Democratic and Popular Algerian Republic

Ministry of Higher Education and Scientific Research

University Dr Moulay Tahar - Saida

Faculty of Sciences

Department of Chemistry

Dissertation

Presented in partial fulfillment of the requirements for the degree of

MASTER

Specialization: CHEMISTRY

Option: Organic Chemistry

Presented by: Miss Nadjet Khaldi

On the theme of

Study of the π-conjugated bridge's effect on the quadratic hyperpolarizability in push-pull organic compounds

Presented on: 23 /05 /2024 in front of the jury composed of :

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Academic Year 2023 – 2024

Acknowledgements

In the name of Allah, the Most Gracious, the Most Merciful. Thanks to Allah that neither success nor victory benefit us except with his consent. All praise is due to Allah, who has not guided us through any path nor spared us any effort except by His grace. To Him is attributed all favor, perfection, and completion.

" وَآخِرُ دَعْوَاهُمْ أَنِ الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِينَ ﴿١٠﴾ "
سورة يونس

All praise is due to Allah, out of love, gratitude, and appreciation. I would not have been able to accomplish this without the grace of Allah Almighty. Praise be to Allah for the beginning and the end.

I would like to extend my deepest gratitude to Professor Boutaleb Miloud, who has never been stingy and who has given his attention and time to this work, without whose efforts I would not have reached this point. Thank you for all the advice and ideas you have given me throughout this work. I ask the Almighty God to protect you from all evil and grant you success in all that you love and desire.

I would also like to express my deepest gratitude to the professors of Moulay Tahar University, President M^{r}. H. brahim, Examiners M^{r}. S. Daoudi and Miss. N. Benhlima, who agreed to serve on and evaluate my thesis.

And finally, I would like to thank everyone who has helped me along the way, my family who have always been by my side, may you be a support to me forever...

Dedication

In the name of my Creator, the Guide of my affairs, and the Protector of my destiny to you all the praise and gratitude.

I dedicate my graduation to the one whose name i bear with pride, to the one who paved the way for me in knowledge after the grace of God. What i am today is due to the man who dedicated his life to making us the best "my father" may God have mercy on him and grant him eternal paradise. How I wish you could be with me in these moments, but this is the will of God and there is no objection to that. But you are always with me in my heart. I ask whoever reads this memoir to pray for my father's mercy and forgiveness.

To the compassionate heart that has supported me throughout my life and endured every moment of pain, "my dear mother."

To the best of my days and the light of my eyes, my brothers Mohammed and Mustafa and my little sister Nour Al-Huda.

To all who have been a support and a pillar in my life, and who have filled the void of my father with their love and affection, my mother's brothers Ahmad, Lakhdar, and Cheikh. Without forgetting my aunt Hanane, my aunt Zahra, my grandparents, and others. Also, my friend and companion on the path of life, Maroua.

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List of abbreviations

List of abbreviations:

NLO: Nonlinear optics.
E: Electric field.
P: Polarization.
Coll: Collaborators.
Al: A group of researchers.
au: Atom unit.
D: Donor group.
A: Acceptor group.
eV: Electron Volt.
esu: Electrostatic unit.
$P^{(1)}$: Linear polarization.
$P^{(2)}$: 2nd order polarization.
$P^{(3)}$: 3rd order polarization.
$P^{(L)}$: Linear polarization.
$P^{(NL)}$: Nonlinear polarization.
SHG: Second-harmonic generation.
SFG: Sum-frequency generation.
DFG: Difference-frequency generation.
ε_0: Permittivity of vacuum.
$\chi^{(1)}$: Linear susceptibility (a tensor of order one).
$\chi^{(2)}$: 2nd order nonlinear susceptibility or quadratic hyperpolarizability.
$\chi^{(3)}$: 3rd order nonlinear susceptibility or cubic hyperpolarizability.
γ: Nonlinear polarizability tensor of order three.
α: Linear polarizability tensor.
β: Nonlinear polarizability tensor of order two (hyperpolarizability).
μ: Dipole moment.
µm: Unit of wavelength.
λ: Wavelength.
ICT: Intramolecular Charge Transfer.
THG: Generation of the third harmonic.
SONLO: Second-order nonlinear optics.

Ej(ω1): The incident electric field j of frequency ω1.

Ek(ω2): The incident electric field k of frequencyω2.

I: The intensity of the light beam.
c: The vacuum speed of light.
n_0 : The refractive index given below.
V/m: Unit of electric field.

nm: Nanometer (unit of wavelength).

QR: Quadratic response.

DFT: Density Functional Theory.

BBO: Bêta-baryta borate.

BTO: Barium titanate.

KDP: Potassium dihydrogen phosphate.

pm. V^{-1}: Unit of the susceptibility coefficients.

GeO_2-P_2O_5: Germanium phosphate glass.

TeO_2: Tellurite glass.

OPO: Optical parametric oscillation.

FWM: Four-wave mixing.

GaP: Gallium phosphide.

FPC: Parametric Frequency Conversion.

OPA: Optical parametric amplification.

PPV: Poly (p-phenylenylvinyl).

PPs: Push-pull compounds.

OPV: Oligo (p-phenylene vinylene).

EPA: Environmental Protection Agency.

MD: Molecular dynamics.

MM: Molecular mechanics.

QM: Quantum methods.

AM1: Austin Model1.

CNDO/2: Complete Neglecting of Differential Overlap/Version 2.

INDO: Intermediate Neglect of Differential Overlap.

NDDO: Neglect of Diatomic Differential Overlap.

MINDO/3: Modified INDO, version 3.

PM3: Parametric method.

HOMO: Highest occupied molecular orbital.

LUMO: The Lowest unoccupied molecular orbital.

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General introduction

General introduction:

The nonlinear optics are one of the important and active fields in our daily lives due to their applications in various fields such as: materials processing, photonic computing, telecommunications and medical imaging. It's the study of phenomena resulting by the modification of the optical properties of a material system in the presence of light where just the laser light is sufficiently intense to modify the optical properties of a material system (1). This phenomenon was called nonlinear optics for the reason that the response of atoms to an intense electromagnetic field could no longer be taken to be linear in the electric field.

The revolutionary invention of the laser by Maiman (2) and his collaborators in 1960 was a major turning point, allowing the meteoric rise of NLO. The year 1961was the start of the nonlinear optic by Franken and coll (3), where the first phenomena observed is an: ultraviolet radiation at 347.1 nm was detected at the exit of a quartz crystal illuminated with a ruby laser beam at 694.2 nm. This was the first demonstration of second harmonic generation at optical wavelength, which is the main nonlinear optical effects (4). the intensity of the light generated at the second-harmonic frequency tends to increase as the square of the intensity of the applied laser light.

Figure1: Professor Peter Franken (1928–1999).

The observation of second harmonic generation in 1961 Open the way for the discovery of many nonlinear processes (5), such as: intensity dependent refractive index, stimulated Brillouin scattering (SBS), the third harmonic generation.

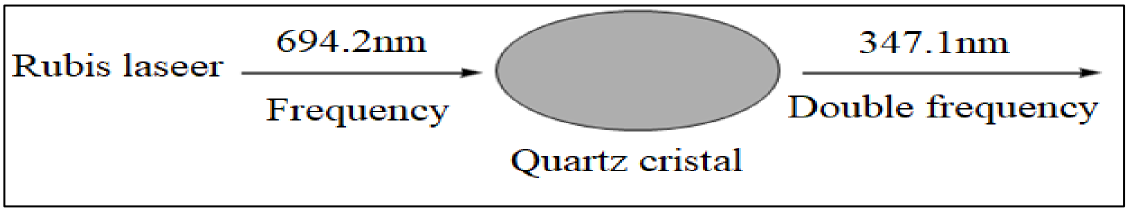

Figure 2: First phenomena observed in NLO.

Nonlinear optics is distinguished by its fascinating and ever-growing exploration (4), ranging from fundamental theories that predict and explain the behaviors of materials when subjected to intense optical fields. These theories then gave rise to many practical applications, such as frequency conversion devices. Also, it can be used to probe structures at scales ranging from microscopic to macroscopic. For example, nonlinear imaging techniques can visualize internal structures of materials with incredible resolution, while macroscopic nonlinear phenomena can be used to control the propagation of light at the scale of several centimeters. It ranges from materials physics to classical and quantum electrodynamics, encompassing a multitude of media, from gases to solids, from minerals to organic compounds.

Inorganic crystals were the first interesting for NLO for example: LiNbO3, (KDP), (KTP). Then, in 1970s Davydov and al (6), propose the use of new material which are the organic for Improving the effects of NLO. The development and the research in NLO services, showed that the organic materials have a better NLO proprieties than mineral materials due to the presence of many effects influence the NLO as the conjugation, especially the organic conjugated compounds for polymeric materials and push pull material (7) which has a donor(D) and acceptor(A).

Another effect that distinguishes organic materials is the bridge effect. Molecules possess π-conjugate systems that allow the delocalization of electrons π, meaning that they are not confined to a single bond but rather distributed throughout the molecular structure. This phenomenon creates a conductive "bridge" that facilitates the interaction between the electric field of light and the electrons of the molecule what gives organic materials their nonlinear optical properties. The bridge effect in NLO is our interesting and this is what we will study in detail throughout this paper.

Our objective in this dissertation is to study the effect of the bridge on the properties of nonlinear optics (hyperpolarizability) for three different bridge cases, The hyperpolarizabilities were calculated using various quantum chemistry modeling methods (AM1, DFT).

This manuscript will then be composed of three chapters. The first chapter provides a review of the definitions and properties of nonlinear optical phenomena.

Also, we will discuss about the importance, principles and Quantum theory of NLO.Then, we're going to present the different materials for the nonlinear optics specially the organic compound by presenting their characteristics and the factors influencing the NLO properties.

In the second chapter, we will provide a chemical overview of the three bridge cases we want to study by presenting the definitions of the different functions, properties, and synthesis methods.

The third chapter summarizes the different molecular modeling methods used to perform this structural analysis. Then discuss the molecular geometry and optimization of the selected structures, and then an interpretation of the calculation results carried out by two different methods, and we end this work by an analysis with HOMO and LUMO presentation.

Finally, we conclude by perceiving the important remarques and results in a general conclusion.

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First Chapter

Theory and materials for nonlinear optical

I.1. Introduction:

Nonlinear optics, which is gaining momentum worldwide, is revolutionizing the telecommunications landscape and opening new possibilities for the storage and computing of tomorrow. Nonlinear optics takes the light-matter interaction to another level, unlocking exciting possibilities for enhancing both efficiency and versatility in various applications. We can take as an example the process of amplifying optical signals in fiber optic cables which have very low absorption, allowing signals to be transmitted over long distances. But over time, the signals become weak and need to be amplified. Generally, this is done by converting the light signal into an electronic signal, amplifying it electronically, and then converting it back into a strong light signal but with nonlinear optics, we can amplify the light beam directly using a laser beam in a suitable medium. And as research continues to push the frontier, we can expect more notable advances in areas ranging from communications and sensing to biophotonics and beyond (1).

The optic field treat the interaction of the light and matter (2), when the light has an important intensity, the optical properties of matter will depend on the intensity of light of the incident beam, this is what we called the nonlinear optic. The microscopic characteristics of materials, such as the nature of the atoms that make up the molecule or the crystalline structure, etc., have important effects on NLO properties.

I.2. Definition of Nonlinear Optics:

The Scottish physicist and mathematician James Clerk Maxwell (3) showed that light is a form of electromagnetic wave (4). This discovery unified the study of light and electromagnetism waves, which are a type of wave that consists of oscillating electric and magnetic fields. The electric and magnetic fields are perpendicular to each other and to the direction of propagation of the wave.

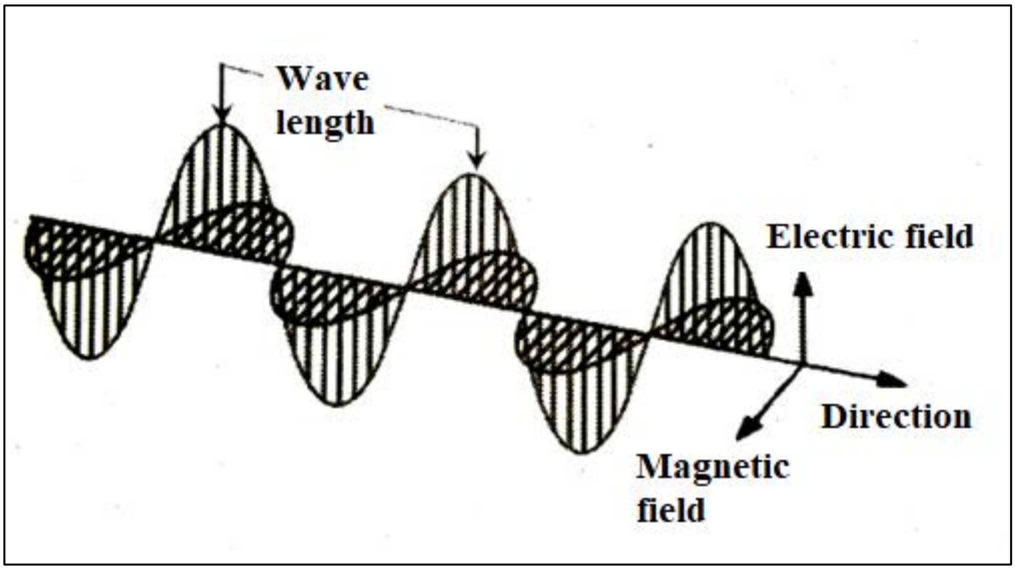


Figure I.1: Electromagnetic waves (5).

Nonlinear optics (NLO) is a branch of optics that studies optical phenomena in which the response of a medium to an electromagnetic field is not proportional to the intensity of that field. In other words, the relationship between the amplitude of the light wave and the intensity of the electric field that generated it is not linear. When matter is subjected to an oscillating electric field E, the positive charges are driven in the direction of the field while the negative charges are driven in the opposite direction of the field, inducing an oscillating dipole. In the case of high frequencies, it can be considered that only the electrons are animated, the nuclei remaining fixed. The magnitude of the dipole moment is proportional to the strength of the electric field and the frequency of the oscillation. In the case of high frequencies, the electrons are unable to follow. the rapid oscillations of the field. As a result, the dipole moment is only created for a short period of time. This is why it can be considered that only the electrons are animated in the case of high frequencies (6).

In the case of lasers, the light intensities are so high that they can cause the electrons in the medium to move in an anharmonic way. Anharmonicity means that the restoring force that pulls the electrons back to their equilibrium positions is not a simple function of the displacement of the electrons. This can lead to the emission of waves of different frequencies from those of the incident light. The response is said to be "nonlinear".

The polarization P must then be developed as a function of the increasing powers of the electric field (6):

$$\mathbf{P} = \mathbf{P}_{(0)} + \boldsymbol{\varepsilon}_{(0)}\left(\boldsymbol{\chi}^{(1)}.\mathbf{E} + \boldsymbol{\chi}^{(2)}.\mathbf{E}^2 + \boldsymbol{\chi}^{(3)}.\mathbf{E}^3..\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I.1)}$$

$$\mathbf{P} = \mathbf{P}_{(0)} + \mathbf{P}_{(1)} + \mathbf{P}_{(2)} + \mathbf{P}_{(3)} + .. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I.2)}$$

$$\mathbf{P} = \mathbf{P}_{(0)} + \mathbf{P}_L + \mathbf{P}_{NL} \ \text{ where:} \mathbf{P}_L = \mathcal{E}_{(0)}\boldsymbol{\chi}^{(1)}.\mathbf{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I.3)}$$

$\mathbf{P}_{(0)}$: Represents static polarization.

$\boldsymbol{\varepsilon}_{(0)}$: The permittivity of free space.

$\boldsymbol{\chi}^{(\mathbf{n})}$: Possibly complex n-order electric susceptibilities.

$\mathbf{P}_{(\mathbf{n})}$: The nth order polarization.

$\mathbf{P}_{(2)}$ refer to the second-order nonlinear polarization and to $\mathbf{P}_{(3)}$ refer to the third-order nonlinear polarization (7).

The quantities $\boldsymbol{\chi}^{(\mathbf{n})}$ are the electric susceptibilities of order n:

linear for n = 1, second order for n = 2, and third order for n = 3.

Linear susceptibility $\boldsymbol{\chi}^{(1)}$ is proportional to the electric field. It is responsible for the linear optical properties of a material, such as refraction, reflection, and absorption. Second-order susceptibility $\boldsymbol{\chi}^{(2)}$ is proportional to the square of the electric field. It is responsible for a variety of nonlinear optical phenomena, such as second-harmonic generation (SHG), sum-frequency generation (SFG), and difference-frequency generation (DFG). Third-order susceptibility$\boldsymbol{\chi}^{(3)}$ is proportional to the cube of the electric field. It is responsible for a variety of nonlinear optical phenomena, such as optical Kerr effect, four-wave mixing, and self-phase modulation (6).

I.2.1. Quadratic nonlinear optics:

In the realm of nonlinear optics, various phenomena arise from the intricate interplay between light and matter. More specifically, these phenomena stem from the interaction between the polarizable electron density within matter and the powerful electric field generated by an intense laser beam (8). Nonlinear optical processes exhibit interesting fields such as quadratic nonlinear optics.

Quadratic nonlinear optics or Second-order nonlinear optics (SONLO) are the easiest to implement. It is a field of nonlinear optics that studies phenomena that depend on the square of the electric field of light. The most common quadratic nonlinear optical effect is the second harmonic generation SHG. In this case, the coherent waves excited in the medium will have frequencies produced by a mixture of frequencies (9).

Nonlinear quadratic optics is a field of optics that studies phenomena that occur when two electric fields of frequency ω1 and ω2 interact with a nonlinear material. The nonlinear polarization is written as follows in these conditions (7):

$$\mathbf{P}_i^{NL} = \boldsymbol{\varepsilon}_{(0)}\boldsymbol{\varepsilon}0\boldsymbol{\Sigma}\mathbf{j},\mathbf{k}\boldsymbol{\chi}\mathbf{ijk}^{(2)}\mathbf{Ej}(\boldsymbol{\omega}1)\mathbf{Ek}(\boldsymbol{\omega}2) \qquad \text{……………………} \ \textbf{(I.4)}$$

with $1 \leq i, j, k \leq 3$

Where: P_i^{NL}: nonlinear polarization.

$\boldsymbol{\varepsilon}_{(0)}$: the permittivity of free space.

Σj, k: the sum on the indices j and k.

Ej(ω1): the incident electric field j of frequency ω1.

Ek(ω2): the incident electric field k of frequencyω2.

I.2.1.1. Second-harmonic generation:

The second harmonic generation was the first considered phenomena in NLO by franken and col (10) in crystals, then it developed by Bloembergen & Pershan in 1962(11). (SHG) is the nonlinear conversion of two photons of frequency (ω) to a single photon of frequency (2 ω). the Studies and research in this phenomenon show that the Fourier component of polarization at frequency 2ω, $P^2(2\omega)$, is responsible for the SHG from the sample and is proportional to the square of the amplitude of the incident electric field (12):

$$P^2(2\omega) = \chi^{(2)} E^2(\omega) \qquad \text{.....................} \ \textbf{(I.5)}$$

I.2.2. Cubic nonlinear optics:

Cubic nonlinear optics is a field of nonlinear optics that studies phenomena that depend on the cubic of the electric field of light. It deals with the interaction of light with materials in which the intensity of the light affects its refractive index. Cubic nonlinear can have several effects: third harmonic generation (THG)and Kerr effect optical (6).

I.2.2.1. Third-harmonic generation:

Third-harmonic generation was subsequently reported by Maker, Terhune, and Savage (13). The first appearance was in crystals, glasses, liquids and gases, Among the gauzes studied (14): helium, neon, argon, xenon, krypton, molecular hydrogen, carbon…

In THG, an intense light beam interacts with a material and generates a new light beam at three times the frequency (3 ω) of the incident light (ω). This means the output light has a significantly shorter wavelength and higher energy compared to the original light.

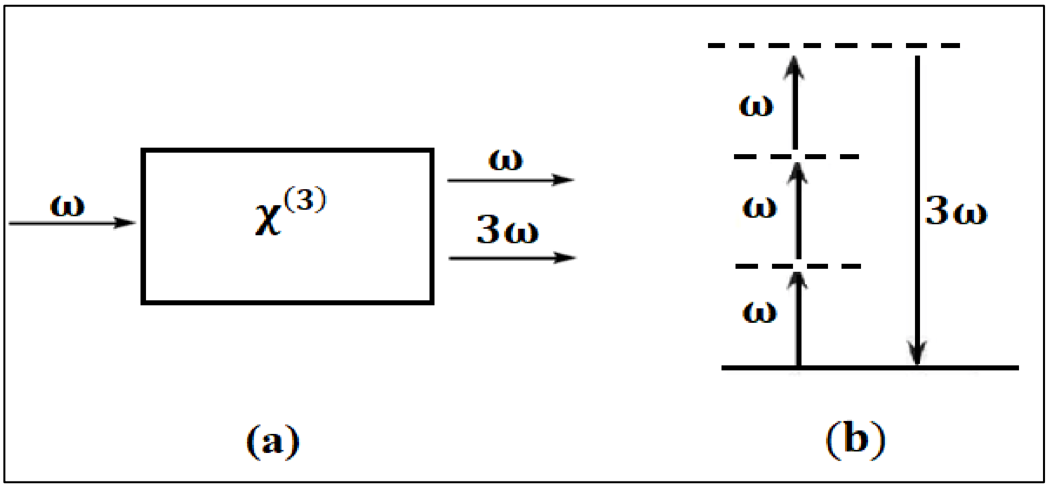


Figure I.2: Third harmonic generation. (a) Geometry of interaction. (b) Energy-level description.

