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AN ANALYSIS OF THE THROUGH-BOND INTERACTION USING THE LOCALIZED MOLECULAR ORBITALS WITH <u>AB</u> <u>INITIO</u> CALCULATIONS -- IV

ROLE OF RELAY ORBITALS IN PERPENDICULAR Π -SYSTEMS

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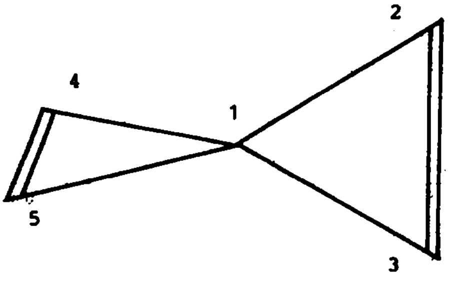
Abstract---The analysis of the through-space/bond interaction using the localized molecular orbitals with ab initio calculation is applied to perpendicular π -system. We have performed the analysis for spiropentadiene and tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene as the models of the perpendicular π -system. The former compound has the spiroconjugation, and the latter one has relay orbitals in the molecule. With use of our method, it is clarified that the relay orbitals play an important role for the determination of the energy levels of perpendicular π -orbitals. It is found that this analysis is useful for the study of the intramolecular long-range interactions.

Since the concept of the "through-bond" and the "through-space" interactions was proposed originally by Hoffmann et al. in 1968,[1-2] this analysis has been used for wide range of the chemistry by many theoretical and experimental chemists. Especially, the photoelectron spectra of various organic molecules were analyzed in terms of the through-space/bond interactions. In previous papers,[3-5] we proposed and examined a method for a qualitative estimation of the "through-bond" interactions using ab initio localized molecular orbitals. For example, this method could qualitatively explain the intramolecular long-range interaction between lone pair orbitals. In this paper we apply the above method to the analysis of the interaction between mutually perpendicular π -orbital systems. For the estimation of the interaction between the perpendicular π -orbitals, Bischof et al. has reported using the MINDO/3 method in comparison with their photoelectron spectral data.[6] In order to get more qualitative and precise knowledge for this object, we performed the ab initio calculations with our through-bond analysis procedure.

As the models of the perpendicular π -system, we choose two compounds, spiropentadiene 1 and tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene 2. These compounds have mutually perpendicular π -orbitals at the both side of the molecules.



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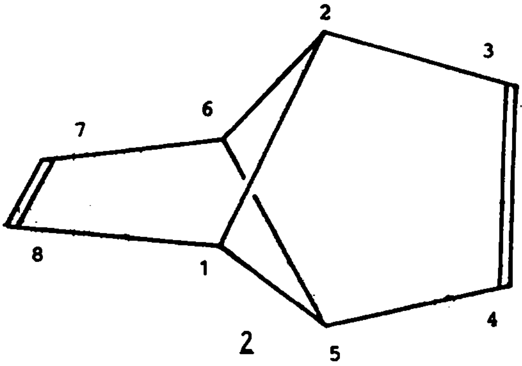

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Fig. 1. Schematic Structures and Atom Numbering of Spiropentadiene 1 and Tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene 2.

In the case of the two mutually perpendicular π-orbital systems, the combined π-orbitals, which are constructed by the linking of the parent π-orbitals, are subjected to the "through-space" interaction. This, which is called spiroconjugation, has been studied by theoretical[6-8] and experimental[6,7,9-11] approaches. The simplest case of the spiroconjugation is spiropentadiene 1. This has two perpendicular cyclopropene rings as shown in Fig. 1(a), so this molecule has D_{2d} symmetry. From the point of view of the symmetry, the space spanned by the total π-orbitals can be divided to three sets of A_2, B_1, and E symmetry. The anti-bonding π-orbitals become the "out of phase" combination a_2 and the "in phase" combination b_1, as shown in Fig. 2, while the bonding orbitals still remain as a degenerate pair. For the anti-bonding π-orbitals, it is expected theoretically that the b_1-orbital will be more stable than the a_2-orbital, since the direct through-space interaction acts as bonding between the parent π-orbitals. However, such orbital splitting is expected to be rather small, because the two parent π-orbitals is placed in a long distance. On the other hand such interaction may be expected to increase for tricyclo compound, as shown in Fig. 1(b), which has cyclobutane ring in middle of two π-orbitals as the so-called "relay orbitals". In this case, however, it was reported that the a_2-orbital is more stable than the b_1-orbitals.[6] In the present study, we try to explain the difference between above two π-systems qualitatively.

