

In the Hückel Method Application Heksatriena Conjugated Molecules

Andre I. Lumempow¹, D. R. Wenas², A. Komansilan³

¹Undergraduate Student, Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Manado

^{2,3}Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Manado

(³alfritskomansilan@gmail.com)

Abstract-One method used in the calculation of molecular orbital is Hückel molecular orbital method. The purpose of this study is to examine the electronics state transitions heksatriena conjugated molecules, the calculation of the amounts to heksatriena conjugated molecules, and the resulting spectrum. Calculation of molecular orbital calculations is one that is very complicated to do because it requires a complex mathematical calculations and stack output which must be analyzed. Hückel method is a method that uses a simple calculation. This method was developed to study the properties of linear hydrocarbon molecules that have conjugated double bonds. This method is part of a computational method semiempirical molecules. The method used is the modeling of the electronics structure and molecular heksatriena calculated by the Hückel approach. This method will compare the complexity of manual calculations with the calculations have been using the Hückel method. This molecular orbital method will facilitate the construction manual of molecular orbital calculations. By using the software package Matlab Hückel program, will result in the output of the heksatriena molecular scales, along with its spectrum. The spectrum will be seen through the electronic transitions of heksatriena molecules.

Keywords- *Hückel Method, Conjugated Molecular, Electronic Transitions*

I. INTRODUCTION

Molecular orbital calculation is a calculation requiring a complex mathematical analysis. However, by using a simple method that can provide specific data and information can be linked with the results of the experimental observations. One of these is a simple calculation, Hückel method. Hückel method is a method developed by Erich Hückel, a German physicist. Erich Hückel tried to understand the concept of aromaticity in benzene, but then the method was developed to study the properties of linear hydrocarbon molecules that had conjugated double bonds.

One of the hydrocarbon molecules is the simplest linear conjugated molecules heksatriena. Heksatriena molecule is a molecule that has six carbon atoms and eight hydrogen atoms (C_6H_8). The material with conjugated double structure has bonded π electrons that are responsive to external electric field

that has a great probability of electrical and optical responses showed that fast. This material can conduct electricity due to the conjugated double bond.

The Hückel method can explain the electronic state transitions that may occur from the ground state to an excited state. This method can also be applied in the calculation of the amount of molecules. This study becomes a complex assessment if done manually. Therefore, Hückel program package with the help of software Matlab v.7 is used not to make it more complex.

Package program can help Hückel molecular orbital calculation from a complex calculation becomes simpler. Scale of molecules heksatriena can also be calculated by the Hückel program package.

Molecular system is the case with multi-atom, so the system is prepared by atom bonded to each other. In predicting the characteristics of molecules in terms of molecular electronic structure can be done by Linear Combination Atomic Orbital (LCAO) approaches. By using the LCAO, molecular orbital can be functioned to the state of a single electron in the core field of the whole molecule so that the wave function that is a linear function approximation can be a combination of atomic orbitals

In the Hückel molecular orbital method, which is sometimes called the Hückel method or HMO (Hückel Orbital Method), shape and orbital energies obtained without integration numerical. Although there are many basic integral equations, various quantities are included in the secular equation is replaced with typical parameters depends on the element or kind of bond. Hückel method is divided into two, namely the method is simple Hückel and extended Hückel method. Simple Hückel method has the disadvantage that cannot be used on systems when chemical bonding position is not clear, although in an easy method. For example, metal complexes and organic compounds that have a structure that is not suitable for simple Hückel method. So the extended Hückel method specifically evaluates the overlap integral, although such an approach is contrary to the desire to avoid numerical integration wherever possible.

In the Hückel method, the assumption being made is part of bonding σ and bonding π in a molecule can be separated

because bonding - π is in the plane perpendicular to the plane of the molecule, the distance between the electron π and σ is large enough so that the interaction between them is relatively smaller than the atomic interaction as type of atom. Also overlap adjacent atomic orbitals are not considered as zero. Moreover, the interaction energy between atoms that are not adjacent considered zero. When these interactions are negligible, then the molecular orbitals of a conjugated molecule can be expressed as a linear combination of $2zp$ orbitals $2zp$. This is the view of the underlying theory of electron - π .

