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Fluorescence behavior of new 3-pyridinecarbonitrile containing compounds and their application in security paper

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Abstract

The fluorescence properties of the newly synthesized 3-pyridinecarbonitrile containing compounds were determined. The application of such compounds for preparation special type of paper was investigated by studying the fluorescence behavior and mechanical properties of treated paper sheets prepared from non-wood fibrous material (bagasse pulp).

Keywords: Ylidenemalononitriles; 3-Pyridinecarbonitrile containing compounds; Fluorescent dyes; High quality paper; Specialist paper

1. Introduction

Paper today still remains the most important information bearer despite the computer age and electronic mail. Striking presentations invariably use color as the most effective means of attracting our attention. Many basic dyes were found to be suitable (e.g. Bismark Brown, Malachite Green, Rhodamine, Auramine, etc.). They are economical and have very bright colors, but have poor light-fastness. Some acid dyes were also used, but they have poor fastness and give colored backwaters, thus wasting a lot of dye, unless fixatives are used. Direct dyes, compared with basic dyes, have a high affinity for wood-free, bleached pulps. The light-fastness is offending superior to that obtained with basic dyes. But they are less suitable for the dyeing of unbleached furnishes; ground wood [1–3].

For protecting the environment from pollution encountered due to using the synthetic dyes, the world now directed to return using of natural dye for coloring the paper as well as textile as ancient time [4–7]. Unfortunately, the natural dyes have some serious disadvantages; only few dyes have good fastness to light and washing, inadequate degree of fixation and higher cost and limited range [8–9].

The requirements of dyes for paper are greatly dependent on the end use of the paper. Packaging grades of paper and board may be colored economically with basic dyes, where the fastness properties may not be important, whereas high quality writing paper or tissue require dyes with higher fastness properties, e.g., mixture from cationic and anionic dyes [10]. Dyeing of speciality papers, e.g. security papers, needs type of dyes, make forgeries more difficult.

In the present work, it is intended to investigate the synthesis as well as the fluorescence properties

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of different 3-pyridinecarbonitrile containing compounds via a facile and simple synthetic approach. The application of the newly synthesized heterocycles on paper sheets prepared from non-wood fibrous material (bagasse pulp) and hence investigation of the fluorescence and mechanical properties of the treated paper will also considered. This is in accord with the well known ability of many 3-pyridinecarbonitriles to be used as dyes for synthetic fabrics [11–13] and paper [14].

2. Experimental

2.1. a- Synthesis and characterization of 3-pyridinecarbonitrile containing compounds

All melting points are uncorrected. IR spectra were recorded (KBr) on a JASCO FT/IR 300E spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL EX 270 (270 Mz) spectrometer. UV as well as fluorescence spectra were recorded on a Shimadzu UV-240 spectrophotometer, and a Jasco FP-777 spectrofluorometer, respectively. Elemental analyses were carried out at the Analytical Chemistry Department, National Research Centre.

The reaction sequence as well as the purity of the isolated products were monitored by silica gel TLC aluminium cards with fluorescence indicator F254 nm using different elutions. The starting compounds **1a,b** were prepared according to the reported procedures [15,16].

The efficiency of fluorescence, the quantum yield (Φ_s) were measured relative to fluorescence quantum yield of quinine sulphate (Φ_r), which used as a reference standard [17].

2.2. Synthesis of 2-ethoxy-3-pyridinecarbonitrile containing compounds *3*, *6* and *8* (Schemes 1 and 2)

A mixture of equimolar amounts of the appropriate ylidenemalononitrile **1** and the corresponding ketone **2**, **5** or **7** (5 mmol) in ethanolic KOH solution (25 ml; 4%) was stirred at room temperature (20–25 °C) for the appropriate time. The solid separated was collected, washed with water and crystallized from a suitable solvent affording the corresponding **3**, **6** or **8**.

2.2.1. 6-(4-Chlorophenyl)-2-ethoxy-4-[4-(1-piperidinyl)phenyl]-3-pyridinecarbonitrile (*3a*)

Reaction time 24 h; yellow crystals from *n*-butanol; mp 186–188 °C; yield 53%. IR: ν 2215 cm^{-1} (C≡N); 1606, 1583 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, CH_3, $J=6.9$ Hz); 1.69 (br., 6H, $3CH_2$); 3.28 [br., 4H, $N(CH_2)_2$]; 4.60 (q, 2H, OCH_2, $J=6.9$ Hz); 6.97 (d, 2H, arom. H, $J=8.9$ Hz); 7.37 (s, 1H, pyridine H-5); 7.42 (d, 2H, arom. H, $J=8.6$ Hz); 7.57 (d, 2H, arom. H, $J=8.9$ Hz); 7.98 (d, 2H, arom. H, $J=8.6$ Hz). Anal. for $C_{25}H_{24}ClN_3O$ (417.91): Calcd. C 71.85, H 5.79, N 10.05; Found: C 71.79, H 5.71, N 10.12%.

