Analysis of Chemical Phenomena by Solving the Constrained Hartree–Fock Equation. II. Relationship between π-Electronic Structure and Its Energy in Benzene

Hiroshi Ichikawa* and **Hirotaka Kagawa**

Hoshi College of Pharmacy, Shinagawa, Tokyo 142

(Received July 1, 1996)

The constrained Hartree–Fock method provides quantum-mechanically acceptable wave functions of an arbitrary electronic structure *without changing the molecular geometry.* We have applied this method to the analysis of the behavior of π electrons in benzene finding that there are two types of resonance energy, simple resonance between double bonds and super-stabilization due to the topology of benzene, which were estimated as 54 and 168 $\mathrm{kJ\,mol^{-1}}$, respectively. According to our method, π electrons in benzene were found to have a propensity for uniform distribution. Namely, the D_{6h} distribution of π electrons gives the minimum values concerning both the π-electronic and total energies, which are brought forth by lowering the kinetic energy of π electrons. The origin of delocalization of π electrons in benzene was attributed to relaxation of the kinetic-energy pressure of π electrons.

Organic compounds have been classified into aliphatics and aromatics. This style of classification goes back to the early 1800s and is still effective today.[2)] Aromatic compounds have been characterized by the tendency to undergo substitution reaction.[3)] Such a characteristic is really applicable to many cyclic conjugated compounds and has been studied topologically[4)] as well as by a variety of molecular orbital methods.[5—7)]

If atoms are arranged in an aromatic compound in such a manner that they induce an appreciable amount of so-called topological resonance energy, this kind of aromaticity is referred to as topological aromaticity. The stability of the topological aromatics has been interpreted to be given by a special arrangement of π electrons. the prototypical compound is benzene.

A number of investigations, however, have thrown doubt on the long-believed extra-stabilization of the π system in benzene. A question came with the analysis of the zero-point vibration in 1950. Horning pointed out the stable Kekulé structure to explain the abnormally low force constant for the B_{2u} vibrations (here, the author seems to use the term Kekulé structure for that of cyclohexatriene).[8)] 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 slight differences 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, making him postulate that the π electrons are not the major source of stability for the regular hexagon; they might well have a lower energy if the ring approaches a cyclohexatriene-like shape.[9)]

More than 20 years later, this was examined by Shaik and co-workers in a series of quantum chemical studies,[10,11)] where the energy difference of π-electrons given by distortion of the benzene geometry towards π-bond alternation was analyzed (we call the analysis of energy components of the total energy 'the energy-component analysis'). The investigation has also been followed by a number of different workers.[12—14)] All results by them seem to support that of the vibrational analysis and seem to question chemical epistemology.[10d)] However, Baird[15)] showed a case in which the conclusion was reversed. Meanwhile, Kollmar proposed a method for direct calculation of resonance energy by substituting π MOs with localized ones obtained in another system. According to this, a considerable amount of resonance energy is figured out.[16)]

Glendenig et al. studied this problem.[17)] 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 largely 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, the π system preferring a distorted geometry. However, it is also shown that the π-energy component contains a sizable and strongly geometry-dependent contribution from the localized (Kekulé) wave function.

Our preceding paper shows that there are countless numbers of reaction coordinates for distortion that either lower or increase the π-electronic energy.[18)] The minimum-energy path (MEP) was found for the distortion from the D_{6h} to D_{3h} benzene and was not the one previously investigated. Along such an MEP, the π-electronic energy was traced. However, the role of π electrons seems to be reversed, i. e., π-electronic energy is most stable at the D_{6h} symmetry.

Why did those conflicting results come out? Reviewing the results so far reported, we noticed two problems. First, we have discussed the benzene problem without a consensus on the definition of 'π energy': according to this definition, any conclusion may come out. It may, however, be at present difficult, among researchers, to obtain a consensus on what π energy is. Second, we are not very sure what we seek in the benzene problems. That is, it is not very certain whether we study the relationship between 'π energy' and π-electronic structure or 'π energy' and benzene's geometry. As will be stated, we can explicitly defined the π-electronic structure and π-electronic energy. Therefore, as a new approach to the benzene problem, *we studied the relationship between the π – electronic energy as well as its partitioned energies and π – electronic structure.*

Theoretical Strategies

As stated in the introduction, we have discussed the benzene problem using concepts with ambiguous meaning. This seems to cause some confusion in the interpretation of the problem. Therefore, first we had better define or specify the meaning of the terms which are used in the discussion. Then we discuss the properties of wave functions that satisfy the quantum-mechanical requirements. Further we will introduce a method which measures the relationship between various energies of π electrons and π-electronic structure without changing the geometry of conjugated hydrocarbons.

Molecular System as a Mechanical System. We are dealing with the benzene or distorted benzene system that is secluded from outer systems. In such circumstances, the total energy (E) is the sum of the kinetic (T) and potential energies (V) of the system considered.

$$E = T + V. \tag{1}$$

In molecular orbital (MO) theories, T and V are given as expectation values of the total wave function (Ψ) concerning the corresponding operators and expressed as $\langle T \rangle$ and $\langle V \rangle$. Thus, E is expressed as

$$E = \langle T \rangle + \langle V \rangle. \tag{2}$$

Any mechanical system must satisfy the following relationship,

$$\langle T \rangle + E + \sum_{\alpha > \beta} R_{\alpha\beta} \frac{\partial E}{\partial R_{\alpha\beta}} = 0, \tag{3}$$

where R is the internuclear distance between atoms α and β, and where the sum runs over all internuclear distances. This is called the molecular virial theorem.[19] It has been proven that Eq. 3 is satisfied in the Hartree–Fock–Roohaan theory[20] if the basis set is complete.[21]

If the geometry of the system is optimized, the third term of the virial theorem turns out to be null since $\partial E / \partial R = 0$ holds concerning any nuclear center, giving simple and familiar relationships,

$$E + \langle T \rangle = 0 \quad \text{or} \quad \langle V \rangle = -2\langle T \rangle. \tag{4}$$

The wave functions of benzene at its optimized geometry are required to satisfy Eq. 4. Most wave functions based on a usual basis set do not meet this requirement. But as will be discussed, the difficulty can be removed by the scaling technique. We use the term 'benzene' when the geometry is optimized, otherwise we call 'distorted benzene'.

SCF Wave Function. Molecular orbitals are obtained by solving the normal SCF equation.[20] By artificially adjusting coefficients of the basis functions, one may obtain the MOs that give an arbitrary electronic structure. However, they are not SCF wave functions. Here, 'SCF' has a special meaning. The SCF wave functions are eigenfunctions of the considered electronic structure and satisfy the variation principle

$$\begin{gathered} \Psi \rightarrow \Psi + \Delta\Psi \Rightarrow E \rightarrow E + \Delta E, \\ \text{where} \\ \Delta E = 0. \end{gathered} \tag{5}$$

Here, Ψ is the total wave function. Equation 5 indicates that the wave function is at an extreme point, i. e., the minimum or maximum or stationary point of E. It also means that the total energy is not changed by a small change of the wave function. Such wave functions are those for the standing wave, which is a necessary condition for molecular orbitals to exist independently of time. In other words, they satisfy the boundary conditions. One may obtain the MOs that give an arbitrary electronic structure by changing coefficients. However, only those which satisfy Eq. 5 are acceptable because they are time-independent.

