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Efficient π-electron conjugated push–pull nonlinear optical chromophore 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one: A vibrational spectral study

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ABSTRACT

As part of the efforts for the design new organic nonlinear optical (NLO) materials with high efficiency for present day technological requirements, a comprehensive investigation on the intramolecular charge transfer (ICT) of an efficient π-conjugated potential push–pull NLO chromophore, 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one to a strong electron acceptor group through the π-conjugated bridge has been carried out from their vibrational spectra. The NIR FT-Raman and FT-IR spectra supported by the density functional theory (DFT) quantum chemical computations have been employed to analyze the effects of intramolecular charge transfer on the geometries and the vibrational modes contributing to the linear electro-optic effect of the organic NLO material. The calculated first hyperpolarizability of DMMC is 6.650×10^{-30} esu, which is 25 times that of urea. The simultaneous IR and Raman activation of the phenyl ring modes of ν(C=C/C–C) mode, ring C=C stretching modes, in-plane deformation modes and the umbrella mode of methyl groups also provide evidences for the charge transfer interaction between the donors and the acceptor group through the π-system. Vibrational analysis indicates the electronic effects such as induction and back-donation on the methyl hydrogen atoms causing the lowering of stretching wavenumbers have also been analyzed in detail. The planar conformations would give an enhanced NLO activity where as any deviations from planarity would decrease the mobility of electrons within the π-conjugated molecular system, resulting a reduction in NLO activity.

1. Introduction

In recent years conjugated organic nonlinear optical (NLO) materials have been attracting attention because of their second- or third-order hyperpolorizablities compared to those of inorganic NLO materials [1]. Many investigations are being done to synthesize new organic materials with large second-order optical nonlinearities in order to satisfy day-to-day technological requirements [2]. They have innumerable potential applications including telecommunications, optical computing, optical data storage, etc. The conjugated molecules consist of a skeleton containing conjugated π-electrons; the conjugated bridge is linked to two end groups with electron donor (D) and electron acceptor (A) character, respectively. The electron acceptor group withdraws electronic charge from the donor through the conjugated bridge: as a consequence the π-electrons of the skeleton become polarized, giving rise to a relevant molecular dipole moment which defines a charge transfer axis roughly coincident with the chain axis of the conjugated system. These molecules are known as push–pull molecules [3,4]. The basic strategy of using electron-donor and electron-acceptor substituents to polarize the π-electron system of organic materials has been illustrious for developing the NLO chromophores possessing large molecular nonlinearity, good thermal stability, improved solubility and processability [5,6]. Recently, much effort is being devoted to understand the origin of nonlinearity in large systems and to relate the nonlinear optical (NLO) responses to electronic structure and molecular geometry for designing and fabricating the NLO materials of large molecular hyperpolarizability [7,8]. In this series, 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one(DMMC) is one of the recently discovered potential organic NLO materials. It belongs to the monoclinic system with high electro optic and nonlinear optical coefficients [9]. Its low dielectric constant suggests that the materials can be used for optical data storage applications.

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The vibrational spectroscopy has been extensively used to understand the factors contributing to the linear electro-optic effect from the vibrational modes in organic materials and to provide deeper knowledge regarding the intermolecular interactions, and the relationship between molecular architecture, nonlinear response and hyperpolarizability [10]. NIR FT-Raman spectra combined with quantum chemical computations have recently been successfully employed in the vibrational analysis of drug molecules, biological compounds, natural products and NLO active compounds [11–14], since fluorescence free Raman spectra and computed results help unambiguous identification of vibrational modes and provide deeper insight into the bonding and structural features of complex organic molecular systems. The present work describes the vibrational spectral studies of 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one (DMMC), to understand the relationship between the molecular structural features and NLO properties, nonlinear optical response and hyperpolarizability of this push–pull prospective NLO chromophore with special emphasis on the role of intramolecular charge transfer (ICT) mechanism in such organic materials.

2. Experimental

2.1. Synthesis of the compound

Commercially available AR grade 3,4-dimethoxybenzaldehyde, 4-methoxy acetophenone and ethanol (99%) were used without further purification to synthesize the DMMC by Claisen–Schmidt condensation method [15]. This is the reaction of substituted acetophenone with substituted benzaldehyde in the presence of an alkali. Solution of para methoxyacetophenone (0.01 mol) in ethanol (30 ml) was mixed with (0.01 mol). 3,4-dimethoxybenzaldehyde in ethanol (30 ml) in the presence of NaOH (5 ml, 30%). After stirring for 3 h, the contents of the flask were poured into ice-cold water (250 ml) and kept aside for 24 h. The resulting crude solid was collected by filtration, dried and purified by repeated recrystallization. Purity of the compound was checked by thin layer chromatography. The melting point of the synthesized material was found to be 93 °C. A supersaturated solution of DMMC was obtained by dissolving the sample in the acetone at ambient temperature. After about 5 days good quality seed crystals appeared and these seed crystals were used to grow larger size crystals of dimension 28 mm × 7 mm × 3mm within a period of 20 days by slow evaporation technique.

