Electronic Spectra of Quinoline and Isoquinoline and the Mechanism of Fluorescence Quenching in These Molecules

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In the previous papers[1,2] we have reported detailed theoretical studies on the electronic structure and the nature of electronic transitions of some nitrogen heterocycles, using the semiempirical SCF method. The detailed Hartree-Fock SCF study has been made only for nitrogen heterobenzenes, and some semiquantitative extentions to larger molecules such as acridine and phenazine have been made on the basis of the results obtained for nitrogen heterobenzenes. Even by the latter very approximate method, the general feature of the electronic spectra is fairly well comprehended. In the present report and also in following one, we shall employ a more rigorous method and give a more detailed interpretation and reasoning on the nature of the electronic transitions in some two and three ring-nitrogen heterocycles such as quinoline, isoquinoline, acridine and phenazine.

Method

The Hartree-Fock self-consistent field method applied to molecules in terms of MO's, determines the best MO's for approximate ground state, and these MO's may also be satisfactory in describing the excited states[3]. As pointed out by McWeeny[4], however, it may be possible that other choices of MO's may give a comparable result for the interpretation of electronic spectra. From such a viewpoint, rather than pursuing a laborious iterative calculation of SCF, we have assumed that SCF MO's of the parent hydrocarbon[5], naphthalene, may be a satisfactory approximation to the MO's of quinoline and isoquinoline for the description of the excited states. Then the orbital energy of the i-th orbital, ε_i, and the excitation energy of the $i\to k$ transition, $E(\chi_{i\to k})$ may be calculated by the following equation[1,2].

$$\varepsilon_i=\int\phi_i^*F\phi_i dv=\sum_{\mu,\nu}c^*_{i\mu}c_{i\nu}F_{\mu\nu} \tag{1}$$

where F is the Fock's Hamiltonian and ϕ_i is the LCAO MO of the parent hydrocarbon,

$$\phi_i=\sum_{\mu}c_{i\mu}\phi_\mu \tag{2}$$

$$F_{\mu\mu}=\alpha_\mu+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \tag{3}$$

$$F_{\mu\nu}=\beta_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \tag{4}$$

The last term in the right hand side of Eq. 3 vanishes because of the uniform charge density, $P_{\kappa\kappa}=1$, in the parent hydrocarbon.

$$F_{\mu\mu}=\alpha_\mu+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} \tag{3'}$$

$$E(^1\chi_{i\to k})=\varepsilon_k-\varepsilon_i-(ik|G|ik)+2(ik|G|ki), \tag{5}$$

$$E(^3\chi_{i\to k})=E(^1\chi_{i\to k})-2(ik|G|ki) \tag{6}$$

where,

$$(ik|G|ik)=\int\phi_i^*(1)\phi_k^*(2)\frac{e^2}{r_{12}}\phi_i(1)\phi_k(2)\,dv_1dv_2 \tag{7}$$

$$(ik|G|ki)=\int\phi_i^*(1)\phi_k^*(2)\frac{e^2}{r_{12}}\phi_k(1)\phi_i(2)\,dv_1dv_2 \tag{8}$$

Expanding ϕ_i's in terms of AO's, and neglecting the differential overlap, Eqs. 7 and 8 become as follows,

$$(ik\mid G\mid ik)=\sum_{\mu,\nu}c^*_{i\mu}c_{i\mu}c^*_{k\nu}c_{k\nu}\gamma_{\mu\nu}, \tag{9}$$

$$(ik\mid G\mid ki)=\sum_{\mu,\nu}c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}\gamma_{\mu\nu}. \tag{10}$$

ε_i and $E(\chi_{i\to k})$ thus calculated for nitrogen heterocycles may be different from the corresponding quantities of the parent hydrocarbon by small amounts $\delta\varepsilon_i$ and $\delta E(\chi_{i\to k})$, because of slight changes in the core potential and electronic repulsion energies due to the hetero-replacement.

The expressions for $\delta\varepsilon_i$ and $\delta E(\chi_{i\to k})$ may be written as follows

$$\delta\varepsilon_i=\sum_{\mu,\nu}c^*_{i\mu}c_{i\nu}(\delta F_{\mu\nu}) \tag{11}$$

$$\delta F_{\mu\mu}=\delta\alpha_\mu+\frac{1}{2}P_{\mu\mu}(\delta\gamma_{\mu\mu}) \tag{12}$$

$$\delta F_{\mu\nu}=\delta\beta_{\mu\nu}-\frac{1}{2}P_{\mu\nu}(\delta\gamma_{\mu\nu}) \tag{13}$$

$$\delta E(^1\chi_{i\to k})=\delta\varepsilon_k-\delta\varepsilon_i-\sum_{\mu,\nu}c^*_{i\mu}c_{i\mu}c^*_{k\nu}c_{k\kappa}(\delta\gamma_{\mu\nu})+2\sum_{\mu,\nu}c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \tag{14}$$

