BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 76—83 (1969)

Electronic Structure of Lone Pairs. I. Azine Compounds and Quinones*1

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(Received June 6, 1968)

Molecular orbital investigations of the electronic structures of lone pairs of some azine compounds and quinones are carried out by the Hückel method and the extended Hückel method for σ and π electron systems. The delocalization and the s–p mixing of lone pairs are investigated. Qualitative discussions of the splitting of the lone-pair levels and the calculated n–π* transitions of these compounds are made. It is revealed that the Hückel method, which does not include direct interactions, gives an incorrect prediction for the symmetry of the energy levels of pyridazine. After comparative discussions, it is concluded that the lone paris couple with each other directly "through-space" as well as "through-bond."

Many theoretical investigations1) of the electronic structures of such azine compounds as pyridine, diazines and triazine have been carried out in order to discuss the n–π* transitions in these compounds.

Since the theoretical procedure for treating the lone pair has never been settled, there exist few theoretical approaches to the problems of the delocalization of the lone pair, its hybridization, and the mode of interaction between two lone pairs in a molecule.

Recently, however, Hoffmann2) proposed an extended Hückel calculation in which all the valence electrons were taken into account and established the delocalization of the lone pair whose 2s character is less than 10%.

These conclusions were further confirmed by Lipscomb3) and his co-workers on the basis of a more rigorous SCF MO treatment. They concluded that an accurate quantitative work should take into account the appreciable amount of delocalization and the smaller 2s participation of the nitrogen lone pair than one would predict on the basis of an sp^2 hybridization.

In the present paper, we make use mainly of two alternative MO methods in order to investigate the problems stated above in azine compounds and some quinones. The first method is the Hückel treatment for σ electronic systems proposed by Sandorfy and Yosizumi4) and developed by some of the present authors.5) This will be abbreviated hereafter to as the H method. Since the resonance integrals between non-adjacent AO's are neglected, this method may be considered to treat the delocalized lone pair with the through-bond interaction.*2 The second method is the extended Hückel method, to be referred to as the E-H method. This method is suitable for discussing the electronic structure of two lone-pair couplings, "through-bond" as well as "through-space."*2

By comparative discussions, the following conclusions are obtained. The delocalization of lone-pair electrons and the appropriate mutual interaction between them must be taken into account in arriving at a better interpretation of the n–π* transitions.

The electron distribution and the splitting of the lone-pair levels due to mutual interaction as calculated by the Hückel method for σ electron systems seems to be adequate. However, as the direct interaction (through-space interaction) of the lone pair is not taken into account in this method, it gives an incorrect prediction for the symmetry of the energy levels, as in the case of pyridazine. Therefore, for a more accurate discussion of, for instance, the 2s participation in the lone pair and the interaction of two separate lone pairs, it seems better to use the extended Hückel method.

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*1 Presented at the 20th Annual Meeting of The Chemical Society of Japan, April, 1967.

1) T. Anno, *J. Chem. Phys.*, **29**, 1161, 1170 (1958); *ibid.*, **32**, 619, 867 (1960); L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

2) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2745 (1964).

3) F. P. Boer, M. D. Newton and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2361 (1966).

4) C. Sandorfy, *Can. J. Chem.*, **33**, 1337 (1955); H. Yoshizumi, *Trans. Farad. Soc.*, **53**, 125 (1957).

5) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 442, 1111 (1962); K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, *ibid.*, **35**, 38 (1962).

*2 On the through-bond and through-space couplings, see the paper by R. Hoffmann, A. Imamura and W. J. Hehre (*J. Am. Chem. Soc.*, **90**, 1499 (1968)).

Theoretical

The parameters used in the Hückel method for σ electron systems are tabulated in Table 1.

TABLE 1. PARAMETERS IN HÜCKEL CALCULATION FOR σ ELECTRON SYSTEMS

Coulomb integrals for σ system		Resonance integrals for σ systems	
C (sp^2)	α	C–C	β
N (sp^2)	$\alpha+0.2\beta$	C (sp^2)	0.38β*
H	$\alpha-0.2\beta$	C–N	β
O	$\alpha+0.3\beta$	N–N	β
		N (sp^2)	0.4β*
		C–H	0.94β
		C–O	1.2β
		O	0.3β*

* Resonance integrals between two σ orbitals belonging to the same atom.

