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Solvent effects on the UV-visible absorption spectra of aryl-2,2'-bifuran derivatives

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ABSTRACT: The effect of solvent polarity on absorption spectra of a series of bifuran carbonitriles and their corresponding carboxamidine hydrochloride salts was investigated. Synthesis of the new thienylbifuran-5-carbonitrile **5** was described through a Stille coupling reaction of the precursor 5'-bromo-[2,2'-bifuran]-5-carbonitrile with 2-tri-n-butylstannylthiophene. Cationic thienylbifuran carboxamidine compound **6** was prepared on treatment its corresponding carbonitrile compound **5** with lithium bis-trimethylsilylamide, followed by de-protection step and subsequent hydrochloride salt formation. The relationship between aryl-2,2'-bifuran structure feature and their corresponding absorption in the UV–visible region was studied. The absorption maxima of the tested aryl-2,2'-bifuran derivatives showed that λ_{max} of the amidine derivatives shifted to higher wavelength than their corresponding carbonitrile derivatives.

Keywords: 2,2'-bifuran-5-carbonitriles, Stille reaction, 2,2'-bifuran-5-amidines, UV/Vis absorption, solvent effect

1. Introduction

There are many different types of chalcophenes. Chalcophenes are classified into: mono-, bi- and oligo-chalcophenes. Bi- as well as oligo-chalcophenes play an important role as advanced materials. These compounds have been incorporated into numerous fields and applications. They can be used as organic semiconductors and radioactive materials due to their luminescent properties [1]. Bifuran and their analogues are important synthetic precursor for biologically active molecules [2-6]. These types of compounds have significant use in solvatochromic, photosensitizing and photovoltaic cells applications [7-9]. The idea depends on the presence of donor- (π-spacer)-acceptor in conjugation with each other consequently [10,11]. These compounds bear cyano group which act as electron withdrawing acceptor, electron donating groups representing in substituents such as (OCH_3, Cl) and suitable π-spacer that support the enhancement of intramolecular charge transfer characteristics and hence, enlargement of the dipole moment [12]. In this paper, we report the effect of different solvents (polar and non-polar solvents) on the UV –visible study of bi- and oligo-chalcophene derivatives. In specific, 5'-aryl-2,2'-bifuran-5-carbonitriles and their corresponding carboxamidine derivatives.

2. Experimental

2.1. General:

Melting points were measured in degree centigrade on Gallenkamp apparatus and are uncorrected. The ultraviolet-visible absorption spectra were measured on a Schimadzu 1700 spectrophotometer in the region of 200–600 nm. The infrared spectra (KBr) were explored on Thermo Scientific Nicolet iS10 FTIR spectrometer. ^{1}H NMR spectra were measured in DMSO-d_6 as a solvent at 500 MHz on JEOL's spectrometer. Perkin-Elmer 2400 analyzer has been used to determine the elemental analyses. 5'-Aryl-2,2'-bifuran derivatives **1a-d** and **2a-d** have been prepared as recently reported [13].

2.2. Preparation of 5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carbonitrile (5).

To a stirred mixture of bromobifuran derivative **4** (1.19 g, 5 mmol), tetrakis-(triphenylphosphine) palladium (100 mg) in 25 mL toluene was added 2-tri-n-butylstannyl-thiophene (2.06 g, 5.5 mmol). The reaction

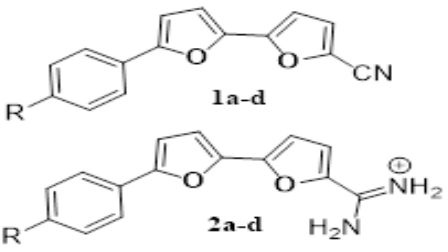
mixture was heated at reflux for 12 hrs. Where after, the reaction mixture was extracted with ethyl acetate (200 mL, 3x). The organic layer was re-extracted with 5 mL concentrated ammonia, dried, and then evaporated to dryness under reduced pressure to furnish the desired thienylbifuran compound **5** in 72% yield as yellow solid, m.p. = 119-120 °C, R_f = 0.58, petroleum ether (60-80 °C)/EtOAc (9:1). IR (KBr) ν/cm^{-1}; 3108 (CH, stretch), 2220 (CN, stretch), 1624, 1570, 1536 (C=C, stretch). ^{1}H-NMR (DMSO-d_6); δ/ppm = 6.96 (d, *J* = 3.5 Hz, 1H), 7.01 (d, *J* = 4.0 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.14-7.16 (m, 1H), 7.51 (d, *J* = 3.5 Hz, 1H), 7.62 (d, *J* = 4 Hz, 1H), 7.72 (d, *J* = 3.5 Hz, 1H). MS (EI) m/e (rel.int.); 241 (M^+, 100). Anal. Calcd. for $C_{13}H_7NO_2S$ (241.26): C, 64.72; H, 2.92; N, 5.81 Found: C, 64.60; H, 2.98; N, 5.70%.

