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Liquid-Crystalline 4-(trans-4′-n-Alkylcyclohexyl) Benzoates. The Effect of Terminal and Lateral Substituents on the Mesomorphic, Thermodynamic and Dielectric Properties

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Liquid-Crystalline 4-(trans-4′-*n*-Alkylcyclohexyl) Benzoates. The Effect of Terminal and Lateral Substituents on the Mesomorphic, Thermodynamic and Dielectric Properties.

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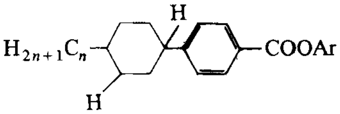
From 4-(trans-4′-*n*-alkylcyclohexyl)-benzoyl chlorides four series of esters of the general formula:

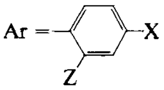
1



have been prepared.

Series I: Ar = α-, β- or γ-pyridyl.

Series II–IV:



II, $n = 5$, Z = H, X = H, F, Cl, Br, I, CHO, $CH(OCH_3)_2$, $COCH_3$, CN, $N(CH_3)_2$, NO_2, NCS, SCN, OH, $OCOCH_3$, CH_2CN, $CH_2{-}CH_2CN$, alkyl, alkoxyl, phenyl;
IIIa and IIIb, $n = 2 - 10$, Z = H, X = CN(a) and X = NO_2(b);
IVa and IVb, $n = 2 - 10$, Z = CN, X = C_5H_{11}(a) and X = C_4H_9(b).

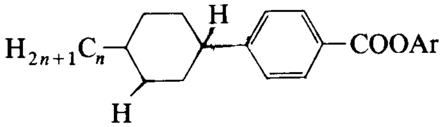
For the series of esters I–IV the phase transition temperatures and the dielectric constants ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) have been determined; for series II the enthalpies of the phase transitions have been determined also. On the basis of the results obtained the effects of the substituents on the stability of the liquid crystalline phases, their kind, and on the enthalpies and entropies of the phase transitions are discussed.

INTRODUCTION

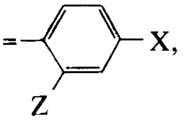
In the recent few years the investigations concentrated on the synthesis of liquid-crystalline compounds including saturated rings.[1-4] Particularly valuable properties, low viscosity and high chemical stability have been found for compounds with a trans-1,4-substituted cyclohexane ring.

In ref. [5] we described a convenient method of obtaining 4-(trans-4′-alkylcyclohexyl)benzoic acids and in a short communication [6] we discussed the mesomorphic and dielectric properties of several esters derived from these acids of the formula

1



$n = 4$–7, Ar =



X = CN, Z = H

or

X = C_5H_{11}, Z = CN

These compounds are nematics of positive (X = CN) or negative (Z = CN) dielectric anisotropy; they reveal high clearing points and fairly low melting temperatures. The wide range of the nematic phase facilitates the measurements of the physical constants of these compounds and renders easy the observation of the changes of these constants due to small modifications of their molecular structure, e.g. change of position of the substituent or introduction of a new substituent. Basing on these premises we decided to use these compounds to study the effects of a large number of various substituents, especially these in the terminal position, on the phase transition temperatures and enthalpies, and on the dielectric constants. For that purpose we synthesized the four enumerated below series of compounds of the general formula **1**:

I: $n = 5$, Ar = α-, β- or γ-pyridyl

II: $n = 5$, Z = H, X = H or F, Cl, Br, I, CHO, $CH(OCH_3)_2$, $COCH_3$, CN, NH_2, $N(CH_3)_2$, NO_2, NCS, SCN, OH, $OCOCH_3$, CH_2CN, CH_2—CH_2CN, alkyl (CH_3, C_2H_5, C_4H_9, C_5H_{11}), phenyl, alkoxy group (OCH_3, OC_8H_{17}).

IIIa: $n = 2$–10, Z = H, X = CN; IIIb: $n = 2$–10, Z = H, X = NO_2.

IVa: $n = 2$–10, Z = CN, X = C_5H_{11}; IVb: $n = 2$–10, Z = CN, X = C_4H_9

In the first and second series of esters, the alkyl substituent at the acid moiety of the esters is constant, while the terminal substituent or ring in the phenol moiety of the esters is varied.

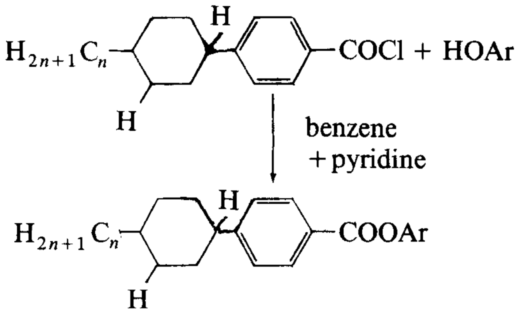
In the third and fourth series of esters tested, the terminal or lateral substituent in the phenol moiety of the molecule is constant, while the length of the alkyl chain in the acid moiety is varied.

The effects of the terminal groups on the features of mesomorphic transitions of compounds containing benzene rings have already been studied by many authors,[6-11] and are fairly well known for Schiff's bases,[6,7] esters[8-10] and biphenyls.[11] In the series of compounds with many substituents studied so far, high melting temperatures and often only monotropic mesomorphic transitions were observed. This renders difficult or even impossible the determination of many constants characterizing the mesophase and comparison of the properties of the particular mesophases. It seems that compounds **1** tested by us reveal more advantageous mesogenic properties, since we have found that with substituents differing largely in character they yield a stable enantiotropic nematic phase.

RESULTS AND DISCUSSION

Synthesis of the compounds

All the esters of the I–IV series, except these with the terminal groups NH_2, $CH(OCH_3)_2$ and OH, have been obtained in a direct, equimolecular reaction of 4-(trans-4′-*n*-alkylcyclohexyl)benzoyl chlorides with phenols (scheme 1) conducted in a benzene-pyridine solution. In the case of ester with an OH group, hydroquinone in a five fold excess was used.



Scheme 1: synthesis of the esters

The ester with the amine (NH_2) terminal group was prepared by reducing the ester with the nitro group with stannous chloride. The ester with the acetal final group was obtained by refluxing in methanol the ester with the formal (CHO) group in the presence of ammonium nitrate. This is a convenient method of preparing acetals.[12] All the esters were crystallized twice from ethanol and once from hexane and next, if necessary, from ethanol or methanol until the thin-layer chromatogram gave one spot, the melting temperature range was less than 1°, and the clearing point was constant. The structure of the esters was confirmed by elementary analysis and IR spectra.

The ester obtained from γ-hydroxypyridine is less stable than those derived from α- or β-hydroxypyridine and undergoes easily partial hydrolysis yielding a complex with the acid molecule. The instability of the esters obtained from γ-hydroxypyridine is a general feature of the esters of that phenol.[13]

MESOMORPHIC PROPERTIES

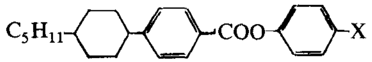
Esters of series I and II

Effects of the terminal substituents on the phase transition temperature and kind of mesophase. Tables I and II list the measured phase transition temperatures of the esters of series I and II. The numbering of the compounds in the text relates to the numbering in the tables.

All the tested esters are mesomorphic, the range of their mesophase is 10–115°, and most of them reveal only the presence of the nematic phase. Enantiotropic smectic phases were observed in the series II esters only for compounds with the terminal groups: $CH(OCH_3)_2$,

TABLE I

Phase transition temperatures of 4-(trans-4′-*n*-pentylcyclohexyl) benzoates:


(series II)

The values in the upper line have been determined using the polarization microscope with heated stage, and those in the lower line by the difference scanning calorimeter (DSC) method

Compound No 1	Terminal substituent X 2	Phase transition temperatures °C K_1 3		K_2 4		S_B 5		S_A 6		N 7		I 8	Mesophase range ΔT_M 9
1	H			·	87.5–88	—		—		·	114	·	26
				·	87.5	—		—		·	113.5		
2	F			·	92–93	—		—		·	156	·	63
		·	82	·	92	—		—		·	156	·	
3	Cl			·	104–104.5	—		—		·	191	·	86.5
		·	95	·	104	—		—		·	191	·	
4	Br			·	115.5–116	—		—		·	193	·	77
		·	111	·	116	—		—		·	193	·	
5	J			·	126.5–127.5	—		·	(126)	·	186	·	58.5
				·	127	—		·		·	185.5	·	
6	CHO			·	92.5–93	—		—		·	201.5	·	108.5
				·	92.5	—		—		·	201	·	
7	$CH(OCH_3)_2$			·	93–94	·	98	·	107.5	·	123	·	29
				·	94	·	98	·	107.5	·	124	·	
8	$COCH_3$			·	127–127.5	—		—		·	209	·	81.5
				·	127.5	—		—		·	208		
9	CN			·	111–111.5	—		—		·	226	·	114.5
		·	82	·	111	—		—		·	225.5	·	
10	NH_2			·	160–161	—		—		·	200.5		39.5
				·	160	—		—		·	200		
11	$N(CH_3)_2$	·	146–147[a]	·	162–163[a]	—		—		·	212	·	49
		·	147	·	163	—		—		·	212	·	
12	NO_2			·	99.5–100	—		—		·	201	·	101
		·	83	·	99.5	—		—		·	200.5	·	
13	NCS			·	118.5–119	—		·	129	·	235	·	106
				·	118.5	—		·	129	·	235	·	