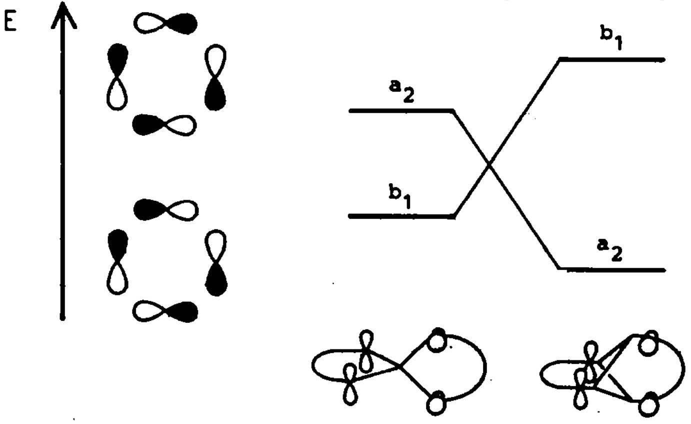


Fig. 2. Orbital Sequence for b_1- and a_2-orbitals in The Spiro Compounds (Left) and The Corresponding Tricyclic Compounds (Right).

<u>Method of calculation</u> The original canonical MO's (CMO's) were obtained from <u>ab initio</u> LCAO MO calculations.[12] The basis set was the STO-3G functions with the standard scale factors developed by Pople <u>et al.</u>,[13] and the program GAUSSIAN 70[14] was used. The localized MO's (LMO's) were obtained from the CMO's by the procedure of Edmiston-Ruedenberg.[15] The detailed procedure of the calculations has been described in the previous paper.[3] The molecular geometric parameters of the carbon skeltons for spiropentadiene and tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene were the same to those determined by Bischof <u>et al.</u>[6] using the MINDO/3 method, and are shown in Table I with the remaining parameters used here.

TABLE I. Structural Parameters of The Calculated Compounds.[a]

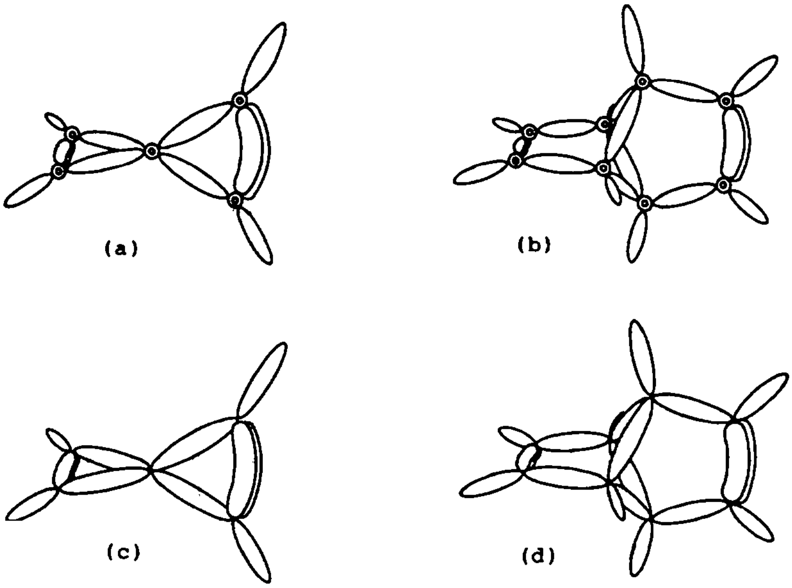
Spiropentadiene		Tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene			
r (C1-C2)	1.49	r (C1-C2)	1.59	α (C2-C3-C4)	103.0
r (C-H)	1.10	r (C2-C3)	1.52	α (C2-C3-H)	128.5
α (C2-C1-C3)	58.0	r (C3-C4)	1.35	α (C3-C2-H)	116.0
α (C1-C2-H)	149.0	r (C-H)	1.10	dihedral angle[b]	104.0

a) Lengths are in angstrom, and angles are in degree.

b) The angle between the planes C1-C2-C6 and C1-C5-C6.

