The Electronic Structures of Azine Compounds. II. The General Considerations on the Electronic Structures of Azine and Dihydroazine Compounds

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Introduction

In the preceding paper[1], the semi-empirical LCAO molecular orbital calculations were made on some azine and dihydroazine compounds. In this paper, for the purpose of generalizing the above conclusions, the scope of the discussions is extended to ten odd azine, dihydroazine, and aza compounds. The results are arranged and investigated systematically from several viewpoints: electronic states, molecular structures, stabilities, etc.

Experimental

With the object of replenishing the spectra data for the sphere of azine compounds, the electronic absorption spectrum was taken on quinoxaline (1, 4-diaza-naphthalene). The sample used was synthesized by the members of Kawai Laboratory of Tokyo University of Education. For the solvent, anhydrous methanol was always employed. The other experimental conditions were similar to that previously described. The result is shown in Fig. 1.

From the standpoint of the transition intensity and the correspondency with the absorption curves of phenazine or quinoline, the strong absorption maximum near 32000 cm^{-1}, may be considered as the π–π transition.

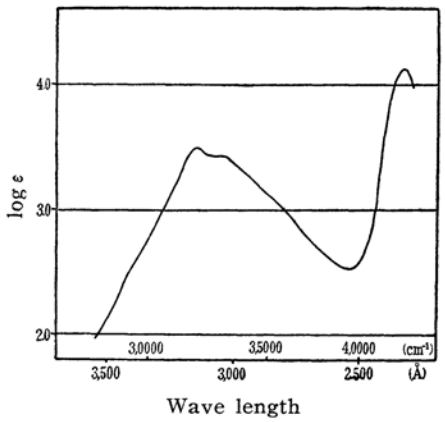


Fig. 1. The absorption spectrum of 1:4-diaza-naphthalene (quinoxaline) (in anhydrous methanol).

1) Y. Akimoto, This Bulletin 29, 460 (1956).

MO Calculation

MO calculations have been carried out for all the molecules shown in Fig. 2. The same calculations were extended to several aza compounds. The π-electron energies of the molecules in the heavy line frames, were calculated by the simplest variation method, and the others by the second order perturbation method, taking as the parent molecules the corresponding molecules which are in the heavy line frames, and for the perturbation term the changes of Coulomb integral values affected by the replacements by N atoms or the introductions of meso–H atoms[2]. According to the conclusions of the previous paper[1], Coulomb integral values are taken as follows:

for every N atom, $\alpha_c+0.6\beta$
for every N_H atom, $\alpha_c+1.2\beta$
for every adjacent atom of
N or N_H atoms (r), $\alpha_c+\frac{1}{8}\sum(\alpha_r-\alpha_c)$

Regarding the other conditions and the detailed explanations of the calculations, the previous paper[1] is to be quoted.

The results of the calculations are summarized in Table I–II, and Fig. 3. Table I shows the results of the variation method calculations applied to the "parent molecules" of the following perturbation calculations. Fig. 3 indicates the π-electron energy states of all molecules referred to above. The underlined column shows the results obtained by the variation method calculations, and the others by the perturbation calculations. In Table II, two calculation methods: variation and perturbation methods, are compared in regard to the numerical results. The first column indicates the electron energies cal-

