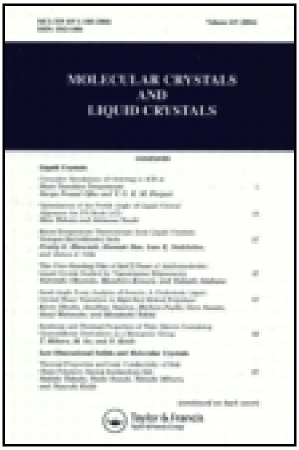

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The Effect of Carbonyl Containing Substituents in the Terminal Chains on Mesomorphic Properties in Some Aromatic Esters and Thioesters. 3. Acyloxy Groups on the Acid End

Mary E. Neubert [a], Cynthia Colby [a], Matthew C. Ezenyilimba [a], Michael R. Jirousek [a] [b], Darrin Leonhardt [a] & Katherine Leung [a] [c]

[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242

[b] Chemistry Department, Case Western Reserve University, Cleveland, Ohio

[c] Uniroyal, Mishawaka, Indiana

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The Effect of Carbonyl Containing Substituents in the Terminal Chains on Mesomorphic Properties in Some Aromatic Esters and Thioesters. 3. Acyloxy Groups on the Acid End

MARY E. NEUBERT, CYNTHIA COLBY, MATTHEW C. EZENYILIMBA, MICHAEL R. JIROUSEK,† DARRIN LEONHARDT and KATHERINE LEUNG‡

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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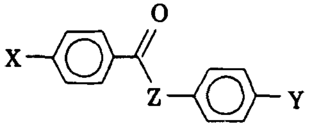
A select number of 4-alkyl and alkoxyphenyl-4′-acyloxybenzoates and phenylthiobenzoates of the type



where X = RCO_2, Y = R′ or OR′, and Z = O or S have been prepared and their mesomorphic properties determined by hot-stage polarizing microscopy. These were compared with the properties for the corresponding alkoxy esters/thioesters (X = RO). Replacement of the acid RO with RCO_2 favors the nematic phase in all series and the smectic C phase in the esters. This latter phase is slightly less favored in the thioesters. Smectic A phases were definitely less favored occurring only in the esters with Y = R′. Smectic B phases were also observed; most were monotropic. All seemed to be crystalline smectic B phases.

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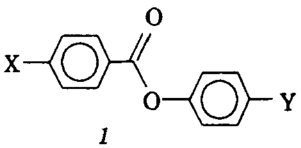
†Current address: Chemistry Department, Case Western Reserve University, Cleveland, Ohio.

‡Current address: Uniroyal, Mishawaka, Indiana.

A comparison of the mesomorphic properties of the esters with X = RCO_2 with those when Y = OCOR′ showed only small differences in these two isomeric series. The types of mesophases which were enhanced were the same in both series. Monotropic smectic B phases seemed more prevalent when Y = OCOR′ than when X = RCO_2, possibly due to lower crystallization temperatures. Melting and clearing temperatures did not vary appreciably in these two series nor from those observed when X and Y are alkyl or alkoxy groups.

INTRODUCTION

Thus far, we have studied the effect of two types of terminal chains having a carbonyl group on the phenolic end: α-keto (*1*, X = R,RO and Y = COR′)[1] and acyloxy (*1*, X = R,RO and Y = OCOR′)[2] on the mesomorphic properties of phenylbenzoates.



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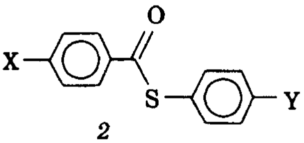


2

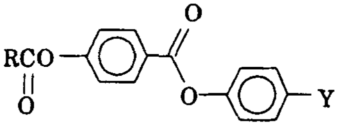
Now we wish to report the effect of an acyloxy group on the acid end in both the phenylbenzoates *1* (X = RCO_2 and Y = R′,OR′) and the thiobenzoates *2* (X = RCO_2 and Y = R′,OR′).† A few select chain lengths were prepared which we felt would give an accurate indication of the trends observed in each series, particularly those of smectic phases. When the trends were not clear from these homologs, additional ones were prepared but rarely did these show a variation from the initial trend. In fact, trends within a homologous series are among the more predictable ones observed in liquid crystals. Incorrect data for one homolog is often easily detected and shown to be wrong when rechecked. Usually the addition or subtraction of mesophases is a gradual one, unless these phases are monotropic where their observation depends on the crystallization temperature. Our choice of a chain length centered around a total number of carbon atoms of ten for RCO_2, with one homolog shorter and one longer, seemed to be adequate when combined with a short (C_3 or C_5), mid (C_7 or C_8), and long (C_{10}, C_{12}) phenolic/thiolic chain.

---

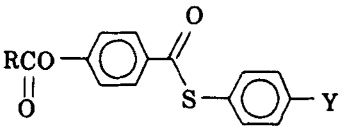
†The corresponding α-keto and acyloxy thioesters *2* (Y = COR′ and OCOR′) have not yet been studied because of the greater difficulty in preparing these compounds.