TABLE I (*Continued*)

Compound No 1	Terminal substituent X 2	Phase transition temperatures °C											Mesophase range ΔT_M 9
		K_1 3		K_2 4		S_B 5		S_A 6		N 7		I 8	
14	SCN			·	104–105	—		—		·	125	·	20
				·	104	—		—		·	124.5	·	
15	OH			·	179–180	—		—		·	218	·	38
		·	114	·	179	—		—		·	218	·	
16	OCH_3			·	122–122.5	—		—		·	212	·	99.5
				·	123	—		—		·	213	·	
17	OC_8H_{17}			·	78–79	·	106	·	158.5	·	178	·	99
				·	78.5	·	105	·	157.5	·	178.5	·	
18	$OCOCH_3$	·	109–110[b]	·	116–117	—		·	(105)	·	234	·	117
		·	109	·	117	—				·	234	·	
19	CH_3			·	106–107	—		—		·	176	·	69
		·	99	·	106	—		—		·	175	·	
20	$C_2H_5^f$			·	91–91.5	·	107	—		·	174	·	82.5
		·	77	·	91	·	107	—		·	173	·	
21	C_4H_9			·	72.5	·	90	·	120.5	·	158	·	85.5
					74	·	87.5	·	118	·	158	·	
22	$C_5H_{11}^c$			·	73.5–74	·	99.5	·	136	·	172.5	·	98.5
				·	75	·	99	·	135.5	·	172	·	
23	CH_2CN			·	129–130	·	(124)[d]	—		·	165.5	·	35.5
		·	97[e], 100[e]	·	129, 130	·	(123)	—		·	165.5	·	
24	CH_2–CH_2–CN			·	110–111	—		—		·	185	·	74
				·	110.5	—		—		·	185	·	
25	C_6H_5			·	154–154.5	·	(121)	·	(142.5)	·	267	·	112.5
		·	111.5[e], 146[e]	·	155	·	(122)	·	(142)	·	266	·	

[a] It is supposed that the first observed transition is the one from the solid to the plastic crystal, and the second one from the plastic crystal to the nematic phase.

[b] Above that temperature the substance flows under pressure.

[c] The phase transition of that compound is according to work[26]: K 97 S 133 N 169 I.

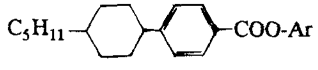
[d] The observed monotropic mesophase has a texture characteristics of a smectic E.

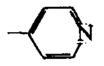
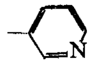
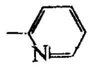
[e] Two polymorphous transformations are observed in the solid phase.

[f] After melting. In that substance a well visible phase transition was observed under the microscope during the first heating at 87–88.5° (directly after crystallization).

TABLE II

Comparison of phase transition temperatures and electric permittivities for phenyl, α-, β- and γ-pyridyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoates



Compound No	Ar	phase transition temp. °C K		N		I	Electric permittivity $\epsilon_\parallel$	$\epsilon_\perp$	$\Delta\epsilon$	ϵ_I
1		·	87.5–88	·	114	·	3.87	3.21	+0.66	3.12
26		·	97.5–98	·	108	·	30.00	15.60	+14.40	17.60
27		·	75.5–76	·	125	·	4.35	3.25	+1.10	3.15
28		·	74.5–75	·	96	·	4.20	4.71	−0.51	4.38

$\epsilon_\parallel$, $\epsilon_\perp$, $\Delta\epsilon$ refer to temperature $t - t_{N-I} = -10°$, ϵ_I refers to temperature $t - t_{N-I} = +10°$.

NCS, C_2H_5, C_4H_9, C_5H_{11} and OC_8H_{17}, and besides monotropic smectic phases were observed for compounds with the terminal groups: I, $OCOCH_3$, CH_2CN, C_6H_5. In most cases the nematic phase revealed a marble texture characterized by light and very bright colours: yellow, green, pink and blue. In esters with OH, NH_2, CHO, $CH(OCH_3)_2$, $OCOCH_3$, alkyl terminal groups a homeotropic texture was obtained, especially during cooling at the clearing point.† Compound **26** (derived from γ-hydroxypyridine) revealed only the homeotropic texture. The esters derived from non-substituted phenol, phenol with a thiocyanate (SCN) or acetal $[CH(OCH_3)_2]$ group or else from hydroxypyridines revealed the smallest range of the nematic phase (20–30°) and its lowest stability.

The widest range of the nematic phase, of 100 and more degrees, was observed for the esters with the following substituents given in the decreasing order:

$$OCOCH_3 > CN > C_6H_5 > CHO > NCS > NO_2$$

These esters have at the same time the highest clearing temperatures. The clearing temperatures of series II esters vary in the following

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†It was found that the tendency to homeotropic alignment decreases with increasing crystallization number.

order depending on the type of substituent:

$$C_6H_5 > NCS \approx OCOCH_3 > CN > OH > OCH_3 \approx N(CH_3)_2 >$$

$$COCH_3 > CHO \approx NO_2 \approx NH_2 > Br > Cl > CH_2{-}CH_2CN >$$

$$I > CH_3 > C_2H_5 > CH_2CN \approx F > SCN \approx CH(OCH_3)_2 > H.$$

Each of the enumerated substituents increases, though in a different degree (from 10° in the case of SCN to 150° in the case of an additional benzene ring) the clearing temperature of the ester if it is placed in position 4- of the phenol ring in the place of hydrogen.

The sequence of clearing temperatures observed in the studied series II of compounds is analogous to that observed in other series of compounds already investigated,[7-11] except for the ester with the group OH (compound **15**). The latter compound reveals a lower clearing temperature than it might be expected from the sequence observed by Dewar and Griffin for non-symmetric hydroquinone diesters.[9,10] The quoted authors found for those compounds the following order according to the clearing temperatures: $OH > CN > CH_3O \approx NO_2 > NH_2 \approx Cl \approx Br > CH_3 > F > CF_3 > H$. This lower clearing point of compound **15** is probably due to the somewhat different angular arrangement of the group OH with respect to the long axis of the molecule in the esters of series II as compared with those tested by Dewar and Griffin. As a result, the shapes of the dimers produced due to hydrogen bonds may also be different.

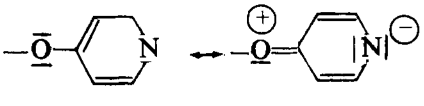
The advantage of series II of the tested esters consists in that we succeeded, for the first time, in observing in one series the enantiotropic transition N → I for such a large number of compounds differing as regards the terminal substituents and in comparing the clearing temperatures of compounds with groups not studied so far (NCS, SCN, $CH(OCH_3)_2$) or seldom studied (OH, NH_2, $N(CH_3)_2$, $COCH_3$, CHO, I, CH_2CN, $CH_2{-}CH_2CN$). The terminal group is largely responsible for the stability of the mesophase, what has been observed by the quoted authors as well as in the present work. It is not easy, however, to explain the observed order of t_{N-I}. Many different factors contribute to that order, among which the more important are: the length of the substituent, its radius and mass, rigidity, the magnitude of the spatial hindrance it presents, the dipole moment, polarizability of the substituent and the adjacent bonds, the donor-acceptor properties and ability to associate. All these factors affect the equilibrium between the attractive and repulsive forces as well as the angular correlation of the arrangement of the molecules. If one of the enumerated features dominates in the substituent introduced then the cause of the observed change of stability of the nematic phase can be defined more precisely, i.e. the high increase of the clearing temperature of ester **25** can be related to the elongation of the molecule by the benzene ring, while the low clearing temperatures of the compounds with the $CH(OCH_3)_2$, CH_2CN or SCN substituents can be related to the spatial hindrance. In the two latter cases, however, the low clearing temperatures can also be ascribed to their non-linear association, considering that the compound with the $N(CH_3)_2$ group yields a stable mesophase despite the fact that that substituent has a fairly large radius.

In the halogen series, the stability of the mesophase varying in the order F < Cl < Br is in accordance with the increasing length of the C—X bond and growing polarizability of the halogen atom and C—X bond as it has been suggested by Van der Veen.[7] The lack of the compound with C—I bond in that sequence may be attributed to that the effect related to the large radius of the iodine atom, responsible for the increase of the repulsive forces, dominates in this group over the increase of polarizability. It is difficult, however to explain as yet why the groups NO_2, NH_2 and CHO, differing so much as regards their donor-acceptor properties, ability to associate, magnitude of their dipole moment, yield esters revealing nematic phases of identical stability.