The resonance integrals between non adjacent AO's are ignored, as is usual with the Hückel method.[5] In the extended Hückel calculations, the resonance integral, H_{rs}, is evaluated by $H_{rs}=\frac{K}{2}S_{rs}(H_{rr}+H_{ss})$, putting $K=1.75$, where S_{rs} is the overlap integral between the atomic orbitals, χ_r and χ_s. The Coulomb integral, H_{rr}, for which the valence state ionization potential is usually used, is modified to improve the overestimated electron distribution in this calculation and to obtain a more reasonable energy for the lone-pair orbital. For this purpose, we refer to the results of the application of the ω_A-technique[6] in the extended Hückel method. These H_{rr} values are listed in Table 2. The bond lengths and angles employed are shown in Fig. 1. These values are adopted with reference to the Table of Interatomic Distances edited by Sutton and the experimental results of Wheatley.[7]

TABLE 2. THE VALUES OF H_{rr}'S IN EXTENDED HÜCKEL CALCULATIONS (eV)

	s	p_x	p_y	p_z
H	-14.9			
C	-21.5	-12.0	-12.0	-11.9
N	-24.2	-11.2	-11.2	-11.9
O	-28.6	-11.7	-11.7	-12.9

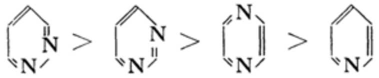
Results and Discussion

Delocalization of Lone Pair. Since the Hückel calculation needs the values of the hybridization of constituent atoms in order to estimate the Coulomb and resonance integrals of a lone-pair AO, an sp^2 hybridization for the nitrogen atom in azine compounds is assumed.

It may be noted that, in the Hückel calculation, the highest occupied σ orbitals in azine compounds are, without exception, remarkably localized on the lone-pair AO of the nitrogen atom. These MO's will be referred as lone-pair MO's hereafter in the present paper.

The electron distributions of these lone-pair MO's as obtained by the Hückel calculation are given in Fig. 2. For the diazines, the distribution is obtained by summing two lone-pair MO's, the highest occupied MO and the next highest occupied MO. For triazine and tetrazine, three and four lone-pair MO's are summed respectively. In view of the partial electron density at the lone-pair AO, about 80%—90% of the lone-pair electrons are localized on that orbital and the electron density increases with a decrease in the distance between nitrogen atoms in diazine compounds. It can also be seen that these partial electron densities run parallel with the observed pK values[8] and also with the blue shifts of the n–π^* bands,[8] accompanied by the change in solvent from cyclohexane to an aqueous solution except in the case of pyridine.

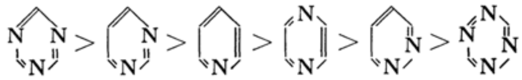
Figure 3 lists the total σ electron densities obtained by the Hückel calculation in these compounds. These electron distributions may also indicate the extent of lone-pair delocalization. Namely, the total electron density at the lone-pair AO is always less than 2, and about a 20%—30% delocalization of lone-pair electrons is observed. The total electron densities of the lone-pair AO in four heteroaromatic compounds decrease in the order:



This order is parallel with the order obtained by the partial electron densities of the lone-pair MO.

Next, for the sake of comparison, let us discuss the electron distribution of the azine compounds obtained by the extended Hückel calculation. The atomic population and the atomic orbital population of lone-pair MO's at the nitrogen atom are shown in Table 3, together with the values obtained by the Hückel calculation.

There exists a definite parallelism between the π-electron densities of the nitrogen atom obtained by the Hückel calculation and the atomic orbital populations of the p_z orbital of the nitrogen atoms in azine compounds. Namely, they decrease in the order:



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[6] H. Konishi, H. Kato and T. Yonezawa, Symposium on the electronic structure of molecules, Osaka, October, 1966.

[7] P. J. Wheatly, *Acta. Cryst.*, **13**, 80 (1960).

[8] S. F. Mason, *J. Chem. Soc.*, **1959**, 1240.