2.3. Preparation of 5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carboxamidine hydrochloride salt (6).

5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carbonitrile (5) (241 mg, 1 mmol) was allowed to react with lithium bis-trimethylsilylamide (1M solution in THF, 6 mL) with stirring for overnight. After which, ethanolic-HCl (gas) solution (10 mL, 1.25 M) was added dropwise with cooling, until a precipitate was formed. The reaction mixture was left to stir at ambient temperature for 6 hr; where after the resultant solid was collected through filtration after it was diluted with ether. The crude solid of thienylbifuran monoamidine derivative was neutralized with 1N NaOH followed by filtration. Finally, the thienylbifuran mono-amidine free base was stirred in ethanolic-HCl(gas) solution for overnight, the solid formed was triturated with ether and filtered off to furnish the target compound 5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carboxamidine hydrochloride salt (**6**) in 63% yield as a yellowish-brown solid, m.p. 210-211 °C. IR (KBr) ν/cm^{-1}; 3378, 3270 (NH, stretch), 3079 (CH, stretch), 1655, 1569, 1531 (C=C, stretch) cm^{-1}. ^{1}H-NMR (DMSO-d_6); δ/ppm = 7.06.-7.08 (m, 1H), 7.10-7.12 (m, 3H), 7.31-7.33 (m, 2H), 8.01 (d, J = 4.0 Hz, 1H), 9.22 (s, 2H, D_2O exchangeable), 9.56 (s, 2H, D_2O exchangeable). MS (EI) m/e (rel.int.); 258 (M^+, 19), 259 (M^+ +1, 53), 241 (M^+ -NH_3, 3), 57 (100). Anal. Calcd. for $C_{13}H_{10}N_2O_2S$-1.0HCl (294.75): C, 52.97; H, 3.76; N, 9.50 Found: C, 52.68; H, 3.84; N, 9.39%.

3. Results and discussion

Preparation of aryl-2,2'-bifuran derivatives **1a-d** and **2a-d** (Figure 1) was recently described on treatment of 5'-bromo-[2,2'-bifuran]-5-carbonitrile with the appropriate arylboronic acids employing a Suzuki coupling conditions [13].



1,2a; R = H **b;** R = OCH_3
c; R = Cl **d;** R = F

Figure 1: 5'-Aryl-2,2'-bifuran-5-carboxamidine derivatives that have been subjected for UV-visible studies

Preparation of 5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carboxamidine hydrochloride salt (**6**) (Figure 2) starts with preparation of the corresponding thienylbifuran derivative **5** *via* treatment of bifuran carbonitrile derivative **4** with 2-tri-n-butylstannylthiophene (**3**) employing a Stille cross-coupling conditions. After which, thienylbifuran carbonitrile **5** was treated with lithium bis-trimethylsilylamide, then de-protection with hydrogen chloride and subsequent neutralization with NaOH. Thienyl-bifuran-5-carboxamidine hydrochloride salt was prepared by treatment of its monoamidine free base with hydrogen chloride in ethanol.

Structure determination of the newly synth-esized thienylbifuran carbonitrile **5** was assured from its spectral and elemental analyses. IR spectrum of compound **5** indicated that appearance of nitrile group with stretching vibration at ν' 2220 cm^{-1}. ^{1}H NMR spectrum of the mononitrile **5** displayed six small doublet signals (each signal integrated for one proton) at δ/ppm 6.96, 7.01, 7.13, 7.51, 7.62, 7.72, respectively, in addition to one multiplet signal at δ/ppm 7.14-7.16 (1H). Furthermore, mass spectrum of mononitrile **5** gave a peak corresponding for its molecular ion peak (M^+) at m/z 241. Structure determination of the newly synthesized thienylbifuran carboxa-

amidine hydrochloride salt **6** was assured from its spectral and elemental analyses. IR spectrum of monoamidine **6** indicated disappearance of the nitrile group and appearance of new peaks corresponding for N-H stretching vibrations at ν' 3378 and 3270 cm^{-1}. ^1H NMR spectrum of monoamidine **6** showed two singlet signals at δ 9.22 (2H) and 9.56 (2H) characteristic to the cationic amidine group and were deuterium exchangeable, one doublet signal integrated for one proton at δ 8.01 ppm, in addition to three multiplet signals integrated for six protons. In addition, mass spectrum and fragmentation pattern of compound **6** gave a peak of its molecular ion peak (M^+) at m/z 258, and m/z peak at 241 corresponding for a fragment that produced from loss a molecule of ammonia.

