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# Synthesis and DFT calculations of linear and nonlinear optical responses of novel 2-thioxo-3-N,(4-methylphenyl) thiazolidine-4 one

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#### ABSTRACT

The aim of this work is to present results of both experimental and theoretical studies of 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one. In this paper, we present the chemical synthesis of 2-thioxo-3-N, (4-methylphenyl) thiazolidine 4-one followed by spectroscopy study. The applying of <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR), ultraviolet-visible (UV-vis) spectroscopy, performed its structural characterization. UV-vis measurements showed absorption between 250 and 350 nm. The optical gap energy is calculated using the Tauc method, which comes out to be around 3.91 eV. Density functional theory (DFT) computations were adopted for the geometry optimization of this compound and to evaluate their static polarizability (the mean polarizability  $\langle \alpha \rangle$  and the polarizability anisotropy  $\Delta \alpha$ ) and static first hyperpolarizability (the electric field-induced second harmonic generation (EFISHG)  $\beta_{//}$  and the hyper–Rayleigh scattering (HRS)  $\beta_{\text{HRS}}$ ) using several functionals. These static electrical properties are studied in detail. An inverse relation between the first hyperpolarizability and the HOMO-LUMO gap has been obtained for the 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one. Based on these results, we can conclude that the synthesized molecule is considered as a good candidate for optoelectronic device applications.

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# 1. Introduction

Rhodanine is a five–membered heterocyclic molecule containing a thioxo group on second carbon and the carbonyl group on fourth carbon with thiazole nucleus. Many molecules are designed and synthesized due to the various possibilities of structural derivatives of the rhodanine ring [1,2]. Since the past ten years, the number of patents and scientific publications describing a plenty of the different biological applications of rhodanine–based compounds are increasing continuously. Rhodanine has been found to possess various biological activities, such as anticancer, antidiabetic, antibacterial, antifungal, anti–infective, pesticidal, antimycobacterial, antineoplastic, and so on [3,4]. They also show antimalarial activities, anti–human immunodeficiency virus (HIV) and antitubercular.

Here we present a bibliographic study on rhodanine–based synthetic materials for medical and physical applications. Derivatives of rhodanine can be used as anticancer. For these applications, novel purine–pyrazole hybrids combining thiazoles, thiazolidinones and rhodanines, were designed and tested as inhibitors. These compounds are potential anticancer and antioxidant agents [1,5–7]. 4–thiazolidinones subtypes [3], 5–isopropylidiene derivatives of 3–dimethyl–2–thio hydantoin, 3–ethyl–2–thio–2, 4–oxazolidinedione, and 5–benzilidene–3–ethyl rhodanine are powerful against leukemic cell line in a concentration–dependent manner [1]. For antibacterial activity, many derivatives rhodanine compounds are presented for a wide spectrum bactericidal agents, furanyl–substituted rhodanine derivatives, rhodanine derivatives containing various substituents at the N3 and C5 positions, arylhydrazone derivatives bearing a rhodanine moiety, 5–aryloxypyrazole derivatives, pyrazole–substituted derivatives bearing rhodanine–3–fatty acid moieties, rhodanine–3–acetic acid derivatives, allyl rhodanine azo dye derivatives [3] are designed, synthesized and tested on large groups of bacteria [1]. For the antifungal activity, rhodanine–3–acetic acid derivatives and a series of benzylidene–rhodanines acting as antifungal agents are reported [1-8]. For the antidiabetic activity, the dispiropyrrolidine derivatives of rhodanine which are found to exhibit attractive antidiabetic properties.

