Studies of Reaction Mechanisms with All-valence Electron Semi-empirical SCF MO Theories. IX.1) The Role of Tetracyclo[4.2.0.0^{2,8}0^{5,7}]oct-3-ene on the Ground State Potential Energy Hypersurfaces of $(CH)_8$ Isomers

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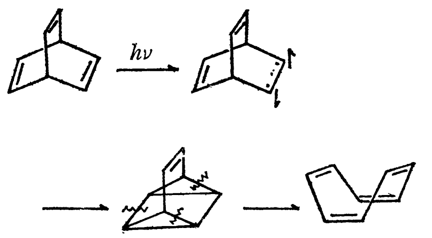
Tetracyclo[4.2.0.0^{2,8}0^{5,7}]oct-3-ene (**1**) is estimated by a MINDO MO calculation to be moderately strained. Interaction between the ethylenic π orbital and the Walsh orbitals of the two cyclopropane rings is extensive in the ground state structure of **1**. The third highest occupied MO is an out-of-phase combination of the ethylenic $2p\pi$ AO's on C_3 and C_4, while the corresponding in-phase combination appears in the lower unoccupied MO's. The interconversion between **1** and bicyclo[4.2.0]octa-2,4,7-triene (**2**) is a typical symmetry-allowed reaction as revealed by a smooth change in bond indices along the reaction coordinates. The isomerization of substituted cyclooctatetraenes *via* **1** and **2** (Eq. (2)) is predicted to be possible at elevated temperatures. The symmetry-allowed degenerate valence isomerization of **1** (Eq. (3)) is energetically less favorable due to skeletal constraint.

While compounds with the tetracyclo[4.2.0.0^{2,8}0^{5,7}]-oct-3-ene structure have never been prepared, the parent hydrocarbon **1** has often been quoted as a possible intermediate in many thermal as well as photochemical interconversions between other $(CH)_8$ isomers. One of the earliest suggestions was that **1** was the intermediate in the singlet excited state reaction of barrelene to give cyclooctatetraene (Eq. (1)).2) Recently Paquette *et al.* found evidence that **1′** was an intermediate in the thermal isomerization between 1,2- and 1,4-disubstituted cyclooctatetraenes (Eq. (2)).3)



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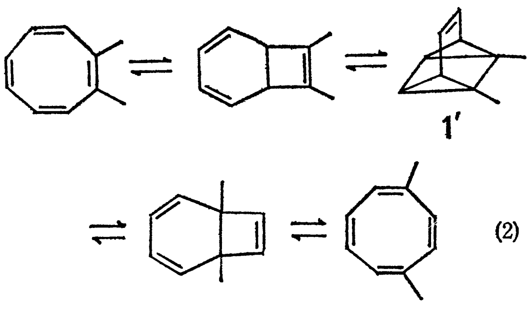
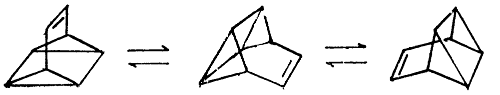


(2)

We have examined the electronic structure of **1** and the ground state potential energy hypersurfaces surrounding the minimum corresponding to structure **1** by MINDO/2 methods.4) Specifically the reaction coordinates for the intramolecular Diels-Alder reaction of bicyclo[4.2.0]octa-2,4,7-triene (**2**) leading to **1** (see Eq. (2)) have been determined. A degenerate valence isomerization of **1** as represented by Eq. (3) has also been examined.



(3)

Method of Calculation

Details of the procedure are nearly the same as reported in the preceding paper.1) Since no experimental data concerning the structure of the molecules studied here are available, the theoretical geometries of the ground states were sought by minimizing the total energies with respect to changes in all bond lengths and angles. It was only assumed that **1** and **2** have C_{2v} and C_s symmetry, respectively. Although a large number of nuclear configurations have to be considered in order to get information on the reaction paths, it would require tremendous effort to take all conceivable intermediate configurations into account. We have, therefore, made some simplifying assumptions to reduce the computational effort in finding the

