Journal of Molecular Structure 1139 (2017) 294-302

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Nonlinear optical studies and *structure-activity* relationship of chalcone derivatives with *in silico* insights

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ABSTRACT

susceptibilities.

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ARTICLE INFO

Article history: Received 29 January 2017 Received in revised form 16 March 2017 Accepted 16 March 2017

Keywords: Chalcones SHG efficiency Degenerate four wave mixing Structure-activity relationship Molecular modeling Theoretical studies

1. Introduction

Various substances/compounds have been studied for optical properties to be used for several optical devices which include optical switching, optical limiting, etc. [1-3]. The main reguirements for the application are high and fast Nonlinear Optical (NLO) responses. Among the large varieties of materials evaluated, organic materials have attracted attention due to their high nonlinear properties and ultrafast response. Conjugated organic systems have delocalized π electrons, which show excellent NLO properties as they can be easily polarized. A structure-activity relationship in this regard helps in the design and modeling of molecules to meet the requirements. The NLO response acquired for organic molecules can be enhanced by various strategies: donor-acceptor-donor (D- π -A- π -D), acceptor-donor-acceptor $(A-\pi-D-\pi-A)$ and donor $-\pi$ -donor $(D-\pi-D)$ types of molecules [4]. There are three features essential for high nonlinear activity (multi photon absorption) in an organic compound: a strong electron donor, a highly polarizable π -conjugated bridge and a strong

* Corresponding author. E-mail address: gnageswararao@sssihl.edu.in (G. Nageswara Rao). π -electron acceptor. Chalcones satisfy these criteria given their π -conjugated bridge that can be manipulated with a wide range of substitutions.

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Chalcones have been studied for various biological properties [5-9] but come into the picture because of their large SHG (Second Harmonic Generation) efficiencies. Also they have noticeable third-order nonlinearity. Due to their ability to crystallize in non-centrosymmetric structure and their blue light transmittance, they have acquired considerable interest [10-12]. Our main focus is to establish a *structure-activity* relationship along with quantitative measurement of these susceptibilities. Further, to evaluate potential physical parameters *in silico* to relate these experimental results.

2. Experimental

2.1. Preparation of the chalcones

General scheme for preparation [13]:

Nine chalcones were prepared via Claisen-Schmidt condensation, and characterized by UV-vis. IR. ¹H

NMR, ¹³C NMR and mass spectrometry. One of the representative member 4-NDM-TC has been studied

via single crystal XRD and the TGA/DTA technique. SHG efficiency and NLO susceptibilities of the chal-

cones have been evaluated by the Kurtz and Perry method and Degenerate Four Wave Mixing techniques

respectively. 3-Cl-4'-HC was noted to possess SHG efficiency 1.37 times that of urea while 4-NDM-TC returned the highest third order NLO susceptibilities with respect to CS_2 . In silico studies help evaluate various physical parameters, in correlating the observed activities. In conclusion, the *structure-activity*

relationship was derived based on the in silico and experimental results for the third order NLO

The chalcones were prepared (Scheme 1) by dissolving the required ketone (0.02 mol) and the aldehyde (0.02 mol) in ethanol (40 ml). Aq. NaOH (30%, 2.7 ml) was added to the above solution and the reaction mixture was stirred at room temperature. The









Scheme 1. General Claisen-Schmidt condensation reaction. X & Y represent various substituents and at different positions.

reaction was monitored by Thin Layer Chromatography (TLC). The reaction time varied depending upon the type of the substituents present. After the reaction was complete, the contents were filtered and washed free of alkali. In case of hydroxy-chalcones, NaOH (30%, 5.04 mL) was taken and the solutions were purged with nitrogen before reaction and nitrogen atmosphere was maintained during the reaction. After the reaction was complete (shown by TLC), the contents of the flask were poured into a beaker containing ice. The pH of the solution was brought to below 7.0 while stirring vigorously to obtain a colored solid. The crude solid was washed with cold water to remove any excess acid. In all cases, the filtered solid was dried and re-crystallized from distilled methanol. The compounds prepared along with their sample code, yield and melting point are shown in Table 1.

2.2. Single crystal growth and XRD analysis

The single crystal for 4-NDM-TC was obtained by slow

Table 1

Structure, IUPAC names, % yield and melting points of the chalcones prepared.



| Substituent | IUPAC name | Code | Yield (%) | Melting point (°C) |
|--|---|--------------|-----------|--------------------|
| $R_{2}^{1} = -H, R^{2} = -H,$ | (E)-1-phenyl-3-(4-N,N-dimethylaminophenyl)prop-2-ene -1-one | 4-NDM-C | 85 | 68–72 |
| $R^{3} = -N(Me)_{2}, R^{4} = -H$ $R^{1} = -H, R^{2} = -OH,$ | (E)-1-(4-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-ene-1-one | 4-MO-4'-HC | 68 | 182-184.2 |
| $R^{3} = -OMe, R^{4} = -H$ $R^{1} = -OH, R^{2} = -H,$ | (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-ene-1-one | 4-MO-2'-HC | 76 | 186.2-188 |
| $R^{3} = -OMe, R^{4} = -H$ $R^{1} = -H, R^{2} = -OH,$ | (E)-3-(4-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-ene-1-one | 4-Cl-4'-HC | 90 | 190.52 |
| $R^{3} = -Cl, R^{4} = -H$ $R^{1} = -H, R^{2} = -OH.$ | (E)-3-(3-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-ene-1-one | 3-Cl-4'-HC | 88 | 198–200 |
| $R^3 = -H, R^4 = -Cl$ $R^1 = -H, R^2 = -OH$ | (F)-3-(4-(N N-dimethylamino)nhenyl)-1-(4-hydroxynhenyl)nron-2-ene-1-one | 4-NDM-4'-HC | 64 | 122 3-124 2 |
| $R^{3} = -N(Me)_{2}, R^{4} = -H$ | (E) 2 (4 (NN dimethylamino)phenyl) 1 (2 hydronyphenyl)prop 2 che 1 one | | 70 | 171.9 172.0 |
| $R^{3} = -OH, R^{2} = -H,$ $R^{3} = -N(Me)_{2}, R^{4} = -H$ | (E)-3-(4-(N,N-dimethylamino)phenyi)-i-(2-hydroxyphenyi)prop-2-ene-i-one | 4-NDM-2'-HC | 78 | 171.8-172.9 |
| $R^{1} = -H, R^{2} = -Br,$ $R^{3} = -N(Me)_{2}, R^{4} = -H$ | (E)-1-(4-bromophenyl)-3-(4-(N,N-dimethylamino)phenyl)prop-2-ene-1-one | 4-NDM-4'-BrC | 80 | 145.2-146.8 |
| | 0 | | | |



