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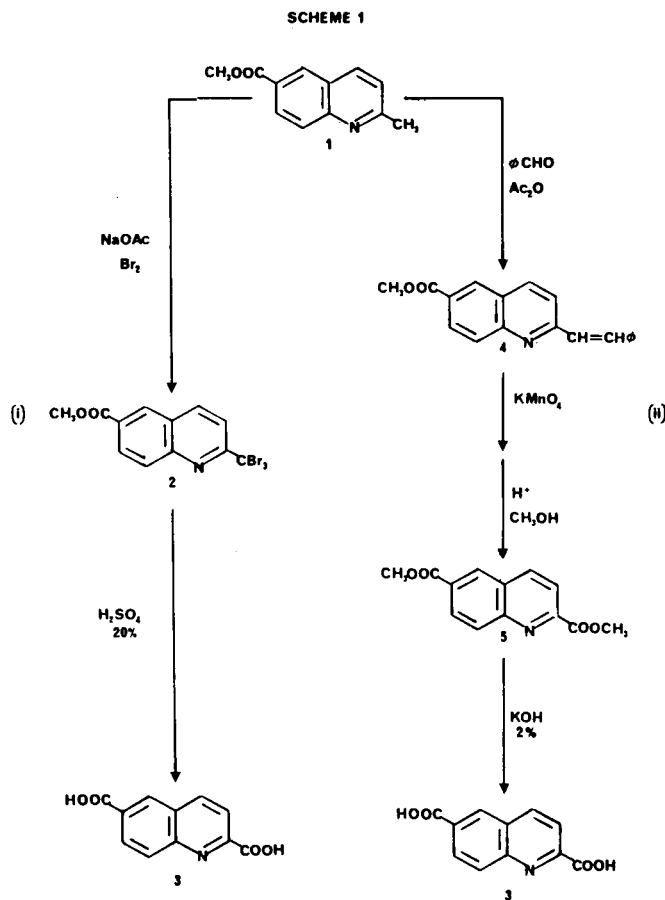
New quinoline-2,6-dicarboxylic acid and 6-aminoquinoline-2-carboxylic acid which are potential monomers for the introduction of quinoline units in commercial polymers such as polyamides, polyesters, *etc.* have been synthesized.

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Polyquinolines with a wide range of chain stiffness, that can be altered from a relatively flexible polymer with a low glass transition temperature to rod-like macromolecules with a high glass transition temperature, have been reported in the literature [1]. The synthetic route used is the Friedlander reaction, under a variety of base or acid-catalyzed conditions, between an aromatic bis-*o*-amino-ketone and an aromatic diketone. All the polymers showed an excellent thermal stability, with initial weight losses occurring between 500 and 600° in air. Most of the materials have a low degree of crystallinity [2,3] except a rigid polyquinoline ( $T_g = 415$ ,  $T_m = 552$ , >60% crystallinity). Thus, the introduction of such quinoline units in the polymer backbone of other polymers such as polyesters, polyamides, *etc.*, could influence the degree of crystallinity, the  $T_m$  and the thermal stability of such materials, but no attempts have been made in the past to synthesize the appropriate monomers.

In this paper we report the synthesis and the characterization of new quinoline compounds such as quinoline-2,6-dicarboxylic acid (**3**) (Scheme 1) and 6-aminoquinoline-2-carboxylic acid (**9**) (Scheme 2) which are potential monomers for the introduction of quinoline units in the polymer chains.

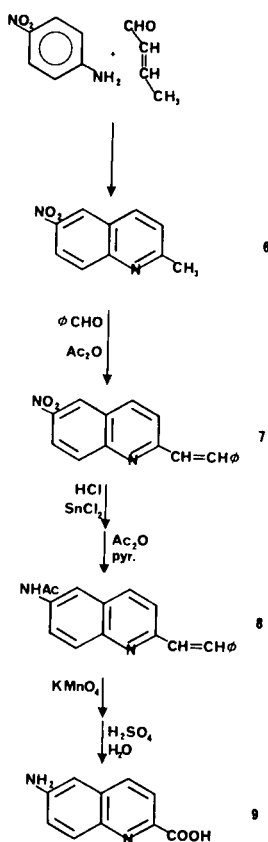
2-Methylquinoline-6-carboxylic acid was prepared following the procedure described in the literature [4,5] and esterified with methanol to obtain the methyl 2-methyl-6-quinolinecarboxylate (**1**). The quinoline-2,6-dicarboxylic acid (**3**) was then obtained by the two following routes (Scheme 1): i) Methyl 2-methyl-6-quinolinecarboxylate was brominated by reaction with bromine and anhydrous sodium acetate in 40% yield and the following hydrolysis with 20% sulphuric acid of the resulting compound **2** yielded the diacid **3** with 15% overall yield. ii) Methyl 2-methyl-6-quinolinecarboxylate was allowed to react with benzaldehyde in acetic anhydride to obtain the methyl 2-styryl-6-quinolinecarboxylate (**4**). Oxidation with potassium permanganate yielded compound **5** and the following esterification with methanol and hydrolysis with



2% aqueous potassium hydroxide gave compound **3** with a 39% overall yield.

