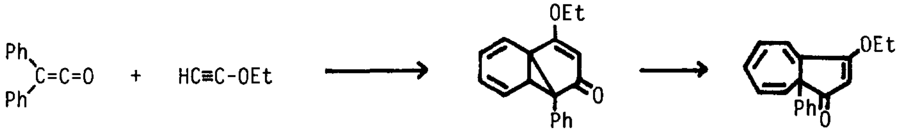
Tetrahedron Letters,Vol.23,No.25,pp 2593-2596,1982 0040-4039/82/252593-04$03.00/0
Printed in Great Britain

MOLECULAR ORBITAL QUANTITIES OF CONJUGATED KETENES AND INFLUENCE OF STRUCTURAL VARIATIONS ON THEIR ELECTRONIC FEATURES

Masayuki Kuzuya,* Fumio Miyake, Kaoru Kamiya and Takachiyo Okuda
Gifu College of Pharmacy, 6-1, Mitahora-Higashi 5-Chome, Gifu, 502, Japan

Abstract: MO quantities by CNDO/2 method on several valence isomeric ketenes and structurally corresponding allene molecules were calculated to evaluate the influence of structural feature on magnitude of back-donation of oxygen n-electrons in ketene, and to rationalize an unusual cycloaddition involved in diphenyl ketene.

In connection with our study of physicochemical properties of o-quinonoid ketene which have been reported to undergo novel intramolecular cycloadditions with an aromatic ring,[1] and to be of interesting molecular orbital quantities,[2] we felt it also of interest and of importance in fully understanding the electronic detail involved in ketenes and probably in all other heterocumulene systems to investigate the structural variation exerting an influence on the molecular orbital quantities of various ketenes. In fact, it has been shown for diphenyl ketene to undergo unusual $[_{\pi}2_a + {}_{\pi}2_a + {}_{\pi}2_s]$ cycloaddition with ethoxyacetylene to give an azulenone derivative along with the usually preferred $[_{\pi}2_a + {}_{\pi}2_s]$ cycloaddition.[3] This experimental fact actually led us to consider possibility of the presence of the special feature concerning the molecular orbiral quantities involved in such a ketene.



From these points of interest, we undertook the molecular orbital calculation of phenyl ketene[4] which is a valence isomer of o-quinonoid ketene, supported by CNDO/2 approximation.[5] Although we focussed here our attention on the MO quantities of phenyl ketene, we also carried out the calculations of p-quinonoid ketene and several other related molecules (necessary for discussions described in this report) for comparison with the same level of approximation and parameterizations.

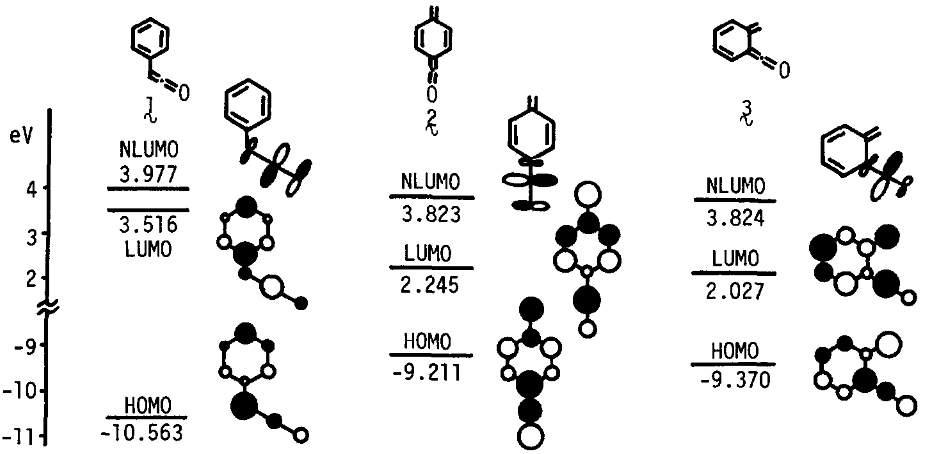
We wish to report here the unique properties of phenyl ketene disclosed by such calculations, by which the above mentioned cycloaddition can be nicely explained in terms of frontier molecular orbital theory, and the influence of structural feature on the magnitude of back-donation of oxygen lone pair electron in ketene.

1. Molecular orbital quantities of valence isomeric ketenes

The molecular orbital calculation on the out of plane deformation considering all valence electrons introduces the complexity of σ-π mixing, resulting in orbitals of unrecognizable shape. Thus, although geometrical optimization of phenyl ketene by MINDO/3 method showed that benzene ring is twisted from the xy plane of the ketene moiety by 42.3°,[6] the geometry of the phenyl ketene with C_S symmetry was taken for simplicity, since the computed energy difference between such structures was in only 0.11 Kcal/mol,[6] and the values of parameters adopted in the CNDO/2 calculations were the same as those in the original paper.[7] These approximations have proved useful in our hand for gaining fundamental insight into the reactivity (vide infra).