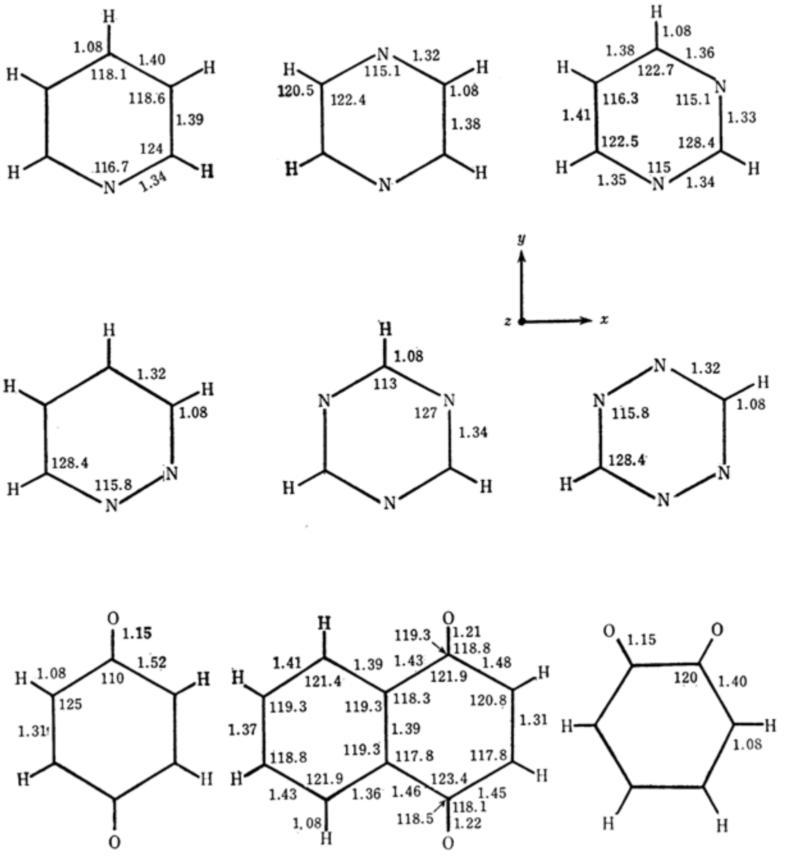


Fig. 1. Bond angles (in degree), bond lengths (in Å) and coordinate axis.

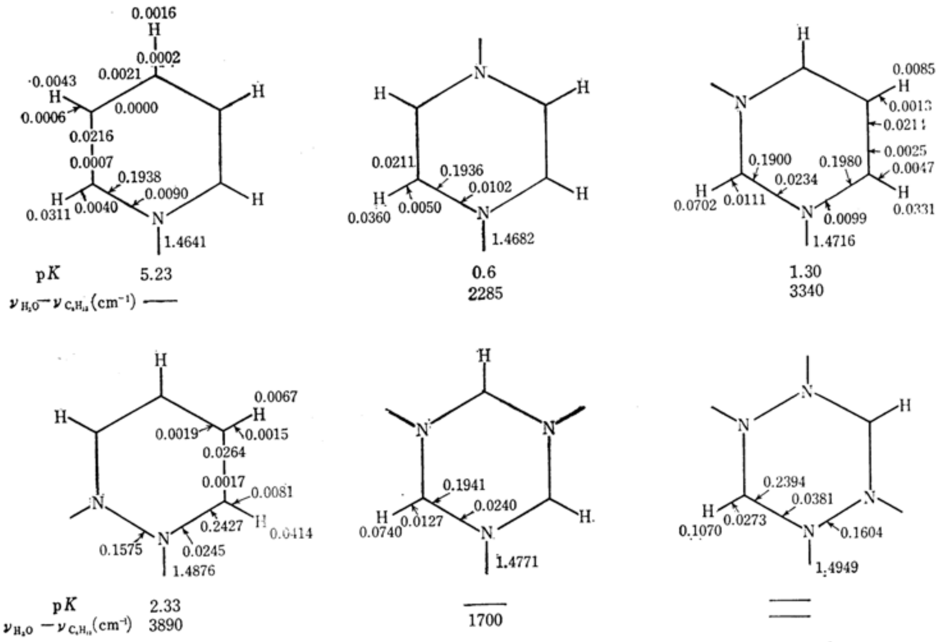


Fig. 2. The electron distribution in the lone-pair MO's of azine compounds.

