A Theoretical Aspect on the Mechanism of Thermal Dimerization of Cyclooctatetraene[1]

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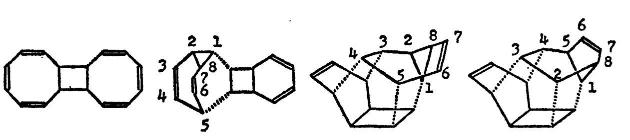
Thermal isomerization of cyclooctatetraene to semibullvalene **6** has been studied theoretically by the MINDO methods. The reaction is predicted to be exothermic by comparison of the calculated heats of formation and to be allowed as a concerted cyclization by constructing a complete MO correlatiom diagram. These findings together with the knowledge of thermal interconversion of cyclooctatetraene and bicyclo[4.2.0]octa-2,4,7-triene **5** suggest a tentative mechanism for thermal dimerization of cyclooctatetraene in which dimers **2**, **3**, and **4** are formed by coupling of the two isomers **5** and **6** of cyclooctatetraene.

It has been shown by Reppe *et al.*,[2] Jones,[3] and Schröder[4] that cyclooctatetraene forms several dimers on heating under various reaction conditions. A mixture of isomers **1**, mp 53°C, and **2**, mp 76°C, for example, is obtained by heating neat cyclooctatetraene at 100° in a sealed tube. Refluxing in *o*-dichlorobenzene and *N*,*N*-diethylaniline as the diluents results in formation of dimers **3**, mp 41.5°C, and **4**, mp 18.5°C, respectively. In spite of their fascinating structures and utility as the excellent intermediates for synthetic works highlighted by preparation of bullvalene,[5] little study has been done on the mechansim of formation of these dimers **1**∼**4**.

We notice by simple inspection of the molecular framework of these dimers that structural units of bicyclo[4.2.0]-octa-2,4,7-triene **5** and semibullvalene **6** are incorporated in **2**, **3** and **4** as shown in Chart 1, and are led to propose a hypothesis that these dimers could be formed by coupling of **5** and **6** which in turn might be produced by thermal valence isomerization of cyclooctatetraene. While thermal interconversion of cyclooctatetraene and **5** has been unambiguously established,[6] the thermal conversion of the former to **6** has been the subject of considerable controversy. Thus **6** can be formed by the acetone sensitized photolysis of cyclooctatetraene.[7] In the case of 1,3,5,7-tetramethylcyclooctatetraene, it is a pyrolytic condition of heating at 250°C for 15 hr rather than irradiation under various conditions which gives the corresponding semibullvalene.[7] Criegee and Askani reported efficient conversion at elevated temperature of octamethylcyclooctatetraene to the semibullvalene.[8]

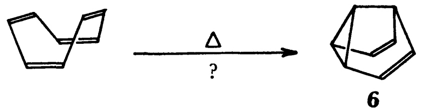


1 2 3 4

Chart 1. Molecular framework of dimers **1**∼**4** of cyclooctatetraene.

With all the findings mentioned above which are suggestive of a possible thermal transformation of cyclooctatetraene to **6**, experimental efforts to detect the latter in the gaseous and condensed phase pyrolysates of the former have proved to be totally unsuccessful. The products are usually styrene and dihydropentalene as well as benzene and acetylene.[9,10] Formal application of the orbital symmetry rule is also controversial; the same 1,3 ; 2,6 concerted multicyclization of cyclooctatetraene has been predicted as an allowed process in the ground state by a group of authors[11] while others reasoned the allowedness in the excited state.[12]

With no operational test available, we began theoretical approach to the problem and present here the analyses of the electronic structure of the molecular reorganization reaction represented by the equation;



6 (1)

Methods of Theoretical Calculation

The theoretical methods employed here are to construct a quantitative molecular orbitals correlation diagram between cyclooctatetraene and semibullvalene **6**, and to see if the occupied MO levels are correlated between the two species. Since the experimental data concerning the geometry of **6** are not available, the theoretical geometry has to be sought by minimizing the molecular energy with respect to all the bond lengths and angles in the molecule. Out of several versions of the semi-empirical SCF MO theories, the MINDO/2

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[1] Part IV of Studies of Reaction Mechanisms by All-valence-electron Semiempirical SCF MO Theories. For Part III, see H. Iwamura, K. Morio, and T. L. Kunii, This Bulletin, **45**, 841 (1972).

[2] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

[3] W. O. Jones, *J. Chem. Soc.*, **1953**, 2036; *Chem. Ind.* (London), **1955**, 16.

