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SYNTHESIS AND LIQUID CRYSTAL PROPERTIES OF SOME 4-n-ALKYLPHENYL 2'-CHLORO-4'-(6-n-ALKYL-2-NAPHTHOYLOXY)BENZOATES

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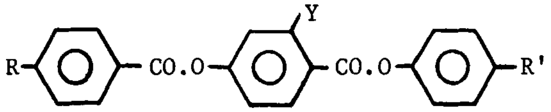
Abstract The preparation and liquid crystal properties of ten 4-n-alkylphenyl 2'-chloro-4'-(6-n-alkyl-2-naphthoyloxy)benzoates are described. The esters exhibit nematic phases of wide range.

Introduction In 1973, Van Meter and Klanderman[1,2] reported the preparation and properties of a series of substituted phenyl 4-benzoyloxybenzoates (I). R and R' were combinations of alkyl, alkoxy, halogeno or cyano substituents, and Y was either hydrogen or a methoxy or a chloro substituent.



(I)

For given terminal substituents, the melting points of the compounds were lower with Y = Cl than with Y = H.

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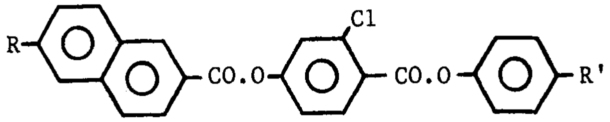
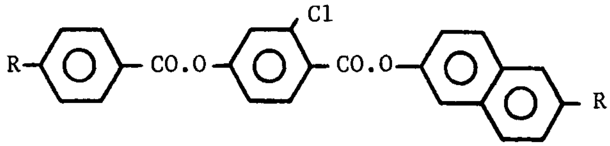
Furthermore, compounds of structure (I) with Y = Cl had lower melting points than analogous esters in which Y occupied other positions in the central ring or in which the central ring had more than one substituent. Esters of structure (I) were also lower melting than those in which the symmetry of orientation of the ester functions was different,[3] e.g., R-Ar-O.OC-Ar'-CO.O-Ar-R. Also, the lowest melting diesters of structure (I), with Y = Cl had both R and R' = alkyl.

From our earlier work[4] on mono-esters, it was known that when a 1,4-phenylene ring was replaced by a 2,6-naphthylene ring, a considerable increase in the nematic-isotropic liquid (N-I) transition temperature was obtained, but the melting point of the compound was not raised as much.

In the present study, we have combined the reasoning behind the earlier work[1,2,3] on the phenylene esters of structure (I) and our own work[4] on 2,6-disubstituted naphthalene esters, and have made the compounds (II) (4-n-alkylphenyl 2'-chloro-4'-(6-n-alkyl-2-naphthoyloxy) benzoates) and (III) (6-n-pentyl-2-naphthyl 2'-chloro-4'-(4-n-pentylbenzoyloxy)benzoate).



(II)



(III)

Results and Discussion Initially, the analogous compounds (II) and (III) with R = R' = n-pentyl were prepared. The constants for the compound (II) were: C-N, 63.8°; N-I, 190.4°, and for the compound (III) were: C-N, 94.8°;

N-I, 193.7°. These N-I values are much higher than those of the di-n-pentyl ester of structure (I). This has the constants:[1] C-N, 39°; N-I, 122°, and is the compound of lowest melting point and widest nematic range (83°) of that series.

It is noted that the N-I values of the di-n-pentyl analogues of structures (II) and (III) are similar. In our previous work[4] on mono-esters such as 4-cyanophenyl 6-alkyl-2-naphthoates (IV) and 6-cyano-2-naphthyl 4-alkylbenzoates (V), we found that when the naphthyl group was used in the phenol moiety (V), much higher (~20°) N-I values were obtained than when it was used in the acid moiety (IV). In the present work this difference is very much smaller (~3°).

The N-I values of the compounds (II) and (III) are about 70° higher than those of the analogous phenyl 2-chloro-4-benzoyloxybenzoate (I). This is also in agreement with our earlier work;[1] when the naphthyl group was in the acid moiety, N-I values 65-75° higher than those of the analogous 4-cyanophenyl 4-alkylbenzoates were obtained. However, when the naphthyl group was in the phenol moiety, the N-I values were 85-95° higher than those of the analogous phenyl benzoates. Thus, in the systems (II) and (III), the naphthyl group gives an increase in N-I value similar to that which it gave when used in the acid moiety of the cyano mono-esters,[4] (IV).

