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ORIGINAL PAPER

# Synthesis, characterization and *structure–activity* relationship of non-linear optical response of chalcone derivatives with in silico insights

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## Abstract

Fifteen chalcone derivatives having D–A–D, D–A–A and A–A–D architectures have been synthesized by Claisen–Schmidt condensation reaction and characterized by UV–Vis, IR, $^1$H-NMR, $^{13}$C-NMR and Mass spectrometry. In order to unambiguously establish the *structure–activity* relationship for the non-linear optical activity of these compounds, for the first time to our knowledge, we use the femtosecond degenerate four wave mixing (DFWM) technique to quantify and compare the third-order non-linear optical (NLO) activity of all the 15 compounds, under identical conditions. The second harmonics generation (SHG) efficiencies for all the compounds have also been evaluated using the Kurtz-Perry powder method. Among the compounds that we have synthesized here, the ones with A–A–D architecture show the highest NLO activity. Our results show that the NLO activity of a compound with A–A–D architecture can be further enhanced by incorporating a substituent with strong electron withdrawing ability on ring A and strong electron donating substituent on ring B. The results of the in silico studies that we have carried out correlate well with our experimental findings. The compounds *(E)*-3-(4-(dimethylamino)phenyl)-1-(4-nitrophenyl)prop-2-en-1-one with the compound code (4-N$(CH_3)_2$–4′-$NO_2$) and *(E)*-3-(4-methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one with the compound code (4-MeO-4′-$NO_2$) show the highest NLO activity among the compounds we have reported here.

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**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s11696-020-01487-6.

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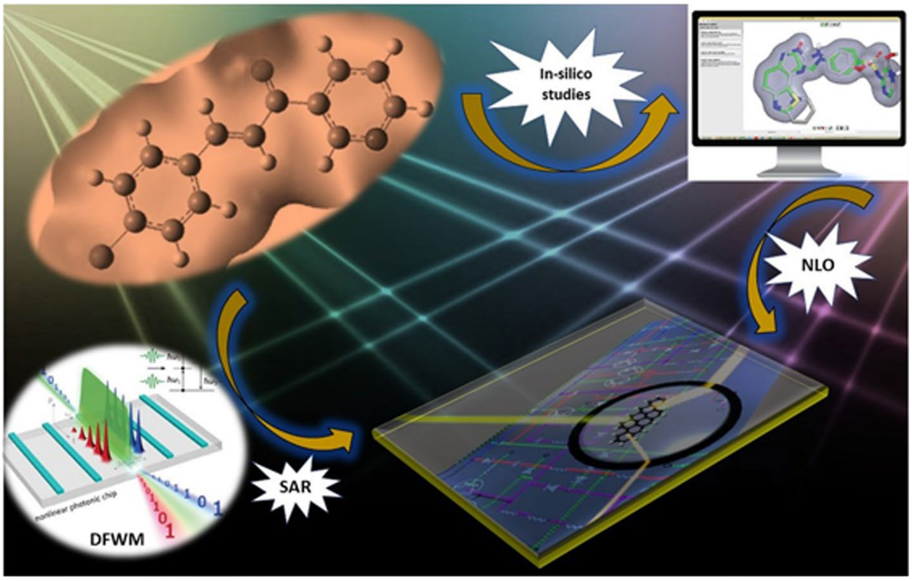
## Graphical abstract



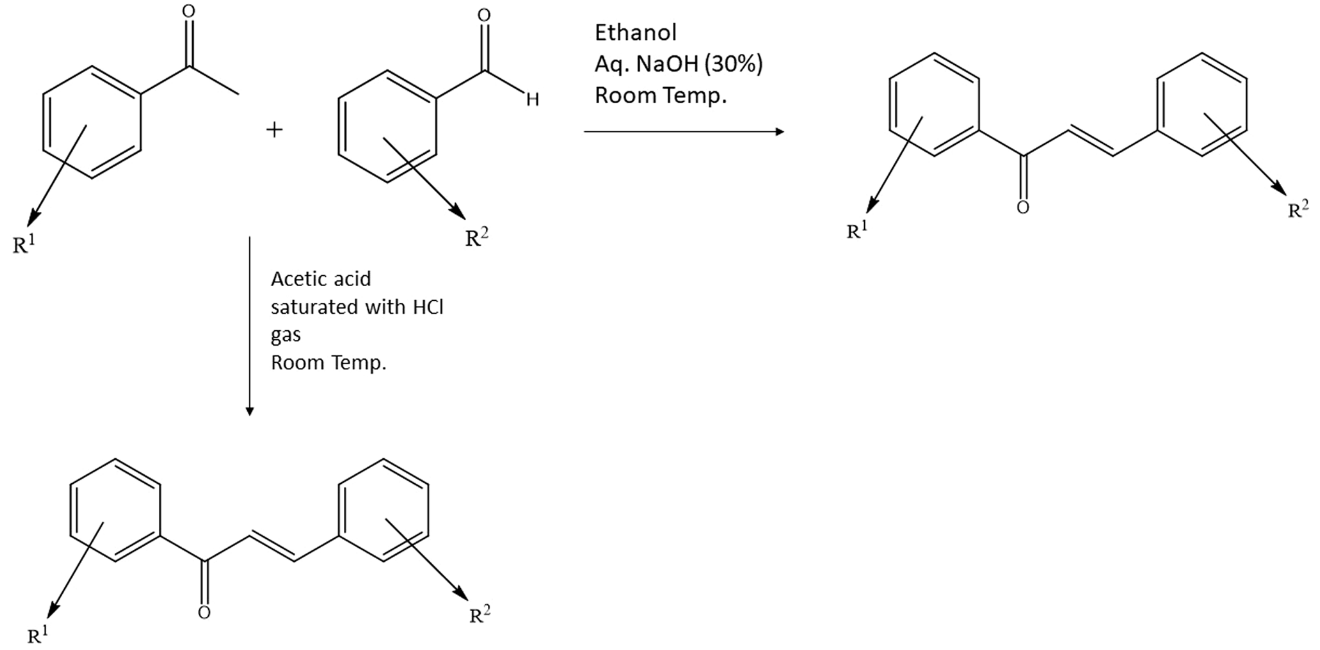
**Keywords** Chalcones · Synthesis and characterization · Second harmonic generation · Degenerate four wave mixing · Molecular modelling

## Introduction

In the quest of active non-linear optical materials for optical devices, the organic compounds with delocalized systems have been widely studied for their non-linear responses. The reason behind these organic compounds taking the spotlight in optical research lies in the fact that the organic compounds can be easily polarised, provide greater flexibility in their syntheses and also render the ability to tune the ultra-fast response through structural modification (Kar et al. 2017; Dhanuskodi et al. 2010). The substances with fast NLO responses find their applications in optical devices which include optical switching, optical limiting, optical storage, etc. (Gupta et al. 2011; Perry et al. 1996). Researchers have developed numerous design strategies such as donor–acceptor–donor (D–A–D), acceptor–donor–acceptor (A–D–A) and donor–pi–donor (D–π–D) architectures for designing the organic compounds with fast non-linear responses (Kiran et al. 2014; He et al. 2008; Rajashekar et al. 2012).

