

Theoretical Studies on Octalene: The Planar and Nonplanar Structures and the Isomerization Reactions among the Nonplanar Structures

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The most stable geometrical structure of the hypothetical planar octalene is determined by using the MNDO and ab initio MO methods. It is revealed that the configuration interactions in the π space, particularly the quadruply excited configuration interactions, play an important role in determining the most stable structure. The molecular symmetry reduction does not occur in the planar octalene, the most stable structure being the D_{2h} structure in which π -electrons are delocalized throughout its periphery. Further, we discuss four nonplanar isomers of octalene, the *R*, *S*, cis, and trans types. All isomers are almost equally stable. The activation energy of the isomerization reaction from the *R*(*S*) type to the cis and trans types is calculated to be about 30 kcal mol⁻¹, which indicates that the cis and trans types would not be able to be synthesized from the *R*(*S*) type by thermal reactions.

Introduction

Bond distortions in the ground states of certain nonalternant hydrocarbons have drawn considerable theoretical attention in late years.¹ For example, pentalene shows no energy minimum for the D_{2h} symmetry suggested by the superposition of the two Kekulé type resonance structures, but has a lower energy if it takes an unsymmetrically distorted nuclear arrangement that corresponds to either of the resonance structures of the C_{2h} type. The experimental information² agrees with this in indicating that π -electrons in this molecule are strongly localized in double bonds, rather than uniformly delocalized over the entire molecule. Theoretical explanations for such anomalous phenomena have been attempted by several authors.³

On the basis of the second-order Jahn-Teller theory, Nakajima et al.⁴ have proposed an energy gap rule for the occurrence of molecular symmetry reduction, which states that if the lowest singlet excitation energy ΔE_1 of a conjugated hydrocarbon, calculated by assuming the full molecular symmetry and by using the Pariser-Parr-Pople type SCF MO method⁵ augmented by the singly excited configuration interaction calculation, is smaller than ca. 1.2 eV, the molecule should be distorted into a less symmetrical nuclear arrangement. In most cases, the effective nuclear deformation is of the bond alternation type. The bond distortions predicted by the above rule in various nonalternant hydrocarbons are in good agreement with those predicted by using the Pariser-Parr-Pople type SCF MO method, together with the variable bond length technique (VBL-PPP).⁶

If octalene is assumed to be planar (Figure 1), ΔE_1 is calculated to be 1.36 eV, which, according to the above rule, indicates that the molecular symmetry reduction does not occur. This is in agreement with the information deduced from the experimental facts.⁸ On the other hand, the

VBL-PPP calculation shows that the C_{2v} structure (C of Figure 1) distorted along the b_{2u} nuclear displacement is most stable. The disagreement between the two predictions may probably be due to the neglect of the electron correlation in the VBL-PPP calculation, which in some cases plays an important role in determining the most stable structure.

In the first half of this paper, we examine the molecular symmetry and the geometrical structure of the hypothetical planar octalene by using the MNDO and ab initio MO methods augmented by the configuration interaction calculation. In the second half, we discuss nonplanar structures of octalene. Oth et al.⁸ have synthesized octalene, whose structure is of the *R* or *S* type, the *R* and *S* structures being a pair of enantiomers (Figure 3). By analogy with the tub-shaped structure of cyclooctatetraene (COT), the cis type (C_{2v}) and the corresponding trans type (C_{2h}) may also be possible (Figure 3), but these types have not yet been synthesized. Allinger et al.⁹ have discussed the relative stabilities of the cis and trans types by using the Pariser-Parr type MO method but have not considered the *R* and *S* types. We discuss the stability of these isomers and estimate the activation energies of the isomerization reactions among them.

Method of Calculation

Planar Structures. The geometry optimizations are carried out by using the MNDO method¹⁰ and the ab initio MO method with the STO-3G basis set.¹¹ All geometry optimizations are followed by the single-point ab initio MO calculations with the 4-31G basis set¹² (denoted 4-31G//MNDO and 4-31G//STO-3G, respectively). Still more, all SCF calculations are followed by the singly and doubly excited configuration interaction calculations in the π space

(1) den Boer-Veenendaal, P. C.; Vliegthart, J. A.; der Boer, D. H. *W. Tetrahedron* 1962, 18, 1325. Snyder, L. C. *J. Phys. Chem.* 1962, 66, 2299. Nakajima, T.; Katagiri, S. *Mol. Phys.* 1963, 7, 149.

(2) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* 1961, 83, 4659.

(3) der Boer-Voenendaal, P. C.; den Boer, D. H. *W. Mol. Phys.* 1961, 4, 33. Nakajima, T.; Saijo, T.; Yamaguchi, H. *Tetrahedron* 1964, 20, 2119.

(4) Nakajima, T. *Top. Curr. Chem.* 1972, 32, 1.

(5) Pople, J. A. *Trans. Faraday Soc.* 1953, 49, 1325.

(6) Dewar, M. J. S.; Gleicher, G. J. *Tetrahedron* 1957, 21, 140. Yamaguchi, H.; Nakajima, T.; Kunii, T. L. *Theor. Chim. Acta* 1968, 12, 349.

