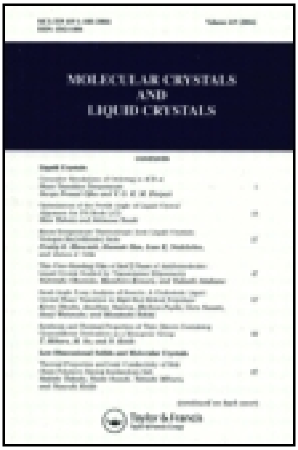

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Synthesis and Mesomorphic Properties of 4-Substituted Phenyl-4′-(4″-*n*-Alkoxy Benzoyloxy) Cinnamates

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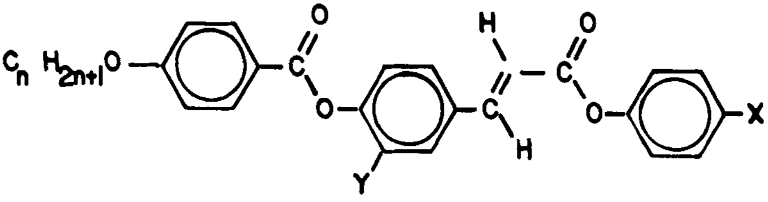
The transition temperatures and the melting enthalpies were measured for 4-substituted phenyl cinnamates. The effects of groups (CN, NO_2, Br) on the persistence of the nematic phase was found to increase with increasing polarity of the group. The lateral substitution of a methoxy group was found to decrease the nematic–isotropic transition temperatures and to inhibit the formation of the smectic phase which was present in the bromine substituted compound. The smectic phase was investigated by X-ray scattering and optical observation and is probably a smectic A phase.

INTRODUCTION

The presence of liquid crystalline phases is directly related to intermolecular forces which are a function of various structural factors, both electronic and stereochemical. These factors depend on molecular geometry, the polarity of the terminal and/or lateral groups and the bridging groups within the molecule.[1,2] Small structural modifications produce large changes in the mesomorphic behavior and can even completely eliminate the mesomorphic properties. Variation of the structure of the molecule not only changes the transition temperatures and the temperature interval of existence of the mesophase but also the type of mesophase.

Compounds with three benzene rings bridged by carboxylate groups and having polar terminal groups are interesting because some compounds of this type have a reentrant nematic especially when the terminal group is cyano.[3,4] Binary mixtures of these compounds have also been known to induce smectic phases or reentrant phases.[5]

In this communication, we will present the effects of terminal polar groups and also the effect of a substituted lateral methoxy group in the central ring of the following structure.



I

	Y	X	n
a:	H	CN	6
b:	H	NO_2	6
c:	H	Br	6
d:	H	CN	12
e:	OCH_3	CN	6
f:	OCH_3	NO_2	6
g:	OCH_3	Br	6
h:	OCH_3	CN	12

RESULTS AND DISCUSSION

The transition temperatures and melting enthalpies of the compounds without a laterally substituted methoxy group are shown in Table I.

For the non-laterally substituted compounds 1a, 1b, and 1c, we observe a high thermal stability of the nematic phase and this stability increases with the increase of polarity of the terminal group, CN > NO_2 > Br. A crystal–crystal transition was observed in all compounds with $n = 6$ and in the case of the brominated compound a smectic phase appeared in detriment of the nematic phase.

The efficiency of polar terminal groups in the formation or stability of a mesophase is very complex due to the different ways in which the group can contribute to molecular properties.[6] They can effect

TABLE I

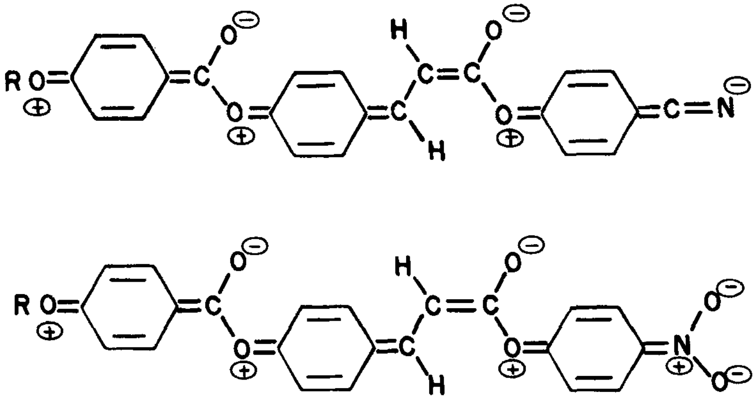
Transition temperature (°C) and corresponding enthalpies of fusion (Cal/g) of the mesogens 1a, 1b, 1c, 1d

Compound	n	Y	X	KK	K	S	N	ΔH_f
1a	6	H	CN	· 96.4	· 125.6	—	· 284.0	· 15.08
1b	6	H	NO_2	· 112.0	· 128.0	—	· 275.5	· 16.68
1c	6	H	Br	· 112.6	· 137.2	· 233.0	· 265.3	· 12.51
1d	6	H	CN	—	· 112.8	· 249.2	—	· 18.00