I.2.2.2. Optical Kerr effect:

The optical Kerr effect is a consequence of cubic optical nonlinearity, it was first observed for molecules with directions of greater polarizability. by French physicists Guy Mayer and François Gires in 1963(16). When an electric field is applied to a material, the refractive index of the material becomes dependent on the strength of the electric field. This dependence can be expressed by the following equation (17):

$$\mathbf{n} = \sqrt{\mathbf{1} + \boldsymbol{\chi}^{(1)}} + \boldsymbol{\chi}^{(3)} \frac{\mathbf{3I}}{\mathbf{2c\varepsilon_{(0)}}\sqrt{\mathbf{1}+\boldsymbol{\chi}^{(1)}}} \quad \text{……………………. (I.6)}$$

Or: $\boldsymbol{n} = \boldsymbol{n}_{0+}\boldsymbol{n}_2.\boldsymbol{I}$ ……………………. (I.7)

where: $\boldsymbol{I} = \frac{1}{2} c\mathcal{E}_{(0)}\boldsymbol{n}_0\boldsymbol{E}^2$

with:

I: the intensity of the light beam.

c: the vacuum speed of light.

$\boldsymbol{n}_0$: the refractive index given below.

I.3. The importance of NLO:

Nonlinear optics has two statuses: modern physics and modern optics. the modern physic is the study of the nonlinear response, that’s mean the relationship between action and reaction of objects under a strong interaction. The nonlinear physic used in different fields, for example in nonlinear acoustics, nonlinear electromagnetism, and nonlinear optics, nonlinear mechanics and nonlinear thermodynamics. the modern optics is the optics based on the laser source with the stimulated radiation where the traditional optics are based on the common light source with the spontaneous radiation. The modern optics and nonlinear optics have a large domain of applications: digital optical information processing, Light pulse compress, elimination of distortion in transmission medium, nonlinear communications and all-optical switch, optical storage, slow light, high resolution spectrum analyze, also Optical telecommunications, Imaging of biological structures and materials with high resolution (18).

I.4. Principle of nonlinear optics:

In NLO, Light changes the optical properties of the material in a way that depends on its intensity. The most immovable principle in NLO is the polarization and hyperpolarization:

I.4.1. Polarization:

Nonlinear optics is concerned with the electric polarization P induced in a material by an electric field E. In the linear optics case, an electromagnetic wave interacts with an anisotropic material (a material whose physical properties vary depending on the direction), It distorts the electron cloud of atoms or molecules in the material. This deformation is due to the Coulomb force, which is the attractive force between electric charges, which leads to an Induced polarization which is the measurement of the intensity of the electric dipole moment created in the material. It is proportional to the electric field of light. This approximation is valid when the electric field is less than 105 V/m. Beyond this value, the induced polarization becomes non-linear.

Polarization is express by (19) (20):

$$\mathbf{P}_{\boldsymbol{L}} = \mathcal{E}_{(0)}\boldsymbol{\chi}^{(1)}.\mathbf{E} \quad = \boldsymbol{\alpha}\mathbf{E} \qquad \text{……………………} \ \textbf{(I.8)}$$

p**:** represents the induced polarization, which is a vector measuring the density of electric dipole moment induced in the material by the electric field. Its unit is C/m² (coulombs per square meter).

α**:** represents the polarizability, which is a scalar measuring the susceptibility of a material to induce a polarization in response to an electric field. Its unit is F/m (farad per meter).

E**:** represents the external electric field, which is a vector describing the electric force per unit charge at a given point in space. Its unit is V/m (volt per meter).

But in nonlinear optics beyond the value 105 V/m the polarization deviates from proportionality which means the response is nonlinear. This polarization represents the moment density electric dipole per unit volume and reflects the displacement of the weakly bound charges of the environment under the influence of the eclectic field (21). The polarization in NLO express P as a series of terms in ascending powers of E:

$$\mathbf{P} = \mathbf{P}_{(0)} + \boldsymbol{\varepsilon}_{(0)}\left(\boldsymbol{\chi}^{(1)}.\,\mathbf{E} + \boldsymbol{\chi}^{(2)}.\,\mathbf{E}^{2} + \boldsymbol{\chi}^{(3)}.\,\mathbf{E}^{3}..\right) \quad \text{…………………….. } \mathbf{(I.1)}$$

$$\mathbf{P} = \mathbf{P}_{(0)} + \mathbf{P}_{(1)} + \mathbf{P}_{(2)} + \mathbf{P}_{(3)} + .. \quad \text{…………………….. } \mathbf{(I.2)}$$

$$\mathbf{P} = \mathbf{P}_{(0)} + \mathbf{P}_{\boldsymbol{L}} + \mathbf{P}_{\boldsymbol{NL}} \ \text{ where:} \mathbf{P}_{\boldsymbol{L}} = \mathcal{E}_{(0)}\boldsymbol{\chi}^{(1)}.\,\mathbf{E} \quad \text{…………………….. } \mathbf{(I.3)}$$

$\mathbf{P}_{(0)}$: Represents static polarization.

$\boldsymbol{\varepsilon}_{(0)}$: The permittivity of free space.

$\boldsymbol{\chi}^{(\mathbf{n})}$: Possibly complex n-order dielectric susceptibilities.

$\mathbf{P}_{(\mathbf{n}):}$ The nth order polarization.

The quantities $\boldsymbol{\chi}^{(\mathbf{n})}$are the electric susceptibilities of order n: linear for n = 1, quadratic for n = 2, and cubic for n = 3.

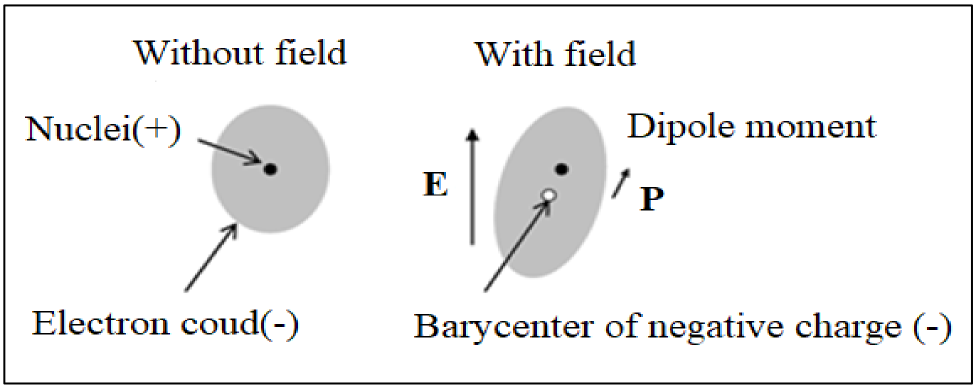


Figure I.3: Effect of an electric field on atom and its electron cloud.

The NLO polarization is determined at the macroscopic or microscopic, the macroscopic nonlinearity of a material originates from the microscopic nonlinearity of the entities that compose the material. In a crystal, one can always choose the unit cell as the microscopic entity, although it is generally preferable to choose to separate the atoms, ions, or molecules within the unit cell. Hence the total dipole moment is written as a series expansion of the E field in the semi-classical formalism as follows (19):

$$\mathbf{\mu i\ (E) = \mu^{0} i + \alpha_{ij}\ Ei + \beta_{\ ijk}\ Ej\ Ek + \gamma_{ijkl}\ Ej\ Ek\ EL + \ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (I.9)}$$

where:

μ^0 : the potential permanent dipole moment of the molecule in the absence of E. α_{ij}: the linear polarizability.

$\beta_{ijk}, \gamma_{ijkl}$: the hyperpolarizabilities of the first (or quadratic) and second order (or cubic), respectively.

Microscopic polarization can be written as a function of the following local electric field the relationship below:

$$\mathbf{P = P0 + (\alpha E^{(1)} + \beta\ E^{(2)} + \gamma\ E^{(3)} + \ldots) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (I.10)}$$

Where: Tensors α, β, and γ are defined by the first, second, and third derivations of the induced dipole moment on the E-field (22).

The Focuses of microscopic polarization are on the individual charges and their local displacements within the material, where the Macroscopic Polarization Focuses on the overall behavior of the material. for a molecular population, this allows the interaction of several electric fields, and thereby modifies the frequency, phase, or polarization of the incident light. The dielectric polarization is expressed in the same way by the following equation:

$$\mathbf{P} = \mathbf{P}_{(0)} + \boldsymbol{\varepsilon}_{(0)}\left(\boldsymbol{\chi}^{(1)}.\mathbf{E} + \boldsymbol{\chi}^{(2)}.\mathbf{E}^{2} + \boldsymbol{\chi}^{(3)}.\mathbf{E}^{3}..\right) \qquad \textbf{………………….. (I.1)}$$

Where the term $\chi^{(1)}$ represents linear susceptibility, The terms $\chi^{(2)}$ and $\chi^{(3)}$ are the non-sensitivities linear of order two and three, respectively.

I.4.2. Hyperpolarizability:

The hyperpolarizabilities are tensors containing information about the system's optical response in different directions, where higher order term β and γ are the first and second hyperpolarizabilities, respectively (23).The first hyperpolarizabilities is an important parameter for the characterization of the molecular material, generally associated with organic molecules consisting of donor group and acceptor separated by a conjugated segment which allows the distortion of the electron cloud to be relayed from one end of the system to the other. First hyperpolarizabilities were calculated with DFT quadratic response (QR) theory using Dalton 2011 at the common laser frequencies of 0.65, 1.165 and 1.55 eV (λ = 1907, 1064 and 800 nm) (23). This nonlinear response can lead to a variety of interesting optical effects, such as second-harmonic generation and electro-optic modulation which is a process in which the intensity or phase of light can be controlled by applying an electric field. This effect is used in a variety of devices, such as optical switches and modulators.

The second hyperpolarizability, often denoted by the symbol $\boldsymbol{\gamma}$**.** A specific type of quadratic hyperpolarizability (β). Describes how an intense electric field induces a third-harmonic polarization in the material. This means the induced polarization oscillates at three times the frequency of the applied electric field. It is related to the third order susceptibility $\boldsymbol{\chi}^{\mathbf{(3)}}$ and describe nonlinear optics like third harmonic generation (24). There are different experimental methods commonly used to measure hyperpolarizabilities, such as Hyper-Rayleigh Scattering, Electric Field Induced Second Harmonic Generation (25-26).

I.4.3. Refractive index:

The refractive index is a fundamental parameter that characterizes how light travels through a material. In nonlinear optics, the refractive index becomes dependent on the strength of the electric field of light (27). This phenomenon is called nonlinear refraction. There are Several mechanisms can contribute to nonlinear refraction us Optical Kerr Effect. The refractive index can be expressed as a Taylor series as a function of the electric field strength (28):

$$n = n_0 + n_2 I + n_3 I^2 + \dots \qquad \dots\dots\dots\dots\dots\dots \text{(I.10)}$$

where:

n_0: the linear refractive index of the material, i.e. the refractive index at low intensity.

n_2: the second-order nonlinear refractive coefficient.

n_3: the third-order nonlinear refractive coefficient.

I: the strength of the electric field.

The higher-order terms of the Taylor series are generally negligible, except for extremely high electric field strengths.

I.5. Nonlinear Optics Theory of response:

Nonlinear optics is the study of phenomena that occur because of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken and col. (1961) (10), shortly after the demonstration of the first working laser by Maiman in 1960. Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field.

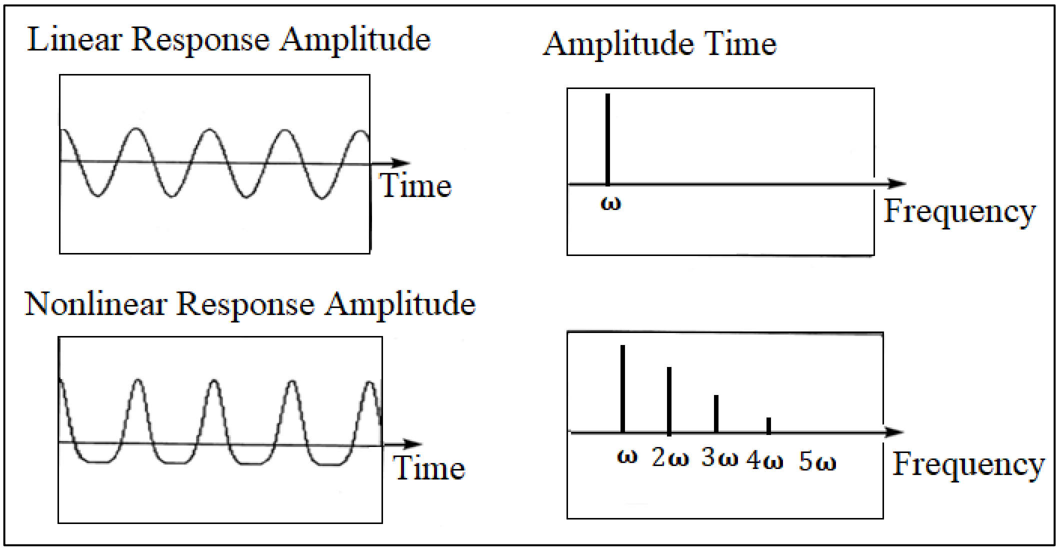


Figure I.4: Linear and nonlinear response (29).

For example, second-harmonic generation occurs because of the part of the atomic response that scales quadratically with the strength of the applied optical field. Consequently, the intensity of the light generated at the second-harmonic frequency tends to increase as the square of the intensity of the applied laser light (7). When light interacts with matter, the electrons of the atoms that make up the matter are deformed. This deformation is called polarization (30). The polarizability of a material is a measure of how easily it can be polarized. It becomes nonlinear when it is exposed to a high-intensity electric field:

$$\mathbf{P} = \mathbf{P}_{(0)} + \boldsymbol{\varepsilon}_{(0)}\left(\boldsymbol{\chi}^{(1)}.\mathbf{E} + \boldsymbol{\chi}^{(2)}.\mathbf{E}^2 + \boldsymbol{\chi}^{(3)}.\mathbf{E}^3..\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(I.1)}$$

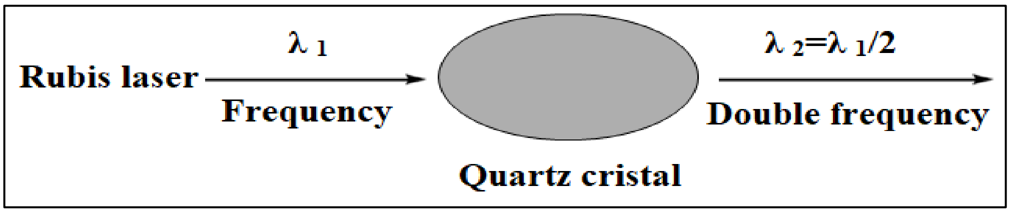


Figure I.5: Double frequency emission.

I.6. Quantum theory of nonlinear optical phenomena:

The quantum theory of nonlinear optical phenomena provides a framework for understanding how light interacts with matter at the microscopic level, leading to various nonlinear optical effects observed in experiments (31). This approach goes beyond the classical description of light and matter, where the response of a material is directly proportional to the intensity of the light field. The results come from the application of quantum equations to nonlinear processes such as phase modeling.

I.7. Materials for NLO:

The nonlinear optic has a longue story, it involves an impressive range of different aspects. From theory to applications, from physics to chemistry, from microscopic to macroscopic aspects, from quantum mechanics of materials to classical and quantum electrodynamics, from gases to solids, from mineral to organic compounds, from bulk to surface, from waveguides to fibers and so on (32).

Non-linear optics started by using inorganic materials when Franken uses a quartz crystal (the discovery of frequency doubling phenomena caused by the interaction of laser with quartz), among the properties that make crystals as materials for NLO are transparency and fluorescence. But after a long search, the researchers find that there are materials that have a great nonlinear response and better than mineral materials, these are organic materials and especially conjugated polymers (33).

I.7.1. Inorganic materials:

The nonlinear optics field began with the use of inorganic materials, which were mainly crystals. They have many properties. For example, they have an ordered and repetitive structure defined by a crystal lattice. They are generally conductors in the molten or dissolved state, but not in the solid state. They are often transparent or translucent, because the ions do not absorb visible light. They also exhibit a high resistance to optical damage and are generally hard and brittle (34). In these materials, Electrons involved in nonlinear phenomena exhibit low polarizability due to their engagement in strong chemical bonds. This means they are less sensitive to external electric fields and their nonlinear response is less pronounced. However, despite their low polarizability, these electrons offer an interesting compromise between transparency, efficiency, and stability. Transparency is important to minimize light losses in the device, while efficiency is essential to maximize the conversion of incident light into nonlinear light. Stability ensures the long-term durability of the device. The favorable compromise between transparency, efficiency, and stability makes these electrons particularly suitable for the realization of nonlinear devices at the industrial scale. Among the most interesting inorganic materials in NLO, we have:

I.7.1.1. Crystals:

Bêta-baryta borate (BBO): a chemical compound with the formula BaB_2O_4, also written $Ba(BO_2)_2$ and $BaOB_2O_3$. Barium borate comes in the form of a white powder or colorless crystals, often in the $BaB_2H_2O_5$ hydrate state. It is a Birefringent crystals and nonlinear optical material with a very wide optical transmission window, ranging from 490 to 3500 nm. It used to achieve frequency doubling (SHG)**(35)(36).** BaB_2O_4 can exist in two phases: the high-temperature phase (α phase) and the low-temperature phase (β phase), with a phase transition temperature of 925°C. Both phases have quasi-identical structures containing the coplanar $[BrO_4]^{4-}$ring. The α and β phases of BBO differ in the positioning of the Ba^{2+} ion: in the α phase, the barium is in a 32-point symmetry site surrounded by six oxygen atoms, while in the case of the β phase, the barium atoms are regularly bonded to eight oxygen atoms. This implies that the β phase is non-centrosymmetric while the α phase is not. The β phase is built around $[B_3O_6]^{3-}$ rings linked to each other and to Ba^{2+} ions by FeO_4 tetrahedra in a rhombohedral structure. BaB_2O_4 is a congruently melting material with a melting temperature between 1095 and 1105 °C (37).

Figure I.6: Bêta-baryta borat (BBO) crystal (38).

The beta hyperpolarizability value of beta-barium borate (BBO) is approximately 2.3 pm²/V². This value is relatively high compared to other optical nonlinear materials (37)(39).

Barium titanate (BTO): a chemical compound with the formula $BaTiO_3$, this crystal is a ferroelectric white solid with pronounced hysteresis that also has a photorefractive and piezoelectric effect (40).because of the nonlinear properties of BTO like the Hight hyperpolarizability and wide bandgap, which allows it to operate at both visible and infrared optical wavelengths, it used for many process like SHG,and it's important to note that the beta hyperpolarizability of BTO is very sensitive to crystal structure and the presence of defects(41).

Cubic structure: at high temperature, this is the stable phase above the Curie temperature, about 130 °C. In this structure, barium (Ba) atoms occupy the corners of a cube, titanium atoms (Ti) occupy the center of the cube, and oxygen atoms (O) occupy the faces of the cube and positions in between. This structure is centrosymmetric, which means that it has a center of symmetry and therefore does not have important optical nonlinear properties (42).

Tetragonal structure: at intermediate temperature (43) below Curie temperature, the cubic structure deforms slightly and becomes tetragonal. In this phase, the titanium atoms move slightly from their central position, which breaks the symmetry and gives the BTO piezoelectric and ferroelectric properties.

Orthorhombic structure: at low temperatures, the tetragonal structure deforms further and becomes orthorhombic. This phase also exhibits piezoelectric and ferroelectric properties (42)(44).

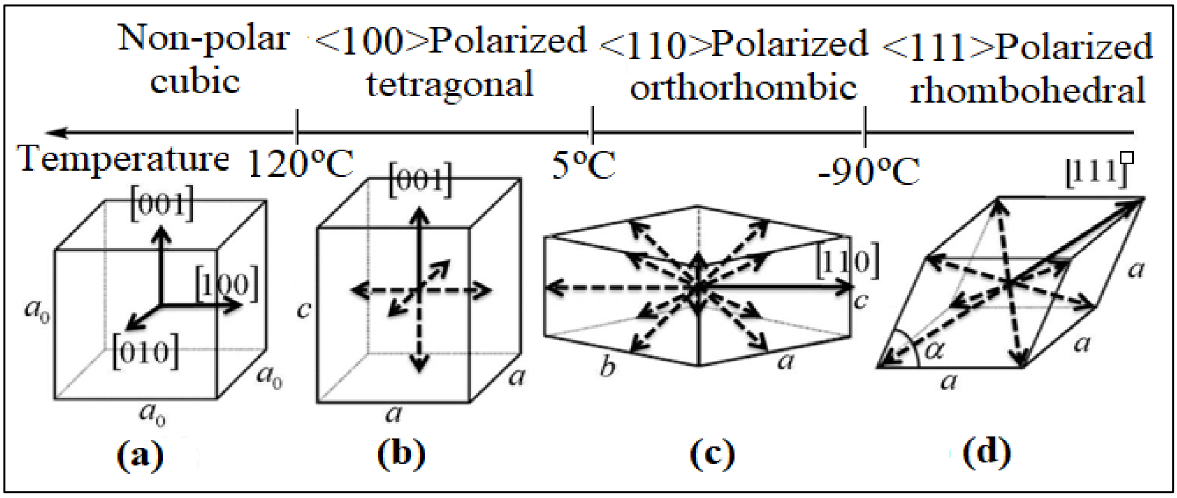


Figure I.7: Phase transformation in barium titanate (45).

So, in the cubic structure, the hyperpolarizability is not well-defined due to its centrosymmetric structure**.** But in the tetragonal, the orthorhombic and rhombohedral it has an interesting hyperpolarizability due to the non-centro symmetry (43).

