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Spectral Shift of Band Origins in the Near Ultraviolet Absorption Spectra of Some 2- and 3-Substituted Pyridines

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The relative shifts in the position of band origin of the lowest singlet π-electron transition in some 2- and 3-substituted pyridines, and monosubstituted benzenes with similar substituents, with respect to those of the parent molecules have been calculated by the method of localized orbitals with configuration interaction. Under certain assumptions, the calculated relative shifts in the 2- and 3-substituted pyridines are found to bear a linear relationship with that of the corresponding monosubstituted benzenes. The experimental data are found to be in agreement with the theoretical expectation.

The close similarity between the near ultraviolet π-electronic absorption spectra of monosubstituted benzenes and similarly substituted pyridines is well known. From the available values of the position of the O–O band of the lowest singlet $\pi \rightarrow \pi^*$ transitions in these compounds in the vapour phase, it is seen that the shifts of the band origin in the near ultraviolet absorption spectra of 2- and 3-substituted pyridines from that of pyridine are closely parallel to those of corresponding monoderivatives of benzene with respect to that of benzene. The π-electronic energy levels of some monosubstituted benzene molecules have been calculated from localized orbital model with configuration interaction by Kimura, Tsubomura, and Nagakura[1] and by Kimura and Nagakura.[2] Similar calculations including inductive effect of the substituent have been made by Favini, Gamba, and Bellobono[3] in amino- and nitro-substituted pyridines. With reasonable values of the ionization potential of the substituent, the electron affinity of benzene and pyridine molecules to which the substituent is attached and the resonance integrals between the substituent and the carbon atom of the respective molecules, these authors have obtained fair agreement between the calculated and experimentally observed values of the π-electronic energy levels in these molecules. SCF calculations of the π-electronic energy level of monosubstituted benzenes have also been reported by several workers.[4–6]

We have applied the localized orbital model with configuration interaction to explain the observed parallelism of the shifts of band origins in the near ultraviolet absorption spectra of some monosubstituted benzenes and 2- and 3-substituted pyridines with the same substituent without going into the actual calculations of the lowest π-electronic energy levels of all these molecules.

Theoretical Considerations

a) Monosubstituted Benzenes. The energy of the lowest excited π-electronic level E_α^X of monosubstituted benzenes with substituent X corresponding to E_α the energy of the α-band in benzene has been obtained from an approximate solution of the 3×3 determinantal equation (which is equivalent to a second order perturbation calculation) of B-species given by Kimura and Nagakura[2] for monosubstituted benzenes, and is given by

$$E_\alpha^X = E_\alpha + \frac{\frac{1}{6}\beta_X^2}{E_\alpha - E_{\mathrm{C.T,b}}} \tag{1}$$

where β_X is the resonance integral corresponding to $\beta + \beta'$ of Kimura and Nagakura[2] and $E_{\mathrm{C.T,b}} = I_X - A - Q_2$ is the energy of the charge transfer state. All these quantities are given in electron volts and the notations used are those of Kimura and Nagakura.[2]

The validity of Eq. (1) is seen from Table 1 where a comparison of the exact values of this energy level in a number of monosubstituted benzene molecules calculated by Kimura and Nagakura[2] and those for the corresponding molecules obtained from Eq. (1) is given. All these values have been calculated with the parameters given by Kimura and Nagalura.[2]

Table 1. Comparison of the energy of the lowest excited state in monosubstituted benzenes
(All values in eV)

Substituent	F	Cl	Br	OH	NH_2
Kimura and Nagakura[2]	4.80	4.70	4.53	4.68	4.40
Equation (1)	4.80	4.71	4.53	4.68	4.35

If the lowering of the ground state energy is neglected, the shift in the position of α-band of benzene with substitution is given by:

$$\Delta E_\alpha^X = E_\alpha - E_\alpha^X,$$

and from Eq. (1) we get

$$\beta_X^2 = 6\Delta E_\alpha^X (E_{\mathrm{C.T,b}} - E_\alpha) \tag{2}$$

b) Monosubstituted Pyridines. The method of calculating the lowest excited π-electron energy levels in 2- and 3-substituted pyridines is the same as that used by Favini, Gamba, and Bellobono[3] in the case of aminopyridines. But instead of solving the 7×7 determinantal equation exactly, an approximate solution as in the case of monosubstituted benzenes has been used for obtaining the energy of the lowest excited state in each of the 2- and 3-substituted pyridines with the

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substituent X. These are respectively given by the following equations:

