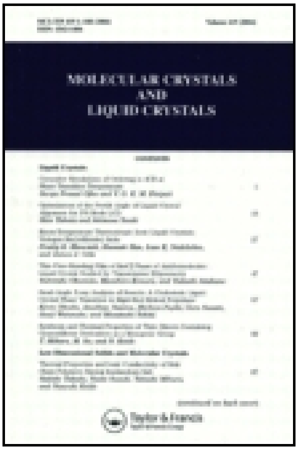

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Liquid Crystalline Properties of 4-*n*-Alkoxyphenyl 4-Nitrobenzoates

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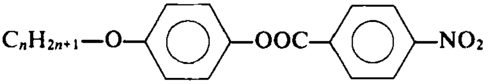
Twelve 4-alkoxyphenyl esters of 4-nitrobenzoic acid have been synthesized. The mesophases have been identified and the transition temperatures and enthalpies determined. The above series shows considerable similarity to the reverse analogues, i.e., the 4-nitrophenyl 4-*n*-alkoxybenzoates.

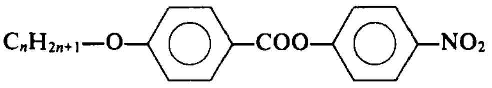
INTRODUCTION

A number of papers dealing with the effects of central and terminal groups on the liquid crystalline properties of several homologous series have been recently published.[1-3] Among others the problem of the structural reversal of the asymmetric central group has been investigated.[4]

In the present work, we decided to check the behavior of these analogues of the 4-nitrophenyl 4-*n*-alkoxybenzoates (II)—to which more and more attention[5-10] has recently been paid—in which the central ester group is reversed (I). Consequently twelve derivatives have been synthesized with alkoxy groups of varying carbon chain length (1–12 carbon atoms). Essential experiments have been carried out to determine the transition temperatures and enthalpies, as well as the macroscopic textures of the mesophases.



(I)



(II)

EXPERIMENTAL

Preparation of materials. 4-*n*-Alkoxyphenyl 4-nitrobenzoates were prepared according to the scheme:

$$C_nH_{2n+1}OH \xrightarrow{PBr_3} C_nH_{2n+1}Br \xrightarrow{HO-C_6H_4-OH} C_nH_{2n+1}-O-C_6H_4-OH$$

$$\xrightarrow[+\ \text{pyridine}]{O_2N-C_6H_4-COOH} C_nH_{2n+1}-O-C_6H_4-OOC-C_6H_4-NO_2$$

n-Alkyl bromides were prepared by using a classical method.[11] 4-Alkoxyphenols were obtained by the method of Klarman *et al.*[12]

The 4-alkoxyphenyl esters were synthesized by mixing the phenols with 4-nitrobenzoyl chloride in dry pyridine. The solution was then treated with a mixture of concentrated HCl and ice. The precipitate, after drying, was crystallized several times alternately from ethanol and hexane until chromatographic purity was achieved. The results of elemental analysis are presented in Table I.

Measuring techniques. Measurements of the transition temperatures and the identification of the mesophases were made by using a Zeiss-Jena AMPLIWAPOL polarization microscope in conjunction with a

TABLE I

Elemental analyses for 4-*n*-alkoxyphenyl 4-nitrobenzoates

Substituent C_nH_{2n+1}	Found C	Found H	Found N	Required C	Required H	Required N
CH_3	61.6	4.4	4.6	61.5	4.1	5.9
C_2H_5	62.0	5.2	5.1	62.7	4.7	4.9
C_3H_7	63.8	5.6	4.0	63.8	5.0	4.7
C_4H_9	64.6	5.3	4.2	64.8	5.4	4.4
C_5H_{11}	65.9	5.9	4.2	65.6	5.8	4.3
C_6H_{13}	66.2	6.5	4.9	66.5	6.2	4.1
C_7H_{15}	66.9	6.2	3.1	67.2	6.5	3.9
C_8H_{17}	68.0	6.8	3.5	67.9	6.8	3.8
C_9H_{19}	68.8	6.8	4.0	68.6	7.1	3.7
$C_{10}H_{21}$	69.0	7.4	3.6	69.2	7.3	3.5
$C_{11}H_{23}$	70.7	7.8	3.3	69.7	7.6	3.4
$C_{12}H_{25}$	71.0	7.9	3.4	70.2	7.8	3.3

Kofler type hot-stage and control unit. Calorimetric measurements were made by using a RIGAKU differential scanning calorimeter.

