An Analysis of the Through-bond Interaction Using the Localized Molecular Orbitals. I. Interactions between Lone-pair Orbitals in Azines: Pyridazine, Pyrimidine, and Pyrazine

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The CNDO/2 and INDO calculations were performed on three azines: pyridazine, pyrimidine, and pyrazine. In order to check the validity of the lone-pair orbital energies, the calculated orbital energies were compared with those obtained by *ab initio* calculations. These molecules have two lone-pairs, which can be transformed into symmetric and antisymmetric combinations. In pyridazine and pyrimidine, the symmetric one is lower than the antisymmetric one in energy, while in pyrazine the reverse is true. These results were subjected to an analysis from the standpoint of the through-bond interaction. That is, we transformed the canonical molecular orbitals obtained by the CNDO/2 method into localized molecular orbitals. By the use of the localized molecular orbitals thus obtained, the variation in the lone-pair orbital energies of these molecules was estimated in terms of the through-bond (and/or the through space) interaction according to a method which selectively considered the particular interaction between the specified localized molecular orbitals in a molecule. As a result of this analysis, it was found that the relative order of the lone-pair orbital energies was determined by the different types of interactions from molecule to molecule, and the energy variation in the lone-pair orbitals was elucidated in terms of the specified through-bond and through-space interactions.

From the early days of the molecular orbital theory, such azines as pyridazine, pyrimidine, and pyrazine have been studied. Most of the previous works were examined by the semi-empirical methods.[1] Recently, *ab initio* molecular orbital methods have also been applied to these molecules.[2]

These molecules are characterized by their two lone-pair orbitals (LPO). These two LPO should be classified into symmetric and antisymmetric combinations on the basis of their symmetry properties. Hoffmann and his coworkers attempted to explain the separation between two lone-pair orbital energies (LPOE)[3] generally in terms of the "through-space" and the "through-bond" interactions in the cases of benzyne and its related compounds.[4] Many researches in this direction have been reported. However, the explicit calculations of the through-bond interactions have never been carried out, although data have been accumulated for the through-space interactions.[5] In the present article, we attempted to evaluate quantitatively the through-bond interactions by using the localized molecular orbitals (LMO) transformed from the canonical molecular orbitals (CMO). There is an advantage for chemists to understanding chemical phenomena in using the LMO- rather than the usual CMO-bases wave function, since the LMO can often be chosen so as to be localized in a certain space region, whereas the CMO are delocalized in most cases.

There are two LPO, n_1 and n_2, in the molecules treated here. These two LPO n_1 and n_2 can be classified into a symmetric or an antisymmetric combination from their symmetry properties, as was mentioned in the previous paragraph. There is an interest in the order of these LPOE, since there are intimate relations between this order and the assignments of the ionization potentials (IP's) and the $n\rightarrow\pi^*$ transition in the photoelectron or absorption spectra. For the IP's and the spectra of these molecules, there are many references available.[6] In connection with this, the order of the LPOE is different from molecule to molecule. Therefore, we have investigated the dominant factors in determining the order of the LPOE by using the LMO; that is, the order of the LPOE was successfully explained in terms of the through-space and the specified through-bond interactions.

Method of Calculations

There are fifteen occupied orbitals in the azines now under consideration. Among them, three are π-molecular orbitals. As a result, twelve occupied σ-orbitals were localized by minimizing the off-diagonal exchange energy according to the procedure of Edmiston-Ruedenberg.[7] The occupied π and all of the virtual orbitals were not transformed into the LMO. The original CMO were obtained from the CNDO/2

TABLE 1. NUCLEAR COORDINATES (in Å units) OF THE AZINES

		x	y	z
Pyridazine[a]	N	0	±0.665	0
	C	−1.18236	±1.32	0
	C	−2.41	±0.6875	0
	H	−1.16619	±2.40988	0
	H	−3.29671	±1.24986	0
Pyrimidine[b]	N	±1.182650	0.668858	0
	C	0	1.243153	0
	C	±1.165980	−0.668858	0
	C	0	−1.393466	0
	H	0	2.293153	0
	H	±2.080520	−1.184725	0
	H	0	−2.443466	0
Pyrazine[c]	N	0	0	±1.404814
	C	0	±1.125714	±0.689018
	H	0	±2.032340	±1.218801

a) From Ref. 6c. b) Recalculated in the light of Ref. 10. c) From Ref. 2c.