Because the N-I values of the di-n-pentyl analogues of structures (II) and (III) were similar, but the compounds had very different melting points, we decided to prepare a range of the lower melting materials of structure (II). The constants for these esters are listed in Table 1.

The widest nematic range and the lowest melting point are in fact found for the di-n-pentyl ester; the nematic range of 126.6° is 43.6° wider than that of the best of the esters of structure (I).

TABLE 1

Transition temperatures (°C) for some 4-n-alkylphenyl 2'-chloro-4'-(6-n-alkyl-2-naphthoyloxy)benzoates (II)

R	R'	C-N (or S_A)	S_A-N	N-I	Nematic range
C_4H_9	C_5H_{11}	74.5		190.4	115.9
C_4H_9	C_6H_{13}	71.1		181.0	109.9
C_5H_{11}	C_4H_9	88.3		189.0	100.7
C_5H_{11}	C_5H_{11}	63.8		190.4	126.6
C_5H_{11}	C_6H_{13}	63.7		182.8	119.1
C_6H_{13}	C_4H_9	74.2	[66.0]	179.9	113.9
C_6H_{13}	C_5H_{11}	68.6	[52.5]	178.9	126.4
C_6H_{13}	C_6H_{13}	55.0	80.4	171.0	90.6
C_7H_{15}	C_4H_9	70.5	93.3	178.5	85.2
C_7H_{15}	C_5H_{11}	52.2	95.6	176.7	81.1

[ ]: a monotropic transition temperature

Experimental 6-n-Alkyl-2-naphthoic acids: These were prepared as described earlier,[4] except for the method of separation of the reaction products from the Friedel Crafts acylation of the 2-alkylnaphthalenes. The modified procedure consisted of distilling the crude product and then isolating the 2-acetyl-6-alkylnaphthalene as its semicarbazone by pouring the isomeric mixture (35 g) into a solution of water (250 ml), anhydrous sodium acetate (35 g), semicarbazide hydrochloride (35 g) and ethanol (500 ml). The solution was stirred at 35-40° for 3 hr. On cooling for some hours, a white mass of crystals formed; these were filtered off and washed with aqueous ethanol. The semicarbazone was heated with concentrated hydrochloric acid (80 ml) and water (80 ml) for 1.5 hr. When cool, the resultant oil was extracted into diethyl ether, dried and distilled. This gave the pure 2-acetyl-6-alkylnaphthalene (50-60%) which was then oxidised to the acid.

4-n-Alkylphenols were available or prepared by standard routes.

6-n-Pentyl-naphth-2-ol: 2-methoxynaphthalene (0.3 mol) was dissolved in a cold solution of anhydrous aluminium trichloride (0.32 mol) in dry nitrobenzene (240 ml). n-Pentanoyl chloride (0.31 mol) was added dropwise with stirring which was continued at room temperature for 48 hr. The purple mixture was poured into ice/concentrated hydrochloric acid and the solvent removed by steam distillation. The residual oil was distilled under reduced pressure to yield 70% of 6-n-pentanoyl-2-methoxynaphthalene. The orientation of substitution was checked by n.m.r. spectroscopy. The ketone group was reduced by normal methods and the final product obtained by heating the 6-n-pentyl-2-methoxynaphthalene (14 g), 45% w/v hydrogen bromide in acetic acid (115 ml) and constant boiling hydrobromic acid (110 ml) for 10 hr. On cooling and diluting the reaction mixture, the precipitated product was filtered off. This was purified by column chromatography (silica gel and dichloromethane as eluent). The 6-n-pentylnaphth-2-ol was finally crystallised from hexane as colourless plates (40-60%), m.p. 104°.

Esters: As previously described,[4] these were made by interacting the acid chloride (Ar.COCl)(0.01 mol), obtained from the 6-n-alkyl-2-naphthoic acid and thionyl chloride, with the substituted phenyl 2-chloro-4-hydroxybenzoate (0.012 mol)(prepared by a standard method) in dry pyridine (80 ml) at 0°. The esters were purified by column chromatography and crystallisation from ethanol until constant transition temperatures were obtained (Mettler FP52 hot stage). Their structures and purities were checked by standard physical techniques.

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References

1 J.P. Van Meter and B.H. Klanderman, Mol. Cryst. Liquid Cryst., 22, 285 (1973).

2 United States Patent, 3, 915, 883.

3 D. Demus, H. Demus and H. Zaschke, Flüssige Kristalle in Tabellen (V.E.B. Deutscher Verlag für Grundstoffindustrie, Leipzig), 1974.

4 D. Coates and G.W. Gray, Mol. Cryst. Liquid Cryst., 37, 249 (1976).