The Electronic Structures of Azine Compounds. I. The Molecular Structures and the Electronic States of Fluoflavine and Fluorubine

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The recent development of the organic chemistry concerning azine compounds has made it possible to offer us some various theoretically interesting problems. This series includes as its purpose the semi-empirical discussions on such problems, in terms of the simple LCAO molecular orbital theory, which would permit us to take a bird's-eye view of the electronic structures of the azine compounds.

As the first venture, fluoflavine (dihydro-5, 6, 11, 12-tetraaza-naphtacene) and fluorubine (dihydro-5, 6, 7, 12, 13, 14-hexaaza-pentacene) were chosen for consideration here. The electronic absorption spectra were observed and discussed. Attention was also paid to the position of *meso*-H atoms of the molecules.

Experimental

Difficulty arises in the selection of a good solvent of fluoflavine and fluorubine, as none of the non-polar solvents dissolve these compounds or do not dissolve them completely. As a result of the solvent test extended to ten odd solvents and their mixtures*, slight solubility was observed on several alcoholic solvents, where the solubility slightly increased as the size of the alkyl group increased**. Here, considering the absorption ranges of the solvents, *n*-propylalcohol was used. Fluoflavine saturates up to 1/20,000 mol, and fluorubine to 1/150,000 mol. already, so the confidence regarding the absolute intensity of the absorption is slight.

For the observation, a Beckman quartz DU-type spectrophotometer was used. Samples used were synthesized by the members of Kawai Laboratory of Tokyo University of Education. Observed curves were shown in Fig. 1.

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* Methyl- to octyl-alcohol, benzene, toluene, $CHCl_4$, CCl_4, dioxane, etc., and their mixtures.

** These samples are slightly soluble in dioxane and in mixtures of CCl_4 and alcohols. But in the former case, the formation of the hydrogen bonds is apprehended, and in the latter, the tendency of deepening of color shows the possibility of the formation of some intermolecular compounds.

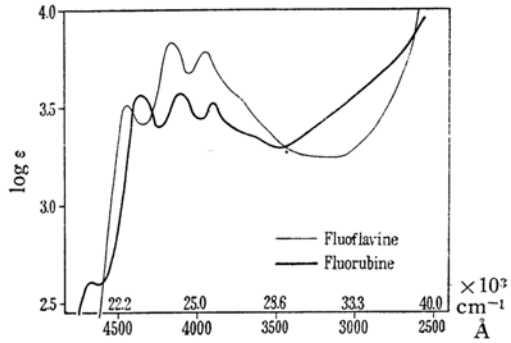

Fig. 1. The absorption curves of fluoflavine and fluorubine.

Interpretation of Spectra

Platt[1] presumed that a weak absorption tail near 24,000 cm^{-1} of phenazine is to be the transition of *n*-type. If we admit his postulate that, with increasing size of the parent conjugated systems, n-π transition moves to the red only about half as far as the longest wave-length π-π transition, we may anticipate that the n-π transition will be hidden when the molecule becomes larger and larger. Moreover, in the case of dihydro-azine as fluoflavine, *n*-electron of the hydrogenated N atoms (N_H atoms) conjugates with the π-electron system increasing the number of the filled orbitals, and so the n-π transition will move farther to the blue side. Because of these aspects, and also from the standpoint of the transition intensity, the longest strong wave-length absorption of fluoflavine may be assumed to be the π-π transition.

In fluorubine, the increase of the number of non-hydrogenated N atoms two to four, will produce some interaction to shift the *n*-band to red, just as the increase of the number of N atom one to two, produced the absorption tail on phenazine which was not present in acridine. Actually, fluorubine has a weak absorption near 21,000 cm^{-1}. If we assume this absorption to be of *n*-type, fluorubine has come to have three absorption maxima in the longest wave-length π-π band just as in the case of fluoflavine.

Such a way of thinking does not conflict with the spectral results of hemofluorindine (dihydro-5, 7, 12, 14-tetraaza pentacene) which was reported by Badger et al.[2] Hemofluorindine has only two nonconjugated *n*-electrons, so n-π transition does not show the independent maximum.

