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Mesomorphic Properties of a Homologous Series of Substituted Benzoyloxybenzoates†

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A homologous series of twelve 4-cyanophenyl-3-methyl-4-(4-*n*-alkylbenzoyloxy) benzoates have been prepared and their mesomorphic properties characterised. All these compounds are colourless, stable and have large positive dielectric anisotropy. The first ten homologues are purely nematic and have a wide thermal range. The undecyloxy and dodecyloxy derivatives exhibit a smectic phase in addition to the nematic phase. A plot of the nematic-isotropic transition temperatures against the number of carbon atoms in the alkyl chain shows the usual odd-even effect.

INTRODUCTION

With the increasing use of liquid crystals in various electro-optical devices attempts are being made in recent years to prepare materials which are liquid crystalline at or below room temperature and also which have a fairly high clearing temperature. In the present work, the following factors were taken into consideration in choosing the system to be investigated. Firstly, it is well known that the introduction of a terminal cyano group into a molecule results in a material of positive dielectric anisotropy. Secondly, the thermal stability of the mesophase may be increased by increasing the number of phenyl rings in the molecule from two to three.[1] Van Meter and Klanderman[2] and Young and Green[3] have reported several compounds derived from phenyl 4-benzoyloxy benzoates. These diesters have alkyl or alkoxy chains at the terminals, have wide nematic ranges and fairly low melting points, in contrast to the *p*-phenylene diesters reported by Dewar and Goldberg[1] and

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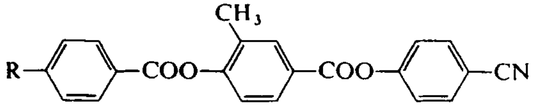
Arora *et al.*[4] The low melting points in the former compounds have been attributed to the dissymmetry associated with these molecules which can be considered to have been derived from *p*-hydroxybenzoic acid. Thirdly, several systems are known[5–9] wherein a lateral substituent either on a phenyl ring or in the α-position of a central linkage has reduced the melting as well as the clearing temperatures, the latter, however, being more marked. Based on a combination of these factors the following system (I) was selected and a homologous series of compounds were synthesized:



I

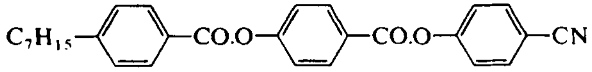
R = *n*-Alkyl

RESULTS AND DISCUSSION

The 4-cyanophenyl-3-methyl-4-(4-*n*-alkylbenzoyloxy) benzoates were prepared in six convenient steps, similar to the procedure described by Young and Green,[3] as shown in the scheme on the following page. In contrast, Van Meter and his co-workers[2,10] synthesized similar compounds in only two teps, one of which involved the esterification of a 4-alkylphenol with 4-hydroxybenzoic acid or one of its chlorinated derivatives to give a substituted 4-hydroxybenzoate. A combination of sulphuric acid and boric acid was used as a catalyst for the esterification.[11] The catalyst was found to be specific, so that only the hydroxyl group of the 4-alkyl phenol was involved in the ester formation. We could not use this method since the reaction of 4-hydroxybenzonitrile with either 4-hydroxybenzoic acid or 3-methyl-4-hydroxybenzoic acid failed to proceed. This is probably due to the presence of a *para*-cyano group in 4-hydroxybenzonitrile which deactivates the ring and resists esterification. However, it must be emphasized that the six step method gives excellent yields.