RESULTS AND DISCUSSION

The rough sketches of the calculated LMO's are shown in Fig. 3. Fig. 3(a) and (b) correspond to the occupied LMO's for compounds 1 and 2, respectively, and (c) and (d) correspond to the virtual LMO's. In Fig. 3(a) and (b), the circles at carbon nuclei mean the 1s core orbitals which strictly localized at carbon nuclei. In Fig. 3(c) and (d), the virtual LMO's have the nodes of the anti-bonding orbitals at the middle of themselves. Since we obtained the LMO's with no restriction for orbital mixing, namely since the σ-orbitals and the π-orbitals could be mixed with each other, the LMO's obtained for the carbon-carbon double bonds had the "banana-like" shapes, so we call them "banana bonds" hereafter.


(a) (b)

(c) (d)

Fig. 3. The Shape of Occupied (Upper Side) and Virtual (Lower Side) LMO's for Spiropentadiene (Left) and Tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene (Right).

Virtual orbitals Fig. 4 shows the change of the orbital energies for anti-symmetric pair of the "banana bonds" in virtual orbital space of spiropentadiene. The left part of Fig. 4 indicates the energy level of the orbital which is an out-of-phase combination of banana bonds within one cyclopropane ring. This energy level is determined only by the interaction between a pair of banana bonds. Of course, the orbital which is constructed by another side bonds exists at the same energy level. As shown in the right side of Fig. 4, where the result of the full interaction between two pairs of banana bonds is given, the interaction between two cyclopropene rings splits two pairs of orbitals into a a_2- and a b_1-orbital. In this spiro compound case, there are no other orbitals which can interact with the banana bonds at both sides, and then only the direct through-space interaction between the banana orbitals has an effect. Because of the long

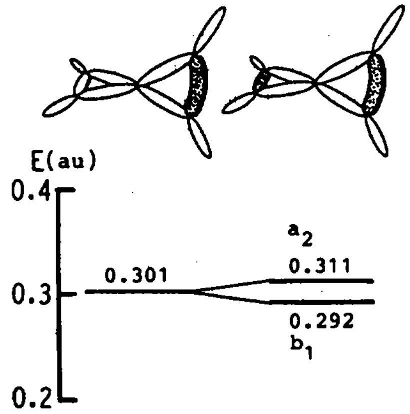


Fig. 4. Orbital Energy Diagram for Virtual LMO's of Spiropentadiene.

distance between two pairs, the energy separation is rather small (0.019au), but the a_2-orbital becomes more unstable while the b_1-orbital becomes more stable.

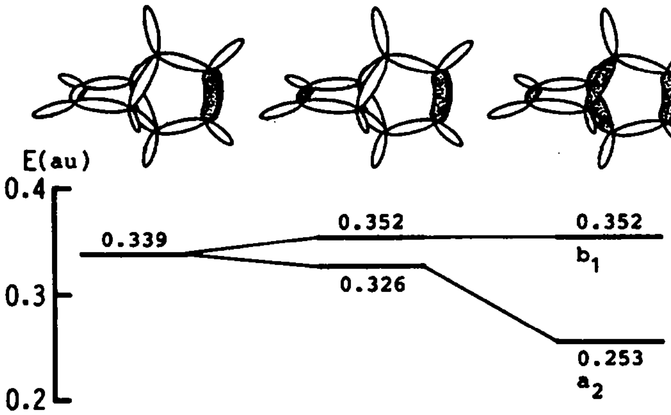


Fig. 5. Orbital Energy Diagram for Virtual LMO's of Tricyclo[$3,3,0,0^{2,6}$]octa-3,7-diene.