For 2-substituted pyridines:

$$E_1^{X(2)} = E_1 - 0.017 I_\pi^X + \frac{0.166\beta_X^2}{E_1 - E_5^{(2)} - 0.132 I_\pi^X} + \frac{0.011\beta_X^2}{E_1 - E_6^{(2)} - 0.27 I_\pi^X} \tag{3}$$

and for 3-substituted pyridines:

$$E_1^{X(3)} = E_1 - 0.083 I_\pi^X + \frac{0.171\beta_X^2}{E_1 - E_5^{(3)} - 0.157 I_\pi^X} + \frac{0.042\beta_X^2}{E_1 - E_6^{(3)} - 0.33 I_\pi^X} \tag{4}$$

where E_1 is the energy of the lowest excited state (A_1) of pyridine, $E_1^{X(2)}$ and $E_1^{X(3)}$ are those of 2- and 3-substituted pyridines, respectively, I_π^X is the inductive parameter of the substituent X given by Godfrey and Murrell,[7] the quantities containing β_X^2 are the square of the Hamiltonian matrix elements between the lowest excited state (A_1) of pyridine and the appropriate charge transfer state T_D^4 and T_D^5 according to the notations used by Favini, Gamba, and Bellobono.[3]

For the two types of substituted pyridines, the following are the energies of these two charge transfer states.

$$\left.\begin{aligned} E_5^{(2)} &= I^X - A - Q_5^{(5)};\; E_6^{(2)} = I^X - A - Q_6^{(2)} \\ E_5^{(3)} &= I^X - A - Q_5^{(3)};\; E_6^{(3)} = I^X - A - Q_6^{(3)} \end{aligned}\right\} \tag{5}$$

If the lowering of the ground state energy is neglected, the substitution of β_X^2 from Eq. (2) into Eqs. (3) and (4) yields, for the values of the shift of the lowest excited energy level for the two kinds of substituted pyridines, the following expressions:

$$\begin{aligned} \varDelta E_2^X &= E_1 - E_1^{X(2)} \\ &= 0.017 I_\pi^X + \left[\frac{E_{\text{C.T,b}} - E_\alpha}{E_5^{(2)} - E_1 + 0.132 I_\pi^X} + \frac{0.066(E_{\text{C.T,b}} - E_\alpha)}{E_6^{(2)} - E_1 + 0.27 I_\pi^X}\right]\varDelta E_\alpha^X \end{aligned} \tag{6}$$

and

$$\begin{aligned} \varDelta E_3^X &= E_1 - E_1^{X(3)} \\ &= 0.083 I_\pi^X + \left[\frac{1.026(E_{\text{C.T,b}} - E_\alpha)}{E_5^{(3)} - E_1 + 0.157 I_\pi^X} + \frac{0.252(E_{\text{C.T,b}} - E_\alpha)}{E_6^{(3)} - E_1 + 0.33 I_\pi^X}\right]\varDelta E_\alpha^X \end{aligned} \tag{7}$$

Assuming that the molecules of monosubstituted benzene and the two types of substituted pyridine as regular hexagons with bond distances 1.39 Å, the values for the bond lengths between the substituent and the substituted carbon atom as those given by Kimura and Nagakura[2] and a point charge approximation for the evaluation of the electrostatic energies Q, it is found $Q_5^{(2)} \approx Q_5^{(3)}$, $Q_6^{(2)} \approx Q_6^{(3)}$, and $Q_6 > Q_5 > Q_2$, Q_6 being greater than Q_5 by about 10% and Q_5 greater than Q_2 by the same amount.

If we assume that for a given substituent $I^X - A$ has the same value for the monosubstituted benzene and the corresponding 2- and 3-substituted pyridines and observing that $E_\alpha \approx E_1$ the Eqs. (6) and (7) may be further simplified. The quantities $(E_{\text{C.T,b}} - E_\alpha)/(E_5^{(2)} - E_1 + 0.132 I_\pi^X)$ etc. will be somewhat larger than unity while though the terms like $(E_{\text{C.T,b}} - E_\alpha)/(E_6^{(3)} - E_1 + 0.271_\pi^X)$ have values appreciably greater than unity their effects will be reduced because in each case they are multiplied by small quantities. Hence the coefficients of $\varDelta E_\alpha^X$ in Eqs. (6) and (7) will be a little larger than 1.066 and 1.278, respectively. These equations may, therefore, be written as

$$\varDelta E_2^X = 0.017 I_\pi^X + 1.1 \varDelta E_\alpha^X \tag{8}$$

and

$$\varDelta E_3^X = 0.083 I_\pi^X + 1.3 \varDelta E_\alpha^X \tag{9}$$

Further, if we assume that I_π^X for the different substituents may be represented by an average value I_π for both types of pyridine molecules considered, then it follows from Eqs. (8) and (9) that the plots of $\varDelta E_2^X$ and $\varDelta E_3^X$ *vs.* $\varDelta E_\alpha^X$ are straight lines with slopes 1.1 for the 2-pyridines and 1.3 for the 3-pyridines and the intercepts have values 0.017 I_π and 0.083 I_π, respectively.

