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MOLECULAR MODELING, REACTIVITY PARAMETERS, AND SPECTROCHEMIC STUDIES OF ε-CAPROLACTAM AND o-PHENANTROLINE

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ABSTRACT

Background: Recently, research has been carried out to improve the efficiency of electronic devices in general. With the commercial search for consolidated materials and the growth in demand with monitoring of costs, research has sought to minimize these effects with the replacement or functionalization of other substances, which may be applied at lower costs without compromising operating yields already achieved. **Objective:** This work aimed to obtain molecular modeling and reactivity parameters of ε-caprolactam and o-phenanthroline to evaluate the interaction capacity in the formation of molecular systems. Conductance measurements were taken to observe the electrolytic behavior. Infrared and UV-visible spectra were recorded to characterize vibrational transitions and evaluate spectrochemical properties. **Methods:** The WebLab® program was used to obtain structural data and calculate reactivity parameters. Conductance was obtained in QUIMIS Q-405 equipment. IR spectra were recorded on PERKIN ELMER FRONTIER equipment. UV-vis spectra were recorded in a SHIMADZU equipment 200 – 1000 nm range to record the main transitions. **Results and Discussions:** Electron donor atoms are centered mainly on oxygen and nitrogen, respectively, which are sterically more favorable. The behavior was non-electrolyte. Groups with vibrational transitions sensitive to chemical interactions are comprised of C=N, C-N, and C=O bonds. The ε parameter indicates transitions in the 190 – 300 nm region and the near-infrared, and the oscillator strength is typical of molecules used as dyes and sensitizers in optical light-emitting systems or light-to-electricity converters. **Conclusions:** We observed that these ligands have a donor capacity for the formation of complex systems that meet the need for electron transfer in optical pumping devices for the intensification of transitions or radiation converters, which can also be applied in radiation-to-electricity converter systems.

KEYWORDS: *oscillator strength, transition dipole moment, spectrochemical properties.*

1. INTRODUCTION:

ε-caprolactam is a cyclic chain amine that has molecular formula $C_6H_{11}NO$, molar mass 113.16 g/mol, soluble in water (50 mg/mL), which in aqueous solution has a pH between 7.0 - 8.5 (333 g/L) (Sigma-Aldrich, 2021). In the chemical industry, it has been used as a precursor of polymers called nylon 6 (Bomfim *et al*., 2009). It has also been used in the synthesis of polymeric polyamide composites (Gong and Yang, 2010), in thermodynamic evaluations of uses in photochemical-photovoltaic-thermochemical (CP-PV-T) systems in the use of high-efficiency full-spectrum solar energy (Fang *et al*., 2010), as well as its derivatives, (N-methyl-ε-caprolactam) in the synthesis of light-emitting compounds (Borges et al. 2016). As a ligand in coordination compounds, according to studies, it can be observed that, due to the delocalization of the unbound electron pair from nitrogen, oxygen behaves as a donor group and is the main binding point of the molecule (Alvarez, 1998; Cardoso *et al*., 2007). Figure 01 illustrates the modeling for ε-caprolactam. It is possible to see a specific steric impediment to forming a metal-ligand bond by the unbound electron pair of the nitrogen atom. At the same time, oxygen has two unbound electron pairs and a privileged position in the molecule's boundary orbitals.

O-phenanthroline, also called 1,10-phenanthroline, is a solid, white, organic heterocyclic compound with the molecular formula $C_{12}H_8N_2$, the molar mass of 180.21 g/mol, and has a solubility of 3.3 g/L (25 ^{o}C) in monohydrated form (Merck, 2021) and has been used as a bidentate binder in coordination chemistry, where it is commonly used as a chelating agent for metallic ions (Vogel *et al*., 1981, Huhey, 1983; Greenwood and Earnshaw, 1986; Cotton and Wilkinson, 1988; Vasconcelos, 2019). The bond strength of o-phenanthroline with metals also comes from its ability as an π electron receptor, which contributes enthalpically to the formation of stable complexes (Maldonado, 2017). In Figure 02, the modeling for orthophenanthroline can be seen. Although 1,10-phenanthroline is widely used for fast, flexible, and reliable analysis with a high scientific reputation in research, other applications are found, such as; using cathodic protective buffer layers as a conventional binder to improve the efficiency of organic solar cells (Sun *et al*., 2014), in the study of efficacy in the Luminol chemiluminescence system in Fenton reactions (Mitsuhiro *et al*., 2014), in complex systems with Cu(I) using mixed ligands to amplify luminescent radiative emissions by electron transfer with a high quantum efficiency (Li *et al*., 2012), in complexes with Cu^{2+} and Pt^{2+} that have antimicrobial properties (Neville *et al*., 2013), in geomicrobiology as an indicator of Fe^{2+} in microbial activities in terrestrial and interstellar minerals (Notini *et al*., 2019), among others that enrich the national and international literature.

