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A Remark on the Importance of Particular Orbital Interaction in the Dimerization of Methylenes

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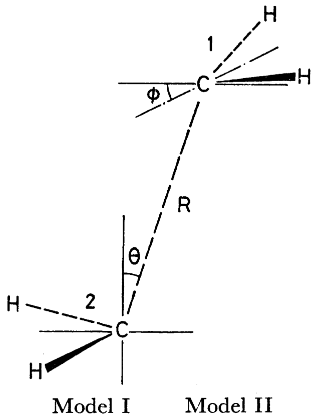
Hoffmann discussed the mode of the approach of two singlet methylenes to form an ethylene molecule, suggesting the preference of a non-least-motion path to the least-motion path.[1] The dimerization of methylenes was also investigated by Kollmar using the CNDO MO method,[2] and by Sustmann and Binsch applying their perturbation calculation method.[3] In our own recent papers,[4,5] the interaction energy between two species has been discussed by dividing it into the Coulomb, exchange, delocalization, and polarization terms, and the important role of the delocalization interaction in representing the bond interchange in chemical reactions has been pointed out. In this note we will present the results of an approximate MO calculation on the dimerization of singlet methylenes.

Table 1 gives the four energies which have been obtained much as in our previous calculation.[6] The necessary variables in order to determine the relative positions of the two singlet methylenes are defined in Fig. 1. We see that Model III is the best among the three. It may also be noted that the superiority of Model III to Model I and to Model II is based mainly on the small unstabilization due to the exchange interaction and to the large stabilization due to the delocalization interaction. The contributions of the Coulomb interaction energy and the polarization interaction energy are both rather small, reflecting the fact that methylene is a neutral species. The exchange interaction energy is supposed to depend on the sum of the squares of the overlap integrals between the occupied MO's of two methylenes.[4] Such a relation can easily be confirmed by comparing the ε_k in Table 1 and the $\sum\limits_{i}^{occ}\sum\limits_{k}^{occ} S_{ik}^2$ in Table 2. The delocalization term comes from the mixing of charge-transferred electron configurations into the adiabatically interacting state. Among the various charge-transferred states, the one in which an electron is transferred from the highest occupied (HO) MO of one molecule into the lowest unoccupied (LU) MO of another molecule, and the converse, are usually the most important in governing the course of chemical reactions. In Table 2 are also presented the absolute values of the overlap integrals between the HOMO of one methylene and the LUMO of another. We find a close parallelism between the magnitudes of the energy, D, and the sums of the squares of the overlap integrals between these particular MO's.

Table 1. The calculated results of the interaction energies

	Model I	Model II	Model III
ε_Q eV	0.102	0.067	0.054
ε_K eV	0.356	0.148	0.139
D eV	0.015	0.223	0.291
Π eV	0.010	0.004	0.003

ε_Q: Coulomb energy, ε_K: exchange energy, D: delocalization energy, Π: polarization energy



	Model I	Model II	Model III
R(Å)	3.0	3.0	3.0
θ(°)	90	44	6
ϕ(°)	0	0	78

Fig. 1. Assumed reaction models. (Model I corresponds to the least-motion path, and Model III to the non-least-motion path.[1])

Table 2. The orbital overlappings between two methylenes

	Model I	Model II	Model III
$\sum\limits_{i}^{occ}\sum\limits_{k}^{occ} S_{ik}^2$	0.00668	0.00285	0.00279
$S_{HO^1,\ LU^2}$	0	0.0346	0.0575
$S_{HO^2,\ LU^1}$	0	0.0346	0.0112

HO^1 means the HOMO of methylene 1 and LU^2 the LUMO of methylene 2. (see Fig. 1) S_{ik} is the overlap integral between the ith MO of one methylene and the kth MO of another methylene. $\sum^{occ}\sum^{occ}$ implies the summation over all the combinations of occupied MO's of two methylenes.

Thus, the present calculation demonstrates that two singlet methylenes favor approaching in such a way as to make small the overlappings of occupied MO's and to gain an effective orbital interaction between the HOMO of one methylene and the LUMO of another. This seems to be a general feature of chemical interactions between two neutral systems.

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