Double-bond Fixation and Aromatic Stability in Cyclic Difulvalene Systems

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On the basis of the second-order Jahn–Teller theory and of the semiempirical Pariser–Parr–Pople type SCF-MO method, we have examined the energetically most favourable ground-state geometrical structures with respect to C–C bond lengths of cyclic difulvalene systems. The cyclic difulvalene systems examined are classified into two groups, one in which a molecule undergoes symmetry reduction from the fully symmetrical nuclear arrangement and the other in which a molecule suffers no symmetry reduction, suggesting that the former behaves as a polyolefin and the other as a typical aromatic hydrocarbon. This marked difference is explained in terms of a polarization stability by cyclization.

Thus far the electronic properties of the fulvalene systems, especially of calicene and sesquifulvalene, have been the subjects of both theoretical and experimental studies.[1-16]

In recent years, the cyclic dicalicene having $4 \times 4\ \pi$ electrons [(3) in Figure 1] and its derivatives have successfully been prepared and their spectroscopic and chemical properties have been examined by Yoneda and his co-workers.[17,18] In spite of being the nonalternant hydrocarbon containing highly strained three-membered rings, the ^1H and ^{13}C n.m.r. spectra reveal that molecule (3) is that of a stable aromatic hydrocarbon. In addition, the *X*-ray study indicates that the molecule has no double-bond fixation in the peripheral carbon skeleton.

Since such experimental facts show a sharp contrast with those obtained for calicene derivatives [9-12] that have strongly localized single and double bonds, it is of great interest to investigate whether or not the relaxation of double-bond fixation is, in fact, a common phenomenon in the cyclic difulvalene systems. In connection with charge separation in the fulvalene systems, it is also intriguing to examine the effect of cyclization on the charge distributions in the cyclic difulvalene systems (Figure 1).

In this paper, we study the above problems by examining the energetically most favourable ground-state geometrical structures with respect to C–C bond lengths of the cyclic difulvalene systems, using the semiempirical Pariser–Parr–Pople (PPP) type SCF-MO approximation [19,20] in conjunction with the variable-bond-length technique.[16]

It will be shown that the origin of a decisive relaxation of the double-bond fixation for certain cyclic difulvalenes which undergo no symmetry reduction is readily ascribed to the occurrence of a large amount of intramolecular charge transfer by cyclization. On the other hand, the appearance of a strong bond-length alternation for other cyclic difulvalenes is shown to be due to the effect brought about by the second-order Jahn–Teller bond distortion.[21] This marked difference between the two groups is explained in terms of a polarization or an anti-polarization stability by cyclization.