KK = Transition crystal–crystal
ΔH_f = Enthalpy of fusion (Cal/g)

the polarizability of the aromatic ring to which they are joined, interact attractively or repulsively with neighboring molecules or with the lateral parts of neighboring molecules. The transition temperatures of these compounds are in agreement with the idea that the presence of polar groups tends to create high melting points and high mesophase transition temperatures[7] which however is not a general rule. As the polarity of the group diminishes, the nematic–isotropic transition temperatures also diminish. This means that the intermolecular attractions increase when the polarity and polarizability of the terminal group are increased. For the compounds with the nitro group (1b) and cyano (1a) without a lateral substituent, the attractive forces are due to the interactions of the polar groups of the ester and the terminal polar group of a given molecule with polar groups of appropriate charge on other molecules. The repulsive forces are in part due to interactions between negative lateral and terminal dipoles of neighboring molecules. The carbonyl, a strongly polar group is one of the groups responsible for the increase of lateral attractions. Alternatively, the lack of repulsive forces could permit an approximation of neighboring molecules increasing the attractive forces and favoring the formation of the smectic phase as in the case of the bromo substituted compound (1c) without a lateral substituent.

The above arguments can be made more explicit as follows. The thermal stability of the nematic mesophase can be attributed to strong conjugation interactions of the aromatic rings with the terminal groups that increase interactions of the polar type. For the compounds with terminal groups, cyano (1a) and nitro (1b), it is possible to write a canonical structure such that the molecule is totally conjugated (Scheme I), and where the groups —CN and —NO_2 have a high localized electron density. However for the terminal substituted bromo compound (1c), it is not possible to write a canonical structure that leads

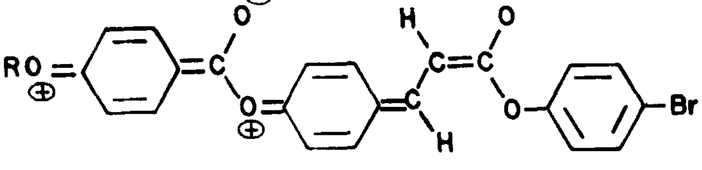


SCHEME I

to a totally conjugated molecule (Scheme II). Therefore, the lateral interaction between carbonyl groups is more important than the interaction between terminal groups which favors the formation of a smectic phase.

Table II shows the transition temperatures and melting enthalpies for the compounds with a lateral substituted methoxy group in the central ring.

The previous arguments given to explain the thermal stability of the nematic mesophase are valid for the mesogenic compounds with a laterally substituted methoxy. However, there is a destabilization of the nematic phase in all the compounds and for the bromo substituted compound (1g) the smectic phase disappears. The lowering of the phase transition temperatures must be attributed to the effect of the lateral methoxy group that increases the breadth of the mol-



SCHEME 2

TABLE II

Transition temperature (°C) and corresponding enthalpies of fusion (Cal/g) of the mesogens 1e, 1f, 1g, 1h

Compound	n	Y	X	KK	K	S		ΔH_f
1e	6	OCH_3	CN	· 123.5	· 137.5		· 203.2	· 16.90
1f	6	OCH_3	NO_2	· 57.0	· 155.3	—	· 194.4	· 21.28
1g	6	OCH_3	Br	· 120.0	· 135.8	—	· 171.5	· 18.66
1h	12	OCH_3	CN	—	· 105.4	· 169.0	· 170.2	· 19.00

KK = Transition crystal–crystal
ΔH_f = Enthalpy of fusion (Cal/g)

ecule and diminishes the attractive van Der Waals forces that are responsible for the parallel alignment of the molecules in the nematic phase. This reduces the temperature interval of the nematic and provokes the disappearance of the smectic phase. The effect of the lateral methoxy on the van Der Waals forces is greater than that of the polar units of the carbonyl groups which are also responsible in part for the stability of the mesophase.

When the alkyl chain is increased to 12 carbon atoms in the compounds with a cyano group with or without the methoxy substituent (Tables I and II), compounds 1d and 1h show a smectic phase; this is in accord with the fact that a longer alkyl chain tends to favor the formation of a smectic phase. However for the compounds 1h with a methoxy group, a nematic phase is observed in a small temperature interval. These mesogenic compounds have all the properties necessary to create favorable conditions for the induction of a reentrant mesophase; that is three rings, carboxylate groups and a terminal cyano group. However a reentrant nematic phase was not observed, not even a reentrant monotropic nematic. The NO_2 and Br groups do not tend to create reentrant mesophases although the nitro group has a dipole similar to the cyano group.

The smectic phases of compound 1c, 1d and 1h were investigated by X-ray diffraction and convergent light observations. The smectic phases show a focal-conic texture or a homeotropic texture; the convergent light observations were made on the homeotropic texture.

