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Synthesis and fluorescent property of some novel benzothiazoyl pyrazoline derivatives containing aromatic heterocycle

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Abstract

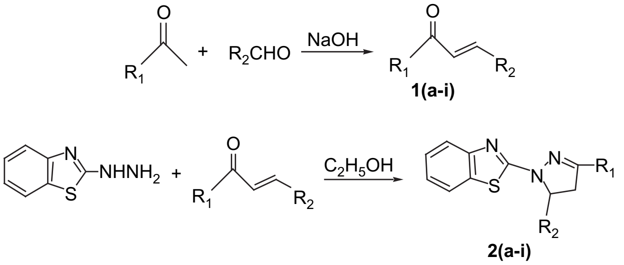
A series of novel benzothiazoyl pyrazoline compounds containing aromatic heterocycle were synthesized, whose structure were confirmed by means of IR, ^{1}H NMR, UV and elementary analysis. The fluorescent spectra showed that these compounds have good blue fluorescence. The fluorescence emission wavelengths are about 450 nm.

Keywords: Pyrazoline; Benzothiazole; Fluorescent compound; Heterocycle

1. Introduction

Organic electroluminescent devices (OELDs) have attracted much interest all over the world. Since Tang and Vanslyke first reported the usage of multi-layer organic thin films for light-emitting devices (LEDs) [1], OLEDs have received considerable attention because of their potential applications in various displays [2–7]. The organic electroluminescence (OEL) devices have shown several advantages over inorganic ones, such as low cost, high luminous efficiency, wide selection of emission colors via molecular design of organic materials, and easy processing. Recently, a lot of works have been focused on blue color emitting materials [8–15].

Pyrazoline derivatives have been investigated in many respects due to their blue light emission with high quantum yield [16–19], ready accessibility, and easily being used as carrier transporting as well as emitting materials [20]. Many 1,3,5-triaryl-2-pyrazolines have been reported as hole transporting or emitting materials in organic EL devices [21–23]. But benzothiazoyl pyrazoline derivatives containing aromatic heterocycle have not been reported. It is well known that the five or six-membered aromatic heterocycle is higher π-electron excessive group. Herein, in this report, we describe the synthesis of some novel benzothiazoyl pyrazoline compounds containing aromatic heterocycle using 2-hydrazinobenzothiazole and chalcones (Scheme 1).



Scheme 1.

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2. Experimental

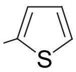
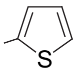
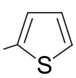
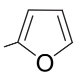
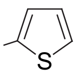
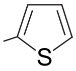
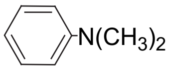
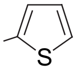
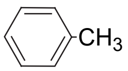
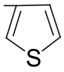
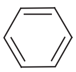
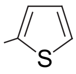
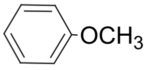
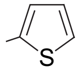
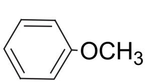
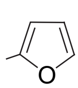
2.1. General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. ^{1}H NMR(400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in $CDCl_3$. IR Spectra were obtained on a Nicolet FT-IR500 spectrophotometer using KBr pellets. Elemental analyses were performed by a Carlo-Erba EA1110 CNNO-S analyzer. X-ray diffraction data were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo Ka; radiation.

2.2. Syntheses

First, we prepared (**1a–i**) according to previous literature, Yield: 92%. 2-Hydrazinobenzothiazole was obtained as described in literature [24] with a yield of 90%. Compounds (**2a–i**) were synthesized by 2-hydrazinobenzothiazole with chalcones as the following procedure: a mixture of 2-hydrazinobenzothiazole (1 mmol) and chalcone (1 mmol) in absolute ethanol was refluxed for 6–7 h. Then, the pyrazoline derivatives were precipitated on cooling or diluting with ethanol. The precipitate was filtered off and recrystallized from ethanol, pure products were obtained. The results are shown in Table 1.

Table 1
The synthesis of benzothiazoyl pyrazoline compounds (**2a–i**)

Entry	R_1	R_2	Product	Time (h)	Yield (%)[a]
1			**2a**	6	65
2			**2b**	6	51
3			**2c**	6	68
4			**2d**	7	71
5			**2e**	7	53
6			**2f**	6	69
7			**2g**	6	69
8			**2h**	7	56
9			**2i**	7	53

[a] Recrystalization yields.

