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Synthesis and Photophysical Characterization of 2'-Aminochalcones †

Cátia I. C. Esteves 1, Luis F. B. Fontes 1,2, A. Filipa N. Borges 1, João Rocha 2, Artur M. S. Silva 1 and Samuel Guieu 1,2,∗

1 LAQV-REQUIMTE, Campus de Santiago, Universidade de Aveiro, 3810-193 Aveiro, Portugal; catiaiesteves@ua.pt (C.I.C.E.); lfontes@ua.pt (L.F.B.F.); filipa.borges@ua.pt (A.F.N.B.); artur.silva@ua.pt (A.M.S.S.); sguieu@ua.pt (S.G.)
2 CICECO-Aveiro Institute of Materials, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal; rocha@ua.pt
∗ Correspondence: sguieu@ua.pt
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Abstract: Chalcones present biological activity and are, therefore, currently studied for their therapeutic potential. They have shown antitumor, anti-inflammatory, antifungal and antibacterial properties. These compounds occur in nature as secondary metabolites of plants and are precursors of flavonoid biosynthesis. Generally, they are not luminescent, but derivatives with some particular patterns of substitution can present fair quantum yields. Excited State Intramolecular Proton Transfer (ESIPT) is a particular case of tautomerization, and some molecules can exhibit ESIPT fluorescence if their structures incorporate an intramolecular hydrogen bonding interaction between a hydrogen donor (–OH or –NH) and a hydrogen acceptor. If the dye is fluorescent, emission from both tautomers may be observed, leading to a dual emission. The chalcones with a strong push–pull character, compounds 2c, 3c and 4c, presented dual emission of keto–enol tautomerism as a consequence of ESIPT.

Keywords: aminochalcones; Excited State Intramolecular Proton Transfer; synthesis; fluorescence

1. Introduction

Chalcone (1,3-diphenylprop-2-en-1-one) is an aromatic ketone, where the two aromatic nuclei are joined by an α,β-unsaturated carbonyl bridge, which forms the central nucleus of a variety of important biological compounds [1]. Chalcone exists as trans (E)- or cis (Z)-isomers, with the most stable and predominant stereoisomer being the (E)-isomer [2]. There are several methods for the synthesis of chalcones, with Claisen–Schmidt condensation being the classic method [3]. Chalcones and their derivatives have been extensively studied because of their wide range of applicability [4]. Chalcones have several applications such as anti-inflammatory, Reference [5] anti-HIV, Reference [6] antibacterial, Reference [7] anticancer, Reference [8] antituberculosis, Reference [9] antileishmanial, Reference [10] therapeutic activity, and Reference [11], among others.

Structural changes in chalcone derivatives can modify different optical properties such as refractive index, absorption magnitude and spectral position, as well as the optical energy gap [4]. These examples indicate that structurally modified chalcones can exhibit variable physical properties.

Within this class of compounds, 2'-aminochalcone derivatives still represent a recent field of investigation [12]. They have antitumor activity [13] and have been shown to be photoprotectors [14].
Generally, they are not luminescent, but derivatives with some particular patterns of substitution can present fair quantum yields [15].

Excited State Intramolecular Proton Transfer (ESIPT) is a particular case of tautomerization, and molecules can exhibit ESIPT fluorescence if their structures incorporate an intramolecular hydrogen bonding interaction between a hydrogen donor (-OH or -NH) and a hydrogen acceptor [16]. The intramolecular hydrogen bond plays a crucial role in the proton transfer process [17]. If the dye is fluorescent, emission from both tautomers may be observed, leading to a dual emission [18]. ESIPT fluorophores have some beneficial photophysical properties such as intense luminescence, photostability and an unusually large Stokes Shift [3]. The proton-transfer tautomer emits fluorescence at longer wavelengths and will result in larger Stokes shifts.

ESIPT is a system with four energy levels (L → L* → E* → E). The two forms of the chalcone (L and ESIPT form) are in equilibrium (Scheme 1). In the ground state, the chalcone is in the L form. After absorption of a photon, the L* suffers an ESIPT tautomerization equilibrium to the E*, and both tautomers can emit light. After relaxation to the E form, the chalcone goes back to the keto form through reverse proton transfer (RPT). This equilibrium may be influenced by the environment of the chalcone, especially the polarity and proticity of the solvent, leading to different proportion of both tautomers, and therefore to different emission intensities in the two bands when dual emission is observed. As such, these fluoroophores may be found in such applications as molecular probes, giving an insight into the properties of their environment, including the polarity of an organelle.