Chalcones are known for their various biological activities (Yin et al. 2014; Liu et al. 2014; Kupcewicz et al. 2014; Shenvi et al. 2013; Agnihotri et al. 2014) but are majorly studied for their photonic applications(Shettigar et al. 2006; Iliopoulos et al. 2012; Ravindra et al. 2007). These compounds show high SHG efficiencies and interesting non-linear properties like high absorption extinction coefficients in the UV region (Abegão et al. 2016). Also, these compounds possess a π conjugated bridge along with strong electron donor and acceptor groups which can be modified to tune the non-linear response (Samoc et al. 1998; Marder et al. 1997; Norman, Luo, and Ågren 1998; Albota et al. 1998).

In the present study, we report the synthesis, characterisation, Second Harmonic Generation (SHG) efficiency and Third Order Non-linear optical (NLO) properties of 15 chalcone derivatives having (D–A–D), (D–A–A) and (A–A–D) architectures with the main focus on establishing the *structure–activity* relationship of these compounds. The third-order non-linear optical studies were done using the Degenerate Four Wave Mixing (DFWM) technique, while the SHG efficiencies were characterized using the Kurtz-Perry powder method. From the literature, we find that the NLO measurements of four of the 15 chalcone derivatives that we have reported here have been carried out using *Z*-scan technique (Ravindrachary et al. 2005); (Janardhana et al. 2013); (Dharmaprakash 2017). A quick look at the existing literature tells one that the reported measured NLO properties of compounds differ by more than an order of magnitude due to the subtle differences in the methods used, differences in the wavelengths used and differences in the pulse widths used. It is not possible to get the right structure–activity relationship using such data. For efficient, uniform and consistent comparison of their structure-activity relationship, for the first time to our knowledge we report the NLO measurements of all thee 15 chalcone derivatives by using the same technique, at the same wavelength. For the third-order nonlinear measurements carried out using dilute solutions, femtosecond



**Scheme 1** Claisen–Schmidt condensation: $R^1$ and $R^2$ represent various substituents at different positions

pulses have been used since they rule out thermal nonlinearities which depend on the bulk thermal properties of the solutions and do not truly reflect the relationship between the molecular structure and the nonlinear activities of the solute molecules. Majority of the work done in this field deals with the study of non-linear optical activity of only one or two organic/inorganic compounds at a time. Therefore, this work on establishing structure–activity relationship of the synthesized compounds with different architectures would lead to a better understanding of the kind of substituents that could be incorporated in the system for better non-linear optical responses. In silico studies of these synthesized chalcone derivatives have also been done to draw correlation with the experimental findings. Finally, thermal stability studies of the new compounds with the highest optical nonlinearities have also been carried out to validate their applicability in the real world.

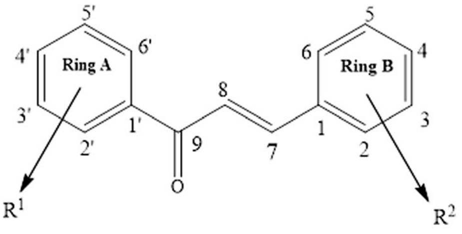


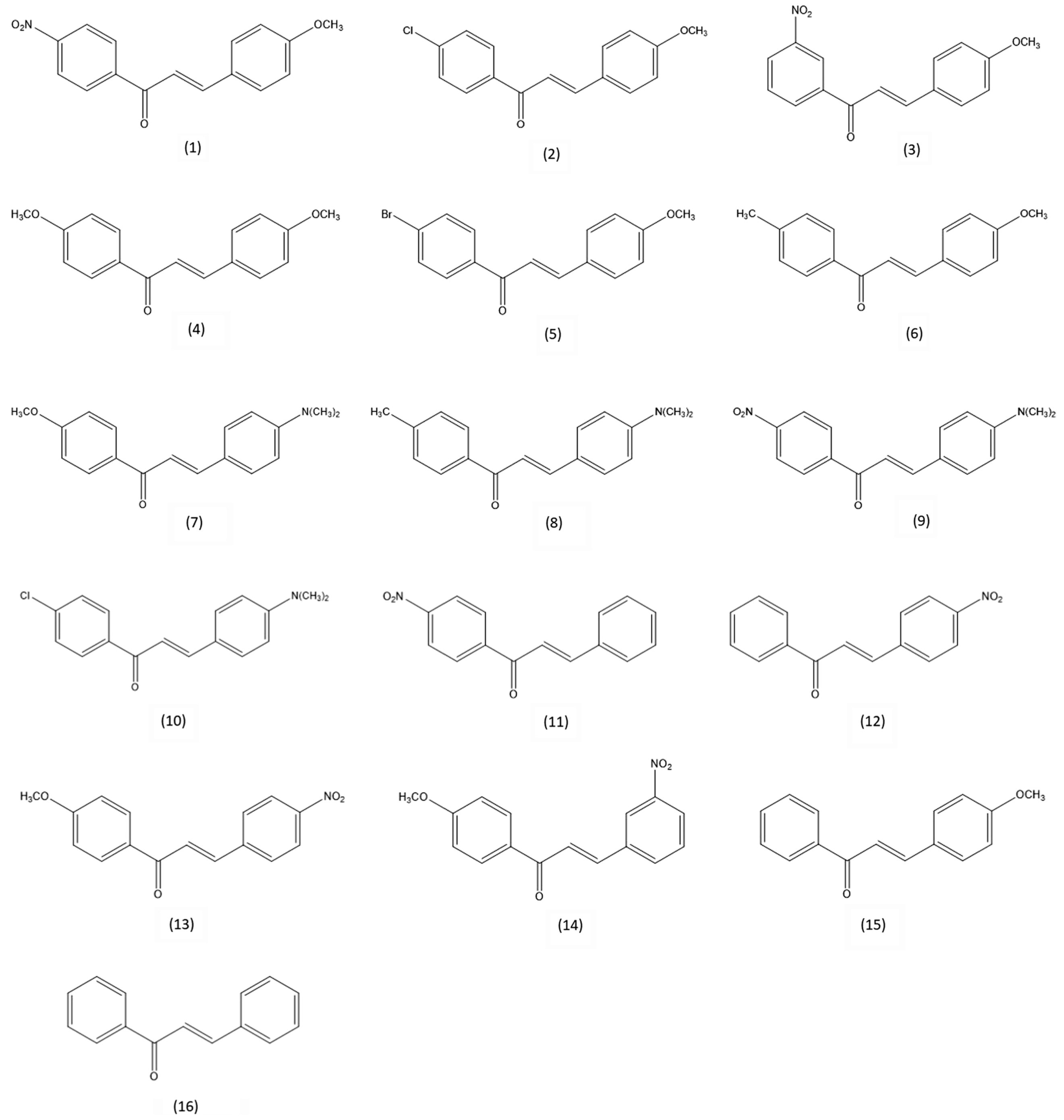
**Fig. 1** General structure of the synthesized compounds

## Experimental studies

### Synthesis

The chalcone derivatives, except for those containing the nitro groups, were synthesized by Claisen–Schmidt condensation between aldehydes and ketones in a base catalysed reaction (Scheme 1). 0.02 mol of aldehyde and 0.02 mol of ketone were added to round-bottom flask containing 40 ml of ethanol. 2.7 ml of 30% aqueous solution of NaOH was then added to the reaction mixture which was then stirred at room temperature for 12 h. The progress of the reaction was monitored by Thin Layer Chromatography. On the completion of the reaction, the contents were poured in ice cold water and the product was filtered. The solid obtained was washed with water till neutral to litmus. The crude chalcone was then dried and weighed and was recrystallized in chloroform–methanol (Furniss 1989).

