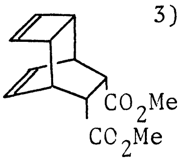
CHEMISTRY LETTERS, pp. 457-460, 1973. Published by the Chemical Society of Japan

ON THE INERTNESS OF SYN-TRICYCLO[4.2.0.0^{2,5}]OCTA-3,7-DIENE UNDER PHOTOLYTIC CONDITIONS. AN APPARENT VIOLATION OF THE ORBITAL SYMMETRY RULE [1]

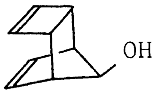
Hiizu IWAMURA, Kazuhiko MORIO, and Hiroshi KIHARA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo

An MO explanation is given to the failure of the intramolecular photocycloaddition reaction of syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene. Due to the presence of the high-lying σ-orbitals of the cyclobutane ring and to the unique topology of the molecule, the electronic excitation could not be related to the ethylenic chromophore and/or a possible degenerate isomerization might be induced by photoexcitation.

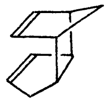
The [2+2] cycloaddition reaction is one of the most widely documented processes which are symmetry-allowed in the electronically excited state, and serves as an excellent guiding principle in designing a synthetic route leading effectively to a cyclobutane ring.[2] The cage compounds which are not easily accessible otherwise are prepared advantageously by the intramolecular photocycloaddition of the corresponding dienes,



[3]



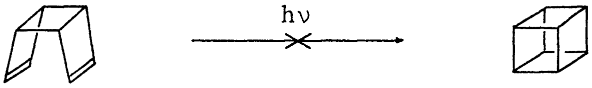
[4]



[5]

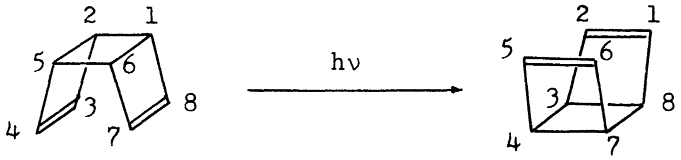
and etc.[2,6]

However, the same tactics fails in the attempted synthesis of cubane according to Eq. 1.[7] We wish to report on the theoretical significance of this resistance to cycloaddition, an apparent exception to the Woodward-Hoffmann rule,[8] as disclosed by the MO study of syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene.



(1)

Although less popular than the corresponding Walsh model of cyclopropane, there is a degenerate e_u set of the highest occupied orbitals of relatively high energy (-10.7 eV) in cyclobutane.[9)] We find that, due to the presence of these σ-orbitals of the cyclobutane and cyclobutene rings as well as to the unique topology of the molecule, mixing of the π- and σ-orbitals is extensive in the syn-tricyclooctadiene. The construction of the higher occupied and lower unoccupied orbitals are approximately described as shown in the Figure. Note that the highest occupied MO is composed mainly of the carbon 2p AO's perpendicular to the $2p\pi$ orbitals on the ethylenic carbons, and is devoid of the latter π-bond character. It is usually the case that, when two ethylene groups interact face to face with each other, the degeneracy of the π-levels is lifted to give an in-phase combination of lower energy and an out-of-phase combination of higher energy as shown in column a of the Figure. As the result of mixing with the high-lying σ orbitals of the cyclobutane ring, the level ordering is reversed in the tricyclooctadiene and the second highest occupied MO is the in-phase combination while the out-of-phase combination appears in the 16th MO of lower energy. The π-type electronic excitation to the lower unoccupied MO does not contribute effectively to the increase in the C_3-C_8 and C_4-C_7 bond orders. When energetically less favorable electronic configurations of the excited state are taken into considerations, the interaction between the two ethylene moieties can be bonding to form a cyclobutane ring at the bottom of the molecular framework, i.e., C_3, C_4, C_7 and C_8. At the expense of the bonding interaction, however, the bond orders between C_1 and C_6, and C_2 and C_5 decrease to effect concomitant cleavage of these bonds as seen from the orbital construction of the 20th and 26th unoccupied MO's. Thus it is expected that the photochemical valence isomerization represented by Eq. 2 might take place in the excited state configurations in which the [2+2] cycloaddition could be induced. Since the starting material and the product are structurally degenerate, it is possible that we could not have observed the net reaction. The overwhelming numbers of examples of the intramolecular photocycloaddition in other dienes[2-6)] can be reasoned in terms of poorer mixing of the σ- and π-orbitals because of lower symmetry in these dienes and/or



(2)

