Electronic Structure and Spectra of s-Tetrazine

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(Received December 18, 1957)

Recently, we have studied the electronic structure and the spectra of some nitrogen heterocycles using a semiempirical LCAO SCF MO method[1]. Our investigation has given a theoretical ground to the classification of the spectra of nitrogen heterocycles which has been made by Zanker[2] in analogy to the spectra of aromatic hydrocarbons. The cause of the intensification of ^1L_b band in a nitrogen heterocycle compared with the corresponding aromatic hydrocarbon, was ascribed by some authors[3,4], for example, in the case of pyridine and benzene, to the mixing of unperturbed $^1B_{2u}$ state to which transition from the ground state is virtually forbidden, with some contribution from $^1E_{1u}$ state to which transition is strongly allowed. Tsubomura[5] has studied the same problem, using an antisymmetrized product of naive MO. He has examined the above described possibility and also another possibility that, in pyridine, the lowering of molecular symmetry compared with benzene, may cause the perturbation on MO in the direction of C_{2v} axis, and this perturbation may also lead to the intensification of ^1L_b band. His conclusion is, however, that the latter effect may be small compared with the former. We have confirmed[1] that the latter effect is negligibly small compared with the former, on the basis of SCF MO. In the present paper, we shall report the results obtained for *s*-tetrazine, a typical nitrogen heterocycle, comparing them with the results for some nitrogen heterobenzenes such as pyridine and pyrazine, and discuss the nature of electonic transition in the *s*-tetrazine molecule.

Theoretical Method[1]

The present section is devoted to a brief description of the main ideas and approximations in the theory.

A) Formulation. — The theoretical method is based on the framework of the LCAO SCF MO method developed by

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[1] N. Mataga and K. Nishimoto, *Z. physik. Chem., N. F.*, **13**, 140 (1957).

[2] V. Zanker, ibid., **2**, 52 (1954).

[3] W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

[4] N. Mataga et al., This Bulletin, **29**, 373 (1956).

[5] H. Tsubomura, *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 293 (1957).

Roothaan[6] and Hall[7], with only the π-electrons considered explicitly. Its computation procedure is similar to that of Pople[8] and Ooshika[9]. The wave function for the π-electron in the ground state was taken as a Slater determinant built up from orthonormal moleculer orbitals which are themselves linear combinations of $2p\pi$ atomic orbitals $\phi_1 \ldots\ldots \phi_{2m}$ of carbon or nitrogen,

$$\psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu} \tag{1}$$

The coefficients $c_{i\mu}$ are chosen to minimize the electronic energy,

$$E = \int \chi_0 \mathbf{H} \chi_0 d\tau \tag{2}$$

where $\mathbf{H}$ is the complete electronic Hamiltonian

$$\mathbf{H} = \sum_i H_i^{core} + \sum_{i<j}^{2m} (e^2/_{ij}) \tag{3}$$

The general set of equations for $c_{i\mu}$ which has been given by Roothaan[6] can be reduced to the following eigenvalue equations, by some simplifying approximations about the integrals that arise[8-10].

$$\sum_{\nu} F_{\mu\nu} c_{i\nu} = \varepsilon_i c_{i\mu} \tag{4}$$

where

$$F_{\mu\mu} = H_{\mu\mu} + \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\kappa(\neq\mu)} P_{\kappa\kappa} \gamma_{\kappa\mu} \tag{5}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \tag{6}$$

$$P_{\mu\nu} = 2 \sum_{j=1}^{m} c_{i\mu} c_{i\nu} \tag{7}$$

$\gamma_{\mu\nu}$ is the interelectronic Coulomb repulsion integral

$$\gamma_{\mu\nu} = \int \phi_{\mu}^*(1) \phi_{\nu}^*(2) \frac{e^2}{r_{12}} \phi_{\mu}(1) \phi_{\nu}(2) \mathrm{d}v_1 \mathrm{d}v_2 \tag{8}$$