The chalcone derivatives with nitro groups were synthesized by Claisen–Schmidt condensation in acid-catalysed reaction (Scheme 1) as nitro compounds were found to decompose in the base catalysed reaction. 0.02 mol of aldehyde and 0.02 mol of ketones (4-nitroacetophenone or 3-nitroacetophenone) were added to round-bottom flask containing 20 ml acetic acid saturated with HCl gas. The reaction mixture was then stirred at room temperature for 12 hrs. The progress of the reaction was monitored by TLC. On the completion of reaction, the contents were poured in ice cold water and the product was filtered. The solid obtained was



(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16)

**Fig. 2** Structures of the synthesized compounds

washed with water till neutral to litmus. The crude chalcone was then dried and weighed and was recrystallized in chloroform–methanol (Furniss 1989) (Figs. 1, 2). In case of 4-$N(CH_3)_2$-4′-$NO_2$, the contents of the reaction were neutralized with aq. NaOH before filtration.

The IUPAC names and other details of the synthesized compounds are given in Table 1.

## Instrumentation

$^1$H-NMR spectra were recorded on VARIAN 200 MHz instrument. The sample preparation was done using $CDCl_3$ as a solvent and TMS as the internal reference. $^{13}$C-NMR spectra were recorded in Bruker Avance 100 MHz instrument using $CDCl_3$ as the solvent and TMS, the internal reference. The FT-IR spectra were recorded on Thermo-Nicolet

**Table 1** Synthesized chalcone derivates with compound code, IUPAC name, architecture type and melting point

| Structure number | Compound code | IUPAC name of chalcone derivatives | Architecture type | Melting point (°C) |
|---|---|---|---|---|
| (1) | 4-MeO-4′-$NO_2$ | (E)-3-(4-methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one | A–A–D | 175.2–176.0 |
| (2) | 4-MeO-4′-Cl | (E)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one | A–A–D | 117.3–117.9 |
| (3) | 4-MeO-3′-$NO_2$ | (E)-3-(4-methoxyphenyl)-1-(3-nitrophenyl)prop-2-en-1-one | A–A–D | 172.4–173 |
| (4) | 4-MeO-4′-MeO | (E)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one | D–A–D | 102.0–102.9 |
| (5) | 4-MeO-4′-Br | (E)-1-(4-bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one | A–A–D | 142.2–142.6 |
| (6) | 4-MeO-4′-Me | (E)-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one | D–A–D | 93.8–94.4 |
| (7) | 4-N$(CH_3)_2$-4′-MeO | (E)-3-(4-(dimethylamino)phenyl)-1-(4methoxyphenyl)prop-2-en-1-one | D–A–D | 125.0–126.0 |
| (8) | 4-N$(CH_3)_2$-4′-Me | (E)-3-(4-(dimethylamino)phenyl)-1-(p-tolyl)prop-2-en-1-one | D–A–D | 119.5–119.9 |
| (9) | 4-N$(CH_3)_2$-4′-$NO_2$ | (E)-3-(4-(dimethylamino)phenyl)-1-(4-nitrophenyl)prop-2-en-1-one | A–A–D | 188.5–188.9 |
| (10) | 4-N$(CH_3)_2$-4′-Cl | (E)-1-(4-chlorophenyl)-3-(4-(dimethylamino)phenyl)prop-2-en-1-one | A–A–D | 138.5–139.0 |
| (11) | 4′-$NO_2$C | (E)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one | A–A–D | 74.5–75.0 |
| (12) | 4-$NO_2$C | (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one | D–A–A | 140.3–140.7 |
| (13) | 4-$NO_2$-4′-MeO | (E)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one | D–A–A | 166.2–167.0 |
| (14) | 3-$NO_2$-4′-MeO | (E)-1-(4-methoxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one | D–A–A | 153.4–153.9 |
| (15) | 4-MeOC | (E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one | D–A–D | 78.1–78.4 |
| (16) | Chalcone | (E)-1,3-(Bisphenyl)- prop-2-en-1-one | – | 55.5–56.0 |

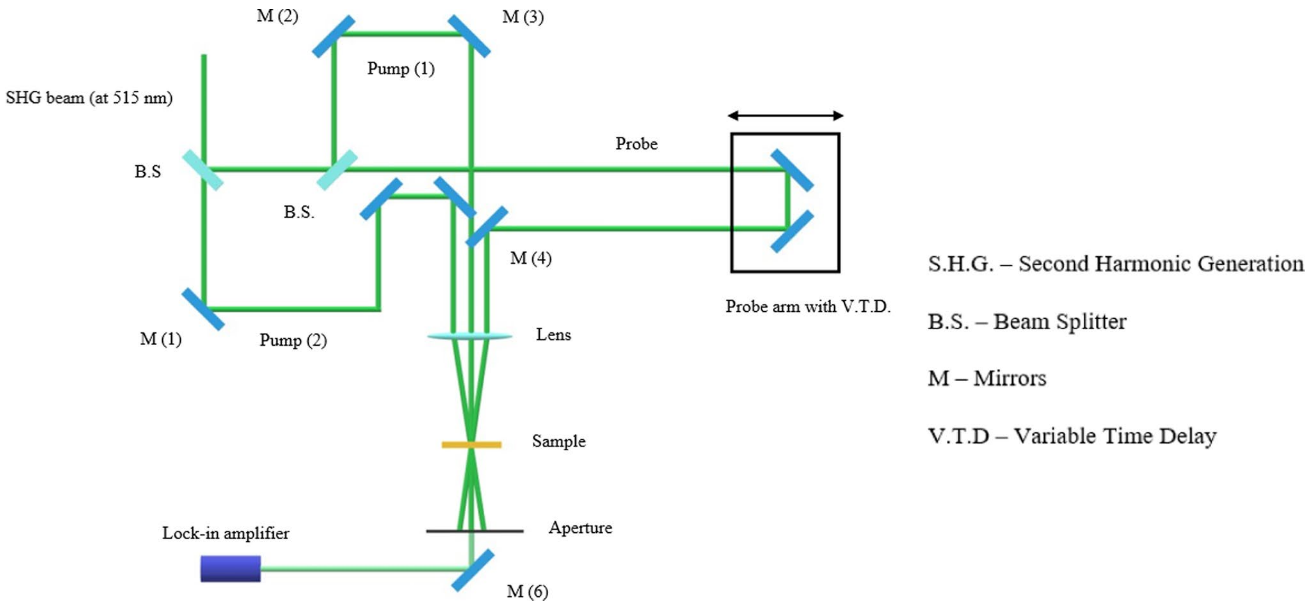


**Fig. 3** Experimental configuration of degenerate four-wave mixing using folded-box CARS geometry

Avatar 370 spectrophotometer between 400 and 4000 cm$^{-1}$ using KBr pellet. The UV–Vis spectra of the chalcone derivatives were recorded using Shimadzu 2450 spectrophotometer in the range of 200–800 nm. For mass spectra, Shimadzu-Q2010MS GC–MS instrument was employed. The thermal studies were carried out in Mettler Toledo TGA/DSC1 STARe System.

