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

LONE-PAIR ORBITAL INTERACTION IN 1,4-DIAZABICYCLO[2.2.2] OCTANE AND ITS MODEL MOLECULES

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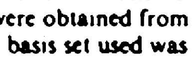
Abstract—*Ab initio* SCF MO calculations using STO-3G basis set were performed on 1,4-diazabicyclo[2.2.2]octane and its model molecules. The canonical MOs obtained for the molecules were then transformed into the localized MOs. With the use of the localized MO's thus obtained, the variation in the lone-pair orbital (LPO) energies (LPOE's) of the molecules were pursued in the light of the through-bond interaction. The through-bond interactions were analyzed systematically. As a result of this analysis, it was found that the two interactions are mainly responsible for the splitting of the two LPOE's, the first one is the interaction between the LPOs and the central C–C bond in the same path, and the second one is the interaction between two neighbouring N–C bonds in different paths. Theoretical grounds for these interactions are discussed by using the usual perturbation method.

The concept of the through-space and the through-bond interactions was first introduced by Hoffmann *et al* in order to explain the energy levels of the lone-pair orbital (LPO).[1,2] This concept has been applied to many fields in chemistry. Heilbronner's group has developed a method for the quantitative estimation of the through-space and the through-bond interactions by using the symmetry adapted localized molecular orbitals (LMO's) and applied to explain the photoelectron spectra of a variety of molecules.[3-10] We have used[11-17] the terms of "through-space" and "through-bond" interactions in a little different meanings from those used for example in Ref 10. That is, when we analyzed so-called "through-bond" interaction in more detail, we found that only one category of the "through-bond" interaction was too simple to clarify the theoretical ground for the interaction between the two LPOs. Consequently, the through-bond interaction should include several terms in it.

In the present paper, we performed the *ab initio* SCF calculations on 1,4-diazabicyclo[2.2.2]octane 3 and two model molecules, and hereafter these refer to 1 and 2. The schematic structures of 1, 2 and 3 are shown in Fig 1. The molecule 3 has been known to have typical large through-bond interaction and a small through-space interaction between the LPO's, and this is suitable for the present analysis in order to unfold the contents of the through-bond interaction.

Method of calculation. The original canonical MO's (CMO's) were obtained from the *ab initio* SCF calculations. The basis set used was the STO-3G type with standard exponents[20] and the program GAUSSIAN 70 was used.[18] The LMO's were obtained from the CMO's by the procedure of Edmiston-Ruedenberg.[19] The detailed procedure of the calculations has been described in the previous paper.[16] The molecular geometries assumed are as follows: $r(C-H) = 1.09$ Å, $r(C-C) = 1.54$ Å, $r(C-N) = 1.47$ Å and $r(N-H) = 1.01$ Å, and the angles around heavy atoms were assumed to be tetrahedral.



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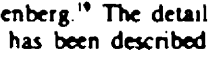

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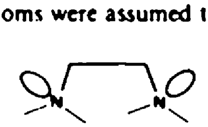

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Fig 1. Schematic structures of 1,4-diazabicyclo[2.2.2]octane 3 and its model molecules, 1 and 2.

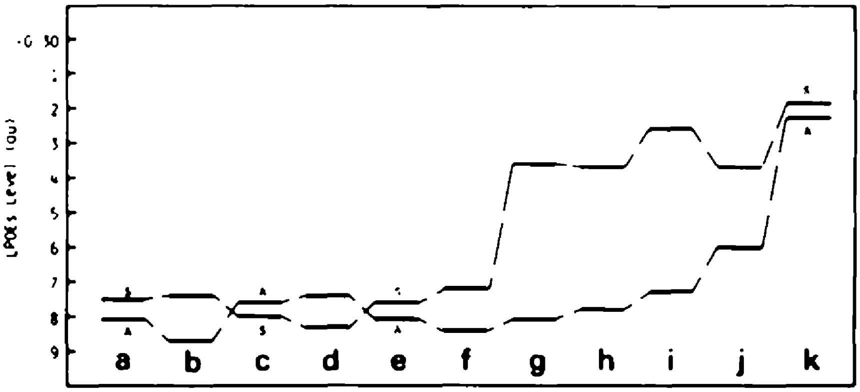

Fig 2 Variation of LPOEs for Model 1 See also Fig 3

RESULTS AND DISCUSSION

In the model 1, the two remote LPO's interact with each other through only one path of bonds, while model 2 has two paths of bonds. The analysis of the LPO energies (LPOE's) in 1 clarifies the interaction scheme in a single path of bonds, and that in 2 the contribution of the inter-path interaction to the splitting of the two LPOE's. The through-bond interaction in 3 is expected to be explained by combination of the above-mentioned two analyses.