$H_{\mu\mu}$ are the diagonal matrix elements of the core Hamiltonian for all atoms,

$$\begin{aligned} H_{\mu\mu} &= \int \phi_{\mu}^* \left\{ -\frac{1}{2} \nabla^2 - \sum_{\kappa} V_{\kappa} \right\} \phi_{\mu} \mathrm{d}v \\ &= \int \phi_{\mu}^* \left\{ -\frac{1}{2} \nabla^2 - V_{\mu} \right\} \phi_{\mu} \mathrm{d}v \\ &\quad - \sum_{\kappa(\neq\mu)} \int \phi_{\mu}^* V_{\kappa} \phi_{\mu} \mathrm{d}v \\ &= \alpha_{\mu} - \sum_{\kappa(\neq\mu)} \gamma_{\kappa\mu}' \end{aligned} \tag{9}$$

where

$$\alpha_{\mu} = \int \phi_{\mu}^* \left\{ -\frac{1}{2} \nabla^2 - V_{\mu} \right\} \phi_{\mu} \mathrm{d}v \tag{10}$$

$$\gamma_{\kappa\mu}' = \int \phi_{\mu}^* V_{\kappa} \phi_{\mu} \mathrm{d}v \tag{11}$$

α_{μ} may be regarded as a quantity characteristic to μ atom in an appropriate valence state and for our purpose, it may be satisfactory to assume, $\gamma_{\kappa\mu}' = \gamma_{\kappa\mu}$[8].

We denote $H_{\mu\nu}$, the off-diagonal matrix elements of the core Homiltonian, as $\beta_{\mu\nu}$,

$$\beta_{\mu\nu} = \int \phi_{\mu}^* \left\{ -\frac{1}{2} \nabla^2 - \sum_{\kappa} V_{\kappa} \right\} \phi_{\nu} \mathrm{d}v \gamma_{\kappa\mu} \tag{12}$$

then the matrix elements of the ground state Fock Hamiltonian may be written as follows, using the approximations described above,

$$F_{\mu\mu} = \alpha_{\mu} + 1/2 P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\kappa(\neq\mu)} (P_{\kappa\kappa} - 1) \tag{13}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 1/2 P_{\mu\nu} \gamma_{\mu\nu} \tag{14}$$

When the self-consistent problem for the ground state has been solved by a cyclic process, the unoccupied orbitals $\psi_{m+1} \ldots\ldots \psi_{2m}$ can be used to construct configurational wave functions for excited states. We shall write ${}^1\chi_{i\to k}$ for the singlet configurational wave function in which one electron is excited from an occupied orbital ψ_i to an unoccupied orbital ψ_k. The corresponding triplet wave function will be written ${}^3\chi_{i\to k}$, and $({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{j\to l})$ and $({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{j\to})$ represent the matrix elements of total Hamilton $\mathbf{H}$ by these wave functions. Then the excitation energies corresponding to the transition $i \to k$ are expressed as follows for singlet and triplet respectively :

$$\begin{aligned} E({}^1\chi_{i\to k}) &= ({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{i\to k}) - (\chi_0|\mathbf{H}|\chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik|G|ik) + 2(ik|G|ki) \end{aligned} \tag{15}$$

$$\begin{aligned} E({}^3\chi_{i\to k}) &= ({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{i\to k}) - (\chi_0|\mathbf{H}|\chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik|G|ik) \end{aligned} \tag{16}$$

where

$$(pq|G|rs) = \int \psi_p^*(1) \psi_q^*(2) \frac{e^2}{r_{12}} \psi_r(1) \psi_s(2) \mathrm{d}v_1 \mathrm{d}v_2 \tag{17}$$

The interconfigurational matrix elements may be written in a similar way

$$({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{i\to k}) = 2(jk|G|li) - (jk|G|il) \tag{18}$$

$$({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{i\to k}) = -(jk|G|il) \tag{19}$$

An excited state wave function Ψ_{α} is approximated by a linear combination of singly excited configuration functions $\chi_{i\to k}$'s.

