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Synthesis, characterization, crystal structure and quantum chemical investigations of three novel coumarin-benzenesulfonohydrazide derivatives

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ABSTRACT

Coumarin derivatives are an important class of heterocyclic compounds due to their physical and biological properties. Coumarin derivatives have been identified with many significant electro-optical properties and biological activities. Three novel coumarin derivatives containing benzene sulfonohydrazide group were synthesized by condensation reaction. The synthesized compounds were characterized by various spectroscopic techniques (Mass, $^{1}H/^{13}C$ NMR and FTIR). Thermal and optical properties were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and UV–Vis spectroscopic studies. Finally their structures were confirmed by single crystal X-ray diffraction (XRD) studies. The three compounds exhibit diverse intermolecular interactions, as observed by the crystal packing and Hirshfeld surface analysis. Further, their structures were optimized by density functional theory (DFT) calculations using B3LYP hybrid functionals with 6-311G+(d,p) level basis set. The Mulliken charge, molecular electrostatic potential (MEP), frontier molecular orbitals (HOMO-LUMO) were investigated. The experimentally determined parameters were compared with those calculated theoretically and they complement each other with a very good correlation. The transitions among the molecular orbitals were investigated using time-dependent density functional theory (TD-DFT) and the electronic absorption spectra obtained showed very good agreement with the experimentally measured UV–Vis spectra. Furthermore, non-linear optical (NLO) properties were investigated by calculating polarizabilities and hyperpolarizabilities. All three compounds exhibit significantly high hyperpolarizabilities compared to the reference material urea, which makes them potential candidates for NLO applications.

1. Introduction

Coumarin (benzopyran-2-one, or chromen-2-one) ring system is one of the very important families of lactones with many significant therapeutic properties. More than 1000 coumarin derivatives, either isolated from plants, fungi, bacteria or synthesized have been studied for their biological importance over the last century. Coumarin derivatives have been identified with diverse biological activities. Coumarin derivatives including coumarin-chalcone hybrids, coumarin 3-(N-aryl) sulfonamides, coumarin substituted hydrazide-hydrazone derivatives have been investigated for their potential anticancer activities [1–5]. Coumarin-3-aminoamides and their alpha lipoic acid adducts, coumarin umbelliprenin, vanillin ethers from 4-(bromomethyl) coumarin and some bi heterocyclic coumarin derivatives have been extensively studied for their antioxidant, anti-inflammatory, analgesic and lipoxygenase activities [6–10]. Some coumarin derivatives have been identified with potent anti-HIV activities [11–13]. They have also been found to possess vasorelaxant, anti-coagulation, anti-retroviral, anti-pyretic activities [14–18].

On the other hand, coumarin derivatives have also shown many other significant physical properties. Many coumarin dyes, and side chain coumarin dye substituted polymers have been identified with nonlinear optical properties [19–23]. Coumarin based

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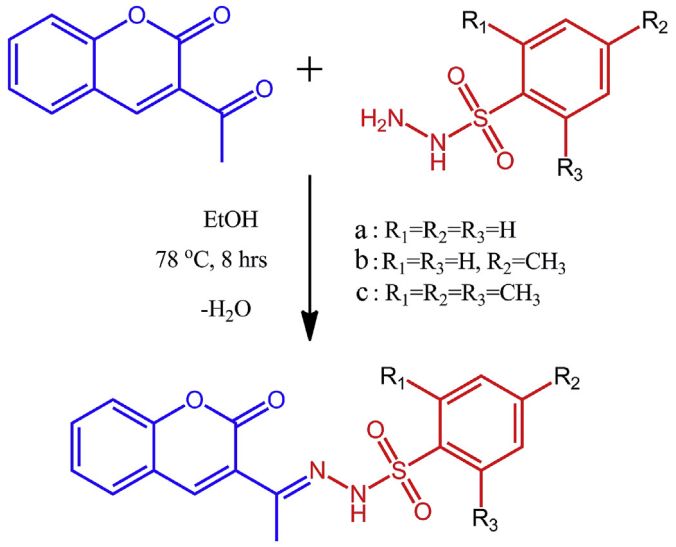