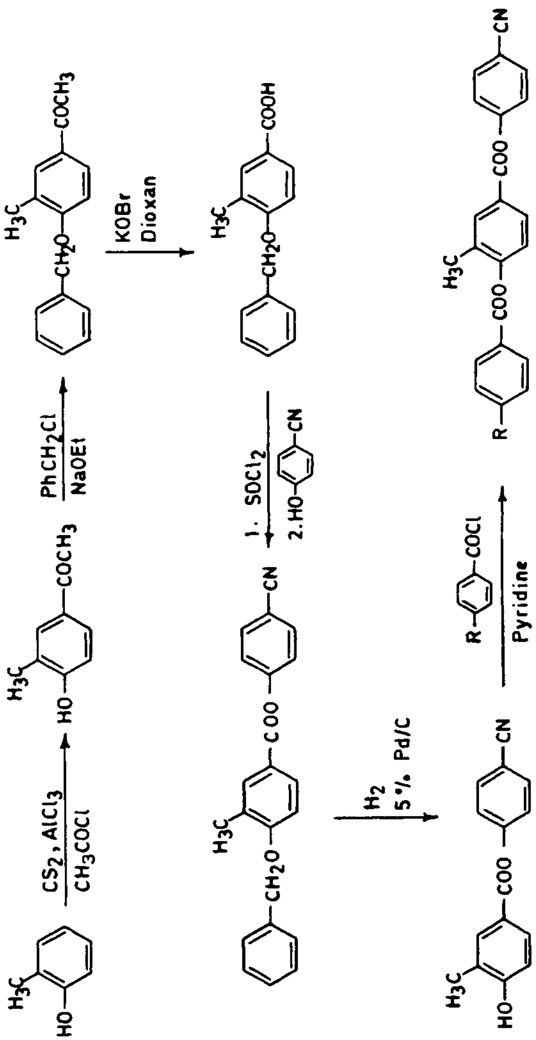
The melting and clearing temperatures for the homologous series of 4-cyanophenyl-3-methyl-4-(4-*n*-alkylbenzoyloxy) benzoates are summarized in Table I. These are colourless, stable materials having wide thermal range and large positive dielectric anisotropy. There is a gradual reduction of the range of the mesophase as the series is ascended. Compound 2 has the widest nematic range, viz., 105.5°C, and compound 4 the lowest melting point.

Van Meter *et al.*[12] have prepared the unsubstituted parent homologue,



K 94 S 111 N 225 I

SCHEME



R = Methyl to n-Dodecyl

TABLE I

Melting and clearing temperatures for 4-cyanophenyl-3-methyl-4-(-4-*n*-alkylbenzoyloxy)benzoates I.

		Temperature of transition to			
Compound number	R[a]	Smectic °C	Nematic °C	Isotropic °C	ΔT, °C Nematic Range
1	CH_3	—	159	219.5	60.5
2	C_2H_5	—	99	204.5	105.5
3	C_3H_7	—	105.5	203.5	98
4	C_4H_9	—	93	191.5	98.5
5	C_5H_{11}	—	108.5	187	78.5
6	C_6H_{13}	—	101.5	175.5	74
7	C_7H_{15}	--	103.5	170	66.5
8	C_8H_{17}	—	106	162	56
9	C_9H_{19}	—	104	159	55
10	$C_{10}H_{21}$	—	100.5	153	52.5
11	$C_{11}H_{23}$	103.5	126	151	25
12	$C_{12}H_{25}$	102	137	147	10

[a] All alkyl groups are normal.

Comparing this compound with the corresponding substituted homologue, it is seen that the lateral methyl group has lowered the nematic-isotropic temperature, eliminated the smectic phase and also increased the melting temperature. We are currently preparing the other unsubstituted parent homologous to make a more detailed study of the substituent effect for the complete series.

Figure 1 shows a plot of the transition temperatures against the number of carbon atoms in the alkyl chain. The nematic-isotropic transition temperature decreases on ascending the series, the points lying on two smooth falling curves; the curve for the odd homologues lies above that for the even homologues. There is an alternation in the melting points from compound 2 to compound 7, a behaviour that has been attributed[13] to a similarity in the crystal structures. The smectic mesophase appears from compound 11 upwards as an enantiotropic phase. The smectic phase exhibits a simple fan shaped texture and is believed to be smectic A, in analogy with what is observed in many other materials of high positive dielectric anisotropy.[9,14,15,16] The curve for the smectic-nematic transition shows the usual initial upward trend.

These diesters have a large positive dielectric anisotropy, evidently because of the Ph-CN group, which has a moment of 4.05 D.[17] The dielectric constants of compound 6 at 120° were experimentally found to be $\varepsilon_{\parallel} = 19.28, \varepsilon_{\perp} = 5.12$, $\Delta\varepsilon = +14$.