Concerning these dihydro-azine compounds, many isomers are possible in regard to the positions of *meso*-H atoms (N_H atoms). Up to the present, no report has been presented about the isolation of these isomer, and the deduction will be drawn that either there is only the most stable isomer or the tautomerism between these isomers. The resemblance of these spectra to that of the corresponding polyacene compounds, seems to favor the former assumption[3]. But according to Badger et al.[4], the absorption curves of azine compounds generally lack the detailed structures as compared to that of polyacene. The measurement of the oscillator strengths will give the information about this problem, while we simply assume the former hypothesis, namely the presence of only one isomer to each dihydro-azine compound, leaving out further detailed discussion.

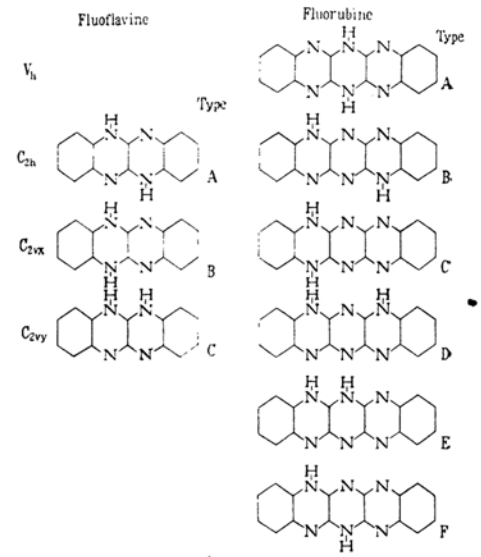

Fig. 2. The quoted isomers of fluoflavine and fluorubine.

MO Calculation

Simple molecular orbital calculations are applied to the various isomers of fluoflavine and fluorbine, as well as to the azine compounds which have the same skeleton with the above dihydro-azine compounds. (see Fig. 2)

The π-orbital energies of the azine compounds: 5, 6, 11, 12-tetraaza-naphtacene and 5, 6, 7, 12, 13, 14-hexaaza-pentacene, are calculated usng the ordinary simple variation method. For each isomer of fluoflavine and fluorubine, the second-order perturbation method is used, taking the changes of Coulomb integral values affected by the introduction of *meso*-H atoms on some N atoms of the former azine molecules, as the pertur-

1) J.R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).
2) G.M. Badger and R. Pettit, *J. Chem. Soc.*, 3211 (1951).
3) A. Buraway, *J. Chem. Soc.*, 1177 (1939).
4) G.M. Badger and R. Pettit., *J. Chem. Soc.*, **1951**, 3211.

bation terms. The adoption of the perturbation method offers us the following advantages:

(1) The labor of calculation is reduced.

(2) The Coulomb integral value of N_H atoms is taken to be changeable easily, as the change of the value of perturbation.

All overlap integrals are neglected.

(1) Variation Method Calculation.—In 1951, P. O. Löwdin discussed the dipole moments of some aza-compounds to determine the most profitable Coulomb integral value α_r, for heterocyclic N atom, which was found to be $\alpha_N=\alpha_C+0.6\beta$[5]. A year later, H. H. Jaffé obtained the same conclusion from facts concerning the reactivity of some aza-compounds[6].

In this calculation we adopt the above value for α_r of every N atom. Inductive effect is assumed on the adjacents of N atoms to be 1/8 of 0.6β. After all concerns about the tolerable changes of the π-electron energies, which may be yielded by the choice of exchange integral values the privation of any reliable data compeles us to take the values as 1β indiscriminately, leaving the detailed discussion hereafter[7]. The results of the calculations are shown in Fig. 3.

(2) Perturbation Method Calculation.—P. O. Löwdin has developed this theory, making it applicable on any changes of Coulomb or exchange integral values of the molecules[8].