Here, we report the synthesis and photophysical characterizations of 2′-aminochalcones, substituted with electron donating or withdrawing groups, which could be used as markers to study the environment of cellular organelles.
2. Experimental

2.1. General Procedure for the Synthesis of 2′-Aminochalcones 2a–c

The 2′-aminochalcone derivatives were obtained via aldol condensation reaction of 2′-aminocacetophenone (2 mmol) with the appropriate substituted benzaldehyde 1a–c (2 mmol) catalyzed by potassium hydroxide (4 mmol) in methanol (5 mL). The reaction mixture was stirred at 60 °C overnight followed by addition of HCl and the solution extracted with CH2Cl2 (3 × 20 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting oil was purified by silica gel column chromatography, using dichloromethane as eluent.

2.1.1. (E)-1-(2-aminophenyl)-3-(4-dimethylaminophenyl)prop-2-en-1-one (2a)

The product was isolated as a yellow solid (1.139 g, 4.81 mmol, 80%). M.p. = 91–92 °C. 1H NMR (300 MHz, CDCl3) δ = 2.39 (s, 3H, CH3), 6.44 (br s, 2H, NH2), 6.71 (d, J = 5.6 Hz, 1H, H-3), 6.72 (dt, J = 8.1 and 1.2 Hz, 1H, H-4), 7.22 (d, J = 8.1 Hz, 2H, H-2′,6′), 7.61 (d, J = 15.6 Hz, 1H, α-H), 7.78 (d, J = 15.3 Hz, 1H, β-H), 7.89 (dd, J = 8.1 and 1.2 Hz, 1H, H-6) ppm. 13C NMR (75 MHz, CDCl3) δ = 31.0 (CH3), 115.8 (C-5), 117.3 (C-3), 117.9 (C-1), 120.8 (α-C), 128.4 (C-2′,6′), 129.7 (C-3′,5′), 130.3 (C-4), 141.9 (C-2), 150.7 (C-2), 151.2 (C-2′), 191.8 (CO) ppm. MS m/z (ESI %): 238.1 ([M+H]+); HMRS: m/z (ESI) calc. for C16H16NO2 238.1226, found 238.1230. UV/Vis (CHCl3, nm): λmax (log ε) = 317 (4.59).

2.1.2. (E)-1-(2-aminophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (2b)

The product was isolated as a dark yellow solid (0.214 g, 0.81 mmol, 43%). M.p. = 68–69 °C. 1H NMR (300 MHz, CDCl3) δ = 3.81 (s, 3H, OCH3), 6.25 (br s, 2H, NH2), 6.65–6.70 (m, 2H, H-3 and H-5), 6.90 (d, J = 8.8 Hz, 2H, H-3′,5′), 7.26 (dt, J = 8.4 and 1.5 Hz, 1H, H-4), 7.48 (d, J = 15.6 Hz, 1H, α-H), 7.56 (d, J = 8.8 Hz, 2H, H-2′,6′), 7.71 (d, J = 15.6 Hz, 1H, β-H), 7.84 (dd, J = 8.4 and 1.5 Hz, 1H, H-6) ppm. 13C NMR (75 MHz, CDCl3) δ = 55.4 (OCH3), 114.4 (C-3′,5′), 115.8 (C-5), 117.3 (C-3), 119.3 (C-1), 120.8 (α-C), 128.0 (C-1′), 130.0 (C-2′,6′), 130.9 (C-6), 131.4 (C-4), 142.8 (β-C), 151.0 (C-2′), 161.3 (C-4′), 191.8 (CO) ppm. MS m/z (ESI %): 254.1 ([M+H]+); HMRS: m/z (ESI) calc. for C17H19N2O 254.1176, found 254.1172. UV/Vis (CHCl3, nm): λmax (log ε) = 333 (4.51).