Potassium dihydrogen phosphate (KDP): a crystalline material widely used in nonlinear optics (NLO). "It has low nonlinear susceptibility coefficients (0.435 pm. V^{-1}) (46). And it has several properties that make it interesting for this application, it is a birefringent crystal, which means that it has two different refractive indices for light polarized in different directions. This property is used to generate harmonic frequencies and to make optical modulators. KDP has high nonlinear coefficients, which means that it can interact with light in a nonlinear way. This property is used to generate harmonic frequencies, to make optical mixers, and to pump parametric lasers. It has good optical transmission in the visible and infrared, which makes it usable for a wide range of NLO applications and a high optical damage threshold, which allows it to withstand high light intensities without deteriorating. The transparency range of KDP is: 0.176 - 1.711nm.

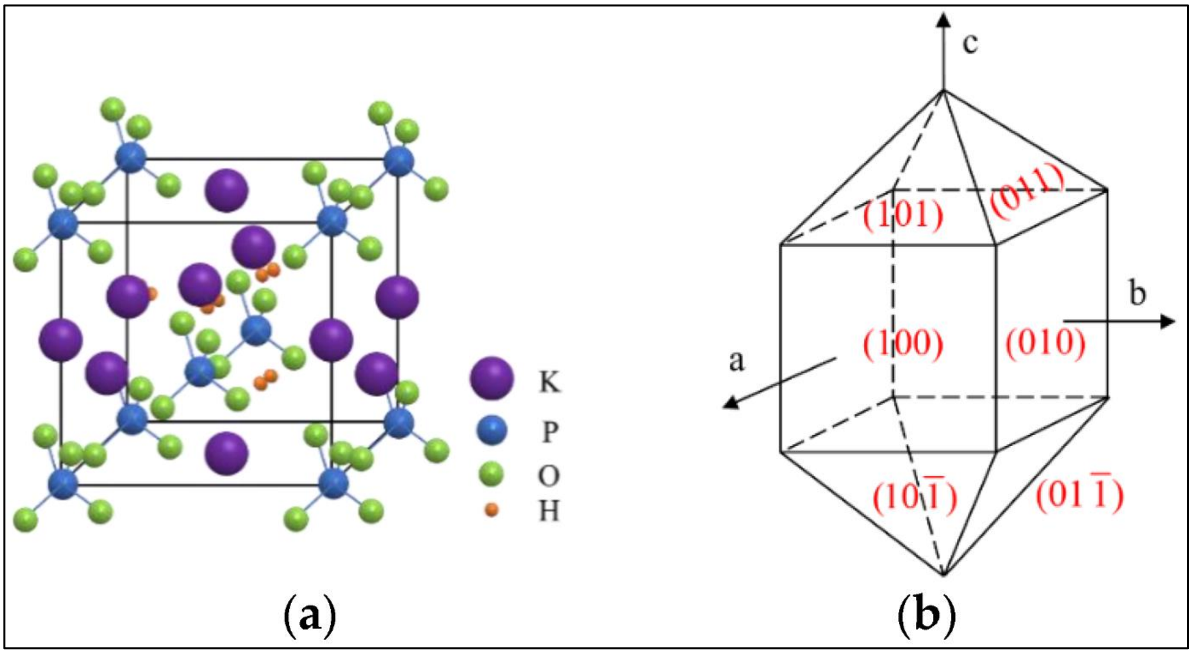


Figure I.8: The structure of KDP crystal:(a) The cell structure, (b) The ideal shape of KDP crystal (47).

I.7.1.2. Glasses:

Germanium phosphate glass (GeO_2-P_2O_5): a glass composed of germanium dioxide (GeO_2) and phosphorus pentoxide (P_2O_5) (48); it is a type of non-linear optical glass that exhibits a non-linear response to light. Their refractive index changes based on the intensity of the light passing through it and it demonstrates good resistance to both chemical and thermal degradation. Thats why Germanium phosphate glass used for Many applications for example: Frequency doubling and Optical parametric oscillators (OPOs) (49).

Tellurite glass (TeO_2): (TeO_2) contain tellurium oxide as the main component. It is a type of non-linear optical glass that exhibits a stronger non-linear response which involves interactions between the light's electric field and the electrons in the Te atoms (50). Among the phenomena presented by (TeO_2) we have: Second-harmonic generation (SHG), Optical parametric oscillation (OPO)which Utilizing the non-linearity to convert a single light source into multiple beams with different wavelengths, allowing for tailored functionalities and, Four-wave mixing (FWM).

Table 1: Hyperpolarizability of TeO2 glass.

		χ (3)	(10^{-13}) esu
Glass	Energy(eV)	Calculated	Observed
TeO_2	6.85	11.20	14.10

I.7.1.3. Semi-conductor:

Gallium phosphide (GaP): Gallium phosphide (GaP) is a Type III-V binary composite semiconductor composed of phosphorus and gallium (51). It has interesting nonlinear optical properties, in a two-photon process, an electron gets excited by absorbing a photon. It can then absorb another photon of the same frequency, which pushes it to a higher energy state. When the electron returns to its original state, it releases a photon with twice the frequency of the original light. (GAP) used for a variety of applications: Parametric Frequency Conversion (FPC) to generate light at new wavelengths (52).

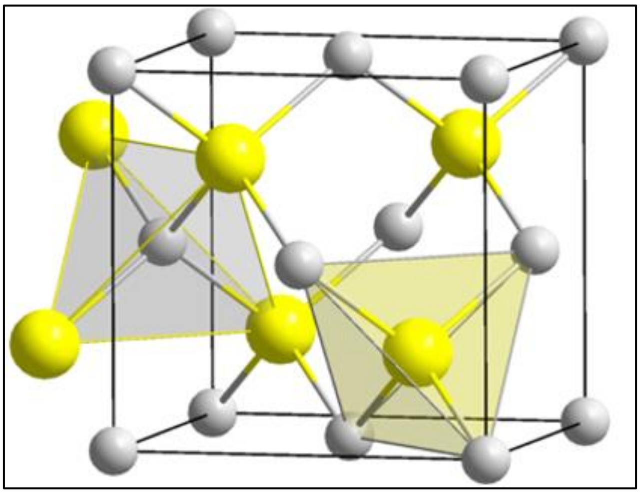


Figure I.9: GAP cubic structure centred on the face, each Ga atom is surrounded by four P atoms, and vice versa.

I.7.2. Hybrid materials:

Hybrid organic–inorganic materials applications in nonlinear optics has emerged as one of the most interesting fields. They have an easy chemistry, easy to shape and pattern, and they have good mechanical and important optical properties. Their nanocomposite structure gives opportunities to fine tune the optical response and to prepare many different types of photonic materials (linear and non-linear optical properties). Particular attention has been paid to hybrid materials for non-linear optics in optoelectronics applications (53). This type of materials is prepared by hydrolytic polycondensation of molecular precursors (54). Organo-mineral hybrid materials are a promising area of research for nonlinear optics (55). They offer potential advantages in terms of efficiency and performance compared to pure organic materials. However, their low thermal stability still limits their field of use. The field of hybrid materials for nonlinear optics is still under development, but it holds great promise for the future. As researchers continue to develop new materials and improve their properties, we can expect to see hybrid materials playing an increasingly important role in a variety of photonic applications. Here are some hybrid materials:

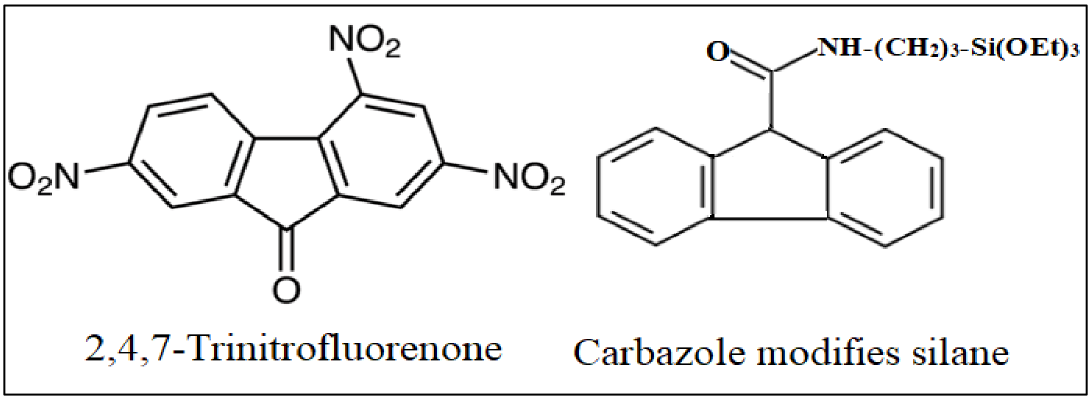


Figure I.10: Structure of some hybrid materials (53).

I.7.3. Organic materials:

Some organic materials, especially Organic materials with aromatic rings have emerged as exciting candidates for nonlinear optics, they have been reported to possess large optical nonlinearities and fast response times. They hold potential advantages over traditional materials like dielectric crystals and semiconductors in terms of how easily they can be manipulated and incorporated into devices (56). They have characteristics comparable to those of inorganic NLO materials, it is possible to design their chemical structures and absorption wavelengths to achieve highly efficient functions for NLO device use. Therefore, they can be applied in many optical devices, such as thin film and fiber waveguides (57).

Organic molecules used for nonlinear optics typically contain a donor-acceptor combination connected by a conjugate bridge i.e. purely organic chromophore (58). The delocalized π electron system connecting the donor and acceptor allows for an intramolecular charge transfer (ICT) between the groups at the ends of the molecule, this charge transfer generates high dipole moments in the ground and excited states of the molecule. The combination of the above characteristics gives these molecules an important hyperpolarizability. This type of organic molecule which contains donor-acceptor groups connected by a conjugate bridge are usually has a strong dipole moment and is called "push-pull". They are molecules with easily polarizable electrons, i.e. electrons π. The length of conjugate systems including groupings (59) is a key factor contributing to the high degree of electron delocalization along the transfer axis and therefore enhancement of non-linear effects.

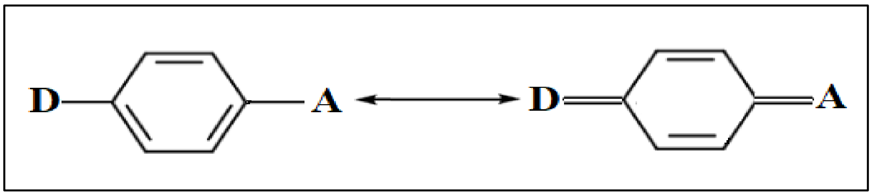


Figure I.11: Schematic representation of X-phenyl-Y molecules. the X and Y groups (donor and acceptor).

I.7.3.1. Heterocyclic organic materials:

Heterocyclic compounds are also among the interesting organic materials of NLO because of the presence of rings and heteroatom like pyrazine, nitrogen, oxygen, or sulfur, they can exhibit strong electron delocalization due to their conjugated structure which allows for easy distortion of the electron cloud under an electric field. Those properties contribute to the molecule's electron-withdrawing character, which is crucial for enhancing NLO responses (60).

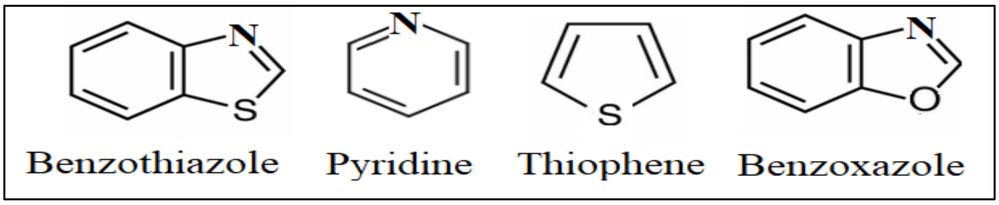


Figure I.12: Some heterocyclic materials for NLO (61).

Table 2: Approximation calculations values of First Hyperpolarizability, (10^{-30}esu), of Heterocyclic Molecules (the values depending on the method of calculation and the experimental conditions):

Molecules	Pyridine	Thiophene	Benzoxazole	Benzothiazole
β (10^{-30} esu)	14.8	8.5	15	8.3

I.7.3.2. Crystals:

Organic crystals hold immense promise for image processing and optical communication due to their remarkable non-linear optical properties**.** This surge in interest stems from their superior performance compared to traditional inorganic crystals, particularly in terms of their ability to handle high laser intensities without sustaining damage. Recent research has specifically focused on exploring unique classes of organic molecular crystals to unlock their full potential in these crucial fields (62).

3-Acetamido-4-(cyclooctylamino) nitrobenzene ($C_{16}H_{23}N_3O_3$) crystals: This crystal have been found to exhibit good nonlinear optical properties, making them potentially useful for a variety of applications such as frequency doubling, optical parametric oscillation (OPO), and optical parametric amplification (OPA) (62). However, more research is needed to determine their suitability for practical applications. This molecule is a benzene derivative with donor-acceptor (D-A) substitutions (push-pull compound). A charge-transfer (CT) interaction occurs between the cyclooctylamino (donor) and nitro (acceptor) groups at the para position. This interaction leads to high molecular non-linearity (63). While the acetamido ($NHCOCH_3$) group has a minor effect on non-linearity, it crucially facilitates non-centrosymmetric crystal growth through hydrogen bonding (64).

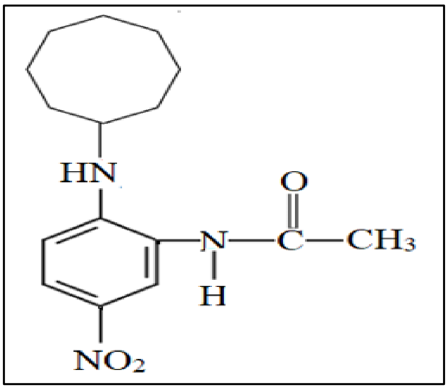


Figure I.13: Structure of ($C_{16}H_{23}N_3O_3$) crystals (64).

I.7.3.3. Polymers:

Conjugated organic polymers are capable of emitting light, they are formed by the regular repetition of monomers containing π-electrons, to obtain a chain with no interruption of the conjugation. The π-electron system is completely extended over the entire chain. Conjugated conducting polymers have experienced a considerable boom which dates to 1977 when Heeger (65), MacDiarmid and Shirakawa demonstrated the existence of metallic conductivity in doped polyacetylene. This discovery was awarded the Nobel Prize in Chemistry in 2000. Another interesting polymer is the azopolymer compounds (66), they possess electron donor and acceptor groups, and separated by a conjugated path which is in this case an azobenzene derivative. The main advantages of polymers for nonlinear optics are their ability to be integrated directly into optoelectronic devices, their adhesion to various substrates, and the possibility of reorienting photochromic molecules under an electric or electromagnetic field, very fast response times, High nonlinear coefficients. They are cheaper and easier to manufacture and process (67).

Poly(p-phenylenylvinyl) (PPV): a conjugated polymer that is of great interest for nonlinear optics applications. Due to its conjugate structure, PPV has a strong nonlinear reactivity, which means that it can interact with light in a nonlinear manner. This property can be used for a variety of applications, for example: SHG and Optical Switching (68). The value of the β hyperpolarizability of poly(p-phenylenylvinyl) (PPV) depends on several factors, including the structure of the polymer, the length of the conjugated chain, and the solvent in which it is dissolved (68)(69):

PPV in solution: β = 10^{-28} to 10^{-26} esu.

Doped PPV: β =10^{-27} to 10^{-25} esu.

PPV in thin film: β =10^{-26} to 10^{-24}esu.

Note: These values are estimates only and the actual value of β may vary significantly from one sample to another.

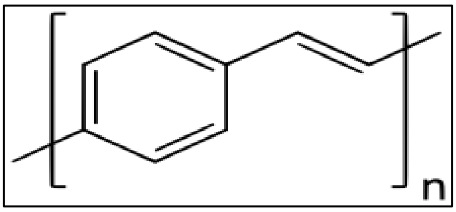


Figure I.14: Structure of PPV.

I.8. Molecularity of Push-Pull Compounds:

Push-pull compounds (or PPs) are organic systems composed of an electron donor (D) and an electron acceptor (A) placed in conjugate positions with the extremities of a conjugate π system. This system allows for electronic interaction between the electron donor and acceptor which translates on the absorption spectrum by a band of intense absorption called intramolecular charge transfer band (ICT) and therefore a strong dipole moment and High hyperpolarizability (70). The strong directionality of the charge transfer within the molecule « push-pull »makes these molecules one-dimensional**.** The Transfer of electrons from donor to acceptor during the intramolecular transition can be partial or total (71) and the complex form is characterized by a new adsorption band called the intramolecular charge transfer spectrum. These complexes generally have an intense color and absorb radiation in the visible region.

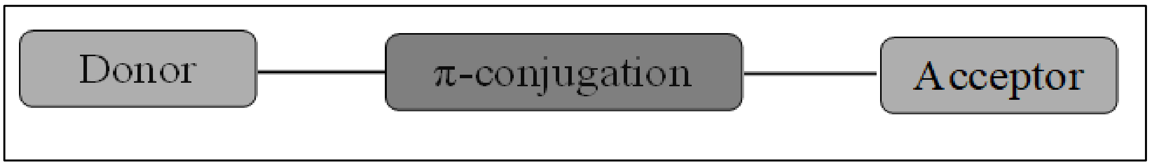


Figure I.15: Structure of Push-pull compounds.

- The donor and acceptor groups (72) of push-pull molecules are functional groups that tend to donate or accept electrons, respectively. Where donor groups are usually high in electrons and have low electronegativity:

$OCH_3 < OH < Br < OC_6H_5 < SCH_3 < N_2H_3 < NH_2 < N(CH_3)_2$

There is other donner complex groups like: Aromatic Amine and Phenolic Hydroxyl.

- Acceptor groups are functional groups that tend to accept electrons. They are usually low in electrons and have high electronegativity:

$SO_2CH_3 < CN < CHO < COCF_3 < NO < NO_2 < CHC(CN)_2 < C_2(CN)_2$

Also, there are acids that consider us an acceptor group like: picric acid.

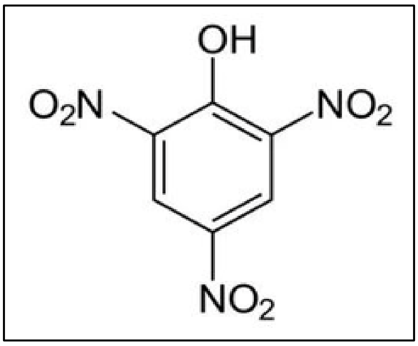


Figure I.16: Picric acid structure.

I.9. Characteristics of organic molecules:

I.9.1. Molecular structure:

Conjugation: Conjugation in organic chemistry refers to the presence of a series of atoms bonded by alternating single and double bonds. This configuration allows the electrons to relocate across the entire conjugate system, giving the material unique electronic and optical properties (73). The conjugation effect automatically increases the load transfer intramolecular of charges (ICT), The existence of chromophore electrons of Type π-π cause strong nonlinearities, where the length of the conjugates system influences the (ICT) (74).

Example: Oligo (p-phenylene vinylene) (OPV)
Dimer (n = 2) : 10^{-30} esu.
Trimer (n = 3) : 2.5 x 10^{-30} esu.
Tetramer (n = 4) : 4.5 x 10^{-30}esu.

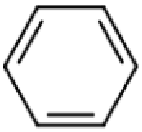
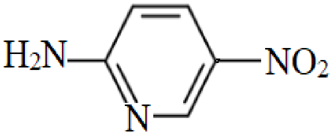
The hyperpolarizability values (75) given above are approximate estimates and may vary depending on the specific structure of the material and measurement conditions.

Non-Centrosymmetric of Organic Molecules: Non-centrosymmetric organic molecules play a crucial role due to their unique ability to exhibit a specific type of nonlinear optical effect called second-harmonic generation (SHG). A molecule is said to be non-centrosymmetric if it does not have a center of inversion. Given that the electric field and polarization vectors are polar vectors (they change sign under space inversion) the inversion of the electric field direction in a non-centrosymmetric medium changes the sign of the second-order electric polarization of that medium (7) which is:

$$P^2(-E) = -P^2(E) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I.11)}$$

The non-centro symmetry molecules possess a strong fundamental dipole moment after excitation by an electromagnetic field or electric so, an important hyperpolarizability.in the centrosymmetric molecules the hyperpolarizability's value is zero (76).

Table 3: β calculation of some molecules.

		 	
β $(10^{-3} esu)$	0	35	34

Donor and Attractor Groups: Donor and attractor groups are groups of atoms that can influence the distribution of electrons in an organic molecule which allows the creation of push-pull structures in an almost unlimited number by modifying the groups (A), (D), or the nature of the transmitting group. It is therefore possible to produce crystals or thin films with strong nonlinearities, since the final arrangement of the molecules remains non-centrosymmetric (77).

We take as an example the 2-pyrazoline Substituted, where the table below explains the group's effects.

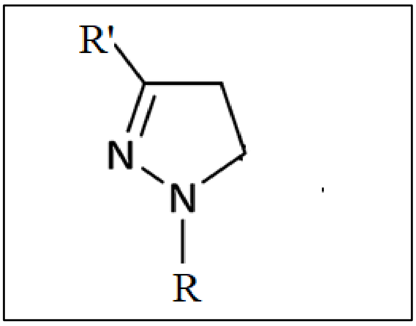


Figure I.17: 2-pyrazoline substituted structure.

