



## Fluorescent Schiff base as molecular rotor with dual-stimuli responsive: Microwave-assisted, ultrasound-assisted, and mechanosynthesis, characterization, and photophysical properties

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### Abstract

The Schiff base (*E*)-2,4-di-*tert*-butyl-6-((pyridin-4-ylimino)methyl)phenol (**1**) was synthesis by three eco-friendly synthetic routes such as microwave irradiation, mechanosynthesis and ultrasounds. Compound **1** was fully chemo-photophysical characterized as well as high-resolution mass spectrometry (HRMS), the title compound showed solvato- and viscochromism, where the Schiff base **1** is influenced by the solvent polarizability and viscosity media. The experimental and theoretical calculation demonstrated the ability of the molecule to act as a molecular rotor.

**Keywords:** Schiff bases, dual-responsive, Solvatochromic, viscochromic, Fluorescent molecular rotor, Microwave assisted.

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### 1. Introduction

In the last decade, stimuli responsive fluorescent organic materials have been widely investigated in both sides, principles, and applications. The applications of these fluorescent materials have been reported from OLEDs[1] to metal sensors [2]. A simple search in the literature, we can find different fluorescent materials from multi-, dual- and mono-stimuli, where the optical properties can be modified by one or various chemical stimuli. The  $\pi$ - conjugated organic compounds have been very attractive to the scientific community due to the easy synthesis, low-cost and high chemical yields where these organic materials show electro-, [3] piezo-, [4] mechano-, [5] halo-, [6] thermo-, [7] solvato-, and photochromism [8]. For example, the Schiff bases have showed stimuli response in solution and in solid state [7,8,9,10,11]. Schiff bases are the compounds carrying imine or azomethine group, obtained by condensation of ketones and aldehydes with a primary amine for the formation of C=N double bond. Schiff bases have been widely used as ligand to generates stable complexes with a large number of metal ions and

metalloids[12,13,14,15]. However, due to quick preparation and synthetic flexibility, Schiff bases by themselves have interesting and attractive properties to be applied in different areas of science, attracting the attention of chemical and biological topics [16,17,18]. In this context, Jiménez-Sánchez *et al.* synthesized a multiresponsive photo, solvato, halo, and ionochromic Schiff base probe, which displays a noticeable solvatochromic effect, changing from 3214 cm<sup>-1</sup> in cyclohexane to 9580 cm<sup>-1</sup> in methanol, influenced dominantly by the solvent acidity parameter [8]. Recently, Ibarra, *et al.* synthesized a Schiff base showing interesting properties of thermo-, vapo-, piezo-, and viscochromism. The viscosity studies presented an increase of 5.5 folds in luminescent quantum yield with the progressive increase in the viscosity medium, using methanol and glycerol binary mixture [7]. On the other hand, it is not only important to generate functional Schiff bases, but it is necessary a green and sustainable synthesis of them and industrial scalable as well, underlining that there are few reports in the literature on this subject. A series of Schiff bases have been prepared using the conventional method as well as mechanochemically, and by <sup>1</sup>H NMR analysis, the authors verified to have the same compounds with both methods, but in a shorter synthesis time and lower solvent consumption by liquid assisted grinding (LAG) method [19]. Haque *et al.* synthesized under microwave irradiation three chitosan Schiff bases at 60°C for 15–20 min in a methanol-water mixture. The authors mentioned the use of microwave synthesis offers benefits, such as, increase the rate of chemical reaction, high yield of the product, and high purity without involving cumbersome purification steps [20]. Bouzayani *et al.* synthesized for a green methods; microwave, ultrasound and under inert conditions (argon), comparing its yields, showing better results the microwave irradiation (100°C, 5 min) [21]. Recently, Tunde *et al.* report the synthesis of Schiff bases derived from nitrobenzaldehyde and aniline in a solvent-free approach, where mechanical grinding results in high yield (>95%) and occurred within five minutes [22]. We are interested in the synthesis of Schiff bases and compounds of groups such as boron and tin by green methods for example microwave-assisted synthesis [23]. Continuing with our research, here we report the syntheses of a Schiff base (**1**) by three different green synthetic routes: microwave, ultrasound and mechanochemistry. Besides, we describe on the dual responsive properties of **1** mediated by solvent nature to modulate emission wavelength (solvatochromism) and the behaviour of the fluorescence against the viscosity (viscochromism). Additionally, the rotational capacity of the molecular structure and frontier molecular orbitals in different solvents was calculated by DFT.