## Non-linear optical measurements

### SHG efficiency

The SHG efficiency measurements of the synthesized chalcone derivatives were done using the Kurtz-Perry method (Giuliani et al. 1971) taking urea as a reference. The

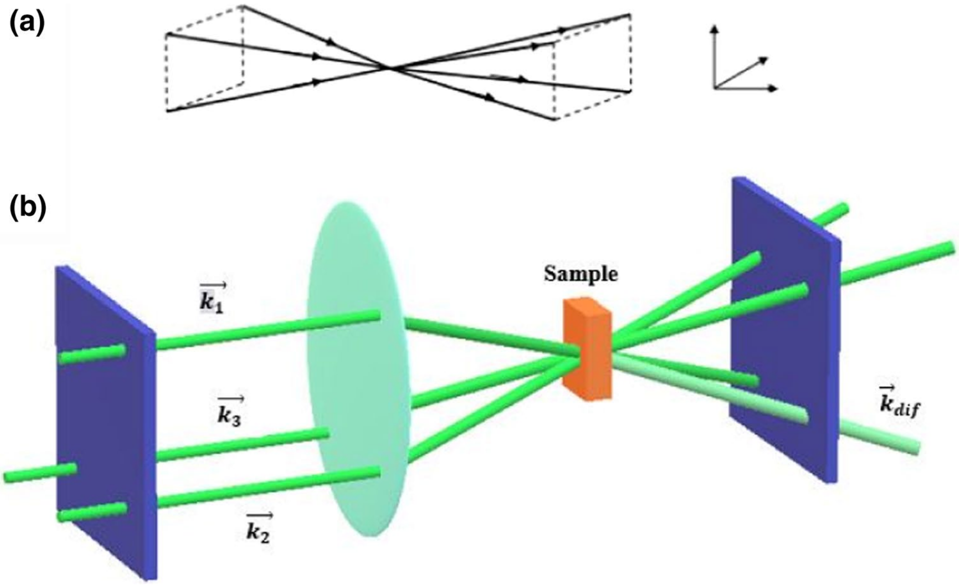


**Fig. 4** Arrangement of beams in folded Box-CARS geometry (Taylor and Saha 2007). **a** Two-dimensional view of the geometry; **b** Three-dimensional view of the geometry

Nd-YAG laser having a fundamental wavelength of 1064 nm, pulse width of 10 ns and a repetition rate of 10 Hz was used for the Second Harmonic Generation studies for the chalcone derivatives. The microcrystalline powder taken in a capillary tube was exposed to the beam which was steered to be incident on the sample. The Second Harmonic (532 nm) generated was detected by a photomultiplier tube which converts the SHG signal to an electrical signal. This electrical signal gets displayed on the oscilloscope.

## Third-order NLO studies

The third-order non-linear studies of the synthesized chalcone derivatives were done using the femtosecond DFWM technique (Sahraoui et al. 1998; Sahraoui and Rivoire 1997). The experimental configuration of DFWM is shown in Fig. 3. This process is known as degenerate since all the four interacting waves have the same frequency. In four wave mixing, the magnitude of the third-order non-linear susceptibility is proportional to the strength of the fourth beam. Thus, measurements of the observed signal yields information about the $\chi^{(3)}$ tensor components of the medium. The molecular second-order hyperpolarizability ($\gamma$) can then be computed knowing the concentrations and the refractive indices. The laser system used for the DFWM studies was a frequency doubled femtosecond ytterbium-doped fiber laser (MenloSystems-BlueCut) with a pulse width less than 500 fs at 515 nm. For our study, we employed the so-called folded-Box CARS geometry. The arrangement of beams in folded-Box CARS geometry is shown in Fig. 4. This configuration gives the advantage of having a background free signal, well separated from the other three beams and is particularly suited for femtosecond applications. In this configuration, the two pumps and the probe are aligned parallel to each other before focusing onto the sample. The alignment is made in such a way that the three incident beams form the three corners of a square on the screen. The folded box CARS geometry gives us the advantages of easy phase matching (Saha 1995). The output signal was detected using a custom-built lock-in technique that used an Arduino microcontroller interfaced to a computer. Since the nonlinear susceptibilities are sensitively dependent on the values of the refractive indices of the compounds, we used a laser-based lateral shift imaging technique (Singh 2002) for measuring these values. With some averaging, this technique is accurate to the third decimal and lends itself to automation.

The solutions of 14 chalcone derivatives in chloroform having the concentration 0.05 mM were prepared for carrying out the study. In case of 4-N$(CH_3)_2$-4′-$NO_2$C, 0.005 mM solution in chloroform was considered in order to avoid the optical dispersion due to its intense colour. The third-order susceptibility of the chalcone derivatives was calculated by using Eq. 1:

$$I_{dif} = \left(\frac{2\pi}{nc}\right)^4 \frac{\omega_{dif}^2}{\varepsilon\left(\omega_{dif}\right)} \left|\chi_{ijkl}^{(3)}\right|^2 I_{pr} I_{pu1} I_{pu2}, \tag{1}$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility, $I_{pr}$, $I_{pu1}$ and $I_{pu2}$ are the intensities of the input pumps and the probe beams, $n$ is the refractive index, $\omega_{diff}$ is the diffracted frequency and $\varepsilon$ is the dielectric constant of the material (Caro and Gower 1982).

The second molecular hyperpolarizability ($\gamma$) was calculated using Eq. 2.

$$\gamma = \frac{\chi^{(3)}_{eff}(solution) - \chi^{(3)}_{eff}(solvent)}{Nf^4}, \tag{2}$$

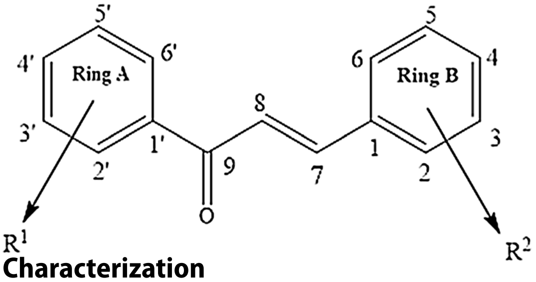
where $N$ is the number density of the solute molecules, $f = \frac{n^2+2}{3}$ is the local field factor (this is due to the difference between the applied macroscopic electric field and the effective electric field, or Lorentz local field, that each atom or molecule experiences) and n is the refractive index of the solution. An Arduino microcontroller-based fully automated refractive index measurement technique that utilizes the lateral displacement of a light beam through the sample was set up and used to measure the refractive index to the third decimal. The details of this will be discussed elsewhere.

The average powers of the two pump beams were 22.3 and 59.7mW, respectively, while the probe beam had an average power of 1.975mW.

### Software strategies for the computational studies

The modelling of the chalcone derivatives was done using Gaussview5 (Dennington et al. 2003) and the energy minimization was carried out using Gaussian09. The chalcone analogues were drawn using the GaussView panel and cleaned appropriately. The molecules were then input into Gaussian and optimized (Opt + Freq) job was considered using the ground state DFT method with the B3LYP functional and the 6-31G (d, p) basis set to a default condition. The charge was 0 and the spin state was set to singlet. For the bromo-substituted chalcone derivative, DFT method was used with the B3PW91 functional and the LanL2MB basis set to a default condition, as the core and inner shell electrons come into play and therefore there was a necessity to factor different electronic condition.

