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Synthesis and spectral characterization of new homologous 1,3,5-triaryl-2-pyrazolines: Influence of alkyloxy chain length on fluorescence

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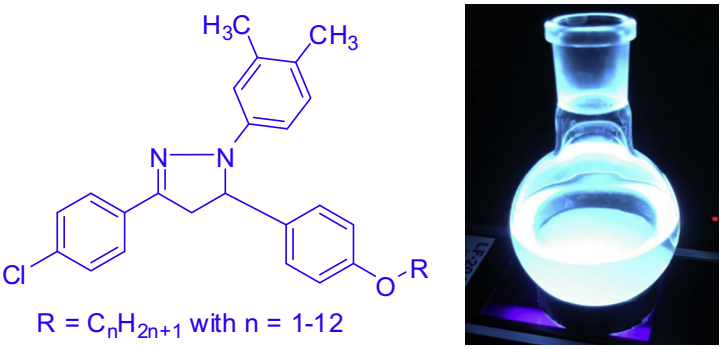
HIGHLIGHTS

- Organic fluorescent compounds are important and attracted considerable attention.
- New 1-(3,4-dimethylphenyl)-3-(4-chlorophenyl)-5-(4-alkoxyphenyl)-2-pyrazolines.
- Synthesis and fluorescence property evaluation.
- Effect of chloro and alkyloxy substituents on fluorescence.

GRAPHICAL ABSTRACT



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ABSTRACT

Twelve new homologous 1,3,5-triaryl-2-pyrazolines (**1c**–**12c**) have been synthesized and characterized on the basis of their spectral (IR, ^{1}H and ^{13}C NMR and MS) data and microanalysis. The influence of alkyloxy chain length on absorption and fluorescence properties of **1c**–**12c** was studied by UV–Vis and emission spectroscopy. For all the compounds, fluorescence was observed in the blue region of the visible spectrum. Furthermore, a strong influence of alkyloxy chain length was found on the emission intensity of 1,3,5-triaryl-2-pyrazolines, without causing any major blue- or red-shift in the emission wavelength (λ_{max}^{em}). The absorption and emission maxima (λ_{max}^{abs} and λ_{max}^{em}) for all the compounds were observed in the range of 408–416 nm and 471–476 nm, respectively. The effect of chloro-substituent present on the conjugated backbone of 1,3,5-triaryl-2-pyrazoline moiety is also discussed.

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Introduction

Organic fluorescent compounds have attracted considerable attention in cosmetics, surface coatings, inks and textile industries [1–3]. They have also been used in sensors [4], solar cells, optoelectronics and electronic displays [5,6]. They are generally considered superior to inorganic fluorescent materials, mainly due to the ease of fabrication and tunability of emission properties by a simple chemical modification, as evidenced by organic electroluminescence devices (OELDs) having low cost, broad range of emission colors, high brightness, high luminous efficiency, good life stability and simple processing [7–9]. However, the major drawback of organic fluorescent materials is aggregation of molecules i.e. the formation of an excimer-like species and H-type

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molecular aggregates, leading to the decrease in fluorescence intensity [10–12]. To circumvent this problem, slight structural changes in fluorescent molecules have been found useful and effective [13–15]. The examples include the introduction of an ethyl group on the conjugated backbone of diphenylbutadiene [13] and incorporation of quinacridone dye molecule into dendrimers [14] leading to enhanced emission efficiency due to decreased molecular aggregation.

Pyrazolines in general [16] and 1,3,5-triaryl-2-pyrazolines in particular [17–20] are typical intramolecular charge transfer compounds of immense importance, not only due to their use in organic electroluminescent devices (OELDs) and optoelectronics [21–25] but also due to their diverse biological applications [26–36]. 1,3,5-Triaryl-2-pyrazolines with blue fluorescence and high quantum yield are described as hole transporting media in photoconductive and emitting materials, organic photovoltaic cells, and in OELDs [37–41]. In addition, they are also used as optical brightening agents for textiles, papers and plastics [42], fluorescent probes in many chemosensors [43,44] and fluorescent switches [45].

In continuation of our previous studies on synthesis and properties of pyrazolines [46–49], herein, we report the synthesis and spectral characterization of new homologous 1,3,5-triaryl-2-pyrazolines having chloro-substituent at 3-aryl and one to twelve carbon alkyloxy side chain at 5-aryl of 2-pyrazoline ring highlighting the effect of alkyloxy side chain on fluorescence property. The study is helpful in understanding the interplay of weak interactions with the change in alkyloxy chain length and their significance in absorption and emission properties. The compounds of the present series with fluorescence properties in the blue region of the visible spectrum are potential future candidates for their use as blue light emitting materials.

Experimental

Materials and methods

All reagents and solvents were used as obtained from the supplier or recrystallized/redistilled as required. Thin layer chromatography (TLC) was performed using aluminium sheets coated with silica gel 60 F_{254} (Merck). Elemental analyses were carried out with a LECO-183 CHNS model. ^{1}H and ^{13}C NMR spectra of compounds were recorded on a Bruker 300 MHz spectrometer using deuterated solvents and TMS as internal standard. IR spectra of compounds were recorded on a Bio-Rad FTS 3000 MX spectrophotometer (400–4000 cm^{-1}). The melting points of compounds were determined using capillary tubes and an electrothermal melting point apparatus, model MP-D Mitamura Riken Kogyo, Japan.

