The B_{1u} and B_{2u} Vibrational Modes Causing a D_{6h} to D_{3h} Transition in Benzene and in [18]- and [30]Annulenes

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Alternation of long and short carbon–carbon bonds in large cyclic polyenes are investigated from the point of view of vibrational analyses. [6(2n+1)]Annulenes, where n is 0, 1, 2,···, are cyclic polyenes that can have planar bond-delocalized D_{6h} or bond-localized D_{3h} structures without severe nonbonded interactions. The B_{1u} and B_{2u} modes of vibration that potentially cause a D_{6h} to D_{3h} transition in benzene, [18]annulene, and [30]annulene are specifically discussed. The delocalized D_{6h} structure is stable in benzene and [18]annulene, but not in [30]annulene. The D_{6h} structure of [30]annulene has an imaginary B_{2u} mode of $416i$ cm^{-1} that has relevance to the so-called Kekulé B_{2u} mode of benzene. The D_{6h} structure of [30]annulene is confirmed to be a transition state that leads to the equivalent D_{3h} global minimum in both the forward and reverse directions.

Alternation of long and short carbon–carbon bonds in π-conjugated systems is a good measure of π-electron delocalization, or aromaticity. Since the work of Ooshika[1)] and Longuet-Higgins and Salem[2)] in the late 1950s, it has been widely believed that linear and cyclic polyenes exhibit remarkable bond-length alternation when their sizes are large. Cizek and Paldus[3)] also predicted from the so-called Hartree–Fock stability condition that delocalized (bond-equalized) structures are unstable for [N]annulenes, $(CH)_N$, when $N \geq 14$. [6(2n+1)]Annulenes are interesting cyclic polyenes that can have planar delocalized D_{6h} or localized D_{3h} structures without severe nonbonded interactions, where n is 0, 1, 2,···. The smallest member of this annulene family is, of course, benzene ([6]annulene) that has a well-known D_{6h} structure; the next smallest member, [18]-annulene (Chart 1), has been confirmed from X-ray structural analyses[4)] and semiempirical[5)] and ab initio[6)] computations to have a nearly D_{6h} structure in which all the C–C distances are close to that of benzene (1.4 Å). The structure of [18]-annulene has been recently reinterpreted from density-functional-theory (DFT) computations by Jiao and Schleyer,[7)] Baldridge and Siegel,[8)] and Kertesz et al.[9)] Thus, the D_{6h} structure of [18]annulene has been well established after a long controversy,[10)] but to the best of our knowledge there has been no X-ray structural information about higher annulenes of this group. Most of higher annulenes are highly colored (red or brown) crystalline substances, but are not stable in the solid state.[11,12)]

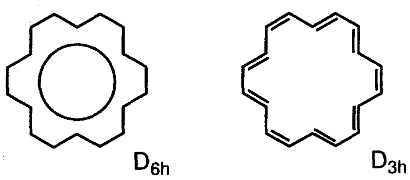


Chart 1.

Nakajima, Toyota, and collaborators[13)] have suggested that the second-order Jahn–Teller effect plays an essential role in determining the structures of the ground and excited states of annulenes. Recently, Choi and Kertesz[14)] carried out systematic DFT computations in respect of the bond-length alternation of large annulenes, predicting that a transition from delocalized D_{6h} to localized D_{3h} structures occurs in [30]-annulene. This is consistent with our earlier predictions[15)] from MNDOC (C for correlation)[5b)] computations coupled with a conventional perturbational treatment. It is reasonable that one-electron-theory methods prefer a bond-alternant structure that leads to a large HOMO–LUMO gap; on the other hand, higher-level methods including second-order energy may prefer a bond-equalized structure because of a resultant small HOMO–LUMO gap. We mentioned in the previous paper[15)] that these two effects strongly compete in determining the preferred structures of the [6(2n+1)]-annulene family, especially in [18]- and [30]annulenes. In this short paper, we present vibrational analyses for the D_{6h} forms of benzene, [18]-, and [30]annulenes, indicating that the D_{6h} structure of [30]annulene is a transition state that connects the equivalent D_{3h} minima.