The Definition of the π-Electronic Energy and Its Components. The molecular energy under the Born–Oppenheimer approximation can be expressed in terms of four energy components that can be clearly defined; Figure 1 shows such fundamental energy components. $\langle T \rangle$, $\langle V_{\mathrm{eN}} \rangle$, and $\langle V_{\mathrm{ee}} \rangle$ are the expectation values of the kinetic energy of electrons, one-electron potential energy (attractive interaction between electrons and nuclei), and two-electron potential energy (repulsive interaction between electrons), while V_{NN} and Z_{A} are the nuclear-repulsion energy and the number of protons at nucleus A (angle brackets indicate expectation values). The total energy (E) is expressed by,

$$\begin{aligned} E &= E^{\mathrm{el}} + V_{\mathrm{NN}} \\ E^{\mathrm{el}} &= \langle T \rangle + \langle V_{\mathrm{eN}} \rangle + \langle V_{\mathrm{ee}} \rangle \end{aligned} \tag{6}$$

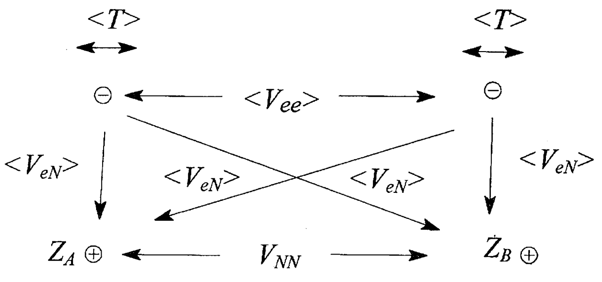


Fig. 1. Fundamental energy components included in a molecular system.

where, E^{el} is defined as 'the total electronic energy'.

To study the role of π electrons in benzene, a convenient method partitions E into the π-energy part (E_π) and the skeletal part ($E_\sigma{}'$) as in Eq. 7.

$$E = E_\pi + E'_\sigma. \tag{7}$$

This is possible because the SCF electronic wave function (Ψ) is a Slater determinant of molecular orbitals (MOs: ψ_i) expanded in terms of a linear combination of AOs (χ_r) and since the total bond order (P_{rs}) is the sum of π- (P^{π}_{rs}) and σ-bond orders (P^{σ}_{rs}) in a planar unsaturated hydrocarbon, Each term in Eq. 7 is further partitioned into energies as follows.

$$E_\pi = \langle T\rangle_\pi + \langle V_{\mathrm{eN}}\rangle_\pi + \langle V_{\mathrm{ee}}\rangle_\pi + \langle V_{\pi-\sigma}\rangle \tag{8}$$

$$E'_\sigma = \langle T\rangle_\sigma + \langle V_{\mathrm{eN}}\rangle_\sigma + \langle V_{\mathrm{ee}}\rangle_\sigma + \langle V_{\sigma-\pi}\rangle + V_{\mathrm{NN}} \tag{9}$$

where, $\langle V_{\pi-\sigma}\rangle = \langle V_{\sigma-\pi}\rangle$ is the electrostatic interaction between π and σ electrons. The term E_π is defined as the π-electronic energy.

Here, it should be pointed out that the π-electronic energy is distinguished from 'π energy' that is calculated by a π MO theory. The π-electronic energy is one clearly defined by Eq. 8, which includes the potential from nuclei as $\langle V_{\mathrm{eN}}\rangle_\pi$ and shield effects of σ and inner-shell electrons as $\langle V_{\pi-\sigma}\rangle$. 'π Energy' by a π MO theory has been generally considered to include the potentials from nuclei as shielded by σ and inner-shell electrons. In this respect, 'π energy' and the π-electronic energy seem to be similar. However, the biggest difference is that 'π energy' is independent of nuclear displacement as seen in the Hückel molecular orbital theory: At present, there is not one accepted idea although some proposals have been made.10g,12,22)

Those partitioned energies for π electrons are obtained as expectation values by a general expression,

$$\begin{aligned}\langle X\rangle_\pi &= 2\sum_i^{\mathrm{occ}}\sum_r\sum_s C_r^{*\pi i} C_{\mathrm{s}}^{\pi i}\int \chi_r^*(1)X\chi_s(1)\mathrm{d}\tau_1 \\ &= \sum_r\sum_s P^{\pi}_{rs}X_{rs},\end{aligned} \tag{10}$$

where $\mathrm{C}_r^{\pi i}$ is the coefficient of χ_r at the ith π MO. X is the operator of the corresponding energy ($\langle T\rangle$, $\langle V_{\mathrm{eN}}\rangle$, or $\langle V_{\mathrm{ee}}\rangle$), while X_{rs} is the element in its matrix form.

Geometry Contribution to Partitioned Energies. If the optimized geometry with the D_{6h} symmetry was distorted to the D_{3h} symmetry to obtain the energy change of π electrons caused by π-bond alternation in benzene, a severe problem emerges, that is the third term of the molecular virial theorem (Eq. 3) comes to play an important role that was not taken into consideration at all in the previous studies.

As stated, if the geometry of the system is optimized concerning all nuclear centers, the third term (which is often called the virial term) turns out to be null to give the simple relationship, $\langle T\rangle + E = 0$ or equivalently $\langle V\rangle/\langle T\rangle = -2$, where $\langle V\rangle$ is the expectation value of the potential energy ($\langle V_{\mathrm{eN}}\rangle + \langle V_{\mathrm{ee}}\rangle + V_{\mathrm{NN}}$). This is reproduced in the Hartree–Fock theory only when the basis set is complete.21) Otherwise, the ratio shifts from -2. Because the T and V operators are of degree -2 and -1 in the coordinates of electrons, by applying a universal scale factor (ζ) to the wave function, one can obtain the simple virial ratio. At the same time, however, the virial term for the unoptimized geometry can also be made zero by applying ζ to the total wave function simply because of the degrees -2 and -1 for the T and V operators: through a single ζ, the simple viral ratio can be fulfilled for the wave function of both incomplete basis sets and unoptimized geometry.

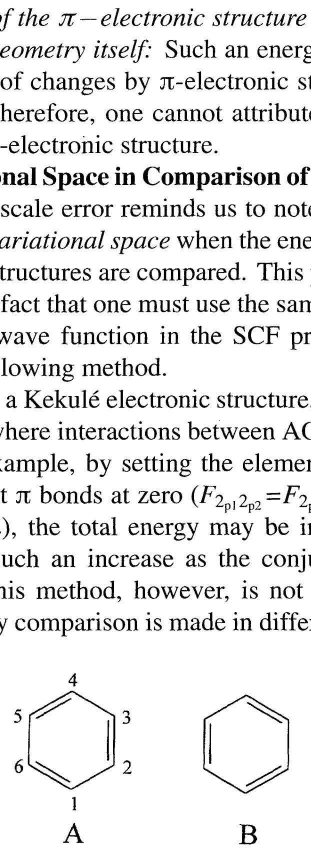
Pedersen and Morokuma studied how much the total energy and its components shift by scaling and found that the total energy deviates in the second-order of the scale error γ ($= \zeta - 1$) while those in the partitioned energies do in the first-order.23) Actual deviations of the partitioned energies were found to be from 10^2 to 10^4 times more than that of the total energy.24,25)

The scale error appears when the geometry is not optimized and the basis set is incomplete. Therefore, those shifts expressed in terms of expansions of the scale error must be regarded as the degree of shift given by a *molecular distortion* as well as by *the incompleteness* of the wave function. The former indicates that the conclusion concerning the role of π electrons totally depends on how to select the reaction coordinate of distortion. If the optimized geometry of benzene is distorted, the third term becomes alive and goes partly to the energy of the π system and partly to the σ frame. This can happen independently of the method of partitioning.