In general, when some Coulomb terms are perturbed by V, the π-orbital energy changes as follows:

$$\varepsilon^j=\varepsilon^{j(0)}+\sum_\mu V_\mu d_\mu^{jj(0)}+1/2\sum_{\mu\nu} V_\mu V_\nu \pi_{\mu\nu}^{jj(0)}$$

where upper indices $j, \alpha,$.....indicate the molecular orbitals, lower indices $\mu, \nu,$.....the atomic orbitals, and (o) the quantities, belonging to the original system. π is known by the name of mutability, defined as follows:

$$\pi_{\mu\nu}^{jj}=\sum_{\alpha\neq j}\frac{2d_\mu^{j\alpha}d_\nu^{j\alpha}}{(j\alpha)}$$

$$d_\mu^{j\alpha}=C_\mu^j C_\mu^\alpha$$

where C is the orbital coefficient, and $(j\alpha)$ indicates the energy difference between j-th and α-th orbitals.

For the perturbation terms, the differences of the Coulomb integral magnitudes, $\alpha_{NH}-\alpha_N=\Delta\alpha_N$, (conventionally taken to be 0.3, 0.6, and 1.2β) and the induction effects (assumed to be 1/8 for all adjacents of the perturbed atoms) are taken. In Fig. 3, the π-orbital energies of all isomers are shown in regard to the case of 0.6β perturbation. In Table II, the relations between the reduced representations of the π-orbitals and the symmetry properties of the perturbed molecules are shown.

TABLE I

THE ORBITAL ENERGIES OF 5,6,11,12-TETRAAZA-NAPHTACENE (X) AND 5,6,7,12,13,14-HEXAAZA-PENTACENE (Y)

(Calculated by the simple variation method)

$x=(\alpha-\varepsilon)/\beta$

$\beta=1$, $\alpha_N=\alpha_C+0.6\beta$, $S=0$

(X)		(Y)	
B_{3g}	−2.2752	B_{3g}	−2.2706
A_{1u}	−2.1147	A_{1u}	−2.1752
B_{3g}	−1.6657	B_{3g}	−1.8704
B_{1u}	−1.2267	A_{1u}	−1.4739
A_{1u}	−1.2056	B_{1u}	−1.2144
B_{2g}	−1.1037	B_{2g}	−1.1491
B_{3g}	−0.9373	B_{3g}	−1.1266
B_{1u}	−0.5886	A_{1u}	−0.9204
B_{2g}	0.0686	B_{1u}	−0.8050
		B_{2g}	−0.3349
A_{1u}	0.6104	B_{1u}	0.2028
B_{3g}	0.8747		
B_{1u}	1.0581	B_{3g}	0.6086
A_{1u}	1.3849	A_{1u}	0.7969
B_{2g}	1.4018	B_{2g}	1.0721
B_{3g}	1.8285	B_{3g}	1.1902
B_{1u}	1.8609	B_{1u}	1.3382
B_{2g}	2.3082	A_{1u}	1.5972
B_{1u}	2.7212	B_{2g}	1.7437
		B_{3g}	1.8939
		B_{1u}	2.1190
		B_{2g}	2.4935
		B_{1u}	2.7842

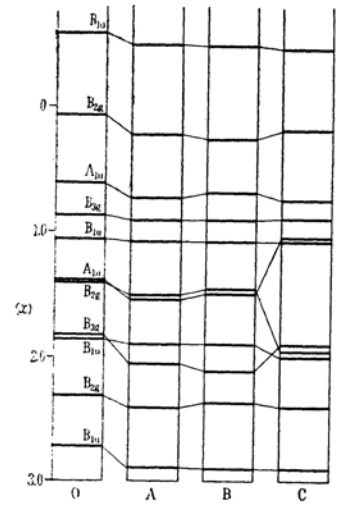

Fig. 3A. The orbital energies of each isomer of fluoflavine. (0 indicates 5, 6, 11, 12-tetraaza-naphtacene (0 was calcalculated by the variation method and the others by the perturbation method)

5) Per-Olov Löwdin, *J. Chem. Phys.*, **19**, 1323 (1951).
6) H.H. Jaffé, *J. Chem. Phys.*, **20**, 1554 (1952).
7) C.A. Coulson and J. der Heer, *J. Chem. Soc.*, **1952**, 482.
8) Per-Olov Löwdin, *J. Chem. Phys.*, **21**, 496 (1953).