In other hand, rhodanine derivatives have several physical applications. Heterocyclic compounds containing five membered rings with nitrogen, sulfur, and oxygen atoms have been investigated since a long time for their important properties. Among these heterocycles, there are the thiazoles, which are an important class. Recently, the push-pull effects of thiazolidinone compounds have been receiving big attention of chemists and physicists for their linear and nonlinear optical (NLO) properties [9-14]. Similar compounds attract attention such as chalcone and derivative for optoelectronic applications studied using combined experimental and theoretical studies [15-17]. These studies explore the potential of these compounds and its derivatives as efficient NLO-phores. A very simple-structured nonfullerene acceptor consisting of a bithiophene core and octyl-substituted rhodanine can be used in the photovoltaic cells [8]. Photovoltaic properties are also investigating with simple-structured non-fullerene acceptor containing alkoxy substituted benzothiadiazole and a rhodanine [18]. Other applications for these kinds of compounds, rhodanine-3-acetic acid can be used in dye-sensitized solar cell as an acceptor group [19]. Supramolecular self-assembly is one of the powerful approaches for the development of dynamic functional soft materials. For optoelectronic properties, supramolecular columnar self-assembly of wedge-shaped rhodanine based dyes is synthesized. This material has a small  $\pi$ -conjugated functional organic molecule capable of forming supramolecular columnar self-assembly [20]. These kinds of molecules can be used as a Red emissive sensor for discriminative detection of  $\mathrm{Ag^{+}}$  and  $\mathrm{Hg^{2+}}$  ions in buffer-free aqueous solutions. For this application, triarylamine rhodanine derivatives are synthetized and tested [21]. Good thermal like our compound, chemical stability, and the control chromophore-chromophore interactions in the solid state, can increase the HRS and EFISH hyperpolarizability measured for unsymmetrical polymethine dyes [22]. These factors possess the required characteristics for electro-optical applications. In the same state, Kong et al. [23] showed that EFISH measurements reveal unprecedented hyperpolarizabilities of twisted  $\pi$ -electron system. Their studies provide quantitative NLO information on the extent of aggregation. The measurement of HRS hyperpolarizabilities for solid-state materials show that the aggregation in the solid state undoubtedly affects the conformation and hence the hyperpolarizability  $\beta$  of the material [24]. Several experimental studies [25-27] of NLO properties in solid state show that the HRS measurements in solid state facilitate the comprehension of the orientational correlation between NLO chromophores in the film.

# 2. Results and discussion

# 2.1. Optical properties

In this work, the energy gap is calculated from the UV–vis spectrum (see Figure S1). An absorption maximum at more than 4 eV (corresponding to the near ultraviolet region) was observed, which highlights the  $\pi - \pi^*$  transition between the highest occupied and the lowest unoccupied electron band of this compound. As shown in Figure S1, the UV–vis



**Figure 1.** Absorption spectrum of 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one as a function of the energy.

spectroscopy confirms that the synthesized compound has a good optical absorption with tunable intensities and regions.

Figure 1 shows the evolution curves of the absorption coefficient  $\alpha$  of the synthesis compound as a function of the incident photon energy E. Referring to this figure; we calculated the band gap energy ( $\Delta \varepsilon$ ) using a Tauc plot method [28–31] based on the linear adjustment of the X-axis intercept, which comes out to be around 3.91 eV. It should be noted that we used a quartz cell with 10 mm thick to obtain the Absorption spectrum. This calculated  $\Delta \varepsilon$  value reflects the semiconductor nature of the 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one.

The absorption spectrum reveals that the 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one, capable of absorbing visible radiation. Therefore, it can be very suitable for optoelectronic device applications.

### 2.2. Static electrical properties results

#### 2.2.1. Computational details

The geometry of this compound has been optimized at the B3LYP functional [32] using the 6–311 + G(d,p) basis set implemented in Gaussian 09 [33]. The optimized molecular geometry and their coordinates are showed in Figure S5 and Table S1, respectively. The Gaussian 09 suite of programs [33] was used for all static electrical properties calculations. The GaussView 5.1 program [34] was used to visualize the structure and HOMO and LUMO orbitals. We are interested in calculating and studying theoretically the dipole moment  $\mu$ , the static polarizability  $\alpha$  and the static first hyperpolarizability  $\beta$  of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one. For  $\alpha$ , we calculated the mean polarizability  $\langle \alpha \rangle$  and the polarizability anisotropy  $\Delta \alpha$ . For the static first hyperpolarizability  $\beta$ , we are interested in the values of the EFISHG  $\beta_{//}$  and the HRS phenomena  $\beta_{\text{HRS}}$ . The B3LYP functional is usually considered a gateway choice to predict the NLO properties of small molecules [35]. The calculation of these static electrical properties was performed using several DFT functionals (PBE0, B3PW91 [36], B3LYP [32], CAM–B3LYP [37], M06 [38], M05–2X and M06–2X [39]). Several theoretical studies showed that corrected XC functionals are more reliable compared to traditional functionals to predict polarizability and first hyperpolarizability [40–42]. For the EFISHG,  $\beta_{//}$  is the central quantity, the vector component of  $\beta$  projected along the dipole moment axis (multiplied by a factor of 3/5),