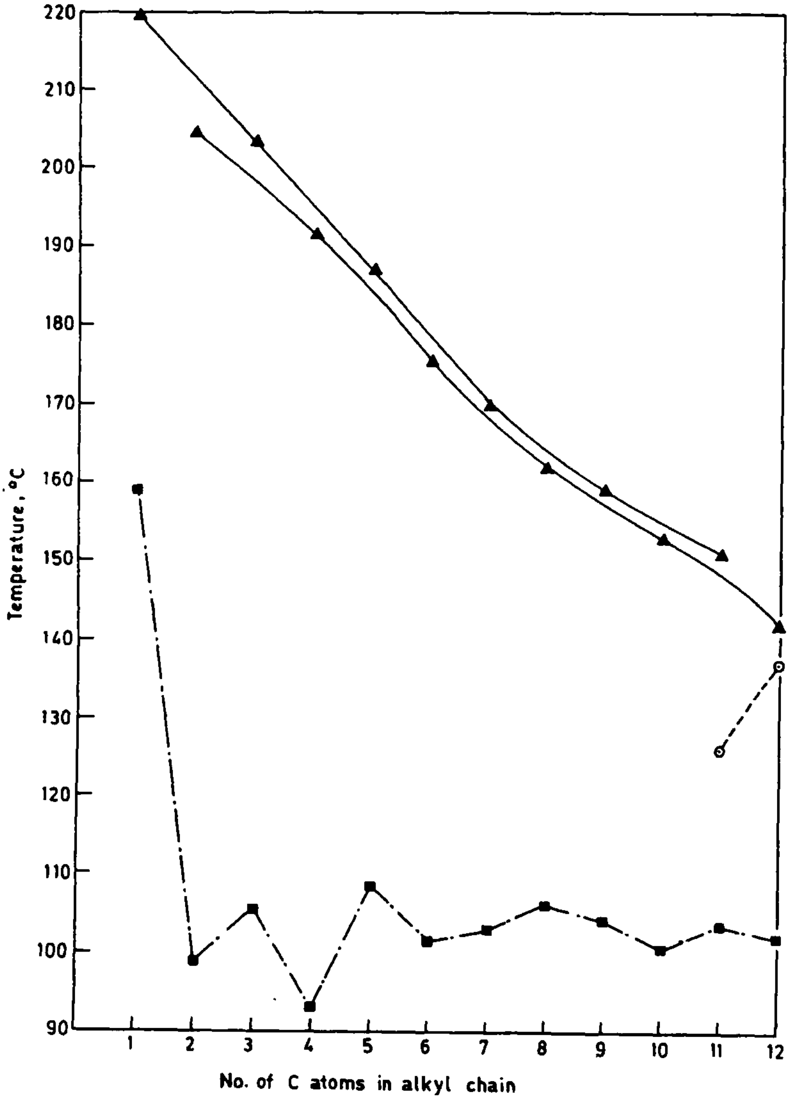


FIGURE 1 Melting behaviour of 4-cyanophenyl 3-methyl-4(4-*n*-alkylbenzoyloxy)benzoates.

■-·-·-·-■ Crystal—mesophase transition
▲———▲ Nematic—isotropic transition
⊙------⊙ Smectic—nematic transition.

EXPERIMENTAL

The melting points and 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 a glass slide and cover slip, under a polarizing microscope.

The synthetic route was essentially that adopted by Young and Green[3] and is described in detail. All the new compounds had satisfactory spectral properties and elemental analyses. The purities of all the final products synthesized and the intermediates were checked by thin layer chromatography. Infrared spectra were recorded on a Leitz double beam prism spectrograph and pmr spectra were taken on a Varian T-60 spectrometer.

p-*n*-Alkyl benzoic acids

Commercial *p*-toluic acid was recrystallized from dilute ethyl alcohol to constant melting point and used. *p*-Ethyl to *p*-*n*-dodecyl benzoic acids were prepared according to the procedure of Weygand and Gabler.[18]

4-Hydroxybenzonitrile

A mixture of 4-bromophenol (17.3 g, 0.1 mole), anhydrous cuprous cyanide (13.43 g, 0.15 mole) and anhydrous dimethyl formamide (100 ml) was refluxed for 8 hours and cooled. The reaction mixture was poured onto a stirred mixture of hydrated ferric chloride (7.5 g), concentrated hydrochloric acid (2.5 ml) and water (100 ml). This was heated to 60°C and maintained at that temperature for about 30 minutes. The cooled reaction mixture was extracted with ether several times and the combined ether extract was washed with water and dried over anhydrous sodium sulfate. Removal of solvent afforded a white material which was recrystallized from benzene. Yield 92.5%, m.p. 113°C (*lit.*[19] m.p. 113°C).

