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THE MOLECULAR-SYMMETRY REDUCTION IN SOME CYCLIC DIFULVALENE SYSTEMS

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The energetically favorable molecular-symmetry groups of some cyclic difulvalene systems are examined by using the theory of double-bond fixation. It is found that molecules 2 and 5 should suffer the symmetry reduction from D_{2h} to C_{2h} and molecules 1, 3, 4, and 6 show no symmetry reduction. Further, a simple rule for predicting the stable molecular shapes of these systems is presented.

For predicting the stable molecular shapes with respect to C-C bond lengths of conjugated hydrocarbons, a general theory of double-bond fixation has been developed by Binsch et al.[1-4] This theory has been applied to a large number of conjugated hydrocarbons, and the predictions are in good agreement with available experimental facts.

Of the cyclic difulvalene systems (Fig. 2), cyclic dicalicene (1) and its derivatives have recently been prepared by Yoneda et al.[5] Since cyclic difulvalene systems are considered to be composed of two fulvalene molecules, it is of interest to examine whether they would exhibit the properties of parent molecules or not.

In the framework of the Huckel MO approximation, we examine the stable molecular shapes of some cyclic difulvalene systems formed of the same two fulvalene molecules using the theory of double-bond fixation. On the basis of the results obtained, we derive a simple rule for predicting the stable molecular shapes of the cyclic difulvalene systems. Further, we briefly refer to the chemical properties of these conjugated hydrocarbons.

Since the theory of double-bond fixation has been well developed in several literatures,[1-4] we give here only the outline of the theory. The information on the most favorable bond distortion in a conjugated system will be obtained by the diagonalization of bond-bond polarizability matrices:

$$\| \pi_{rs,tu} - \lambda \delta_{rs,tu} \| = 0$$

The eigenvalue and the associated eigenvector provide a measure of the force constant for distortion from the symmetrical nuclear configuration and the type of bond distortion, respectively. The most favorable type of bond distortion is given by the eigenvector corresponding to the largest eigenvalue λ_{max}. If λ_{max} is greater than a certain critical value, ca. 1.80 β_0^{-1}, the molecule will lose its original full symmetry.

In Fig. 1 we show the dependence of the calculated largest eigenvalues λ_{max} on the number n of general formula $C_{4n}H_{4n-8}$ for the cyclic difulvalene systems (Fig. 2). It is seen that λ_{max} values for molecules 2 and 5 are definitely larger than the critical value, while those for molecules 1, 3, 4, and 6 are smaller than the critical value, showing a trend of increase with n. Since all of the eigenvectors D_{max} corresponding to λ_{max} are found to be of b_{3g} symmetry, molecules 2 and 5 are predicted to undergo the second-order Jahn-Teller distortion from D_{2h} to C_{2h}, whereas molecules 1, 3, 4, and 6 undergo no symmetry reduction. The bond distortion is predicted from the pattern of the normalized components of the eigenvector D_{max} shown in Fig. 2. It is found that the type of distortion is bond-length alternation in the peripheral carbon skeleton. It is noted that in spite of being 4n π-electron systems the cyclic difulvalene systems examined are classified into two groups, one in which there occurs a second-order double-bond fixation and the other in which there exists only a moderate first-order double-bond fixation.

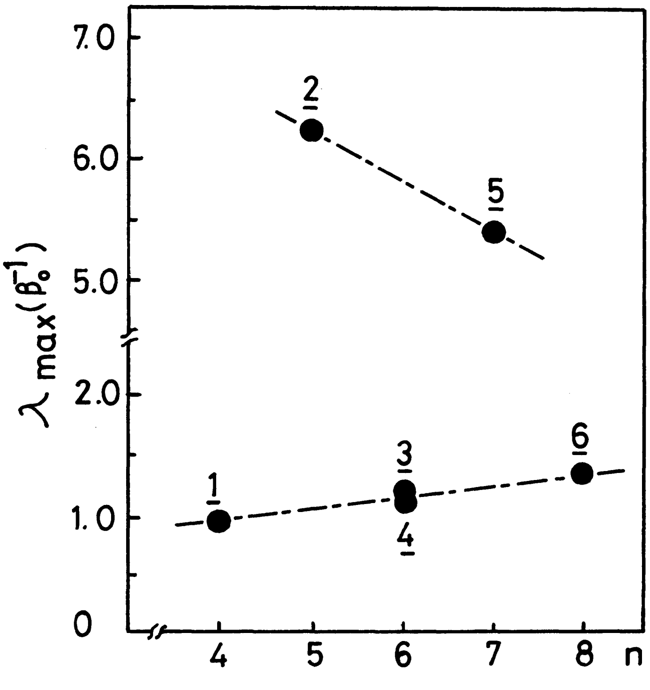


Fig. 1. The dependence of the largest eigenvalues λ_{max} on the number n of the $C_{4n}H_{4n-8}$ systems.