This discussion shows that *the energy change of π electrons obtained by a geometry distortion is not only given by the change of the π − electronic structure but also by the change of the geometry itself:* Such an energy change is, in fact, a mixture of changes by π-electronic structure and by the σ frame. Therefore, one cannot attribute it only to the change of the π-electronic structure.

The Variational Space in Comparison of Energy. The problem of the scale error reminds us to note that *one must keep the same variational space* when the energies of canonical electronic structures are compared. This practically corresponds to the fact that one must use the same basis set and the same trial wave function in the SCF procedure. This rules out the following method.

To reproduce a Kekulé electronic structure, a method may be considered where interactions between AOs are forced to be null. For example, by setting the elements between 2p AOs of adjacent π bonds at zero ($F_{2_{\mathrm{p}1}2_{\mathrm{p}2}} = F_{2_{\mathrm{p}3}2_{\mathrm{p}4}} = F_{2_{\mathrm{p}5}2_{\mathrm{p}6}} = 0$, see **A** in Fig. 2), the total energy may be increased. One may consider such an increase as the conjugation energy in benzene. This method, however, is not acceptable because the energy comparison is made in different variational



A B

Fig. 2. Kekulé structures of benzene.

spaces: such an increase includes the effects from different variational spaces.

Kekulé Electronic Structure. Kekulé structures of benzene are expressed as **A** and **B**. Originally, Kekulé structures were considered to rapidly convert by a 'mechanical motion'.[26] Later, the methods of quantum mechanics were shown to be successful to account for the stability problem of benzene: Both the molecular orbital (MO) and valence bond (VB) methods[27] are based on the Born–Oppenheimer approximation. This inevitably makes one accept that such a conversion is not the one of geometry but of electronic structure.

We have to make clear what we are investigating to account for the stability problem of benzene: The relationship between 'π energy' and the geometry of benzene or the relationship between 'π energy' and π-electronic structure. Most researches would agree that we are supposed to look into the relationship between 'π energy' and π-electronic structure. If so, we cannot distort the geometry of benzene to localize π bonds, since, as we have seen, the influence of geometry distortion to 'π energy' is inevitable. Here, we use the term 'Kekulé electronic structure' for benzene with completely localized π bonds, where the geometry is exactly the same as normal benzene.

Constraint on π-Electronic Structure. Each π MO is normalized as

$$\langle \psi_i^* | \psi_i \rangle_\pi = \sum_r \sum_s C_r^{*\pi i} C_s^{\pi i} S_{rs} = 1, \tag{11}$$

where S_{rs} is the element of the overlap matrix between AOs χ_r and χ_s. The π-Electron distribution between AOs χ_r and χ_s is described as

$$2 \sum_i^{\mathrm{occ}} C_r^{*\pi i} C_s^{\pi i} S_{rs} = P_{rs}^{\pi} S_{rs}. \tag{12}$$

Here, $P_{rs}{}^{\pi}$ is the element between χ_r and χ_s of the π-bond order matrix.

Constraint on the π-electronic structure is equivalent to seeking SCF π MOs that give a pre-determined π-electronic structure. For example, to obtain the energies of non-conjugative benzene (Kekulé electronic structure), we look for the SCF π MOs which reproduce every other $P_{rs}{}^{\pi}$ being zero ($P_{12}^{\pi}=P_{34}^{\pi}=P_{56}^{\pi}=0$).

How to Obtain SCF Wave Functions of the Pre-determined Electronic Structure. From above discussion, the benzene problem is reduced to how to obtain the SCF wave functions that reproduce the pre-determined π-electronic structure without changing the variational space and the geometry of benzene.

In 1963, Mukherji and Karplus introduced the constrained variation method in molecular quantum mechanics.[28] The purpose of this theory was to obtain a wave function that is constrained to give the known theoretical or experimental expectation values of operators rather than the total energy. The method was generalized by Brown,[29] and was applied to the SCF theory. We found that the total energy of nonresonating cyclohexatriene can be obtained by solving the constrained Hartree–Fock (HF) equation, replacing the constraints for the desired expectation values to those for canceling delocalization of the π electrons on resonating bonds.[30]

Constrained Hartree–Fock Equation. Inclusion of constraints in the SCF variational procedures results in a slight modification in the ordinary SCF equation. Such an equation was derived by Björnå in the early 1970s for the constraints that yield accurate expectation values for physical properties.[31] The logic of our method is essentially the same, although *the constraints of this method are not to give the desired expectation value for a physical property but to control the distribution of π electrons on (a) certain bond(s).* The detail of the derivation has been presented in our previous paper[30] and here only the resultant equations are shown.

$$\begin{cases} P_{rs} = 2 \sum_i^{\mathrm{occ}} C_r^{*i} C_s^{i} = p_k, \\ (F + \lambda) C = \varepsilon' S C. \end{cases} \tag{13}$$

Here, F, C, and S are matrices of Fock operator, MO (ψ) coefficients, and overlap integrals while ε' is the fictitious orbital energy associated with ψ. Matrix, λ, is a parameter that constrains the electron distribution to be controlled. The bond-order (P_{rs}) between atomic orbitals (AOs) r and s is a function of λ_{rs}, an element of λ, where the λ_{rs} value is so chosen that P_{rs} becomes null (p_k=0) to cancel the delocalization between AOs r and s.

How to Realize the Concept of Canonical Structure in Conjugation Using the Constrained HF Method. Let us examine the concept of conjugation in organic chemistry, taking butadiene for example. Conjugation is expressed as **A** in Fig. 3. To express **A**, canonical structures **B**, **C**, and **D** are used. The resonance energy corresponds to the energy difference between **A** and **B**, where *the geometry difference between those structures is not taken into account.* Delocalization between two double bonds is expressed by superposition of **B**, **C**, and **D** in which double bond(s), cation, and anion are isolated. Such structures are, of course, hypothetical and are introduced to understand conjugation in terms of chemically-expressible structures. The problem is how to realize this image in terms of the Hartree–Fock–Roothaan theory. For the reality is that all 2p AOs that consist of the π system interact with each other, not only adjacent orbitals but also those at a distance.

A Hartree–Fock calculation, independent of the adopted basis set, reproduces well such a normal electronic structure as **A** in which long-range interactions are small enough to be ignored. However, a difficulty may appear when adjacent

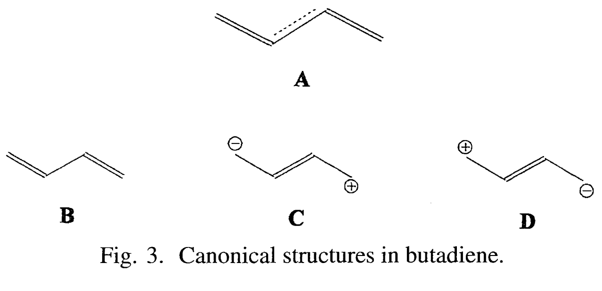


Fig. 3. Canonical structures in butadiene.

interactions are forced to stop to create **B**. When the current of π-electrons between two double bonds is nullified, the π electrons would find other paths to delocalize themselves. As a result, nonbonding interactions are increased. This happens in the constrained HF method and may be a natural outcome due to the nature of electrons.