In a class of organic chemical compounds known hydrocarbon called conjugated compounds, such as ethylene C_2H_4 , butadiene C_4H_6 , benzene C_6H_6 , and heksatriena C_6H_8 . In compounds - of each carbon atom having sp^2 hybridization. The third hybrid form bonding σ with atom neighbors. Orbital $2p_z$ left, forming a bond with the π orbitals of the atoms neighboring $2p_z$. π -bonds is in use within the field perpendicular to the molecular plane, the plane formed by the bond σ . Electrons are involved in bonding σ , called electron - σ , localized in space. Electrons are involved in bond π called electron π ; electron is not localized but rather easy to move along the molecule. Ease of move that's caused by the unidirectional molecular polarizability bond - π . Hückel developed a calculation method that can provide understanding - a very useful basic understanding of a conjugated compound, in this method, the molecular orbitals ψ is expressed as a linear combination of orbital $2p_z$, of all the carbon atoms in the molecule, namely:

$$\psi = \sum_i c_i \phi_i$$

Where ϕ_i is orbital $2p_z$ in the i -carbon atom.

Scale of molecules which can be calculated by the Hückel method:

- Total π -electron density (q)

$$Q_i = \sum_R n_r c_{ri}^2$$

- Bond order (p)

$$p_{ij} = \sum_r n_r c_{ri} c_{rj}; i \neq j$$

- Bond length between carbon atoms (r)

$$r_{ij} 1,5 - 0,15 p_{ij} \text{ (Angstrom)}$$

- Free valence-electron π (F)

$$F_i = 1,732 - p_i$$

- Total π -electron energy $-\pi$ (E_0)

$$E_0 = \sum_r n_r \epsilon_r$$

- Energy localization (E_{lok})

$$E_{lok} = g_1(2\alpha + 2\beta) + g_2\alpha$$

- Delocalization energy molecules (E_d)

$$E_d = E_0 - E_{lok}$$

Energy has UV rays that can cause the displacement of electrons or the so-called electronic transition. Electronic transitions can be interpreted as a transfer of electrons from one orbital to another orbital. Called the electronic transitions due to electrons occupying an orbital with the lowest energy can be transferred to another orbital has a higher energy if it absorbs energy. In the other hand, electrons can move from orbital that have lower energy if the energy releases Received or absorbed energy in the form of electromagnetic radiation. In quantum mechanics electronic transitions are allowed or not allowed (forbidden) called selection rules. Based on the selection rules, generally electronic transitions include:

- Transitions are allowed when the value of ϵ is 10^3 to 10^6
- Transitions are forbidden when the value of ϵ is 10^{-3} to 10^3

In addition to seeing the price ϵ can be expressed by the selection rules and spin symmetry. Based on the symmetry and spin electronic transition, allowed if:

- Takes place between orbitals in the same field
- During the orientation of the spin transition should be fixed.

In one molecule there are two kinds of orbitals, bonding orbital and antibonding orbitals. Bonding orbitals are divided into several types namely sigma bonding orbitals (σ , single bonds) and orbital phi (π , double bonds), while the non-bonding orbitals form of free electrons usually denoted by n. Non-bonding orbitals are generally found in molecules that contain nitrogen atoms, oxygen, sulfur and halogen groups. The electronic transition from orbital bonding to anti-bonding orbitals does not lead to dissociation or termination of bond.

Many benefits to be gained from this research. Completion of a simple molecular orbital is one of its benefits. The output data from the program Hückel package can be used to learn heksatriena molecular structures and the scale of molecular heksatriena.

II. RESEARCH METHOD

A. Kind of Research

This type of research is a research that focuses on the theoretical studies of the structure of conjugated organic materials with the aid of software Matlab v.7.

B. Place and Time Research

Location of the study carried out in the laboratory of Physics, Faculty of Mathematics and Natural Sciences, Manado State University. Particularly in materials physics laboratory.

C. Objects and Methods

Objects that were examined in this study are heksatriena which is linear conjugated molecule that has six carbon atoms and eight hydrogen (C₆H₈). The method used is heksatriena and molecular electronic structure which were calculated by the Hückel approach. This calculation was aided by using a software program package Matlab v.7 Hückel.

