PMO Analysis of Cycloadditions, IV [+)]

Regioselectivity and Reactivity in Cycloadditions of Diazomethane

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The program PERVAL, based on an all-valence electron perturbation treatment, is applied to the evaluation of cycloadditions of diazomethane. The reactive complexes are modeled after the ab-initio calculated transition state for the reaction of ethylene with diazomethane. The results show the type-I behavior of diazomethane. The reactivity of dipolarophiles in these cycloadditions is determined by CT interactions, the regioselectivity, including the electron-rich methyl vinyl ether, is explained by non-covalent interactions.

Eine PMO-Analyse von Cycloadditionen, IV [+). – Regioselektivität und Reaktivität bei Cycloadditionen des Diazomethans

Das Programm PERVAL, das auf einer alle Valenzelektronen berücksichtigenden Störungstheorie basiert, wird auf Cycloadditionen des Diazomethans angewendet, wobei die reaktiven Komplexe dem ab-initio berechneten Übergangszustand der Umsetzung von Diazomethan mit Ethylen angepaßt werden. Die Ergebnisse zeigen, daß sich Diazomethan dem Typ I der Klassifikation von Cycloadditionen entsprechend verhält. Während die Reaktivität der Dipolarophile gegenüber Diazomethan befriedigend mit CT-Wechselwirkungen erklärt werden kann, läßt sich die Regioselektivität, einschließlich der bei der Cycloaddition des elektronenreichen Enolethers beobachteten, am besten mit nichtkovalenten Wechselwirkungen deuten.

Huisgen[1-4] showed in elegant experimental investigations that diazoalkanes as 1,3-dipoles may belong to type I or type II of the classification of these cycloadditions[5]. Thus, diazomethane displays high reactivity towards electron-deficient olefins but low reactivity towards the electron-rich vinyl ether[1]. As predicted by the frontier molecular orbital (FMO) treatment of reactivity in 1,3-dipolar cycloadditions, a gradual move from type I to type II characteristics takes place with the replacement of the hydrogen atoms of diazomethane by one or two electron-withdrawing groups like alkoxycarbonyl or phenylsulfonyl[2-4].

Diazoalkane cycloadditions have been studied by molecular orbital methods several times. Fukui[6] carried out a PMO analysis of the addition of diazomethane to ethylene and Leroy performed ab-initio calculations on the STO-3G level for the transition state of the cycloaddition of diazomethane to ethylene[7] and substituted olefins[8]. In the calculated transition state (**1**), diazomethane has no longer a linear structure and ethylene is also distorted. Better quality calculations with a more precise determination of the transition state structure would be possible but the general features should remain unchanged. Recently[9] an evaluation of kinetic data for the cycloadditions of several diazoalkanes was published which is based on PMO theory. Linear correlations of the log k values with the second order charge-transfer stabilisation energy were obtained if other π orbitals than the frontier molecular orbitals were included. A drawback of this study is that the CNDO/2-calculated orbital energies of the reacting molecules had to be adjusted empirically in order to obtain this result. Some years ago[10] we applied within the CNDO/2 approximation an all-valence electron perturbation procedure to diazomethane cycloadditions and showed that a linear correlation of log k values with the total second order π-MO interaction can be obtained without additional assumptions.

Regiochemistry is explained by FMO theory on the basis of the structure of the frontier molecular orbitals. The procedure has been applied to diazomethane cycloadditions originally by Houk[11] and Bastide[12], later it was exploited extensively by Huisgen[4]. If it is possible to identify the dominating FMO interaction or if both predict the same regiochemistry, then this method works satisfactorily in many cases. In cycloadditions where it is difficult to select one FMO interaction as predominating and when in addition the two lead to antagonistic orientational predictions one may encounter difficulties. In diazomethane cycloadditions the procedure fails, for instance, in explaining the regiochemistry for vinyl ether cycloadditions[4,9,13]. As no steric effects can be invoked in this case the deficiency may be a hint that the explanation of regiochemistry based on second-order perturbation theory is incomplete or may not be based on the underlying physical effect. The success of FMO theory in this area might perhaps be fortuitous because the real cause and the results of second-order perturbation theory correlate with each other. On the other hand it may be that we have to use more than one factor to explain regioselectivity. It has been demonstrated in a number of cases that there are other effects operating, for instance steric effects[14] which are not considered by FMO theory.