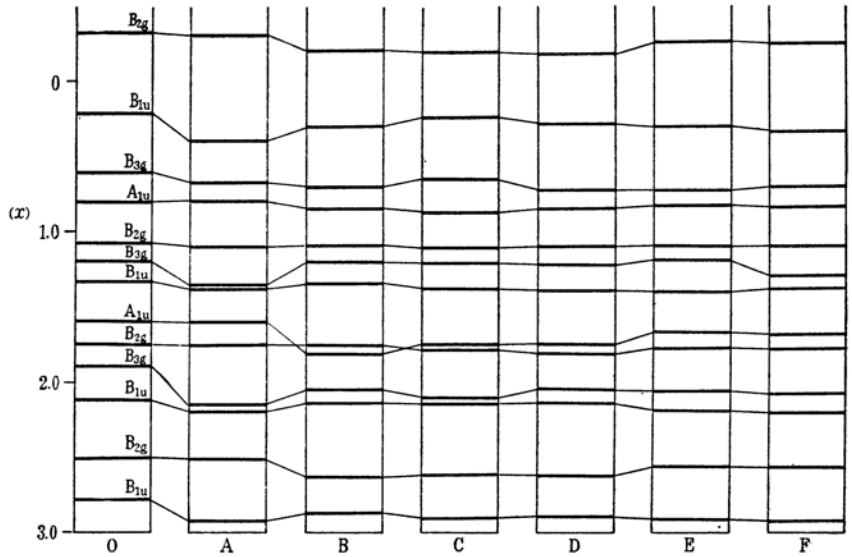

Fig. 3B. The orbtial energies of each isomer of fluorubine. (0 indicates 5: 6: 7: 12: 13: 14-hexaaza-pentacene) 0 was calculated by the variation method, and the others by the perturbation method.

TABLE II

THE RELATION BETWEEN THE REDUCED ORBITAL REPRESENTATION AND THE SYMMETRY PROPERTY OF THE MOLECULE

Symmetry property	V_h	C_{2h}	C_{2vx}	C_{2vy}
Reduced representation	A_{1u}	A_u	A_2	A_2
	B_{1u}	A_u	B_2	B_2
	B_{2g}	B_g	B_2	A_2
	B_{3g}	B_g	A_2	B_2

Discussion

1) Delocalization Energy.—The comparison of the stability are performed between the isomers using the terms of the vertical delocalization energy, defined as follows[9]:

$$\Delta\varepsilon=\varepsilon(L)-\varepsilon(D)$$

In spite of habitual suspicions which are entertained on the propriety of making it the criterion of the molecular stability, the identity of the skeletons such as between the isomers, is observed to offer us the considerable confidence in it. In Fig. 4, the delocalization energies are compared with the changes of $\Delta\alpha_N$.

In the case of fluoflavine, A-type isomer retains invariably the highest stability, but in fluorubine, the stability of A-type isomer is surpassed by B-type isomer over the $\Delta\alpha_N$ of 0.75β.

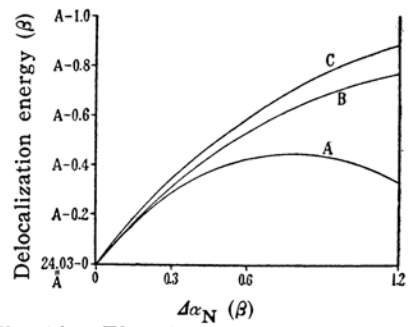

Fig. 4A. The delocalization energy of each isomer of fluoflavine.

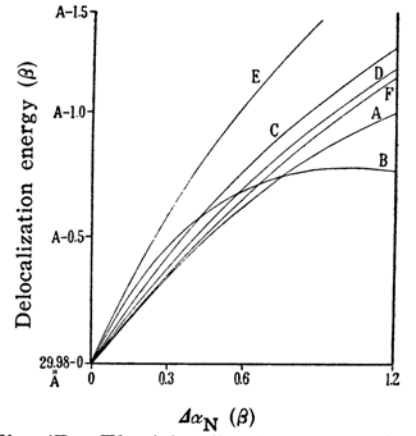

Fig. 4B. The delocalization energy of each isomer of fluorubine.