$$\beta_{//}(-2\omega;\omega,\omega) = \beta_{//} = \frac{1}{5} \sum_{i} \frac{\mu_i}{|\vec{\mu}|} \sum_{j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$
(1)

In the static limits, the component  $\beta_{ijj} = \beta_{jij} = \beta_{jji}$ and so,

$$\beta_{//} = \frac{3}{5} \sum_{i=x,y,z} \frac{\mu_i \beta_i}{|\vec{\mu}|}$$
(2)

$$|\vec{\mu}|$$
 is the norm of the dipole moment

 $\mu_i$  and  $\beta_i$  the *i*th components of the  $\mu$  and  $\beta$  vectors, respectively, with:

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$$

and

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zzz}$$

All these contributions ( $\beta_{xxx}$ ,  $\beta_{xxy}$ ,  $\beta_{xyy}$ ,  $\beta_{yyy}$ ,  $\beta_{xxz}$ ,  $\beta_{yyz}$ ,  $\beta_{xzz}$ ,  $\beta_{yzz}$  and  $\beta_{zzz}$ ) can be calculated using Gaussian 09 [33]. We provide in Table S2 in SI each value as taken from output file for all eight DFT calculations.

In HRS, the depolarization ratios DR were also calculated. For a non–polarized incident signal, and for the reason that both polarizations are detected with equal sensitivity, the orientational average over  $\beta$  is

$$|\beta_{\rm HRS}| = \sqrt{\beta_{\rm HRS}^2} = \sqrt{\beta_{ZZZ}^2 + \beta_{ZXX}^2}$$
(3)

and

$$DR = \frac{I_{VV}^{2\omega}}{I_{HV}^{2\omega}} = \frac{\beta_{ZZZ}^2}{\beta_{ZXX}^2}$$
(4)

 $\langle \beta_{ZZZ}^2 \rangle$  and  $\langle \beta_{ZXX}^2 \rangle$  are orientational averages of the  $\beta$  tensor components, describing the HRS intensities when the incident light is vertically or horizontally polarized, respectively. These two invariants  $\langle \beta_{ZZZ}^2 \rangle$  and  $\langle \beta_{ZXX}^2 \rangle$  are calculated without assuming Kleinman's

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conditions and are defined as [43]:

$$\beta_{ZZZ}^{2} = \frac{1}{7} \sum_{\zeta}^{x,y,z} \beta_{\zeta\zeta\zeta}^{2} + \frac{4}{35} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta}^{2} + \frac{2}{35} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\zeta} \beta_{\zeta\eta\eta} + \frac{4}{35} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\eta\zeta\zeta} \beta_{\zeta\zeta\eta} + \frac{4}{35} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\eta\zeta\zeta} \beta_{\zeta\eta\eta} + \frac{4}{35} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\eta\varepsilon\varepsilon} + \frac{1}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\eta\varepsilon\varepsilon} + \frac{1}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\eta\zeta\zeta} \beta_{\eta\varepsilon\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\eta} \beta_{\eta\varepsilon\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\eta} \beta_{\eta\varepsilon\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\eta\varepsilon} \beta_{\eta\eta\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\eta\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\eta\varepsilon} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} \beta_{\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} \beta_{\zeta\zeta\eta} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,y,z} + \frac{4}{105} \sum_{\zeta\neq\eta}^{x,$$

$$-\frac{2}{105}\sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z}\beta_{\zeta\zeta\eta}\beta_{\eta\varepsilon\varepsilon} + \frac{2}{35}\sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z}\beta_{\zeta\eta\varepsilon}^2 - \frac{2}{105}\sum_{\zeta\neq\eta\neq\varepsilon}^{x,y,z}\beta_{\zeta\eta\varepsilon}\beta_{\eta\zeta\varepsilon}$$
(5)

#### 2.2.2. Dipole moment

The dipole moment values obtained using B3LYP/6–311 + G(d,p) level act in parallel with the hyperpolarizability results (Table 1). We can see that the dipole moment values obtained with the M06 functional are systematically smaller than those obtained with other functionals. The results show that by using hybrid functionals B3LYP, PBE0 and B3PW91, the  $\mu$  values are in the range of 1.62–1.77 D. In fact, the PBE0 functional gives the high dipole moment value.