Comparison with Experiment

In order to find out how far the conclusions drawn from the theoretical considerations agree with the experimental data obtained by various workers[8–22] the shifts in the positions of O-O band (expressed in units of electron volt) for the 2- and 3-substituted pyridines with respect to that of pyridine are plotted against

TABLE 2. POSITION OF O–O BAND (cm^{-1}) IN THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE, MONOSUBSTITUTED BENZENES, PYRIDINE, 2-SUBSTITUTED AND 3-SUBSTITUTED PYRIDINES

Substituent	Monosubstituted benzenes	2-Substituted pyridine	3-Substituted pyridine
H	38090[8]	38350[9]	
F	37819[10]	38000[11]	37320[11]
CH_3	37477[12]	37620[13]	37380[13]
Cl	37052[14]	37115[15]	36469[15]
Br	36996[16]	36958[17]	36300[17]
OH	36350[18]	36420[19]	36247[19]
NH_2	34035[20,21]	34324[22]	33854[22]

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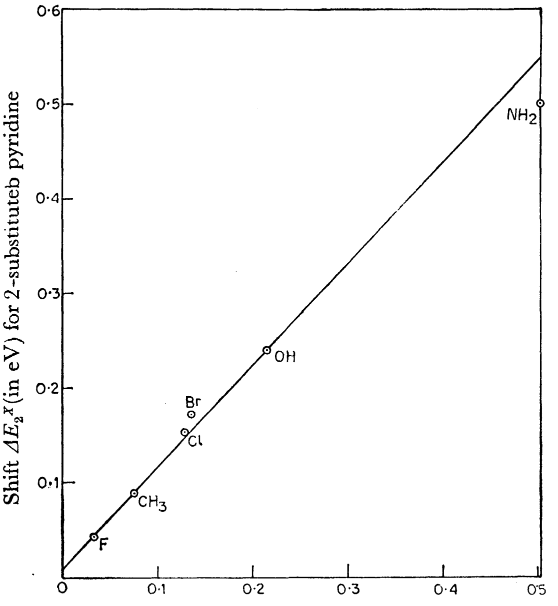

Fig. 1.

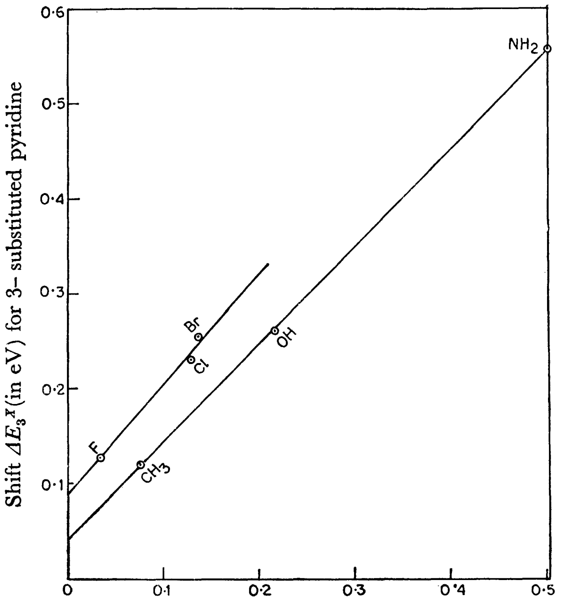

Fig. 2.

those of the corresponding monosubstituted benzene with respect to benzene in Figs. 1 and 2, respectively. For this purpose the positions of the O–O band in the near ultraviolet absorption spectra of monosubstituted benzenes and some 2- and 3-substituted pyridines with similar substitutions, taken from available data, are shown in Table 2.

It is seen from Figs. 1 and 2 that the plots of $\Delta E_2{}^X$ *vs.* $\Delta E_\alpha{}^X$ and $\Delta E_3{}^X$ *vs.* $\Delta E_\alpha{}^X$ give straingt lines. In the case of 2-substituted pyridines all the points corresponding to different substituents fall on the same line (Fig. 1) with a slope of 1.07 and an intercept of 0.01 eV. This value of the slope compares favourably with the expected value 1.1 of Eq. (8). The average value of I_π obtained from the same equation is about 0.6 eV. For the 3-substituted pyridines the points corresponding to F, Cl, and Br as substituents and those with CH_3, OH, and NH_2 as substituents fall on two different straight lines (Fig. 2). The former has an inclination of 1.16 and an intercept of 0.09 eV while for the latter these values are 1.02 and 0.04 eV, respectively. The value of the slope for either of the straight lines is smaller than 1.3 expected from Eq. (9) while the average values of I_π for the two groups of compounds are respectively about 1.0 and 0.5 eV. The value 0.6 eV of I_π obtained from 2-substituted pyridine compares favourably with the values 1.0 eV and 0.5 eV for this quantity in the case of 3-substituted pyridines. The values of $I_\pi{}^X$ given by Godfrey and Murrell7) for these substituents vary from 0.54 eV for the methyl group to 1.74 eV for the amino group. The values obtained in the present case lie within these limits.