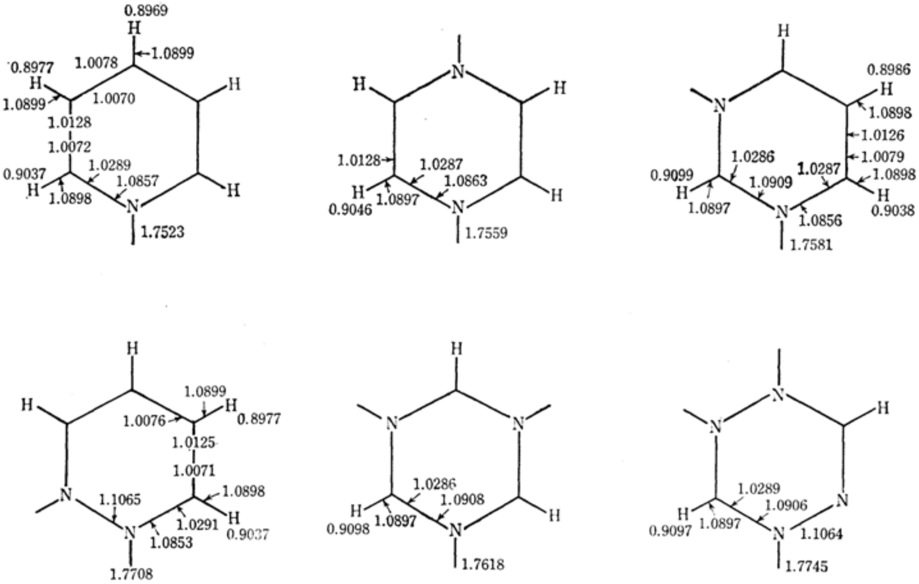


Fig. 3. Total σ electron density of azine compounds.

TABLE 3. AO POPULATIONS AND ATOM POPULATIONS OF THE NITROGEN ATOM OF AZINE COMPOUNDS

Compound	E-H					H*		
	Atomic orbital population				Atom population	$\sum_r^{\mathrm{on N}} q_r$	$\sum_r^{\mathrm{on N}} q_r^{\sigma}$	q_N^{π}
	s	p_x	p_y	p_z				
Pyridine	1.4212	0.9974	1.7820	1.0060	5.2066	5.2935	3.9238	1.3697
Pyrazine	1.4175	1.0083	1.7838	0.9736	5.1832	5.2172	3.9285	1.2887
Pyrimidine	1.4256	1.0168	1.7623	1.0203	5.2250	5.3085	3.9347	1.3738
Pyridazine	1.4742	0.9241	1.7499	0.9065	5.0547	5.2260	3.9626	1.2634
s-Triazine	1.4239	1.0413	1.7439	1.0333	5.2425	5.3224	3.9434	1.3790
s-Tetrazine	1.4729	0.9315	1.7401	0.8773	5.0218	5.1158	3.9715	1.1443

* q^{π}; Total π electron density of the nitrogen atom N.

$\sum_r^{\mathrm{on N}} q_r^{\sigma}$; Summation of the σ electron density of AO's belonging to the nitrogen atom

$$\sum_r^{\mathrm{on N}} q_r = q_r^{\pi} + q_r^{\sigma}$$

An agreement is also observed between the atom population and the total density obtained by summing all the σ electron densities and the π electron density around the nitrogen atom in the Hückel calculation.

However, it should be noted that the parallelism between the sum of the AO populations of s, p_x, and p_y and the summed σ electron density around the nitrogen atom, $\sum_r^{\mathrm{on N}} q_r^{\sigma}$, obtained by the H-method does not hold.

Electron Distribution of Some Quinones. The lone-pair electron densities of *p*- and *o*-benzoquinones, 1,4-naphthoquinone, and 9,10-anthraquinone have been calculated by the H method and E-H method. In the H calculation a lone pair of the 2p type is assumed on the oxygen atom.[*3] The highest occupied and the next highest occupied σ orbitals obtained are considerably localized on the lone-pair AO of the oxygen atom of these quinones.