The changes of the clearing temperatures of series I esters (compounds **26, 27, 28**), which have a pyridine ring instead of a benzene one, with respect to ester **1** can be related primarily to electron effects, since the geometry of compounds **1** and **26–28** is the same. The observed changes of the mesophase stability in this series of compounds are small (10–20°) and depend on the position of the nitrogen atom in the pyridine ring with respect to the ester bond. The clearing temperature of these compounds varies in the order:

$$\beta\text{-pyridyl} > \text{phenyl} > \gamma\text{-pyridyl} > \alpha\text{-pyridyl}$$

depending on the position of the nitrogen atom in the phenol fragment of the ester. Byron *et al.* have also observed in the course of their studies of 4-(2′-pyridyl) phenyl and 4-(4′-pyridyl) phenyl alkoxybenzoates[14] that esters with α- and γ-pyridyl groups reveal lower clearing temperatures than the analogous ones with a phenyl group. The lower stability of the mesophase in compounds with α- and γ-pyridyl groups is probably also due to the relatively easy intramolecular charge displacement. This effect is strong in the case of the ester with a γ-pyridyl ring what is revealed by the large positive anisotropy of electric permittivity,



That mesomorphic effect does not occur in the β-pyridyl ring so that ring has a more pronounced electron acceptor or electron donor character in intermolecular interactions. As regards other liquid-crystalline compounds, e.g. alkylphenyl cyanobenzoates or cyanobenzylideneanilines, in which intramolecular charge displacement does not occur, higher clearing temperatures are observed as compared with analogous cyanophenyl benzoates or benzylidene-cyanoanilines in which such displacements are possible. This observation may point to a marked contribution of electron donor-acceptor forces to the mesophase stability, and is in accordance with the results obtained from studies of the properties of systems consisting of pairs of compounds which yield induced and enhanced smectics.[15–17]

Compounds with terminal groups: $CH(OCH_3)_2$, OC_8H_{17}, C_6H_5, C_4H_9, C_5H_{11} revealed two identical smectic phases (all four compounds show miscibility in both phases). The phase existing at the lower temperature was identified as smectic phase B and the one succeeding it as phase A. This was done by testing their miscibility with known smectics A and B and observing their characteristic textures. In the esters with groups OC_8H_{17} and C_6H_5 a fan texture was chiefly observed in the phases A and B, while the esters with groups $CH(OCH_3)_2$, C_4H_9 and C_5H_{11} often become arranged spontaneously in thin layers assuming a pseudoisotropic texture which is preserved in the S_A–S_B transition. The proper assignment of the phases was next confirmed by X-ray investigations of compounds with C_5H_{11} and OC_8H_{17} groups, when X-ray diagrams characteristic of smectics A and B were obtained. The results of X-ray investigations will be discussed in detail in a separate work.[18]

Compound **20**, with the ethyl group, revealed the presence of one enantiotropic smectic phase, which was identified as phase B, and one monotropic phase which was identified as G. The increase of the length of the alkyl chain causes that phase B coexists with the less ordered smectic phase A. Such a dependence of polymorphism in the smectic phase on the length of the alkyl chain was also observed in other homologous series of liquid-crystalline substances, e.g. refs. [19, 20]. Compound **20** differs from the remaining analogous compounds with a longer alkyl substituent in that it crystallizes from solvents in metastable form, which on melting transforms into a more stable crystalline modification of higher melting temperature. The DSC plot (Figure 1) shows that the compound begins to melt at 87°, upon which

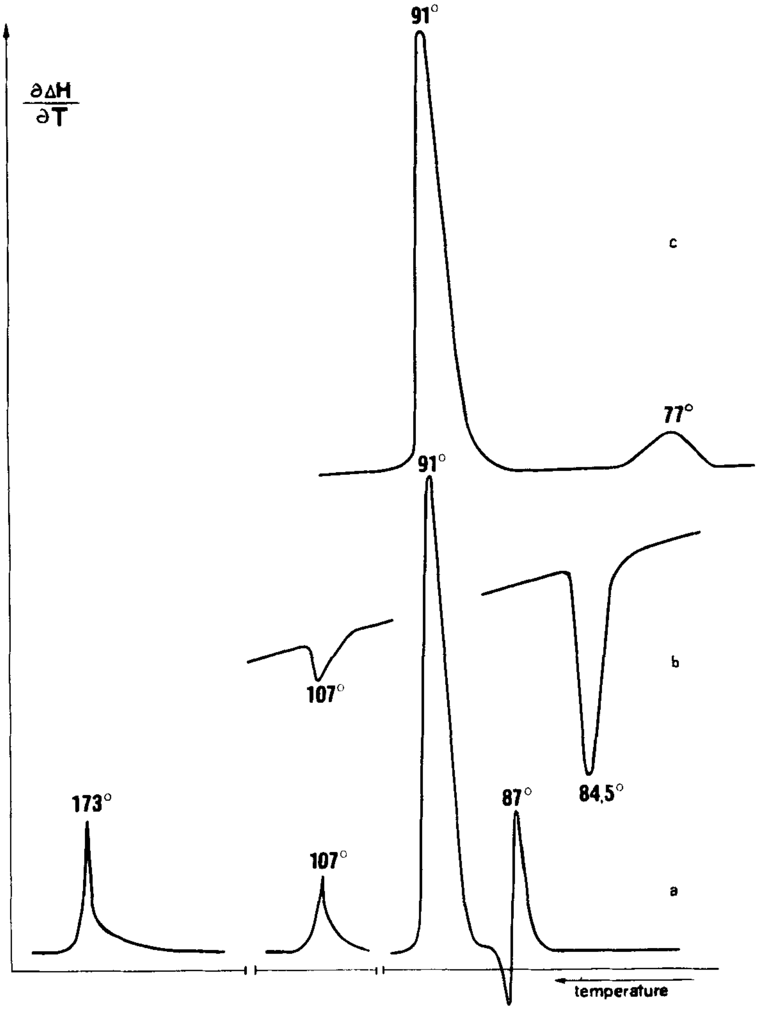


FIGURE 1 DSC plots for 4″-enthylphenyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate: (a) first heating of the sample, (b) cooling of the sample, (c) repeated heating of the sample after its preliminary crystallization.

it crystallizes transforming into a modification whose melting point is 91–91.5°. The first melting point is also well visible in microscopic observations. When a melted sample is cooled, we observe a monotropic transition at 84.5° from smectic phase B to another smectic phase. After crystallization of the sample, we observe in consecutive heating cycles one, higher melting temperature of 91.0–91.5°.

In esters of series II with polar terminal groups: I, NCS, $OCOCH_3$ we observed only one smectic phase which was identified as S_A phase (a fan texture was observed for the first two compounds, and a pseudoisotropic one for the third one). The three compounds mix readily and the phase transition $S_A \rightarrow N$ and $N \rightarrow I$ temperatures obey the additivity rule. In the range of phase S_A they are also miscible with esters substituted with groups: $CH(OCH_3)_2$, OC_8H_{17}, C_4H_9 and C_5H_{11}, however, the $S_A \rightarrow N$ transition temperatures are additive only for any pair of compounds containing group $OCOCH_3$ or $CH(OCH_3)_2$. For the remaining pairs of compounds we observe a strong increase of stability of the smectic phase A.

In ester **23** (with the CH_2CN group) we observed on cooling a monotropic, reversible phase transition N → S which is accompanied by an exothermic effect of 9.1 kJ/mole. The smectic phase produced has a mosaic texture characteristic of a smectic E. Also initial X-ray studies point to the possibility of such a structure existing. This compound differs from the remaining ones in that it has two melting points, observed both in microscopic and DSC studies. In the course of the first heating of the sample the DSC diagram reveals in the region of melting two maxima: one, stronger at 129° and one, weaker at 130°. On cooling and crystallization of the sample, repeated heating gives a diagram with both transitions better separated; the 129° maximum weakens to the advantage of the 130° one. Probably the compound consists of two rotamers which melt at two different, closely lying temperatures. That compound also reveals a transition in the solid phase in the region of 97–110° which is the result of two endothermic effects overlapping. The observed effects in kJ/mole are presented in the scheme:

Heating

$$\underbrace{K_1 \xrightarrow{97} K_2' \xrightarrow{100}}_{+10.3} K_2'' \xrightarrow[+9.1]{129} K_2''' \xrightarrow[+18]{130} N \xrightarrow[+0.9]{166.5} I$$

Cooling

$$\text{Crystallization} \underset{-16.4}{\overset{116}{\rule{2em}{0.4pt}}} S \xleftarrow[-9.1]{123} N \xleftarrow[-0.9]{166.5} I$$

The inhibition of rotation on the phenyl—CH_2CN bond was postulated by us in ref. [11] as a conclusion from the analysis of electron spectra.

In many esters from series II we observed within the solid phase range one or two polymorphous transformations.