The importance of molecular modeling of the studied compounds is because it provides relevant structural data and better visualization of the chemical environment around these compounds. In addition, modeling is widely used to interpret experimental results and construct materials with specific properties (Coelho *et al*., 1999; Lima^1 et al., 2015; Lima^2 et al., 2015).

The reactivity parameter has also been found to be useful in evaluating and understanding the properties of substances, facts that allow a better understanding of which metals will form more stable coordination compounds, and which location is most likely for the formation of the metal-ligand bond, which can be verified experimentally through spectrochemical studies, in addition to other techniques (Lima^1 et al., 2015; Lima^2 et al., 2015).

Molar conductivity measurements were obtained for the electrolytic evaluation of these compounds in an aqueous solution to observe what influence they could attribute to the formed complex systems (Geary, 1971; Crockford and Knight, 1977; Belarmino, 1998; Lima *et al*., 1998; Costa *et al*., 2013; Lima^1 *et al*., 2015; Lima^2 *et al*., 2015).

Infrared (IR) spectroscopy is a spectroscopic technique that, in addition to identifying the structure and bonds and recognizing groups of atoms in compounds, is also used in qualitative analysis, mainly in the areas of synthesis, organic transformations, and in the chemistry of natural products (Smith, 1961; Silverstein *et al*., 2007; Pavia *et al*., 2010; Marin, 2013; Maciel and Filho, 2015).

The technique of the interaction of electromagnetic radiation as molecules, atoms, or ions, the technique of electronic absorption spectroscopy in the UV-vis region, is used. This technique is based on the absorption of radiation that promotes electrons from a lower energy state to another higher energy state, and it is possible to determine physicochemical properties useful in the field of scientific and technological applications (Vogel *et al*., 1981; Moore, 1991; Silverstein *et al*., 2007; Pavia *et al*., 2010; Levine, 2014; LIMA *et al*., 2017; Fang *et al*., 2020). Furthermore, according to the literature, the electronic spectra of molecules allow evaluation of some of their spectral properties, making it possible to calculate the oscillator strength, which aims to quantify the intensity of a transition, and thus evaluate the influence of the chemical environment on the dynamics of the spectra (Drago, 1965; Figgs, 1966. Heslop and Jones, 1976; Lima et al., 1996; Lima et al., 2017).

Given the above, the purpose of this work was to obtain the molecular modeling, define the reactivity parameters of ε-caprolactam and orthophenanthroline, obtain measurements of molar conductivity, record infrared and UV-visible spectra, evaluate the spectrochemical properties related to the oscillator strength and the induced dipole moment, to sequence the investigation of their functionalities as electron donor species in compounds applied in radiation converter systems or light-to-electricity converters.

2. MATERIALS AND METHODS:

2.1 Molecular Modeling and Reactivity Parameters

Molecular modeling, theoretical reactivity parameters, electrostatic potential cloud, bonding distances, bonding angles, and partial charges were obtained from the WebLab ViewerPro©

program. The parameters were calculated using the following expression (Lima *et al.*, 2020):

$$\Re = \frac{\int q_i \, d\tau}{\sum_{i=1}^{n} \left| \int q_i \, d\tau \right|}$$

(Eq. 01)

2.2 Conductance, Conductivity, and Molar Conductivity

Molar conductivity measurements were performed for aqueous solutions of millimolar concentration using a QUIMIS Q-405 conductivity meter at a temperature of 25.0 ± 1 °C, after calibration of the cell constant with freshly prepared standard solutions millimolar of NaCl and KCl. The molar conductivity was calculated using the expression below:

$$\Lambda_M = \frac{(L_{sol} - L_{solv}).Kc.10^3}{M} = \frac{(k_{sol} - k_{solv}).10^3}{M},$$

(Eq. 02)

Table 01 – Comparative values of the type of electrolyte with acceptable ranges of molar conductivities in aqueous solution for solutions of concentration M = 1.00×10^{-3} mol L^{-1} (Belarmino *et al.*, 1998; Lima *et al.*, 1998; Costa *et al.*, 2013; Lima *et al.*, 2020).

