Through-Space Interactions in Non-Kekulé Biradicals

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Through-space interactions in non-Kekulé biradicals were analyzed. We defined $PNBMO_{i,j}$ as a product of i-th and j-th NBMO of non-Kekulé biradicals. Whereas through-space interactions between non-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ were negligible in so-called disjoint-type biradicals, antibonding-through-space interactions between second-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ destabilized the singlet states in so-called nondisjoint-type biradicals. The instabilities in the singlet states contributed to the triplet state preference for nondisjoint-type biradicals.

Non-Kekulé hydrocarbons have attracted the interest of many quantum chemists. Non-Kekulé hydrocarbons are π-conjugated compounds of which molecular structures cannot be drawn only by C=C double bonds. Non-Kekulé hydrocarbons have non-bonding molecular orbitals (NBMOs), of which the eigenvalues are zero with respect to the Coulomb integral α in the Hückel molecular orbital method. The number of NBMOs in non-Kekulé hydrocarbons has been predicted by Longuet–Higgins,[1] and their coefficients are obtained by using the NBMO method.[1,2] We can expect high-spin states of the non-Kekulé hydrocarbons from the Hund's rule, because the NBMOs are degenerate. The spin-quantum number S of non-Kekulé hydrocarbons predicted by the Hunt's rule is expressed by Eq. 1:[1]

$$S = \frac{N - 2T}{2}, \tag{1}$$

where N and T are number of carbon atoms and classical double bonds, respectively.

Mataga proposed the possibilities of organic ferromagnets based on a molecular orbital method[3] that takes into account the topological degeneracy[4] coming from the unique linkage of the carbon atomic sites of *m*-phenylene skeleton. Ovchinikov has also proposed the possibilities of organic ferromagnets based on valence bond theory.[5] The theory is related to the spin polarization concept of hydrocarbon, which plays an important role in the intermolecular spin alignment.[6] Tyutyulkov and co-workers have also proposed various non-Kekulé polymers with ferromagnetic properties.[7]

Non-Kekulé biradicals are the simplest candidates for high-spin organic molecules. They have two NBMOs and two unpaired electrons. From Eq. 1, their ground states are predicted to be triplet with spin-quantum number 1. Some non-Kekulé biradicals, however, have singlet ground states in violation of Hund's rule. The theoretical aspects of the violation of Hund's rule in non-Kekulé biradicals have been theoretically studied by Borden and Davidson.[8,9] Their work has made it possible to design not only high-spin organic molecules but also organic ferromagnets using so-called disjoint and nondisjoint concepts. Although the NBMOs of ground-state singlet biradicals can be made to span no common atoms, which is a disjoint type, the NBMOs of ground-state triplet biradicals can be made to span common atoms, which is a nondisjoint type.[8–10] Since simultaneous occupancy of two electrons with parallel spin at the same carbon atomic orbital is forbidden by the Pauli principle, the triplet stabilities of nondisjoint-type biradicals are due to reduction of Coulombic repulsion.[8] Disjoint/nondisjoint analysis has been confirmed by ab initio calculations including electron correlation.[8]

Recently, a sophisticated procedure to find nondisjoint-NBMO-degenerate systems has been suggested by Aoki and Imamura,[10] and the quantitative index L_{ij}, which represents ferromagnetic degree of general NBMO-degenerate systems, has also been suggested by them.[10] The L_{ij} index has been applied to the design of organic ferromagnets.[11,12] Many high-spin organic molecules have been designed and realized using such spin-preference rules,[13–16] and there has been increasing interest in not only high-spin hydrocarbons but also organic ferromagnets, including hetero-atom-containing systems.[17–21]

In this paper, it is shown that antibonding-through-space interactions between second-nearest-neighbor carbon atomic sites play a significant role in the instability of singlet states in nondisjoint-type biradicals. We defined $PNBMO_{i,j}$ as a product of i-th and j-th NBMO of non-Kekulé biradicals. Whereas through-space interactions between non-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ were negligible in disjoint-type biradicals, antibonding-through-space interactions between second-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ destabilized the singlet states in nondisjoint-type biradicals. The instability in the singlet states contributed to the preference for triplet states in nondisjoint-type biradicals. The through-space interactions were analyzed within the framework of the Hückel molecular orbital method. Qualitative interpretations of through-space interactions in $PNBMO_{i,j}$ are emphasized. The formulation and estimation of the through-space interactions in $PNBMO_{i,j}$ are also discussed.

Theoretical

In order to explain the through-space interactions in $PNBMO_{i,j}$, we analyzed well-known non-Kekulé biradicals:

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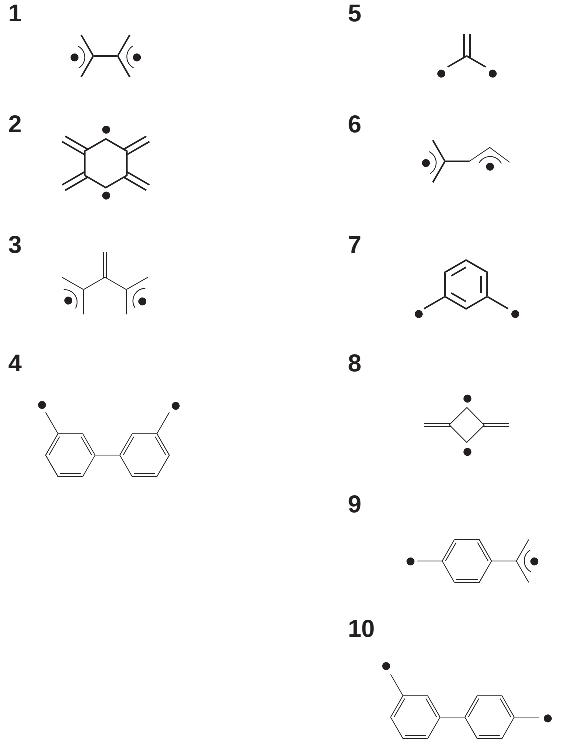

