Laboratory Session 7: Quantum-Chemical Study of Electronic Transfer in Polyenic and Polycyclic Conjugated Molecular Wires

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Objectives: The study shows the student the main methods of semi-empirical calculations. The PM3 method will be used to obtain the electronic structure and properties of the ground state, and the INDO/S method is used to obtain properties related to the excited states. The determination of these properties will allow the student to analyze the change in intramolecular electronic transfer (IET) that occurs in molecular wires with conjugated π spacers of different nature and length. The student will be able to establish the factors that facilitate the transport of electrons and, therefore, their ability to behave like good molecular wires.

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1. Introduction

Quantum Chemistry is, together with Spectroscopy, the main form of research at the molecular level; the former has the advantage that it's able to determine molecular properties that in a conventional laboratory would be very complicated to measure. Some of these properties are: molecular geometries, especially in molecules whose structures are not available; relative energies, which indicate their stability; electrical and magnetic molecular properties or spectra.

Thecalculation methods used for the study of electronic structure and molecular properties could be divided into two large groups: those that use semi-classical models, which include the Molecular Mechanics and Molecular Dynamics methods; and a second group related to methods using quantum-chemical models. Within this second group, we can differentiate between *ab initio* and semi-empirical methods. We class *ab initio* methods as those that calculate exactly all the integrals appearing in the calculations, while in semi-empirical methods, some of them are not directly evaluated, but are adjusted using experimental data or values from *ab initio* calculations. In this practical, we will use two semi-empirical quantum-chemical methods in the study of conjugated polyenes and polycyclic aromatic hydrocarbons. The main goal is to investigate how the electronic transfer capacity depends on its nature and length, in order to assess whether they can be used as molecular wires. We will use the PM3 method to obtain the geometric structure of the systems under study and the INDO/S method to calculate their electronic spectra.

1.1. The INDO/S method

The INDO (Intermediate Neglect of Differential Overlap) method is an improvement of the CNDO method (Complete Neglect of Differential Overlap). Pople and collaborators developed the CNDO method in 1965. In order to calculate electronic spectra, Jaffé and Del Bene made a modification of the CNDO/2 method, which they called CNDO/S. This methodology was a great advance as it was not restricted to the calculation of π-electronic spectra. From the CNDO/S method, the INDO/S method was formulated, in which parameters were adjusted to reproduce the maximum absorption values instead of the origin of the absorption spectrum bands, as in the CNDO/S model. In both cases, the parameters were obtained from results at the CIS level, that is, an *ab initio* method implying the interaction of configurations with only monoexcitations. The two methods (CNDO/S and INDO/S), lead to similar energy values for the $\pi \rightarrow \pi^*$ excitations in molecules containing hydrogen and other first series atoms. In contrast, the INDO/S method gives more satisfactory values in the calculation of $n \rightarrow \pi^*$ excitations. In addition, the INDO/S method has been extended to practically all atoms of the periodic table, even including the lanthanide elements. In general, the INDO/S model reproduces the values of excitation energies below 40000 cm^{-1} with an accuracy of about 2000 cm^{-1} with respect to the CIS level. However, this model is not able to adequately reproduce transitions that appear above 2 eV and below the first ionization potential. The values of the transition moment calculated at the INDO/S level are reasonably accurate for weak transitions, that is, for values below 0.2 for the oscillator strength, but they are usually too large for very intense bands. The inclusion of higher order excitations in the configuration interaction usually improves oscillator strength values. Nowadays, many research groups use the INDO/S model which can be applied to systems with a size of the order of 1000 atoms.

1.2. The PM3 method

In 1975, Dewar and collaborators developed the MINDO/3 model, the third version of a modified INDO model. *This model was developed to reproduce various experimental properties such as molecular geometries, formation heats, dipole moments and ionization potentials*. In 1983, the first version of the MOPAC program was presented, containing the MINDO/3 and MNDO models. This program allowed geometric optimizations, the characterization of transition states using the "reaction coordinate", and the calculation of vibrational frequencies. In 1985, Dewar developed the AM1 model (Austin Model 1). The most important improvement of this method with respect to the MNDO approach is the inclusion of a new term in order to correct the excess of repulsions at van der Waals distances.

The PM3 (Parametric Method 3), introduced by Stewart in 1990, is a variation of the AM1, with a different procedure for determining the parameters.

