



# Synthesis, structural characterization and optical nonlinear properties of two azo- $\beta$ -diketones



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## ABSTRACT

Synthesis, structural characterization and Density Functional Theory (DFT) studies of two azo- $\beta$ -diketones, (3-((4-bromophenyl)diazenyl)pentane-2,4-dione and 2-((4-bromophenyl) diazenyl)-1-phenylbutane-1,3-dione prepared by coupling reaction of dizonium salt of 4-bromoaniline with acetylacetone and benzoylacetone. The products are characterized by FTIR, Mass, <sup>1</sup>H NMR and <sup>13</sup>CNMR spectra. Density Functional Theory with B3LYP method in the level of basis sets 6-311 G (d,p) is used to optimize the geometry of the synthesized azo- $\beta$ -diketone dyes. The energy of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and  $\Delta E$  gap energies from the DFT/B3LYP - 6-311G(d,p) basis set are calculated. The lower value for  $\Delta E$  (HOMO-LUMO) gap energy is 0.14756 eV of the first compound. The Z-scan method is adopted to study the optical nonlinear properties of the two compounds using a continuous wave laser beam at 473 nm wavelength. The two compounds showed high nonlinear refractive indexes of the order of  $10^{-8}$  cm<sup>2</sup>/W. We showed that the origin of nonlinearity of the two samples is thermal. The two compounds showed the properties of the optical limiter with limiting threshold values of 15.5 and 16.7 mW respectively. A mechanism for the optical limiter that the two samples showed is discussed.

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## 1. Introduction

Continuous efforts in the search and/or synthesis of new materials are in progress during the last three decades, required in a wide range of applications viz., optical high density storage, optical computing, optical communications, all-optical modulation, optical limiting, optical switching, optical delays, etc. [1-26].

The light induced index of refraction changes of a medium usually described by the relation that relate the medium index of refraction,  $n$ , in the presence of the laser beam, the linear index of refraction,  $n_0$ , the intensity of laser beam,  $I$ , and the nonlinear index of refraction,  $n_2$ , as follows:

$$n = n_0 + n_2 I \quad (1)$$

( $\pm$ ) signs refer to self-focusing and self-defocusing respectively. The  $n_2$  contains number of nonlinear optical effects viz., grating induced by the laser beam, optical switching, self-phase modulation, optical bi-stability, self-diffraction, self-focusing, self-defocusing

and optical soliton. The refractive index can be altered by the absorption of part of the incident laser beam energy which is due to non-radiative decays that transferred to heat in the shape of bell Gaussian distribution of the laser beam. A gradient in the heat occurs due to the thermal conduction effect. A refractive index gradient resulted from the temperature profile which can be related to the nonlinear medium thermo-optic coefficient.

Vast number of materials were found to show, under irradiation with laser beam, induced refractive indexes, viz., liquid crystals [27], fullerenes [28], curcumin and its derivatives [29-31], organic materials [32,33], etc., using three different methods viz., diffraction ring pattern [34], thermal lens [35] and Z-scan [36,37]. The first one required a change in the laser beam phase of  $\geq 2\pi$  radians while the second and third ones required that a change in the laser beam phase less than  $2\pi$  radians.

Para bromo aniline and its derivatives have received much attention in different directions viz., in minor method for measuring pentoses [38], in electrochemical polymerization and analysis of some aniline derivatives [39], in third order nonlinear optical materials [40], morphology and photovoltaic properties [41], as a novel nonlinear optical material with a (3 + 1)-dimensional incommensurately modulated structure [42], in nano composite thin

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