(7) Reference deleted.

(8) Vogel, E.; Runzheimer, H. V.; Hogrefe, F.; Baasner, B.; Lex, J. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 871. Oth, J. F. M.; Muellen, K.; Runzheimer, H. V.; Mues, P.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 872.

(9) Allinger, N. L.; Gilardeau, C. *Tetrahedron* 1967, 23, 1569.

(10) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899. Modified version of Quantum Chemistry Program Exchange (QCPE No. 353).

(11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1969, 51, 2657. Modified version (IMSPACK) of GAUSSIAN 70, available from QCPE No. 236.

(12) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Soc.* 1971, 54, 724.

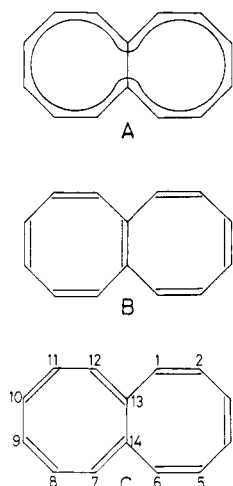


Figure 1. Kekulé type resonance structures of octalene.

(π -SDCI), and the influence of the quadruple excitations is estimated by using the following correction¹³ (denoted MNDO + π -SDQ*CI, STO-3G + π -SDQ*CI, and 4-31G + π -SDQ*CI).

$$E_{Q^*} = E_{SD}(1 - C_0^2)/(2C_0^2 - 1)$$

E_{SD} is the correlation energy estimated by using the π -SDCI calculation and C_0 is the coefficient of the reference state.

Nonplanar Structures. The geometry optimizations are carried out by using the MNDO method. The energies of the optimized geometries are estimated by using the ab initio MO methods with the STO-3G basis set and the 4-31G basis set (denoted STO-3G//MNDO and 4-31G//MNDO, respectively).

The geometries of the transition states and their energies in the isomerization reactions among the nonplanar isomers are estimated by using the MNDO method. All the optimized geometries are checked by calculating and diagonalizing the Hessian (force constant) matrix by using Cartesian coordinates.¹⁴

Results and Discussion

Hypothetical Planar Structures. The optimized geometrical structures of the hypothetical planar octalene are given in Figure 2. There are three equilibrium geometries, A, B, and C.

Geometrical Structures A and C. The bond length alternation in the C type obtained by using the STO-3G basis set is fairly larger than that obtained by using the MNDO method (bond lengths and bond angles obtained by using the latter method are shown in parentheses). As for the A type, both the methods produce almost the same geometries.

The relative energies of the three structures obtained by using various methods are given in Table I. The C type is more stable than the A type by 29.2 kcal mol⁻¹ if STO-3G//STO-3G is used. The difference in energy between the A and C types calculated by using 4-31G//STO-3G is much smaller than the above value, and the energy difference obtained by using 4-31G//MNDO is almost the same as that obtained by using 4-31G//STO-3G. All the above results show that the A type is less stable than the

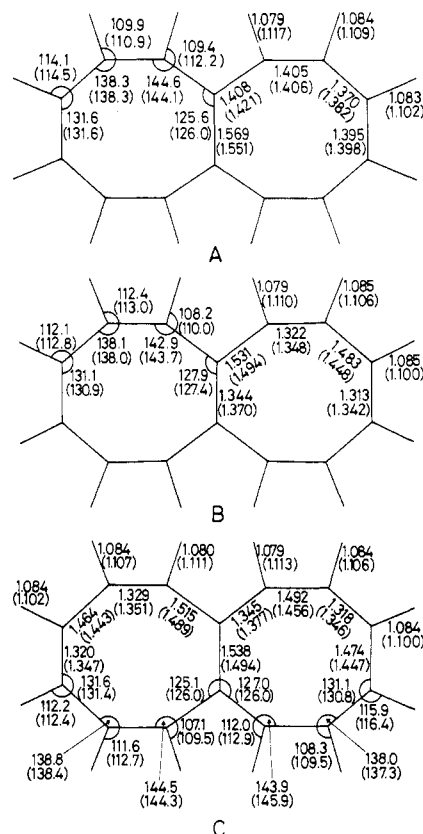


Figure 2. Optimized geometries of the planar octalene (bond lengths in angstroms, and bond angles in degrees) calculated by using the ab initio MO method with the STO-3G basis set and the MNDO method (in parentheses). The A, B, and C types correspond to those in Figure 1.

Table I. Relative Energies of the Planar Octalene (kcal mol⁻¹)

method	A type	B type	C type
	D_{2h}	D_{2h}	C_{2v}
MNDO	0.0	-20.7	-19.7
MNDO + π -SDCI	0.0	-12.8	-11.8
MNDO + π -SDQ*CI	0.0	+4.6	+4.9
STO-3G//MNDO	0.0	-19.5	-24.2
4-31G//MNDO	0.0	-4.4	-11.8
STO-3G//STO-3G	0.0	-25.3	-29.2
STO-3G + π -SDCI	0.0	-26.7	-28.2
STO-3G + π -SDQ*CI	0.0	-0.5	-2.3
4-31G//STO-3G	0.0	-3.6	-10.6
4-31G + π -SDCI	0.0	-2.6	-7.6
4-31G + π -SDQ*CI	0.0	+7.0	+3.0

C type, which does not agree with the experimental information.⁸ We then take into account the π -electron correlation, assuming the effect of σ -electron correlation to be almost the same between the relevant two structures.

