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A Convenient Method for the Preparation of 4-*n*-Alkyl-4″-cyano-*p*-Terphenyl

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A new and general procedure for the preparation of 4-*n*-alkyl-4″-cyano-*p*-terphenyl is described starting from *p*-terphenyl. This procedure consists of the Friedel–Crafts reaction on *p*-terphenyl with an acyl halide and reducing the resulting ketone by the Wolff–Kishner method to the 4-*n*-alkyl-*p*-terphenyl. This is acylated with acetyl chloride to the corresponding 4-*n*-alkyl-4″-acetyl-*p*-terphenyl, which in turn is oxidised to the carboxylic acid. This acid is converted to the amide through its acid chloride. Dehydration of this amide affords the desired 4-*n*-alkyl-4″-cyano-*p*-terphenyl. This convenient method offers better yields than the procedure of Gray *et al.*[1] and could also be utilised for the preparation of 4-*n*-alkoxy-, and 4-*n*-alkyl-4′-cyano biphenyls. In addition to the cyano derivatives, some intermediate compounds also exhibit mesomorphic properties.

INTRODUCTION

It has been fairly well established that 4-*n*-alkoxy- and 4-*n*-alkyl-4′-cyano biphenyls[1] and 4-*n*-alkyl-4″-cyano-*p*-terphenyls[2] are very stable materials and suitable mixtures from these compounds satisfy the stringent conditions required in some of the electrooptic devices. The procedure of Gray *et al.*[2] for the preparation of 4-*n*-alkyl-4″-cyano-*p*-terphenyl presented a problem. It was difficult to isolate the pure mono bromo *p*-terphenyl in good yield. This varying low yields in obtaining this intermediate prompted us to adopt a simple and convenient method in preparing these 4-*n*-alkyl-4″-cyano-*p*-terphenyls. The method is shown schematically in the chart. It consists of the Friedel–Crafts reaction on *p*-terphenyl I with an acyl halide, which gave the

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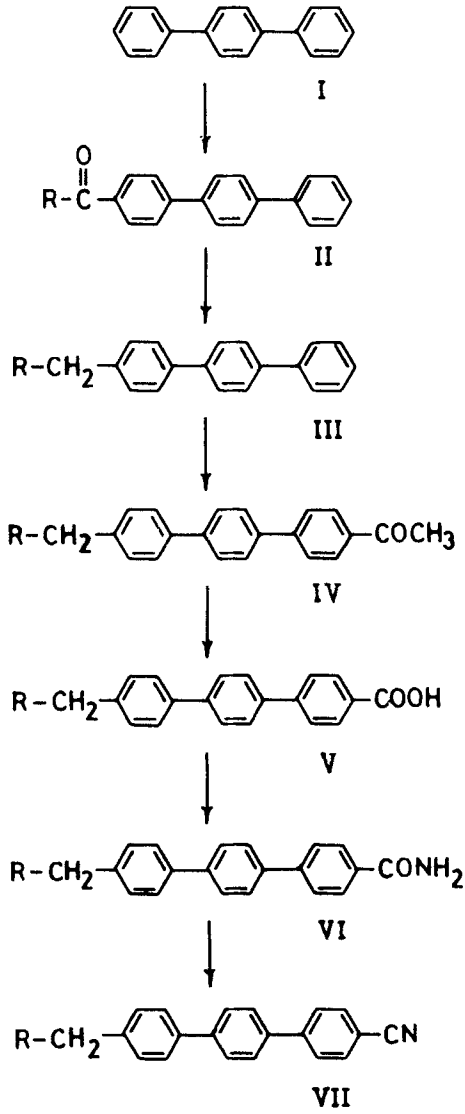
CHART I



R = n-C_4H_9 or n-C_5H_{11} or n-C_6H_{13} or n-C_7H_{15}

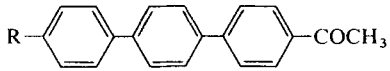
4-acyl-*p*-terphenyl II. This ketone on Wolff–Kishner reduction afforded the 4-alkyl-*p*-terphenyl III, which was again acylated with acetyl chloride to the corresponding 4-alkyl-4″-acetyl-*p*-terphenyl IV. This in turn was oxidised to the carboxylic acid V and was finally converted to the desired 4-alkyl-4″-cyano-*p*-terphenyl VII, through its caboxylic acid amide VI. The yields were good in all the steps. This procedure has the advantage of not utilizing the hazardous bromine or the poisonous cuprous cyanide, especially when working on a large scale.

