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AN ANALYSIS OF THE THROUGH-BOND INTERACTION USING THE LOCALIZED MOLECULAR ORBITALS WITH *AB INITIO* CALCULATIONS—I

LONE-PAIR ORBITAL INTERACTIONS IN *CIS*- AND *TRANS*-HYDRAZINES

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Abstract—*Ab initio* SCF MO calculations using STO-3G basis set were performed on the *cis*- and *trans*-hydrazines. The cannonical MOs obtained by these calculations were then transformed into the localized MOs. With the use of the localized MOs thus obtained, the variation in the lone-pair orbital energies of the molecules were pursued in the light of the through-space and/or the through-bond interactions between the specified localized MOs. As a result of this analysis, it was found that; (a) the effect of the inner shell orbitals, 1 s electrons of N atoms, is not negligibly small, (b) the effect of the through-bond interaction is not so larger than the through-space interaction, and (c) the large contribution of the through-space interaction is caused from the indirect as well as direct interactions between two lone-pairs.

The concept of the through-space and the through-bond interactions was first introduced by Hoffmann *et al.* in connection with the discussions on the height of the energy levels of the lone-pair orbitals (LPOs).[1,2] This concept has been applied to many fields such as chemical reactivity, electron spin distribution and so on. Heilbronner *et al.* developed a method for the quantitative calculation of the through-space and the through-bond interactions by using the symmetry adapted localized orbitals and applied to bicyclo compounds with semi-empirical MOs.[4] We have also developed a method[3] to evaluate the through-space and the through-bond interactions by making use of the LMOs and this method has been successfully applied to explain the long-range hyperfine spin coupling constants in alkyl radicals,[5,6] to explain lone-pair orbital interaction in azines,[3,7] and to explain the long-range effect of the LPO to optical rotatory strength of the CO $n \rightarrow \pi^*$ transition in keto-piperidines.[8] In these papers,[3,5–8] the procedure is to estimate quantitatively the through-bond and/or the through-space interaction by using the semi-empirical method.[9,10]

$$\mathbf{D} = \begin{pmatrix} d_{11} & d_{12} & \cdots & d_{1n} \\ d_{21} & d_{22} & \cdots & d_{2n} \\ \cdots & \cdots & \cdots & \vdots \\ d_{n1} & d_{n2} & \cdots & d_{nn} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \begin{pmatrix} \epsilon_1 & & & 0 \\ & \epsilon_2 & & \\ & & \ddots & \\ 0 & & & \epsilon_n \end{pmatrix} \begin{pmatrix} a_{11} & a_{21} & \cdots & a_{n1} \\ a_{12} & a_{22} & \cdots & a_{n2} \\ \cdots & \cdots & \cdots & \vdots \\ a_{1n} & a_{2n} & \cdots & a_{nn} \end{pmatrix} \qquad (2)$$

In the present work, in order to confirm and to support the validity of the previous procedure, and to obtain separately new information, we have developed the method by the aid of *ab initio* SCF MO calculations.

Method of calculation. The original CMOs were obtained from the *ab initio* SCF calculations. The basis set used was the STO-3G and the program GAUSSIAN 70[11] was used. The LMOs were obtained from the CMOs by the procedure of Edmiston–Ruedenberg.[12] The SCF calculations based on the LMOs were carried out in order to evaluate various types of the through-bond/space interaction energies.

Theory. For the analysis of the through-bond/space interactions, Fock matrix elements between LMOs are obtained. These Fock matrix elements are easily calculated by the following convenient procedure.

First, the LMOs $\psi_{L1}, \psi_{L2}, \ldots, \psi_{Ln}$ are expressed by eqn (1) from the CMOs $\psi_1, \psi_2, \ldots, \psi_n$ which are obtained from the usual SCF MO calculation,

$$\begin{pmatrix} \psi_{L1} \\ \psi_{L2} \\ \vdots \\ \psi_{Ln} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \cdots a_{1n} \\ a_{21} & a_{22} \cdots a_{2n} \\ \cdots & \cdots \vdots \\ a_{n1} & a_{n2} \cdots a_{nn} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{pmatrix} \qquad (1)$$

Together with the CMOs, the orbital energies $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$ can be obtained from the SCF calculations.

