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Optical nonlinearity of D-A-π-D and D-A-π-A type of new chalcones for potential applications in optical limiting and density functional theory studies

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ABSTRACT

Two new chalcones namely, (2*E*)-1-(3-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one and (2*E*)-3-(4-chlorophenyl)-1-(3-fluoro-4-methoxyphenyl)prop-2-en-1-one were synthesized and grown as single crystals by slow evaporation technique in methanol. The FTIR spectrum recorded confirms the presence of functional groups in these materials. The molecular conformation of the compounds was achieved by single crystal X-ray diffraction studies. The thermal stability of the crystals was determined from TGA/DSC curve. The third order optical nonlinearity of the chalcone compounds in DMF solution has been carried out using an Nd:YAG laser at 532 nm as the source of excitation. The nonlinear optical response was characterized by measuring the intensity dependent refractive index n_2 of the medium using Z-scan technique. It is seen that the molecules exhibit a negative (defocusing) nonlinearity and large nonlinear refractive index of the order of -1.8×10^{-11} esu. The third-order nonlinearity of the studied chalcones is dominated by nonlinear refraction, which leads to strong optical limiting of laser. The result reveals that these two new chalcone molecules would be a promising material for optical limiting applications. In addition, the optimized molecular geometry, vibrational frequencies in gas, and the Molecular Electrostatic Potential (MEP) surface parameters of the two molecules were calculated using DFT/B3LYP method with 6–311++G(d,p) basis set in ground state. All the theoretical calculations were found in good agreement with experimental data.

1. Introduction

A large number of nonlinear optical (NLO) organic molecules with delocalized electron and conjugated double bond systems and a large dipole moment have been developed due to their prominent applications in optical limiting and optical switching [1–3]. Optical limiting is a NLO process in which the transmitted intensity of a material decreases with increased incident light intensity. Optical limiting performance will be enhanced by coupling two or more of the NLO mechanisms. Excited state absorption (ESA) and reverse saturable absorption (RSA) are the most common mechanisms for the NLO behavior of organic materials [4]. NLO effects can be employed for the design and performance of optical limiter [5–7]. It has been demonstrated that optical limiting can be used for the protection of eyes and sensors from intense lasers [8]. Chalcones are of great interest because their structure can be tailored to

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enhance their optical nonlinearity. In chalcones, the nonlinearity arises because of the delocalization of 'π' electrons in the structure. In this paper, the optical nonlinearity and optical limiting action of chalcone molecules in DMF solvent was studied using Nd:YAG laser operating at the wavelength of 532 nm in nanosecond regime. In addition, quantum chemical calculations were used to gain a better understanding on the molecular and electronic structures, and vibrational spectra of (2*E*)-1-(3-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (FMOC-3) and (2*E*)-3-(4-chlorophenyl)-1-(3-fluoro-4-methoxyphenyl)prop-2- en-1-one (FMOC-7) focusing on the comparison of calculated and the experimental results.

2. Experimental

2.1. Synthesis

The target chalcone compounds were synthesized by standard Claisen Schmidt condensation method [9–11]. The reactants were purchased from Sigma Aldrich. 1-(3-fluoro-4-methoxyphenyl) ethanone (0.01 mol), 4-dimethoxybenzaldehyde (0.01 mol), and 4-chlorobenzaldehyde (0.01 mol) were used to prepare FMOC-3 and FMOC-7 respectively. The mixture was dissolved in 20 cm^3 methanol; a catalytic amount of sodium hydroxide (NaOH) was added drop-wise to the solution with vigorous stirring. The reaction mixture was stirred for about 4 h at ambient temperature. The progress of the reaction was monitored by Thin Layer Chromatography (TLC). The obtained products were filtered, washed several times with double distilled water and recrystallized. The purity of the synthesized materials was confirmed by TLC using Merck silica gel 60 F254 coated aluminum plates. The reaction scheme is shown in Fig. 1.