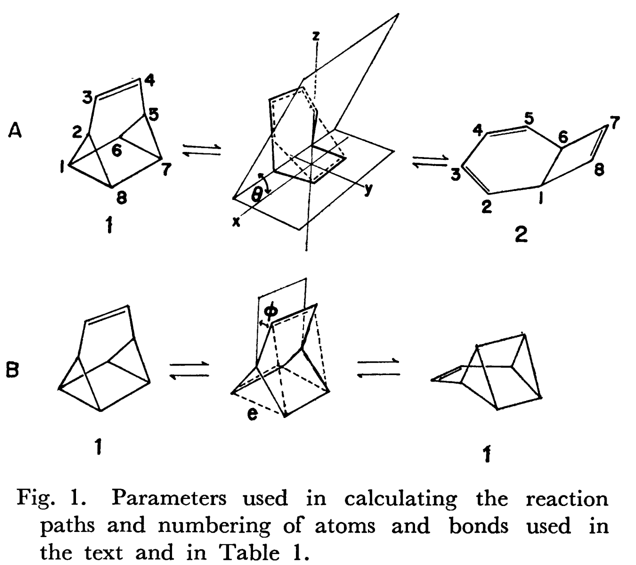


Fig. 1. Parameters used in calculating the reaction paths and numbering of atoms and bonds used in the text and in Table 1.
A: s is a smoothing parameter to describe a profile of **1** (**2**) in passing from **1** (**2**) into **2** (**1**) in the (retro) Diels-Alder reaction. All other geometrical parameters except θ are assumed to vary linearly with s from their values at the end points $s=0.0$ (=**1**) and $s=1.0$ (=**2**), respectively.
B: φ describe the inclination of C_2-C_3-C_4-C_5 plane towards C_7-C_8.

transition state geometries. A few parameters were chosen to describe the most relevant reaction coordinates. These parameters are detailed in Fig. 1. The eigenvalues and eigenfunctions were computed using a set of numerical values of these parameters, and the total energy was minimized by varying these parameters empirically to arrive at the transition state geometries.

An energy partitioning analysis was also made. The total energy (E) of a molecule can be expressed as a sum of one-center terms (E_A) and two-center terms (E_{AB}). The former sum was subdivided into one due to carbon atoms (E^C_A) and one due to hydrogen atoms (E^H_A). The two-center terms were divided into resonance (E^R_{AB}), exchange (E^X_{AB}), and electrostatic (E^S_{AB}) terms. Terms E_{AB} can also be divided into neighboring (E^N_{AB}) and non-neighboring (E^{NN}_{AB}) terms. The definition of each term and standard integrals representations in MINDO/2 formalism were given in the preceding paper.[1] A FORTRAN program was written for a HITAC 8700/8800 system at the Computer Centre of the University of Tokyo.

Results and Discussion

The Optimized Structure, Energy and Bond Parameters. Table 1 shows the equilibrium geometries, two-center energies, Wiberg bond indices, W_{AB},[5] and bond populations defined by taking into account the overlap, P^s_{AB}, defined in Eq. (5).

$$W_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu}^2 \tag{4}$$

$$P^s_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu} S_{\mu\nu} \tag{5}$$

The numerical values of W_{AB} are close to the conventional bond orders: 2 for double bonds and 1 for single bonds. The calculated geometries are generally in good agreement with those observed for many hydrocarbons possessing three or four-membered rings, except for slightly shorter C–C single bond lengths. Energies and ionization potentials obtained by using Koopmans' theorem are listed in Table 2.

The absolute values of the heats of formation obtained for **1** and **2** by MINDO/2 might be considerably lower than the actual values, since this method is reputed to underestimate the strain energies of small rings and compounds having a compact skeleton.[4,6] The MINDO/1 method is thought to be more acceptable in calculating the heats of formation.[6] Heats of formation of 12.3 and 54.5 kcal/mol were obtained for **1** and **2** by Franklin's group-equivalent method.[7] The strain energy of **1** was therefore estimated to be 65.6 kcal/mol (the heat of formation from the MINDO/1 method minus that from Franklin's). The strain energy value so obtained is around mid-value among those estimated for all the possible $(CH)_8$ isomers.

*Molecular Orbitals of **1**.* **1** may be regarded formally as being constructed of two cyclopropane rings, a cyclobutane ring and an ethylenic double bond. The ability of cyclopropanes to conjugate with an adjacent unsaturated center is well known. Structure **1** has a most desirable configuration for the cyclopropyl and vinyl moieties allowing them to interact adequately (*i.e.* bisected conformation). It is obvious from Table 1 that the C_2–C_3 (and C_4–C_5) bond has double bond character to some extent while the C_1–C_8 (and C_6–C_7) bond is slightly weakened as a result of the cyclopropyl-vinyl-cyclopropyl conjugation. A close inspection of the AO coefficients of the molecular orbitals reveals that the orbital interactions between the Walsh type orbitals of cyclopropane e′ and localized orbitals (π_{CC}, π_{CH_2}, σ_{CC}) of the ethylenic moiety and additional interactions between the orbitals resulting from the interactions described above are evident in the molecular orbital profile of **1**. This qualitative molecular orbital description can be obtained by considering in-phase and out-of-phase combinations between those localized orbitals with the same symmetry. Some higher occupied and lower unoccupied molecular orbitals are illustrated in Fig. 2. It is interesting to note that the third highest occupied