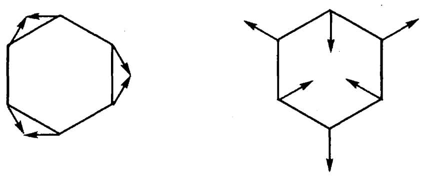
Computational Details. We first optimized the D_{6h} structures of benzene and [18]annulene and both the D_{6h} and D_{3h} structures of [30]annulene at the B3LYP[16—18)] levels of density functional theory. The 6-31G** basis set[19)] was used for DFT computations. The B3LYP method, a hybrid Hartree–Fock and DFT method, consists of the Slater exchange, the Hartree–Fock exchange, the exchange functional of Becke,[16)] the LYP correlation functional,[17)] and the local correlation functional of Vosco, Wilk, and Nusair.[20] This hybrid method has been proposed to provide, in general, excellent descriptions of many reaction profiles, particularly in molecular geometries, heats of reaction, and activation energies of transition state.[21] Vibrational mode analyses were conducted for the optimized D_{6h} structures of benzene, [18]annulene, and [30]annulene in order to characterize the molecular potential energy surfaces in the vicinity of the D_{6h} structures. All computations were performed using the Gaussian 94 ab initio program.[22]

Clearly, computations of high quality are necessary to reach a final conclusion in respect of the preferred structures of these annulenes. Schaefer and collaborators[23] indicated that neither second-order Møller–Plesset perturbation theory[24] nor DFT methods can adequately describe the potential energy surface of [10]annulene and that the problem on the preferred structures of similar systems should be treated with extreme caution and verified at higher ab initio levels of theory where possible. Unfortunately, the annulenes of our interest are so large that we currently cannot perform definite calculations using a post-Hartree–Fock multiconfigurational method. DFT methods which adequately include electron correlation effects are current possibility of studying such large electronic systems. We consider a possible D_{6h} to D_{3h} transition in benzene, [18]-, and [30]annulenes from different points of view of molecular vibration and energetics.

The B_{1u} and B_{2u} Modes of Vibration in the D_{6h} Annulenes. As mentioned above, the preference of the D_{6h} structure over the D_{3h} one has been well established in [18]-annulene from recent DFT computations.[7—9] In fact, the D_{3h} structure is *not* a stationary point on the potential energy surface of [18]annulene. Our main interest in this work is the global minimum on the potential energy surface of [30]-annulene. In contrast to [18]annulene, in which only the D_{6h} structure is a stable point, both D_{6h} and D_{3h} structures of [30]annulene were recently reported,[14] the D_{3h} structure being 2.3 $\mathrm{kcal\,mol^{-1}}$ more stable than the D_{6h} one at the B3LYP/6-31G* level. The D_{3h} structure exhibits remarkable bond-length alternation whereas the D_{6h} structure has nearly equal carbon–carbon distances of 1.4 Å, as expected.

The controversy over the issue of this paper, whether or not the π electrons of the $[6(2n+1)]$annulenes possess a tendency to localize leading to D_{3h} structures with significant bond-length alternation, already starts from benzene. According to the papers of Schaik, Hiberty, and collaborators[25] and Jug and Köster,[26] the well-known D_{6h} structure of benzene originates from the dominating σ-electrons which tend to equalize the carbon–carbon bond distances. This effect overcomes the tendency of the π electrons which tend to cause bond-length alternation. This view may be in contrary to the traditional one that the D_{6h} symmetry of the benzene molecule is ascribed to the π-electron delocalization.[27]

Since vibrational analyses were not carried out in Ref. 14, it is useful to consider the controversy from a viewpoint of molecular vibration. There are two types of in-plane vibrational modes that can cause a D_{6h} to D_{3h} transition in benzene. One is the B_{2u} mode of vibration (Chart 2, left) that leads to a D_{6h} to D_{3h} transition concomitant with significant bond-length alternation. Haas and Zilberg[28] indicated that this vibrational mode undergoes a significant upward shift in the first excited state of benzene. The other is the B_{1u} mode (Chart 2, right); although this vibration does not cause bond-length alternation, it actually leads to a D_{6h} to D_{3h} transition through benzene-ring deformation. It is thus of interest to look in detail at the B_{1u} and B_{2u} modes in [18]- and [30]-annulenes because a D_{6h} to D_{3h} transition actually occurs in [30]annulene.[14]



B_{2u} (1310 $\mathrm{cm^{-1}}$)　B_{1u} (1010 $\mathrm{cm^{-1}}$)

Chart 2.

