An MO Calculation of 1,3-Dipolar Cycloaddition between Ethylene and Diazomethane

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A semiempirical SCF MO calculation of the reaction between ethylene and diazomethane was carried out as an example of 1,3-dipolar cycloaddition. A calculation of the interaction energy and electron population by the use of the configuration interaction wave function showed that the formation of the two new bonds in this reaction is concerted but non-synchronous. This result is attributable to the extension of the highest occupied molecular orbital of diazomethane.

The molecular orbital (MO) approach can be used to interpret the chemical reactivity of organic molecules, both saturated[1] and unsaturated.[2] Most of the MO criteria for the chemical reactivity are based upon the use of various reactivity indices.[3] These indices agree fairly well with the experimental results. Therefore, the study of electronic effects appears to lead to the elucidation of the reaction mechanism. We will study 1,3-dipolar cycloaddition through calculations of the electron states of ethylene and diazomethane.

1,3-Dipolar cycloaddition is the union of a 1,3-dipole (a—b—c) with a multiple bond system (d—e), the so-called dipolarophile, to form a five-membered ring.[4,5] A 1,3-dipole a—b—c is described by a zwitterionic octet structure, *e.g.*:

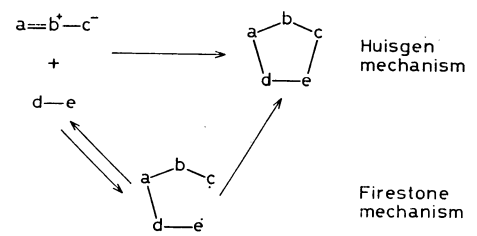
$$a \equiv b^+ - c^- \longleftrightarrow a^- = b^+ = c \quad (b=N)$$

$$a = b^+ - c^- \longleftrightarrow a^- - b^+ = c \quad (b=N\text{-}R,\ O)$$

Specific classes of molecular 1,3-dipoles include diazoalkanes ($R_2C{=}N^+{=}N^-$), nitrile oxides (Ar–C≡N^+–O^-), azides (Ar–N=N^+=N^-), nitrones (Ar–CH=N^+(Me)–O^-) and nitrile amines (Ar–C≡N^+–N^-–Ar).

The concept of this reaction was first suggested by Smith.[6] The generality of the reaction was recognized by Huisgen[4] in a splendid series of researches, during which many new reactions were predicted and discovered. The picture of the reaction mechanism which Huisgen's group drew was that of a single-step, concerted cycloaddition, in which the concerted formation of the two new bonds (*i.e.*, a—d and c—e) is not necessarily synchronous.[4]

Woodward-Hoffmann rules for the conservation of orbital symmetry[7] supply the theoretical basis and, taken with most of the experimental results,[4] provide support for Huisgen's earlier predictions.[8] That is, the rules reveal that 1,3-dipolar cycloaddition is symmetry-allowed for the ground state. Recently Firestone has argued in favour of a two-step mechanism involving biradical intermediates.[9]



The nature of orientation in the reaction (*i.e.*, unsymmetrical dipolarophiles can add to the unsymmetrical 1,3-dipole in two directions, (I) and (II)) has not been adequately interpreted and predicted.

(I) (II)

However, Houk qualitatively discussed the regioselectivity in 1,3-dipolar cycloaddition in terms of the extension of particular MO's, and his conclusion is consistent with the experimental results.[10,11] Furthermore, he and his co-workers[11] qualitatively discussed nonsynchroneity in the formation of two new bonds; this nonsynchroneity seems to play a part in the determination of the orientation of the concerted mechanism.[12]

Considering these circumstances, we will undertake a more detailed perturbational MO calculation of the nonsynchronous formation of new bonds in the course of the 1,3-dipolar cycloaddition reaction between olefin and diazoalkane.

Here olefin (dipolarophile) and diazoalkane (1,3-dipole) will be typified by ethylene and diazomethane for the sake of simplicity of calculation.

