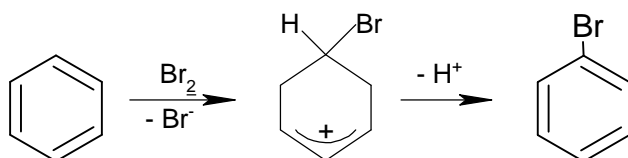


Are the π electrons in a benzene molecule in an unstable state?

Benzene rings do not break in normal chemical reactions. It is a very stable system, and most organic chemists believe that its stability is due to π electrons. Papers that challenged this common sense were published by Shaik et al. between 1985 and 1995, mainly in journals such as the American Chemical Society.¹ The main ones are first seven references. The Journal of the American Chemical Society is a leading research journal in the field of chemistry, so it is easy to imagine how confused organic chemists must have been.

However, upon closer investigation, it became clear that their conclusion was incorrect, and that the cause of the error was the incorrect application of molecular orbital methodology as a research method. This was due to a lack of basic knowledge of quantum mechanics and a failure to thoroughly examine the literatures already published.

What is surprising is that none of the paper's reviewers noticed such a simple error and allowed it to be published. The reviewers for the Journal of the American Chemical Society are chemists who are generally considered to be first-rate (?). This reveals that even amongst so-called first-rate theoretical chemists, the basic knowledge of quantum mechanics has not been properly disseminated. I will edit and report this history in as easy-to-understand a manner as possible.



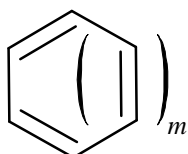
Example of substitution reaction: Substitution reaction occurs due to the retention of the 6π electron system of the benzene ring. This shows the stability of the π electron system of benzene.

Figure 1. Examples of addition and substitution reactions

Aromaticity

Aromaticity is a fundamental concept in organic chemistry, so it is found in any organic chemistry textbook. Here are some examples from specialized textbooks.² Benzene is a very stable unsaturated hydrocarbon. Unsaturated hydrocarbons usually undergo addition reactions, but benzene undergoes substitution reactions (reactions in which a hydrogen atom of benzene is replaced by another atom (group)). In other words, while normal unsaturated hydrocarbons undergo reactions that eliminate unsaturated bonds, benzene reacts to maintain the cyclic unsaturated bond structure of the benzene ring. There are many cyclic unsaturated hydrocarbons that exhibit this property, and they are called

aromatic compounds. In addition to benzene, these include naphthalene, anthracene, and phenanthrene and so on. The word "aroma" in aromatics comes from the fact that such compounds have a relatively pleasant smell (chain unsaturated hydrocarbons generally have a foul smell like rotten onions). However, nowadays it does not refer to a "pleasant smell" but to the special stability of unsaturated cyclic compounds.



Cyclic unsaturated hydrocarbons

Regardless of the number of ring members (value of m), when the number of π electrons is $4n+2$, it is stable.

When the number of π electrons is $4n$, it is unstable.

$n=(0),1,2,\dots$

Figure 2. Relationship between the number of π electrons in cyclic unsaturated hydrocarbons and the stability of the compound.

Following the discovery of Hückel's rule, it has long been believed that the stability of aromatic compounds is due to the conjugation of π electrons. The relationship between the stability of cyclic unsaturated hydrocarbons and the number of π electrons was investigated, and it was found that when the number of π electrons is $4n+2$ ($n=0,1,2,\dots$), they are more stable than linear hydrocarbons with the same number of unsaturated bonds, and when the number of π electrons is $4n$ ($n=1,2,4,\dots$), they are unstable. This is called Hückel's rule or the $4n/4n+2$ rule and is one of the most fundamental concepts in organic chemistry. Benzene is a typical example of a stable system with $n=1$.

Among cyclic unsaturated hydrocarbons, some are very chemically reactive and quickly react with other molecules and disappear (e.g., cyclobutadiene), while others have a curved structure rather than a planar structure to avoid conjugation of the π electrons (e.g., cyclooctatetraene). However, if π electrons are removed or added to make the number of π electrons the number of stable systems according to Hückel's rule, the system will have a planar structure that is favorable for conjugation. Such an example is shown in Figure 3. The ions shown in the bottom row of Figure 3 have a regular tetragonal, pentagonal, hexagonal, heptagonal, or octagonal structure. In other words, instead of $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ bonds, all C-C bonds are uniform bonds with no distinction between single and double bonds.

Furthermore, there is the following fact: The C-H bond in benzene has an electronegativity of 2.5 for carbon atoms and 2.1 for hydrogen atoms, so it polarizes like $\text{C}^{\delta-}-\text{H}^{\delta+}$. The polarized structure is called a dipole moment. Its magnitude (μ) is expressed as the amount of polarized charge (Q) and the distance r (in this case, the bond distance), $Q \times r$, and is called dipole efficiency (unit: Debye D). Dipole efficiency has a direction as a vector amount, and takes the direction from - to + positively (there are some textbooks that define the direction inversely).

