ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
https://www.icf.ro/rrch/

Rev. Roum. Chim.,
2022, *67*(4-5), 263–270
DOI: 10.33224/rrch.2022.67.4-5.05

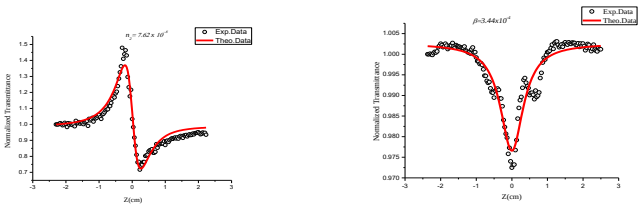
SYNTHESIS AND NONLINEAR OPTICAL PROPERTIES OF IONIC LIQUIDS LIKE BY Z-SCAN TECHNIQUE

Mohammed D. ZIDAN,[*,a] Atef ARFAN[b] and Ahmad ALLAHHAM[a]

[a] Department of Physics, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria
[b] Department of Chemistry, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria

Received November 28, 2019

A new 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate and 8-hydroxyquinolin-1-ium2-carboxybenzoate salts were synthesized, later, they were characterized using different spectroscopic techniques such as: UV–Visible, FTIR and NMR. Then, the nonlinear optical measurements were performed using single z-scan technique in order to determine the nonlinear optical absorption coefficient (β) and nonlinear refractive index (n_2) of the new ion liquid salts. The calculation of the 3rd order nonlinearity (χ^3) indicates that the group of thiazolidine-4-carboxylate has higher value than the carboxybenzoate. Our results allow us to propose these ionic liquids as good candidates for the development of nonlinear optical devices.



INTRODUCTION

Many optical applications have motivated the scientists to search for materials exhibiting nonlinear optical effects. The organic materials (OM) with large nonlinear optical response has attracted considerable attention to be used in different photonic applications.[1-4] Among the different kinds of the OM, a class of organic salts called ionic liquids (IL), which have been widely used in many fields such as: in catalysis,[5] batteries,[6] Nano-chemistry[7] and nanoparticles.[8] Recently, the investigations of a new organic ionic liquid systems (using z-scan technique) have been reported such as: ([BMI]BF4) and ([BMI]PF6),[9] Quinotoxine salts[10-12] and (8-HQ) salts.[13] However, the IL compounds have large nonlinear optical responses, but, their nonlinear optical properties are still under considerations.

It was reported about designing, synthesizing of new hybrid imidazole (benzimidazole) and pyridine (quinoline) derivatives.[14] These new compounds are core scaffolds widely present in many classes of drugs as well as various pharmacological activities. The structure of imidazole is a planar five-membered heterocyclic ring system with three carbon and two nitrogen atoms, and the benzimidazole is bicyclic in nature which consists of the fusion of benzene and imidazole. The heterocyclic quinoline is a fusion of benzene and pyridine. These ring systems are undoubtedly aromatic. So, certain possible modifications on the heterocyclic ring by the addition of diverse substituents may lead to new products with better biological profiles.[15]

The simple z-scan setup[16-17] has been used for estimating the nonlinear optical coefficients "the nonlinear optical refractive index (n_2) and the nonlinear optical absorption (β)". Continuing to our

* Corresponding author: Fax: +963116112289; E-mail: PScientific8@aec.org.sy (M. D. ZIDAN)

work on the ionic liquids, we have presented our results concerning the investigations of spectroscopic characterizations and the nonlinear optical properties of two 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate and 8-hydroxyquinolin-1-ium2-carboxybenzoate salts. To our knowledge, there is no report of studying the two salts using z-scan setup.

EXPERIMENTAL

1. Materials and procedures

All reactions and manipulations were carried out in air with reagent grade solvents. 8-hydroxyquinolin was purchased from MERCK and (R)-thiazolidine-4-carboxylic acid was purchased from MERCK. Phthalic acid was purchased from FLUKA and used as received. IR spectrum was recorded on a Jasco FTIR 300E instrument. ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra were recorded on a Bruker Bio spin 400 spectrometer The Ultra-Violet-Visible (UV-Vis) absorption spectrum was recorded in the wavelength range of 190-1100 nm using UV-1601 PC Shimadzo Spectrophotometer.

For the synthesis of **8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate (I)**, a mixture of 8-hydroxyquinolin (C_9H_7NO; 1 g, 6.9 mmol) and (R)-thiazolidine-4-carboxylic acid. ($C_4H_7NO_2S$; 0.9 g, 6.7 mmol) in 15 mL ethanol was prepared, and agitated well for 2 h at room temperature. The new solid product was separated by filtration and washed with ethanol to give the product (I) in 35% yield, the melting point was determined to be 198.5^0C.