For tricyclo compound 2, Bischof et al.[6] reported that the order of energies of the a_2- and the b_1-orbitals within the virtual space was opposite to that of spiropentadiene 1 from their MINDO/3 calculation. The most right side of Fig. 5 is the orbital levels with the full interactions. In this case all orbitals within the B_1 and the A_2 symmetries, respectively, are allowed to interact with each other. As is shown in this diagram, our ab initio calculation gave the same result that the a_2-orbital is more stable (0.099au) than the b_1-orbital. In order to analyze the role of relay orbitals, we cut the interactions between the banana bonds and the relay orbitals and still considered the direct interaction between the both banana orbitals. As is shown in the middle diagram of Fig. 5, the energy ordering is the same as that in the full-interaction case against the prediction that the splitting is similar with the spiro compound, though the separation between these orbitals is small (0.026au). In order to understand this contradiction, we carried out a calculation for two ethylene molecules which are placed at the same positions with the double bonds of tricyclo compound. Fig. 6 shows that in this case the a_2-orbital is higher in energy than the b_1-orbital, though the separation is very small (0.0016au) because of the little overlap. This means that the pure direct through-space interaction between two banana bonds may give the same result with the spiropentadiene which has no relay orbitals. Therefore it may be probable that the above contradiction is due to the "tailing" of the LMO's, namely the penetration of the banana bond LMO's to the relay orbital region. Generally speaking, the Edmiston-Ruedenberg method used for the LMO's can not so strictly localize the Hartree-Fock-Roothaan orbitals to the so-called "chemical bonds" between two nuclei.

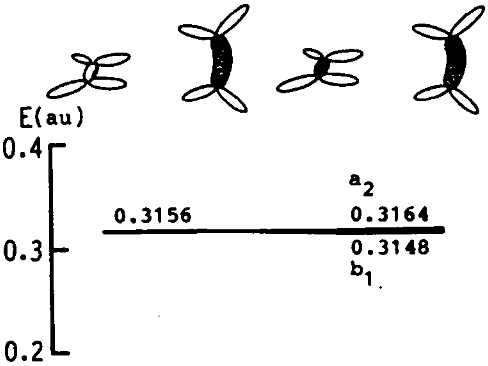


Fig. 6. Orbital Energy Diagram for Virtual LMO's of Two Ethylene Molecules.

In Fig. 5 the b_1-orbital does not change its energy level by the interaction with the relay orbitals. (See the middle and the right diagrams of Fig. 5.) Though this is caused by the absence of other b_1-orbitals in the virtual orbital space within the minimal basis set approximation used in the present calculation, it seems to be true that the b_1-orbital suffers a smaller influence from the relay orbitals than the a_2-orbital even if a better basis set was used.

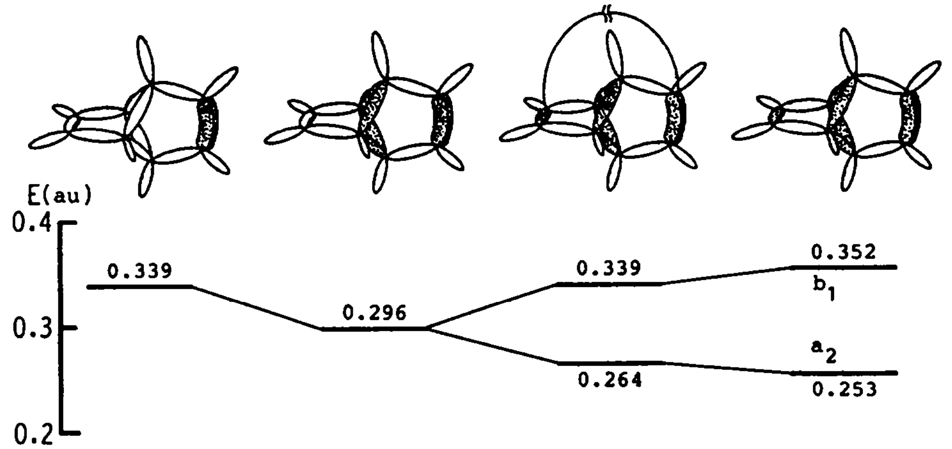


Fig. 7. Effect of Relay Orbitals for Virtual LMO's of Tricyclo[3,3,0,0^{2,6}]octa-3,7-diene.