Fig. 1. Molecular structures of **1**–**10**.

tetramethyleneethane (**1**), 1,2,4,5-tetramethylenebenzene (**2**), pentamethylenepropane (**3**), biphenyl-3,3′-bismethylene (**4**), trimethylenemethane (**5**), 1,1-dimethylenebutadiene (**6**), *m*-phenylene (**7**), 1,3-dimethylenecyclobutadiene (**8**), α,α,4-trimethylenetoluene (**9**), and biphenyl-3,4′-bismethylene (**10**). The molecular structures of **1**–**10** are shown in Fig. 1. **1**, **2**, **3**, and **4** are disjoint-type biradicals with singlet ground states. On the other hand, **5**, **6**, **7**, **8**, **9**, and **10** are nondisjoint-type biradicals with triplet ground states. Many theoretical studies including ab initio calculations have established the spin states of the compounds. For example, the spin states of **1**, **2**, **3**, **5**, **7**, and **8** have been discussed in a review by Borden[9] and the literature there in. **4** and **10** have been theoretically studied by Yamaguchi and co-workers.[6] **6** and **9** have been theoretically studied by Aoki and Imamura.[10] The schematic NBMOs of **1**–**4** and **5**–**10** are shown in Figs. 2 and 3, respectively. The method of the construction of the NBMOs follows.

Since the NBMOs of non-Kekulé biradicals cannot be determined uniquely due to the topological degeneracy, we proposed that the product of two NBMOs is localized as much as possible. Such a choice of NBMOs was based on the Borden–Davidson rule,[8] which has been expanded by Aoki and Imamura.[10] The exchange integrals between two NBMOs are minimized by this choice.[10] We call these NBMOs "localized NBMOs" for convenience. The localized NBMOs lead to very small singlet-triplet energy gaps in disjoint-type biradicals and large singlet–triplet energy gaps in nondisjoint-type biradicals, because the exchange integrals are approximately zero in disjoint-type biradicals and significantly positive in nondisjoint-type biradicals within the Hartree–Fock method.[10] This is consistent with experimental studies based on ESR spectra[13,14] and ab initio calculations[9] on many non-Kekulé biradicals. Therefore, the electronic states of non-Kekulé biradicals are well described by localized NBMOs. In the case of simple non-Kekulé biradicals such as **1**, we can easily find the localized NBMOs by using the usual NBMO method.[1] However, using the theoretical procedure, it is necessary to prove a certain product of NBMOs of general non-Kekulé biradicals to be truly localized as much as possible. The general procedure to obtain the localized NBMOs has already been established by Aoki and Imamura.[10] We constructed the product of *i*-th and *j*-th localized NBMOs as $PNBMO_{i,j}$ referring to the literature[10] as described below.

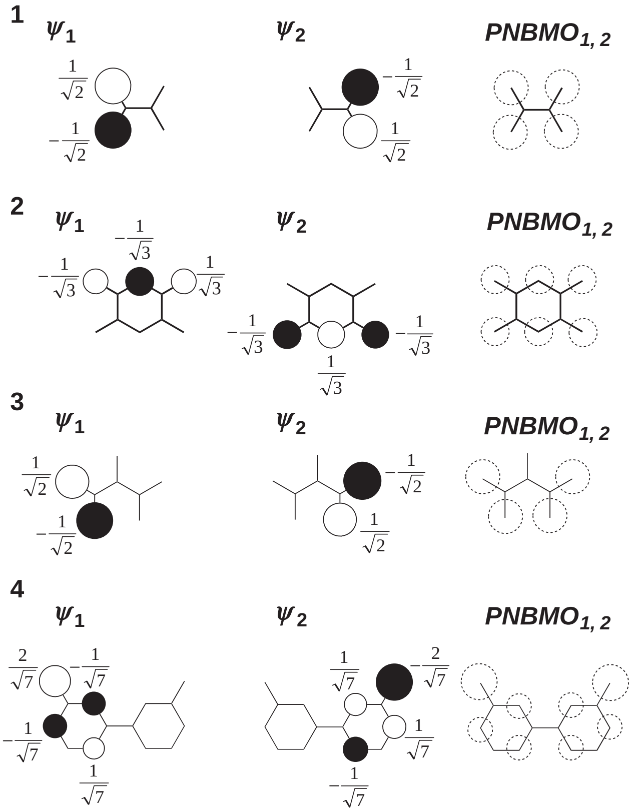

Fig. 2. Schematic localized NBMOs and $PNBMO_{i,j}$ of disjoint-type biradicals. $PNBMO_{i,j}$ vanished under the NDO approximation.