Spectroscopic data

IR (KBr, n, cm^{-1}): 3173 (OH) , 1508 (COO^{-}); ^{1}H NMR (400 MHz, *DMSO-d6)* 2.78-2.98 (m, 2H), 3.73-3.98 (m, 3H), 7.08-7.10 (m, 1H), 7.37-7.45 (m,2H), 7.51-7.64 (m,1H), 8.29-8.32 (m,1H), 8.83-8.84 (m,1H).

^{13}C NMR (100 MHz, *DMSO-d6)d* ppm 35.45, 52.33, 69.45, 114.35, 119.15, 122.3 127.96, 129.62, 136.51., 138.90, 148.60, 173.4.

For the synthesis of **8-hydroxyquinolin-1-ium2-carboxybenzoate(II)** 8-hydroxyquinolin (C_9H_7NO; 1. g, 6.8 mmol) was added to phthalic acid ($C_8H_6O_4$; 0.64 g, 3.8 mmol) in 15 ml ethanol, the mixture was stirred at room temperature for 2 h. The product was separated and washed with ethanol in order to get the product **(II)** in 68% yield, the melting point was determined to be 130^0C.

Spectroscopic data

IR (KBr, n, cm^{-1}): 3423 (COOH), 1603 (COO^{-}).^{1}H NMR (400 MHz, *DMSO-d6)d* ppm 7.94-7.01 (m, 2H), 8.18-8.07 (m, 1H), 8.33 (dd, J = 8.34, 1.66 Hz, 2H), 8.56-8.48 (m, 4H), 8.66-8.57 (m, 1H), 8.84 (dd, J = 4.20, 1.66 Hz, 1H), 9.11-9.02 (m, 1H) ^{13}C NMR (100 MHz, *DMSO-d6*) ppm 111.92, 118.23, 122.31, 128.08, 128.91, 129.30, 131.21, 133.36, 136.92, 138.56, 148.45, 153.56, 169.14.

2. NMR, FTIR and UV-Vis characterizations

8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate **(I)** was purely isolated as: white powder and it was characterized by multi-nuclear NMR, FTIR. The spectroscopic data were very informative and consistent with the molecular structure of the product (Fig.1). The FTIR spectra (Fig. 2) show two characteristic bands at 3423cm^{-1} and 1603 cm^{-1}, that were assigned to the OH and COO^{-} groups, respectively.

The ^{1}H NMR spectrum shows seven region of complex peaks in ratio 1:3:1:2:1:1:1 for different proton environment represent different proton groups of 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate. The ^{13}C $\{^{1}H\}$ NMR spectrum gave twelve peaks that represented the C nuclei of the 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate.

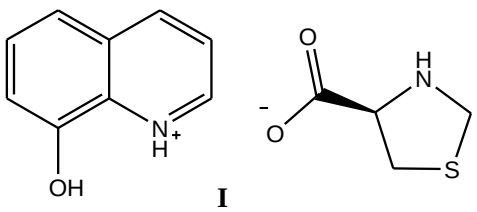
8-hydroxyquinolin-1-ium2-carboxybenzoate **(II)** was purely isolated as: yellow powder and characterized. In this case, two characteristic bands at 3423 1603 were identified and assigned to COOH and COO^{-} groups respectively. In addition, the spectrum of compound (II) was characterized by relatively high intensity absorption bands.

The ^{1}H NMR spectrum shows seven complex peaks for different proton groups that represented the H nuclei of the 8-hydroxyquinolin-1-ium2-carboxybenzoate.

The ^{13}C $\{^{1}H\}$ NMR spectrum shows thirteen singlets for Seventeen environmentally different C centers; that represented the C nuclei of the 8-hydroxyquinolin-1-ium2-carboxybenzoate were present.

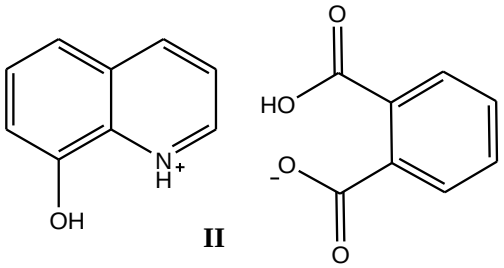
For briefing of the a new compounds names, the obtained white powder of 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate (I) is named as 8HQZCA salt, and the yellow powder of 8-hydroxyquinolin-1-ium2-carboxybenzoate (II) is named as 8HQPhAC salt.