It would be desirable, therefore, to come up with a more comprehensive explanation of regiochemistry. One might carry out ab-initio calculations for each reactant pair. For

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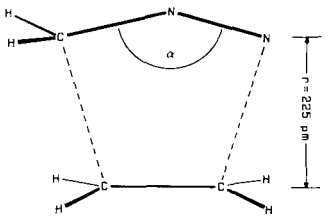
a few cases Leroy[8] performed such calculations and found differences in activation energies for the regioisomers in the expected direction. In other cases the method was reported not to lead to conclusive results[15]. Regardless of the success of such a procedure it provides small numbers as differences of big total energies and the origin of the small numbers may be difficult to identify. A better solution should be improved perturbational methods. Such attempts would consist in the direct calculation of the FMO stabilisation or perhaps in the evaluation of the total second order π-MO stabilisation for regiochemical isomers. The latter procedure, limited to the atoms involved in the bond making process, has been applied by Bastide[12] and in the above-mentioned study of diazoalkane cycloadditions[9]. Even though this approach requires some knowledge about the structure of the activated complex it seems to be attractive. Due to a number of elaborate calculations on transition states for cycloadditions[16] one could rely in the perturbation calculation on these structures and remove in this way ambiguities concerning the molecular complexes on which the perturbation calculations should be performed. A more advanced technique, however, should not be restricted to π-electron interactions and to the reacting atoms, but it should be based on an all-valence electron treatment and should include all atoms of the reacting molecules. We have followed this path and have developed a program PERVAL for an IBM-AT personal computer which makes use of graphical evaluations of the numerical results[17]. The underlying perturbation theory, developed by us a number of years ago[18,19] and applied to some cycloadditions[10,18,20], is based on the MINDO/3 approximation. One of its advantages is that it allows to discern between covalent and non-covalent interactions in a molecular complex. Another feature is that it can be used reliably for molecular complexes which are modeled after or even correspond to ab-initio calculated transitions states[21]. We have demonstrated successful applications to cycloadditions of formonitrile oxide[22]. There, and also in an earlier analysis of the regiochemistry in cycloadditions of diazomethane to substituted butadienes[20], we concluded that non-covalent interactions may be important and in some cases perhaps a better measure of regioselectivity than rationalisations based on FMO theory.



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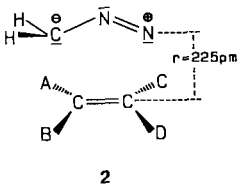


2

The present investigation deals with the regiochemistry and reactivity in diazomethane cycloadditions using the program PERVAL. We analyse first the transition state of the cycloaddition of ethylene to diazomethane (**1**). Then we proceed to cycloadditions of diazomethane to substituted olefins. The structure of the dipolarophiles in the latter calculations are based on standard bond lengths and bond angles[23], the structure of the molecular complexes is shown in formula **2**.

The separation of the line connecting the terminal atoms of the 1,3-dipole and the CC double bond is 225 pm as in the calculated transition state **1**. The structure of diazomethane in **2** corresponds to that in **1**.

Results

Addition of Diazomethane to Ethylene: MINDO/3 calculations were performed for the transition state **1** (ΔH_f = 78.52 kcal/mol) and for the components diazomethane (ΔH_f = 27.42 kcal/mol) and ethylene (ΔH_f = 23.53 kcal/mol) in the structures shown in **1**. The perturbation energies between the components of **1** in the arrangement of the transition state according to the PERVAL calculation are 47.26 kcal/mol and −18.86 kcal/mol for the first and second order contribution, respectively. A very satisfactory agreement is observed between the heat of formation of **1** and the sum of the ΔH_f values for diazomethane and ethylene plus the perturbation energy. Within ca. 1% the same numbers are obtained, a good demonstration for the applicability of perturbation calculations at a separation of 225 pm of the interacting molecules. Consequently the interaction at this point of the reaction coordinate is not too big in order to apply perturbation theory. This result helps to remove ambiguities in the choice of the structure for the molecular complex in the perturbation calculations for the substituted dipolarophiles. In the following applications we use as indicated above in **2** the distance of 225 pm of the reactants and replace ethylene by the corresponding olefins in their ground state structure.