Next we examined the role of the relay orbitals in more detail. Fig. 7 shows the orbital energies for four types of the interactions between LMO's. The energy level on the far left means the case of the single-side banana bonds alone, and the next one is the case in which the interaction between the banana bonds and the relay orbitals was added. Only the through-space interaction between the banana and the relay orbitals is acting because of the symmetry restriction, but the stabilization of the orbital energy is rather large (0.043au). Adding the

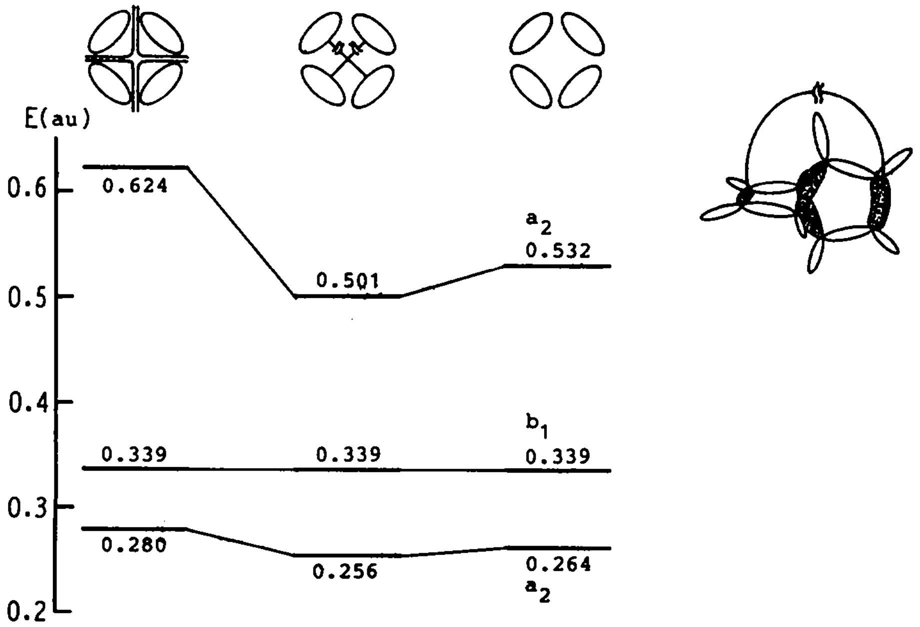


Fig. 8. Parallelism Between Orbital Energies of Relay Orbitals and Perpendicular π-orbitals.

interaction from the banana bonds on the opposite side through the relay orbitals, we obtained the splitting to the b_1- and the a_2-orbitals. The splitting of this is 0.075au. Furthermore, the addition of the direct through-space interaction between the banana bonds at both sides of the molecule caused the instabilization of the b_1-orbital (0.013au) and the stabilization of the a_2-orbital (0.011au). It is worth noting that the sum of the direct interaction effects to both the b_1- and the a_2-orbitals (0.024 au) is nearly equal to this type of the effect obtained without involving the relay orbitals as is shown in the middle diagram of Fig. 5.

Furthermore, in order to investigate the effect of the existence of the relay system, we cut the interactions among the relay orbitals as is shown in Fig. 8. The left diagram indicates the energy levels after taking four carbon-carbon bonds of the relay orbitals to pieces, the middle corresponds to the case to cut only the interactions between the opposite sides of cyclopropane ring, and the right one is the same with the third one in Fig. 7. The upper side diagrams of Fig. 8 are the orbital energies which are mainly made from the relay orbitals, and the lower side corresponds the orbitals which include the banana bonds. There is a parallelism between the relay orbital energies and the a_2-orbital energies, though the b_1-orbital energies do not change during above artificial process. It is the reason of this tendency of the b_1-orbital that there are no b_1 symmetry virtual orbitals of the relay cyclopropane ring in the minimal basis set approximation as mentioned before. In contrast to this the a_2-orbitals can interact with the virtual orbitals of the relay system.

