Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: D. Coates & G. W. Gray (1978): The Liquid Crystal Properties of Some Aromatic Esters Derived From Naphthalene, Molecular Crystals and Liquid Crystals, 41:7, 197-202

To link to this article: http://dx.doi.org/10.1080/00268947808070299

Mol. Cryst. Liq. Cryst. Vol. 41 (Letters), pp. 197-202
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Printed in the United States of America

THE LIQUID CRYSTAL PROPERTIES OF SOME AROMATIC ESTERS DERIVED FROM NAPHTHALENE

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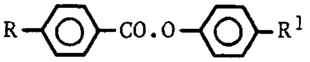
(Submitted for publication: 10th February 1978)

Abstract The 2,6-naphthylene ring system has been used to replace each of the 1,4-phenylene rings in various 4-substituted-phenyl 4-substituted-benzoates, where the substituents were alkyl and/or alkoxy. For the dialkyl esters, the N-I temperatures were increased by 60-80^{o} compared with the simpler, analogous phenyl benzoates, irrespective of the position of the 2,6-naphthylene ring. For the esters with one alkyl and one alkoxy substituent, the N-I temperatures were again higher than those of the corresponding phenyl benzoates (~60^{o}); S_A properties were quite pronounced in the 6-alkyl-2-naphthyl 4-alkoxybenzoates. When both substituents were alkoxy groups, S_C phases of quite wide thermal range were exhibited, usually preceded on cooling by a nematic and a S_A phase.

Introduction Di-substituted phenyl benzoate esters (I) are well known liquid crystal materials.[1,2] When both terminal groups, R and R^1, are alkyl groups, the esters are particularly low melting and some form enantiotropic nematic (N) phases.



(I)

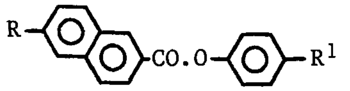
where R and/or R^1 = alkyl and/or alkoxy

The dialkoxy esters exhibit smectic C (S_C) phases, smectic A (S_A) phases and N phases. When R = alkyl and R^1 = alkoxy, N and S_C phases are exhibited, and when R = alkoxy and R^1 = alkyl, N and S_A phases are formed. The liquid crystal phases of the esters (I) are however usually of short thermal range, and indeed are, in many cases, monotropic.

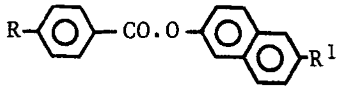
In earlier work,[3] we showed the effect of replacing a 1,4-phenylene ring in esters of type I, but where R = alkyl or alkoxy and R^1 = CN, with a 2,6-naphthylene ring. The N-I temperatures were greatly increased, the increase depending on whether the ring system of the acid moiety (increase of 65-75°) or the phenol moiety (increase of 85-95°) was replaced. The increases in melting point were much smaller (25-35°). We have now examined the situation in the cases where R and/or R^1 = alkyl and/or alkoxy.

Results and Discussion

Di-alkyl esters: Two types of ester are possible - (II) and (III).



(II)



(III)

The di-n-pentyl ester (II) gives C-N, 52.9°; N-I, 93.2° and the analogous ester (III) gives C-N, 69.5°; N-I, 91.6°. The N-I values are therefore similar. This was not the case for the alkyl-substituted cyano-esters, for which the N-I temperatures were about 20° higher for the cyanonaphthyl esters ((III) R^1 = CN) than for the corresponding cyanophenyl esters ((II) R^1 = CN). This was explained by the more extended conjugative interactions between the oxygen of the ester linkage and the cyano group in the case of the naphthyl ester. In the present case, however, the situation is different in that R^1 is a weakly electron donating alkyl group.

The melting point of the di-n-pentyl ester (III) was considerably higher than that of the analogous ester (II), and the nematic thermal range was therefore much narrower. We therefore prepared more esters of type (II), and their transition temperatures are listed in Table 1.

These esters therefore have nematic thermal ranges of up to 42.2°, whereas the corresponding phenyl benzoates usually exhibit monotropic nematic phases.

Alkyl/alkoxy esters: When the alkyl substituent on the acid moiety is replaced by an alkoxy substituent, a large difference in the properties of the two types of ester

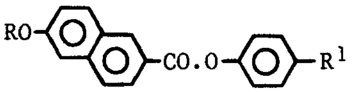
TABLE 1

Transition temperatures (°C) for some 4-alkylphenyl 6-alkyl-2-naphthoates (II)

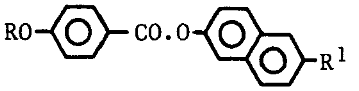
R	R^1	C-N	N-I[*]	Nematic range
n-C_4H_9	n-C_5H_{11}	40.7	82.9	42.2
n-C_4H_9	n-C_6H_{13}	47.8	72.0	24.2
n-C_5H_{11}	n-C_4H_9	47.3	84.3	37.0
n-C_5H_{11}	n-C_5H_{11}	52.9	93.2	40.3
n-C_5H_{11}	n-C_6H_{13}	49.0	82.0	33.0
n-C_6H_{13}	n-C_4H_9	53.0	75.2	22.2
n-C_6H_{13}	n-C_5H_{11}	47.8	84.4	36.6
n-C_6H_{13}	n-C_6H_{13}	57.4	77.2	19.8

[*] Compared with the corresponding phenyl benzoates, the N-I values are higher by 60-80°

((IV) and (V)) is found (see Table 2).



