Double-bond Fixation in Tricyclopenta[*cd,f,h*]azulene and its Higher Homologues

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The C–C bond distortions in tricyclopenta[*cd,f,h*]azulene and its higher homologues have been examined by using the symmetry rule and the semiempirical Pariser–Parr–Pople (PPP)-type SCF MO method. In tricyclopenta[*cd,f,h*]azulene and tricyclohepta[*a,c,ef*]heptalene, it is predicted that a molecular-symmetry reduction ($C_{2v} \longrightarrow C_s$) accompanied by a marked double-bond fixation should occur in the carbon skeleton. In contrast, other homologues are expected to show a moderate bond fixation, retaining the full molecular symmetry group. This difference is explained in terms of a pseudo-Jahn–Teller effect.

Bond distortions and related phenomena in the cata-condensed non-alternant hydrocarbons are of considerable theoretical interest to theoretical chemists.[1–11] Of these molecular systems, pentalene has been of particular interest since it can be regarded as a prototype of the weakly perturbed [4*n*]annulenes. The stable ground-state nuclear arrangement is predicted to assume a skew C_{2h} structure corresponding to either of the Kekulé-type resonance ones. This has been confirmed by the spectroscopic data[6,7,12–15] such as the temperature-dependent ^{13}C n.m.r. spectrum and *X*-ray analysis.

Recently, dicyclopenta[*a,e*]pentalene considered as being composed of two fused pentalene molecules has been prepared by Stowasser and Hafner.[16] Theoretically, the molecule is shown to undergo molecular-symmetry reduction from C_{2h} to C_s, taking on a bond-alternated nuclear arrangement. In contrast, in dicyclohepta[*a,e*]pentalene synthesized by Toda *et al.*,[17] no such a symmetry reduction is expected to occur. The molecule is, however, shown to possess two heptafulvene-like moieties with double-bond fixation. The predictions[9] are in good agreement with the available experimental information. This marked difference has been interpreted in terms of pseudo-Jahn–Teller effect.[5,18]

In this connection, it is intriguing to investigate whether or not tricyclopenta[*cd,f,h*]azulene (**1**) shows an energy minimum at the fully symmetrical C_{2v} nuclear arrangement suggested by the superposition of the three Kekulé-type resonance structures, since the molecule contains a pentalene-like skeleton of interest (Figure 1). On the basis of the pseudo-Jahn–Teller theory[18] and of the semiempirical PPP-type SCF MO method,[19] we thus examine here the energetically favourable ground-state geometrical structures with respect to the C–C bond lengths of molecule (**1**) and its higher homologues: cyclopenta[*cd*]dicyclohepta[*f,h*]azulene (**2**), dicyclopenta[*a,e*]cyclohepta[*ef*]heptalene (**3**), and tricyclohepta[*a,c,ef*]heptalene (**4**). Further, we discuss the pseudo-Jahn–Teller effect on bond distortions and concomitant properties of these polycyclic non-alternant hydrocarbons (Figure 2).

The Symmetry Rule.—The pseudo-, or second-order, Jahn–Teller effect[18] is the stabilization which occurs when a certain nuclear deformation mixes two nearly degenerate electronic states in a symmetrical nuclear arrangement. On the basis of this theory, we have derived a symmetry rule[5] for predicting the energetically favourable molecular shapes of conjugated hydrocarbons. Since the symmetry rule has been well discussed in our previous papers,[5,9] we give here the essence briefly. The symmetry rule states that if the lowest singlet excitation energy of a conjugated molecule calculated by assuming the full molecular symmetry with the PPP-type SCF MO method is smaller than the critical value, *ca.* 1.2 eV, the molecule should be distorted into a less symmetrical nuclear arrangement through an unsymmetrical nuclear deformation. The symmetry of nuclear displacement is identical with that of the lowest excited singlet state. The actual type of distortion is predicted from the distribution of the two centre components of transition density ρ_{01}. When the lowest excited singlet state is represented by a one-electron transition between molecular orbitals φ_i and φ_j, ρ_{01} is given by $\sqrt{2}\varphi_i\varphi_j$.

Table. Energy gaps and symmetries of the lowest excited singlet states and the lowest eigenvalues and symmetries of the eigenvectors

Molecule (point group: C_{2v})	Energy gap/eV	Symmetry	Lowest eigenvalue (β_0^{-1})	Symmetry
(1)	0.35	B_2	2.78	B_2
(2)	1.53	B_2	1.35	B_2
(3)	1.58	A_1	1.04	B_2
	1.75[a]	B_2[a]		
(4)	0.43	B_2	2.57	B_2

[a] Energy gap and symmetry of the second excited singlet state.