Method of Calculation

In this paper, the means of calculation is based upon one[13] of the isolated molecule approximations that Fukui *et al.* have developed. That is, the wave function (Ψ) of a chemically-interacting state in a reaction between ethylene and diazomethane is represented by means of the configuration interaction (CI) procedure;

$$\Psi = C_0\Psi_0 + \sum_{i=1}^{6}\sum_{l=9}^{14} C_{i\to l}\Psi_{i\to l} + \sum_{k=1}^{8}\sum_{j=7}^{12} C_{k\to j}\Psi_{k\to j} + \sum_{i=1}^{6}\sum_{j=7}^{12} C_{i\to j}\Psi_{i\to j} + \sum_{k=1}^{8}\sum_{l=9}^{14} C_{k\to l}\Psi_{k\to l} \qquad (1)$$

where Ψ_0 means the adiabatically-interacting state in which all valence electrons occupy the MO's of ethylene (i) and those of diazomethane (k), both doubly-occupied in their initially-isolated state. $\Psi_{i\to l}$ implies the charge-transferred state, with one electron in the i-th occupied MO of ethylene transferred into the l-th unoccupied one of diazomethane, while $\Psi_{k\to j}$ implies a back charge-

transferred state in which one electron in the k-th occupied MO of diazomethane jumps up into the j-th unoccupied one of ethylene. $\Psi_{i\to j}$ is a locally-excited state in which an electron in the i-th MO of ethylene is excited into the j-th MO of ethylene and $\Psi_{k\to l}$ indicates a locally-excited state in diazomethane as does $\Psi_{i\to j}$ in ethylene. These wave functions are constructed by means of Slater determinants, composed of the semiempirical LCAO SCF MO's,[14] including all valence electrons and overlap integrals. C_0, $C_{i\to l}$, $C_{k\to j}$, $C_{i\to j}$, and $C_{k\to l}$ in Eq. (1) are the CI coefficients obtained by solving the usual CI secular equation.

When the CI seqular equation is expanded in the approximate sense that the interaction is not too strong, the total stabilization energy (ΔW) due to the CI effect mentioned above can be partitioned into the following four terms: Coulombic (E_Q), exchange (E_K), delocalization (D), and polarization (π) terms.[13]

$$\Delta W = E_Q + E_K - D - \pi \qquad (2)$$

E_Q is the electrostatic interaction energy between ethylene and diazomethane. E_K is the exchange repulsion energy between two closed-shell molecules[15] resulting from the overlap between the occupied MO's of two molecules; it increases unfavorably as the reaction proceeds. D is the stabilization energy due to the mixing-in of the charge-transferred states ($\Psi_{i\to l}$ and $\Psi_{k\to j}$) with the adiabatically-interacting state (Ψ_0); it works to promote the reaction. The last term in Eq. (2), π, is also the stabilization energy due to the mixing-in of local excited states ($\Psi_{i\to j}$ and $\Psi_{k\to l}$). π is usually less important than the others on the right-hand side of Eq. (2).[15]

The electron density ($\rho(1|1)$) of the interacting state (Ψ) is given by:[16]

$$\rho(1|1) = 28\int \Psi^*(1, 2, \cdots, 28)\Psi(1, 2, \cdots, 28) \times d\varepsilon_1 d\tau_2 \cdots d\tau_{28} \qquad (3)$$

where the number "28" indicates the total valence electrons in the whole system, where $d\varepsilon_1$ is the integral over the spin coordinate of the 1 electron, and where $d\tau_i$ is the integral over both the spin and space coordinates of the i electron. Furthermore, $\rho(1|1)_{C_2H_4}+\rho(1|1)_{CH_2N_2}$ signifies the simple sum of the electron density of ethylene and that of diazomethane. Of course, $\rho(1|1)$ is different from $\rho(1|1)_{C_2H_4}+\rho(1|1)_{CH_2N_2}$.

Results and Discussion

The molecular geometry of ethylene and diazomethane which we have employed comes from Herzberg[17] without any deformation, because it seems that the interaction between ethylene and diazomethane is sufficiently weak at the early stage of the reaction. Figure 1 illustrates the geometry of the assumed reaction models. M in Fig. 1 represents the center of the linear C_3–N_4–N_5 line of diazomethane. Theta (θ) in Fig. 1 represents the angle between the C_3–N_4–N_5 line and the X-axis. The restrictions adopted in the selection of the geometry in Fig. 1 are as follows. The two molecular planes (*i.e.*, two Y–Z planes) to which ethylene and diazomethane respectively belong are parallel at $\theta=90°$. The distance between the planes is 2.7 Å. M moves horizontally along the C_3–N_4–N_5 line of diazomethane from a position just above the C_1 of ethylene to one above the C_2 of ethylene in order to determine the relative position of the two parallel molecules. Therefore, the geometry of the assumed reaction model is selected in terms of the position of M which gives the lowest total energy by the CNDO/2 method.[18] This geometry ($\theta=90°$) is defined as Model 1. Furthermore, diazomethane is rotated about M by $\pm5°$; we define the geometry at $\theta=85°$ as Model 2 and the geometry at $\theta=95°$ as Model 3.