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[6] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).
[7] G. G. Hall, *Proc. Roy. Soc.*, **A205**, 541 (1951).
[8] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).
[9] Y. Ooshika, *J. Phys. Soc. Japan*, **12**, 1238 (1957)
[10] J. A. Pople, *Trans. Faraday. Soc.*, **49**, 1357 (1953).

The oscillator strength, f, is calculated by the method described by Mulliken and Rieke,

$$f=1.085\times10^{11}\omega_{0\alpha}\sum_{r=x,y,z}[Q_{0\alpha}{}^{r}]^{2} \qquad (20)$$

where $\omega_{0\alpha}$ is the frequency of the $\chi_0\rightarrow\Psi_\alpha$ transition in cm^{-1}.

B) Semiempirical Evaluation of Integrals.—Molecular integrals appeared in Eqs. 13 and 16 are evaluated by semiempirical procedure analogous to, but somewhat different from those given by Pariser and Parr[11], Ooshika[9] and Pople[10].

B1. The value of α_μ was taken to be equal to $-I_\mu$, where I_μ is the ionization potential of μ atom in the appropriate atomic valence state[12]. $\beta_{\mu\nu}$ for C–N and N–N were taken from Pariser and Parr[11] and Paoloni[13], respectively, for nearest neighbours and neglected for more distant neighbors:

$$\beta_{\mathrm{CN}}=-2.576\,e.v.,\quad \beta_{\mathrm{NN}}=-2.35\,e.v.^{*}$$

B2. To estimate the two center Coulomb repulsion integrals of the type $\gamma_{\mu\nu}$, we used the following approximation,

$$\gamma_{\mu\nu}=e^2/R_{\mu\nu} \qquad (21)$$

$$R_{\mu\nu}=a+r_{\mu\nu} \qquad (22)$$

where $r_{\mu\nu}$ is the interatomic distance between μ and ν atoms. a is a parameter, which is determined in the following way, using valence state ionization potential I_μ and electron affinity A_μ in the same valence state. For homonuclear two centers, we put

$$\gamma_{\mu\mu}=e^2/R_{\mu\mu}=e^2/a=I_\mu-A_\mu \qquad (23)$$

In the case of heteronuclear two centers, i.e. carbon and nitrogen, we take as $e^2/R_{\mu\mu}$, simple arithmetic mean of $e^2/R_{\mu\mu}$'s for carbon and nitrogen. The values of a thus evaluted are, $a_{\mathrm{CC}}=1.328\,\text{Å}$, $a_{\mathrm{CN}}=1.212\,\text{Å}$ and $a_{\mathrm{NN}}=1.115\,\text{Å}$. The geometrical structure of s-tetrazine has been determined by Bertinotti, Giacomello and Liquori[14], by means of X-ray diffraction. The values of $r_{\mu\nu}$'s necessary for the evaluation of $\gamma_{\mu\nu}$'s and oscillator strength were taken from this work.

Results and Discussion

As pointed out previously[1], the replacement of —CH= with —N= can be regarded as a small perturbation, and the SCF MO's of nitrogen hetrocycles are nearly close to the naive MO's obtained by ordinary procedure, assuming the Coulomb integral at nitrogen atom, α_{N}, to be equal to $\alpha+0.5\beta$.

We have chosen the naive MO's of s-tetrazine obtained in this way as a starting MO's for the SCF calculation. Thus the self-consistent problem for s-tetrazine has been solved and the resulting SCF MO's and MO energies are collected in Table I.

