On the Intramolecular Charge Transfer Spectra and Structure of Isomeric Aminopyridines

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(Received November 6, 1958)

In a series of papers, we have reported detailed theoretical studies on the electronic structure and the nature of electronic transitions of nitrogen heterocycles[1-5]. The detailed Hartree-Fock SCF study has been made only for nitrogen heterobenzenes such as pyridine[1], pyrazine[1], *sym*-triazine[1] and *sym*-tetrazine[2]. In addition, some extensions to larger molecules such as quinoline[3,5], isoquinoline[3,5], phthalazine[5], quinoxaline[5], acridine[4,5] and phenazine[4,5] have been made on the basis of the results obtained for nitrogen heterobenzenes, employing the perturbation method based on the Hartree-Fock SCF theory. Thus a theoretical ground for the classification and interpretation of the electronic spectra of nitrogen heterocycles has been given. As an extension of these investigations, we have studied the electronic structure and the spectra of some substituted nitrogen heterocycles. Among these, we have taken up the isomeric aminopyridines. There have been some disputes concerning the molecular forms of these molecules, especially 2- and 4- aminopyridines, i. e., imine-enamine tautomerism[6]. However, the possibility of the existence of imino-form was rejected by Anderson and Seeger[7] by spectral studies of these and related molecules and also Angyal and Angyal[8] reported that these compounds exist predominantly in the amino-form by critically surveying the foregoing data and arguments and also by the measurement of pK_a values of these molecules and related ones. Nevertheless, there seem to remain some ambiguities about this problem, even now. Morita[9] has calculated the electronic spectra of 4-aminopyridine by a method analogous to Dewar and Paoloni[10], assuming various models with respect to the molecular forms of this molecule. However, no definite conclusion about the form of this molecule has been derived from his calculation. We have tried to make clear the interrelation among the isomeric aminopyridines and their relation to aniline, pyridine and benzene, with respect to the electronic structure and spectra. We have assumed the amino-form of these isomers and attempted to interpret the observed spectra. It will be expected that some contributions to the problem of the tautomerism of these molecules will be made also by such a study even if it is by an indirect method.

1) N. Mataga and K. Nishimonto, *Z. physik. Chem. N. F.*, **13**, 140 (1957).
2) N. Mataga, This Bulletin, **31**, 453 (1958).
3) N. Mataga, ibid., **31**, 459 (1958).
4) N. Mataga, ibid., **31**, 463 (1958).
5) N. Mataga, *Z. physik. Chem. N. F.*, **18**, 285 (1958).
6) See, for example, E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948).
7) L. C. Anderson and N. V. Seeger, ibid., **71**, 340 (1949).
8) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, **1952**, 1461.
9) T. Morita, presented at the "Symposium on the Electronic States of Molecules", held by Chem. Soc. Japan and Phys. Soc. Japan on october 13, 1958.
10) M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.*, **53**, 261 (1957).

Method

Previously, Tsubomura[11] has studied the electronic spectra of substituted pyridines by the electron migration theory of Sklar and Herzfeld[12]. The general features of the substituted pyridine spectra have been well comprehended by his study. As pointed out by Goodman and Shull[13] in the case of substituted benzene spectra, however, for certain very strongly conjugating substituents, e. g., $-NH_2$, such a simplified perturbation method may be essentially invalid, and a more rigorous method will be needed. In the present study we have used the method developed by Longuet-Higgins and Murrell[14] for the study of the composite system. An excellent treatment based on an analogous idea has been developed independently by Nagakura and Tanaka[15]. Hereafter the outline of the method will be mentioned briefly.

Generally speaking, the electron transfer states are of two kinds, according as the electron is transferred from pyridine to the substituent or from the substituent to pyridine. In the present case, however, the substituent is a fairly strong electron donor and accordingly the configuration in which the electron is transferred from pyridine to the substituent will have a very high energy compared with the opposite case and may be neglected.

With this approximation, the problem is reduced to an evaluation of the interaction between the locally excited states of pyridine and one set of electron transfer states in which the electron is transferred from the substituent to pyridine.

If the SCFMO's of pyridine are written $\phi_1 \cdots\cdots \phi_p$ and those of the substituent $\theta_1 \cdots\cdots \theta_s$, then the energy of the electron transfer configuration $\chi_{s\to k}$ where one electron is transferred from an occupied orbital θ_s to an unoccupied orbital ϕ_k, is given by

$$E(\chi_{s\to k}) = \varepsilon_k - \varepsilon_s - \int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_k^2(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (1)$$

where ε_k and ε_s are SCFMO energies of ϕ_k and θ_s, respectively, and ϕ_k's are linear combinations of $2p\pi$ AO's $\phi_1 \cdots\cdots \phi_p$ of carbon or nitrogen

$$\phi_k = \sum_\mu c_{k\mu} \phi_\mu \quad (2)$$

Now, in actual computation, ε_s will be given, to a good approximation, by the ionization potential of ammonia. The difference of the observed[16] and calculated[17] values of electron affinity of benzene, $\Delta A = A_{\text{benz}}^{\text{obs}} - A_{\text{benz}}^{\text{calc}}$ has been added to the calculated values of ε_k's.