2.1.3. (E)-1-(2-aminophenyl)-3-[4-(dimethylamino)phenyl]prop-2-en-1-one (2c)

The product was isolated as an orange solid (1.210 g, 4.51 mmol, 75%). M.p. = 120–121 °C. 1H NMR (300 MHz, CDCl3) δ = 3.00 (s, 6H, N(CH3)2), 6.26 (br s, 2H, NH2), 6.67 (d, J = 8.7 Hz, 2H, H-3′,5′), 6.66–6.71 (m, 2H, H-3 and H-5), 7.25 (dt, J = 8.1 and 1.2 Hz, 1H, H-4), 7.41 (d, J = 15.4 Hz, 1H, α-H), 7.52 (d, J = 8.7 Hz, 2H, H-2′,6′), 7.73 (d, J = 15.4 Hz, 1H, β-H), 7.86 (dd, J = 8.1 and 1.2 Hz, 1H, H-6) ppm. 13C NMR (75 MHz, CDCl3) δ = 40.2 (N(CH3)2), 111.9 (C-3′,5′), 115.8 (C-5), 117.3 (C-3), 117.9 (C-1), 121.0 (C-1′), 132.0 (C-2′,6′), 130.8 (C-6), 133.7 (C-4′), 144.0 (β-C), 150.7 (C-2′), 151.8 (C-4′), 192.0 (CO) ppm. MS m/z (ESI %): 267.1 ([M+H]+); HMRS: m/z (ESI) calc. for C17H18N2O 267.1499, found 267.1492. UV/Vis (CHCl3, nm): λmax (log ε) = 418 (4.59).

2.2. General Procedure for the Synthesis of 2′-(methanesulfonfonyl)amino)chalcones 3a–c

2′-Aminochalcone derivatives 2a–c (1 mmol), methane sulfonyl chloride (1 mmol) and triethylamine (1 mmol) were stirred in dichloromethane (5 mL) overnight at room temperature. Following the addition of H2O (50 mL), the pH was neutralized with dilute HCl and the solution extracted with CH2Cl2 (3 × 20 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting oil was purified by silica gel column chromatography, using dichloromethane as eluent.
2.2.1. (E)-N-[2-3-(4-methylphenyl)acryloyl]phenyl)methanesulfonamide (3a)

The product was isolated as a yellow solid (0.148 g, 0.47 mmol, 56%). M.p. = 125–126 °C. 
¹H NMR (300 MHz, CDCl₃) δ = 2.40 (s, 3H, CH₃), 3.06 (s, 3H, SO₂CH₃), 7.21 (dt, J = 7.8 and 1.2 Hz, 1H, H-5), 7.24 (d, J = 8.4 Hz, 2H, H-3′,5′), 7.55 (d, J = 15.5 Hz, 1H, α-H), 7.56 (d, J = 8.4 Hz, 2H, H-2′,6′), 7.57 (dt, J = 7.8 and 1.2 Hz, 1H, H-4), 7.79 (dd, J = 8.4 and 1.2 Hz, 1H, H-3), 7.83 (d, J = 15.5 Hz, 1H, β-H), 8.03 (dd, J = 7.8 and 1.2 Hz, 1H, H-6), 11.27 (br s, 1H, NH) ppm. 
¹³C NMR (75 MHz, CDCl₃) δ = 21.6 (CH₃), 40.1 (SO₂CH₃), 118.8 (C-3), 120.7 (α-C), 122.8 (C-5), 123.6 (C-1′), 128.8 (C-2′,6′), 129.8 (C-3′,5′), 131.1 (C-6), 131.7 (C-2), 134.8 (C-4), 140.6 (C-1), 141.8 (C-4′), 146.4 (β-C), 192.7 (CO) ppm. MS m/z (ESI %): 316.1 ([M+H]+); HMRs: m/z (ESI) calc. for C₁₇H₁₈NO₃S 316.1002, found 316.1008. UV/Vis (CHCl₃, nm): ε = 361 (4.57).

2.2.2. (E)-N-[2-3-(4-methoxyphenyl)acryloyl]phenyl)methanesulfonamide (3b)

The product was isolated as a yellow solid (0.109 g, 0.33 mmol, 42%). M.p. = 155–156 °C.