D. Bahan dan Alat

- Matlab v.7 Software
- Package of Hückel Program

E. Research Design

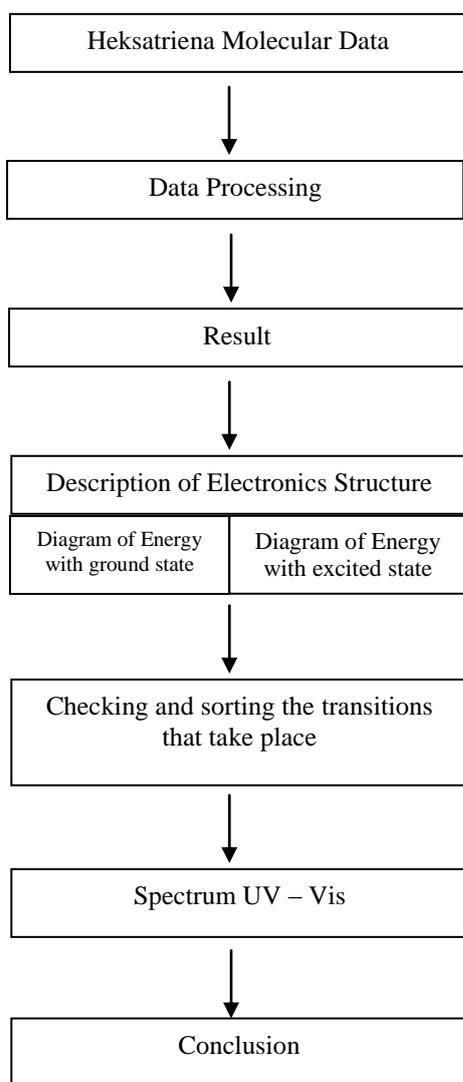


Figure 1. Diagram of Research Flows

III. RESULTS AND DISCUSSION

A. Hückel Method on Heksatriena Molecular

Heksatriena C₆H₈ has six carbon atoms.

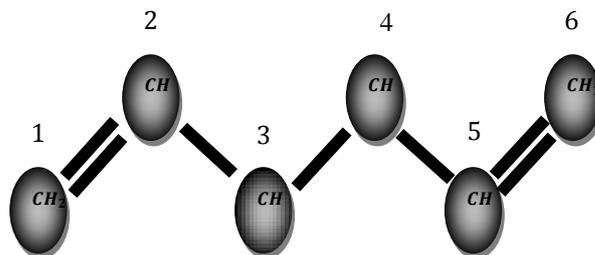


Figure 2. Numbering the Heksatriena Molecular

Starting from the left end, carbon atoms are numbered 1, 2, 3, 4, 5, 6.

Heksatriena has similar approximation wave:

$$\psi_i = c_{i1}p_{z1} + c_{i2}p_{z2} + c_{i3}p_{z3} + c_{i4}p_{z4} + c_{i5}p_{z5} + c_{i6}p_{z6}$$

Of the secular $\sum_{i,j}(H_{ij} - \epsilon S_{ij})c_j = 0$ then heksatriena wave equation can be substituted with α and β to form the matrix so that the secular determinant for this molecule is:

$$\begin{vmatrix} \alpha - \beta & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha - \beta & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - \beta & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - \beta & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - \beta & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha - \beta \end{vmatrix} = \beta \begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

with

$$x = \frac{\alpha - \epsilon}{\beta} \rightarrow \epsilon = \alpha - x\beta$$

Obtained from the secular determinant equation that $x^6 - 5x^4 + 6x^2 - 1 = 0$, with Matlab program, the roots are $x = -1.802, -1.247, -0, 445, 0,445, 1,247, 1,802$. If this price is distributed into eigen equation, then the energy of the molecular orbital is:

- $\epsilon_1 = \alpha + 1,802\beta$ Bonding
- $\epsilon_2 = \alpha + 1,247\beta$ Bonding
- $\epsilon_3 = \alpha + 0,445\beta$ Bonding
- $\epsilon_4 = \alpha - 0,445\beta$ Anti - Bonding
- $\epsilon_5 = \alpha - 1,247\beta$ Anti - Bonding
- $\epsilon_6 = \alpha - 1,802\beta$ Anti - Bonding