The computed frontier molecular orbital coefficients and energies of **1** and **2** were shown in Figure 1, together with those of o-quinonoid ketene, **3**, for comparison.[2a]

Figure 1



Inspection of Figure 1 showed that variables in structural feature leave the nodal property and coefficient distribution of FMO in ketene moiety as well as the energies of in plane π^*-orbital essentially unchanged due to orthogonality between the two π-systems. Major difference is in the pattern of frontier molecular orbital energies of **1** as shown. But, perhaps the most interesting properties of **1** is in the distribution of the LUMO coefficient; the ipso-carbon (the site of substitution) of benzene ring has the largest coefficient, suggestive for high reactivity at this carbon in case of that the reaction mainly involves the LUMO of phenyl ketene.

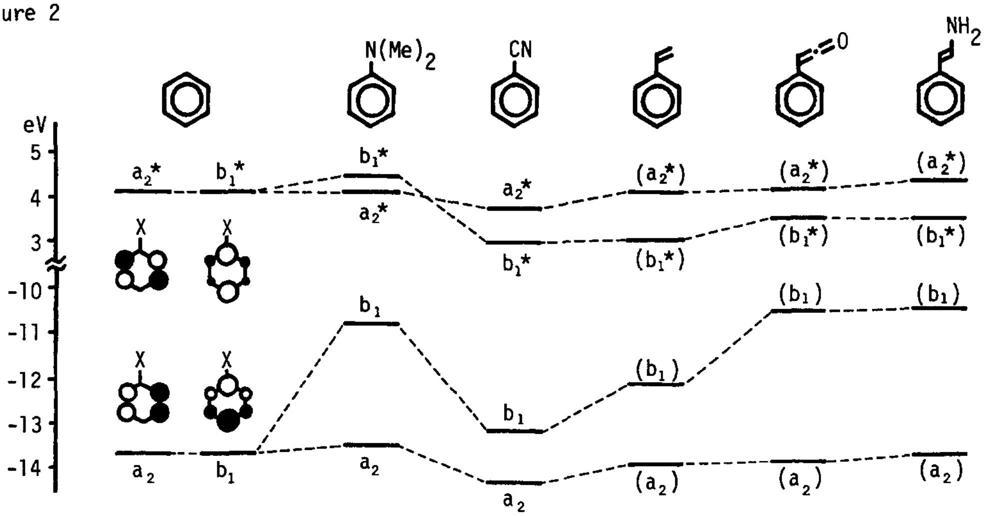
2. Concerning magnitude of back-donation of oxygen lone pair involved in conjugated ketenes

Contrary to well established property that the propensity of ketene to undergo cycloadditions in an antarafacial fashion is the result of the electrophilicity of the central carbon of the ketene induced by in plane π^*-orbital, the back-donating nature and magnitude of oxygen lone pair electron in ketene, which is in a π-type orbital with a node in the molecular plane, are poorly understood and, to our best knowledge, theoretical considerations have never been systematically examined.

The computed FMO energy pattern and nodal properties of an aromatic portion of phenyl ketene, **1**, were compared with those of mono-substituted benzene bearing typical three types of substituent; electron-donating group (dimethylaniline), electron-withdrawing group (benzonitrile) and conjugative group (styrene and ω-aminostyrene).

As is shown in Figure 2, the orbital patterns of the HOMO and LUMO in the benzene moiety of phenyl ketene corresponds to b_1 and b_1^* in C_{2v} symmetry[8] which is in the same pattern as styrene and benzonitrile. However, the HOMO energy is considerably higher than those of such compounds. This fact is indicative of a rather strong back-donation of oxgen lone pair in view of the substituent effect derived from "the general principle of orbital interaction". In fact, the

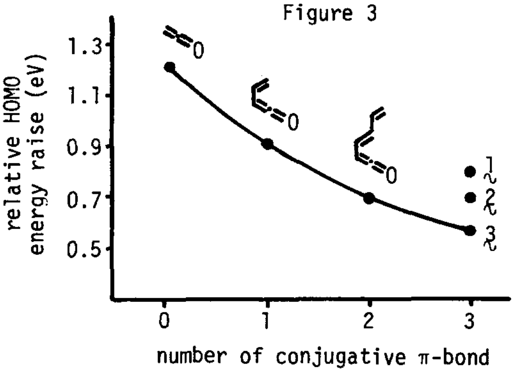
Figure 2



energy pattern of phenyl ketene is close to those of trans ω-aminostyrene as is shown.

Furthermore, in order to evaluate the influence of the structural feature on magnitude of the back-donation, MO calculations of the structurally corresponding allene molecules were also carried out. The plot of the HOMO energy raise of ketene relative to the corresponding allenes as a function of the number of π-bonding showed hyperbora relation, but the plot of **1** was largely deviated from such a line, indicating again on this point the unique properties of phenyl ketene, as shown in Figure 3.

Figure 3



3. FMO analysis of [$\pi 2_a + \pi 2_a + \pi 2_s$] cycloaddition involved in diphenyl ketene

For an analysis of this cycloaddition, the MO calculation on methoxy acetylene was also carried out. The MO energies calculated were shown in Figure 4.