As regards the ester with the $N(CH_3)_2$ group [compound (**11**)], some features of the transition observed in the solid phase differ from those of the remaining compounds. In the temperature interval 146–147°, where a weak endothermal effect is observed, compound **11** softens distinctly and is deformed under pressure, flowing the easier the higher is its temperature. That state reminds the smectic phase or a plastic crystal.[†] At 161–162° we observe a transition to the nematic phase accompanied by a very strong endothermal effect (22 kJ/mole). When the sample was heated not more than 1–2° above that temperature, it was found that the transition is reversible and on cooling a solid-like body is obtained with a mosaic texture resembling smectic E. However, if the sample is heated to a higher temperature, then on cooling we observe transitions at 161°. The nematic phase was observed up to about 130°, i.e. to the temperature at which the compound crystallizes. The thermal effects in kJ/mole of the described cycle of transformations can be presented by the scheme:

Heating

$$\text{Solid} \xrightarrow[+2.5]{147} \text{smectic or plastic crystal} \xrightarrow[+22]{163}$$

$$\text{nematic} \xrightarrow[+1.8]{200} \text{isotropic liquid}$$

Cooling

$$\text{Solid} \xleftarrow{130} \text{nematic} \xleftarrow{200} \text{isotropic liquid}$$

Similar properties are revealed by the ester with group $OCOCH_3$.

Series III and IV esters

Effect of the alkyl chain length on the phase transition temperature. In Table III the phase transition temperatures are compared of two homologous series of esters with terminal groups CN and NO_2. In

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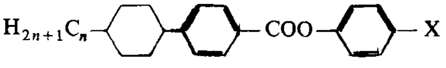
[†] The phase diagram also reminds that of the melting of a mixture of compounds whose components constitute an eutectic. It was not ascertained however that the sample consists of several compounds.

TABLE III

Phase transition temperatures for esters (III)



	Phase transition temperatures, °C													
	X = CN							X = NO_2						
Number Carbon of atoms *n*	K		S_A		N		I	K		S_A		N		I
2	·	114.5–115.5	—		·	216	·	·	114–114.5	—		·	180.5	·
3	·	123.5–124	—		·	236.5	·	·	134–134.5	—		·	205	·
	·	122^a	—		·	227^a	·							
4	·	105–106	—		·	228	·	·	97.5–98	—		·	197.5	·
	·	104^a	—		·	224^a	·							
5	·	111–111.5	—		·	226	·	·	99.5–100	—		·	201	·
	·	108^a	—		·	217^a	·							
6	·	100–101	—		·	216	·	·	98–99	—		·	191	·
	·	101^a	—		·	208^a	·							
7	·	103–104	—		·	211.5	·	·	104.5–105	—		·	193	·
8	·	99–100	·	148	·	204	·	·	98–99	·	145	·	181	·
9	·	96.5–97^b	·	165	·	298	·	·	99.5–96	·	159	·	182	·
10	·	93–94	·	167	·	183	·	·	94–95	·	165	·	174	·

[a] After patent [26].

[b] At 101° a transition to the smectic phase S_A is observed. Between 97° and 101° a smectic phase exists observable only during the heating of the sample.

both series the clearing points and melting points vary in a similar way with the growing number (*n*) of carbon atoms in the alkyl chain substituted in the cyclohexane ring. The clearing points of the series of esters with group NO_2 are lower than those of the esters with group CN by 10 to 30°. That difference is greater for the compounds with the shorter alkyl chain and decreases with the length of the alkyl. The clearing points decrease fairly quickly with the increase of *n* (see Figure 2). As a result the alternation of the clearing points as a function of the even or odd numbers *n*, characteristic of the homologous series, is observed though fairly weakly. An analogous alternation is better seen as regards the melting temperatures (what is seldom encountered) which also decrease in a very moderate way with the increasing number of carbon atoms in the alkyl chain. In both series of compounds the presence of one smectic phase is observed when the number of carbon atoms is $n \geq 8$. The mesomorphic properties of series III esters are very similar to those of the homologous series of esters obtained from 4-(4′-*n*-alkylphenyl) benzoic acid[21] (see comparison in Figure 2).

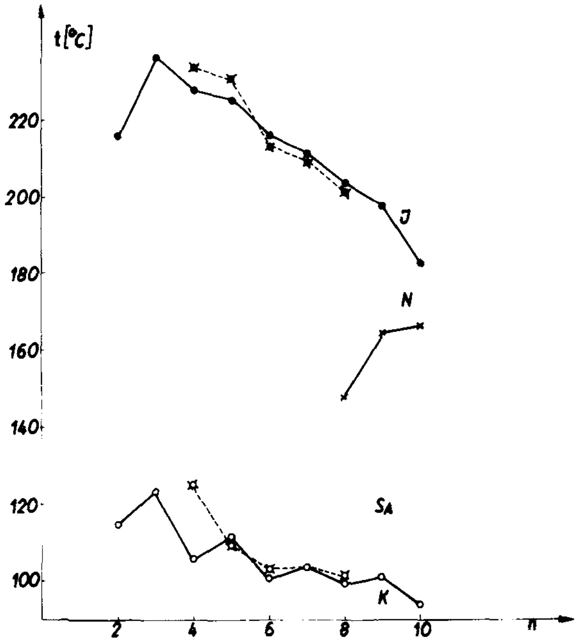


FIGURE 2 Comparison of the phase transition temperatures of the esters: 4″-cyanophenyl 4-(trans-4′-*n*-alkylcyclohexyl) benzoates obtained in the present work (solid line), and 4″-cyanophenyl 4-(4′-*n*-alkylphenyl) benzoates obtained from ref. 21 (dashed line).

The diffractogram† of the smectic phase obtained for the esters with group CN or NO_2 and $n = 10$ is characteristic of smectic phase A, what finds confirmation in the observed textures (fan-shaped, pseudo-isotropic). The mixtures of series III esters with substituents NO_2 and CN reveal additive phase transition temperatures: S → N and N → I, while their mixtures with esters belonging to series II with such terminal substituents as: alkyl, alkoksyl or phenyl reveal an enhanced smectic phase A (positive departure from additivity). Mixtures of smectic esters of series III with smectic esters of series II with terminal groups: I, NCS, $OCOCH_3$ reveal different properties. In equimolar mixtures of those esters we observe no smectic phase but only the nematic one. The destroying of the smectic structure indicates that these are different smectic phases A. In order to explain this peculiarity we measured the thicknesses (d) of the smectic layers in ester **13**

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†The X-ray scattering measurements were carried out by Dr. J. Przedmojski.

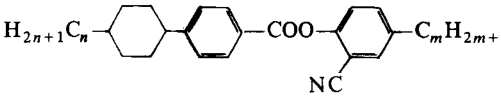
belonging to series II (X = NCS) and in esters III (n = 10, X = NO_2 or CN). It was found that d amounts to 26.7, 39.1 and 41.1 Å, respectively. Thus in the first compound the thickness of the smectic phase approximates the calculated length of the single molecule (l = 27.6 Å) while in the latter two compounds it is much larger (l = 31.1 or 31.6 Å). On this basis it can be assumed that the smectic phase in esters of series II is of A_1 type for compounds with terminal substituents X = NCS, $OCOCH_3$ or I, while in esters of series III it is of A_d type for compounds with n = 8 to n = 10 and X = NO_2 or CN. Suggestions as to the arrangement of molecules in the smectic phase will be presented in greater detail in another work.[22] The observed by us properties of the smectic phases of series II and III esters are in agreement with the earlier known properties of smectics A_1 and A_d. Sigaud *et al.* observed two different smectic phases A in a binary system composed of 4″-n-pentylphenyl 4-(4′-cyanobenzoyloxy) benzoate and terephthalidene-bis-butylaniline which differed as regards their layer thickness. The phase transition from A_1 to A_d was not accompanied by a change of texture.[22] Separation of the induced smectic regions (type A_1) from the pure component ones (type A_d) by a nematic phase was observed by Oh in the diagram of the ester-biphenyl binary system[24] and by Engelen *et al.* for the ester-Schiff bases systems.[25]

In Table IV the phase transition temperatures are summarized for two homologous series with the CN group in lateral position. Introduction of the CN group into the phenol ring in position 2 with respect to the ester bond lowered the clearing point by about 50° with respect to analogous esters without the CN group (Z = H) studied in the present work and in ref. [26]. As regards series IV of the esters, if one alkyl substituent is constant (X = C_5H_{11}), the change of the length of the other substituent from n = 2 to n = 10 hardly affects the melting temperature, since they all melt in the vicinity of 70 °C. The clearing points increase for small values of n and decrease slowly for $n \geq 5$; the alternation of the melting and clearing temperatures is well visible (Figure 3). In the analogous esters in which X = C_4H_9 is constant the melting and clearing temperatures are by about 10° lower, the former varying in a very irregular manner.

The lowest melting temperature of 36.5–37° is observed for the compound with m = 4 and n = 2. A characteristic feature of both groups of series IV (a and b) compounds are their relatively low melting temperatures when the alkyl chains are short (n = 2 to 3) and the absence of smectic phases even if the values of n are high. In the compound with n = 10 no smectic phase was observed even if the melted sample was supercooled to 0°.