calculations,[8] since an *ab initio* calculation consumes a lot of computation time. The INDO calculations[9] were also carried out in order to compare the order of the LPOE with the *ab initio* one. The atomic coordinates used are summarized in Table 1.[2c,6c,10]

Pyridazime, pyrimidine, and pyrazine belong to the C_{2v}, C_{2v}, and D_{2h} point groups respectively. In order to express the symmetric character of the LPO, only the two-fold axis, which bisects the LPO and interchanges n_1 and n_2 with the symmetry operation, is used. The two symbols, S(Symmetric) and A(Antisymmetric), are named according to their symmetry properties in terms of the transformation around the two-fold axis.

When there is no interaction between n_1 and n_2, the two LPOE should be equal. If there are some interactions between them, S and A should be separated into two different energy levels; the separation width $\Delta = |E(S)-E(A)|$ expresses the magnitude of the interactions between them.

Now we will attempt to explain the procedure for estimating the effect of a particular through-bond interaction in the molecule. For the purpose of this procedure, the atomic orbital, χ_r, is represented by a linear combination of the LMO in the CNDO or INDO approximation, as is shown below. That is, the LMO, ϕ_i, is given by

$$\phi_i = \sum_s c_{is}\chi_s. \tag{1}$$

Equation 1 is multiplied by the coefficient, c_{ir}, for all the i and the equations are added:

$$\sum_i c_{ir}\phi_i = \sum_i c_{ir}\sum_s c_{is}\chi_s = \sum_s \chi_s \sum_i c_{ir}c_{is} = \sum_s \chi_s \delta_{rs}. \tag{2}$$

Thus,

$$\chi_r = \sum_i c_{ir}\phi_i. \tag{3}$$

By using Eq. 3, we can represent a core resonance integral between atomic orbitals, χ_r and χ_s, as the summation of the core resonance integrals between the LMO, ϕ_i and ϕ_j:

$$I^\circ_{rs} = \int \chi_r h^\circ \chi_s d\tau = \sum_i \sum_j c_{ir}c_{js}\int \phi_i h^\circ \phi_j d\tau = \sum_i \sum_j c_{ir}c_{js}I_{ij}, \tag{4}$$

where I°_{rs} and I_{ij} are the core resonance integral between the atomic orbitals, χ_r and χ_s, and that between the LMO, ϕ_i, and ϕ_j, respectively, and where h° denotes a one-electron Hamiltonian. By modifying Eq. 4, we can obtain the value of the core resonance integral between the atomic orbitals which gives zero for the core resonance integrals between the specified LMO, and which gives the core resonance integral between the other LMO correctly. That is,

$$I_{rs} = I^\circ_{rs} - \sum_{(i_1-j_1)} (c_{i_1r}c_{j_1s} + c_{i_1s}c_{j_1r})I_{i_1j_1}, \tag{5}$$

where $(i_1\text{-}j_1)$ means that the summation should cover only definite pairs of the specified LMO. It can easily be proved that the core resonance integral, I_{rs}, obtained by Eq. 5 gives zero for the core resonance integral between the specified LMO, $I_{i_1j_1}$, and the correct values for the others as is shown below.

$$\begin{aligned} I'_{ij} &= \sum_r \sum_s c_{ir}c_{js}\int \chi_r h^\circ \chi_s d\tau = \sum_r \sum_s c_{ir}c_{js}I_{rs} \\ &= \sum_r \sum_s c_{ir}c_{js}I^\circ_{rs} - \sum_r \sum_s c_{ir}c_{js}\sum_{(i_1-j_1)} (c_{i_1r}c_{j_1s} \\ &\quad + c_{i_1s}c_{j_1r})I_{i_1j_1} \\ &= I_{ij} - \sum_{(i_1-j_1)} I_{i_1j_1}[(\sum_r c_{ir}c_{i_1r})(\sum_s c_{js}c_{j_1s}) \\ &\quad + (\sum_r c_{ir}c_{j_1r})(\sum_s c_{js}c_{i_1s})] \\ &= I_{ij} - \sum_{(i_1-j_1)} I_{i_1j_1}(\delta_{ii_1}\delta_{jj_1} + \delta_{ij_1}\delta_{ji_1}), \\ &\begin{cases} = 0 & (i = i_1,\ j = j_1 \text{ or } i = j_1,\ j = i_1) \\ = I_{ij} & (\text{otherwise}). \end{cases} \end{aligned} \tag{6}$$