From the experimental reactivity pattern of diazomethane cycloadditions[1] we expect that the interaction between ethylene and the 1,3-dipole is governed by HOMO-(CH_2N_2)−LUMO(C_2H_4), the other FMO interaction should be smaller. This is confirmed by the actual numbers of −11.05 kcal/mol for HOMO(CH_2N_2)−LUMO(C_2H_4) and −2.91 kcal/mol for HOMO(C_2H_4)−LUMO(CH_2N_2). The sum of these two stabilisations corresponds to 74% of the total second-order stabilisation underlining the importance of the HOMO-LUMO interactions in the transition state. The factor 3.8 between the two frontier molecular orbital interactions derives not only from different orbital energy separations but is mainly the result of the structure of the involved MO's. In Figure 1 we display the structures of the HOMO-LUMO pairs together with their MINDO/3 energies.

The representations in the lower part of Figure 1 visualize by the area of the circles the contribution of each atom to the HOMO-LUMO interaction. Full or open circles signify numbers of opposite sign. As a consequence of the phase distribution in the MO's we observe values of the same sign from the reacting atoms indicating bonding relations between them. However, other atoms, particularly N-2 in HOMO(C_2H_4)−LUMO(CH_2N_2), lead to contributions of

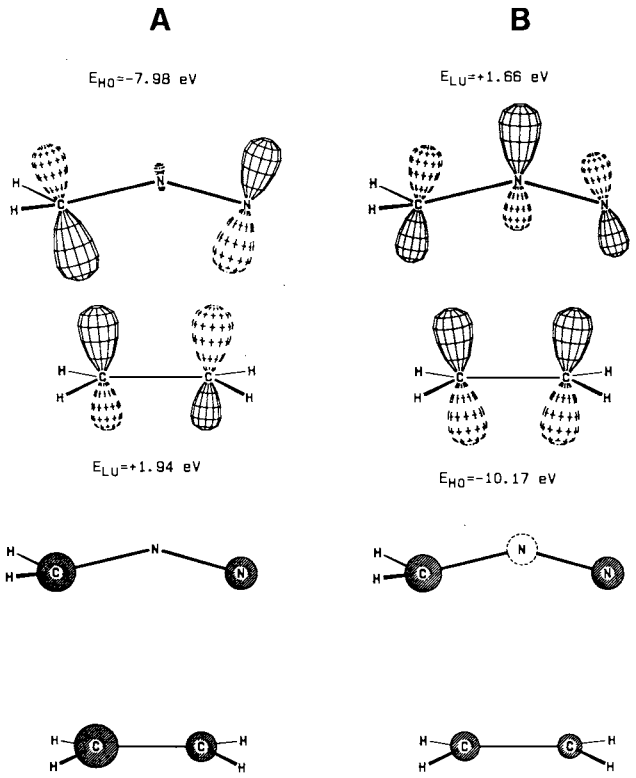


Figure 1. $HOMO(CH_2N_2)-LUMO(C_2H_4)$ (A) and $HOMO(C_2H_4)-LUMO(CH_2N_2)$ (B)
Representations (upper part) and atom contributions to the FMO interactions (lower part)

opposite sign thus decreasing the total bonding. Here we find one of the major reasons for the lower $HOMO(C_2H_4)-LUMO(CH_2N_2)$ stabilisation. However, as will be shown below, the stronger the 1,3-dipole bends in the transition state the more favorable this interaction will become. This can be interpreted as one of the reasons that the 1,3-dipole assumes a bent structure in the transition state. With higher contributions from the atoms forming the new CC bond we would anticipate an unsymmetrical bond forming process favoring the CC bond. Similar conclusions were reached by Fukui[6] in his PMO analysis of this reaction.

Table 1. Perturbation energies [kcal/mol] for complexes of structure **1** and **2** in which the angle is 150°, 140°, and 130°

Complex	Angle	1st Order	2nd Order	Sum	$HOMO(CH_2N_2)-LUMO(C_2H_4)$	$HOMO(C_2H_4)-LUMO(CH_2N_2)$
1	150°	47.3	−18.9	28.4	−11.0	−2.9
1	140°	45.7	−21.7	24.0	−10.9	−5.1
1	130°	44.8	−24.8	20.0	−10.1	−7.6
2	150°	50.0	−17.5	32.5	−9.8	−2.3
2	140°	48.3	−20.3	28.0	−9.6	−4.3
2	130°	47.3	−23.3	24.0	−8.8	−6.6

The angle α in **1** corresponds to 150° according to Leroy's[7,8] calculation. In order to see the effect of further bending we carried out MINDO/3 and perturbation calculations for symmetrical complexes like **1**, retaining the structural features in diazomethane and ethylene but reducing the angle to 140° and 130°, respectively (Table 1). For the purpose of comparison and as justification of our choice of the structure for the reactive complex in the case of substituted olefins we present also values for complex **2** with ethylene in its ground state structure using the same angles α. Both series of numbers are very similar.