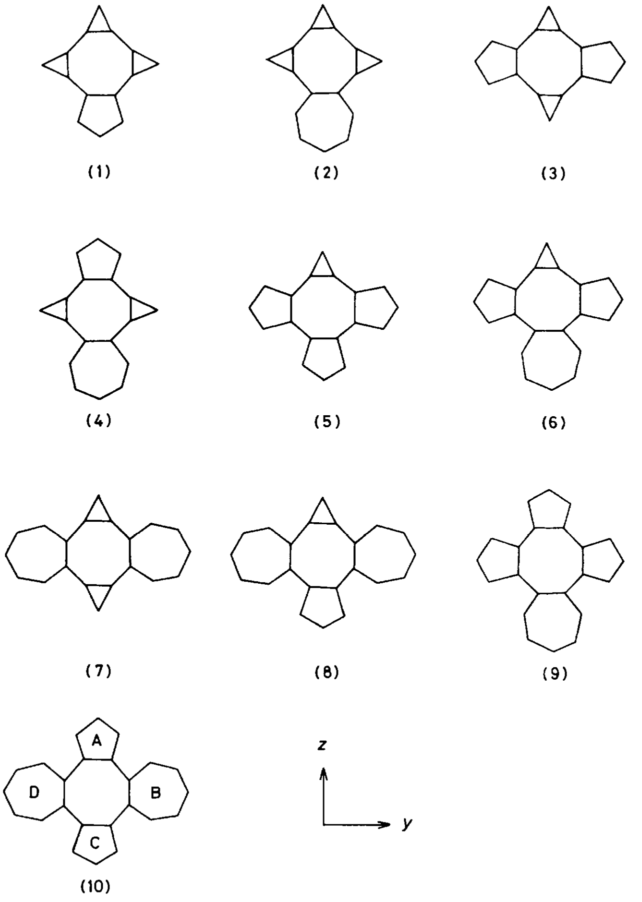


Figure 1. Carbon skeletons of the cyclic difulvalene systems and choice of molecular axis. Rings in each molecule are labelled as A, B, C, and D, as illustrated in molecule (10)

Theory

The Symmetry Rule.—Since the symmetry rule [22-24] for predicting the energetically most favourable molecular-symmetry groups of conjugated hydrocarbons has been well discussed in previous papers, we give here only the outline of the theory.[21,25-29] Let us start by assuming a fully symmetrical nuclear arrangement as the unperturbed configuration for a conjugated molecule. We further assume that in the unperturbed nuclear configuration all the symmetrical bond distortions have been taken into account. The unperturbed electronic wavefunctions ψ_0, $\psi_1 \ldots \psi_n \ldots$ and the corresponding eigenvalues E_0, $E_1 \ldots E_n \ldots$ are assumed to be known. If we distort the nuclei from the symmetrical nuclear arrangement by means of the *i*th C–C stretching normal mode Q_i, the energy of the ground state after nuclear deformation can be written as equation (1), where *k* and *V* represent the force constant for C–C σ-bond and the one-electron operator for nuclear-electron potential energy, respectively.

$$E(Q_l) = E_0 + \frac{1}{2}\left\{k - 2\sum_n{}' \frac{|\langle\psi_n|(\partial V/\partial Q_l)_0|\psi_0\rangle|^2}{(E_n - E_0)}\right\}Q_l^2 \qquad (1)$$

According to equation (1), the force constant for the normal vibration Q_l can be identified with the term in the braces and can be negative if the second term, *i.e.* the sum over excited states, is larger than k. If the force constant is negative, the energy should be lowered by the bond distortion Q_l, and a second-order Jahn–Teller bond distortion[21] from the fully symmetrical nuclear arrangement would occur spontaneously.

The symmetry rule for predicting the most favourable molecular shape of the ground state is stated as follows.[22-24] The symmetry of the bond distortion with the smallest force constant is identical with that of the direct product $\Gamma(\psi_0) \times \Gamma(\psi_1)$, where ψ_0 and ψ_1 are the wavefunctions for the ground and the first excited singlet state, respectively. If the energy gap $E_1 - E_0$ calculated by assuming the fully symmetrical nuclear arrangement is smaller than the critical value, *ca.* 1.2 eV, the molecule should be distorted into a less symmetrical nuclear configuration. Of the several types of bond distortion belonging to the same symmetry, the most favourable one is predicted from the distribution of the two-centre components of transition density ρ_{01} over the molecular skeleton. When the first excited singlet state is represented by a one-electron transition between molecular orbitals φ_i and φ_j, ρ_{01} is given by $\sqrt{2}\,\varphi_i\varphi_j$.

Computational Method.—In order to obtain the energy gap $E_1 - E_0$ for the fully symmetrical nuclear arrangement of a molecule, we calculate the geometrical structure by using the PPP-type SCF-MO method in conjunction with the variable bond-length technique.[16,19,20] For the excited state, we perform the CI calculations including 64 singly excited configurations. In calculating the lengths for the bonds in the three-membered ring, for the bonds joining the three-membered ring and the five- or seven-membered ring, we use the bond order–bond length relationship proposed by Yamaguchi *et al.*[16]