2.2.2. 6-(4-Chlorophenyl)-2-ethoxy-4-[4-(4-morpholinyl)phenyl]-3-pyridinecarbonitrile (*3b*)

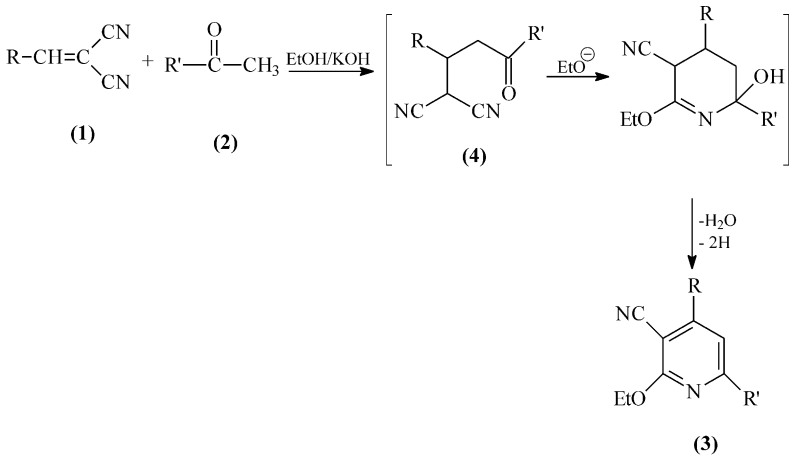
Reaction time 24 h; yellow crystals from *n*-butanol; mp 217–218 °C; yield 53%. IR: ν 2221 cm^{-1} (C≡N); 1608, 1585 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, CH_3, $J=6.9$ Hz); 3.25 [t., 4H, $N(CH_2)_2$, $J=4.6$ Hz]; 3.86 [t, 4H, $O(CH_2)_2$, $J=4.6$ Hz]; 4.61 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 6.98 (d, 2H, arom. H, $J=8.6$ Hz); 7.37 (s, 1H, pyridine H-5); 7.43 (d, 2H, arom. H, $J=8.3$ Hz); 7.59 (d, 2H, arom. H, $J=8.6$ Hz); 7.98 (d, 2H, arom. H, $J=8.2$ Hz). Anal. for $C_{24}H_{22}ClN_3O_2$ (419.89): Calcd. C 68.65, H 5.28, N 10.01; Found: C 68.34, H 4.96, N 9.60%.

2.2.3. 2-Ethoxy-6-(4-fluorophenyl)-4-[4-(1-piperidinyl)phenyl]-3-pyridinecarbonitrile (*3c*)

Reaction time 24 h; pale yellow crystals from *n*-butanol; mp 150–151 °C; yield 55%. IR: ν 2213 cm^{-1} (C≡N); 1602, 1508 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.49 (t, 3H, CH_3, $J=6.9$ Hz); 1.69 (br., 6H, $3CH_2$); 3.28 [br., 4H, $N(CH_2)_2$]; 4.60 (q, 2H, OCH_2, $J=6.9$ Hz); 6.96–8.07 (m, 9H, arom. H). Anal. for $C_{25}H_{24}FN_3O$ (401.46): Calcd. C 74.79, H 6.03, N 10.47; Found: C 74.52, H 5.67, N 10.29%.

2.2.4. 2-Ethoxy-6-(4-fluorophenyl)-4-[4-(4-morpholinyl)phenyl]-3-pyridinecarbonitrile (*3d*)

Reaction time 24 h; pale yellow crystals from *n*-butanol; mp 214–215 °C; yield 55%. IR: ν 2215 cm^{-1} (C≡N); 1610, 1581 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.54 [t, 3H, CH_3, J = 7.3 Hz); 3.29 [t, 4H, $N(CH_2)_2$; $J=4.6$ Hz]; 3.91 [t, 4H, $O(CH_2)_2$, $J=4.6$ Hz]; 4.66 (q, 2H, $O\underline{CH_2}CH_3$, $J=7.3$ Hz);



1a; R = 4-(1-piperidinyl)C_6H_4
1b; R = 4-(4-morpholinyl)C_6H_4

2a; R = 4-ClC_6H_4
2b; R = 4-FC_6H_4
2c; R = 4-$H_3CC_6H_4$
2d; R = 4-$H_3COC_6H_4$
2e; R = 2-thienyl
2f; R = 2-furanyl

3a; R = 4-(1-piperidinyl)C_6H_4, R' = 4-ClC_6H_4
3b; R = 4-(4-morpholinyl)C_6H_4, R' = 4-ClC_6H_4
3c; R = 4-(1-piperidinyl)C_6H_4, R' = 4-FC_6H_4
3d; R = 4-(4-morpholinyl)C_6H_4, R' = 4-FC_6H_4
3e; R = 4-(1-piperidinyl)C_6H_4, R' = 4-$H_3CC_6H_4$
3f; R = 4-(4-morpholinyl)C_6H_4, R' = 4-$H_3CC_6H_4$
3g; R = 4-(1-piperidinyl)C_6H_4, R' = 4-$H_3COC_6H_4$
3h; R = 4-(4-morpholinyl)C_6H_4, R' = 4-$H_3COC_6H_4$
3i; R = 4-(1-piperidinyl)C_6H_4, R' = 2-thienyl
3j; R = 4-(4-morpholinyl)C_6H_4, R' = 2-thienyl
3k; R = 4-(1-piperidinyl)C_6H_4, R' = 2-furanyl
3l; R = 4-(4-morpholinyl)C_6H_4, R' = 2-furanyl

Scheme 1.

