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Single X-ray crystal and spectroscopic investigation of novel biologically active donor–acceptor chalcones as specific application for opto-electronics and photonics

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ABSTRACT

Chalcones were synthesized by reaction of 3-acetyl-2,5-dimethylthiophene with corresponding active aldehyde in ethanolic NaOH. The structure of these compounds was established by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and EI-MS spectral analysis. UV–Vis and fluorescence spectroscopy measurements provided that compounds are good absorbent and fluorescent. Fluorescence polarity study demonstrated that the compound 1 & 2 was sensitive to the polarity of the microenvironment provided by different solvents. In addition, spectroscopic and physicochemical parameters, including electronic absorption, extinction coefficient, Stokes shift, oscillator strength, transition dipole moment and photochemical quantum yield were investigated in order to explore the analytical potential of synthesized compound 1 & 2. The anti-bacterial activity of the compound 1 & 2 were first tested *in vitro* by the disk diffusion assay against two Gram-positive (*Aeromonas hydrophila and Yersinia enterocolitica)* and two Gram-negative (*Listeria Monocytogenes and Pseudomonas aeruginosa*) bacteria, and then the minimum inhibitory concentration was determined with the reference of standard drug tetracycline. The results showed that compound **2** is better inhibitor of both types of the bacteria (Gram-positive and Gram-negative) as compared to tetracycline.

1. Introduction

α, β-unsaturated carbonyl compounds are also known as chalcones which are mostly present in isoflavonoids, flavonoids and other natural occurring compounds which are regarded as cyclic chalcones and have closely related physiological and medical relevancies [1]. Chalcones are the condensation product of acetophenone with aromatic aldehydes in the presence of strong base [2]. They exhibit a wide range spectrum of biological activities such as anti-bacterial [3], anti-oxidant [4], anti-inflammatory [5], anti-cancer [6] and anti-viral [7]. Cyclization of chalcones gives the various heterocyclic compounds such as pyrazole, pyrimidine and pyridine by a nucleophilic addition reaction which enhanced the biological activities [8–11]. Chalcones based ligands and their metal complexes with Cu(II), Ni(II), Co(II), Pt (II), Pd(II), Cd(II) and (Zn (II) play a prominent role in modern coordination chemistry [12]. These compounds possessing novel structure interesting spectral and magnetic properties have been the subject of intensive research due to their importance in analytical, biological and industrial fields [13]. Over the past decades because of л-conjugated bridges chalcone is using in the field of material science such as, third order non-linear optics (NLO) [14], optical switching [15], electrochemical sensing [16], langmuir films and photoinitiated polymerization [17]. Physicochemical characteristics, such as, solvatochromic, piezochromic, oscillator strength, dipole moment, florescent quantum yield and photostability, are also the most important studies for determining the behavior of compounds [18]. In accordance, the present study was aimed to synthesis of heterocyclic chalcones and to investigate their *in-vitro* antibacterial activity. In addition, the analytical efficiency of heterocyclic chalcones was investigated by studying spectroscopic and physicochemical parameters.

2. Experimental

2.1. Chemicals and reagents

The appropriate 3-acetyl-2,5-dimethylthiophene and corresponding active aldehyde were purchased from Acros Organic. Other reagents and solvents (A.R.) were obtained commercially and used without further purification, except dimethylformamide (DMF), ethanol and methanol.

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2.2. Apparatus

Melting points were recorded on a Thomas Hoover capillary melting apparatus without correction. FT-IR spectra were recorded on a Nicolet Magna 520 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR experiments were performed in $CDCl_3$ on a Brucker DPX 600 MHz spectrometer using tetramethyl silane (TMS) as internal standard at room temperature. UV–Vis electronic absorption spectra were acquired on a Shimadzu UV-1650 PC spectrophotometer. Absorption spectra were collected using a 1 cm quartz cell. Steady state fluorescence spectra were measured using Shimadzu RF 5301 PC spectrofluorphotometer with a rectangular quartz cell. Emission spectra were monitored at right angle. All fluorescence spectra were blank subtracted before proceeding in data analyses.

2.3. (2E)-1-(2,5-dimethylthiophen-3-yl)-3-(1-methyl-1H-pyrrol-2-yl) prop-2-en-1-one (1)

A solution of 3-acetyl-2,5-dimethythiophene (2 g, 0.012 mol) and 1-methyl-1*H*-pyrrole-3-carbaldehyde (1.30 g, 0.012 mol) in ethanolic solution of NaOH (3 g in 10 ml of ethanol) was stirred for 6 h at room temperature. The solution was poured onto ice-cold water of pH ~ 2 (pH adjusted by HCl). The separated solid was filtered off, washed several times with a saturated solution of $NaHCO_3$ and left to dry. The residual was recrystallized from methanol/chloroform. Light-yellow solid: m.p. 85.6°C; IR (KBr) ν_{max} cm^{-1}: 3104 (Ar-H), 2912 (C-H), 1642 (C=O), 1546 (C=C); ^{1}H NMR (600MXz, $CDCl_3$) (δ/ppm): 7.71 (d, C=CH, J = 15.6 Hz), 7.04 (d, CO=CH, J = 16.0 Hz), 7.26 (s, 1H, thiophene), 7.05 (d, CH, J = 7.8 Hz), 6.79 (d, CH, J = 4.8 Hz), 6.21 (d, CH, J = 7.2 Hz), 3.74 (s, 3H, N-CH_3), 2.70 (s, 3H, thiophene 2-CH_3), 2.43 (s, 3H, thiophene 5-CH_3); ^{13}CNMR ($CDCl_3$) δ: 186.11 (C=O), 146.43 (C-β), 137.13, 135.13, 131.07, 130.26, 127.47, 125.93, 119.86 (C-α), 111.95, 109.60, 43.38, 15.88, 15.07; EI-MS *m/z* (rel. int.%): 247 (72) [M+1] $^{+\cdot}$; Anal. calc. for $C_{14}H_{15}NOS$: C, 68.54, H, 6.16, N, 5.71. Found: C, 68.48, H, 6.08, N, 5.65.