Since the symmetry rule is based on the second-order perturbation theory, it gives only the type of the most favourable bond distortion. In order to examine the possibility of symmetry reduction and, if it occurs, in order to obtain information about the equilibrium bond lengths at which the nuclei of the molecule will settle, we perform the PPP type SCF-MO calculations by taking into account,[30] as a starting geometry, a distorted structure suggested by the symmetry rule. When self-consistency is achieved at the geometrical structure with a lower symmetry, it is, in principle, lower in energy than the fully symmetrical nuclear arrangement. We define the stabilization energy as the difference in total energy between the nuclear arrangements with the full symmetry and a reduced symmetry. The total energy is assumed to be the sum of the π-bond and σ-bond energies, the latter being calculated by assuming the harmonic oscillator model with the force constant equal to 714 kcal mol^{-1} A^{-2} for σ-bond compression.[31]

Results and Discussion

Ground-state Molecular-symmetry Groups.—The energy gaps and the symmetries of the ground and the first excited singlet states of the cyclic difulvalene systems obtained by assuming the fully symmetrical nuclear arrangements are summarized in Table 1. On the basis of the symmetry rule and Table 1, we now discuss the problem of the molecular-symmetry reduction.

Table 1. Energy gaps and symmetries of the ground and first excited singlet states of the cyclic difulvalene systems

Molecule (point group and ground-state symmetry)	First excited singlet state Energy gap ($E_1 - E_0$) (eV)	Symmetry
(1) (C_{2v}, A_1)	1.48	B_2
(2) (C_{2v}, B_2 [a])	0.30	A_1
(3) (D_{2h}, A_g)	2.13	B_{3g}
(4) (C_{2v}, A_1)	0.58	B_2
(5) (C_{2v}, A_1)	0.82	B_2
(6) (C_{2v}, A_1)	1.71	B_2
(7) (D_{2h}, B_{3g} [a])	0.22	A_g
(8) (C_{2v}, A_1)	1.04	B_2
(9) (C_{2v}, A_1)	0.76	B_2
(10) (D_{2h}, A_g)	1.44	B_{3g}

[a] The symmetry of the lowest singlet state. If we take into account the doubly excited configuration corresponding to the orbital jumps from the HOMO to the next LUMO,[32] we believe that the lowest singlet state turns out to be the closed-shell singlet state with the A_1 (A_g) symmetry.