The total and partial lone-pair electron densities on the oxygen atoms of quinones are shown in Fig. 4. The partial electron densities in the lone-pair MO's are shown by the parentheses. About 98% of the lone-pair electrons are localized on the lone-pair AO of the oxygen atom; this magnitude is larger than that of the nitrogen atom of azines.

Both the total and partial electron densities at

[*3] This assumption is made with reference to the conclusion on the s nature of the lone-pair orbital at the oxygen atom to be presented below.

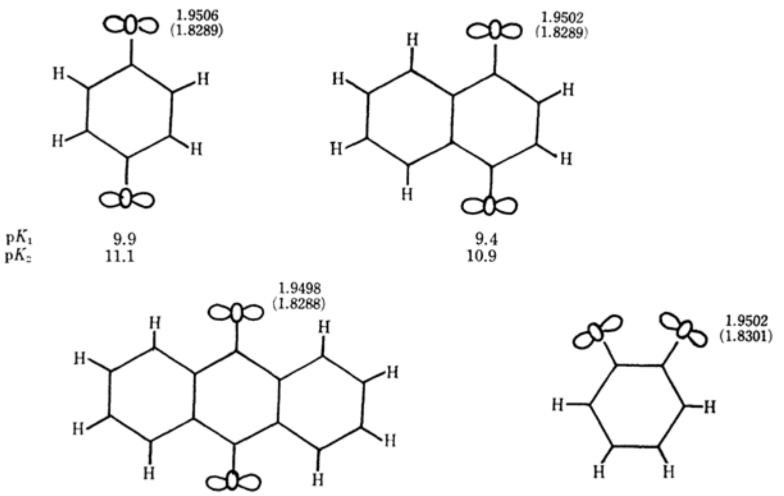


Fig. 4. Total and partial lone-pair electron densities of some quinones.

TABLE 4. AO POPULATIONS AND ATOM POPULATIONS OF THE OXYGEN ATOM OF SOME QUINONES

Compound	E-H					H		
	Atomic orbital population				Atom population			
	s	p_x	p_y	p_z		$\sum_r^{\mathrm{onO}} q_r$	$\sum_r^{\mathrm{onO}} q_r^\sigma$ *	q_0^π **
p-Benzoquinone	1.6391	1.9401	1.6770	1.2686	6.5248	6.5811	5.0811	1.500
1,4-Naphthoquinone	1.6873	1.9701	1.6492	1.3638	6.6704	6.6221	5.0801	1.542
9,10-Anthraquinone	—	—	—	—	—	6.6461	5.0791	1.567
o-Benzoquinone	1.6473	1.2005	1.6313	1.7224	6.2016	6.5428	5.0798	1.463

* The value 2 is added as the contribution of two 2s electrons.
** A. Kuboyama, This Bulletin, **31**, 752 (1958); *ibid.*, **32**, 1226 (1959).

TABLE 5. MOLECULAR OTBITAL COEFFICIENT OF THE LONE-PAIR MO'S OF PYRAZINE AND *p*-BENZOQUINONE

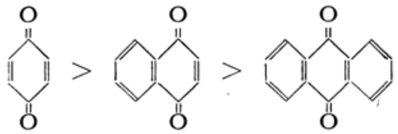
Compound	Atom	HO* next HO (eV)	The coefficient of the AO's in the lone-pair MO's			
			s	p_x	p_y	p_z
Pyrazine	N	−10.53	0.162	0.000	0.639	0.000
		−11.91	0.164	0.000	0.659	0.000
p-Benzoquinone	O	−10.94	0.000	0.644	0.000	0.000
		−11.25	0.000	0.676	0.000	0.000

* HO; Highest occupied MO.