We tentatively determined $PNBMO_{i,j}$ of non-Kekulé biradicals using NBMOs ϕ_i and ϕ_j by Eqs. 2–4, where C_{ri} and C_{sj} are the NBMO coefficients on the carbon atomic site *r* and *s* in ϕ_i and ϕ_j, respectively. χ represents $2p_z$ atomic orbitals on the carbon atomic sites. The summations included all carbon atomic sites.

$$\phi_i = \sum_r C_{ri}\chi_r, \tag{2}$$

$$\phi_j = \sum_s C_{sj}\chi_s, \tag{3}$$

$$\begin{aligned} PNBMO_{i,j} = \phi_i\phi_j &= \sum_r \sum_s C_{ri}C_{sj}\chi_r\chi_s \\ &\cong C\sum_r C_{ri}C_{rj}\chi_r\chi_r. \end{aligned} \tag{4}$$

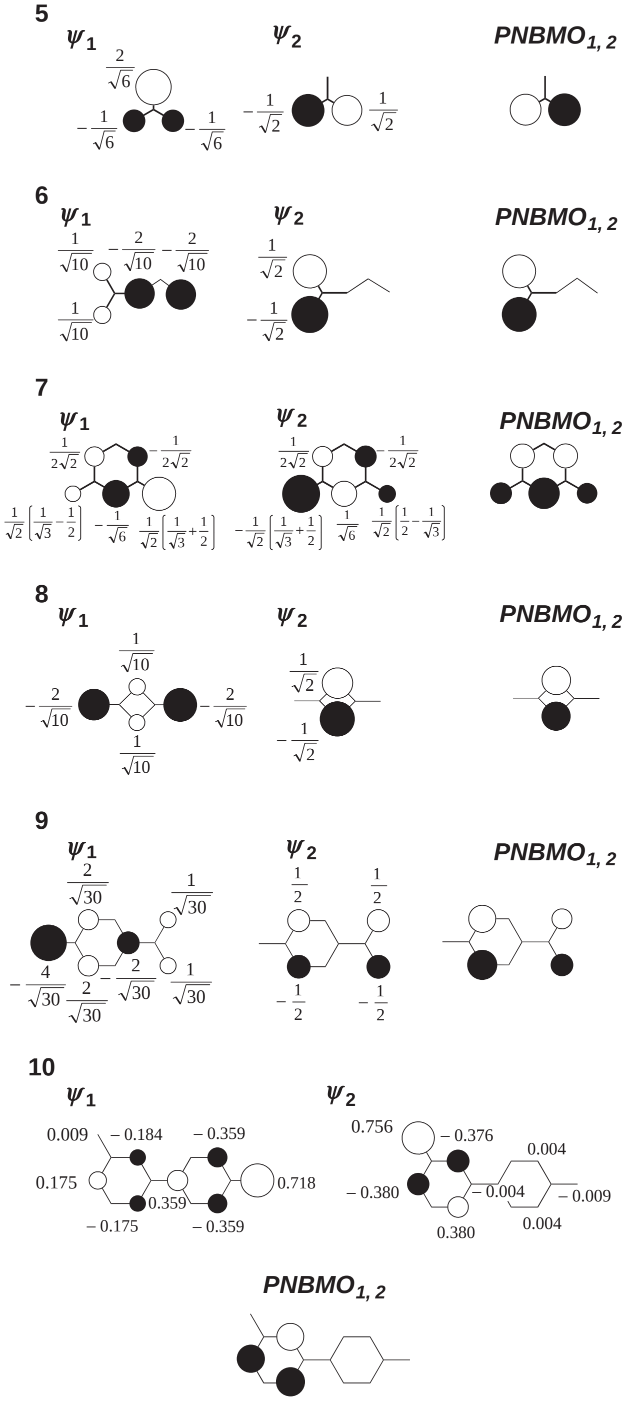

Fig. 3. Schematic localized NBMOs and $PNBMO_{i,j}$ of non-disjoint-type biradicals. The coefficients of $PNBMO_{i,j}$ are omitted.

The last approximation resulted from the "neglect of differential overlaps" (the NDO approximation). C was chosen so that the $PNBMO_{i,j}$ was normalized under the NDO approximation. The cross terms $\chi_r\chi_s$ were acceptably small, because they were created between non-nearest-neighbor carbon atomic sites due to the non-bonding characters of ϕ_i and ϕ_j. This is why the NDO approximation is reasonable. The NDO approximation makes it possible to obtain the schematic $PNBMO_{i,j}$ by simple product between the coefficients on the same carbon atomic site of each NBMO. Of course, the $PNBMO_{i,j}$ can be constructed without any approximation, but the NDO-approximated $PNBMO_{i,j}$ is sufficient for our purpose.

The tentative NBMOs ϕ_i and ϕ_j were chosen arbitrarily due to the degeneracy. In order to obtain localized NBMOs ψ_i and ψ_j, we transformed them so that the sum of the squared amplitudes of $PNBMO_{i,j}$ was minimized using unitary transformation expressed by Eq. 5.

$$\begin{pmatrix} \psi_i \\ \psi_j \end{pmatrix} = \begin{pmatrix} \sin\theta & \cos\theta \\ -\cos\theta & \sin\theta \end{pmatrix} \begin{pmatrix} \phi_i \\ \phi_j \end{pmatrix}. \tag{5}$$

The sum of the squared amplitudes of $PNBMO_{i,j}$ is degree of localizability of a certain product of NBMOs. Under the NDO approximation, this was proportional to the L_{ij} index, which has been introduced by Aoki and Imamura.[10] θ dependence of the index L_{ij} is expressed by Eq. 6, that is,

$$|PNBMO_{i,j}|^2 \propto L_{ij} = \sum_r (C'_{ri}C'_{rj})^2 = \frac{1}{8}(\alpha_{ij} + 4\beta_{ij}) - A\sin(4\theta + \varphi), \tag{6}$$

where C'_{ri} and C'_{rj} are new coefficients of the NBMOs ψ_i and ψ_j after the unitary transformation and the first and second terms are related each other by the following Eqs. 7–11.[10]

$$\pm A = \frac{1}{2}\sqrt{\gamma_{ij}^2 + \frac{1}{16}(\alpha_{ij} - 4\beta_{ij})^2}, \tag{7}$$

$$\varphi = \tan^{-1}\frac{\alpha_{ij} - 4\beta_{ij}}{4\gamma_{ij}}, \tag{8}$$

$$\alpha_{ij} = \sum_r (C_{rj}^2 - C_{ri}^2)^2, \tag{9}$$

$$\beta_{ij} = \sum_r C_{ri}^2 C_{rj}^2, \tag{10}$$

$$\gamma_{ij} = \sum_r (C_{rj}^2 - C_{ri}^2) C_{ri} C_{rj}. \tag{11}$$

If A is positive, L_{ij} is minimized when

$$4\theta + \varphi = \frac{\pi}{2}. \tag{12}$$

Thus, the parameter θ which leads to the localized NBMOs is given by Eq. 13.