1) N. Mataga and K. Nishimoto, *Z. physik. Chem.*, N. F. in press.
2) N. Mataga, This Bulletin **31**, 453 (1958).
3) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).
4) R. McWeeny, *Proc. Phys. Soc.*, **A70**, 593 (1957).
5) We have calculated the electronic spectra of some unsaturated hydrocarbons by the self-consistent field method, using our semiempirical parameters described in refs. 1) and 2). N. Mataga and K. Nishimoto, to be published elsewhere.

$$\delta E(^3\chi_{i\to k}) = \delta E(^1\chi_{i\to k}) - 2\sum_{\mu,\nu} c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \qquad (15)$$

In addition, we have taken into consideration some amount of configuration intereactions, which is restricted only to those invoked in the calculation of parent hydrocarbon.

The interconfigurational matrix elements may be expressed as follows.

$$(^1\chi_{i\to k}|\mathbf{H}|^1\chi_{j\to l}) = -(jk|G|il) + 2(jk|G|li) \qquad (16)$$

$$(^3\chi_{i\to k}|\mathbf{H}|^3\chi_{j\to l}) = (^1\chi_{i\to k}|\mathbf{H}|^1\chi_{j\to l}) - 2(jk|G|li) \qquad (17)$$

where,
$$(jk \mid G \mid il) = \sum_{\mu,\nu} c^*_{j\mu}c_{i\mu}c^*_{k\nu}c_{l\nu}\gamma_{\mu\nu}, \qquad (18)$$

$$(jk \mid G \mid li) = \sum_{\nu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}\gamma_{\mu\nu}. \qquad (19)$$

The difference between these quantities and the corresponding ones of the parent hydrocarbon may be written as

$$\delta(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l}) = -\sum_{\mu,\nu} c^*_{j\mu}c_{i\mu}c^*_{k\nu}c_{l\nu}(\delta\gamma_{\mu\nu}) + 2\sum_{\mu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \qquad (20)$$

$$\delta(^3\chi_{i\to k} \mid \mathbf{H} \mid {}^3\chi_{j\to l}) = \delta(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l}) - 2\sum_{\mu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \qquad (21)$$

It will be shown in the next paragraph that $\delta\varepsilon_i$, $\delta E(_{i\to k})$ and $\delta(\chi_{i\to k} \mid \mathbf{H} \mid \chi_{j\to l})$ are really very small and only a small percent of ε_i, $E(\chi_{i\to k})$ and $(\chi_{i\to k} \mid \mathbf{H} \mid \chi_{j\to l})$, respectively.

Therefore, our present treatment may be regarded also as a kind of perturbation theory*.

Previously, Pariser and Parr[6] calculated the electronic spectra of some nitrogen heterobenzenes by their semiempirical ASMO method including configuration interaction, using, however, MO's of benzene.

Our procedure described above may be equivalent to theirs, but ours is in terms of Hartree-Fock SCF theory, involving configuration interaction. In view of the approximate nature of our treatment and also for lack of experimental data, values of $\gamma_{\mu\nu}$ necessary for the evalution of electronic repulsion integrals $\gamma_{\mu\nu}$ and oscillator strengths are taken from those of naphthalene. The method of the semiempirical evalution of $\gamma_{\mu\nu}$ and the calculation of oscillator strength are the same as in the previous reports[1,2].

Results and Discussions

In Table I, the orbital energies of highest and second highest occupied levels and lowest and second lowest vacant levels which are responsible for transitions to lower excited states, are given together with their $\delta\varepsilon_i$.

In the case of isoquinoline, all levels are more or less depressed ; in the case of quinoline, however, fourth and sixth levels are depressed on the one hand and fifth and seventh levels are lifted on the other hand. The perturbation caused by the hetero-replacement on α-position is different from that on β-position, in this way.

TABLE I*
(in unit of e. v.)

	Quinoline		Isoquinoline	
i	ε_i	$\delta\varepsilon_i$	ε_i	$\delta\varepsilon_i$
4	−10.791	−0.205	−11.196	−0.611
5	− 9.494	0.120	− 9.767	−0.153
6	− 2.734	−0.348	− 2.518	−0.133
7	− 1.209	0.205	− 1.442	−0.027

* $\delta\varepsilon_i = \varepsilon_i - \varepsilon^0_e$, where ε^0_i is the corresponding orbital energy of naphtalene.