## Results and discussion



### Characterization

The $^1$H-NMR spectra of these compounds were analysed. The proton H-8 was observed in the range of $\delta$ 7.62–7.72 as doublet. Similarly, the proton H-7 was observed in the range of $\delta$ 7.80–7.84 as a doublet. The coupling constants of these protons ranged between $J = 14$ and 16 Hz indicating that these are trans to each other. The proton at H-7 had greater chemical shift as it is in the $\beta$ position with respect to the carbonyl group. The protons H-2′ and H-6′, H-3′ and H-5′, H-2 and H-6, H-3 and H-5 were found to be equivalent in case of para substitutions. The chemical shifts of these protons are dependent on the substituents present. In case of methoxy group as a substituent, the shift of protons at H-3′ and H-5′ and/or H-3 and H-5 were seen in the range $\delta$ 7.1–7.3 due to the shielding from the methoxy group. Similarly, for chalcones containing –$NO_2$ group, H-3′ and H-5′ and/or H-5 and H-3 were seen in the range of $\delta$ 8.20–8.40 due to the electron withdrawing effect of the –$NO_2$ substituent. The protons attached to the methoxy group were observed as a singlet between $\delta$ 3.10–3.20. The ones attached to the –$N(CH_3)_2$ group were seen ~ $\delta$ 3.05. The chemical shift of the protons attached to the carbon of methyl group were seen between $\delta$ 2.3–2.7.

The $^{13}$C-NMR spectra of these compounds were analysed. The carbonyl carbon was observed at around $\delta$ 188. The aromatic carbon signals were observed in the range $\delta$ 120–165. For the compounds with the methoxy substituents, the aromatic carbon attached to the methoxy group was observed in the range of $\delta$ 160–165. In case of the compounds with nitro groups, the aromatic carbon attached to the nitro group appeared at around $\delta$ 154. Similarly, the aromatic carbon attached to the –$N(CH_3)_2$ group was observed in the range of $\delta$ 150–152 and the carbon at the beta position to the carbonyl group appeared at around $\delta$ 145. The carbon at the alpha position to the carbonyl group was seen in the range of δ 118–122. The methoxy carbon was observed at around $\delta$ 55 and N,N-dimethylamino carbons were observed at around $\delta$ 40.

The UV–Vis spectra showed absorptions at different wavelengths corresponding to the absorption by aromatic rings at a lower wavelength at around 205 nm, followed by the absorption by carbonyl group ($\pi \rightarrow \pi^*$ transition) between 320 and 430 nm. In the IR spectra, some of the prominent peaks were observed at 1650–1660 cm$^{-1}$ indicating the presence of a carbonyl group. The three bands of medium intensity were observed between 1500 and 1600 cm$^{-1}$ which corresponds to aromatic C = C stretch. In case of 1, 4-disubstituted chalcones, peak was observed at 815–830 cm$^{-1}$ (aromatic C–H oop bending). The presence of methoxy groups as substituent can be concluded by the peak at 1100–1300 cm$^{-1}$. The peak was observed at 1000–1300 cm$^{-1}$ when dimethyl amine was one of the substituents present in the chalcone derivatives. This is due to C–N stretching. In these chalcone derivatives, peak due to sp$^2$ C–H stretch is observed between 3050 and 3010 cm$^{-1}$.

**Table 2** SHG efficiency of synthesized chalcone derivatives with respect to urea

| | Structure number | Compound code | SHG value with respect to urea |
|---|---|---|---|
| Methoxy group compounds | (5) | 4-MeO-4′-Br[a] | 20 |
| (Methoxy group on Ring B) | (1) | 4-MeO-4′-$NO_2$[c] | 5 |
| | (2) | 4-MeO-4′-Cl[d] | 1.4 |
| | (4) | 4-MeO-4′-MeO[a] | 0.9 |
| | (6) | 4-MeO-4′-Me[b] | 0.5 |
| | (3) | 4-MeO-3′-$NO_2$ | 0 |
| *N*, *N*-dimethyl amino group compounds | (7) | 4-$N(CH_3)_2$-4′-MeO[a] | 4 |
| (*N*, *N*-dimethyl amino group on Ring B) | (8) | 4-$N(CH_3)_2$-4′-Me | 0.5 |
| | (9) | 4-$N(CH_3)_2$-4′-$NO_2$ | 0 |
| | (10) | 4-$N(CH_3)_2$-4′-Cl[e] | 0 |
| Other compounds in a series | (15) | 4-MeO[a] | 8.5 |
| | (12) | 4-$NO_2$C | 2.1 |
| | (11) | 4′-$NO_2$C | 0 |
| | (13) | 4-$NO_2$-4′-MeO[a] | 0 |
| | (14) | 3-$NO_2$-4′-MeO | 0 |
| | (16) | Chalcone[a] | 0 |

SHG efficiencies of some of the chalcone derivatives have been already reported in the literature

[a] Reported by (Zhao et al. 2000)

[b] Reported by (Ravindrachary et al. 2005

[c] Reported by (Dharmaprakash 2017)

[d] Reported by (Prabu et al. 2014

[e] Reported by (Janardhana et al. 2013)

The mass spectra of the compounds showed molecular ion peak as $[M+1]^+$ peaks. In case of 4-$N(CH_3)_2$-4′Cl, $[M+2]^+$ peak with 33% intensity was observed indicating the presence of chloro group. Similarly, the mass spectrum of 4MeO-4′Br showed $[M]^+$ and $[M+2]^+$ peaks of equal intensities indicating the presence of bromo group.

## SHG efficiency

The values obtained from the SHG measurements of the chalcone derivatives that we have studied are shown in Table 2

Apart from the non-centrosymmetric crystal structure, the SHG efficiency of a molecule is influenced by various factors that include conjugation, π–π stacking of the aromatic moieties and hydrogen bonding (Kiran et al. 2014). The compounds that we have reported here exhibit cross conjugation between the benzene–π electrons and the carbonyl compound.

It was previously reported in the literature that the compound 4-MeO-4′-Br is 20 times more active than urea. The compounds with bromo group as a substituent exhibit greater SHG effects (Zhao et al. 2000). In our present study, the SHG efficiency was found to increase in the order of compounds 4-MeO-4′-Me < 4-MeO-4′-MeO < 4-MeO-4′-Cl < 4-MeO-4′-$NO_2$. Thus, the SHG efficiency was found to increase with the increase in the electron withdrawing ability of the substituent group in ring A, thereby showing that A-A-D architecture (4-MeO-4′-$NO_2$ and 4-MeO-4′-Cl) gives better SHG efficiency than D–A–D architecture (4-MeO-4′-Me and 4-MeO-4′-MeO) for the methoxy group of compounds. Also, 4MeO-3′$NO_2$ has no SHG efficiency, whereas its isomer 4-MeO-4′-$NO_2$ shows SHG efficiency five times that of urea. This shows that the position of the substituent in ring A also affects the SHG efficiency of a given compound.