2.2.1. 1-(2-Benzothiazole)-3,5-bis(2-thiophene)-2-pyrazoline (**2a**)

M.p.: 165–166 °C. Anal. Calcd. (%) for $C_{18}H_{13}N_3S_3$: C, 58.83; H, 3.57; N, 11.43. Found (%): C, 58.30; H, 3.61; N, 11.78. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.46–3.51 (m, 1H), 3.89–3.97 (m, 1H), 6.08–6.12 (m, 1H), 6.94 (t, $J = 4$ Hz, 1H), 7.08–7.30 (m, 6H), 7.50 (d, $J = 4$ Hz, 1H), 7.59 (d, $J = 7.2$ Hz, 1H), 7.65 (d, $J = 8$ Hz, 1H). IR (KBr, cm^{-1}): 3067, 1599, 1538, 1444, 698.

2.2.2. 1-(2-Benzothiazole)-3-(2-thiophene)-5-(2-furan)-2-pyrazoline (**2b**)

M.p.: 149–151 °C. Anal. Calcd. (%) for $C_{18}H_{13}N_2S_2O$: C, 61.52; H, 3.73; N, 11.96. Found (%): C, 61.51; H, 3.75; N, 12.08. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.61–3.67 (m, 1H), 3.79–3.86 (m, 1H), 6.32 (d, $J = 1.6$, 1H), 7.11–7.16 (m, 3H), 7.27–7.33 (m, $J = 5.6$ Hz, 4H); 7.47 (d, $J = 4.4$ Hz, 1H); 7.64 (d, $J = 7.6$ Hz, 2H). IR (KBr, cm^{-1}): 3052, 1597, 1538, 1444, 753.

2.2.3. 1-(2-Benzothiazole)-3-(2-thiophene)-5-phenyl-2-pyrazoline (**2c**)

M.p.: 170–172 °C. Anal. Calcd. (%) for $C_{20}H_{15}N_3S_2$: C, 66.45; H, 4.18; N, 11.62. Found (%): C, 66.20; H, 4.49; N, 11.48. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.28–3.34 (m, 1H), 3.93–4.00 (m, 1H), 5.82 (s, 1H), 7.06–7.10 (m, 2H), 7.21 (d, $J = 4$ Hz, 1H), 7.33 (t, $J = 8$ Hz, 5H), 7.43 (d, $J = 4$ Hz, 1H), 7.50 (d, $J = 8$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 1H). IR (KBr, cm^{-1}): 3098, 3067, 1597, 1537, 1444, 712.

2.2.4. 1-(2-Benzothiazole)-3-(2-thiophene)-5-(4-dimethylamine-phenyl)-2-pyrazoline (**2d**)

M.p.: 255–257 °C. Anal. Calcd. (%) for $C_{22}H_{20}N_4S_2$: C, 65.32; H, 4.98; N, 13.85. Found (%): C, 65.24; H, 4.98; N, 13.68. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.91 (s, 6H), 3.28–3.33 (m, 1H), 3.87–3.94 (m, 1H), 5.71–5.75 (m, 1H), 6.67 (d, $J = 8$ Hz, 2H), 7.08 (d, $J = 3.8$ Hz, 2H), 7.27 (t, $J = 9.4$ Hz, 4H), 7.43 (d, $J = 4.8$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H). IR (KBr, cm^{-1}): 3067, 2883, 2801, 1613, 1531, 1444, 812, 750, 721.

2.2.5. 1-(2-Benzothiazole)-3-(2-thiophene)-5-(4-methyl-phenyl)-2-pyrazoline (**2e**)

M.p.: 182–184 °C. Anal. Calcd. (%) for $C_{21}H_{17}N_3S_2$: C, 67.17; H, 4.56; N, 11.19. Found (%): C, 67.14; H, 4.53; N, 11.21. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.31

(s,3H), 3.26–3.32 (m, 1H), 3.91–3.98 (m, 1H), 5.76–5.80 (m, 1H), 7.07–7.15 (m, 4H), 7.21–7.27 (m, 4H), 7.43 (d, $J = 5.2$, 1H), 7.50 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8$ Hz, 1H). IR (KBr, cm^{-1}): 3067, 2919, 1596, 1537, 1444, 813, 750.

2.2.6. 1-(2-Benzothiazole)-3-phenyl-5-(3-thiophene)-2-pyrazoline (*2f*)

M.p.: 170–171 °C. Anal. Calcd. (%) for $C_{20}H_{15}N_3S_2$: C, 66.45; H, 4.18; N, 11.62. Found (%): C, 65.92; H, 4.29; N, 11.52. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.36–3.42 (m, 1H), 3.85–3.92 (m, 1H), 5.94 (d, $J = 8.4$ Hz, 1H), 7.06–7.13 (m, 2H), 7.26–7.31 (m, 3H), 7.47 (t, $J = 2.4$ Hz, 3H), 7.57 (d, $J = 8$ Hz, 1H), 7.64 (d, $J = 8$ Hz, 1H), 7.79 (t, $J = 3.6$ Hz, 2H). IR (KBr, cm^{-1}): 3093, 2924, 1597, 1565, 1538, 1443, 757.