Table 4: The effect of donor and attractor groups on the value of hyperpolarizability of 2-pyrazoline (β_0 is the value calculated at $w_0 = 0$ to avoid resonance effects, β is the value for input wavelength w = 1.06 μm):

R	R’	β_0	B
H	H	1.7	2.9
NH_2	NO_2	28.6	137.6

I.9.2. High Nonlinear Optical Response:

Organic materials offer considerable potential for nonlinear optics due to their unique properties; their Molecular structure Allows an intramolecular charges transfer (ICT) which favors non-linear effects (increase the hyperpolarizability). Organic materials exhibit ultra-fast (femtosecond scale) response times to light, while inorganic materials do not, which is crucial for high-speed applications. They can also be easily made into different shapes (thin films, optical fibers, polymers) for the manufacture of ONL devices (78,79).

Organic materials offer the possibility of more cost-effective solutions than inorganic technologies, that’s why they are used for different application us: Optical Frequency Conversion, Optical Switches & Modulators and Organic Dye Lasers (79).

I.10. Factors Influencing Hyperpolarizability:

I.10.1. Positional effects:

Let's take as an example a benzene substituted by an attractor group (NO_2) and a donor group (NH_2) in different positions: Ortho, meta and para. The position of the groups ortho, meta and para influences hyperpolarizability where the para position facilitates the ICT better then Ortho and meta position due to the asymmetric distribution of charges (80).

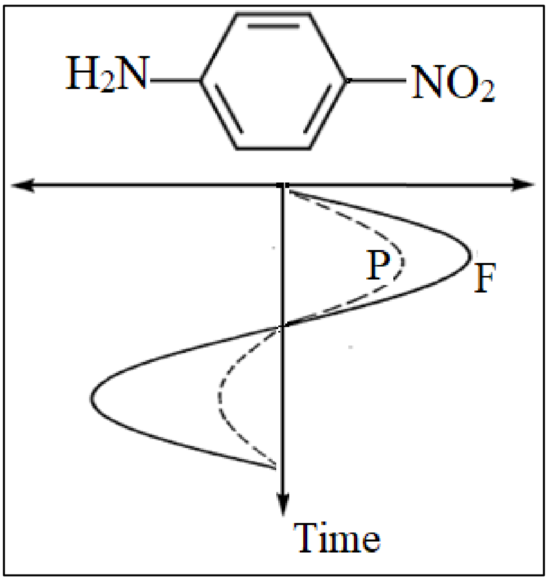


Figure I.18: P polarization induced by an oscillating field F on the molecule of Para nitroaniline.

Table 5: Hyperpolarizability beta measured by second harmonic generation Static subfield of substituted benzenes values given in $10^{-4}mv^{-1}$(81).

Position	D	A	B
Ortho	NH2	NO2	26.8
Metha	NH2	NO2	17.6
Para	NH2	NO2	88.3

I.10.2. The effects of donor and acceptor groups:

In a push-pull system, the donor group is usually linked to an attractor group by a conjugate chain. The conjugated chain allows electrons to delocalize between the two groups, increasing the hyperpolarizability of the molecule. a proportional relationship between the donor and attractor group strength and coefficients hyperpolarizability β.

We take as an example this molecule:

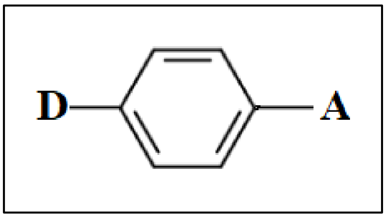


Figure I.19: Substituted benzenes by a donor and acceptor groups.

Table 6: Donor and acceptor effects in Substituted benzenes on para position.

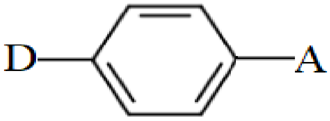
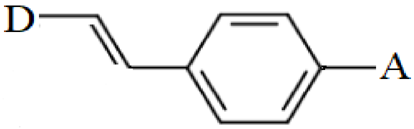
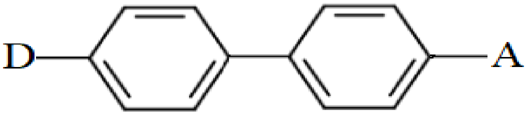
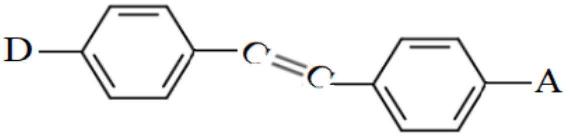
Nomenclature	Donnor	Acceptor	$\beta 10^{-30}$(esu)
1-Metoxy-4- nitrobenzen	Ome	NO_2	5.1
N-Methyl-4-nitroaniline	NMe	NO_2	12
4-Nitroaniline	NH2	NO_2	10.3
4-(Methyl sulfonyl)aniline	NH2	SO_2CH_3	1.6

From the result given by this table, we can resume that the structure of donor or acceptor groups influence the hyperpolarizability β by a proportional way

I.10.3. Conjugation:

The hyperpolarizability coefficient β rises when conjugation increases so, a proportional relationship between conjugation and coefficients hyperpolarizability β (59) that's what we can confirm using the table below which present the hyperpolarizability of some conjugate molecules.

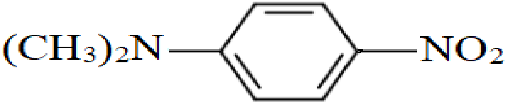
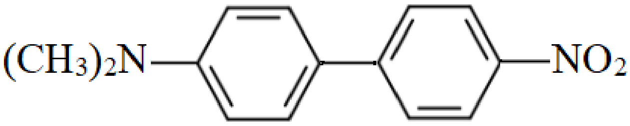
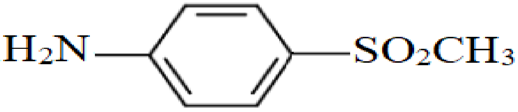
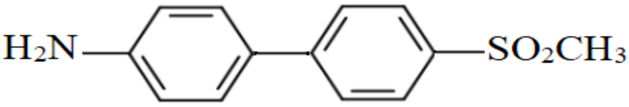
Table 7: The hyperpolarizability of some conjugate molecules.

Molecules	Donnor	Acceptor	$\beta 10^{-30}$(esu)
	OMe	NO2	5.1
	OMe	NO2	17
	OMe	NO2	9.2
	OMe	NO2	28

I.10.4. The effects of aromatic rings:

The coefficient of hyperpolarizability β increases when the number of cycles increases, and the donor and attractor group strength therefore increase the relationship between them is a corresponding relationship. The table below confirms that the relation between the number of cycles and the argumentation of hyperpolarizability β is proportional:

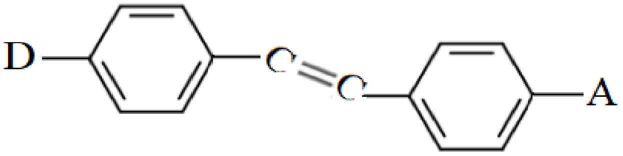
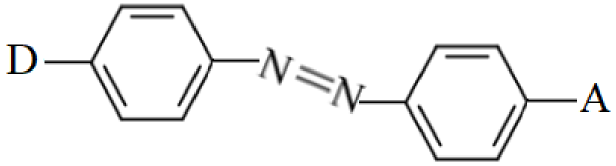
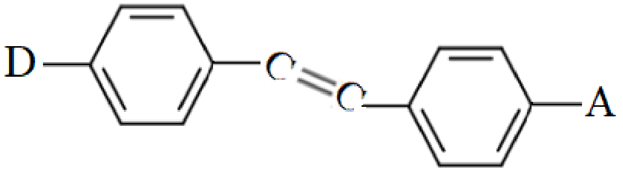
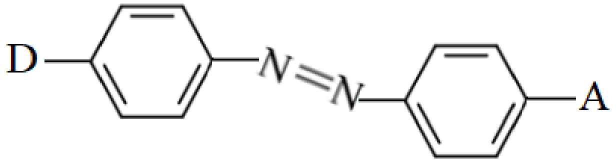
Table 8: Cycles effects on hyperpolarizability.

N. of cycles	Structure	$\beta 10^{-30}$esu
1		12
2		50
1		1.6
2		9.1

I.10.5. The Effects of the Bridge:

Conjugated bridges play an important role in increasing the hyperpolarizability of molecules (82). A conjugate bridge is a chain of atoms connected by alternating single and double bonds. This configuration allows the delocalized π electrons to move freely through the conjugate chain. The delocalization of electrons increases a molecule's ability to respond to an external electric field, resulting in higher hyperpolarizability. The value of the β hyperpolarizability coefficients is influenced by the nature of the bridge used between the two aromatic rings in the push-pull system. When you set a stilbene bridge C=C the values of β will increase better then azo N=N bridge.

Table 9: bridge's effect on hyperpolarizability.

Structure	D	A	$\beta 10^{-30}$esu
	N(CH3)2	NO_2	73
	N(CH3)2	NO_2	59.4
	N(CH3)2	SO_2CH_3	62.1
	N(CH3)2	SO_2CH_3	27.8

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Second chapter

Chemical overview and chromophore’s reactions

II.1. Introduction:

The organic materials specially the push-pull compounds are the most interesting for the nonlinear optics due to their different properties, that's why they are the most widely used in different fields of application.

Our interesting in this dissertation is the study of the effect of bridge in push-pull molecules on the nonlinear optics properties in all three cases: the azo compounds which are organic compounds bearing the functional group diazinyl (R−N=N−R′), Olefin molecules which is a class of organic compounds characterized by the presence of one or more carbon-carbon double bonds (R1R2C=CR3R4) and the third case is imine or Schiff- bases , in this case, the carbon and nitrogen atoms are bound by two covalent bonds: a σ bond and a π bond(R1R2C=NR3). But before this, we will study the structure and synthesis of these three categories: azo, olefin and imine structures.

II.2. Azo compounds:

II.2.1. Definition:

Azo compounds, also known as diazenes, are a broad class of organic compounds characterized by the presence of the azo functional group, denoted:(-N=N-). This group connects two aromatic rings, either heterocyclic rings (containing atoms other than carbon) or aliphatic groups (carbon chains) (1). The azo group discovered around 1860 by the Anglo-German chemist Johann Griess (2), he was influential in the formation of modern dyes, first formulating the diazotization reaction of aryl amines (the key reaction in the synthesis of the azo dyes). where the repetition of the azo group in a molecule is possible, resulting in disazoic, triazoic, etc. The number of azo groups present in the molecule affects its properties, such as its solubility and color which make them widely used in different domains, in food coloring, printing and textiles.

Examples:

a. Monoazoic compounds:

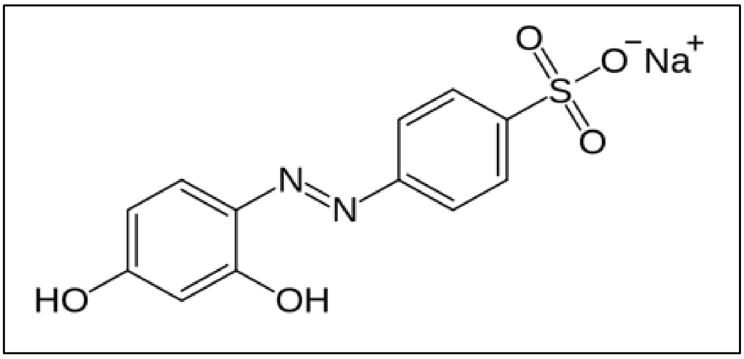


Figure II.1: Cyrosine S (or resorcin yellow).

b. Disazoic compounds :

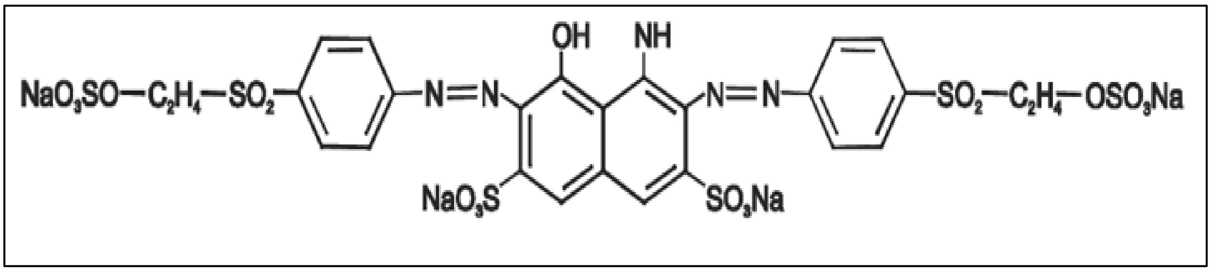
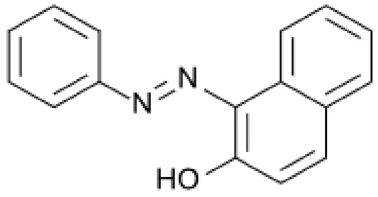
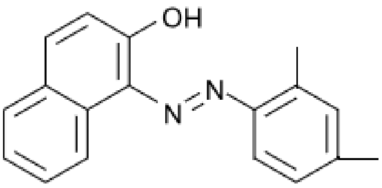


Figure II.2: Diss Dissymmetric diazo dye Remazol Black 5(3).

II.2.2. Properties of azo Compounds:

II.2.2.1.Color: Azo compounds are characterized by their excellent coloring properties due to the presence of chromophore group (-N=N-) which form bridges attached with aromatic or heterocyclic systems (4) mostly reds, oranges, and yellows, where Yellows are easily obtained from pyrazolones or acetoacetylated derivatives, simple naphthols lead to oranges and reds, while blues, browns and blacks are derived from aminonaphthols but achieving beautiful green shades is more difficult, as the bathochrome displacement is most often accompanied by a widening of the bands, thus reducing the purity and vividness of shades (5). This diversity of colors is due to the delocalization of π electrons within the molecule. There are many factors influencing the color of azo compounds such as the structure of the aromatic nucleus, where the nature and position of substituents on aromatic rings affect the wavelength of light absorbed, and therefore, the color of the compound. Another factor influencing the color is the presence of auxochromes (6) which are groups such as -OH, -NH2, -SO3H change the color by intensifying or shifting the absorption band. Color is due to the fraction of light that is not absorbed and is reflected, and this is what gives color to matter (7).

Table 10: Some azo dyes.

Structure		
Name	Sudan I (Sudan Yellow)	Sudan II (Sudan Orange)
IUPAC name	1-[(E)-phenylazo] -2naphthol	2-(E)-(2,4-dimethylphenyl)diazenyl-1-naphthol

A typical dye molecule is usually made up of three parts: a chromophore, an auxochromic group and a solubilizing group (8), the chromophore is the portion responsible for the color of compounds, the auxochrome is the part influencing the intensity of the coloration and it fixes with efficiency the dye on the substrate and finally the solubilizing group improves the solubility of the dye and thus, it can potentially be applied in an aqueous medium(9).

II.2.2.2. Stability and reactivity: Azo compounds have two isomeric forms, trans and cis. We take us an example azobenzene, the cis form is unstable and can be obtained from the trans form by photoisomerization (10).

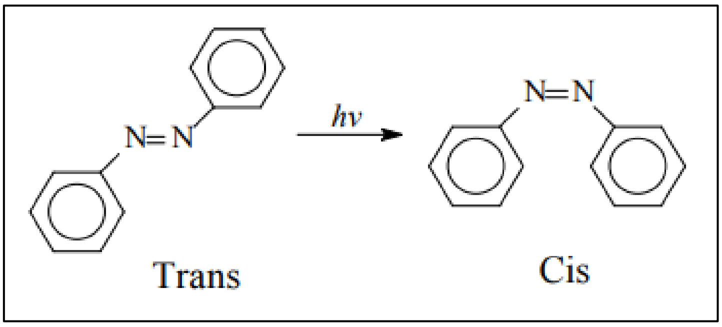


Figure II.3: Azobenzene isomeric forms.

In the trans isomer, the shape of the molecule is very unfolded, while in the cis isomer it is well folded on itself. As a result, the intensity of electronic absorption, which is very sensitive to the dimensions of the conjugated system transition, varies considerably when going from one form to the other**.**

Table 11: Absorptivity in cis and trans isomer of azobenzene.

forms	λ max (nm)	ε (L.Cm-1.mol-1)
Trans isomer	319	22000
Cis isomer	280	5260

The azo unit can react with a variety of chemical agents, and it is a leaving group, which means that it can be easily eliminated from a molecule, and it can present in different reactions, they can in principle, be sulphonated, nitrated, halogenated, etc…, allowing them to be used in many industrial applications. The introduction of a hydroxy group in the ortho or para position of the azo function creates the possibility of azophenol-quinonehydrazone tautomerism, studied by spectroscopic methods (11).

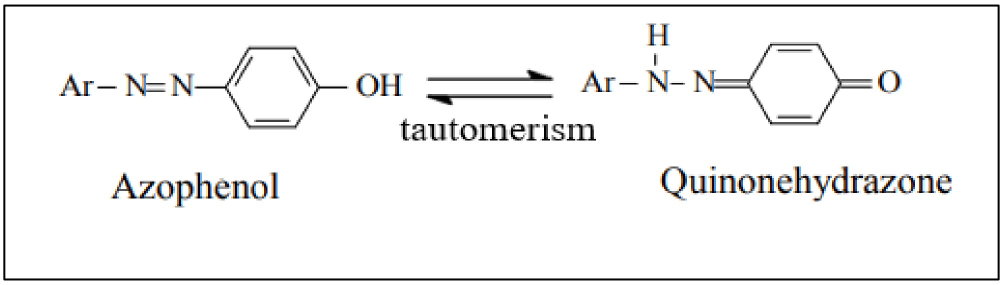


Figure II.4: Azophenol-quinonehydrazone tautomerism.

Among the addition reactions on the N=N double bond, we have hydrogenation leading to hydrazo benzene (a) and oxidation by hydrogen peroxide and peracids giving rise to the corresponding azo compounds (b)(12).

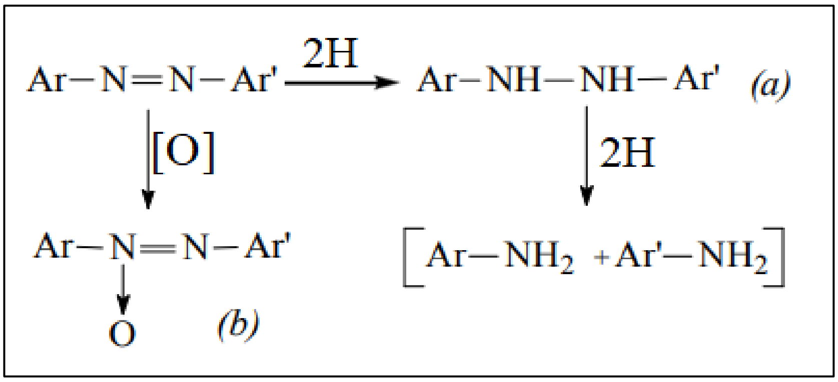


Figure II.5: Addition reactions on the N=N double bond.

II.2.3. Synthesis of azo compounds:

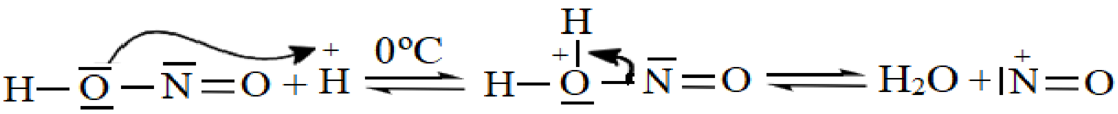
The synthesis of the azo group is mainly done by 2 steps which are diazotaion and copulation.

II.2.3.1. Diazotation reactions: Diazotization is the reaction of nitrous acid with amines to form diazonium salts. Aryldiazonium salts are generally prepared by reacting aniline with nitrous acid, which is generated from mineral nitrite. Their aryldiazonium ions are stable enough to exist in solution at room temperature and even above because of an electronic delocalization with the aromatic ring and it seems to carry its charge predominantly on the nitrogen atom bonded to the ring, they can be isolated as salts with non-nucleophilic anions such as tetrafluoroborate. On the other hand, alkyldiazonium ions decompose rapidly into molecular nitrogen and carbocation. The formation of diazonium involves the addition of NO^+ to the amino group, followed by the elimination of a water molecule (13-15). Nitrous acid is not thermodynamically stable in aqueous solution from a redox point of view:

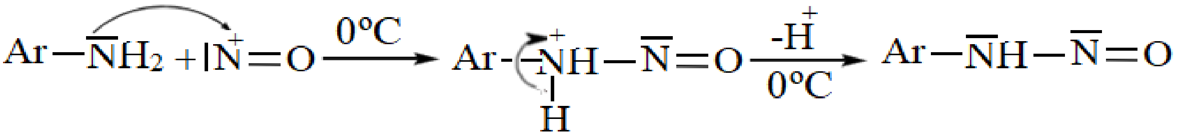
$$3HNO_2 \longleftrightarrow NO^-_3 + 2NO\uparrow + H_3O^+$$

To prepare it, we use a strong acid HCl or H_2SO_4 and a $NaNO_2$ nitrite (sodium nitrite) in aqueous solution at 0°C because the acidic environment promotes protonation and the appearance of the electrophilic NO^+.