We carried out vibrational analyses in respect of the delocalized D_{6h} structures. As indicated previously,[29] the B3LYP method is appropriate for molecular vibrational analyses for π-conjugated systems, giving reasonable values that agree with experiment. Table 1 lists computed wavenumbers ($\mathrm{cm^{-1}}$) of the B_{1u} and B_{2u} modes for the D_{6h} structures of benzene, [18]-, and [30]annulenes. The definition of the B_{1u} and B_{2u} modes under D_{6h} symmetry is dependent on the way of taking the C_2' axis and the σ_d plane and concomitantly the C_2'' axis and the σ_v plane.[30] Although both kinds of vibrational modes cause a D_{6h} to D_{3h} structural change, in a usual definition only B_{2u} modes can lead to a bond-alternant structure. The D_{6h} structures of benzene and [18]annulene are global minima on the potential energy surfaces because the two annulenes have no imaginary vibrational mode. However, the D_{6h} structure of [30]annulene is not a stable point because it has one imaginary mode of 461i $\mathrm{cm^{-1}}$. This imaginary mode is of B_{2u} symmetry and others are all real, as we expect. Therefore the D_{6h} structure of [30]annulene is a transition state that correctly connects the equivalent D_{3h}

Table 1. Computed Frequencies (in $\mathrm{cm^{-1}}$) of the B_{1u} and B_{2u} Modes in Benzene, [18]-, and [30]annulenes of D_{6h} Form at the B3LYP/6-31G** Level
The values in the parentheses for benzene are reference values.[31]

Benzene		$(CH)_{18}$		$(CH)_{30}$	
B_{1u}	B_{2u}	B_{1u}	B_{2u}	B_{1u}	B_{2u}
3172 (3068)	1356 (1310)	3186	3169	3158	3170
1018 (1010)	1180 (1150)	3152	1511	3148	3158
		1483	1288	3145	1563
		1276	1180	1631	1420
		688	781	1370	1309
		233	296	1305	1238
				1289	1054
				635	496
				492	114
				95	461i