evaporation method at room temperature. The recrystallized substance was used for this purpose and methanol was found to give the best single crystals. The X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Ka radiation $(\lambda = 0.71073 \text{ Å})$ with ω -scan method [14]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5382 reflections. Integration and scaling of intensity data were accomplished using SAINT program [14]. The structures were solved by Direct Methods using SHELXS97² and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7 [15]. Anisotropic displacement parameters were included for all nonhydrogen atoms. H bound to N atom was located from the difference Fourier map. All H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms.

2.3. Instrumentation

The ¹HNMR spectra were obtained on VARIAN 400 MHz, ¹³CNMR on VARIAN 101 MHz using TMS as the internal standard. The NMR spectra for 4-MO-4'-HC, 4-Cl-4'-HC and 3-Cl-4'-HC were recorded using DMSO- d_6 as the solvent whereas CDCl₃ was used for the other chalcones. For mass spectra AGILENT 6430 Triple Quad LC/MS was employed. The FT-IR spectra were recorded between 400 and 4000 cm⁻¹ using KBr pellets on Thermo-Nicolet Avatar 370 spectrophotometer. UV–vis spectra in methanol were recorded in the wavelength range 200–600 nm using Shimadzu 2450 spectrophotometer. The single crystal X-ray diffraction pattern of the reported sample was recorded using Bruker Smart Apex CCD diffractometer. The thermal studies were carried out in SDT Q600 (V20.9 Build 20) instrument with the standard DSC-TGA module.

2.4. Nonlinear optical measurements

2.4.1. Powder SHG measurement

Based on the popular Kurtz and Perry [16,17] powder SHG technique that measures the SHG efficiency of materials using urea or potassium dihydrogen phosphate (KDP) as standard, 8 ns pulses of 1064 nm from Nd:YAG laser working at a repetition rate of 10 Hz was used for SHG measurement. The microcrystalline powdered samples taken in glass capillary were smeared with laser pulses of 3.1 mJ/pulse energy. A photomultiplier tube was used to detect the second harmonic wave of 532 nm produced from the sample and the resultant signal was fed into an oscilloscope. Urea crystals with uniform particle size were used as reference for the SHG experiment.

2.4.2. Degenerate four wave mixing technique

A solution of 3 mg/ml of each chalcone dissolved in a mixture of tetrahydrofuran; methanol ($30:70 \ %v$) was prepared for carrying out the study.

The third order studies were done using the degenerate four wave mixing technique [18–21]. Fig. 1 displays the experimental configuration. The input beam is second harmonic (532 nm) of fundamental 1064 nm wavelength of a Q-switched Nd:YAG laser, with a pulse width of 7 ns. The experimental setup is shown in Fig. 1.

This beam is divided by beam splitters so that the two counter propagating pump beams have the same energy(18 mJ) and the probe beam has 5 mJ.The $\chi^{(3)}$ measurements were made using the reference sample CS₂.

The magnitude of the third order nonlinearity was calculated

using formula [22]:

$$\frac{\left|\chi_{eff}^{(3)}(sample)\right|^{2}}{\left|\chi_{eff}^{(3)}(CS_{2})\right|^{2}} = \left(\frac{n_{sample}}{n_{CS_{2}}}\right)^{4} \times \frac{I_{sample}}{I_{CS_{2}}} \times \frac{L_{CS_{2}}^{2}}{L_{sample}^{2}} \times \frac{\left(1 - R_{CS_{2}}\right)^{4}}{\left(1 - R_{sample}\right)^{4}}$$

where.

 $\chi_{eff}^{(3)}$ is the third order nonlinear susceptibility, *R* is surface reflectance, *n* is Refractive Index of the medium, *L* is the path length and *I* is the intensity of the phase conjugate signal.

2.5. Computational studies

All the chalcones used for the studies were modelled using GaussView (3.09) [23]. The energy minimization of these molecules has been carried out using DFT theory using Gaussian 03 [24].

3. Results and discussion

3.1. Characterization

3.1.1. Structural analysis

Fig. 2 shows the ORTEP diagram obtained from the single crystal XRD study of 4-NDM-TC.

Crystal data for 4-NDM-TC: $C_{15}H_{15}NOS$, M = 257.34, 0.48 × 0.18 × 0.09 mm³, monoclinic, space group P_{21}/c (No. 14), a = 6.3037(5), b = 10.1112(8), c = 21.6280 Å, $\beta = 103.795(2)^{\circ}$, V = 1338.76(18) Å³, Z = 4, $D_c = 1.277$ g/cm³, $F_{000} = 544$, CCD area detector, MoK α radiation, $\lambda = 0.71073$ Å, T = 293(2)K, $2\theta_{max} = 52.5^{\circ}$, 13782 reflections collected, 2695 unique ($R_{int} = 0.025$), Final *GooF* = 1.19, R1 = 0.0619, wR2 = 0.1505, R indices based on 2518 reflections with $I > 2\sigma(I)$ (refinement on F^2), 165 parameters, $\mu = 0.229$ mm⁻¹, Min and Max Resd. Dens. = -0.25 and 0.31 e/Å³. CCDC 1453426 contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://summary.ccdc.cam.ac.uk/structure-summary-form or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ ccdc.cam.ac.uk.

Given the role of the structure in the consequential property of the non-linear optics evaluated extensively in our study, we confirmed the structure using the XRD of the single crystal. Further, to establish the reliability of the *in silico* strategy used, we compared the simulated bond lengths and bond angles obtained from the least energy conformation of 4-NDM-TC in G03. The



Fig. 1. The DFWM set-up.



Fig. 2. ORTEP diagram of 4-NDM-TC with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

complete comparison values are tabulated in the supplementary data (Table SD1 and SD2). The significant correlation of 0.97 and 0.89 with respect to the bond lengths and bond angles respectively provide the confirmation of the proposed structure and help us visualize its D-A- π -D system.