The interpretation of the increase in the $HOMO(C_2H_4)-LUMO(CH_2N_2)$ stabilization can be deduced directly from Figure 2 where we show the change in energy and structure of the FMO's of diazomethane with bending. The pictures reproduce the MINDO/3 molecular orbitals and the orbital drawings are linear combinations of the AO contributions. The smaller the angle becomes the farther N-2 will be removed from the double bond of ethylene in **1** and **2**. The overlap of the orbital at N-2 with the HOMO of ethylene, therefore, decreases, diminishing its antibonding effect in the $HOMO(C_2H_4)-LUMO(CH_2N_2)$ interaction. The bending process is thus very favorable in terms of the FMO stabilization.

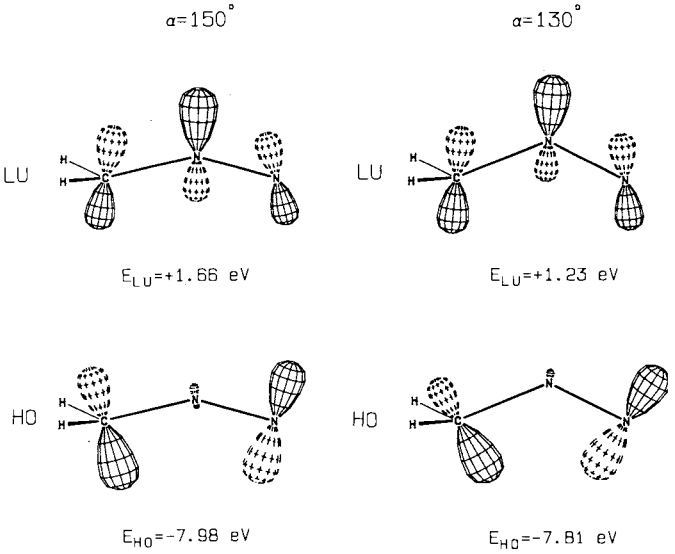
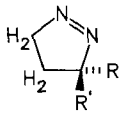


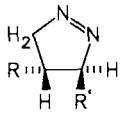
Figure 2. Structure of the FMO's of diazomethane as f(α)

Other effects can be noticed also in Figure 2. The lobes of the orbital at N-2 in $LUMO(CH_2N_2)$ are different in size as a consequence of the bending, in such a way that the bigger portion appears on the side opposite to the dipolarophile. This unequal orbital extension is more pronounced at α = 130° and leads to a decrease of the antibonding effect of N-2 in the $HOMO(C_2H_4)-LUMO(CH_2N_2)$ interaction. In the final product, 1-pyrazoline, this angle will be roughly 110−115°[7] and this orbital of N-2 then houses a lone pair of electrons. In the α = 130° structure we observe for the orbitals at the terminal atoms of the 1,3-dipole a direction which is better suited for overlap with the AO's of ethylene than in the α = 150° structure. This is a further argument for the increase in stabilisation from the interaction $HOMO(CH_2N_2)-LUMO(C_2H_4)$.

Regiochemistry in Diazomethane Cycloadditions: Experimentally predominant formation of 3-substituted 1-pyr-

azolines (**3**) is observed for monosubstituted olefins regardless of the electronic nature of the substituents[4]. This causes problems for the theoretical model which relies on the size of the eigenvector coefficients in the dominant FMO interaction. The seemingly exclusive formation of 3-ethoxy-1-pyrazoline (**3a**) in the cycloaddition of ethyl vinyl ether to diazomethane is not in accord with this model (see above). Methyl crotonate and methyl cinnamate are reported to yield **4a** and **4b**.





3	R'	R
a	H	OC_2H_5
b	H	CO_2CH_3
c	CH_3	CO_2CH_3
d	H	C_6H_5

4	R	R'
a	CH_3	CO_2CH_3
b	C_6H_5	CO_2CH_3

For a set of nine different dipolarophiles we carried out PMO calculations using molecular complexes of structure **2**. The results are collected in Table 2. The individual energy values describe the non-covalent contribution, – first-order energy change with the exemption of the coulombic interaction due to the partial charges of the atoms in the molecules –, charge interaction, total covalent stabilisation, FMO interactions, and the sums of the interactions of occupied π- with unoccupied π-MO's.