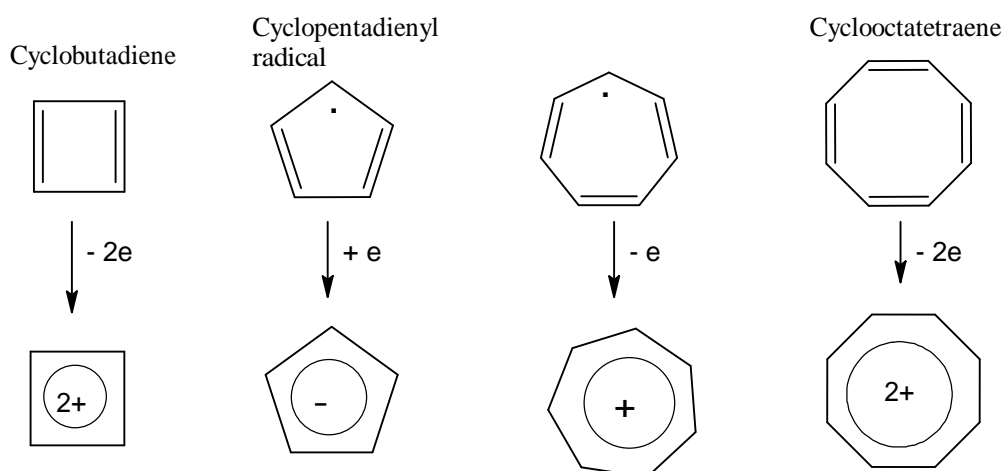


Figure 3. Even if the system is unstable, if the number of π electrons is set to a stable number according

to Hückel's rule, the π electron system becomes completely conjugated.

In the case of benzene, each C-H bond has a dipole, but due to the symmetry of the molecule, there is always a dipole in the opposite direction. These cancel each other out, so the dipole moment of the entire benzene molecule is 0. However, certain cyclic unsaturated hydrocarbons can have peculiar dipole moments as a whole molecule. Figure 4 shows an example. The μ value is the dipole moment of the molecule, and the number assigned to the carbon atom in the structural formula is the electron density of π electrons calculated using a method called the Hückel molecular orbital method.

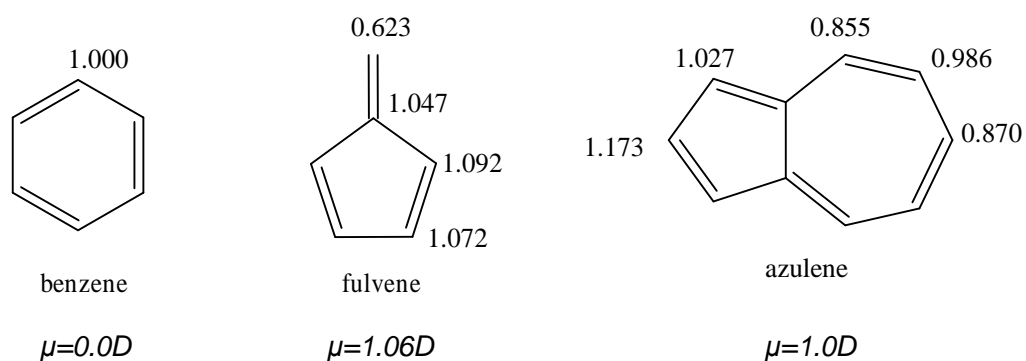


Figure 4. Fulvene and azulene have large dipole moments as whole molecules.

The number of π electrons in the ring of a fulvene is five, but if one π electron is introduced from the terminal methylene into the ring, the number of π electrons in the ring becomes six. The azulene molecule has a structure in which the π electron system of a five-membered ring and the π electron system of a seven-membered ring are fused together, with the numbers of π electrons being five and

seven, respectively (the π electrons of the carbon atoms in the environment are counted in the number of π electrons of both rings). In an azulene molecule, if one π electron of the seven-membered ring is transferred to the five-membered ring, both rings will have six π electron systems. Considering these, the π electrons move so that the π electron system of a cyclic unsaturated hydrocarbon becomes $4n+2$ ($n=1$), which is the stable system of Hückel's rule, and a large dipole moment is generated. The results of molecular orbital calculations also support such a transfer of π electrons.

Let us return to the subject of benzene. The unique stability of benzene is seen as a special form of conjugation and has long been accepted by organic chemists and theoretical chemists alike. As an aside, E. Hückel introduced the famous Hückel molecular orbital method to explain this special stability of benzene.³ To reiterate, the stability of the π electron system has gained absolute confidence among organic chemists.

The bond distance of a single bond between carbon atoms is approximately 1.54 \AA , and that of a double bond is 1.35 \AA , so essentially (if there is no special conjugation known as aromaticity) it should have an irregular shape like structure **A**. (Structure **A** is represented by the symbol D_{3h} , as a convention for expressing molecular symmetry.) However, as you know, benzene molecules take the regular hexagonal structure **B**. This is represented as D_{6h} . Moreover, the bond distance is 1.4 \AA . This is because the double bonds are completely conjugated, and π electrons are distributed equally in both the single bonds and double bonds between the double bonds, making it impossible to distinguish between these bonds.

These facts left little doubt about the idea that the special stability of benzene and its D_{6h} structure are due to π electrons. Therefore, the announcement by Shaik et al. is a serious problem that could shake the basic concept of aromaticity in organic chemistry.

