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Nonlinear optical investigations of Quinine and Quinotoxine salts by *Z*-scan technique

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ABSTRACT

Z-scan technique was used to investigate the nonlinear optical properties of Quinine and 1-(carboxymethyl)-6-methoxy-4-(3-(3-vinylpiperidin-4-yl) propanoyl) quinolin-1-ium chloride (Quinotoxine) salts. The two salts were characterized using UV–visible, FTIR and NMR measurements. The characterization spectra confirm the expected molecular structure of the prepared "Quinotoxine " salt. The z-scan measurements were performed with a CW Diode laser at 635 nm wavelength and 26 mW power. The nonlinear absorption coefficient (β), nonlinear refractive index (n_2), the ground-state absorption cross sections (σ_g), the excited-state absorption cross sections (σ_{ex}) and thermo-optic coefficient of the samples were determined. Our results reveal that the σ_{ex} is higher than the σ_g indicating that the reverse saturable absorption (RSA) is the dominating mechanism for the observed absorption nonlinearities. The results suggest that this material should be considered as a promising candidate for future optical devices applications.

1. Introduction

The nonlinear optical properties of organic materials have attracted much attention in the past decades due to their potential applications in the development of photonic and optical devices, such as human eyes and optical sensors protection from high power laser pulses [1–4]. It is well known that the organic molecules with high π–electron delocalization can exhibit large nonlinear effects; arise from the interaction between light and electrons within individual molecular units, giving greater and faster nonlinear optical responses. The ionic organic compounds have several advantages such as: large nonlinear absorption hyperpolarizability, crystal structure controllability, high melting point and hardness when compared with the organic non-ionic compounds. These advantages have motivated many researchers to carry on more investigations related to the ionic organic materials [5,6].

Nonlinear optical properties of different organic materials have been characterized by z-scan technique, including: chalcones and their derivatives [7], and fullerenes [8,9], carbon nanotubes [10], organo-tellurium compounds [11], oxazol compounds [12] and red BS dye [13]. The single beam z-scan technique introduced by Sheik-Bahae et al. [14,15] is the simplest method to measure both the nonlinear absorption coefficient (NLA) and the nonlinear refractive index (NLR). This method is considered to be sensitive to all nonlinear optical mechanisms that give rise to a change of the refractive index and absorption coefficient.

The present article reports on the use of z-scan technique at 635 nm to measure the 3rd nonlinear optical properties of Quinine and Quinotoxine (as a new salt) in ethanol. To our knowledge, there is no report of an investigation of the z-scan measurements of Quinine and Quinotoxine.

2. Experimental techniques

2.1. Materials and methods

All reactions and manipulations were carried out in air with reagent grade solvents. Quinine was purchased from FLUKA, Chloroacetic acid was purchased from MERCK and used as received. IR spectra were recorded on a Jasco FT-IR 300E instrument using the KBr method and the DTGS detector, at a resolution of 4 cm^{-1} and a total of 64 scans in the wave number range from 400 to 4000 cm^{-1}. A background spectrum was subtracted in each collection. ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra were recorded on a Bruker Bio spin 400 spectrometer a solution of 2% (w/v) was prepared in D_2O. The Ultra-Violet-Visible (UV–Vis) absorption spectrum was recorded in the wavelength range 190–1100 nm using UV–vis1601 PC Shimadzu Spectrophotometer.

For the synthesis of **1-(carboxymethyl)-6-methoxy-4-(3-(3-vinylpiperidin-4-yl)propanoyl)quinolin-1-ium chloride**

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(Quinotoxine**)**, a mixture of Quinine ($C_{20}H_{24}N_2O_2$; 0.5 g, 1.5 mmol) was added to Chloroacetic acid ($C_2H_3ClO_2$; 0.14 g, 1.5 mmol) in 25 mL chloroform, the mixture was refluxed for 72 h. The precipitant was isolated by filtration, and purified by recrystallization from absolute ethanol to produce the product 0f Quinotoxine in 78% yield.

IR (KBr, ν, cm^{-1}): 3404 (OH), 1730 (COOH), 1699 (-CO-), 1617 (C=C); ^{1}H NMR (400 MHz, D_2O) δ ppm 1.36–1.9 (m, 6H), 2.03 (m, 2H), 2.6–2.8 (m, 2H), 3.7 (s, 2H), 3.83 (d, *J*=15.44 Hz, 2H), 4.0 (s, 3H), 5.0–5.2 (m, 2H), 5.4–5.6 (m, 1H), 6.98–7.10 (m, 1H), 7.5–7.6 (m, 1H), 7.98–8.06 (m, 1H), 8.10–8.19 (m, 1H), 9.03–9.1 (m, 1H). ^{13}C NMR (100 MHz, D_2O) δ ppm 25.99, 26.1, 34.73, 36.21, 39.01, 46.31, 56.17, 56.85, 67.31, 105.03, 116.36, 120.55, 122.87, 127.16, 133.54, 137.91, 140.50, 145.89,146.55, 160.24, 176.14, 204.4.

