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AN MO APPROACH TO THE DIMERIZATION OF METHYLENE

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The very recent paper of R. Hoffmann [1] on EHT calculations of the dimerization of methylene prompts us to report the results of our CNDO calculations regarding this matter [2]. In addition, we add some general remarks concerning the problem of forbidden reactions according to the Woodward-Hoffmann rules [3].

With the assumption of a D_{2h} (as well as D_{2d}) transition state, the dimerization reaction of singlet methylenes is predicted to be thermally forbidden, as can be seen from an MO correlation diagram. However, if only C_i symmetry is conserved, the reaction should be allowed (Fig. 1).

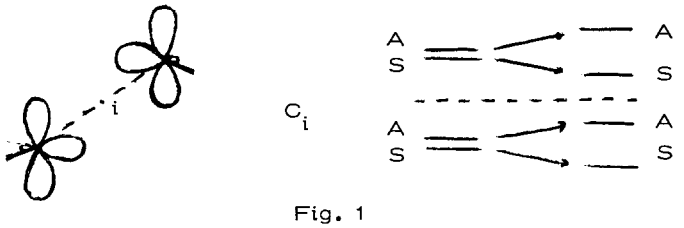

Fig. 1

Calculations with our modified CNDO procedure [4] yielded the following results:

For methylene an equilibrium geometry with a C-H bond length of 1.09 Å and a H-C-H angle of 120° is obtained. The heat of atomization is calculated to be 216 kcal/mol. The energy of dimerization of methylenes comes out to be 131 kcal/mol, a value which is close to the usually assumed energy of the C-C double bond.

With a reaction path of D_{2h} symmetry, an activation energy for the dimerization of methylenes of about 200 kcal/mol is calculated. Exact values for the activation energy and the transition state geometry cannot be given, because the total energy does not vary steadily with the reaction coordinate. This principal difficulty can only be overcome with configuration interaction methods.

If the two methylenes approach each other with C_i symmetry, one obtains with mod. CNDO the very low activation energy of 8 kcal/mol. The transition state is reached at a C-C distance of 2.84 Å and an angle of the carbene planes versus the C-C bond of 67°. All bond lengths and angles have been minimized within the symmetry restriction. In the transition state there is a bonding interaction between the two carbon atoms: The bond energies E_{CC} and E^{R}_{CC} (notations see ref. [5]) are both equal to -0.002 a.u.

However, the optimum energy reaction path may lack symmetry completely. In fact, EHT predicts an approach with the two methylenes planes perpendicular to each other at large distance. With CNDO we do not find any considerable difference in energy. The perpendicular approach is favored over the C_i approach by 0.1 kcal/mol and the C-C distance in the transition state is 2.88 Å.

An additional consequence of the C_i reaction path is that trans bending of ethylene needs less energy than cis bending. This might be an important factor in the steric control of elimination reactions.

The essential characteristic of the optimum energy approach is the penetration of the empty p_π orbital of one methylene and the occupied hybrid orbital of the other. This point will be discussed in detail.

With the notation φ_1 and φ_2 for the occupied hybrid orbitals and φ^*_1 and φ^*_2 for the unoccupied p_π orbitals of the carbenes, the localized orbitals φ_3 and φ_4 of the C-C bond of the ethylene can be approximately written as (bent bonds from the C_i approach)

$$\varphi_3 = \frac{1}{\sqrt{2}} (\varphi_1 + \varphi^*_2)$$
$$\varphi_4 = \frac{1}{\sqrt{2}} (\varphi^*_1 + \varphi_2)$$

Thus for the formation of the C-C bond one needs an equal amount of occupied and unoccupied orbitals of the reactants. The reaction will proceed without considerable activation energy if a steady mixing of the occupied and unoccupied orbitals along the reaction path is possible, i.e. if the occupied orbitals can be written in the form

$$\frac{1}{N} (\varphi_1 + \lambda \varphi^*_2) \quad ; \quad N^2 = 1 + \lambda^2$$

with steadily increasing λ along the reaction coordinate.

This steady mixing can be symmetry forbidden as in the case of the reaction path with D_{2h} symmetry and it can be symmetry allowed as in the case of the reaction path with C_i symmetry. The reaction coordinate that allows optimal mixing of the occupied and unoccupied orbitals will be energetically most favorable. Another example for a reaction where empty and filled orbitals are mixed steadily is the 2,1 hydrogen migration in primary carbonium ions [6].