The study of SHG efficiency of the compounds with N, N-dimethylamino group fixed at one end of the ring (B ring) and various substituents incorporated at the other end (A ring) has been done. The SHG efficiency increases in the order of compounds: 4-$N(CH_3)_2$-4′-$NO_2$ ~ 4-$N(CH_3)_2$–4′-Cl < 4-$N(CH_3)_2$–4′-Me < 4-$N(CH_3)_2$–4-MeO. This leads us to the conclusion that in case of the compounds with dimethyl amino group, the SHG efficiency increases with the increase in the electron donating ability of the substituent group at ring A rendering superior SHG efficiency of compounds wit h dimethyl amino group having D–A–D architecture (4-$N(CH_3)_2$-4′-Me and 4-$N(CH_3)_2$-4′-MeO) over their A–A–D (4-$N(CH_3)_2$-4′-$NO_2$ and 4-$N(CH_3)_2$-4′-Cl) counterpart.

**Table 3** Third-order non-linear susceptibility, second-order hyperpolarizability and refractive index (in $CHCl_3$) of the synthesized chalcone derivatives

| | Structure number | Compound code | $\chi^3$ ($10^{-14}$ esu) | Second order hyperpolarizability ($10^{-31}$ esu) | Refractive index |
|---|---|---|---|---|---|
| Methoxy group compounds | (1) | 4-MeO-4′-$NO_2$ | 3.37 ± 0.52 | 2.03 ± 0.05 | 1.485 ± 0.002 |
| (Methoxy group in Ring B) | (2) | 4-MeO-4′-Cl | 3.35 ± 0.53 | 1.95 ± 0.03 | 1.486 ± 0.002 |
| | (3) | 4-MeO-3′-$NO_2$ | 3.30 ± 0.42 | 1.53 ± 0.36 | 1.433 ± 0.002 |
| | (4) | 4-MeO-4′-MeO | 3.24 ± 0.41 | 1.28 ± 0.40 | 1.418 ± 0.002 |
| | (5) | 4-MeO-4′-Br | 2.97 ± 0.45 | 0.42 ± 0.27 | 1.418 ± 0.002 |
| | (6) | 4-MeO-4′-Me | 2.94 ± 0.44 | 0.32 ± 0.28 | 1.413 ± 0.002 |
| N,N-dimethylamino group compounds | (7) | 4-$N(CH_3)_2$-4′-MeO | 3.16 ± 0.45 | 1.06 ± 0.28 | 1.433 ± 0.002 |
| (N,N-dimethylamino group in Ring B) | (8) | 4-$N(CH_3)_2$-4′-Me | 3.02 ± 0.46 | 0.60 ± 0.22 | 1.431 ± 0.002 |
| | (9) | 4-$N(CH_3)_2$-4′-$NO_2$* | 2.99 ± 0.47 | 4.36 ± 1.80 | 1.431 ± 0.002 |
| | (10) | 4-$N(CH_3)_2$-4′-Cl | 2.99 ± 0.47 | 0.48 ± 0.19 | 1.432 ± 0.002 |
| Other compounds in a series | (11) | 4′-$NO_2$C | 3.38 ± 0.39 | 1.72 ± 0.46 | 1.418 ± 0.002 |
| | (12) | 4-$NO_2$C | 3.14 ± 0.45 | 0.98 ± 0.28 | 1.432 ± 0.002 |
| | (13) | 4-$NO_2$-4′-MeO | 3.35 ± 0.42 | 1.71 ± 0.38 | 1.434 ± 0.002 |
| | (14) | 3-$NO_2$-4′-MeO | 3.02 ± 0.47 | 0.59 ± 0.20 | 1.433 ± 0.002 |
| | (15) | 4-MeOC | 3.50 ± 0.41 | 2.23 ± 0.43 | 1.437 ± 0.002 |
| | (16) | Chalcone | 3.32 ± 0.42 | 1.57 ± 0.39 | 1.429 ± 0.002 |

*The NLO measurement of 4-$N(CH_3)_2$-4′-$NO_2$ was done at 0.005 mM concentration solution in $CHCl_3$ in order to avoid the optical dispersion due to its intense colour

For all other compounds, NLO measurement was done at 0.05 mM concentration solution in $CHCl_3$

An interesting observation was made in the case of the compounds 4-$NO_2$C and 4′-$NO_2$C. The SHG values of these two compounds are found to be 2.16 and 0.01 times that of urea, respectively. This indicates that the position of a substituent in a particular ring (ring A or B) also affects the SHG efficiency of a molecule. The presence of nitro group in A ring renders greater SHG efficiency than its presence in the B ring. Though, as mentioned earlier, SHG efficiency of a molecule is mainly influenced by its crystal structure, this study led us to the conclusion that the substituents and their positions introduced in a molecule also have an effect on its SHG efficiency.

## Third order non-linear optical susceptibility measurements

The experimental results of the chalcone derivatives that we have reported here are shown in the Table 3.

The chalcone derivatives we have reported here have D–A–A, D–A–D and A–A–D architectures. Considering the molecules with A–A–D architecture, methoxy group is incorporated in ring B and at the other end on ring A, the incorporated substituent group is varied in terms of its electron withdrawing ability. It has been observed that the increase in the electron withdrawing/accepting ability of a substituent group in A–A–D type molecules result in better second-order hyperpolarizability value and hence the better third-order non-linear optical activity. In the methoxy group of compounds with A–A–D architecture, the second-order hyperpolarizability increases in the order of compounds 4-MeO-4′-Br < 4-MeO-3′-$NO_2$ < 4-MeO-4′-Cl < 4-MeO-4′-$NO_2$. The greater the electron accepting ability of a substituent group at 4′ position (in A-ring), the greater the second-order hyperpolarizability. The extended conjugation in case of 4-MeO-4′-$NO_2$ results in its greater second-order hyperpolarizability value than 4-MeO-3′-$NO_2$. Evaluating the methoxy group of compounds with D–A–D architecture where methoxy group is fixed in ring B, the second-order hyperpolarizability value was found to increase with the increase in the electron donating ability of the substituent at ring A. Thus 4-MeO-4′-MeO showed greater second-order hyperpolarizability value than 4-MeO-4′-Me. However, it was observed that 4-MeOC has highest second-order hyperpolarizability among the methoxy groups of compounds. The simple chalcone was also found to have an appreciable third-order optical activity.

Evaluating p-dimethyl amino group of chalcone derivatives, the second-order hyperpolarizability of the molecules of type A–A–D, in which p-dimethyl amino group was attached at ring B, was observed to increase with the increasing electron withdrawing ability of the substituent group at ring A. Thus 4-$N(CH_3)_2$-4′-$NO_2$ showed greater second-order hyperpolarizability than 4-$N(CH_3)_2$-4′-Cl. In case of the p-dimethyl amino group of compounds of type D–A–D, the second-order hyperpolarizability was observed to increase with the increase in electron donating ability of the substituent group at A ring. Experimentally, it was observed that 4-N(CH$_3$)$_2$-4′MeO showed greater second-order hyperpolarizability than 4-N(CH$_3$)$_2$-4′Me.

For the molecules with D–A–A architecture, it was observed that the non-linear optical activity of a compound increases with the increase in the electron donating ability of a substituent on ring A as observed in case of the compounds 4-NO$_2$-4′-MeO and 4-NO$_2$C, where the former has greater second-order hyperpolarizability than the latter. Also, it was experimentally found that 4-NO$_2$-4′-MeO has greater non-linear activity than 3-NO$_2$-4′-MeO. This clearly indicates that the position of the substituent in the ring also influences the non-linear activity of the compound. The presence of extended conjugation in 4-NO$_2$-4′-MeO results in its greater second-order hyperpolarizability than that of 3-NO$_2$-4′-MeO. The difference in the non-linear optical activity was also observed when the same substituent group was incorporated on one of the either rings (ring A or ring B) as in case of 4′-NO$_2$C (A–A–D architecture) and 4-NO$_2$C (D–A–A architecture). 4′-NO$_2$C, i.e. nitro group when introduced in the ring A, showed better non-linear activity than 4-NO$_2$C where nitro group is placed on the ring B.