Results

It was found that 4-*n*-alkyl-4″-acetyl-*p*-terphenyls and 4-*n*-alkyl-*p*-terphenyl-4″-carboxylic acids also exhibit mesomorphic properties, the latter decomposing owing to their high melting points. The transition temperatures for the acetyl derivatives are summarized in Table I. Compounds 1 to 4 melt to a smectic phase on heating of the respective solids and go to the isotropic phase without the formation of any nematic phase. It may be mentioned that even the first members of a series of several 4-*n*-alkyl- and 4-*n*-alkoxy-4′-*n*-alkanoyl biphenyls[3] show a similar behaviour wherein the smectic phases pass on to the isotropic liquid. All the compounds in the present study show a mosaic texture. However, the kind of smectic phase has not yet been identified. The 4-*n*-alkyl-*p*-terphenyl-4″-carboxylic acids are expected to show liquid crystalline properties. All the four acids are indeed mesomorphic, but the mesophases are unstable due to thermal decomposition. These colourless acids became dark brown on heating, exhibiting both smectic and nematic phases. The transition temperatures are not quite reversible (due to decomposition) and consequently have not been given. However, they appear to have very high nematic–isotropic transition temperature, viz., $>350°C$.

TABLE I

Transition temperatures of 4-*n*-alkyl-4″-acetyl-*p*-terphenyls

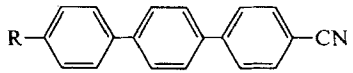


Compound number	R	C—S °C	S—I °C	ΔT°C thermal range
1	n-C_5H_{11}	231.5	258.5	27.0
2	n-C_6H_{13}	229.0	253.0	24.0
3	n-C_7H_{15}	233.5	258.0	24.5
4	n-C_8H_{17}	230.5	249.5	19.0

The transition temperatures for the 4-*n*-alkyl-4″-cyano-*p*-terphenyls agree quite well with those reported by Gray *et al.*[4] and are given in Table II. Regarding the smectic phases of the octyl derivative 8, no miscibility studies were made. The change in the texture pattern, at the temperature mentioned, indicated the polymesomorphism in this compound.

TABLE II

Transition temperatures of 4-*n*-alkyl-4″-cyano-*p*-terphenyls



Compound number	R	C—N or S_3 °C	S_3—S_2 °C	S_2—S_1 °C	S_1—N °C	N—I °C
5	*n*-C_5H_{11}	130.0	—	—	—	239
6	*n*-C_6H_{13}	124.5	—	—	—	227
7	*n*-C_7H_{15}	134.0	—	—	(124.5)	222
8	*n*-C_8H_{17}	126.0	127.0	131.5	195.0	215

Experimental

The melting points are all uncorrected. The transition temperatures were determined in open capillary tubes using a microscope (Franz Kustner Nacht KG, Dresden, Model HMK 70/3171) provided with a heating stage. The mesophase textures were observed in thin films, by sandwiching samples between glass slide and cover slip, under a polarizing microscope. Infrared spectra were recorded on a Leitz double beam prism spectrograph and nmr spectra were obtained on a Varian T-60 spectrometer. The purity of the materials at each stage was investigated by thin layer chromatography.

The procedure used for the preparation of 4-*n*-pentyl-4″-cyano-*p*-terphenyl is described in full. The physical constants of the remaining three homologues are given at appropriate places.