TABLE 1. GROUND STATE GEOMETRIES, TWO-CENTER ENERGY TERMS, BOND POPULATION, AND WIBERG'S BOND INDICES OF TETRACYCLO[4.2.0.0^{2,8}0^{5,7}]OCT-3-ENE **1** AND BICYCLO[4.2.0]OCTA-3,5,7-TRIENE **2**

		C_1–C_2	C_2–C_3	C_3–C_4	C_1–C_8	C_7–C_8	C_2–C_8
1	Bond length (Å)	1.50	1.47	1.36	1.51	1.49	1.50
	E^R_{AB} (eV)	−12.456	−15.091	−19.792	−10.794	−13.570	−12.456
	E^N_{AB} (eV)	−12.988	−15.728	−22.421	−11.572	−14.161	−12.988
	P^s_{AB}	0.6414	0.7591	1.0275	0.5833	0.6813	0.6414
	W_{AB}	0.9115	1.0066	1.8441	0.9586	0.9504	0.9115
2	Bond length (Å)	1.54	1.34	1.47	1.49	1.33	2.333
	E^R_{AB} (eV)	−14.368	−20.362	−15.135	−13.328	−20.004	−0.219
	E^N_{AB} (eV)	−14.971	−22.720	−15.841	−13.956	−22.437	−0.060
	P^s_{AB}	0.7269	1.0527	0.7650	0.6825	1.0423	0.0151
	W_{AB}	0.9752	1.8432	1.0279	0.9594	1.8949	0.0218

1: Cyclobutane-cyclopropane dihedral angle = 119.4°. **2**: Cyclohexadiene-cyclobutane dihedral angle = 103.1°.

TABLE 2. DISSECTED TOTAL ENERGIES, HEATS OF FORMATION AND IONIZATION POTENTIALS OF **1** AND **2**

	$\sum E_A$ (eV)	$\sum\sum E_{AB}$ (eV)	ΔH_f (kcal/mol)	I_p (eV)	ΔH_f (MINDO/1)
1	−904.341	−247.446	35.99	7.97	77.9
2	−905.876	−245.605	43.02	8.58	76.8

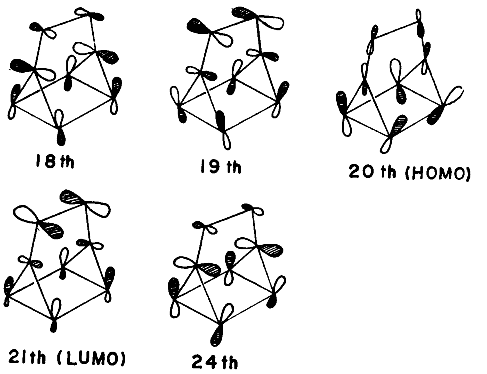


Fig. 2. Higher occupied and lower unoccupied molecular orbitals of **1**. The atomic orbital sizes present only approximately the magnitude of the relevant coefficients; their direction is similarly idealized.

molecular orbital is an out-of-phase combination of the ethylenic $2p\pi$ AO's on C_3 and C_4, while the corresponding in-phase combination appears among the lower unoccupied molecular orbitals.

*Potential Energy Surfaces and Reaction Paths for **1** and **2**.* By calculating a large number of nuclear configurations, the energies of their electronic ground states along the reaction paths was obtained as a function of θ and s. A two dimensional presentation of the energy (in units of the heat of formation) as a function of θ and s is shown in Fig. 3. The most probable reaction path for the interconversion of **1** and **2** is indicated by the dotted line. A clearer picture of this cross section of the potential energy surface is given in Fig. 4 together with the change of bond indices. A smooth change of the bond indices for the bonds, which are formed or broken as the reaction proceeds along the reaction coordinates, is characteristic of symmetry-allowed reactions. Symmetry-forbidden reactions show, in contrast, abrupt changes in bond index.[1] This can be easily understood in terms of the well-known orbital correlation diagram.[8] In the case of allowed reactions, no alternation of occupied and unoccupied orbitals occurs anywhere along the reaction paths. In other words, all the occupied orbitals of the reactant can be transformed into the occupied orbitals of the product with continous changes in their shapes. The smooth change of bond indices results from the continuous change of the corresponding AO coefficients of the occupied molecular orbitals. An abrupt change of bond index indicates that alternation of occupied and unoccupied levels takes place somewhere in the reaction path.[9]