Fig. 3 shows the UV-Vis absorption spectra of the 8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate and 8-hydroxyquinolin-1-ium2-carboxybenzoate (II). In the compound (I) spectrum, there are two maximum absorption peaks at 260 and 330 nm. While, the compound (II) shows two maximum absorption peaks around 250 and 320 nm. These bands are attributed to $\pi \rightarrow \pi^*$ transitions.[18-21]



I

8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate



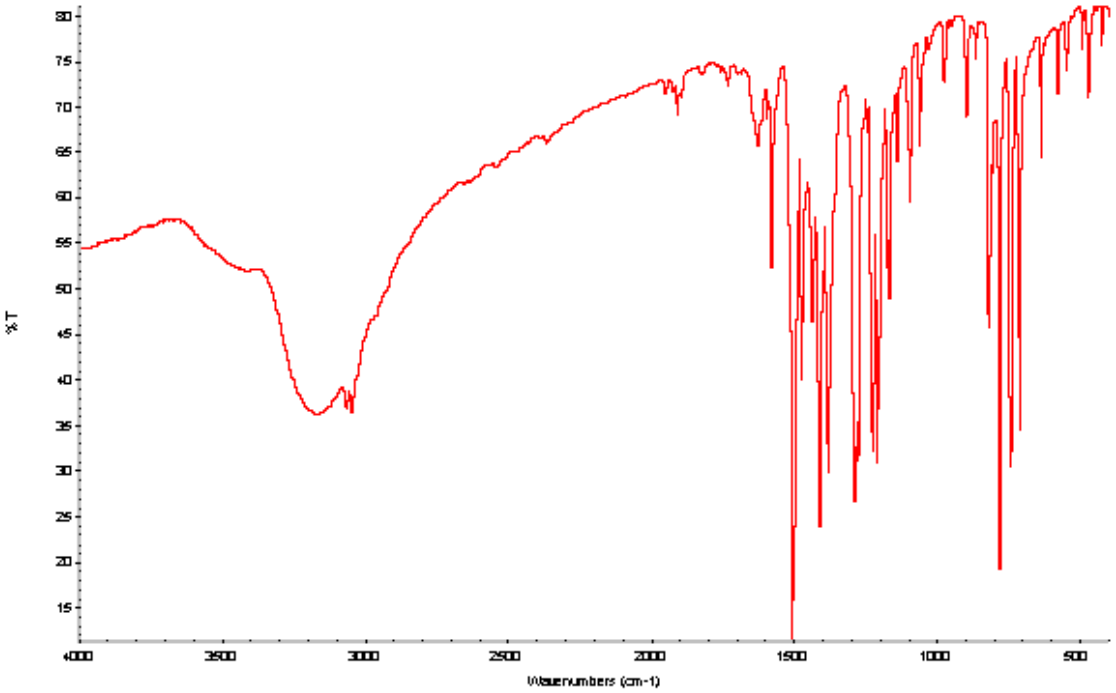
II

8-hydroxyquinolin-1-ium2-carboxybenzoate

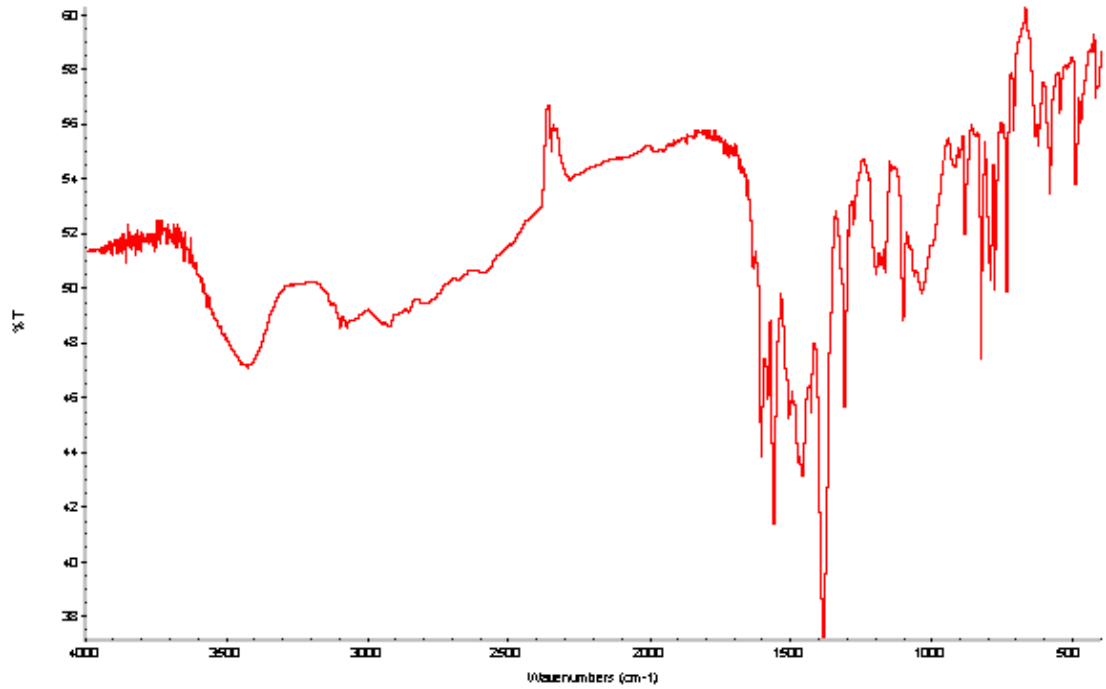
Fig. 1 – The molecular structure of 8HQZCA and 8HQPhAC salts.

