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Relationship between the π-Electron Distribution and the Symmetry of Cyclic C_6H_6 Systems

Hiroshi Ichikawa* and Hirotaka Kagawa

Hoshi College of Pharmacy, Shinagawa-ku, Tokyo 142

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In an attempt to comfirm the role of π electrons in benzene, the relationship between the π-electron distribution and the preferred symmetry in C_6H_6 systems was examined. It was shown that under the restriction of being planar, the $C_6H_6{}^{6+}$ system has a D_{6h} geometry, which is fragile towards shrinking as well as a distortion, and is also fragile at saddle points towards bending. When π electrons are added to such a system, the π electrons distribute in the way of either D_{6h} or D_{2h} symmetry according to the number of electrons. When the π-electron distribution is D_{6h}-symmetric, non-distortive (i.e., those along the A_{1g} coordinate) forces are produced; when it is D_{2h}-symmetric, distortive forces, i.e., those that break the D_{6h} symmetry, appear. Optimization leads to a symmetry which is pre-determined by the π-electron distribution. In this way, it was elucidated that π electrons in benzene have a tendency to form a uniform distribution.

Recently, the role of π electrons in benzene has been actively discussed, although the question may go back to the early 1950s; when Horning first pointed out the stable Kekulé structure to explain the abnormally low force constant concerning B_{2u} vibrations.[1)] Namely, since a force constant represents the curvature of the potential-energy function in the vicinity of the equilibrium configuration, it was expected that when relatively stable configurations with only a slight difference in geometry exist, the potential energy would change slowly, giving rise to an abnormally low force constant. Ten years later, Berry estimated the amplitude of motion for a carbon atom in the B_{2u} mode of the zero-point vibration, obtaining a large figure, as much as 0.031 or 0.033 Å.[2)] The question immediately arises as to the origin of such a large-amplitude, low-energy motion. The same author postulated that the π electrons are not the major source of stability for a regular hexagon, and approaches cyclohexatriene-like shapes.

More than twenty years later, this problem was examined by Shaik and Hiberty as well as their co-workers, who investigated the changes in the π and σ energies when D_{6h} benzene is deformed to D_{3h}. Their results are summarized in a very recent paper, as follows.[3)] The π-bonding energy of benzene is stabilized by a localizing B_{2u} distortion. Benzene is the site of two opposing driving forces: the π driving force tends to distort the molecule while the stronger σ driving force opposes this, imposing a regular geometry.[4)]

The investigation has also been followed by a number of different workers.[5)] A number of results seem to support that of the vibrational analysis to question the chemical epistemology. However, in one case such a conclusion was reversed.[6)] Glendenig et al. studied this problem.[7)] They found that benzene favors a bond-alternating geometry when its canonical π MOs are replaced by three localized ethylenic orbitals, revealing that delocalization is evidently responsible for the equilibrium symmetric structure. In contrast, a σ–π energy partitioning analysis suggests that the σ framework of benzene is responsible for the symmetric structure.

We have shown that the change in the π energy obtained by a geometry-distortion (GD) method includes a large contribution from the changes in the nuclear coordinates, and, therefore, the role of the π electrons depends on the reaction coordinate of the distortion: *The GD method does not give the relationship between the π-electronic structure and its energy.*[8)] We also gave an answer to the question why the energies are invariant along the B_{2u} coordinate. Any energy terms around the optimized geometry are almost linear with respect to a small change in the distortion along the B_{2u} coordinate; since the B_{2u} vibration modes involve an equal amount of expansion and shrinkage of the skeletal bond at the same time, the energy changes caused by expansion are almost canceled by those caused by shrinking to give small changes.

Reviewing the results so far reported, we have noticed that we have discussed the benzene problem without a consensus concerning the definition of the π energy, and that the discussion based on the π-orbital symmetries has not been applied to the problem. According to π-energy definition, any conclusion may result. Besides, it may be at present difficult, among researchers, to obtain a consensus concerning the nature of the π energy. We thus turned to a discussion based on the symmetries of the π orbitals, including the characteristics of the skeletal σ-frame, itself (i.e., $C_6H_6{}^{6+}$ ion). In a sense, this may be a direct way to understand the role of the π electrons and the relationship between the form of the π-electron distribution and the preferred geometry of the $C_6H_6{}^{n+}$ system. We thus performed an investigation using the even-electron cases from $C_6H_6{}^{6+}$ to C_6H_6 in the singlet ground state based on the restricted Hartree–Fock theory.