Second, we now define a new datrix $\mathbf{D}$ (d_{ij}) by using the transformation matrix as in eqn (2),

This matrix $\mathbf{D}$ is nothing but the Fock matrix represented on the basis set of the LMOs, since the orbital energies, $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$, are the matrix elements between the CMOs.

Off-diagonal matrix elements in the matrix $\mathbf{D}$ correspond to the interaction between the two specified LMOs which concentrate in the specified bond/atom.

Consequently, we can detect the contribution of the through-bond/space interactions to the orbital energies by dropping the relevant matrix element followed the diagonalization to obtain orbital energies. When the two LMOs localized on the two adjacent bonds, the corresponding off-diagonal elements should be responsible for the through-bond interaction, while the two LMOs localized on two remote parts of the molecule, this matrix element should relate to the through-space interaction. By combining appropriate off-diagonal matrix elements, we can evaluate a relevant through-bond/space interaction. It should be noteworthy that the transformation matrix obtained by the above-mentioned procedure for the analysis of the through-bond/space interactions is orthogonal, so that the density matrix as well as the total energy is invariant under this transformation.[16] In the preceding series of the papers,[3] we have evaluated the through-bond/space interactions by dropping the relevant core resonance integrals and the two-electron integrals were not varied. This definition may be rationalized because of the approximation of the neglect of differential overlaps used in the semi-empirical method. However in the *ab initio* method, this definition is very difficult, since differential overlaps are included explicitely in the calculation. Accordingly, in the present paper, the through-space/bond interactions are evaluated by dropping the relevant Fock matrix elements instead of the core resonance integrals.

Application to the actual molecules. The procedure developed is now applied to the actual molecules *cis*- and *trans*-hydrazines. Molecular geometries used are shown below: $r(\text{N–N}) = 1.47$ Å, $r(\text{N–H}) = 1.04$ Å; angles around N atoms were assumed tetrahedral. Although molecular structures of hydrazine and related compounds have been estimated spectroscopically,[13–15] we have treated here hydrazine in the typical *cis*- and *trans*-forms only.

There are two LPOs, n_1 and n_2, in the molecules treated here. These two LPOs, n_1 and n_2, can be classified into a symmetric, $n_1 + n_2$, or an anti-symmetric, $n_1 - n_2$, combination from their symmetry properties. We will pursue the orbital energies of these two combinations in the present work.

RESULTS AND DISCUSSION

cis-*Hydrozine.* Figure 1 shows the variation in the lone-pair orbital energy (LPOE) of *cis*-hydrazine. The LPOEs are raised up by interacting with neighbouring N–H bonds (**a** and **b**). By comparing with the diagrams **b** and **c**, we can see that the effect of the inner shell orbitals, 1s electrons of N atoms, is not negligibly small, although the effect is not so large. This cannot be recognized by the previous procedure with the semi-empirical method.[3] To examine the diagrams **a**, **c**, and **d**, we can notice that the through-bond interaction is rather small. This result differs from the case of pyridazine,[3,7] although the situations are somewhat different between the *cis*-hydrazine and pyridazine.

From the diagrams **a**, **c**, **e**, and **f**, we can see that the through-space interaction is responsible for the energy difference between the two LPOs. This is also true in the case of pyridazine.[3,7]

We will now discuss in more details the through-bond interaction using Fig. 2. From the diagrams **c** and **g**, it is