[4] G. Schröder, *Chem. Ber.*, **97**, 3131 (1964); *Angew. Chem.*, **78**, 117 (1966).

[5] G. Schröder, *ibid.*, **75**, 91, 722 (1963); W. von E. Doering and W. R. Roth, *ibid.*, **75**, 27 (1963); W. von E. Doering and W. R. Roth, *Chem. Ber.*, **97**, 3140 (1964).

[6] R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964); E. Vogel, H. Kiefer, and W. R. Roth, *ibid.*, **76**, 432 (1964).

[7] H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.* **90**, 4763 (1968); **92**, 2015 (1970).

[8] R. Criegee and R. Askani, *Angew. Chem.*, **80**, 531 (1968).

[9] M. Jones, Jr. and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968).

[10] H. E. Zimmerman and H. Iwamura, unpublished work.

[11] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, Inc., New York, N. Y. (1970) p. 81.

[12] K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971); R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971).

method[13] proposed by Dewar *et al.* is considered to reproduce the best geometry; the geometry which gave the minimum value of total energy by the MINDO/2 method was taken as the equilibrium geometry of the actual molecule. For the sake of consistency of comparison, the optimized geometry of cyclooctatetraene was also employed in the present study.

Correlation between the MO's of the species in either side of Eq. (1) is not straightforward because cyclooctatetraene and **6** lack any common symmetry element. It is, however, rendered possible to find the MO correlation by imposing in the reaction coordinate close to the end product the intermediate which corresponds to the transition state structure for the degenerate Cope rearrangement of **6**.[1] The C_2 symmetry operation is kept for the first half of the reaction, and the C_s symmetry element holds throughout the last half of the reaction coordinate (see Chart 2). Since the activation energy for the Cope rearrangement is known to be exceptionally low,[14] the above specification of the reaction as passing through this intermediate does not necessarily mean the restriction of the course of the reaction to a stepwise reaction; the intermediate and **6** are energetically too close to be separated on the entire potential energy surface interrelating the $(CH)_8$ isomers.

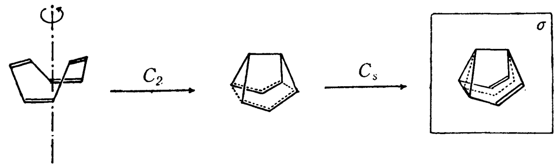

Chart 2. Symmetry elements along the reaction coordinates.

Estimation of heats of formation of cyclooctatetraene and **6** is considered to be illuminative as a measure of the exothermicity of the forward reaction of Eq. (1). The MINDO/2 approximation is reputed to underestimate heats of formation of the cyclopropane ring by about 10 kcal/mol.[13] In this respect, it is worthwhile to recourse to the original version (MINDO/1) of the approximation which, although artificially parametrized, gives best results of the theoretical heats of formation with the use of the standard bond lengths; even a seriously strained cyclobutene deviates only by 3.4 kcal/mol from the experimental value.[15] Therefore more reliable estimation of heats of formation of cyclooctatetraene and **6** was made by the MINDO/1 calculations in which the optimal lengths reached by the MINDO/2 approximations were replaced by the standard bond lengths of Baird and Dewar.[15] Heats of formation are by definition given by total bonding energies minus heats of formation of the free atoms in the molecule in the standard state. The total bonding energies are in turn calculated by subtracting the sum of isolated atom energies from the total valence shell energies.

Partitioning of the total valence shell energy (E) of a molecule into the terms due to one-center (E_A) and two-center (E_{AB}) was performed at the level of MINDO approximations analogously to the method elaborated by Gordon in the CNDO/2.[16]

$$E = \sum_{A} E_A + \sum_{A<B}\sum E_{AB} \tag{2}$$

The one-center terms can be expressed in terms of standard integrals as

$$\begin{aligned} E_A = {} & \sum_{\mu}^{A}\left[P_{\mu\mu}U_{\mu\mu} + \frac{1}{2}P_{\mu\mu}{}^2\langle\mu\mu|\mu\mu\rangle\right] \\ & + \sum^{A}\sum_{\nu\neq\mu}^{A}\left\{P_{\mu\mu}P_{\nu\nu}\left[\langle\mu\mu|\nu\nu\rangle - \frac{1}{2}\langle\mu\nu|\mu\nu\rangle\right]\right. \\ & \left. + P_{\mu\nu}{}^2\left[\frac{3}{2}\langle\mu\nu|\mu\nu\rangle - \frac{1}{2}\langle\mu\mu|\nu\nu\rangle\right]\right\} \end{aligned} \tag{3}$$