Table 1 shows long-range interactions of π electrons in terms of kinetic energy and its change by constraint of the π-electron flow between C_2 and C_3 in butadiene, where we adopted single zeta STO-3G[32] and split-valence 4-31G[33] to see the difference. Interactions between outer orbitals are generally stronger than that between inner and inner or between outer and inner orbitals. Such outer interactions are greatly increased by constraint of the π-electron flow between double bonds. From the table, we may guess that the more flexible the basis set, the more long-range interactions are intensified. This may be natural because outer functions are close to each other.

There are two ways to represent **B** by the constrained Hartree–Fock method: (1) to constrain all interactions except the bonding 2p orbitals and (2) to use such a rigid basis set as the single-zeta basis set. The difficulty of the former method is that a large number of constraints must be adopted to express a pure canonical structure. For example, to express **B** using the 4-31G basis set,16 (=$n^2 \times m$, n: number of split-valence, m: number of interactions to be canceled) interactions must be canceled. Such a calculation is impractical in usual molecules.

Table 1. Long-Range Interaction of π Electrons in Terms of Kinetic Energy and Its Change by Constraint (*trans*-Butadiene)[a)]

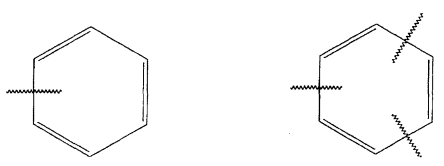
	C_3/C_{3-i}	C_{3-o}	C_4/C_{4-i}	C_{4-o}	RE[b)]
STO-3G					
C_1: SCF	0.7		0.4		16.8
Δ[c)]	0.1		−0.2		
4-31G					
C_{1-i}: SCF	0.1	0.4	0.0	0.2	12.4
Δ	0.1	−0.1	0.0	−0.1	
C_{1-o}: SCF	0.3	−1.7	0.2	1.2	
Δ	0.1	0.4	−0.1	−0.3	

a) In kJ mol^{-1}. b) Calculated resonance energy ($E^{\text{constrained}}-E^{\text{SCF}}$ in kJ mol^{-1}). c) Change given by constraint on the π-electron flow between C_2 and C_3.

The latter is to make use of the rigidity of the basis set, where long-range interactions are limited due to inability of swelling of the basis function.[34] From Table 1 it is seen that changes of long-range interactions given by 4-31G are 1.5 to 4 times larger than those of STO-3G. This is because in 4-31G, long-range interactions are intensified by constraint, resulting in delocalization of π electrons through space.

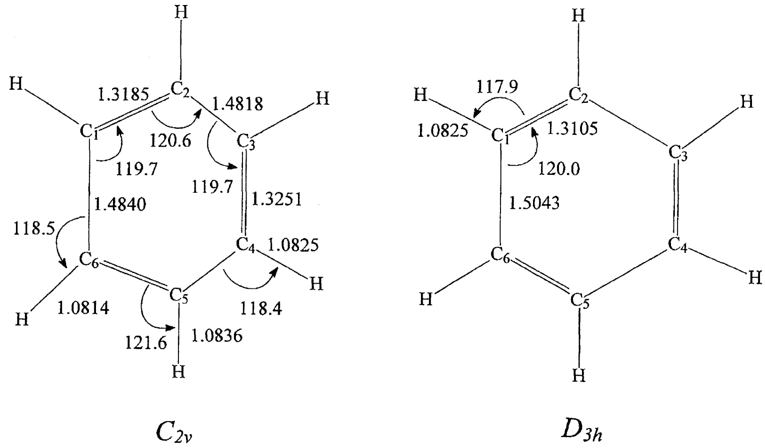
Geometry Change by Constraint. Now let us look at how the geometry of benzene with the D_{6h} symmetry is changed by constraints. Two types of constraints were considered to figure out resonance energies. They are shown in Fig. 4. A single constraint indicates only one resonating bond being nullified while a triple constraint shows that three resonating bonds are constrained at the same time.

Geometry optimization of benzene by STO-3G gives the D_{6h} structure with the bond lengths of 1.38679 Å (C–C) and 1.08261 Å (C–H). This is denoted as G_0. Resonance in benzene can be interrupted by a constraint on the π-electron flow to give a *cyclohexatriene*. Geometry optimization of such



single constraint triple constraint

Fig. 4. Two types of constraints on π-electron flow.



a: Single constraint **b**: Triple constraint

Fig. 5. Optimized geometries of single-(SCC) and triple-constraint cyclohexatriene (TCC). Bond lengths and bond angles are in Å and degrees.

cyclohexatriene gives a different structure (G_1). Figure 5-a, Fig. 5-b are the optimized geometries for single- (SCC(G_1)) and triple-constraint cyclohexatriene (TCC(G_1)).

As seen in the figure, bond lengths for single and double bonds reasonably reproduced as those of the usual single and double carbon-carbon bonds. Single constraint gives the cyclohexatriene without resonation at C_1–C_6 (Fig. 5-a), Comparison with that of benzene shows that resonating single and double bonds are, respectively, shortened and lengthened. However, the constrained bond (C_1–C_6) is short if compared with the isolated C–C bond between double bonds. This and the fact that the inner angles are not exactly 120° indicate that there is a kind of strain in the skeleton. As will be quoted, this may slightly affect the resonance energy.

How Coefficients of π MO's Vary by Constraint. Table 2 shows coefficients of π MOs of benzene, single-constraint cyclohexatriene at G_0 and G_1, triple-constraint cyclohexatriene at G_0 and G_1, and hexatriene. The constraint was put on C_1–C_6 in single constraint or on C_1–C_6, C_2–C_3, and C_4–C_5 in triple constraint. Single constraint on benzene is expected to give a hexatriene-like π electronic structure. This is easily ascertained by comparing the signs and ab-

Table 2. Coefficients of π MOs of the Normal and Constrained Solutions in Benzene, Cyclohexatriene, and *trans*-Hexatriene