TABLE I

SCF MO'S AND MO ENERGIES OF *s*-TETRAZINE

Symmetry	$\varepsilon_i(e.v.)$	
b_{2u}	−15.531	$\phi_1=0.4277\sigma_1+0.3667\sigma_2$
b_{1g}	−12.759	$\phi_2=0.5000\sigma_3$
b_{3g}	−11.973	$\phi_3=0.3256\sigma_4+0.5365\sigma_5$
a_{1u}	− 2.899	$\phi_4=0.5000\sigma_6$
b_{2u}	− 1.573	$\phi_5=0.2592\sigma_1-0.6046\sigma_2$
b_{3g}	0.975	$\phi_6=0.4374\sigma_4-0.3424\sigma_5$

$\sigma_1=(\phi_2+\phi_3+\phi_5-\phi_6)$, $\sigma_3=(\phi_1+\phi_4)$, $\sigma_5=(\phi_2+\phi_3-\phi_5-\phi_6)$

$\sigma_2=(\phi_2-\phi_3-\phi_5+\phi_6)$, $\sigma_4=(\phi_1-\phi_4)$, $\sigma_6=(\phi_2-\phi_3+\phi_5-\phi_6)$

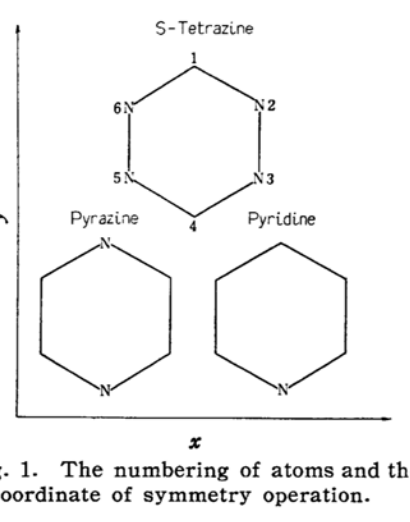

Fig. 1. The numbering of atoms and the coordinate of symmetry operation.

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[11] R. Pariser and R. G. Parr, (a) *J. Chem. Phys.*, **21**, 466 (1953): (b) ibid., **21**, 767 (1953): (c) ibid., **23**, 711 (1955); (d) R. Pariser, ibid., **24**, 250 (1956).

[12] The values of ionization potentials and electron affinities in the valence state are taken from: H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

[13] L. Paoloni, *J. Chem. Phys.*, **25**, 1277 (1956).

*) Note added in proof: Paoloni has used the ASMOCI method. Although he has employed the value −2.34 e.v. in ref. 13), he has pointed out in another place§ that β_{NN} could be as low as −1 e.v. if one invokes the configuration interaction among χ_0, $\chi_{2\rightarrow6}$ and $\chi_{1\rightarrow4}$. However, in our present theory which takes into consideration only a limited amount of configuration interaction, the best choise of β_{NN} value seems to be the one employed here. The author is grateful to Dr. L. Paoloni of Rome University for illuminating discussions on this point.

§ L. Paoloni, Gazz. chim. ital., **87**, 313 (1957).

[14] F. Bertinotti, G. Giacomello and A. M. Liquori, *Acta Cryst.*, **8**, 513 (1955); ibid., **9**, 510 (1956).

TABLE II

THE ENERGIES OF CONFIGURATIONS AND THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS*

$$\Psi({}^1B_{3u}{}^-)=0.8691{}^1\chi_{3\to4}-0.4945{}^1\chi_{2\to5} \qquad E({}^1\chi_{3\to4})=5.7479$$

$$\Psi({}^1B_{3u}{}^+)=0.4945{}^1\chi_{3\to4}+0.8691{}^1\chi_{2\to5} \qquad E({}^1\chi_{2\to5})=7.2810$$

$$({}^1\chi_{3\to4}\mid \mathbf{H}\mid {}^1\chi_{2\to5})=1.2901$$

$$\Psi({}^3B_{3u}{}^-)=0.2181{}^3\chi_{3\to4}-0.9759{}^3\chi_{2\to5} \qquad E({}^3\chi_{3\to4})=3.4231$$

$$\Psi({}^3B_{3u}{}^+)=0.9759{}^3\chi_{3\to4}+0.2181{}^3\chi_{2\to5} \qquad E({}^3\chi_{2\to5})=5.8077$$