The diffraction pattern of the brominated compound (1c) shows one sharp small angle peak that corresponds to a distance, using Bragg's law, of $d = 29.6$ Å. A drawn-to-scale design of the molecule gives a calculated length of $l = 28.9$ Å. The ratio d/l is therefore approximately 1. Convergent light observation shows the phase to be uniaxial positive. These results imply that the phase should probably be classified as smectic A. The compounds 1d and 1h give a diffraction pattern with a sharp small angle peak corresponding to d = 45.8 Å. The calculated length of both molecules is l = 34.0 Å. The ratio $d/l \approx 1.4$ indicates layers formed of two molecules as already described for other cyano compounds.[8–12] Convergent light observation shows these phases to be unaxial positive, also. Therefore the smectic phase of these compounds should probably be classed as an interdigitated bilayer smectic A.

EXPERIMENTAL

Transition temperatures were measured and microscopic observations of textures were made using a Leitz-ortholux polarizing microscope together with a Mettler FP-2 hot stage. Transition temperatures and heats were determined with a Perkin-Elmer DSC-2. X-ray measurements were made with the sample in 0.7 mm Lindemann glass capillaries in a oven controlled to ± 1° K. The radiation was nickel filtered Cu K_α and the pattern was recorded on a flat plate camera. I.R. spectra were recorded for a KBr disc with a Perkin-Elmer model 283. NMR^{1}H spectra were measured in $CDCl_3$ solutions with tetramethylsilane as the standard on a Varian T60 spectrometer.

The 4-*n*-alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chorides were prepared as described by Neubert *et al.*[13]

The 4(4′-*n*-alkoxybenzoyloxy) benzaldehydes and 4(4′-*n*-alkoxybenzoyloxy)-3-methoxy benzaldehydes were prepared by the methods of Reference 14.

The 4(4-*n*-alkoxybenzoloxy) trans cinnamic acids and 3-methoxy-4-(4-*n*-alkoxybenzoyloxy) trans cinnamic acids were prepared by method described in Ref. 15.

The 4-substituted phenyl-4′(4″-*n*-alkoxybenzoyloxy) cinnamates(1a,b,c,d) and 4-substituted phenyl-3-methoxy 4′(4″-*n*-alkoxybenzoyloxy) cinnamates (1e, f, g, h) were prepared by the reaction of the substituted cinnamonoyl chloride with the 4-substituted phenol in pyridine solution at room temperature.

All products were purified by recrystallization from ethanol. Yields and elemental analysis results are shown in Table III. The spectroscopic data for the 4-cyano-4′(4″-*n*-hexyloxybenzoyloxy) cinnamates (1a) are: I.R. ν_{max} (K Br) 2962–2870 (CH_3), 2860–2850 (CH_2), 2220 (—CN), 1759 vs. (CO) 1605–1590 (C═C), 1280 (CO_2) 980 (C═C) and 730, rock (CH_2) cm^{-1}. ^{1}H n.m.r. δ_H (60 MHz solvent $CDCl_3$, standard Me_4Si) 0.90 (3H, *t*, CH_3), 1.16–2.00 (8H, br. m, $((CH_2)_4)$,

TABLE III

Yields and elemental analyses of compounds a,b,c,d,e,f,g.

No. Compound	Molecular Formula	Crude Yields %	Found (%) (Required)			
			C	H	N	Br
a	$C_{29}H_{27}NO_5$	85%	74.1	5.8	2.8	—
			(74.2	5.7	3.0)	—
b	$C_{28}H_{27}NO_7$	80%	68.6	5.4	2.7	—
			(68.7	5.5	2.9)	—
c	$C_{28}H_{27}O_5Br$	83%	64.3	5.1	—	15.5
			(64.3	5.3	—	15.3)
d	$C_{35}H_{39}NO_5$	81%	76.1	6.8	2.4	—
			(76.0	7.0	2.5)	—
e	$C_{30}H_{29}NO_6$	86%	72.0	5.9	2.7	—
			(72.1	5.8	2.8)	—
f	$C_{29}H_{29}NO_8$	88%	67.2	5.7	2.7	—
			(67.1	5.6	2.7)	—
g	$C_{29}H_{29}O_6Br$	83%	63.1	5.1	—	14.3
			(62.9	5.2	—	14.4)
h	$C_{36}H_{41}NO_6$	89%	74.2	7.0	2.2	—
			(74.1	7.0	2.4)	—

4.00 (2H, *t*, OCH_2), 6.83–7.96 (12H, 3q. Ar), 6.23 (H, *d*, = CH) and 8.26 (H, *d*, = CH).

The spectroscopic data for the 4-cyanophenyl-3′-methoxy-4′(-hexyloxybenzoyloxy) cinnamates. (1e) are: I.R. ν_{max} (K Br) 2960–2872 (CH_3), 2860–2859 (CH_2), 2220 (—CN), 1725 vs. (CO), 1600–1590 (C=C), 1475–1385 (CH_3), 1280 (CO_2), 980 (C=C) and 720, rock (CH_2) cm^{-1}. ^1H n.m.r. δH (60 MHz solvent $CDCl_3$, standard Me_4Si) 0.90 (3H, *t*, CH_3), 1.14–2.20 (8H, br. m, $(CH_2)_4$), 3.90 (3H, s, OCH_3), 4.10 (2H, *t*, OCH_2), 6.80–8.00 (12H, m, Ar), 6.21 (H, *d*, = CH) and 8.25 (H, *d*, = CH).

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