Full expression for the bi-centric terms (E_{AB}) are

$$E_{AB} = E_{AB}{}^{R} + E_{AB}{}^{X} + E_{AB}{}^{E} \tag{4}$$

where:

$$E_{AB}^{R} = 2\sum_{\mu}^{A}\sum_{\nu}^{B}P_{\mu\nu}\beta_{\mu\nu} \tag{5}$$

$$E_{AB}^{X} = -\frac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{B}P_{\mu\nu}{}^2\gamma_{AB} \tag{6}$$

$$E_{AB}^{E} = (P_AP_B - P_AZ_B - P_BZ_A)\gamma_{AB} + Z_AZ_BR_{AB}^{-1} \tag{7}$$

and E_{AB}^{R}, E_{AB}^{X}, and E_{AB}^{E} represent the resonance, exchange and electrostatic energies, respectively.

Results and Discussion

In Fig. 1 is summarized the MO correlation diagram obtained by application of symmetry operation and the noncrossing rule to the final MO's. We notice that the occupied MO levels are satisfactorily correlated between the starting cyclooctatetraene and product **6**.

The second clear-cut criterion obtained in the present study which supports the thermal route of Eq. (1) is, as shown in Table 1, that the heats of formation of cyclooctatetraene is higher than that of **6** by 13.4 kcal/mol; the forward reaction is predicted to be exothermic.

Turning now to the consideration of the driving force of the exothermic reaction, we note that the MO numbers 1, 8 and 20 of cyclooctatetraene are mostly responsible for lowering the electronic energy as the reaction proceeds. Nature of these levels is not obvious at a glance over the eigen vectors of the all-valence-electron SCF MO method, since separation of the σ and π character of a given MO is not clear. In this respect, it is instructive to go back to the correlation diagram constructed on the π-orbital approximation. Starting from cyclooctatetraene in which the occupied levels are made of four ethylene groups weakly overlapped through σ-bonds, we end up, as illustrated in Fig. 2, with two σ- and two π-orbitals of **6** with the aid of the bonding levels of two interacting allylic orbitals of the intermediate. In reality all

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13) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

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

15) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969).