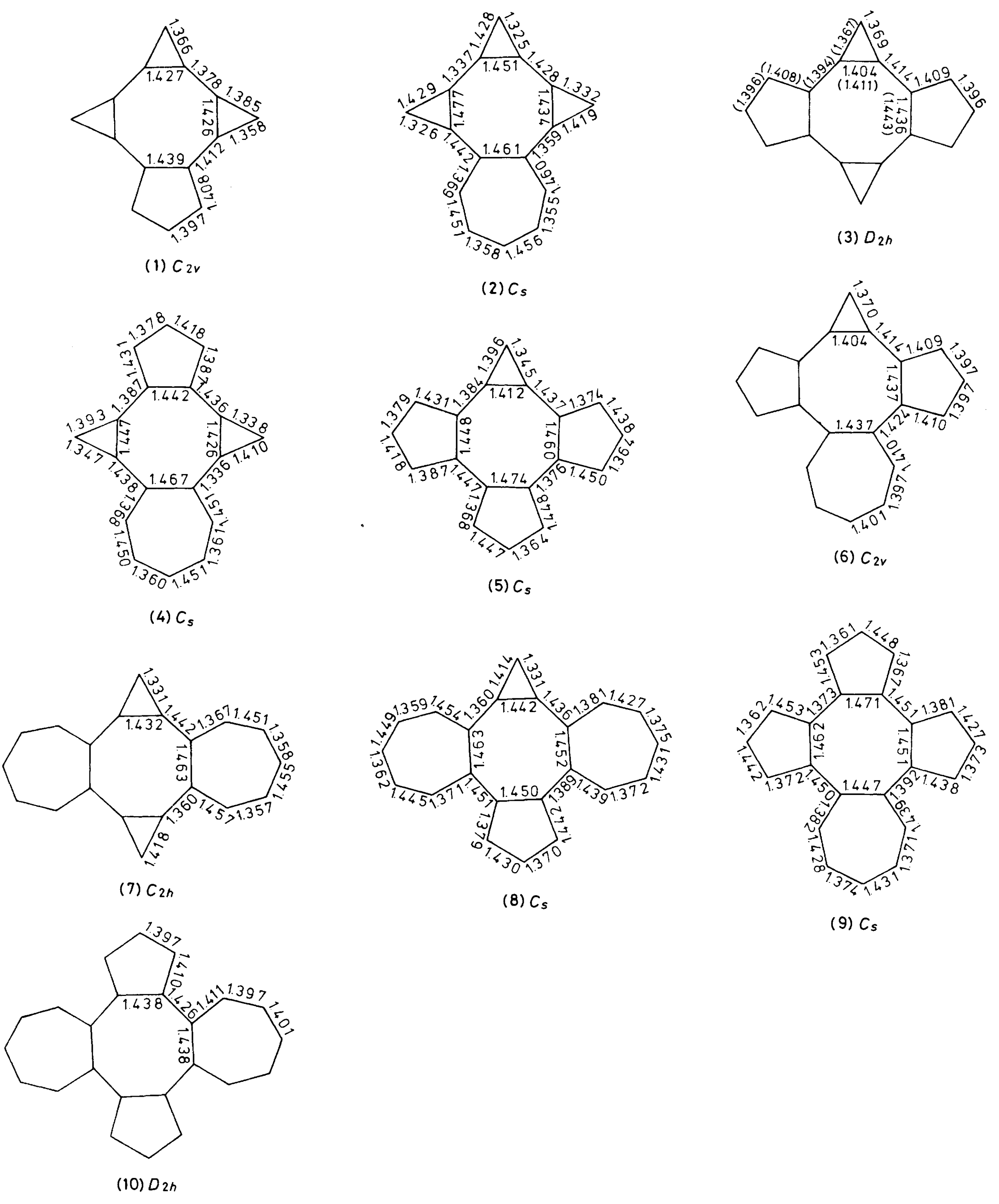
(i) *Molecules* (1), (3), (6), *and* (10). The energy gaps $E_1 - E_0$ for these molecules are all larger than the critical value (*ca.* 1.2 eV) for symmetry reduction, irrespective of whether they are the $4n$ or $4n + 2$ π-electron systems. Hence, these molecules are expected to undergo no symmetry reduction, retaining their original fully symmetrical nuclear arrangements.[33]

(ii) *Molecules* (2) *and* (7). The ground state of a molecule having an even number of electrons is usually a closed-shell singlet state. However, it turns out that in the symmetrical C_{2v} nuclear arrangement of molecule (2) the ground state is an open-shell $^3B_2$ state corresponding to a single MO transition from the HOMO to the LUMO and the lowest singlet is a $^1B_2$ state arising from the same occupancy of orbitals. The $^1B_2$ state is predicted to lie only 0.15 eV above the $^3B_2$ state. Further, as is shown in Table 1, the first excited $^1A_1$ state, which corresponds to the closed-shell structure, is nearly degenerate with the lowest singlet state, the energy separation between the two states being 0.30 eV. On the basis of the symmetry rule, we can expect that the nuclear arrangement of the lowest singlet state undergoes a strong second-order Jahn–Teller distortion from the C_{2v} to the C_s nuclear arrangement by the vibronic interaction between the two singlet states through the nuclear displacement of b_2 symmetry. Our question in such a case is whether the energy of the lowest singlet state may be lowered by the interaction to such an extent that it lies below the symmetric (C_{2v}) triplet ground state. As for molecule (7), the situation is quite similar to the case of molecule (2) and molecule (7) is also expected to lose its original full molecular-symmetry group (D_{2h}) and have a bond-alternating structure with the C_{2h} symmetry.[33]

(iii) *Molecules* (4), (5), (8), *and* (9). For these molecules which have ($4n + 2$) π electrons and the closed-shell ground states, the energy gaps are small as compared with the critical value for symmetry reduction. Since the most favourable bond distortion is of b_2 symmetry, all the molecules are predicted to undergo the symmetry reduction from C_{2v} to C_s. Inspection of transition density reveals that the type of the most favourable nuclear displacement is the bond-length alternation in the carbon skeleton.