2.2. IR and Raman measurements

The Raman spectra of polycrystalline samples (Fig. 2) and saturated acetone solution (Fig. 3) were measured using a Nicolet Magna 760 FT-IR spectrometer equipped with Nicolet Nexus FT-Raman module. The measurements were carried out in the range of 100–3700 cm^{-1} (Happ–Genzel apodization, 2 cm^{-1} resolution, 1064 nm Nd:YVO_4 laser excitation, 450 mW power at the sample). The spectra were processed using the OMNIC software [16]. FT-IR spectrum (Fig. 4) of the synthesized material was recorded in the wavenumber range 400–4000 cm^{-1} by KBr pellet technique (Thermo Nicolet AVATAR 370 DTGS FT-IR spectrophotometer).

3. Computational details

The geometry optimization and calculation of the harmonic vibrational wavenumbers were performed using the Gaussian 98 program [17], within the density functional theory (DFT) approach, in order to properly account for the electron correlation effects (particularly important in this kind of conjugated systems) [18]. The widely employed hybrid method denoted by B3LYP, which includes a mixture of HF and DFT exchange terms and the gradient corrected correlation functional of Lee, Yang and Parr, as proposed and parameterised by Becke [18], was used, along with the double-zeta split valence basis set 6-311G(d,p) [19]. The calculations are performed at B3LYP level using 6-311G(d,p) basis set and the vibrational wavenumbers are scaled by 0.9614 to account for the error caused by harmonic approximation [20]. Molecular geometries were fully optimized by the Berny algorithm, using redundant internal coordinates [19]. The bond lengths to within ca. 0.1 pm and the bond angles to within ca. 0.1°. The final root-mean-square (rms) gradients were always less than 3×10^{-4} hartree $bohr^{-1}$ or hartree $radian^{-1}$. No geometrical constraints were imposed on the molecules under study. The first hyperpolarizability (β_0) of this of novel molecular system, and related properties (β, α_0 and $\Delta\alpha$) of DMMC are calculated using B3LYP/6-311G(d,p) basis set, based on the finite-field approach. The calculated first hyperpolarizability of DMMC is 6.650×10^{-30} esu, which is 25 times the corresponding value for urea.

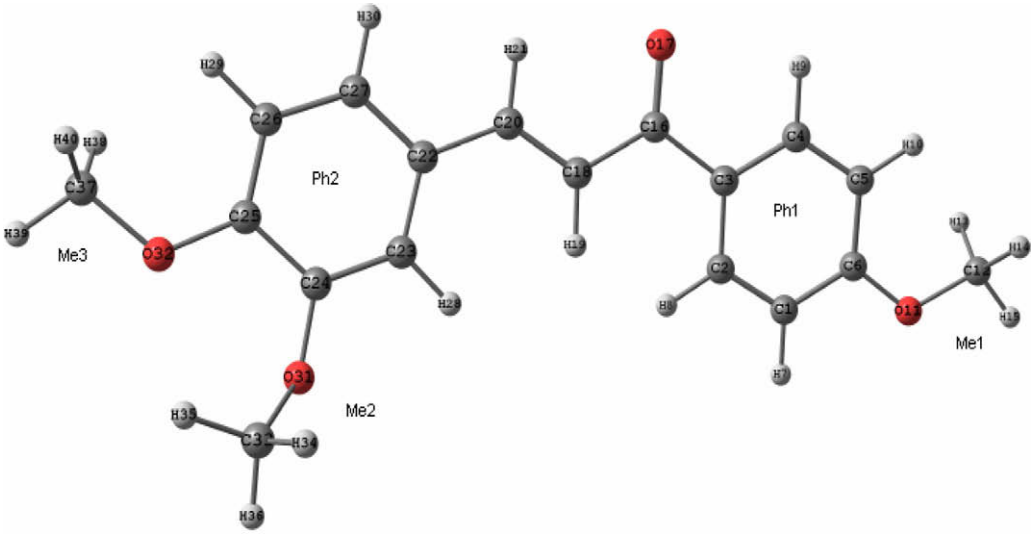

Fig. 1. Molecular structure of DMMC.