Equation 6 indicates that I'_{ij} is equal to zero when $i=i_1$, $j=j_1$, or $i=j_1$, $j=i_1$, and is equal to the correct value otherwise. Consequently, when the LMO, ϕ_i and ϕ_j, which specified the bonds i and j, are picked up in Eq. 5, the core resonance integral between ϕ_i and ϕ_j should be cut off; that is, the through-bond interaction between the bonds i and j can be considered to be cut off.[11] Thus, the SCF calculations using the core resonance integrals in Eq. 5 give the total energy without the appropriate through-bond interactions. The difference between the total energies calculated with and without the specified through-bond interactions should be a measure of the specified through-bond interactions.[12]

Previously, in order to describe the π-hyperconjugative interactions, the through-space and the through-bond interactions were treated separately by removing the core resonance integrals by the use of the semi-empirical method;[5] the present procedure is the first attempt to analyze the LPO interactions including a σ-system quantitatively.

Results and Discussion

The LPOE of these molecules, as calculated by the CNDO/2 and INDO methods, together with an *ab initio* calculation,[2f] are summarized in Table 2. From this table we can see that the order of S and A, and the separation width between them as calculated by the semi-empirical method, correspond with the results of the *ab initio* calculations. The tendencies of the separation width between S and A are also very similar to each other in the cases of the semi-empirical and non-empirical methods. Therefore, we can recognize that

Table 2. Orbital energies (au) for the lone-pairs in the azines[a]

		CNDO/2	INDO	*ab initio*[b]
Pyridazine		−0.5091 S	−0.4732 S	−0.4727 S
		−0.4705 A	−0.4036 A	−0.3919 A
	Δ	0.0386	0.0696	0.0808
Pyrimidine		−0.5075 S	−0.4676 S	−0.4621 S
		−0.4689 A	−0.4139 A	−0.4039 A
	Δ	0.0386	0.0537	0.0582
Pyrazine		−0.6128 A	−0.5362 A	−0.4900 A
		−0.4582 S	−0.3996 S	−0.3953 S
	Δ	0.1546	0.1366	0.0947

a) S: Symmetric; A: Antisymmetric; $\Delta = |E(S)-E(A)|$.
b) From Ref. 2f.

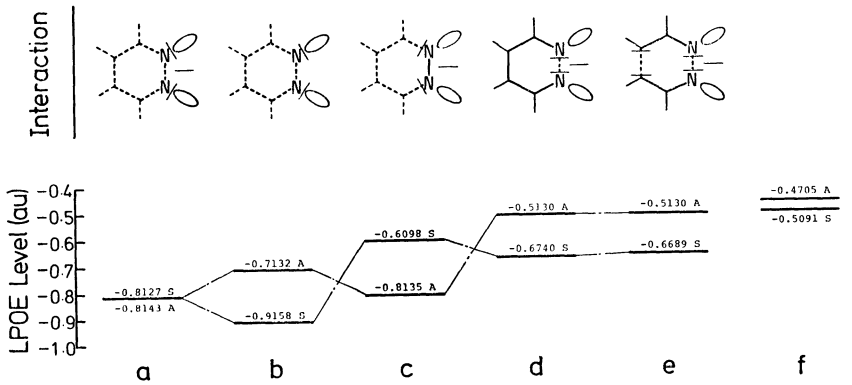

Fig. 1. LPO interaction diagram for pyridazine.
a: LPO are "cut off", **b**: LPO are "cut off" and N···N direct-through space interaction is allowed, **c**: short path is allowed, **d**: long path is allowed, **e**: short path is "cut off" and long path is "cut off" at the C–C bond parallel to the N–N bond, **f**: CMO level.

the semi-empirical method used here is sufficient to explain the energy variation in the LPOE or the change in the symmetry property of the LPO in these molecules.