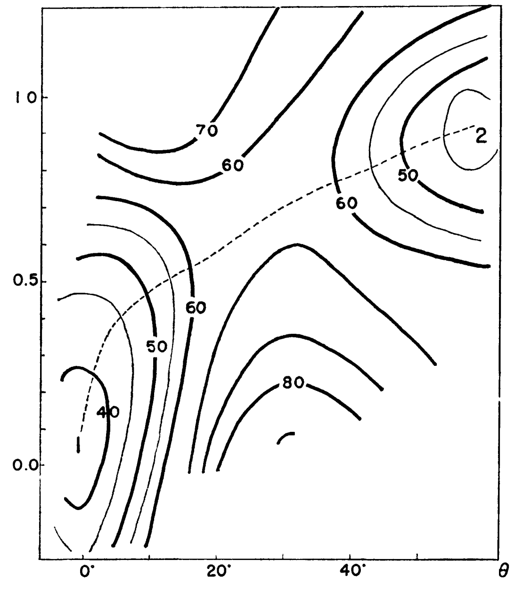


Fig. 3. The potential energy surface for the interconversion of **1** and **2**.

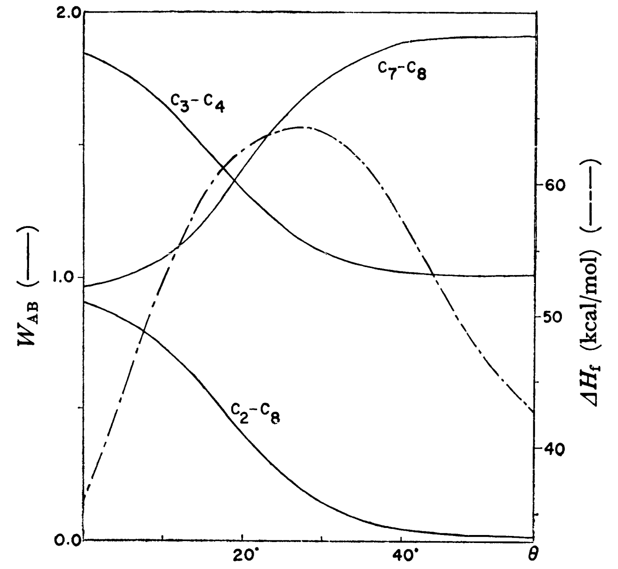


Fig. 4. The energy and the bond indices during the reaction of **1** and **2**.

Figure 5 shows the calculated geometry and (in parentheses) Wiberg's bond indices for the transition state of the reaction, **2** to **1**. Note that the bond indices are about 1.6 for bonds C_2–C_3 (and C_4–C_5) and C_1–C_8, 1.17 for C_3–C_4, and 0.2 for C_2–C_8 (and C_5–C_7). As shown in Table 3, the two-center energy terms E_{AB} for the transition state geometry are more in pararell with those of **2**. The dihedral angles 83° and 200° of the transition state structure correspond to 57° and 213° in **1** and 104° and 180° in **2**. Thus the configuration of the transition state is electronically similar to **2**, while it is similar to **1** in terms of skeletal displace-

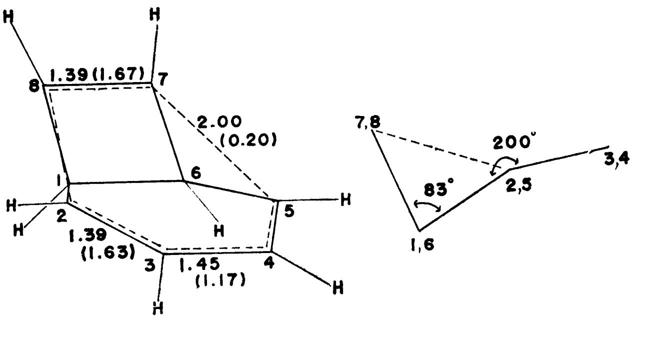


Fig. 5. The calculated geometry and the Wiberg's bond indices (in parentheses) for the transition state of the reaction of **2** to **1**.

