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ORIGINAL ARTICLE

Synthesis and fluorescence of new 3-biphenylpyrrolo [1,2-*c*]pyrimidines

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1,3-dipolar cycloaddition;
Stokes shift;
Fluorescence quenching;
Quantum yield

Abstract New pyrrolo[1,2-*c*]pyrimidines derivates having a biphenyl moiety at position 3 have been synthesized by 1,3-dipolar cycloaddition of their corresponding *N*-ylides with activated alkynes. FTIR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis have been used to characterize the structures of the new nine pyrrolo[1,2-*c*]pyrimidine derivates. Absorption and fluorescence spectra have been recorded. The appropriate solvent for the photoluminescence properties of the studied compounds has been found to be chloroform:acetonitrile mixture (1:1). The main spectral features such as molar extinction coefficients (ε), Stokes shifts, quantum yields using quinine sulphate as standard, fluorescence quenching in the presence of benzoquinone and Stern-Volmer constants have been calculated. The substituent effects on intensity of absorption, maximum absorbance wavelengths and fluorescence parameters have been discussed. The highest quantum yield value was found for ethyl 3-(4-biphenylyl)-7-(3,4-dimethoxybenzoyl)pyrrolo[1,2-*c*]pyrimidine-5-carboxylate (0.55). The obtained results suggest that the studied compounds are promising candidates for future study in order to evaluate their use in practical applications in fluorescent chemical sensors.

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1. Introduction

Fluorescence (Valeur, 2001) raised a special interest among the most important physical-chemical properties of heterocycles due to its applicative potential spanning from medical applications (Firmino and Goncalves, 2012; Perin et al., 2011; Yin and Yoon, 2015) to high-tech materials as, for example, organic light emitting diodes

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(OLEDs) (Chen et al., 2014; Buckley, 2013; Oh et al., 2012). In this context nitrogen-containing heterocycles have been proved to be very useful in obtaining fluorescent chemical sensors (Zhang et al., 2014; Goswami et al., 2013), bioprobes (El Aissi et al., 2014), dyes for solar cells (DSSCs) (Li et al., 2012; Ying et al., 2014; Huckaba et al., 2014), or LASER dyes (Srividya et al., 1998). In particular pyrroloazines (Rotaru et al., 2009; Vlahovici et al., 1999; Dumitrascu et al., 2011) or pyrrolodiazines (Zbancioc and Mangalagiu 2006; Vasilescu et al., 2008; Tumkevicius et al., 2010; Skardziute et al., 2013; Bucevicius et al., 2015) were studied for their fluorescence with promising results.

The pyrrolo[1,2-*c*]pyrimidine framework was studied for its bioactivity (Rise et al., 1996; Ono et al., 2004; Mangalagiu et al., 2001; Kristafor et al., 2011; Kim et al., 2006) as it is present as a substructure in some natural products (Perry et al., 1994; Bondu et al., 2012; Elliott and Long 2002). Its synthetic methods reported in the literature are rather scarce (Minguez et al., 1996; Alvarez et al., 1999; Weidner et al., 1991; Copar et al., 1993; Romashin et al., 2000; Baumann et al., 2015; Iuhas et al., 2002; Mangalagiu et al., 2000; Georgescu et al., 2013; Georgescu et al., 2012), the 1,3-dipolar cycloaddition reaction of the pyrimidinum *N*-ylides being one of the most lucrative (Iuhas et al., 2002; Mangalagiu et al., 2000; Georgescu et al., 2013; Georgescu et al., 2012).

Herein we present the synthesis and fluorescence studies of 9 new 3-biphenyl-pyrrolo[1,2-*c*]pyrimidines synthesized by 1,3-dipolar cycloaddition reaction of their corresponding cycloimmonium *N*-ylides with electron-deficient alkynes. To our knowledge this is the first study regarding the fluorescence of substituted pyrrolo[1,2-*c*]pyrimidines till now.

2. Materials and methods

2.1. General

Melting points were determined on a Boëtius hot plate microscope. The elemental analysis was carried out on a COSTECH Instruments EAS32 apparatus. The IR spectra were recorded on a Bruker Vertex 70 ATR spectrometer or Nicolet Impact 410 spectrometer, in KBr pellets. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. UV–VIS spectra were recorded with a JASCO V550 spectrophotometer. Fluorescent excitation and emission spectra were measured with a Jasco FP6500 spectrofluorimeter, with reading at an angle of 90°. The refractive indexes were measured at room temperature using a refractometer (Abbe from CETI Belgium).

2.2. Synthesis of the starting 4-Biphenylpyrimidine

4-Biphenylpyrimidine was obtained from 4-acetylbiphenyl and trisformylaminomethane according to the reported method for the synthesis of 4-phenylpyrimidine (Brederek et al., 1965). 2-Bromo-3′,4′-dimethoxyacetophenone was obtained by the brominating of corresponding acetophenone with bromine in diethyl ether. Other reagents used for synthesis were commercially available products. Acetonitrile and chloroform (Fluka) were used as received. Quinine sulphate (Buchler) was used as reference to calculate the quantum yield.

2.3. General procedure for syntheses of 3-biphenylpyrrolo[1,2-c] pyrimidines *4a–i*

A mixture of 4-biphenylpyrimidine **1** (2 mmol), bromoacetyl derivative **2** (2 mmol) and a non-symmetrical electron-deficient alkyne **3** (2 mmol) in 30 mL of 1,2-epoxybutane was heated at reflux temperature for 24 h. The solvent was partly removed under vacuum, 3 mL of MeOH was added under a gentle stirring, and the mixture was left overnight in the refrigerator. The solid formed was filtered off and recrystallized from $CHCl_3$/MeOH giving 3-biphenyl-pyrrolo[1,2-*c*]pyrimidines **4a–i**. In the case of symmetrical dipolarophiles, the procedure is similar with the small modification that the dipolarophile was added to the reaction mixture after an hour of reflux.

2.3.1. 3-(4-Biphenylyl)-5-acetyl-7-(4-chlorobenzoyl)pyrrolo [1,2-c]pyrimidine (*4a*)

Yellow crystals. FT-IR (ATR, cm^{-1}): 3096, 1667, 1610, 1513, 1467, 1328, 1219, 1194;^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.56 (s, 3H, CH_3); 7.38–7.41 (m, 2H, 2H-Ph); 7.46–7.51 (m, 1H, 1H-Ph); 7.70 (s, 1H, H-6); 7.67–7.69 (m, 2H, 2H-Ph); 7.55, 7.82 (2d, J = 8.4 Hz, H-2″, H-3″, H-5″, H-6″); 7.77 (d, J = 8.4 Hz, 2H, H-2′, H-6′); 8.30 (d, J = 8.4 Hz, 2H, H-2′, H-6′); 8.93 (d, J = 1.1 Hz, 1H, H-4); 10.62 (d, J = 1.1 Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 28.1 (Me); 109.3 (C-4); 115.4 (C-5); 127.7, 127.9, 128.9, 129.5, 130.3, (C-2″, C-3″, C-5″, C-6″, 5C-Ph); 121.9, 135.2, 137.4, 138.6, 140.2, 140.8, 143.1, 151.2 (C-7, C-4a, C-3, C-1′, C-4′, C-1″, C-4″ Cq-Ph); 127.1, 127.5 (C-2′, C-3′, C-4′, C-6′); 129.0 (C-6); 140.7(C-1); 183.9 (COAr), 193.01 (COMe); Anal. calcd. $C_{28}H_{19}ClN_2O_2$ (450.91): C 74.58; H 4.25; N 6.21. Found: C 74.64, H 4.29, N 6.17.