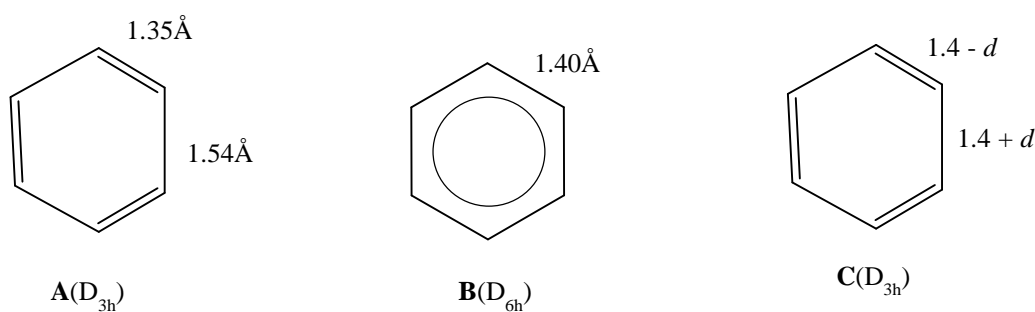


Figure 5. Structures of the benzene molecule

The argument made by Shaik et al.

The total energy (E) of planar unsaturated hydrocarbons can be separated into the energy of the sigma (σ) electrons (E^σ) and the energy of the π electrons (E^π). This is possible because the bond

order (P) can be expressed as the sum of the bond order of the σ electrons (P^σ) and the bond order of the π electrons (P^π): $P = P^\sigma + P^\pi$.

$$E = E_\sigma + E_\pi \quad (1)$$

Shaik et al. extended every other bond in D_{6h} benzene by a distance d and shortened every other bond by d (structure **C** of D_{3h}) and observed the changes in E_σ and E_π . Compared to D_{6h} benzene, E_π decreased and E_σ increased. From this fact, they concluded that the π electrons in benzene prefer a localized electronic structure rather than an even distribution. They subsequently published numerous papers to support this conclusion. At first glance, this is a very reasonable claim. However, there are often unexpected hidden meanings behind "seemingly reasonable" phenomena. This is why researchers are so enthusiastic about research.

$$\begin{aligned} \Delta E_\pi &= E_\pi^{D_{3h}} - E_\pi^{D_{6h}} \\ \Delta E_\sigma &= E_\sigma^{D_{3h}} - E_\sigma^{D_{6h}} \end{aligned} \quad (2)$$

This attracted the interest of many theoretical chemists. Some papers agreed with Shaik's conclusion,⁴ others disagreed,⁵ and some questioned the fact that different research methods led to different conclusions.⁶

This problem was solved by a series of papers by Ichikawa et al.⁷ They pointed out that, first, E^π , as expressed in Eq. 1, does not really represent the energy of only the π electronic structure. In other words, when structure **B** is changed to **C**, the value of E^π changes, but this includes not only the energy change due to the change in the π electronic structure, but also the energy changes due to the changes in the position of the atomic nuclei. Therefore, it cannot be said that E^π decreases in general due to the change in electronic structure.

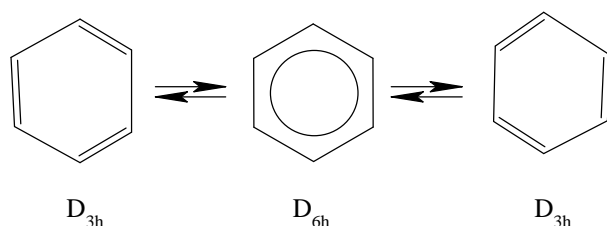


Figure 6. D_{3h} symmetry-preserving vibrations of benzene (b_{2u}).

Honig's Question⁸

In 1950, Honig noticed something strange when he looked at the vibrational spectrum (infrared region) of benzene. There are two types of vibration that maintain the planar structure of benzene.⁸ One is a vibration that maintains the regular hexagonal structure (D_{6h}) of benzene, in which the benzene nucleus expands and contracts, and is called an a_{1g} type vibration. The other is a vibration in which the distance between every other bond increase and every other bond contract at the same rate. This is a vibration that maintains the D_{3h} structure and is called a b_{2u} type vibration.

The frequency of the b_{2u} vibration is very low (1311, 1147 cm^{-1}), and the frequency corresponds to vibrational energy. Honig pointed out that " b_{2u} vibration occurs with small energy. This is because the Kekulé electronic structure (electronic structure in which the π bonds are not completely conjugated and the properties of single and double bonds are maintained) resulting from benzene's D_{3h} structure is stable. In other words, he deduced that the π electrons of benzene are more stable when they are not completely conjugated and consist of double bonds and single bonds."

Ten years later, Berry supported Honig's claim based on the results of molecular orbital calculations.⁹ The author then looked into the method of molecular orbital calculations that Berry spoke of, but it was a quote from a presentation (oral presentation) at a symposium by someone named Snyder, and he was unable to find out what method Snyder used for calculations or what results he obtained.

Can we accept Honig's conclusion as it is? In fact, it is natural that the frequency of the b_{2u} vibration does become small (it vibrates with less energy). As an example, let's consider the energy of internuclear repulsion. In the b_{2u} vibration, when every other bond is lengthened by d , every other bond is shortened by d . The internuclear repulsion energy is given by $36e^2/R$, where R is the distance between carbon nuclei (e is the charge of an electron (proton)). (See that each carbon atom has six protons in its nucleus.) If R is extended to $R+d$ by the b_{2u} vibration, the energy decreases by $36e^2d/R(R+d)$, but the adjacent bond becomes $R-d$, and the energy increases by $36e^2d/R(R-d)$. If d is small, the net energy change is almost 0. Therefore, it is not because the Kekulé structure of the π electrons is particularly stable. For this reason, we will ignore Honig and Berry's paper.