The variations of the dipole moment as a function of the exchange–correlation functionals (B3LYP, PBE0, B3PW91, CAM–B3LYP,  $\omega$ B97X–D, M06, M05–2X and M06–2X) attain 15%. Kulinich et al. [44] showed that the dipole moment of rhodanine derivatives increases under excitation. In this paper, we calculate dipole moment at the ground state and not under excitation.

$\frac{1}{1}$						
	μ	$\langle \alpha \rangle$	$ \alpha $	$eta_{//}$	$\beta_{ m tot}$	$eta_{HRS}$ (DR)
B3LYP	1.62	167.89	75.55	-234.24	435.45	212.56 (3.61)
	1.64 <sup>a</sup>	171.28 <sup>a</sup>			509.71 <sup>a</sup>	212.56 (3.61)
PBE0	1.77	173.12	82.67	-281.34	535.42	248.17 (3.97)
B3PW91	1.69	166.14	75.62	-230.17	427.73	206.52 (3.37)
CAM-B3LYP	1.61	164.11	70.15	-208.71	363.72	192.61 (2.88)
ωB97X–D	1.69	163.91	70.17	-228.24	396.63	200.66 (3.10)
M06	1.25	167.39	75.42	-234.27	434.44	210.87 (3.34)
M05–2X	1.56	163.26	71.17	-223.59	381.06	190.75 (3.22)
M06–2X	1.59	163.78	71.52	-204.66	349.76	188.00 (2.82)
<sup>a</sup> [52].						

**Table 1.** Dipole moment  $\mu$ , mean polarizability  $\langle \alpha \rangle$ , anisotropy polarizability  $|\alpha|$ , gas phase EFISHG  $\beta_{//}$ , the HRS first hyperpolarizability  $\beta_{\text{HRS}}$  and the depolarization ratios DR obtained using eight DFT functionals at 6–311 + G(d,p) basis set.

#### 2.2.3. Polarizability

The average polarizability was calculated using the polarizability components by the formula

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{6}$$

and the anisotropy of polarizability by the formula:

$$|\Delta \alpha| = \sqrt{\frac{1}{2}} \left[ ((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2) \right]$$
(7)

Using several DFT functionals at the same 6-311 + G(d,p) basis set, the mean polarizability values  $\alpha$  for the 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one is shown in Table 1. The analysis of the results in Table 1 shows that, similarly for dipole moments, the values of the polarizability  $\alpha$  depend on the method used. By using the B3LYP, PBE0 and B3PW91 functionals, the  $\alpha$  values are in the range of 166–173 a.u. The corrected functionals CAM-B3LYP and  $\omega$ B97X-D display  $\alpha$  value in the range of 163–164 a.u. Not a significant difference between the results obtained with the two functionals M05–2X and M06–2X.

Unusual enhancement of the mean polarizability  $\langle \alpha \rangle$  and the anisotropy polarizability  $\Delta \alpha$  is shown using the Perdew–Burke–Ernzerhof (PBE0) calculation. Theoretical papers [45,46] show the efficiency of the PBE0 functional to predict mean polarizability  $\langle \alpha \rangle$  and the anisotropy polarizability  $\Delta \alpha$ . A PBE0 calculation is more appropriate according to the paper of Adamo et al. [45]. In addition, Sabirov et al. [46] showed that for all the studied multi-cage nanostructures, the PBE0 functional gives polarizability with high accuracy and are in perfect agreement with the measured values. Our results show that, when passing from the traditional functionals B3LYP, PBE0 and B3PW91 to the long-range functionals CAM–B3LYP and  $\omega$ B97X–D, small changes are observed. In the case of C<sub>60</sub> [47], the PBE0 polarizability value is in extraordinary agreement with the experimental value using experimental photoabsorption cross sections and the density-of-states technique. The authors showed that this functional gives accurate polarizability compared to other DFT functionals used in their paper and MP2 level. Other examples of the reliability of the PBE0 functional to reproduces the polarizability values like the work of Hornberger et al. [48] and Sabirov et al. [49], the authors showed that the PBE0 method reproduces the measured  $\Delta \alpha$  of fullerene halogenides (C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub>).