TABLE IV

Phase transition temperatures in series IV esters:



Number of carbon atoms n	Phase transition temperatures, °C										
	$m = 5$						$m = 4$				
	K		N		I	ΔT^b	K		N		I
2	·	66–66.5	·	90	·		·	36.5–37	·	76.5	·
3	·	71.5–72.5	·	121	·		·	54.5–55	·	113.5	·
4	·	60.5–61	·	114.5	·	50[c]	·	59–60	·	106.5	·
5	·	69–69.5	·	123	·	49	·	49.5–50.5	·	115.5	·
6	·	61.5–62.5	·	115	·		·	52–52.5	·	107	·
7	·	70–70.5	·	115.5	·	47[c]	·	60.5–61	·	107	·
8	·	69.5–70.5	·	109.5	·						
9	·	72.5–73[a]	·	110	·						
10	·	71–72	·	106	·						

[a] Stable form; the compound crystallized from solution, melts the first time at 65.5 ÷ 66 °C and after melting crystallizes again to melt at 72.5 ÷ 73 °C.

[b] The clearing temperature difference between the non-substituted laterally with group CN ester analog of series III and ester of series III.

[c] For calculation of the temperature difference data for esters not substituted laterally were taken from patent.[26]

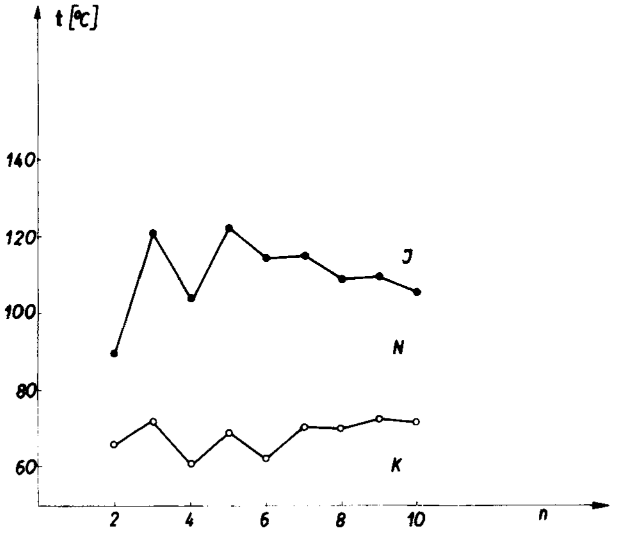


FIGURE 3 Variation of the phase transition temperature with the alkyl chain length in the homologous series of 2″-cyano-4″-pentylphenyl 4-(trans-4′-n-alkylcyclohexyl) benzoates.

Phase transition enthalpy and entropy

The phase transition enthalpies of all esters of series II were measured by the DSC method. The values of the enthalpies and entropies for compounds in which the phase transition sequence K → N → I was observed are listed in Table V, while those for compounds in which the sequence K → S → N → I occurred are summarized in Table VI. The enthalpies of all the observed phase transitions depend largely on the character of the terminal substituent in the phenol moiety of the 4-(trans-4′-*n*-pentylcyclohexyl) benzoate.

The enthalpy of polymorphous transformations observed in a solid varies from a very small value for the compound with Cl as terminal

TABLE V

Molar melting and clearing enthalpies and entropies for esters of series II. The numbering as in Table I.

Compound No	$\Delta H_{K_1 \to K_2}$ kJ mole^{-1}	$\Delta H_{K_2 \to N}$ kJ mole^{-1}	$\Delta S_{K_2 \to N}$ kJ mole^{-1} K^{-1}	$\Delta H_{N \to I}$ kJ mole^{-1}	$\Delta S_{N \to I}$ kJ mole^{-1} K^{-1}
1		23.4	64.9	0.53	1.37
2	1.8	28.5	78.1	0.88	2.05
3	very small	31.9	84.6	0.92	1.98
4	8.4	22.3	57.3	1.13	2.42
5		31.5	78.8	1.20	2.62
6		22.1	60.5	1.27	2.68
7		—	—	0.60	1.51
8		39.0	97.4	0.91	1.89
9	5.4	19.0	49.5	1.35	2.71
10		25.7	59.4	1.20	2.54
11	2.5	22.4	51.4	1.82	3.75
12	9.0	20.8	55.9	0.84	1.77
13		—	—	0.94	1.88
14		33.1	87.8	0.73	1.84
15	9.0[a]	30.7	67.9	0 ÷ 2.2[b]	0 ÷ 4.41
16		27.8	70.3	0.90	1.80
17		—	—	1.30	2.88
18	1.05	22.7	58.2	1.30	2.56
19	6.1	17.9	47.2	0.87	1.94
20	2.7	—	—	0.85	1.90
21	—	—	—	0.65	
22	—	—	—	1.01	2.30
23	10.3	27.1	67.3	0.90	2.05
24		28.4	74.0	1.32	2.88
25	5.9 0.12	29.7	69.4	1.23	2.29

[a] The DSC peak is wide.

[b] At a heating rate of 1 deg/min it is ≈ 0, and at 10 deg/min it is ≈ 2.2 kJ/mole.

group (ca. 0.1 kJ/mole) to a fairly large value for the compound with the phenyl group (13 kJ/mole). Its values are thus similar to those observed in the same compounds for phase transitions between liquid-crystalline phases (see Tables V and VI). The melting enthalpy to the mesophase ($\Delta H_{K\to N}$ and $\Delta H_{K\to S}$) in series II of the studied esters varies from 39 kJ/mole to 18 kJ/mole, and the melting entropy —from the maximum value of 97 kJ/mole · K to 47 kJ/mole · K, respectively. Those compounds can be arranged according to their molar heat of melting to the nematic phase $\Delta H_{K\to N}$ in the order:

$$\mathrm{COCH_3} > \mathrm{SCN} > \mathrm{Cl} \geq \mathrm{I} > \mathrm{OH} > \mathrm{C_6H_5} > \mathrm{F} \geq \mathrm{CH_2{-}CH_2CN}$$

$$> \mathrm{OCH_3} > \mathrm{CH_2CN} \geq \mathrm{NH_2} > \mathrm{H} > \mathrm{OCOCH_3} > \mathrm{Br} > \mathrm{CHO} > \mathrm{NO_2}$$

$$> \mathrm{CN} > \mathrm{CH_3}$$

The molar melting entropy $\Delta S_{K\to N}$ varies in the same order except for the two compounds (with terminal groups OH and C_6H_5) which probably have a different crystalline lattice ·

$$\Delta S_{K\to N}\text{:}\quad \mathrm{COCH_3} > \mathrm{SCN} > \mathrm{Cl} > \mathrm{I} > \mathrm{F} > \mathrm{CH_2{-}CH_2CN} >$$

$$\mathrm{OCH_3} > \mathrm{C_6H_5} > \mathrm{OH} > \mathrm{CH_2CN} > \mathrm{NH_2} > \mathrm{H} >$$

$$\mathrm{OCOCH_3} > \mathrm{Br} > \mathrm{CHO} > \mathrm{NO_2} > \mathrm{CN} > \mathrm{CH_3}.$$

TABLE VI

Molar phase transition enthalpy in the smectic phase range for esters of series II.

Compound No	Enthalpy (kJ mole^{-1})				
	$\Delta H_{K\to S_B}$	$\Delta H_{K\to S_A}$	$\Delta H_{S_B\to S_A}$	$\Delta H_{S_B\to N}$	$\Delta H_{S_A\to N}$
5	—	—	—	—	(0.1)
7	30.2	—	3.2	—	1.3
13	—	24.3	—	—	0.1
17	25.9	—	2.4	—	1.1
20[a]	24.9	—	—	0.45	—
21	18.6	—	0.18	—	0.53
22	18.6	—	2.6	—	0.55

[a] In the second heating cycle. In that compound we have for the monotropic transition $S_2 \to S_B$, $\Delta H = 2.7$ kJ mole^{-1}.

A part of the compounds with polar substituents of large polar moment such as CHO, NO_2 or CN require for destroying of the crystalline lattice as much energy as the compounds with groups of small dipole moments such as H or CH_3. To explain this we can assume that the crystalline lattice is built of dimers and when it melts the molecules pass to the mesomorphic phase also in dimer form. The forces keeping the dimer molecules composed of compounds with polar terminals in the crystalline lattice are analogous to those binding in that lattice the molecules with non-polar terminals. In many works it has been shown that the smectic phases consisting of molecules with terminal groups CN or NO_2 reveal a bimolecular structure;[27,28] in nematic phases associated molecules corresponding to dimers are observed;[29,30] the dimer structure of these compounds is preserved after their dissolution in non-polar solvents.[31] The low melting enthalpy and entropy is thus a consequence and at the same time a further confirmation of such a molecular structure of the compounds with groups NO_2, CN or CHO.

In the studied series II of esters the clearing enthalpies are small (0.5 to 1.0 kJ/mole) and their values are close to those found in earlier works[8-10] for other series of compounds in which the N → I transition is observed and the nematic phase exists in a wide temperature range.