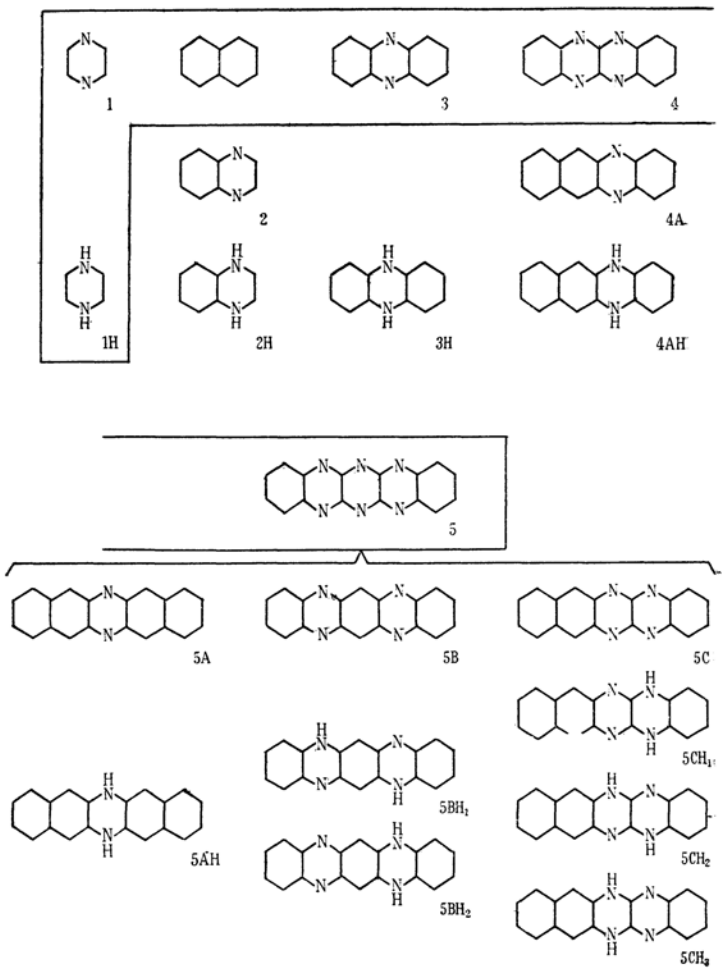


Fig. 2. The model numbers of azine and dihydroazine compounds quoted for the calculations.

2) Per-Olov Löwdin, *J. Chem. Phys.*, **21**, 496 (1953).

culated by the second order perturbation method taking anthracene as the parent molecule, and the second column by the simplest variation method. The result is in a satisfactory agreement.

TABLE I

THE ORBITAL ENERGIES OF "PARENT MOLECULES" CALCULATED BY THE SIMPLE VARIATION METHOD

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

Pyrazine (x)		Naphthalene (x)		Phenazine (x)	
				B_{3g}	−2.2834
				A_{1u}	−1.9760
		B_{3g}	−2.0000	B_{3g}	−1.3384
		B_{1u}	−1.6180	B_{1u}	−1.2493
B_{3g}	−1.5716	A_{1u}	−1.6180	B_{2g}	−0.9878
A_{1u}	−0.8500	B_{3g}	−0.6180	A_{1u}	−0.9618
B_{1u}	−0.2394	B_{2g}	−0.6180	B_{1u}	−0.1565
B_{2g}	1.1500	A_{1u}	0.6180	B_{3g}	0.6132
B_{3g}	1.9216	B_{1u}	0.6180	A_{1u}	1.0129
B_{1u}	2.5894	B_{2g}	1.6180	B_{2g}	1.0368
		B_{3g}	1.6180	B_{1u}	1.4908
		B_{1u}	2.0000	B_{3g}	1.6836
				B_{2g}	2.0261
				B_{1u}	2.5900

On 5, 6, 11, 12-tetraaza-naphtacene, and 5, 6, 7, 12, 13, 14-hexaaza-pentacene, cf. ref. (1).

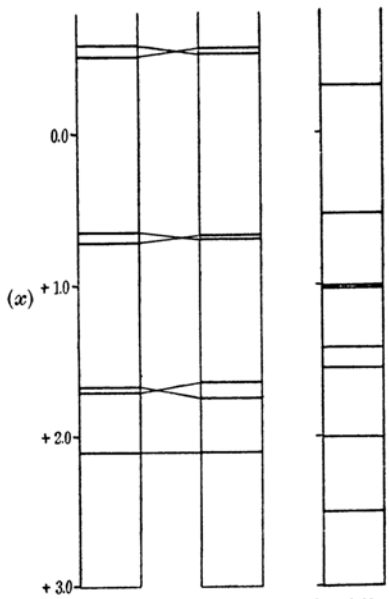


Fig. 3a. The electronic states of some aza compounds.

$x=\frac{\varepsilon-\alpha}{\beta}$ (Calculated by the perturbation method).