## 2. Experimental section

### 2.1 General remarks

All starting materials were purchased from Aldrich Chemical Company. Solvents were used without further purification. The syntheses of the Schiff base were performed with an Anton Paar Monowave 300 microwave reactor, a Retsch mixer mill MM 200 and an ultrasonic Branson 2510. Melting point was determined on an Electrothermal Mel-Temp apparatus and is uncorrected. The high-resolution mass spectrum (HRMS) was acquired with an Agilent Technologies LC/MSD TOF instrument with atmospheric pressure chemical ionization (APCI). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of samples in CDCl<sub>3</sub> were recorded with a Bruker Avance DPX 400 spectrometer (<sup>1</sup>H 399.78 MHz and <sup>13</sup>C 100.52 MHz).

### 2.3 General procedure for reaction for Schiff base

*(E)-2,4-di-tert-butyl-6-((pyridin-4-ylimino)methyl)phenol*

**Synthesis route A (Microwave)** A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde 0.234 g (1.0 mmol), 4-aminopyridine 0.0941 g (1.0 mmol), in methanol was irradiated for

20 minutes at 500 W. The reaction mixture was slowly cooled to room temperature and the precipitated was filtrated off and washed with hexane, followed by crystallization in the same solvent to give 0.2912g (94%) of yellow crystals. M. p. 182-184°C. <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ: 1.33 (s, 9H, H-14, H-15, H16), 1.47 (s, 9H, H-18, H-19, H-20), 7.15 (d, 2H, H-1,H-5), 7.24 (d, 1H, H-8), 7.51 (d, 1H, H-10), 8.62 (d, 2H, H-2, H-4), 8.64 (s, 1H, H-6), 13.10 (s, H-OH) ppm. <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>) δ: 29.22 (C-18, C-19, C-20), 31.25 (C-14, C-15,C-16),34.06(C-17),34.98(C-13),116.06(C-1,C-5),117.68(C-7),127.21(C-8),129.23(C-10),137.19(C-11),140.94(C-9),150.86(C-6),155.56(C-3),158.42(C-12),166.56(C-2,C-4)ppm.HSQC[H/C]:1.33/31.25(H-14,H-15,H-16/C-14,C-15,C-16),1.47/29.22(H-18,H-19, H-20/C-18, C-19, C-20), 7.15/16.06 (H-1, H-5/C-1, C-5), 7.24 (H-8/C-8), 7.51/129.23 (H-10/C-10). HRMS *m/z* (%): C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O: Calcd. 310.4430 g/mol, found: 311.211790, (error: 0.140881 ppm).

**Synthesis route B (Ultrasonic)** *Applying the same procedure for synthesis route A.* of 3,5-di- *tert*-butyl-2-hydroxybenzaldehyde (1.0 mmol), 4-aminopyridine (1.0 mmol), for ultrasonic assisted synthesis was prepared in methanol for 1 hour at 60 °C with a drop of acetic acid was employed as catalyst. Yield: 0.267 g (86%).

**Synthesis route C (Mechanochemical)** *Applying the same procedure for synthesis route A.* of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.0 mmol), 4-aminopyridine (1.0 mmol), CaCl<sub>2</sub> (1 mmol) by mechanochemical without solvent in a mixer ball mill for 2 hours. Yield: 0.27g (87%).

## 2.4 Photophysical characterization

Photophysical characterization was carried out in spectroscopic grade CHCl<sub>3</sub>, THF, CH<sub>2</sub>Cl<sub>2</sub>, MeOH from Aldrich. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda365 spectrophotometer. Emission spectra have been recorded with a Horiba Scientific Fluorolog-3 spectrofluorimeter; the excitation wavelength was 10 nm lower than the absorption maximum. Fluorescence quantum yields (Φ) were determined in solution at 25 °C with the dilute method, according to the reported procedure[24] and using quinine sulphate in H<sub>2</sub>SO<sub>4</sub> 0.1 M (Φ = 0.54 at 310 nm) as the standard. Three solutions with absorbance at the excitation wavelength lower than 0.1 were analysed for each sample and the quantum yield was averaged. The viscosity study was carried out with a solvent mixture (methanol/glycerol) using different ratios.