Among the synthesized compounds that we have reported here, the compounds having A–A–D architecture showed better non-linear optical activity. From this study, we conclude that the electron withdrawing group and the electron donating group should be incorporated in ring A and ring B, respectively, at the para positions for better non-linear optical activity.

The NLO measurements of the four chalcone derivatives 4-MeO-4′-MeO, 3-NO$_2$-4′-MeO, 4-N(CH$_3$)$_2$-4′-Cl, 4-MeO-4′-NO$_2$ have been reported in the literature where the measurements have been done by using *Z*-scan technique (Ravindra et al. 2007); (Janardhana et al. 2013); (Dharmaprakash 2017). In the mentioned studies, the Re $\chi^3$ values of 4-MeO-4′-MeO, 3-NO$_2$-4′-MeO and 4-N(CH$_3$)$_2$-4′-Cl have been reported as $-1.923\times10^{-13}$esu, $-1.619\times10^{-13}$esu and $-1.89\times10^{-20}$ m$^2$ V$^{-2}$, respectively. For the compound 4-MeO-4′-NO$_2$, the second-order hyperpolarizability has been reported to be $2.9\times10^{-31}$ esu. In our study, we obtained almost the same second-order hyperpolarizability value of $2.031\times10^{-31}$esu for 4-MeO-4′-NO$_2$. The third-order susceptibility values of the synthesized compounds that we have reported here are in the order of $10^{-14}$esu.

For this experiment, carbon disulphide was used as a reference to optimize the setup. The third-order susceptibility value and the refractive index of carbon disulphide were found to be ($5.30\pm0.38\times10^{-12}$) esu and ($1.63\pm0.002$), respectively. Thus, the work we have reported here gives an idea as to what kind of substituent group should be introduced in the most suitable position so as to design and synthesize the organic compounds with good non-linear optical activity.

## Thermal studies of 4-N(CH$_3$)$_2$-4′NO$_2$ and 4-MeO-4′NO$_2$

The thermal stability of a nonlinear compound is critically important when it comes to real-world applications. We, therefore, carried out the thermal analysis of 4-N(CH$_3$)$_2$-4′-NO$_2$ and 4-MeO-4′-NO$_2$ as these showed higher NLO activities than all the other compounds that we have reported here. The TGA–DSC analysis of the dried crystals of 4-N(CH$_3$)$_2$-4′-NO$_2$ and 4-MeO-4′-NO$_2$ were performed under nitrogen flow of 100 ml/min. The equilibrate temperature was 30 °C and the instrument was heated up to 600 °C at heating rate of 10 °C/min.

The results obtained from the thermal analysis are depicted in Fig. 5.The endothermic peak in DSC curves shown in Fig. 5. implies that the compounds

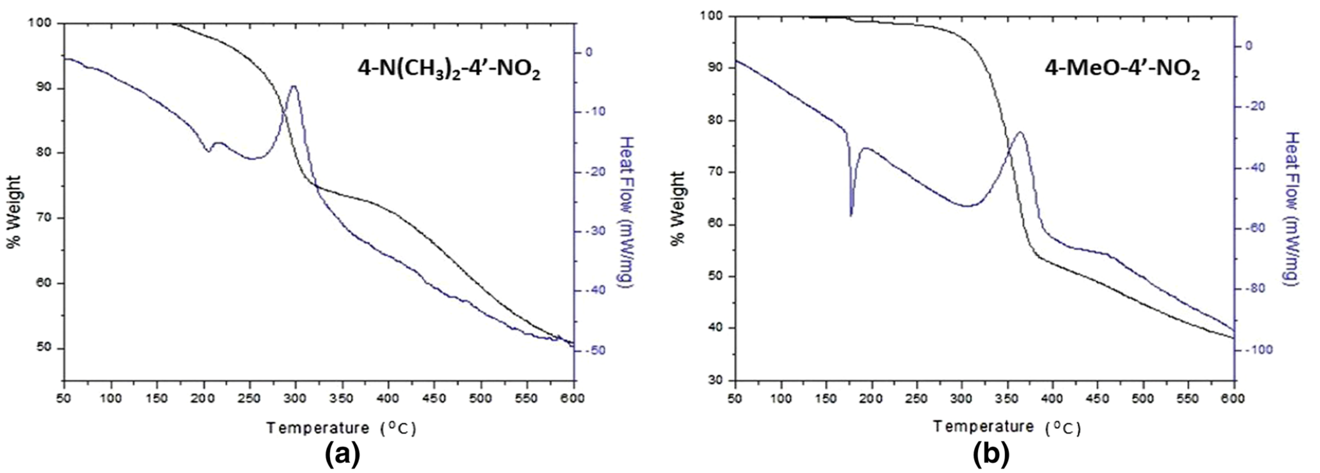


**Fig. 5** TGA–DSC Curve for: **a** 4-N(CH$_3$)$_2$-4′-NO$_2$ and **b** 4-MeO-4′-NO$_2$

**Table 4** Parameters obtained from in silico studies of the synthesized chalcone derivatives

| Structure number | Compounds | Energy gap (AU) in $CHCl_3$ | Static dipole moment (in Debye) | Ionisation potential (AU) | Hardness (AU) |
|---|---|---|---|---|---|
| − 9 | 4-$N(CH_3)_2$-4′-$NO_2$ | 0.0918 | 13.1647 | 0.19514 | − 0.0459 |
| − 10 | 4-$N(CH_3)_2$-4′-Cl | 0.1174 | 5.1217 | 0.19212 | − 0.0587 |
| − 7 | 4-$N(CH_3)_2$-4′-MeO | 0.1224 | 6.0261 | 0.18878 | − 0.0612 |
| − 8 | 4- $N(CH_3)_2$-4′-Me | 0.1211 | 7.8197 | 0.1898 | − 0.0606 |
| − 3 | 4-MeO-3′-$NO_2$ | 0.1244 | 10.5973 | 0.21978 | − 0.0622 |
| − 13 | 4-$NO_2$-4′-MeO | 0.1244 | 7.0817 | 0.23291 | − 0.0622 |
| − 1 | 4-MeO-4′-$NO_2$ | 0.1247 | 7.4651 | 0.20953 | − 0.0624 |
| − 11 | 4′-$NO_2$C | 0.1296 | 7.2269 | 0.23972 | − 0.0648 |
| − 14 | 3-$NO_2$-4′-MeO | 0.1332 | 10.0639 | 0.23194 | − 0.0666 |
| − 2 | 4-MeO-4′-Cl | 0.1365 | 6.1478 | 0.21713 | − 0.0682 |
| − 6 | 4-MeO-4′-Me | 0.1399 | 4.1085 | 0.21457 | − 0.07 |
| − 4 | 4-MeO-4′-MeO | 0.141 | 2.346 | 0.21312 | − 0.0705 |
| − 12 | 4-$NO_2$C | 0.1426 | 5.4762 | 0.25326 | − 0.0713 |
| − 5 | 4-MeO-4′-Br | 0.1459 | 7.2976 | 0.14505 | − 0.073 |
| − 15 | 4-MeOC | 0.1389 | 4.4986 | 0.21549 | − 0.0695 |
| − 16 | Chalcone | 0.1519 | 3.8602 | 0.23394 | − 0.0759 |