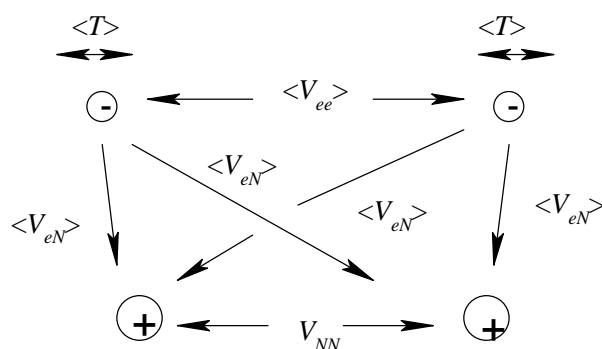


Figure 7. The energy of a molecule consists of the kinetic energy of electrons ($\langle T \rangle$), the one-electron potential

energy ($\langle V_{eN} \rangle$), the electron-electron repulsive energy ($\langle V_{ee} \rangle$), and the nuclear repulsive energy (V_{NN}).

Doubts about Shaik et al.'s claims

As already mentioned, the fundamental questions raised by Ichikawa et al.⁷ regarding the conclusions of Shaik et al. were as follows: (1) whether the E_{π} given in Eq. 1 truly represents the

energy of the π electrons only, and (2) whether it is possible to compare the energies of π electrons in different atomic geometries. The second point apparently ignores the Born-Oppenheimer approximation, which is a basic assumption of molecular orbital theory.

$$E = E^{el} + V_{NN} \quad (3)$$

$$E^{el} = \langle T \rangle + \langle V_{eN} \rangle + \langle V_{ee} \rangle \quad (4)$$

The total energy (E) of a molecule can be divided into the total electronic energy (E^{el}) and the nuclear repulsion energy (V_{NN}). E^{el} is divided into the kinetic energy of the electrons ($\langle T \rangle$: in classical mechanics, it corresponds to the energy of the motion of the electrons), the one-electron potential energy ($\langle V_{eN} \rangle$: the energy based on the electrostatic attraction between the negative charge of the electrons and the positive charge of the nuclei), and the electron repulsion energy ($\langle V_{ee} \rangle$: the energy based on the repulsion between the negative charges of the electrons) (Figure 7). The terms enclosed as ' $\langle X \rangle$ ' represent quantum mechanical expectation values. There are expectation values and eigenvalues in quantum mechanics, and there is a profound difference between the two, but the author will not explain them here.

In unsaturated hydrocarbons with a planar structure such as benzene, E^{el} can be further divided into the energy related to π electrons (E_{π}) and the part related to σ electrons (E_{σ}) and can be expressed by the following formula.

$$E^{el} = \langle T \rangle_{\pi} + \langle V_{eN} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi\sigma} + \langle T \rangle_{\sigma} + \langle V_{eN} \rangle_{\sigma} + \langle V_{ee} \rangle_{\sigma} + \langle V_{ee} \rangle_{\sigma\pi} \quad (5)$$

Here, $\langle T \rangle_{\pi}$, $\langle V_{eN} \rangle_{\pi}$ etc. denote the kinetic energy of the π electron, the single-electron potential energy of the π electron, etc. Additionally, $\langle V_{ee} \rangle_{\pi\sigma}$ denotes the interelectronic (double-electron) repulsive energy that the π electrons experience from the σ electrons, and $\langle V_{ee} \rangle_{\sigma\pi}$ denotes the interelectronic repulsive energy that the σ electrons experience from the π electron. However, according to the law of action and reaction, $\langle V_{ee} \rangle_{\pi\sigma} = \langle V_{ee} \rangle_{\sigma\pi}$. For information on the division of the total energy, see reference [10].

Shaik et al. defined the energy of the π electrons and the energy of the σ skeleton in Eqs. 6 and 7. This is thought to be based on the interpretation that "the energy obtained from the Hückel molecular orbital (described later) is the energy of the π electron moving in the potential created by the atomic nucleus, the (fixed) σ electrons, and other π electrons."

$$E_{\pi}^{Shaik} = \langle T \rangle_{\pi} + \langle V_{eN} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi\sigma} + \langle V_{ee} \rangle_{\sigma\pi} \quad (6)$$

$$E_{\sigma}^{Shaik} = \langle T \rangle_{\sigma} + \langle V_{eN} \rangle_{\sigma} + \langle V_{ee} \rangle_{\sigma} + V_{NN} \quad (7)$$

However, since σ electrons also move, it seems more reasonable to define it as follows ;

$$E_{\pi}^{el} = \langle T \rangle_{\pi} + \langle V_{eN} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi} + \langle V_{ee} \rangle_{\pi\sigma} \quad (8)$$

$$E'_\sigma = \langle T \rangle_\sigma + \langle V_{eN} \rangle_\sigma + \langle V_{ee} \rangle_\sigma + \langle V_{ee} \rangle_{\sigma\pi} + V_{NN} \quad (9)$$

In either method, it is necessary to carefully consider whether it truly represents the energy of the π electrons. This is because divided energies are directly affected by the position coordinates of the nucleus as $\langle V_{eN} \rangle$.

