



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

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## ABSTRACT

Nine chalcones were prepared via Claisen-Schmidt condensation, and characterized by UV–vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C 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 chalcones 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<sub>2</sub>. *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 susceptibilities.

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## 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 requirements 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  $\pi$  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– $\pi$ –A– $\pi$ –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  $\pi$ -conjugated bridge and a strong

$\pi$ -electron acceptor. Chalcones satisfy these criteria given their  $\pi$ -conjugated bridge that can be manipulated with a wide range of substitutions.

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

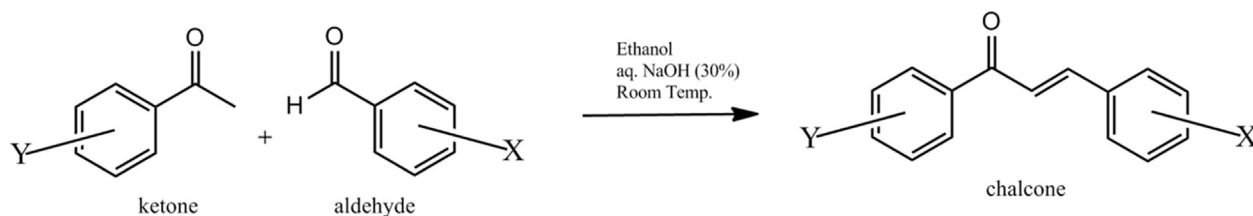
### 2.1. Preparation of the chalcones

General scheme for preparation [13]:

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

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**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.

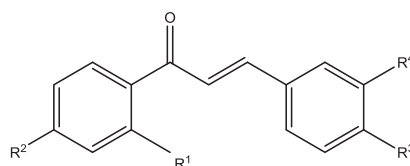
## 2.2. Single crystal growth and XRD analysis

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

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-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\omega$ -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 SHELXS97<sup>2</sup> and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7 [15]. Anisotropic displacement parameters were included for all non-hydrogen 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  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}$  for methyl atoms.

**Table 1**

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



Substituent	IUPAC name	Code	Yield (%)	Melting point (°C)
$R^1 = -\text{H}, R^2 = -\text{H}, R^3 = -\text{N}(\text{Me})_2, R^4 = -\text{H}$	(E)-1-phenyl-3-(4- <i>N,N</i> -dimethylaminophenyl)prop-2-ene-1-one	4-NDM-C	85	68–72
$R^1 = -\text{H}, R^2 = -\text{OH}, R^3 = -\text{OMe}, R^4 = -\text{H}$	(E)-1-(4-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-ene-1-one	4-MO-4'-HC	68	182–184.2
$R^1 = -\text{OH}, R^2 = -\text{H}, R^3 = -\text{OMe}, R^4 = -\text{H}$	(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-ene-1-one	4-MO-2'-HC	76	186.2–188
$R^1 = -\text{H}, R^2 = -\text{OH}, R^3 = -\text{Cl}, R^4 = -\text{H}$	(E)-3-(4-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-ene-1-one	4-Cl-4'-HC	90	190.52
$R^1 = -\text{H}, R^2 = -\text{OH}, R^3 = -\text{H}, R^4 = -\text{Cl}$	(E)-3-(3-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-ene-1-one	3-Cl-4'-HC	88	198–200
$R^1 = -\text{H}, R^2 = -\text{OH}, R^3 = -\text{N}(\text{Me})_2, R^4 = -\text{H}$	(E)-3-(4-( <i>N,N</i> -dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-ene-1-one	4-NDM-4'-HC	64	122.3–124.2
$R^1 = -\text{OH}, R^2 = -\text{H}, R^3 = -\text{N}(\text{Me})_2, R^4 = -\text{H}$	(E)-3-(4-( <i>N,N</i> -dimethylamino)phenyl)-1-(2-hydroxyphenyl)prop-2-ene-1-one	4-NDM-2'-HC	78	171.8–172.9
$R^1 = -\text{H}, R^2 = -\text{Br}, R^3 = -\text{N}(\text{Me})_2, R^4 = -\text{H}$	(E)-1-(4-bromophenyl)-3-(4-( <i>N,N</i> -dimethylamino)phenyl)prop-2-ene-1-one	4-NDM-4'-BrC	80	145.2–146.8
–	(E)-3-(4-( <i>N,N</i> -dimethylamino)phenyl)-1-(thiophen-2-yl)prop-2-ene-1-one	4-NDM-TC	91	101–103

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