If the orbital energy Heksatriena described by setting the price $\alpha = -11$ and $\beta = -2.5$, then would come his energy level diagram:

$$\begin{aligned} \varepsilon_1 &= \alpha + 1,802\beta = -6,4952eV \\ \varepsilon_2 &= \alpha + 1,247\beta = -7,8826eV \\ \varepsilon_3 &= \alpha + 0,445\beta = -9,8874eV \\ \varepsilon_4 &= \alpha - 0,445\beta = -12,1126eV \\ \varepsilon_5 &= \alpha - 1,247\beta = -14,1174eV \\ \varepsilon_6 &= \alpha - 1,802\beta = -15,5048eV \end{aligned}$$

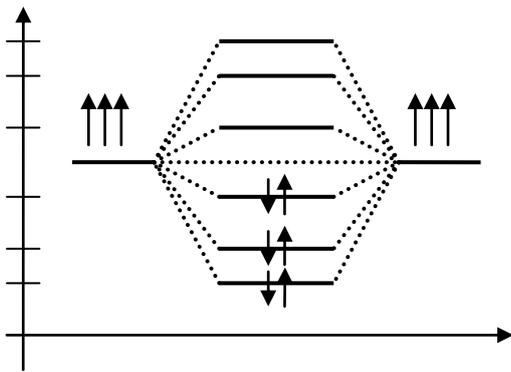


Figure 3. Diagram of Energy with ground state

$$\psi_6 = 0,232\phi_1 - 0,418\phi_2 + 0,512\phi_3 - 0,521\phi_4 + 0,418\phi_5 - 0,232\phi_6$$

$$\psi_5 = 0,418\phi_1 - 0,521\phi_2 + 232\phi_3 + 0,232\phi_4 - 0,521\phi_5 + 0,418\phi_6$$

$$\psi_4 = 0,521\phi_1 - 0,232\phi_2 - 0,418\phi_3 + 0,418\phi_4 + 0,232\phi_5 - 0,521\phi_6$$

$$\psi_3 = 0,521\phi_1 + 0,232\phi_2 - 0,418\phi_3 - 0,418\phi_4 + 0,232\phi_5 + 0,521\phi_6$$

$$\psi_2 = 0,418\phi_1 + 0,521\phi_2 + 232\phi_3 - 0,232\phi_4 - 0,521\phi_5 - 0,418\phi_6$$

$$\psi_1 = 0,232\phi_1 + 0,418\phi_2 + 0,512\phi_3 + 0,521\phi_4 + 0,418\phi_5 + 0,232\phi_6$$

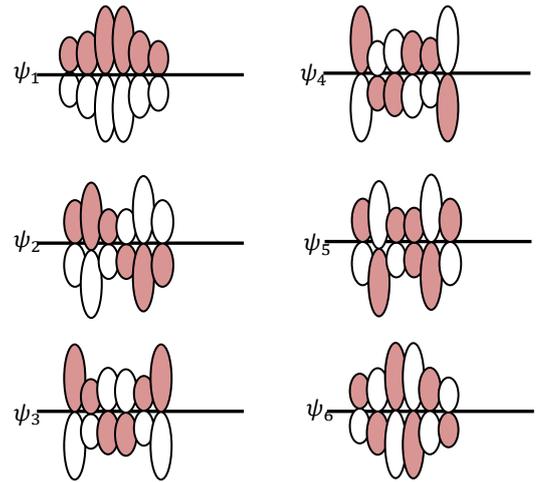


Figure 4. Heksatriena Molecular Orbital

B. Electron Transition

Examination of the π -electron transitions from the ground state Ψ_0 to the excited ground Ψ_n , done by considering the price of a state representation of the situation. Opportunity of proportional transition the square of the transition can be expressed by.