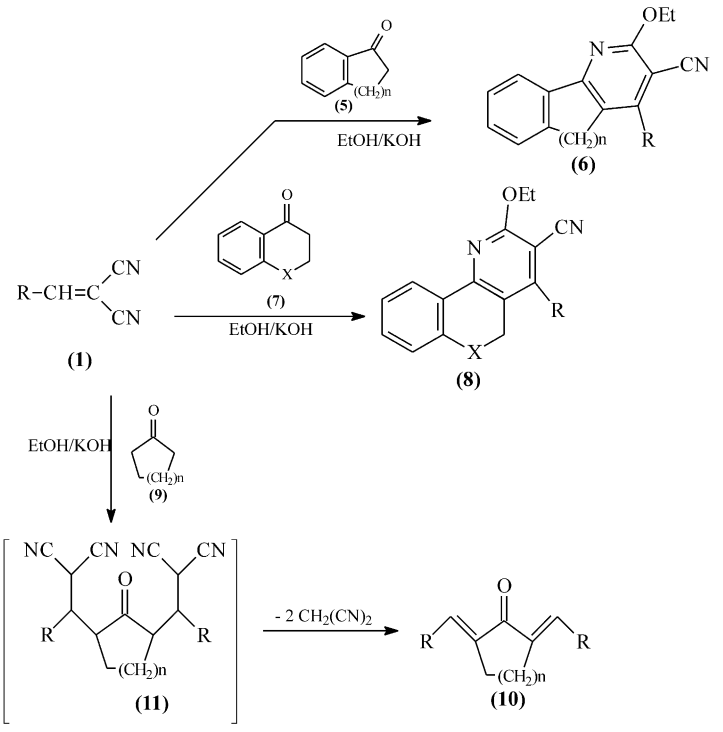
7.01–8.12 (m, 9H, arom. H). Anal. for $C_{24}H_{22}FN_3O_2$ (403.44): Calcd. C 71.45, H 5.50, N 10.42; Found: C 71.26, H 5.69, N 10.22%.

2.2.5. 2-Ethoxy-6-(4-methylphenyl)-4-[4-(1-piperidinyl)phenyl]-3-pyridinecarbonitrile (**3e**)

Reaction time 24 h; almost colourless crystals from *n*-butanol; mp 144–145 °C; yield 50%. IR: ν 2215 cm^{-1} (C≡N); 1585, 1511 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.49 (t, 3H, $\underline{CH_3}CH_2$, $J = 6.9$ Hz); 1.7 (br., 6H, $3CH_2$); 2.4 (s, 3H, CH_3); 3.28 [br., 4H, $N(CH_2)_2$]; 4.62 (q, 2H, $O\underline{CH_2}CH_3$, $J = 6.9$ Hz); 6.99 (d, 2H, arom. H, $J = 8.9$ Hz); 7.27 (d, 2H, arom. H, $J = 8.3$ Hz); 7.39 (s, 1H, pyridine H-5); 7.59 (d, 2H, arom. H, $J = 8.9$ Hz); 7.96 (d, 2H, arom. H, $J = 8.3$ Hz). Anal. for $C_{26}H_{27}N_3O$ (397.5): Calcd. C 78.56, H 6.85, N 10.57; Found: C 78.13, H 6.62, N 10.84%.

2.2.6. 2-Ethoxy-6-(4-methylphenyl)-4-[4-(4-morpholinyl)phenyl]-3-pyridinecarbonitrile (**3f**)

Reaction time 24 h; yellow crystals from *n*-butanol; mp 186–188 °C; yield 55%. IR: ν 2221 cm^{-1} (C≡N); 1608, 1585 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.49 (t, 3H, $\underline{CH_3}CH_2$, J = 6.9 Hz); 2.40 (s, 3H, CH_3); 3.24 [br., 4H, $N(CH_2)_2$]; 3.86 [br., 4H, $O(CH_2)_2$]; 4.62 (q, 2H, $O\underline{CH_2}CH_3$, $J = 6.9$ Hz); 6.98 (d, 2H, arom. H, $J = 8.6$ Hz); 7.26 (d, 2H, arom. H, $J = 7.9$ Hz); 7.38 (s, 1H, pyridine H-5); 7.60 (d, 2H, arom. H, $J = 8.6$ Hz); 7.95 (d, 2H, arom. H, $J = 7.9$ Hz). Anal. for $C_{25}H_{25}N_3O_2$ (399.47): Calcd. C 75.16, H 6.31, N 10.52; Found: C 74.93, H 6.17, N 10.15%.