TABLE 6. OSCILLATOR STRENGTHS OF n–π^* TRANSITIONS IN AZINE COMPOUNDS

Compound	Transition (allowed)	Transition energy obs. (cm^{-1})[8]	Oscillator strength			
			obs.[8]	H	E-H	Localized model
Pyridine	$n_{a_1} \rightarrow \pi_{b_1}$	37000	0.0030	0.0062	0.0032	0.0100
Pyrazine	$n_{a_{1g}} \rightarrow \pi_{b_{3u}}$	30515	0.0104	0.0042	0.0025	0.0169
Pyrimidine	$n_{b_2} \rightarrow \pi_{a_2}$	33500	0.0069	0.0029	0.0011	0.0102
Pyridazine	$n_{b_2} \rightarrow \pi_{a_2}$	29410	0.0058	0.0075	0.0033	0.0176

the lone-pair AO of the oxygen atom decrease in the order:



Moreover, the electron density at the lone-pair AO runs parallel with the observed pK values9) cited in Fig. 4 for *p*-benzoquinone and 1,4-naphthoquinone.

The electron distributions of these compounds as obtained by the H and E-H calculations are given in Table 4 In the E-H calculation, the highest and next highest occupied σ orbitals of the quinones are lone-pair MO's, as in the H calculation. The atomic orbital populations of p_x and $s+p_x$ of the oxygen atom, which would correspond to the population of the lone-pair AO, increase in an order reverse to that of the H calculation.

However, a parallelism is observed between the π-electron densities of the oxygen atom of quinones obtained by the H calculation for π electron systems and the AO population of p_z of the oxygen atom obtained by the E-H calculation. Furthermore, in the 6th and 7th columns, there is a parallelism between the atom population obtained by the E-H calculation and the total density obtained by summing all the σ and π electron densities around the oxygen atom in the H calculation.

2s Participation in the Lone-pair MO. Since the hybridizations of the atoms are assumed *a priori*, the Hückel calculation is not applicable to a discussion of the s contribution of the nitrogen atom to the lone-pair orbital. Hence, the extended Hückel treatment is adopted for investigating the hybridizations of the nitrogen and oxygen atoms. The molecular orbital coefficients of the lone-pair MO's of pyrazine and *p*-benzoquinone are listed in Table 5.

In pyrazine, the lone-pair MO's consist of only 2s and $2p_y$ AO's of the nitrogen atom. This indicates that the nitrogen atom has a sp^n-type hybridization. On the other hand, in the lone-pair MO's of *p*-benzoquinone, only the $2p_x$ orbital of the oxygen atom is involved in the highest and the next highest occupied MO's. Therefore, the lone pairs of the diazine and *p*-benzoquinone may be referred to as a hybridized-type and a *p*-type lone pair respectively. Hence, it can be pointed out that the lone pairs of azine compounds, ammonia, and hydrogen cyanide belong to the former type, while those of aldehydes, quinones, and alcoholes belong to the latter type.

To estimate the s character of these compounds, the oscillator strength of n-π^* transition, which depends mainly on the s character of the lone pair is calculated.

Some of the oscillator strengths calculated by the three different methods are listed in Table 6. In the table, the values in the last column are the results obtained by combining the ordinary Hückel procedure for π electrons with the Hückel treatment based upon a completely-localized sp^2 hybridized lone-pair model. The results are in a poor agreement with the experimental results, so further improvement is required to make a quantitative discussion. However, it may be generally remarked that the results calculated by three methods decrease in the order:

$$\text{HD method} > \text{H method} > \text{E-H method}$$

This order is parallel with the decrease in the s contribution of the lone pair in the three methods and also with the increase in the delocalization of lone-pair electrons.

In these circumstances, it can easily be understood that, since the magnitude of the oscillator strength depends on the 2s contribution, the n-π^* transitions due to the pure p-type lone pair has an approximately zero or a very small oscillator strength, in accordance with the experimental results.[*4]

Interaction between Lone Pairs. In the molecules in which more than two lone-pair AO's are involved, the interaction between these lone-pair AO's should be taken into account. The mode of the interaction between two lone-pair AO's has, however, never been studied comprehensively. In the present paper this problem is studied by the three different methods described above.

The characteristics of the three methods are illustrated in Fig. 5. In the HD method, only the direct interaction of the lone pair is considered, as it is based upon the localized model. In the Hückel approach, only the through-bond interaction is taken into account. In the extended Hückel method, however, both interactions, through bond and through space (direct), are considered.