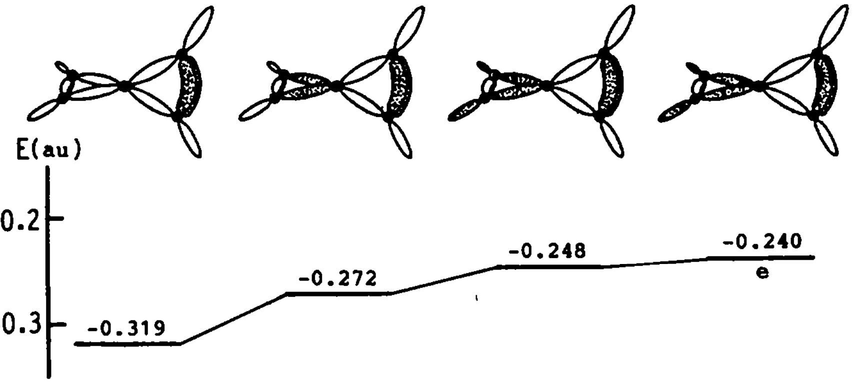


Fig. 9. Orbital Energy Diagram for Occupied LMO'S of Spiropentadiene.

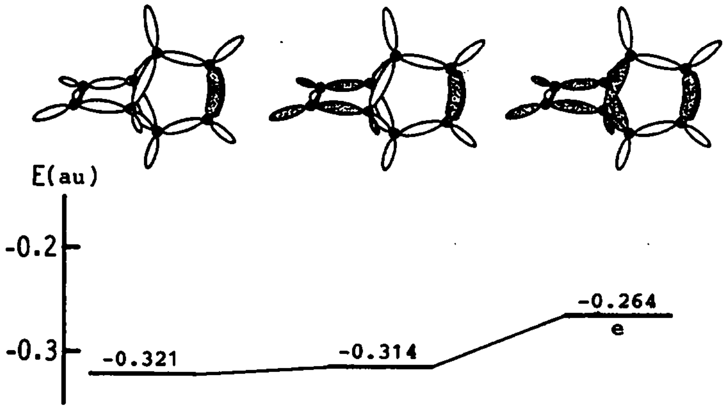


Fig. 10. Orbital Energy Diagram for Occupied LMO's of Tricyclo[3,3,0,$0^{2,6}$]octa-3,7-diene.

Occupied orbitals Fig. 9 shows the orbital energy change of the occupied orbitals for spiropentadiene against four types of the interaction schemes. We picked up only the orbitals which are mainly constructed from occupied banana bonds within the E symmetry. Of course, another degenerate pair of the banana orbitals exists for each orbital drawn in Fig. 9. The far left one is the energy level of a pair of banana bonds belonging to the single cyclopropene. As shown in the next diagram, this becomes 0.047au unstable by the through-space interaction with the C-C σ -bonds of the opposite side triangle. In a similar way, the addition of the C-H bonds causes the destabilization of the banana bonds, but its magnitude (0.024au) is rather small as is shown in the third diagram. Furthermore the right most diagram shows the level which is determined by the inclusion of the two C-H bonds and the 1s core orbitals of two opposite side carbons to the interaction with the banana bonds. The 1s core orbitals of carbons play a little role (0.008au) in the destabilization of the e symmetry banana bonds as is easily found. This tendency is essentially inherited to the tricyclo compounds as shown in Fig. 10. The left of the figure shows the orbital energy of the e symmetry banana bonds alone. This level is nearly equal to that of the spiro compound. As shown in next diagram, however, the destabilization by the σ -bonds (both two C-C and four C-H) and two 1s core orbitals within another half of the molecule is rather small (0.007au), because the distance between the banana orbitals and such orbitals becomes large. In contrast to this, the interaction with the relay cyclopropane ring is strong (0.050au) because of the large overlap. (See the right most column of Fig. 10.) In the case of spiropentadiene, the interaction to the banana bonds from the symmetry-allowed nearest neighbor orbitals (i. e. the C-C σ -bonds of the opposite side cyclopropene ring) is smaller (0.047au) than that of the tricyclo compound (0.050au), but in the former case the C-H σ -bonds push the orbital energy of the e symmetry banana bonds up (0.024au). As a result, the banana bond level of spiro compound is higher than that of tricyclo one.