In the following, we shall give a detailed account only about the transition to the lowest excited singlet state, the intensity of which is most remarkably influenced by the hetero-replacement. We shall also give some arguments on the corresponding triplet state, i. e. ^3L_b, in relation to the mechanism of fluorescence quenching in quinoline.

The excited state wave functions, energies of configurations and the values of interconfigulational matrix elements as well as their differences from the corresponding quantities of the parent hydrocarbon are given in Table II.

In Table III, the calculated excitation energies and oscillator strengths indicated in comparison with the observed values.

The calculated values of excitation energies are in a satisfactory agreement with observed ones and the slight difference between the observed spectra of quinoline and isoquinoline is well interpreted, i. e., the theory predicts that the excitation energy of isoquinoline is slightly smaller than that of quinoline, in agreement with the observation.

The experimental values of oscillator strengths of these molecules are uncertain, and only the values of log ε_{max} are given in Table III.

By an inspection of this table, the observed intensity of quinoline seems almost the same as that of isoquinoline. The ^1L_b band of quinoline, however, is strongly superposed by ^1L_b band, the intensity of which may be scarcely affected by the hetero-replacement*, in contradistinction to the case of isoquinoline, where the superposition is not so much remarkable

* The present writer is now pursuing a calculation on the electronic structure of nitrogen heterocycles, which is based on stadard method of the perturbation theory.

6) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

* The results for ^1L_a state together with those for ^1B_b and ^1B_a states will be published shortly.

TABLE II
(in units of *e. v.*)

Quinoline

$\Psi(^1L_b)=0.757\,^1\chi_{4\to6}-0.652\,^1\chi_{5\to7}$, $E(^1\chi_{4\to6})=4.864$, $E(^1\chi_{5\to7})=5.092$

$\Psi(^3L_b)=0.537\,^3\chi_{4\to6}-0.843\,^3\chi_{5\to7}$, $E(^3\chi_{4\to6})=3.857$, $E(^3\chi_{5\to7})=4.085$

$(^1\chi_{4\to6}\mid \mathbf{H}\mid {}^1\chi_{5\to7})=0.763$, $(^3\chi_{5\to6}\mid \mathbf{H}\mid {}^3\chi_{5\to7})=-0.244$.

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}\gamma_{\mu\nu}=4.199,$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}=0.503.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu},\quad \sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}\gamma_{\mu\nu}=0.244.$$

$\delta E(^1\chi_{4\to6})=-0.176$, $\delta E(^1\chi_{5\to7})=0.052$, $\delta(^1\chi_{4\to6}\mid \mathbf{H}\mid {}^1\chi_{5\to7})=0.000$,

$\delta E(^3\chi_{4\to6})=-0.149$, $\delta E(^3\chi_{5\to7})=0.079$, $\delta(^2\chi_{4\to6}\mid \mathbf{H}\mid {}^3\chi_{5\to7})=0.003$.

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}(\delta\gamma_{\mu\nu})=\sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}(\delta\gamma_{\mu\nu})=0.033.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}(\delta\gamma_{\mu\nu})=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}(\delta\gamma_{\mu\nu})=0.000.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}(\delta\gamma_{\mu\nu})=0.000.$$

Isoquinoline

$\Psi(^1L_b)=0.410\,^1\chi_{4\to6}-0.911\,^1\chi_{5\to7}$, $E(^1\chi_{4\to6})=5.513$, $E(^1\chi_{5\to7})=4.101$

$\Psi(^3L_b)=0.883\,^3\chi_{4\to6}-0.469\,^3\chi_{5\to7}$, $E(^3\chi_{4\to6})=4.454$, $E(^3\chi_{5\to7})=3.043$

$(^1\chi_{4\to6}\mid \mathbf{H}\mid {}^1\chi_{5\to7})=0.798$, $(^3\chi_{4\to6}\mid \mathbf{H}\mid {}^3\chi_{5\to7})-0.260$.

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}\gamma_{\mu\nu}=4.224.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}=0.529.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu},\quad \sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}\gamma_{\mu\nu}=0.260.$$

$\delta E(^1\chi_{4\to6})=0.473$, $\delta E(^1\chi_{5\to7})=-0.393$, $\delta(^1\chi_{4\to6}\mid \mathbf{H}\mid {}^1\chi_{5\to7})=0.035$.