What is the energy of π electrons?

Most organic chemists are probably familiar with the Hückel molecular orbital method for calculating the energy of π electrons in conjugated double bonds, so we will not go into a detailed explanation of the calculation method. This molecular orbital method is also the basis of the Woodward-Hoffmann rule. The energy obtained using the Hückel molecular orbital method has long been called the π electron energy, and as already mentioned, it is understood to be the energy of the π electrons moving within the potential created by the atomic nucleus, the (fixed) σ electrons, and other π electrons.

By the way, when we look at the system $\text{CH}_2=\text{CH}-(\text{CH}=\text{CH})_n-\text{CH}=\text{CH}_2$, we find that the energy of the π electrons has a strange property in that every time n increases by one, the energy increases by a fixed amount. This is called energy additivity and is used to quantitatively determine aromaticity. Why is this strange? Because even though it is the energy of the π electrons, it also includes the repulsive energy between atomic nuclei. In other words, when n increases by one, $\text{CH}=\text{CH}$ is added, but this also includes two carbon nuclei and two hydrogen nuclei.

To investigate this issue, Ichikawa et al. divided the total energy (E) into the sum of Eq. 5 and $\langle V_{NN} \rangle$ and searched for terms that are proportional to the energy of the π electrons by the Hückel molecular orbital (the Hückel energy). As a result, they found that it was the total energy (E), the kinetic energy of the electrons ($\langle T \rangle$), and the kinetic energy of the π or σ electrons ($\langle T \rangle_\pi$ and $\langle T \rangle_\sigma$). Of these, the one related to the π electrons is $\langle T \rangle_\pi$, so they claimed that this term, the kinetic energy of the π electrons, corresponds to the Hückel energy.^{11,12}

The relationship between the total energy (E) and $\langle T \rangle_\pi$ is explained as follows: For chain unsaturated hydrocarbons, the ratio of $\langle T \rangle_\pi$ to $\langle T \rangle$ is 0.0021, and is constant regardless of the length of the chain. According to the Virial theorem,¹³ $E = -\langle T \rangle$, and so there is a proportional relationship between E and $\langle T \rangle_\pi$. They then carried out more detailed research into the additivity of the energy of π electrons, but we will not go into that here.

Conclusion for "What are the energy of π electrons?": The energy of π electrons is the kinetic energy of π electrons ($\langle T \rangle_\pi$), and E_π^{Shaik} does not correspond to the energy of π electrons.

When the atomic arrangement in benzene is changed, can the energy of the π electrons be compared?

In Figure 5, suppose the bond distance of D_{6h} benzene (**B**) is changed by d on the b_{2u} coordinate. (This means that every other bond is extended by d , and every other bond is shortened by d to create benzene with **C** structure.) If this structural change does not affect the energy of the π electrons, then the π electron energy change between structures **B** and **C** can be said to be due to the change in the π electronic structure.

Ichikawa et al. have theoretically shown that the energy change due to a small change in the geometric structure is larger than the total energy in the case of the energy expectation value (E_π , etc., which divides the total energy, corresponds to the expectation value), and they actually calculated the changes in total and divided energies when the optimal structure of benzene is changed by a small amount on the b_{2u} coordinate. The results are quoted in Table 1.¹⁴

Table 1. Energy changes when benzene is deformed on the b_{2u} coordinate system^a

term	benzene ^b	distorted ^c	dif. ^d
E	-230.131181	-230.130948	0.6
E^{el}	-434.895341	-434.899241	-10.2
V_{NN}	204.764160	204.768293	10.9
$\langle T \rangle$	229.990483	229.992533	5.4
$\langle V_{eN} \rangle$	-946.860745	-946.869539	-23.1
$\langle V_{ee} \rangle$	281.974922	281.977766	7.5
$E_\pi^{el\ e}$	-40.067251	-40.068398	-3.0
$E_\pi^{Shaik\ f}$	-6.405036	-6.405731	-1.8
$\langle T \rangle_\pi$	7.471762	7.471929	0.4
$\langle V_{eN} \rangle_\pi$	-85.535949	-85.537529	-4.1
$\langle V_{ee} \rangle_\pi$	4.334722	4.334535	-0.5
$E_\sigma^{el\ g}$	-394.828090	-394.830843	-7.2
$\langle T \rangle_\sigma$	222.518721	222.520603	4.9
$\langle V_{eN} \rangle_\sigma$	-861.324796	-861.332010	-18.9
$\langle V_{ee} \rangle_\sigma$	210.315770	210.317897	5.6
$2X \langle V_{ee} \rangle_{\pi\sigma}$	67.324430	67.325334	2.4
E'_σ^h	-190.063930	-190.062550	3.6
$E'_\sigma^{Shaik\ i)}$	-223.726145	-223.725217	2.4

^aSTO-6G. ^bAu. Geometry-optimized benzene (D_{6h}). The bond lengths of C-C and C-H are 1.38585 and 1.07867 Å. ^cAu. Displacement by 0.01Å along the b_{2u} coordinate (D_{3h}). ^dDifference in kJ/mol. ^e π Electronic energy. ^f' π Energy' defined by Shaik. ^g σ Electronic energy. ^hSkeletal energy ($E - E_\pi^{el}$). ⁱSkeletal energy by Shaik.