2.2.7. 1-(2-Benzothiazole)-3-phenyl-5-(2-thiophene)-2-pyrazoline (*2g*)

M.p.: 158–159 °C. Anal. Calcd. (%) for $C_{20}H_{15}N_3S_2$: C, 66.45; H, 4.18; N, 11.62. Found (%): C, 64.31; H, 4.64; N, 11.23. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.49–3.54 (m, 1H), 3.90–3.97 (m, 1H), 6.16 (s, 1H), 6.95 (t, $J = 4.2$ Hz, 1H), 7.13 (t, $J = 4.2$ Hz, 1H), 7.19 (d, $J = 4$ Hz, 2H), 7.26–7.32 (m, 1H), 7.46 (d, $J = 4.8$ Hz, 3H), 7.61–7.67 (m, 2H), 7.80 (t, $J = 4$ Hz, 2H). IR (KBr, cm^{-1}): 3108, 3053, 2921, 1597, 1537, 1443, 756.

2.2.8. 1-(2-Benzothiazole)-3-(4-methoxy-phenyl)-5-(2-thiophene)-2-pyrazoline (*2h*)

M.p.: 171–173 °C. Anal. Calcd. (%) for $C_{21}H_{17}N_3OS_2$: C, 64.42; H, 4.38; N, 10.73. Found (%): C, 64.78; H, 4.69; N, 10.67. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.46–3.51 (m,2H), 3.87–3.95 (m, 3H), 6.15 (s, 1H), 6.93–6.98 (m, 3H), 7.12 (t, $J = 7.2$ Hz, 1H), 7.19 (d, $J = 4.8$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.60–7.66 (m, 2H), 7.75 (d, $J = 8.8$ Hz, 2H). IR (KBr, cm^{-1}): 3101, 3062, 2933, 2833, 2836, 1650, 1588, 1540, 716.

2.2.9. 1-(2-Benzothiazole)-3-(4-methoxy-phenyl)-5-(2-furan)-2-pyrazoline (*2i*)

M.p.: 169–172 °C. Anal. Calcd. (%) for $C_{21}H_{17}N_3O_2S$: C, 67.18; H, 4.56; N, 11.19. Found (%): C, 67.24; H, 4.74; N, 11.09. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.57–3.63 (m, 1H), 3.87 (m, 4H), 6.31–6.37 (m, 1H), 6.92–7.97 (m, 11H). IR (KBr, cm^{-1}): 3267, 2965, 2837, 1669, 1599, 1543, 1444, 755.

3. Result and discussion

3.1. Absorption spectra

The UV–Vis spectra of (**2a–i**) are shown in Fig. 1. As shown in Fig. 1, the absorptions of the pyrazoline derivatives were the results of the combination of two chromophores, and they all had similar absorption bands in the range of 300–450 nm. The maximum absorption of **2d** was located at 366 nm and the others appeared at 344–365 nm. The red-shift phenomenon of **2d** was due to the electron affinity, such as dimethylamine on 4-positioned phenyl, which was included in the *p*-conjugated system. As to the methoxy groups, which did not belong to the conjugated system, they could not lead to the shift of n–p∗ transition bands of **2d**.