Figure 1 shows the variation in the LPO energy levels of pyridazine.

a. When both LPO n_1 and n_2 were cut off from the interactions, S and A go to considerably lower energy levels. In this case, the N···N direct through-space interaction is not allowed. From the LPOE we can see that there is no interaction between n_1 and n_2.

b. Then the N···N direct through-space interaction was added to the **a** state; under these circumstances, A goes up about 0.1 au, while S lowers. This gives the magnitude of the direct through-space interaction between the LPO.

c. When the through-bond interaction *via* the N–N direct path (short path) was taken into consideration, S was found to go drastically up, but A scarcely varies from the **a** state. From the consideration of the orbital symmetry, it seems that this type of through-bond interaction does not have any effect on the energy level of A, as has already been pointed out by Hoffmann *et al.*[4]

d. When the interaction through the path N–C–C–C–C–N (long path) is taken into consideration, A goes up to around the CMO level, but S does not. The order of S and A is reversed from the **c** state.

e. In addition to the **d** state, the long path is cut off at the C–C bond parallel to the N–N bond; both S and A levels scarcely vary from the **d** state. Accordingly, it is obvious that the LPOE in the **d** state are not due merely to the through-bond interaction, but to a combination of the through-bond and through-space interactions, as will be discussed later in detail.

Figure 2 shows the variation in the LPO energy levels of pyrimidine.

a. Two LPO, n_1 and n_2, were cut off from the interactions; when this happens the energy levels of the LPO go lower, and S and A degenerate.

b. When we added the N···N direct through-space interaction to the **a** state, there were no variations in the energies of S and A from the **a** state. This shows that the N···N direct through-space interaction between two N atoms at the meta-position is almost zero. The same is true in pyrazine, as will be shown later.

c. Only the short path is allowed; S and A go upper,

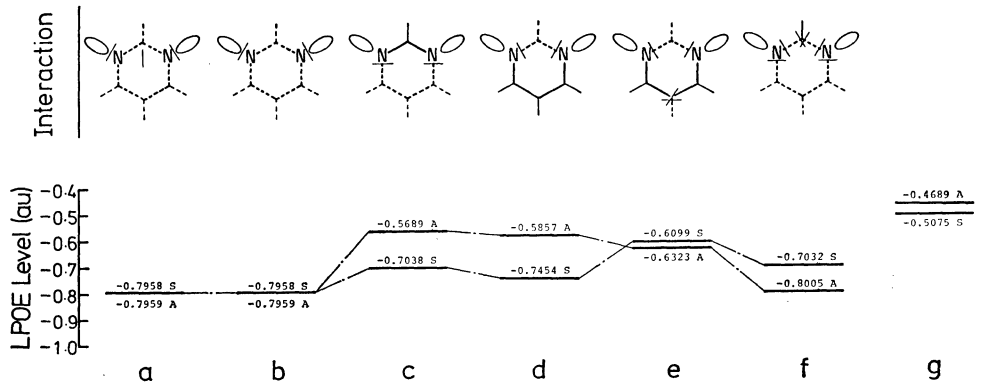

Fig. 2. LPO interaction diagram for pyrimidine.
a: LPO are "cut off", **b**: LPO are "cut off" and N···N direct through-space interaction is allowed, **c**: short path is allowed, **d**: long path is allowed, **e**: short path is "cut off" and long path is "cut off" at its central point, moreover C–H bond bonded at this point is "cut off", **f**: long path is "cut off" and short path is "cut off", but one C–H interaction with two LPO in the short path is allowed, **g**: CMO level.

but the variation is larger in A than in S. Therefore, it is noteworthy that the present situation is quite different from that in pyridazine.

d. The long path is allowed; both S and A vary from the **b** state. However, the variation in this case is less than that of the **c** state. One of the differences between the **c** and **d** states may be a result of the difference of the through-bond interactions *via* two and four bonds.