$$\mu_{0 \rightarrow n} = \int \Psi_0 \hat{\mu} \Psi_n dv$$

In this equation $\hat{\mu}$, the electric dipole operator expressed by components $\hat{\mu} = e(\hat{x} + \hat{y} + \hat{z})$, so that equation $\mu_{0 \rightarrow n} = \int \Psi_0 \hat{\mu} \Psi_n dv$ can be expressed on components separately:

$$\mu_{0 \rightarrow n}^{(x)} = \int \Psi_0 \hat{x} \Psi_n dv$$

$$\mu_{0 \rightarrow n}^{(y)} = \int \Psi_0 \hat{y} \Psi_n dv$$

$$\mu_{0 \rightarrow n}^{(z)} = \int \Psi_0 \hat{z} \Psi_n dv$$

Based on the above equation, it can be said that one of the three transitions can occur only if the representation of one of the components of x, y, z, for example to apply component z obtained $\Gamma(z) = \Gamma(\Psi_0)\Gamma(\Psi_n)$.

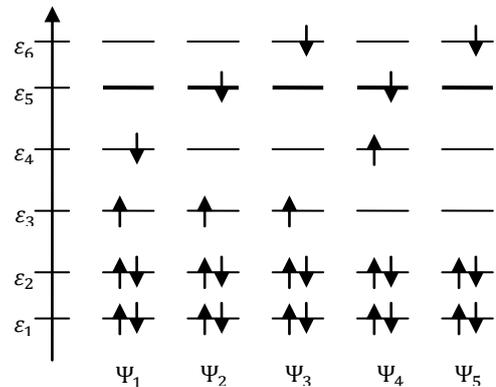


Figure 5. Diagram of Energy with Excited State

In the ground state of this molecule has π electron configuration $\psi_1^2, \psi_2^2, \psi_3^2$. So the excited state can be written as following:

1. Ground state $\Psi_0 \equiv \psi_1^2 \psi_2^2 \psi_3^2$ and energy $E_0 = 2\varepsilon_1 + 2\varepsilon_2 + 2\varepsilon_3$
2. Excited state 1 $\Psi_1 \equiv \psi_1^2 \psi_2^2 \psi_3^1 \psi_4^1$ and energy $E_1 = 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_3 + \varepsilon_4$
3. Excited state 2 $\Psi_2 \equiv \psi_1^2 \psi_2^2 \psi_3^1 \psi_5^1$ and energy $E_2 = 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_3 + \varepsilon_5$
4. Excited state 3 $\Psi_3 \equiv \psi_1^2 \psi_2^2 \psi_3^1 \psi_6^1$ and energy $E_3 = 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_3 + \varepsilon_6$
5. Excited state 4 $\Psi_4 \equiv \psi_1^2 \psi_2^2 \psi_4^1 \psi_5^1$ and energy $E_4 = 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_4 + \varepsilon_5$
6. Excited state 6 $\Psi_5 \equiv \psi_1^2 \psi_2^2 \psi_4^1 \psi_6^1$ and energy $E_5 = 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_4 + \varepsilon_6$

Transitions above must fulfill the equation,

$$\Gamma(\hat{\mu}) = \Gamma(\Psi_0)\Gamma(\Psi_n)$$

So, the transitions from ground state to the excited state will come to the result,

$$\Gamma(\hat{\mu}_{0 \rightarrow 1}) = \Gamma(\Psi_1) \rightarrow \text{allowed}$$

$$\Gamma(\hat{\mu}_{0 \rightarrow 2}) = \Gamma(\Psi_2) \rightarrow \text{forbidden}$$

$$\Gamma(\hat{\mu}_{0 \rightarrow 3}) = \Gamma(\Psi_3) \rightarrow \text{allowed}$$

$$\Gamma(\hat{\mu}_{0 \rightarrow 4}) = \Gamma(\Psi_4) \rightarrow \text{allowed}$$

$$\Gamma(\hat{\mu}_{0 \rightarrow 5}) = \Gamma(\Psi_5) \rightarrow \text{forbidden}$$

C. Calculation of Molecular States

1) Total π -electron density (q)

Calculation of load density on each atom according to the equation is as follows:

$$q_i = \sum_r n_r c_{ri}^2$$

$$q_1 = 2c_{11}^2 + 2c_{21}^2 + 2c_{31}^2 = 1$$

$$q_2 = 2c_{12}^2 + 2c_{22}^2 + 2c_{32}^2 = 1$$

$$q_3 = 2c_{13}^2 + 2c_{23}^2 + c_{33}^2 = 1$$

$$q_4 = 2c_{14}^2 + 2c_{24}^2 + 2c_{34}^2 = 1$$

$$q_5 = 2c_{15}^2 + 2c_{25}^2 + 2c_{35}^2 = 1$$

$$q_6 = 2c_{16}^2 + 2c_{26}^2 + 2c_{36}^2 = 1$$

Meaning, to every carbon atom, there is one electron.