$\varepsilon^{a)}$	C_1	C_2	C_3	C_4	C_5	C_6
Benzene						
−0.46090 a_{2u}	0.33333	0.33333	0.33333	0.33333	0.33333	0.33333
−0.28265 e_{1g}	0.20163	0.52648	0.32485	−0.20163	−0.52648	−0.32485
−0.28265 e_{1g}	0.49152	0.07114	−0.42038	−0.49152	−0.07114	0.42038
0.27076 e_{2u}	0.50983	−0.61749	0.10766	0.50983	−0.61749	0.10766
0.27076 e_{2u}	0.41867	0.23219	−0.65086	0.41867	0.23219	−0.65086
0.50910 b_{1g}	0.52439	−0.52439	0.52439	−0.52439	0.52439	−0.52439
Single constraint (G_0)						
−0.44668 a_u	0.21210	0.34508	0.41717	0.41717	0.34508	0.21210
−0.26657 b_g	0.47127	0.44450	0.16209	−0.16209	−0.44450	−0.47127
−0.27243 a_u	0.42085	0.23597	−0.44866	−0.44866	0.23597	0.42085
0.26515 b_g	0.58542	−0.29436	−0.46443	0.46443	0.29436	−0.58542
0.26876 a_u	0.45770	−0.60955	0.32720	0.23720	−0.60955	0.45770
0.48010 b_g	0.32732	−0.52250	0.65574	−0.65574	0.52250	−0.32732
Single constraint (G_1)						
−0.44431 a_u	0.24713	0.34119	0.40153	0.40154	0.34119	0.24713
−0.28906 b_g	0.45839	0.45474	0.12423	−0.12422	−0.45474	−0.45839
−0.28846 a_u	0.38608	0.23900	−0.47042	−0.47042	0.23899	0.38607
0.28235 b_g	0.54397	−0.29830	−0.51613	0.51613	0.29829	−0.54397
0.28691 a_u	0.49059	−0.61045	0.18454	0.18453	−0.61045	0.49059
0.48434 b_g	0.38151	−0.51065	0.63454	−0.63454	0.51065	−0.38151
Triple constraint (G_0)						
−0.44798 a_{2u}	0.33333	0.33333	0.33333	0.33333	0.33333	0.33333
−0.26132 e	0.28117	0.20877	−0.54981	−0.54492	0.26864	0.33614
−0.26132 e	0.47253	0.50868	0.00723	−0.07354	−0.47977	−0.43514
0.25200 e	0.49970	−0.62535	0.10237	0.17838	−0.60207	0.44697
0.25200 e	0.40671	−0.15507	−0.63611	0.61910	0.22940	−0.46404
0.49724 b_{1g}	0.52439	−0.52439	0.52439	−0.52439	0.52439	−0.52439
Triple constraint (G_1)						
−0.44282 a_{2u}	0.33514	0.33514	0.33514	0.33514	0.33514	0.33514
−0.28941 e	0.41114	0.36430	−0.50664	−0.52549	0.09550	0.16119
−0.28941 e	0.34764	0.39646	0.18224	0.11727	−0.52988	−0.51372
0.28275 e	0.36669	−0.52588	0.28557	−0.07368	−0.65226	0.59956
0.28275 e	0.54146	−0.38869	−0.58829	0.64977	0.04683	−0.26108
0.49121 b_{1g}	0.52312	−0.52312	0.52312	−0.52312	0.52312	−0.52132
Hexatriene						
−0.42082 a_u	0.23864	0.33167	0.43040	0.43040	0.33167	0.23864
−0.34887 b_g	0.42150	0.44826	0.11229	−0.11229	−0.44826	−0.42150
−0.24544 a_u	0.41910	0.27840	−0.44665	−0.44665	0.27840	0.41910
0.22065 b_g	0.49216	−0.31380	−0.50906	0.50906	0.31380	−0.49216
0.35051 a_u	0.54827	−0.60306	0.17635	0.17635	−0.60306	0.54827
0.45213 b_g	0.33650	−0.50236	0.64347	−0.64347	0.50236	−0.33650

a) Corrected orbital energy (au).[31)]

solute values of hexatriene with those of single-constraint cyclohexatrienes at G_0 and G_1.

Triple constraint gives nonresonating cyclohexatriene; it may be supposed that this gives triply degenerative ethylene-like π systems. However, this is not true since there exist through-space interactions between ethylene units resulting in two pairs of doubly-degenerated π MOs like those in benzene. One may see that the π bond-orders of C_1–C_6, C_2–C_3, and C_4–C_5 are all null.

Thus, one may understand that the constrained HF method creates the MOs with coefficients that make the specific bond-order zero. An important point is that *they are obtained by the variational principle with respect to the total energy*. That is, they are *eigenfunctions* of the Hamiltonian of the pre-determined electronic structure.

Influence of the Scale Factor on the Partitioned Energies. If the adopted basis set is complete and if a geometry is optimized with respect to any nuclear coordinate, the virial ratio, $\langle V\rangle/\langle T\rangle$, must be exactly −2 according to the quantum mechanical virial theorem for molecules.[19] Most basis sets, such as STO-3G, do not meet this requirement even if the geometry is strictly optimized. However, it can be met by using a universal scale factor, ζ; this parameter for a usual wave function shifts from 1 to satisfy the simple ratio. As stated, the changes of E, $\langle T\rangle$, and $\langle V\rangle$ of the unscaled wave function from the scaled one can be expressed in a power series of the scale error, γ ($=\zeta-1$), to show that the deviation of the total energy is in the second order while those of $\langle T\rangle$ and $\langle V\rangle$ are in the first order.[21] The energy components are supposed to include a large amount of shift; partitioned energies largely depend on the scale error of the wave function. Therefore, one must use the scaled wave function or carefully examine the effects of the scale factor before energy-components analysis is done.

We optimized of ζ on benzene, obtaining $\zeta=1.004566$. Table 3 shows the total and partitioned energies by the usual wave function based on STO-3G and those by the scaled wave function. The virial ratio by the unscaled wave function was −2.008093, which was improved to −2.000001 by scaling.

Table 3. Changes of Energies by Scaling[a]

	Unscaled	Scaled[d]	ΔE
Virial ratio	2.008093	2.000001	
E	−227.891360[b]	−227.895534[b]	−11.0[c]
V_{NN}	204.532841	205.013523	1262.0
$\langle T\rangle$	226.061948	227.895367	4813.6
$\langle V_{\mathrm{eN}}\rangle$	−939.897167	−942.988423	−8116.1
$\langle V_{\mathrm{ee}}\rangle$	281.411017	282.184000	2029.5
$\langle T\rangle_\pi$	7.452712	7.523611	186.1
$\langle V_{\mathrm{eN}}\rangle_\pi$	−85.393002	−85.671476	−731.1
$\langle V_{\mathrm{ee}}\rangle_\pi$	4.329395	4.342673	34.9
$\langle T\rangle_\sigma$	218.609236	220.371756	4627.5
$\langle V_{\mathrm{eN}}\rangle_\sigma$	−854.504164	−857.316948	−7385.0
$\langle V_{\mathrm{ee}}\rangle_\sigma$	209.852511	210.409816	1463.2
$2\times\langle V_{\mathrm{ee}}\rangle_{\pi-\sigma}$	67.229110	67.431510	531.4

a) STO-3G. b) In au. c) In kJ mol^{-1}. d) Scale factor $\zeta=1.004566$.

Since ζ is one of variational parameters, the total energy is lowered by 11 kJ mol^{-1} by scaling. Look at the energy components. Deviations of those energies are several hundred times larger than that of the total energy. This is because the deviations of $\langle T\rangle$ and $\langle V\rangle$ ($=\langle V_{\mathrm{eN}}\rangle+\langle V_{\mathrm{ee}}\rangle+V_{\mathrm{NN}}$) are given by the first order of γ. Now let us consider the case when E is partitioned into E_π and E'_σ according to Eqs. 8 and 9. The deviations for them are substantial enough to be −244.4 and 233.4 kJ mol^{-1}, respectively. These facts indicate how important the scaling of the wave function is in the analysis of the components of the total energy.