When STO-3G//STO-3G is used (STO-3G + π -SDQ*CI), the effect of electron correlation makes the energy difference much smaller (-2.3 kcal mol⁻¹) but does not reverse their relative stability even if the effect of the quadruply excited configurations is included. On the other hand, when 4-31G//STO-3G is used (4-31G + π -SDQ*CI), their relative stability is reversed by the inclusion of the effect of the quadruply excited configurations. The result is in qualitative agreement with the experimental fact though the calculated energy difference (+3.0 kcal mol⁻¹) is smaller than the experimental value (ca. 15 kcal mol⁻¹).⁸ The similar calculation made by using the MNDO method (MNDO + π -SDQ*CI) also shows that the A type is more stable than the C type by 4.9 kcal mol⁻¹. Thus, it is revealed that the effect of electron correlation, particularly

(13) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* 1974, 8, 61. Langhoff, S. R.; Davidson, E. R. *Ibid.* 1976, 10, 917. Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* 1977, 52, 403. Siegbahn, P. E. M. *Chem. Phys. Lett.* 1978, 55, 386.

(14) McIver, J. W.; Komornicki, A., Jr. *J. Am. Chem. Soc.* 1972, 94, 2625.

of the quadruply excited configurations, is quite important in determining the most stable structure of the planar octalene.

We have studied the effect of electron correlation on the prediction of geometrical structures of pentalene and heptalene, which belong to the homologous series of octalene, by using the ab initio MO method augmented by the π -SDCI and π -SDQ*CI calculations.¹⁵ The results show that the correlation energy in the D_{2h} structure is smaller than that in the C_{2h} one, and that the inclusion of electron correlation does not reverse the relative stability predicted without the correlation effect being included. The reason for this is explained as follows: the lowest unoccupied molecular orbital (LUMO) of the D_{2h} type pentalene and the highest occupied molecular orbital (HOMO) of the D_{2h} type heptalene are nonbonding (NBMO), and the electronic configurations involving the excitations to LUMO or from HOMO do not make valuable contributions to the correlation energy. On the other hand, in the C_{2h} structures these electronic configurations make larger contributions, since HOMO or LUMO loses the nonbonding character. In the D_{2h} type octalene, HOMO and LUMO are not nonbonding, and the correlation effect is different from that in pentalene and heptalene. Moreover, it has been known that the effect of electron correlation in [18]annulene¹⁶⁻²⁰ and [10]annulene²¹ is the same as that in the planar octalene.

Thus, we can group conjugated hydrocarbons, from the view point of the electron correlation effect, into the two classes. In molecules belonging to the first class, the relative stability between the fully symmetrical structure and the bond-distorted one predicted by using the Hartree-Fock approximation is enhanced by taking into account the effect of electron correlation and, consequently, remains correct at least qualitatively as in pentalene and heptalene. In molecules belonging to the second class, the relative stability predicted by using the Hartree-Fock approximation is reversed by taking into account the effect of electron correlation as in octalene, [18]annulene, and [10]annulene.

Kekulé Type Structure B. Some annulenoannulenes which possess $4n$ π -electrons, e.g., pentalene and heptalene etc., have only two Kekulé type structures with the C_{2h} symmetry, while those which possess $4n + 2$ π -electrons, e.g., naphthalene and octalene etc., have two Kekulé type structures with the C_{2v} symmetry and one with the D_{2h} symmetry.

It has been well-known that the most stable geometrical structure (D_{2h}) of naphthalene has a relatively short central bond expected from the superposition of three Kekulé type structures. However, the present results show that the A type octalene (D_{2h}) has a distinctly longer central bond than the other bonds and seems to be constructed from the superposition of the only two Kekulé type structures with the C_{2v} symmetry. In order to clarify this point, we made the geometry optimization by assuming a very short central bond as the initial geometry. The geometrical

structures thus optimized by using the STO-3G basis set and the MNDO method are of the B type, which corresponds to the Kekulé type structure with D_{2h} symmetry (Figure 2). Thus, octalene has two optimized geometries with D_{2h} symmetry. The reason for the existence of these two geometries are given as follows: In naphthalene, the HOMO of the D_{2h} structure is smoothly connected with those of the three Kekulé type structures, so that no energy barriers are expected among their ground states. On the other hand, in octalene the next HOMO of the A type, which is energetically very close to HOMO, belongs to the same irreducible representation as LUMO of the B type, and LUMO of the A type belongs to the same irreducible representation as HOMO of the B type. Consequently, it is expected that there exists a relatively high energy barrier between the two structures.

However, the present results finally show that the B type is most unstable among the three structures, and moreover, our rough configuration interaction calculations made by using the MNDO method show a tendency to remove the barrier between the A and B types. Therefore, the B type cannot be considered to be the true equilibrium geometry.