The sum of the perturbation energies is positive in all cases signalising that the activated complexes are destabilised relative to the separated molecules. The interaction due to the partial charges of the atoms is negligible and will not be considered further. Of interest is the comparison of the total perturbation energy for the possible regioisomers. We notice smaller positive values for the orientation leading to the 3-substituted 1-pyrazoline for all monosubstituted dipolarophiles indicating that this isomer should be formed preferentially. Also for the 1,2-disubstituted olefins we find lower positive values for the experimentally favored regioisomer (**4a** and **4b**). The difference in the numbers varies from 1.2 kcal/mol for methyl cinnamate and 15.2 kcal/mol for methyl methacrylate. Obviously, the cases with the smaller differences should be predestined to yield mixtures of isomers. Experimentally known[24] is the formation of a 80:20 mixture of 3- and 4-methyl-1-pyrazoline for propene (ΔE = 4.4 kcal/mol). On this basis we might expect the formation of regioisomers for methyl cinnamate and methyl crotonate. The literature[25,26] does not report the formation of a mixture of isomers in these two cases although it is not clear how intensive one has looked for another isomer. It might be interesting and at the same time a good test for our procedure to check again very carefully the cycloadditions of methyl cinnamate and methyl crotonate with diazomethane. Noteworthy seems that these two dipolarophiles yield mixtures of isomers in 1,3-dipolar cycloadditions of formonitrile oxide[27], benzonitrile oxide[28] and 1,3-diphenylnitrilimine[29]. Diazomethane forms also a mixture with methyl phenylpropiolate as dipolarophile[26].

Can one deduce the observed regiochemistry from the FMO interactions? All cycloadditions which we considered have a strong HOMO(CH_2N_2) – LUMO(olefin) interaction. According to the simple model we should therefore compare the stabilization HOMO(CH_2N_2) – LUMO(olefin). The appropriate numbers in column 6 of Table 2 show differences of 0.1 to 0.8 kcal/mol for the regioisomers. More important is whether the higher stabilization reproduces qualitatively the experimentally observed regiochemistry. In all but one example this expectation is fulfilled. As in the model based solely on the size of the eigenvector coefficients in the dominant HOMO – LUMO interaction[11] methyl vinyl ether should produce the 4-alkoxy-substituted 1-pyrazoline preferentially. This is in line with the results of Gandolfi and Rastelli[9]. We may test two further approximations. Firstly we can add the stabilization from both HOMO – LUMO interactions (columns 6 and 7) and secondly we can consider the interaction of all occupied π-MO's with the π*-MO's (columns 8 and 9). The first approach improves the results in many cases but leads to wrong predictions for butadiene and styrene. The second approach gives very poor correla-

Table 2. Perturbation energies [kcal/mol] for molecular complexes **2** with varying olefins

$H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N$ |	1st Order Charge	1st Order Non-cov.	2nd Order Covalent	Sum	HOMO(CH_2N_2) – LUMO(olefin)	HOMO(olefin) – LUMO(CH_2N_2)	HOMO(CH_2N_2) – $\Sigma\pi^*_{olef.}$	$\Sigma\pi_{olef.}$ – LUMO(CH_2N_2)
$H_2C=CH-OCH_3$	0.06	56.5	−16.5	40.4	−7.6	−1.6	−7.6	−2.4
$H_3CO-HC=CH_2$	−0.03	63.1	−17.1	46.0	−8.0	−1.1	−8.0	−2.2
$H_2C=CH-CH_3$	−0.01	58.7	−17.9	40.8	−9.2	−1.7	−9.2	−1.7
$H_3C-HC=CH_2$	−0.04	63.0	−17.8	45.2	−9.1	−1.5	−9.3	−1.5
$H_2C=CH_2$	−0.01	50.0	−17.5	32.5	−9.8	−2.3	−9.8	−2.3
$H_2C=CH-CH=CH_2$	0.02	54.5	−17.1	37.4	−6.8	−1.6	−9.1	−2.2
$H_2C=HC-HC=CH_2$	−0.02	61.5	−16.9	44.6	−6.7	−2.2	−8.9	−2.5
$H_2C=CH-C_6H_5$	−0.01	54.5	−16.3	38.4	−4.3	−1.5	−8.4	−2.1
$H_5C_6-HC=CH_2$	−0.03	62.9	−16.3	46.6	−4.2	−1.6	−8.3	−2.2
$H_5C_6-HC=CH-CO_2CH_3$	−0.02	65.7	−20.2	45.5	−9.4	−0.8	−11.8	−2.1
$H_3CO_2C-HC=CH-C_6H_5$	−0.31	66.8	−20.1	46.7	−8.8	−0.8	−11.0	−1.6
$H_3C-HC=CH-CO_2CH_3$	−0.51	69.1	−21.9	47.2	−11.5	−0.8	−11.9	−2.0
$H_3CO_2C-HC=CH-CH_3$	−0.60	72.6	−21.8	50.8	−10.7	−0.9	−11.0	−1.8
$H_2C=C(CH_3)CO_2CH_3$	−0.50	63.3	−22.3	41.0	−11.8	−1.0	−12.3	−1.8
$H_3CO_2C(H_3C)C=CH_2$	−0.61	78.5	−22.3	56.2	−11.0	−1.2	−11.4	−2.0
$H_2C=CH-CO_2CH_3$	−0.01	52.8	−22.1	30.7	−13.3	−1.5	−13.9	−1.8
$H_3CO_2C-HC=CH_2$	−0.26	62.0	−21.8	40.2	−12.5	−1.4	−13.0	−1.9