With neglect of differential overlap, the integral in 1 is reduced to

$$\sum_\mu \gamma_{s\mu} = \sum_\mu \int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_\mu^2(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (3)$$

These integrals have been replaced by the interaction energy of point charges centered on the substituent and on the μ atom, taking the length of bond joining the substituent and pyridine to be 1.46 Å. The matrix elements of the interaction between the various configurations have been evaluated from the following formulae,

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_{j\to l}) = -\delta_{kl} \int \theta_s(i) H(i) \phi_j(i) \mathrm{d}v(i) \quad (4)$$

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_0) = \sqrt{2} \int \theta_s(i) H(i) \phi_k(i) \mathrm{d}v(i) \quad (5)$$

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_{s\to l}) = -(sk|G|sl) = -\int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_k(j) \phi_l(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (6)$$

The integral $\int \theta_s(i) H(i) \phi_j(i) \mathrm{d}v(i)$ can be reduced to $c_{jr} \int \theta_s(i) H(i) \phi_r(i) \mathrm{d}v(i)$ the substitutent being attached to carbon atom 'r'.

We have used a reasonable value for $\beta_{RS} = \int \theta_s(i) H(i) \phi_r(i) \mathrm{d}v(i) = -1.6$ eV. which is the same value as that used by Murrell[14] for the study of aniline. The wave functions and energies above the ground state of locally excited states of pyridine to be used in the present calculation are as follows[1]:

11) H. Tsubomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 293 (1957).
12) A. L. Sklar, *J. Chem. Phys.*, **7**, 987 (1939); K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 72 (1951).
13) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).
14) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, A68, 601 (1955); J. N. Mureell, ibid., **68**, 969 (1955).
15) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).
16) Blackedge and Hush, quoted in N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).
17) N. Mataga, K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).

	E (eV.)
$\Psi(L_b)=0.8202\chi_{3\to4}-0.5720\chi_{2\to5}$	5.009
$\Psi(L_a)=0.8688\chi_{3\to5}+0.4951\chi_{2\to4}$	6.248
$\Psi(B_a)=0.4951\chi_{3\to5}-0.8688\chi_{2\to4}$	7.229
$\Psi(B_b)=0.5720\chi_{3\to4}+0.8202\chi_{2\to5}$	7.159

Results and Discussion

The interactions which occur between the various electronic states are shown in Table I.

As shown in Table I, in the case of 4-amino-pyridine, the seventh order matrix splits off into fourth and third order matrices, owing to the c_{2v} symmetry of the molecule.

Now, the wave functions and energies of the electronic states of 4-amino-pyridine are easily obtained as shown in Table II by solving the secular equations. In Table II, the corresponding quantities for aniline* are also indicated for the purpose of comparison.

TABLE I. THE MATRIX ELEMENTS OF THE INTERACTIONS BETWEEN THE ELECTRONIC STATES DUE TO THE CHARGE TRANSFER

2-Amino-pyridine

χ_0	L_b	L_a	B_a	B_b	$\chi_{s\to4}$	$\chi_{s\to5}$
0	0	0	0	0	−0.765	1.138
	5.009	0	0	0	0.652	0.166
		6.248	0	0	−0.144	0.691
			7.229	0	0.252	0.394
				7.159	0.455	−0.238
					5.554	0.696
						5.286

3-Amino-pyridine

χ_0	L_b	L_a	B_a	B_b	$\chi_{s\to4}$	$\chi_{s\to5}$
0	0	0	0	0	−0.617	−1.125
	5.009	0	0	0	0.660	−0.330
		6.248	0	0	0.286	0.699
			7.229	0	−0.502	0.398
				7.159	0.460	0.474
					5.593	−0.405
						5.313

4-Amino-pyridine

χ_0	L_a	B_a	$\chi_{s\to4}$	L_b	B_b	$\chi_{s\to5}$
0	0	0	1.333	5.009	0	−0.559
	6.248	0	0.484		7.159	0.802
		7.229	−0.850			6.221
			4.643			

TABLE II. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF 4-AMINO-PYRIDINE AND ANILINE

4-Amino-pyridine

Energy (eV.)		χ_0	L_a	B_a	$\chi_{s\to4}$
−0.364	Ψ_0	0.963	0.019	−0.029	−0.263
4.609	$\Psi_I(A_1)$	0.255	−0.261	0.286	0.885
6.352	$\Psi_{II}(A_1)$	0.043	0.954	0.198	0.205
7.522	$\Psi_{III}(A_1)$	0.057	0.122	−0.934	0.322
		L_b	B_b	$\chi_{s\to5}$	
4.750	$\Psi_I(B_1)$	0.898	−0.138	0.416	
5.990	$\Psi_{II}(B_1)$	0.425	0.511	−0.746	
7.651	$\Psi_{III}(B_1)$	0.109	−0.846	−0.519	