3. Z-scan measurements

The present measurements were performed with similar experimental setup, which was used in our previous work[18]. The used laser model is **CUBE™** Diode Laser System, Coherent-635-30QE (I = 635 nm; the power is up to 26 mW). A special optical filter was inserted in front of the laser beam to get very good high quality TEM_{00} Gaussian beam. The z-scan measurements in an open aperture/closed aperture configurations were carried out with the input intensity of I_0=1134 W/cm^2. The new IL salts were dissolved in chloroform solvents to prepare new samples with concentrations of 10^{-3}M.



8-hydroxyquinolin-1-ium(R)-thiazolidine-4-carboxylate



8-hydroxyquinolin-1-ium2-carboxybenzoate (II)

Fig. 2 – The FTIR spectra of 8HQZCA salt (upper), and 8HQPhAC salt (lower).

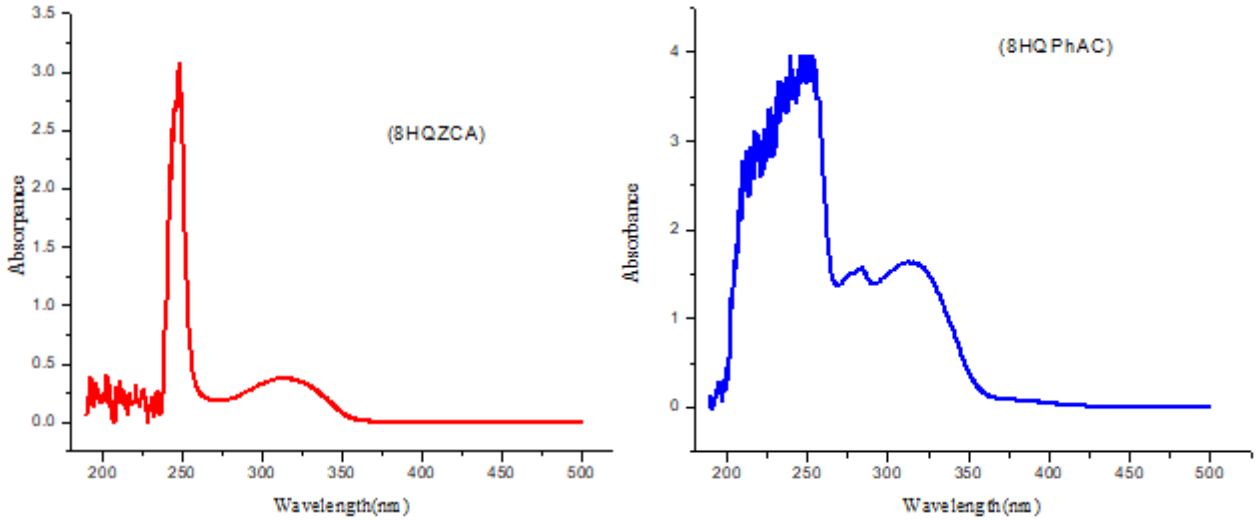


Fig. 3 – The UV-Vis absorption spectra of 8HQZCA salt (upper) and 8HQPhAC salt (lower).

RESULTS AND DISCUSSION

1. Nonlinear measurements

The z-scan setup was performed in the open-aperture (OA) configuration to estimate the nonlinear absorption coefficients "β". Figure 4 shows the normalized transmittance curves of the open aperture (OA) scan of 8HQZCA salt in Chloroform and 8HQPhAC salt in Ethanol with concentration at 10^{-3}M. The shape of the curve is symmetrical with respect to focal point (z=0), that indicates to the presence of nonlinear optical absorption (NLA) effect.

The NLA coefficient (β) was evaluated by fitting the experimental data of OA measurements to the following equation[22]:

$$T(z) = 1 - \frac{(I_0 L_{eff} \beta)}{[2^{\frac{3}{2}}(1+\frac{z^2}{z_0^2})]} \qquad (1)$$

here, $L_{eff} = (1- \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, α_0 is the linear absorption coefficient, $z_0 = \pi\omega^2_0/\lambda$ is diffraction length of the beam, λ is the laser wavelength, and I_0 is the laser intensity at z = 0. The symbols present the experimental data, while the "solid lines" is the fitting curves.