16) M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

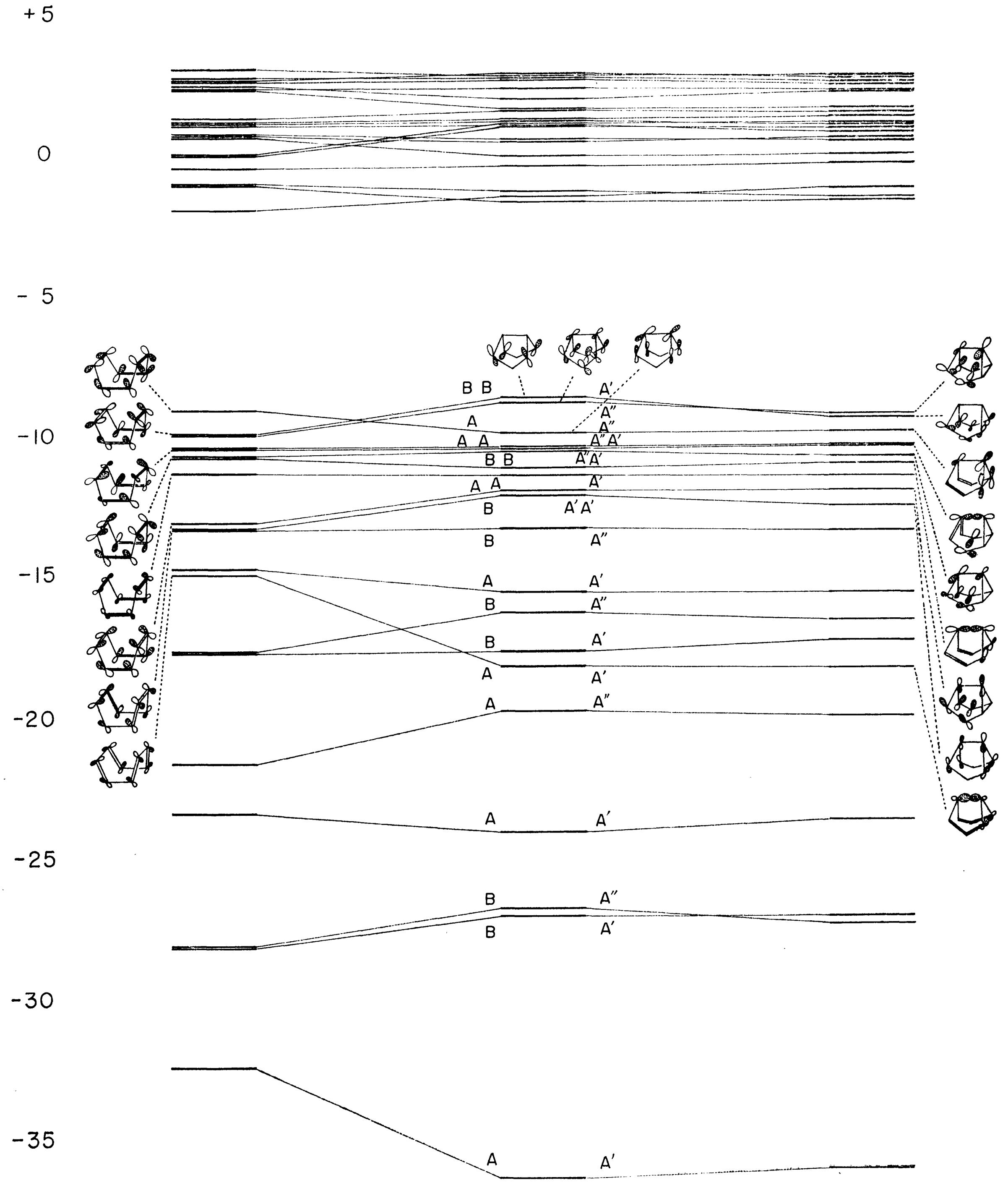

Fig. 1. Correlation diagram of the MINDO MO's for the isomerization of cyclooctatetraene to semibullvalene. (In some pairs of degenerate MO's of cyclooctatetraene, slight deviation from D_{2d} symmetry was imposed in the Figs. 1 and 2 to show the fate of the MO's during the course of the reaction.)

Table 1. Heats of formation and dissected values of total valence shell energies

	Heats of formation (kcal/mol)		Total valence shell energies			
			$\sum_{A} E_A$ (eV)	$\sum\sum_{A<B} E_{AB}$ (eV)		
	MINDO/2	MINDO/1		Resonance	Exchange	Electrostatic
Cyclooctatetraene	56.7	66.4	−921.9	−153.4	−75.0	−0.13
Intermediate[a]	45.4	53.6	−922.3	−155.1	−73.3	−0.15
6	27.1	53.0	−922.9	−154.0	−73.9	−0.21

a) Transition state structure of the Cope rearrangement of **6**.

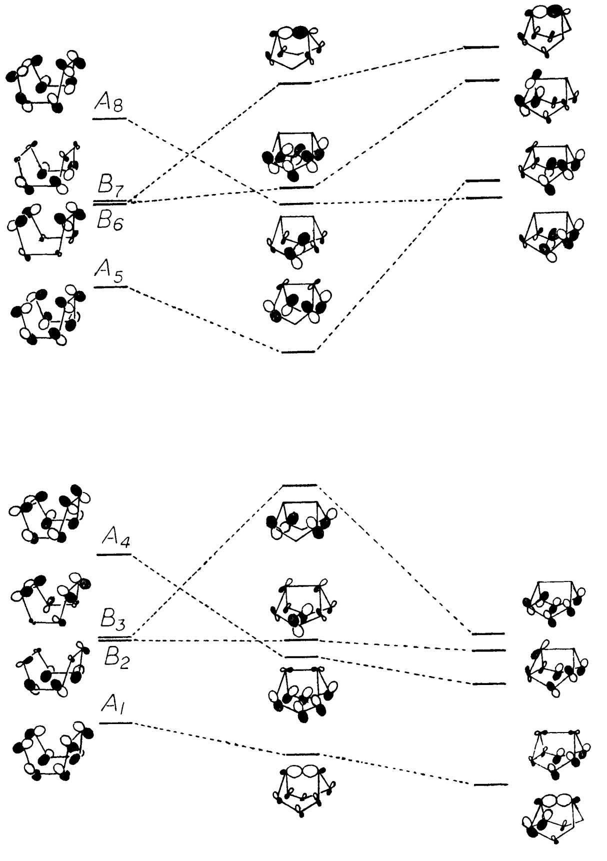

Fig. 2. Approximate correlation diagram of the π MO's of cyclooctatetraene for its isomerization to semibullvalene.