4-n-Pentanoyl-p-terphenyl In a two litre three-necked flask fitted with a reflux condenser, a mercury-sealed mechanical stirrer and a dropping funnel were placed *p*-terphenyl (46 g, 0.2 mole) and "analar" nitrobenzene (350 ml). Anhydrous aluminium chloride (29.37 g, 0.22 mole) was added and the mixture stirred at room temperature. *n*-Pentanoyl chloride (24.1 g, 0.2 mole) was introduced drop by drop to the stirred mixture during forty-five minutes. Stirring was continued after addition for two hours at room temperature and then at 55–65°C for two more hours and left at room temperature overnight.

The dark complex was hydrolyzed with concentrated hydrochloric acid (100 ml) and ice water (250 ml) and the reaction mixture steam distilled to remove nitrobenzene. The solid mass was filtered off, washed with water and air-dried. It was recrystallized from 1,4-dioxan using norit. Yield 90%, m.p. 177–178°C, IR (nujol). 1686 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.96 (t – 3, CH_3 of C_4H_9) 1.3–1.93 (m – 4, $-CH_2-CH_2-$ of $-C_4H_9$) 2.96 (t – 2, CH_2 of $-\overset{O}{\overset{\|}{C}}-CH_2-$) 7.1–8.05 ($m$ – 13, aromatic).

Anal. calcd. for $C_{23}H_{32}O$: C, 87.9; H, 7.006%

Found: C, 87.58; H, 7.211%

By the same method we prepared 4-*n*-hexanoyl-*p*-terphenyl, m.p. 195–197°C (calcd. for $C_{24}H_{24}O$: C, 87.8; H, 7.316%. Found: C, 87.50; H, 7.6%), 4-*n*-heptanoyl-*p*-terphenyl, m.p. 194–197°C (calcd. for $C_{25}H_{26}O$: C, 87.719; H, 7.602%. Found: C, 87.64; H, 7.50% and 4-*n*-octanoyl-*p*-terphenyl, m.p. 190–193°C (calcd. for $C_{26}H_{28}O$: C, 87.64; H, 7.865%. Found: C, 87.56; H, 7.886%).

4-n-Pentyl-p-terphenyl A mixture of 4-*n*-pentanoyl-*p*-terphenyl (53.38 g, 0.17 mole), diethylene glycol (300 ml), potassium hydroxide pellets (28.77 g, 0.51 mole) and 90% hydrazine hydrate (36 ml) was heated at 110°C for 2 hours. The temperature was gradually raised to 180°C, distilling off the volatile matter in the process and held at this temperature for 4 hours. The mixture was cooled when a solid separated out. This was dissolved in chloroform, water added and the mixture extracted several times with chloroform. The organic phase was washed with water and dried over anhydrous sodium sulfate. Removal of solvent afforded a pale brown material which was crystallised from *n*-heptane using norit, to remove colouring matter, in colourless flakes yield 86%, m.p. 177°C, (IR (nujol) there was no absorption in the 1680–1690 cm^{-1} region). nmr ($CDCl_3$) δ 0.91 (t – 3, CH_3 of C_5H_{11}) 1.15–1.91 (m – 6, 3 methylenes of C_5H_{11}) 2.68 (t – 2, benzyl methylene) and 7.11–7.75 (m – 13, aromatic)

Anal. Calcd. for $C_{23}H_{24}$: C, 92; H, 8%

Found: C, 92; H, 7.998%.

By a similar procedure we prepared 4-*n*-hexyl-*p*-terphenyl, m.p. 170–172°C (calcd. for $C_{24}H_{26}$: C, 91.73; H, 8.28%, Found: C, 91.50; H, 8.399%), 4-*n*-heptyl-*p*-terphenyl, m.p. 170–171°C (calcd. for $C_{25}H_{28}$: C, 91.463; H, 8.536%, Found: C, 91.33; H, 8.41%) and 4-*n*-octyl-*p*-terphenyl, m.p. 158–160°C (calcd. for $C_{26}H_{30}$: C, 91.228; H, 8.771% Found: C, 91.45; H, 8.5%).