2.4. (2E)-3-(3,5-Dimethyl-1-phenyl-1H-pyrazol-4-yl)-1-(2,5-dimethyl-3-thienyl)prop-2-en-1-one (2)

A solution of 3-acetyl-2,5-dimethythiophene (2 g, 0.012 mol) and 3,5-dimethyl-1-phenylpyrazole-4-carboxaldehyde (2.50 g, 0.012 mol) in ethanolic solution of NaOH (3 g in 10 ml of ethanol) was stirred for 6 h at room temperature. The solution was poured onto ice-cold water of pH ~ 2 (pH adjusted by HCl). The separated solid was filtered off, washed several times with a saturated solution of $NaHCO_3$ and left to dry. The residual was recrystallized from methanol/chloroform. Light-yellow solid: Light-yellow solid: m.p. 111–112 °C; IR (KBr) ν_{max} cm^{-1}: 3055 (Ar-H), 2918 (C-H), 1638 (C=O), 1575 (C=C); ^{1}H NMR (600MXz, $CDCl_3$) (δ/ppm): 7.71 (d, C=CH, J = 15.6 Hz), 7.35 (d, CO=CH, J = 16.0 Hz), 7.19(s, 1H, thiophene), 7.24–6.93 (m, 5H, Ph), 2.65 (s, 3H, pyrazole 3-CH_3), 2.44 (s, 3H, pyrazole 5-CH_3), 2.37 (s, 3H, thiophene 2-CH_3), 2.36 (s, 3H, thiophene -CH_3); ^{13}CNMR ($CDCl_3$) δ: 185.43 (C=O), 145.59 (C-β), 140.04 137.90, 136.00, 134.25, 133.86, 128.32, 127.74, 124.82, 123.89 (C-α), 117.92, 114.32, 28.67, 14.92, 13.94, 11.96, 10.62; EI-MS *m/z* (rel. int.%): 337 (65) [M+1] $^{+\cdot}$; Anal. calc. for $C_{20}H_{20}N_2OS$: C, 71.40, H, 5.99, N, 8.33. Found: C, 71.36, H, 5.95, N, 8.28.

2.5. Crystallography

Single crystal of **1** was selected under microscope from the raw crystalized sample and fixed on a glass tip supported by copper pin and magnetic base. Data collection was performed on an Agilent SuperNova CCD diffractometer with mirror monochromated Cu–K_α radiation at 296 K. The structure was solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [19] from within the X-seed [20] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. All H atoms were located geometrically with C-H = 0.93 Å for aromatic and C-H = 0.98 Å for methyl groups and then treated as riding atoms with *Uiso*(H) = *1.2*Ueq(*C*) and *Uiso*(H) = *1.5*Ueq(*C*) for aromatic and methyl carbon atoms respectively. The diagrams were created PLATON [21]. The parameters for data collection and structure refinement of **1** are listed in Table 1. Similarly, the selected bond lengths and bond angles are given in Tables 2 and 3. The data have been submitted to CCDC with CCDC code 1026537 and it can be obtained freely from http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx.

Table 1
Crystal data and structure refinement for 14058.

Identification code	1
Empirical formula	$C_{14}H_{15}NOS$
Formula weight	245.33
Temperature/K	296.15
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	8.4960(4)
b/Å	12.0897(6)
c/Å	12.8499(7)
α/°	90.00
β/°	91.905(5)
γ/°	90.00
Volume/Å^3	1319.14(12)
Z	4
ρ_{calc}mg/mm^3	1.235
m/mm^{-1}	2.036
F(000)	520.0
Crystal size/mm^3	0.2785 × 0.1012 × 0.0862
2Θ range for data collection	6.88–152.42
Index ranges	$-5 \le h \le 10$, $-15 \le k \le 13$, $-15 \le l \le 16$
Reflections collected	8162
Independent reflections	2758[R(int) = 0.0349]
Data/restraints/parameters	2758/0/157
Goodness-of-fit on F^2	1.126
Final R indexes [I>=2σ (I)]	$R_1 = 0.0855$, $wR_2 = 0.2582$
Final R indexes [all data]	$R_1 = 0.0983$, $wR_2 = 0.2725$
Largest difference peak/hole/e Å^{-3}	0.59/−0.26

Table 2
Selected bond lengths for 14058.

Atom	Atom	Length/Å
S1	C1	1.720(4)
S1	C4	1.716(4)
O1	C5	1.236(4)
N1	C8	1.391(4)
N1	C11	1.350(5)
N1	C14	1.445(5)

Table 3
Selected bond angles for 14058.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/
C4	S1	C1	93.39(18)	C13	C4	S1	119.2(3)
C8	N1	C14	125.9(3)	O1	C5	C3	120.1(3)
C11	N1	C8	108.9(3)	O1	C5	C6	121.0(3)
C11	N1	C14	125.2(3)	C6	C5	C3	118.9(3)
C12	C1	S1	121.1(3)	N1	C8	C7	121.3(3)

2.6. Organism culture and in vitro screening

Anti-bacterial activity was studied by the disk diffusion method with minor modifications. *Aeromonas hydrophila, Yersinia enterocolitica, Listeria Monocytogenes* and *Pseudomonas aeruginosa* were subcultured in brain-heart infusion broth (BHI, Himedia, India) medium