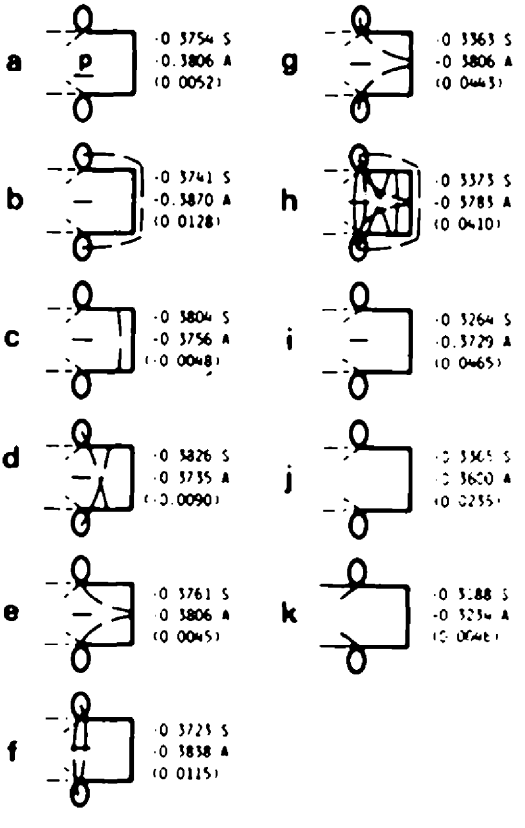

Fig 3 Typical interactions and LPOEs for Model 1 Broad line part shows the interaction allowed part p only the neighbouring through-bond (geminal bond) is allowed — through-space interaction between the LPO is not allowed

Model 1

Figure 2 shows the diagram of the LPOE variation for 1 The orbital energies and the difference of the orbital energies between the symmetric (S) and antisymmetric (A) combinations are summarized in Fig 3

(a) Pure through-bond, only the through-bond interaction between the neighbouring bonds, i.e. geminal bonds, is allowed This can be taken up as the starting point In this state, the direct through-space interaction between the LPOs is forbidden, and the four N H bond-localized orbitals are isolated from the others Consequently, we concentrate our attention only to the through-bond interaction along the path from one nitrogen LPO through two CH_2 groups to another LPO This scheme is retained from the state **a** to the state **i** It is noteworthy that the pure through-bond interaction gives a relatively small splitting of the two LPOs

(b) In addition to the state **a**, the interaction via the C H bond is allowed The S level varies scarcely but the A level lowers from the state **a**

(c) In addition to the state **a**, the interaction between the two N–C bonds is allowed The order of S and A level varies from that of the state **a**. Obviously, an interaction between two remote N–C bonds through-space lowers the S level and raises the A level, which leads to the variation of the order of S and A levels That is, the through-bond interaction along one path can be considered to include a kind of the through-space interaction

(d) In addition to the state **a**, the interaction between LPO and N C bond which does not locate in the neighbouring position is allowed The situation is similar to the case of c

(e) In addition to the state **a**, the interaction between N_H and the C C bond is allowed There is no remarkable change from the state **a**

(f) In addition to the state **a**, the interaction between N_H and LPO, which is not in a neighbouring position, is allowed, then the S level is destabilized while the A level is stabilized from the state **a**

(g) In addition to the state **a**, the interaction between LPOs and the central C C bond, jumping interaction, is allowed The S level is largely destabilized but the A level is not with reference to the state **a**. It is needless to say that this type of the interaction has no contributions to the A level in