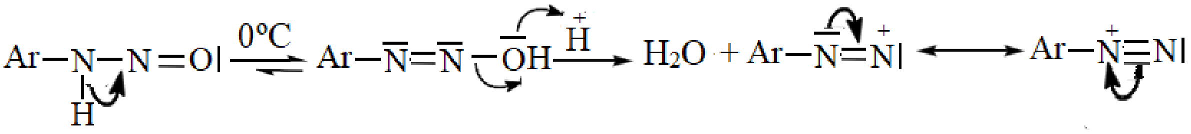
$$HCl + NaNO_2 \xrightarrow{0°C} NaCl + HNO_2$$



In aromatic amines (easy diazotation according to their basicity), the nitrosyl ion reacts at the nucleophilic amine site of the substrate and not on the aromatic ring, because the latter requires the presence of a strong electrophile, which is not the case with NO^+, a weak electrophile that does not react practically on Ar-H**.** The attack leads to N-nitrosoaniline:

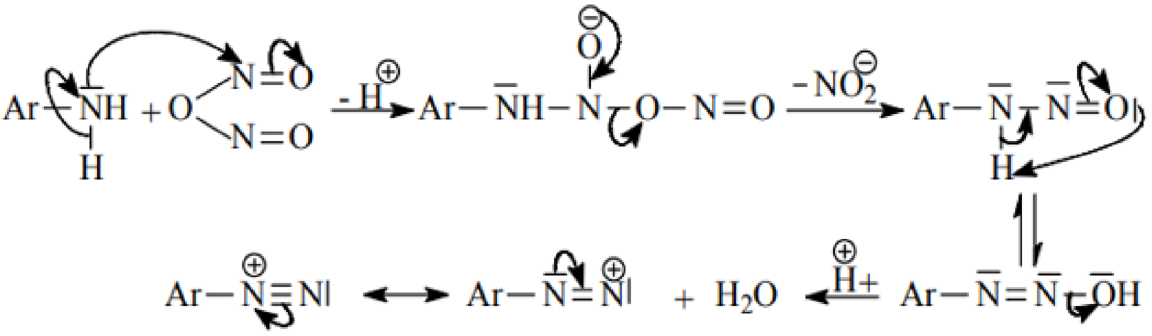


Tautomerism then occurs by acid-base internal rearrangement:

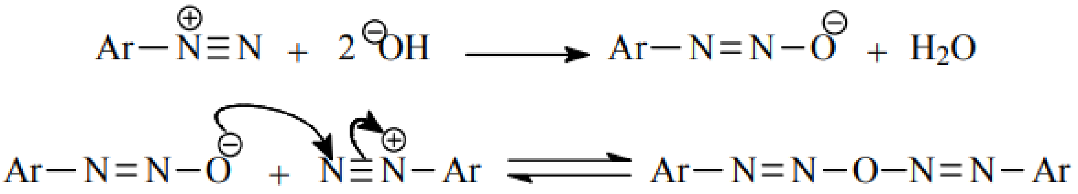


In a low-acid environment, the true nitroso agent N_2O_3 (in the form of anhydride) depending on the reaction:

$$HNO_2 \rightleftharpoons ON-ONO+H_2O$$



In alkaline solution, diazonium ions are converted into diazoate anions, which are in equilibrium with diazooxides:



There are other good methods of diazotation that can also be applied to amino sulfonic compounds, aminophenols, also certain aromatic compounds other than amines primary by the action of nitrous acid in a sulphuric medium in the presence of salts mercurics as a catalyst (16)(17).

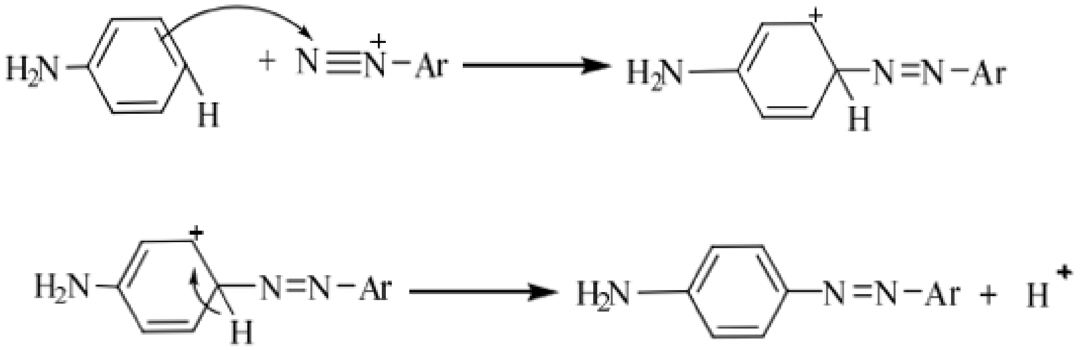
II.2.3.2. Copulation reactions: Azo coupling reaction is an electrophilic substitution reaction of the diazonium cation which is a weak electrophile reagent with a coupling component either with a phenol or with an aromatic amine, a colored compound is obtained: an azo phenol or an azo amine (18)(19).

II.2.3.2.1. Copulation with phenol:

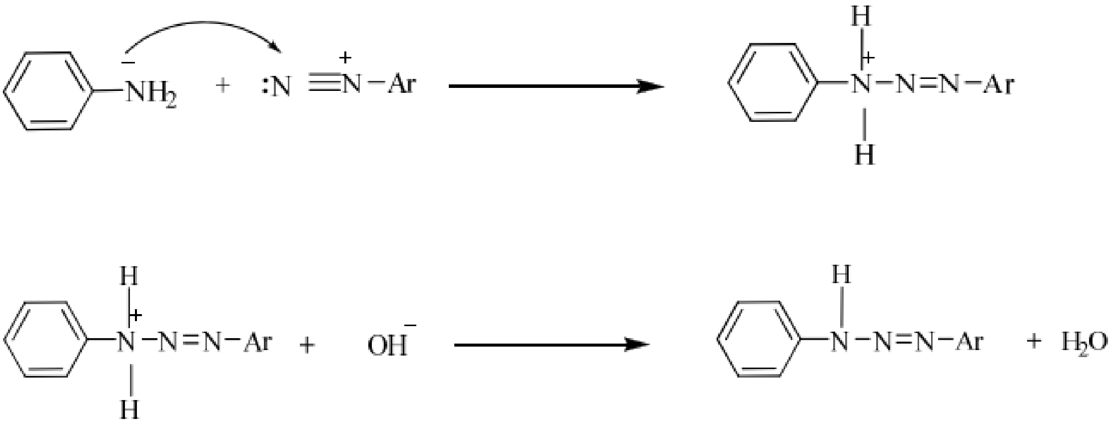
In a basic medium, it is the phenoxy ion that reacts with the diazonium ion.

II.2.3.2.2. Copulation with amines:

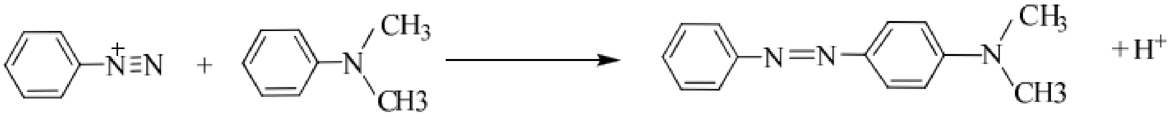
Primary and secondary amines with an excess of amine and in an acidic environment:



Primary and secondary amines in an alkaline or weak acid medium (ethanoic acid), leads to a triazine:



Tertiary amine in an acidic medium:



There are other methods for the synthesis of azoic (20) for example: Reduction of nitro aromatic derivatives in an alkaline medium, reduction of nitrosated compounds by $AlLiH_4$ and condensation of hydrazines and quinones.

II.2.4.application of azo compounds:

Azoic compounds are used in different domains. They are used as dyes for example Sudan Red B is an azo dye used to color textiles, plastics, and food. It has also been used as a dye in lipsticks and other cosmetic products. Chromium yellow is an azo pigment used in paints, inks, and plastics. It is also used as a food coloring agent. Another interesting domain which uses azo compound is medicine, some azo compounds are used as medicines for example, sulfasalazine is a drug used to treat ulcerative colitis and rheumatoid arthritis. Azo compounds have their vital role in medical field for example azo resveratrol and oxyresveratrol exhibited high tyrosine's inhibiting activity, useful for cancer treatment (21). also used in manufacture of rubber, plastics and explosives (22), photoelectronic (23), light and weather fastness and other.

II.2.5. Toxicity of azo compounds:

The toxicity of azo acids is increased by the presence of substituents on the aromatic ring, in particular nitro (-NO2) and halogen (particularly Cl) groups. According to the EPA (24). Some azo compounds are highly toxic, which can be carcinogenic, mutagenic or interfere with the reproductive system. Others pose little or no risk. Inhalation, ingestion and dermal contact are the main routes of exposure to azo compounds. Some azo compounds can disrupt the hormonal system and affect fertility or fetal development. (25).

II.3. Olefinic compounds:

II.3.1. Definition:

Olefinic compounds, also called ethylene carbides, are organic molecules characterized by the presence of a carbon-carbon double bond (C=C) in their chemical structure. This means that two adjacent carbon atoms, in sp2 hybridization, exchange two bonds between them and, in addition, are each only linked to two other atoms (tri-coordination of sp2 carbon atoms. The oldest known olefin is ethylene C_2H_4 discovered in 1669 by Johann Joachim Becher (26) obtained by heating a mixture of ethyl alcohol and concentrated sulphuric acid to 160 0C (27).

Olefins can be classified according to the length of their carbon chain, the type of functional group present and the arrangement of atoms in the molecule(28)(29**):** Linear alkenes are characterized by a linear carbon chain containing at least one carbon-carbon double bond, branched alkenes that have a carbon chain containing one or more branches, dienes are hydrocarbons that contain two carbon-carbon double bonds in their molecular structure. They can be linear or branched, and they can present different geometric configurations of the double bonds, Cyclic alkenes are compounds that have a cyclic structure with one or more carbon-carbon double bonds. These compounds have a double bond inside the ring, which gives them specific properties and reactivities and functionalized alkenes that contain functional groups other than carbon and hydrogen atoms.

Examples:

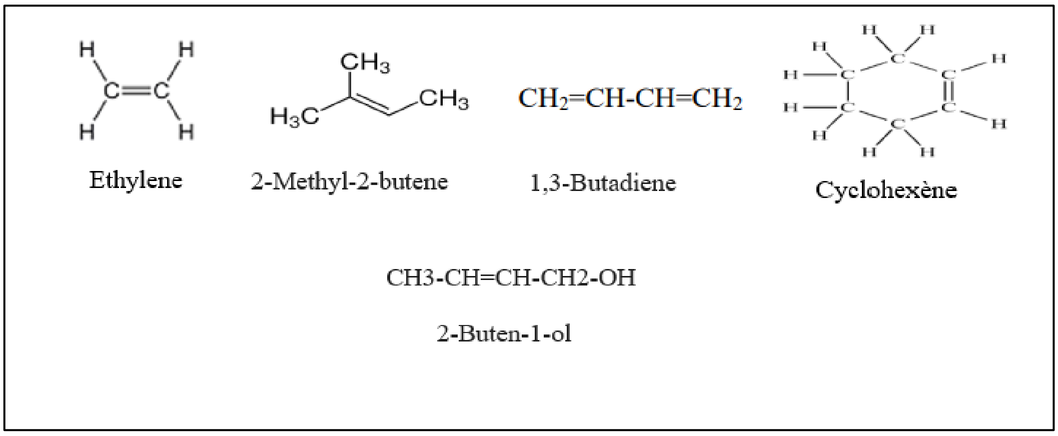


Figure II.6: Some olefins structure.

II.3.2. Properties of olefinic compounds:

Olefins are less dense than water and float on it. They are nonpolar and do not dissolve in water. They are soluble in nonpolar organic solvents such as hexane, pentane, and ether**.** The presence of the double bond in the molecule of olefin gives it various possibilities for chemical reactions in the synthesis of a wide range of chemical products and intermediates. They can undergo various chemical reactions such as: addition reaction, oxidation and polymerization.

Addition reaction: reactions where a molecule adds across the double bond of an alkene. This process often results in a new molecule with a single bond between the two previously doubly bonded carbon. There are different types of addition reactions depending on the adding molecule for example: Hydrogenation, Halogenation, Hydrohalogenation ...

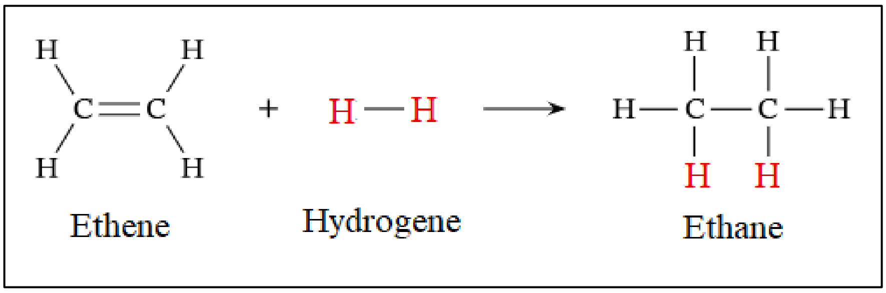


Figure II.7: Hydrogenation reaction.

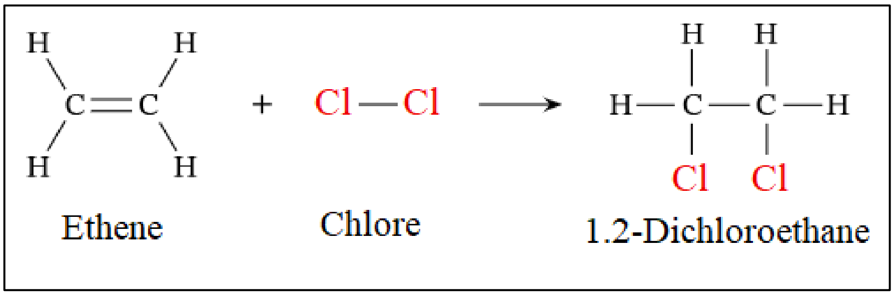


Figure II.8: Halogenation reaction.

Oxidation reaction: Olefins can be oxidized by strong oxidizing agents like potassium permanganate ($KMnO_4$) to form diols, aldehydes, or ketones.

The following chemical equation shows how ethene molecules can react with a cold, dilute, acidic solution of potassium permanganate; However, this reaction is also possible under acidic conditions. The symbol [O] is used to represent the oxygen atoms provided by permanganate ions. This equation is a simplification of a more complicated reaction scheme that is beyond the scope of this explainer.

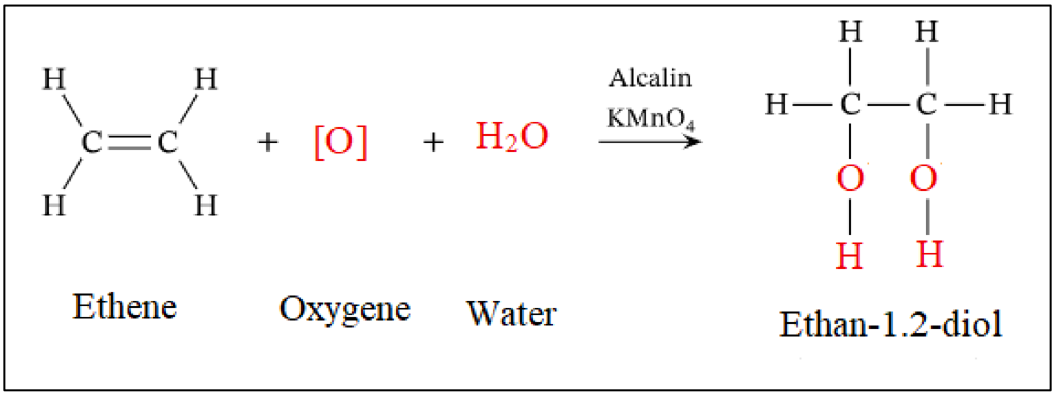


Figure II.9: Oxidation reaction.

Polymerization reaction: Olefins can undergo a polymerization reaction to form polymers, which are large molecules made up of multiple repeating monomer units:

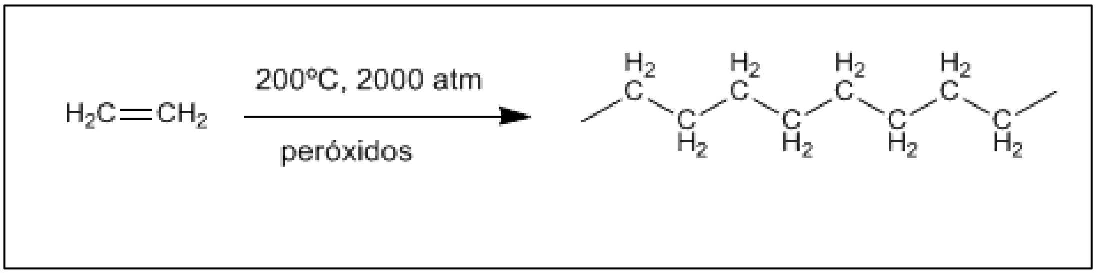


Figure II.10: Radical polymerization (30).

Another type of polymerization occurs with the formation of carbocations, it is called cationic polymerization which has 3 steps (30).

II.3.3. Olefin manufacturing processes:

There are several processes for obtaining olefins, among the most common we have:

II.3.3.1. Dehydrogenation: Dehydrogenation is a process that converts paraffins (saturated chain hydrocarbons) into olefins by removing hydrogen. The reaction is generally carried out at high temperature (around 500°C) in the presence of a catalyst. Dehydrogenation is used to produce a variety of olefins, including ethylene, propylene, and butylene. These olefins are used as feedstocks for a variety of chemicals and plastics.

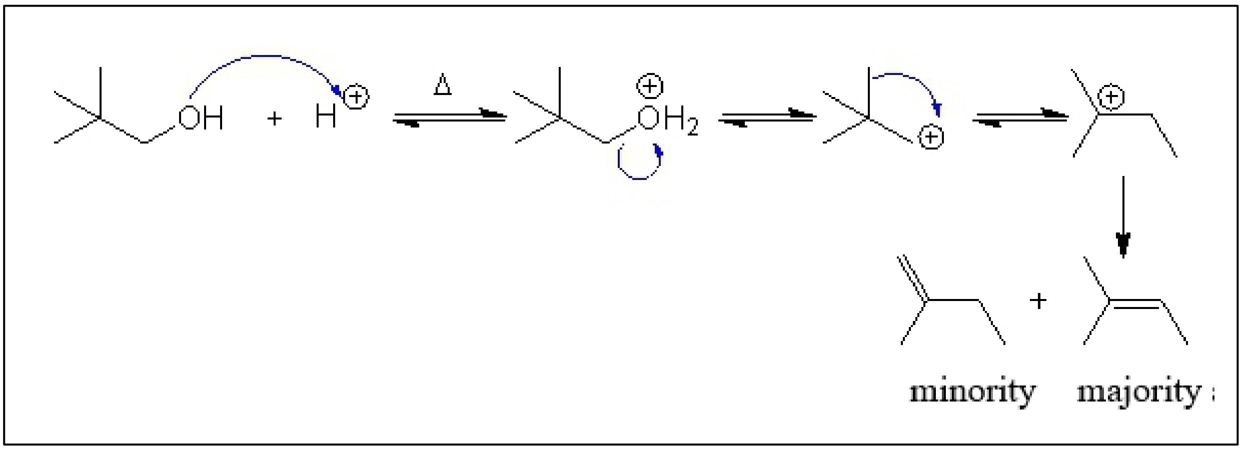


Figure II.11: Dehydrogenation reaction (31).

II.3.3.2. Cracking methods: cracking refers to the process of breaking down large, complex molecules into smaller, simpler ones. This is especially important in the petroleum industry, where cracking is used to convert heavy crude oil into more usable products.

Steam cracking: Steam cracking is a chemical process used to produce olefins on a large scale. It was first developed in the 1990s 1910 by Friedrich Bergius and Hans Goldschmidt. The process uses steam and catalysts to break down hydrocarbon molecules into lighter chemicals, such as ethylene and propylene. The working principle of steam cracking is based on breaking the bonds between carbon atoms (C) and the hydrogen atoms (H) inside the hydrocarbon molecules. This thermal process is carried out at high temperatures in the absence of oxygen, which favors the formation of molecules unsaturated (32).

Catalytic cracking: Catalytic cracking is a chemical process used in the petrochemical industry to Convert heavy hydrocarbons into lighter, more valuable petroleum products. It involves the use of a catalyst that accelerates the reaction of cracking, i.e. the breaking of chemical bonds within hydrocarbon molecules. Under the action of the catalyst, the hydrocarbons break down into smaller fragments, mainly by breaking the C-C and C-H bonds. This leads to the formation of products lighter petroleum products, such as alkanes, olefins, and aromatic compounds. Catalyst also promotes side reactions, such as the reduction of sulphur compounds and the Rearrangement of products. (33)

II.3.4. Applications:

Olefins are used in a variety of fields such as Cosmetics and personal care products, Pharmaceuticals, including basic chemicals used in drug synthesis. Olefins are used in the production of products agrochemicals such as herbicides, insecticides and fertilizers and above all are the main raw material of the petrochemical industry. They are used to produce a wide variety of chemicals such as plastics, synthetic fibres, rubbers.

II.3.5. Toxicity of olefins:

Olefins have varying toxicity depending on the type of olefin and the duration of exposure. Most single olefins have an irritating effect on the eyes, respiratory tract and skin. Exposure can cause redness, watery eyes, throat irritation, coughing and skin irritation, also at high concentrations and with prolonged exposure, some olefins can affect the central nervous system, causing headaches, dizziness, drowsiness, and loss of coordination. Some olefins, especially butadiene, are suspected of being carcinogenic. Long-term exposure can increase the risk of certain cancers (34)(35).

II.4. Schiff- bases compounds:

II.4.1. Definition:

Schiff bases, named by Hugo Schiff in 1864 (36) are a type of organic compounds containing a functional group with a carbon-nitrogen double bond (C=N). In contrast to a regular imine, the nitrogen atom in a Schiff base is connected to an aryl or alkyl group, rather than a hydrogen atom, so they are organic compounds with imine or imide functions secondary. Schiff bases have a well-defined chemical structure that promotes their use as ligands in complex chemistry. These ligands are components of containing the imine function:

(-C=N-) (37).