$$\theta = \frac{1}{4}\left(\frac{\pi}{2} - \varphi\right). \tag{13}$$

For example, the construction of the localized NBMOs ψ_1 and ψ_2 of **1** is shown in Fig. 4. The localized NBMOs consisted of two allyl-NBMOs moieties. The resultant $PNBMO_{i,j}$ did not contain any ionic term $\chi_r\chi_r$, because the localized NBMOs span no common atoms. Then, $PNBMO_{i,j}$ vanished under the NDO approximation, as schematically depicted in Fig. 4. Such a consideration is generally extended to general disjoint-type biradicals, in which each NBMO can be localized at no common atoms. In disjoint-type biradicals, the localized NBMOs consist of two spaciously-separated-NBMO fragments. For instance, for **2**, the orbital patterns of two pentadienyl radicals were conserved in the localized NBMOs, and the resultant $PNBMO_{i,j}$ vanished as described in Fig. 2. Similarly, for **3**, the orbital patterns of two allyl radicals were conserved, and for **4**, the orbital patterns of two benzyl radicals

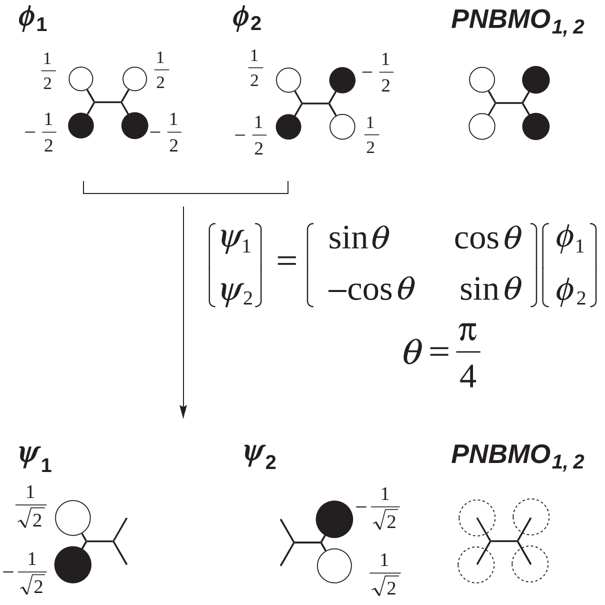

Fig. 4. Construction of localized NBMOs of **1**.

were conserved to form the localized NBMOs. Thus, the *PNBMO*$_{i,j}$ of disjoint-type biradicals vanished under the NDO approximation.

On the other hand, localized NBMOs in nondisjoint-type biradicals, such as **5**, span common atoms. Then, *PNBMO*$_{i,j}$ does not vanish. The *PNBMO*$_{i,j}$ of **5**–**10** created by the localized NBMOs are schematically shown in Fig. 3.

As a prototype of nondisjoint-type biradicals, here, we discuss fundamental properties of the NBMOs of **5** referring to Fig. 5. We focused our attention on the amplitude pattern of the *PNBMO*$_{i,j}$. From Fig. 5, second-nearest-neighbor carbon atomic sites with out-of-phase amplitudes appeared in *PNBMO*$_{i,j}$ of **5**. We denote such an out-of-phase moiety as "P_{anti}-fragment." Although we were able to show that the P_{anti}-fragment in *PNBMO*$_{i,j}$ of general nondisjoint-type biradicals results from orbital mixing, we only paid attention to amplitude patterns of *PNBMO*$_{i,j}$ of **5** after the unitary transformation. ϕ_1 and ϕ_2 depicted in Fig. 5, were already the localized NBMOs, because the value A in Eq. 7 became coincidently zero. This can be easily confirmed using Eqs. 7 and 9–11. Therefore, the index L_{ij} of **5** was independent of any unitary transformation. In relation to group theory, the NBMOs of **5** were chosen arbitrarily, because they belong to the e$''$ representation of the D_{3h} point group. Nevertheless, at least one P_{anti}-fragment always appeared in the *PNBMO*$_{i,j}$ of **5** after any unitary transformation as described below.

The two NBMOs of **5** are described concretely as Eqs. 14 and 15:

$$\phi_1 = \frac{2}{\sqrt{6}}\chi_1 - \frac{1}{\sqrt{6}}\chi_2 - \frac{1}{\sqrt{6}}\chi_3, \tag{14}$$

$$\phi_2 = -\frac{1}{\sqrt{2}}\chi_2 + \frac{1}{\sqrt{2}}\chi_3, \tag{15}$$

where χ_r ($r = 1$–3) are 2p$_z$ atomic orbitals of the peripheral carbon atomic sites. Under the NDO approximation, the *PNBMO*$_{i,j}$ of **5** becomes the following apart from the normalization factor.