2.2. Solubility study

The solubility study was performed in various solvents like acetone, chloroform, methanol and toluene to choose the best solvent. A known volume of the methanol solvent was taken in a clean and moisture free 25 cm^3 beaker. The finely powdered sample was added slowly to the methanol solvent with constant stirring until saturation point is reached. About 10 cm^3 of this saturated solution of FMOC-3/FMOC-7 were transferred to a pre-weighed specific gravity bottle and weighed again. The difference in the weight of the empty bottle and bottle containing the solution gives the actual weight of the solution taken. The solution of FMOC-3/FMOC-7 was transferred from the specific gravity bottle to clean beakers, evaporated to dryness and weighed to get the amount of solute present in the solution. The percentage solubility can be determined using formula [8]:

$$Solubility\ (wt\%) = \frac{Weight\ of\ Solute}{Weight\ of\ (Solute + Solvent)} \times 100$$

The solubility process was repeated thrice to get the accurate results at different temperatures in acetone. The solubility of FMOC-3 and FMOC-7 measured in methanol as a function of temperature is depicted in Fig. 2.

2.3. Crystal growth

Single crystals of the FMOC-3 and FMOC-7 were grown by the slow evaporation technique at ambient temperature. A saturated solution of the FMOC-3 and FMOC-7 in methanol was prepared and warmed slightly to get a homogeneous mixture. The solution was filtered and was kept undisturbed for a period of 5 days. The beaker mouth was covered with filter paper to avoid fast evaporation. The defect free seed crystals so obtained were used for growing bulk crystals. The grown crystals are shown in Fig. 3.

2.4. Characterization

Fourier Transform Infrared (FTIR) spectrum of FMOC-3/FMOC-7

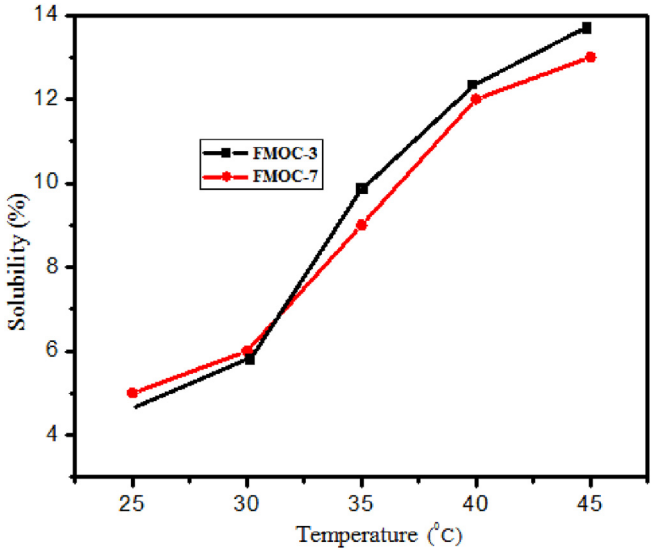

Fig. 2. The solubility curves of FMOC-3 and FMOC-7.

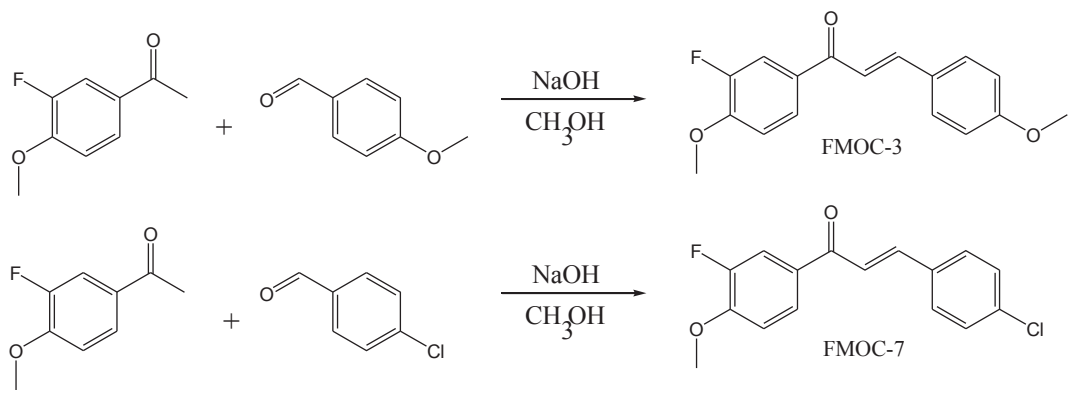

Fig. 1. Synthesis of FMOC-3 and FMOC-7.