these levels split further on coupling with a combination of σ-orbitals of the same symmetry. As a result, none of the MO's in Fig. 1 can be exactly equivalent to any one MO in Fig. 2. Closer inspection of the MO coefficents reveals, however, that the 8th and 20th MO's of cyclooctatetraene in Fig. 1 are most reasonably approximated by the A_4 orbital in Fig. 2.[17] The behavior of the two MO's of cyclooctatetraene during the course of the reaction indicates that 1,3 ; 2,6 interaction of the π-orbitals of cyclooctatetraene is of bonding in nature. The reaction may figuratively be regarded as an intramolecular Diels-Alder ($2_\pi + 4_\pi$) reaction between the C-1, C-2 ene unit and the diene C-3$\sim$C-6. Instead of suprafacial overlap between the front lobes of C-2 and C-3, and C-1 and C-6 which leads to **5**, the opposite lobes of the p-orbitals on C-1 and C-2 are involved to form the new σ-bonds of **6** with the bottom lobe of C-3 and the top p-lobe of C-6, respectively (Chart 3).

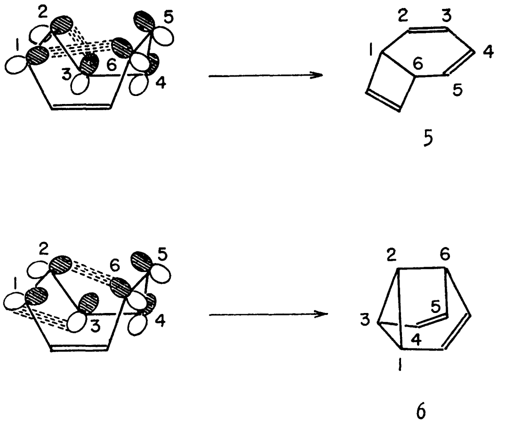

Chart 3. Two modes of thermally allowed closure.

Another aspect of the origin of the driving force for the reaction of Eq. (1) can be found in Table 1. In terms of resonance energy, the transition state structure of the Cope rearrangement of **6** is most favored (-155.16 eV) by the aromaticity of the Hückel type array of the 6π electrons. Cyclooctatetraene (-153.40 eV) is presumably destabilized to some extent by its anti-aromaticity due to cyclic array of 8π electrons. It is also interesting to note that contribution of the non-bonded interaction to the bi-centric resonance energy in cyclooctatetraene is -0.0074, -0.0038, and $+0.3485$ eV for the atomic pair of $C_1\sim C_6$, $C_2\sim C_6$, and $C_1\sim C_3$, respectively; a nagative value for E_{AB} implies bonding between atoms A and B while a positive value implies an anti-bonding interaction. It is also apparent in Table 1 that the one center terms are largely responsible for the total energy difference between cyclooctatetraene and **6**. The main contribution comes from the terms for C_2, $C_4(C_8)$, and C_5-(C_7) of **6**, and the effect appears to be associated with an increase in electron density and consequently one-center core binding energy of these carbon atoms. Of special importance is the high p_y electron density at C_2 of **6** which characterizes the electronic structure of this molecule (the y axis is taken parallel to the C_1—C_3 bond. The numbering system is given for **6** in Chart 3 only to clarify the original positions of atoms in the precursor, and does not conform to the IUPAC rules).

It is now conclusive on the theoretical bases that the reaction of Eq. (1) is an allowed process as a concerted cyclization in the ground state. Prediction to the contrary in Ref. 12 is found to be due to wrong drawing of the orbitals in which ring closure should lead to unrealistic semibullvalene with the cyclopropane ring fused trans (Chart 4).

Chart 4. Double cyclization of cyclooctatetraene according to the drawings in Ref. 12.

So far is rationalization of the thermally allowed conversion of cyclooctatetraene to semibullvalene. We are now halfway to give full theoretical account for the hypothesis that dimers **2**$\sim$**4** could be formed by way of coupling between **5** and **6**. In Chart 5 are shown one of the conceivable modes in which the coupling takes place. By application of the mnemonics of

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[17] The highest occupied orbital A_4 in Fig. 2, for example, appears to split into the MO's 20, 13, and 8 in Fig. 1 by mixing with a combination of σ orbitals in the ethylenic double bonds which has A symmetry for C_2 operation.

