



Synthesis, characterization of novel cyclohexenone derivatives and computation of their optical response



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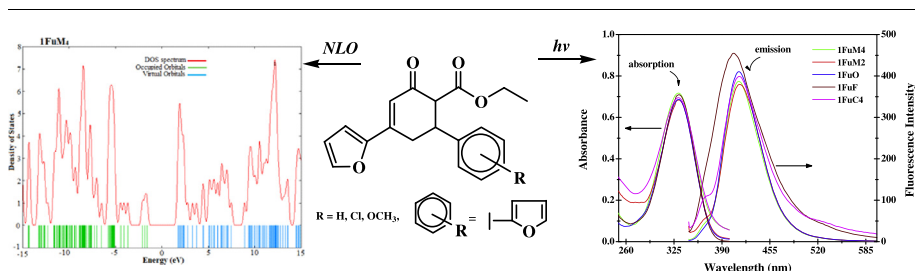
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HIGHLIGHTS

- A viable approach for the synthesis of five new cyclohexenone derivatives from Robinson annulation is described.
- Micro- and spectral analysis have been effectively operated to confirm the molecular structures of cyclohexenones.
- As-synthesized cyclohexenones exhibit intense violet fluorescence and display high hyperpolarizability values.
- The computed and experimental electronic transitions are in good agreement.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study reports the successful development of five new cyclohexenone derivatives (CDs) using rational design synthesis principles and quantum chemical calculations. These new CDs were synthesized by following a convenient route of Robinson annulation, and the molecular structure of these CDs were later confirmed by various analytical techniques such as ¹H NMR, ¹³C NMR, FT-IR, UV-Vis spectroscopy and Mass spectrometry. The results from spectroscopic studies show that the as-synthesized CDs molecules apparently emit violet light at about 406–414 nm. Moreover, polarizability (α) and first static hyperpolarizability (β) were computed by density functional theory (DFT). In addition, the UV-Vis spectra, transition character and electronic structures of these CDs were computed by using the time dependent density functional theory (TD-DFT). It was interesting to note that the values of computed and experimental electronic transitions (λ_{max}) were in good agreement. Finally, the measurements of higher non-linear optical (NLO) response of our newly synthesized CDs suggest their potential for application in photonic devices.

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Introduction

At present, the developments of materials that exhibit second-order nonlinear optical (NLO) responses are receiving significant

attention, primarily due the potential applications of these materials in the area of optoelectronic technology [1]. On the basis of theoretical and experimental investigations, several principles have been suggested to improve the second-order NLO response. These principles include planar donor- π -conjugated bridge-acceptor (D- π -A) type [2], bond length alternation (BLA) theory [3], auxiliary donor and acceptor representation of heterocycles [4], and twisted π -electron systems [5]. Literature suggests that the large second-order NLO response can be attained by optimizing the D/A strength and/or by extending the conjugated bridge [6]. Owing to the flexibility of altering the molecular structure, the organic molecules are therefore investigated as the potential candidates for optimizing the NLO properties in optical signal processing, data storage, sensor protection and imaging [7,8].

Among a variety of organic molecular systems, the chalcones are open chain flavonoids with two aromatic rings attached by an unsaturated carbonyl moiety [9–11]. Though, the chalcones are notorious due to their biological properties, in several cases, the presence of extensive conjugation in these molecules also provides charge transfer axis. In addition, one can easily incorporate the appropriate functionalities on the two aromatic rings of the chalcones and thereby can tune one aromatic ring as donor and second as acceptor [12,13]. This charge transfer from donor to acceptor can take place through charge transfer axis [14]. Since, they display NLO responses, chalcones with delocalized π -electron systems are superior candidates as NLO materials compared to the standard p-nitroaniline [15].

A number of studies show that the cyclic chalcones display different types of pharmacological activities [16,17]. Michael additions of ethyl acetoacetate to numerous chalcones, followed by internal aldol condensation, have compelled them as effective synthons in various projected synthesis of azoles and cyclohexenones derivatives [18–22]. Extensive optical properties and various chemical functions of cyclohexenone derivatives also make them valuable compounds for applications such as organic light-emitting devices (light emitting laser, laser pointers, light-emitting diodes etc.) [23] and fluorescent probes for membranes [24,25].

This work demonstrates the synthesis and characterization of some novel cyclohexenone derivatives (CDs) via a convenient route of Robinson annulations. In order to fully explore the properties of these newly synthesized CDs, non-linear optical properties and absorption spectra of these compounds were calculated using quantum chemical methods. Our results revealed that the investigated molecules are likely to have interesting NLO properties as their hyperpolarizability values etc. are high. Moreover, in the present work, we were also able to generate some high responsive optical moieties in our newly synthesized CDs that may possibly lead to the molecular and material engineering pathways in future.