TABLE II

THE COMPARISON OF TWO CALCULATION METHODS ON THE ORBITAL ENERGIES OF ANTHRACENE

	Calculated by perturbation method (A)	Calculated by variation method (B)	Differences (A)-(B)
B_{3g}	0.415	0.414	+0.01
A_{1u}	1.000	1.000	0
B_{2g}	1.000	1.000	0
B_{1u}	1.414	1.414	0
B_{3g}	1.412	1.414	−0.02
B_{2g}	2.000	2.000	0
B_{1u}	2.416	2.414	−0.02

Discussion

1) **Delocalization Energy.**—In consideration of the previous paper's results[1], the positions of meso–N atoms are determined in comparing the vertical delocalization energy values (vertical delocalization energy $\Delta\varepsilon$ is defined as follows:

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

cf. ref. (1))

over all isomers of each compound (see Table III). Underlined isomers are the most stable ones.

Through the considerations continued from the preceeding paper[1], as far as dihydroazines are concerned, the following practical principle may be established. *The stabilities of dihydroazine isomers increase according to the following order of molecular symmetry:* $C_{2v}\rightarrow C_{2h}\rightarrow V_h$. In Table IV, the vertical delocalization energy of the most stable isomer of each dihydroazine compound is compared with that of its parent azine compound.

In general, the reactivities and the stabilities of meso dihydro derivatives increase rapidly with the increase of the number of rings of azine compounds[3]: It is impossible to oxidize fluoflavine to parent azine compound[4], while quinoxaline has not any stable dihydroazine derivatives. Table IV shows that delocalization energies of all dihydroazine compounds are smaller than those of the corresponding azine compounds, nevertheless on account of the differences which the number of atoms or π-electrons make, the direct comparisons can not provide the conclusion that all dihydroazine compounds are less stable than the corresponding azine compounds. However, the tendency to contract the difference of both energies according to the increase of molecular sizes, enables

3) G.M. Badger and R. Pettit, *J. Chem. Soc.*, **1951**, 3211.

4) S. Kawai and S. Noguchi, private communication.