Λ_M S cm^2 mol^{-1}	Type of electrolyte $xA^+ : yB^-$ $A_xB_y \leftrightarrow xA^+ + yB^-$	Species predominant
0 - 100	Não eletrólito	A_xB_y
100 - 200	1:1	$A^+ + B^-$
200 - 300	1:2 or 2:1	$A^+ + 2B^-$ or $2A^+ + B^-$
300 - 500	1:3 or 3:1	$A^+ + 3B^-$ or $3A^+ + B^-$
500 -?	1:4 or 4:1	$A^+ + 4B^-$ or $4A^+ + B^-$

2.3 Spectroscopy in the Infrared Region

The infrared spectra of the two samples were recorded in a PERKIN ELMER FRONTIER equipment, in KBr pellets, in the range of 700 – 4000 cm^{-1} and resolution of 4 cm^{-1}.

2.4 Spectroscopy in the UV-Visible Region

The UV-vis spectra were recorded in a SHIMADZU UV model spectrophotometer in the range of 200 - 1000 nm, quartz cuvette with a 1 cm optical path for aqueous ε-caprolactam solutions (1.18×10^{-2} mol L^{-1}), aqueous o-Phenanthroline (1.15×10^{-2} mol L^{-1}) and ethanolic o-Phenanthroline (1.01×10^{-2} mol L^{-1}). Samples needed to be diluted. The oscillator strength f was calculated by Drago's and Figgs method and described methodologies (Lima *et al.*, 2020) according to the expressions:

DRAGO: $f = 4,6 \times 10^{-9} \int \varepsilon_{(\sigma)} d\sigma$ (Eq. 03)

FIGGS: $f = 4,32 \times 10^{-9} \int \varepsilon_{(\sigma)} d\sigma$ (Eq. 04)

The area under the absorption band =

$$\int A_{(\sigma)} d\sigma = A_{máx}.(1/\lambda_1 - 1/\lambda_2) \quad \text{Eq. 05}$$

The importance of using the oscillator force in evaluating optical properties in spectroscopy is that there is a theoretical connection with the initial and final state wave functions of a chemical system involved in an electronic transition. The μ_{if} transition dipole, generally, is a complex vector quantity that includes some phase factors associated with the two states. The direction of its magnitude guides the polarization of a transition, which has the consequence of determining the interaction of the system with an electromagnetic wave of a certain polarization, and the square of its magnitude indicates the strength of this interaction due to the distribution of charge in the system. In a way, it is related to the initial states ψ_i and final states ψ_f, and is defined unidimensionally as:

$$\mu_{xif} = \int \psi_i^* . \mu_x . \psi_f \, dx, \quad \text{(Eq. 06)}$$

where

$$\mu_x = \sum_{i=1}^{n} e_i . x_i \quad \text{(Eq. 07)}$$

and e_i, it is (or are) the electron(s) involved in the transition, and x_i the displacement performed in the space provided by the system, being a measure of the dipole moment associated with the charge displacement when there is a redistribution of an electron into a configuration, brought about by the interaction between electromagnetic radiation and matter. The oscillator strength f is associated with the three-dimensional dipole moment through the equation below,

$$f = \frac{8\pi^2 . \mathrm{M_e} \nu}{3\mathrm{he}^2} \left[\mu_{xif}{}^2 + \mu_{yif}{}^2 + \mu_{zif}{}^2 \right],$$

(Eq. 08)

Where M_e is the electron mass, ν the transition frequency, h the Planck constant, e the electron charge and μ_{if} the transition dipole moment in three dimensions (Kauzmann, 1957; Drago, 1965; Pitzer, 1965; Figgis, 1966; Atkins, 1990; Atkins and Friedman, 2011; Levine, 2014).