tions of the stabilization energies with the experimental results. The consideration of the dominant HOMO–LUMO interaction is still the best heuristic principle to rationalise the regiochemistry on the basis of second-order perturbation theory.

We have proposed earlier[17] the definition of a quantity which we termed reactivity measure (RM value, Eq. 1). It is an approximate interpretation of the full FMO expression and is similar to Fukui's superdelocalizability[30]. κ and λ signify the AO's of the reacting atoms k and l, $\beta_{\kappa\lambda}$ is the resonance integral. $h\nu_{CT}(HO-LU)$ corresponds to the HOMO–LUMO charge-transfer excitation energy.

$$RM = -2 \frac{\{\sum_{\kappa}\sum_{\lambda} c_{HO\kappa} \cdot c_{LU\lambda} \cdot \beta_{\kappa\lambda}\}^2}{h\nu_{CT}\,(HO-LU)} \qquad \text{Eq. 1}$$

We list for both reacting atom pairs the sum of these values for the dominant HOMO–LUMO interaction in Table 3. The conclusion is that the RM values are as good a measure of the observed regiochemistry as the complete HOMO–LUMO stabilization. Methyl vinyl ether still remains the famous exemption.

Table 3. Sum of the RM values (Eq. 1) [kcal/mol] for the reacting atoms in regioisomeric complexes of structure **2**

$H_2\underline{C}-\overset{\oplus}{N}\equiv N\vert$	RM value (× 10)
$H_2C=CH-OCH_3$	−8.03
$H_3CO-HC=CH_2$	−8.89
$H_2C=CH-CH_3$	−8.67
$H_3C-HC=CH_2$	−8.43
$H_2C=CH_2$	−9.38
$H_2C=CH-CH=CH_2$	−5.41
$H_2C=HC-HC=CH_2$	−4.62
$H_2C=CH-C_6H_5$	−2.88
$H_5C_6-HC=CH_2$	−2.28
$H_5C_6-HC=CH-CO_2CH_3$	−5.86
$H_3CO_2C-HC=CH-C_6H_5$	−5.47
$H_3C-HC=CH-CO_2CH_3$	−9.34
$H_3CO_2C-HC=CH-CH_3$	−7.59
$H_2C=C(CH_3)CO_2CH_3$	−9.59
$H_3CO_2C(H_3C)C=CH_2$	−7.63
$H_2C=CH-CO_2CH_3$	−10.64
$H_3CO_2C-HC=CH_2$	−8.75

From the discussion we may conclude that the regiochemistry is most comprehensively rationalised on the basis of the non-covalent interactions. As the energy content of the transition state is the sum of a number of different contributions we should not, however, exclude the covalent portion. But the question remains whether we can devise a simple method to predict the predominant regioisomer. So far it seems that in the 1,3-dipolar cycloadditions studied here and earlier[20,22] the non-covalent contribution to the energy of the transition state gives the best rationalization. There may be cases, however, where the covalent interaction provides the decisive contribution. Further tests have to be carried out in order to see the generality of this approach. The tests are very simple because they do not require the knowledge of the wave function of the involved molecules, only the carthesian coordinates of the molecular complex are required.