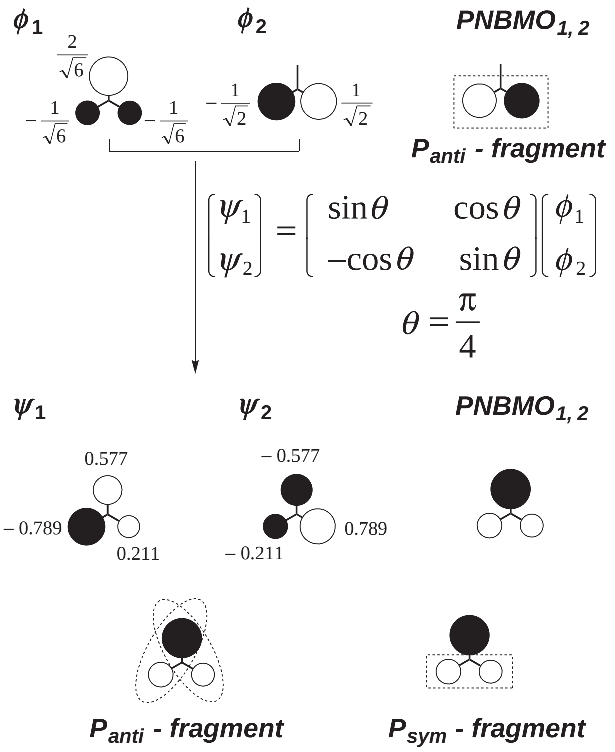

Fig. 5. Construction of localized NBMOs of **5**.

$$\phi_1\phi_2 \propto \frac{1}{\sqrt{12}}\chi_2\chi_2 - \frac{1}{\sqrt{12}}\chi_3\chi_3. \tag{16}$$

After the unitary transformations in Eq. 5, the *PNBMO*$_{i,j}$ created by the new NBMOs ψ_1 and ψ_2 becomes the following:

$$\begin{aligned}\psi_1\psi_2 &= (\sin\theta\phi_1 + \cos\theta\phi_2)(-\cos\theta\phi_1 + \sin\theta\phi_2)\\ &= \frac{1}{2}(\phi_2^2 - \phi_1^2)\sin 2\theta - \phi_1\phi_2\cos 2\theta\\ &\propto -\frac{1}{3}\sin 2\theta\chi_1\chi_1 + \left(\frac{1}{6}\sin 2\theta - \frac{1}{\sqrt{12}}\cos 2\theta\right)\chi_2\chi_2\\ &\quad + \left(\frac{1}{6}\sin 2\theta + \frac{1}{\sqrt{12}}\cos 2\theta\right)\chi_3\chi_3.\end{aligned} \tag{17}$$

The sum of the first, second, and third term became zero. In short, the sum of *PNBMO*$_{i,j}$ amplitudes was coincidently zero. Therefore, at least one amplitude having plus sign and one amplitude having minus sign always appeared in the *PNBMO*$_{i,j}$ for any θ. Thus, at least one P_{anti}-fragment always appeared in the *PNBMO*$_{i,j}$ of **5** after any unitary transformation. A typical unitary transformation with $\theta = \pi/4$ is shown in Fig. 5. After the unitary transformation, two P_{anti}-fragments appeared in the *PNBMO*$_{i,j}$ of **5**. In addition, second-nearest-neighbor carbon atomic sites with in-phase amplitudes also appeared in *PNBMO*$_{i,j}$. We denote such an in-phase moiety as "P_{sym}-fragment." The roles of P_{anti}-fragment and P_{sym}-fragment are clarified later.

In general, nondisjoint-type biradicals, the sum of *PNBMO*$_{i,j}$ amplitudes were not always zero, because the θ dependence was different from that of the sum of the squared amplitudes of *PNBMO*$_{i,j}$ (Eq. 6). The θ dependence of the sum of *PNBMO*$_{i,j}$ amplitudes is as follows:

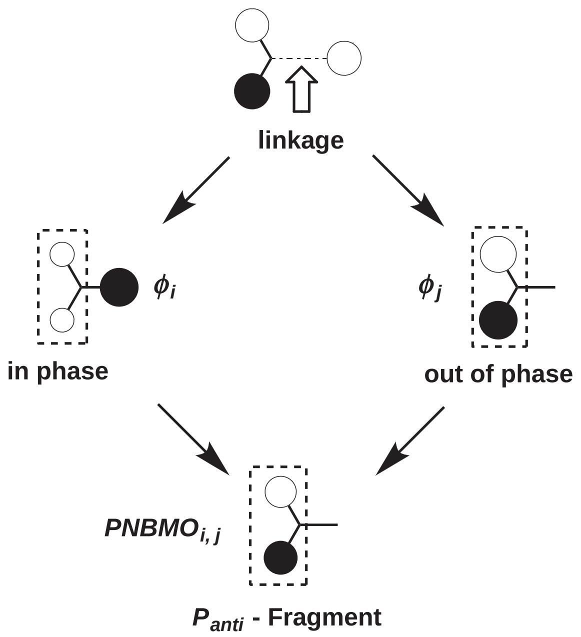

Fig. 6. Formation of P_{anti}-fragment by orbital mixing.

$$\sum_r (C'_{ri}C'_{rj}) = \frac{1}{2}\sum_r (C_{ri}^2 + C_{rj}^2)\sin(2\theta + \tau), \tag{18}$$

where τ is expressed by Eq. 19.

$$\tan^{-1}\tau = -\frac{2\sum_r C_{ri}C_{rj}}{\sum_r (C_{rj}^2 - C_{ri}^2)}. \tag{19}$$

