



NLO properties of 1, 4-naphthoquinone, Juglone and Lawsone by DFT and Z-scan technique – A detailed study



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ARTICLE INFO

Article history:

Received 17 May 2017

Received in revised form

26 June 2017

Accepted 28 June 2017

Keywords:

1, 4-Naphthoquinone

Lawsone

Juglone

Nonlinear optical

DFT

Z-scan

ABSTRACT

1, 4-Naphthoquinone, 2-hydroxy-1,4-naphthoquinone (Lawsone) and 5-hydroxy-1,4-naphthoquinone (Juglone) have been investigated for their nonlinear optical (NLO) properties using Z-scan technique and Density Functional Theory (DFT) method. The Z-scan results show that all the three compounds have appreciable NLO properties. Among the three molecules Juglone showed the highest static hyperpolarizability value. The functional CAM-B3LYP performed better than BHHLYP and B3LYP in computing NLO properties. Solvent environment plays a decisive role in NLO properties of naphthoquinone derivatives. Polar solvent environment enhanced the NLO characteristics.

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1. Introduction

Extensive use of sensitive spectrophotometers and high-power lasers in various applications have triggered interest in the search for materials with linear and nonlinear optical (NLO) properties [1–4].

Studies in organic dyes possessing nonlinear optical (NLO) properties have been an active area of research [5–8]. Organic natural dyes exhibit NLO properties and have a distinct scope in the field of optical storage, optical switching, optical communications and harmonic generation, optical power limiting and optical computing [4,9–13]. The natural dyes possess a large molecular hyperpolarizability due to their electron delocalisation along the conjugated system, and they have large nonlinearities having nonlinear coefficients of 10^4 – 10^6 times higher than that of carbon disulphide [14].

Electric field induced second harmonic generation (EFISHG), hyper-Rayleigh scattering (HRS) often at the Nd: YAG fundamental

wavelength (1064 nm) or elsewhere in the near infrared, involving femtosecond laser pulses, Z-scan techniques and solvatochromic methods are used for the experimental measurement of NLO properties [14–23].

Theoretical computations have been employed in recent years as an *a priori* tool to compute the NLO properties of organic molecules alongside the other experimental methods [8,24,25]. The computational methods are beneficial as we get the prior understanding of the influence structure in relation to the properties and the factors governing the efficiency of NLO properties, such as the contribution of the donor/acceptor fragments within the molecule as well as the solvent effects [8,26–28].

For the measurement of nonlinear refractive index and nonlinear absorption coefficients Z-scan method has become a standard tool due to its simplicity, its immediate indication of the sign type of nonlinearity, its high sensitivity [16,29,30]. Sheik-Bahae et al. originally proposed the technique and has been implemented since then to the study of several nonlinear composite glasses and semiconductor materials. Many organic compounds including natural dyes (conjugated π -electron systems) such as anthocyanin [31], bixa orellana [32], chlorophyll [33], laccic acid dye [14,34], carotenoids [35], betanines [17,36], curcumin

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[8] and hibiscus sabdarifa [37,38] have been investigated through these techniques these techniques which have with a conjugated π -electronic system.

Studies carried out over the last three decades show that the high molecular nonlinearities can be achieved if a molecule contains donor and acceptor groups connected through the π -electron delocalized bridge [39–42]. By increasing the donor-acceptor capability of the substitutions attached to the π -conjugated system, nonlinearity can be increased. The position of the substitutions is of vital important in terms of NLO activity [43]. Donor substitute quinonoid compound are likely to have appreciable NLO properties. Anthraquinone derivatives have been studied for their NLO properties [44–46].

Naphthoquinone derivatives such as 1, 4 Naphthoquinone, 5-hydroxy-1, 4-naphthoquinone (Juglone) and 2-hydroxy-1, 4-naphthoquinone (Lawsone) (Fig. 1) have the conjugated π -electrons and likely to be good NLOphores. So we have studied here naphthoquinone and their derivatives.