## 2.5 Computational details

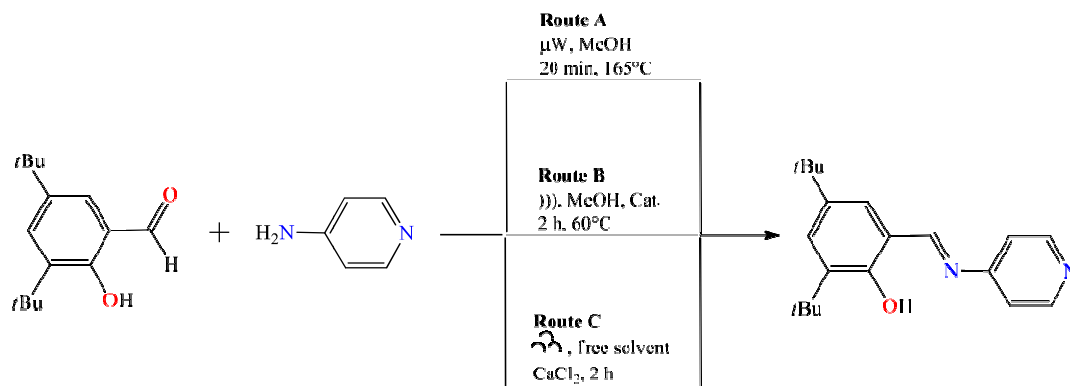
We have explored the potential energy surface (PES) to find the lowest energy structure for compound **1**. The structure of **1** was optimized using the Gaussian 09 program, with the B3LYP/6-31G(d,p) method [25]. The global minimum was characterized by calculating their vibrational modes at the same level of theory. Subsequently, a single point calculation, was performed to the lowest energy structure previously obtained to compute the UV spectra. Finally, the energy rotation barrier values were computed by rotating every 20° the N-C<sub>Ph</sub> bond. All results were visualized with the Chemcraft v1.8 program.

## 3. Results and discussion

### 3.1 Synthesis

Schiff base **1** was prepared by three different methods, microwave irradiation, ultrasound, and mechanochemical, through the condensation reaction of the corresponding aryl aldehyde and the 4-aminopyridine (Scheme 1). Using microwave-assisted synthesis in 20 minutes of radiation, at 165°C, compound **1** was obtained the best chemical yield (94%)

(Table 1). Probably the mechanochemical and ultrasound present a low yield due to lack of solubility in the medium and the type of energy that can promote the synthesis.[26] The high-resolution mass spectra (HRMS) of **1** shows that the molecular ion peak corresponds to molecular weight, and the first fragmentation of the compound is given by removing of the two *tert*-butyl groups to 182.95 *m/z* (see spectra inESI).



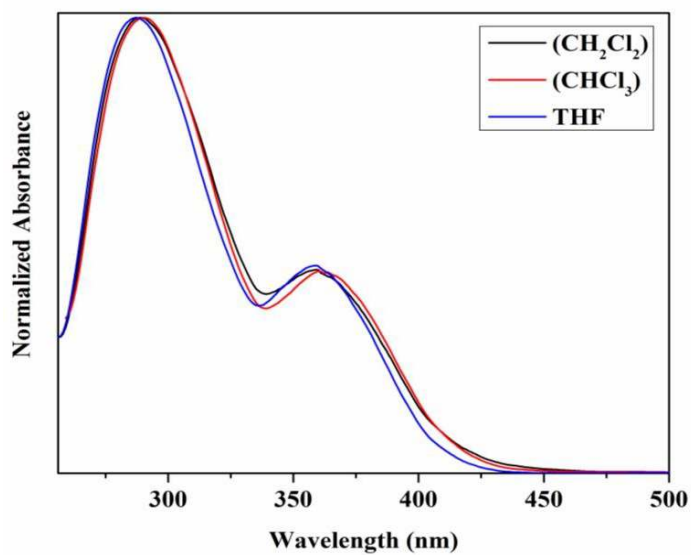
**Scheme 1.** Synthesis of Schiff base **1**.

**Table 1.** Main parameters of different synthetic routes of **1**.

	Solvent	Yields (%)	Time	Temperature (°C)
<b>Microwave</b>	Methanol	94	20 min	165
<b>Ultrasound</b>	Methanol	86	1 h	60
<b>Mechanochemical</b>	None	87	2 h	-