Rearranging variables and writing the transition dipole moment variation in a more simplified way for an isotropic approximation, we will have:

$$\mu_{if}{}^2 = \frac{3\mathrm{he}^2}{8\pi^2 . \mathrm{M_e} \nu} . f \rightarrow$$

$$\mu_{if} = 8{,}422 \mathrm{x} 10^{-22} (\mathrm{m\ s^{-1/2} C}) . \sqrt{\frac{f}{\nu}} \quad (\mathrm{C\ m})$$

(Eq. 09)

This expression allows, in these terms, to evaluate the experimental transition dipole moment from the oscillator strength and the transition frequency corresponding to the maximum of the absorption band (or the transition barycenter) and certainly takes with it the contributions of the transfer mechanisms of charge (electric dipole moment, magnetic dipole and electric quadrupole), which contribute to its occurrence.

One of the direct applications mentioned in the literature of the dipole moment is that it can be related to; (1) the extent to which an intramolecular bond is polarized and (2) with a more detailed understanding of the geometry of molecules, as mentioned by some researchers (Moore, 1991). In the case of this work, the induced dipole moment can guide us concerning the reactivity of the binding groups that we intend to manipulate in the formation of complex chemical systems, especially the lower energy transitions that certain molecules present in their spectra, which reveals, in some magnitude, the ease or difficulty of polarizing its electrons situated in the molecule's boundary orbitals, where the most important chemical interactions that precede bond formation or electron transfer in electronic devices usually occur.

From the UV-vis electronic spectra of solutions of ε-caprolactam and o-phenanthroline compounds, the oscillator strength is calculated by the Gaussian (or half-band) method and by applying the expressions described by Drago and Figgs (Drago, 1965; Figgs, 1966; Barrow, 1982), it was possible to evaluate the transition dipole moment, also called the induced dipole moment, for the transitions resolved in the electronic absorption bands, recorded and shown in Figure 05. This magnitude reveals the connection that exists with the system's wave functions, modified by the interaction of electromagnetic radiation with the chemical environment of the compounds under the influence of the solvents chosen for this study in the first analysis, and indeed, the same ones that will be used in the synthesis of the alleged complexed systems in the adducts, to assess their understanding in the chemical modification of the spectroscopic properties of these and others similar, with potential application in light-emitting devices and radiation-to-electricity converters, such as those mentioned in the literature.

3. RESULTS AND DISCUSSION:

3.1 Molecular modeling, obtaining structural data and reactivity parameters.

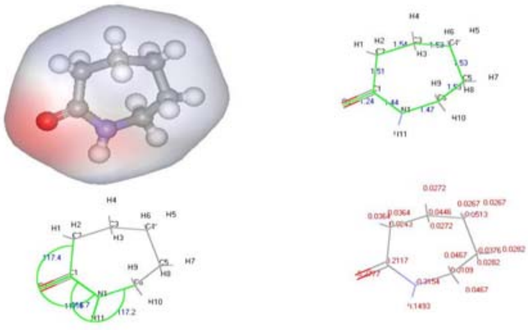

Figure 01 - Modeling obtained for ε-Caprolactam, $C_6H_{11}NO$, using the WebLab ViewerPro program©.

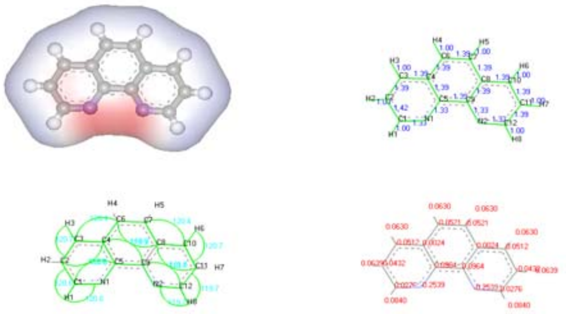

Figure 02 *- Modeling obtained for o-Phenanthroline, $C_{12}H_8N_2$, using the WebLab ViewerPro program©.*

Table 02 *- Partial charges and PRM for ε-Caprolactam, $C_6H_{11}NO$.*(main atoms)

Atoms	*Partial charges*		PRM	
	δ^-	δ^+	$\Re^-$	$\Re^+$
O_1	-0,2777		-0,3822	
C_1		0,2117		0,2913
H_1		0,0364		0,0501
H_{10}		0,0467		0,0643
N_1	-0,3154		-0,4341	
H_{11}		0,1493		0,2054

PRM - Molecular Reactivity Parameters

Table 03 *- Partial charges and PRM for o-Phenanthroline, $C_{12}H_8N_2$. (main atoms)*