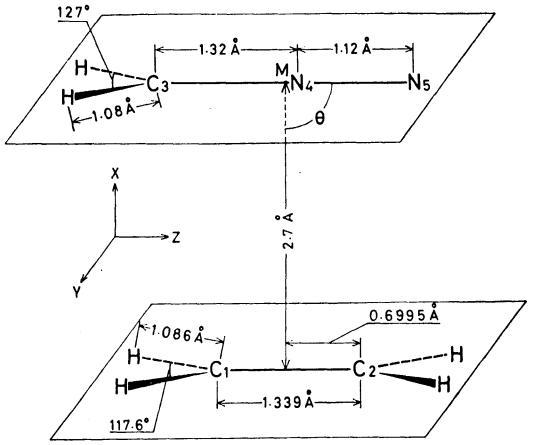


Fig. 1. Assummed interacting models between ethylene and diazomethane at the initial stage of the reaction. The former molecule holds D_{2h} symmetry and latter has C_{2v} one.

The MO energy levels of the ethylene and diazomethane obtained by the SCF procedure are given in Fig. 2.

First let us consider Model 1 at $\theta=90°$, in which

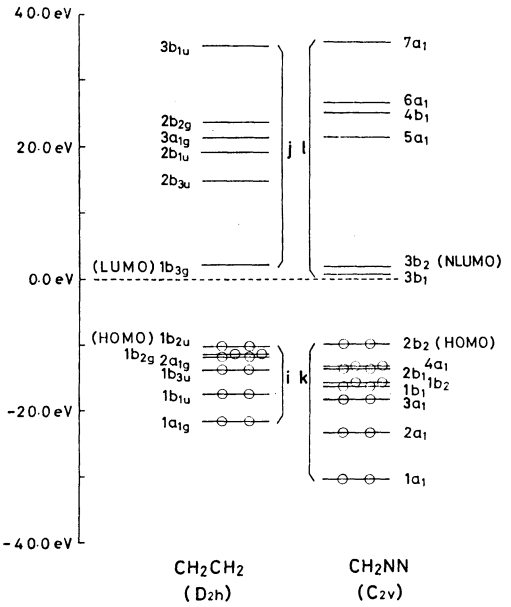


Fig. 2. Schematic presentation of MO levels of ethylene and diazomethane. NLUMO in this figure represents the next unoccupied MO of the lowest unoccupied MO.

two molecular planes are parallel. The interaction energy, ΔW, was calculated for Model 1; the results are given in Table 1. Table 1 shows that, in this reaction model, E_Q and π are small in value because the two reactants we use are *neutral* molecules. E_K and D are larger than the former two terms. E_K is found to hinder the progress of the reaction. On the other hand, D greatly stabilizes this reaction system, thus prompting the reaction.

Table 1. Interaction energies between diazomethane and ethylene

	Model 1	Model 2	Model 3
θ[a] (°)	90	85	95
E_K (eV)	2.769	2.588	3.260
E_Q (eV)	−0.015	−0.014	−0.015
D (eV)	1.325	1.141	1.958
π (eV)	0.040	0.044	0.053
ΔW (eV)	1.389	1.389	1.234

a) θ is shown in Fig. 1.