The normal vibrational analysis using the MNDO method gives imaginary frequencies for the b_{2g} , a_u , b_{1u} , and b_{3u} modes of the A type, for the b_{2g} , a_u , and b_{3u} modes of the B type, and for the two a_2 and two b_1 modes of the C type. The vibrational motion b_{1u} of the A type leads to the symmetry reduction to the C type. However, it is shown that the frequency of this mode becomes real if the normal vibrational analysis using the MNDO + π -SDQ*CI or 4-31G + π -SDQ*CI method is carried out. The other three modes of the A type, the three of the B type, and the four of the C type are all out-of-plane vibrations.

Nonplanar Structures. The optimized geometries of the R, S, cis, and trans types are given in Figure 3 and Table II. The relative energies of the isomers obtained by using the MNDO method, STO-3G//MNDO, and 4-31G//MNDO are given in Table III. All the eigenvalues of the force constant matrices of these four structures are positive. All the calculations show that the cis and trans types are more stable than the R and S types, though the energy differences are all very small. On the other hand, the thermochemical estimation shows that the R and S types are more stable than the cis and trans types by 5-6 kcal mol⁻¹.⁸ This energy difference has been obtained by assuming that the ring strain in the R(S) type is much the same as in the cis(trans) type and that the energy difference is given by the gain in the conjugation energy for the planar butadiene fragment C5C6C14C7 in the R(S) type. However, the dihedral angle of C5C6C14C7 obtained by using the MNDO method is equal to 148.7°, and there should be little gain in conjugation energy. Moreover, the ring strain in the R(S) type may probably be larger than that in the cis(trans) type, because in the former the σ orbitals of C atoms seem to be more distorted from the sp² hybridization than in the cis(trans) type.

Thus, our conclusion concerning the relative stability is that all the isomers are equally stable. We believe that the cis and trans types are not too unstable to be synthesized. However, to our knowledge, there is no report that the cis or trans type has been synthesized.

Ring-Inversion Reactions. We consider two types of ring-inversion reactions since the R and S types have two different fragments, the cyclooctatetraene and cyclooctatriene rings.

Inversion of the Cyclooctatriene Fragment. The stereochemistry remains unchanged after the inversion of the cyclooctatriene fragment. The transition state of this

(15) Jean, Y. *Nouv. J. Chim.* 1980, 4, 11. Kataoka, M.; Koseki, S.; Nakajima, T., to be published.

(16) Haddon, R. C. *Chem. Phys. Lett.* 1980, 70, 210.

(17) Bregman, J.; Hirschfeld, F. L.; Rabinovich, D.; Schmidt, G. M. J. *Acta Crystallogr.* 1965, 19, 227.

(18) Jackman, L. M.; Sondheimer, F.; Amiel, Y.; Ben-Efraim, D. A.; Gaoni, Y.; Wolovsky, R.; Bothnerby, A. A. *J. Am. Chem. Soc.* 1962, 84, 4307. Sondheimer, F. *Pure Appl. Chem.* 1963, 7, 363.

(19) Baumann, H. *J. Am. Chem. Soc.* 1978, 100, 7196.

(20) Thiel, W. *J. Am. Chem. Soc.* 1981, 103, 1420. Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* 1980, 52, 1431.

(21) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* 1982, 104, 3516.

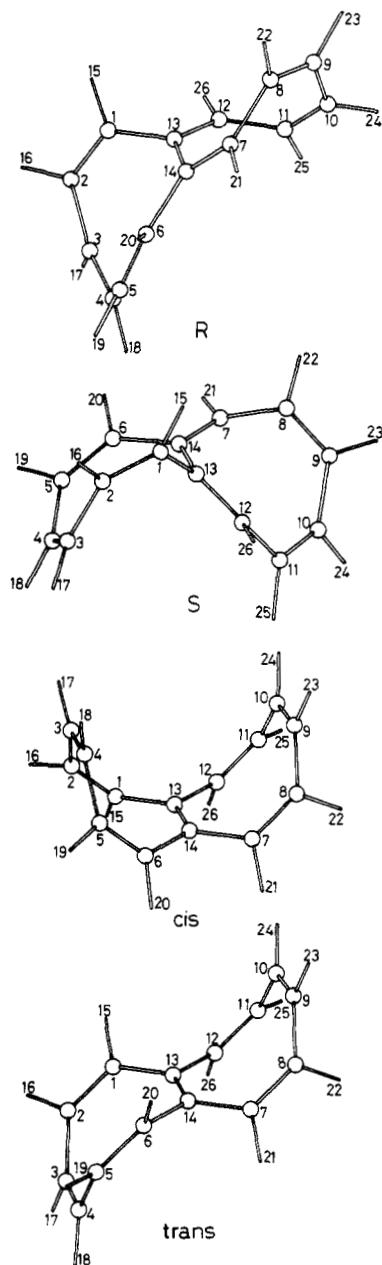


Figure 3. Optimized geometries of the R, S, cis, and trans types. Geometrical parameters are given in Table II.

ring-inversion reaction is assumed to have the planar cyclooctatriene fragment.