$$({}^3\chi_{3\to4}\mid \mathbf{H}\mid {}^3\chi_{2\to5})=-0.5607$$

$$(34\mid G\mid 34)=5.6509, \qquad (34\mid G\mid 43)=1.1624,$$

$$(25\mid G\mid 25)=5.3782, \qquad (25\mid G\mid 52)=0.7366$$

$$\Psi({}^1B_{1u}{}^-)=0.0927{}^1\chi_{2\to4}-0.9957{}^1\chi_{3\to5} \qquad E({}^1\chi_{2\to4})=6.8708$$

$$\Psi({}^1B_{1u}{}^+)=0.9957{}^1\chi_{2\to4}+0.0927{}^1\chi_{3\to5} \qquad E({}^1\chi_{3\to5})=9.9633$$

$$({}^1\chi_{2\to4}\mid \mathbf{H}\mid {}^1\chi_{3\to5})=-0.2899$$

$$\Psi({}^3B_{1u}{}^-)=0.1598{}^3\chi_{2\to4}-0.9871{}^3\chi_{3\to5} \qquad E({}^3\chi_{2\to4})=3.1924$$

$$\Psi({}^3B_{1u}{}^+)=0.9871{}^3\chi_{2\to4}+0.1598{}^3\chi_{3\to5} \qquad E({}^3\chi_{3\to5})=6.5663$$

$$({}^3\chi_{2\to4}\mid \mathbf{H}\mid {}^3\chi_{3\to5})=-0.5607$$

$$(24\mid G\mid 24)=6.6683, \qquad (24\mid G\mid 42)=1.8392,$$

$$(35\mid G\mid 35)=3.8329, \qquad (35\mid G\mid 53)=1.6985$$

* The energies are in unit of *e. v.*

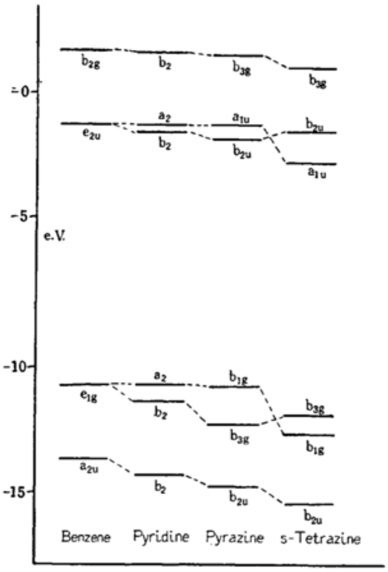

Fig. 2. SCFMO energies of benzene, pyridine, pyrazine and *s*-tetrazine.

The numbering of atoms and the coordinate for the symmetry operation are shown in Fig. 1. For the purpose of comparison, the SCF MO energies are indicated in Fig. 2 together with those of benzene, pyridine and pyrazine[1].

It is evident from Fig. 2 that both of the doubly degenerate benzene MO's e_{1g} and e_{2u} are split into two MO's with different energies in pyridine, pyrazine and *s*-tetrazine owing to the lowering of molecular symmetry. In pyrazine, b_{1g} is higher than b_{3g} in the occupied MO's, and in the vacant MO's a_{1u} is higher than b_{2u}. When molecular symmetry is reduced from D_{2h} in pyrazine to C_{2v} in pyridine, a_{1u} and b_{1g} become a_2, and b_{2u} together with b_{3g} become b_2. In addition, the former is higher than the latter, in the case of pyridine, both in the occupied and the vacant MO's. In the case of *s*-tetrazine, the relative order of the coresponding levels is reversed. The cause of this reversal may plausibly be attributed to the strengthening of the core potential, resulting from the increase of the number of nitrogen atoms. The excited state wave functions, energies of configarations and the values of interconfigurational matrix elements are given in Table II.