	Partial charges		PRM	
Atoms	δ^-	δ^+	$\Re^-$	$\Re^+$
C_1		0,0276		0,0345
C_{12}		0,0276		0,0345
C_5		0,0964		0,1204
C_9		0,0964		0,1204
N_1	-0,2539		-0,3171	
N_2	-0,2539		-0,3171	

PRM - Molecular Reactivity Parameters

3.2 Conductivity measurements and the associated electrolyte type.

Table 04 *– Conductivities obtained for millimolar aqueous solutions at 25.0 ± 1 °C.*

	k x10^{-6}	M Mol/L	Λ_M	Type of electrolyte
H_2O	17,6	55,5	31,7x10^{-5}	n-electrol
NaCl	121	0,001	103,4	1:1
KCl	150	0,001	132,4	1:1
ε-capro	34,4	0,001	16,8	n-electrol
o-fen	33,0	0,001	15,4	n-electrol

Units: k (S cm^{-1}); Λ_M (S cm^2 mol^{-1})

3.3 Spectra in the infrared region.

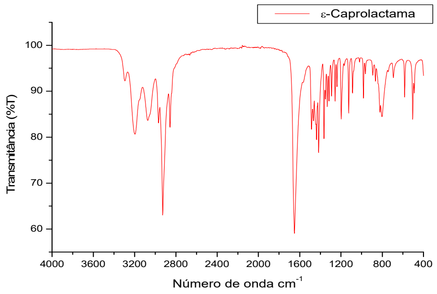

Figure 03 *- Infrared spectrum of ε-Caprolactam*

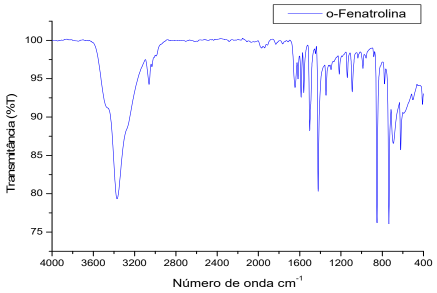

Figure 04 *- Infrared spectrum of o-Phenanthroline*

Table 05 - *Vibrational transition assignments for ε-Caprolactam (main)*

vib. modes	Silverstein 2007	Pavia 2010	Cardoso *et al* 2017	Exper
N-H	3350	3300		3294 w
	3180			3197 m
		3100		3073 m
C=O	1720	1680	1663	1652 s
	1706	1630		
C-N			1461	1467 m
C-N		1400		1417 m

w (weak); m (medium); s (strong)

Table 06 - *Vibrational transition assignments for o-Phenanthroline (main)*

vib. modes	Smith, 1961	Martins 2010	Maciel 2015	Exper
νC=N	1616			1616 m
ν_{sim}C=C			1600	
νC=N	1585			1586 w
	1558			1561 m
νCC	1508			
		1501		1503 s
νC=C	1418			
νCN		1419		1421 s
C-N_{arom}	1340			1345 w
δ C=N		621		622 m

w (weak); m (medium); s (strong)

3.4 Spectra in the UV-Visible region in aqueous and ethanolic solution.

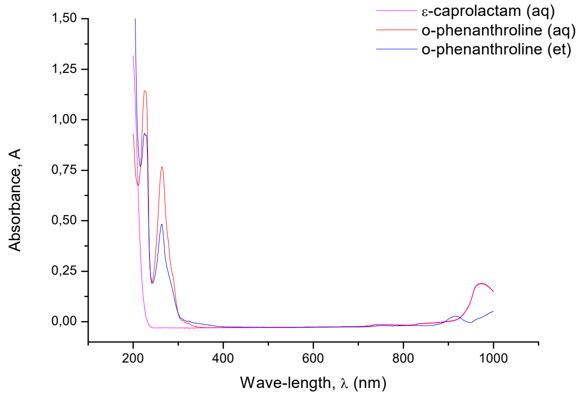

Figure 05 - *UV-vis spectrum of ε-caprolactam and o-phenanthroline.*

Table 07 - *Oscillator strength and ligand transition dipole moment.*

Ligand	Range Spectral (nm)	*f* (x10^{-3}) (adim)		μ_{if} (x10^{-30}) C m (Debye)	
		D	F	D	F
ε-cap (aq)	948–999	3,9	3,68	3,0 (0,90)	2,91 (0,872)
o-phe (aq)	217-234	1,5	1,44	28 (8,4)	27,7 (8,30)
	251 -278	1,2	1,11	27 (8,1)	26,4 (7,91)
	948-1000	42	39,2	9,8 (2,9)	9,50 (2,85)
o-phe (et)	215-234	1,6	1,50	29 (8,7)	28,3 (8,48)
	249-278	0,91	0,852	24 (7,2)	23,0 (6,89)
	900-930	4,5	4,22	3,1 (0,93)	3,22 (0,905)