Reactivity in Diazomethane Cycloadditions: Is the FMO model suited for a discussion of reactivity in cycloadditions of diazomethane? The kinetic data for diazomethane cycloadditions reveal that the addition reactions of diazomethane belong to type I of the cycloaddition classification. A reproduction of this result can be recognized in the HOMO(CH_2N_2)–LUMO(olefin) stabilisations of Table 2. By factors ranging from 3 to 9 it is higher than the interaction of HOMO(olefin)–LUMO(CH_2N_2). In Table 2 the dipolarophiles are arranged according to increasing reactivity[1] from the top to the bottom of the table. It can be seen that the increase in reactivity follows the increase in stabilization. The electron-deficient dipolarophile methyl acrylate exhibits the highest stabilization. Not only is this the case but also methyl vinyl ether on the other side of the reactivity scale is well-behaved. Its HOMO(CH_2N_2)–LUMO(olefin) interaction is the smallest (except for butadiene and styrene) and relatively its HOMO(olefin)–LUMO(CH_2N_2) interaction is higher than for the electron-deficient dipolarophiles. As expected the HOMO(olefin)–LUMO(CH_2N_2) stabilization exhibits a trend opposite to the other frontier molecular orbital interaction. The data in Table 2 indicate also the difficulties encountered with conjugated systems like butadiene and styrene. Here it is not sufficient to restrict the discussion to the FMO's, other π orbitals must be considered. A detailed analysis of this phenomenon has been given in ref.[22].

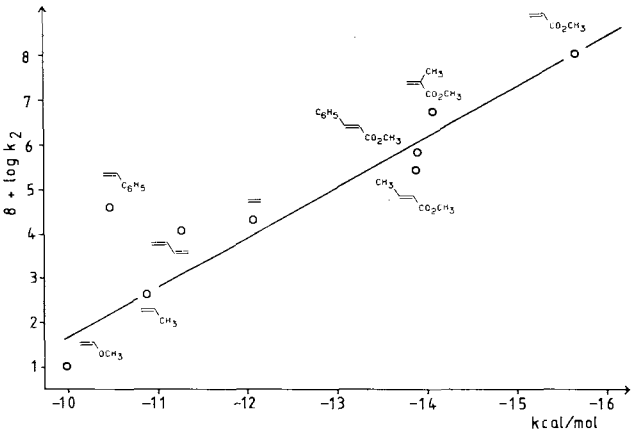


Figure 3. Correlation of log k_2 values with the sum of the second order π-CT interactions. The log k_2 values of ethylene and butadiene were corrected by a statistical factor of 2; for propene we used log k_2 of 1-hexene, for methyl vinyl ether that of *n*-butyl vinyl ether

Our perturbation program PERVAL takes not only care of the FMO's but provides all the other interactions of occupied with unoccupied MO's. In columns 8 and 9 of Table 2 we have singled out the interactions of the π- with the π^*-MO's of the two reactants. Their sum should correlate with the log k_2 values for the cycloadditions. In Figure 3 we present such a plot from which one can see that seven of the nine data points give a good linear fit ($r^2 = 0.94$) and

that two of the olefins, butadiene and styrene, deviate. The total spread in stabilization is ca. 5 kcal/mol. This result was obtained without making any further assumptions like corrections to the orbital energies and is in agreement with our earlier CNDO/2-based analysis[10]. It seems to be very satisfactory in the light of the approximations still present, for instance the identical model for the reactive complex for all dipolarophiles.

Conclusion

The analysis of 1,3-dipolar cycloadditions of diazomethane by our all-valence electron perturbational method has confirmed the type-I behavior of this 1,3-dipole. The second-order covalent interaction, including all π-MO's, describes the reactivity correctly. The simple reactivity model from which the classification of cycloadditions is derived, finds itself reproduced in the FMO interactions. Thus, our calculations support this reactivity model. Regioselectivity is not explained as well by the FMO model. Within the limits of validity of our approach, non-covalent interactions seem to be better suited to rationalise orientational phenomena, at least they provide a comprehensive picture. Being electrostatic in nature, the range of these repulsive forces stretches further out than the covalent interactions. The latter depend on orbital overlap and decrease exponentially. If this conclusion is generally correct, it facilitates further applications. It is very easy to evaluate the non-covalent interactions and to accumulate data for comparison.