The calculated excitation energies and oscillator strengths are collected in Table III, in comparison with the observed values. Unfortunately, the experimental

TABLE III

EXCITATION ENERGIES AND OSCILLATOR STRENGTHS

Symmetry		Excitation energy (*e.v.*)		Oscillator strength	
Group theory	Platt	calc.	obs.	calc.	obs.
${}^1B_{3u}{}^-$	${}^1L_b$	5.013	4.96[a]	0.11	—
${}^1B_{1u}{}^+$	${}^1L_a$	6.842	—	0.43	—
${}^1B_{3u}{}^+$	${}^1B_b$	8.015	—	1.35	—
${}^1B_{1u}{}^-$	${}^3L_a$	9.990	—	0.73	—
${}^3B_{1u}{}^+$	${}^3L_a$	3.101	—	0	—
${}^3B_{3u}{}^+$	${}^3B_b$	3.298	—	0	—
${}^3B_{3u}{}^-$	${}^3L_b$	5.933	—	0	—
${}^3B_{1u}{}^-$	${}^3B_a$	6.657	—	0	—

a) Ref. 15)

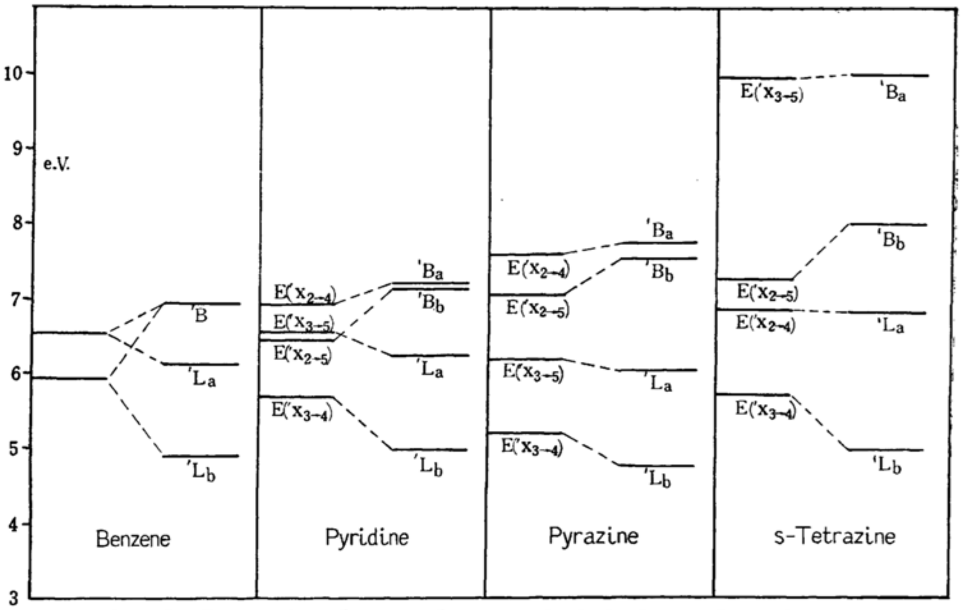

Fig. 3. Interactions between lower excited singlet configurations.

data are not sufficient, and only the value of excitation energy for the lowest singlet $\pi\to\pi$ transition is available[15]. For this transition, the calculated excitation energy agrees satisfactorily with the observed one.

The configuration integration between the singlet excited configurations are illustrated in Fig. 3 together with results[1] for benzene, pyridine, for the purpose of comparison. It is clear, from the results given in Fig. 3, that the configuration interaction plays a very important role for the determination of the spectra. Let us consider, for example, the case of the lowest singlet excited state, $^1B_{3u}$. The two configurations, $^1\chi_{3\to4}$ and $^1\chi_{2\to5}$ are degenerate in benzene, and the degree of splitting due to configuration interaction is very large. The two configurations are no longer degenerate in pyridine, *s*-tetrazine and pyrazine, and the energy difference between the two configurations becomes larger in this order. The magnitude of the splitting is, however, the smaller, the larger is the energy difference between the two configurations. Thus the relative hight of $^1B^-{}_{3u}$ state in this series of nitrogen heterocycles is approximately unchanged, and almost the same as that in benzene. This circumstance of the configuration interaction in nitrogen heterocycles has already been discussed qulitatively by Tsubomura[5], and his conclusion is confirmed by our quantitative study described above. It may be a very interesting problem whether such an argument is still applicable to the electronic spectra of pyridinium ion, the lowest excited state of which has almost the same excitation energy as that of pyridine*.