Nevertheless, for nondisjoint-type biradicals, P_{anti}-fragments result from orbital mixing characteristic of nondisjoint NBMOs. The P_{anti}-fragment spread over second-nearest-neighbor carbon atomic sites of **5** was deduced using the perturbational molecular orbital method.[2] In short, **5** was constructed by linkage of a carbon atom and an allyl radical. As is well known, this type of linkage, that is, combination of so-called "stared atoms and unstared atoms," does not lead to not a simple linear combination of original NBMOs but orbital mixing of the original molecular orbitals.[8,10] This situation is schematically depicted in Fig. 6. Orbital mixing created a NBMO with an in-phase moiety and another NBMO with an out-of-phase moiety. Therefore, the resultant $PNBMO_{i,j}$ of **5** contained a P_{anti}-fragment spread over second-nearest-neighbor carbon atomic sites. Thus, analogous to **5**, a P_{anti}-fragment spread over second-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ of any nondisjoint-type biradical results from orbital mixing. Indeed, from Fig. 3, **6**, **7**, **8**, **9**, and **10** as well as **5** contained at least one P_{anti}-fragment spread over second-nearest-neighbor carbon atomic sites. In general, both P_{anti}-fragments and P_{sym}-fragments simultaneously appear in a nondisjoint-type biradicals by unitary transformation.

Through-Space Interactions in $PNBMO_{i,j}$

As is shown in Fig. 2, in **1**, **2**, **3**, and **4**, the $PNBMO_{i,j}$ vanished under the NDO approximation. Therefore, as a rough estimation, through-space interactions between non-nearest-neighbor carbon atomic sites in the $PNBMO_{i,j}$ are zero.

On the other hand, in **5**, the $PNBMO_{i,j}$ had a P_{anti}-fragment spread over the second-nearest-neighbor carbon atomic sites, as described in Fig. 3. The P_{anti}-fragment is expected to bring about through-space interactions in antibonding fashion. Similarly, **6** had a P_{anti}-fragment spread over the second-nearest-neighbor carbon atomic sites. In **7**, the $PNBMO_{i,j}$ had four P_{anti}-fragments spread over the four pairs of second-nearest-neighbor carbon atomic sites inside the molecule. We note that, in **7**, there were three pairs of second-nearest-neighbor carbon atomic sites with in-phase amplitudes, that is, P_{sym}-fragments also appeared in the $PNBMO_{i,j}$. Although the P_{sym}-fragments seem to bring about through-space interactions in bonding fashion, we show later that the magnitude of through-space interactions in P_{sym}-fragment is smaller than that in P_{anti}-fragment. In **8**, the $PNBMO_{i,j}$ had a P_{anti}-fragment spread over the second-nearest-neighbor carbon atomic sites. In **9**, two P_{anti}-fragments were spread over the second-nearest-neighbor carbon atomic sites. **10** had two large P_{anti}-fragments and one P_{sym}-fragment. The coefficients of the localized NBMOs cannot be expressed analytically due to the asymmetric character. The coefficients were obtained by computational procedure.

Thus, antibonding-through-space interactions in P_{anti}-fragments seem to destabilize the singlet states of nondisjoint-type biradicals. In short, the singlet instabilities caused by the through-space interactions in P_{anti}-fragments seem to contribute to the preference for the triplet states of nondisjoint-type biradicals. The formulation and estimation of the through-space interactions are described below.

Discussion

The $PNBMO_{i,j}$ is the product of two NBMOs. Therefore, $PNBMO_{i,j}$ is a total wavefunction containing frontier two electrons within the framework of the NBMO method. Therefore, through-space interactions in $PNBMO_{i,j}$ are different from usual through-space interactions in molecular orbitals. Since through-space interactions in disjoint-type biradicals are trivial, as mentioned above, we focused on through-space interactions in nondisjoint-type biradicals.

The amplitudes of P_{sym}-fragments can interact in bonding fashion between second-nearest-neighbor carbon atomic sites, as schematically depicted in Fig. 7. Bonding interactions in

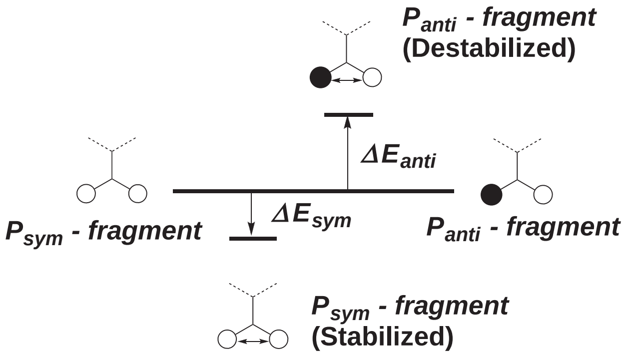

Fig. 7. Energy diagrams of through-space interactions in P_{sym}-fragment (bonding fashion) and P_{anti}-fragment (antibonding fashion).

P_{sym}-fragments stabilize the singlet states of nondisjoint-type biradicals. On the other hand, through-space interactions of P_{anti}-fragments are not bonding but antibonding, as depicted in Fig. 7. The P_{anti}-fragments destabilize the singlet states of nondisjoint-type biradicals.

Supposing that the absolute values of P_{sym}-fragment amplitudes and P_{anti}-fragment amplitudes are equal, as schematically shown in Fig. 7, the magnitude of the instabilities ΔE_{anti} caused by the antibonding interactions is slightly larger than that of the stabilities ΔE_{sym} caused by the bonding interactions. This situation is clarified later taking account of overlap integrals.