In order to seek for the CI configuration ($i \rightarrow l$ and $k \rightarrow j$ combinations) which is the most contributive to D, the calculated CI coefficients of Eq. (1) are given in Eq. (3). Here, the polarization effect is neglected because the effect is sufficiently small, as may be understood from the value of π in Table 1.

$$\Psi_{\text{Model 1}} = 0.883\Psi_0 + 0.342\Psi_{2b_2 \rightarrow 1b_{3g}} + 0.129\Psi_{2a_{1g} \rightarrow 3b_2} - 0.059\Psi_{2a_1 \rightarrow 1b_{3g}} - 0.034\Psi_{1b_{2u} \rightarrow 3b_2} \quad (3)$$

The terms with a CI coefficient whose absolute value is smaller than 0.03 are neglected. Equation (3) shows that the largest CI coefficient except C_0 (=0.883) that is contributive to D is that of the charge-transferred state from the highest occupied (HO) MO of diazomethane ($2b_2$) to the lowest unoccupied (LU) MO of ethylene ($1b_{3g}$). Therefore, there is no doubt that the charge-transfer interaction between the particular MO's, *i.e.*, the HOMO of diazomethane and the LUMO of ethylene, plays a remarkably important role in promoting the reaction.[2]

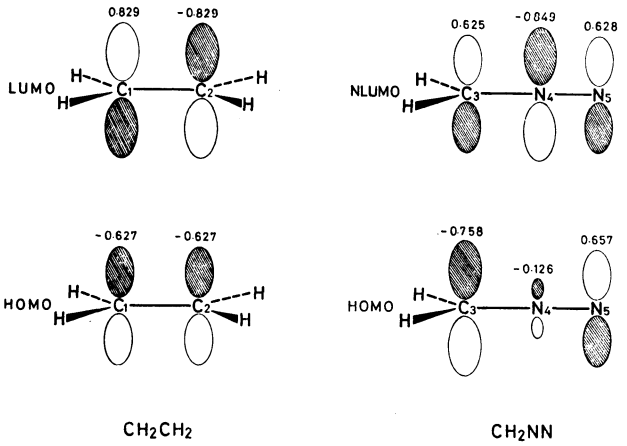


Fig. 3. The nodal property of the particular MO's in ethylene and diazomethane. The values in this figure are the AO coefficients.

The *frontier* MO's* nodal property of ethylene and diazomethane is given in Fig. 3. The values represent the atomic orbital (AO) coefficients of the *fronitier* MO's. Figure 3 shows that the AO coefficient of C_3 (−0.758) is larger than that of N_5 (0.657) in the HOMO of diazomethane.

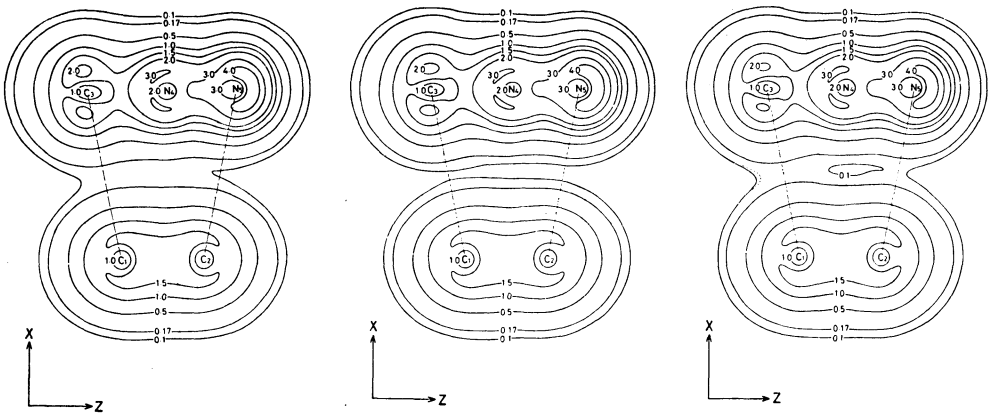
Here, the electron-density contour maps, which make it easy to understand the new bond formation and the old bond disappearance along the reaction course, are considered at the stage of the reaction shown in Fig. 1 by the use of the CI coefficients of Eq. (3). These contour maps are given in Fig. 4 with respect to Model 1. All the electron density lines are pictured on the X–Z plane of Y=0.0.

Figure 4(a) shows the simple sum of the electron density of ethylene and diazomethane, without any interaction between them. This electron density is defined as $\rho(1|1)_{C_2H_4} + \rho(1|1)_{CH_2N_2}$.