Results and Discussion

The symmetries and energy gaps of the lowest excited singlet states for the fully symmetrical C_{2v} nuclear arrangements of the polycyclic non-alternant hydrocarbons (**1**)—(**4**) are calculated using the PPP-type SCF MO CI method in conjunction with the variable-bond-length technique.[19] The results are summarized in the Table.

In molecule (**1**), the lowest excitation energy of 0.35 eV is markedly smaller than the critical value for symmetry reduction. This suggests that the molecule should undergo the pseudo-Jahn–Teller distortion from C_{2v} to C_s by the interaction of the ground state with the lowest excited singlet state through

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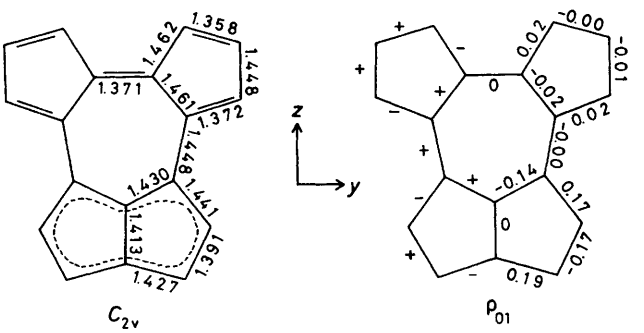
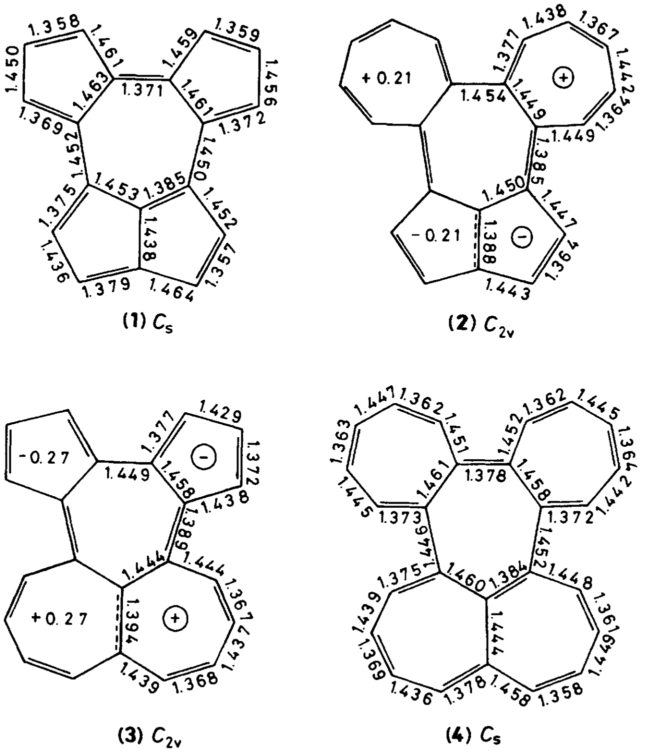


Figure 1. Distributions of the transition density ρ_{01} over the molecular skeleton (*right*) and bond lengths (in Å) at the C_{2v} nuclear arrangement of molecule (**1**)



(**1**) C_s (**2**) C_{2v} (**3**) C_{2v} (**4**) C_s

Figure 2. Predicted bond lengths (in Å), molecular-symmetry groups, and ring charges for molecules (**1**)—(**4**)

the b_2 nuclear deformation. The distribution of the transition density shown in Figure 1 indicates the type of bond distortion. Interestingly, the transition density is localized essentially on the pentalene-like moiety and, consequently, the bond distortion should take place primarily in this region. It is notable that in the C_{2v} structure a first-order double-bond fixation [1,2] occurs on the fulvalene-like skeleton alone (Figure 1). Also in molecule (**4**), the symmetry reduction ($C_{2v} \longrightarrow C_s$) is expected to occur through the b_2 nuclear deformation since the lowest excitation energy is remarkably smaller than the critical value.

In molecule (**2**), on the other hand, the lowest excitation energy of 1.53 eV is large compared with the critical value. Hence, the molecule is expected to undergo no symmetry reduction, retaining the original fully symmetrical nuclear arrangement.

In molecule (**3**), the situation is slightly different because the lowest excited state is of A_1 symmetry. In such cases, we must take into account the second excited singlet state of B_2 symmetry. However, the second excitation energy of 1.75 eV is appreciably greater than the critical value, so that the molecule should suffer no pseudo-Jahn–Teller bond distortion.

In the Table are also listed the results obtained using the double-bond-fixation theory proposed by Binsch *et al.*[1,2] In this theory, information on the bond distortion is obtained by the diagonalization of the bond–bond polarizability matrix. If the largest eigenvalue $\lambda_{max.}$ is greater than *ca.* 1.8 β_0^{-1}, the molecule will lose its original full symmetry. The type of bond distortion is given by the eigenvector corresponding to the $\lambda_{max.}$ value.