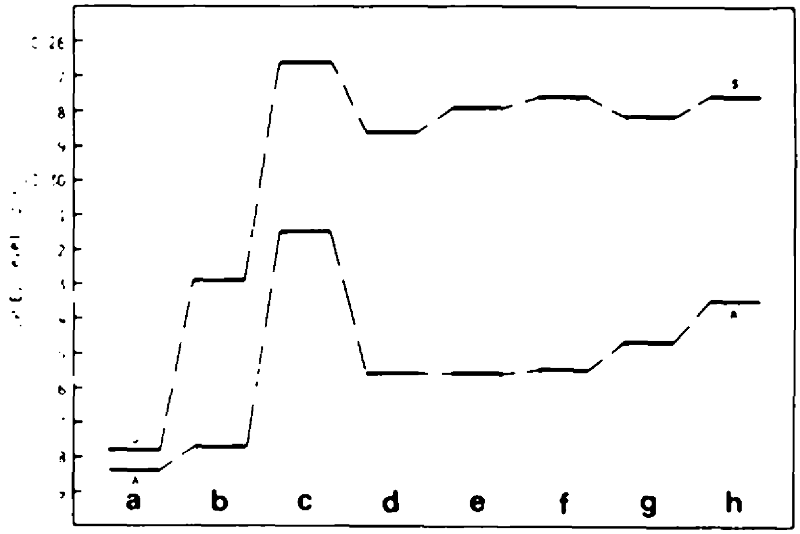

Fig 4 Variation of LPOEs for Model 2 See also Fig 5.

virtue of the antisymmetricity of this level. It is this interaction that is responsible for the destabilization of the S level in the through-bond interaction of **1**. This conclusion is very interesting in relation to the analysis of the through-bond interaction.

(h) **b** + **c** + **d** + **e** + **f** + **g**, as can be expected, the situation is similar to the case of **g**. This shows again that the dominant interaction to destabilize the S level is the interaction shown in the diagram **g**, and the other interactions are not so important to govern the height of the LPOEs of the S combination. In other words, diagrams **b**, **c**, **d**, **e**, **f** and **g** contribute to the change of the S and A levels, but these contributions cancelled approximately with each other leading to the dominant contribution of the diagram **g**.

(i) From the full interaction state (state **k**), only two N H bonds and the direct through-space interaction between the LPOs were cut off. This state corresponds to so-called "through-bond" interaction. The height of the S and A levels are close to those in the state **h**, indicating that the state **h** (and also the state **g**) includes almost all of the main parts of the through-bond interaction which is included in the state **i**.

(j) In addition to the state **i**, the direct through-space interaction between the LPO's is added, then the S level lowers largely and the A level rises considerably as is expected from the usual behavior of the through-space interaction. In other words, **1** has large through-bond interaction leading to the large energy splitting between the LPOs with the lower A level, and this large splitting was decreased remarkably by the direct through-space interaction between the LPOs.

(**k**) In addition to the state **j**, the system is allowed to interaction with two remaining N–H bonds. This state is nothing but the full interaction state. In comparison with the state **j**, two N–H bonds also contribute to decrease the splitting of the two LPOEs. Consequently, the energy splitting for the case of the full interaction is remarkably small (0.0046 au) as the result of the cancellation of several interaction terms as mentioned previously.

Model 2

Figs 4 and 5 show the variation of the LPOE's and the interaction diagram of LPOs for **2**, respectively.

(a) Pure through-bond interaction along single path. This state can be considered as the starting point, and corresponds to the state **a** for **1**. As is done in the molecule **1**, the direct through-space interaction is cut off and two N–H bond-localized orbitals are isolated from the other part of the molecule in the state from **a** to **f** with the same reason as for **1**. It should be pointed out that the value of the splitting of the two LPOEs of the state **a** in **2** is nearly equal to that in **1**.

(b) Single through-bond path and corresponds to the diagram **i** for **1**. Again the value of the splitting of the state **b** in **2** is quite close to that of the state **i** in **1**. Consequently, we can expect the transferability of the localized orbitals in these molecules.