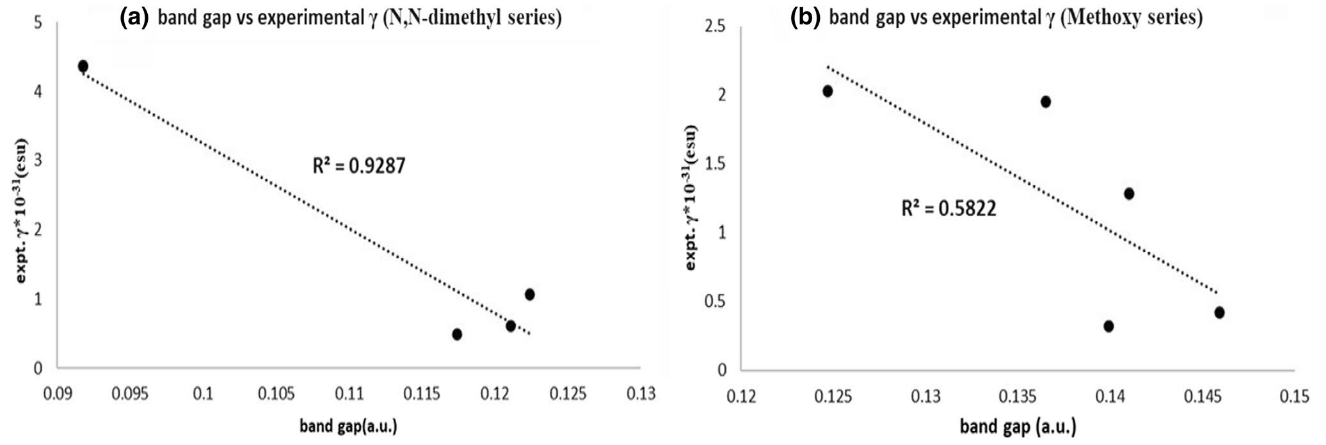


**Fig. 6** Plot of calculated band gap vs experimentally obtained second-order hyperpolarizability(γ) for: **a** N, N-dimethyl amino series of compounds; **b** Methoxy series of compounds

4- $N(CH_3)_2$-4′-$NO_2$ and 4-MeO-4′-$NO_2$ undergo irreversible endothermic transition at 188 and 175 °C, respectively. The peak of the endothermic transition represents the melting point of the said compound which is 188.5 °C for 4-$N(CH_3)_2$-4′-$NO_2$ and 175.2 °C for compound 4-MeO-4′-$NO_2$. There is no phase transition of the aforementioned compounds observed before melting. The exothermic peak observed at 290 °C for 4-$N(CH_3)_2$-4′-$NO_2$ and 366 °C for 4-MeO-4′-$NO_2$ indicates that the compounds 4-$N(CH_3)_2$-4′-$NO_2$ and 4-MeO-4′-$NO_2$ undergo decomposition at 290 and 366 °C, respectively.

## Results obtained from computational studies

The in silico studies of the reported chalcone derivatives have been done. The values of global reactivity parameters like dipole moment, ionisation potential and hardness that are related to the energy gap of a molecule have been shown in Table 4. Lower energy gap corresponds to higher polarizability which in turn results in the better non-linear activity of a molecule. As is already known, the compounds with larger HOMO–LUMO energy gap are considered to be hard molecules having lower reactivity. Thus, the lower the chemical hardness of a molecule, the better is its NLO response

(Khazaal et al. 2020; Khalid et al. 2020).Our experimental results follow the same trend.

From the in silico studies, for the methoxy group of compounds, the energy gap was found to increase in the order 4-MeO-4′-$NO_2$ < 4-MeO-4′-Cl < 4-MeO-4′-Me < 4-MeO-4′-MeO < 4-MeO-4′-Br. It was observed that the compounds having lowest energy gap showed the highest third-order susceptibility value obtained experimentally. The correlation between the calculated band gap and the experimentally obtained second-order hyperpolarizability value has been shown in Fig. 6. The fact that large differences in the energy gap results in a noticeable change in the hyperpolarizability values is evident in these experimental observations.

For p-dimethyl amino group compounds, the energy gap was found to increase in the order of compounds 4-$N(CH_3)_2$-4′-$NO_2$ < 4-$N(CH_3)_2$-4′-Cl < 4-$N(CH_3)_2$-4′-Me < 4-$N(CH_3)_2$-4′-MeO. Thus, the low energy gap obtained computationally for 4- $N(CH_3)_2$–4′- $NO_2$ correlates with our experimental finding of the said compound having greater non-linear activity than the other compounds in p-dimethyl amino series as is shown in Fig. 6. Similarly, 4′-$NO_2$C was found to have smaller energy gap than 4-$NO_2$C which is in correlation with our experimental finding of 4′-$NO_2$C having greater non-linear activity than 4-$NO_2$C.

The compound 4-$N(CH_3)_2$-4′-$NO_2$ which was found to have the highest third-order susceptibility among all the synthesized compounds reported here showed the highest dipole moment value. Among the methoxy group of compounds, 4-MeO-4′-$NO_2$ and 4-MeO-3′-$NO_2$ showed dipole moments greater than other methoxy group of compounds like 4-MeO-4′-Br, 4-MeO-4′-Cl, 4-MeOC and 4-MeO-4′-Me. The reactivity parameters like ionisation potential and hardness correlate with the energy gap and hence the non-linear optical activity.

## Conclusion

We have reported the synthesis, characterization and structure–activity relationship of 15 chalcone derivatives with the architectures A–A–D, D–A–D and D–A–A. These derivatives were synthesized by the Claisen–Schmidt condensation reaction and characterized by NMR, IR, UV–Vis and Mass spectrometry. For the first time to our knowledge, we have used the femtosecond degenerate four wave mixing (DFWM) technique to quantify and compare the third-order non-linear optical (NLO) activity of all the 15 compounds, under identical conditions, in order to establish the structure–activity relationship. The second harmonic generation (SHG) efficiencies for all the compounds have also been evaluated using the Kurtz-Perry powder method. Among the compounds that we have synthesized here, the ones with A–A–D architecture show the highest NLO activity. Our results show that the NLO activity of a compound with A–A–D architecture can be further enhanced by incorporating a substituent with strong electron withdrawing ability in ring A and strong electron donating substituent in ring B. The results of the in silico studies that we have carried out correlate well with our experimental findings. The *structure activity* relationship has mainly been established on the basis of the effect of substituent incorporated on the non-linear response of a compound which eventually enabled us to determine the best architecture for better non-linear response of the chalcone derivatives. 4-$N(CH_3)_2$-4′-$NO_2$ and 4-MeO-4′-$NO_2$ show the highest NLO activity among the compounds we have reported here and hence these compounds can be explored for their photonic applications.

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## Compliance with ethical standards

**Conflict of interest** The author states no conflict of interest.

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