We have further examined the stable molecular shapes of molecules 7 and 8, both of which are formed of two different fulvalene molecules. The λ_{max} values for molecules 7 and 8 are calculated to be 3.65 and 1.15 β_0^{-1}, respectively. It is therefore expected that molecule 7 will lose its original full symmetry (C_{2v}) and has

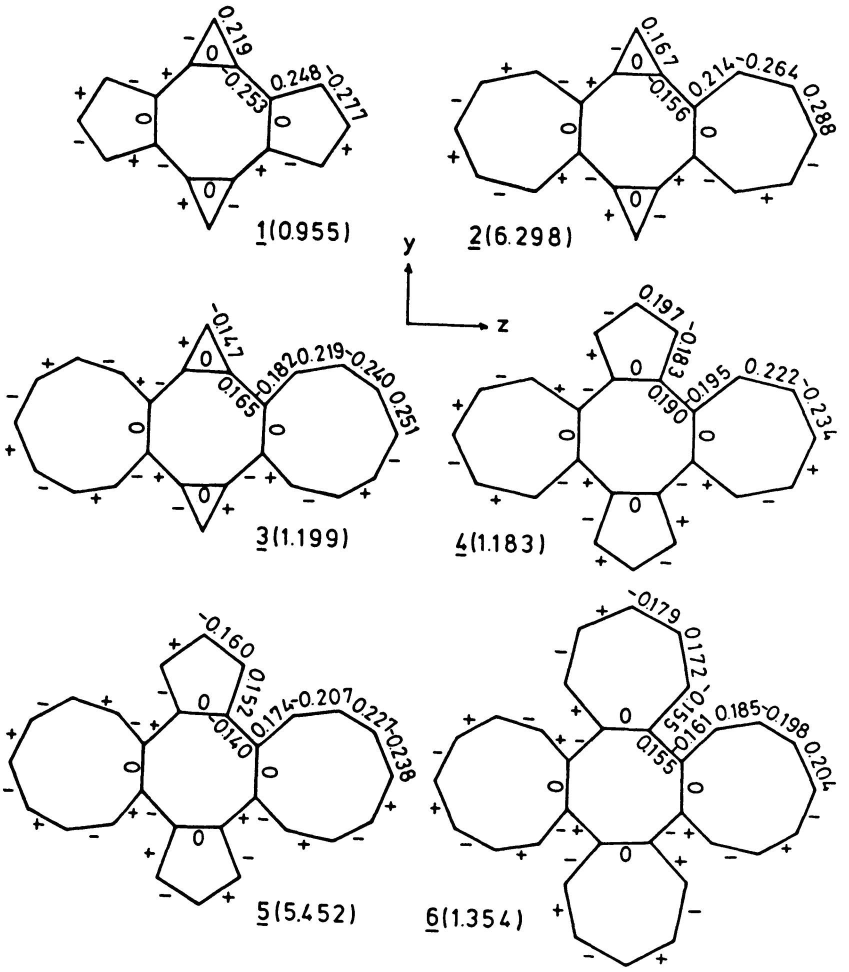
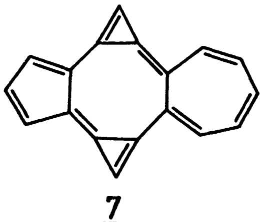


Fig. 2. The largest eigenvalues λ_{max} (in parentheses) and the corresponding eigenvectors D_{max} for the systems examined and the choice of molecular axes.

a bond alternating structure with the C_s symmetry, while molecule 8 retains its original full symmetry (C_{2v}).



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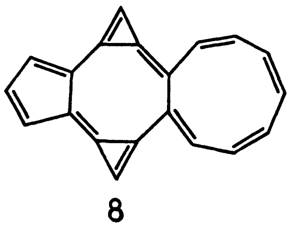

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On the basis of the results obtained above, we can derive a simple rule for predicting the stable molecular shapes of the cyclic difulvalene systems, which can be simply stated: if a Kekule' structure for a molecule contains at least one component corresponding to triaheptafulvalene or pentanonafulvalene, the molecule has a double-bond fixation and will lose, in general, its original full symmetry.

The justification and extension of the rule as well as the application to the other cyclic difulvalene systems, in which a Kekule' structure contains a component, such as triafulvalene, pentafulvalene, or heptafulvalene, will be discussed in detail in the forthcoming paper.

Further, we briefly refer to the chemical properties of these cyclic difulvalene systems. A conjugated system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation.1-4) On the basis of this criterion, molecules 2 and 5 would behave as polyolefins, reflecting the properties of the parent fulvalene molecules. In contrast with them, molecules 1, 3, 4, and 6 are expected to exhibit aromatic characters. As to molecule 1, this is in good agreement with the available experimental information.5)

Finally, it is added that since the theory of double-bond fixation is based on the second-order perturbation theory, it gives only the type of the most favorable bond distortion. In order to obtain information on the actual magnitude of distortion or the equilibrium C-C bond lengths at which the nuclei of the molecule will settle, we have to perform the SCF MO calculations.6,7) Detailes of these results will be reported elsewhere together with those obtained by the symmetry rule.8,9)

References

1) G. Binsch, E. Heilbronner, and J. N. Murrell, Mol. Phys., 11, 305 (1966).

2) G. Binsch and E. Heilbronner, Tetrahedron, 24, 1215 (1968).

3) G. Binsch, I. Tamir, and D. Hill, J. Am. Chem. Soc., 91, 2466 (1969).

4) G. Binsch and I. Tamir, J. Am. Chem. Soc., 91, 2490 (1969).

5) S. Yoneda, S. Kida, K. Shibata, and Z. Yoshida, 12th Symposium on Nonbenzenoid Aromatic Compounds (Abst.), p. 29 (1979).

6) T. Nakajima and A. Toyota, Chem. Phys. Lett., 3, 272 (1969).

7) H. Yamaguchi, T. Nakajima, and T. L. Kunii, Theor. Chim. Acta (Berl.), 12, 347 (1969).

8) T. Nakajima, A. Toyota, and S. Fujii, Bull. Chem. Soc. Jpn., 45, 1022 (1972).

9) A. Toyota and T. Nakajima, to be published.

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