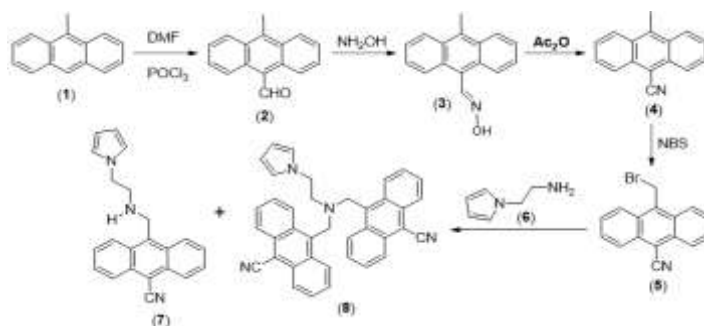


SYNTHESIS OF PYRROLE DERIVATIVES WITH PENDANT ANTHRACENE GROUPS

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Electro-polymerization of pyrrole and substituted pyrroles containing redox centres has received considerable attention because of the useful properties of the resulting polymers. Anthracene is a photoactive molecule, but its reduction potential is quite negative. To make it more positive, a cyanide group was introduced on to the anthracene moiety. With a view to finding a pyrrole derivative/s with electroactive group/s, it was decided to prepare pyrrole derivatives 1-[2-(9-cyanoanthracen-10-yl-methylamino)ethyl] pyrrole (**7**) and 1-[2,2'-di(9-cyanoanthracen-10-yl-methyl)]aminoethyl pyrrole (**8**), containing 9-cyanoanthracene group/s. Synthetic routes to compounds (**7**) and (**8**) are summarised below.



Vilsmeier formylation of 9-methylanthracene (**1**) with POCl_3/DMF yielded 10-methylanthracene-9-carboxaldehyde (**2**), as yellow crystals in 75% yield. The proton resonances of the methyl and aldehyde protons appeared as singlets at 3.16 and 11.31 ppm, respectively. Compound (**2**) was converted into its oxime (**3**) by treating it with hydroxylamine. The singlets at 7.82 and 9.19 ppm were assigned to $=\text{NOH}$ and $\text{CH}=\text{O}$ protons, respectively. With the addition of D_2O , the peak at 7.82 ppm exchanged with deuterium, confirming the presence of $=\text{NOH}$ group. Dehydration of (**3**) with acetic anhydride (Ac_2O) afforded 9-cyano-10-methyl-anthracene (**4**) as yellow needles in 91% yield. The ^1H NMR spectrum showed a singlet at 3.11 for the methyl group and the absorption peak in the IR spectrum at 2208 cm^{-1} was assigned to $\text{n}(\text{C}\equiv\text{N})$. 9-Bromomethyl-10-cyanoanthracene (**5**) was obtained by the reaction between (**4**) and N-bromosuccinimide (NBS) in dry carbon tetrachloride. The reaction between (**5**) and 1-(2-aminoethyl)pyrrole (**6**) in dry benzene gave a mixture containing the secondary amine (**7**) and tertiary amine (**8**). These two pyrrole derivatives were separated by column chromatography on silica using dichloromethane as the solvent. The compound (**8**) eluted first and was isolated as a yellow solid. The second fraction containing compound (**7**) was collected and the secondary amine (**7**) was isolated as yellow needles in moderate yield. In conclusion, two N-substituted pyrrole derivatives (**7**) and (**8**) containing pendant anthracene groups were successfully prepared.

Keywords: Amines, Anthracene, Pyrrole

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INTRODUCTION

Electro-polymerization of pyrrole and substituted pyrroles containing redox centres has received considerable attention because of the useful applications of the resulting polymers [1-5]. Anthracene is a photoactive molecule, but its reduction potential is quite negative. To make it more positive, a cyanide group was introduced on to the anthracene moiety. With a view to finding a pyrrole derivative/s with electroactive group/s it was decided to prepare pyrrole derivatives 1-[2-(9-cyanoanthracen-10-yl-methylamino)ethyl]pyrrole (**7**) and 1-[2,2'-di(9-cyanoanthracen-10-yl-methyl)]aminoethyl pyrrole (**8**), containing 9-cyanoanthracene group/s. In this communication we report the synthetic routes to compounds (**7**) and (**8**).