In what follows, we show the actual geometrical structures of these cyclic difulvalenes obtained by using the PPP type SCF-MO method.

Ground-state Geometrical Structures and Properties.—For



(1) C_{2v} (2) C_s (3) D_{2h} (4) C_s (5) C_s (6) C_{2v} (7) C_{2h} (8) C_s (9) C_s (10) D_{2h}

Figure 2. Predicted molecular-symmetry groups and bond lengths (in Å) of the cyclic difulvalene systems. For molecule (3), the bond lengths in the parentheses refer to the experimental values [18]

molecules (1), (3), (6), and (10), the iterative procedure for self-consistency, started at a given asymmetrical bond distortion, has converged into the unique set of C–C bond lengths of the fully symmetrical nuclear arrangement. On the other hand, for other molecules self-consistency has been achieved at a set of C–C bond lengths corresponding to a lower symmetrical nuclear arrangement. This indicates that the former undergoes no symmetry reduction, whereas the latter suffers the second-order Jahn–Teller effect. Without exception, the results are in complete agreement with those predicted by the symmetry rule. It should be noted that at the reduced C_s and C_{2h} nuclear arrangements for molecules (2) and (7), respectively, the ground

Table 2. Charges of rings A, B, C, and D of the cyclic difulvalene systems

Molecule (point group)	Ring charge [a]			
	A	B	C	D
(1) (C_{2v})	0.015	0.260	−0.535	0.260
(2) (C_s)	0.007	0.156	−0.213	0.050
	(0.083)	(0.103)	(−0.288)	(0.103)
(3) (D_{2h})	0.480	−0.480	0.480	−0.480
(4) (C_s)	−0.453	0.218	−0.190	0.425
	(−0.518)	(0.327)	(−0.137)	(0.327)
(5) (C_s)	0.430	−0.067	0.024	−0.387
	(0.498)	(−0.244)	(−0.010)	(−0.244)
(6) (C_{2v})	0.477	−0.454	0.430	−0.454
(7) (C_{2h})	0.190	−0.190	0.190	−0.190
	(0.151)	(−0.151)	(0.151)	(−0.151)
(8) (C_s)	0.151	0.268	−0.308	−0.111
	(0.167)	(0.151)	(−0.469)	(0.151)
(9) (C_s)	0.013	−0.301	0.334	−0.046
	(−0.024)	(−0.227)	(0.478)	(−0.227)
(10) (D_{2h})	−0.422	0.422	−0.422	0.422

[a] The values in the parentheses refer to ring charges for the unstable, fully symmetrical nuclear arrangement.

state turns out to be the usual closed-shell singlet state lower in energy than the symmetric triplet ground state.

Here, it should be remembered that for calicene and sesquifulvalene the net ring charges calculated within the semi-empirical π-electron approximation are ±0.424(e) and ±0.313, respectively.[16] As to triaheptafulvalene, they are ±0.187, the three-membered ring being charged positively. Since aromatic stabilities in such conjugated systems are closely related to the amount of charge transfer, we discuss the properties of the cyclic difulvalenes in view of the charge separation.

The calculated C–C bond lengths (in Å units) for the most favourable geometrical structures of the cyclic difulvalenes are shown in Figure 2. The associated charges of rings A, B, C, and D, labelled as shown in Figure 1, are given in Table 2.