Fig. 1. Schematic synthesis scheme of the compounds **a**, **b** and **c**.

copolymers have been demonstrated with two photon optical data storage property [24]. The coumarin derivatives have been reported for their potential usage in dye sensitized solar cells with a promising efficiency up to 8% [25–28]. Also, some coumarin derivatives have been shown to possess fluorescence sensing properties and be potential candidates for in cell applications [29–31]. Inspired by the above diverse physical, chemical and biological properties of coumarins, we designed and synthesized three novel coumarin derivatives, (E)-N'-(1-(2-oxo-2H-chromen-3-yl) ethylidene) benzenesulfonohydrazide (**a**), (E)-4-methyl-N'-(1-(2-oxo-2H-chromen-3-yl) ethylidene) benzenesulfonohydrazide (**b**), (E)-2,4,6-trimethyl-N'-(1-(2-oxo-2H-chromen-3-yl) ethylidene) benzenesulfonohydrazide (**c**). They were characterized using spectroscopic techniques and finally the structure was confirmed using single crystal XRD studies. Optical and thermal properties of all the compounds were also investigated. Further geometrical optimization of all the three compounds were carried out using DFT calculations. Frontier molecular orbitals, the electronic absorption spectra and non-linear optical properties were investigated by the DFT calculations.

2. Experimental section

2.1. General instrumentations and materials

All the chemicals used were purchased from Sigma-Aldrich and TCI, and were used without any further purification. Thin layer chromatography was used to monitor the reaction, was carried out with precoated aluminum-backed plate (Merck Silica Gel 60 F_{254}) and visualized under UV light ($\lambda = 256$ nm). Melting point was determined using Chemiline melting point apparatus CL725. The mass spectra were recorded on Agilent 7890A GC system. CHNS analysis was carried out on Vario EL III Elementar. NMR spectra were recorded on a Bruker Avance spectrometer at 300 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. Signals are abbreviated as

Table 1
Crystal data and structure refinement details.

Parameter	a	b	c
Empirical formula	$C_{17}H_{14}N_2O_4S$	$C_{18}H_{16}N_2O_4S$	$C_{20}H_{20}N_2O_4S$
Formula weight	342.36	356.39	383.43
Temperature (K)	293(2)	293(2)	293(2)
Radiation	MoKα	MoKα	MoKα
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	Pcab	Pcab	$P\bar{1}$
a (Å)	11.904(8)	11.680(3)	8.399(5)
b(Å)	15.580(2)	15.450(3)	9.691(6)
c (Å)	16.715(2)	17.890(4)	12.161(8)
α (°)	90	90	68.449(3)
β (°)	90	90	81.91(2)
γ (°)	90	90	83.62(2)
Volume (Å^3)	3100(4)	3228(3)	909.6(1)
Z	8	8	2
ρ_{calc} (Mg m^{-3})	1.467	1.466	1.4
μ (mm^{-1})	0.234	0.228	0.207
F_{000}	1424	1488	402
Crystal size (mm)	0.30 × 0.27 × 0.25	0.28 × 0.32 × 0.30	0.20 × 0.25 × 0.32
θ limits (°)	6.506–55.036	6.314–55.446	6.462–55.158
Index ranges	$-9 \le h \le 15$	$-15 \le h \le 15$	$-10 \le h \le 9$
	$-20 \le k \le 17$	$-19 \le k \le 8$	$-9 \le k \le 12$
	$-21 \le l \le 16$	$-23 \le l \le 19$	$-11 \le l \le 15$
Reflections measured	10191	13222	5380
Unique reflections	3548	3718	4103
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full matrix least-squares on F^2	Full matrix least squares on F^2	Full matrix least-squares on F^2
Parameters	221	231	251
Goodness-of-fit on F^2	1.064	1.002	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0431, 0.1182	0.0843, 0.2242	0.0448, 0.1165
R_1, wR_2 (all data)	0.0501, 0.1257	0.1325, 0.2748	0.0546, 0.1247
Residual (e Å^{-3})	0.24 and −0.54	0.83 and −0.42	0.24 and −0.38
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