METHODOLOGY

Elemental analysis was carried out on a Perkin-Elmer PE-240 automatic analyser. IR spectra were recorded on Perkin-Elmer model 598 and 983G IR spectrometers, using KBr discs. Mass spectral data were obtained using a VG updated MS902 spectrometer operating at 70 eV. NMR spectra were recorded at 250 MHz using a Bruker WH250 instrument. Chemical shifts are in ppm with respect to TMS and coupling constants are in Hz. 9-Methyl anthracene was purchased from Sigma Aldrich.

10-Methylantracene-9-carboxaldehyde (**2**)

Phosphorous oxychloride (8.0 g, 0.052 mol) was added dropwise to a mixture of *ortho*-dichlorobenzene (12 mL) and dimethylformamide (7.3 g, 0.1 mol). 9-Methylantracene (9.7 g 0.05 mol) was then added, and the temperature was raised to 100 °C. After 2.5 h, the solution was cooled, neutralized with aqueous sodium acetate, and diluted with water to a volume of 500 mL. After standing overnight in a refrigerator, the solution was extracted with chloroform (3x500 mL). The chloroform extract was dried over anhydrous sodium sulphate and concentrated to give (**2**) as yellow crystals (8.4 g, 75%). It was recrystallized from dichloromethane as yellow needles. m.p. 172-173 °C. ¹H NMR (δ, CDCl₃): 3.16 (3H, s, CH₃), 7.47 (4H, m, ArH), 8.37 (2H, d, J(HH) 8.5 Hz, ArH); 8.98 (2H, d, J(HH) 8.5 Hz, ArH), 11.31 (1H, s, CHO). Mass m/e (%): 220 (M⁺, 100), 219 (45), 205 (26) and 191 (39). IR ν_{max}: 1655, 1551, 1256, and 1059 cm⁻¹.

10-Methylantracene-9-carboaldehyde oxime (**3**)

A solution of hydroxylamine hydrochloride (2.85 g, 0.04 mol) neutralized with sodium acetate (3.4 g, 0.04 mol) in water (35 mL) was added to a solution of (**2**) (8.25 g, 0.04 mol) in boiling methanol (350 mL). After 30 min, the solution was diluted with water (50 mL) until solution became cloudy and it was cooled. The resulting yellow needles were filtered and dried in vacuum (7.8 g, 88%), m.p. 218-219 °C. ¹H NMR (δ, CDCl₃): 3.15 (3H, s, CH₃), 7.55 (4H, m, ArH), 7.82 (1H, s, -OH, D₂O exchange), 8.38 (4H, m, ArH) and 9.19 (1H, s CH=N). Mass m/e (%): 235 (M⁺, 93), 218 (100), 217 (98) and 189 (42). IR ν_{max}: 3306, 1441 and 1297 cm⁻¹.

9-Cyano-10-methylantracene (**4**)

The oxime (**3**) (7.7 g, 0.03 mol) was refluxed in acetic anhydride (50 mL) for 30 min and allowed to cool. The resulting yellow crystals (**4**) were filtered, washed with petroleum ether (40-60 °C) and recrystallized from methanol/dichloromethane as yellow needles (6.5 g, 91%), m.p. 211-212 °C. ¹H NMR (δ, CDCl₃): 3.11 (3H, s, CH₃), 7.47 (4H, m, ArH), 8.35 (4H, m, ArH). Mass m/e (%): 217 (M⁺, 100), 216 (32) and 189 (10). IR ν_{max}: 2208 cm⁻¹.