3.1.2. Spectroscopic analysis

The ¹H NMR spectra of these compounds were completely analyzed. The –OH protons which are highly de-shielded due to chelation in 2'-hydroxy chalcones were observed at δ 12.95 and δ 13.21 as singlets. Whereas for –OH proton in 4'-hydroxy chalcones, the shifts were observed to be relatively less (δ 9.85–10.46). In the case of the 4'-substituted chalcones H-3 and H-5 were observed as doublets (δ 6.90–7.10). These lower values are due to shielding from the 4' substituent. Whereas H-2 and H-6 were observed as doublets between δ 7.50 and δ 8.20. In 2'-hydroxy chalcones H-3, H-4, H-5 and H-6 had different chemical shifts. The two olefinic protons H-8 ($\delta 6.85 - 7.45$) and H-9 ($\delta 7.60 - 7.97$) signals appeared as doublets with a large coupling constant (J = 13-16 Hz)indicating the trans double bond. The chalcones with p-substition showed signals for H-12 and H-14 as doublets in the range δ 6.80–7.40. H-11 and H-15 were observed between δ 7.45 and δ 7.83. The spectra are pretty symmetric in case of 4 and 4'substituted chalcones. In 3-Cl-4'-HC, H-11, H-12, H-13 and H-15 showed different shifts which resulted in a multiplet due to both meta and ortho couplings. In case of 4-NDM-TC we have doublets for H-1 and H-3 at δ 7.83 and δ 7.63 respectively, whereas H-2 was identified as a doublet of doublet at δ 7.19. The protons in *N*,*N*dimethylamino group were identified by the singlet between δ 3.08–3.04 (6H). Similarly for the methoxy group, singlet between δ 3.82–3.87 (3H).

The ¹³CNMR spectra of these chalcones indicated the presence of C==O by the signal between δ 182 and 193. Other signals as expected for olefinic carbons and the aryl ring are observed in sp² C region of δ 111 to 165 as given in the data. The ¹³CNMR signal of the methoxy and the *N*,*N*-dimethylamino group are observed at around δ 55.39 and δ 40.12 respectively.

All the compounds in the present study showed molecular ions in their ESI-mass spectra as $[M+H]^+$ peaks. In 4-NDM-TC the $[M+2]^+$ peak of around 4–5% intensity is observed which indicates the presence of Sulphur. In case of 3-Cl-4'-HC and 4-Cl-4'-HC with $[M+2]^+$ peaks around 33% intensity was observed which indicated the presence of 'Cl'. In 4-NDM-4'BrC, the $[M]^+$ and $[M+2]^+$ peaks were of the same intensity.

The IR spectra for all compounds have the carbonyl absorption around $1680 - 1660 \text{ cm}^{-1}$. Other features include the hydrogen

above 3000 cm^{-1} attached to sp² carbons. The C=C stretch is seen at 1600 cm⁻¹. The out of plane bending vibrations of aromatic system with para substitutions are seen in the 900 cm⁻¹ to 700 cm⁻¹ range. The chalcones with halogen substitutions have peaks around 650 cm⁻¹ for Br and 720 cm⁻¹ for Cl. Strong band in the region 850–800 cm⁻¹ shows benzene rings with para disubstitutions [25–27]. The UV–vis spectra for all the chalcones have been overlaid in Fig. 3.

Characterization data of the prepared chalcone analogues:



4-NDM-C: ¹H NMR(400 MHz, CDCl₃) *δ*, ppm 8.01 (m, 2H, H-2 and H-6), 7.81 (m, 2H, H-3 and H-5), 7.79 (t, 1H, H-4), 7.61 (m, 2H, H-11 and H-15), 7.52 (d, 1H, *J* = 16 Hz, H-9), 7.48 (d, 1H, *J* = 16 Hz, H-8), 6.70 (d, 2H, H-12 and H-14), and 3.04 (s, 6H, -N(CH₃)₂); ¹³C NMR(101 MHz, CDCl₃) *δ*, ppm 139.06 (C1), 128.32 (C2, C6), 128.46 (C3, C5), 132.16 (C4), 190.71 (C7), 121.3 (C8), 145.84 (C9), 116.96 (C10), 130.42 (C11, C15), 111.89 (C12, C14), 152.12 (C13), and 40.20 (-N-CH₃); IR (KBr disc): 3094-w (alkene C-H stretch), 2941-w, 1680-s(C=O stretch) 1615-s (C=C stretch), 1532,1515-m (aromatic skeletal bands), 1426 (aromatic C-H bend), 840-s, 822-s (C-H oop bend); UV-vis (MeOH) λ_{max} nm: 202, 264, 420; Mass: [M+H]⁺ = *m*/*z* 252.0.

4-MO-4′-**HC:** ¹H NMR(400 MHz, CDCl₃) δ, ppm 10.40 (s, 1H, 4-



Fig. 3. UV-vis spectra for all the samples.

OH), 8.77 (d, 2H, H-2 and H-6), 7.83 (m, 2H, H-3 and H-5), 7.80 (d, 1H, J = 16 Hz, H-9), 7.60 (d, 1H, J = 16 Hz, H-8), 7.10 (d, 2H, H-11 and H-15), 6.90 (d, 2H, H-12 and H-14), and 3.82 (s, 3H, -OCH₃); ¹³C NMR(101 MHz, CDCl₃) δ , ppm 129.76 (C1), 131.45 (C2, C6), 115.73 (C3, C5), 162.42 (C4), 187.44 (C7), 119.96 (C8), 143.112 (C9), 127.92 (C10), 130.96 (C11, C15), 114.77 (C12, C14), 161.52 (C13), and 55.74 (-O-CH₃); IR (KBr disc): 3099-w (alkene C-H stretch), 2932-w, 1678-s(C=O stretch) 1615-s (C=C stretch), 1548,1530-m (aromatic skeletal bands), 1418 (aromatic C-H bend), 1360-m, 1240-s, 1176-s (C=O stretch), 838-s, 826-s, 733-s (C-H oop bend); UV-vis (MeOH) λ_{max} nm: 201, 234, 344; Mass: [M]⁺ = m/z 254.9.