Figure 4(b) shows the electron density with only the adiabatic interaction included; this density is defined as $\rho(1|1)_{0,0}$. It may be noted by observing the 0.1 e/Å^3 density line that the electron density in the intermolecular region, especially that between C_1 of ethylene and C_3 of diazomethane, and that between C_2 of the former molecule and N_5 of the latter, decreases as a result of the inclusion of the electron-exchange interaction in Fig. 4(b), compared with that in Fig. 4(a). This reflects the fact that E_K works repulsively between the two molecules. This is essential to the interaction between two closed-shell systems, as in the case of two helium atoms.

Figure 4(c) shows the electron density with both adiabatic interaction and charge-transfer interaction; this density is defined as $\rho(1|1)$. The comparison of the 0.1 e/Å^3 density line in Fig. 4(c) with that in Fig. 4(a) shows that the electron density between C_1 of ethylene and C_3 of diazomethane, and that between C_2 of the former and N_5 of the latter, overcome the electron density decrease caused by the electron-exchange interaction, thus resulting in an increasing electron density in the reaction zone on account of the mixing-in of the charge-transferred state. We can see that the decrease in the intermolecular electron density between N_4 of diazomethane and ethylene in Fig. 4(b) by the exchange interaction is still preserved in Fig. 4(c). As the overlap between the diazomethane HOMO on N_4 and the ethylene LUMO is small, as Fig. 3 shows, the charge-transfer effect does not appear on N_4 and ethylene. This causes the bending of 1,3-dipole which was adopted in Huisgen's model.[4] Furthermore, Fig. 4(c) also gives us the information that the electron density between C_3 and N_4 of diazomethane decreases, shown, for instance, by the 1.5 e/Å^3 density line which indicates the weakening of the C_3–N_4 bond. The electron density between C_1 and C_2 of ethylene is calculated to decrease in Fig. 4(c), but the decrease is too small to be observed in the figure. Figure 4(c) demonstrates that the electron density increases in the neighborhood of C_1 and C_2 of

* The LUMO of diazomethane is not the *frontier* MO, because it ($3b_1$) can not overlap with the HOMO of ethylene ($1b_{2u}$).



(a) (b) (c)

Fig. 4. Total electron density (in e/Å^3) of Model 1.
(a): $\rho(1|1)_{C_2H_4}+\rho(1|1)_{CH_2N_2}$, (b): $\rho(1|1)_{0,0}$,(c): $\rho(1|1)$.
The dotted line is the 0.1 e/Å^3 density line of (a).

ethylene and decreases in the neighborhood of C_3 of diazomethane. This shows that the carbon of diazomethane is *nucleophilic*.[4c]

Figure 4 shows that the formation of two intermolecular new bonds, C_1–C_3 and C_2–N_5, and the weakening of the old bonds, C_3–N_4 in diazomethane and C_1–C_2 in ethylene, can be described approximately in terms of the mixing-in of the charge-transferred state with the adiabatically-interacting one. That is, at the early stage of this reaction the two bonds are formed by the charge-transfer interaction corresponding to D in the energy expression and the N_4 atom is repulsed from ethylene by the exchange interaction (E_K). The five-membered ring can, then, be pictured by this scheme. At the same time, the HOMO–LUMO interaction is most important, as is shown by the CI coefficients in Eq. (3).

The AO coefficient of C_3 is larger than that of N_5 in the HOMO of diazomethane, as is shown in Fig. 3. To see how this difference in the values influences the reactivity, we prepared Model 2 ($\theta=85°$) and Model 3 ($\theta=95°$).

The interaction energy of Model 2 and that of Model 3 are evaluated, in comparison with that of Model 1 in Table 1. Here the most preferable reaction path may be defined as the model that makes ΔW the smallest.[15] Therefore, the results in Table 1 show that Model 3 is the most reasonable among the three models considered here at the early stage of this reaction.

The wave functions with respect to Model 2 and Model 3 corresponding to Eq. (3) of Model 1 are given by Eqs. (4) and (5):

$$\begin{aligned}\Psi_{\text{Model 2}} = {} & 0.898\Psi_0 + 0.310\Psi_{2b_2\to 1b_{3g}} + 0.128\Psi_{2a_{1b}\to 3b_2} \\ & - 0.058\Psi_{2a_1\to 1b_{3g}} - 0.042\Psi_{1b_{2u}\to 3b_2} \\ & + 0.039\Psi_{1b_{2g}\to 3b_1} \qquad (4)\end{aligned}$$

$$\begin{aligned}\Psi_{\text{Model 3}} = {} & 0.843\Psi_0 + 0.411\Psi_{2b_2\to 1b_{3g}} + 0.130\Psi_{2a_{1g}\to 3b_2} \\ & - 0.059\Psi_{2a_1\to 1b_{3g}} - 0.056\Psi_{1b_{1u}\to 3b_2} \\ & - 0.033\Psi_{3a_1\to 1b_{3g}} \qquad (5)\end{aligned}$$