*General procedure for the synthesis of compounds **(1c–12c)***

The respective 4-alkoxychalcone (0.01 mol) (**1a–12a**) [50] in 25 mL acetic acid containing a few drops of hydrochloric acid was heated at 60–65 °C for half an hour with constant stirring in a round bottom flask before the addition of (3,4-dimethylphenyl)hydrazine hydrochloride (3.45 g, 0.02 mol) (**1b**). After the addition of **1b** to the reaction flask, the reaction mixture was heated to reflux for 5–6 h. The reaction mixture was then cooled to room temperature and poured onto the crushed ice. The precipitates thus appeared, were filtered, washed thoroughly with distilled water and dried. To get highly pure compounds (**1c–12c)** for spectral characterization and fluorescence properties**,** the obtained crude products were subjected to silica gel column chromatography using petroleum ether/ethyl acetate (4:1) as the mobile phase.

For better understanding of ^{1}H NMR chemical shift values, the different protons of compounds **1c–12c** are differentiated according to the labeling shown in Fig. 1.

*1-(3,4-Dimethylphenyl)-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-2-pyrazoline **(1c)***

Yield 87%; pale yellow solid; m.p. 144–147 °C; R_f = 0.85 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1688, 1295, 1492, 1255, 1047, 1080, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H, N-Ar-4-CH_3), 2.22 (s, 3H, N-Ar-3-CH_3), 3.07 (dd, 1H, J = 7.5, 16.6 Hz, H_a), 3.80 (dd, 1H, J = 12.3, 16.8 Hz, H_b), 3.84 (s, 3H, —O—C***H***$_3$), 5.22 (dd, 1H, J = 7.5, 12.0 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N-ArH_g), 6.87 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, J = 8.1 Hz, N-ArH_h), 7.04 (s, 1H, N-ArH_i), 7.24 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.36 (d, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.66 (d, 2H, J = 8.7 Hz, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 20.1, 43.4, 55.2, 64.4, 110.8, 114.4 (2C), 115.2, 126.7(2C), 127.0 (2C), 127.4, 128.7 (2C), 129.9, 131.5, 133.9, 134.5, 137.0, 142.9, 144.9, 158.3, EIMS: m/z 390 (M$^{+\cdot}$, base peak). Anal. calcd. for $C_{24}H_{23}ClN_2O$: C, 73.74; H, 5.93; N, 7.17; Found: C, 73.71; H, 5.90; N, 7.22%.

*1-(3,4-Dimethylphenyl)-3-(4-chlorophenyl)-5-(4-ethoxyphenyl)-2-pyrazoline **(2c)***

Yield 84%; pale yellow solid; m.p. 128–131 °C; R_f = 0.86 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1686, 1297, 1495, 1253, 1042, 1087, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (t, 3H, J = 7.0 Hz, —O—CH_2—C***H***$_3$), 2.17 (s, 3H, N-Ar-4-CH_3), 2.22 (s, 3H, N-Ar-3-CH_3), 3.07 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.75 (dd, 1H, J = 12.3, 16.8 Hz, H_b), 4.02 (q, 2H, J = 7.0 Hz, —O—C***H***$_2$—), 5.21 (dd, 1H, J = 7.5, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N-ArH_g), 6.87 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, J = 8.1 Hz, N-ArH_h), 7.04 (s, 1H, N-ArH_i), 7.24 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.36 (d, 2H, Ar$H_{f=f'}$), 7.66 (d, 2H, J = 8.7 Hz, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 18.8, 20.1, 43.2, 63.4, 64.4, 110.8, 115.0 (2C), 115.2, 126.7(2C), 127.0 (2C), 127.4, 128.7 (2C), 129.9, 131.5, 133.9, 134.5, 137.0, 142.9, 144.9, 158.3, EIMS: m/z 404 (M$^{+\cdot}$, base peak). Anal. calcd. for $C_{25}H_{25}ClN_2O$: C, 74.15; H, 6.22; N, 6.92; Found: C, 74.11; H, 6.18; N, 6.99%.

*1-(3,4-Dimethylphenyl)-3-(4-chlorophenyl)-5-(4-propyloxyphenyl)-2-pyrazoline **(3c)***

Yield 81%; pale yellow solid; m.p. 98–101 °C; R_f = 0.89 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1684, 1292, 1493, 1250, 1044, 1081, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, 3H, J = 7.25 Hz, —O—CH_2—CH_2—C***H***$_3$), 1.81 (sextet, 2H, J = 7.2 Hz, —O—CH_2—C***H***$_2$—CH_3), 2.17 (s, 3H, N-Ar-4-C***H***$_3$), 2.22 (s, 3H, N-Ar-3-C***H***$_3$), 3.07 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.76 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.91 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.21 (dd, 1H, J = 7.5, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N-ArH_g), 6.87 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, J = 8.1 Hz, N-ArH_h), 7.04 (s, 1H, N-ArH_i), 7.24 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.36 (d, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.66 (d, 2H, J = 8.4 Hz, Ar$H_{e=e'}$); ^{13}C NMR (75 MHz, $CDCl_3$)

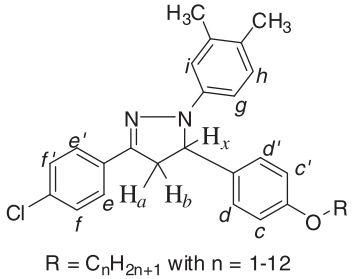

Fig. 1. Labelling scheme for protons of compounds (**1c–12c**).

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