The optimized geometry SS' (RR') of the transition state is given in Figure 4 and Table IV. Its energy is about 37 kcal mol⁻¹ higher than that of the $R(S)$ type. However, the normal vibrational analysis gives two imaginary frequencies (ν_1 and ν_2 in Figure 4), and it is not a geometry of the transition state. The vibrational motion ν_1 leads to the product and the reactant (the R or S type), while the other vibrational motion ν_2 , which is a torsional motion, does not lead to them.

When the geometry of the reactant is carefully compared with that of the product (Figure 5), we notice that C_1 and C_6 remain at almost the same positions. Therefore, we can assume that six carbon atoms ($C_1, C_2, C_3, C_4, C_5,$ and C_6) except C_{13} and C_{14} are arranged in a plane. The optimized geometry SS (RR) of the transition state under this condition is given in Figure 5 and Table IV, and its energy is only 5 kcal mol⁻¹ higher than that of the $R(S)$ type. The normal vibrational analysis gives only one imaginary frequency, which leads to the $R(S)$ type.

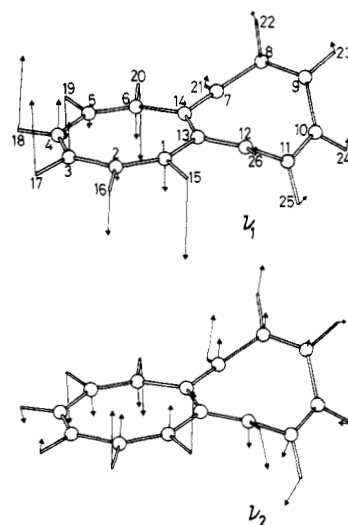


Figure 4. Optimized geometry SS' and the vibrational motions ν_1 and ν_2 corresponding to the imaginary frequencies. Geometrical parameters are given in Table IV.

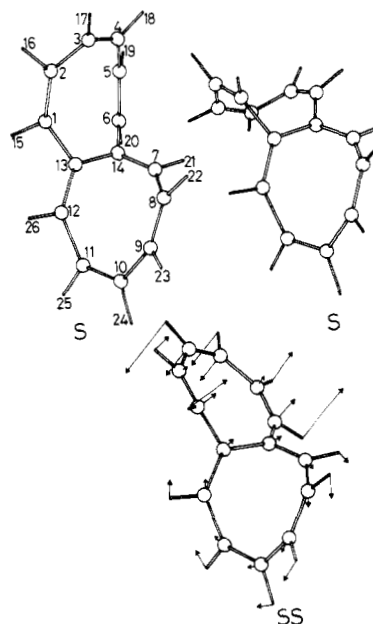


Figure 5. Reactant S, transition state SS , and product S in the ring-inversion reaction of the cyclooctatriene fragment. Arrow heads stand for the vibrational motion corresponding to the imaginary frequency. Geometrical parameters of SS are given in Table IV.

Thus, the activation energy of this reaction is about 5 kcal mol⁻¹, which is somewhat smaller than the experimental value (ca. 8 kcal mol⁻¹).⁸

Inversion of the Cyclooctatetraene Fragment. One enantiomeric structure is converted into the other by the ring inversion of the cyclooctatetraene fragment. The geometry of the transition state is optimized under the assumption that eight carbon atoms of the cyclooctatetraene fragment are arranged in a plane.

The optimized geometry of the transition state (RS) is given in Figure 6 and Table IV. The normal vibrational analysis gives only one imaginary frequency. The energy barrier of this reaction is calculated to be 16 kcal mol⁻¹.

This reaction is similar to the ring-inversion reaction of cyclooctatetraene (COT). The experimental energy barrier of ring-inversion reaction without the π -bond shift in COT²² has been estimated to be ca. 10 kcal mol⁻¹. The