(c) Double through-bond paths without interaction between them. In comparison with the state **b**,

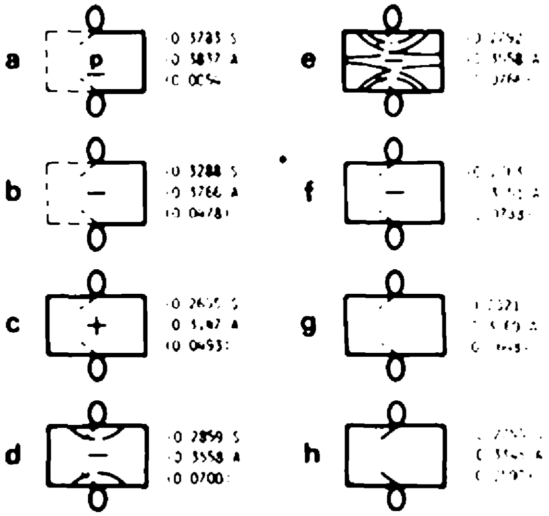

Fig 5. Typical interactions and LPOEs for Model 2 | interaction between the paths is not allowed. The other notations see Fig 3

both S and A level are destabilized, however the energy separation between the S and A levels does not vary very much. This is very interesting and its theoretical ground is discussed in the following paragraph.

(d) In addition to the state c, the interactions between two neighbouring N-C bonds are allowed. In comparison with the splitting of the state c, it is noteworthy that the great increase in the separation of the state **d** is obviously brought about by the interaction between two neighbouring N-C bonds in different paths. The theoretical ground for the increase of the energy separation is also explained by using the perturbation method.

(e) In addition to the state **d**, we added the interaction between two N-C bonds in a path and the central C-C bond in another path and vice versa. It is found that these interactions increase the splitting between the S and A levels.

(f) All of the inter-path interactions are taken into account. In comparison with the state **e**, main part of the inter-path interactions are already included in the state **e**. The value of the splitting (0.0788 au) is considered to be the value for the two through-bond interactions, and then this value is much larger than that by the single through-bond interaction (0.0465 au in the state **l** of Fig. 3).

(g) In addition to the state **f** the direct through-space interaction between two LPOs is allowed. As is theoretically expected, the S level lowers while the A level raises. This type of interaction, therefore, leads to the narrowing of the energy splitting somewhat, in analogy with **1**.

(h) Full interaction case—in other words, we added the interactions between two N-H bonds and the other part of the molecule in addition to the state **g**. Thus, this interaction leads to further narrowing of the energy splitting somewhat, in analogy with that in **1**.

From the above-mentioned analyses, the inter-path interactions shown in the state **d** is the most responsible for the larger energy separation between the S and A levels of the molecule **2** than those of the molecule **1**.

Molecule 3

The splitting of the LPOE's of **3** is reasonably expected to be explained by combining the analyses of the models **1** and **2**, since **3** has the intra-path as well as the inter-path interactions. Consequently, **3** is subjected to the analysis in the same manner as for **2**. Figs. 6 and 7 show the variation of the LPOEs and the interaction diagram of LPOs for **3**, respectively.

(a) Pure through-bond corresponds to the state **a** in Figs. 3 and 5, and the value of the splitting between the S and A levels also nearly corresponds to the previous ones.

(b) Taking into account all of the through-bond interactions along single path, and this state as well as its value of splitting between the S and A levels correspond with those in the state **l** in Fig. 3 and in the state **b** in Fig. 5, respectively.

(c) Double (two) through-bond paths without interaction between them. The separation of the LPOE's of this state is not so much different from that of the state **b**. However both energy levels shifted upward. This state corresponds to the state c in Fig. 5.

(d) Three through-bond paths are allowed and the interactions among them are not allowed. The separation of the S and A levels keeps fairly constant but the energies themselves shifted upward largely.

(e) In addition to the state c, the interaction between two neighbouring N-C bonds in different paths is allowed. As is the case of **2**, the large separation between the LPOE's is obtained.

(f) In addition to the state **e**, the inter-path interactions between two N-C bonds and the central C-C bond are allowed. As is the case of the state **e** in Fig. 5, large separation between the two levels is obtained.

(g) Taking into account all of the inter-path interaction between two paths the energy separation becomes wide. To compare with the state **f**, we can notice that the magnitude of the energy separation is close to that of the state **f**.