We encountered difficulties in determining the clearing enthalpy of the compound with group OH. At heating rates of 1 deg/min or 2 deg/min no endothermic effect was observed in the N → I transition range, irrespective of the sensitivity of the measuring instrument used. At heating rates of 5 deg/min a small endothermic effect of about 0.1 kJ/mole is observed, whereas at a heating rate of 10 deg/min the N → I transition is accompanied by a large endothermic effect whose maximum value was estimated as equal to 2.2 kJ/mole and minimum value—assuming significant changes of the specific heat before and after the transition—as 0.7 kJ/mole. The exothermic effect observed in the course of cooling the sample is lower than the endothermic effect observed during heating and its value is not strictly reproduced. This behaviour points to internal changes taking place in the sample at temperatures close to the clearing point. Similar conclusions can be drawn from microscopic observations of the N → I transition. If a very small quantity of the tested compound is placed between the microscope slides, then instability of the clearing point is observed. Its variation in time occurs, and its value increases as the time of heating is extended. However, if a greater quantity of the compound is used, so that after melting it fills completely the space between the microscope slides, then the transition N → I is easy to detect both on cooling and on heating the sample and the transition temperature is constant. It can be supposed that this compound probably transforms into a diester releasing a hydroquinone molecule.

The series II compounds can be arranged in the following orders of decreasing molar clearing enthalpies and entropies:

$\Delta H_{N \to I}$

$N(CH_3)_2 > CN \approx CH_2{-}CH_2CN \geq OCOCH_3 > CHO > C_6H_5 >$

$NH_2 \approx I > Br > NCS > Cl \geq OCH_3 \approx COCH_3 \geq CH_2CN \approx$

$OCH_3 > F \geq CH_3 \geq \geq C_2H_5 > NO_2 > SCN > CH(OCH_3)_2 > H;$

$\Delta S_{N \to I}$

$N(CH_3)_2 > CH_2{-}CH_2CN > CN > CHO > I > OCOCH_3 \geq$

$NH_2 > Br > C_6H_5 > F > Cl > CH_3 > C_2H_5 > COCH_3 >$

$NCS > SCN > OCH_3 > NO_2 > CH(OCH_3)_2 > H$

Substitution of the hydrogen atom in the terminal position by any of the considered substituents increases the interaction energy in the nematic phase augmenting at the same time its ordering as it is seen from the greater changes of entropy accompanying the transition from the isotropic to the nematic liquid.

If one compares the orders of $\Delta H_{N \to I}$ and $\Delta S_{N \to I}$ observed in the studied series of esters with these found for other series of compounds, agreement is observed only for some of the substituents, e.g. NO_2, H, F and NH_2. Greatest differences in the order are observed for the CN and CH_3 groups. Dewar and Griffin[10] obtained relatively high values of $\Delta H_{N \to I}$ for the compounds with group CH_3 and small values for those with group CN; for the series of compounds tested by us we found the opposite. It may be a specific feature of series II of esters which have in their molecules large paraffin fragments (the pentylcyclohexyl radical), as compared with the other so far tested series of compounds, and therefore react weakly to the change of hydrogen for a CH_3 group. The high value of $\Delta H_{N \to I}$ for the ester with group CN is probably due to that the dimerization constant strongly changes with the phase transition. Low clearing enthalpies are characteristic of compounds with low thermal stability of the nematic phase, e.g. those with F, SCN, $CH(OCH_3)_2$ or H groups, as well as of compounds with high thermal stability of the nematic phase, e.g. those with groups NO_2, NCS, $COCH_3$. As we see, also in the present work we observe no correlation between $t_{N \to I}$ and $\Delta H_{N \to I}$, what is in agreement with the results of earlier works.[9,10] It can be supposed that this lack of correlation is due to that $\Delta H_{N \to I}$ is a quantity not directly proportional to the total energy of interaction in the mesophase, but only indicating the increase of energy of that interaction. The molecules in the isotropic phase have a close-range order which is different for different liquids; especially liquids composed of molecules with polar groups or groups of donor acceptor character or else groups yielding hydrogen bonds may contain a certain number of associated molecules. Transition from such a fairly well ordered isotropic liquid to the nematic liquid is followed by further, small changes of ordering and, in consequence, the ensuing energy effects are also small. In the case of liquid crystals with a large proportion of multimers in the isotropic liquid one should not expect, in our opinion, correlation between $\Delta H_{N \to I}$ and $t_{N \to I}$. However, such a correlation may probably be observed in substances which in the isotropic liquid state are poorly organized and do not yield associated molecules of greater stability. This conception is, however, solely a working hypothesis requiring verification.

DIELECTRIC PROPERTIES

Series I esters

Effect of replacement of the benzene ring by the pyridine one.

In Table 2 the values are summarized of the electric permittivity tensor components $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for the meso- and isotropic phases of series I esters at temperatures by 10° distant from the N → I phase transition temperature. In Figure 4 the temperature dependences of electric permittivity are compared for two esters: phenyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate (compound **1**) and α-pyridyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate (compound **28**).

Ester **1** reveals a moderate positive anisotropy of electric permittivity, $\Delta\epsilon = +0.66$ at temperature t, where $t - t_{N \to I} = 10°$. This is a value that should have been expected for the ester of that type. For instance Klingbiel *et al.* give the value of $\Delta\epsilon = 0.28$ for 4′-*n*-pentylphenyl 4-propylbenzoate at $t - t_{N \to I} = 19°$.[32]

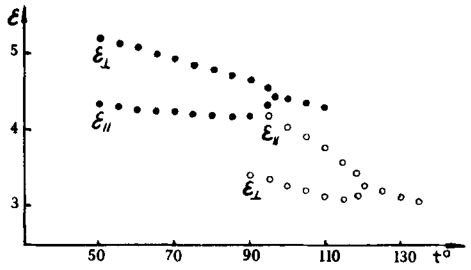


FIGURE 4 Dependence of electric permittivity on temperature for α-pyridyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate (full circles) and phenyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate (empty circles).

Replacement of phenyl by β-pyridyl in the phenol part of ester **1** produces a slight growth of $\epsilon_{\parallel}$ and in consequence leads to the increase of the positive $\Delta\epsilon$ value. Introduction of α-pyridyl caused, as it could have been expected, a somewhat greater increase of $\epsilon_{\perp}$ than of $\epsilon_{\parallel}$. As a result ester **28** reveals a weak negative anisotropy of electric permittivity, $\Delta\epsilon = -0.51$. γ-Pyridyl 4-(trans-4′-pentylcyclohexyl) benzoate (ester **26**) reveals quite different properties. It has very large values of the electric permittivity tensor parallel ($\epsilon_{\parallel} = 30.0$) and perpendicular ($\epsilon_{\perp} = 15.6$) components and a high anisotropy of electric permittivity ($\Delta\epsilon = +14.4$). This shows that the distribution of the electric charge is quite different in the γ-pyridyl group than in the α- and β-pyridyl ones. This supports the suggestion discussed earlier in the present work that intramolecular charge transfer takes place in that compound. The high values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ point at the same time to that the pyridine ring (more generally, the rings of the phenol moiety of the esters) is at a considerable angle to the long axis of the ester molecule.

Series II esters

All the esters of series II studied in the present work reveal positive anisotropy of electric permittivity, what could have been expected from theoretical considerations.[33] $\Delta\epsilon$ varies from a small (close to 0) positive value for esters with the alkyl group as terminal substituent to about +15 for the ester with the CN group. The measured values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for series II esters are summarized in Table VII for one temperature t at a chosen distance from the clearing point. For esters with clearing points below 200°, $t - t_{N\to I} = -10°$, while for esters with clearing points above 200°, $t - t_{N\to I} = -30°$ and $-70°$, the choice of the latter temperatures was due to the limitation of the measuring range maximally to 200°.

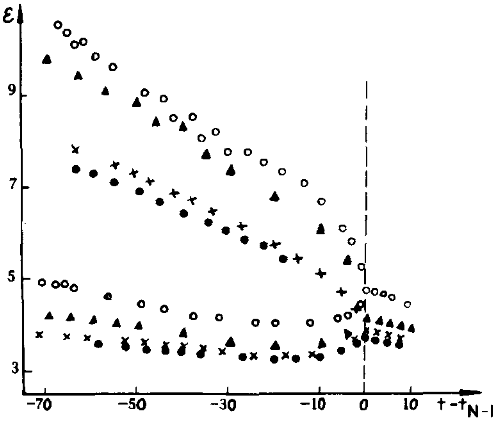


FIGURE 5 Dependence of electric permittivity on temperature for series II esters, X = F (empty circles), Cl (full triangles), Br (crosses), I (full circles).

The results obtained regarding the dielectric properties of series II esters at temperatures above 120° are still of preliminary character, since they may be burdened with a considerable error, what is explained in the experimental part. Nevertheless, we are of the opinion that they can be fully utilized for qualitative comparison of the effects of various functional groups.

The dependence of the electric permittivity of series II esters on temperature varies, as is shown in Figure 5 if they have only the nematic phase, and as is shown in Figure 6 if they have smectic phases at lower temperatures. The esters with terminal groups OCH_3, $OCOCH_3$, OH, CH_2CN, $N(CH_3)_2$ constitute an exception, and their electric permittivity as a function of temperature varies as shown in Figure 7. In these compounds, directly before the temperature at which the monotropic smectic phase exists or the compound crystallizes but still in the nematic phase, a rapid growth of the electric permittivity by several hundred per cent occurs. Further studies, having for aim a more precise explanation of the causes of that phenomenon, are in progress.