5a; **9a**; n = 1

5b; **9b**; n = 2

8a; R = 4-(1-piperidinyl)C_6H_4, X = O

8b; R = 4-(4-morpholinyl)C_6H_4, X = O

8c; R = 4-(4- morpholinyl)C_6H_4, X = S

6a; R = 4-(1-piperidinyl)C_6H_4, n = 1

6b; R = 4-(4-morpholinyl)C_6H_4, n = 1

6c; R = 4-(1-piperidinyl)C_6H_4, n = 2

10a; R = 4-(1-piperidinyl)C_6H_4, n = 1

10b; R = 4-(4-morpholinyl)C_6H_4, n = 1

10c; R = 4-(1-piperidinyl)C_6H_4, n = 2

7a; X = O

7b; X = S

Scheme 2.

*2.2.7. 2-Ethoxy-6-(4-methoxyphenyl)-4-[4-(1-piperidinyl)phenyl]-3-pyridinecarbonitrile (**3g**)*

Reaction time 24 h; colourless crystals from *n*-butanol; mp 144–145 °C; yield 53%. IR: ν 2217 cm^{-1} (C≡N); 1610, 1585 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.46 (t, 3H, $\underline{CH_3}CH_2$, $J = 6.9$ Hz); 1.67 (br., 6H, $3CH_2$); 3.26 [br., 4H, $N(CH_2)_2$]; 3.86 (s, 3H, OCH_3); 4.60 (q, 2H, $O\underline{CH_2}CH_3$, $J = 6.9$ Hz); 6.94–8.04 (m, 9H, arom. H). Anal. for $C_{26}H_{27}N_3O_2$ (413.50): Calcd. C 75.52, H 6.58, N 10.16; Found: C 75.68, H 6.62, N 9.99%.

*2.2.8. 2-Ethoxy-6-(4-methoxyphenyl)-4-[4-(4-morpholinyl)phenyl]-3-pyridinecarbonitrile (**3h**)*

Reaction time 24 h; pale yellow crystals from *n*-butanol; mp 181–183 °C; yield 53%. IR: ν 2223 cm^{-1} (C≡N); 1608, 1583 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, $\underline{CH_3}CH_2$, $J = 6.9$ Hz); 3.23

[t, 4H, $N(CH_2)_2$, $J=5.0$ Hz]; 3.85 [t., 7H, $O(CH_2)_2+OCH_3$]; 4.61 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 6.97 (d, 4H, arom. H, $J=8.6$ Hz); 7.33 (s, 1H, pyridine H-5); 7.59 (d, 2H, arom. H, $J=8.6$ Hz); 8.02 (d, 2H, arom. H, $J=8.9$ Hz). Anal. for $C_{25}H_{25}N_3O_3$ (415.47): Calcd. C 72.27, H 6.07, N 10.11; Found: C 71.93, H 5.94, N 9.96%.

*2.2.9. 2-Ethoxy-4-[4-(1-piperidinyl)phenyl)-6-(2-thienyl)-3-pyridinecarbonitrile (**3i**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 144–145 °C; yield 57%. IR: ν 2217 cm^{-1} (C≡N); 1608, 1577 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, CH_3, $J=6.9$ Hz); 1.69 (br., 6H, $3CH_2$); 3.28 [br., 4H, $N(CH_2)_2$]; 4.58 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 6.96–7.67 (m, 8H, arom. H). Anal. for $C_{23}H_{23}N_3OS$ (389.49): Calcd. C 70.92, H 5.95, N 10.79; Found: C 70.71, H 5.82, N 10.80%.

*2.2.10. 2-Ethoxy-4-[4-(4-morpholinyl)phenyl)-6-(2-thienyl)-3-pyridinecarbonitrile (**3j**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 202–204 °C; yield 56%. IR: ν 2221 cm^{-1} (C≡N); 1602, 1581 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 [t, 3H, CH_3, $J=6.9$ Hz]; 3.24 [t, 4H, $N(CH_2)_2$, $J=5.0$ Hz]; 3.86 [t, 4H, $O(CH_2)_2$, $J=5.0$ Hz]; 4.58 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 6.96–7.67 (m, 8H, arom. H). Anal. for $C_{22}H_{21}N_3O_2S$ (391.47): Calcd. C 67.49, H 5.41, N 10.73; Found: C 67.16, H 5.21, N 10.60%.

*2.2.11. 2-Ethoxy-6-(2-furanyl)-4-[4-(1-piperidinyl) phenyl]-3-pyridinecarbonitrile (**3k**)*

Reaction time 48 h; yellow crystals from methanol; mp 132–134 °C; yield 38%. IR: ν 2219 cm^{-1} (C≡N); 1598, 1515 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.46 (t, 3H, CH_3, $J=6.9$ Hz); 1.68 (br., 6H, $3CH_2$); 3.27 [br., 4H, $N(CH_2)_2$]; 4.55 (q, 2H, OCH_2, $J=6.9$ Hz); 6.53–7.60 (m, 8H, arom. H). Anal. for $C_{23}H_{23}N_3O_2$ (373.43): Calcd. C 73.97, H 6.21, N 11.25; Found: C 74.02, H 6.29, N 11.34%.