4-MO-2'-HC: ¹H NMR(400 MHz, CDCl₃) *δ*, ppm 12.95 (s, 1H,-OH), 7.93–7.89 (m, 2H, H-6 and H-9), 7.63 (d, 2H, H-11 and H-15), 7.56–7.46 (m, 2H, H-4 & H-8), 7.02 (d, 1H, H-3), 6.96–6.92 (m, 3H, H-4, H12 & H-14), and 3.87 (s, 3H, -OCH₃); ¹³C NMR(101 MHz, CDCl₃) *δ*, ppm 120.11 (C1), 163.54 (C2), 118.77 (C3), 136.17 (C4), 117.56 (C5), 129.53 (C6), 193.68 (C7), 118.59 (C8), 145.37 (C9), 127.32 (C10), 130.57 (C11, C15), 114.52 (C12, C14), 162.02 (C13), and 55.47 (-O-CH₃); IR (KBr disc): 3095-w (alkene C-H stretch), 2902-w, 1668-s(C=O stretch) 1610-s (C=C stretch), 1545,1525-m (aromatic skeletal bands), 1422 (aromatic C-H bend),1361-m, 1242-s, 1166-s (C=O stretch), 835-s, 822-s, 737-s (C-H oop bend); UV–vis (MeOH) λ_{max} nm: 201, 241, 365; Mass: [M]⁺ = *m*/*z* 254.9.

4-Cl-4'-HC: ¹H NMR(400 MHz, CDCl₃) δ , ppm 10.46 (s, 1H,-OH), 8.09 (d, 2H, H-2 and H-6), 7.93 (m, 3H, H-9, H-11 and H-15), 7.67 (d, 1H, H-8), 7.51 (d, 2H, H12 &H-14), and 6.91 (d, 2H, H-3 and H-5); ¹³C NMR(101 MHz, CDCl₃); δ , ppm 130.82 (C1), 131.68 (C2, C6), 115.80 (C3, C5), 162.70 (C4), 187.40 (C7), 123.26 (C8), 141.66 (C9), 134.29 (C10), 129.42 (C11, C15), 129.31 (C12, C14), and 135.18 (C13); IR (KBr disc): 3098-w (alkene C-H stretch), 1675-s(C=O stretch) 1606-s (C=C stretch), 1558,1555-m (aromatic skeletal bands), 1420 (aromatic C-H bend),1376-m, 1238-s, 1160-s (C=O stretch), 826-s, 812-s, 727-s (C-H oop bend); UV–vis (MeOH) λ_{max} nm: 201, 229, 321; Mass: [M]⁺ = 258.9, [M+2]⁺ = m/z 260.9.

3-Cl-4'-HC: ¹H NMR(400 MHz, CDCl₃) δ , ppm 10.47 (s, 1H, -OH), 8.11 (d, 2H, H-2 and H-6), 8.07 (m, 2H, H-11 &H-15), 7.80 (d, 1H, J = 15.6, H-9), 7.66 (d, 1H, J = 15.6, H-8), 7.48 (m, 2H, H-13 and H-14) and 6.91 (d, 2H, H-3 and H-5); ¹³C NMR(101 MHz, CDCl₃) δ , ppm 131.06 (C1), 131.78(C2, C6), 115.80 (C3, C5), 162.77 (C4), 187.36 (C7), 124.05 (C8), 141.44 (C9), 137.60 (C10), 128.21 (C11), 130.27 (C12), 129.35 (C13), 134.12 (C14), 128.17(C15); IR (KBr disc): 3099-w (alkene C-H stretch), 2926-w, 1670-s(C=O stretch) 1605-s (C=C stretch), 1548,1535-m (aromatic skeletal bands), 1430 (aromatic C-H bend),1371-m, 1232-s, 1170-s (C=O stretch), 825-s, 812-s, 727-s (C-H oop bend); UV–vis (MeOH) λ_{max} nm: 202, 233, 318; Mass: [M]⁺ = m/z 258.9, [M+2]⁺ = m/z 260.9.

4-NDM-4′-**HC:** ¹H NMR(400 MHz, CDCl₃) δ , ppm = 9.85 (s, 1H, -OH), 7.98 (d, 1H, H-9), 7.41–7.79 (m, 5H),7.05 (d, 2H, H-3 and H-5), 6.74 (d, 2H, H-12 and H-14) and 3.05 (s, 6H, -N(CH₃)₂); ¹³C NMR(101 MHz, CDCl₃) δ , ppm = 130.59 (C1), 131.37 (C2, C6), 116.45 (C3, C5), 164.32 (C4), 189.77 (C7, C=O), 121.45 (C8), 145.18 (C9), 124.78 (C10), 129.56 (C11, C15), 111.75 (C12, C14), 153.5 (C13), and 40.39(-N-CH₃); IR (KBr disc): 3094-w (alkene C-H stretch), 2906-w, 1660-s(C=O stretch) 1600-s (C=C stretch), 1548,1535-m (aromatic skeletal bands), 1432 (aromatic C-H bend),1371-m, 1232-s, 1164-s (C=O stretch), 825-s, 812-s, 727-s (C-H oop bend); UV–vis (MeOH) λ_{max} nm: 202, 241, 341; Mass: m/z [M+H]⁺ = 268.0.

 C15), 111.82(C12, C14), 152.23 (C13), and 40.12(-N-CH₃); IR (KBr disc): 3060-w, 2911-w, 1632-s (C=O stretch), 1611-s (C=C stretch), 1559-m, 1487-s(aromatic skeletal bands), 1434-s, 1417-s (aromatic C-H bend), 1340-s, 1277-s, 1177-s (C=O stretch), 1035-s, 989-s, 814-s, 768s(C-H oop bend); UV–vis (MeOH) λ_{max} nm: 202, 275, 435; Mass: m/z [M+H]⁺ = 268.0.