An energy-level diagram of the lone pair as determined by the H calculation is shown in Fig. 6. In the figure, the orbital symmetries, the observed n-π^* transition energies8) (in cm^{-1}), the splitting of the lone-pair levels as estimated by Mason8) (written in parentheses in cm^{-1}), and the observed ionization potentials10) are cited. The Hückel approximation does not include electronic interactions explicity; therefore, only a qualitative discussion is possible. For diazines a rough linear

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9) M. E. Peover, *J. Chem. Soc.*, **1962**, 4540.

[*4] Nagakura (*Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **74**, 499 (1953)) and Sidman (*J. Am. Chem. Soc.*, **78**, 2363, 4567 (1956)) reported values of 10—100 for the molar extinction coefficient of the n-π^* transitions of *o*- and *p*-benzoquinones, 1,4- and 1,2-naphthoquinones, and 9,10-anthraquinone.

10) I. Omura, H. Baba, K. Higasi and Y. Kanaoka, This Bulletin, **30**, 633 (1957).

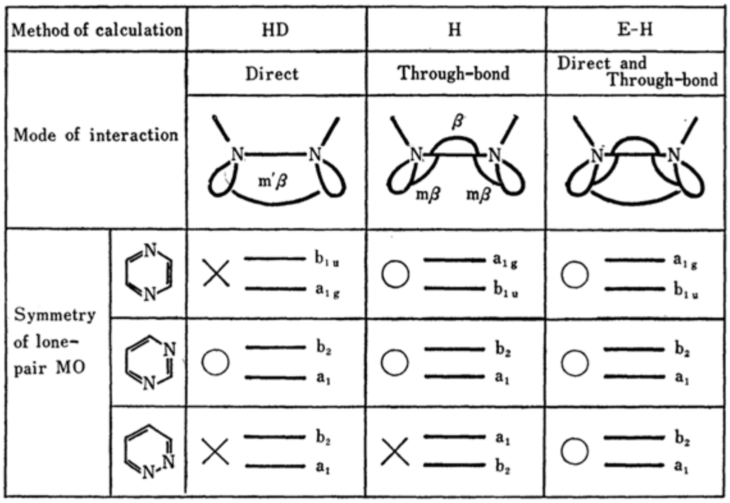

Fig. 5. Interaction between lone-pairs.

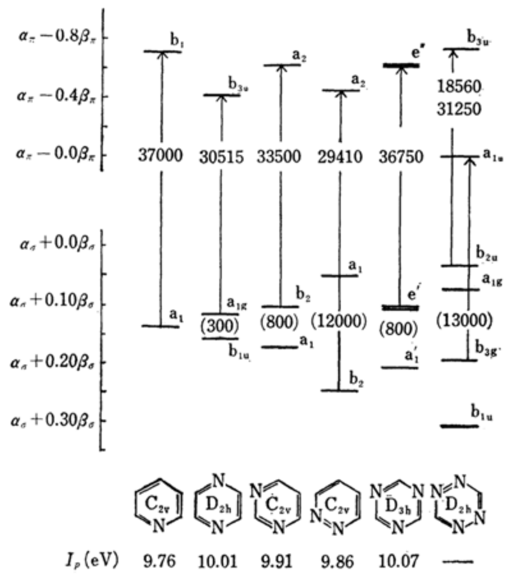

Fig. 6. Lone-pair MO's and lowest vacant orbitals of azine compounds.