*2.2.12. 2-Ethoxy-6-(2-furanyl)-4-[4-(4-morpholinyl) phenyl]-3-pyridinecarbonitrile (**3l**)*

Reaction time 24 h; yellow crystals from ethanol; mp 147–148 °C; yield 48%. IR: ν 2221 cm^{-1} (C≡N); 1579, 1519 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.46 (t, 3H, CH_3, $J=7.3$ Hz); 3.23 [t, 4H, $N(CH_2)_2$, $J=4.6$ Hz]; 3.85 [t, 4H, $O(CH_2)_2$, $J=4.6$ Hz]; 4.55 (q, 2H, $O\underline{CH_2}CH_3$, $J=7.3$ Hz); 6.54–7.62 (m, 8H, arom. H). Anal. for $C_{22}H_{21}N_3O_3$ (375.41): Calcd. C 70.38, H 5.64, N 11.19; Found: C 70.33, H 5.60, N 11.24%.

*2.2.13. 2-Ethoxy-4-[4-(1-piperidinyl)phenyl]-5H-indeno[1,2-b]pyridine-3-carbonitrile (**6a**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 200–202 °C; yield 51%. IR: ν 2211 cm^{-1} (C≡N); 1606, 1560 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.50 (t, 3H, CH_3, $J=7.3$ Hz); 1.71 (m, 6H, $3CH_2$), 3.28 [br., 4H, $N(CH_2)_2$]; 3.77 (s, 2H, CH_2); 4.65 (q, 2H, $O\underline{CH_2}$, $J=7.3$ Hz); 6.98–8.02 (m, 8H, arom. H). Anal. for $C_{26}H_{25}N_3O$ (395.48): Calcd. C 78.96, H 6.37, N 10.63; Found: C 78.81, H 6.42, N 10.76%.

*2.2.14. 2-Ethoxy-4-[4-(4-morpholinyl)phenyl]-5H-indeno[1,2-b]pyridine-3-carbonitrile (**6b**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 179–181 °C; yield 55%. IR: ν 2215 cm^{-1} (C≡N); 1573, 1519 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.55 (t, 3H, CH_3, $J=6.9$ Hz); 3.30 [t, 4H, $N(CH_2)_2$, $J=5.0$ Hz]; 3. 80 (s, 2H, CH_2); 3.90 [t, 4H, $O(CH_2)_2$, $J=5.0$ Hz]; 4.70 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 6.94–8.08 (m, 8H, arom. H). Anal. for $C_{25}H_{23}N_3O_2$ (397.45): Calcd. C 75.54, H 5.83, N 10.57; Found: C 75.39, H 5.70, N 10.54%.

*2.2.15. 5,6-Dihydro-2-ethoxy-4-[4-(1-piperidinyl) phenyl]benzo[h]quinoline-3-carbonitrile (**6c**)*

Reaction time 24 h; pale yellow crystals from *n*-butanol; mp 217–218 °C; yield 54%. IR: ν 2219 cm^{-1} (C≡N); 1606, 1552 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.49 (t, 3H, CH_3, $J=6.9$ Hz); 1.71 (br., 6H, piperidinyl $3CH_2$); 2.75 (br., 4H, $2CH_2$); 3.25 [br.., 4H, $N(CH_2)_2$]; 4.62 (q, 2H, $O\underline{CH_2}CH_3$, $J=$ 6.9 Hz); 6.97–8.28 (m, 8H, arom. H). Anal. for $C_{27}H_{27}N_3O$ (409.51): Calcd. C 79.18, H 6.65, N 10.26; Found: C 79.10, H 6.52, N 10.31%.

*2.2.16. 2-Ethoxy-4-[4-(1-piperidinyl)phenyl]-5H-[1]benzopyrano[4,3-b]pyridine-3-carbonitrile (**8a**)*

Reaction time 24 h; almost colourless crystals from *n*-butanol; mp 214–215 °C; yield 44%. IR: ν 2227 cm^{-1} (C≡N); 1606, 1590 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, CH_3, $J=6.9$ Hz); 1.55–1.85

(m, 6H, $3CH_2$); 3.27 [br., 4H, $N(CH_2)_2$]; 4.62 (q., 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 5.06 (s, 2H, OCH_2); 6.90–8.17 (m, 8H, arom. H). Anal. for $C_{26}H_{25}N_3O_2$ (411.48): Calcd. C 75.89, H 6.12, N 10.21; Found: C 75.82, H 6.02, N 10.34%.

*2.2.17. 2-Ethoxy-4-[4-(4-morpholinyl)phenyl]-5H-[1]benzopyrano[4,3-b]pyridine-3-carbonitrile (**8b**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 224–225 °C; yield 44%. IR: ν 2227 cm^{-1} (C≡N); 1608, 1590 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.48 (t, 3H, CH_3, $J=6.9$ Hz); 3.24 [t, 4H, $N(CH_2)_2$, $J=4.6$ Hz]; 3.86 [t, 4H, $O(CH_2)_2$, $J=4.6$ Hz]; 4.62 (q., 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 5.04 (s, 2H, OCH_2); 6.90–8.17 (m, 8H, arom. H). Anal. for $C_{25}H_{23}N_3O_3$ (413.45): Calcd. C 72.62, H 5.61, N 10.16; Found: C 72.43, H 5.36, N 9.94%.