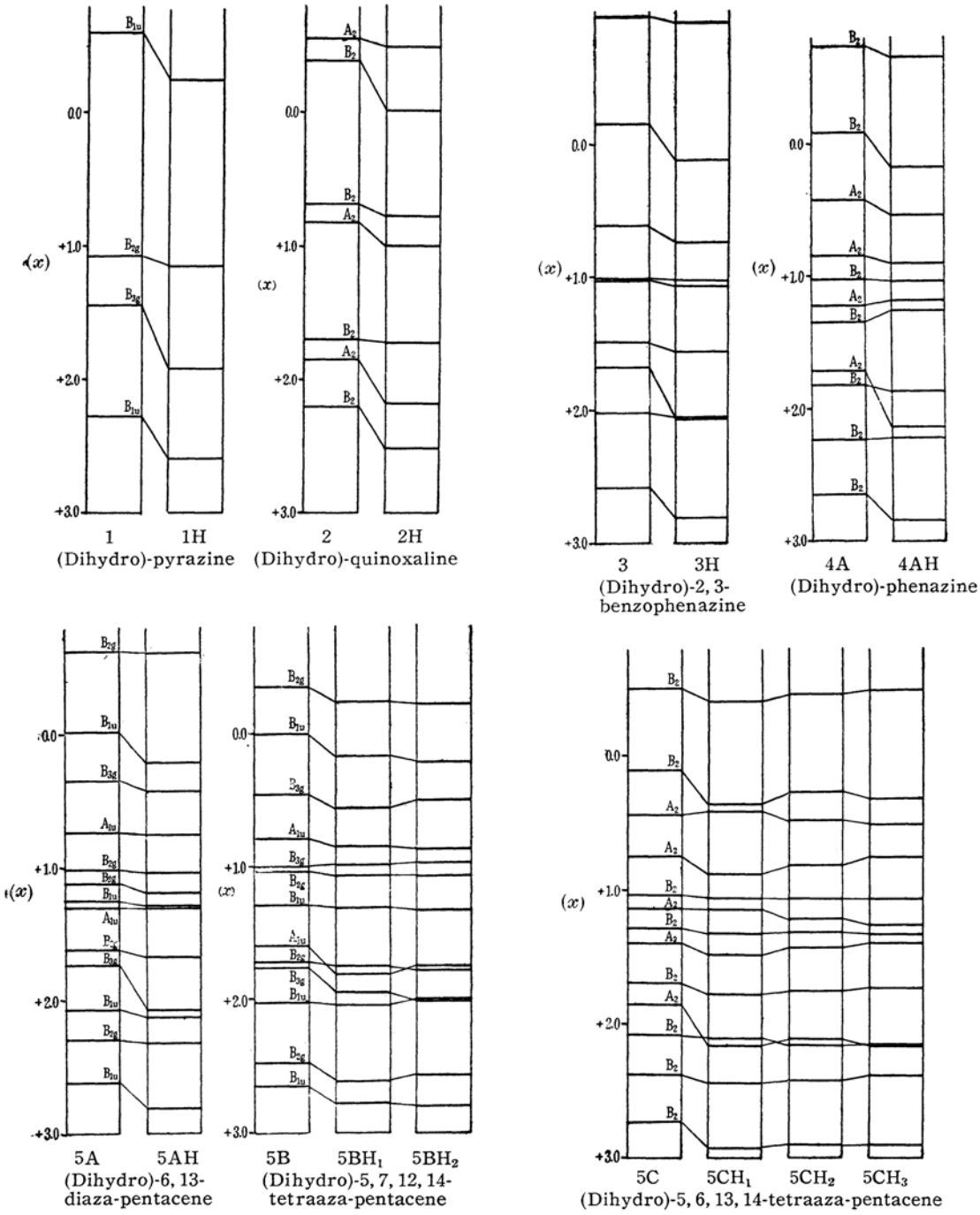


Fig. 3b. The electronic states of some azine and dihydroazine compounds.

$$x = \frac{\varepsilon - \alpha}{\beta}$$

us to predict the stabilities from the ground of the vertical delocalization energies. The reduction rates of the energies, shown in the last column of Table IV, seem to give us some criteria. None of the molecules which have the reduction rates over 17% have any stable dihydroazine derivatives, and less than 6% of any azine compounds. About 9% of the rate seems to correspond to the equal stability between azine and dihydroazine compounds.

In 1926, Dutt reported on his accomplishment of synthesis of 5, 7, 12, 14-tetraza-pentacene[5]. But the result of the re-examination which was followed by Badger et al.[3] was negative. On 5, 6, 11, 12-tetraza-naphtacene, since Hinsberg had reported on his success of the syntheses in 1896[6], no report has been presented, while, the recent result of the re-examination performed by Kawai and Noguchi is negative[4]. Such being the case, the prediction of the stability based on the reduction rates of the delocalization energies, may, though it has not any close theoretical backing, be put to the practical uses.

TABLE III
THE COMPARISONS OF THE DELOCALIZATION ENERGIES ON DIHYDROAZINE ISOMERS

Compounds	Position of meso-H atoms (Model number)	Delocalization energy (β)
Dihydro-5, 7, 12, 14-tetraaza-pentacene	5, 14 ($5BH_2$)	28.920
	5, 12 ($5BH_1$)	28.979
Dihydro-5, 6, 13, 14-tetraaza-pentacene	5, 14 ($5CH_1$)	29.296
	5, 13 ($5CH_2$)	29.205
	6, 13 ($5CH_3$)	29.201

2) The position of the Longest Wave-length Absorption.—Supposing that only the most stable isomer exists on each molecule, the longest wave-length π-π absorption is calculated. In Table V, these values are compared with the observed ones. The conversion rates are chosen so that the calculated transition energies of the corresponding polyacene molecules, agree with the observed absorptions[7] (see ref. (1)). In Fig. 4, these

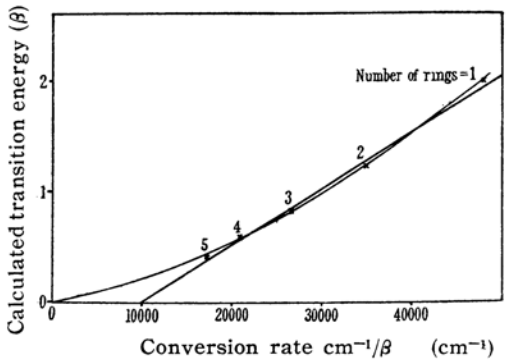
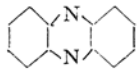
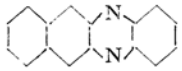
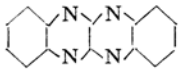
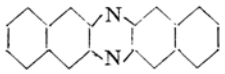
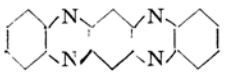
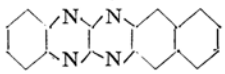
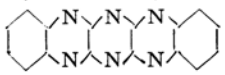


Fig. 4. The conversion rates for the absorption wave number calculations.

