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MOLECULAR ORBITALS OF CONJUGATED KETENES AND ANALYSIS OF THE INTRAMOLECULAR CYCLOADDITION

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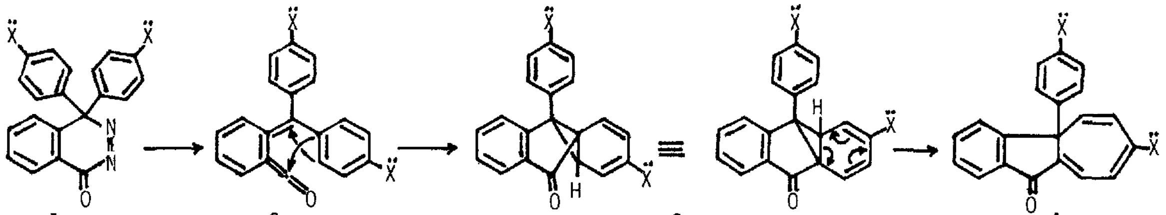
Summary: MO calculations by CNDO/2 method on some conjugated ketenes were carried out. Several special features obtained and the evaluation of a role of the in plane π*-orbital for the intramolecular ene-ketene cycloaddition are described.

We have recently reported the first example of an antarafacial role of an aromatic ring, by which the ene-ketene 2, thermally generated from 1, undergoes a facile and regiospecific $[{}_{\pi}4_a + {}_{\pi}2_a]$ intramolecular cycloaddition with N,N-dimethylaniline to result in the novel formation of norcaradiene 3, followed by the ring opening to an azulenone derivative 4, and dimethylamino group on the para position of benzene ring appears to render a striking substituent effect to divert the reaction completely from the usually prefered 6π-electrocyclization.[1]



1 $\ddot{X}=N(CH_3)_2$ 2 3 4

An antarafacial character of ketene in terms of orbital symmetry has been the object of much discussion for several years. It is now widely believed on the basis of theoretical analyses[2] and experimental evidences[3] that the propensity of ketene to undergo a thermally allowed $[{}_{\pi}2_a + {}_{\pi}2_s]$ cycloaddition is the result of the electrophilicity of the central carbon of the ketene induced by in plane π*-orbital. Contrary to this well investigated ketene cycloaddition, the nature and reactivity of conjugated ketenes are poorly understood, and some ambiguities remain particularly as to how the orthogonal two plane π-systems of the ene-ketene come into play on the intramolecular cycloaddition in terms of frontier molecular orbital theory.

In order to gain better understanding on such cycloadditions, we have carried out preliminary MO calculation by CNDO/2 method[4] on some conjugated ketenes,[5,6] and wish to report here the special features disclosed by these calculations. In the light of the inherent limitation of CNDO/2 approximation, the calculated absolute values might be little reliable. Nevertheless, the relative energies and coefficients would provide insight into the regioselective criterion for choosing between two processes involved in the intramolecular ene-ketene cycloaddition.

The frontier molecular orbitals, coefficients and energies relevant to the reaction are shown in Figure 1 with those of ketene[7] for comparisons. The plane geometry for the molecules with all bond angles fixed at 120° except for $C_4C_3C_8(=C_3C_8C_7)$ on 7 were assumed.[8]

The relative energy diagram shows that the LUMO of the ene-ketene 7 and the HOMO of dimethylaniline 8 has the smallest separation in energy[9] and therefore should yield the dominant stabilization in the transition state for the intramolecular cycloaddition of 2.

For **6** and **7**, the perturbation in coefficient distribution on the HOMO and LUMO due to the carbonyl function of the ketene moiety appears to exert the influences of a rather electron-donating substituent on the carbon-carbon π-system, although it plays a role of an electron-withdrawing substituent on the carbonyl π-bonding. This indicates that the ene-ketene would have an inherent aptitude of periselectivity of the 4π component, when the LUMO is involved in the reaction.

Furthermore, the especially interesting feature worthy of note is that the energy level of in plane π*-orbital of the carbonyl group for the conjugated ketene remains largely unaltered, relative to that of ketene, and the potentiality for the orbital interaction would also be unchanged, although the increase in conjugation of the carbon-carbon π-system loweres the unoccupied molecular orbital in energy. As a result, the in plane π*-orbital has been moved to NLUMO for **7** unlike LUMO for **5** and **6**, and yet it underwent the antarafacial pathway.