Table II. Geometrical Parameters for the *R(S)*, *Cis*, and *Trans* Types^a

type	sym	geometrical parameters
<i>R(S)</i>	C_1	C13-C14 1.488, C13-C1 1.489, C1-C2 1.349, C2-C3 1.471, C3-C4 1.353, C4-C5 1.465, C5-C6 1.351, C6-C14 1.482, C14-C7 1.364, C7-C8 1.471, C8-C9 1.348, C9-C10 1.466, C10-C11 1.346, C11-C12 1.471, C12-C13 1.359, C1-H15 1.095, C2-H16 1.094, C3-H17 1.095, C4-H18 1.095, C5-H19 1.100, C6-H20 1.100, C7-H21 1.098, C8-H22 1.097, C9-H23 1.095, C10-H24 1.095, C11-H25 1.096, C12-H26 1.098, C14C13C1 116.7, C13C1C2 125.3, C1C2C3 124.5, C13C14C6 119.1, C14C6C5 131.2, C6C5C4 131.1, C13C14C7 123.8, C14C7C8 129.4, C7C8C9 128.0, C14C13C12 126.0, C13C12C11 129.0, C12C11C10 127.2, C13C1C15 114.6, C1C2H16 120.4, C2C3H17 114.2, C5C4H18 114.4, C6C5H19 117.0, C14C6H20 113.2, C14C7H21 119.2, C7C8H22 112.7, C8C9H23 119.6, C11C10H24 120.3, C12C11H25 113.2, C13C12H26 119.1, C1C13C14C7 133.8, C1C13C14C6 -42.8, C7C14C13C12 -47.7, C14C13C1C2 85.0, C13C1C2C3 -1.9, C13C14C6C5 -34.5, C14C6C5C4 11.7, C13C14C7C8 -5.7, C14C7C8C9 61.4, C14C13C12C11 -6.3, C13C12C11C10 62.4, C12C13C1H15 85.0, H15C1C2H16 -1.3, H16C2C3H17 -52.5, H19C5C4H18 49.8, H20C6C5H19 3.0, C7C14C6H20 -26.4, C6C14C7H21 -3.8, H21C7C8H22 53.4, H22C8C9H23 -1.0, H25C11C10H24 -0.6, H26C12C11H25 55.2, C1C13C12H26 -3.6
<i>cis</i>	C_{2v}	C13-C14 1.365, C13-C1 1.486, C1-C2 1.347, C2-C3 1.470, C3-C4 1.347, C1-H15 1.098, C2-H16 1.097, C3-H17 1.094, C14C13C1 124.4, C13C1C2 129.2, C1C2C3 128.1, C13C1H15 112.9, C1C2H16 118.5, C2C3H17 114.6, C1C13C14C7 180.0, C1C13C14C6 0.0, C14C13C1C2 -55.6, C13C1C2C3 -0.3, C12C13C1H15 -55.4, H15C1C2H16 1.2, H16C2C3H17 53.0
<i>trans</i>	C_{2h}	C13-C14 1.365, C13-C1 1.486, C1-C2 1.347, C2-C3 1.470, C3-C4 1.348, C1-H15 1.098, C2-H16 1.097, C3-H17 1.094, C14C13C1 124.4, C13C1C2 129.2, C1C2C3 128.2, C13C1H15 112.9, C1C2H16 118.6, C2C3H17 114.6, C1C13C14C7 180.0, C1C13C14C6 0.0, C14C13C1C2 55.6, C13C1C2C3 0.3, C12C13C1H15 55.4, H15C1C2H16 -1.2, H16C2C3H17 -53.2

^a Bond lengths in angstroms, and bond angles in degrees. *Ck-Cl*, *Ck-Hl* = bond lengths. *CkC1Cm*, *CkC1Hm* = bond angles. *CkC1CmCn* = dihedral angles.

Table III. Relative Energies of the Nonplanar Isomers (kcal mol⁻¹)

method	<i>R</i> and <i>S</i> C_1	<i>trans</i> C_{2h}	<i>cis</i> C_{2v}
MNDO	0.0	-2.1	-1.7
STO-3G//MNDO	0.0	-1.2	-1.8
4-31G//MNDO	0.0	-2.4	-1.6

MNDO method gives the result that the planar structure of COT is higher than the tub-shaped structure by about 8 kcal mol⁻¹, which is in good agreement with the above value. The difference of 8 kcal mol⁻¹ between the energy barriers of the ring-inversion reaction in the *R(S)* type (16 kcal mol⁻¹) and in COT (8 kcal mol⁻¹) can be attributed mainly to the steric effect of the cyclooctatriene fragment.

Isomerization Reaction between the *Cis* and *Trans* Types. The isomerization reaction between the *cis* and *trans* types is the ring-inversion reaction of the cyclooctatetraene fragment. Therefore, we assume that the geometry of the transition state of this reaction has a planar cyclooctatetraene fragment.

The normal vibrational analysis of the optimized geometry of the transition state (TC) shown in Figure 7 and Table IV gives only one imaginary frequency. The transition state is higher in energy than the *cis* and *trans* types by 16 kcal mol⁻¹, which is the same as the barrier of the inversion reaction of the cyclooctatetraene fragment in the *R(S)* type.

Allinger et al.⁹ have estimated, using the Pariser-Parr type MO method, the activation energy for this isomerization reaction to be 10–12 kcal mol⁻¹.

The Possibility of the Isomerization Reaction from the *R(S)* Type to the *Cis(Trans)* Type. It is a difficult task to draw the correlation diagram between the MO's of the *R(S)* type and the *cis(trans)* type, because the *R(S)* type has no symmetry. However, by analogy with the correlation diagram between MO's of the planar structures, it is expected that a crossing should occur between an occupied MO and a vacant MO along the reaction path from the *R(S)* type to the *cis(trans)* type. Therefore, we expect that this isomerization reaction has a relatively large energy barrier and that the reaction cannot occur thermally.

Reaction via the RS and TC Types. The π -bond shift in COT takes place thermally though a crossing occurs

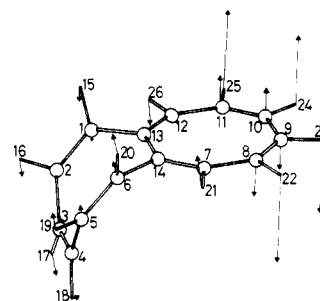


Figure 6. Transition state RS in the ring-inversion reaction of the cyclooctatetraene fragment. Arrow heads stand for the vibrational motion corresponding to the imaginary frequency. Geometrical parameters of RS are given in Table IV.