Table 3. Neighboring two-center energies (eV) for the transition state **t**

C_1–C_2	C_2–C_3	C_3–C_4	C_1–C_8	C_7–C_8	C_2–C_8
−14.133	−20.969	−17.231	−13.453	−20.181	−2.464

Table 4. One-center and two-center terms in the activation energies (eV) for the reaction of **1** and **2**

	1	$\Delta E_{1\to t}$	**t**	$\Delta E_{2\to t}$	**2**
E_A^H	−84.1694	0.1038	−84.0656	0.2804	−84.3460
E_A^C	−820.1734	−1.9006	−822.0740	−0.5424	−821.5316
E_A	−904.3411	−1.7976	−906.1387	−0.2627	−905.8760
E_{AB}^N	−259.5897	4.4817	−255.1080	1.0959	−256.2039
E_{AB}^{NN}	12.1428	−1.4348	10.7080	0.1093	10.5987
E_{AB}	−247.4469	3.0469	−244.4000	1.2052	−245.6052
E	−1151.788	1.249	−1150.539	0.943	−1151.481

Table 5. Difference in electron populations on the carbon atoms and dissection of one-center contribution to the activation energy (eV) for rearrangement of **1** and **2**

	1		**2**	
	Δq_A	ΔE_A^C	Δq_A	ΔE_A^C
C_1 (C_6)	−0.077	0.5844	0.010	−0.0194
C_2 (C_5)	0.071	−1.0399	−0.020	0.0099
C_3 (C_4)	0.001	0.0567	0.021	−0.1449
C_8 (C_7)	0.013	−0.5515	0.009	−0.1168

ments. This is in accord with Hammond's postulate[11] and is also reasonable when the geometrical constraints imposed on the molecule in attaining the transition state are considered. It is noted that partial bonds C_2–C_8 (and C_5–C_7) are considerably weaker than those occurring in more facile reactions, *e.g.*, the Cope rearrangements of bridged homotropilidenes.[12] In the latter, the partial bonds in the transition states have a W_{AB} value of 0.4. The smaller W_{AB} value corresponds to the fact that the resonance energy of the aromatic transition state is not large in the present case.

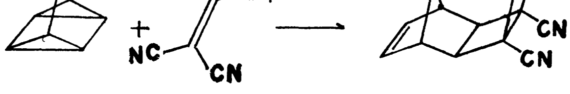
In order to fully characterize the electronic structure of the transition state, the total contribution to the activation energy of the one-center term (ΔE_A) and of the two-center terms (ΔE_{AB}) are given in Table 4. Those were obtained by taking differences between the corresponding values for the ground state and transition state.

The stabilizing contribution to the activation energy comes from changes (ΔE_A) in the one-center terms on passing from the reactants to the transition state. Further inspection reveals that the contribution of hydrogen atoms is very small and that the ΔE_A values are governed by changes in the one-center terms for carbons. The first and third columns of Table 5 show the change (Δq_A) in the electron population of atom A in passing from the reactant to the transition state. A positive Δq_A implies an increase in electron density and also in negative charge. It is seen that the variation of ΔE_A values correlates with those of Δq_A.[13] Note that the terms leading to smaller activation energy are those for the carbon atoms in the "aromatic ring" of the transition state, *e.g.*, atoms 2,3,4,5,7 and 8. In other words, the six carbons involved become effectively more electrogative in going from the reactants to the transition state and the transition state is correspondingly stabilized by a drift of negative charge to those six carbons from the rest of the molecule. On the contrary, the net change in the two-center neighboring terms ΔE_{AB}^N is relatively large with positive sign. Thus the relief of steric strain is not contributing much to the driving force of the reaction.

The activation energy for the valence isomerization of **1** to **2** is estimated at 29 kcal/mol by taking the difference in the energies of **1** and the transition state. Thus the isomerization of substituted cyclooctatetraene *via* **1** and **2** (see Eq. (2)) is predicted theoretically to be possible at elevated temperatures. It is also concluded that **1** is reasonably stable kinetically as well as thermodynamically (see Section A). The height of the potential energy barrier is large enough to give **1** a reasonable life-time at room temperature once prepared by an authentic route.