Materials and methods

Reagents

The reagents; ethyl acetoacetate, 4-Chlorobenzaldehyde, 2-Methoxybenzaldehyde, 4-Methoxybenzaldehyde, 2-Furfural and 2-Acetylfuran were purchased from Fluka (Germany). The liquid reagents were distilled at their boiling points and the solid reagents were characterized by recording their melting points. No further purification was required. Sulfuric acid and hydrochloric acid (37%) were obtained from Stedee Ltd. The solvents chloroform, ethyl acetate, absolute ethanol and pet ether were purchased from Sigma Aldrich (Germany). All the solvents were used after necessary purification and drying according to the standard procedures. The dried solvents were stored over molecular sieves (4 Å).

Compound characterization techniques

R_f values were calculated by using precoated silica gel aluminum backed plates Kiesel gel 60F₂₅₄ Merck (Germany) using ethylacetate: pet-ether (1:4) as developing solvents. Melting points of the compounds were determined in open capillaries using Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectral data were recorded on Bio-Rad Merlin Spectrophotometer using KBr disks. ¹H NMR and ¹³C NMR spectra were recorded on Bruker (300 MHz) AM-250 spectrometer in CDCl₃ solution using TMS as internal standard. EIMS was recorded on Agilent mass spectrometer. Purity of each compound was ascertained by thin layer chromatography. The purification of synthesized compounds was achieved mostly through recrystallization, the use of solvent extraction, or by making preparative thin layer chromatography or column chromatography whenever required.

Steady-state fluorescence measurements

Steady-state fluorescence (SSF) was performed on a Perkin Elmer LS 55 Luminescence Spectrometer with PC controlled software FinWinLab. The Photo Multiplier tube (PMT) voltage was kept at 665 V. The emission and excitation slits were fixed at 6.0 nm each. The excitation wavelength was taken as 331 nm. The scan range used was from 350 to 600 nm. Polarizers were kept clear and no cutoff was operating during the scan. The temperature of the cell was fixed with the help of an external circulator water bath.

Spectrophotometric (UV-Vis) measurements

Spectrophotometric measurements were performed on a Perkin-Elmer Lambda 20 ultraviolet-visible spectrophotometer with 1.0 cm quartz cells at a temperature of 25.0 ± 0.1 °C. The scan range used was from 200 to 400 nm.

General synthetic methods

The synthetic strategy for the titled compounds is outlined in the following Scheme 1. Furanyl-containing chalcone analog 1 (3 mmol) and ethyl acetoacetate 2 (0.39 g, 0.40 mL, 3 mmol) were refluxed for 2 h in 10–15 mL ethanol in the presence of 0.5 mL 10% NaOH aqueous solution. The reaction mixture was then poured with good stirring into 200 mL ice-cold water and kept at room temperature until the reaction product separated as a solid, which was filtered off and recrystallized from ethanol.

The molar ratio, physical, FTIR, ¹H NMR, ¹³C NMR and EIMS data for these compounds are given below:

Ethyl-6-(4-methoxyphenyl)-4-(furan-2-yl)-2-oxocyclohex-3-ene-1-carboxylate (1FuM₄)

Carmel solid, Yield 3.0 g (65%); m.p.: 83–85 °C. ¹H NMR (CDCl₃, 300 MHz): δ 1.07 (t, J = 6.9 Hz, 3H), 4.06 (q, J = 6.9 Hz, 2H), 3.00 (dd, J_1 = 2.5 Hz, J_2 = 16.5, 1H), 2.80–2.86 (m, 1H), 3.72 (dd, J_1 = 2.7 Hz, J_2 = 6.75, 2H), 6.60 (s, 1H), 7.57 (d, J = 1.7 Hz, 1H), 6.53 (dd, J_1 = 1.8 Hz, J_2 = 3.4, 1H), 6.76 (d, J = 3.6 Hz, 1H), 7.24 (dd, J_1 = 2.1 Hz, J_2 = 6.6, 2H), 6.89 (dd, J_1 = 2.1 Hz, J_2 = 6.6, 2H), 3.81 (s, 3H). ¹³C NMR (CDCl₃, 300 MHz): δ 193.42, 168.71, 151.09, 145.84, 145.69, 138.45, 134.00, 128.99, 127.94, 126.90, 126.85, 126.09, 114.00, 112.49, 61.16, 60.25, 58.41, 42.90, 31.98, 14.06. IR (KBr, cm⁻¹): 1075, 1545, 1607, 1659, 1736, 2978. MS (EI): m/z (%) = 268(30), 134(100), 106(5), 51(4), 39(3), 240(10), 209(1), 119(10), 91(9), 65(5).

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