#### 2.2.4. Hyperpolarizability

It is well known that conjugated molecules generally have a much larger NLO effect than unconjugated molecules, indicating a dominant contribution of  $\pi$ -delocalized electrons.

For the  $\beta_{\text{HRS}}$ , the average  $\langle \beta_{\text{HRS}} \rangle$  made on the equiprobable orientations taken by a molecule. The calculations hyperpolarizability show that the contributions along the *x*-axis are the majority, also, because *x*-axis is the major charge transfer axis in our designed compound. The molecule is placed in the *xy*-plane with the groups along the *x*-axis (Figure 2).

In our compound, the theoretically calculated  $\beta$  values for the 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one (Table 1 and Figure 3) are 5.8 times larger than the values for hyperpolarizability of urea [50]. Bureš [51] showed in their study of



Figure 2. Orientation of the studied molecular system during calculations.



**Figure 3.**  $\beta_{//}$  (left) and  $\beta_{\text{HRS}}$  (right) of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one determined at different levels of approximation.

structure–properties relationships in push–pull compounds that compounds with thiazol acceptor have high first hyperpolarizability  $\beta$ . Indeed, the author showed that substitution of 4–nitrophenyl by the 5–nitrothiazole and 6–nitrobenzo[d]thiazole increase the first hyperpolarizability  $\beta$  values from 50 to 70 esu. He noted that push–pull compounds connected to thiazol acceptor are thermally stable (near to 300°C). In this paper, we also confirmed that the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one is thermally stable.

Due to their important charge distribution and high first hyperpolarizabilities  $\beta$  of this type of molecular framework, recent studies [52,53] have shown the importance of rhodanine derivatives in the synthesis and design of NLO compounds. Anbarasan *et al.* [52] have shown that the total first hyperpolarizability value of the (E)-5-benzylidine-2-thioxothiazolidine-4-one (E5BTTO) is twelve times greater than

that of urea. Their obtained total first hyperpolarizability results are in good accordance with our results for the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one using the same B3LYP/6–311 + G(d,p) level of theory. Indeed, the obtained dipole moment  $\mu$  and the mean polarizability  $\langle \alpha \rangle$  obtained for the rhodanine derivative (E5BTTO) [52] are in perfect accordance with our results (Table 1). The study [52] shows the importance of the presence of rhodanine derivatives in materials for the NLO applications. If we compare the results obtained with the different functionals, we find that are little differences between the functionals CAM–B3LYP, M05–2X and M06–2X. The same assessment has been obtained by Hadji and Champagne [54] in their detailed study of the HRS first hyperpolarizability  $\beta_{\text{HRS}}$  using several DFT functionals. The authors showed that the  $\beta_{\text{HRS}}$  values obtained using M05–2X and M06–2X DFT functionals at the same aug–cc–pVDZ basis set are quite similar. In this study, the PBE0 functional contains amount 40% of HF exchange displays the highest first hyperpolarizability  $\beta_{\text{HRS}}$  values, whereas, the M06–2X DFT functional, which contains amount 54% of HF exchange, gives the smallest  $\beta_{\text{HRS}}$  values (Table 1 and Figure 3).

Among the NLO applications that have been investigated for rhodanine derivatives, we can cite the study of Svetlichnyi *et al.* [55]. The authors showed the suitability of rhodanine derivatives for NLO applications using two–photon absorption investigations. Indeed, the study [55] showed that the two–photon absorption cross sections of two rhodanine derivatives are measured and equal to 115 and 125 GM, respectively. Our static first hyperpolarizability calculations show that the  $\beta_{\text{HRS}}$  is inversely proportional to the  $\beta_{//}$  values. The  $\beta_{\text{HRS}}$  values of 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one is 248.17 a.u. using M06–2X/6–311 + G(d,p) calculation, which is the lowest  $\beta_{\text{HRS}}$  value obtained for this rhodanine derivative, while the  $\beta_{//}$  value of the same compound becomes the largest (–204.66 a.u.) using the same calculation level (Table 1 and Figure 3).