The shape of the curves reveal that the 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol exhibited a reverse saturable absorption (RSA) mechanism, when the $\sigma_{ex} >> \sigma_g$ (where the σ_g is cross-sections of the ground state and σ_{ex} is the excited state. However, RSA mechanism was explained in full details.[23-24] The σ_{ex} and σ_g at λ=635 nm were calculating according to ref.[20] and tabulated in Table 1. Our results have shown that the σ_{ex} is higher than the σ_g (all the values are tabulated in Table 1).

The closed-aperture (a small aperture is located in front of the detector) configuration was used to calculate the nonlinear refractive index (n_2). Usually, in the case of CA configuration, the data profile comes from two components: β and n_2. The division method[13] was applied to eliminate the effect of β. Our results (Figure 5) show the pure experimental data (the symbols) of the 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol at concentration of $10^{-3}M$. The fitting curves were obtained by inserting the experimental data into the following equation:[16-17]

$$T(z, \Delta\varphi) = 1 - \frac{4\,\Delta\varphi_0\ X}{(X^2+9)\,(X^2+1)} \qquad (2)$$

where is X = (Z/Z_0), and T is the normalized transmittance for the pure (n_2), and $\Delta\varphi_0$ is the on–axis nonlinear phase shift. The $\Delta\varphi_0$ can be inserted in the formula 3 to determine the value of n_2.

$$[n_2 = \frac{\lambda\,\Delta\varphi_0}{2\pi I_0 L_{eff}}] \qquad (3)$$

The value of $|\chi^3|$ was calculated from the real and the imaginary parts of the third-order nonlinear susceptibility $|\chi^3| = [Re(\chi^3)^2 + Im(\chi^3)^2]^{1/2}$.
where:

$$Re|\chi^3\ (esu)| = (10^{-4}\ \varepsilon_0 c^2 n_0^2/\pi)\ n_2\ (cm^2/w) \qquad (4)$$

and

$$Im|\chi^3\ (esu)| = (10^{-2}\ \varepsilon_0 c^2 n_0^2 \lambda/4\pi^2)\ \beta\ (cm/w) \qquad (5)$$