Next let us examine *how the scaling affects those energy changes by constraint*. The energy differences in the vertical and adiabatic processes are calculated by both scaled and unscaled wave functions and are shown in the columns under ΔE^{vert} of Table 4. It is found that the differences in the vertical process are almost the same in both single and triple constraints as found in linear polyenes.[31] This is because the incompleteness of the basis set is not changed between them. That is, the deviations caused by the scale error are canceled out by taking the differences between the normal and constrained solutions. Thus, we may use unscaled wave functions for further discussion.

Results and Discussion

Does Super Stabilization Energy Exist in Benzene? The resonance energy in benzene consists of three units of resonance energy between double bonds (E_{R}) and, if it exists, super stabilization energy (E_{S}) due to the topology of benzene. We will figure out those energies using data in Table 4. We use unscaled wave functions. The vertical single constraint raises the total energy by 222 kJ mol^{-1} while triple constraint does 330 kJ mol^{-1}. The total energy of benzene is stabilized by delocalization of π electrons by such amounts. Simple arithmetic indicates that the energy needed for breaking one resonation between double bonds (denoted as $E_{\mathrm{R}}^{\mathrm{vert}}$) is 54 kJ mol^{-1} and *the super stabilization energy* ($E_{\mathrm{S}}^{\mathrm{vert}}$) *is 168 kJ mol*$^{-1}$. These values seem to be very large. However, this is understood as the bond length in benzene is substantially shorter than the single bond between two double bonds, like one in hexatriene.

Let us look at the changes of partitioned energies. In both single and triple constraints, the π part of the energy components vary greatly while the change of the σ part is from one twentieth to one fiftieth. This is because the skeleton is maintained in the vertical process. A major increase appears in the kinetic energy of π electrons while a major decrease does in the one-electron potential energy of π electrons. It is interesting that the next major increase is given by the π–σ interaction energy, indicating that *the energy of π electrons is greatly changed through this term when the geometry is changed.*

Does Super Stabilization Energy Exist in Cyclohexatriene? Table 4 also shows the energy changes from D_{6h} benzene to cyclohexatrienes. The adiabatic process gives energy increases of 128 and 181 kJ mol^{-1} by single and triple constraints. This indicates that the adiabatic resonance

Table 4. Changes of Energies by Constraint[a)]

	ΔE^{vert}				ΔE^{adia}	
	Single		Triple		Single	Triple
E	221.9[b)]	(224.5[b,c)])	329.5[c)]	(333.5[b,c)])	128.0[b)]	180.5[b)]
V_{NN}	0.0	(0.0)	0.0	(0.0)	−4122.0	−5693.3
$\langle T\rangle$	432.4	(435.6)	683.9	(689.3)	219.7	333.9
$\langle V_{\mathrm{eN}}\rangle$	−381.2	(−382.6)	−602.7	(−605.0)	7904.8	10889.7
$\langle V_{\mathrm{ee}}\rangle$	170.8	(171.4)	248.2	(249.1)	−3874.4	−5349.8
$\langle T\rangle_\pi$	440.4	(444.1)	698.6	(704.5)	313.1	452.5
$\langle V_{\mathrm{eN}}\rangle_\pi$	−404.3	(−406.2)	−640.7	(−643.9)	718.4	963.6
$\langle V_{\mathrm{ee}}\rangle_\pi$	−5.7	(−5.7)	−33.9	(−34.1)	−126.4	−181.2
$\langle T\rangle_\sigma$	−8.1	(−8.4)	−14.6	(−15.2)	−93.4	−118.2
$\langle V_{\mathrm{eN}}\rangle_\sigma$	23.1	(23.6)	38.0	(38.9)	7189.4	9926.1
$\langle V_{\mathrm{ee}}\rangle_\sigma$	−11.5	(−11.7)	−19.6	(−19.9)	−2992.2	−4138.9
$2\times\langle V_{\mathrm{ee}}\rangle_{\sigma\text{–}\pi}$	187.9	(188.8)	301.7	(303.1)	−755.9	−1029.6

a) STO-3G. b) In kJ mol^{-1}. c) Values in parentheses are the results by the scaled wave function ($\zeta=1.004566$).

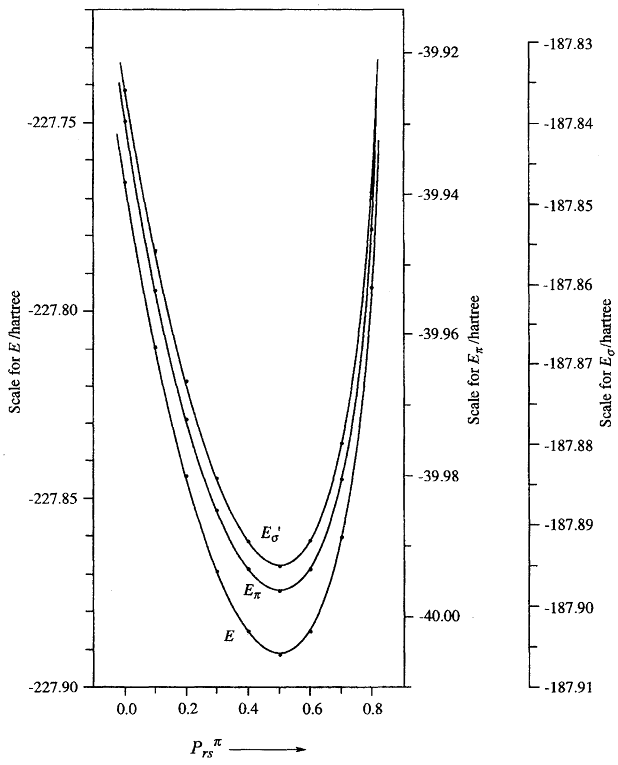


Fig. 6. Change of the total energy as a function of the π-bond order (P^{π}_{rs}). At $P^{\pi}_{rs}=0.50446$ (bottom), there is no constraint against the π-electron flow. Note that at the uniform delocalization of π electrons, the total energy as well as E_π and E'_σ are all minimum.

energy per resonation ($E^{\mathrm{adia}}_{\mathrm{R}}$) is 26 kJ mol^{-1} and *the super-stabilization energy* ($E^{\mathrm{adia}}_{\mathrm{S}}$) *is 102 kJ mol*$^{-1}$. The $E^{\mathrm{adia}}_{\mathrm{R}}$ value has been calculated to be 20 kJ mol^{-1} in linear polyenes.[31)] The difference may be caused by the skeletal distortion in the resonating cyclohexatriene (SCC, see Fig. 6-a). The total energy of **a** is made higher because of skeletal distortion.

The adiabatic process changes both σ and π energies by large amounts. The greatest change appears in the potential energy due to the geometry change. Although it is difficult to interpret the behaviors of all of the partitioned energies, two items must be pointed out: (1) The kinetic energy of the π electrons is a steady contributor to the increase of the total energy. (2) The σ–π interaction energy ($E_{\sigma\text{–}\pi}$) plays substantial roles when the total energy is partitioned into σ and π energies. The adiabatic process involves a geometry change. Therefore, this is direct evidence for our insistence that the energy of π electrons is greatly changed through the σ–π interactions when the geometry is changed.