RESULTS

The majority of the compounds prepared exhibit liquid crystalline properties, although some of them $n = 4, 5, 6$ form only monotropic

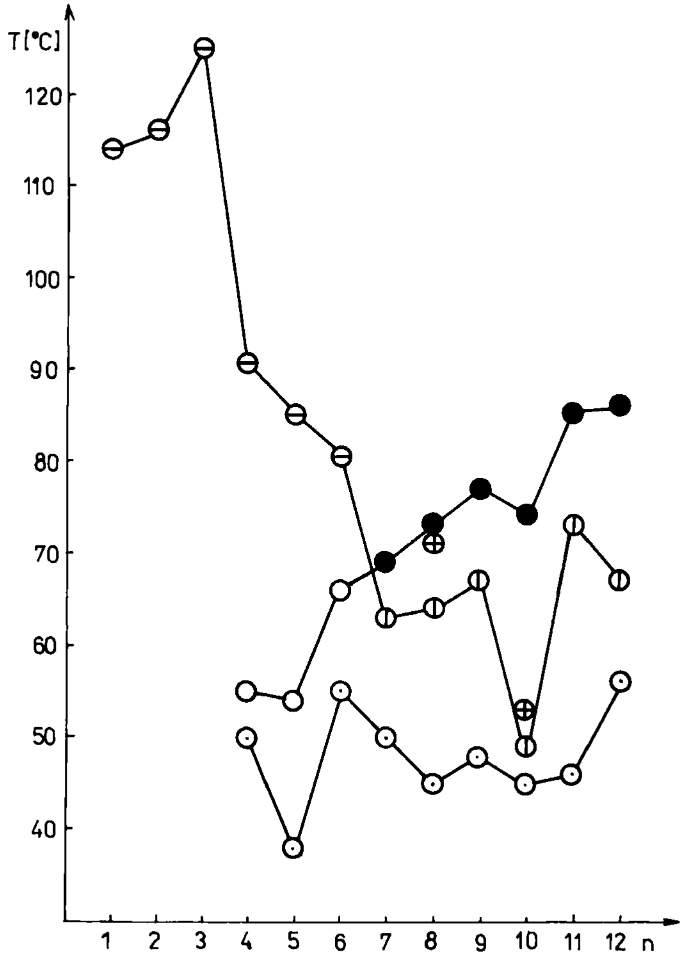


FIGURE 1 Phase transition points: transition (solid → isotropic liquid), ⊖; isotropic → nematic, ○; nematic (smectic A) → isotropic, ●; solid → nematic (smectic A), ⦶; recrystallization, ⊙; nematic → smectic A, ⊕;

TABLE II

Transition temperatures and enthalpies

	Recrystallization		Solid → S(N)		S → N		S(N) → isotropic		Solid → isotropic	
n	T[°C]	$\left[\frac{\text{kcal}}{\text{mol}}\right]$	T[°C]	$\Delta H\left[\frac{\text{kcal}}{\text{mol}}\right]$	T[°C]	$\Delta H\left[\frac{\text{kcal}}{\text{mol}}\right]$	T[°C]	$\Delta H\left[\frac{\text{kcal}}{\text{mol}}\right]$	T[°C]	$\Delta H\left[\frac{\text{kcal}}{\text{mol}}\right]$
1	—	—	—	—	—	—	—	—	114.0	—
2	—	—	—	—	—	—	—	—	116.0	—
3	—	—	—	—	—	—	—	—	125.0	—
4	50.0	—	—	—	—	—	54.8	—	90.5	—
5	38.0	6.8	—	—	—	—	54.0	0.17	85.0	13.0
6	54.8	2.3	—	—	—	—	66.0	0.17	80.5	4.14
7	50.0	3.34	63.0	2.57	—	—	69.0	0.45	—	—
8	45.0	5.46	64.0	5.46	71.0	0.01	73.2	0.55	—	—
9	48.0	8.1	67.0	10.4	—	—	77.0	0.97	—	—
10	45.3	4.85	49.0	1.41	53.0	3.93	74.0	1.05	—	—
11	46.0	5.3	73.0	11.0	—	—	85.0	0.85	—	—
12	56.0	11.26	67.0	13.0	—	—	86.0	0.86	—	—

nematic phases. The heptyl and octyl derivatives show a normal nematic liquid crystalline phase, although the temperature ranges are narrow. This is particularly true for the octyl member of the investigated series which reveals a smectic phase. Presumably it is a S_A phase because of the focal-conic texture seen using the polarization microscope. Surprisingly however, the nonyl member does not apparently show any smectic properties, but these reappear (with a low S–N transition temperature) in the decyl member. Thereafter, the undecyl and dodecyl members are purely smectic.

A plot of transition temperatures against the number of carbon atoms in the alkoxy group is shown in Figure 1. All data including transition enthalpies are collected in Table II. The results indicate that the reversal of the central ester group leads to little changes in the mutual molecular interactions. This is reflected both in the transition temperatures and, most probably, in the structures of the mesophases. The observation is very similar to that reported by Gray *et al.*[4] for other liquid crystalline compounds.

The very unexpected behavior of the C_{10} compound, as compared with its neighbors, is difficult to interpret, although analogous anomalies have been reported previously for other nitro-derivatives. Any even distribution of the S–N and S–I transition temperatures with increasing chain length is destroyed by the low S–N temperature for the C_{10} member and the absence of a smectic phase for the C_9 member. It should however be noted that (a) the occurrence of a very narrow smectic phase (too small to detect by standard techniques) for the C_9 member cannot be totally ruled out, and (b) that there is no proof that all the phases are S_A in character, i.e., a change in smectic phase type could offer some explanation of the anomalies.

The drastic drop in the smectic transition temperature for the C_{10} member is shown clearly in Figure 1 where the lower plot corresponds to the freezing points on cooling.

Acknowledgments

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