e. The short path is cut off, and the long path is cut off at its central point; moreover, the C–H bond combined at this point is cut off from the interactions. With this state, A goes lower than the **d** state, but S goes up. The energy difference between S and A becomes fairly small, and the order of S and A is reversed from the **d** state. From the **d** and **e** states, it is obvious that the energy variation in the LPO of the **e** state from the **d** state is caused by the through-bond interaction itself. This situation is also quite different from that of the **d** and **e** states in pyridazine.

f. The long path is cut off, as is the short path, but in the short path one C–H interaction is allowed. Therefore, in this state, only the through-space interaction between the two LPO (indirect through-space interaction) is allowed *via* the central C–H bond. With this interaction, S goes up from the **b** state; this new S level is nearly the same in energy as that of the **c** state. By comparing the energy levels in the **c** and **f** states, the variation in energy of S should mainly be derived not from the through-bond interaction (short path), but from the through-space interaction *via* the central C–H bond, while the variation of A is mostly the result of the through-bond interaction.

Figure 3 shows the variation in the LPO energy levels of pyrazine.

a. Two LPO on N atoms are cut off from the interactions; the energy levels of two LPO then go to lower levels and degenerate.

b. Even when we added the N···N direct through-space interaction to the **a** state, S and A showed no change in energy. The same phenomena had already been seen in pyrimidine.

c. When we cut off the right-hand side of C–C bond from the interactions (the same is true on the left-hand side), A goes up to the CMO level, but S does partly.

d. When the C–C bonds on both sides are cut off from the interactions, A does not vary from the **c** state, but S goes lower. The energy difference between the **c** and **d** states shows the magnitude of the C–C direct through-bond interaction. The order of S and A is reversed from the **c** state. From the **c** and **d** states, the energy level of S depends much on the through-bond interaction, while that of A does not, as is predicted from the consideration of the orbital symmetry. It is also noteworthy that the through-space interaction is not responsible for the energy difference between S and A, since the energy difference in the **d** state is rather small. This situation is quite different from that shown in pyridazine.

e. When the interactions were permitted only between the "cut-off" LPO and their neighboring four N–C bonds, A goes beyond the CMO level, but S still retains much below the CMO level. This result indicates that the energy level of S is determined not only by the direct through-bond interaction, but also by the through-space interaction combined with the through-bond interaction, since the energy level for S in the **e** state is much different from that of CMO, and the **e** state can be considered to include only the direct through-bond interaction.

Now we will discuss the roots of the LPO interactions. In the case of pyridazine, S is mainly destabilized through the short path, whereas A mainly interacts with the long path. Moreover in this molecule, the direct through-space interaction between n_1 and n_2 is larger than that of pyrimidine or pyrazine. Let us examine in more detail the **c**, **d**, and **e** states of Fig. 1. A indeed goes up by means of interactions *via* the long path. However, in comparison with the **d** and **e** states, both S and A retain nearly the same levels in spite of their different interactions. Therefore, in this molecule, it may be concluded that the interactions between the upper half and the lower half of a molecule *via* the through-space interaction are very important, as was

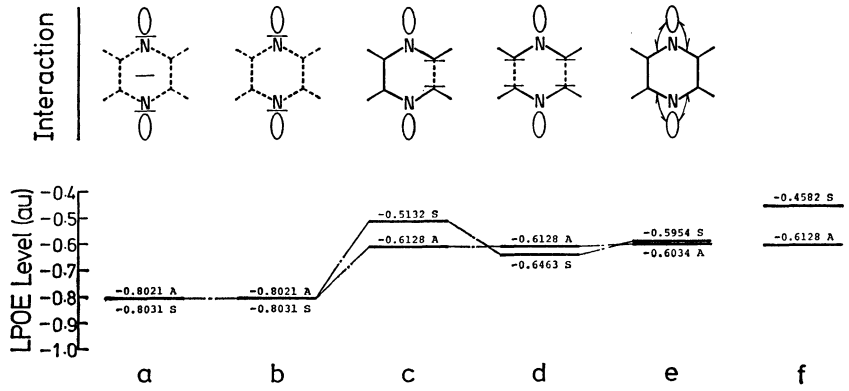

Fig. 3. LPO interaction diagram for pyrazine.
a: LPO are "cut off", **b**: LPO are "cut off" and N···N direct through-space interaction is allowed, **c**: one path is allowed but the other path is "cut off" at the C–C bond, **d**: both C–C bonds are "cut off", **e**: LPO are "cut off" and interactions between LPO and four N–C bonds are allowed, **f**: CMO level.