The absolute values of the CI coefficients smaller than 0.03 are neglected, as in Eq. (3). A comparison of Eqs. (4) and (5) indicates that the charge-transfer effect works most successfully in Model 3. When C_3 which has the largest AO coefficient of the HOMO of diazomethane, approaches C_1 of ethylene, the MO overlap between the HOMO of diazomethane and the LUMO of ethylene is extended. Therefore, Model 3 is favorable to the charge-transfer interaction.

Furthermore, the contour maps are depicted for Model 2 and Model 3. Figure 5 indicates the electron density of Model 2 in the X–Z cross section. Figure 5(a) shows the sum of the electron density of ethylene and diazomethane, corresponding to Fig. 4(a) of Model 1. Figure 5(b) shows the electron density with the adiabatic and the charge-transfer interactions, corresponding to Fig. 4(c) of Model 1. Model 2 is an unfavorable reaction path, as may be understood from the interaction energy in Table 1; a comparison of Fig. 5(a) with Fig. 5(b) gives the information that the electron-density increase in the intermolecular region of Model 2 as a result of the mixing-in of the charge-transferred state with Ψ_0 is similar in appearance to that of Model 1.

Figure 6 indicates the electron density of Model 3 in the X–Z cross section. Figure 6(a) shows the sum of the electron density of ethylene and diazomethane, corresponding to Fig. 4(a) of Model 1 and Fig. 5(a)

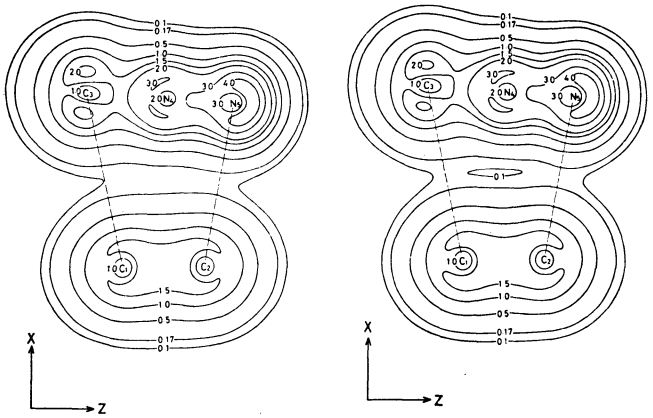


Fig. 5. Total electron density (in e/Å^3) of Model 2.
(a): $\rho(1|1)_{C_2H_4}+\rho(1|1)_{CH_2N_2}$, (b): $\rho(1|1)$.

of Model 2. Figure 6(b) shows the electron density with the adiabatic and the charge-transfer interactions, corresponding to Fig. 4(c) of Model 1 and Fig. 5(b) of Model 2. Model 3 is found, from the findings on interaction energy in Table 1, to be the most favorable reaction model. In this model, the electron density in the intermolecular region, especially C_1–C_3, shows a considerable increase as a result of a more effective mixing-in of the charge-transferred state with Ψ_0 than the others, as the comparison of the 0.17 e/Å^3 density line in Fig. 6(a) with that in Fig. 6(b) shows. Therefore, a concerted cycloaddition of diazomethane to ethylene may be expected to show an unequal progress of the bond formation, as Houk and his co-workers proposed.[11]

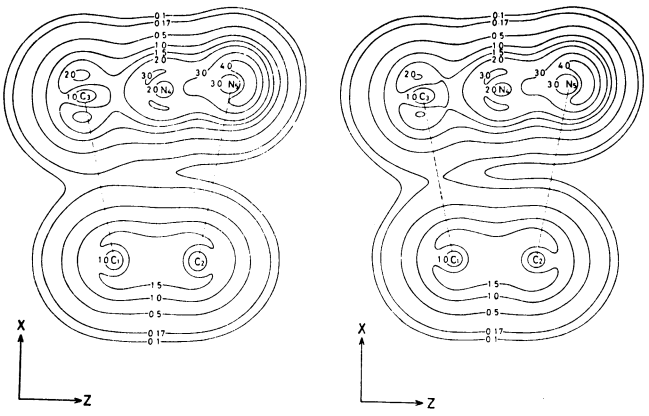


Fig. 6. Total electron density (in e/Å^3) of Model 3.
(a): $\rho(1|1)_{C_2H_4}+\rho(1|1)_{CH_2N_2}$, (b): $\rho(1|1)$.