2.3.2. 3-(4-Biphenylyl)-5-acetyl-7-(3-nitrobenzoyl)pyrrolo[1,2-c]pyrimidine (*4b*)

Yellow-mustard crystals. FT-IR (KBr, cm^{-1}): 3085, 1664, 1617, 1600, 1530, 1515, 1481, 1416, 1350, 1329, 1219, 1196, 1110, 1006. ^{1}H NMR ($CDCl_3$ + TFA, 300 MHz, δ): 2.76 (s, 3H, CH_3); 7.44–7.54 (m, 4H, H-5″, 3H-Ph); 7.66–7.70 (m, 2H, 2H-Ph); 7.89 (s, 1H, H-6); 7.86–7.90 (m, 2H, H-3′, H-5′); 8.05 (d, J = 8.4 Hz, 2H, H-2′, H-6′); 8.23–8.25 (m, 1H, H-4″); 8.57–8.60 (m, 1H, H-6″); 8.72 (t, J = 1.9 Hz, 1H, H-2″); 8.06 (d, J = 8.4, 2H, H-2′, H-6′); 9.01 (d, J = 1.1 Hz, 1H, H-4); 11.25 (d, J = 1.1 Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$ + TFA, 75 MHz, δ): 27.5 (Me); 112.0 (C-4); 116.4 (C-5); 123.9 (C-2″) 127.3, 127.8, 128.1, 128.5, 128.6, 129.1, 132.7, 134.7 (C-2′, C-3′, C-5′, C-6′, C-4″, C-5″, C-6″, 5C-Ph); 123.3, 138.6, 139.3, 141.0, 143.5, 145.5, 148.4 (C-7, C-4a, C-3, C-1′, C-4′, C-1″, C-3″, Cq-Ph); 130.7 (C-6); 141.0 (C-1); 184.9 (COAr), 197.3 (COMe); Anal. calcd. $C_{28}H_{19}N_3O_4$ (461.47): C 72.88; H 4.15; N 9.10. Found: C 72.93, H 4.18, N 9.03.

2.3.3. Ethyl 3-(4-biphenylyl)-7-(4-fluorobenzoyl)pyrrolo[1,2-c] pyrimidine-5-carboxylate (*4c*)

Yellow crystals. FT-IR (KBr, cm^{-1}): 3068, 2976, 1700, 1616, 1523, 1470, 1416, 1330, 1230, 1199, 1154, 1085, 1052. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 1.45 (t, J = 7.1 Hz, 3H, CH_3); 4.43 (q, J = 7.1 Hz, 2H, CH_2); 7.21(t, J = 8.6 Hz, 2H, H-3″, H-5″); 7.35–7.49 (m, 3H, 3H-Ph); 7.63–7.70 (m, 2H, 2H-Ph); 7.72 (d, J = 8.5 Hz, 2H, H-3′, H-5′); 7.75 (s, 1H, H-6); 7.86–7.88 (m, 2H, H-2″, H-6″); 8.21 (d, J = 8.5 Hz, 2H, H-2′, H-6′); 8.62 (d, J = 1.1 Hz, 1H, H-4); 10.54 (d, J = 1.1 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 14.7 (Me); 60.8 (CH_2); 107.2 (C-5); 108.5 (C-4); 115.9 (J = 21.8 Hz, C-3″, C-5″); 122.2, 135.3, 135.5 140.3, 140.9, 142.9, 149.6 (C-7, C-4a, C-3, C-1′, C-4′, C-1″, Cq-Ph); 127.2, 129.0 (C-2′, C-3′, C-5′, C-6′);

129.8 (C-6); 127.4, 127.7, 128.0 (5C-Ph); 131.5 (J = 8.9 Hz, C-2″, C-6″); 140.8 (C-1); 165.2 (J = 263.4 Hz, C-4″); 163.7 (CO); 183.8 (COAr); Anal. calcd. $C_{29}H_{21}FN_2O_3$ (464.50): C 74.99; H 4.56; N 6.03. Found: C 75.05, H 4.52, N 5.99.

2.3.4. Ethyl 3-(4-biphenylyl)-7-(4-bromobenzoyl)pyrrolo[1,2-c]pyrimidine-5-carboxylate (**4d**)

Yellow crystals. FT-IR (KBr, cm^{-1}): 3108, 3054, 2985, 1698, 1620, 1600, 1521, 1472, 1430, 1351, 1327, 1300, 1253, 1202, 1087, 1048; ^1H NMR ($CDCl_3$ + TFA, 300 MHz, δ): 1.49 (t, J = 7.1 Hz, 3H, CH_3); 4.50 (q, J = 7.1 Hz, 2H, CH_2); 7.41–7.53 (m, 3H, 3H-Ph); 7.66–7.69 (m, 2H, 2H-Ph); 7.73–7.74 (m, 4H, H-2″, H-3″, H-5″, H-6″); 7.83 (d, J = 8.6 Hz, 2H, H-2′, H-6′); 8.03 (d, J = 8.6 Hz, 2H, H-2′, H-6′); 8.04 (s, 1H, H-6); 8.69 (d, J = 1.1 Hz, 1H, H-4); 11.08 (d, J = 1.1 Hz, 1H, H-1); Anal. calcd. $C_{29}H_{21}BrN_2O_3$ (525.39): C 66.29; H 4.03; N 5.33. Found: C 66.36, H 4.10, N 5.28.