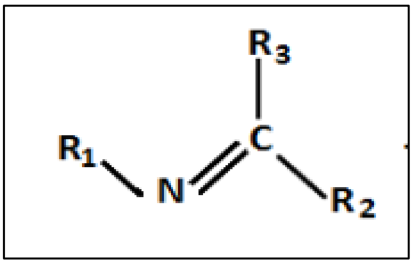


Figure II.12: General structure of Schiff bases.

Schiff bases have a general formula: $R_1R_2C=NR_3$, where R is an organic chain. In this definition, Schiff base is synonymous with azomethin. Some restrict the definition to secondary aldimines (azomethines where carbon is bound only to a single hydrogen), and therefore have the general formula RCH=NR'. The carbon chain on the nitrogen atom makes the Schiff bases a stable imine. Schiff bases derived from aniline, where R_3 is therefore a phenyl, or substituted phenyls are called aniles (38).

II.4.2. Synthesis of Schiff bases:

Schiff bases are formed by the condensation of a primary amine with an aldehyde or ketone accompanied by the elimination of a water molecule. The reaction is reversible because of the presence of water molecules (hydrolysis), and the equilibrium constant determines the yield of the Schiff base. This reaction is usually carried out in an alcoholic or sometimes reflux environment (39) (40).

Figure II.13: Synthesis of a Schiff basis (39).

The primary amine acts as a nucleophile due to the lone electron pair on the nitrogen atom, which attacks the carbonyl carbon (C=O) of the aldehyde or ketone, forming a carbon-nitrogen bond (C-N) and an intermediate alcoholate. The intermediate alcoholate loses a proton (H^+) to the reaction medium (acid-catalyzed) and a water molecule (H_2O) is removed. This forms the carbon-nitrogen double bond (C=N) characteristic of a Schiff base.

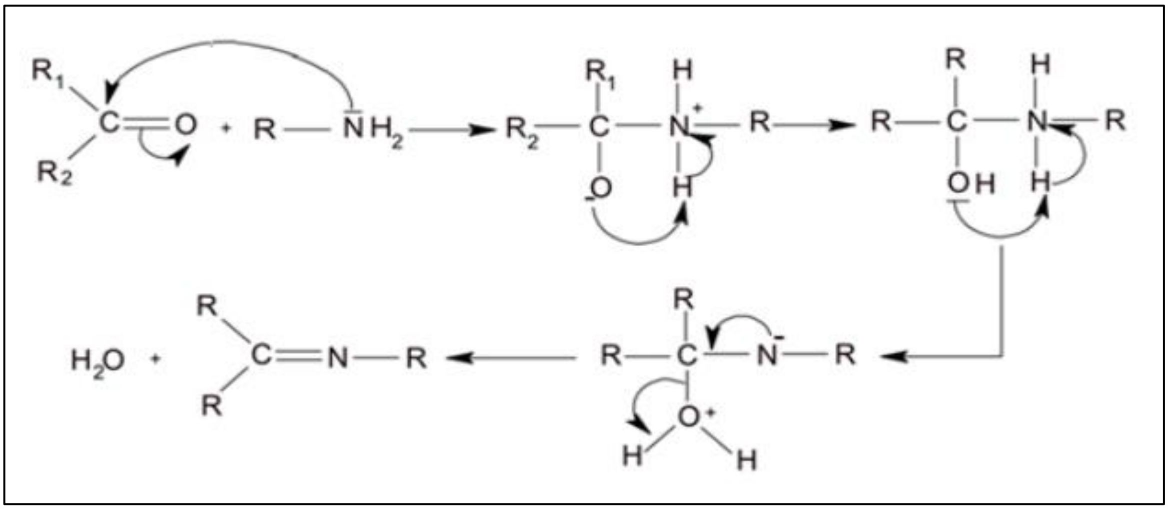


Figure II.14: Reaction mechanism of Schiff base formation (41).

II.4.3. Classification of Schiff bases:

a. Aldimine: An imine in which the carbon atom bonded to the nitrogen atom bears an alkyl group and a hydrogen atom. When the nitrogen atom is bonded to a hydrogen atom or a hydrocarbon group, it is called a "primary aldimine" or "secondary aldimine", respectively. (42)

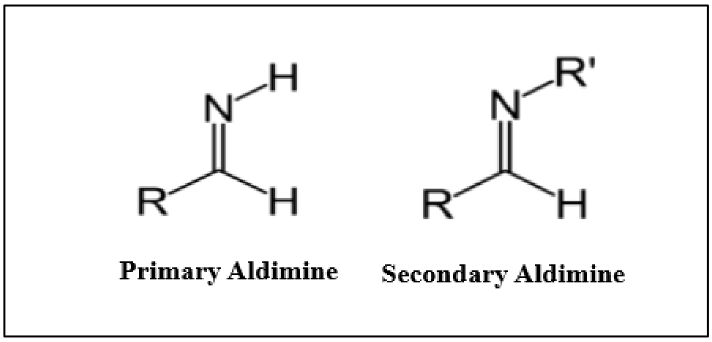


Figure II.15: Structure of aldimine.

b. Ketimine: An imine in which the carbon atom bonded to the nitrogen atom is attached to two alkyl groups is called a "ketimine". Similarly, depending on the nature of the substituent on N, it will be called a "primary ketimine" or "secondary ketimine". (42)

II.4.4. Properties and applications:

The vibration frequencies of the azomethin group of the Schiff base ligands range from 1603 to 1680 cm^{-1} depending on the nature of the different substitutions on the carbon and nitrogen atoms. This property makes infrared spectroscopy a technique of choice for the identification of this group. They have a great interest in the field of chemistry, especially coordination chemistry (43), also in analysis and catalysis (44). Schiff bases are also used in medicine and the business industry biological agents such as antibacterial and antifungal agents and in the field of new electronics due to their wide magnetic properties (45).

II.4.5. Toxicity:

Many Schiff bases are not inherently toxic. In fact, some are even used in medications or dyes, but the toxicity of Schiff bases varies widely depending on their specific structure such us the presence of certain functional groups like Schiff bases with nitro groups (NO_2) tend to be more toxic by Nitro increasing toxicity through various mechanisms, such as disrupting cellular processes or generating reactive oxygen species that damage cells.

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Third chapter

Theory and result’s interpretations

III.1. Introduction:

The twentieth century was marked by a major discovery: light does not only behave like a wave, as was previously thought, but it can also behave like a particle. This wave-particle duality, evidenced by numerous experiments, has revolutionized our understanding of the nature of light and paved the way for new fundamental research**.** This led Broglie (1) to propose that this duality should be generalized to all known particles. Broglie's hypothesis was brilliantly confirmed by later experiments, demonstrating that electrons, indeed, produced interference fringes. This discovery validated the wave-particle duality and opened a new perspective in quantum physics. Broglie used the relationship between the energy and momentum of a photon to derive a relationship between the energy **E**, momentum of the particle **p**, frequency **ν**, wavelength **λ** of a particle, and Planck's constant (6.626 x 10^-34 J s) **h**, this relationship is known as the de Broglie wavelength:

$$\begin{cases} E = h\nu \\ p = h/\lambda \end{cases}$$

In 1925, Erwin Schrödinger (2) brought Louis de Broglie's ideas to life by formulating the Schrödinger equation. This revolutionary equation is based on the principle of wave-particle duality to describe the behavior of matter at the quantum scale. At the heart of this theory is the wave function, a mathematical entity that encapsulates the complete state of a quantum system, including the position and momentum of its particles. Calculating the wave function of an N-electron quantum system is a major challenge in quantum chemistry and materials physics. This can be obtained from the Schrödinger equation but, in practice, it is impossible to solve the exact Schrödinger equation for an N-electron system because each electron is influenced by the motion of all the others. This makes the equation extremely complex, with 10^{23} simultaneous differential equations to solve. So, the use of approximations is verry necessary (3).

The Molecular modeling is a technique that allows to represent the properties and chemical reactions, to manipulate the models of structures in two or three dimensions, determine the graphical representation of the geometry or configuration of the atoms of a molecule and evaluate the physicochemical properties of the molecule. Molecular modelling relies on sophisticated theoretical computational methods, such as (Molecular Dynamics, Ab-initio quantum mechanics...).

Molecular Modeling Methods can be classified into three categories (4):

- Molecular dynamics (MD).
- Molecular mechanics (MM).
- Quantum methods (QM).

This last category is our interesting in this chapter, we will be exhibiting the different levels of approximations required to solve the Schrödinger equation. Then discussing some methods of calculation: Density functional theory (DFT) and AM1 (Austin Model 1) method.

III.2. Structural study by quantum chemistry calculations:

The structural study through quantum chemistry calculations is a field of research that uses quantum chemistry methods to predict and understand the structure of molecules. This field of chemistry defines molecular structure as a nucleus around which gravitate electrons, which are described by their probability of presence at a point and represented by orbitals (5). Quantum chemistry methods are based on the Schrödinger equation.

III.2.1. The Schrödinger equation:

Quantum chemistry methods are based on the Schrödinger equation which is written for steady state (6):

$$\hat{H}\Psi = E\,\Psi \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; \text{(III.1)}$$

Where**:**

$\hat{H}$**:** The Hamiltonian operator, which describes the total energy of the quantum system.

Ψ : Wave function of the molecule.

E : Total System Energy.

In a molecule with N nuclei and n electrons, the total Hamiltonian, represented by Ĥ, encapsulates its complete energy picture. This equation comprises five key terms, it is simplified into the form (7):

$$\hat{\mathbf{H}} = \hat{\mathbf{T}}_{\mathbf{N}}(\mathbf{R}) + \hat{\mathbf{T}}_{\mathbf{e}}(\mathbf{r}) + \hat{\mathbf{V}}_{\mathbf{NN}}(\mathbf{R}) + \hat{\mathbf{V}}_{\mathbf{Ne}}(\mathbf{R},\mathbf{r}) + \hat{\mathbf{V}}_{\mathbf{ee}}(\mathbf{r}) \dots\dots\dots.(\mathbf{III}.2)$$

Where:

$\hat{\mathbf{T}}_{\mathbf{N}}(\mathbf{R}) = -\sum_{\mathbf{k}} \frac{1}{2\mathbf{M}_{\mathbf{K}}} \nabla_{\mathbf{k}}^{2}$ the kinetic energy of the nuclei.

$\hat{\mathbf{T}}_{\mathbf{e}}(\mathbf{r}) = \sum_{\mathbf{i}} \frac{1}{2} \nabla_{\mathbf{i}}^{2}$ the kinetic energy of the electrons.

$\hat{\mathbf{V}}_{\mathbf{NN}}(\mathbf{R}) = \sum_{\mathbf{k}} \sum_{\mathbf{l}>\mathbf{k}} \frac{\mathbf{Z}_{\mathbf{k}}\mathbf{Z}_{\mathbf{l}}}{\mathbf{R}_{\mathbf{ij}}}$ the potential energy of interaction between the nuclei.

$\hat{\mathbf{V}}_{\mathbf{ee}}(\mathbf{r}) = \sum_{\mathbf{j}} \sum_{\mathbf{i}>\mathbf{j}} \frac{1}{\mathbf{R}_{\mathbf{kl}}}$ the potential energy of repulsion between the electrons.

$\hat{\mathbf{V}}_{\mathbf{Ne}}(\mathbf{R},\mathbf{r}) = \sum_{\mathbf{i}} \sum_{\mathbf{k}} \frac{\mathbf{Z}_{\mathbf{k}}}{\mathbf{d}_{\mathbf{ik}}}$ the potential energy of attraction between Nuclei-electron.

The solution of Schrödinger's equation, based on Hamiltonian is possible for the hydrogen atom and single electron systems but, its complexity increases considerably when it comes to polyatomic molecules, i.e. molecules composed of several atoms. So, approximations must therefore be introduced to solve the equation.

III.2.2. Calculation Methods:

III.2.2.1. Ab initio method:

1.The Mono-Determinantal Approximation:

The Born-Oppenheimer approximation:

To be able to work on solving the Schrödinger equation Born-Oppenheimer (Max Born (1882-1970) and Robert Oppenheimer (1904-1967) consider the probability of separating the motion of nuclei from that of electrons which is the base of the Born-Oppenheimer approximation (8). Assume that nuclei are very heavy and therefore slower than electrons, which mean that electrons can move through solid much faster than nuclei. So, the motion of nuclei is negligible, their kinetic energy is zero and the potential energy of interaction between the nuclei becomes constant. the Born-Oppenheimer approximation is based on the adiabatic approximation known as the "adiabatic BO approximation"(9). The electronic Hamiltonian can thus be defined as:

$$\mathbf{H_e = T_e + T_{(n-e)} + V_{(e-e)} \dots . (III.3)}$$

So, The Schrödinger equation be:

$$\mathbf{H_e\,\Psi_e = E_e\,\Psi_e \dots\dots (III\,.4)}$$

Where: Ψe is Electron Wave Function.

And: $\mathbf{E_{total} = E_e + E_{nucl}}$

Orbital approximation:

The central idea of the orbital approximation is to neglect, or at least not to deal explicitly, with the term electronic interaction. In other words, electrons are considered to evolve independently of each other, as if they were under the influence of a field created by nuclei and other electrons. It is a way of allowing a numerical solution of the many-body problem by a field-type approximation Medium (10).

If 2n is the number of electrons,Ψ is a function to (2n) ×3 variables that are commonly noted Ψ (1, 2... 2n). The orbital approximation introduced by Hartree in 1928(9) consists of decoupling the 2n electrons by developing the function Ψ(1, 2...,2n) in a product of 2n monoelectronic functions.

2. Hartree-Fock Method:

The Hartree-Fock method is the simplest ab initio calculation method, in which the electron-electron Coulomb repulsion is not specifically considered. Hartree proposed a method for calculating approximate polyelectronic wavefunctions by writing them as products of single electron wavefunctions (11):

$$\Psi_{\text{approximate}} = \Psi_1(r1) \times \Psi_2(r2) \times \ldots \Psi_N(rN) \text{ ……….. (III.5)}$$

This equation is based on the free electron hypothesis, which means that the Interactions between electrons are not considered.

The Hartree-Fock Method allows an approximate solution for Schrödinger's equation of a quantum system with n electrons and N nuclei where the approximate polyelectronic wavefunctions is written as a Slater determinant (12).

III.2.2.2. Semi-empirical methods:

The Semi-empirical methods are computational techniques used in quantum chemistry to study the properties of molecules. They combine principles of quantum mechanics (part of the calculations necessary for Hartree-Fock calculations) with experimental data in order to simplify the calculations and make them accessible for medium-sized molecular systems. The Semi Methods empirical (13) consider only valence electrons.

CNDO/2 method:

Complete Neglecting of Differential Overlap/Version 2 is a method proposed by Pople Santry and Segal in 1965-1966. (14), only valence electrons are treated explicitly. This method based on Value approximation and ZDO (Zero-differential Overlap)

INDO Method:

INDO stands for Intermediate Neglect of Differential Overlap, this method allows to distinguish between singlet and triple states of a system by preserving the integral exchanges. It is an improved version of the simpler CNDO/2(14).

NDDO method:

NDDO stands Neglect of Diatomic Differential Overlap, proposed by Pople in 1965(14), the principle of this method is that all bi-centered bi-electronic integrals are retained.

MINDO/3 method:

Modified INDO, version 3 method developed by Michael Dewar and collaborators (15). It is based on the Intermediate Neglect of Differential Overlap (INDO) method and is an improved version of it. It is set to reproduce experimental data and uses a Davidon-Fletcher algorithm.

AM1 Method:

Austin Model 1 is a method developed by Michael Dewar and co-workers in 1985(16), it is based on the MNDO method and aims to improve its accuracy. This method is adjusted on experimental data to improve the accuracy of the results. This includes data on molecular geometries, binding energies, enthalpies of formation, and electron spectra. AM1 offers better accuracy then MNDO and INDO methods (16).

PM3 method:

PM3 stands for parametric method. It is method developed by J. J. P. Stewart in 1989(17), It is based on the AM1 (Austin Model 1) method and aims to improve its accuracy for systems with heavy elements.

III.2.2.3. The density functional theory (DFT):

The DFT is a theory that uses electron density **ρ(r)** which is the probability of the presence of an electron in a volume (**ρ(r)** is a positive function depending only on the three coordinates (x, y, z)) (18). While identifying the different contributions to the Hamiltonian, we have defined electrons as being indistinguishable and indiscernible particles. Indeed, an electron cannot be localized as an individual particle, on the other hand its probability of presence in a volume element can be estimated and corresponds to the electron density **ρ(r)**. Electrons must therefore be considered in their collective aspect (electron cloud), where electron density allows us to know the regions of space where electrons reside the most. more often. These electrons are in the vicinity of nuclei (18,19).

III.3. Molecular geometry:

The following figure represents the molecules we want to study, where these molecules have a push-pull structure by the presence of a donor group which is in our case the dimethylamine group, and an acceptor group which is the nitro group. These two groups are fixed on the extremities of a conjugated system that contain two aromatic cycles connected by the bridge (X=Y):

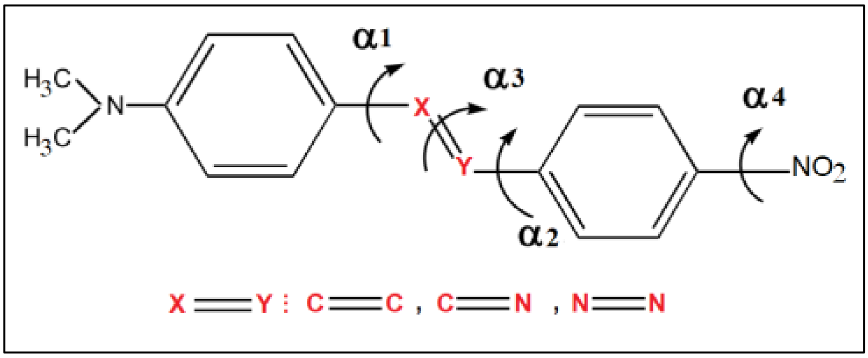

Figure III.1: The geometry of the molecule to be studied.

The following materials have been chosen as examples for the study of the bridge's effects in nonlinear optics. Where each material presents a different bridge (the three cases we've seen):

a. N, N-dimethyl-4-[(4-nitrophenyl) diazenyl] aniline:

Also called 4-N, N-Dimethylamino-4'-nitroazobenzene, an organic molecule belonging to the class of aromatic azo compounds with the molecular Formula $C_{14}H_{14}N_4O_2$ and a molecular weight of 270.29 g/mol.

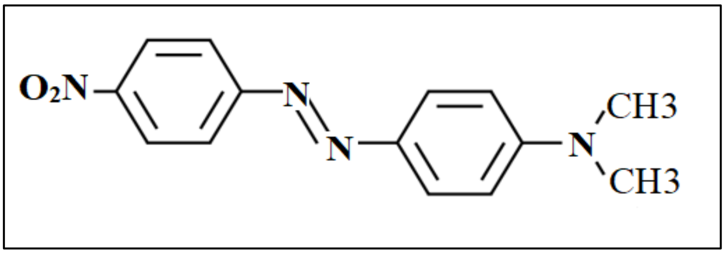

Figure III.2: Push-Pull compound with N=N bridge.

b. N, N-Dimethyl-4-(4-nitrostyryl) aniline:

The 4-Dimethylamino-4'-nitrostilbene(C16H16N2O2) is an organic compound consists of a nitro group, a styryl group and an aniline group, with a molecular weight approximately 268.31 g/mol.

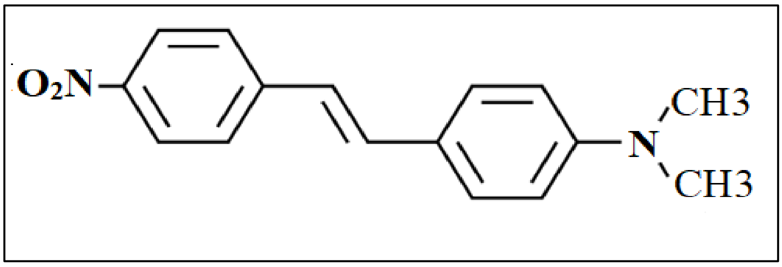

Figure III.3: Push-Pull compound with C=C bridge.

c. N, N-Dimethyl-N'-(4-nitrobenzylidene)-1.4-benzenediamine:

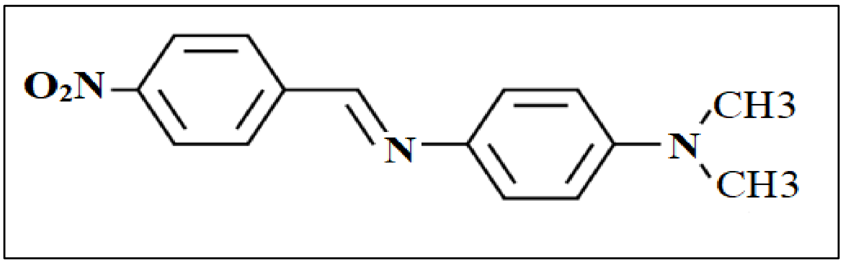

Figure III.4: Push-Pull compound with C=N bridge.

III.3.1 Geometry optimization:

Our geometry optimization tests on the three structures led to the results listed in the following table. All three structures perfectly confirmed the planarity due to the presence of sp2 hybridization provided by the benzene ring and the double bond existing in the bridge connecting the two aromatic rings. The proposed model includes two orthogonal sp2 planes that are not parallel. This is justified by the very different values of the torsion angles α1, α2 and α3 in table 1.

This proposed structure gives the material a very asymmetric structure, ensuring perfect polarization, which makes their dipole moment efficiency very high. Therefore, the intramolecular charge transfer (ICT) in the proposed system is ensured by the presence of a long carbon chain and by the double π-bond that is repeated on this carbon chain by the intra-cycle sp2 hybridization and the extra-cycle sp2 hybridization located in the different bridges C=C, N=N and C=N.