Results and Discussion

Geometry of the $C_6H_6^{6+}$ Ion. The $C_6H_6^{6+}$ system may be the smallest sextuplicatedly-charged cyclic ion that maintains its shape without a 'coulombic explosion'. Keeping the planarity of this system, the geometry was optimized. The basis set was 6-311G.[9)] The plane-restricted $C_6H_6^{6+}$ ion has the geometry of a D_{6h} symmetry with lengths of 1.723071 Å for C–C. The fact that the symmetry was kept at D_{6h} indicates that the σ framework favors a regular-hexagon structure. This is easily expected, since the system consists of sp^2 carbons, which have three equivalent valences. However, such a geometry has three imaginary frequencies at -325.16, -196.31, and -196.31 cm^{-1}, which are all out of the molecular plane, indicating that the system is at saddle points towards bending. As a matter of fact, if the restriction of planarity was removed, it resulted in a chair-form structure (Fig. 1).

The C–C bondlength of the plane-restricted $C_6H_6^{6+}$ ion is considerably long due to the lack of π electrons. Since the tightness of the bonding is roughly proportional to the shortness of the bondlength, *the skeletal σ-frame is fragile towards shrinking/expansion and distortion.* Then, since the geometry is optimized (i.e., $\partial E/\partial R = 0$ for any nuclear coordinates), *there are no forces against any distortion at this geometry.* Moreover, *it is at cols towards breaking its planarity.*

Geometry of the $C_6H_6^{4+}$ Ion. The *topology* of the C_6H_6 system determines the phases of unoccupied π MOs, as shown in Fig. 2. The LUMO of the planar $C_6H_6^{6+}$ ion was the lowest unoccupied π MO ($\psi_{\pi1}$), which may accept electrons when two electrons are added. Since $\psi_{\pi1}$ is an a_{2u} symmetry species, the π-electron distribution must be of D_{6h} symmetry. Two electrons were put into this system. Since the initial geometry was not optimized as the $C_6H_6^{4+}$ ion, there appeared forces of displacement on the skeletal carbon atoms. The directions were all shrinking with an equivalent value (0.0598 au (hartree/Bohr)); no distortive forces were found (Fig. 3A). When such a $C_6H_6^{4+}$ ion was optimized under the condition of planarity, the obtained geometry was shorter in bondlengths (1.499949 Å) with D_{6h} symmetry.[10)]

Geometry of $C_6H_6^{2+}$ Ion. High-level ab initio molecular-orbirtal calculations have already been carried out on this system by Krogh–Jespersen in order to understand its geometry.[11)] The second and third π MOs of the geometry-optimized planar $C_6H_6^{6+}$ ion are degenerate; since both have the symmetry species of e_{1g}, the π-electron distribution of either $\psi_{\pi2}$ or $\psi_{\pi3}$ ought to have a symmetry of D_{2h}. Four electrons were added to the system. The electrons occupy $\psi_{\pi1}$ and $\psi_{\pi3}$ at D_{6h}, where the force directions appear as shown in Fig. 3B. Contrary to the former case, distortive forces appeared. Since $\psi_{\pi3}$ has nodes on C_1 and C_4, if the electron configuration were kept during optimization, it would lead to a geometry with short bonds on C_2–C_3 and C_5–C_6 and long ones for the others. Actually, however, when the geometry of this ion was deformed, the π-electron configuration was switched to be $(\psi_{\pi1})^2(\psi_{\pi2})^2$; by allowing optimization, it resulted in a geometry with a D_{2h} symmetry and with bondlengths of 1.377161 and 1.535244 Å for short and long C–C bonds.[12)] This suggests that the *dynamic* distribution of π electrons determines the resultant symmetry.

Geometry of C_6H_6. We then examined what happens to the geometry-optimized $C_6H_6^{2+}$ ion (D_{2h}) when two more electrons were added. The LUMO ($\psi_{\pi3}$) of this ion has nodes on the C_1 and C_4 atoms (as that of $\psi_{\pi3}$ in Fig. 2). This indicates that such bonds connecting those atoms are elongated by accepting electrons in this MO. The addition of two electrons brought forth shortening and elongating forces concerning long and short bonds (Fig. 3C), respectively. They are the directions to lead the structure to the D_{6h} symmetry of benzene; optimization resulted in the D_{6h} benzene. Namely, the π-electron distribution of $\psi_{\pi3}$ is the source of