$\delta E(^3\chi_{4\to6})=0.448$, $\delta E(^3\chi_{5\to7})=0.095$, $\delta(^3\chi_{4\to6}\mid \mathbf{H}\mid {}^3\chi_{5\to7})=-0.013$.

$$\sum_{\mu,\alpha} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}(\delta\gamma_{\mu\nu})=\sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}(\delta\gamma_{\mu\nu})=0.058.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}(\delta\gamma_{\mu\nu})=\sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}(\delta\gamma_{\mu\nu})=0.026.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}(\delta\gamma_{\mu\nu})=0.016.$$

TABLE III

	Excitation Energy (*e.v.*)		Oscillator Strength	
	Calcd.	Obsd.[a,b]	Calcd.	Obsd.[a] (log ε_{max})
		Quinoline		
^1L_b	4.207	3.96	0.01	3.4
^3L_b	4.240	—	0.00	—
		Isoquinoline		
^1L_b	3.742	3.86	0.16	3.6
^3L_b	4.592	—	0.00	—

a) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley and Sons, 1951.

b) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

because ^1L_a band is shifted to a somewhat shorter wave length side and ^1L_b band to a longer wave length side in some degree compared with those of quinoline.

Therefore, in reality, the oscillator strength of quinoline may be far smaller than that of isoquinoline, in qualitative agreement with the theoretical prediction.

Now, some considerations on the mechanism of the fluorescence quenching in nitrogen heterocycles will be given on the basis of the present theoretical calculation. Previously, we have studied the hydrogen bonding effect on the fluorescence of quinoline and acridine in non-polar solvent mixed with various proton donors, in order to elucidate the mechanism of inner quenching in these molecules[7]. The results were as follows. The larger the relative fluorescence yields of hydrogen bonded nitrogen heterocycles become, the stronger the donating powers of proton donors are, and from this fact, it has become clear that the cause of the remarkable inner quenching in these molecules compared with the parent aromatic hydrocarbons may be attributable to the interaction between n- and π-electrons in the

7) N. Mataga and S. Tsuno, This Bulletin, **30**, 368 (1957).

excited state, which may probably induce the radiationless transition to the ground state, directly or indirectly.

Moreover, we have found an interesting fact that the difference in the emitting π-electronic state leads to the different behavior of these nirogen heterocycles in fluorescene quenching by a halogen atom.

Although the increase in fluorescence yields of quinoline and acridine by hydrogen bonding with ethanol or by proton addition in aqueous solution is almost the same, the fluorescence yield of quinoline hydrogen bonded with trichloracetic acid is rather small compared with the fluorescence yield in ethanol solution, in contradistinction to the fact that the fluorescence yield of acridine is greatly enhanced by hydrogen bonding with trichloracetic acid. This distinction in these two molecules was ascribsd to the difference of emitting π-electronic state as follows[7].

In aromatic hydrocarbons, such as benzene, naphthalene and anthracene, there exists ^3L_b state which has the same energy as ^1L_b, but for ^1L_a, there exists no such circumstance, the energy of ^3L_a state being considerably different from that of ^1L_a[5,8,9]. If the lowest singlet excited state is ^1L_b, the phosphorescence transition occurs with relative ease probably by the process, $^1L_b \rightarrow {}^3L_b \rightarrow {}^3L_a \rightarrow$ ground state. However, when the lowest singlet excited state is ^1L_a, phosphorescence transition may be very difficult. We have assumed[7] that the analogous situation probably prevails also in these heterocyclic molecules, because of the close similarity of the electronic spectra of the latter with those of isoelectronic aromatic hydrocarbons. Now, as shown in Table III, the results of the present calculation clearly indicate that, at least in the case of quinoline, there exists ^3L_b state which has almost the same energy as ^1L_b. Thus, on the basis of the present results, it is confirmed that, at least in the case of quinoline, the near-by existence of a halogen atom may easily accelerate $^1L_b \rightarrow {}^3L_b$ process owing to the spin orbital perturbation, but it may be difficult for such a situation to be realized in acridine*. The circumstance in the case of isoqunoline may be somewhat different from the situation described above, because ^3L_b is somewhat higher than ^1L_b. Unfortunately, such an experimental observation for the case of isoquinoline is not yet available. After all, the close spectral similarity of quinoline and isoquinoline with naphthalene and also the intensification of ^1L_b band due to heteroreplacement are well comprehended by the present perturbation method. Moreover, the assumed effect of emitting π-electronic state on the quenching phenomenon, has been confirmed on the theoretical ground.

Summary

1. A pertubation theory based on the Hartree-Fock SCF theory including a limited number of configuration interactions was applied to quinoline and isoquinoline.

2. The theory satisfactorily interprets the excitation energies and oscillator strengths of ^1L_b bands of these nitrogen heterocycles.

3. The previous assumption concerning the effect of π-electronic state on the fluorescence quenching in nitrogen heterocycles due to the near-by existence of a halogen atom, was confirmed for the case of quinoline, on the basis of the theoretical calculation.

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8) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
9) J. A. Pople, *Proc. Phys, Soc.*, **68A**, 81 (1955).

* Detailed discussions on acridine will be given in a following paper.