9-Bromomethyl-10-cyanoanthracene (5)

9-Cyano-10-methylanthracene (1.88 g, 8.6 mmol) and N-bromosuccinimide (1.58 g, 8.8 mmol) were refluxed in carbon tetrachloride (200 mL) for 3 h and cooled. The resulting precipitate was filtered and extracted with chloroform (3 x 25 mL). The chloroform extracts and filtrate were combined, evaporated to dryness and recrystallized from dichloromethane to yield (5), (1.55 g, 60%), m.p. 230-232 °C. Found: C, 64.4; H, 2.9; N, 4.3. Calc. for C₁₆H₁₀NBr. C, 64.9; H, 3.4; N, 4.7%. ¹H NMR (δ, CDCl₃): 5.48 (3H, s, CH₂Br), 7.52 (4H, m, ArH), 8.37 (2H, m, ArH) and 8.48 (2H, m, ArH). Mass m/e (%): 297 (M+2, 5.3), 295 (M⁺, 5.4), 217 (20) and 216 (100). IR ν_{max}: 2215 and 1695 cm⁻¹.

1-[2-(9-Cyanoanthracen-10-yl-methylamino)ethyl]pyrrole (7)

1-(2-aminoethyl) pyrrole (6) [5] (0.85 g, 7.7 mmol), 9-bromomethyl-10-cyanoanthracene (1.5 g, 5.1 mmol) and excess potassium carbonate (1.2 g) were refluxed in benzene (70 mL) for 30 h. After cooling, the solution was filtered and evaporated to dryness (1.6 g) and this contained a mixture of compounds (7) and (8). Upon column chromatography on silica using dichloromethane as the eluent a pure sample of (7) was isolated and was recrystallized from methanol-dichloromethane as yellow prisms (1.0 g, 61%), m. p. 107-108 °C. Found: C, 81.2; H, 5.7; N, 13.2. Calc. for C₂₂H₁₉N₃. C, 81.2; H, 5.9; N, 12.9%. ¹H NMR (δ, CDCl₃): 3.20 (2H, t, J(HH) 5.9 Hz, CH₂N), 4.06 (2H, t, J(HH) 6.0 Hz, pyrrole-CH₂), 4.65 (2H, s, NCH₂-anthracene), 6.15 (2H, t, J(HH) 2.0 Hz, pyrrole), 6.68 (2H, t, J(HH) 2.0 Hz, pyrrole), 7.62 (4H, m, ArH), 8.31 (2H, d, J(HH) 4.9 Hz, ArH), 8.40 (2H, d, J(HH) 6.9 Hz, ArH). Mass m/e (%): 325 (M⁺, 17), 217 (21) and 216 (100). IR ν_{max}: 3429, 2211, 1473, 756 and 734 cm⁻¹.

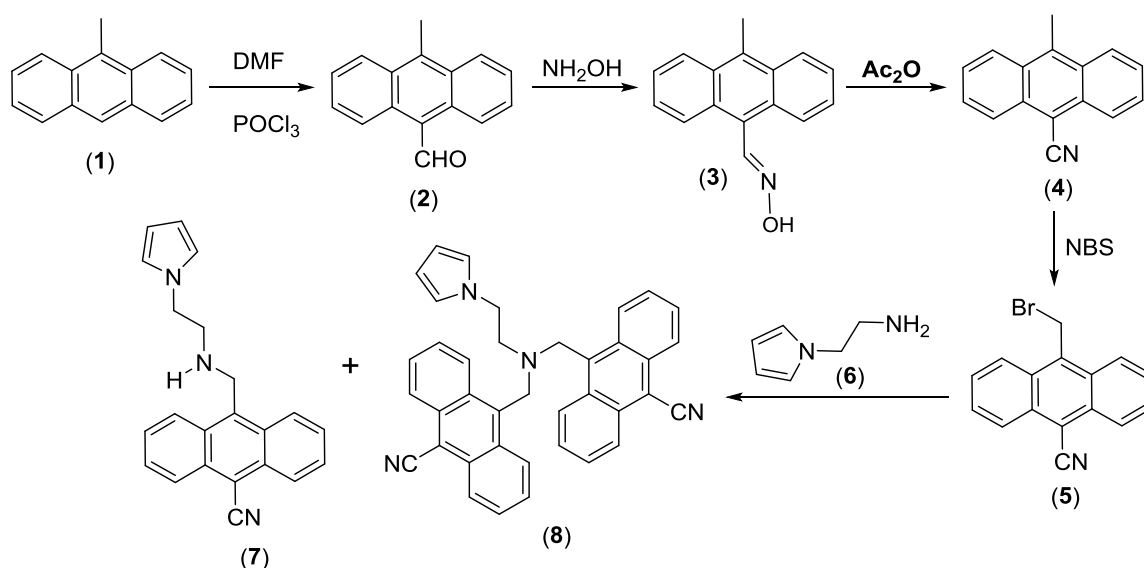
1-[2,2'-Di(9-cyanoanthracen-10-yl-methyl)]aminoethyl pyrrole (8)