2.2. Z-scan measurements

In order to investigate the nonlinear optical properties of the samples, the single beam z-scan technique was applied. A linearly polarized TEM_{00} Gaussian beam from the CW diode laser (λ=635 nm, with 26 mW) was used as the excitation source. The laser beam was focused using a 7.5 cm converging lens. The radius of the beam (ω_0) and Rayleigh length (z_0) were 27 μm and 3.6 mm respectively. The radius of the aperture (r_a) was 0.4 mm and the radius of the beam waist (ω_a) on the aperture was 1.25 mm. The sample cell was 2 mm thick quartz, which was fixed on a computer-controlled translation stage is precisely moved through the focal region of the laser beam over a length of 6 cm. At the same time, the reference beam energy, and transmitted beam energy were measured using an energy meters (Thorlabs PM300E). Consequently the detected signals were acquired, stored, and later on processed by a computer. The studied samples were prepared by an accurately weighed amount of the Quinine and Quinotoxine salts and dissolving them in ethanol to obtain samples of a concentration of 10^{-3} M. The ethanol was used as a solvent because the Quinine and Quinotoxine salts can only be dissolved in ethanol. The z-scan experimental set-up was analogous to that described in Ref. [16], the molecular structure of the Quinine and Quinotoxine in Fig. 1.

3. Results and discussion

3.1. NMR, FTIR and UV–vis characterizations

Quinotoxine was isolated as russet powder and characterized by multi-nuclear NMR, FTIR and UV–vis spectroscopies (see experimental). The reaction was followed by the FTIR spectroscopy, and this is shown in Fig. 2, the spectrum of the Quinotoxine reveals the presence of four characteristic bands at 3404, 1730, 1699 and 1617 cm^{-1}, that are assigned to the OH, COOH, (–C=O), and (C=C) groups, respectively. The presence of the new carbonyl group at 1699 cm^{-1} is indicative of rearrangement of the Quinine molecule. The ^{13}C{1H} NMR spectrum gave twenty-two singlets for twenty-two environmentally different C centers, a peak at 67.31 (CH_2 of carboxymethyl), and two peaks at 176.14, 204.4 that represented the C nuclei of the COOH and CO groups [17]. This confirms the previous FTIR analysis.

The UV–vis absorption spectrum of Quinine in ethanol (Fig. 3) shows three maximum absorption peaks centered at 246, 282 and 335 nm. While, for the Quinotoxine in ethanol (Fig. 3), there are three maximum absorption peaks at 263, 324, and 475 nm. These peaks are assigned to π→π* transitions [18,19].

3.2. Nonlinear measurements

In the present investigation, z-scan experiments were performed in order to determine the nonlinear absorption coefficient β, without aperture (or with open aperture "OA") and the nonlinear refractive index n_2 (with closed aperture "CA") of Quinine and Quinotoxine solutions at an input intensity of I_0=700 W/cm^2.

3.2.1. Open aperture

In open aperture z-scan experiment, the transmitted light measured by the detector is sensitive only to the intensity variation. The open aperture data of Quinine and Quinotoxine salts in ethanol at concentration of 10^{-3} M are shown in Fig. 4. Here, the transmission is symmetric with respect to focus (z=0), where it reaches a minimum value, showing intensity dependent absorption effect.

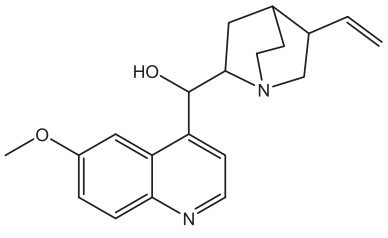
The nonlinear absorption coefficient β can be obtained from a best fitting performed on the open-aperture measurements of normalized transmittance with the following equation [14,15]:

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{\frac{3}{2}}} \quad (1)$$

For $q_0 < 1$, Where q_0 (z) is a parameter function of I_0, L_{eff} and β:

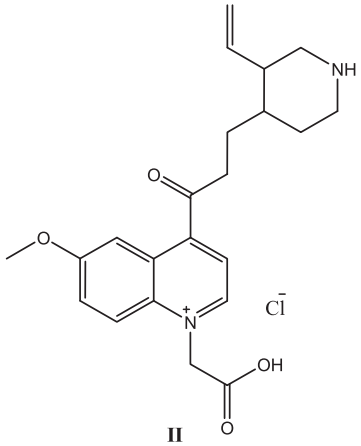
$$q_0(z) = \frac{I_0 L_{eff} \beta}{\left(1 + \frac{z^2}{z_0^2}\right)} \quad (2)$$

Solving the summation and for $\alpha_0 \ll 1$;



I

Quinine



II

1-(carboxymethyl)-6-methoxy-4-(3-(3-vinylpiperidin-4-yl)propanoyl)quinolin-1-ium chloride

Fig. 1. Molecular structure of (I) Quinine and Quinotoxine.