When $d=0.01\text{\AA}$, the change in total energy is only 0.6kJ/mol. In general, the change in energy on the b_{2u} coordinate is "slight" for the reasons mentioned above, but the change in the divided energy is still large, up to 39 times the total energy change. The effect of nuclear arrangement on the energy of the π electron is expressed in $\langle V_{eN} \rangle_{\pi}$. The change in this value (absolute value) is 4.1kJ/mol. The change in the energy of the π electrons is 1.8kJ/mol according to Shaik's definition, so the main energy change in Shaik et al.'s argument is due to the change in the geometric structure, not the change in the π electronic structure. Although they were supposed to be trying to find the relationship between the π electronic structure and the π electronic energy, they looked at the relationship between the geometric structure of benzene and the energy of the π electrons.

Conclusion of this section: Most of the energy change of the π electrons that occur when the geometric structure is changed is due to the change in the nuclear arrangement, not the change in the π electronic structure.

So how do we solve the benzene problem?

Since we know that the energy of the π electrons is the kinetic energy of the π electron ($\langle T \rangle_{\pi}$), we need to focus on $\langle T \rangle_{\pi}$. Ichikawa et al. have used two methods to solve the problem that it is not possible to compare the energy of the π electrons by changing the geometric structure. One method is to change the electronic structure without changing the geometric structure and obtain the total and partitioned energies as a function of the electronic structure. This is called the constrained Hartree-Fock method.¹⁵ The other method is to partially differentiate the energy with respect to the nuclear configuration or bond order (partial differentiation method).¹⁶

Constrained Hartree-Fock method

It is the wave function that determines the electronic structure. The wave function cannot be arbitrary; it must be a standing wave in the electrostatic field¹⁷ created by the charges of the atomic nuclei and electrons. A standing wave is a wave that exists over time, and this is important. Atomic orbitals contain principal quantum numbers, azimuthal quantum numbers, and magnetic quantum numbers, but for example, an atomic orbital (wavefunction) with a principal quantum number of 1.5 is not considered because such a wave cannot exist. The problem is how to find the standing wavefunction that corresponds to an arbitrary electronic structure.

The standing wavefunction is obtained as an eigenfunction of the operator (Hamiltonian) corresponding to the energy of the electron. Therefore, by manipulating the Hamiltonian to change it to a specific electronic structure and finding its eigenfunction, the standing wavefunction corresponding to that electronic structure can be obtained.¹⁸ Once the wave function is obtained, the total energy or its components can also be obtained. In the case of the commonly used molecular orbital method, the Hamiltonian is the Fock operator. Manipulating the Fock operator to obtain the

wavefunction for a specific electronic structure is equivalent to solving the constrained Hartree-Fock equation, which is the following equation.

$$(F + \lambda)C = SC\varepsilon \tag{10}$$

The usual Hartree-Fock equation is one where λ is a $\mathbf{0}$ (vector). Here, F , C , S , and ε are the Fock operator, the coefficient representing the contribution of the basis function to the molecular orbital, the overlap integral, and the energy of the molecular orbital, respectively. λ is an operator that defines the electronic structure of the system (molecule). For example, to find the wave function of the electronic structure of unconjugated benzene, it can be considered as an operator that sweeps out the π electrons on every other C-C bonds. Details of this method are given in reference [15], and the results are presented here.