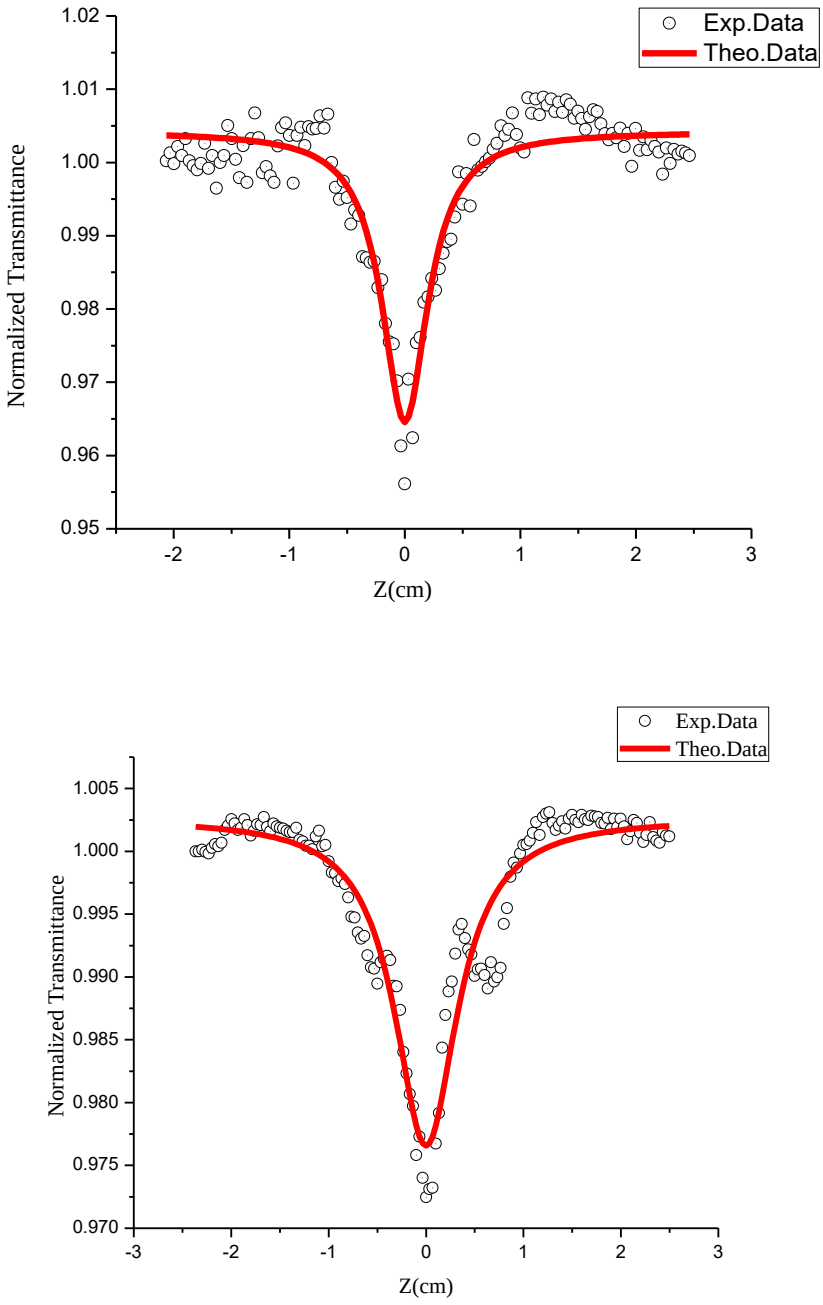


Fig. 4 – Open aperture z-scan data of 8HQZCA salt in chloroform (upper), and 8HQPhAC salt in ethanol (lower).

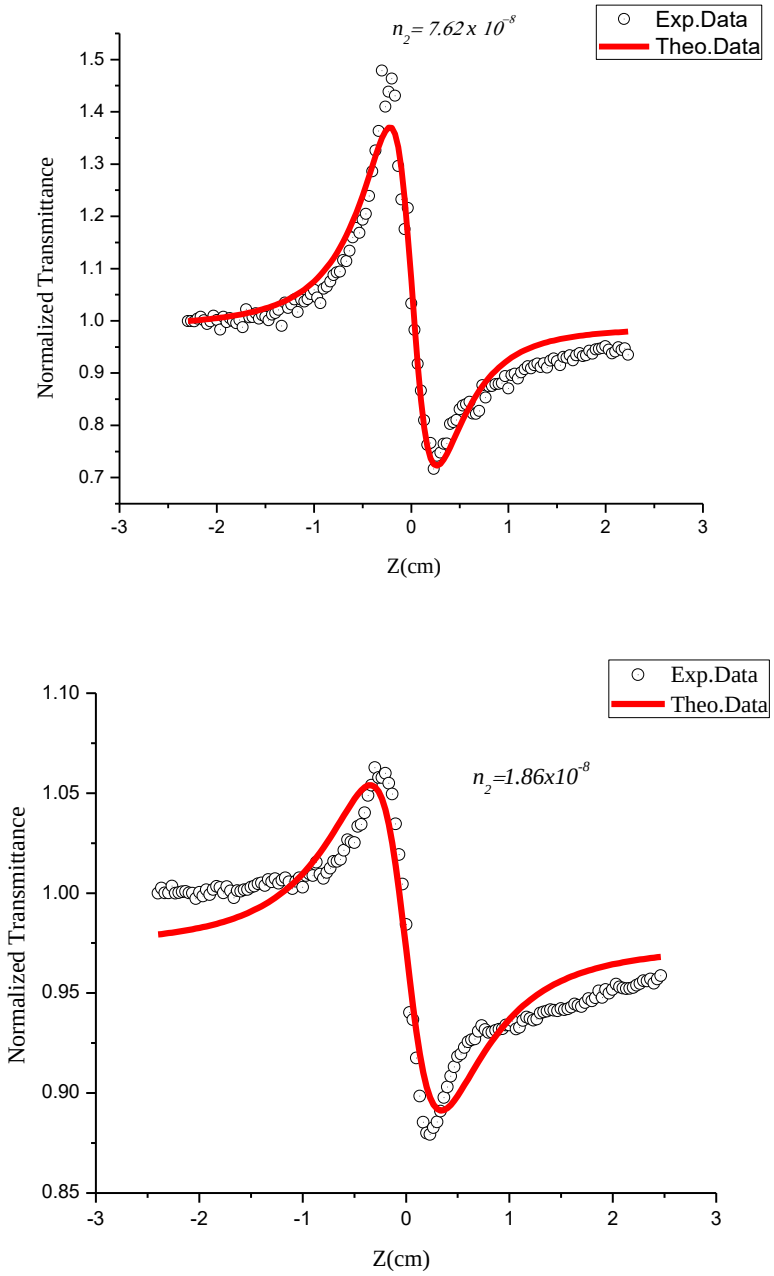


Fig. 5 – Close/open aperture z-scan data of 8HQZCA salt in chloroform (upper), and 8HQPhAC salt in ethanol (lower).

