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THE GROUND-STATE GEOMETRICAL STRUCTURES OF THE TRIPLE-LAYERED AND THE QUADRUPLE-LAYERED syn-AZULENOPHANE

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Abstract: The semiempirical model calculations predict that in the triple-layered and the quadruple-layered syn-azulenophane every azulene molecule has a bond-alternated structure and the bond alternations in all the adjacent azulene subsystems are out of phase.

Recently, syn-[2.2](2,6)azulenophane has been prepared and its spectroscopic properties have been investigated.[1] The experimental facts can well be interpreted by assuming the azulene subsystems to have the delocalized structures. In the triple-layered and quadruple-layered syn-azulenophanes (1 and 2, respectively), the stronger transannular interaction is expected to produce the second-order Jahn-Teller (SOJT) bond distortion[2,3] due to the smaller first excitation energy.

In this paper, we examine the bond distortions in the azulene subsystems of (1) and (2) by using the trimer and tetramer models, the Pariser-Parr-Pople-type SCF MO method with the variable bond-length technique,[3-5] and the SOJT theory. The distances between the adjacent subsystems are all assumed to be 3.3 Å, which is the average distance of [2.2](2,6)azulenophane.[6] The effect of the bridging ethylene on the pi-electronic system is not explicitly considered. The maximum symmetries of the phanes considered are assumed to be C_{2v}.

We have optimized the bond lengths of the subsystems of the C_{2v} phanes, and calculated the first excited singlet states: the excitation energy and the symmetry are 1.0 eV and B_2 for (1), and 1.1 eV and A_2 for (2). The small energy gap induces the strong vibronic coupling between the ground and the first excited singlet state through the b_2 and the a_2 distortion, and , consequently, the molecular symmetry reduction: $C_{2v} \rightarrow C_s$ in (1) and $C_{2v} \rightarrow C_2$ in (2). From the transition densities of the phanes, we find that the actual distortion is the bond alternating mode bringing about the alternations between the adjacent azulenes are out of phase.

We now take the bond-alternated nuclear configurations predicted by the transition densities as starting geometries of the variable bond-length SCF MO method, and optimize the less symmetrical structures with respect to the C-C bond lengths of the subsystems. The optimum geometrical structures in Figure 1 are such that in all the adjacent azulenes the two identical Kekulé-type structures are out of phase. Such bond-alternated structures are in marked contrast to the delocalized structure of azulene itself.[6] The stabilization energies favoring the distorted structures are calculated to be 1.1 and 1.5 kcal/mol for (1) and (2), respectively. If the total energies of the phanes are the simple sum of the energies of the subsystems, the phanes do not undergo any bond distortions. The out-of-phase bond alternation should thus provide the bonding interaction between the adjacent subsystems and lower the ground-state energy.

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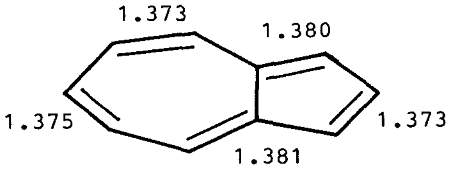

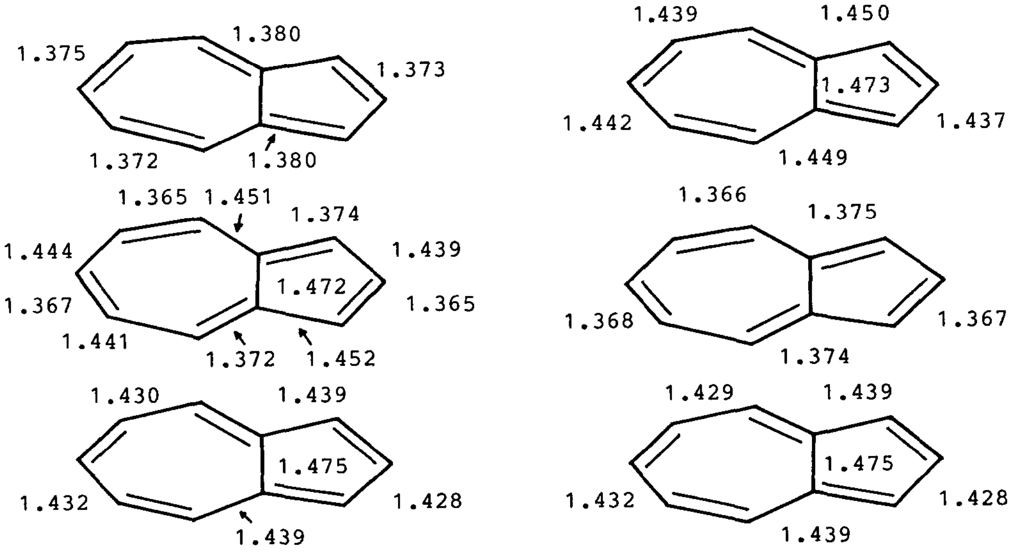

(1) C_s (2) C_2

Figure 1. The optimized bond lengths (Å) of the less symmetrical forms for the trimer and the tetramer model of the triple-layered (1) and the quadruple-layered (2) syn-azulenophane. The other bond lengths can be obtained by using the reflection in (1) and the C_2 rotation in (2).

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