2.3.5. Ethyl 3-(4-biphenylyl)-7-(4-nitrobenzoyl)pyrrolo[1,2-c]pyrimidine-5-carboxylate (**4e**)

Orange crystals. FT-IR (KBr, cm^{-1}): 2983, 1701, 1617, 1591, 1523, 1471, 1415, 1347, 1327, 1254, 1203, 1089, 1053. ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.45 (t, J = 7.1 Hz, 3H, CH_3); 4.44 (q, J = 7.1 Hz, 2H, CH_2); 7.40–7.52 (m, 3H, 3H-Ph); 7.67–7.70 (m,2H, 2H-Ph); 7.77 (d, J = 8.4 Hz, 2H, H-3′, H-5′); 7.78 (s, 1H, H-6); 8.00 (d, J = 8.8 Hz, 2H, H-3″, H-5″); 8.27 (d, J = 8.4 Hz, 2H, H-2′, H-6′); 8.41 (d, J = 8.8 Hz, 2H, H-2″, H-6″); 8.71 (d, J = 1.1 Hz, 1H, H-4); 10.64 (d, J = 1.1 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 27.7 (Me); 60.6 (CH_2); 107.7 (C-5); 108.4 (C-4); 123.8, (C-3″, C-5″); 121.5, 135.0, 140.0, 141.4, 143.0, 144.2, 149,6, 150.3 (C-7, C-4a, C-3, C-1′, C-4′, C-1″, C-4″, Cq-Ph); 130.2 (C-6); 127.0, 127.3, 127.6, 127.8, 128.9, 129.7 (C-2′, C-3′, C-5′, C-6′, C-2″, C-6″,5C-Ph); 140.6 (C-1); 163.2 (CO); 184.9 (COAr); Anal. calcd. $C_{29}H_{21}N_3O_5$ (491.49): C 70.87; H 4.31; N 8.55. Found: C 70.82, H 4.28, N 8.61.

2.3.6. Ethyl 3-(4-biphenylyl)-7-(3,4-dimethoxybenzoyl)pyrrolo[1,2-c]pyrimidine-5-carboxylate (**4f**)

Yellow crystals. FT-IR (KBr, cm^{-1}): 2935, 2839, 1706, 1619, 1602, 1516, 1475, 1416, 1328, 1266, 1198, 1172, 1140, 1091, 1050, 1024. ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.38 (t, J = 7.1 Hz, 3H, CH_3); 3.90 (s, 3H, OMe); 3.91 (s, 3H, OMe); 4.36 (q, J = 7.1 Hz, 2H, CH_2); 6.90 (d, J = 8.4 Hz, 1H, H-5″); 7.30–7.48 (m, 5H, H-2″, H-6″, 3H-Ph); 7.58–7.60 (m, 2H, 2H-Ph); 7.68 (d, J = 8.5 Hz, 2H, H-3′, H-5′); 7.78 (s, 1H, H-6); 8.17 (d, J = 8.5 Hz, 2H, H-2′, H-6′); 8.57 (d, J = 1.1 Hz, 1H, H-4); 10.46 (d, J = 1.1 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 14.6 (Me); 56.1 (2OMe); 60.5 (CH_2); 106.8 (C-5); 108.4 (C-4); 110.2, 111.6, 123.6 (C-2″, C-5″, C-6″); 122.4, 131.6, 135.5 140.3, 140.6, 142.7, 149.2 (C-7, C-4a, C-3, C-1′, C-4′, C-1″, Cq-Ph); 127.2, 127.3 (C-2′, C-3′, C-5′, C-6′); 129.3 (C-6); 127.1, 127.6, 128.9 (5C-Ph); 140.8 (C-1); 149.3, 152.8 (C-3″, C-4″); 163.7 (CO); 184.0 (COAr); Anal. calcd. $C_{31}H_{26}N_2O_5$ (506.55): C 73.50; H 5.17; N 5.53. Found: C 73.61, H 5.22, N 5.49.

2.3.7. Dimethyl 3-(4-biphenylyl)-7-(4-nitrobenzoyl)pyrrolo[1,2-c]pyrimidine-5,6-dicarboxylate (**4g**)

Orange crystals. FT-IR (KBr, cm^{-1}): 3072, 2957, 1739, 1697, 1619, 1601, 1529, 1508, 1497, 1445, 1387, 1350, 1337, 1251, 1205, 1176, 1106. ^1H NMR ($CDCl_3$ + TFA, 300 MHz, δ): 3.47 (s, 3H, CH_3); 4.03 (s, 3H, CH_3); 7.43–7.54 (m, 3H, 3H-Ph); 7.55–7.66 (m, 2H, 2H-Ph); 7.84–8.02 (m, 6H, H-2′, H-3′, H-5′, H-6′, H-2″, H-6″); 8.38 (d, J = 8.5 Hz, 1H, H-3″, H-5″); 8.69 (d, J = 1.5 Hz, 1H, H-4); 10.96 (d, J = 1.5 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$ + TFA, 75 MHz, δ): 53.4, 53.9 ($2CH_3$); 107.0 (C-5); 111.4 (C-4); 121.0, 131.2, 135.3, 139.4, 142.6, 143.6, 145.1, 148.0, 150.4 (C-6, C-7, C-4a, C-3, C-1′, C-4′, C-1″, C-4″, Cq-Ph); 127.3, 128.0, 128.5, 128.6, 129.2 (C-2′, C-3′, C-5′, C-6′, 5C-Ph); 123.9, 129.9 (C-2″, C-3″, C-5″, C-6″); 139.4 (C-1); 163.3, 165.0 (2CO); 185.0 (COAr); Anal. calcd. $C_{30}H_{21}N_3O_7$ (535.50): C 67.29; H 3.95; N 7.85. Found: C 67.35, H 3.99, N 7.81.

2.3.8. Diethyl 3-(4-biphenylyl)-7-(4-phenylbenzoyl)pyrrolo[1,2-c]pyrimidine-5,6-dicarboxylate (**4h**)

Yellow crystals. FT-IR (KBr, cm^{-1}): 2972, 1734, 1700, 1611, 1605, 1490, 1431, 1395, 1371, 1333, 1243, 1196, 1103. ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.04 (t, J = 7.1 Hz, 3H, CH_3); 1.38 (t, J = 7.1 Hz, 3H, CH_3); 3.74 (q, J = 7.1 Hz, 2H, CH_2); 4.38 (q, J = 7.1 Hz, 2H, $2CH_2$); 7.38–7.51 (m, 6H, 6H-Ph); 7.62–7.84 (m, 10H, H-2′, H-6′, H-2″, H-3″, H-5″, H-6″ 4H-Ph); 8.24 (d, J = 8.4 Hz, 2H, H-3′, H-5′); 8.67 (d, J = 1.5 Hz, 1H, H-4); 10.29 (d, J = 1.5 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 13.6, 14.3 (2Me); 60.8, 62.0 ($2CH_2$); 104.9 (C-5); 108.5 (C-4); 120.4, 132.8, 135.2, 137.6, 139.6, 139.8, 140.9, 143.0, 145.3, 149.6 (C-6, C-7, C-4a, C-3, C-1′, C-4′, C-1″, C-4″, 2Cq-Ph); 127.3, 127.4, 129.1, 129.5 (C-2′, C-3′, C-5′, C-6′, C-2″, C-3″, C-5″, C-6″); 126.9, 127.1, 127.7, 127.9, 128.3, 128.9 (10C-Ph); 140.4 (C-1); 162.7, 164.2 (2CO); 186.0 (COAr); Anal. calcd. $C_{38}H_{30}N_2O_5$ (594.65): C 76.75; H 5.08; N 4.71. Found: C 76.80, H 5.11, N 4.66.