Table 1

The calculated nonlinear optical parameters of 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol at concentration of 10^{-3} *M*

Sample	**α_0 (cm^{-1})**	**n_0**	**n_2 (cm^2/W)**	**β (cm/W)**	**Re (χ^3) (esu)**	**Im (χ^3) (esu)**	**dn/dt×10^{-5}**	**σ_g (cm)**	**σ_{ex} (cm)**
8HQZCA salt in Chloroform	0. 783	**1.4394**	**7.62×10^{-8}**	**5.24×10^{-4}**	**4×10^{-6}**	**1.38×10^{-5}**	**5.23**	**1.3×10^{-18}**	**4.18×10^{-14}**
8HQPHAC salt in Ethanol	0. 422	**1.3557**	**1.86×10^{-8}**	**3.44×10^{-4}**	**8.66×10^{-7}**	**8.06×10^{-6}**	**3.14**	**7×10^{-19}**	**5.09×10^{-14}**

The values of α_0 and n_0 were determined by similar[23] and listed in Table 1. Also, the values of n_2, β, |Re χ^3| and |Im χ^3| are given in Table 1.

As the Figure 6 has peak-valley shape, this is indication to the negative value of n_2. This reveals that our sample is considered to be a self-defocusing material at the wavelength λ=635nm. The thermal lens effect is raised from absorption of tightly CW laser beam propagating through the absorbing medium producing a spatial distribution of temperature.[9] As the CW laser was used in our work, the present results indicate to the fact that the thermal lens effect is responsible for the obtained of the large optical nonlinearity in the studied salts. The term of n_2 is related to the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ by the following formula:

$$\left[\left(\frac{dn}{dT}\right) = \frac{4\, n_2 \kappa}{\alpha_0\, \omega_0^2}\right] \qquad (6)$$

where κ is the thermal conductivity of the solvent: κ =0.129 *(W/m K)* for the Chloroform and κ =0.171*(W/m K)* for the ethanol. The values of the $\left(\frac{dn}{dT}\right)$ of 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol are listed in Table 1.

To clarify the suitability of the materials for photonic devices, there are many requirements, such as: large Kerr nonlinearity, low linear and nonlinear losses and ultrafast response time. These requirements are expressed by two figures of merit, W (one photon) and T (two-photon):[26]

$$W = n_2 I/\alpha \qquad (7)$$

$$T = b\, I/n_2 \qquad (8)$$

The two figures of merit should have the following characteristics: W>>1 and T<<1. Our samples have given the following values: W= 1.74 and T=0.434 for 8HQZCA salt in chloroform, whereas: W= 0.79 and T= 1.16 for 8HQPHAC salt in ethanol. These satisfy the conditions of all optical switching. So, we can consider the 8HQZCA salt in chloroform suitable to be used in all-optical switching devices.

It well known, that the form of the molecular structure affects the NLO response of the 8HQZCA and 8HQPHAC salts.[27] And, it has been shown that the IL compounds show large optical nonlinearities due to their expanded of π-electron system. As we expected, our 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol show large third –order nonlinear optical properties due to the delocalized electronic states formed by $\pi \rightarrow \pi^*$.[28,29] Our sample (8HQZCA) is considered to be as good candidate for future application for photonic devices.

Our reported results for n_2 and β of the new 8HQZCA salt in chloroform and 8HQPhAC salt in ethanol are given in Table 1 which can be compared with others new values in literature for molecules with CW laser excitation.[9-12]

CONCLUSIONS

We have presented the z-scan measurements of novel 8HQZCA salt and 8HQPhAC salt, using a CW diode Laser at 635 nm wavelength. Depending on the experimental results, values of α_0, n_0, n_2, β, Re χ^3, and Im χ^3 are calculated. Our results show that 8HQZCA has better nonlinear optical properties than the 8HQPHAC salts. That may be due to presence of thiazolidine-4-carboxylate group. As well as, our measurements indicate that 8HQZCA and 8HQPhAC salts have negative sign of the nonlinear refractive index (n_2) at λ=635 nm wavelength with potential applications in optoelectronic devices.

Acknowledgements. The Authors would like to thank Prof. I. Othman for his permanent encouragement and support, also to Prof. M. K. Sabra and to Prof. A.W. Allaf for their useful discussions.