Although the relative energy diagram shows that the LUMO of alkoxy acetylene and the HOMO of ketene, **1**, has the smallest separation in energy, the computed LUMO (4.267 eV) is largely polarized to the alkoxy moiety and the NLUMO (6.845 eV) is largely mixed with s-orbital at acetylene moiety, i.e., σ-bond character. Thus, we believe that the leading orbital interaction in the transition state should be in the LUMO of ketene and the HOMO of alkoxy acetylene, which is an orbital of full π-character with the same phase, provided that the transition state assumes to involve mainly single configuration. And also, it is known that in plane π*-orbital of central carbon atom of ketene, which is not directly involved in the reaction, is responsible for inducing an orthogonal approach of each reactant with a charge-transfer stabilization by the three center bonding with 2π component. This type stabilization also gives rise to the interaction of 2π system with the orthogonal Pz orbital of the central carbon atom, the magnitude of which necessarily correlates with that of the HOMO coefficient of 2π system.[2,9]

In these views, it can be best understood that the cycloaddition arises from the initial bond formations between the central carbon of ketene moiety and the carbon atom apart from alkoxy group in acetylene due to the larger HOMO coefficient (bond a), and also ipso-carbon of benzene ring and the other carbon atom of acetylene due to the large LUMO coefficient of phenyl ketene (bond b). Such bond formations bring about concomitant clockwise rotation of benzene ring and counterclockwise rotation of ketene axis, whose rotations also make the bond formation between C_3 and C_5 favorable with respect to orbital dihedral angle due to the opposite sign of the LUMO (bond c), as shown in Figure 5.

Figure 4

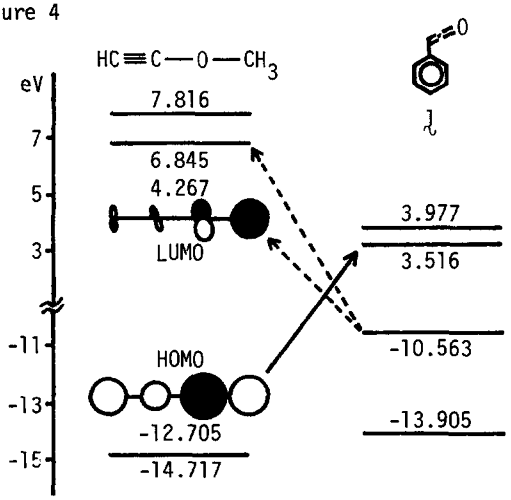
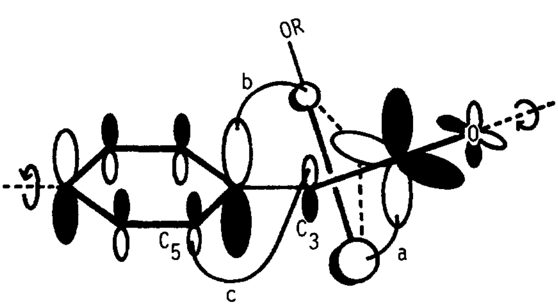


Figure 5



It should be noted that introduction of the second phenyl group to C_3-position, i.e., diphenyl ketene would force the benzene ring to twist further with respect to the ketene xy plane due to a repulsive contribution from each other. This effect reduces the magnitude of the conjugative interaction between the ketene π_z-system and aromatic π-system but the net effect leads to lower the LUMO energy and the resulting conformation would favor the bond formation of C_3 and C_5 in an antarafacial fashion. These combined factors led to the completion of unusual $[{}_{\pi}2_a + {}_{\pi}2_a + {}_{\pi}2_s]$ cycloaddition along the predicted regiospecificity.

REFERENCES AND FOOTNOTES

1. a) M. Kuzuya, F. Miyake and T. Okuda, Tetrahedron Lett., 21, 1043 (1980)
   b) M. Kuzuya, F. Miyake and T. Okuda, Chemistry Lett., 1593 (1981)
2. a) M. Kuzuya, F. Miyake and T. Okuda, Tetrahedron Lett., 21, 2185 (1980)
   b) M. Kuzuya, S. Ito, F. Miyake and T. Okuda, Chem. Pharm. Bull., in press.
3. J. D. Wuest, Tetrahedron, 36, 2291 (1980), references cited therein.
4. MO calculation of phenyl ketene was reported as a part of study for reactions of thioketones but the detailed quantities and features were not presented; J. C. Meslin, Y. T. N'Guessan, H. Quiniou and F. Tonnard, Tetrahedron, 31, 2679 (1975)
5. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York 1970
6. M. Kuzuya, F. Miyake and T. Okuda, unpublished results.
7. a) J. A. Pople, D. P. Santry and G. A. Segal, J. Chem. Phys., 43, 129 (1965)
   b) J. A. Pople and G. A. Segal, J. Chem. Phys., 43, 136 (1965)
8. Although introduction of non-linear substituent to benzene ring reduces the molecular symmetry to C_s, the point we discuss here is in the qualitative nodal properties of an aromatic ring.
9. R. Sustmann, A. Ansmann and F. Vahernholt, J. Am. Chem. Soc., 94, 8099 (1972)

(Received in Japan 15 March 1982)