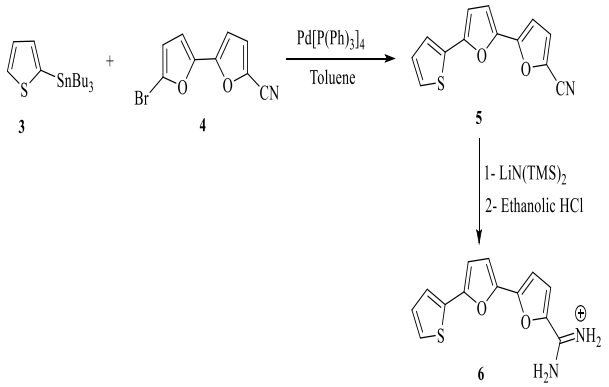


Figure (2): Synthesis of 5'-(thiophen-2-yl)-[2,2'-bifuran]-5-carboxamidine hydrochloride salt.**3.1.**

The solvent effect on theUVvisibleabsorption spectra

The study of solvent effect on the electronic spectra of aryl-2,2'-bifuran derivatives in the UV-visible region was investigated using different solvents with different polarities. The wavelength at maximum absorption (λ_{max}) of the studied aryl-2,2'-bifuran derivatives were determined in four different solvents with various polarities (ethanol, dimethylformamide, 1,4-dioxane, and methylene chloride), the effect of different solvents with different substituents (H, OCH_3, Cl, F) of aryl-2,2'-bifuran derivatives can be briefly introduced in the following points:

- The change of solvent from ethanol, DMF, methylene chloride and dioxane did not bring remarkable change in the absorption λ_{max} values of the tested 5'-aryl-2,2'-bifuran-5-carbonitrile derivatives **1a-d** and **5**. Whereas, the absorptions of 5'-aryl-2,2'-bifuran-5-carboxamidine salts **2a-d** and **6** in DMF announced higher wavelengths than the other solvents.
- The introduction of chlorine or fluorine substituent at the benzene ring of the studied 5'-aryl-2,2'-bifuran-5-carbonitriles **1c** and **1d** did not cause remarkable change in the absorption λ_{max} values. In all used solvents, the absorption maxima announced a narrow range of λ_{max} values (338-346 nm).
- The introduction of methoxy group at the phenyl ring of the tested 5'-aryl-2,2'-bifuran-5-carbonitrile derivative **1b** provided absorption maxima very close to that observed by the 5'-thienyl-2,2'-bifuran-5-carbonitrile derivative **5** with wavelengths range from 348 to 352 nm.
- From table **(2)** it was observed that the carboxamidine compounds **2a-d** and **6** exhibited higher absorption wavelengths λ_{max} than their corresponding nitrile compounds **1a-d** and **5**.
- The replacement of benzene ring by thiophene as shown in compounds **5** and **6 (Tables 1** and **2)** on the π-conjugated bridge shifted the absorption maxima to higher wavelengths (bathochromic shift).
- The increase of aromatic character when benzene ring replaced by the thiophene heterocycle may be attributed to the bathochromic effect that resulted from the enhanced π-overlap between bifuran and thiophene units.

Table (1): UV-visible absorption wavelength (λ_{max}, nm) for the 5'-aryl-2,2'-bifuran-5-carbonitrile derivatives **1a-d** and **5.**

Cpd No	EtOH		DMF		CH_2Cl_2		Dioxane	
1a	340	214	344	258	342	224	342	242
1b	348	260	350	258	352	234	348	238
1c	342	252	346	260	346	298	344	244
1d	338	248	342	258	342	234	340	296
5	350	258	352	274	354	260	350	260

Table (2): UV-visible absorption wavelength (λ_{max}, nm) for the new 5'-aryl-2,2'-bifuran-5-carboxamidine derivatives **2a-d** and **6.**

Cpd No.	EtOH		DMF		CH_2Cl_2		Dioxane	
2a	352	222	392	326	388	240	350	264
2b	378	356	396	344	380	240	376	346
2c	372	352	388	340	374	352	372	350
2d	356	220	384	340	388	352	352	194
6	374	206	378	270	360	230	374	258

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