2.3.9. Diethyl 3-(4-biphenylyl)-7-(2-naphthoyl)pyrrolo[1,2-c]pyrimidine-5,6-dicarboxylate (**4i**)

Yellow crystals. FT-IR (KBr, cm^{-1}): 2979, 1739, 1697, 1619, 1508, 1489, 1431, 1383, 1334, 1245, 1200, 1183, 1128, 1093. ^1H NMR ($CDCl_3$, 300 MHz, δ): 0.9 (t, J = 7.1 Hz, 3H, CH_3); 1.39 (t, J = 7.1 Hz, 3H, CH_3); 3.40 (q, J = 7.1 Hz, 2H, CH_2); 4.41 (q, J = 7.1 Hz, 2H, CH_2); 7.38–7.56 (m, 3H, 3H-Ph); 7.57–7.77 (m, 7H, H-2′, H-6′, 2H-Ph, 4H-Naphthoyl); 7.90–7.98 (m, 2H, 2H-Naphthoyl); 8.26 (br s, 1H, 1H-Naphthoyl); 8.27 (d, J = 8.4 Hz, 2H, H-3′, H-5′); 8.72 (d, J = 1.5 Hz, 1H, H-4); 10.35 (d, J = 1.5 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 13.1, 14.1 (2Me); 60.6, 60.7 ($2CH_2$); 104.8 (C-1); 108.3 (C-8); 120.4, 130.3, 131.7, 132.8, 135.0, 135.8, 139.5, 140.1, 142.2, 149.2 (C-6, C-7, C-4a, C-3, C-1′, C-4′, 1Cq-Ph, 3Cq-Naphthoyl); 127.2, 129.1 (C-2′, C-3′, C-5′, C-6′); 124.4, 126.8, 126.9, 127.4, 127.5, 127.7, 128.2, 128.4, 128.7, 130.3 (5C-Ph, 7C-Naphthoyl); 140.2 (C-1); 162.5, 164.0 (2CO); 186.0 (COAr); Anal. calcd. $C_{36}H_{28}N_2O_5$ (568.62): C 76.04; H 4.96; N 4.93. Found: C 75.99, H 4.92, N 4.89.

3. Results and discussion

3.1. Synthesis of 3-biphenylpyrrolo[1,2-c]pyrimidines

The new 3-biphenylpyrrolo[1,2-*c*]pyrimidines **4a–i** have been obtained by 1,3-dipolar cycloaddition reactions of the corre-

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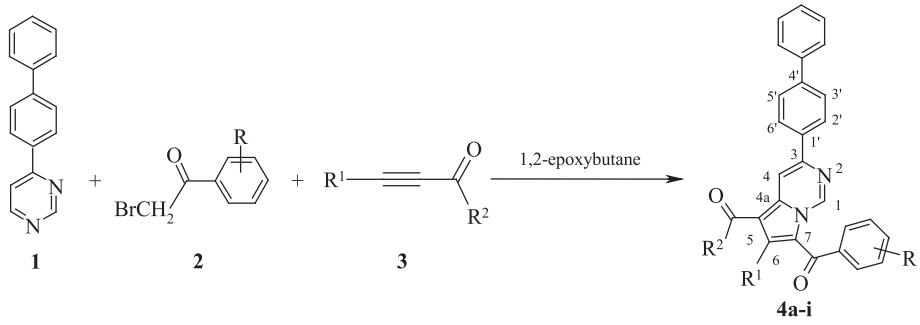
sponding 4-biphenylpyrimidinium-*N*-ylides (generated *in situ* from the corresponding salts) with electron-deficient alkynes, in the 1,2-epoxybutane at reflux (Georgescu et al., 2013; Georgescu et al., 2012; Popa et al., 2015). The advantage of performing the reaction in a one-pot three-component approach is the direct formation of the final aromatic compounds, avoiding the formation of dipyrimidino-pyrazinic inactivated products. The 3-biphenylpyrrolo[1,2-*c*]pyrimidines have been synthesized according to Scheme 1 with medium to good yields (Table 1).

The reaction mechanism (Scheme 2) for obtaining the new 3-biphenylpyrrolo[1,2-*c*]pyrimidines implies the attack of the bromide ion of the pyrimidinium bromide of type **5** on the oxirane ring of 1,2-epoxybutane with formation of an alkoxide (Popa et al., 2015). This reactive alkoxide extracts one of the methylene protons in the bromide salt, generating the pyrimidinium-*N*-ylide **6** which reacts in the form of the mesomeric 1,3-dipole **7**. In the next step, 1,3-dipolar cycloaddition between the pyrimidinium-*N*-ylide **7** and the activated acetylenic dipolarophile leads to the formation of the primary cycloadduct **8** which gives the final aromatic pyrrolo[1,2-*c*] pyrimidine **9** by oxidation in the reaction conditions.

The structural characterization of the new compounds was performed by FTIR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. All methods present evidence for the structure of the new compounds. The main features of ^{1}H NMR spectra are the signals of the two hydrogen atoms in pyrimidine, H-1 and H-4, which appear as two doublets with coupling constants ranging from 1.1 to 1.5 Hz. In the case of unsymmetrical dipolarophiles the signal for H-6 appears as a sharp singlet at around 7.80 ppm or 8.0 ppm (when trifluoroacetic acid (TFA) was added). The main features of ^{13}C NMR spectra are given by the presence of aliphatic carbons and carbonyl carbon atoms in the expected ranges. C-1 carbon atom appears the most deshielded at around 140 ppm due to its direct coupling with two nitrogen atoms. All the other signals and the corresponding multiplicities (for the ^{1}H NMR spectra) are in good agreement with the proposed structures.

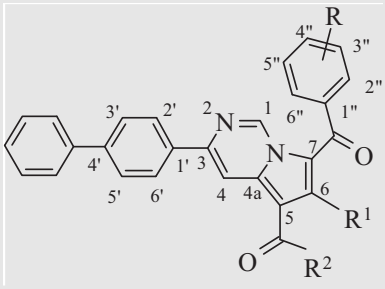
3.2. Absorbance studies

UV–VIS spectra of the compounds have been recorded in order to evaluate the excitation wavelength for the study of the pyrrolo[1,2-*c*]pyrimidine framework fluorescence. Acetoni-



Scheme 1 Synthesis of 3-biphenylpyrrolo[1,2-*c*]pyrimidines.

Table 1 Structures, melting points and synthesis yields for the new pyrrolo[1,2-*c*]pyrimidine **4a–i**.