a b

Fig. 4. **a**: Through-space interaction, and **b**: through-bond interaction, in pyridazine. After combining **a** and **b**, it becomes the "through-space interaction after through-bond" or "through-bond interaction after through-space".

mentioned above. In the case, the through-bond interaction is also included, of course. That is, in other words, this may be named the "through-space after through-bond" or "through-bond after through-space" interaction. Some of interaction courses are shown in Fig. 4.

We shall now return to the discussion of pyrimidine by examining the **d**, **e**, and **f** states of Fig. 2 in more detail. In the case of pyridazine, we have already shown that the LPOE in the **d** and **e** states do not vary very much, as is shown in Fig. 1. However, in the case of pyrimidine, the LPOE are different in the **d** and **e** states, as is shown in Fig. 2. From this we can conclude that, in pyrimidine, the through-bond interaction *via* the N–C–C–C–N course is one of the most important interaction courses, unlike the case of pyridazine. That is, by cutting off the interactions between the C_1–C_2 and C_2–C_3 bonds, and the interaction of C_2–H in the N–C_1–C_2–C_3–N group, the LPO become less interactive.

With pyrazine from the **c** and **d** states shown in Fig. 3, we can recognize that S interacts intimately with the central C–C bonds. Usually the LPO energy order is S<A, but in pyrazine this order is reversed. Hoffmann *et al.*[4] have explained that this reverse order is attributable to the destabilization of the S level as a result of the interaction with the parallel σ C–C levels. Hackmeyer and Whitten[2c] have described that, in the case of the $n\rightarrow\pi^*$ transition, the two combinations of LPO n_1 and n_2 correspond to the $S\simeq n_1+n_2+\lambda\sigma$ and $A\simeq n_1-n_2$ relations. They have also concluded that the higher energy of S is attributable to the interaction with the pyrazine-ring σ system. The case in which the LPO do not interact with the σ C–C bond is shown by, for example, **d** of Fig. 3. In this case the energy order is S<A, indicating that the lack of interaction between the LPO and the central σ C–C bonds leads to a reversion of the levels of S and A. Therefore, the reverse order of S and A in pyrazine is explained quantitatively by the present analysis, and the present analysis confirms the previous hypotheses. In the **d** state, the LPOE are −0.6463 S and −0.6128 A (au), with a difference Δ= 0.0335 (au). The order of the difference agrees well with those of the CMO levels of pyridazine and pyrimidine, although the reason for it remains obscure.

The reversion of S and A is, of course, to be seen in pyridazine and pyrimidine also. In these molecules, however, the reversion cannot be explained only by the hypotheses of Hoffmann and his coworkers.[4] For example, with a pyridazine-type molecule, they proposed that the "through-space" interaction between LPO is dominant and that this lowers the S combination. According to the present analysis, it was found that the N–N direct through-bond interaction also plays an important role (the **c** state in Fig. 1), and in the **d** and **e** states of Fig. 1, the order is S below A even though the N···N direct through-space interaction is cut off.

Palmer *et al.* have reported on the photoelectron spectra of oxygen, sulfur, and nitrogen heterocycles, and they have discussed the variations in the LPOE at O, S, and N atoms.[13] In their paper they suggested that the "through-bond" interactions may play an important role in azines. In that paper, however, we cannot obtain a clear image of the interactions. The present investigation showed that the interactions between LPO are indeed very complicated. However, the interactions can be investigated very simply and clearly using the present procedure.

In conclusion, the present procedure for analyzing orbital interactions is very helpful to analyze the interactions between or among LPO in other molecules with very clear chemical images. The procedure is also applicable to analyzing the orbital interactions in such diradicals as benzynes. For such molecules the analyses are now in progress. This method will also be applied in an *ab initio* calculation. The details will be published elsewhere in the near future.

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12) The through-space and/or through-bond interactions used in the present article are named on the basis of the LMO. Therefore, the definition used here is one of convenience.

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