As mentioned above, we have pointed out previously[1], that the perturbation on MO by hetro-replacement may have only small influence on the oscillator strength, and almost all the part of the latter may arise from the inequality of *a* and *b* in Eq. 24.

$$\Psi(\Gamma)=a\chi_1+b\chi_2 \tag{24}$$

where $\Psi(\Gamma)$ is an excited-state wave function and χ_1 and χ_2 are two configurations interacting upon each other.

That the same circumstance prevails also in the case of *s*-tetrazine is evident from the following analysis. Let us put $a=b$ in Eq. 24, then the oscillator strengths of *s*-tetrazine become as follows.

Γ	f
$^1B^-{}_{3u}$	0.01
$^1B^+{}_{1u}$	0.008

In fact, these values of f are very small compared with the actual values of

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[15] A. M. Liquori and A. Vaciago, *Ric. Scient.*, **26**, 181 (1956); *Gazz. chim. ital.*, **86**, 759 (1956).

* In this respect, the present author, in collaboration with Miss S. Tsuno, is now working out the electronic structure of pyridinium ion.

calculated oscillator strength and are almost negligible.

Now let us refer to the polarizations of transitions in this molecule, though there are no such experimental data available at present.

With the results and reasonings described hitherto, the polarization of transition to the lowest excited state may be polarized in x direction of Fig. 1, where, in addition to *s*-tetrazine, pyridine and pyrazine are pictured for the convenience of comparison, their corresponding transitions being polarized also in x direction of the figure. The transition to the second excited state, however, is polarized in y direction in *s*-tetrazine as well as in pyridine and pyrazine.

Eventually, the spectral similarity of *s*-tetrazine with the parent hydrocarbon and the other nitrogen heterocycles such as pyridine and pyrazine originates from the close correspondence of the MO's of the former with those of the latter, though the MO energies of *s*-tetrazine are considerably different from those of the others. Whereas the relative order of b_{1g} and b_{3g} or a_{1u} and b_{2u} orbitals in energy scale is reversed in *s*-tetration compared with those in pyrazine or pyridine, the result of configuration interaction gives the excitation energy of the transition to the lowest excited state which is almost the same as those of pyrazine, pyridine and benzene, in good agreement with the experimental observation.

Summary

(1) π-Electronic structure and the nature of the electronic transitions in the *s*-tetrazine molecule has been elucidated using the semiempirical LCAO SCF MO method.

(2) There is satisfactory agreement between the calculated and the observed values of the excitation energy for the transition to the lowest excited state.

(3) Tsubomura's qualitive argument concerning the influence of configuration interaction on the lowest energy transition of nitrogen heterocycles has been confirmed by the quantitative calculation.

(4) The cause of the intensification of ^1L_b band compared with the parent hydrocarbon has been analysed by the same method employed previously[1], and it has been confirmed that, also in the case of *s*-tetrazine the perturbation on MO by hetero-replacement has only a small influence on the oscillator strength.

(5) The spectral simirarity of nitrogen heterocycles with the parent hydrocarbon has been ascribed to the fact that their MO's correspond closely each other, and it has been pointed out that the configuration interaction plays a very important role in the determination of spectra, which is also a cause for the spectral similarity.

The autor expresses his gratitude to Professor S. Mizushima of Tokyo University for his encouragement. He also expresses his cordial thanks to Professor R. Fujishiro for his interest and encouragement during the present study. He is grateful to Dr. S. Nagakura of Tokyo University and Dr. H. Tsubomura of Tokyo University for their illuminating discussions. He also express his hearty thanks to Mr. K. Nishimoto and Miss S. Tsuno for their helpful discussions.

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