### 3.2 Photophysical properties

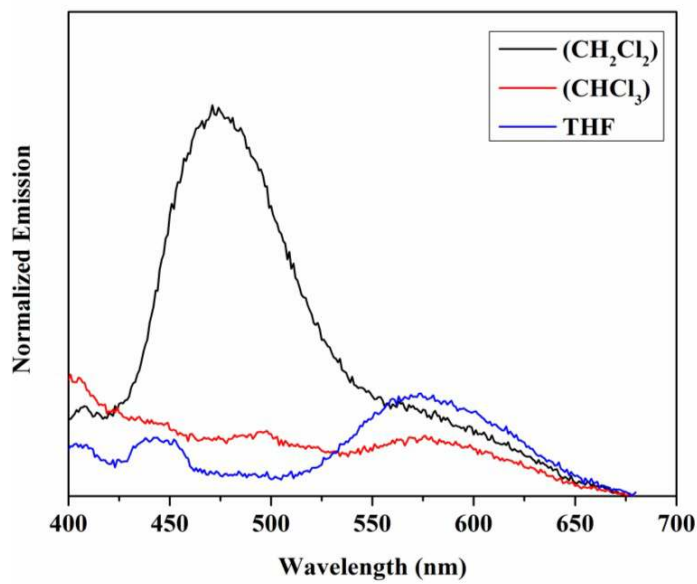
In order to evaluate solvatochromic behavior, the photophysical properties were obtained in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF (Table 2). The absorption and emission spectra of the Schiff base at a concentration of 1x10<sup>-5</sup> M are shown in Figures 1 and 2. In general, compound **1** presents two absorption peaks around 289 and 390 nm corresponding to HOMO–LUMO electronic transitions (Figure 1). The fluorescence spectrum of **1** in CHCl<sub>3</sub> shows a weak emission of around 570 nm and almost null emission in THF, while CH<sub>2</sub>Cl<sub>2</sub> presents a higher intensity of emission at 476 nm (Figure 2). Besides, compound **1** exhibits the least Stokes shift in dichloromethane too. This behavior is mainly influenced by the solvent polarizability, as has been observed in other solvatochromic studies of Schiff bases.[8]



**Figure 1.** UV-Vis spectra of Schiff base in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and THF at  $3.5 \times 10^{-5}$  M.

**Table 2.** Photophysical properties of compound **1**.

Solvent	Polarity index	$\lambda_{\text{abs}}$ [nm]	$\epsilon * 10^4$ [ $\text{M}^{-1}\text{cm}^{-1}$ ]	$\lambda_{\text{em}}$ [nm]	$\Phi$ (%)	Stokes shift ( $\text{cm}^{-1}$ )
$\text{CH}_2\text{Cl}_2$	3.1	287	1.2	476	0.69	13835
$\text{CHCl}_3$	4.1	289	2.2	577	0.15	17271
THF	4.0	290	1.2	569	0.16	16908

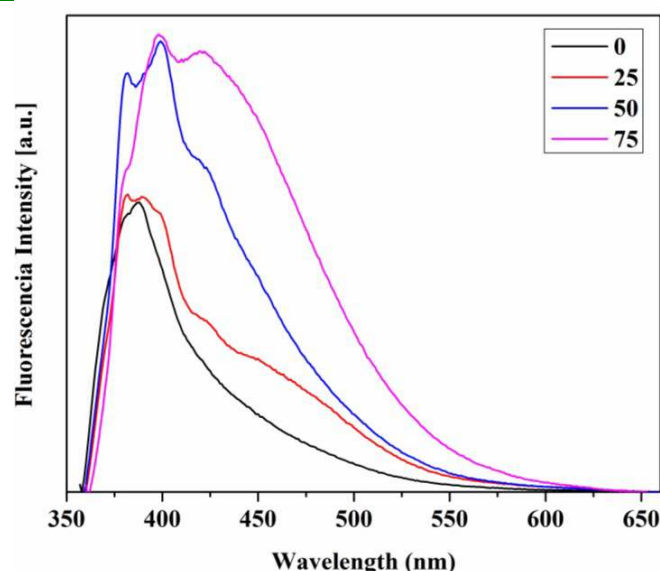


**Figure 2.** Emission spectra of compound **1** in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and THF at  $3.5 \times 10^{-5}$  M.

On the other hand, due to the molecule **1** presents free rotation across the aminopyridine group, the ability to stop this rotation in high viscosity medium and improved fluorescence quantum yield was evaluated, according to studies of fluorescent molecular rotors (FMR's) reported in the literature [27,28]. Fluorescence measurements of **1** in methanol/glycerol mixtures with different viscosities (% of glycerol) show that the fluorescent intensity increases with increasing solvent viscosity (Figure 3). The observed increase in fluorescence intensity of **1** is consistent with the restricted rotation of the aminopyridine group in the medium of high viscosity and dissipated energy by intramolecular rotation, and the photoactivated molecule might relax by nonradiative decay processes [28,29].