2-Methyl-6-nitroquinoline (**6**), 6-nitro-2-styrylquinoline (**7**) and 6-acetylamino-2-styrylquinoline (**8**) (Scheme 2) were prepared following the procedures described in the literature [6-8]. Oxidation of the 6-acetylamino-2-styrylquinoline with potassium permanganate followed by hydrolysis with sulphuric acid gave the 6-aminoquinoline-2-carboxylic acid (**9**) with an overall yield (starting from 2-methyl-6-nitroquinoline) of 44%.

SCHEME 2



The synthesis of new polymers (polyesters and polyamides) by using these quinoline monomers are in progress.

## EXPERIMENTAL

All melting points were determined on a Buchi 530 capillary melting point apparatus and are uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on a Perkin Elmer 684 spectrometer, and nuclear magnetic resonance (nmr) spectra were obtained with a Bruker WP-80 (80 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded on a LKB 9000 S spectrometer.

### Methyl 2-Methyl-6-quinolinecarboxylate (1).

2-Methylquinoline-6-carboxylic acid (18.7 g) was added to 150 ml of methyl alcohol and 9 ml of concentrated sulphuric acid. The mixture was allowed to reflux for 24 hours, then cooled, added to 500 ml of crushed ice, stirred and filtered. The methyl carboxylate was precipitated neutralizing the solution with sodium carbonate at 0°. The cream solid was filtered washed with cold water and dried (mp 105°, yield 74%); <sup>1</sup>H-nmr (deuteriochloroform): δ 2.65 (3H, s, 2-CH<sub>3</sub>), 3.83 (3H, s, 6-COOCH<sub>3</sub>), 6.98-8.22 (5H, m, ArH); ms: m/e 201 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.54; H, 5.37; N, 7.02.

### i) Methyl 2-Tribromomethylquinoline-6-carboxylate (2).

Finely powdered anhydrous sodium acetate (36.6 g) was added with stirring to a solution of 14.9 g of this methylcarboxylate in glacial acetic acid (120 ml) at 70-80°. Bromine (20.4 g) in acetic acid (15 ml) was added while stirring in 15 minutes time at the same temperature. The mixture was stirred for 1 hour at 90-95° and then allowed to stand overnight, filtered off and the remaining solid 2 was washed with water, and dried (yield 41%, mp 150°); <sup>1</sup>H-nmr (deuteriochloroform): δ 4.02 (3H, s, 6-COOCH<sub>3</sub>), 6.8-8.64 (5H, m, ArH).

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>Br<sub>3</sub>NO<sub>2</sub>: C, 32.91; H, 1.84; N, 3.20. Found: C, 32.79; H, 1.71; N, 3.28.

### Quinoline 2,6-Dicarboxylic Acid (3).

Two g of this brominated compound were heated under reflux with 20% sulphuric acid (20 ml) for 20 hours. The cooled mixture was filtered and aqueous ammonia was added slowly to the filtrate to give a white precipitate that was collected, washed with water, solubilized in 0.1N sodium hydroxide, precipitated with dilute hydrochloric acid, washed with water and dried (mp > 300°, yield 50%); <sup>1</sup>H-nmr (DMSO-d<sub>6</sub>): δ 8.29 (3H, m, ArH), 8.83 (2H, m, ArH); ir (potassium bromide): 1720 cm<sup>-1</sup> (6-C=O), 1655 cm<sup>-1</sup> (2-C=O), 3440 cm<sup>-1</sup> (OH).

*Anal.* Calcd. for C<sub>11</sub>H<sub>7</sub>NO<sub>4</sub>: C, 60.83; H, 3.25; N, 6.45. Found: C, 60.65; H, 3.22; N, 6.37.