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CAS Registry Numbers

H_2CN_2: 334-88-3 / $H_2C{=}CHOCH_3$: 107-25-5 / $H_2C{=}CHCH_3$: 115-07-1 / $H_2C{=}CH_2$: 74-85-1 / $H_2C{=}CHCH{=}CH_2$: 106-99-0 / $C_6H_5CH{=}CH_2$: 100-42-5 / $C_6H_5CH{=}CHCO_2CH_3$: 103-26-4 / $CH_3CH{=}CHCO_2CH_3$: 18707-60-3 / $H_2C{=}C(CH_3)CO_2CH_3$: 80-62-6 / $H_2C{=}CHCO_2CH_3$: 96-33-3

1) J. Geittner, R. Huisgen, R. Sustmann, *Tetrahedron Lett.* **1977**, 881.
2) L. Fišera, J. Geittner, R. Huisgen, H.-U. Reißig, *Heterocycles* **10** (1978) 153.
3) W. Bihlmaier, R. Huisgen, H.-U. Reißig, S. Voss, *Tetrahedron Lett.* **1979**, 2621.
4) R. Huisgen, in *1,3-Dipolar Cycloadditions* (A. Padwa, Ed.), vol. 1, Wiley-Interscience, London, New York 1984.
5) R. Sustmann, *Tetrahedron Lett.* **1971**, 2721; *Pure Appl. Chem.* **40** (1974) 569.
6) T. Minato, S. Yamabe, S. Inagaki, H. Fujimoto, K. Fukui, *Bull. Chem. Soc. Jpn.* **47** (1974) 1619.
7) G. Leroy, M. Sana, *Tetrahedron* **31** (1975) 2091.
8) G. Leroy, M. Sana, *Tetrahedron* **32** (1976) 709.
9) M. Burdisso, R. Gandolfi, S. Quartieri, A. Rastelli, *Tetrahedron* **43** (1987) 159.
10) R. Sustmann, E. Wenning, R. Huisgen, *Tetrahedron Lett.* **1977**, 877.
11) K. N. Houk, J. Sims, C. R. Watts, L. J. Luskus, *J. Am. Chem. Soc.* **95** (1973) 7301.
12) J. Bastide, N. El Ghandour, O. Henri-Rousseau, *Bull. Soc. Chim. Fr.* **1973**, 2290; J. Bastide, O. Henri-Rousseau, *ibid.* **1973**, 2294; **1974**, 1037.
13) R. A. Firestone, *J. Org. Chem.* **41** (1980) 2212.
14) See ref.[4], p. 141 ff.
15) K. N. Houk, K. Yamaguchi, in *1,3-Dipolar Cycloadditions* (A. Padwa, Ed.), vol. 2, p. 407, Wiley-Interscience, New York, London 1984.
16) See ref.[15] for a review.
17) R. Sustmann, W. Sicking, *Chem. Ber.* **120** (1987) 1323.
18) R. Sustmann, A. Ansmann, F. Vahrenholt, *J. Am. Chem. Soc.* **94** (1972) 8099.
19) R. Sustmann, F. Vahrenholt, *Theor. Chim. Acta* **29** (1973) 305.
20) J. Martelli, F. Tonnard, R. Carrie, R. Sustmann, *Nouv. J. Chim.* **2** (1978) 609.
21) R. Sustmann, W. Sicking, *J. Am. Chem. Soc.*, submitted for publication.
22) R. Sustmann, W. Sicking, *Chem. Ber.* **120** (1987) 1471.
23) L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions, Chem. Soc. Publ.* **11** (1958), **18** (1965).
24) R. A. Firestone, *Tetrahedron Lett.* **21** (1980) 2209.
25) H. v. Pechmann, E. Burkard, *Ber. Dtsch. Chem. Ges.* **33** (1900) 3590; D. E. McGreer, W. Wan, G. Carmichael, *Can. J. Chem.* **38** (1960) 2410.
26) J. Bastide, O. Henri-Rousseau, L. Aspart-Pascot, *Tetrahedron* **30** (1974) 3355.
27) R. Huisgen, M. Christl, *Chem. Ber.* **106** (1973) 3291.
28) M. Christl, R. Huisgen, R. Sustmann, *Chem. Ber.* **106** (1973) 3275.
29) R. Huisgen, R. Sustmann, G. Wallbillich, *Chem. Ber.* **100** (1967) 1580.
30) K. Fukui, *Fortschr. Chem. Forsch.* **15** (1970) 1.

[113/87]