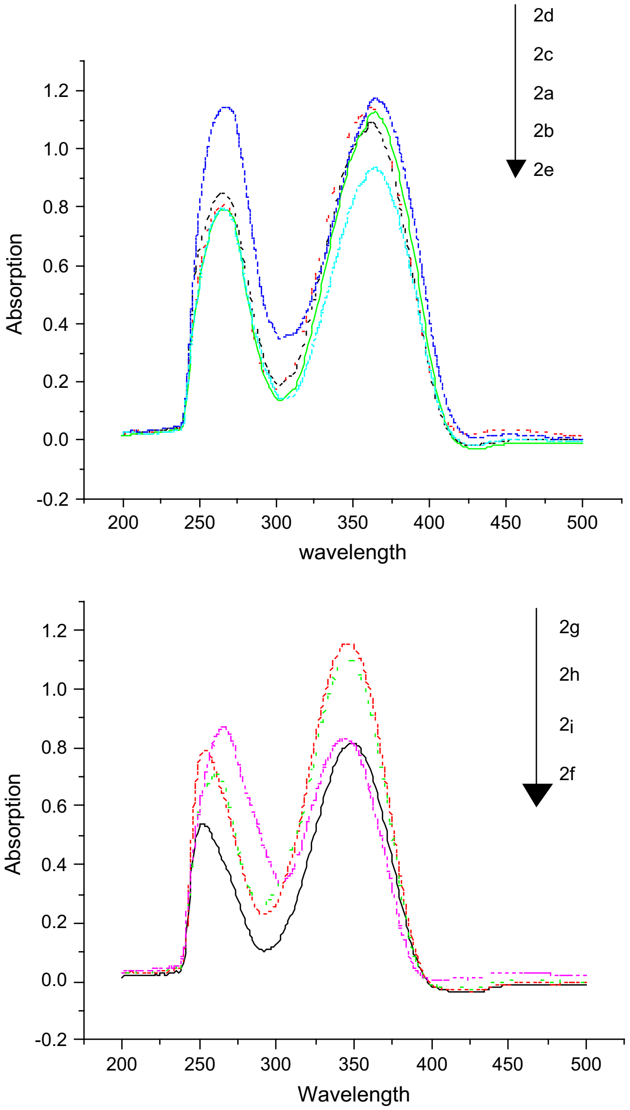


Fig. 1. The normalized UV–Vis spectra of pyrazoline derivatives (**2a–k**) in chloroform solution with the concentration of 1×10^{-5} M.

3.2. Fluorescence

Fig. 2 presented the excitation and emission spectra of (**2a–i**) in chloroform solution (1×10^{-5} M) (Table 2). Their excitation wavelengths neared about 360 nm. It can be found that they all have strong fluorescence.

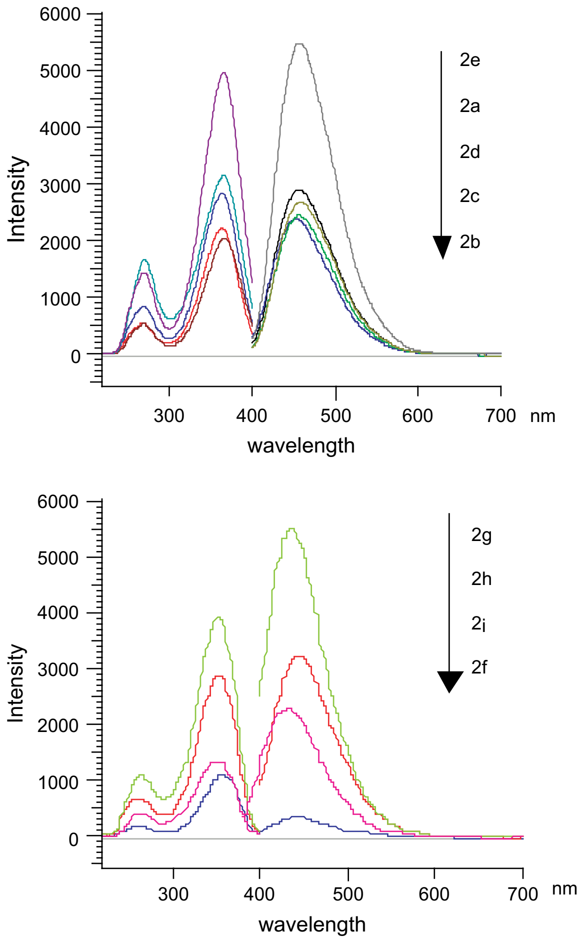


Fig. 2. The excitation spectra and emission spectra of pyrazoline derivatives (**2a–k**) in chloroform solution with the concentration of 1×10^{-5} M.

From the fluorescence of (**2a–e**), it can also be found that these five pyrazoline compounds have the same group of thiophene at position 3, and have different groups at position 5. The emission bands all neared about 460 nm, which showed no obvious change with different groups at position 5, indicating that the group at position 5 had little influence on the emission. On the contrary, we also found that (**2a–e**) red shifted from (**2f–i**). The red-shift resulted from the electron affinity of thiophene as indicated in UV–Vis absorption spectra. So the group at position 3 had very strong influence on the emission of pyrazoline compounds.

Table 2
Absorption and fluorescence spectra of compounds (**2a–i**)

Compound	E_{max}^{ex} (nm)	E_{max}^{em} (nm)	E_{max}^{abs} (nm)
2a	364	456	363
2b	363	454	363
2c	366	457	364
2d	366	459	366
2e	365	457	365
2f	357	442	349
2g	352	444	348
2h	353	435	348
2i	351	432	344

4. Conclusion

A series of novel benzothiazoyl pyrazoline compounds containing aromatic heterocycle have been synthesized. Their absorption and photoluminescence in chloroform solution are studied. They have stronger fluorescence, and the emission bands were about 450 nm. It was found that the group at position 3 of pyrazoline has strong influence on the emission of pyrazoline compounds.

Acknowledgement

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