A similar situation is found for the depolarization ratios DR. The DFT functionals used in this work give close DR values for the same studied compound. Their DR values range from 3 to 4 using M06–2X and PBE0 levels, respectively. These data, in combination with the chemical topology of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one structure, is congruent with the representative C<sub>s</sub> molecular point group. Indeed, in general, the DR property covers a broad range of octupolar-dipolar characters of compounds; this factor makes it possible to characterize the microscopic symmetry of the molecule when it has a few elements of the non-zero hyperpolarizability tensor.

#### 2.3. Frontier Molecular Orbitals (FMOs) and their energy gaps

This theoretical study showed that the gap|HOMO–LUMO| or ( $\Delta \varepsilon$ ) varied from 2.80 to 8.31 eV using PBE0 and  $\omega$ B97X–D functionals (Table 2 and Figure 4), respectively, which implies the eventual charge transfer interaction–taking place within the rhodanine derivative: The 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one studied in this work. The low  $\Delta \varepsilon$  value (2.80 eV) has been obtained using the PBE0 level at the 6–311 + G(d,p) basis set. Good agreement has been obtained between the experimental obtained values using the Tauc plot method [28–31] noted above ( $\Delta \varepsilon_{exp} = 3.91 \text{ eV}$ ) and their obtained using theoretical levels B3LYP, B3PW91 and the PBE0 functionals at 6–311 + G(d,p) basis set ( $\Delta \varepsilon_{PBE0} = 4.38$ , 2.80 and 4.74 eV), respectively. Recent theoretical study [56] of the  $\beta_{HRS}$ 

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**Figure 4.** HOMO and LUMO orbitals of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one and their  $\Delta \varepsilon$  (in eV) estimated by several DFT functionals at the 6–311 + G(d,p) basis set.

and the gap|HOMO–LUMO| of heteroleptic bis–cyclometalated iridium(III) complex containing 2–phenylpyridine and picolinate ligands showed that the PBE0 functional gives similar experimental gap values compared to CAM–B3LYP and M06–2X levels. The same assessment has been obtained in this study.

According to the FMOs illustrated in the Figure 4, the electron density in HOMO is delocalized on the cycle carries the two sulfur atoms and the phenyl. Both functionals PBE0, B3LYP, M05–2X and M06–2X well represent this delocalization (Figure 4). Whereas, all

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	E <sub>HOMO</sub>	E LUMO	gap HOMO–LUMO	$\beta_{\rm HRS}$
B3LYP	-6.14	-1.76	4.38	212.56
PBE0	-5.19	-2.39	2.80	248.17
B3PW91	-6.26	-1.85	4.74	206.52
CAM-B3LYP	-7.70	-0.51	7.18	192.61
ωB97X–D	-8.29	0.01	8.31	200.66
M06	-6.34	-1.52	4.81	210.87
M05–2X	-7.70	-0.73	6.96	190.75
M06-2X	-7.64	-0.81	6.83	188.00
Exp			3.91	

**Table 2.** HOMO, LUMO, gap|HOMO–LUMO| and the  $\beta_{\text{HRS}}$  obtained using eight DFT levels at the 6–311 + G(d,p) basis set.

DFT functionals used in this paper showed that the electron density of the LUMO is localized on the cycle carries the two sulfur atoms. The study showed that higher values of the  $\beta_{\text{HRS}}$  as well as lower energy gap ( $\Delta \varepsilon$ ) for the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one (Table 2). Therefore, an inverse relation between the gap|HOMO–LUMO| and the HRS first hyperpolarizability  $\beta_{\text{HRS}}$  has been obtained. The same findings were obtained in our previous studies [54,56–58].