High positive values of anisotropy of electric permittivity (see Table VII) are observed beside the ester with the terminal group CN also for compounds with the groups: NO_2, $COCH_3$ and CHO. It is interesting to note that in the given series of compounds highest parallel components of electric permittivity are observed for the ester with the terminal group $COCH_3$ and not for the one with group CN as it might

TABLE VII

Anisotropy ($\Delta\epsilon$) and electric permittivity constants for esters of series II.

Compound No	X	$t - t_{N-I}$	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$
1	—H	−10	3.87	3.21	0.66
		−30	4.44	3.52	0.92
2	—F	−10	6.65	4.05	2.60
		−30	8.00	4.10	3.90
3	—Cl	−10	6.05	3.55	2.50
		−30	7.35	3.60	3.75
4	—Br	−10	5.10	3.35	1.75
		−30	6.20	3.40	2.80
5	—J	−10	4.90	3.25	1.65
		−30	6.00	3.30	2.70
6	COH	−30	11.8	5.8	6.0
		−70	16.8	7.3	9.5
7	—$CH(OCH_3)_2$	−10	3.8	3.3	0.5
8	$COCH_3$	−30	19.5	10.0	9.5
		−70	23.0	10.7	12.3
9	—CN	−30	13.7	5.8	7.9
		−70	24.4	7.5	16.9
10	—NH_2	−30	3.1	2.8	0.3
11	—$N(CH_3)_2$	−30	3.4	3.2	0.2
12	—NO_2	−30	19.5	6.5	13.0
		−70	26.2	7.0	18.2
13	—NCS	−30	6.7	3.3	3.4
		−70	9.3	3.8	5.5
14	—SCN	−10	9.7	5.2	4.5
15	—OH	−30	4.9	4.5	0.4
16	—OCH_3	−30	3.7	3.4	0.3
17	—OC_8H_{17}	−10	2.9	2.7	0.2
18	$OCOCH_3$	−30	3.6	3.4	0.2
		−70	4.0	3.6	0.4
19	—CH_3	−10	3.46	3.06	0.30
		−30	3.65	3.13	0.52
20	—C_2H_5	−10	3.15	2.86	0.29
		−30	3.30	2.96	0.34
21	—C_4H_9	−10	3.30	3.23	0.07
22	—C_5H_{11}	−10	3.18	2.98	0.20
		−30	3.40	3.20	0.20
23	—CH_2CN	−10	13.6	9.2	4.4
		−30	15.0	9.6	5.4
24	—CH_2CH_2CN	−10	11.0	6.8	4.2
		−30	12.3	7.1	5.2
25	—C_6H_5	−70	4.0	3.0	1.0

6

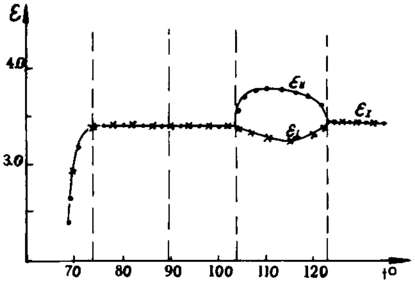


FIGURE 6 Dependence of electric permittivity on temperature for ester 7 (series II, X = $CH(OCH_3)_2$). Parallel ordering of samples (full circles), perpendicular ordering of samples (crosses). In the smectic phase random ordering of the sample was obtained.

have been expected from the values of the dipole momento of these groups ($\mu_{COCH_3} = -2.96$ D and $\mu_{CN} = -4.05$ D). The higher anisotropy of electric permittivity of the ester with group CN as compared with that with group $COCH_3$ is due to that the former has smaller perpendicular components of electric permittivity. The above facts are obvious, since we know that the esters with group CN form antiparallel pairs yielding dimers, while the molecules of esters with the terminal group $COCH_3$ probably do not have that ability.

Esters of series II with $\Delta\epsilon \geq 2$ can be arranged in the orders of decreasing values of electric permittivity anisotropy, as well as of the parallel and perpendicular components of electric permittivity as follows:

$\Delta\epsilon$ CN > NO_2 > $COCH_3$ > CHO > CH_2CN > SCN > NCS > F > Cl

$\epsilon_{\parallel}$ $COCH_3$ > CN > NO_2 > CHO > CH_2CN > CH_2—CH_2CN > SCN > NCS > F > Cl

$\epsilon_{\perp}$ $COCH_3 \gg CH_2CN$ > CN ≈ CH_2—CH_2CN > $NO_2 \geq$ CHO > SCN > F > NCS ≈ Cl

Series IV esters

For esters of this series with $n = 3$ to 7 and $m = 4$ or 5 we measured the electric permittivity in the temperature range of 60–140°. The

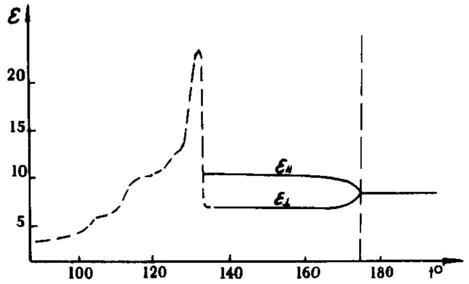


FIGURE 7 Dependence of electric permittivity on temperature for ester 23 (series II, $X = CH_2CN$).

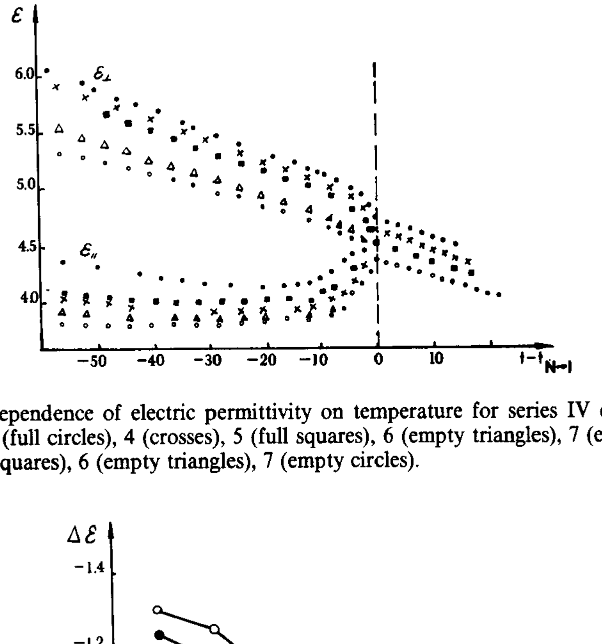


FIGURE 8 Dependence of electric permittivity on temperature for series IV esters ($m = 4$): $n = 3$ (full circles), 4 (crosses), 5 (full squares), 6 (empty triangles), 7 (empty circles). 5 (full squares), 6 (empty triangles), 7 (empty circles).

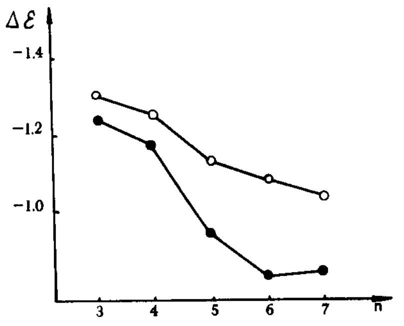


FIGURE 9 Variation of the electric permittivity anisotropy with the number of carbon atoms in alkyl chain for series IV esters and constant $m = 4$ (empty circles) or $m = 5$ (full circles).

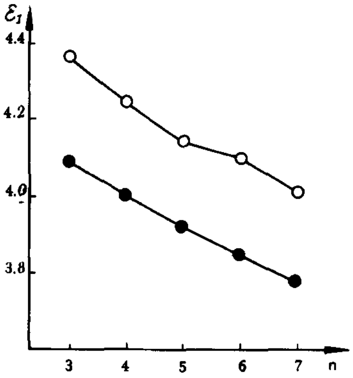


FIGURE 10 Dependence of electric permittivity in the isotropic phase for esters of series IV on the number of carbon atoms n at constant $m = 4$ (empty circles) or $m = 5$ (full circles).

electric permittivities for esters of the series with constant $m = 4$ are summarized in Figure 8. For esters IV with $m = 5$ the electric permittivity varies in a similar way. All esters of series IV show negative anisotropy in the nematic phase. For both groups of series IV esters we plotted in Figures 9 and 10 the correlations between $\Delta\epsilon$ and ϵ, and the number of carbon atoms in the alkyl chain of the acid moiety of the ester. In Table VIII the values are summarized of $\epsilon_\perp$, $\epsilon_\parallel$ and $\Delta\epsilon$ as measured at temperatures t where $t - t_{N\to I} = -20°$, and of ϵ_I for $t - t_{N\to I} = +20°$. The growth of the number of carbon atoms in the terminal alkyl chain leads in the homologous series of esters IV with negative $\Delta\epsilon$ values, as it was observed in work[34] for homologous series with positive $\Delta\epsilon$ values, to a small lowering of $\Delta\epsilon$ as well as of $\epsilon_\parallel$, $\epsilon_\perp$ and ϵ_I. This effect is probably due chiefly to the decrease of density and of the number of molecules in unit volume.