4-NDM-4′-**BrC**: ¹H NMR(400 MHz, CDCl₃) δ, ppm = 7.87 (d, 2H, J = 8 Hz, H-2 and H-6), 7.77 (d, 1H, J = 16 Hz, H-9), 7.62 (d, 2H, J = 8 Hz, H-3 and H-5), 7.55 (d, 2H, J = 7.8 Hz, H-11 and H-15), 7.29 (d, 1H, J = 16 Hz, H-8), 6.71 (d, 2H, J = 7.8 Hz, H-12 and H-14) and 3.04 (s, 6H, -N(CH₃)₂); ¹³C NMR(101 MHz, CDCl₃) δ, ppm = 137.80(C1), 130.58 (C2, C6), 131.71 (C3, C5), 127.08(C4), 189.39 (C7, C=O), 116.14 (C8), 146.42 (C9), 122.08 (C10), 129.88(C11, C15), 111.84 (C12, C14), 152.11 (C13), and 40.17(-N-CH₃); IR (KBr disc): 3080-w, 1647-s (C=O stretch),1610(C=C stretch) 1581-m, 1479-s(aromatic skeletal bands), 1430-s 1410-s (aromatic C-H bend), 1067-s, 982-s, 810-s, 809-s(C-H oop bend), 690-m (C-Br stretch); UV-vis (MeOH) λ_{max} nm: 202, 275, 428; Mass: m/z [M+H]⁺ = 330.0 and [M+H+2]⁺ = 332.0.



4-NDM-TC: ¹H NMR(400 MHz, CDCl₃) δ , ppm = 7.83 (d, 1H, J = 4.0 Hz, H-1), 7.82 (d, 1H, J = 15.2 Hz, H-7), 7.62 (d, 1H, J = 4.0 Hz, H-3), 7.55 (d, 2H, J = 8.0 Hz, H-9 and H-13), 7.24 (d, 1H, J = 15.2 Hz, H-6), 7.16 (dd, 1H, J = 4.0 Hz, 4.8 Hz, H-2), 6.72 (d, 2H, J = 8.0 Hz, H-10 and H-12) and 3.04 (s, 6H, -N(CH₃)₂); ¹³C NMR(101 MHz, CDCl₃) δ , ppm = 144.95(C1), 130.94 (C2), 132.90 (C3), 146.34 (C4), 182.13 (C=0, C5), 151.98 (C11), 111.88 (C6), 130.50 (C7), 116.28(C8), 130.48 (C9 and C13), 128.08 (C10 and C12), and 55.39 (-N(CH₃)₂); IR (KBr disc): 3080-w (alkene C-H stretch), 1632-s (C=0 stretch), 1611-s (C=C stretch), 1559-m (aromatic skeletal bands), 1434-s, 1417-s (aromatic C-H bend), 1295-m, 1206-s, 859-s, 839-s, 809-s (C-H oop bend); UV-vis (MeOH) λ_{max} nm: 203, 280, 430, 428; Mass: *m*/*z* [M+H]⁺ = 258.0, [M+2+H]⁺ = 260, [M+H-CH₃]⁺ = 243 and [M-C₄H₃S]⁺ = 174.

3.2. Thermal studies for 4-NDM-TC

Thermal analysis of a material gives useful information regarding the thermal stability of that material [28]. To find the thermal stability of 4-NDM-TC, thermo gravimetric analysis was carried out. Dried crystals of 4-NDM-TC were selected for this purpose and the analysis was carried out under nitrogen flow of 100 mL/min 30 °C was chosen as the temperature to equilibrate and then the instrument was heated to 600 °C at a heating rate of 10 °C/ min in the SDT Q600 TGA/DTA analyzer.

The results obtained from this analysis are depicted in Fig. 4. The DTA curve implies that the material undergoes an irreversible endothermic transition at 101 °C, where melting begins. The endothermic peak represents the temperature at which the melting terminates, which corresponds to its melting point at 103 °C. Further it indicates that there is no phase transition before melting. The peak shows the good degree of crystallinity and purity of the sample. The TGA curve of this sample indicates that the sample is stable upto 310 °C and above this temperature the weight loss is not due to self-degradation of 4-NDM-TC, but merely due to evaporation after its melting. The exothermic peak at 335.0 °C indicates that the sample undergoes decomposition at this temperature.



Fig. 4. TGA/DTA curve for 4-NDM-TC.

3.3. Nonlinear optical properties

3.3.1. SHG efficiency

The chalcones were evaluated for their SHG efficiency and the values obtained from the SHG measurement are shown in Table 2. It is known that the SHG values depend upon various factors for a given compound. Some of the factors are conjugation, hydrogen bonds, parallel stacking and $\pi - \pi$ interactions apart from the non-centrosymmetric crystal structure [29].

In this study, we find that 3-Cl-4'-HC is 1.37 times more active than urea followed by 4-MO-2'-HC with a relative gain of 1.30 [30]. Reduced activity is seen in 4-NDM-TC (0.45 times urea), 4-NDM-C (0.35 times urea), 4-NDM-4'-BrC (0.33 times urea), and 4-Cl-4'-HC (0.25 times urea). It is interesting to note that among the chalcones containing the *N*,*N*-dimethylamino group, all show SHG activity other than 4-NDM-4'-HC and 4-NDM-2'-HC. This indicates that the *N*,*N*-dimethylamino group is essential for SHG activity whereas presence of hydroxyl along with the *N*,*N*-dimethylamino group leads to inactivity. 3-Cl-4'HC and 4-Cl-4'-HC are isomers where only the position of the –Cl substituent is different. The role of the position of the substituent is evident from the difference in the SHG values, where 3-Cl-4'-HC has the highest SHG efficiency (1.37 times urea) while 4-Cl-4'-HC has lowest observed SHG efficiency (0.25 times urea).

A thienyl chalcone named T-CHL-2T has shown a SHG value of 52 times that of urea which is attributed to its symmetrical structure. Whereas chalcone T-CHL-CAN showed lower activity of 0.27

Table 2SHG efficiency of the chalcones.

| - | |
|--------------|--------------------|
| Sample | SHG values vs urea |
| 3-Cl-4'-HC | 1.37 |
| 4-MO-2'-HC | 1.30 |
| 4-NDM-TC | 0.45 |
| 4-NDM-C | 0.35 |
| 4-NDM-4'-BrC | 0.33 |
| 4-Cl-4'-HC | 0.25 |
| 4-NDM-4'-HC | 0 |
| 4-NDM-2'-HC | 0 |
| 4-MO-4'-HC | 0 |

times urea [31] and in our case 4-NDM-TC showed activity 0.45 times urea which indicates that symmetric structures in thienyl chalcones is essential for higher SHG efficiency.