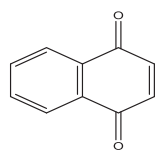
In this study, we have evaluated NLO properties of these three molecules using the functionals, B3LYP, CAM-B3LYP and BHHLYP in combination with the three basis sets 6-311+G (d), 6-311++G (d) and 6-311++G (d, p) in eleven solvent environments in order to study the NLO behaviour under solvent microenvironment, as well as to understand the basis set and functional dependence on the NLO properties of naphthoquinone derivatives. We have also done the z-scan measurements to assess the NLO properties of these dyes in three solvents.

2. Computational procedure

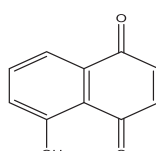
The ground state (S_0) geometry of the dyes under investigation was optimized in vacuum using DFT method. We have calculated the static first hyperpolarizability (β_0) and its related properties (μ , α_0 , α , γ) by employing three DFT functionals with different percentage of Hartree-Fock (HF) exchange. It is highly demanding that there is the proper functional in computational approach to calculate the molecular hyperpolarizability. The functionals used are the choice of hybrid functional which uses a fixed amount of exchange at all interelectronic distances or a long-range corrected (LC) functional which uses a larger fraction of generalised gradient approximation (GGA) DFT exchange at short range and larger fraction of exact exchange at long range interelectronic distances [47–49]. Self-consistent reaction field (SCRf) incorporated in the Polarizable Continuum Model (PCM) was used for all the computations in solvents of different polarities [25,50].

The complete equations (equations (1)–(5)) for calculating the magnitude of total static dipole moment (μ), the mean polarizability (α_0), the anisotropy of the polarizability (α), the mean first hyperpolarizability (β) and static second hyperpolarizability (γ), using the x, y, z components are defined as [51–53].

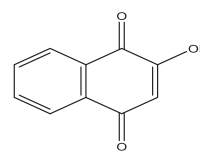
$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$



Naphthoquinone



Juglone



Lawsone

Fig. 1. Structure of 1, 4 Naphthoquinone, juglone (5-hydroxy-1, 4-naphthoquinone) and lawsone (2-hydroxy-1, 4-naphthoquinone).

$$\alpha_0 = (1/3)[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad (2)$$

$$\alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2} \quad (3)$$

$$\beta_{\text{total}} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2 \right] \quad (4)$$

$$\gamma = (1/5) \left[(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx}) \right] \quad (5)$$

The total static dipole moment (μ), the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$), the mean first hyperpolarizability (β) and static second hyperpolarizability (γ), of the Juglone, Lawsone and 1, 4-Naphthoquinone in different solvent environments were calculated using Equations (1)–(5). The results obtained are summarised in [Supplementary information](#). The computations were carried out using Gaussian 09 program [54].

3. Result and discussion

3.1. Choice of functionals and basis sets

It has been known that DFT functionals with a large fraction of HF (like BHHLYP) and RSHs (like CAM-B3LYP) perform with semi-quantitative precision and a reasonable computational while the global hybrid B3LYP overestimates the hyperpolarizability values [28,55,56]. The CAM-B3LYP functional [47], uses coulomb-attenuating method and includes 19% and 65% of short- and long-range HF exchange with $m = 0.3$ adding a long-range correction, and it is therefore appropriate for the computation of molecular NLO properties of large systems.

In [Table 1](#), we list the total static first hyperpolarizabilities (β_{tot}), polarizability (α_0) and dipole moment (μ) computed at B3LYP, BHHLYP and CAM-B3LYP levels of theory for Lawsone, Juglone, and naphthoquinone. The β_{tot} values are functional-dependent but they show a similar trend ([Fig. 2a](#)). Among the three functionals, the B3LYP functional overestimates the β_{tot} values for all the three molecules under investigation. The overestimation of the hyperpolarizabilities is expected due to the incorrect electric field dependence of the “response part” of the exchange–correlation potential, which lacks a linear term counteracting the applied electric field [57,58]. Further, one can easily see that the increasing percentage of Hartree–Fock (HF) exchange within the hybrid DFT methods results in a monotonic decrease of β_{tot} values in the order: B3LYP (20%HF exchange) > BHHLYP (50% HF exchange). The amount of HF exchange in hybrid DFT is relation to the variation of β_{tot} values are reported [59–61].

Contrariwise, the β_{tot} values obtained using long-range correction functionals (CAM-B3LYP) are noticeably smaller than those obtained with B3LYP.

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