Entry	R	R^1	R^2	Mp (°C)	Yield (%)
4a	4-Cl	H	Me	234–235	53
4b	3-NO_2	H	Me	286–288	49
4c	4-F	H	OEt	222–224	58
4d	4-Br	H	OEt	234–235	53
4e	4-NO_2	H	OEt	267–269	47
4f	3,4-diMeO	H	OEt	216–218	55
4g	4-NO_2	CO_2Me	OMe	286–288	62
4h	4-C_6H_5	CO_2Et	OEt	216–218	51
4i	3,4-benzo	CO_2Et	OEt	215–217	44

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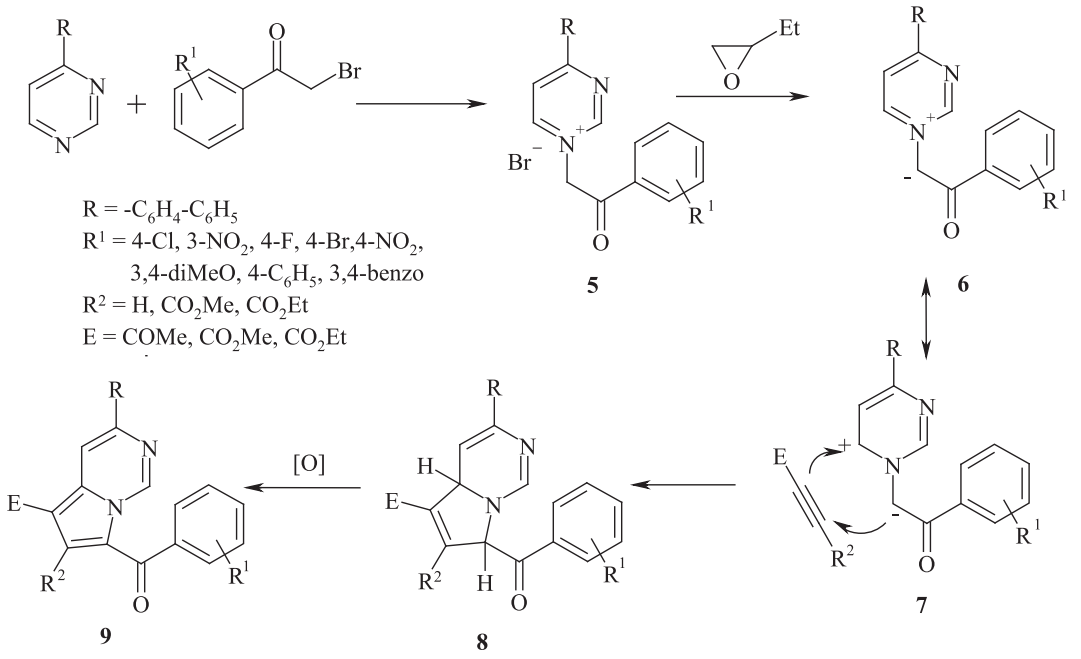

Scheme 2 Reaction mechanism for the 1,3-dipolar cycloaddition of pyridinium N-ylides with activated acetylenes.

trile:chloroform mixture (1:1) has been found as the appropriate solvent. For instance Fig. 1A shows the obtained spectra at increasing concentrations of compound **4d** in acetonitrile:chloroform (1:1) and Fig. 1B shows the linear dependences on concentration of the recorded absorbances at the main maximum wavelengths λ_{max1} = 268 nm and λ_{max2} = 384 nm. The extinction coefficients (ε_1, ε_2) at the two wavelengths (λ_{max1} and λ_{max2}) have been calculated from the slopes of the linear dependences of absorbance on concentration, and they are shown in Fig. 1B.

Fig. 2 shows the absorption spectra for all compounds **4a–i** at the same concentration (5 μmol/L) in acetonitrile:chloroform (1:1). It can be seen that absorption maxima show big differences in intensity varying between 0.1 and 0.8 for the investigated structures. All spectra have two main absorption maxima λ_{max1}, in the range 262–280 nm, and λ_{max2}, in the range 366–398 nm. The extinction coefficients (ε_1, ε_2) at the two maximum wavelengths (λ_{max1} and λ_{max2}) have been calculated for all compounds from the slopes of the linear dependences in a similar way as shown in Fig. 1B for **4d**. The results are summarized in Table 2 where are given also the equations for the linear dependences of the absorbances at λ_{max1} and λ_{max2} on concentration (**[I]**) ($A_{\lambda max1}$ and $A_{\lambda max2}$ *vs* **[I]** respectively).

Fig. 2 shows that the nature of substituents R connected to the pyrrolo[1,2-*c*]pyrimidine framework induces significant differences in their spectra. R nature has an important influence both on λ_{max} and ε. The replacement of fluorine atom (from compound **4c**) with a bromine atom (in compound **4d**) and chlorine atom (in compound **4a**) induces a bathochromic shift (to higher wavelengths) of λ_{max1} and λ_{max2}; this is the effect of electronegativity of the atoms. By comparing the compound **4h**

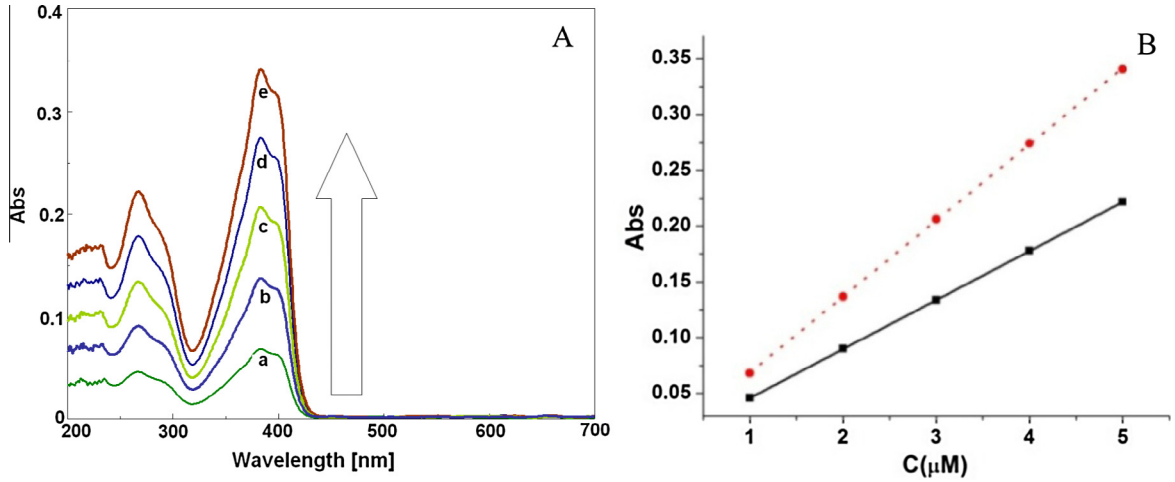

Figure 1 A: Spectra of **4d** in acetonitrile:chloroform (1:1) at increasing concentrations (μmol/L): 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) B: Linear dependences of the absorbance on concentration for **4d** at λ_{max1} = 268 nm (solid line) and λ_{max2} = 384 nm (dotted line).