1.3. Molecular wires

Molecular wires are essential components in molecular electronics, where they are used to connect functional units within an electronic circuit. They have a highly conjugated structure that facilitates the transfer of charge along the wire. There are many types of molecular wires, but the simplest ones are conjugated hydrocarbon chains since the delocalized π structure makes the conduction of electrons easy.

A simple procedure to evaluate the possibilities of new materials as molecular wires is the study of intramolecular electronic transfer (IET) between the ends of the system when they act as a linker between a donor and acceptor (Figure 1).

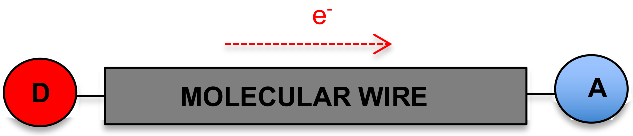

Figure 1. Molecular wires as a linker between a donor (D) and an acceptor (A)

The quantum-chemical study of the structural and electronic properties of these molecular systems leads to specific information on the electron transfer process of and the potential conductive capacity of the systems studied. Thus,

- **Molecular geometry:** this provides information on the length of the CC bonds. In conjugated systems, the CC bond lengths indicate the level of delocalization in the π electron system between the ends of the molecular wire and, therefore, its ability to transfer electric charge through the molecule. However, there are theoretical methods that excessively localize the geometries and do not allow us to appreciate this effect.
- **Dipole moment:** this indicates the polarization of the electronic density produced by the intramolecular charge transfer, and provides information on the propensity and direction of the displacement of charge.
- **Frontier Molecular Orbitals (FMO):** the shape and energy of the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) molecular orbitals are important parameters to evaluate the electronic transfer through a molecule. A HOMO of high energy indicates a molecule with a donor character and a LUMO of low energy suggests an acceptor character. The energy difference between HOMO and LUMO (gap) is a measure of electronic mobility. A smaller gap facilitates IET.
- **Electronic distribution and atomic charge** (Q): the variations in charge between the donor, the bridge, and the acceptor in potential molecular wires can be used to analyze how intramolecular electronic transfer takes place and how favorable it is.
- **Electronic spectra**: as the conjugation increases in polyenes, the energy difference between HOMO and LUMO decreases, absorbing at longer wavelengths. There is a bathochromic shift (redshift) of the optical transitions from UV to visible associated with a higher IET. In addition, charge transfer bands corresponding to a donor-acceptor transfer may

appear.

- **Frontier Electron Indices**: studying of the reactivity of molecular wires provides information about its interaction with other molecular units. Thus, the approach "frontier electron" gives information about the preferential sites where a reagent can attack, as well as the oxidizing and reducing character.
  - **Electrophilic and nucleophilic attack**: an electrophilic reagent searches for electrons and will react with the electrons in the highest occupied orbital (HOMO), and it will do in the position where there is more electronic density $\rho_{\acute{a}tom}^{HOMO} = n_{occupation} c_{\acute{a}tom}^2 = 2c_{\acute{a}tom}^2$. On the contrary, a nucleophilic reagent provides electrons, which will place in the lowest unoccupied MO (LUMO), in the position with a greater capacity to accept them. $\rho_{\acute{a}tom}^{LUMO} = n_{occupati\acute{o}n}\, c_{\acute{a}tom}^2 = 2c_{\acute{a}tom}^2$.
  - **Oxidizing and reducing character**: a reducing agent (electron donor) gives electrons and is oxidized in the process. The electrons are taken from its HOMO; therefore, better reducing agents have higher energy HOMOs. An oxidizing (an electron acceptor) receives electrons and is reduced. The electrons are put into its LUMO; accordingly, it will be better oxidizing agent if its LUMO is lower in energy.

In this theoretical work, the intramolecular electronic transfer (IET) will be studied using semiempirical methods. The study includes conjugated polyene-type bridges (ethene, butadiene, and hexatriene) and aromatic polycyclic-type wires (benzene, naphthalene, and anthracene). In addition, the NH_2 group will be used as a donor and the NO_2 as an acceptor. Moreover, the IET will be examined as a function of the nature and length of the linker.

2. Calculation procedure

Determine the geometric and electronic structure, as well as the electronic absorption spectra of the following polyenes and aromatic polycycles:

R_1-(CH=CH)-R_2, R_1-$(CH=CH)_2$-R_2, R_1-$(CH=CH)_3$-R_2, R_1-C_6H_4-R_2, R_1-$C_{10}H_6$-R_2 and R_1-$C_{14}H_8$-R_2, con R_1=NO_2 y R_2=NH_2 located at the beginning and end of the chain (Figure 2).