The role of relay orbitals Now we can summerize the role of the relay orbitals for the determination of the orbital energy levels of the perpendicular π -system. The upper part of Fig. 11 is a schematic sketch of the perpendicular π -system in the D_{2d} symmetry. The two occupied π -orbitals, which are shown in the center of Fig. 11, construct the E symmetry space, and the two virtual π^*-orbitals split to the b_1 and the a_2 symmetry orbitals. In the case of the spiroconjugation, the virtual orbital of the B_1 symmetry is more stable than the a_2-orbital because of the direct through-space interaction between the π^*-orbitals. On the other hand, the relay orbitals of the tricyclo compound split to the b_1, e and a_2 symmetry orbitals. (See the lower part of Fig. 11.) The split width between the b_1- and the a_2-orbital energy levels of the relay orbitals is larger than that of the π^*-orbitals because of the short distance of the interacting orbitals. Consequently, the b_1-orbital is included into the occupied orbital space. As shown in Fig. 12, when the π -electron system interacts with the relay orbitals, the a_2-orbital of the π^* becomes stable and that of the relay orbitals becomes unstable. The b_1-orbital of the π -orbitals, however, can not interact with the b_1-orbitals of the relay system, since the occupied space and the virtual space are not mixed each other in the present method based on the Hartree-Fock orbital scheme. Thus, the inversion of the orbital levels of the a_2- and the b_1-orbitals occured in the tricyclo compound which has the relay orbitals.

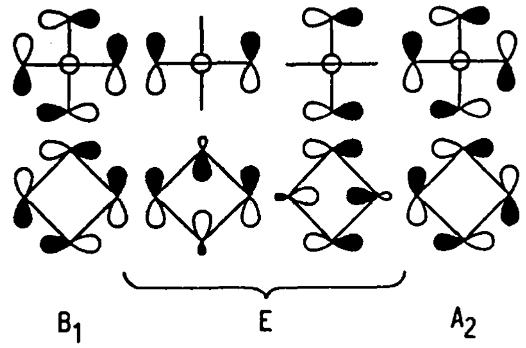


Fig. 11. Symmetry Behavior for Perpendicular π -systems (Above) and Relay Orbitals (Below) in D_{2d} Symmetry.

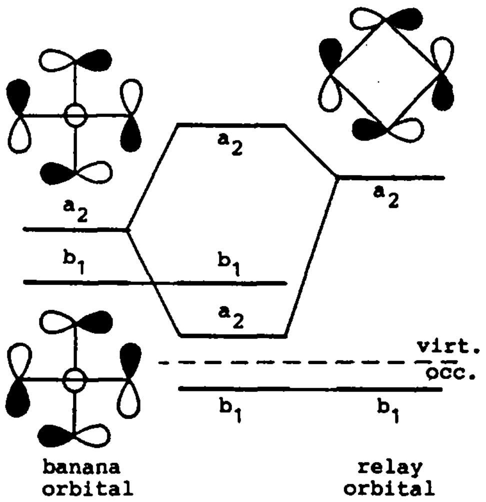


Fig. 12. Interaction Diagram Between Banana Bonds and Relay Orbitals.

CONCLUSION

From the present study, it was found quantitatively that the interaction from the relay orbitals is important in the determination of the orbital energy of the perpendicular π -system. In the virtual orbitals, especially, the order of energy level of the a_2 and the b_1 orbitals in the tricyclo compound is opposite to that of the spiro compound. This effect is not an enhancement of the direct through-space interaction between the banana bonds but a stabilization of the a_2 banana bonds because of the interaction with the relay orbitals. In the case that the relay orbitals were artificially forced to be unstable, the energy level of the perpendicular π -orbitals became unstable synchronously. The present method should be a very powerful tool for the understanding of the through-space/bond interactions.

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