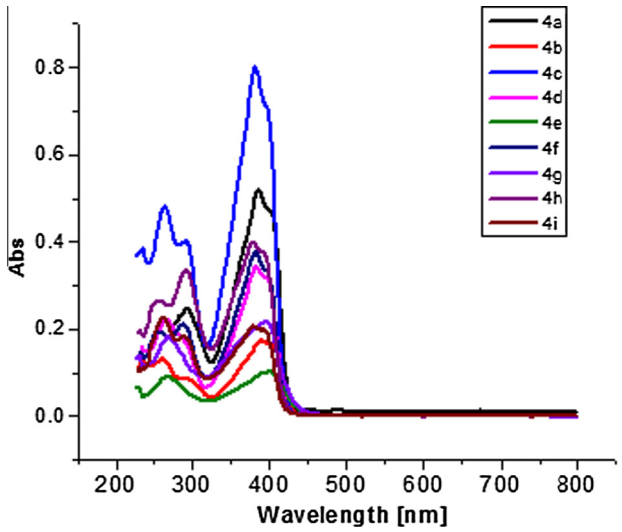

Figure 2 Absorption spectra for compounds **4a–i** in 5 μmol/L solutions acetonitrile:chloroform (1:1).

with **4i** it can be concluded that the hypsochromic shift (to lower wavelengths) for compound **4h** is caused by the disturbance of conjugation due to deviation from co-planarity of the aromatic rings imposed by steric impediments.

3.3. Fluorescence studies

The emission spectra of compounds **4a–i** were recorded in acetonitrile:chloroform (1:1) solutions (Tatu et al., 2015). For each compound the spectra were recorded at the corresponding absorption maxima λ_{max1} and λ_{max2} (Table 2). The emission spectra for λ_{max1} have fluorescence intensities smaller (less than 50%) than for λ_{max2} (Figs. 3Aand B). The spectra obtained at the same concentration with excitation at λ_{max2} are shown in Fig. 4.

All compounds present one single emission band in the blue range domain (430–465 nm) as seen also in Table 3. The spectra in Fig. 3B have been grouped in 3 categories (A, B, C), in agreement with the compounds structure: **4c–f** (A), **4g–i** (B), **4a–b** (C), and the values of their fluorescence intensity are given at the end of discussion. Studies regarding their fluorescence characteristics (Stokes shift, quantum yield and fluorescence quenching) have been performed.

3.4. Stokes shifts

For practical applications, an important feature of the fluorescence is given by the Stokes shift ($\Delta\bar{\nu}$) which is equal with the difference between the wavelength of excitation and emission (Yang et al., 2015).

Stokes shifts were calculated (Table 3) using Eq. (1) for all compounds **4a–i** on the basis of absorption-emission properties. Eq. (1) gives errors of 5–20%. The Stokes shifts were cal-

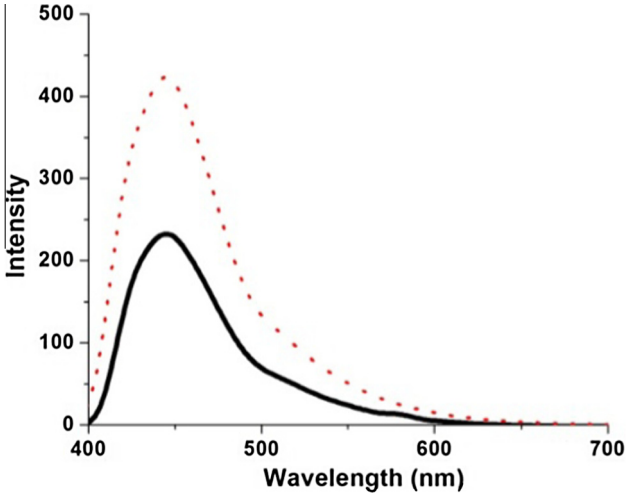

Figure 3A Emission spectra of compounds **4f** for excitation at λ_{max1} = 290 nm (solid line) and λ_{max2} = 380 nm (dot line) in solutions (10^{-6} mol/L) in acetonitrile:chloroform (1:1).

Table 2 Characteristics of the absorption spectra for compounds **4a–i** in acetonitrile:chloroform(1:1).

Compound	λ_{max1} (nm)	ε_1 L/(mol*cm)	Equation $A_{\lambda max1}$ *vs* [I], *(R^2)	λ_{max2} (nm)	ε_2 L/(mol*cm)	Equation $A_{\lambda max2}$ *vs* [I], *(R^2)
4a	293	49,337	49,337*[I] + 0.004 R^2 = 0.9994	386	105,456	105,456*[I] + 0.002 R^2 = 0.9999
4b	263	25,640	25,640*[I] + 0.001 R^2 = 0.9991	389	34,200	34,200*[I] + 0.001 R^2 = 0.9992
4c	262	87,480	87,480*[I] + 0.044 R^2 = 0.9914	381	144,430	144,430*[I] + 0.078 R^2 = 0.9935
4d	266	43,920	43,290*[I] + 0.02 R^2 = 0.9999	384	68,180	68,180*[I] R^2 = 0.9999
4e	270	18,880	18,880*[I] + 0.003 R^2 = 0.9953	399	20,706	20,706*[I] + 0.004 R^2 = 0.9943
4f	290	38,272	38,272*[I] - 0.004 R^2 = 0.9833	383	68,795	68,795*[I] - 0.01 R^2 = 0.979
4g	268	34,200	34,200*[I] + 0.013 R^2 = 0.984	398	44,780	44,780*[I] + 0.003 R^2 = 0.9842
4h	262	65,250	65,250*[I] + 0.005 R^2 = 0.998	380	77,820	77,820*[I] + 0.005 R^2 = 0.9979
4i	292	39,784	39,784*[I] - 0.003 R^2 = 0.9994	380	34,836	34,836*[I] + 0.003 R^2 = 0.9999

* Coefficient of determination.

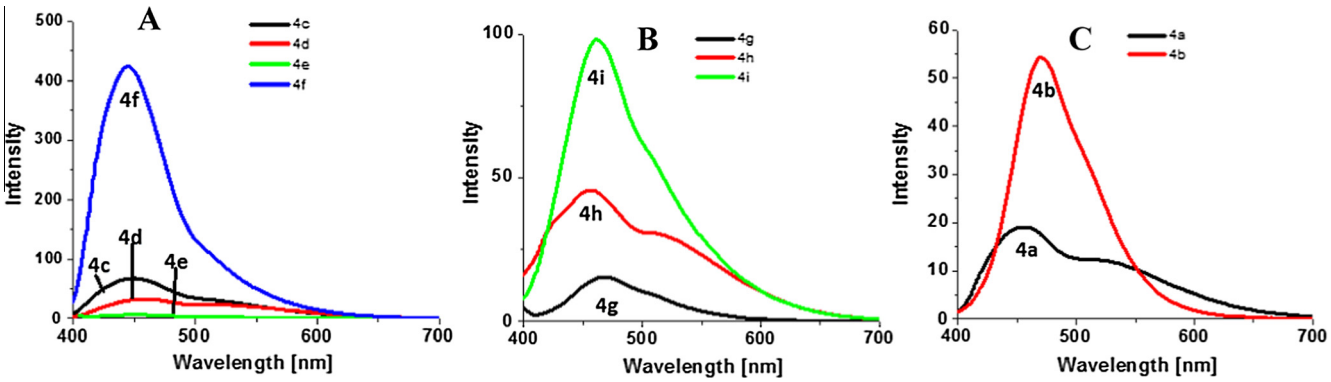

Figure 3B Emission spectra of compounds **4c-f** (A), **4g–i** (B), **4a–b** (C) in solutions (10^{-6} mol/L) in acetonitrile:chloroform (1:1); each spectrum has been recorded for excitation at the specific wavelength λ_{max2} (given in Table 2).