relation is obtained between the highest occupied level and the ionization potential. From Fig. 6, it can be seen that the splitting of lone-pair levels becomes larger with a decrease in the mutual distance of two nitrogen atoms; this is in accordance with Mason's estimation.[8)] These results suggest an interpretation of the long-wavelength n-π^* band. In the case of pyridazine, however, the symmetry of the two lone-pair orbitals is inverse to the experimental suggestion[8)] that the highest occupied must be B_2, and the next one, A_1. This is probably because the allowed transition of pyridazine is $n(B_2)\rightarrow\pi^*(A_2)$ and because its absorption band is at the longest wavelength among these azines. This discrepancy seems to be a defect of the method, in which the direct interaction of the adjacent lone pairs of the nitrogen atom, which may have sizable overlaps,[*5] is not taken into account. These circumstances are shown in Fig. 5. "Circle" denotes the agreement of the level sequence obtained by the experiment and by calculation, while "Cross" denotes their disagreement. In the E-H method the higher one is B_2, and the lower one is A_1, they agree with the experimental suggestions, in contrast to the results of H calculation. However, the trend of the splitting expected from the experiment, that is a small splitting for pyrazine, a large one for pyridazine, and an intermediate one for pyrimidine, can not be interpreted. The splittings calculated by the E-H method are pyrazine (1.38 eV), pyrimidine (0.63 eV), and pyridazine (0.66 eV). In the localized model, as is shown in Fig. 5, the higher one is B, the antibonding orbital of two lone pairs, and the lower one is A, the bonding orbital, for all the azines; these results contradict the experimental suggestions regarding pyrazine.[*6]

Summarizing these discussions, it may be concluded that the lone-pairs interact directly through space as well as through bond. When two lone pairs lie in close proximity to each other, as in pyridazine, the through-space interaction should not be neglected. On the other hand, when two lone pairs are separated by several bonds,

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[*5] It is estimated as 0.08β by the use of tables (R. S. Mulliken and C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949)) for the sp^2-type lone-pair orbitals of pyridazine.

[*6] Mason mentioned (Ref. 8) in his localized model, in which the through-bond interaction is not considered, that the higher-energy lone-pair molecular orbital of pyrazine is b_{1u} in D_{2h} and that the lower one is a_g.

as in pyrazine, the through-bond interaction should not be neglected.

The Direct Interaction. In the preceding section we mentioned that the H method, which does not include direct interactions among lone-pair orbitals, gives incorrect level sequences for the symmetry of pyridazine. In order to test the effect of the direct interaction, we modified the H calculation by including that of the neighboring lone pairs of pyridazine. Though interactions among all the non-bonding orbitals should be taken into account, we picked up only one interaction, that between lone-pairs, as the most important direct interaction that affects the lone-pair levels. The calculated lone-pair levels of two methods are illustrated in Fig. 7. In method I, the direct interaction is not considered. In the method II, a direct interaction of 0.2β is assumed. It may be noted that the lower level of method I becomes the upper one of method II and coincides with the orbital sequence obtained by the E-H method, as had been anticipated. On the other hand, the sequence of the other occupied levels is not changed.

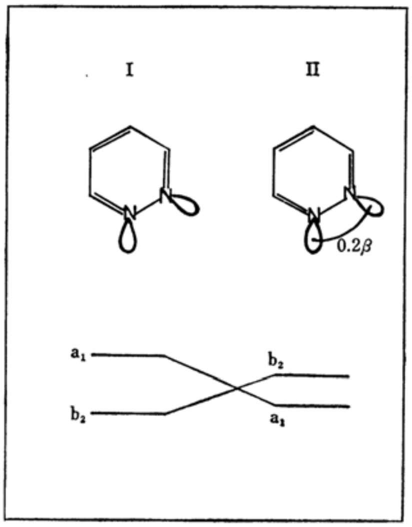

Fig. 7. Direct interaction of lone-pairs of pyridazine.

The electron distribution of method II is shown in Fig. 8. When it is compared with the electron distribution of method I in Fig. 3, it is noted that the value, 1.7910, of the lone-pair electron density in Fig. 8. deviates conspicuously from the value in the series of diazines shown in Fig. 3. When the direct interaction of lone pairs is included, the Coulomb and resonance integrals should be evaluated newly, taking into account the main direct interactions among orbitals other than lone pairs.

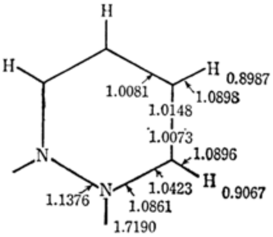

Fig. 8. Total σ electron density of pyridazine in including the direct interaction of 0.2β.

The calculations have been carried out on an IBM 7090 computer at the Japan IBM CO., with the permission of the UNICON committee, and on an HITAC 5020 computer at the Computation Center of the University of Tokyo.