3.3.2. Nonlinear optical susceptibilities measurements

The 3rd order NLO values obtained for the chalcones via the Degenerate Four Wave Mixing technique are shown in Table 3.

When all the interacting waves in four wave mixing have same frequency the process is said to be degenerate. This process results from nonlinear index of refraction. DFWM provides information about the magnitude and response of the third-order nonlinearity. The strength of the fourth beam depends on a coupling constant that is proportional to effective $\chi^{(3)}$ (third order nonlinear susceptibility). Thus measurements of the observed signal will yield information about the $\chi^{(3)}$ tensor components of the medium. As a technique, DFWM is the most frequently used method to characterize third nonlinearity of novel materials. Although third order NLO using z-scan has been reported for chalcones, we report the first NLO measurements via DFWM for these set of chalcones.

These chalcones possess a D-A- π -D type of arrangement. 4-NDM-TC has highest NLO activity ($\chi^{(3)}_{xxxx} = 0.679$) with respect to CS₂ as the reference whereas others have lower $\chi^{(3)}$ values.

Firstly, examining the Chalcones containing the N,N-dimethylamino substituent only, we have one fixed aldehyde side with the -NMe₂ group. Hence, the 4-NDM-C is the simplest of all the chalcones containing the -NMe₂ group. In the ketone side we have 4'-OH, 4'-Br, 2'-OH substituents and also a different aromatic ketone, i.e. 2-Acetyl thiophene. The chalcone resulting from 2-acetyl thiophene, 4-NDM-TC demonstrates the highest activity. Upon further examination, it is observed that these substituents pump electrons to the ring. Thus, we infer that substituents with +R effect decrease the NLO activity. But the bromo substituent has -I effect also because of which there is a sharp rise in the activity from 4-NDM-4'-HC to 4-NDM-4'-BrC. The position of these functional groups is para. On similar lines another study reports the third order NLO values of three chalcones using the Z-scan technique where the chalcones have fixed B ring and substituents vary on the A ring [32]. In the mentioned study the compound 4Br4MSP has a Re $|\chi^{(3)}|$ value of 2.27 \times 10⁻²² m²/V² and the compound 4N4MSP has a Re $|\chi^{(3)}|$ value of 2.36 \times 10^{-22} $m^2/V^2.$ In both 4Br4MSP and 4N4MSP, the -Br

| Sample | Refractive index | $\chi^{(3)}_{xxxx}$ (observed) | $\chi^{(3)}_{xxxx}$ (relative) | $\chi^{(3)}_{yxyx}$ (observed) | $\chi^{(3)}_{yxyx}$ (relative) |
|-----------------|------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| CS ₂ | 1.620 | 16.57 | 1 | 10.030 | 1 |
| 4-NDM-TC | 1.351 | 9.718 | 0.679 | 5.971 | 0.688 |
| 4-NDM-C | 1.342 | 6.940 | 0.523 | 5.495 | 0.656 |
| 4-NDM-2'-HC | 1.346 | 5.946 | 0.440 | 4.717 | 0.589 |
| 4-NDM-4'-BrC | 1.332 | 5.244 | 0.406 | 4.114 | 0.466 |
| 4-NDM-4'-HC | 1.365 | 3.805 | 0.274 | 3.652 | 0.399 |
| 4-MO-4'-HC | 1.342 | 3.013 | 0.233 | 3.013 | 0.233 |
| 4-MO-2'-HC | 1.463 | 2.950 | 0.218 | 2.333 | 0.291 |
| 4-Cl-4'-HC | 1.343 | 2.457 | 0.182 | 2.344 | 0.293 |
| 3-Cl-4'-HC | 1.345 | 2.245 | 0.166 | 2.145 | 0.268 |

 Table 3

 Observed and Relative 3rd order NLO susceptibilities of the chalcones along with their measured refractive indices.

Note: The order for $\chi^{(3)}$ is 10^{-21} m²/V².

and the $-NO_2$ functional groups are present in the *para* (4th) position. The nitro group is a stronger electron withdrawing group as compared to bromo, resulting in the higher $Re|\chi^{(3)}|$ value of 4N4MSP as compared to that of 4Br4MSP. As observed in our work and also in the mentioned study, electron withdrawing group (-I or -R effect) at the *para* position increase the NLO activity as compared to an electron pumping substituent, the effect observed in Fig. 5.

Secondly, we observe that all the molecules containing the *N*,*N*-dimethylamino substituent have NLO susceptibilities higher than the other molecules. This indicates that the *N*,*N*-dimethylamino group owing to its higher +R effect increases NLO activity, followed by the methoxy substituent, and the chloro substituent at last. Overall, we can conclude that substituents with +R effect on the B-ring increase the activity. A similar kind of work has also been reported using the Z-scan method, supporting our claim that an electron pumping group in the phenylene ring (B ring) increase activity [33]. Hence, this study makes the role of substituents very important in the 3rd order NLO activity, helping establish a certain *structure-activity* relationship.



Fig. 5. Plot of $\chi(3)$ xxxx of molecules containing *N*,*N*-dimethylamino substituent only.

| Tabl | e 4 | |
|------|-----|--|
|------|-----|--|

Various parameters obtained with respect to the molecular orbitals

3.3.3. *Computational studies*

The molecules were built and minimized using GaussView (3.09). The obtained output files were studied extensively. The various calculations were determined [34] and the values obtained are summarized in Tables 4 and 5 given below.

The predicted MO energy gap correlated with the observed NLO values. It is observed that the sample 4-NDM-TC, with the highest 3rd order NLO susceptibilities has the lowest energy gap whereas 3-Cl-4'-HC has the lowest 3rd order NLO susceptibilities with relatively higher energy gap. This trend continues barring a few exceptions. The plot of observed values vs the energy gap depicted in Fig. 6 demonstrated a significant correlation with the R² value of 0.9327. We know that the hardness or the softness of the molecule is directly related to its reactivity. Here we have obtained a specific trend being followed in case of the obtained hardness and softness values. The hardness increases with decreasing 3rd order NLO susceptibilities whereas the softness of the samples increase. 4-NDM-TC has the lowest hardness of 0.07449 units and the highest softness of 6.71231 units while, 4-Cl-4'-HC has the highest hardness of 0.088895 units and the least softness of 5.624613 units. Another feature to notice is that 4-NDM-TC also has the highest static dipole moment. And also all the molecules containing the *N*,*N*-dimethylamino substituent have higher dipole moments than the other molecules. This is reflected in their higher third order NLO susceptibilities and better SHG efficiency in most cases. This fact helps us conclude that higher static dipole moments in molecules lead to better activity.