4-n-Pentyl-4″-acetyl-p-terphenyl In a one litre 3-necked flask fitted with a reflux condenser, a mercury-sealed mechanical stirrer and a dropping funnel, were placed 4-*n*-pentyl-*p*-terphenyl (42 g, 0.14 mole), "analar" carbon tetrachloride (300 ml) and anhydrous aluminium chloride (24.03 g, 0.18 mole). The mixture was kept below 20°C and during stirring was added freshly distilled acetyl chloride (10.99 g, 0.14 mole), drop by drop, during 1 hour. Stirring was continued for 4 hours at the same temperature and left to stand for 36 hours. The dark coloured complex was decomposed with concentrated hydrochloric acid (75 ml) and ice-water (150 ml). Chloroform (100 ml) was added and the mixture extracted twice. The organic phase was washed with water and dried over anhydrous sodium sulfate. Removal of solvent and recrystallisation of the product from toluene afforded the desired acetyl derivative. [Any unconverted starting material can be recovered by chromatography.] Yield 85%, m.p. 231.5°C, IR (nujol) 1687 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.91 (t − 3, CH_3 of $-C_5H_{11}$) 1.18–1.88 (m − 6, three methylenes of C_5H_{11}) 2.48–2.88 (t − 5, benzylic $-CH_2$ and $-\overset{O}{\overset{\|}{C}}-CH_3$) 7.08–8.15 ($m$ − 12, aromatic)

Anal. calcd. for $C_{25}H_{26}O$: C, 87.72; H, 7.603%
Found: C, 87.46; H, 7.568%

By the same procedure we obtained 4-*n*-hexyl-4″-acetyl-*p*-terphenyl, m.p. 229°C (calcd. for $C_{26}H_{28}O$: C, 87.66; H, 7.856% Found: C, 87.34; H, 7.809%), 4-*n*-heptyl-4″-acetyl-*p*-terphenyl, m.p. 233.5°C (calcd. for $C_{27}H_{30}O$: C, 87.567; H, 8.108%, Found: C, 87.82; H, 8.33%) and 4-*n*-octyl-4″-acetyl-*p*-terphenyl, m.p. 230.5°C (calcd. for $C_{28}H_{32}O$: C, 87.5; H, 8.333%, Found: C, 87.34; H, 8.426%).

4-n-Pentyl-p-terphenyl-4″-carboxylic acid A solution of sodium hypobromite prepared at 0–5°C by adding bromine (54.6 g, 0.35 mole) to sodium hydroxide (49 g, 1.225 mole) in water (245 ml) was added slowly to a stirred solution of 4-*n*-pentyl-4″-acetyl-*p*-terphenyl (23.94 g, 0.07 mole) in dioxan (800 ml) maintained at 30°C during 1 hour. The sodium salt separated out during the addition and stirring was continued for a further $1\frac{1}{2}$ hours during which period the temperature was slowly raised to 55°C to ensure completion of reaction. Enough aqueous sodium metabisulfite solution was added to remove the excess of hypobromite and the mixture was diluted with water (1200 ml). About 300 ml of the liquid was distilled and the mixture cooled. Acidification by concentrated hydrochloric acid afforded pale yellow crystals of the acid. This was filtered off, dried and recrystallised from dioxan; yield

76.5% m.p. 308°C, IR (nujol) 1680 cm^{-1} (—C=O).

Anal. calcd. for $C_{24}H_{24}O_2$: C, 83.71; H, 6.976%

Found: C, 83.75; H, 6.913%.

By a similar procedure we prepared 4-*n*-hexyl-*p*-terphenyl-4″-carboxylic acid, m.p. 287°C (calcd. for $C_{25}H_{26}O_2$: C, 83.79; H, 7.263%, Found: C, 84.03; H, 7.422%), 4-*n*-heptyl-*p*-terphenyl-4″-carboxylic acid, m.p. 285°C (calcd. for $C_{26}H_{28}O_2$: C, 83.87; H, 7.52%, Found: C, 84.3; H, 7.40%) and 4-*n*-octyl-*p*-terphenyl-4″-carboxylic acid, m.p. 302°C (calcd. for $C_{27}H_{30}O_2$: C, 83.93; H, 7.77%, Found: C, 84.3; H, 8.0%).