Do π Electrons in Benzene Have a Distortive Propensity? As we saw, one cannot investigate the energetics of π electrons by changing the geometry simply because *most of the change concerning the π electrons is given by that of the geometry directly through nuclear coordinates and indirectly through the* $\langle V_{\mathrm{ee}}\rangle_{\sigma\text{–}\pi}$ *and* $\langle V_{\mathrm{ee}}\rangle_{\pi\text{–}\sigma}$ *terms.* What we are looking for is the relationship between the energy and electronic structure in π electrons where it is shown by the virial theorem that the geometry *must* not be changed.

Figure 6 shows the relationships between energies and π-electronic structure in triple constraint, where at $P^{\pi}_{rs}=0$, the system corresponds to the nonresonating cyclohexatriene with the geometry of benzene. At $P^{\pi}_{rs}=0.50446$ (bottom), there is no constraint of the π-electron flow, the value of which is exactly equal to that of benzene. This indicates that the uniform (D_{6h}) distribution of π electrons in benzene produces the lowest total energy, E_π, and even E'_σ: *any* D_{3h} *distribution of π electrons causes higher energies.* This simply indicates that π electrons in benzene do not have what is called a distortive propensity at all at this geometry.

Figure 7 shows the changes in the kinetic energy of σ electrons ($\langle T\rangle_\sigma$) and π electrons ($\langle T\rangle_\pi$) as functions of π-bond order, P^{π}_{rs}. The behaviors of partitioned energies are suggestive. The change of $\langle T\rangle_\pi$ exactly accords with that of the total energy assuring that resonance is given by the lowering of this term. On the other hand, $\langle T\rangle_\sigma$ behaves against that of $\langle T\rangle_\pi$: This could be regarded as a minor phenomenon since the energy scale is around one-fiftieth.

Figure 8 shows changes of potential energies for σ ($V_\sigma=\langle V_{\mathrm{eN}}\rangle_\sigma+\langle V_{\mathrm{ee}}\rangle_\sigma$) and π electrons ($V_\pi=\langle V_{\mathrm{eN}}\rangle_\pi+\langle V_{\mathrm{ee}}\rangle_\pi$) and the

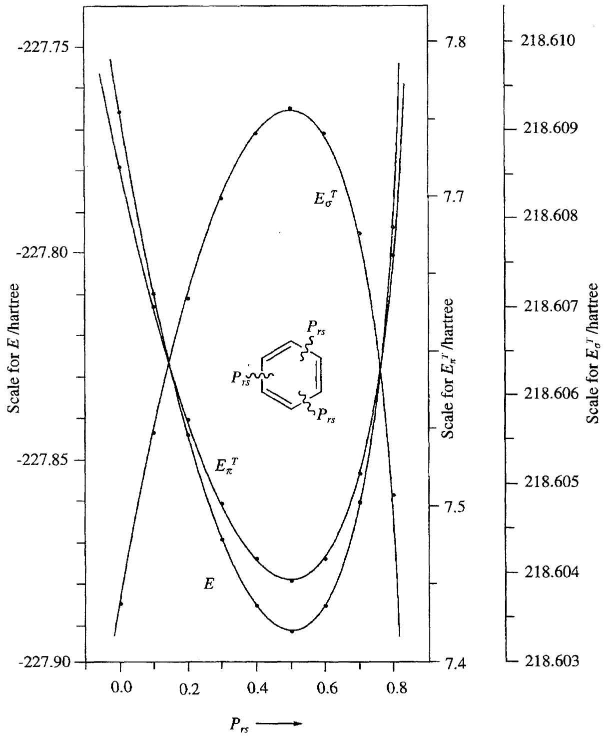


Fig. 7. Changes of the total (E), kinetic energies of σ-electrons, E_σ^T ($\equiv\langle T\rangle_\sigma$), and π-electrons, E_π^T ($\equiv\langle T\rangle_\pi$) as functions of π-bond order, P_{rs}.

σ–π interaction energy ($\langle V_{ee}\rangle_{\pi-\sigma}+\langle V_{ee}\rangle_{\sigma-\pi}$). As commonly observed, potential energies behave against kinetic energies. The σ–π interaction energy has the minimum at the uniform electron distribution. Among the changes of partitioned energies, those of π electrons are major contributors because of the constraint being put on the π-electron flow. Behaviors of those partitioned energies are explained as follows: delocalization of π electrons lowers the kinetic energy, i. e., release of the kinetic-energy pressure[35] causes delocalization of π electrons. Such delocalization raises the potential energy of π electrons because π electrons are distributed much farther from nuclei. It also minimizes the σ–π interaction energy (since σ electrons are mostly distributed near the nucleus). Now, we might have an answer to the title question: *The π electrons in benzene are the most stable at their uniform distribution.*

Concluding Remarks We thought that it would be nice if we could calculate the molecular energies of a pre-determined electronic structure, since it directly makes clear the relationship between them. If a method for this is established, important problems of organic chemistry would be solved. The prototypical example is benzene. Benzene has particular properties very different from other unsaturated hydrocarbons. Organic chemists have explained them as the character of π electrons in the cyclic-conjugate structure.

To understand such a behavior of π electrons in benzene, it was necessary to disturb the π electronic structure since examining the change of the π-electron energy by such a disturbance seemed to reveal its role. To this end, the geometry of benzene *was* changed. The pitfall of this method is that the change of energy includes contributions both from the electronic structure and from the geometry, since π and σ electrons are strongly correlated and all electrons move in the field created by nuclei; consequently, the change of π energy is a mixture of those of the π system and the σ frame.

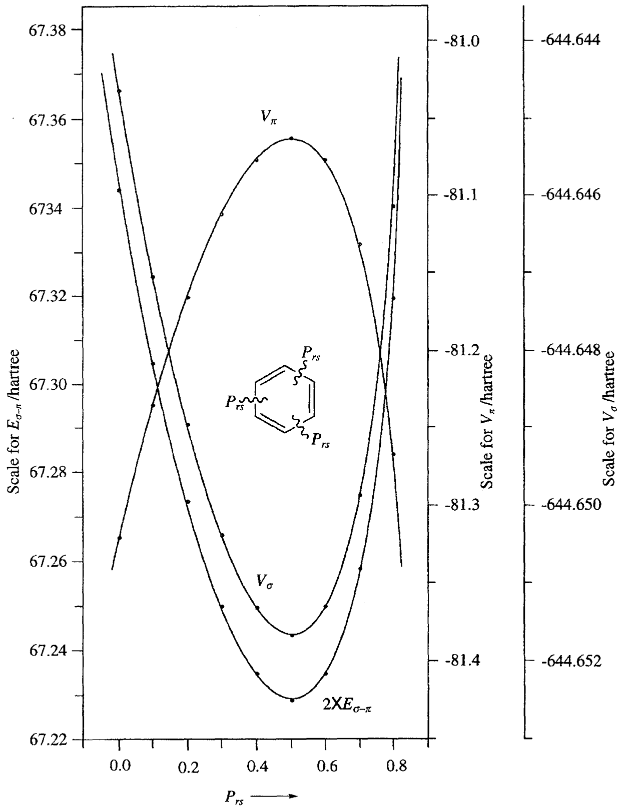


Fig. 8. Changes of one-electron ($\langle V_{eN}\rangle$) plus two-electron energies ($\langle V_{ee}\rangle$) of σ-electrons (V_σ) and π-electrons (V_π) and σ–π interaction energy ($E_{\sigma-\pi}(\equiv\langle V_{ee}\rangle_{\sigma-\pi})$) as functions of P_{rs}.