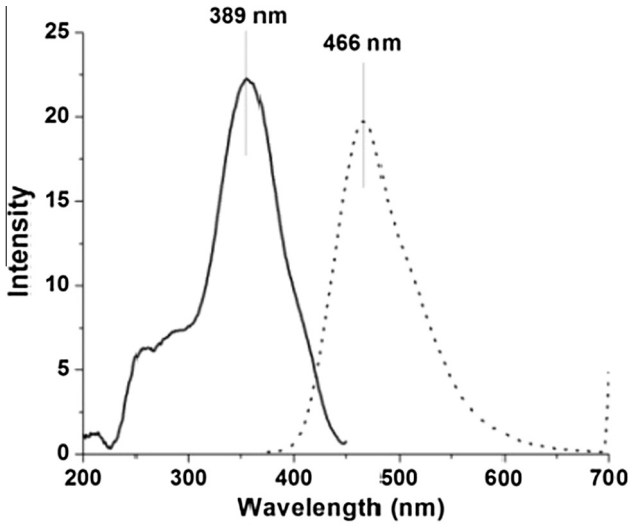

Figure 4 Excitation spectrum (solid line, with maximum at 389 nm) and emission spectrum (dot line, with maximum at 466 nm) for the compound **4b** in solution (10^{-6} mol/L) in acetonitrile:chloroform (1:1).

culated at each maximum wavelength ($\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_2$) at the same concentration (10^{-6} mol/L). All these compounds have fluorescence in the range of 430–470 nm. The data from Table 3 show higher Stokes shifts for excitation at $\lambda_{max,exc1}$ in comparison with $\lambda_{max,exc2}$ for all the investigated compounds.

$$\Delta\tilde{\nu} = \frac{1}{\lambda_{max,exc}} - \frac{1}{\lambda_{max,em}} \quad (1)$$

3.5. Quantum yield

The fluorescence quantum yield (QY) is among the most important characteristics of fluorescence being defined as the efficiency of a fluorophore to convert the absorbed light into fluorescence. QY has been calculated (Table 4) for all compounds **4a–i** using Eq. (2) (Brower, 2011; Fery-Forgues and Lavabre, 1999; Maree et al., 2002) in order to evaluate their fluorescence intensity. QY was measured for diluted acetonitrile:chloroform (1:1) solutions ($3.5 * 10^{-6}$ mol/ L) using quinine sulphate as standard (Tatu et al., 2015). In (2), QY, A, I, and n are quantum yield, maximum value of the absorbance at the emission wavelength $\lambda_{max,em2}$, area of the emission peak and refractive index for the solution of investigated compound, and QY_{ref}, A_{ref}, I_{ref}, n_{ref} are the corresponding values for the standard solution respectively. The following values are constant: $n = 1.3942$, and $I_{ref} = 16{,}463$; $n_{ref} = 1.339$; $QY_{ref} = 0.6$ (for the quinine sulphate standard solution) in the case of diluted solutions of all compounds **4a–i** in acetonitrile:chloroform (1:1).

$$QY = QY_{ref} \times \frac{I}{A} \times \frac{A_{ref}}{I_{ref}} \times \frac{n}{n_{ref}} \quad (2)$$

Table 3 Maximum wavelengths of absorption ($\lambda_{max,exc}$) and emission ($\lambda_{max,em}$) and the corresponding Stokes shifts ($\Delta\tilde{\nu}_1$, $\Delta\tilde{\nu}_2$) for the compounds **4a–i** (10^{-6} mol/L) in acetonitrile:chloroform(1:1).

Group	Compound	$\lambda_{max,exc1}$ (nm)	$\lambda_{max,em1}$ (nm)	$\lambda_{max,exc2}$ (nm)	$\lambda_{max,em2}$ (nm)	$\Delta\tilde{\nu}_1$ (cm^{-1})	$\Delta\tilde{\nu}_2$ (cm^{-1})
C	**4a**	268	453	383	454	15,238	4083
	4b	262	459	354	466	16,381	6789
A	**4c**	262	462	381	463	16,522	4648
	4d	268	462	389	466	15,668	4536
	4e	270	457	400	462	15,155	3354
	4f	290	435	380	446	11,494	3894
B	**4g**	262	451	360	463	15,994	6179
	4h	263	430	380	460	14,767	4576
	4i	264	455	380	464	15,900	4764

Table 4 Absorption and fluorescent parameters for the compounds **4a–i** in acetonitrile:chloroform (1:1) solutions ($3.5 * 10^{-7}$mol/L) using quinine sulphate as standard.

Group	Compound	R	R^1	R^2	A	I	A_{ref}	QY (%)	K_{SV} (M^{-1})
C	**4a**	4-Cl	H	Me	0.05263	2146	0.03	4.64	637
	4b	3-NO_2	H	Me	0.059	4025	0.0248	6.42	223
A	**4c**	4-F	H	OEt	0.04859	6479	0.0376	**19.02**	**5748**
	4d	4-Br	H	OEt	0.0867	3750	0.0387	6.35	206
	4e	4-NO_2	H	OEt	0.06875	166	0.02	0.18	202
	4f	3,4-diMeO	H	OEt	0.079	29,733	0.0387	**55.27**	**2942**
B	**4g**	4-NO_2	CO_2Me	OMe	0.03223	989	0.0298	3.47	249
	4h	4-C_6H_5	CO_2Et	OEt	0.06017	3380	0.0418	8.91	749
	4i	3,4-benzo	CO_2Et	OEt	0.08411	8152	0.0418	15.37	987

3.6. Fluorescence quenching

The fluorescence quenching of the new synthesized pyrrolo[1,2-*c*]pyrimidines in presence of the quencher 1,4-benzoquinone (BQ) has been examined. This is a very important property of a specific chromophore which may lead to interesting applications in the investigation of supramolecular assemblies for example (Wang et al., 2002). The fluorescence quenching curves for compounds **4a–i** in the presence of BQ have been recorded. For instance Fig. 5 presents the fluorescence decrease in intensity (quenching) for the compound **4f** in the presence of increasing concentrations of BQ.