#### 3. Experimental section

#### 3.1. Synthesis of 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one

The synthesis of the title compound was performed according to Schemes 1 and 2. The synthesis was carried out in two steps; the first is to produce dithiocarbamate salt as follows. 0.1 mole of paratoulidine (a) was introduced into 10 ml of triethylamine. After, 0.11 mole of carbon disulfide was added to form the N paramethyltoulidine triethylammonium dithiocarbamate (b). The resulting solid was washed and dried to be used in the second step.

The dithiocarbamate salt (**b**) was solubilized in 50 ml of water with magnetic stirring for one hour at 0°C. Sodium chloroacetate was then added. The mixture is put ender mechanical stirring for 15 min at 0°C. Concentrated HCl (0.1-0.2 N) was added to acidify the medium. The reaction mixture was refluxed ender ( $100^{\circ}$ C).

The precipitate was filtered off to give the title compound with a moderate yield 65%. The melting point of this compound is 152°C.



Scheme 1. Synthesis of N paramethyltoulidine triethylammonium dithiocarbamate.



Scheme 2. Synthesis of 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one (C).

# 3.2. Spectroscopic data of 2-thioxo-3-N, (4-methylphenyl) thiazolidine-4-one

Electronic spectra were recorded on a spectrum instrument SP–UV 200 S spectrophotometer with quartz cell of 10 mm at 25°C. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured in CDCl<sub>3</sub> and TMS with a Bruker AC–DPX–200 (300 MHz) spectrometer at 25°C. The UV–vis analysis and NMR characterizations of the synthesized molecule are as follows and presented in Figure S2, Figure S3, Figure S4 and Figure S5.

NMR <sup>1</sup>H (300 MHz, CDCl<sub>3</sub>/TMS)  $\delta$ ppm, J Hz: 2.44 (s, 3H); 4.17 (s, 2H); 7.21–7.35 (dd, 4H, AB, J = 7.75). NMR <sup>13</sup>C (300 MHz, CDCl<sub>3</sub>/TMS)  $\delta$ ppm: 21.42 (CH<sub>3</sub>); 36.46 (CH<sub>2</sub>); (128.07;130.41;132.41;140.03)(C-aryl); 173.61 (C = S); 201.52 (C = O).

UV-visible  $\lambda$ (nm): 264 (C = C); 304 (C = S).

# 4. Conclusions

In this paper, we have reported synthesis of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one that has been characterized by means <sup>1</sup>H and <sup>13</sup>C NMR, UV–vis spectroscopy. The synthesis was carried out in two steps; the first is to produce dithiocarbamate then the second for obtaining the final product. The optical gap energy is calculated using the Tauc method, which comes out to be around 3.91 eV.

On the other hand, a theoretical calculation of the NLO properties of the 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one was performed theoretically by using DFT computations. For this we are using eight functionals at the 6–311 + G(d,p) basis set. The high values of the obtained HRS first hyperpolarizabilities  $\beta_{\text{HRS}}$  show the suitability of this rhodanine in the NLO field, where the  $\beta$  values for 2–thioxo–3–N, (4–methylphenyl) thiazolidine–4–one is 5.8 times greater than that of urea using PBE0/6–311 + G(d,p) calculation. The PBE0 functional gives the highest HRS first hyperpolarizability  $\beta_{\text{HRS}}$ , and the lowest gap|HOMO – LUMO| compared to other functionals used in this study. An inverse relationship between the two properties ( $\Delta \varepsilon$  and  $\beta_{\text{HRS}}$ ) was obtained. The B3LYP functional performed better to estimate the gap|HOMO – LUMO|, indeed, a small difference was obtained between the calculated values ( $\Delta \varepsilon_{\text{B3LYP}}$ ) and that of the experiment. To enhance the first hyperpolarizability for this compound, a strategy consists in investigating the push–pull configuration, which is a rudimentary principle to design efficient NLO-phores, as this was carried out by Muhammad *et al.* [59–61] in the case of chalcone

derivatives and dinitrophenol derivatives [62]. These derivatives have already been synthesized and the structure-NLO property relationships were studied using DFT and TD–DFT functionals. Basing on the experimental and the theoretical study, we conclude that this compound appears to be potentially good candidates for application in the field of the solar cells and nonlinear optics.

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# **Disclosure statement**

No potential conflict of interest was reported by the author(s).

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