(h) In addition to the state **d**, only the interaction between neighbouring N-C bonds among three paths are allowed. The energy separation increases remarkably as is expected, because the relation between the states **d** and **h** corresponds to that between c and **e**.

(i) In addition to the state **h**, the interactions between the N-C bonds in a path and the non-neighbouring C-C bond in another path are allowed. The relation between **h** and **i** corresponds to that of **e** and **f**.

(j) All of the inter-path interactions are taken into

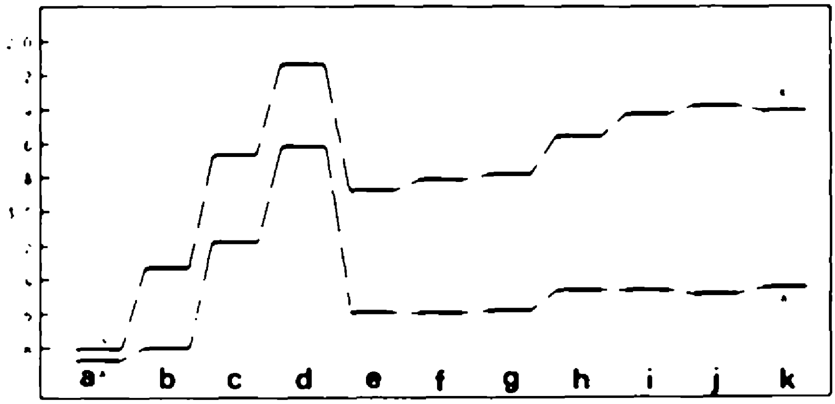

Fig. 6. Variation of LPOEs for **3**. See also Fig. 7.

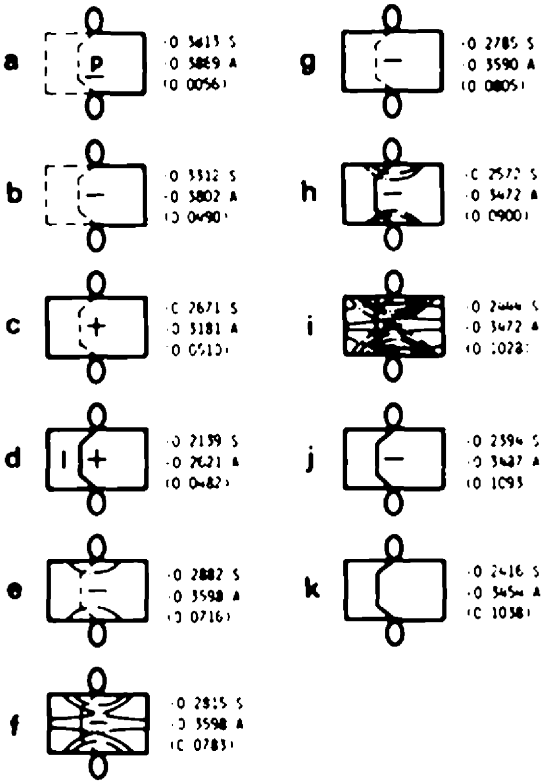

Fig 7 Typical interactions and LPOEs for 3. Notations see Figs. 3 and 5.

account. The energy separation for this state is close to that for the state *i*.

(k) In addition to the state j, the direct through-space interaction is allowed, that is, full interaction case. The S and A levels shift as is theoretically expected, but the effect of the direct through-space interaction is fairly small.

From the above-mentioned analyses, the energy splitting between the S and A levels in 3 was found to be explained in the same way as that for the model molecules 1 and 2. The large energy separation between the S and A levels in 3 is caused mainly by the inter-path interactions between neighbouring N–C bonds as is shown in the states d and h in Fig. 7. As for the intra-path interaction, the interaction between the LPO's and the central C–C bond is responsible for the splitting of the energy which is included in the states a and g of Fig. 3. Consequently, the energy splitting by the through-bond interaction in 3 was found to be beautifully explained by the above-mentioned two factors.