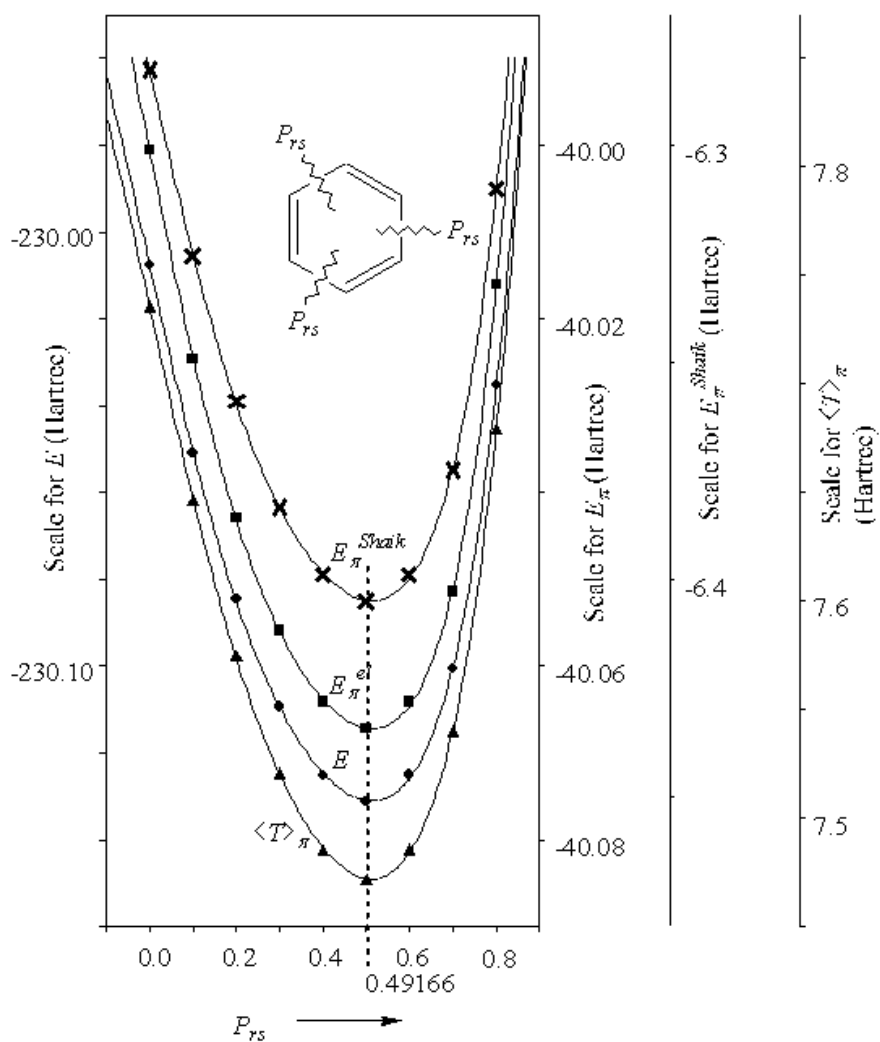


Figure 8. Various energies as a function of alternate π bond orders (P_{rs})

The constrained Hartree-Fock method allows us to obtain the total energy and its components as a function of bond order without changing the geometry of benzene. Figure 8 shows the energy change

as a function of every other π bond order (P_{rs}) of benzene. The basis set is STO-6G. When $P_{rs} = 0$, the double bond of benzene is completely isolated, and the energy minimum is $P_{rs} = 0.49166$, which coincides with the value given by the standard Hartree-Fock method. It is noteworthy that the total energy (E) and the splitting terms (including the energy of the π electrons defined by Shaik) are all minimum when $P_{rs} = 0.49166$. This means that the energy of the π electrons is also the lowest at that time, i.e., when it is uniformly distributed. Although this is not an appropriate way of saying it, using Shaik's expression, the π electrons of benzene prefer to be uniformly distributed.

Partial Differential Method Results

Let's consider the ratio of the change in energy (E) (ΔE) when only one of the variables q (q) changes by Δq . The ratio when Δq is infinitesimal is called the partial derivative of E with respect to q .

$$\frac{\Delta E}{\Delta q} = \frac{E(q+\Delta q)-E(q)}{\Delta q} \rightarrow \frac{\partial E}{\partial q} \quad (11)$$

Since vector q has direction, so $\partial E/\partial q$ does. Therefore, the partial differential coefficient (value) is a vector quantity with direction and magnitude. (Note that energy is a scalar quantity without directional information.) If the nuclear coordinate of an atom is q , then $\partial E/\partial q$ is the force acting on the nucleus at that position. When the geometric structure is optimized, the partial differential coefficient with respect to the total energy of all nuclear coordinates is 0. Also, since the total energy of a molecule is a function of the nuclear coordinates, the (geometric) structure of a molecule is such that the positions of the nuclei are in a "depression" of energy that has a small value in its vicinity. There are generally multiple such "depressions" of energy, which correspond to the existence of various compounds with the same molecular formula. From the viewpoint of energy, such a point is called a local minimum of energy. There is also a term called a global minimum of energy, which refers to the smallest of the multiple local minimums.

Now, by using partial differential calculus, we can clarify the causes of chemical phenomena. Since E can be divided into the sum of Eq. 5 and V_{NN} , Eq. 6 can be expressed as follows.

$$\frac{\partial E}{\partial q} = \frac{\partial}{\partial q} \langle T \rangle_{\pi} + \frac{\partial}{\partial q} \langle V_{eN} \rangle_{\pi} + \frac{\partial}{\partial q} \langle V_{ee} \rangle_{\pi} + \frac{\partial}{\partial q} \langle V_{ee} \rangle_{\pi\sigma} +$$

$$\frac{\partial}{\partial q} \langle T \rangle_{\sigma} + \frac{\partial}{\partial q} \langle V_{eN} \rangle_{\sigma} + \frac{\partial}{\partial q} \langle V_{ee} \rangle_{\sigma} + \frac{\partial}{\partial q} \langle V_{ee} \rangle_{\sigma\pi} +$$

$$\frac{\partial}{\partial q} V_{NN} \quad (12)$$

If we take the nuclear coordinate as q , then the right-hand side of Eq. 12 becomes the component of the force acting on the nucleus. Because chemical reactions are accompanied by changes in the position of the nuclei, analyzing the right-hand side of Eq. 12 will tell us what type of force is inducing the reaction. An analytical differentiation method for the variable q of the energy partition component as in Eq. 12 has been given by Tokiwa et al.,¹⁹ but it can also be easily found using numerical differentiation.

When benzene is in the D_{6h} structure, E has a minimum value, so if we deform benzene to D_{3h} on the b_{2u} coordinate and then analyze the force trying to return to D_{6h} , the cause of the D_{6h} structure of benzene should become clear. The values when deformed by 0.06 Å on the b_{2u} coordinate are shown in Table 3.