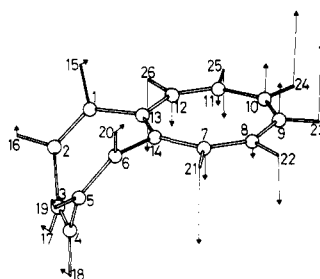


Figure 7. Transition state TC in the isomerization reaction between the *cis* and *trans* types. Arrow heads stand for the vibrational motion corresponding to the imaginary frequency. Geometrical parameters are given in Table IV.

between HOMO and LUMO. This reaction is considered to be initiated by the ring inversion of COT followed by the π -bond shift. The analysis of the temperature-dependent ¹³C NMR spectra shows that the activation energy of this reaction is ca. 14 kcal mol⁻¹ and the energy barrier of the π -bond shift in the planar form is about 4 kcal mol⁻¹.²² Therefore, we expect that the energy barrier of the π -bond shift in the planar cyclooctatetraene fragment of the RS or TC type is larger than 4 kcal mol⁻¹, because of the steric effect of the cyclooctatriene fragment.

According to the above discussion, the energy barrier of the isomerization reaction from the *R(S)* type to the *cis* and *trans* types should be larger than 20 kcal mol⁻¹, which is the sum of the energy difference (16 kcal mol⁻¹) between

Table IV. Geometrical Parameters for the Transition States^a

type	sym	geometrical parameters
SS' (RR')	C ₁	C13-C14 1.484, C13-C1 1.480, C1-C2 1.350, C2-C3 1.444, C3-C4 1.348, C4-C5 1.444, C5-C6 1.350, C6-C14 1.480, C14-C7 1.382, C7-C8 1.469, C8-C9 1.344, C9-C10 1.461, C10-C11 1.344, C11-C12 1.468, C12-C13 1.381, C1-H15 1.110, C2-H16 1.106, C3-H17 1.101, C4-H18 1.101, C5-H19 1.106, C6-H20 1.110, C7-H21 1.103, C8-H22 1.100, C9-H23 1.094, C10-H24 1.094, C11-H25 1.100, C12-H26 1.103, C14C13C1 127.7, C13C1C2 142.4, C1C2C3 137.6, C13C14C6 127.6, C14C6C5 142.4, C6C5C4 137.7, C13C14C7 122.7, C14C7C8 133.2, C7C8C9 130.6, C14C13C12 122.8, C13C12C11 133.3, C12C11C10 130.5, C13C1H15 109.5, C1C2H16 113.1, C2C3H17 112.0, C5C4H18 112.1, C6C5H19 113.0, C14C6H20 109.5, C14C7H21 118.0, C7C8H22 110.8, C8C9H23 120.3, C11C10H24 120.5, C12C11H25 110.8, C13C12H26 118.0, C1C13C14C7 186.5, C1C13C14C6 0.0f, C7C14C13C12 13.3, C14C13C1C2 0.0f, C13C1C2C3 0.0f, C13C14C6C5 0.0f, C14C6C5C4 0.0f, C13C14C7C8 31.6, C14C7C8C9 -75.3, C14C13C12C11 32.0, C13C12C11C10 -75.5, C12C13C1H15 0.0f, H15C1C2H16 0.0f, H16C2C3H17 0.0f, H19C5C4H18 0.0f, H20C6C5H19 0.0f, C7C14C6H20 0.0f, C6C14C7H21 22.6, H21C7C8H22 -58.2, H22C8C9H23 1.9, H25C11C10H24 1.5, H26C12C11H25 -58.3, C1C13C12H26 23.2
SS (RR)	C ₁	C13-C14 1.487, C13-C1 1.476, C1-C2 1.351, C2-C3 1.450, C3-C4 1.352, C4-C5 1.448, C5-C6 1.352, C6-C14 1.472, C14-C7 1.365, C7-C8 1.469, C8-C9 1.349, C9-C10 1.471, C10-C11 1.350, C11-C12 1.469, C12-C13 1.362, C1-H15 1.100, C2-H16 1.103, C3-H17 1.101, C4-H18 1.105, C5-H19 1.104, C6-H20 1.104, C7-H21 1.097, C8-H22 1.095, C9-H23 1.096, C10-H24 1.095, C11-H25 1.095, C12-H26 1.098, C13C14C6 120.2, C14C6C5 135.3, C6C5C4 135.6, C5C4C3 136.3, C4C3C2 133.2, C3C2C1 133.1, C13C14C7 121.4, C14C7C8 128.2, C7C8C9 125.7, C14C13C12 122.3, C13C12C11 128.2, C12C11C10 125.6, C2C1H15 116.6, C3C2H16 111.1, C4C3H17 115.1, C5C4H18 119.4, C11C10H24 119.7, C12C11H25 114.5, C13C12H26 119.6, C13C14C6C5 -38.6, C14C6C5C4 5.8, C6C5C4C3 0.0f, C5C4C3C2 0.0f, C4C3C2C1 0.0f, C6C14C13C12 250.1, C12C13C14C7 65.6, C13C14C7C8 -5.2, C14C7C8C9 -59.5, C14C13C12C11 -5.4, C13C12C11C10 -59.0, H16C2C1H15 5.0, H17C3C2H16 12.3, H18C4C3H17 -0.4, H19C5C4H18 3.5, H20C6C5H19 1.7, C7C14C6H20 -32.8, C6C14C7H21 -8.8, H21C7C8H22 -55.5, H22C8C9H23 1.0, H25C11C10H24 0.5, H26C12C11H25 -56.3, C1C13C12H26 -8.1
RS	C _s	C13-C14 1.485, C13-C1 1.497, C1-C2 1.347, C2-C3 1.468, C3-C4 1.349, C13-C12 1.364, C12-C11 1.458, C11-C10 1.345, C10-C9 1.453, C1-H15 1.098, C2-H16 1.097, C3-H17 1.093, C10-H24 1.102, C11-H25 1.104, C12-H26 1.107, C14C13C1 118.9, C13C1C2 129.1, C1C2C3 127.9, C14C13C12 131.1, C13C12C11 139.3, C12C11C10 136.2, C13C1H15 118.6, C2C3H17 115.9, C11C10H24 115.5, C12C11H25 109.8, C13C12H26 114.0, C1C13C14C7 180.0f, C1C13C14C6 0.0f, C7C14C13C12 0.0f, C14C13C12C11 0.0f, C13C12C11C10 0.0f, C14C13C1C2 63.6, C13C1C2C3 -5.0, C12C13C1H15 61.8, H15C1C2H16 -3.3, H16C2C3H17 -56.9, H25C11C10H24 0.0f, H26C12C11H25 0.0f, C1C13C12H26 0.0f
TC	C _s	C13-C14 1.365, C13-C1 1.498, C1-C2 1.348, C2-C3 1.471, C3-C4 1.349, C13-C12 1.479, C12-C11 1.347, C11-C10 1.454, C10-C9 1.345, C1-H15 1.098, C2-H16 1.095, C3-H17 1.093, C10-H24 1.101, C11-H25 1.105, C12-H26 1.106, C14C13C1 120.7, C13C1C2 128.8, C1C2C3 126.0, C14C13C12 131.9, C13C12C11 138.0, C12C11C10 136.9, C13C1H15 113.0, C1C2H16 119.6, C2C3H17 115.7, C11C10H24 111.4, C12C11H25 113.5, C13C12H26 110.5, C1C13C14C7 180.0f, C1C13C14C6 0.0f, C7C14C13C12 0.0f, C14C13C12C11 0.0f, C13C12C11C10 0.0f, C14C13C1C2 64.7, C13C1C2C3 -5.1, C12C13C1H15 63.2, H15C1C2H16 -3.6, H16C2C3H17 -56.4, H25C11C10H24 0.0f, H26C12C11H25 0.0f, C1C13C12H26 0.0f