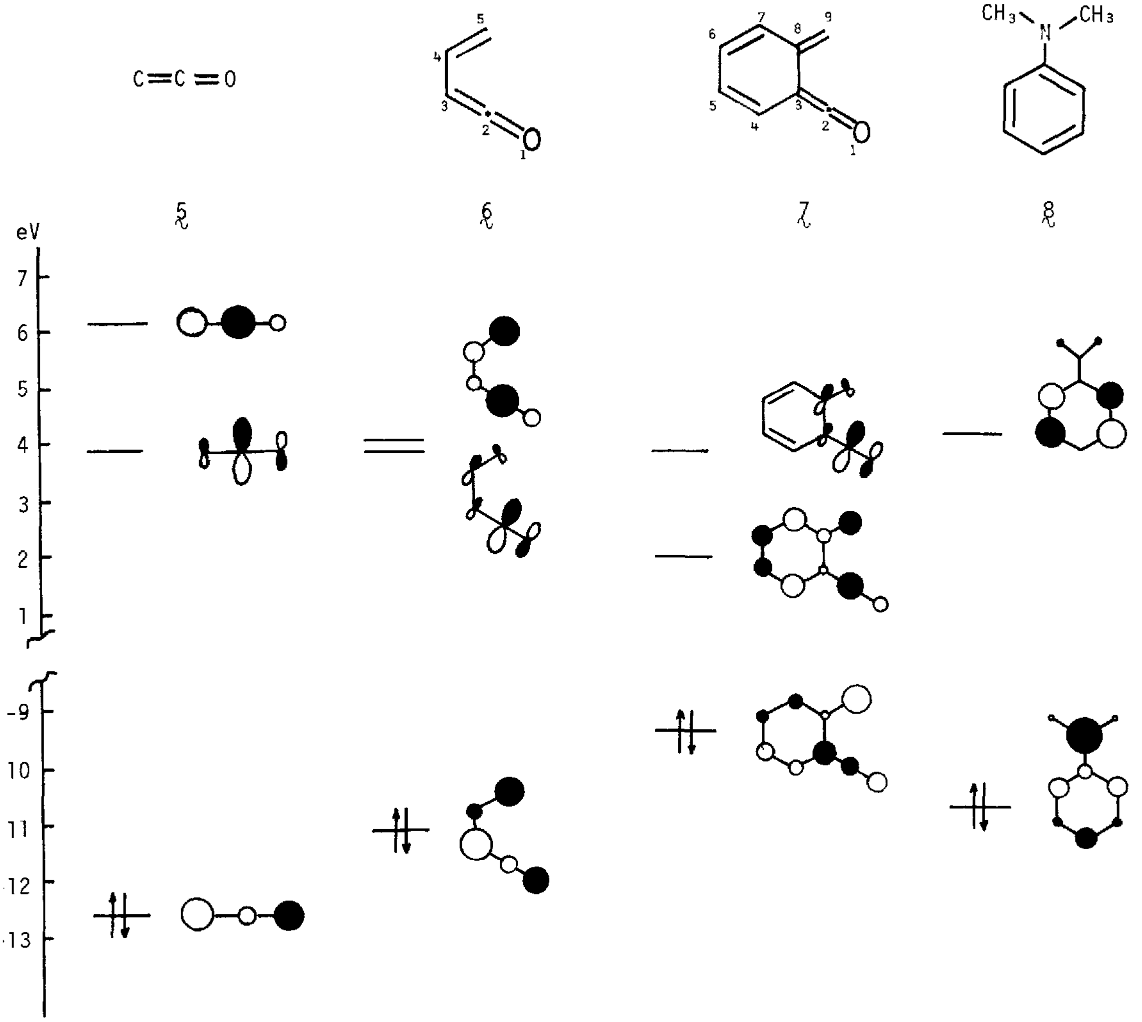


Figure 1. Frontier Molecular Orbital Energies and Coefficients by CNDO/2 Method

To further asscess the configuration interaction of each component, total energies of cis-cis diene-ketene 9 as a model molecule were also evaluated by CNDO/2 approximation as a function of rotation about C_5-C_6bond.[8]

From the relative total energies diagram shown in Figure 2, it is clear that out of plane deformation of the diene-ketene 9 by 45° is energetically feasible. Rotation of C_5-C_6bond from its 45° conformation toward the plane conformer results in a steep energy increase. The very high electron- and core-repulsive contributions of hydrogen atom (inside)of C_7 with C_2atom are responsible for this destabilization. Thus, the geometry rotated 90° is far more stable than the plane geometry despite the decrease in contribution of conjugation.