D – Drago; F – Figgs; 1 Debye = 3,336x10^{-30} C m
(aq) aqueous solution, (et) ethanolic solution.

4. CONCLUSIONS:

Molecular modeling, partial charge δ and reactivity parameters ℜ for elements with higher negative densities corroborate that these species have a Lewis base characteristic, which can function as electron donor molecules in systems that are deficient in pumping electrons, to enhance the inductive and resonance effects, to optimize preconceived chemical systems that have optical properties.

Molar conductivity measurements confirmed the non-electrolyte behavior for the compounds in an aqueous solution of ε-caprolactam and o-phenanthroline, as described in Table 04. These analyzes are intended to evaluate further the influence of these species on the electrochemical behavior of complex systems.

The spectra in the infrared region accurately identify these species and are presented with good resolution, which allows the characterization of these molecules present in new chemical environments to be analyzed. The transitions that occur for ε-caprolactam NH, C=O, CN, $CC_{(axial)}$ and $CC_{(ang)}$ at 3294, 3073, 1652, 1467, 1437, 1417, 1365, 1351, 1333, 1257, 1198, 1125 , 803, 505 and 490 cm^{-1}, identified in Table 05, are particularly useful in recognizing these species for the free molecule and in complex systems. In the spectrum of orthophenanthroline, the transition at 3369 cm^{-1} is attributed to the water molecule of the o-phenanthroline monohydrate, and the transition at 3060 cm^{-1} is attributed to the ν_{sym} C-H transition. Its main C=N, CN, and C=C transitions that occur around 1645, 1616, 1421, 1420, 1345, 1217, 1139, 778, 736 cm^{-1}, shown in Table 06, are also of particular interest in recognition spectral for the free molecule as well as indicative when bound in other compounds.

The UV-vis spectra clearly show that both ε-caprolactam and o-phenanthroline do not absorb in the visible between 400 - 760 nm, which can be interesting in certain situations, and therefore they are white compounds in solid-state, and their solutions are colorless. However, they absorb with great intensity in the ultraviolet region in the range of 200 - 280 nm and with less intensity in the near-infrared region, in the range of 940 - 1000 nm, which can provide these species with a tendency to act as pumpers of electrons in optical devices and in complex systems, mainly due to the values obtained for their spectrochemical parameters of molar absorptivity ε_{max}, oscillator strength f and transition dipole moment μ_{if}.

We observed that in these evaluated concentrations, which allowed the adequate resolution to detect the best resolution of the spectrum, the values of the induced dipole moment, obtained through the oscillator force by the half-band method using the expressions of Drago and Figgs (Drago, 1965; Figgs, 1966), guided us to state that the boundary electrons in o-phenanthroline in aqueous solution have higher values (2,9 – 2,85 Debye), than when compared to the same o-phenanthroline in solution ethanolic (0,93 – 0,905 Debye) and ε-caprolactam in aqueous solution (0,90 – 0,872 Debye). It is possible to conclude, based on the behavior of o-phenanthroline, that the solvent change will not only influence the dynamics of the transitions and intensities of the dipole moment but especially the chemical interactions, which may favor the application of the dipole moment of transition, as an additional or alternative parameter, for the choice of ligands and solvents, to facilitate the efficiency of electron transfer and the energy performance of some reactions, as well as help in the choice of pairs (solvents/ligands), that contribute to the formation of chemical interactions and bonds in complex systems that show more excellent stability.

5. DECLARATIONS

5.1. Study Limitations

No limitations were known at the time of the study.

5.2. Acknowledgements

Our thanks to the Institute of Chemistry at UFRN for supporting the infrared and UV-visible equipment.

5.3. Funding source

The authors funded this research

5.4. Competing Interests

There are no conflicts of interest in this work that we are aware of currently.

5.5. Open Access

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