The constrained Hartree–Fock method provides quantum-mechanically acceptable wave functions of an arbitrary electronic structure *without changing the molecular geometry.*[30] Analysis of energy changes by this method can be purely attributed to the change of the electronic structure. Application to benzene led to the conclusions that (1) the resonance energy in benzene consists of three units of the resonance energy between double bonds (E_R) and super stabilization energy (E_S) due to the topology of benzene, which were estimated as 54 and 168 kJ mol^{-1}, respectively. (2) π Electrons in benzene have a propensity for uniform distribution at its geometry. (3) The D_{6h} distribution of π electrons in benzene gives the minimum values of both the π electron and total energies, which are brought forth by the lowering in the kinetic energy of π electrons.

A large amount of research on aromaticity based on the Hückel molecular orbital theory led to the conclusion that there is a quantitative relationship between the Hückel energy and the topological aromaticity. It was also shown that the Hückel energy quantitatively represents the amount of kinetic energy of π electrons in linear and cyclic polyenes.[36] Thus, it may be a natural consequence that both vertical and adiabatic resonance energies are given by relaxation of the kinetic-energy pressure[35] of π electrons.

This research is supported by The Otani Research Prize.

References

1) For Part I, see Ref. 31.

2) For review: a) E. D. Bergmann and B. Pullmann, "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," The Israel Acad. Sci. Humanities, Jerusalem (1971); b) P. J. Garrat, "Aromaticity," John Wiley & Sons, New York (1986).

3) R. Robinson, *Tetrahedron*, **3**, 323 (1958).

4) J. Aihara, *Bull. Chem. Soc. Jpn.*, **56**, 1935 (1983).

5) By Hückel MO methods: a) R. Breslow and E. Mohasci, *J. Am. Chem. Soc.*, **85**, 431 (1963); b) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 302 (1983).

6) By a PPP (Pariser-Parr-Pople) MO method: M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

7) By ab initio MO methods: a) R. C. Haddon and J. Starnes, *Adv. Chem. Ser. A*, **169**, 333 (1978); b) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **105**, 7500 (1983); c) H. Ichikawa and Y. Ebisawa, *J. Am. Chem. Soc.*, **107**, 1161 (1985).

8) D. F. Horning, *J. Am. Chem. Soc.*, **72**, 5772 (1950).

9) R. S. Berry, *J. Chem. Phys.*, **35**, 2253 (1961).

10) a) S. S. Shaik and R. Bar, *Nouv. J. Chim.*, **8**, 411 (1984); b) S. S. Shaik and P. C. Hiberty, *J. Am. Chem. Soc.*, **107**, 3089 (1985); c) P. C. Hiberty, S. S. Shaik, J. -M. Lefour, and G. Ohanessian, *J. Org. Chem.*, **50**, 4657 (1985); d) S. S. Shaik, P. C. Hiberty, J. -M. Lefour, and G. Ohanessian, *J. Am. Chem. Soc.*, **109**, 363 (1987); e) G. Ohanessian, P. C. Hiberty, J. -M. Lefour, J. -P. Flament, and S. S. Shaik, *Inorg. Chem.*, **27**, 2219 (1988); f) S. S. Shaik, P. C. Hiberty, G. Ohanessian, and J. -M. Lefour, *J. Phys. Chem.*, **92**, 5086 (1988); g) P. C. Hiberty, D. Danovich, A. Shurki, and S. Shaik, *J. Am. Chem. Soc.*, **117**, 7760 (1995).

11) P. C. Hiberty, *Top. Curr. Chem.*, **153**, 27 (1990).

12) K. Jug and A. Köster, *J. Am. Chem. Soc.*, **112**, 6772 (1990).

13) R. Janoschek, *J. Mol. Struct. (Theochem)*, **229**, 197 (1991).

14) T. Nakajima and M. Kataoka, *Theoret. Chim. Acta*, **84**, 27 (1992).

15) N. C. Baird, *J. Org. Chem.*, **51**, 3908 (1986).

16) H. Kollmar, *J. Am. Chem. Soc.*, **101**, 4832 (1979).

17) E. D. Glendenig, R. Faust, A. Streitwieser, K. P. C. Vollhardt, and F. Weinhold, *J. Am. Chem. Soc.*, **115**, 10952 (1993).

18) H. Ichikawa and H. Kagawa, *J. Phys. Chem.*, **99**, 2307 (1995).

19) R. G. Parr and J. E. Brown, *J. Chem. Phys.*, **49**, 4849 (1968).

20) D. R. Hartree, *Proc. Cambridge Philos. Soc.*, **24**, 89 (1928); V. Fock, *Z. Phys.*, **61**, 126 (1930); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

21) See e. g., I. N. Levine, "Quantum Chemistry," 3rd ed, Allyn and Bacon, Inc. (1983), p. 393.

22) Interesting and comprehensive relationship between the π energy by the Hückel MO theory and the kinetic energy of π electrons has been reported. Besides, the kinetic energy of π electrons was shown not to be very susceptible to nuclear displacement (H. Ichikawa and Y. Ebisawa, *J. Am. Chem. Soc.*, **107**, 1161 (1985); H. Ichikawa and K. Sameshima, *Bull. Chem. Soc. Jpn.*, **63**, 3248 (1990).

23) L. Pedersen and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).

24) D. E. Magnoli and J. R. Murdoch, *Int. J. Quantum Chem.*, **22**, 1249 (1982).

25) H. Ichikawa and A. Shigihara, *Bull. Chem. Soc. Jpn.*, **61**, 1837 (1988).

26) For detailed discussion of the historical aspects of benzene, see: J. R. Partington, "A History of Chemistry," Macmillan, New York (1964), Vol. 4; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y. (1969); P. J. Garrat, "Aromaticity," John Wiley & Sons, New York (1986), Chap. 1.

27) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, New York (1962); J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "The Chemical Bond," Wiley, New York (1978); L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York (1966); K. Yates, "Hückel Molecular Orbital Theory," Academic Press, New York (1978).

28) A. Mukherji and M. Karplus, *J. Chem. Phys.*, **38**, 44 (1963).

29) W. B. Brown, *J. Chem. Phys.*, **44**, 567 (1966).

30) H. Ichikawa and H. Kagawa, *Int. J. Quantum Chem.*, **52**, 575 (1994).

31) a) N. Björnå, *J. Phys. B*, **4**, 424 (1971); *J. Phys. B*, **5**, 721 (1972); *J. Phys. B*, **5**, 732 (1972); b) N. Björnå, *Mol. Phys.*, **24**, 1 (1972).

32) W. J. Hehre, R. F. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).

33) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, **56**, 4233 (1972); J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975).

34) Swelling means that importance of the outer shell is intensified.

35) a) M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, "Advances in Quantum Chemistry," ed by P. Löwdin, Academic Press, New York (1970), Vol. 5, p. 27; b) K. Ruedenberg, "Localization and Delocalization in Quantum Chemistry," ed by O. Chalvet, R. Daudel, S. Diner, and J. R. Malrieu, Reidel, Dordrecht (1975), Vol. 1, pp. 223—245.

36) H. Ichikawa and K. Sameshima, *Bull. Chem. Soc. Jpn.*, **63**, 3248 (1990).