Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 144 (2015) 29–42

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, spectroscopic investigation and computational study of 3-(1-(((methoxycarbonyl)oxy)imino)ethyl)-2H-chromen-2-one

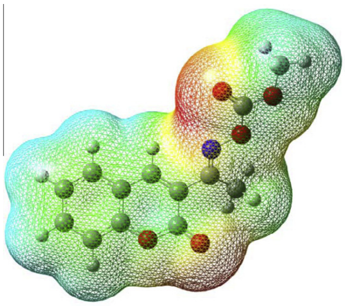
K. Gokula Krishnan [a], R. Sivakumar [a], V. Thanikachalam [a,*], H. Saleem [b], M. Arockia doss [a]

[a] Department of Chemistry, Annamalai University, Annamalainagar 608 002, Tamil Nadu, India
[b] Department of Physics, Annamalai University, Annamalainagar 608 002, Tamil Nadu, India

HIGHLIGHTS

- Oxime carbonate was synthesized from oxime with methyl chloroformate.
- Small HOMO–LUMO band gap indicate that charge transfer occurs in the title compound.
- NLO analysis shows that the title compound as an effective NLO material.
- Intramolecular hyperconjugative interactions in the benzene ring causes more delocalization in the ring.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 July 2014
Received in revised form 4 February 2015
Accepted 5 February 2015
Available online 18 February 2015

Keywords:
3-Acetylcoumarin oxime carbonate
Vibrational assignments
NBO
Non-linear optical
HOMO–LUMO

ABSTRACT

The molecular structure and vibrational modes of 3-acetylcoumarin oxime carbonate (abbreviated as 3-ACOC) have been investigated by FT-IR, FT-Raman, NMR spectra and also by computational methods using HF and B3LYP with 6-311++G(d,p) basis set. The optimized geometric parameters (bond lengths, bond angles and dihedral angles) were in good agreement with the corresponding experimental values of 3-ACOC. The calculated vibrational frequencies of normal modes from DFT method matched well with the experimental values. The complete assignments were made on the basis of the total energy distribution (TED) of the vibrational modes. NMR (^{1}H and ^{13}C) chemical shifts were calculated by GIAO method and the results were compared with the experimental values. The other parameters like dipole moment, polarizability, first order hyperpolarizability, zero-point vibrational energy, E_{HOMO}, E_{LUMO}, heat capacity and entropy have also been computed.

Introduction

Oxygen containing heterocycles such as coumarins are a promising structural moiety for drug designing [1]. Coumarins are chemical derivatives of benzopyrone analogous and they are subdivided into benzo-2-pyrones to which the coumarins belong and benzo-4-pyrones, of which the flavonoids are the principal members. Coumarins are abundant in nature and their related compounds have proven significant therapeutic activities [2]. Both natural as well as synthetic coumarins have attracted much attention due to their numerous therapeutic applications such as anticoagulant, anti-inflammatory, anti-cancer, anti-HIV and anti-oxidant [3–7]. Moreover, coumarin nucleus exhibits unique photochemical and photophysical properties [8], and used as chemosensors, dyes, phototriggers, fluorescent labels and probes in biology and medicine. In addition, 3-acyl derivatives of coumarins were widely examined for their specificity to neuropsychiatric disorders [9,10].

---

* Corresponding author. Tel.: +91 9488476098.
E-mail address: profvt.chemau@gmail.com (V. Thanikachalam).

http://dx.doi.org/10.1016/j.saa.2015.02.021
1386-1425/

Organic carbamates and carbonates are versatile compounds used as solvents or reagents in the chemical industry, as electrolytes in lithium ion batteries and fuel additives [11]. They have been used as protecting groups for amines and alcohols [12] and as intermediates [13] in organic synthesis. They are also frequently encountered as endower molecules in pharmaceuticals and agrochemicals [14,15].

Several authors have extensively studied the different aspects of coumarin derivatives [16]. The theoretical *ab initio* and DFT analyses give information regarding the electronic structure, functional groups, orbital interactions and mixing of skeletal frequencies which are typically larger than their experimental counterparts. Hence, in the present investigation, an extensive experimental and quantum chemical calculations of 3-acetylcoumarin oxime carbonate (abbreviated as 3-ACOC) derivative have been carried out.