*2.2.18. 2-Ethoxy-4-[4-(4-morpholinyl)phenyl]-5H-[1]benzothiopyrano[4,3-b]pyridine-3-carbonitrile (**8c**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 199–201 °C; yield 56%. IR: ν 2227 cm^{-1} (C≡N); 1608, 1590 (C=N, C=C). ^{1}H-NMR ($CDCl_3$): δ 1.53 (t, 3H, CH_3, $J=6.9$ Hz); 3.29 [t, 4H, $N(CH_2)_2$, $J=5$ Hz]; 3.81 (s, 2H, SCH_2); 3.91 [t., 4H, $O(CH_2)_2$, $J=5$ Hz]; 4.65 (q, 2H, $O\underline{CH_2}CH_3$, $J=6.9$ Hz); 7.02–8.39 (m, 8H, arom. H). Anal. for $C_{25}H_{23}N_3O_2S$ (429.51): Calcd. C 69.90, H 5.40, N 9.78; Found: C 69.69, H 5.26, N 9.84%.

2.3. Synthesis of diarylmethylenecycloalkanones 10 (Scheme 2)

A mixture of equimolar amounts of the appropriate ylidenemalononitrile **1** and the corresponding cycloalkanone **9** (5 mmol), was stirred at room temperature (20–25 °C) in ethanolic KOH solution (25 ml; 4%) for the appropriate time. The solid separated was collected and crystallized from a suitable solvent affording the corresponding **10a–c**.

*2.3.1. 2,5-Bis[4-(1-piperidinyl)phenylmethylene]cyclopentanone (**10a**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 260–262 °C; yield 56%. IR: ν 1675 cm^{-1} (C=O); 1589, 1515 (C=C); 981 (trans out-of-plane deformation C=C). ^{1}H-NMR ($CDCl_3$): δ 1.65 (br., 12H, piperidinyl $6CH_2$); 3.04 (s, 4H, $2CH_2$); 3.28 [br., 8H, $2N(CH_2)_2$]; 6.90 (d, 4H, arom. H, $J=8.9$ Hz); 7.50 (d, 6H, 4 arom. H + 2 olefinic CH). Anal. for $C_{29}H_{34}N_2O$ (426.58): Calcd. C 81.65, H 8.03, N 6.57; Found: C 81.72, H 8.11, N 6.49%.

*2.3.2. 2,5-Bis[4-(4-morpholinyl)phenylmethylene]cyclopentanone (**10b**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 275–277 °C; yield 56%. IR: ν 1677 cm^{-1} (C=O); 1594, 1515 (C=C); 983 (trans out-of-plane deformation C=C). ^{1}H-NMR ($CDCl_3$): δ 3.04 (s, 4H, $2CH_2$); 3.24 [br., 8H, $2N(CH_2)_2$]; 3.84 [br., 8H, $20(CH_2)_2$]; 6.90 (d, 4H, arom. H, $J=8.3$ Hz); 7.52 (d, 6H, 4 arom. H + 2 olefinic CH). Anal. for $C_{27}H_{30}N_2O_3$ (430.53): Calcd. C 75.32, H 7.02, N 6.51; Found: C 75.20, H 6.96, N 6.66%.

*2.3.3. 2,6-Bis[4-(1-piperidinyl)phenylmethylene]cyclohexanone (**10c**)*

Reaction time 24 h; yellow crystals from *n*-butanol; mp 230–232 °C; yield 55%. IR: ν 1654 cm^{-1} (C=O); 1585, 1511 (C=C); 968 (trans out-of-plane deformation C=C). ^{1}H-NMR ($CDCl_3$): δ 1.50–1.85 (m, 14H, $7CH_2$); 2.90 (br., 4H, $2CH_2$); 3.25 [br., 8H, $2N(CH_2)_2$]; 6.88 (d, 4H, arom. H, $J=8.6$ Hz); 7.40 (d, 4H, arom. H, $J=8.6$ Hz); 7.72 (s, 2H, olefinic CH). Anal. for $C_{30}H_{36}N_2O$ (440.61): Calcd. C 81.77, H 8.24, N 6.36; Found: C 81.70, H 8.10, N 6.58%.

2.4. Paper making and its treatment with 3-pyridinecarbonitrile containing compounds

Handsheets were prepared from bleaching kraft-bagasse pulp [α-cellulose 77.2% [18], pentosans 20.4% [19] and lignin 0.7% [20], according to the Swedish Standard Method (SCA). Unbleached kraft-bagasse pulp was kindly provided by Edfo Mill, Egypt. The treatment by fluorescence materials was carried out by dipping the prepared bagasse hand-sheets for few seconds in 0.1% (wt./vol. of $CHCl_3$) of 3-pyridinecarbonitrile containing compounds (dip dyeing process). The handsheets were then air-dried and conditioned for 24 h in a room controlled at 23 °C and 50% relative

humidity. The hand-sheets were tested for their mechanical properties [21], as well as fluorescence behavior.