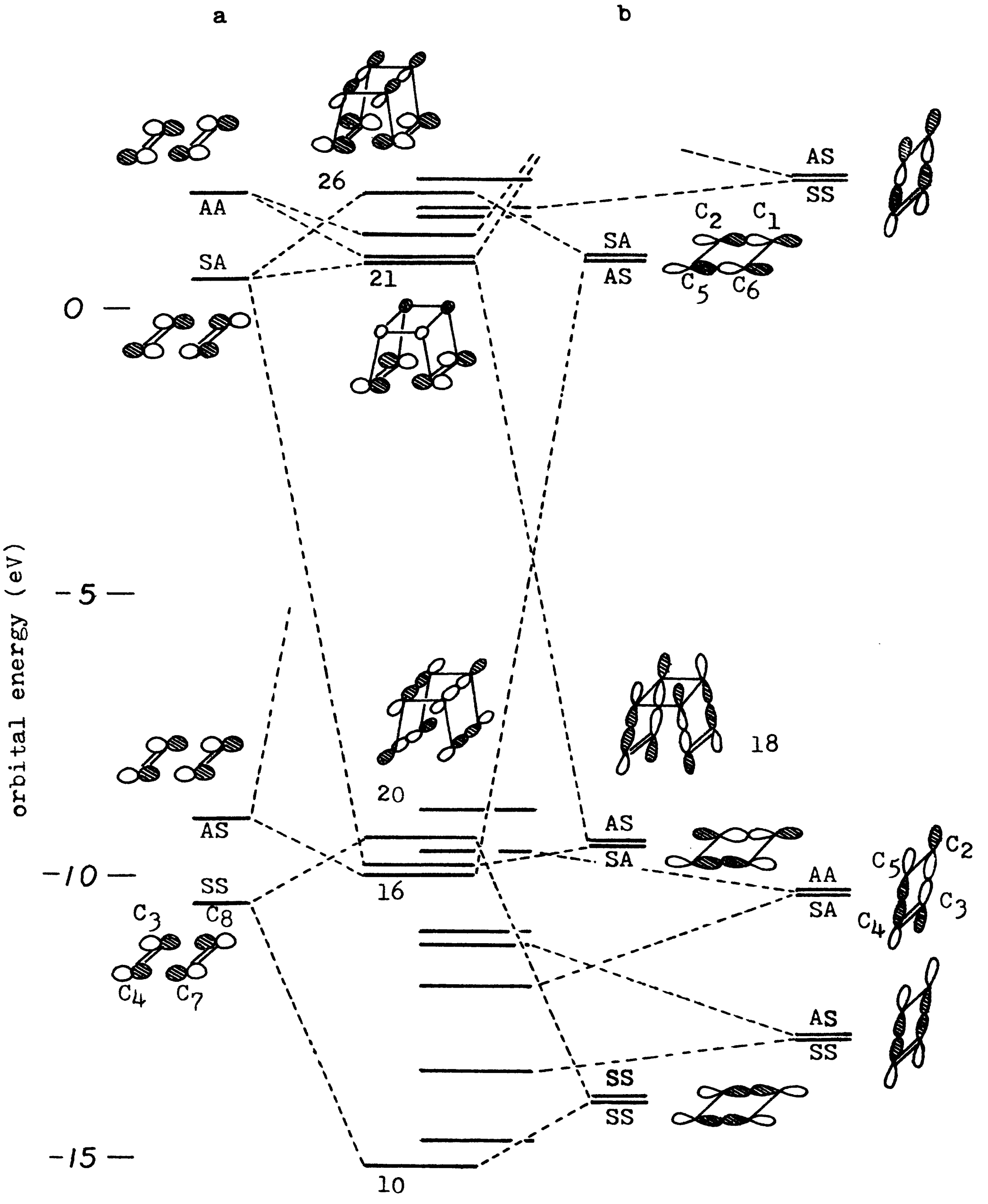


Figure. The construction diagram of the higher occupied and lower unoccupied MINDO/2 molecular orbitals of the syn-tricyclooctadiene. Classifications S and A are due to the symmetry with respect to the planes perpendicular to the $C_1C_2C_5C_6$ plane and bisecting the C_1C_2 and C_5C_6 bonds, and the C_1C_6 and C_2C_5 bonds, respectively.

of the violation of the Bredt rule encountered when these dienes undergo the rearrangement corresponding to Eq. 2.

The way of dissipation of the excitation energy of the tricyclooctadiene and detection of the possible degenerate valence isomerization by labeling technique are under current investigation.

REFERENCES

1) Part VII of "Studies of Reaction Mechanisms by All-valence-electron Semi-empirical SCF MO Theories." For Part VI, see H. Iwamura, Tetrahedron Letters, 369 (1973).

2) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Co., New York, N. Y. (1967), Chapt. 6; N. J. Turro, "Technique of Organic Chemistry, Vol. 14, Energy Transfer and Organic Photochemistry," ed. by A. Weissberger, Interscience Publishers, New York, N. Y. (1969), Chapt. 3; R. N. Warrener and J. B. Bremner, Rev. Pure Appl. Chem., 16, 117 (1966); W, L. Dilling, Chem. Rev., 66, 384 (1966).

3) E. E. van Tamelen and D. Carty, J. Amer. Chem. Soc., 89, 3922 (1967); S. Masamune, H. Cuts, and M. G. Hogben, Tetrahedron Letters, 1017 (1966).

4) W. G. Dauben and D. L. Whalen, ibid., 3743 (1966).

5) G. O. Schenck and R. Steinmentz, Chem. Ber., 96, 520 (1963).

6) R. C. Cookson and E. Crundwell, Chem. and Ind., 1004 (1958).

7) R. Criegee, Angew. Chem., 74, 703 (1962); H. Iwamura, to be published elsewhere.

8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press Inc., New York, N. Y. (1970), Chapt. 6.

9) L. Salem and J. S. Wright, J. Amer. Chem. Soc., 91, 5947 (1969); R. Hoffmann and R. B. Davidson, ibid., 93, 5699 (1971); P. Bischof, E. Haselbach, and E. Heilbronner, Angew. Chem., 82, 952 (1970); J. S. Wright and L. Salem, J. Amer. Chem. Soc., 94, 322 (1972).

(Received January 17, 1973)