2) The Correspondency with the Absorption Curve.—The above results are examined from the aspect of correspondency with the

9) C.A. Coulson and Altmann, *Trans. Faraday Soc.*, 48, 293 (1952).

conclusion deduced from the positions of absorptions of absorption maxima. On the conversions of the π-electron transition energies of polyacene molecules (in β unit) into the positions of the longest wave-length absorptions (in wave number unit), good agreements are obtained in taking the exchange rates increasing with the size of molecular skeletons. Here, the rates are taken to agree with the transition energies of naphtacene and pentacene (polyacene molecules which have the same skeletons with fluoflavine and fluorubine respectively) calculated by the simplest MO calculations, with the observed positions of the longest wave-length absorptions: naphtacene 35,500 cm^{-1}/β, and pentacene 39,000 cm^{-1}/β. In Fig. 5, calculated positions of the longest wave-length absorption of each isomer is shown with the magnitude of $\Delta\alpha_N$.

We saw in Fig. 1, the so called blue shift with increase of molecular size: fluoflavine to fluoflavine. In Fig. 4, the curve of the most stable isomer of fluorubine A-type, rises up rapidly with the increase of $\Delta\alpha_N$ to cross to that of fluoflavine A-type about the position of $\Delta\alpha_N=0.4\beta$. Consequently, so long as the $\Delta\alpha_N$ is larger than 0.4β, a satisfactory explanation is obtained on the observed blue shift. (Fluorubine B-type does not explain the blue shift, in removing to further red side with increase of the perturbation.)

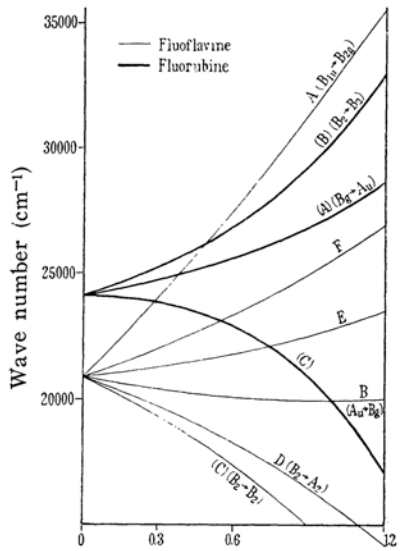

Fig. 5. The calculated longest-wave π-π transition energies of fluoflavine and fluorubine.

3) Conclusion.—As the result of the above discussions, unless we assume the existence of only one isomer, only A-types of both molecules satisfy all the conditions quoted here, and in this case, $\Delta\alpha_N$ must be larger than 0.4β and smaller than 0.75β.

If we set on Fig. 5, the calculated difference between the absorption positions of both molecules, 500 cm^{-1}, the perturbation is concluded by 0.45β. The observed values, 33,500 cm^{-1} for fluoflavine, and 23,000 cm^{-1} for fluorubine, are somewhat smaller than the calculated values corresponding to the perturbation of 0.45β, but within the permissible ranges.

Summary and Conclusion

1) The absorption spectra of fluoflavine and fluorubine were observed in *n*-propyl alcohol solution.

2) The longest wave-length π-π transitions were observed in 22,500 cm^{-1} for fluoflavine, and in 23,000 cm^{-1} for fluorubine.

3) The n-π transition was observed near 21,000 cm^{-1} in fluorubine, while no independent n-π absorption was observed in fluoflavine.

4) The simple MO calculations were applied to 5, 6, 11, 12-tetraaza-naphtacene and 5, 6, 7, 12, 13, 14-hexaaza-pentacene.

5) The π-orbital energies of all isomers of fluoflavine and fluorubine were calculated using the second- order perturbation-method.

6) Supposing that only one isomer exists on each molecule, the blue shift, appearing in fluoflavine to fluorubine, was explained by setting the following structures: 5, 11-dihydro-5, 6, 11, 12-tetraaza-naphtacene for fluoflavine, and 6, 13-dihydro-5, 6, 7, 12, 13, 14-hexaaza-pentacene for fluorubine.

7) The above conclusion was consistant with the conclusion from the comparisons of the vertical delocalization energies.

8) To satisfy the conclusions 6) and 7), the Coulomb integral value of N_H atom must be between $\alpha_C+1.0\beta$ and $\alpha_C+1.35\beta$. Consequently, twice the Coulomb integral value as large as that of N atom will be the most appropriate.

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