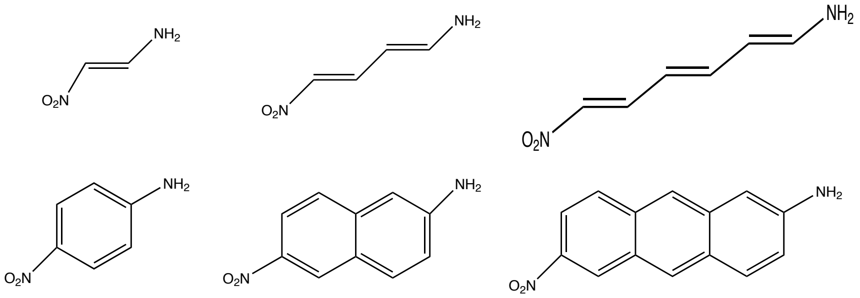

Figure 2. Molecules under study.

The first step is the determination of the molecular geometry with minimum energy. The geometry optimization will be carried out using the PM3 method. Once we arrive at the optimized geometry, we will compute the electronic absorption spectra using the INDO/S method.

2.1. Geometry Optimization

- Program WINMOPAC
- File → New (red button) Background → White
- **Build the molecule**: for linear polyenes select {sp^2 (2H)}, adding as many groups as necessary; for aromatic cycles, build the molecule starting from a template(program models) {template}. At the beginning of the chain, add an NH_2 {sp^3(2H)} group and at the end a NH_2 {sp^2(2H)} and replace the H atoms for O.

- **Measure the initial values** of the carbon-carbon bond distances, bond angles, and dihedral angles, before and after optimizing the geometry in order to verify that they have been optimized.

Go to the *Information* column → click *Atom type* (numbering)

Choose Measure, select atom 1 and atom 2 → distance between atoms

In the same way, the bond angle (1-2-3) and the dihedral (1-2-3-4) are obtained

- **Optimize the geometry** of the molecule with the PM3 method (MOPAC97 program).

The geometry can be optimized by choosing the Z-matrix option in the Edit column.

The name of the molecule is written in Name and the keywords are chosen:

- keywords (if more than one line, add "+" sign on the line 1):
  PM3 EF PRECISE VECTORS ALLVEC BONDS LET GNORM=0.001
- comments: your names
- the name of the molecule (total 2 lines)

→ *Apply and Accept*

→ *Calculation (Click Start)*

- **Write down the values** of energy, dipole moment, optimized distances, and atomic charges
- **Save the optimized molecule** with the name of "molecule-opt.dat".

When performing the calculation, several files are generated; important information can be obtained from the files molecula.arc and molecula.out

- To represent **MOs** → *Information Menu* → *Molecular Orbital*

- **Represent schematically the molecular orbital diagram**. Indicate the energy and symmetry of each orbital, as well as its type σ or π. The file molecula.out contains the MOs. Remember that the σ molecular orbitals are a combination of atomic orbital s and p (s-s, p-p, s-p or p-s), while the π orbitals are combination of atomic orbitals p perpendicular to the bond axis.

◆ Analyze the **shape of the molecular orbitals** of type π : H-1, H, L, L+1.

At the optimized geometry, determine the electronic absorption spectrum with the INDO/S method.

2.2. Calculation of Excited States. Absorption Spectrum

◆ Open the file “molecule-opt.dat”.

◆ Choose the MOS-F program in “Z-matrix (edit)”, in the method: “INDO/S”, in the calculation type: “difference electron density”. *Apply and Accept. Calculation (Start), Information* → Excited States, enter “coord=Mcart” in keywords.

◆ Open the file molécula-opt.oms to obtain the Table of electronic transitions that includes the ΔE between states, oscillator strength, composition of transitions, etc.

◆ To obtain the graph of oscillator strength versus λ (nm) for each of the transitions ⇒ If “Excited States” is active in the Information Menu, cut the corresponding graph directly.

Alternative: Open the molecule-opt.wms file with the WinMOPAC program and if “Excited States” is active in the Information Menu, cut the corresponding graph directly.

3. Results

3.1. Geometric and electronic structure of molecular wires

Determine the geometric and electronic structure of each of the molecules studied using figures and tables that you will have to discuss. Study the smallest molecule in each group (ethylene wire and benzene wire) in detail and the other two together.