2.2.3. General Procedure for the Synthesis of 2

Following the addition of H₂O (50 mL), the pH was neutralized with dilute HCl and the solution was concentrated to dryness. The resulting solid was purified by silica gel column chromatography, using dichloromethane as eluent.

2.3. General Procedure for the Synthesis of 2′-(Acetylamino)Chalcones 4a–c

2′-Aminoacanthone derivatives 2a-c (1 mmol), acetyl chloride (1 mmol) and triethylamine (1 mmol) in dichloromethane (5 mL) were stirred overnight at room temperature. Following the addition of H₂O (50 mL), the pH was neutralized with dilute HCl and the solution was extracted with CHCl₃ (3 × 20 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting solid was purified by silica gel column chromatography, using dichloromethane as eluent.

2.3.1. (E)-N-[2-3-(4-methylphenyl)acryloyl]phenyl)acetamide (4a)

The product was isolated as a yellow solid (0.118 g, 0.42 mmol, 84%). M.p. = 121–122 °C. 
¹H NMR (300 MHz, CDCl₃) δ = 2.25 (s, 3H, COCH₃), 2.41 (s, 3H, CH₃), 7.16 (dt, J = 8.2 and 1.2 Hz, 1H, H-5), 7.25 (d, J = 8.4 Hz, 2H, H-3′,5′), 7.52 (d, J = 15.6 Hz, 1H, α-H), 7.55 (d, J = 8.4 Hz, 2H, H-2′,6′), 7.56 (dt, J = 8.2 and 1.2 Hz, 1H, H-4), 7.79 (d, J = 15.6 Hz, 1H, β-H), 7.97 (dd, J = 8.2 and 1.2 Hz, 1H, H-3), 8.70 (d, J = 8.2 Hz, 1H, H-6), 11.55 (br s, 1H, NH) ppm. 
¹³C NMR (75 MHz, CDCl₃) δ = 21.6 (CH₃), 25.5 (COCH₃), 121.2 (C-6), 121.8 (α-C), 122.4 (C-5), 123.5 (C-1), 128.7 (C-2′,6′), 129.8 (C-3′,5′), 130.5 (C-3), 131.9 (C-1′), 134.6 (C-4), 141.0 (C-2), 141.6 (C-4′), 145.8 (β-C), 169.4 (COCH₃), 193.5 (CO) ppm. MS m/z (ESI %): 280.1
(\([\text{M}+\text{H}]^{+}\)); HMRS: \text{m/z} (\text{ESI}) \text{ calc. } \text{for } \text{C}_{18}\text{H}_{18}\text{NO}_{2} 280.1332, \text{found } 280.1337. \text{ UV/Vis (CHCl}_{3}, \text{nm}): \lambda_{\text{max}} \text{(log } \varepsilon) = 334 \text{ (4.49).}

2.3.2. (E)-N-{2-[3-(4-methoxyphenyl)acryloyl]phenyl}acetamide (4b)

The product was isolated as a yellow solid (0.101 g, 0.34 mmoL, 43%). M.p. = 121–122 °C. 1H NMR (300 MHz, CDCl\(_3\) \(\delta= 2.23 \text{ (s, 3H, COC}_{6}\text{H}_{3}), 3.84 \text{ (s, 3H, OCH}_{3}), 6.93 \text{ (d, } J = 8.7 \text{ Hz, 2H, H-3',5'), 7.13 \text{ (dt, } J = 8.1 \text{ and 1.2 Hz, 1H, H-5), 7.42 } \text{ (d, } J = 15.6 \text{ Hz, 1H, } \alpha -\text{H}), 7.53 \text{ (dt, } J = 8.1 \text{ and 1.2 Hz, 1H, H-4), 7.59 } \text{ (d, } J = 8.7 \text{ Hz, 2H, H-2',6'), 7.76 } \text{ (d, } J = 15.6 \text{ Hz, 1H, } \beta -\text{H}), 7.94 \text{ (dd, } J = 8.1 \text{ and 1.2 Hz, 1H, H-3), 8.69 \text{ (dd, } J = 8.1 \text{ and 1.2 Hz, 1H, H-6) 11.58 (br s, 1H, NH) ppm. 13C NMR (75 MHz, CDCl}_{3} \text{)} \(\delta= 25.5 \text{ (COC}_{6}\text{H}_{3}), 55.4 \text{ (OCH}_{3}), 114.5 \text{ (C-3',5'), 120.3 (C-1), 121.1 (C-6), 122.4 (C-5), 123.6 (C-1'), 127.3 (C-1'), 130.4 (C-3), 130.5 \text{ (C-2',6'), 134.4 (C-4), 140.9 (C-2), 145.5 (C-1'), 162.0 (C-4'), 169.3 (C O CH}_{3}), 193.3 \text{ (CO) ppm. MS m/z (ESI %): 296.1 ([M+H]^+); HMRS: m/z (ESI) calc. for C}_{18}\text{H}_{18}\text{NO}_{3} 296.1281, \text{found } 296.1272. \text{ UV/Vis (CHCl}_{3}, \text{nm): } \lambda_{\text{max}} \text{(log } \varepsilon) = 359 \text{ (4.54).}