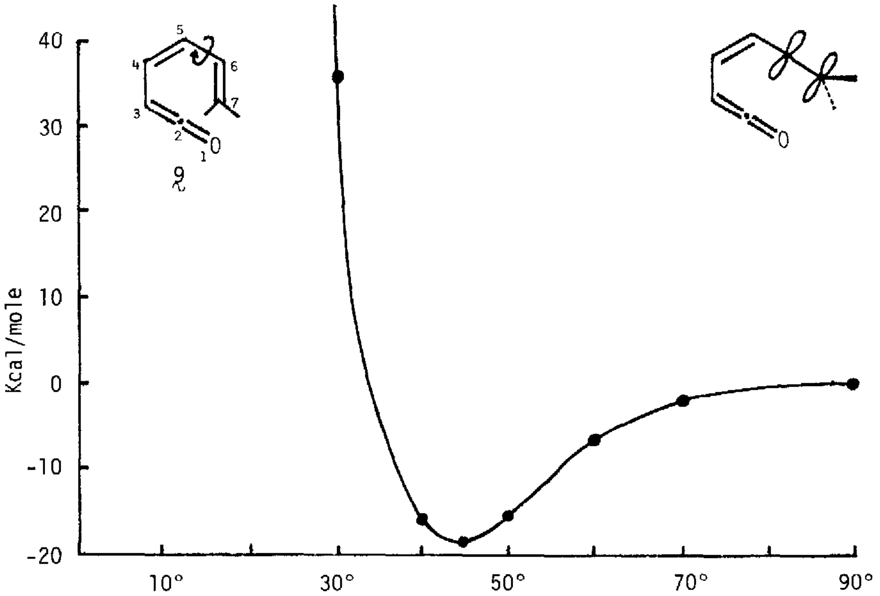
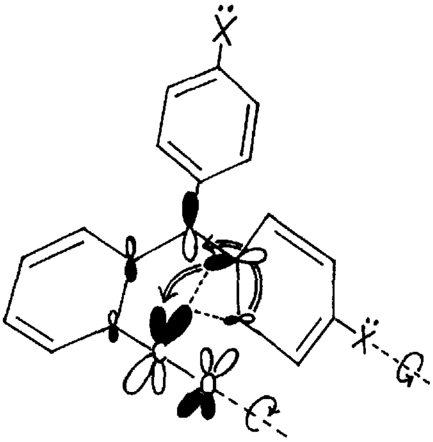


Figure 2. Relative total energies of 9 resulting from rotation about the C_5-C_6 bond; The zero of energy corresponds to the 90° conformer.

Based on these results, it can be best understood in FMO terms for the intramolecular cycloaddition of the ene-ketene that in plane π*-orbital, regardless of being LUMO or NLUMO, is not directly involved in the reaction but is responsible for inducing an orthogonal or orthogonal-like approach of each component with an electrostatic (charge-transfer) stabilization by the three center bonding of the central carbon atom wtih 2π component.[10] This type stabilization also gives rise to the interaction of 2π component with the orthogonal p_z orbital of the central carbon atom.[12] But, of more importance is the fact that the magnitude of such a interaction depends on the extent of magnitude of the interaction between the two p orbitals in the three center bonding.[13] This seems to be a critical feature for the regioselectivity for this cycloaddition process. The site of the preferential bond formation would turn out to correlate with the magnitude of the HOMO coefficient of 2π component, even if it is the part of an aromatic ring.

The regiospecific $[{}_{\pi}4_{a} + {}_{\pi}2_{a}]$ intramolecular ene-ketene cycloaddition for 2, therefore, arises from the initial bond formation between the central carbon atom of the ketene and the carbon atom on the para position of dimethylaniline due to the much greater magnitude of the HOMO coefficient on the para position. Such a bond formation also brings about concomitant disrotatory motion as shown, leading to the completion of [$_{\pi}4_a$ + $_{\pi}2_a$] process.

However, it remains to be answered from what difference of the HOMO coefficient magnitude one can have it undergo an antarafacial pathway. Further strudies directed toward this matter are in progress.



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5. Calculation on the out of plane deformation of the full molecule **2** introduces the complexity of σ-π mixing, which gives orbitals of unrecognizable shapes. Therefore, we separate the molecule into two components; the ene-ketene as 4π-component and dimethylaniline as 2π-component.
6. MO calculation on dimethylaniline was also carried out for comparison of the relative energies with the same level of approximation.
7. K.N.Houk, R.W.Strozier and J.A.Hall, Tetrahedron Lett., 897 (1974)
8. The following standard bond lengths were used; r_{CH}=1.08 Å, $r_{C\text{-}C}$=1.46 Å, $r_{C=C}$=1.33 Å, $r_{C_2=C_3}$= 1.31 Å, $r_{C=O}$=1.16 Å.
9. LUMO(**7**) - HOMO(**8**) = 12.826 eV; For the reverse pair; LUMO(**8**) - HOMO(**7**) = 13.512 eV. Introduction of an aromatic ring at the end of the ene-ketene as is for **2** would further lower the LUMO energy level.
10. It should be pointed out that this configuration bears some resembrance to that between 4π- and 2π-system in cyclooctatetraene framework, the permethylated derivative of which also undergoes regiospecific [$_{\pi}4_a$ + $_{\pi}2_a$] intramolecular cycloaddition.[11]
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13. This was deduced from the results calculated by R.Sustmann et al.[12]

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