3-Methyl-4-hydroxyacetophenone

To a one litre 3-necked flask, fitted with a mercury-sealed mechanical stirrer, a refluxing condenser and a pressure equalizing separatory funnel, was introduced dry carbon disulfide (300 ml), anhydrous aluminium trichloride (146.85 g, 1.1 mole) and *o*-cresol (54.0 g, 0.5 mole). The mixture was stirred and freshly distilled acetyl chloride (39.25 g, 0.5 mole) was added drop by drop during 45 minutes. The reaction mixture was refluxed for 4 hours and left at room temperature overnight. Carbon disulfide was distilled off, and the dark brown complex was decomposed with crushed ice and concentrated hydrochloric acid. The mixture was extracted with ether a few times and the ethereal solution was washed with 10% hydrochloric acid once, to ensure complete removal of acid soluble material, and water and dried over anhydrous sodium sulfate. Removal of ether gave a pale brown material which was distilled under reduced pressure. The white product was recrystallized from benzene. Yield 65.25 g, (87%), b.p. 175–180°C/1 mm, m.p. 110–112°C (lit.[20] m.p. 104°C).

3-Methyl-4-benzyloxy acetophenone

A solution of sodium ethoxide was prepared in a one litre three-necked flask, fitted with a reflux condenser and a pressure equalizing separatory funnel, by dissovling sodium (6.9 g, 0.3 mole) in absolute ethyl alcohol (100 ml). To this solution was added 3-methyl-4-hydroxy acetophenone (45.0 g, 0.3 mole) in absolute ethyl alcohol (250 ml) through the separatory funnel. The mixture was stirred magnetically and refluxed for 30 minutes and to this was added freshly distilled benzyl chloride (39.21 g, 0.31 mole) drop by drop during 45 minutes. The mixture was refluxed for a further 8 hours and alcohol (200 ml) was distilled off. Water (500 ml) and hydrochloric acid (100 ml) were added to the cooled reaction mixture and extracted several times with ether. The combined ethereal extract was washed with 10% sodium hydroxide solution and water and then dried over anhydrous sodium sulfate. Removal of solvent afforded a pale yellow material which was recrystallized from petroleum ether (b.p. 60–80°C). Yield, 90%, m.p. 77.5–78.5°C.

3-Methyl-4-benzyloxybenzoic acid

A solution of potassium hypobromite prepared at 0°C, by dissolving bromine (128 g, 0.8 mole) in a solution of potassium hydroxide (89.6 g, 1.6 moles) in water (800 ml) was added to a stirred solution of 3-methyl-4-benzyloxy acetophenone (48 g, 0.2 mole) in 1,4-dioxan (400 ml). The addition was carried out at 30–35°C during 30 minutes. Stirring was continued and the temperature was raised to 50°C and held there for one hour to ensure completion of the reaction. Enough aqueous sodium metabisulfite was added to destroy the excess of hypobromite. Water (1000 ml) was added and about 400 ml of the liquid was distilled. The residual clear solution was cooled and acidified with concentrated hydrochloric acid. The snow white product was filtered off, washed thoroughly with water and air dried. This was recrystallized from ethyl alcohol. Yield, 87.6%, m.p. 183–184°C.