**Table 3.** Photophysical properties in binary mixtures of methanol and glycerol.

Glycerol fraction (v/v)	$\lambda_{\max}$ [nm]	$\lambda_{\text{em}}$ [nm]	$\Phi$ (%)
0	273, 360	390	1.82
25	273, 359	381	1.73
50	273, 362	381	2.83
75	273, 360	398	3.58



**Figure 3.** Fluorescence spectra of compound **1** in binary mixtures of methanol and glycerol in different ratios.

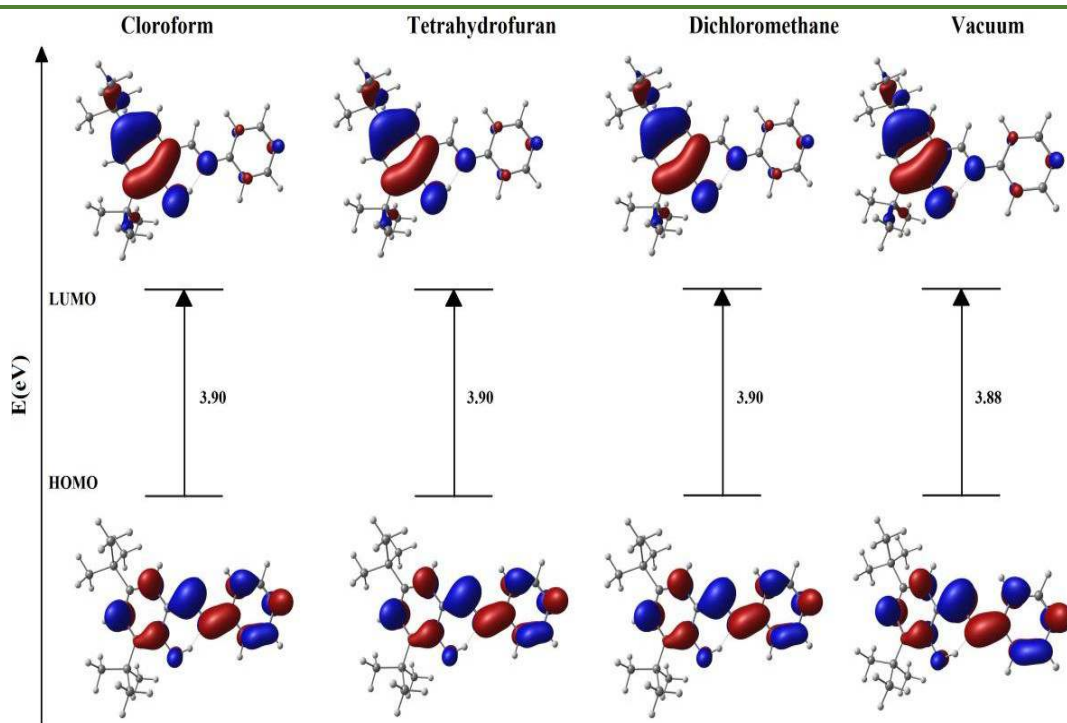
### 3.3 DFT Calculations

We have located the lowest energy structure of compound **1**, using the B3LYP/6-31G(d,p) method. Subsequently, we have calculated the energies of the rotation barriers, and the UV-Vis spectra, in order to compare the values with those obtained in laboratory. UV-vis spectra calculations were carried out without solvent and with the solvents involved in the

lab experiments. The obtained data are collected in Table 4. The results shown in Table 5 are very similar to those obtained experimentally. The calculated absorption values are almost 10 units above the experimental ones. Structures calculated with solvent do not have significant difference. The value of the excited state belongs to the transition from HOMO orbital toward LUMO orbital, which can be observed in Figure 4. The band gap is the same in all cases with solvent ( $\Delta E = 3.90$  eV), while in vacuum it is 3.88 eV.