Aniline

		χ_0	L_a	B_a	$\chi_{s\to4}$
−0.297	Ψ_0	0.972	−0.022	0.020	0.221
5.185	$\Psi_I(A_1)$	0.192	0.550	−0.282	−0.762
6.404	$\Psi_{II}(A_1)$	0.078	−0.793	−0.460	−0.384
7.315	$\Psi_{III}(A_1)$	0.084	−0.250	0.839	−0.471
		L_b	B_b	$\chi_{s\to5}$	
4.704	$\Psi_I(B_1)$	0.942	−0.092	0.316	
6.348	$\Psi_{II}(B_1)$	0.296	0.702	−0.646	
7.588	$\Psi_{III}(B_1)$	0.169	−0.704	−0.689	

As shown in Table II, in both 4-amino-pyridine and aniline, $\Psi_I(B_1)$ is mainly contributed by L_b of pyridine and benzene, respectively, and accordingly the band due to the transition to this state may be regarded as a slightly modified L_b band in both of these molecules.

Contrary to this, $\Psi_I(A_1)$ is mainly contributed by $\chi_{s\to4}$. Although the contribution of L_a to this state is still fairly great in the case of aniline, it becomes less prominent in the case of 4-amino-pyridine, and the contribution of $\chi_{s\to4}$ becomes more predominant (~80%). Therefore, the band due to the transition to this state in the case of 4-amino-pyridine may be called an intramolecular charge transfer band according to the naming of Nagakura and Tanaka[15].

Such a clear-cut classification of band character, however, does not hold in the case of the other isomers, various configurations being mixed in each state.

Now, whereas the MO ϕ_5 has the nodal plane through the C_2 axis of pyridine, the coefficient of AO at nitrogen has fairly great value in the MO ϕ_4. Accordingly, the increase of π-electron density or ring nitrogen caused by the substitution of an amino group for hydrogen may be determined by the degree of contribution of $\chi_{s\to4}$ to the ground state. This contribution is the greatest in the case of 4-amino-pyridine and the smallest in the case of

* The wave functions and energies of elctronic states of aniline collected in Table II are slightly different from those calculated by Murrell[14] because, in the present work, our parameters[1-5] have been used to calculate the wave functions and energies of benzene.

18) H. C. Longuet-Higgins, *J. Chem. Phys.*, 18, 275 (1950).

TABLE III. THE WEIGHT (%) $\chi_{s\to4}$ IN THE GROUND STATE WAVE FUNCTIONS OF ISOMERIC AMINOPYRIDINES

	% weight of $\chi_{s\to4}$	pK_a at 20°C
4-Amino-pyridine	6.9	9.17
2-Amino-pyridine	2.3	6.86
3-Amino-pyridine	1.4	5.98

3-amino-pyridine as shown in Table III. This is in accordance with the conclusion obtained by the qualitative discussion of resonance theory. In addition, this is in good correspondence with the experimental pK_a values as indicated in Table III, if it is allowed to be assumed that pK_a is proportional to the π-electron density on ring nitrogen[18],**. In Table IV, the calculated and observed spectra are compared, where only the two bands which originate from the transitions to the lowest and second lowest excited states are shown, because of the lack of experimental values for the other states.

TABLE IV. CALCULATED AND OBSERVED SPECTRA OF ISOMERIC AMINO-PYRIDINES

Excitation energy (eV.) Calcd.	Obsd.[a]	Obsd. intensity[a] (ε_{max})
	2-Amino-pyridine	
4.865	4.20	4000
5.266	5.26	12000
	3-Amino-pyridine	
4.845	4.13	3000
5.137	5.18	10000
	4-Amino-pyridine	
5.114	~4.6	weak
4.973	5.1	14000

a) Ref. 6.

In Table IV, we have assigned the 5.114 eV. band of 4-amino-pyridine to the observed lowest energy band because, according to the calculated result, this band can be regarded as a slightly modified L_b band and consequently is likely to be weak. Contrary to this, the 4.973 eV. band is likely to be strong since it is the intramolecular charge transfer band. Accordingly we have assigned this band to the observed strong band at 5.1 eV.

It is evident from Table IV that the calculated two excitation energies in the case of 4-amino-pyridine are close to each other, while those in the case of the other isomers are more separated. This theoretical prediction is in qualitative or semiquantitative agreement with the experimental observation. Eventually, the general features of electronic spectra and structure of the isomeric amino-pyridines are well comprehended by the present calculation assuming the amino-form of these molecules.

Summary

The electronic spectra and structure of isomeric amino-pyridines have been studied theoretically employing the general method for the study of a composite system. The calculated results correspond satisfactorily with the experiment, in general, and the nature of electronic transitions in these molecules has been made clear. Thus it is evident that there is no difficulty in assuming the amino-form of these molecules in interpreting theoretically their electronic spectra and structure.

We are grateful to Dr. S. Nagakura of the University of Tokyo, Mr. T. Morita of Tokyo Metroporitan University and Mr. T. Kubota of Shionogi Co., Ltd. for their fruitful discussions.

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** Of course, this is no more than a limited and very approximate treatment as pointed out elesewhere[a].

a) S. Mataga and N. Mataga, *Z. physik. Chem. N. F.*, in press; S. Tsuno and N. Mataga, *Busseiron Kenkyu*, **3**, Ser. 2, 665 (1958).