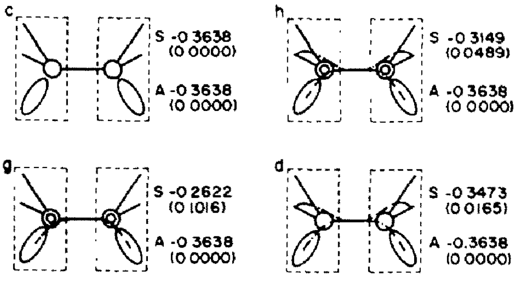


Fig. 2. LPO through-bond interaction diagram for *cis*-hydrazine. The figures in parenthesis show the difference in orbital energies between the diagram **c** and each diagram. The larger value indicates the larger effect in the interaction. The diagram **c** is the starting one. The other notations : see Fig. 1. **c** and **d**: see Fig. 1. **g**: in addition to the diagram **c**, the through-bond interaction between the LPOs via the central N–N bond is allowed, and in this diagram 1s electrons of N atom are not included in the interaction, **h**: in addition ot the diagram **g**, the N–H bonds are allowed to interact with the central N–N bond, and in this diagram also 1s electrons on N atom are not included in the interaction.

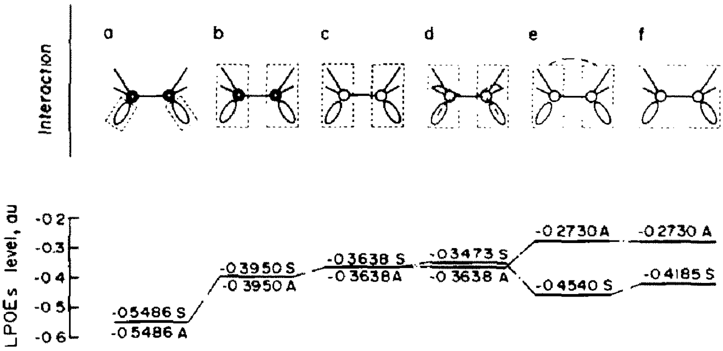


Fig. 1. Typical LPO interaction diagram for *cis*-hydrazine. The part surrounded by broken line is allowed to interact with each other. Nitrogen: ⊚, 1s electrons are not included in the interaction, and ○, they are included. ---: interaction allowed path. In the interaction diagram including N–H bonds to avoid complexity only single line as a whole is used to represent the interaction with two N–H bonds. **a**: LPOs are cut off from all the types of interactions, **b**: interactions in the N–H bonds and LPO are allowed in each NH_2 group except 1s electrons of N atom, **c**: interactions are allowed between the LPO and N–H bonds including 1s electrons of N atom in each NH_2 group, **d**: in addition to the diagram **c**, all the types of through-bond interactions between the two NH_2 groups are allowed, and 1s electrons of N atom are included in the interaction, **e**: in addition to the diagram **c**, all the types of through-space interactions between the two NH_2 groups are allowed, but the through-bond interactions are not allowed, **f**: full interaction case.

found that the direct through-bond interaction via the central N–N bond raises up the symmetric LPOE considerably to lead to the large difference in energy for the two LPOs. When we include the indirect[17] through-bond interaction via the N–H bonds as well as the direct one, the energy difference in the two LPOs decreases remarkably as shown in the diagram **h**. This tendency is straightened by including the indirect through-bond interaction via the inner-shell 1s orbitals of two N atoms as shown in the diagram **d**. Thus, the coupling between the direct through-bond interaction and the indirect through-bond interactions lead to small energy difference between the two LPOs as the whole through-bond interaction.

