ , whose  $pK_a$  values were newly determined here at  $25 \pm 0.1^\circ C$  by spectroscopic methods. Alternatively, we employed the  $pK_a$  value of  $X=COOCH_3$  for  $X=COOC_2H_5$ . It is already known [8, 15, 23, 28] that these  $pK_a$  values are due to proton addition to the  $N$ -oxide group oxygen atom for all the  $N$ -oxides listed in Table 2. We can now see clearly in Fig. 9 that  $\log K$  values pertinent to the iodine complex stability are in good linear agreement with all the  $pK_a$  values throughout all the substituents, supporting the discussion made at the beginning of this section. In other words we can safely say that in the course of proton addition reactions like  $pK_a$  and hydrogen bonding, the contribution from an  $n-\sigma$  type CT interaction must play an important part in the proton addition complex formation.

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