The formulation of the through-space interactions in $PNBMO_{i,j}$ is as follows. Taking into account the overlap integrals, $PNBMO_{i,j}$ is described as Eq. 20:

$$PNBMO_{i,j} \cong \frac{C\sum_r C'_{ri}C'_{rj}\chi_r\chi_r}{\sqrt{C^2\sum_r (C'_{ri}C'_{rj})^2 + 2C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2}}, \quad (20)$$

where s_{rs} is the overlap integral between r-th and s-th carbon atomic orbitals. s_{rs} is positive value. Although the first term in the root symbol becomes unity from the normarization condition Eq. 4, we did not exclude the term analytical for convenience. Eq. 20 resembles the extended Hückel wavefunction.[22,23] Our treatment was, however, different from usual extended Hückel method in that the overlap integrals were introduced not in NBMOs but in the product of NBMOs, that is, $PNBMO_{i,j}$.

Here, we explain why through-space interactions in $PNBMO_{i,j}$ influence the singlet-state energy. $PNBMO_{i,j}$ was a two-electron wavefunction constructed by NBMOs. Under the NDO approximation, the wavefunction contained only ionic terms, that is, $\chi_r\chi_r$. The ionic terms correspond to simultaneous occupancy of two electrons. Since simultaneous occupancy of two electrons with parallel spin at the same carbon atomic orbital is forbidden by the Pauli principle, resultant reduction of the Coulombic repulsion leads to triplet preference of nondisjoint-type biradicals.[8] That is, the squared amplitude of NDO-approximated $PNBMO_{i,j}$ represents the instability of the singlet states. Therefore, if the degree of simultaneous occupancy of two electrons with parallel spin at the same carbon atomic orbital decreases, the singlet state will be stabilized. Oppositely, if degree of simultaneous occupancy of two electrons with parallel spin at the same carbon atomic orbital increases, the singlet state will be destabilized. This situation is theoretically described as follows.

$PNBMO_{i,j}$ in Eq. 20 is further approximated as Eq. 21.

$$PNBMO_{i,j} \cong C\left(\sum_r C'_{ri}C'_{rj}\chi_r\chi_r\right) \times \left(1 - C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2\right). \quad (21)$$

In Eq. 21, the normalization condition (Eq. 4) was applied, and the square of $PNBMO_{i,j}$ became:

$$\begin{aligned} PNBMO_{i,j}^2 &\cong C^2\left(\sum_r\sum_s C'_{ri}C'_{rj}C'_{si}C'_{sj}\chi_r(1)\chi_r(2)\chi_s(1)\chi_s(2)\right) \\ &\quad\times\left(1 - C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2\right)^2 \\ &\cong C^2\left(\sum_r C'^2_{ri}C'^2_{rj}\chi_r(1)^2\chi_r(2)^2\right) \\ &\quad\times\left(1 - C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2\right)^2. \end{aligned} \quad (22)$$

In Eq. 22, the NDO approximation was applied. The electron number 1 and 2 were added for clarification. Thus, the degree of simultaneous occupancy of two electrons with parallel spin at r-th carbon atomic orbital is:

$$\begin{aligned} |PNBMO_{i,j}|_r^2 &\cong C^2C'^2_{ri}C'^2_{rj} \\ &\quad\times\left(1 - C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2\right)^2 \\ &\cong C^2C'^2_{ri}C'^2_{rj} \\ &\quad\times\left(1 - 2C^2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})s_{rs}{}^2\right), \end{aligned} \quad (23)$$

where the forth-order terms with respect to s_{rs} are ignored.

The cross term $(C'_{ri}C'_{rj})(C'_{si}C'_{sj})$ in the last expression in Eq. 23 is product of $PNBMO_{i,j}$ amplitudes between r-th and s-th carbon atomic sites. This term is positive when the r-th and s-th $PNBMO_{i,j}$ amplitudes have the same sign. Oppositely, the term is negative when the r-th and s-th $PNBMO_{i,j}$ amplitudes have different sign. Therefore, the term $(C'_{ri}C'_{rj})(C'_{si}C'_{sj})$ is positive in P_{sym}-fragments and negative in P_{anti}-fragments, respectively. Thus, from Eq. 23, P_{sym}-fragments decrease the degree of simultaneous occupancy of two electrons with parallel spin at r-th carbon atomic orbital. That is, the singlet instability is decreased. In other words, bonding interactions in P_{sym}-fragments stabilize singlet states. Oppositely, P_{anti}-fragments increase the degree of simultaneous occupancy of two electrons with parallel spin at r-th carbon atomic orbital. That is, the singlet instability is increased, i.e., antibonding interactions in P_{anti}-fragments destabilize the singlet states. This is the reason why through-space interactions influence the singlet-state energy.

We next show energy expressions of $PNBMO_{i,j}$. We first note that the simple NDO-approximated $PNBMO_{i,j}$, that is, the last expression in Eq. 4 is an eigenfunction of the sum of one-electron effective Hamiltonian containing frontier two electrons as expressed by Eq. 24.

$$h_{eff} = h(1) + h(2). \quad (24)$$

The corresponding expectation value is 2α, where α is the simple-Hückel-sense Coulomb integral and overlap integrals are ignored.

Similarly, the expectation value E corresponding to the Eq. 20 is expressed by Eq. 25,

$$E = \langle \psi_i(1)\psi_j(2)|h_{\mathrm{eff}}|\psi_i(1)\psi_j(2)\rangle = \frac{2\sum_r (C'_{ri}C'_{rj})^2 H_{rr} + 4\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})H_{rs}}{\sum_r (C'_{ri}C'_{rj})^2 + 2\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj}){s_{rs}}^2}, \quad (25)$$

where H_{rr} and H_{rs} are the extended-Hückel-sense Coulomb integral and the resonance integral between non-nearest-neighbor carbon atomic sites r and s. Both H_{rr} and H_{rs} are negative values. Eq. 25 is an extensional energy expression of the simple NDO-approximated $PNBMO_{i,j}$.