2.3.3. (E)-N-{2-[3-(4-(dimethylamino)phenyl)acryloyl]phenyl}acetamide (4c)

The product was isolated as an orange solid (0.162 g, 0.52 mmoL, 66%). M.p. = 129–131 °C. 1H NMR (300 MHz, CDCl\(_3\) \(\delta= 2.23 \text{ (s, 3H, COCH}_{3}), 3.04 \text{ (s, 6H, N(CH}_{3})_{2}), 6.67 \text{ (d, } J = 8.7 \text{ Hz, 2H, H-3',5'), 7.13 \text{ (dt, } J = 8.1 \text{ and 1.2 Hz, 1H, H-5), 7.34 \text{ (d, } J = 15.3 \text{ Hz, 1H, } \alpha -\text{C}), 7.51 \text{ (dd, } J = 8.1 \text{ and 1.2 Hz, 1H, H-4), 7.54 \text{ (d, } J = 8.7 \text{ Hz, 2H, H-2',6'), 7.78 } \text{ (d, } J = 15.3 \text{ Hz, 1H, } \beta -\text{H}), 7.95 \text{ (dd, } J = 8.1 \text{ and 1.2 Hz, H-3), 8.68 \text{ (dd, } J = 8.1 \text{ and 1.2 Hz, 1H, H-6), 11.66 (br s, 1H, NH) ppm. 13C NMR (75 MHz, CDCl}_{3} \text{)} \(\delta= 25.5 \text{ (COC}_{6}\text{H}_{3}), 3.04 (N(CH}_{3})_{2}), 111.8 \text{ (C-3',5'), 117.2 (C-1), 117.2 (C-6), 122.3 (C-5), 122.3 (C-1'), 122.3 \text{ (C-5), 123.4 (C-3), 130.2 (C-2',6'), 133.8 (C-4), 140.7 (C-2), 146.8 (C-1'), 152.3 (C-4'), 169.3 (C O CH}_{3}), 193.2 \text{ (CO) ppm. MS m/z (ESI %): 309.2 ([M+H]^+); HMRS: m/z (ESI) calc. for C}_{19}\text{H}_{21}\text{N}_{2}O_{2} 309.1598, \text{found } 309.1595. \text{ UV/Vis (CHCl}_{3}, \text{nm): } \lambda_{\text{max}} \text{(log } \varepsilon) = 432 \text{ (4.61).}

2.4. Photophysical Characterization of 2'-aminochalcones 2, 3 and 4

Solutions of 2'-aminochalcones 2a–c, 3a–c and 4a–c \((10^{-4} \text{ to } 10^{-6} \text{ M})\) were prepared in solvents with different character (polar-apolar, protic-aprotic), and their absorption and emission spectra were recorded. Relative fluorescence quantum yields were calculated using fluorescein \((\Phi_F = 0.95 \text{ in NaOH } 0.1 \text{ M})\) and anthracene \((\Phi_F = 0.27 \text{ in ethanol})\) as standard [19].