### ii) Methyl 2-Styryl-6-quinolinecarboxylate (4).

Methyl 2-methyl-6-quinolinecarboxylate (18.7 g), benzaldehyde (29.9 g) and acetic anhydride (21.35 g) were heated for 4 hours in an oil bath at 165-170°. The mixture was then cooled and the yellow crystals filtered, washed with a small amount of glacial acetic acid, water and dried (mp 186°, yield 75%); <sup>1</sup>H-nmr (deuteriochloroform): δ 3.97 (3H, s, 6-COOCH<sub>3</sub>), 7.24-8.51 (12H, m, ArH, CH=); ms: m/e 289 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>: C, 78.87; H, 5.22; N, 4.84. Found: C, 78.72; H, 5.09; N, 4.92.

The reaction was also carried out using anhydrous zinc chloride instead of acetic anhydride but the product was less pure and the yield lower.

### Dimethyl Quinoline-2,6-dicarboxylate (5).

Potassium permanganate (23.7 g) was added slowly (2 hours) to a stirred mixture of this compound (16 g), pyridine (110 ml) and water (25 ml) at 0°. Water (70 ml) was added when necessary to improve stirring, which was continued for 1 hour. The mixture was then allowed to stand overnight, acidified to pH 4 with dilute sulphuric acid and decolorized by addition of a solution of sodium metabisulphite. The solid was collected, washed with water, dried and added to a solution of 25 ml of methanol containing 1 ml of concentrated sulphuric acid. After reflux for 8 hours, the mixture was allowed to cool to room temperature, filtered and the precipitate was washed with cold water and with a cold solution of sodium bicarbonate and dried. The crude product was recrystallized from toluene (charcoal) (mp 188°, yield 79%); <sup>1</sup>H-nmr (deuteriochloroform): δ 4.10 (3H, s, 2-COOCH<sub>3</sub>), 4.01 (3H, s, 6-COOCH<sub>3</sub>); ms: m/e 245 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>NO<sub>4</sub>: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.59; H, 4.45; N, 5.75.

### Quinoline-2,6-dicarboxylic Acid (3).

Five g of this pure dimethyl quinoline-2,6-dicarboxylate and

100 ml of 2% potassium hydroxide solution were reacted at 60° for 2 hours. The solution was acidified to pH 3-4 with dilute hydrochloric acid and the white solid collected, washed with water and dried (mp > 300, yield 89%); <sup>1</sup>H-nmr (DMSO-d<sub>6</sub>): δ 8.29 (3H, m, ArH), 8.83 (2H, m, ArH); ms: m/e 217 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>11</sub>H<sub>7</sub>NO<sub>4</sub>: C, 60.83; H, 3.25; N, 6.45. Found: C, 60.73; H, 3.29; N, 6.48.

2-Methyl-6-nitroquinoline (6), 6-nitro-2-styrylquinoline (7) and 6-acetylamino-2-styrylquinoline (8) were prepared following the procedure described in the literature [6-8].

#### 6-Aminoquinoline-2-carboxylic Acid (9).

To a mixture of obtained compound 8 (34 g) in pyridine (240 ml) and water (52 ml), vigorously stirred, powdered potassium permanganate (51 g) was added during 1 hour, keeping the internal temperature at 18-20°. Water was then added to permit stirring when necessary, due to the thickness of the inorganic material. Stirring was continued for 30 minutes, then the mixture was acidified to Congo paper with dilute sulphuric acid and decolorized by the addition of sodium hydrogen sulphite. The precipitate was collected, washed with ether and extracted with a 2N sodium carbonate solution. Concentrated hydrochloric acid was then added to the extracted solution in order to precipitate the acid. Crystallization from water (600 parts) gave 6-acetylaminoquinoline-2-carboxylic acid as yellow coloured crystals (mp 229.5-230°, yield 65%); <sup>1</sup>H-nmr (DMSO-d<sub>6</sub>): δ 2.15 (3H, s, COCH<sub>3</sub>), 7.84-8.54 (5H, m, ArH), 10.42 (1H, s, NH).

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.39; H, 4.31; N, 12.21.

6-Acetylaminoquinoline-2-carboxylic acid (14 g) was added to water (25 ml) and concentrated sulphuric acid (25 ml), and heated under reflux at 208-210° for 2.5 hours. The solution was poured into water (50 ml) and ammonium hydroxide solution was added to precipitate the acid, that was solubilized in 0.1N sodium hydroxide and precipitated with dilute hydrochloric acid. Crystallization from water (50 parts) gave 6-aminoquinoline-2-carboxylic acid as yellow coloured crystals (mp 241-242°, yield 95%); <sup>1</sup>H-nmr (DMSO-d<sub>6</sub>): δ 6.22 (2H, broad signal, NH<sub>2</sub>), 6.85 (1H, d, ArH), 7.29 (1H, dd, ArH), 7.78-8.11 (3H, m, ArH).

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.43; H, 4.37; N, 14.80.

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