3. Results and discussion

From all the above data it is obvious that, reaction of arylidenemalononitriles **1** with aryl methyl ketones **2** in ethanolic potassium hydroxide solution at room temperature afforded exclusively the corresponding 4,6-diaryl-2-ethoxy-3-pyridine carbonitriles **3**. The structure of the products was established through spectroscopic (IR, ^{1}H-NMR) and elemental analyses data. The IR spectra of 3 reveal the presence of a nitrile stretching vibration band at 2213–2223 cm^{-1} region and lack any band assignable for a carbonyl function. The ^{1}H-NMR spectra of **3** exhibit the presence of the ethoxide moiety ($\delta = 1.46$–1.54 "triplet of CH_3", $\delta = 4.55$–4.66 "quartet for OCH_2") as well as the pyridine H-5 at $\delta = 7.27$–7.40 confirming the cyclized form structure.

The reaction was assumed to take place through addition of **2** to the β-carbon of ylidene **1** affording the Michael adduct intermediate 4. The latter due to attack of the ethoxide anion at one of the nitrile groups underwent cyclization followed by dehydration and subsequent dehydrogenation giving finally the isolable product **3** (Scheme 1).

Similarly, reaction of arylidenemalononitriles **1a,b** with 1-indanone **5a** or α-tetralone **5b** in ethanolic KOH solution gave the 4-aryl-2-ethoxy-5*H*-indeno[1,2-*b*]pyridine-3-carbonitriles **6a,b** and 4-aryl-5,6-dihydro-2-ethoxybenzo[*h*]quinoline-3-carbonitrile 6c, respectively. Meanwhile, 4-aryl-2-ethoxy-5*H*-[1]benzopyrano[4,3-*b*]-pyridine-3-carbonitriles **8a,b** and its thio-analogue **8c** were obtained through the reaction of arylidenemalononitriles **1a,b** with either 4-chromanone 7a or 4-thiochromanone **7b** under the same reaction conditions (Scheme 2).

On the other hand, reaction of arylidenemalononitriles **1a,b** with either cyclopentanone **9a** or cyclohexanone **9b** in ethanolic KOH solution at room temperature afforded the corresponding diarylidene derivatives **10a–c**. The structure of the products was inferred through the appearance of just one singlet signal in ^{1}H-NMR spectra at $\delta = 7.50$–7.72 assignable for the chemically and magnetically equivalent olefinic protons. The IR spectra of **10a–c** exhibit the presence of trans out-of-plane deformation band at 968–983 cm^{-1} region confirming the trans form configuration. The reaction was assumed to proceed through addition of the cycloalkanone active methylenes to two molecules of arylidene 1 giving the adduct intermediate 11. The latter via elimination of two malononitrile molecules afforded the diarylidenes 10 (Scheme 2).

3.1. Fluorescence behavior of the prepared 3-pyridinecarbonitrile containing compounds

From the results obtained (Table 1) it has been found that, either 3-pyridinecarbonitriles 3 or their fused systems **6**, **8** show considerable fluorescence properties. Some of the prepared compounds exhibit remarkable fluorescence characters or in other words, high relative quantum yield with respect to quinine sulfate which used as a reference standard such as **3d**, **3f**, **3g**, **3h** and **6b**. Generally, it could be concluded that attachment of an electron-donating group to the phenyl function oriented at the 6-position of 3-pyridinecarbonitriles **3e–h** enhances the fluorescence properties and in turn gives high relative quantum yield. Also, it could be concluded that, the substituted phenyl function attached to the 6-position of **3a–h** shows better fluorescence properties than the five-membered heterocycles **3i–l**.

3.2. Properties of bagasse treated paper sheets with 3-pyridinecarbonitrile containing compounds

Tables 2 and 3 show the mechanical and fluorescence properties of paper sheets treated with some pre-mentioned prepared new fluorescence compounds.

For the case of mechanical properties, it is clear that (Table 2) there is an increment in tensile and tear indices and an improvement in burst index of paper sheets treated with fluorescence compounds, particularly for the case of 6-(4-chlorophenyl)-(**3a**) and 6-(4-methylphenyl)-(**3e**) 3-pyridinecarbonitriles. The deterioration properties of some treated paper sheets is also noticed when 6-(4-methoxy

Table 1
The absorption and emission maxima together with relative quantum yield of fluorescence materials in chloroform

Compd. no.	Absorption λ_{max} (nm)	ϕ_s	ϕ_s/ϕ_r*	Emission** λ_{max} (nm)
3a	240, 270, 298, 325, 370	0.380	0.6536	368
3b	239, 277, 330	0.238	0.4079	442
3c	240, 265, 290, 325, 365	0.395	0.7239	456
3d	238, 275, 327	0.506	0.86995	448
3e	239, 285, 330	0.442	0.7592	378
3f	275, 335	0.612	1.0708	448
3g	293, 340	0.648	1.1344	442
3h	244, 285, 340	0.508	0.8899	418
3i	239, 298, 348	0.249	0.4313	460
3j	298, 348	0.360	0.6246	442
3k	290, 345	0.219	0.3826	483.5
3l	297, 345	0.436	0.7637	464
6a	290, 338	0.192	0.3363	472
6b	240, 274, 340	0.477	0.8346	460
6c	240, 275, 343	0.264	0.4615	450
8b	240, 277, 357	0.244	0.4222	446
8c	240, 257, 330	0.035	0.0598	484.5
10a	270, 458	0.013	0.022	364
10c	267, 425	0.011	0.0194	367

ϕ_r: quantum yield of the tested compound, phi;$_s$: quantum yield of the reference standard (quinine sulfate).
*The relative quantum yield of the fluorescence samples with respect to quinine sulfate.
**Excitation wavelength correponding to the lowest wave-length absorption maxima were used.