It can also be shown for the case of electrocyclic additions that the decisive factor

for the height of the activation energy is not the use of unoccupied orbitals of the reactants in forming the binding orbitals of the product, but the possibility of steady mixing of empty and filled orbitals.

For this purpose the molecular orbitals are written as a linear combination of symmetrical bonding orbitals φ_i and the corresponding antibonding orbitals φ_i^* instead of atomic orbitals χ_i. We make the assumption, usually made in MO correlation diagram considerations, that the product orbitals are formed from the p orbitals of the π system of the reactants. Hence, also the product orbitals can be represented as a linear combination of the bonding orbitals of the reactants.

1) The electrocyclic dimerization of ethylene.

If φ_1 and φ_2 are the π orbitals of two ethylenes and φ_1^* and φ_2^* the corresponding excited orbitals, the localized orbitals ψ_1 and ψ_2 of the two σ-bonds formed by the dimerization can be written as (see Fig. 2)

$$\psi_1 = \frac{1}{\sqrt{2}}(\chi_2 + \chi_4) = \frac{1}{2}(\varphi_1 - \varphi_1^* + \varphi_2 - \varphi_2^*)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) = \frac{1}{2}(\varphi_1 + \varphi_1^* + \varphi_2 + \varphi_2^*)$$

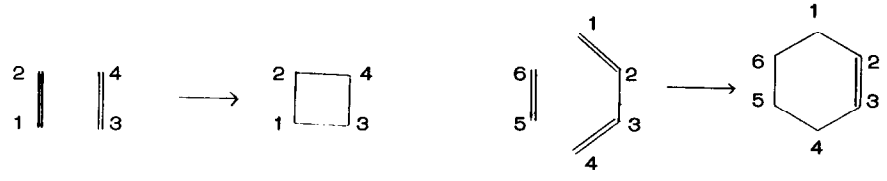

Fig. 2

The same amounts of occupied and unoccupied orbitals of the reactants are used to form the orbitals of the product. If a symmetry plane perpendicular to the ethylenes is assumed the localized orbitals must be symmetry adapted to obtain the canonical orbitals:

$$\frac{1}{\sqrt{2}}(\psi_2 + \psi_1) = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$$

$$\frac{1}{\sqrt{2}}(\psi_2 - \psi_1) = \frac{1}{\sqrt{2}}(\varphi_1^* + \varphi_2^*)$$

The first orbital contains only occupied orbitals, while the second is built only from unoccupied orbitals of the reactants. Thus, a reaction path of D_2 symmetry obviously does not allow the forming of the product orbitals by steady mixing of occupied and unoccupied orbitals of the reactants and the reaction is symmetry forbidden. A reaction path in which the ethylenes are nonequivalent should be more favorable [3].

2) The electrocyclic addition of ethylene to butadiene.

The assumption is made that with $\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$ and $\varphi_2 = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4)$ the two occupied π orbitals of butadiene are $\frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$ and $\frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$. (This neglect of conjugation does not affect the conclusions). The localized orbitals of the product formed by the reaction can be written as

$$\psi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_6) = \frac{1}{2}(\varphi_1 + \varphi_1^* + \varphi_3 - \varphi_3^*)$$
$$\psi_2 = \frac{1}{\sqrt{2}}(\chi_4 + \chi_5) = \frac{1}{2}(\varphi_2 - \varphi_2^* + \varphi_3 + \varphi_3^*)$$
$$\psi_3 = \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) = \frac{1}{2}(\varphi_1 - \varphi_1^* + \varphi_2 + \varphi_2^*)$$

Also in this case, the same amounts of occupied and unoccupied orbitals are used to form the product orbitals. However, after adaption to C_2 symmetry (symmetrical and antisymmetrical combinations of ψ_1 and ψ_2) all orbitals still contain empty and filled reactant orbitals. Thus, they can be formed during the reaction by steadily admixing the excited orbitals and the reaction is symmetry allowed.

The principle of steady mixing of occupied and unoccupied orbitals along a reaction path includes sterical and topological considerations and can be applied to systems which lack symmetry.

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