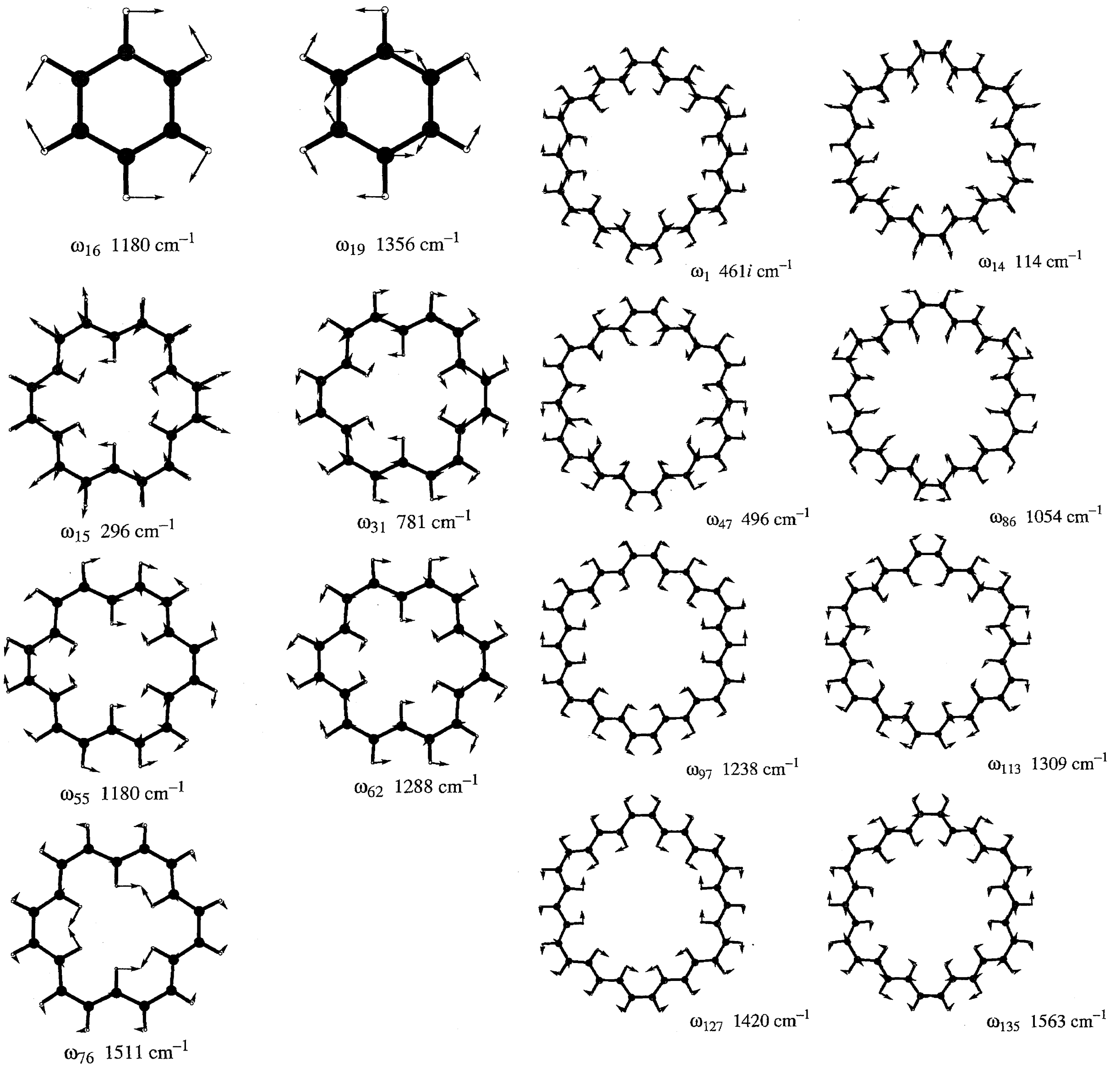


Fig. 1. B_{2u} vibrational modes for the D_{6h} structures of benzene, [18]-, and [30]annulenes at the B3LYP/6-31G** level of theory.

structures in both the forward and reverse directions.

Figure 1 demonstrates computed atomic displacements of the B_{2u} vibrational modes of the three D_{6h} annulenes except C–H stretching modes. The so-called Kekulé mode of benzene (1356 cm^{-1}), the 781 cm^{-1} mode of [18]annulene, and the imaginary 461i cm^{-1} mode of [30]annulene are expected to play a role in the structural transition because the C–C stretching motions in adjacent C–C bonds are 180° out of phase in these special modes. Such atomic motions can lead to a bond-alternant structure. In fact, the D_{3h} structure with distinct bond-length alternation is the global minimum on the potential energy surface of [30]annulene, which is in remarkable contrast to benzene and [18]annulene. However, the energy difference between the D_{6h} and D_{3h} structures was computed to be only 0.2 kcal mol^{-1} at the B3LYP/6-31G** level.

Conclusions. Alternation of long and short carbon–carbon bonds in benzene, [18]-, and [30]annulenes are investigated at the B3LYP level of density functional theory, in respect of the B_{1u} and B_{2u} modes of vibration that potentially cause a D_{6h} to D_{3h} transition. In contrast to benzene and [18]annulene, the D_{6h} structure of [30]annulene has one imaginary mode of 461i cm^{-1}, and it is of B_{2u} symmetry. The D_{6h} structure of [30]annulene is thus a transition state that correctly leads to the equivalent D_{3h} minimum in both the forward and reverse directions. The D_{6h}–D_{3h} energy separation of [30]annulene is 2.3 kcal mol^{-1}[14] and 0.2 kcal mol^{-1} at the B3LYP/6-31G* and B3LYP/6-31G** levels, respectively.

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Laboratory of Kyoto University and at the Computer Center of the Institute for Molecular Science.

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