The changes in the fluorescence intensity related to BQ concentration are expressed by Stern-Volmer (S-V) Eq. (3) (Rose, 1964; Lakowicz, 2006) where: F_0 = fluorescence intensity in the absence of quencher; F = fluorescence intensity in the presence of quencher; K_{SV} = Stern-Volmer constant; [BQ] = concentration of the quencher (1,4-benzoquinone).

$$\frac{F_0}{F} = 1 + K_{SV} \cdot [BQ] \quad (3)$$

The ratios of F_0/F were calculated and plotted (Fig. 6) against [BQ], and K_{SV} were determined according to (3) from their slopes (Table 4).

Looking at the values from Table 4, it can be seen that two of the compounds (**4c** and **4f**) have higher values of QY and K_{SV} (their values are highlighted with bold figures in Table 4). These higher values of QY and K_{SV} could be the result of a π electron conjugated system expansion for this compound. This assumption is confirmed by the high values of the fluorescence quantum yield for the two compounds.

3.7. Structure-fluorescence properties relation in the series of pyrrolo[1,2-c]pyrimidines *4a–i*

The fluorescence and the related properties of the pyrrolo[1,2-*c*]pyrimidine derivatives **4a–i** certainly are influenced by the nature of the substituents and this is discussed further. When comparing the compounds **4c, 4d, 4e** and **4f** of the group A (in which R is a substituted phenyl in position 4 with F, Br, NO_2 and $(MeO)_2$, respectively), it can be noticed that their fluorescence varies in the order of **4f** > **4c** > **4d** > **4e**; this order corresponds to the influence of the following substituents: MeO > F > Br > NO_2. Compound **4f** has the highest fluorescence intensity, witch can be attributed to the presence of the two repulsive methoxy groups. Compound **4c** presents a lower degree of fluorescence then **4d** due to the smaller volume

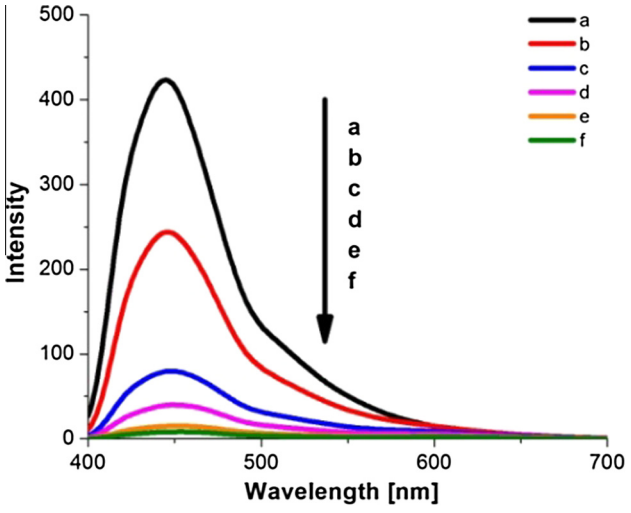

Figure 5 Fluorescence quenching curves of **4f** (10^{-5} mol/L) in acetonitrile:chloroform (1:1) upon addition of increasing concentrations mol/L of BQ: 0 (a), 0.006 (b), 0.012 (c), 0.018 (d), 0.024 (e), and 0.030 (f).

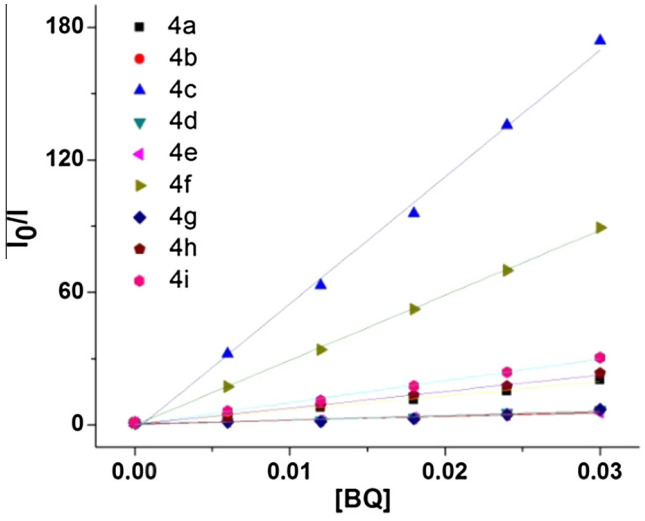

Figure 6 Stern-Volmer plots for benzoquinone (BQ) quenching of the studied compounds in solutions (10^{-5} mol/L) in acetonitrile: chloroform (1:1); the quenching curves have been recorded at $\lambda_{max,em2}$.

of the fluorine atom (in compound **4c)** in comparison with bromine atom (in compound **4d)**. This is an example of the *heavy atom effect* (Guilbault, 1973), which suggests that the probability of intersystem crossing increases as the size of the molecule increases. The presence of bromine atom (compound **4d**), leads to a loss of excitation energy by collision between molecules due to its big volume, which is the consequence of the fluorescence intensity decrease.

In group B, **4i**, **4h** and **4g** which have biphenyl, 2-naphthyl and 4-nitrophenyl as substituent R and $R^1 = R^2$, compound **4g** presents the lowest fluorescence intensity. This might lead to the conclusion that the moieties presenting an extended degree of conjugation such as naphthyl and biphenyl induce a high degree of fluorescence. The difference between **4i** and **4h** could be explained by the free rotation of the two phenyl rings in **4h**, which can place the two phenyls out of the plane, thus decreasing the degree of conjugation and leading to a decrease in fluorescence. The lower fluorescence of **4g** compared to that of the other two structurally analogous compounds **4i** and **4h** can be attributed to an increased tendency to aggregate in solution, due to the presence of nitro group (the polarized structure of the nitro group favours the appearance of compact supramolecular structures).

The compounds **4a** and **4b** of the group C, present low fluorescence intensities due to the presence of electron withdrawing substituents such as NO_2 and Cl. The low fluorescence intensities seen in the experimental fluorescence spectra (Fig. 3) are expressed also by the calculated values of fluorescence quantum yield and K_{SV} (Table 4).

4. Conclusion

New pyrrolo[1,2-*c*]pyrimidines were synthesized by one-pot 1,3-dipolar cycloadditions of their pyrimidinium-*N*-ylides with electron-deficient alkynes. Their absorption and emission spectra have been recorded in acetonitrile:chloroform (1:1) and the main spectral features have been evaluated. The substituent effects on the fluorescence (Stokes shift, quantum yield and fluorescence quenching) of the pyrrolo[1,2-*c*]pyrimidine derivatives have been discussed. The highest quantum yield value was found for ethyl 3-(4-biphenylyl)-7-(3,4-dimethoxybenzoyl)pyrrolo[1,2-*c*]pyrimidine-5-carboxylate (0.55). Correlations between the fluorescence of the pyrrolo[1,2-*c*]pyrimidines and the substituents of the benzoyl moiety attached to the C-3 atom from the pyrrole moiety have been proposed.

Further studies will be directed toward the investigations of the fluorescence and electrical properties of all synthesized compounds in view of their direct relevance in practical applications.

Acknowledgements

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