2) Order Bonding Between Atoms Carbon (p)

Calculation of bond order between two nearest neighboring atoms according to the equation is as follows:

$$p_{ij} = \sum_r n_r c_{ri} c_{rj}; \quad i \neq j$$

$$p_{12} = 2c_{11}c_{12} + 2c_{21}c_{22} + 2c_{31}c_{32} = 0,871$$

$$p_{23} = 2c_{12}c_{13} + 2c_{22}c_{23} + 2c_{32}c_{33} = 0,483$$

$$p_{34} = 2c_{13}c_{14} + 2c_{23}c_{24} + 2c_{33}c_{34} = 0,785$$

$$p_{45} = 2c_{14}c_{15} + 2c_{24}c_{25} + 2c_{34}c_{35} = 0,483$$

$$p_{56} = 2c_{15}c_{16} + 2c_{25}c_{26} + 2c_{35}c_{36} = 0,871$$

3) Bonding Between Atoms Carbon Length (r)

From the equation, then the distance between two adjacent carbon atoms is as follows:

$$r_{ij} = 1,5 - 0,15 p_{ij} \quad (\text{Angstrom})$$

$$r_{12} = 1,5 - 0,15 p_{12} = 1,369 \text{ \AA} = r_{56}$$

$$r_{23} = 1,5 - 0,15 p_{23} = 1,428 \text{ \AA} = r_{45}$$

$$r_{34} = 1,5 - 0,15 p_{34} = 1,382 \text{ \AA}$$

From the above data, it appears that heksatriena ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$) has a bond length between carbon atoms $r_{12} = r_{56} = 1,369 \text{ \AA}$ and $r_{23} = r_{45} = 1,428 \text{ \AA}$. That is, the bond between C1 and C2, between C5 and C6 are double bonds (σ and π) and between C2 and C3, C4 and C5 is the single bond (σ). Between C3 and C4 is a double bond, but not as strong as between C1 and C2 or C5 and C6.

4) Free-electron valence $-\pi$ (F)

Free valence of each atom fit equation is as follows:

$$F_i = 1,732 - P_i$$

$$F_1 = F_6 = 0,861$$

$$F_2 = F_5 = 0,378$$

$$F_3 = F_4 = 0,464$$

Thus, the atoms C1 and C6 are the tip-end of the molecule is more reactive than the other C atom at the center.

5) *Total Electron energy* $- \pi(E_0)$

From the equation

$$E_o = \sum_r n_r \varepsilon_r$$

Energy with ground state: $E_o = 2\varepsilon_1 + 2\varepsilon_2 + 2\varepsilon_3 = 6\alpha + 6,988\beta = -83,5 \text{ eV}$

with $\alpha = -11 \text{ eV}$, dan $\beta = -2,5 \text{ eV}$.

6) *Local Energy* E_{lok}

From the equation:

$$E_{lok} = g_1(2\alpha + 2\beta) + g_2\alpha$$

The amount of localization energy is $E_{lok} = 3(2\alpha + 2\beta) = 3(-22 + (-5)) = -81 \text{ eV}$

7) *Energi Delokalisasi Molekul* (E_d)

The amount of delocalization energy is the measurement of molecular stability, that is:

$$E_d = E_o - E_{lok} = 0,988\beta = -2,5 \text{ eV}.$$

IV. CONCLUSION

1. Hückel method and assistance with Matlab 7.0 software, as well as the molecular orbital calculation of the amount of heksatriena becomes easier.
2. Seen from the diagram that the excited state, automatically has selected that excited state is forbidden.
3. With the help of Matlab software, can be output from the absorption spectrum UV / Vis.

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