The reaction of **2** to **1** is favored in terms of orbital interaction owing to the proper geometry in the transition state. It would lead to activation energy of the same order as a typical Diels-Alder reaction of butadienes with ethylenes.[14]

*A Degenerate Valence Isomerization of **1** (Eq. (3)).* The reaction represented by Eq. (3) is a symmetry-allowed process. A precedent for the analogous [$_\pi 2_s + {}_\sigma 2_s + {}_\sigma 2_s$] reactions may be found in the bimolecular reaction of quadricyclene with TCNE:[15]



However, the ethylenic pπ orbitals are not suitably disposed for overlap with those of the cyclopropane ring in **1**. Inclination of the etheno bridge by 20° is attained only at the expense of 18 kcal/mol strain. The calculated energy values rise nearly in direct proportion to the increase in the values of φ and e. This is illustrated in Fig. 6. The ethylenic pπ orbitals cannot interact sufficiently with those of the cyclopropane

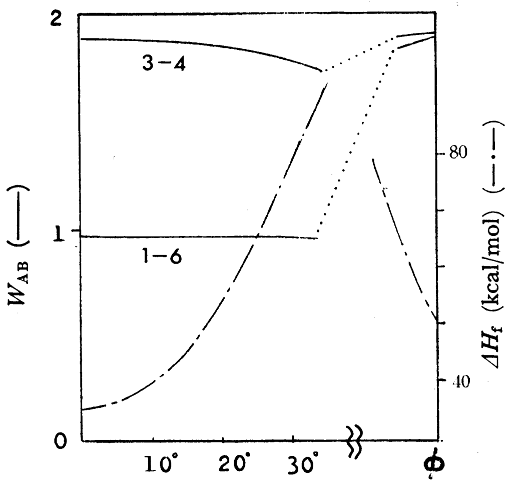


Fig. 6. The energy and the bond indices for the degenerate valence isomerization of **1**.

rings even when a large increase in energy due to strain is imposed. Therefore this formally symmetry-allowed valence isomerization will not take actually place even under severe conditions. Instead, the reaction coordinate represented by the elongation of the bond between C_1 and C_8 (C_6 and C_7), *e*, leads to an unexpected product, barrelene, across a high energy barrier demanded by symmetry considerations.[16]

References and Notes

1) Part VIII: H. Iwamura, H. Kihara, K. Morio, and T. L. Kunii, This Bulletin, **46**, 3248 (1973).

2) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

3) L. A. Paquette and R. E. Wingard, Jr., *ibid.*, **94**, 4398 (1972); L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 9274 (1972).

4) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

5) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

6) H. Iwamura, K. Morio, and T. L. Kunii, *Chem. Commun.*, **1971**, 1408.

7) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

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

9) We find it more advantageous to utilize this criterion to predict the allowedness or forbiddenness of concerted reactions of complex systems which have little or no elements of symmetry. While "snap-shot" calculations on a reaction path are often not sufficient to give acceptable activation energy values, they are adequate to show changes in bond index. The conclusion on the allowedness of the reaction under discussion must of necessity agree with the rule obtained more easily by application of the "Conservation of Orbital Symmetry."[8] We prefer the latter rule to be expressed in terms of the concept of the continuity of phase or nodal characteristic of orbitals, since the transition states of concerted reactions are not necessarily symmetric in general.[10]

10) J. W. McIver, Jr., *Accounts Chem. Res.*, **7**, 72 (1974).

11) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1953).

12) (a) H. Iwamura, K. Morio, and T. L. Kunii, This Bulletin, **45**, 841 (1972); (b) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **93**, 7201 (1971).

13) This can be readily understood as follows. When q_A increases (accumulation of electron density on atom A), the one-center core attraction energy increases, while the one-center Coulomb repulsion increases. Since both terms vary with q and in opposite directions, they almost cancel one another. The values ΔE_A for the individual carbon atoms pararell quite closely those for the one-center exchange term ΔE_A^x and the latter is correlated with Δq_A. Thus an increase in electron density on carbon A makes E_A^x more negative and consequently E_A more negative.[12b]

14) W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, **94**, 3833 (1973) and references cited therein.

15) C. D. Smith, *ibid.*, **88**, 4273 (1966).

16) Lastly, [1,5]sigmatropy in **2** which might be also one of the possible paths taking part in the substituent migration of cyclooctatetraene, has been shown to be a very energetically unfavorable path because of peculiar electronic and steric factors, *i. e.*, additional pπ orbitals and the length of the migrating carbon chain. Results on energetically unfavorable sigmatropic reactions will appear in a forthcoming paper.