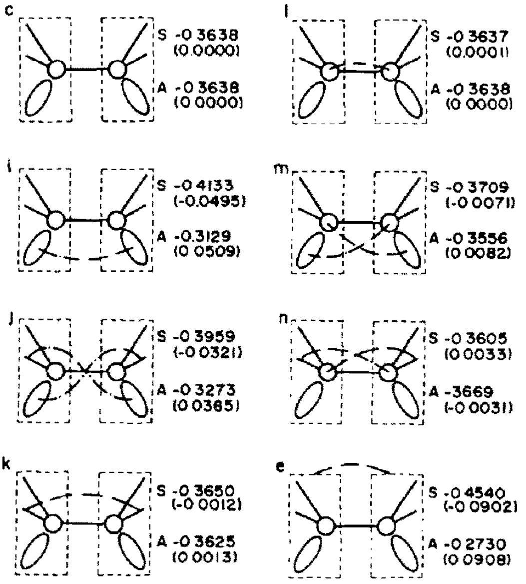


Fig. 3. LPO through-space interaction diagram for *cis*-hydrazine. The figures in parenthesis show the difference in orbital energies between the diagram c and each diagram. The larger value indicates the larger effect in the interaction. The diagram c is the starting one. The other notations: see Fig. 1. c and **e**: see Fig. 1. **i**: in addition to the diagram c, the through-space interaction between the LPOs is allowed. **j**: in addition to the c diagram, the through-space interactions between the LPOs and N–H bonds are allowed, **k**: in addition to the c diagram, the through-space interactions between the N–H bonds of the two NH_2 groups are allowed, **l**: in addition to the c diagram, the through-space interaction between 1s electrons of N atoms is allowed, **m**: in addition to the c diagram, the through-space interactions between 1s electron of N atom and LPO are allowed, **n**: in addition to the c diagram, the through-space interactions between 1s electron of N atom and the N–H bonds are allowed.

We will then discuss in more details the through-space interaction by using Fig. 3. In Fig. 3, we list different kinds of through-space interaction diagrams. From these we can easily see that the dominant ones to determine the through-space interaction are the interactions written in the diagrams **i** and **j**. These two diagrams cover over 90% of the whole through-space interaction (see diagrams **i**, **j** and **e**). That is, the direct through-space interaction between the two LPOs and the indirect through-space interactions via the N–H bonds are responsible for the magnitude of the whole through-space interaction.

trans-*Hydrazine.* Figure 4 shows the variation in the LPOE levels of *trans*-hydrazine. From the diagrams **a** to **d**, it is found that the situations of the *trans*-hydrazine are similar with those of the *cis*-hydrazine. By comparing the diagrams **e** and **f**, the order of the LPOEs is in reverse order from that of *cis*-hydrazine. By the more detailed analysis of the through-bond interaction shown in Fig. 5, it is also found that the situation of the *trans*-hydrazine is quite similar with that of *cis*-hydrazine.

As for the through-space interaction, by comparing Figs. 3 and 6, difference appeared in the diagrams of **i**, **j**, **k**, **m**, and **e**. Among these, the largest one is the diagram **j**, but not in the diagram **i**. This is very interesting, because we can usually expect that the direct through-bond interaction (diagram **i**) should be the most dominant one.

For reader's information, the values of the interaction matrix elements (d_{ij}) are listed in Table 1.

GENERAL DISCUSSION

We have now turned again to the energy levels of the LPOs. The reverse of the energy level ordering for the symmetric and the anti-symmetric combinations of the LPOs for *cis*- and *trans*-hydrazines is caused from the direction of LPOs, which determine the magnitude and the sign of the through-space interaction. Among many

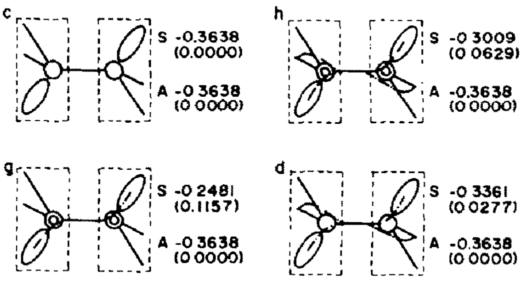


Fig. 5. LPO through-bond interaction diagram for *trans*-hydrazine. Notations: see Fig. 2.

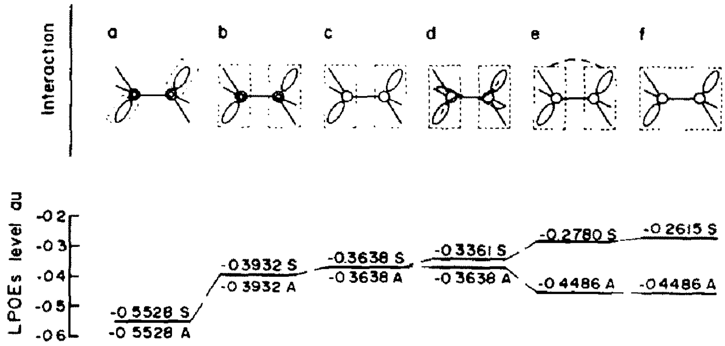
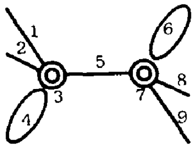


Fig. 4. Typical LPO interaction diagram for *trans*-hydrazine. Notations: see Fig. 1.