^a Bond lengths in angstroms and bond angles in degrees. Ck-Cl, Ck-Hl = bond lengths. CkC1Cm, CkC1Hm = bond angles. CkC1CmCn = dihedral angles. f = fixed.

the *R(S)* and *RS* types and the energy barrier (4 kcal mol⁻¹) of π -bond shift in the cyclooctatetraene fragment. More precisely, we estimate it to be almost 30 kcal mol⁻¹, which is obtained by taking into account the error of the MNDO method (2-3 kcal mol⁻¹) and the steric effect of the cyclooctatriene fragment (8 kcal mol⁻¹). Thus, we conclude that the isomerization reaction via the *RS* and *TC* types cannot occur thermally, though the ring-inversion reaction with the π -bond shift in COT occurs thermally.

Reaction via a Planar Structure. The experimental result⁸ shows that the planar structure A is less stable than the *R(S)* type by 20 kcal mol⁻¹. Therefore, the A type is more stable than the transition state of the above reaction. This fact can be accepted, because the transition state has 8 π -electrons in the conjugated region, while the A type has 14 π -electrons in the periphery. Therefore, the reaction path via the A type seems to be more favorable than that via the *RS* and *TC* types. However, the π -electrons in the A type need to be localized like in the B type, the latter type being less stable than the A type by about 7 kcal mol⁻¹ (Table I). Thus, it is expected that the activation energy along this reaction path is about 27 kcal mol⁻¹, which is

also too large for the reaction from the *R(S)* type to the *cis* and *trans* types to occur thermally.

Thus, the large barriers obtained above provide one of the main reasons for the experimental fact that the *cis* and *trans* types cannot be synthesized from the *R(S)* type even at the high temperature (+120 °C).

Conclusion

The most stable structure of the hypothetical planar octalene is the A type, in which π -electrons are delocalized throughout the periphery. In the planar octalene the correlation effect plays an important role in determining the most stable structure. The *cis* and *trans* types are as stable as the *R(S)* type. However, the former cannot be synthesized from the latter by thermal reactions because of the existence of the large energy barriers.

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