4-Cyanophenyl-4-methyl-4-(4-benzyloxy)benzoate

A mixture of 3-methyl-4-benzyloxy benzoic acid (24.2 g, 0.1 mole) and freshly distilled thionyl chloride (100 ml, excess) was refluxed for 6 hours and the excess thionyl chloride was removed by distillation under reduced pressure. 4-Hydroxybenzonitrile (11.9 g, 0.1 mole) in anhydrous pyridine (150 ml) was added to the crude acid chloride and the mixture stirred magnetically at room temperature for 20 hours and at 100°C for 2 hours and cooled. The reaction mixture was poured onto a stirred mixture of crushed ice and concentrated hydrochloric acid (200 ml) when a precipitate was obtained. It was filtered off, washed with water, 10% aqueous sodium hydroxide solution, water and dried. The pale brown material was chromatographed on silica gel and eluted with benzene-petroleum ether mixture. Removal of solvent from the eluate afforded a white product which was recrystallized from absolute ethyl alcohol into white shining needles. Yield, 86%, m.p. 122–123°C. IR(Nujol) 2235 cm^{-1} (C≡N stretching) 1740 cm^{-1} (COO stretching); pmr ($CDCl_3$) δ 2.7 (s-3, —CH_3) 5.2 (s-2, —CH_2—) 6.8–8.1 (m-12, aromatic). Found: C, 76,86; H, 4.83; N, 4.1% $C_{22}H_{17}O_3N$ requires C, 76.96; H, 4.95; N, 4.08%

4-Cyanophenyl-3-methyl-4-hydroxybenzoate

A mixture of 4-cyanophenyl-3-methyl-4(4-benzyloxy) benzoate (10.3 g, 0.03 mole), ethyl alcohol (150 ml) and a catalyst, 5% Pd/C (3 g) was stirred and heated at 50°C in an oil bath in an atmosphere of hydrogen in a hydrogenation apparatus until the theoretical quantity of hydrogen was absorbed. The reaction mixture was filtered and the alcohol was removed by distillation under reduced pressure. This afforded a white residue which was recrystallised from toluene. Yield, 87%, m.p. 170–172°C. IR(Nujol) 3400 cm^{-1} (OH stretching) 2240 cm^{-1} (C≡N stretching) 1730 cm^{-1} (COO stretching); pmr (DMSO-d_6) δ 2.26 (s-3, ring CH_3) 6.86–7.9 (m-7, aromatic) and 9.96 (s-1, phenolic OH).

Found: C, 71.05; H, 4.3; N, 5.46% $C_{15}H_{11}O_3N$ requires C, 71.14; H, 4.34; N, 5.53%.

4-Cyanophenyl-3-methyl-4(4-*n*-hexylbenzolyoxy)benzoate

A mixture of 4-*n*-hexylbenzoic acid (2.06 g, 0.01 mole) and freshly distilled thionyl chloride (6 ml) was refluxed for 4 hours and the excess thionyl chloride was distilled under reduced pressure. A solution of 4-cyanophenyl 3-methyl-4-hydroxybenzoate (2.53 g, 0.01 mole) in anhydrous pyridine (20 ml) was added to the crude acid chloride. The mixture was stirred magnetically at room temperature for 24 hours and poured onto a stirred mixture of crushed ice and concentrated hydrochloric acid when a pale brown precipitate was obtained. This was filtered, washed with water, 10% aqueous sodium hydroxide solution, water and air dried. This material was chromatographed on silica gel (BDH, India, 60–120 mesh) and eluted with chloroform. Removal of solvent from the eluate afforded a white material which was recrystallized several times from absolute ethyl alcohol until the transition temperatures were constant. Yield, 3.53 g (80%), m.p. 101.5°C. IR(Nujol) 2222 cm^{-1} ($C{\equiv}N$ stretching) 1740 cm^{-1} and 1725 cm^{-1} (COO stretching), pmr ($CDCl_3$) δ 0.95 (t-3, CH_3 of $-C_6H_{13}$) 1.1–2.0 (m-8, four CH_2's of C_6H_{13}) 2.33 (s-3, ring CH_3) 2.73 (t-2, benzyl methylene) and 7.2–8.33 (m-11, aromatic.)

Found: C, 76.17; H, 6.05; N, 3.49% $C_{28}H_{27}O_4N$ requires C, 76.19; H, 6.12; N, 3.17%.

The other members of the homologous series were prepared in an analogous manner and purified as described for compound 6 above.

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