(i) *Molecules* (1), (3), (6), *and* (10). In molecule (1), a negative charge flows into the five-membered ring from the nearest neighbouring three-membered rings (B and D). It is noted that of the cyclic difulvalenes examined, the negative charge of −0.535 on the five-membered ring is the largest and the C–C bond lengths of this ring are considerably smoothed out, as those of benzene. Of particular note is cyclic dicalicene (3), which suffers no symmetry reduction. In the stable D_{2h} nuclear arrangement, the amount of charge transfer from the three-membered ring to the five-membered one is increased as compared with that of calicene, and the C–C bond lengths of the five-membered rings are almost the same as those of benzene. The predicted bond lengths shown in Figure 2 are in good quantitative agreement with the *X*-ray data.[18] For molecule (6), the charges of each ring, especially of the seven-membered one, are large, to an appreciable extent, as compared with those of the component fulvalene molecules. The carbon atoms of the three- and seven-membered rings have a positive charge and, interestingly, the associated ring charge is larger in the former than in the latter, showing a similar trend of electron-releasing powers of the three- and seven-membered rings in triaheptafulvalene. The C–C bonds of the five- and seven-membered rings have been markedly smoothed out in length, as those of benzene. As to molecule (10), the situation is quite similar to the case of molecule (3): the increment of ring charges by cyclization from those of the free sesquifulvalene amounts to *ca.* ±0.11, and the peripheral bond lengths are nearly equalized.

For the above cyclic difulvalenes, since the charge separation is increased by cyclization, the origin of a striking relaxation of the double-bond fixation can be ascribed to the occurrence of a relatively large intramolecular charge transfer. In this sense, these molecules are said to have a pronounced polarization stability by cyclization, suggesting that they belong to novel non-benzenoid aromatic hydrocarbons having a great aromatic stability. As to cyclic dicalicene (3), this is in good agreement with the experimental facts.[17,18]

(ii) *Molecules* (2) *and* (7). For molecules (2) and (7), the stabilization energies due to the symmetry reduction are calculated to be 29.6 and 8.7 kcal mol^{-1}, respectively. As to molecule (2), the second-order Jahn–Teller effect has brought about a strong bond-alternating structure with the C_s symmetry. The examination of the distribution of the peripheral C–C bond lengths reveals that molecule (2) consists of the triafulvalene- and triaheptafulvalene-like skeletons. Similarly, the stable nuclear arrangement (C_{2h}) of molecule (7) is considered to consist of the two triaheptafulvalene-like skeletons. From the amounts of charge transfer shown in Table 2, it is seen that in a cyclic difulvalene, which contains only the rings having the so-called electron-releasing power, the charge polarization is effectively precluded. For this reason, both of the molecules are predicted to have little aromatic stability.

(iii) *Molecules* (4), (5), (8), *and* (9). The stabilization energies which favour the lower-symmetry nuclear arrangements for molecules (4), (5), (8), and (9) are calculated to be 9.7, 5.5, 8.5, and 9.0 kcal mol^{-1}, respectively. From the distributions of C–C bond lengths shown in Figure 2, it is readily found that these cyclic difulvalenes are regarded as the perturbed systems consisting of two fulvalene molecules. As to molecule (5), for example, the stable nuclear arrangement (C_s) is composed of two distinguishable parts, one the pentafulvalene-like skeleton having less charge separation and the other the calicene-like skeleton polarized to the same extent as in the free molecule.

It is remarked that the variation in charge on each ring due to the second-order Jahn–Teller effect takes place mostly in the direction opposite to that of the so-called Hückel ($4n + 2$) rule. As for molecule (4), the molecular-symmetry reduction from C_{2v} to C_s results in decreases in negative and positive charges of the five-membered (A) and the three-membered (B) ring, respectively, and an increase in negative charge of the seven-membered (C) ring. For the other cyclic difulvalenes, it is seen that the second-order Jahn–Teller effect brings about similar changes in ring charge on the whole. In this sense, these molecules are said to suffer an anti-polarization stability by cyclization and are expected to behave as polyolefins, undergoing addition reactions rather than substitution reactions.

Conclusions

From the above considerations, it has become apparent that the cyclic difulvalene systems examined are distinctly classified into two groups; one in which a molecule has a polarization stability, showing a sharp relaxation of the bond distortion inherent to the component fulvalene systems, the other in which a molecule suffers the second-order Jahn–Teller effect, having a strong double-bond fixation in the carbon skeleton.