The first fraction of the above column was collected and slow evaporation of the solvent led to the isolation of a pure sample of (8) as a yellow solid (0.5 g), which is a yield of 92% with respect to unreacted compound (5) available in the reaction mixture. Found: C, 84.9; H, 5.1; N, 9.9. Calc. for C₃₈H₂₈N₄. C, 84.4; H, 5.2; N, 10.35%. m.p. 255-6 °C. ¹H NMR (δ, CDCl₃): 3.15 (2H, t, J(HH) 6.4 Hz, NCH₂C), 3.76 (2H, t, J(HH) 6.4 Hz, pyrrole-CH₂), 4.59 (4H, s, NCH₂-anthracene), 5.98 (2H, t, J(HH) 2.0 Hz, pyrrole), 6.18 (2H, t, J(HH) 2.0 Hz, pyrrole), 7.31 (4H, m, ArH), 7.61 (4H, m, ArH), 8.15 (4H, d, J(HH) 8.5 Hz, ArH), 8.34 (4H, d, J(HH) 8.5 Hz, ArH). Mass m/e (%): 540 (M⁺, 1.2), 460 (10) and 216 (100). IR ν_{max}: 2210, 1443, 749 and 722 cm⁻¹.

RESULTS AND DISCUSSION

Synthesis of N-substituted pyrrole derivatives (7) and (8) containing 9-cyanoanthracene group(s) is summarised in Scheme 1. Vilsmeier formylation of 9-methylanthracene (1) with POCl₃/DMF yielded 10-methyl-anthracene-9-carboxaldehyde (2) as yellow crystals in 75% yield. The proton resonances of the methyl and aldehyde protons appeared as singlets at 3.16 and 11.31 ppm, respectively. Compound (2) was converted into its oxime (3) by treating it with hydroxylamine. The singlets at 7.82 and 9.19 ppm were assigned to =NOH and CH= protons, respectively. With the addition of D₂O, the peak at 7.82 ppm exchanged with deuterium, confirming the presence of =NOH group.

Dehydration of (3) with acetic anhydride afforded 9-cyano-10-methyl-anthracene (4) as yellow needles in 91% yield. The ¹H NMR spectrum showed a singlet at 3.11 for the methyl group and the absorption peak in the IR spectrum at 2208 cm⁻¹ was assigned to ν(C≡N). 9-Bromomethyl-10-cyanoanthracene (5) was obtained by the reaction between (4) and N-bromosuccinimide in dry carbon tetrachloride.



Scheme 1 Preparation of N-substituted pyrrole derivatives (7) and (8)

The reaction between (5) and 1-(2-aminoethyl) pyrrole (6) [5] in dry benzene gave a mixture containing the secondary amine (7) and tertiary amine (8). These two pyrrole derivatives were separated by column chromatography on silica using dichloromethane as the solvent. The compound (8) eluted first and was isolated as a yellow solid. The second fraction containing compound (7) was collected and the secondary amine (7) was isolated as yellow needles in moderate yield.

CONCLUSIONS

Two N-substituted pyrrole derivatives (7) and (8), containing pendant anthracene groups were successfully prepared.

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