Table 1. Interaction matrix elements (d_{ij}) for trans-hydrazine

	H_{1s} 1	H_{1s} 2	N_{1s} 3	N_{LPO} 4	N-N 5	N_{LPO} 6	N_{1s} 7	H_{1s} 8	H_{1s} 9
1[a]	-0.7530	0.1793	0.7190	-0.2074	0.1562	0.0221	-0.0787	-0.0510	0.0095
2		-0.7530	-0.7190	0.2074	-0.1562	-0.0221	0.0787	-0.0095	0.0510
3			-15.1260	1.2220	-0.6293	0.0206	0.0104	0.0787	0.0787
4				-0.5528	0.1912	-0.0642	-0.0206	0.0221	0.0221
5					-0.7989	-0.1912	-0.6293	-0.1562	-0.1562
6						-0.5528	-1.2220	-0.2074	-0.2074
7							-15.1261	-0.7190	-0.7190
8								-0.7530	-0.1793
9									-0.7530

[a] LMO numberings are shown below.



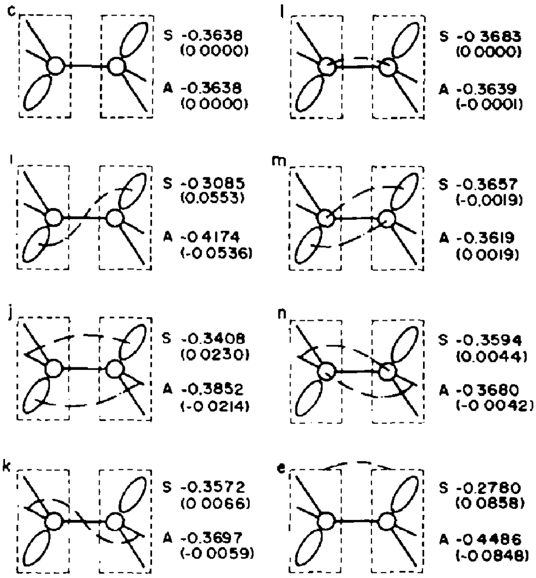


Fig. 6. LPO through-space interaction diagram for *trans*-hydrazine. Notations: see Fig. 3.

types of the through-space interactions, the direct through-space interaction between the two LPOs play an important role. Moreover, it should be stressed that the indirect through-space interactions via the N–H bonds also contribute to the energy separation of the two LPOs. Actually the molecular conformation is not the *cis*- or the *trans*- one,[13,15] but it is in the intermediate conformation between these two forms, that is the dihedral angle between lone-pairs is about 90–110°. Therefore in the actual molecule, the interactions between the LPOs may be somewhat different from those now analyzed in the present paper. Nevertheless, the present result is very interesting as the model for the analysis of the typical through-bond/space interactions between two remote lone-pair orbitals.

In conclusion, the present procedure is very helpful to analyse the interaction between or among definite orbitals (chemical bonds) in the other molecules with very clear chemical images. In the present procedure, we can also treat the inner shell electrons, 1s electrons of N atom, explicitely which is not taken into consideration in the previous semi-empirical method.[3,7] The present procedure will also be used for the analysis of the chemical reaction processes.

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[17] In the present paper, the direct through-bond interaction is denoted for the interaction of two lone-pair orbitals through the central N–N bond, while the indirect one is for the interaction of two lone-pair orbitals through two N–H bonds as well as the central N–N bond. The direct through-space interaction is for the interaction of two lone-pair orbitals without any intervening orbitals while the indirect one is for the through-space interaction between two lone-pair orbitals via two N–H bonds, inner shell orbitals and so on.