REFERENCES

1. P. Karuppasamy, T. Kamalesh, K. Anitha, S. Abdul Kalam, M. S. Pandian, P. Ramasamy, Sunil Verma and S. V. Rao, *Optical Materials*, **2018**, *84*, 475–489.
2. F. Mostaghni and Y. Abed, *Mater. Sci.-Poland*, **2018**, *36*, 445-451.
3. K. Rodriguez, A. Pérez and F. Racedo, *J. Physics: Conf. Series*, **2017**, *786*, 012004-012009.
4. S. Raghavendra, C. S. Chidankumar, A. Jayarama and S. M. Dharmaprakash, *Mater. Chem. Phys.*, **2015**, *149–150*, 487–494.
5. C. E. Song, *Chem. Commun.*, **2004**, *1033*, 43-48
6. T. E. Sutto, *J. Electrochem. Soc.*, **2007**, *154*, 101–107.
7. M. Antonietti, D. B. Kuang, B. Smarsly and Z. Yong, *Angew. Chem. Int. Edn*., **2004**, *43*, 4988–4992
8. J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner and S. R. Teixeira, *J. Am. Chem. Soc.*, **2002**, *124*, 4228–4229
9. R. F. Souza, M. A. R. C. Alencar, M. R. Meneghetti, J. Dupont and J. M. Hickmann, *J. Phys.: Condens. Matter*., **2008**, *20*,155102-155108.
10. M. D. Zidan, A. Arfan, A. Allahham and D. Naima, *Opt. Laser Tech*., **2016**, *76*, 85-90.

11. M. D. Zidan, A. Arfan and A. Allahham., *Opt. Laser Tech*., **2016**, *86*, 79-84.
12. M. D. Zidan, A. Arfan and A. Allahham, *Opt. Laser Tech.*, **2017**, *89*,137-142.
13. M. D. Zidan, A. Arfan and A. Allahham, *Spectrochim. Acta Part A: Molec. and Biomolec. Spectroscopy*, **2018**, *190*,135-139.
14. D. Mantu, V. Antoci, C. Moldoveanu, G. Zbancioc and I. I. Mangalagiu, *J. Enzyme Inhibition and Medicinal Chem.*, **2016**, *3*1, 96–103.
15. S. Maruthamuthu, S. Rajam, C. R. Stella, A. G. Bharathi Dileepan and R. Ranjith, *J. Chem. Pharm. Research*, **2016**, *8*, 505-526.
16. C. Bosshard, M. Bosch, I. I. Liakas, M. Jager and P. Gunter, "Second-Order Nonlinear Optical Organic Materials: Recent Developments", in "Nonlinear Optical Effects and Materials", Springer Verlag, New York, 2000, p. 163.
17. M. Bass, J. M. Enoch, E. W. Vanstryland and W. L.Wolfe, "Hand books of optics IV: fiber optics and nonlinear optics", McGraw-Hill, NewYork, 2001.
18. M. D. Zidan, A. W. Allaf, A. Allahham and A. AL-Zier, *Optik*, **2020**, *200*,163-175.
19. D. Jiang, S. Chen, Z. Xue, Y. Li, H. Liu, W. Yang, Y. Li, *Dye & Pigments*, **2016**, *125*, 100-105.
20. "Spectrometric Identification of Organic Compounds", 7th Edition Silverstein, R.M. and Webster, F.X. and Kiemle, Publisher Wiley, 2005.
21. A. Vlcek, *Coord. Chem. Rev.*, **2002**, *230*, 225–242.
22. S. Zafar, Z. H. Khan and M. S. Khan, *Spectrochim. Acta Part A: Molec. and Biomolec. Spectroscopy*, **2013**, *114*, 164-169.
23. P. G. L. Frobel, S.R. Suresh, S. Mayadevi, S. Sreeja, C. Mukherjee and C. I. Muneera, *Mater. Chem. Phys*., **2011**, *129*, 981-986.
24. A. K. C. A. Reis, D. R. Paiva, M. M. Reginato and S. I. Alves, "8th Iberoamerican Optics Meeting and 11th Latin American Meeting on Optics, Lasers, and Applications", M. Filipe and P. C. Martins Costa (Eds.), Porto, Portugal, 2013, p. 8785, 87853Q.
25. H. A. Badran, Q. M. Ali Hassan and A. Imran, *J. Mater. Sci.: Mater. Electron.*, **2015**, *26*, 5958-5963.
26. T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, S. Li, Y. Zhai, S. You, Q. Wang and J. Qin, *Chem. Phys. Lett.*, **2008**, *451*, 213–217.
27. Z. Li, F. Gao, Z. Xiao, G. Ao, X. Wu, Y. F., Z. Nie, T. Wei, J. Yang, Y. Wang, X. Zhang, J. Zuo and Y. Song , *Dyes and Pigments*, **2015**, *119*, 70-74.
28. G. Gasser, I. Ott and N. Metzler-Nolte, *J. Med. Chem*., **2011**, *54*, 3–25.
29. O. Novakova, H. Chen, O. Vrana, A. Rodger, P. J. Sadler and V. Brabec, *Biochemistry*, **2003**, *42*, 11544–11554.