TABLE VIII

Anisotropy ($\Delta\epsilon$) and electric permittivity constants for esters of series IV.

m	4				5			
n	$\epsilon_\parallel$	$\epsilon_\perp$	$\Delta\epsilon$	ϵ_I	$\epsilon_\parallel$	$\epsilon_\perp$	$\Delta\epsilon$	ϵ_I
3	4.05	5.35	−1.30	4.37	3.76	5.00	−1.24	4.10
4	3.98	5.22	−1.24	4.25	3.78	4.95	−1.17	4.00
5	4.02	5.15	−1.13	4.15	3.81	4.75	−0.94	3.94
6	3.85	4.93	−1.08	4.10	3.72	4.64	−0.82	3.85
7	3.80	4.84	−1.04	4.02	3.58	4.42	−0.84	3.78

CONCLUSIONS

The 4-(trans-4′-alkylcyclohexyl) benzoates show a characteristic, wide range of the mesophase and a high tendency to yield nematic phases in the presence of largely differing terminal substituents. In the present work it has been shown that nematics of high thermal stability of the mesophase can be obtained not only when in the terminal position we have the group CN or NO_2, but also if the NCS, $COCH_3$, CHO, $N(CH_3)_2$, $OCOCH_3$ group is present. The mesophase is also observed in compounds with the terminal groups OH or NH_2 (what is rarely encountered) as well as with the terminal groups such as SCN, CH_2CN, $CH(OCH_3)_2$ or $CH_2—CH_2CN$, which have not been studied as yet or studied only preliminarily. High anisotropy of electric permittivity is revealed not only by esters with group CN or NO_2 in the terminal position but also by those with the $COCH_3$ or γ-pyridyl group. The latter compound being, however, of low stability. The 4-(trans-4′-*n*-alkylcyclohexyl) benzoates are very suitable for carrying out investigations of the effect of various terminal and lateral groups on the mesomorphic properties of molecules and the dielectric and thermodynamic properties of the resultant liquid-crystalline phases.

An important result of the present work is, in our opinion, the finding that the esters with terminal groups NCS, $OCOCH_3$ or I have smectic phases of thicknesses corresponding to a monomolecular arrangement in the layer. These esters, however, in distinction from other monomolecular smectics, do not mix with smectics of bimolecular type characteristic of compounds with terminal groups: CN or NO_2. In the phase diagram of the binary system consisting of, e.g., 4″-isothiocyanatophenyl 4-(trans-4′-*n*-pentylcyclohexyl) benzoate and, e.g., 4″-cyanophenyl 4-(trans-4′-*n*-decylcyclohexyl) benzoate the smectic phases of the pure components are separated by a region in which only the nematic phase exists. More detailed results regarding the properties of such binary systems will be published soon.

EXPERIMENTAL

Measurement of the phase transition temperatures and enthalpies

The phase transition temperatures and enthalpies were measured by means of a difference scanning Du Pont 910 calorimeter with a temperature programming device and Du Pont 990 recorder under isobaric conditions in an nitrogen atmosphere under normal pressure. Pure Al_2O_3 was used as reference, and the instrument was calibrated against the heat of melting of tin and indium. The calibration was checked by measuring the known diheptyloxyazoxybenzene phase transition enthalpies.[35] Weighed portions of about 10 mg were used. The heating rate was constant in the phase transition region (±15°) and amounted to 1 deg/min. The DSC diagrams obtained were integrated graphically; the integration error was 0.1% and 10% for high and small effects (clearing heats), respectively. The temperature of the endothermic effect peak maximum on the DSC diagram was assumed as the phase transition temperature.

The phase transition temperatures were determined independently by another method in which the changes of textures in polarized light of samples placed between two microscope slides are observed. A VEB Analytic (Dresden) heated stage model PHMK microscope was used, and the heating rate in the melting region was less than 1 deg/min. The phase transitions S → N and N → I were observed in a heating and cooling cycle, tending to establish thermal equilibrium between the sample and the stage.

Measurement of electric permittivity

The static electric permittivity was determined from measurements of the volume of the measuring cell, which was a flat condenser filled with the tested ester. The cell construction is described with greater detail in refs. 34, 36. The thickness of the liquid crystal layer was 220 μm, the varying measuring voltage had an amplitude of 3V and frequency 1592 Hz. The samples were ordered by means of magnetic field of induction equal to 1 T. The dependence of the electric permittivity tensor components and $\epsilon_\perp$ in the mesophase and of ϵ_I in the isotropic phase on temperature were determined up to maximally 200°. At temperatures above 120° the relative error of determining $\epsilon_\perp$, $\epsilon_\parallel$ and ϵ_I may reach in our measurements 20%. This comparatively high error is due to that it is not possible to provide fully for the effect of temperature on the working volume of the empty cell $C_0(T)$ and mounting volume $C_M(T)$. The absolute error of determining the electric permittivity anisotropy, $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$, reaches the value of 0.1. When using the measuring cell 220 μm thick (what results from the limited amounts of esters available), it was not possible to determine the electric permittivity anisotropy in the smectic phases of the tested esters. In the smectic phases we measured only a certain electric permittivity $\epsilon_S(T)$ which characterized a completely incidental ordering of the smectic, despite attempts to "freeze" the orientation.

Synthesis of the esters

General procedure. A 0.03 mole portion of the respective phenol was dissolved in 200 ml of dry benzene and 0.12 mole of anhydrous pyridine was added. Next 0.03 mole 4-(4′-*n*-pentylcyclohexyl) benzoyl chloride was added dropwise with agitation. The temperature increased by about 5° and pyridine hydrochloride precipitated. After the whole quantity of the chloride was introduced, the contents were heated for 2 hours at 60° and after cooling poured into 1 l of a 5% hydrochloric acid solution or water in the cases of compounds with a dimethylamine or pyridyl group. The benzene layer was separated, washed with water, 1% NaOH (with the exception of the compound with the OH group), again with water and dried over anhydrous $MgSO_4$. Next the contents were filtered through a layer of silica gel. After distilling off benzene in a vacuum evaporator, the compound was crystallized from ethanol, then from *n*-hexane (the hexane solution was heated at the boil with a small quantity of silica gel) and finally from ethanol. The purity of the compound was checked by thin-film chromatography, using foils coated with Merck silica gel. If the presence of contaminants was detected or the compound did not melt sharply, then the compound was repeatedly crystallized from ethanol or methanol until the melting temperature range was less than 1° and the clearing temperature constant. IR spectra were recorded for all esters and their elementary composition was determined.

The combustion data are in very good agreement with the theoretical results found from the formulae. The IR spectra also confirm the structure of the obtained esters and their high purity. In the majority of cases the purified esters have been obtained with a yield of 60–80% of the theoretical. The yields depended chiefly on the phenol purity, which affected the losses of purification of the esters by crystallization. Solely the esters obtained from γ-hydroxypyridine and 4-isothiocyanatophenol were obtained with a lower yield, i.e. 50%, what was related to their lower chemical stability.

Synthesis of the ester with the acetal group (*compound* **7**). 3 g of aldehyde-ester 6 were mixed in a mortar with 0.5 g ammonium nitrate and next heated at the boil in 400 ml methanol for 20 minutes. After cooling to room temperature, the crystals were filtered off, washed with water and recrystallized from methanol (analytical grade). The IR spectrum of the ester obtained does not reveal the band characteristic of the aldehyde group (1670 cm^{-1}) observed in ester **6**.

Anal.calcd.for $C_{27}H_{36}O_4$:

C – 76.38, H – 8.55

Found: C – 76.50, H – 8.51

Synthesis of the ester with the amine group (*compound* **10**). A mixture consisting of 5 g nitroester **12**, 7 g $SnCl_2$, 100 ml ethanol and 15 ml of concentrated hydrochloric acid is heated at the boil for 1.5 hour. Ester **12** dissolves completely, and after heating for 0.5 hour crystals precipitate. After cooling of the mixture the precipitate is filtered off and recrystallized from ethanol. The compound obtained is the aminoester hydrochloride melting with decomposition in the range of 220–240°. The compound was dissolved in hot ethanol, and the solution was cooled to 40° and treated with 25% aqueous ammonia diluted with ethanol till a basic reaction was obtained. The precipitate was filtered, dried in a desiccator over solid KOH and recrystallized from *n*-hexane.

IR spectrum, KBr: 1700 cm^{-1} ($-CO$), 3200 cm^{-1} wide ($-NH_2$); the bands at 1350 cm^{-1} and 1520 cm^{-1}, corresponding to the nitro group in compound **12**, disappear.

Anal.calcd.for $C_{24}H_{31}NO_2$:

	C – 78.86%,	H – 8.55%,	N – 3.83%
Found:	C – 78.80,	H – 8.62,	N – 3.84

In the synthesis either commercial phenols were used, or these synthesized by us according to procedures given in the literature: 4-isothiocyanatophenol,[37] 4-thiocyanatophenol,[38] octyloxyphenol,[39] 4-alkylphenols and 2-cyano-4-alkylphenols,[40] 4-cyanomethylenephenols[41] and 4-(2-cyanoethylene) phenol.[42]

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