This nonsynchroneity of the two new bond formations may be explained as follows. In ΔW, the largest stabilization comes from D; it is the charge-transfer interaction from the HOMO of diazomethane to the LUMO of ethylene that is the most contributive to D, as is shown by the comparison of the CI coefficients. Therefore, the reaction will take place along the path which maximizes the MO overlap between the HOMO and the LUMO. The HOMO of diazomethane has a larger extension on C_3 than on N_5. Therefore, it is favorable that the approach of C_3 to C_1 occurs first.

If steric complications are not considered it is reasonable to assume that, in an asymmetric dipolarophile, the largest HOMO-coefficient atom of diazomethane (*i.e.*, the carbon atom) unites with the largest LUMO-coefficient atom of the dipolarophile.[10,11,19] Diels-Alder reactions between two dissymmetrical reagents are also most likely to be non-synchronous, as has been suggested by Woodward and Katz.[20] As Diels-Alder reactions have been shown to be under *frontier* control,[21] it seems reasonable to think that the first bond would link the largest HOMO-coefficient atom of diene and the largest LUMO-coefficient atom of dienophile.[12,22]

Conclusion

An approximate MO calculation of the 1,3-dipolar cycloaddition of diazomethane to ethylene has been carried out by a CI method. The results of the present calculation have proved nonsynchroneity in the formation of two new bonds. This result can be explained on the basis of the fact that the extension of the HOMO of diazomethane is different on different constituting atoms. Therefore, the extension of the HOMO is important in any consideration of the reaction path.

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References

1) K. Fukui, "Modern Quantum Chemistry," Vol. I, ed. by O. Sinanoğlu, Academic Press, New York (1965), and the references cited therein.
2) K. Fukui, "Molecular Orbitals in Chemistry, Physics and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press, New York (1964).
3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961), Chapter 11 and the references cited therein.
4) a) R. Huisgen, *Angew. Chem.*, **75**, 604, 742 (1963); b) R. Huisgen, *Proc. Chem. Soc.* (London), **1961**, 357; c) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," ed. by S. Patai, Interscience, London (1964), p. 739; d) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).
5) G. W. Cowell and A. Ledwith, *Quart. Rev.*, **24**, 119 (1970).
6) L. I. Smith, *Chem. Rev.*, **23**, 193 (1938).
7) a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).
8) A. Ledwith, *Ann. Reports (B)*, **65**, 143 (1968).
9) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968).
10) K. N. Houk, *J. Amer. Chem. Soc.*, **94**, 8953 (1972).
11) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Amer. Chem. Soc.*, **95**, 7301 (1973).
12) O. Eisenstein, J.-M. Leffour, and N. T. Anh, *Chem. Commun.*, **1971**, 969.
13) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).
14) H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, *ibid.*, **40**, 2761 (1967).
15) H. Fujimoto, S. Yamabe, and K. Fukui, *Tetrahedron Lett.*, **1971**, 439.
16) H. Fujimoto, S. Yamabe, and K. Fukui, This Bulletin, **44**, 2936 (1971).
17) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., New York (1966).
18) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).
19) J. Bastide, N. El Grandour, and O. Henri-Rousseau, *Tetrahedron Lett.*, **1972**, 4225.
20) R. B. Woodward and T. J. Kats, *Tetrahedron*, **5**, 70 (1959).
21) a) K. Fukui, This Bulletin, **39**, 498 (1966); b) L. Salem, *J. Amer. Chem. Soc.*, **90**, 553 (1968).
22) a) A. Devaquet and L. Salem, *ibid.*, **91**, 3793 (1969); b) T. Inukai, H. Sato, and T. Kojima, This Bulletin, **45**, 891 (1972); c) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 5624 (1973).