**Table 4.** Electronic transitions calculated at B3LY/6-31G(d,p) in vacuum and with different solvents.

Solvent	Excited State	Coefficient	$E_{calc}$ [eV]	$\lambda_{calc}$ [nm]
Vacuum	HOMO $\rightarrow$ LUMO	0.69682	3.37	367.65
Chloroform	HOMO $\rightarrow$ LUMO	0.70032	3.35	369.58
THF	HOMO $\rightarrow$ LUMO	0.70012	3.36	368.87
Dichloromethane	HOMO $\rightarrow$ LUMO	0.70020	3.36	368.83



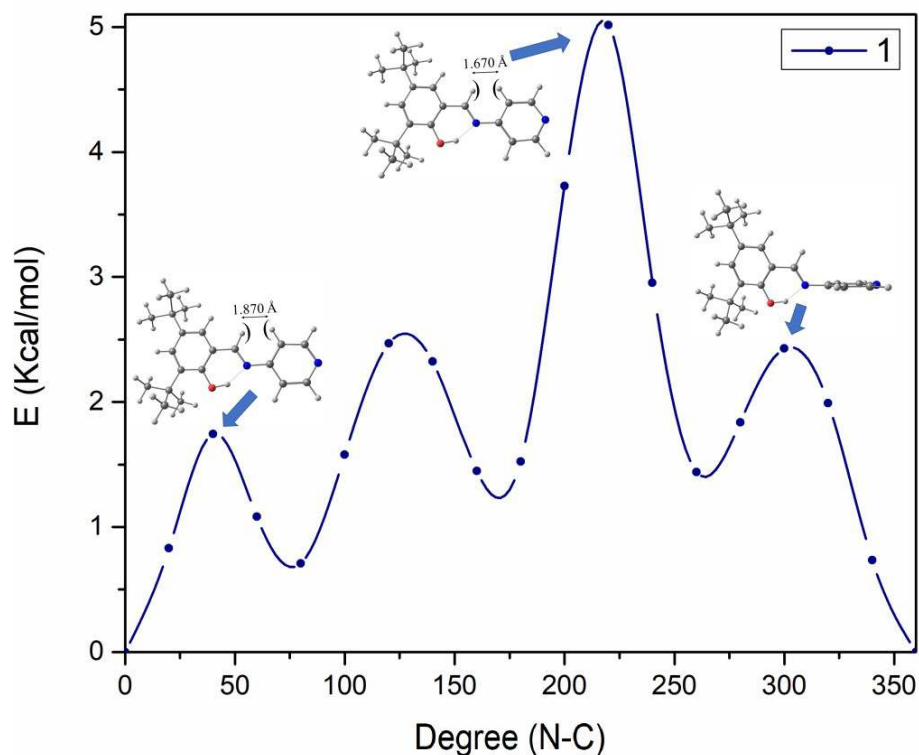
**Figure 4.** Energy diagram of HOMO and LUMO orbitals. Energy values are given in eV.

On the other hand, the structure was evaluated by rotating the pyridinic ring every  $20^\circ$ , of which four relevant energies can be seen, at  $40^\circ$ ,  $120^\circ$ ,  $220^\circ$  and  $300^\circ$ , with associated energies of 1.74, 2.46, 5.01 and 2.42 kcal/mol, respectively. Structures at  $40^\circ$  and  $220^\circ$  are in a coplanar arrangement, however, have different energies, this is due to the repulsion of the hydrogens in position 6-2 ( $40^\circ$ ) and 6-4 ( $220^\circ$ ), with distances of 1.87 and 1.67, and

energies of 1.74 and 5.01 kcal/mol, respectively (Figure 5). The dihedral angle (C6-N2-C3-C2) of the X-ray structure and the optimized structure are 40.2 and 36.8°, respectively.

#### 4. Conclusions

In summary, a comparative study of ultrasound, mechanochemical, and microwave-assisted synthesis of compound **1** was developed, where the last route gave best chemical yield (94 %) in a short time (20 min). Remarkably, compound **1** presents dual-stimuli responsive: solvato- and viscochromism. The asymmetric Schiff base showed solvatochromic behavior influenced by the solvent polarizability. In addition, compound **1** acts as a fluorescent molecular rotor (FMR) exhibiting the ability to detect viscosity, where the fluorescent intensity increases up to twice with increasing solvent viscosity. By DFT calculations, UV-Vis spectra were computationally determined for **1**, without presenting a great difference with that obtained experimentally. Also, the excellent properties as a molecular rotor was demonstrated computationally, due to the aminopyridine ring has a rotational restriction of less than 5 kcal/mol.



**Figure 5.** Rotation barrier energies of complex **1**.

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**Authors' Contributions.** A. A. M. P.: synthesis, experiments, and manuscript writing; V. M. J. P.: experiments and data treatment; J. A. L. C; measurements of fluorescence; A. L. S. Y. RMN analysis; M. S.: computational calculations; B. M. M. F.: study design and manuscript writing.



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**Data Availability.** The data used to support the findings of this study are included within the article.

Compliance with ethical standards

**Competing Interests.** The authors declare no competing interests.

**Ethical Approval.** Not applicable.

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