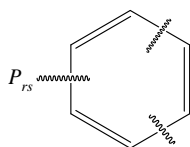
Table 3. The force ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{Å}^{-1}$) that returns benzene to its original shape when it is deformed by 0.06Å on the b_{2u} coordinate system (molecular orbital method: STO-6G)¹⁴

E	$\langle T \rangle_{\pi}$	E_{π}^{el}	E_{π}^{Shaik}	E_{π}^{el}	E_{σ}'	$E_{\sigma}'^{Shaik}$
0.33	0.10	-1.29	-0.80	-3.36	1.62	2.12

Positive values correspond to a force trying to return to the original state, and negative values correspond to a force leading to the Kekulé structure. If the definition of the π electron energy by Shaik et al. is correct, then one would conclude that the π electrons prefer the Kekulé structure, i.e., the energy of the π electrons oppose it. However, since the energy of the π electrons is $\langle T \rangle_{\pi}$, the conclusion is the opposite, i.e., the π electrons have the force to return the system to D_{6h} .

Table 4 shows the results for the same deformed structure when the coordinate q is changed to P_{rs} . In this geometric structure, the π electron distribution in the single bond parts of every other bond is reduced, with the optimized value being $P_{rs} = 0.35450$, and 0.49166 for D_{6h} . The π electrons are quite localized.

Table 4. Partial derivatives of energy components in deformed benzene ($\partial X/\partial P_{rs}$) when benzene is distorted along the b_{2u} coordinate by 0.06Å



E	$\langle T \rangle_{\pi}$	E_{π}^{el}	E_{π}^{Shaik}	E_{π}^{el}	E_{π}'	$E_{\pi}'^{Shaik}$
0.0	-500.7	198.4	6.95	-198.4	-198.4	-389.9

Unit: $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{e}^{-1}$

In Table 4, positive values indicate an increase in E due to an increase in P_{rs} , and negative values indicate a decrease. We can see that $\langle T \rangle_{\pi}$ reduces energy significantly in the direction of equal distribution. In other words, we can understand that the π electrons are trying to be evenly distributed.

Conclusion: In regular hexagonal benzene, π electrons prefer equal distribution. In benzene whose geometric structure has been deformed into the Kekulé form, the π electrons have the power to return the geometric structure to a regular hexagon, and the distribution of the π electrons also tries to be even.

What was the problem?

Mistakes are inevitable in research, but incorrect research does not necessarily mean that the research was meaningless. By analyzing the causes of failure, we can contribute to "avoiding the repeat of mistakes" in new research, either our own or that of others. In that sense, let us consider the causes of this uproar. There are three points to mention:

1. The definition of π electron energy was not a "yardstick" for aromaticity. It was discovered in the 1960s that the standard energy yardstick for aromaticity must be additive.^{20,21} This additivity was studied in detail by Hess and Schaad in 1971.²² Although these papers are well known, Shaik et al. overlooked them. Furthermore, they did not cite Honig's paper, which pointed out a similar point more than long years before them, the author feels that it is "all I can say." Research must be started after examining past literature.
2. The ambiguity of chemical structural formulas brought ambiguity to the definition of the system. Chemical structural formulas are convenient because they concisely express molecular information, but even if the structure changes from the original structure, the expression is the same, so it is often thought that there is no significant change in the energy relationships that make up the molecule. However, even if the geometric structure changes slightly, the energy relationships within the molecule can change significantly. This is related to the next point 3.
3. The Born-Oppenheimer approximation was not properly understood. The molecular orbital method is based on the Born-Oppenheimer (BO) approximation. This is an approximation that the movement of electrons is infinitely faster than the movement of atomic nuclei. The mass of an atomic nucleus is 1,840 to tens of thousands of times that of an electron, so this is a natural approximation, and in fact most chemical phenomena can be applied without any problems with the BO approximation. The BO approximation is equivalent to "when an atomic nucleus moves, the electron distribution is optimized (the wave that determines the distribution of electrons becomes a standing wave) at the same time as the movement." Therefore, if the position of the atomic nucleus changes slightly, the system becomes different from the original system. What is different is that the

potential for electrons is different. Even if the electronic structure is similar, if the potential is different, the energy will be different. Therefore, comparing the energies of different systems gives the relationship between the geometric structure of the molecule and the energy, it is meaningless to investigate the relationship between electronic structure and energy using this method.

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13. Virial theorem: The energy (E) of a system is expressed as the sum of kinetic energy (T) and potential energy (V) ($E=T+V$). In a steady state (a state in which E does not change over time), $V=-2T$ holds, and therefore $E=-T$. This is called the Virial theorem, and it holds in both classical and quantum mechanics. It is an important theorem when discussing the state of molecules. $-V/T$ is called the Virial ratio, and in the steady state (in the case of molecules, when the geometric structure is optimized), it is exactly 2. During a reaction, this ratio does not become 2. When calculating with the molecular orbital method, it becomes 2 only when the basis set is a complete system (one that has a sufficient number and properties of basis functions to describe the electronic structure of the molecule). However, there is a technique called scaling, so the basis set does not have to be a complete system.
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17. Electrostatic field: For example, if there is a proton and an electron a distance r away from it, a force (f) acts between them, which is expressed by the following equation.

$$f = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{(e)(-e)}{r^2}$$

$-e$ is the charge of the electron, e is that of the proton, ϵ_0 is a constant called the dielectric constant of vacuum, and depending on the units used (e.g. cgs units) the first parentheses will be 1. Excluding the charge of the electron,

$$\left(\frac{1}{4\pi\epsilon_0} \right) \frac{(e)}{r^2}$$

is called the electric field E created by the proton at position r . When an electron is placed at position r , a force (vector) of $f=eE$ acts on it. The direction of the force should be aligned with the direction of r .

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