4-n-Pentyl-p-terphenyl-4″-carboxylic acid amide A mixture of 4-*n*-pentyl-*p*-terphenyl-4″-carboxylic acid (13.76 g, 0.04 mole) and redistilled thionyl chloride (60 ml) was refluxed for 4 hours when the evolution of hydrogen chloride gas ceased. Exess thionyl chloride was removed by distillation under reduced pressure and liquor ammonia (75 ml, sp. gr. 0.9) was added to the crude acid chloride and the mixture agitated for $\frac{1}{2}$ hour. The solid material was filtered, washed with water and dried. Recrystallisation from cyclohexanone afforded the desired material, Yield 78.5%, m.p. 315–317°C, IR (nujol) 1640 cm^{-1} (C=O) 3180 cm^{-1} and 3410 cm^{-1} (NH_2)

Anal. calcd. for $C_{24}H_{25}ON$: C, 83.97; H, 7.28; N, 4.08%

Found: C, 84.26; H, 7.21; N, 4.38%.

Following a similar procedure we obtained 4-*n*-hexyl-*p*-terphenyl-4″-carboxylic acid amide, m.p. 285–288°C (calcd. for $C_{25}H_{27}NO$: C, 84.03; H, 7.56; N, 3.92%, Found: C, 83.93; H, 7.48%, N, 3.86%) 4-*n*-heptyl-*p*-terphenyl-4″-carboxylic acid amide, m.p. 312–315°C (calcd. for $C_{26}H_{29}ON$: C, 84.097; H, 7.816; N, 3.77%, Found: C, 84.03; H, 7.658; N, 3.87%) and 4-*n*-octyl-*p*-terphenyl-4″-carboxylic acid amide, m.p. 308–312°C (calcd. for $C_{27}H_{31}ON$: C, 84,15; H, 8.05; N, 3.63% Found: C, 83.85; H, 8.431; N, 3.90%).

4-n-Pentyl-4″-cyano-p-terphenyl An intimate mixture of 4-*n*-pentyl-*p*-terphenyl-4″-carboxylic acid amide (8.575 g, 0.025 mole) and phosphorous pentoxide (10.65 g, 0.075 mole) was heated in an electrical bath at 200°C for 2 hours and cooled. The dark brown material was carefully treated with moist chloroform. Ice-water was added and the mixture extracted several times with chloroform. The organic phase was washed with 25% hydrochloric acid, water, 10% sodium hydroxide solution and water. It was finally dried over anhydrous sodium sulfate for 2 hours. Removal of solvent afforded a pale brown material which was chromatographed on silica gel (60–120 mesh, BDH, India) and eluted with benzene. Removal of solvent from the

eluate gave a white material which was sublimed under high vacuum at a bath temperature of 185°C. Yield 60%. m.p. 130°C, IR (nujol) 2234 cm^{-1} (—C≡N); NMR ($CDCl_3$) δ 0.88 (t – 3, CH_3) 1.1–1.83 (m – 6, methylenes) 2.61 (t – 2, Ar—CH_2—) 6.93–7.7 (m – 12, aromatic)

Anal. calcd. for $C_{24}H_{23}N$: C, 88.61; H, 7.07; N, 4.30%

Found: C, 88.41; H, 6.92; N, 4.39%.

By a similar procedure we prepared 4-*n*-hexyl-4″-cyano-*p*-terphenyl, m.p. 124.5 (calcd. for $C_{25}H_{25}N$: C, 88.49; H, 7.37; N, 4.13%, Found: C, 88.36; H, 7.32; N, 4.08%), 4-*n*-heptyl-4″-cyano-*p*-terphenyl, m.p. 134°C (calcd. for $C_{26}H_{27}N$: C, 88.38; H, 7.64; N, 3.96%, Found: C, 88.31; H, 7.58; N, 3.95%) and 4-*n*-octyl-4″-cyano-*p*-terphenyl, m.p. 126°C (calcd. for $C_{27}H_{29}N$: C, 88.28; H, 7.90; N, 3.81% Found: C, 88.20; H, 7.92; N, 3.80%).

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