Experimental

Synthesis of 3-acetylcoumarin oxime carbonate

To a stirred solution of 3-acetylcoumarin oxime (0.51 g, 2.5 mmol) in dry tetrahydrofuran (5 mL), potassium carbonate (0.51 g, 3.75 mmol) was added. After stirring for 15 min, methyl chloroformate (0.3 mL, 3.75 mmol) was added drop wise to the reaction mixture in a period of 15 min. It was stirred at ambient temperature for 2 h and progress of the reaction was monitored by thin layer chromatography. Upon completion of reaction, the reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL), brine solution (20 mL), dried over anhydrous sodium sulphate (2.5 g), filtered and concentrated under reduced pressure. The crude product was then recrystallised in ethanol to get the pure 3-acetylcoumarin oxime carbonate (0.53 g, 81%) [17].

Spectral measurements

The melting point was measured in open capillary and is uncorrected. FT-IR spectrum was recorded on an AVATAR-300 FT-IR spectrometer using KBr. The spectral features are reported in wavenumber (cm^{-1}). FT-Raman spectrum was recorded on a Bruker RFS 27: Stand alone FT-Raman Spectrometer in solid state. The laser source used for the analysis was Nd: YAG 1064 nm. NMR (^{1}H and ^{13}C) were recorded on a Bruker 400 MHz spectrometer. Chemical shifts values are reported in parts per million (ppm) from tetramethylsilane (TMS).

Computational details

The entire set of calculations have been performed at *ab initio* HF and DFT-B3LYP methods with 6-311++G(d,p) basis set using Gaussian 03 program package [18]. Initially, we have utilized the HF level calculation and then gradient corrected density functional theory (DFT) with the three parameter hybrid functional (B3) for the exchange part and the Lee–Yang–Parr (LYP) correlation function [19], accepted as a cost effective approach, for the energies of optimized structure and computation of vibrational frequencies. The optimized geometry was determined by minimizing the energy with respect to all geometry parameters without imposing molecular symmetry constraints. The optimized structural parameters were used in vibration frequency, electronic properties, and isotropic chemical shift calculations. The validity of the optimized geometry was confirmed by frequency calculations, which gave real values for all the obtained frequencies. The frequency values computed at these levels contain known systematic errors. Therefore, we have used the scaling factor values of 0.9608 for B3LYP. NMR chemical shifts were computed at the B3LYP/6-311++G(d,p) level using the Gauge-Invariant Atomic Orbital (GIAO) calculations [20]. The ^{1}H and ^{13}C isotropic chemical shifts were referenced to the corresponding values for TMS, which was calculated at the same level of theory.

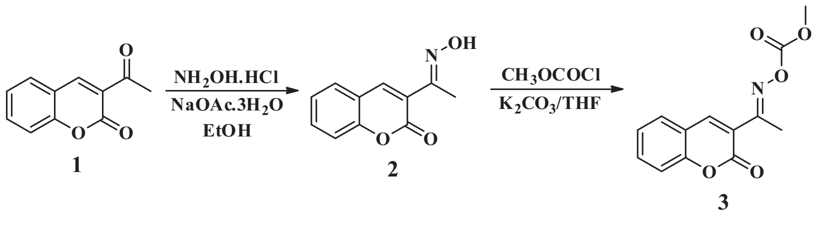
Results and discussion

Synthesis

In the present work, three consecutive steps were adopted for the synthesis of compound 3-ACOC. The key unit of the compound 3-acetylcoumarin (**1**) was synthesized by Knoevenagel condensation [21] of salicylaldehyde and ethyl acetoacetate in 1:1 molar ratio, followed by oximation [22] of (**1**) using hydroxylamine hydrochloride in the presence of sodium acetate trihydrate in ethanol. In the final step, we examined the feasibility of the reaction of 3-acetylcoumarin oxime with methyl chloroformate [17] using K_2CO_3 as base and THF as solvent. The reaction afforded the corresponding oxime carbonate (**3**) with good yield. The synthetic route of 3-ACOC is outlined in Scheme 1.

Potential energy surface scan analysis

The conformational analysis of 3-ACOC was carried out through the potential surface scan with B3LYP/6-311++G(d,p) level of theoretical approximation for determining the most stable geometry. The preliminary search of low energy structures was performed for the dihedral angles C8-C9-C12-N14 and C12-N14-O15-O16 of 3-ACOC, which is also relevant coordinate for conformational flexibility within the molecule. During the calculation all the geometrical parameters have been simultaneously relaxed with C8-C9-C12-N14 and C12-N14-O15-O16 dihedral angles which were varied in steps of 10° from 0° to 360° during the scan. The potential energy barrier obtained by the rotation of the imine and carbonate groups with the dihedral angle is shown in Fig. 1. From Fig. 1, the oxime carbonate has attained minimum energy at −141.6° and 218.4° in the imino group rotation whereas in carbonate group showed minimum energy at 174.6° and 534.6°.



Scheme 1. Synthesis of 3-ACOC.