Theoretical grounds for the intra-path and inter-path interactions

In the following section, the theoretical grounds for the intra-path and inter-path interactions shown in Figs. 3 and 5 are derived by using the perturbation method.[21] MO's can be represented by the linear combination of the LMO's as

$$\Psi = \sum_{r(L)} C_{ir(L)} \chi_{r(L)} \tag{1}$$

where r(L) denotes the rth LMO. The first order perturbation energy is obtained by using the usual manner as

$$\epsilon_i^{(1)} = \sum_{r(L)} \sum_{s(L)} C_{ir(L)} C_{is(L)} F^{(1)}_{r(L)s(L)} \tag{2}$$

where $F^{(1)}_{r(L)s(L)}$ is the first order perturbed Fock matrix. It must be emphasized that the analysis in the present article is only concerned with the orthogonal transformation among occupied orbitals and then gives rise to no changes in the charge populations. In other words, an iterative procedure is not required for the calculation of the perturbed Fock matrices, and we can use eqn 2 straightforwardly.

The second order perturbation energy is given in eqn 3

$$\epsilon_i^{(2)} = -\sum_j{}' \frac{\left(\sum_{r(L)} \sum_{s(L)} C^{(0)}_{jr(L)} C^{(0)}_{is(L)} F^{(1)}_{r(L)s(L)}\right)^2}{\epsilon_j^{(0)} - \epsilon_i^{(0)}} \tag{3}$$

where Σ_j' denotes the summation on j except for i, and $\epsilon_i^{(0)}$ the ith orbital energy of the 0-th order.

First of all, the theoretical ground for the intra-path interaction is analysed, that is, great increase in splitting of the S and A levels from the state a to the state g in Fig. 3 is the most important part of the intra-path interaction. The coefficients of the LMOs in the state a are given together with the necessary first order Fock matrix $F^{(1)}_{r(L)s(L)}$ in Fig. 8. Obviously in the S level, we obtain a remarkably large positive value of $\epsilon_i^{(1)}$ and this results in the upper shift of the S level, while in the A level there is no contribution of $\epsilon_i^{(1)}$ by virtue of the antisymmetricity of the orbital and no change in the height of the A level.

Next, we pay our attention to the behavior of the S and A levels of the states b and c in Fig. 5, that is, the splitting of the two levels in the state b has nearly equal value to that in the state c in spite of the different numbers of paths between the LPOs. In this case, energy change from the state b to the state c is obtained by using the second order perturbation energy given by eqn 3. In Fig. 9, coefficients of the LMO's of two isolated parts of 2 are given together

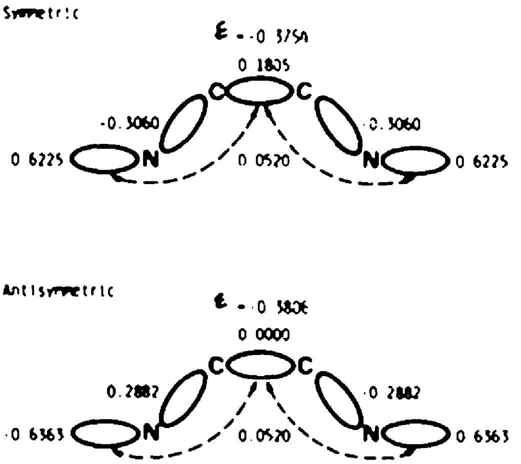

Fig 8 The coefficients and the first order Fock matrices in the S and A levels of the state a in Fig 3. The numbers written close to the dotted line with arrows are the values for the first order Fock matrices.