The power of this charge transfer is supported by the existence of both donor and acceptor groups. The electrons are well-oriented in the direction of the acceptor group under the influence of the pushing force of the donor group and the attractive force of the acceptor group.

Table 12: The torsion angles of the three cases.

		α1	α2	α3	α4
C=C	**AM1**	-6,58	-36,78	168,24	1,49
	DFT	-8,23	-14,28	162,28	2,87
C=N	**AM1**	-5,81	-5,11	182,08	25,48
	DFT	-1,66	1,23	-168,59	8,61
N=N	**AM1**	-8,77	-28,45	168,97	-0,79
	DFT	-2,21	-1,82	169,88	-1,61

III.4. Calculation methods:

The three molecules previously selected which are a D– π –A conjugated chromophores are optimizing by using two methods based on optimized structures: AM1and DFT methods of the MOPAC package which is a versatile computational chemistry software that offers various methods for calculating nonlinear optical (NLO) properties (20). In principle (21,22), these methods involve diagonalizing a molecular Hamiltonian (Hartree-Fock) that incorporates a static electric field perturbation. This diagonalization is performed within a wave function space constructed from Slater-type atomic orbitals. The first static hyperpolarizability is denoted as **β** (0; 0, 0) and the second-harmonic generation (**SHG**), it is denoted as **β** (−2ω; ω, ω).

The values of frequency dependent first average hyperpolarizability were obtained by calculations of **β** (−2ω; ω, ω) for energies of 0.0001to 1.2 eV by using the AM1 and DFT. The polarizabilities and hyperpolarizabilities of increasing order are obtained by the iterative diagonalization procedure, and by differentiation of **μ(F)** with respect to **F**, as allowed by the Hellman-Feynman theorem (23,24).

$$\boldsymbol{\alpha}_{\mathbf{ij}} = \frac{\partial \boldsymbol{\mu}_{\mathbf{i}}}{\partial \mathbf{F}_{\mathbf{j}}}\bigg| \mathbf{F} = 0 \qquad \boldsymbol{\beta}_{\mathbf{ijk}} = \frac{\partial^2 \boldsymbol{\mu}_{\mathbf{i}}}{\partial \mathbf{F}_{\mathbf{j}} \partial \mathbf{F}_{\mathbf{k}}}\bigg| \mathbf{F} = 0$$

The conversion factors for **α** polarizability, **β** first hyperpolarizability and the highest occupied molecular orbital (HOMO), the Lowest unoccupied molecular orbital (LUMO) energies in atomic and **cgs** units: 1 atomic unit (**a.u**) = $0.1482.10^{-24}$ electrostatic unit (**esu**) for polarizability; 1 a.u. = $8.641.10^{-33}$ esu for first hyperpolarizability, 1 a.u. = 27.2116 eV (electron volt) for HOMO and LUMO energies.

This study employed computational tools to evaluate beta (β) and analyze molecular conformations: The QCPE program by J.J.P. Stewart (Unix version for Data General under X windows) was used to calculate β with both AM1 and DFT parameterizations (25,26), Molecular modeling and conformational analysis were performed using the SPARTAN program (version 5) from Wavefunction (27), California University. Here, MNDO parameters are recommended for obtaining good correlations with polarizability and hyperpolarizability. The values of torsion angles between aromatic rings obtained by PM3 optimization are used for MNDO optimization leads to very large torsion angles between the aromatic rings. Indeed, if these torsion angles are too large for the studied molecules, the structure loses length conjugation and the β diminish (28-30).

III.5. Results and interpretations:

The results of the first hyperpolarizability calculations as a function of the incident ray energy in (eV) of the three selected molecules: N, N-dimethyl-4-[(4-nitrophenyl) diazenyl] aniline, N, N-Dimethyl-4-[(4-nitrophenyl) ethynyl] aniline and N, N-Dimethyl-N’-(4-nitrobenzylidene)-1.4-benzenediamine.

III.5.1. Results of AM1 geometry:

The calculations on the three compounds with the AM1 geometry transferred from Spartan version 5 to Mopac 93 are listed in the following table.

Table 13: AM1 Calculation of hyperpolarizability coefficients β.

Energie en (eV)	**Beta**					
	Au	**10^{-30} esu**	**Au**	**10^{-30} esu**	**Au**	**10^{-30} esu**
0.0001	300	2.592	375	3.240	149	1.287
0.01	302	2.609	377	3.257	151	1.304
0.1	305	2.635	379	3.274	155	1.339
0.2	310	2.678	385	3.326	160	1.382
0.3	318	2.747	390	3.369	164	1.417
0.4	327	2.825	398	3.439	173	1.494
0.5	345	2.981	407	3.516	184	1.589
0.6	364	2.989	415	3.586	200	1.728
0.65	377	3.257	423	3.655	209	1.805
0.7	394	3.404	451	3.897	223	1.926
0.75	410	3.542	473	4.087	237	2.047
0.8	430	3.715	495	4.277	256	2.212
0.85	449	3.879	518	4.476	271	2.341
0.9	478	4.130	536	4.631	298	2.575
0.95	509	4.398	576	4.977	327	2.825
1	530	4.579	598	5.167	365	3.153
1.1	567	4.899	652	5.633	430	3.715
1.2	645	5.573	787	6.800	518	4.476
material	**N=N**		**C=C**		**C=N**	

This table has made it possible to draw the following curves of the three cases C=C, N=N and C=N.

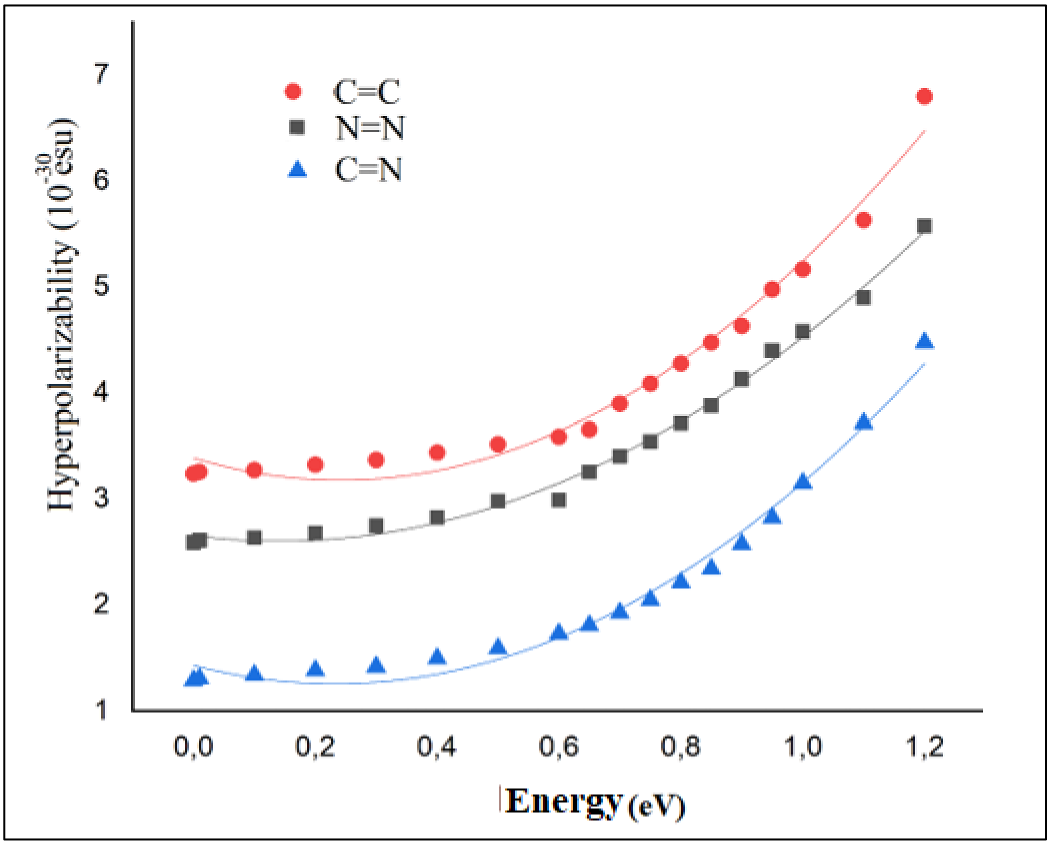

Figure III.5: 1st Order hyperpolarizability: AM1 geometry.

The figure III.6 presents the hyperpolarizabilities values as a function of the applied field during excitation in the three cases discussed earlier using the AM1 method. Upon initial observation, it is noted that the hyperpolarizability values increase with the excitation field strength. This increase starts gradually and becomes more pronounced as the applied energy values become significant, indicating a nonlinear function. This implies that our materials exhibit a favorable response to higher fields. Based on the hyperpolarizability β values presented in this figure we notice that these three molecules exhibit strong nonlinearities. The molecule with the C=C bridge exhibits the most pronounced values for the coefficients β reaching a maximum value of 6.800 x 10^{-30} esu. This is followed by the molecule with the N=N bridge, with a maximum value of 5.573 x 10^{-30} esu. Where the molecule with the C=N bridge has a value of 4.476 x 10^{-30} esu, which is lower compared to the values for the C=C and N=N bridges. So based on these observations and values, it can be concluded that the C=C bridge exhibits stronger nonlinear optical properties compared to the N=N bridge and the C=N bridge where this last is considered as a weak NLO material.

III.5.2. Results of DFT geometry:

The calculations on the three compounds with the DFT geometry transferred from Spartan version 5 to Mopac 93 are listed in the following table.

Table 14: DFT Calculation of hyperpolarizability coefficients β.

Energie en (eV)	**Beta**					
	Au	**10^{-30} esu**	**Au**	**10^{-30} esu**	**Au**	**10^{-30} esu**
0.0001	550	4.752	677	5.849	498	4.303
0.01	563	4.864	687	5.936	510	4.406
0.1	582	5.029	703	6.074	524	4.527
0.2	609	5.262	728	6.290	533	4.605
0.3	641	5.538	761	6.575	572	4.942
0.4	699	6.040	833	7.197	612	5.288
0.5	820	7.085	949	8.200	695	6.005
0.6	965	8.338	995	8.597	769	6.644
0.65	1103	9.531	1245	10.758	935	8.079
0.7	1233	10.654	1467	12.676	1015	8.770
0.75	1418	12.252	1618	13.981	1239	10.706
0.8	1520	13.134	1743	15.061	1390	12.010
0.85	1792	15.484	2105	18.189	1583	13.678
0.9	2045	17.670	2458	21.239	1903	16.443
0.95	2415	20.868	2834	24.488	2198	18.992
1	2765	23.892	3284	28.377	2372	20.496
1.1	3117	26.933	4366	37.726	2621	22.648
1.2	3707	32.032	4942	42.703	3158	27.288
material	**N=N**		**C=C**		**C=N**	

The table has made it possible to draw the following curves of the three cases C=C, N=N and C=N.

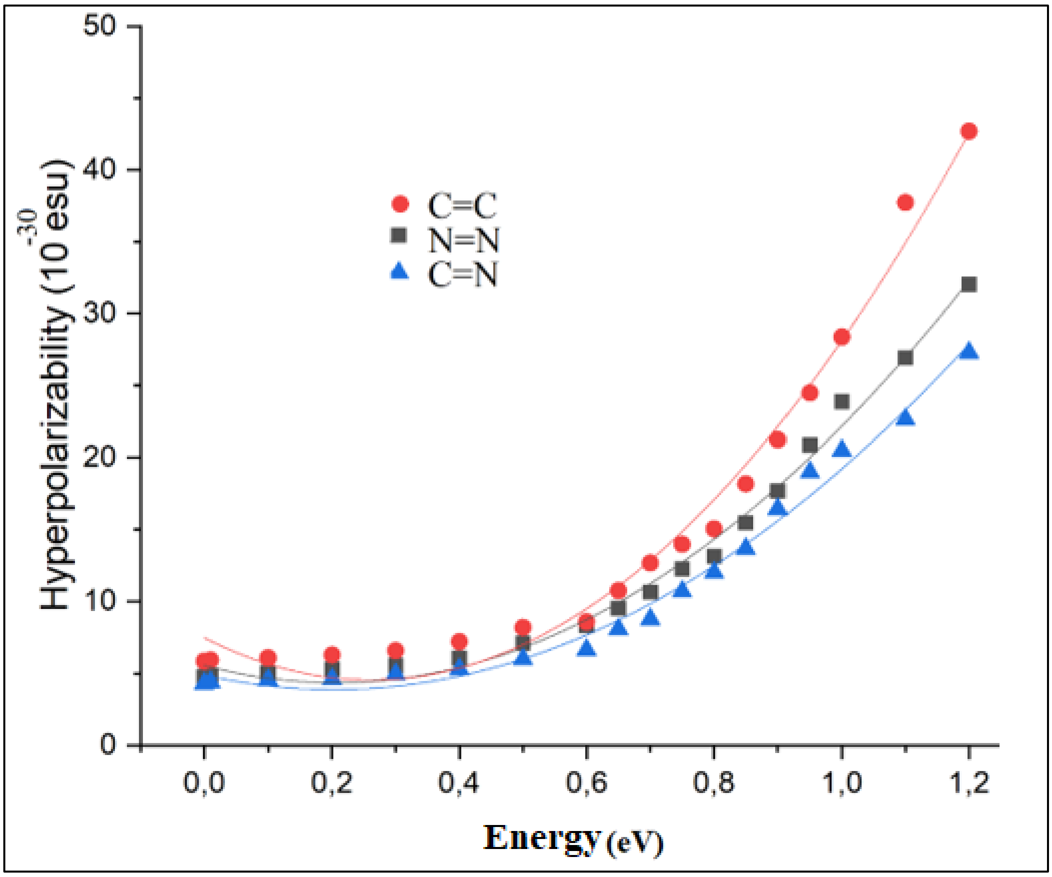

Figure III.6: 1st Order hyperpolarizability: DFT geometry.

The figure III.7 presents the hyperpolarizability values as a function of the applied field during excitation in the three cases discussed earlier using the DFT method. The plots generated by the DFT method show similar trends to those obtained using the AM1 method. The hyperpolarizability values increase with the excitation field strength where it starts gradually and becomes more pronounced as the applied energy values become significant, indicating a nonlinear function. Also, we can notice that the DFT method gives the real role of the bridge only at higher values of incident field but, at a lower values of incident field the three molecules present nearly the same hyperpolarizability ignoring the effects of bridge. We sign that the molecule with the C=C bridge exhibits the most pronounced values for the coefficients β reaching a maximum value of 42.703 x 10^{-30} esu. Followed by the molecule with the N=N bridge, with a maximum value of 32.032 x 10^{-30} esu. Where the molecule with the C=N bridge has a value of 27.288 x 10^{-30} esu, which is lower compared to the values for the C=C and N=N bridges.

So Based on these observations and values, we confirm that the C=C bridge are stronger nonlinear optical properties compared to the N=N bridge and the C=N bridge where this last is considered as a weak NLO material.

III.5.3. Comparison between the AM1 and DFT methods:

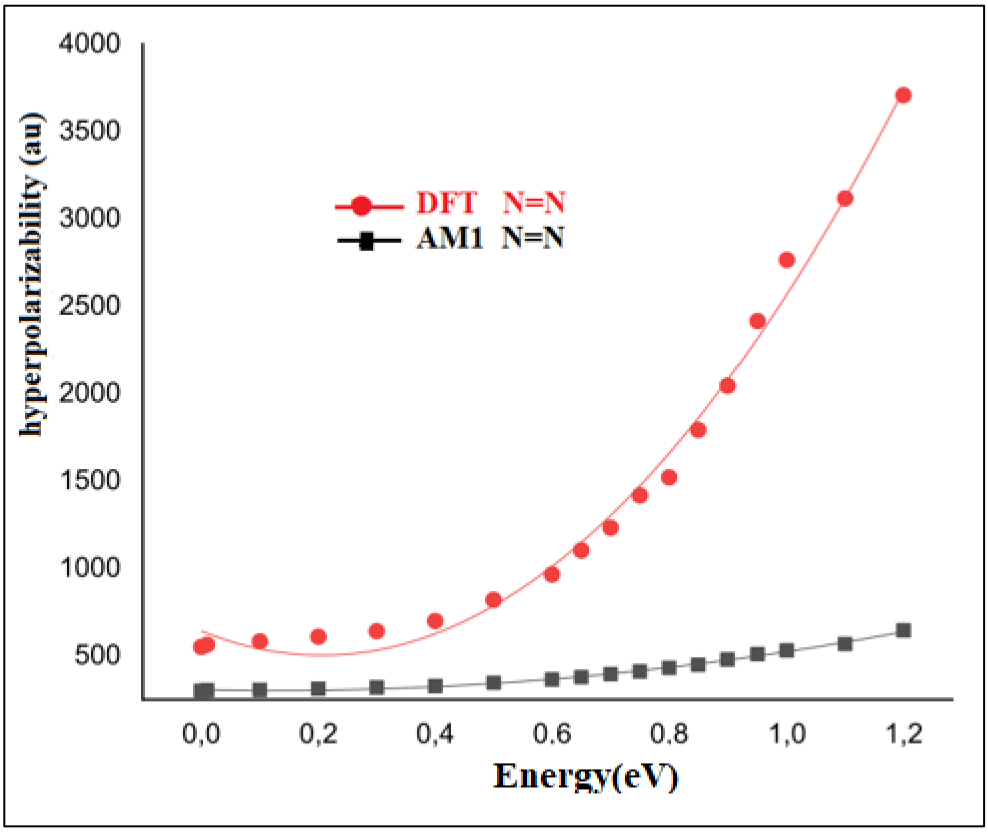

Figure III.7: N=N bridge comparison.

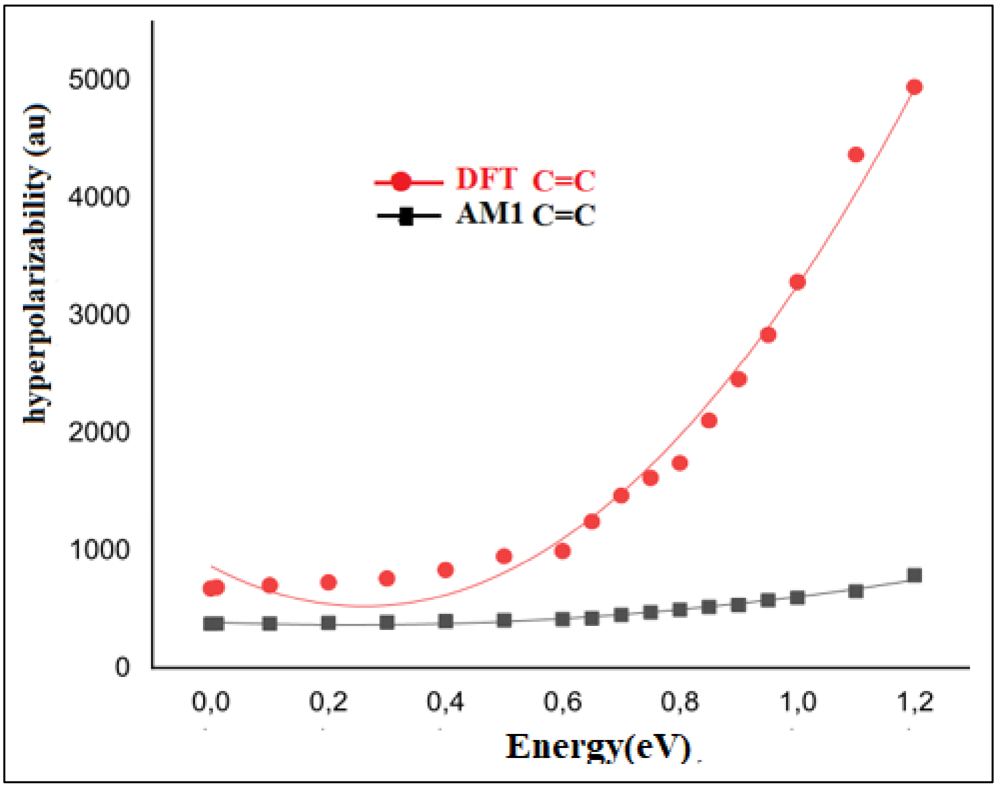

Figure III.8: C=C bridge comparison.

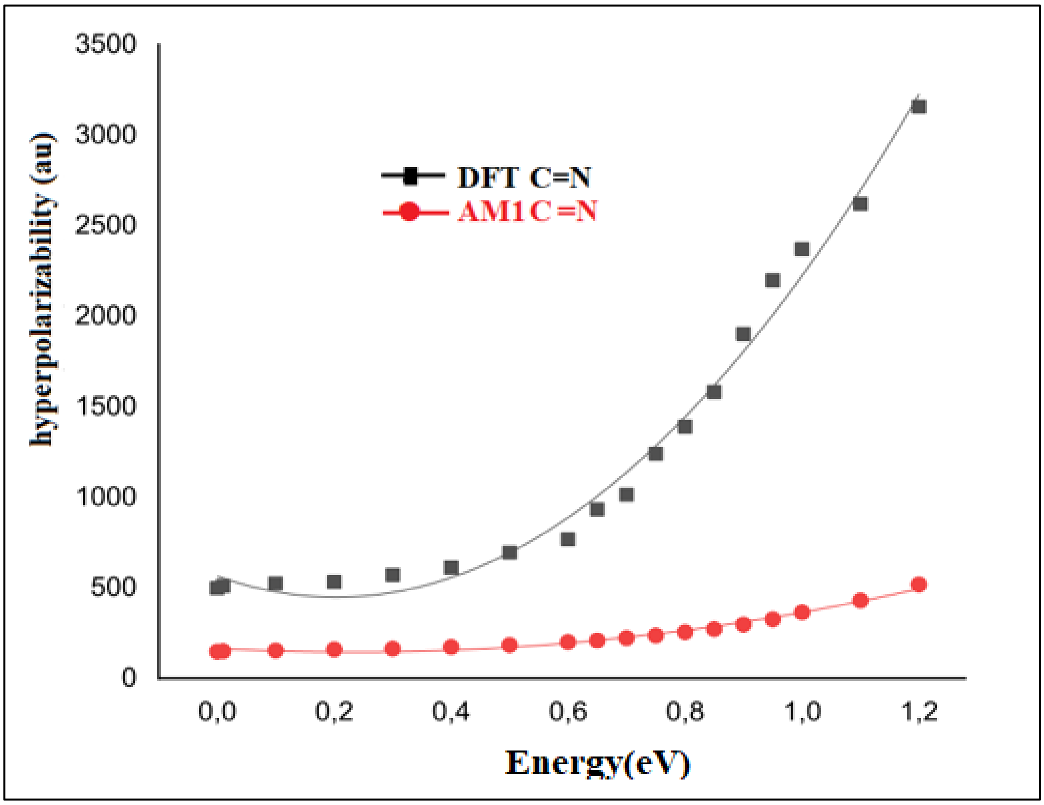

Figure III.9: C=N bridge comparison.