These observations are from the calculations obtained from isolated gaseous molecule where we do not observe any specific trend in the second order hyperpolarisability values which is directly related to the $\chi(3)$ values of the molecule. However, the calculations in a solvent medium when done as in accordance with the experimental studies in methanol as the solvent, returns a change in the second order hyperpolarisability values. These values now follow a trend proportional to their $\chi(3)$ values. Barring 4-NDM-4'-BrC, the second order hyperpolarisability values for the molecules obtained from the solvent phase calculations increase as

| · · · · · · · · · · · · · · · · · · · | | | |
|---------------------------------------|-------------------------|-----------------------|-----------------------|
| Sample | Energy gap in AU (MeOH) | Hardness in AU (MeOH) | Softness in AU (MeOH) |
| 3-Cl-4'-HC | 0.17469 | 0.088825 | 5.629046 |
| 4-Cl-4'-HC | 0.17444 | 0.088895 | 5.624613 |
| 4-MO-2'-HC | 0.17482 | 0.089280 | 5.600358 |
| 4-MO-4'-HC | 0.16698 | 0.089015 | 5.617031 |
| 4-NDM-4'-HC | 0.15389 | 0.079290 | 6.305965 |
| 4-NDM-4'-BrC | 0.15044 | 0.076845 | 6.506604 |
| 4-NDM-2'-HC | 0.15241 | 0.078280 | 6.387328 |
| 4-NDM-C | 0.14813 | 0.078755 | 6.348803 |
| 4-NDM-TC | 0.14443 | 0.074490 | 6.712310 |

| Table | 5 |
|-------|---|
|-------|---|

Parameters obtained with respect to polarizability in gaseous and solvent phase.

| Sample | Static dipole moment (Gas phase) debye | Second order hyperpolarisability (Gaseous) debye-ang**3 | Second order hyperpolarisability (MeOH) Debye-ang**3 |
|--------------|---|---|--|
| 3-Cl-4'-HC | 2.5991 | - 10998.05024 | -10640.09080 |
| 4-Cl-4'-HC | 1.8861 | - 12445.73106 | -10833.18972 |
| 4-MO-2'-HC | 2.4033 | - 11374.39172 | -11411.69180 |
| 4-MO-4'-HC | 0.8405 | - 11603.24782 | -11417.75892 |
| 4-NDM-4'-HC | 2.4775 | - 13827.04074 | -12993.25620 |
| 4-NDM-4'-BrC | 3.9909 | - 18869.80974 | -19079.00120 |
| 4-NDM-2'-HC | 3.6802 | - 13276.69886 | 13565.89724 |
| 4-NDM-C | 3.9622 | - 13204.40990 | 13851.18242 |
| 4-NDM-TC | 4.3634 | - 13052.21288 | 13933.13580 |



Fig. 6. Plot of $\chi(3)$ xxxx of molecules vs the calculated energy gap.

their $\chi(3)$ values also increase. 3-Cl-4'-HC has the lowest $\chi(3)$ values and second order hyperpolarisability values.

Thus, a thorough *in silico* investigation of the molecules gives a broad idea about the various physical parameters for the molecules, enabling their correlation unto observed 3rd order NLO susceptibilities.

4. Conclusions

We have presented nine chalcones which have been prepared by the Claisen-Schmidt condensation, characterized with spectroscopic techniques and one of the representative member has been studied via single crystal XRD. Further its purity by thermal profiling was studied using the TGA/DTA technique. The SHG and NLO activities have been studied, with the NLO properties being evaluated using the Degenerate Four Wave Mixing technique. We also have established the effect of various substituents on the NLO properties, thus establishing a *structure-activity* relationship never done before using the DFWM technique. This study concludes that in these chalcones electron withdrawing groups (-I or -R effect) on the A-ring at the para (4') position increase the NLO activity as compared to an electron pumping group. On the other hand substituents with +R effect on the B-ring increase the activity. These chalcones have been evaluated extensively by in silico techniques to obtain various parameters which are useful to predict different activities and patterns which in turn help us to design molecules with enhanced activities. The resonance of the computed and experimental values shows the accuracy of the in silico calculations. The NLO studies have indicated that these chalcones have potential applications in optical switching, photonic devices, etc.

Acknowledgements

The authors are grateful to Bhagawan Sri Sathya Sai Baba, Founder Chancellor, SSSIHL, for His constant inspiration. The authors thank Dr. D Rajesh Babu, Department of Chemistry, SSSIHL for providing the TGA/DTA data. The authors acknowledge the valuable inputs and help given by Sri C. Sai Manohar, Department of Chemistry, SSSIHL and Sri Parth Gupta, Department of Chemistry, IIT-Madras.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.03.064.