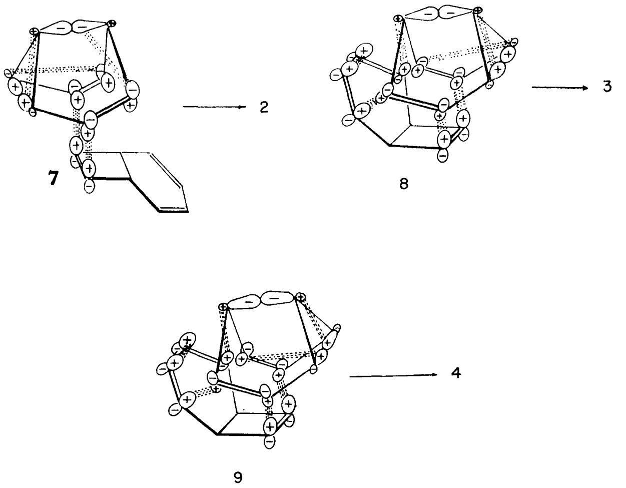

Chart 5. Mechanism I of the dimer formation of cyclooctatetraene from **5** and **6**.

Zimmerman for determining the allowedness or forbiddenness of symmetry controlled reactions, **7** is described as containing a cyclic array of ten atomic orbitals in which there are zero or even numbers of sign inversion resulting from plus-minus overlaps.[7,18] The type of the system is classified as Hückel and the process is predicted to be symmetry allowed in a ground state reaction. In the terminology of Woodward and Hoffmann,[11] the process can be described as $[{}_{\pi}2_s+{}_{\pi}2_a+{}_{\sigma}2_a+{}_{\sigma}2_a+{}_{\pi}2_a]$ processes. In **8** and **9** there are 14 AO's overlapping next to each other to form a cyclic array of orbitals. Irrespective of the choices of the sign of the basis set AO's, the total number of sign inversion resulting from plus-minus overlaps is zero or even. The Hückel system is again predicted to be allowed. Thus the modes of closure given in Chart 5 are proposed as a tentative mechanism for thermal dimerization of cyclooctatetraene.

In view of the multi-center interaction between **5** and **6** in the transition states **7**∼**9** the proposed mechanism should require a large negative entropy of activation. Although no quantitative study has yet been carried out, the fact that the dimers are formed only in condensed phases and that in neat or moderately concentrated solution is in accord with the expectation.[2-4] When the entropy requirement of mechanism I is seriously taken as a disadvantage, an alternative mechanism of the intermediacy of **10** followed by intramolecular closure to give **1**∼**4** may be considered as another candidate (Chart 6). The first step is a typical Diels-Alder reaction— the $[{}_{\pi}4_s+{}_{\pi}2_s]$ cycloaddition. The routes to **3** and **4** include internal closure of the cyclooctatriene moiety to the dihydrosemibullvalene. The theoretical argument developed in the first half of the present paper can similarly be applied to predict the allowedness of this part of the reactions.[7] Thus mechanisms I and II differ only in the chronology of the ring closure and can not be differentiated from the standpoint of orbital symmetry control of electrocyclic reactions.

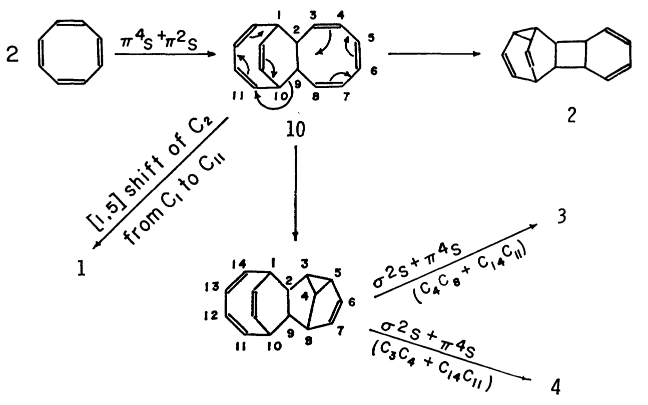

Chart 6. Mechanism II of the dimer formation of cyclooctatetraene.[19]

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[18] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); *ibid.*, **88**, 1566 (1966); *Science*, **153**, 837 (1966); *Accounts Chem. Res.*, **4**, 272 (1971).

[19] Dimers **1** and **2** formed at relatively low temperatures are not precursors of **3** and **4**. Prolonged heating of **2** has been shown to give a tetramer instead of an isomeric dimer.[4]