TABLE IV
THE DELOCALIZATION ENERGIES OF AZINE AND DIHYDROAZINE COMPOUNDS

Group model number	Molecular structure	Delocalization energy (β) Azine (A)	Dihydroazine (B)	A-B	$\frac{A-B}{A}$
1		8.081	(5.743)	2.338	28.9
2		13.060	(10.807)	2.253	17.25
3		19.407 >	17.482	1.924	9.91
4A		25.084 <	23.103	1.981	7.89
4		/25.097/	23.614	1.483	5.91
5A		(30.808)	29.126	1.682	5.46
5B		/30.677/	28.979	1.698	5.54
5C		(30.723)	29.296	1.427	4.64
5		(30.775)	29.353	1.422	4.62

( ) Not yet synthesized.
/ / Accomplishment of synthesis was reported, but negotiated by the re-examination.
> The stability tendency.

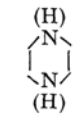
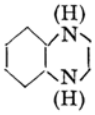
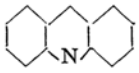
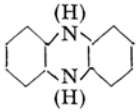
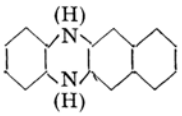
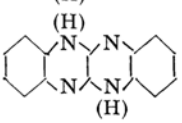
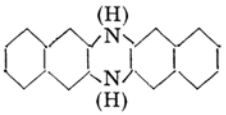
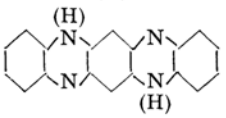
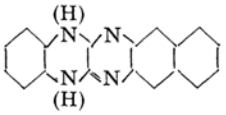
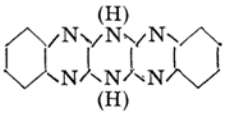
5) O. Dutt, *J. Chem. Soc.*, **1926**, 1178.
6) O. Hinsberg and J. Pollak, *Ber.*, **29**, 784 (1896).
7) E. Clar, *Ber.*, **69**, 607 (1936).

rates are shown: The smooth relations are observed between them.

The lack of the spectra data in this sphere, obstructs the overall examinations, while the presented observed values show almost perfect agreements with the calculated ones.

TABLE V

THE COMPARISONS OF THE CALCULATED LONGEST WAVE-LENGTH ABSORPTION POSITIONS WITH THE OBSERVED ONES

Group model number	Molecular skeleton	Conversion rate	Azine compounds				Dihydroazine compound				Reference
			calcd.		obs.	calcd. −obs.	calcd.		obs.	calcd. −obs.	
		(cm^{-1}/β)	(β)	(cm^{-1})	(cm^{-1})	(cm^{-1})	(β)	(cm^{-1})	(cm^{-1})	(cm^{-1})	
1		24,000	1.672	40100	38000	+2100	0.511	12300			(8)
		28,500	1.156	32900	31900	+1000	—	—			(9)
		28,500	1.198	34100	31300	+3000	—	—			(9)
2		28,500	1.070	30500	31700	−1200	0.490	14000			Present paper
		32,500	0.840	27300	28000	− 700	—	—			(10)
3		32,500	0.770	25000	27800	−2800	1.047	34000			(10)
4A		35,500	0.520	18500			0.825	29300			
4		35,500	0.542	19200			0.723	25700	22500	+3200	(1)
5A		39,000	0.377	14700			0.826	32200			
5B		39,000	0.409	16000			0.409	16000	17700	−1700	(3)
5C		39,000	0.542	21100			0.706	27500			
5		39,000	0.406	15800			0.707	27600	23000	+4600	(1)

8) W.K. Miller, S.B. Knight and A. Roe, *J. Am. Chem. Soc.*, **72**, 1629 (1950).