It is readily found that the predictions by the symmetry rule are compatible with those obtained using the theory of Binsch *et al.*

Since both the symmetry rule and the theory of double-bond fixation are based on the second-order perturbation theory, they give only the most favourable bond distortion. In order to examine the possibility of symmetry reduction and, if it occurs, to obtain information on the magnitude of distortion, we carried out variable-bond-length SCF MO calculations by taking into account as the starting geometry,[20] a distorted structure suggested by the symmetry rule.

Figure 2 shows the molecular-symmetry groups and bond lengths corresponding to the most favourable nuclear arrangements of molecules (**1**)—(**4**). In molecules (**1**) and (**4**), self-consistency is achieved at a set of bond lengths corresponding to a lower symmetrical nuclear arrangement shown in Figure 2. This means that, as expected, both the molecules undergo the pseudo-Jahn–Teller distortion from C_{2v} to C_s and, consequently, the C_{2v} structure does not represent a minimum, but a saddle point of the potential-energy surface of the system. In the C_s structure, a strong second-order double-bond fixation is seen on the whole carbon skeleton. In view of the distribution of C–C bond lengths, the geometrical structure of molecule (**1**) can be said to consist of two distinguishable parts, one a pentalene-like region and the other a fulvalene-like region. In this sense, the molecule may be regarded as a perturbed system composed of pentalene and fulvalene molecules. Similarly, molecule (**4**) may be considered to be a perturbed system composed of heptalene and heptafulvalene molecules. In connection with the molecular-symmetry reduction, we refer briefly to the lowest excited singlet states. In the distorted C_s structures of molecules (**1**) and (**4**), the lowest excitation energies are predicted to be 1.11 and 1.31 eV, respectively, using the PPP-type SCF MO CI method. Evidently, these excitation energies are considerably larger than those calculated by assuming the symmetrical C_{2v} nuclear arrangements (see the Table). This is due only to the effect exerted by the pseudo-Jahn–Teller bond distortion. In contrast, molecules (**2**) and (**3**) suffer no molecular-symmetry reduction, but a first-order bond fixation, retaining the original full molecular symmetry group. The distribution of C–C bond lengths shown in Figure 2 indicates that both molecules assume geometrical structures formally consisting of two fused sesquifulvalene molecules.[21] This is supported by the ring charge distribution in the five- and seven-membered rings: the former ring being negatively charged and the latter positively. The ring charges in molecules (**2**) and (**3**) are ±0.21 and ±0.27 e, respectively. The magnitude of charge separation compares quite well with that in the free sesquifulvalene molecule (±0.31 e).[19] Accordingly, both the molecules may be expected to have polarization stabilities similar to those in sesquifulvalene[21] and cyclic bifulvalene systems.[22]

We then calculated the stabilization energy due to the symmetry reduction, which is defined as the difference in total energy between the fully symmetrical and the distorted nuclear arrangement. Here, the total energy is assumed to be the sum of the π-bond and σ-bond energies, the latter being calculated using the harmonic-oscillator model[23] with a force constant of 714 kcal mol^{-1} Å^{-2}. As a result, the stabilization energies for molecules (**1**) and (**4**) are estimated to be 2.1 and 7.5 kcal mol^{-1}, respectively. In molecule (**1**), the stabilization energy is ascribed to the bond distortion in the pentalene-like region, since the geometrical parameters of the fulvalene-like moiety in the unstable C_{2v} structure (Figure 1) are almost the same as those for the stable C_s structure (Figure 2). Hence, the stabilization energy is regarded as the activation energy of the dynamic double-bond shift for the pentalene-like moiety. It is notable that the present activation energy is of the order of the observed value[7] for the π-bond shift in 1,3,5-tri-(t-butyl)pentalene, *ca.* 4 kcal mol^{-1}. In molecule (**4**), the situation is quite similar to the case in molecule (**1**). As to the heptalene molecule of interest, Vogel *et al.*[24] have observed an activation energy of *ca.* 3.5 kcal mol^{-1} for the isodynamic π-bond shift. A comparision indicates that the activation energy of the dynamic π-bond shift for the heptalene-like moiety in molecule (**4**) is comparable, in magnitude, to that for the free heptalene molecule.[25]

Conclusion

From these considerations, the present polycyclic non-alternant hydrocarbons having $4n + 2$ π electrons can be classified into two groups, one in which a molecule undergoes symmetry reduction and the other in which a molecule undergoes no symmetry reduction. In spite of this, it is shown that all of these non-alternant hydrocarbons exhibit a marked double-bond fixation on the carbon skeleton, the degree of bond fixation being larger in the former group than in the latter. In conclusion, it can be said that these hydrocarbons should possess polyene characteristics rather than aromatic ones, reflecting the properties inherent in the component molecular systems. We hope that the present results will stimulate organic chemists to attempts to prepare such polycyclic non-alternant molecules.

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