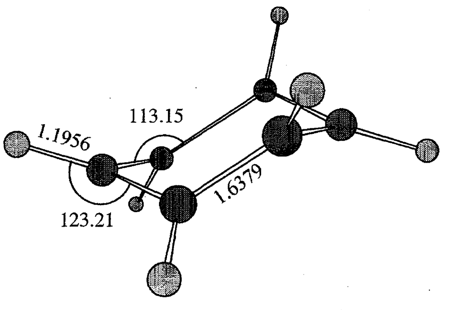
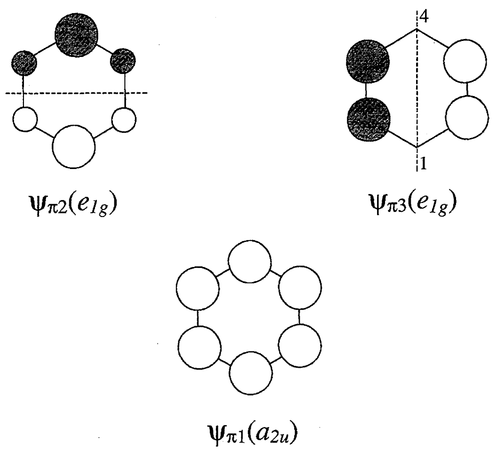


Fig. 1. Optimized geometry of the $C_6H_6^{6+}$ ion (D_{3d}). The values are in Å and degree.



$\psi_{\pi2}(e_{1g})$ $\psi_{\pi3}(e_{1g})$

$\psi_{\pi1}(a_{2u})$

Fig. 2. Phases of three energetically lower π MOs in C_6H_6 system. The symbol in bracket indicates the symmetry species of MO when the system takes a D_{6h} symmetry.

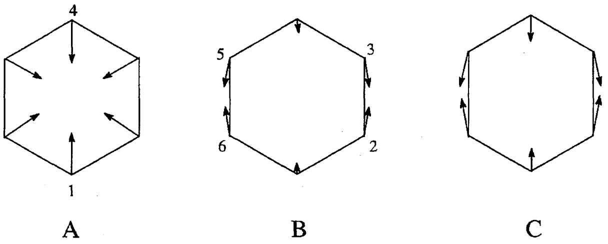


Fig. 3. Types of displacement direction imposed on the skeletal atoms.

the *geometry correction*.

The Relationship of Symmetry between Benzene and the Distribution of π Electrons. Six electrons were added to the optimized planar $C_6H_6{}^{6+}$ system. Those electrons occupy π MOs as $(\psi_{\pi1})^2(\psi_{\pi2})^2(\psi_{\pi3})^2$ to lead a D_{6h} symmetry of the π-electron distribution. Strong forces appeared. All forces have the same quantity (0.1047 au) with the direction on the pure A_{1g} coordinate (Fig. 3A). Optimization leads to the familiar D_{6h} benzene with a bond length of 1.387775 Å. There are, of course, no imaginary frequencies that lead to a bent structure.

We have examined the relationship between the π-electron distribution and the preferred symmetry in C_6H_6 systems. Under the restriction of being planar, the $C_6H_6{}^{6+}$ system has a D_{6h} symmetry. The framework is fragile towards shrinking as well as distortion. It is also at saddle points towards bending: *the skeleton cannot keep its geometry without π electrons*. When π electrons are added to such a system, the π electrons distribute in the way of either D_{6h} or D_{2h} symmetry according to the number of electrons. There appeared forces of displacement on the skeleton. When the π-electron distribution is D_{6h}-symmetric, non-distortive (i.e., those along the A_{1g} coordinate) forces are produced and when it is D_{2h}-symmetric distortive forces, i.e., those that break the D_{6h} symmetry, appeared. Optimization leads to the symmetry which is pre-determined by the π-electron distribution, where if the configuration of π electrons is altered during geometry optimization, the geometry is altered according to the distribution given by the new configuration.

Thus, if we look at the relationships between the ways for the π-electron distribution and the favored geometrical structures, it may be very reasonable to conclude that π electrons in a cyclic C_6H_6 system always determine the symmetry of the system, and that the symmetry of benzene is determined by its π electrons.

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4) Actually, they used 'force' without obtaining $\partial E/\partial R$ or $\mathrm{d}E/\mathrm{d}R$ (where E and R are an energy and a nuclear coordinate). Therefore, it is not clear what 'force' means in their works.

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12) One imaginary frequencies were observed at $-300.63\ \mathrm{cm}^{-1}$, which was also towards breaking the planarity.