References

- R.L. Sutherland, Handbook of Nonlinear Optics, second ed., Dekker, New York, 1996.
- [2] J.W. Perry, K. Mansour, I.Y.S. Lee, X.L. Wu, P.V. Bedworth, C.T. Chen, et al., Organic optical limiter with a strong nonlinear absorptive response, Science 273 (1996) 1533–1536.
- [3] S. Dhanuskodi, T.C.S. Girisun, N. Smijesh, R. Philip, Two-photon absorption and optical limiting in tris-thiourea cadmium sulphate, Chem. Phys. Lett. 486 (2010) 80–83.
- [4] M. Sai Kiran, Benoy Anand, S. Siva Sankara Sai, G. Nageswara Rao, Second- and third-order nonlinear optical properties of bis-chalcone derivatives, J. Photochem. Photobiol. A Chem. 290 (2014) 38–42.
- [5] B.T. Yin, C.Y. Yan, X.M. Peng, S.L. Zhang, S. Rasheed, R.X. Geng, C.-H. Zhou, Synthesis and biological evaluation of α-triazolyl chalcones as a new type of potential antimicrobial agents and their interaction with calf thymus DNA and human serum albumin, Eur. J. Med. Chem. 71 (2014) 148–159.
- [6] Z. Liu, L. Tang, P. Zou, Y. Zhang, Z. Wang, Q. Fang, L. Jiang, G. Chen, Z. Xu, H. Zhang, G. Liang, Synthesis and biological evaluation of allylated and prenylated mono-carbonyl analogs of curcumin as anti-inflammatory agents, Eur. J. Med. Chem. 74 (2014) 671–682.
- [7] B. Kupcewicz, A.A. Jarzęcki, M. Małecka, U. Krajewska, M. Rozalski, Cytotoxic activity of substituted chalcones in terms of molecular electronic properties, Bioorg. Med. Chem. Lett. 24 (2014) 4260–4265.
- [8] S. Shenvi, K. Kumar, K.S. Hatti, K. Rijesh, L. Diwakar, G.C. Reddy, Synthesis, anticancer and antioxidant activities of 2,4,5-trimethoxy chalcones and analogues from asaronaldehyde: structure-activity relationship, Eur. J. Med. Chem. 62 (2013) 435–442.
- [9] R. Shivahare, et al., Synthesis, structure–activity relationships, and biological studies of chromenochalcones as potential antileishmanial agents, J. Med. Chem. 57 (2014) 3342–3357.
- [10] V. Shettigar, et al., Crystal growth and characterization of new nonlinear optical chalcone derivative: 1-(4-Methoxyphenyl)-3-(3, 4-dimethoxyphenyl)-2-propen-1-one, J. Cryst. Growth 295 (2006) 44–49.
- [11] Konstantinos Iliopoulos, et al., Nonlinear absorption reversing between an electroactive ligand and its metal complexes, Opt. Express 23 (2012) 25311–25316.
- [12] H.J. Ravindra, H.J. Ravindra, A. John Kiran, K. Chandrasekharan, H.D. Shashikala, S.M. Dharmaprakash, Third order nonlinear optical properties and optical limiting in donor/acceptor substituted 4'-methoxy chalcone derivatives, Appl. Phys. B 88 (2007) 105–110.
- [13] A.I. Vogel, B.S. Furniss, Vogel's Textbook of Practical Organic Chemistry, fourth ed., Longman, USA, 1989.
- [14] SMART, SAINT, Software Reference Manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc, Madison, Wisconsin, U.S.A., 2001.
- [15] G. M. Sheldrick, SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac. gwdg.de/SHELX/index.php.
- [16] J. Giuliani, L. Goldberg, F. Von Batchelder, An evaluation of nonlinear optical materials by the second-harmonic powder technique, in: DTIC Document, 1971.
- [17] S. Kurtz, T. Perry, A powder technique for the evaluation of nonlinear optical materials, J. Appl. Phys. 39 (2003) 3798–3813.
- [18] G. Rivoire, Modern Nonlinear Optics, Part 1, Wiley, New York, 1993.

- [19] J.P. Bourdin, Phu X. Nguyen, G. Rivoir, J.M. Nunz, Polarization properties of the orientational response in phase conjugation, Nonlinear Opt. 7 (1994) 1–6.
- [20] B. Sahraoui, Phu X. Nguyen, M. Salle, A. Gorgues, Electronic and nuclear contributions to the third-order nonlinear optical susceptibilities of new p-N, N'-dimethylaniline tetrathiafulvalene derivatives, Opt. Lett. 23 (1998) 1811–1813.
- [21] B. Sahraoui, G. Rivoire, Degenerate four-wave mixing in absorbing isotropic media, Opt. Commun. 138 (1997) 109–112.
- [22] R.G. Caro, M.C. Gower, Phase conjugation by degenerate four wave mixing in absorbing media, IEEE J. Quantum Electron 18 (1987), 1376–1982.
- [23] R.I.I. Dennington, et al., GaussView, Version 3.09, Semichem, Inc., Shawnee Mission, KS, 2003.
- [24] M.J. Frisch, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [25] R.M. Silverstein, F.X. Webster, D.J. Kiemle, Spectrometric Identification of Organic Compounds, seventh ed., John Wiley & Sons, USA, 2005.
- [26] D.L. Pavia, G.M. Lampman, G.S. Kriz, J.R. Vyvyan, Introduction to Spectroscopy, fourth ed., Cengage Learning, USA, 2009.
- [27] P. Menezes, A. Jayarama, W.N. Seik, Synthesis, Crystal growth and characterization of a D-π-A type novel organic nonlinear optical single crystal, J. Cryst. Growth 402 (2014) 130–137.
- [28] P.J. Haines, in: Thermal Analysis Principle; Applications and Problems, Blackie,

Academic & Professional London, 1987.

- [29] K. Naseema, Vijayalakshmi Rao, K.V. Sujith, Balakrishna Kalluraya, Crystal growth and characterization of an NLO organic crystal: N'-[(Z)-(4methylphenyl)methylidene]-4-nitrobenzohydrazide, Curr. Appl. Phys. 10 (2010) 1236–1241.
- [30] Y. Goto, A. Hayashi, Y. Kimura, M. Nakayama, Second harmonic generation and crystal growth of substituted thienyl chalcone, J. Cryst. Growth 108 (1991) 688–698.
- [31] G. Nageswara Rao, et al., D-A-π-D Synthetic approach for thienyl chalcones NLO – a structure activity study, J. Photochem. Photobiol. A Chem. 324 (2016) 33–39.
- [32] E.D. D'silva, G. Krishna Podagatlapalli, S. Venugopal Rao, S.M. Dharmaprakash, Study on third-order nonlinear optical properties of 4-methylsulfanyl chalcone derivatives using picosecond pulses, Mater. Res. Bull. 47 (2012) 3552–3557.
- [33] H.J. Ravindra, K. Chandrashekaran, W.T.A. Harrison, S.M. Dharmaprakash, Structure and NLO property relationship in a novel chalcone co-crystal, Appl. Phys. B 94 (2009) 503–511.
- [34] N. Günay, H. Pir, D. Avcı, Y. Atalay, NLO and NBO analysis of sarcosine-maleic acid by using HF and B3LYP calculations, J. Chem. 2013 (2013), http:// dx.doi.org/10.1155/2013/712130.