(IV)



(V)

TABLE 2

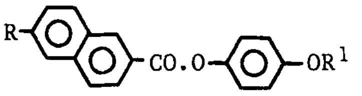
Transition temperatures (°C) for some esters of types (IV) and (V)

Type	R	R^1	C-N	S_A-N	N-I
(IV)	n-C_6H_{13}	n-C_6H_{13}	64.4	-	118[*]
(V)	n-C_6H_{13}	n-C_5H_{11}	81.0	84.9	120[†]
(V)	n-C_8H_{17}	n-C_7H_{15}	73.0	106.1	111.3

[*] The analogous phenyl benzoate has C-N, 45°; N-I 59°
The analogous phenyl benzoate has C-N, 50°; N-I 63°

The N-I temperatures for the esters (IV) and (V) are therefore similar, and about 60° higher than those of the corresponding phenyl benzoates. The S_A thermal stabilities of the esters (V) are however very much enhanced compared with the ester (IV) and its analogue in the phenyl benzoate series.

When the alkoxy and alkyl groups are reversed in the esters (V), the esters (VI) are obtained (see Table 3).



(VI)

TABLE 3

Transition temperatures (°C) for esters of type (VI)

R	R^1	C-N	S_C-N	N-I
n-C_6H_{13}	n-C_6H_{13}	76.1	-	109.7
n-C_7H_{15}	n-C_7H_{15}	83.1	(~58)	109.5

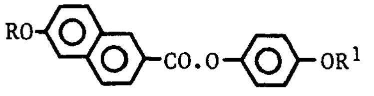
Compared with the esters (V), the esters (VI) have much lower smectic tendencies, and the type of smectic phase has changed to S_C; this change also occurs in the case of the analogous phenyl benzoates.[2] The N-I temperatures for the esters (VI) are a little lower than those of the esters (V) or the esters (IV). This agrees with results of our previous work[3,4] which showed that a terminal substituent (in the acid moiety) which is capable of conjugation with the carbonyl group of the ester function elevates the N-I temperatures.

Di-alkoxy esters: The phenyl benzoates of type (I) with R and R^1 = alkoxy, exhibit S_C, S_A and N phases. It is the S_C properties of these esters which make them interesting, and so we have prepared a range of naphthalene analogues having moderately long alkyl chains, ie, 5 to 9 carbons. The chains of each alkoxy group have been chosen of similar length, since S_C phases often attain a maximum in thermal stability when the end groups are of moderate and similar lengths.[5] The transition temperatures for the esters (VII) are given in Table 4.

These esters represent a range of interesting new materials ranging from purely nematic, to nematic plus S_C to nematic plus S_A and S_C. The S_C phases persist individually for about 20° in the temperature range 82-115°, and the esters and their eutectic mixtures are useful in studies of the S_C phase, particularly as they are rather stable compounds. The S_C phases of the analogous phenyl benzoates (I, where R and R^1 = alkoxy) occur at longer chain lengths and are of shorter thermal range (up to about 15°), with S_C-S_A temperatures which are some 20° lower than

TABLE 4

Transition temperatures (°C) for
4-alkoxyphenyl 6-alkoxy-2-naphthoates



(VII)

R	R^1	C-S	S_C-S_A	S_A-N	N-I
n-C_5H_{11}	n-C_8H_{17}	88.4	-	-	131.4
n-C_6H_{13}	n-C_7H_{15}	82.0	88.4	-	133.4
n-C_6H_{13}	n-C_8H_{17}	85.1	89.1	-	133.3
n-C_7H_{15}	n-C_7H_{15}	88.9	94.7	105.5	129.8
n-C_7H_{15}	n-C_8H_{17}	82.5	103.8	110.7	132.2
n-C_7H_{15}	n-C_9H_{19}	90.4	103.0	113.8	128.0
n-C_8H_{17}	n-C_7H_{15}	84.7	93.8	115.7	129.7
n-C_8H_{17}	n-C_8H_{17}	85.5	101.8	119.8	131.0
n-C_8H_{17}	n-C_9H_{19}	90.0	104.2	122.4	131.8
n-C_9H_{19}	n-C_8H_{17}	87.0	106.3	122.5	129.8
n-C_9H_{19}	n-C_9H_{19}	89.4	115.5	125.7	128.4

those of the esters (VII). The N-I temperatures of the corresponding phenyl benzoates are about 50-70° lower, in accordance with the results given earlier.

Experimental Esters were prepared by standard experimental methods and purified by column chromatography and crystallisation. Each product gave a single spot on thin layer chromatography and its structure was confirmed by mass spectrometry and infra-red spectroscopy.

The following information relates to the starting acids and phenols:

6-n-Alkyl-2-naphthoic acids were prepared as described earlier.[6]

6-n-Alkoxy-2-naphthoic acids were prepared by the methods of Gray and Jones.[7]

4-n-Alkylbenzoic acids. These known materials were prepared by acetylation of the n-alkylbenzenes,[8] followed by oxidation[7] of the 4-n-alkylacetophenones to the corresponding acids.

4-n-Alkoxybenzoic acids were prepared[7] from 4-hydroxybenzoic acid.

4-n-Alkylphenols were either commercially available or prepared by standard methods.

4-n-Alkoxyphenols were prepared by the method of Neubert *et al.*[9]

6-n-Alkyl-2-naphthols were prepared by the method described[6] for 6-n-pentyl-2-naphthol, mp 104°. 6-n-Heptyl-2-naphthol had mp 101°.

Acknowledgments We thank SM Kelly for technical assistance and the Ministry of Defence (UK) for financial support and permission to publish these results.

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