According to the figures Figure III.8, Figure III.9 and Figure III.10 comparing the hyperpolarizability values calculated using the AM1 and DFT methods for the three cases, it is observed that the hyperpolarizabilities obtained with DFT geometry calculations are more pronounced in terms of numerical values. This is attributed to the approximations inherent in this method. DFT will consider the planarity of the molecules more than AM1 method, and the presence of a bridge will favor intramolecular charge transfer to the attractor pole. The electron cloud of this transferred optical density will be more highly populated and more extended when using DFT. This will be encouraged by the presence of π bonds in the conjugated system.

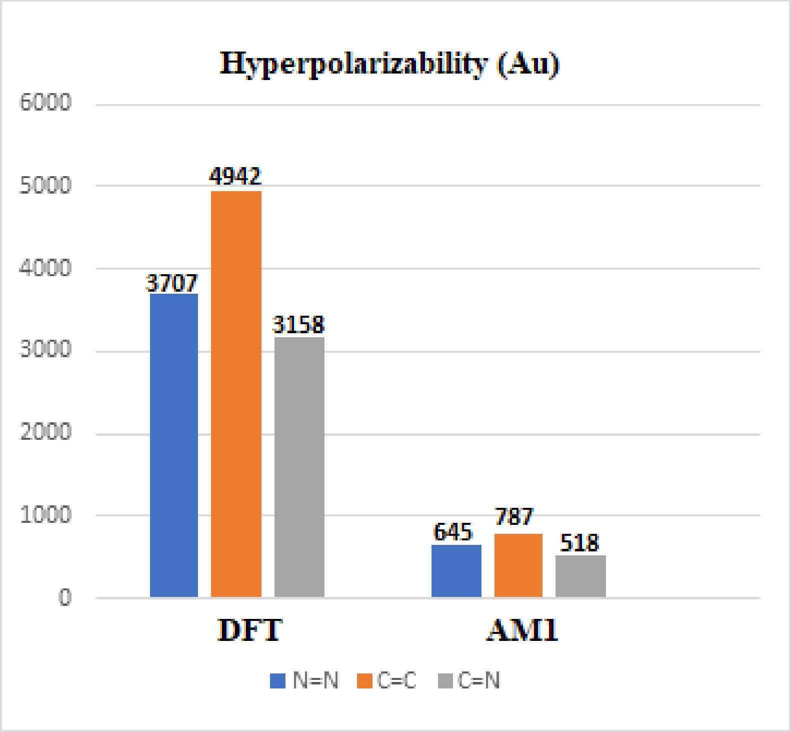

Figure III.10: Histogram of hyperpolarizabilities of the three compounds.

Based on this summarizing Figure III.11, it can be concluded that the C=C bridge exhibits a stronger hyperpolarizability value than the other two bridges. The C=N bridge is considered the weakest bridge. It is also noteworthy that DFT calculations are always more significant compared to AM1.

III.5.4. Analysis with HOMO and LUMO:

We enhance our study by analyzing the atomic orbitals to track and understand the distribution of the electric cloud following the excitation of our materials, examining it along the molecular skeleton by using the analysis based on the two representations HOMO (highest occupied molecular orbital) and LUMO (Lowest unoccupied molecular orbital) (31-34).

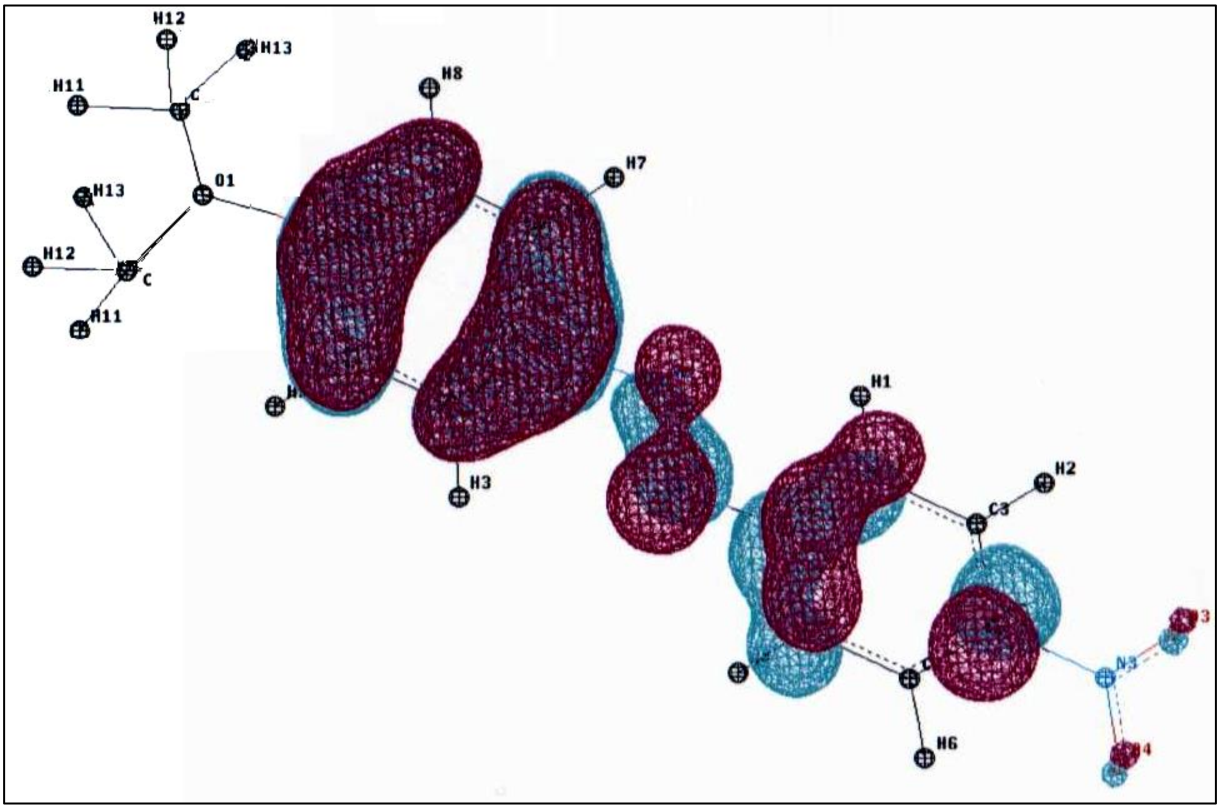

Figure III.11: HOMO Form of C=C compound by AM1 analysis.

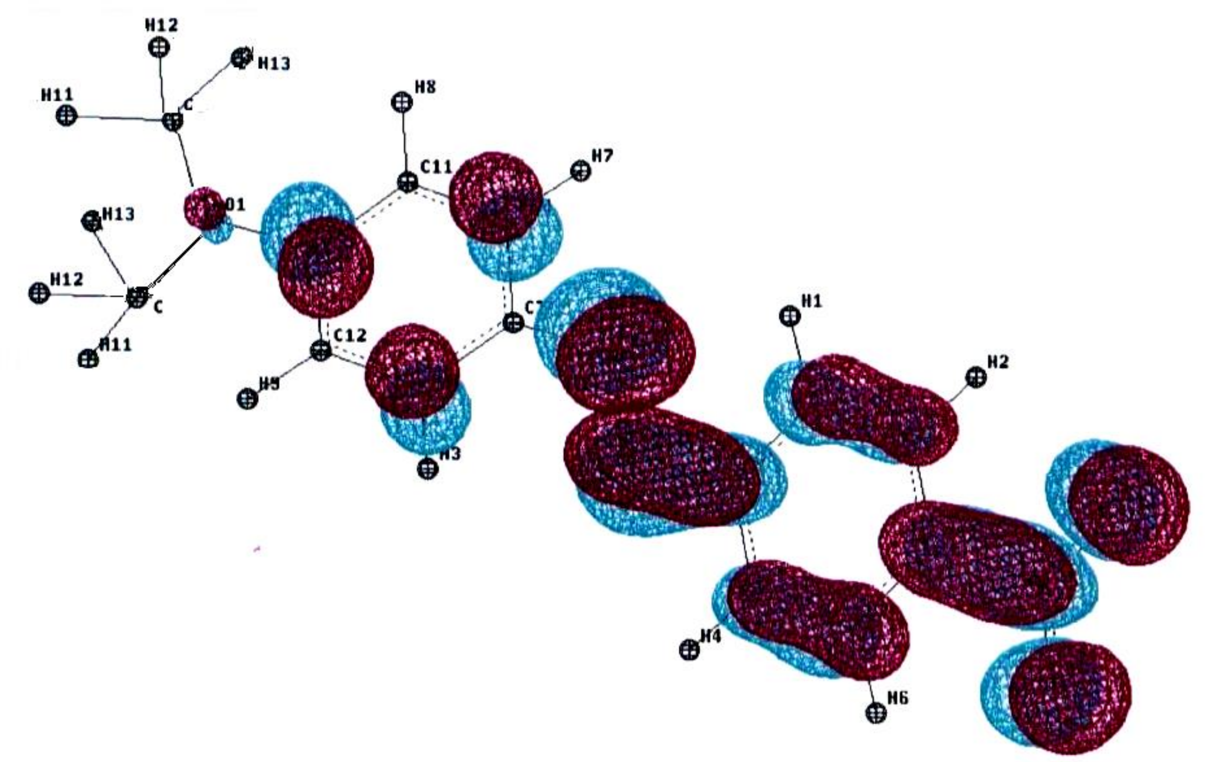

Figure III.12: LUMO Form of C=C compound by AM1 analysis.

The two representations confirm that our materials are perfectly flat and assured a good conjugation on their structures. The existence of π-bond makes the transfer of charge easy, that is clearly observed in the distribution of the density of charge transfer between the donor and attractor groups. HOMO and LUMO diagrams of C=C compounds as a model by DFT and AM1 geometries represented in the following figures III-12 – III-15 show that the distribution of electric cloud along the molecular structure is not identical. These two methods explain that our materials have important electrical properties and can be used in electrical industries.

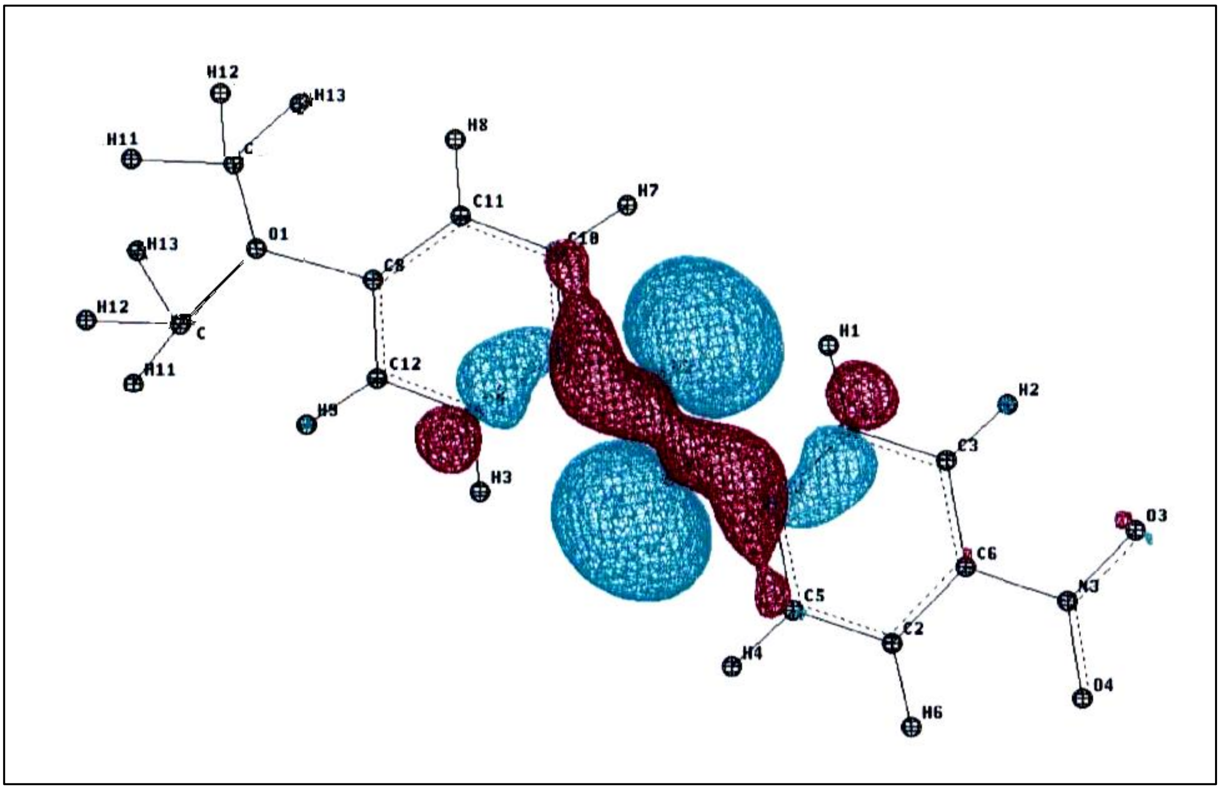

Figure III.13: HOMO Form of C=C compound by DFT analysis.

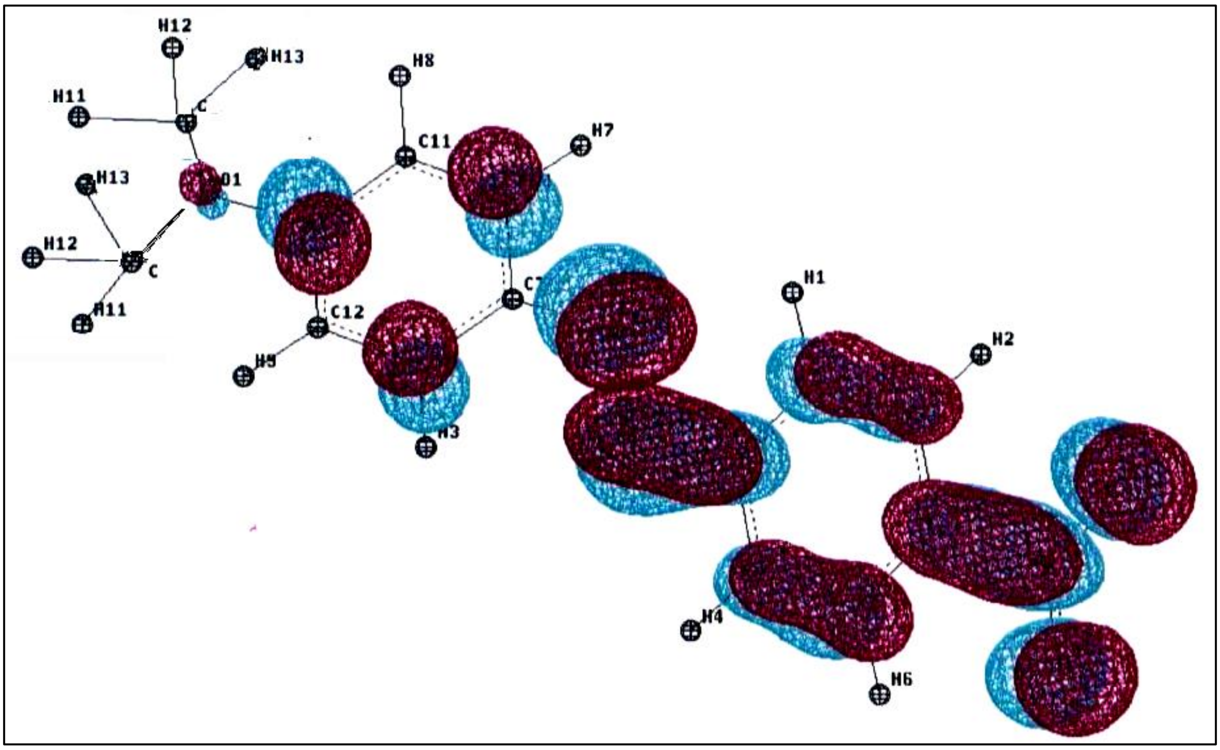

Figure III.14: LUMO Form of C=C compound by DFT analysis.

The HOMO representation by DFT analysis concentrates in the interest zone of distribution charge density which is the C=C bridge. While the HOMO analysis by AM1 method illustrate that the electron density of charge distributed along the molecular structure. This last assure by the presence of SP2 hybridization located on intracycle of aromatic rings and on C=C bridge make the deformation of electronic cloud easier between the donor and attractor groups.

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General conclusion

General conclusion:

The interaction of matter with light presents several phenomena, among them polarization. We have tried to show how this matter reacts with the intensity of the incident field and to see the influence of the behavior of the matter from the point of view of molecular, organic or mineral structure, by studying the molecular skeleton of our matter in detail especially the molecular chain and chemical bonds.

The response of organic compounds after excitation by an incident field shows a different behavior than that of inorganic crystals., this comes back to the nature of the bond within the molecular structure. Mineral compounds exhibit solid bonds of an ionic nature where electrons are highly engaged and require significant energy to break or excite them. While, organic compounds generally possess weak bonds, especially conjugate system bonds that are brittle and require medium energy to transition to their excitation states.

Organic synthesis is an effective tool for designing and modulating the molecular chain according to industrial requirements. We opted for a well-known model with an excitation range compatible with the light used, namely push-pull compounds where the intramolecular charge transfer is facilitated by the presence of two donor and acceptor groups at the ends of these organic compounds. This molecular structure favors the deformation of the electron cloud after excitation in a very short time.

We approached a theoretical study about the nonlinear optical properties in a series of push-pull organic materials, varying the bridge connecting the biaryl system (C=C, N=N and C=N) based on two calculation methods AM1 and DFT.

The results of calculations showed that the response of our three materials was of a perfectly nonlinear order and was highly sensitive to high field values. The hyperpolarizability values of our organic materials are influenced by the conjugated system along the molecular structure and the strengths of the attractor (nitro) and donor (dimethyl amino) groups.

In this work, we have focused on the effect of the bridge that change in each molecule of the three (C=C, N=N and C=N) by calculating the hyperpolarizability values. The results giving by spartan showed that the stilbene bridge dominates both compounds along with the azo and imine bridge. This study was then completed with an analysis of occupied (HOMO) and unoccupied (LUMO) boundary orbitals to better explain the importance of our materials as potential candidates in opto-optical and opto-electronic applications.

Study of the π-conjugated bridge's effect on the quadratic hyperpolarizability in push-pull organic compounds

Résumé :

A travers cette étude, nous avons approfondi nos connaissances en théorie d'optique non linéaire et avons acquis un aperçu chimique des fonctions azoïque, alcène et imine. Nous avons mené une étude sur l'effet du pont dans trois composés de type push-pull de même structure, en changeant le pont dans chaque cas (C=C, N=N et C=N). L'hyperpolarisabilité quadratique a été calculée à l'aide de deux méthodes, AM1 et DFT, en utilisant le programme Spartan version 5. Les résultats du calcul indiquent que le pont C=C est le plus performant, ou celui qui donne la valeur la plus élevée par rapport aux autres ponts.

Mots-clés : Composés organiques, non linéaires, pont.

Summary:

Through this study, we have deepened our knowledge of nonlinear optics theory and have gained a chemical overview of azobenzene, alkene, and imine functions. We conducted a study on the effect of the bridge in three push-pull compounds of the same structure, by changing the bridge in each case (a C=C, N=N and C=N bridge). The quadratic hyperpolarizability was calculated using two methods, AM1 and DFT, using the Spartan software version 5. The calculation results indicate that the C=C bridge is the most efficient, or the one that gives the highest value compared to the other bridges.

Keywords: Organic compounds, non-linear, bridge.

ملخص :

من خلال هذه الدراسة ، قمنا بتعميق معرفتنا بنظرية البصريات غير الخطية واكتسبنا نظرة عامة كيميائيه على وظائف الآزوبنزين والألكين والإيمين. أجرينا دراسة حول تأثير الجسر في ثلاثة مركبات دفع وسحب من نفس الهيكل ، عن طريق تغيير الجسر في كل حالة (C = N و N = N و C = C جسر). تم حساب فرط الاستقطاب التربيعي باستخدام طريقتين ، DFT و AM1 باستخدام الإصدار 5 من برنامج Spartan ، تشير نتائج الحساب إلى ان C = C هو الأكثر كفاءة ، أو الذي يعطي أعلى قيمة مقارنة بالجسور الأخرى

الكلمات المفتاحية: المركبات العضوية ، غير الخطية ، الجسر .