For ethylene you must include the following information:

1- Analysis of the structure: Represent the optimized molecule with numbered atoms to be able to refer to them in the tables and in the text. Indicate the plane in which the C atoms are located to be able to analyze the OMs and give a brief description of the system.

2- Analysis of its characteristics: Include a table with the dipole moment, optimized distance C-C, the total load of the carbon structure and the gap. Explain the direction of the dipole moment. Indicate which is the OM HOMO and which is the LUMO and calculate the gap.

3- Variation of the atomic charges along the molecular thread: Include a figure of the molecule with the graphic and also numerical charges and analyze it.

4- Electronic structure: Make an energy diagram of the three highest occupied molecular orbitals and the three lowest virtual ones. Include next to the energy level only HOMO-1, HOMO, LUMO and LUMO + 1 the representation of the OM to which it corresponds. Indicate approximately the symmetry of the orbitals, if they are σ or π type. Discuss the shape of the molecular orbitals and their spatial distribution.

5- Analysis of the reactivity of the cable: Determine by means of the atomic charges and also, by means of the electron densities of HOMO and LUMO, with the boundary electron method, the carbon atoms that are most susceptible to electrophilic and nucleophilic attack. Compare both methods.

6- Analysis of the optical properties: Include the electronic absorption spectrum and a table of the 3 or 4 most important allowed electronic transitions (highest oscillator force) containing: Excitation wavelength (nm), oscillator force and description of the transitions identifying the OMs between which it occurs (H→L, H-1→L, ...). Remember that the description of the OM is in the file *molecula.out*. Compare to the experimental spectrum of ethylene that you have looked up in the literature.

For butadiene and hexatriene, analyze the two molecules **together** with the following information:

7- Analysis of electronic structure: Include a table with dipole moment, total charge of the carbon structure and gap of the two molecules.

8- Optical properties. Include the electronic absorption spectrum and a table with the 3 or 4 most important allowed electronic transitions (highest oscillator force) containing: Excitation wavelength (nm), oscillator force and description of the transitions identifying the OMs between the produced (H→L, H-1→L, ...). Remember that the description of the OM is in the file *molecula.out*. Compare with the experimental spectra of butadiene and hexatriene that you have looked up in the literature.

For polycyclic aromatic cables, analyze the benzene cable analogously to ethylene (points 1-6) and naphthalene and anthracene together and in less detail as you did for the larger conjugated polyene cables (points 7-8).

3.2. IET in conjugated polyenic wires

From the information of the electronic structures and the spectra of the previous sections, analyze how the IET varies as a function of the length of the polyene for the different molecular cables studied of this type. Compare dipole moment, atomic charges of carbons attached to donor and acceptor groups, gap and bathochromic shift of the transitions of the UV spectrum.

1- Collect the information for all six molecules in a single table for easy comparison. Discuss the evolution of the dipole moment, carbon structure charge and gap.

2- Represent in a single diagram the evolution of the energy of HOMO and LUMO as a function of the length of the polyene for the six cables studied.

3- Analyze the evolution of the redox properties. How does the oxidizing and reducing character vary with the length of the polyene?

4- Analyze the evolution of the optical properties with the length of the length of the polyene, that is, how the position of the most important bands of the UV spectrum varies.

3.3. Effect of the nature of the π system on the IET

Make a comparative analysis of the IET in the two types of wires studied, linear and cyclic, as a function of their nature and length. Discuss what type of wire seems to be most efficient for the design of electronic devices on a nanometric scale.

4. Questions

4.1 Preliminary Questions

1- Calculate the number of electrons and MOs occupied for each molecule.

2- Calculate the number of occupied and virtual MOs in the PM3 calculation, and predict the HOMO and LUMO in each molecule.

3- Find the experimental distance C-C in ethane (single bond), in ethene (double bond), and in butadiene; analyze the differences. Give the values with your bibliographic reference.

4- Find the experimental UV spectrum of ethene, t-butadiene, 1,3,5-hexatriene, benzene, naphthalene, and anthracene, giving the wavelength and intensity of the most important absorption bands.

4.2 Post-laboratory Questions

1- How does conjugation change in the compounds studied by increasing the length of the chain?

2- What effect does π–conjugation have on the UV absorption bands?

3- How does the length of the chain affect the color of the compound forming the molecular wire? Predict the colors of the different compounds.

4- Which compound of those studied has a higher IET? Why?

References

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