The first term in the denominator in Eq. 25, that is, $\Sigma(C'_{ri}C'_{rj})^2$, is identical to L_{ij}. This value is not zero in nondisjoint-type biradicals, because the NBMOs span common atoms. Therefore, E is approximated as follows:

$$E = \frac{2H_{rr} + \dfrac{4}{\sum_r (C'_{ri}C'_{rj})^2}\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})H_{rs}}{1 + \dfrac{2}{\sum_r (C'_{ri}C'_{rj})^2}\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj}){s_{rs}}^2}$$
$$= (2H_{rr} + \Lambda_{ij})(1 - Z_{ij} + Z_{ij}^2 - Z_{ij}^3 + \ldots)$$
$$\cong 2H_{rr} + (\Lambda_{ij} - 2H_{rr}Z_{ij}) - Z_{ij}(\Lambda_{ij} - 2H_{rr}Z_{ij}), \quad (26)$$

where Λ_{ij} and Z_{ij} are defined by Eqs. 27 and 28.

$$\Lambda_{ij} = \frac{4}{\sum_r (C'_{ri}C'_{rj})^2}\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj})H_{rs}, \quad (27)$$

$$Z_{ij} = \frac{2}{\sum_r (C'_{ri}C'_{rj})^2}\sum_{r\neq s}(C'_{ri}C'_{rj})(C'_{si}C'_{sj}){s_{rs}}^2. \quad (28)$$

Again, the cross term $(C'_{ri}C'_{rj})(C'_{si}C'_{sj})$ in Eqs. 27 and 28 is product of $PNBMO_{i,j}$ amplitudes between r-th and s-th carbon atomic sites. Therefore, $(C'_{ri}C'_{rj})(C'_{si}C'_{sj})$ is positive in P_{sym}-fragments and negative in P_{anti}-fragments, respectively.

Λ_{ij} is decreased by P_{sym}-fragments and increased by P_{anti}-fragments. In contrast to Λ_{ij}, Z_{ij} increases due to P_{sym}-fragments and decreases due to P_{anti}-fragments. From Eq. 26, ΔE_{anti}, caused by the P_{anti}-fragments, is larger than ΔE_{sym} caused by P_{sym}-fragments, similar to the usual extended Hückel molecular orbital method.[22,23]

Supposing that the Coulomb integral H_{rr} is $-11.4\,\mathrm{eV}$[22] and the second-nearest-neighbor overlap integral s_{12} is 0.0339 (corresponding to each C–C bond length 1.40 Å and C–C–C bond angle 120°),[24] the second-nearest-neighbor resonance integral H_{12} was estimated to be $-0.676\,\mathrm{eV}$ using the Wolfsberg–Helmholtz approximation,[22]

$$H_{12} = \frac{1.75}{2}s_{12}(H_{11} + H_{22}), \quad (29)$$

where H_{11} and H_{22} are identical to H_{rr} in the case of non-Kekulé hydrocarbons.

The energy of through-space interactions ΔE are obtained by subtracting $2H_{rr}$, that is, non-perturbed energy from E as expressed by Eq. 30.

$$\Delta E = E - 2H_{rr}. \quad (30)$$

Table 1. Through-Space Interactions ΔE in Non-Kekulé Biradicals **1–10**

Biradical	ΔE	Spin state
1	0	Singlet[8,9]
2	0	Singlet[9]
3	0	Singlet[8,9]
4	0	Singlet[6,10]
5	−1.96	Triplet[8,9,21]
6	−1.96	Triplet[8,10]
7	−1.42	Triplet[9]
8	−1.96	Triplet[8,9]
9	−1.96	Triplet[10]
10	−1.38	Triplet[6]

a) ΔE are expressed in units of the second-nearest-neighbor resonance integral H_{12} ($H_{12} < 0$).

The calculated ΔE for **1–10** are summarized in Table 1. In the calculations, only the second-nearest-neighbor carbon atomic sites was taken into account. ΔE are expressed in units of the second-nearest-neighbor resonance integral H_{12}. For disjoint-type biradicals **1–4**, the through-space interaction energies were zero, as mentioned above. On the other hand, for nondisjoint-type biradicals **5–10**, the interaction energies were positive. Although our estimation is qualitative, it can clearly be seen from Table 1 that antibonding-through-space interactions in P_{anti}-fragments contribute to the instabilities of the singlet states in nondisjoint-type biradicals.

We concluded that the perturbations caused by antibonding-through-space interactions between the second-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ led to the instabilities of the singlet states of nondisjoint-type biradicals. In other words, the instabilities in the singlet states contribute to the triplet state preference of nondisjoint-type biradicals.

Concluding Remarks

Through-space interactions in non-Kekulé biradicals were analyzed using the product of the NBMO (non-bonding molecular orbital)s. We defined $PNBMO_{i,j}$ as a product of i-th and j-th NBMO of non-Kekulé biradicals. Although through-space interactions between non-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ were negligible in so-called disjoint-type biradicals, antibonding-through-space interactions between second-nearest-neighbor carbon atomic sites in $PNBMO_{i,j}$ destabilized the singlet states in so-called nondisjoint-type biradicals. The instabilities of the singlet states contribute to the preference for the triplet states of nondisjoint-type biradicals.

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