3. Results and Discussion

3.1. Synthesis

The synthetic route chosen to obtain the 2'-aminochalcones comprised two steps (Scheme 2). First, the aminochalcones were synthesized by base-catalyzed aldol condensation using potassium hydroxide, in 43–80% yields. Then, the electron-withdrawing groups were introduced to obtain the final compounds 3 (sulfonamide formation) and 4 (acylation), in 42–84% yields. All new compounds were fully characterized by \(^1\text{H}-\text{NMR, }\text{^{13}C-NMR and MS.}

\[ \begin{array}{c}
\text{NH} \\
\text{O} \\
\end{array} + \begin{array}{c}
\text{R} \\
\text{O} \\
\end{array} \xrightarrow{\text{MeCH, KH}} \text{NH} \\
\text{O} \\
\begin{array}{c}
\text{1a-c} \\
\text{2a-c} \\
\end{array} \xrightarrow{\text{ESN, DCM, rt}} \text{3a-c} \\
\text{4a-c} \\
\end{array} \]

Scheme 2. Synthesis of the 2'-aminochalcones 2a–c, 3a–c and 4a–c.
The main features of the ¹H NMR spectra of compounds 2, 3 and 4 are the signals corresponding to the vinylic protons of their characteristic α,β-unsaturated moieties. The protons H-α and H-β appear at δ 7.34–7.61 and 7.71–7.83 ppm, respectively, as two doublets with a coupling constant of ca. 15 Hz, which indicates an (E)-configuration for the vinylic system. Another important characteristic of the ¹H NMR spectra of 3 and 4 is a singlet with high frequency values (δ 11.27–11.66 ppm) attributed to 2′-NH₂, due to the intramolecular hydrogen bond with the carbonyl group. This signal is not observed for compounds 2a–c that have a broad singlet with lower frequency values, between 6.25 and 6.44 ppm.

3.2. Photophysical Study of 2′-Aminochalcones 2, 3 and 4

The photophysical properties of the chalcones 2a–c, 3a–c and 4a–c were evaluated. First, the absorption and emission spectra of all compounds were measured in acetonitrile (Figures 1 and 2). The 2′-aminochalcones 2-4 show low to moderate fluorescence quantum yields, and large Stokes’ shifts (5058–9883 cm⁻¹) (Table 1). The influence of the electron-donating group is observed, and compounds 2c, 3c and 4c, bearing a dimethylamino substituent, present a red shift on the absorption and emission maxima. They are also more emissive, with higher quantum yields of 0.03–0.35. For some compounds, the emission profile is not symmetric, and a second emission band appears with a lower intensity. This is consistent with the proposed ESIPT model.

Table 1. UV-visible absorption and emission data for 2′-aminochalcones 2, 3 and 4 in organic solvents with different characteristics.