In conclusion, cyclic difulvalenes (1), (3), (6), and (10) are said to be good candidates for the non-benzenoid aromatic hydrocarbons that form a new series of the stable cyclic difulvalene systems. On the other hand, the remaining members are predicted to reflect properties quite similar to those of the free fulvalene molecules.

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References

1 W. von E. Doering, 'Theoretical Organic Chemistry, Kekulé Symposium,' Butterworths, London, 1959, p. 35.

2 H. Prinzbach, H. Knofel, and E. Woischnik, 'Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity,' The Israel Academy of Sciences and Humanities, Jerusalem, 1971, p. 269 and references cited therein.

3 W. M. Jones and R. S. Pyron, *J. Am. Chem. Soc.*, 1965, **87**, 1608.

4 A. S. Kende and P. T. Izzo, *J. Am. Chem. Soc.*, 1965, **87**, 1609, 4162.

5 M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Lett.*, 1965, 2967.

6 E. D. Bergmann and I. Agranat, *Chem. Commun.*, 1965, 512; *Tetrahedron*, 1966, **22**, 1275.

7 Y. Kitahara, I. Murata, M. Ueno, K. Sato, and H. Watanabe, *Chem. Commun.*, 1966, 180.

8 A. S. Kende, P. T. Izzo, and W. Fulmor, *Tetrahedron Lett.*, 1966, 3697.

9 I. Murata, M. Ueno, Y. Kitahara, and H. Watanabe, *Tetrahedron Lett.*, 1966, 1831.

10 A. S. Kende, P. T. Izzo, and P. T. McGregor, *J. Am. Chem. Soc.*, 1966, **88**, 3359.

11 H. Shimanouchi, T. Ashida, Y. Sasada, I. Murata, and Y. Kitahara, *Tetrahedron Lett.*, 1967, 61.

12 O. Kennard, D. G. Watson, J. K. Fawcett, K. A. Kerr, and C. Romers, *Tetrahedron Lett.*, 1967, 3885.

13 E. K. von Gustorf, M. C. Henry, and P. V. Kennedy, *Angew. Chem.*, 1967, **79**, 616.

14 G. Seitz, *Angew. Chem.*, 1969, **81**, 518.

15 M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, 1965, **21**, 3423.

16 H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, 1968, **12**, 349 and references cited therein.

17 S. Yoneda, S. Kida, K. Shibata, and Z. Yoshida, '12th Symposium on Nonbenzenoid Aromatic Compounds,' 1979, Abstracts, p. 29, Japan.

18 M. Shibata, S. Yoneda, Z. Yoshida, Y. Kai, K. Miki, and N. Kasai, '14th Symposium on Nonbenzenoid Aromatic Compounds,' 1981, Abstracts, pp. 138, 142, Japan.

19 R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 446.

20 J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1357.

21 H. A. Jahn and E. Teller, *Proc. R. Soc. London, Sect. A*, 1933, **161**, 220.

22 T. Nakajima, A. Toyota, and S. Fujii, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1022.

23 T. Nakajima, *Top. Curr. Chem.*, 1972, **32**, 1.

24 T. Nakajima, A. Toyota, and M. Kataoka, *J. Am. Chem. Soc.*, 1982, **104**, 5610.

25 R. F. Bader, *Mol. Phys.*, 1960, **3**, 137.

26 L. Salem, *Chem. Phys. Lett.*, 1969, **3**, 99.

27 R. G. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 1252, 4947.

28 L. S. Bartell, *J. Chem. Educ.*, 1969, **45**, 754.

29 A. Toyota and T. Nakajima, *Tetrahedron*, 1981, **37**, 2575 and references cited therein.

30 T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, 1969, **3**, 272.

31 L. C. Snyder, *J. Phys. Chem.*, 1962, **66**, 2299.

32 A. Toyota and T. Nakajima, *Theor. Chim. Acta*, 1979, **53**, 297.

33 A. Toyota and T. Nakajima, *Chem. Lett.*, 1982, 1049.

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