Table 2
Mechanical properties of the treated paper sheets

Compd. no.	FM* g/m^2	Tensile index (Nm/g)		Tear index (mNm^2/g)		Burst index kPa m^2/g	
		Value	R**	Value	R	Value	R
Untreated	–	35.605	1.0	5.02	1.0	2.147	1.0
3a	0.380	34.668	0.974	4.076	0.812	2.321	1.081
3b	0.391	37.037	1.040	4.589	0.914	3.034	1.413
3c	0.231	36.884	1.036	4.449	0.886	2.846	1.325
3d	0.311	36.624	1.029	4.199	0.836	2.506	1.167
3e	0.366	34.009	0.955	3.991	0.7948	2.296	1.069
3f	0.300	33.209	0.933	3.977	0.792	2.278	1.061
3g	0.4632	25.191	0.708	2.782	0.554	1.809	0.843
3h	0.456	37.958	1.066	4.858	0.968	3.255	1.516
3i	0.206	30.601	0.859	3.494	0.696	1.982	0.923
3j	0.291	32.422	0.911	3.879	0.772	2.052	0.956
3k	0.369	28.754	0.808	3.2314	0.643	1.990	0.927
3l	0.457	39.320	1.104	4.9023	0.976	3.365	1.567
6a	0.3506	33.828	0.950	3.5874	0.714	1.971	0.918
6b	0.445	43.522	1.222	6.0933	1.214	3.438	1.601
6c	0.440	25.350	0.712	3.06933	0.611	1.872	0.872

*The weight of fluorescence materials binded paper sheets of basis weight 70 g /m^2.
**$R = \frac{\text{Reading value}}{\text{Initial value}}$.

Table 3
Fluorescence behavior of treated paper sheets

Compd. no.	Excitation maxima λ_{max} (nm)	Emission λ_{max} (nm)	Fluorescence intensity
Untreated	–	–	–
3a	331, 347, 376	501.5	8.61×10^3
3b	330, 346, 377.5	486	6.40×10^3
3c	329, 345.5, 376.5	481	5.48×10^3
3d	329, 345.5, 376.5	485	2.98×10^3
3e	330, 347.5, 377.5	484.5	1.13×10^3
3f	332.5, 346, 375.5	483	4.57×10^3
3g	331, 346.5, 378	484	4.17×10^3
3h	311, 327, 354.5	483	3.45×10^3
3i	328.5, 343.5, 377.5	484.5	4.760×10^3
3j	331, 348, 376.5, 505.5	505.5	6.56×10^3
3k	329, 344.5, 379	485.5	1.55×10^3
3l	329.5, 344, 377	486	4.25×10^3
6a	331.5, 347.5, 372.5	484	8.22×10^2
6b	331, 379.5, 443.5	541.5	9.1×10^3
6c	331, 346.5, 376.5	481	4.27×10^3

phenyl)-(**3g**), 6-(2-thienyl)-(**3i**) and 6-(2-furanyl)-(**3k**) 3-pyridinecarbonitrile derivatives were used. Similar results were obtained when the fused heterocycles **6b** and **6c** were considered. The reverse results, i.e. improvement in mechanical properties, instead of tear index, were obtained when 6-(4-fluorophenyl)-3-pyridinecarbonitrile (**3c**) was used for treatment of paper sheets.

As can be seen that, substituting the piperidinyl group of **3a**, **3c**, **3e**, **3g**, **3i**, **3k** and **6a** by morpholinyl function (**3b**, **3d**, **3f**, **3h**, **3j**, **3l** & **6b**) improves the mechanical properties, and decreases the deterioration effect of such compounds on strength properties of paper sheets, especially tear index.

The deterioration in most strength properties of dip dyeing paper sheets with the prepared pyridinecarbonitrile containing compounds, especially those containing electron donating group (OCH_3) as a chromophore, this is probably related to the adsorption of the dyes, on the surface of paper and their binding with the fibers via hydrogen and van der waals bonds, as well as hydrophobic interactions, due to the presence of alkoxy chain. These forces weaken the fiber–fiber bonding. While, the presence of a morpholinyl group instead of a piperidinyl group enhances the ability of bonding the fibers via two oxygen atoms of methoxyl and morpholinyl groups in the same compound. However, for the case of compound **6b** the binding ability with cellulosic fibers is probably due to van der waals forces and hydrophobic interactions.

For the case of fluorescence behavior of the finished paper sheets, Table 3 shows that, not only the relative quantum yield of the prepared 3-pyridinecarbonitrile containing compounds affects on the fluorescent intensity of paper sheets but also their amounts adsorbed on paper-hand-sheets.

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