9) G.W. Ewing and E.A. Steck, *J. Am. Chem. Soc.*, **68**, 2181 (1946).

10) G.M. Badger, R.S. Pearce and R. Pettit, *J. Chem. Soc.*, **1951** 3198.

3) **Molecular Diagram.**—On several molecules, the charge densities and the bond orders are calculated (see Fig. 5). Except 6, 13-dihydro-5, 6, 7, 12, 13, 14-hexaaza-pentacene, all diagrams are calculated by the simplest variation method. On the former molecule, perturbation method is used in applying the following relations[1,2].

$$q_\mu^j = q_\mu^{j(0)} + \sum_\kappa V_\kappa \pi_{\mu\mu,\kappa}^{jj(0)}$$

$$p_{\mu\nu}^j = p_{\mu\nu}^{j(0)} + \sum_\kappa V_\kappa \pi_{\mu\nu,\kappa}^{jj(0)}$$

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

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

where q indicates the charge density, p, bond order, V, perturbation terms, C, orbital coefficient, and π, mutability. Upper indices j, α,……indicate the molecular orbitals, lower indices μ, ν, κ,……the atomic orbitals, (0) the quantities belonging to the original system, and $(j\alpha)$ the energy difference between j-th and α-th orbitals.

The unification of the exchange integral to 1β, takes away the significance of bond order considerably[11], while the tendency to prejudicing the orders according to the increase of azine molecule size, and to compensate the prejudice in introducing the meso-H atoms explains the above mentioned tendency which is observed on the reactivities or the stabilities of azine compound series. This tendency will support the conclusions deduced from the former vertical delocalization energy discussions. In any way, the MO recalculation based on the above diagrams, will make more reliable the conclusions stated above.

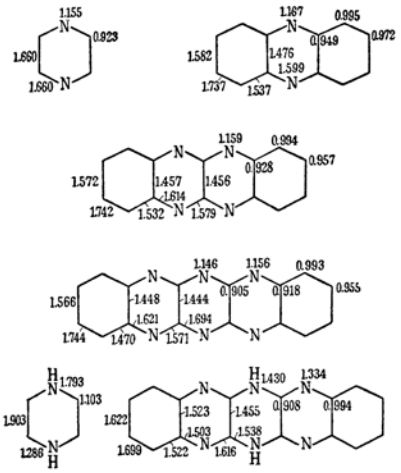


Fig. 5. The molecular diagrams of several azine and dihydroazine compounds.

11) C. A. Coulson, J. de Heer, *J. Chem. Soc.*, **1952** 482.

Summary and Conclusions

1) The absorption spectrum of quinoxaline was observed in anhydrous methanol solution.

2) The longest wave-length π-π transition was observed near 31000–33000 cm^{-1}.

3) The MO calculations were made on ten odd aza, azine, and dihydroazine compounds.

4) Comparing the vertical delocalization energies, the most stable isomer was decided as follows.

molecules	positions of meso-H atoms
dihydro-5, 7, 12, 14-tetraaza-pentacene	5, 14
dihydro-5, 6, 12, 13-tetraaza-pentacene	5, 12.

5) Concerning the stabilities of each dihydroazine isomers, the following tendency was observed. *The stabilities of dihydroazine isomers, increase according to the certain order of molecular symmetry:* $C_{2vx} \rightarrow C_{2h} \rightarrow V_h$.

6) The reduction rates of the delocalization energies, azine to dihydroazine compounds, could be a criterion to predict the stabilities of dihydroazine compound as compared with the corresponding azine compounds. When the rate was less than 6%, only the dihydroazine form could exist steadily; more than 17%, the only stable form was the azine form; and between 6–17%, both forms could exist, while the stability of the azine form was surpassed by that of the dihydroazine form near the rate of 9%.

7) The positions of the longest wave-length absorption were predicted or compared with the observed ones. Agreements were satisfactory in the permissible ranges.

8) The molecular diagrams were drawn on several azine and dihydroazine molecules, which could possibly explain the higher stabilities of dihydroazines, the larger skeletons of molecules.

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