| Cpd | Solvent (π*) | UV/Vis | Fluorescence |
|-----|--------------|--------|--------------|
|     |              | λmax (nm) | log ε | λem (nm) | Stokes' Shift (cm⁻¹) | Φ_F |
| 2a  | Diethyl ether (0.27) | 308 | 4.58 | --- | --- | --- |
|     | Chloroform (0.58) | 317 | 4.59 | 459 | 9759 | <0.01 |
|     | ACN (0.75) | 311 | 4.57 | 449 | 9883 | <0.01 |
|     | DMSO (1.00) | 317 | 4.57 | 460 | 9807 | <0.01 |
| 2b  | Diethyl ether (0.27) | 324 | 4.51 | --- | --- | --- |
|     | Chloroform (0.58) | 333 | 4.51 | 455 | 8052 | <0.01 |
|     | ACN (0.75) | 327 | 4.52 | 448 | 8260 | <0.01 |
|     | DMSO (1.00) | 335 | 4.52 | 454 | 7824 | <0.01 |
| 2c  | Diethyl ether (0.27) | 404 | 4.58 | 493 | 4468 | <0.01 |
|     | Chloroform (0.58) | 418 | 4.59 | 497/532 | 3803/5126 | 0.03 |
|     | ACN (0.75) | 418 | 4.57 | 540 | 5405 | 0.03 |
|     | DMSO (1.00) | 429 | 4.58 | 540 | 4792 | 0.03 |
| 3a  | Diethyl ether (0.27) | 329 | 4.57 | 417/441 | 6414/7719 | <0.01 |
|     | Chloroform (0.58) | 336 | 4.56 | 440 | 7035 | <0.01 |
|     | ACN (0.75) | 333 | 4.59 | 438 | 7199 | <0.01 |
|     | DMSO (1.00) | 332 | 4.58 | 413/438 | 5907/7289 | <0.01 |
| 3b  | Diethyl ether (0.27) | 354 | 4.53 | --- | --- | --- |
|     | Chloroform (0.58) | 361 | 4.57 | 454 | 5674 | <0.01 |
|     | ACN (0.75) | 358 | 4.50 | 445 | 5461 | <0.01 |
|     | DMSO (1.00) | 363 | 4.52 | 455 | 5570 | <0.01 |
| 3c  | Diethyl ether (0.27) | 424 | 4.62 | --- | --- | --- |
|     | Chloroform (0.58) | 439 | 4.66 | 535 | 4087 | 0.10 |
|     | ACN (0.75) | 437 | 4.60 | 561 | 5058 | 0.10 |
|     | DMSO (1.00) | 445 | 4.61 | 537 | 4519 | 0.11 |
| 4a  | Diethyl ether (0.27) | 325 | 4.51 | --- | --- | --- |
Considering the results obtained in acetonitrile, the photophysical properties of 2'-aminochalcones 2, 3 and 4 were evaluated in other organic solvents presenting different polarity. The solvents tested were dimethylsulfoxide, chloroform and diethyl ether, as examples of solvents with different polarity and proticity, with $\pi^*$ values determined by Kamlet and Taft [20] indicating the ability of a particular solvent to stabilize a charge or a dipole due to its dielectric effect, normalized between cyclohexane ($\pi^* = 0$) and DMSO ($\pi^* = 1$). The collected data revealed similar maxima wavelengths of absorption, but some differences in the emission maxima wavelengths (two maxima can be observed in some solvents, for compounds 2c, 3a, 3c and 4c) and the fluorescence quantum yield do not vary significantly (Table 1). The general trend revealed that 2'-aminochalcone 4c (para-position of ring B with dimethylamine and in ring A the acetyl-protected amine group) is the most fluorescent (with $\Phi_F$ in the range of 0.32–0.36).

The absorption and emission spectra of 2c and 4c in different solvent are presented in Figures 3 and 4. For both compounds, a small shift is observed in the absorption spectra in different solvents, probably due to the solvatochromism expected for push–pull dyes. Two emission bands are clearly visible for 2c, with variable intensities depending on the solvent. They are less obvious for 4c. In diethyl ether (less polar solvent), the band at shorter wavelengths is predominant, corresponding to the L form (Scheme 1). In DMSO and ACN (more polar), the band at longer wavelengths is predominant, corresponding to the E form. In Chloroform, both bands are present, witnessing the ESIPT equilibrium. These bands are probably merged into a single one for 4c.
Figure 1. Normalized absorption spectra of 2’aminochalcones 2, 3 and 4 in acetonitrile.

Figure 2. Normalized emission spectra of 2’aminochalcones 2, 3 and 4 in acetonitrile.
Figure 3. Normalized absorption and emission spectra of chalcone 2c in acetonitrile, diethyl ether, chloroform and dimethyl sulfoxide (λ<sub>exc</sub> = 418 nm, 404 nm, 418 nm and 429 nm, respectively; absorption, full line; emission, dotted line).

Figure 4. Normalized absorption and emission spectra of chalcone 4c in acetonitrile, diethyl ether, chloroform and dimethyl sulfoxide (λ<sub>exc</sub> = 428 nm, 417 nm, 432 nm and 437 nm, respectively; absorption, full line; emission, dotted line).

4. Conclusions

The 2′aminochalcones 2, 3 and 4 are emissive, especially derivatives c (N,N-dimethylamine as a substituent) with moderate fluorescence quantum yields (Φ<sub>F</sub> = 0.03 for 2c; Φ<sub>F</sub> = 0.10 for 3c; Φ<sub>F</sub> = 0.35 for 4c) and large Stokes’ shifts (5405, 5058 and 5379 cm<sup>-1</sup>, respectively) in acetonitrile. Compound 4c (acetyl group as a substituent on the amine) displayed the highest fluorescence. Fluorophores 2c and 4c present an interesting ESIPT, with a dual emission. The intensity of each emission band is strongly influenced by the solvent and witnesses a dramatic shift in the ESIPT equilibrium. These compounds could, therefore, find applications as molecular probes of organelles polarity, and this study is ongoing.
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