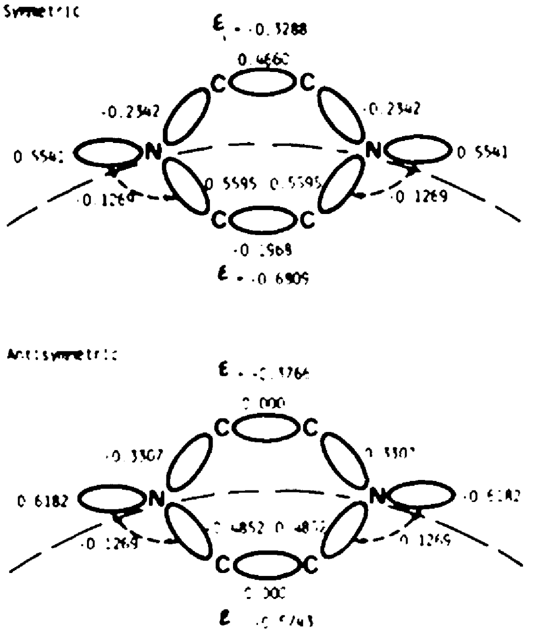

Fig. 9. The coefficients and the first order Fock matrices of the state **b** in Fig. 5 for two isolated parts of the molecule **2**. Two isolated parts are separated by the line. - The orbital energies for two isolated parts are indicated. The other notations see Fig. 8.

with the corresponding orbital energies for the S and A energy levels. The state **c** can be obtained by the interaction between two parts through the first order Fock matrix of − 0.1269 (indicated by the arrow in the figure). In this figure, only the most important level is shown to estimate approximately the contribution of another path to the energy separation. From eqn 3, we can reasonably expect that the second order energies for the S and A levels are fairly large positive values and nearly equal with each other. Consequently, the S and A levels shift upward with nearly equal magnitude in changing from the state **b** to the state **c** and results in the nearly constant value of the energy separation between the S and A levels in good correspondence with the numerical results in Fig. 5.

Finally, we analyze the theoretical ground for large increase in the splitting between the S and A levels in comparing the state **c** with the state **d** in Fig. 5. This is reasonably explained by using the first order perturbation energy given by eqn. In Fig. 10, the coefficients of the LMO's in the state **c** are given for both S and A levels together with relevant first order Fock matrices. Among inter-path interactions, the interaction between two neighbouring N-C bonds must be the most important one. This interaction in the A level is no more than that in the S level because of larger coefficient of the A level (0.2790) in comparison with the S level (0.1969). Thus, the splitting between the two levels is predicted to increase by this interaction. Moreover, both levels have to shift downward from eqn (2). These analyses are in complete agreement with the numerical results shown in the states **c** and **d** of Fig. 5. The interaction between C-N bonds and the central C-C bond make the S level shift upward slightly because of the different signs of the coefficients of relevant LMOs (− 0.3256 and 0.1969 in Fig. 10). On the other hand, the above-mentioned interaction gives the A level no change because of no coefficient for the central C-C bond LMO in the A level of Fig. 10. These conclusions are also coincident with the numerical results shown in the states **d** and **e** of Fig. 5.

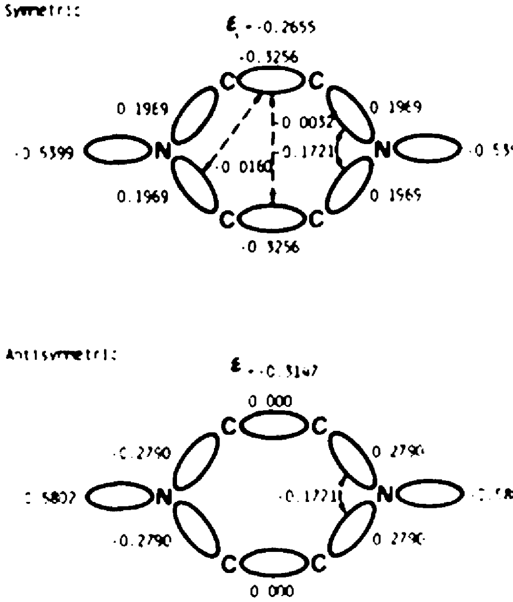

Fig. 10. The coefficients and the first order Fock matrices in the S and A levels of the state **c** in Fig. 5. Notations see Fig. 8.

CONCLUSION

From the present analysis, it was found that the splitting of the LPO's is governed mainly by the two factors: one is the interaction between LPO's and the central C-C bond in the intra-path interaction and another one is the interaction between two neighbouring N-C bonds in the inter-path interaction. The theoretical grounds for the contribution of the interactions to the splitting are satisfactorily explained by using the usual simple perturbation method. The present procedure for the analysis should certainly be very useful to understand the nature of the through-bond interaction.

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