SYNTHESIS

The esters, *3*, and thioesters, *4*



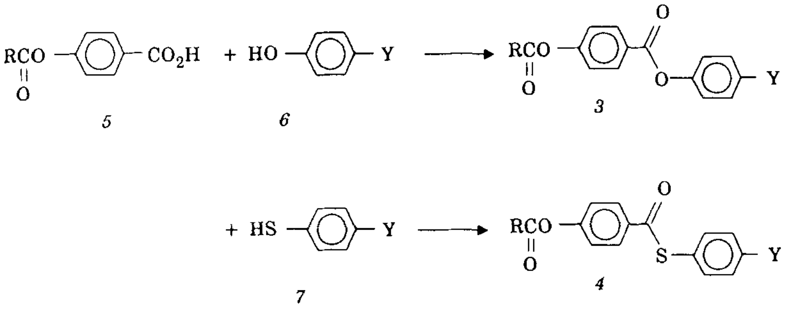
3a: Y = R'
b: Y = OR'



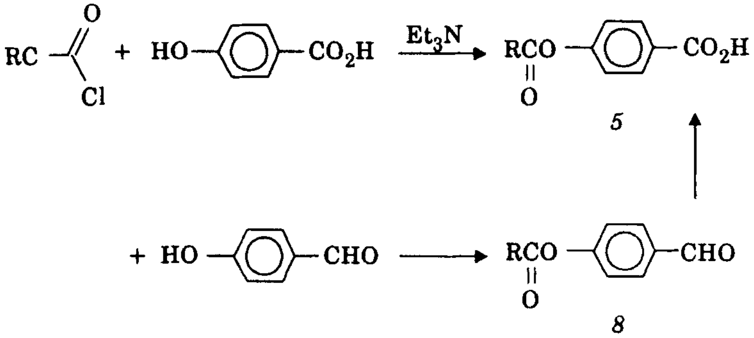
4a: Y = R'
b: Y = OR'

were prepared by esterification of the acyloxy acid, *5*, with either the phenol, *6*, or the thiol, *7*, using the carbodiimide method[2] (Scheme 1). In a few instances, an *in situ* acid chloride method was used successfully. Crude yields ranged from 86–95% and purified ones from 38–64%. Most of these compounds were purified by three recrystallizations from absolute ethanol and showed only one spot by TLC. However, with several compounds, a faint spot slightly under that for the ester/thioester was observed and could not be removed by recrystallization. It could be removed by column chromatography, but this did not seem to appreciably affect the transition temperatures.

The acyloxy acids, *5*, were prepared by acylating 4-hydroxybenzoic acid with an acid chloride using the triethylamine method[2] (Scheme 2). Crude yields ranged from 70–90% and purified ones from 17–67%. Melting points were determined by polarizing microscopy to check for mesophases, but none were observed (Table I). Melting temperatures were not always sharp. Detection of impurities in such polar compounds by TLC is difficult. The acid chloride could be prepared from these acids but distillation gave a mixture of com-



SCHEME 1



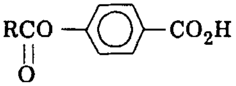
SCHEME 2

pounds. Thus, the acid chloride method was not usually used. However, when done *in situ* using crude acid chloride, it seemed to give good results.

In an attempt to eliminate the impurity observed in the esters and to be better able to control the purity of the acid, another approach was tried. Acylation of 4-hydroxybenzaldehyde gave the aldehyde, *8*, in a purified yield of 89.3% (R = C_9H_{19}) (Scheme 2). Synthesis of shorter homologs by the pyridine method was reported earlier.[3] We used the triethylamine method without any problems. The aldehyde was oxidized to the acid, *5*, in a purified yield of 72.8%. This approach allows for the removal of any unreacted starting phenol or aldehyde by extraction which could not be done in the esterification of 4-hydroxybenzoic acid. However, esters/thioesters prepared using

TABLE I

Transition Temperatures (°C) for


$RC(=O)O-C_6H_4-CO_2H$

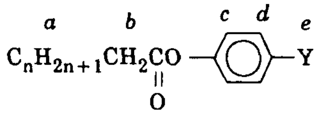
R	C	I
C_6	141.2	134.8-145.3
C_7	129.9	114.3-135.4
C_9	140.9	143.3-145.3
C_{11}	140.3	141.5-142.0

acid synthesized from the aldehyde still showed the trace of impurity by TLC.† We have been unable to obtain enough of this impurity to identify it.

IR and NMR spectra were obtained on all compounds prepared in this work to confirm their structures. The esters, *3*, showed a strong, broad singlet at 1730 cm^{-1} for the two ester absorptions whereas the thioesters, *4*, showed a strong singlet at 1750 cm^{-1} for the ester and another one at 1665 cm^{-1} for the thioester. Typical examples of NMR data are given in Table II. As we have prepared more different types of esters and thioesters, the differences in the aromatic and α-methylene regions have become more refined[4] so that these can now be used to accurately assign the protons for this region. For example, the NMR data for the ester, *3a*, shows only slightly different chemical shifts for the two types of α-CH$_2$, protons, *b* and *g*. A comparison

TABLE II

NMR Data for



Y = CHO

δ	no. of protons	multiplicity	J(Hz)	ID
9.89	1	s	---	e
7.80	2	d	9.0	d
7.15	2	d	9.0	c
2.49	2	t	7.0	b
2.03-0.5	2n + 1	m	---	a

Y = CO_2H ($CDCl_3$)

10.02	1	s	---	e
8.18	2	d	9.0	d
7.21	2	d	9.0	c
2.8	2	t	7.0	b
2.10-0.4	2n + 1	m	---	a

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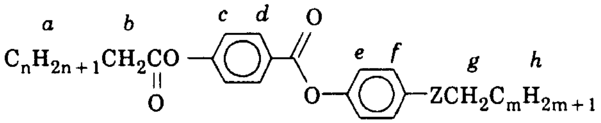
†The possibility that this impurity comes from the phenol has not been eliminated.

TABLE II

(*continued*)



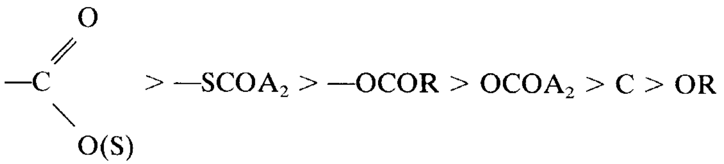
Z = nothing

8.10	2	d	9.0	d
7.10	6	d*	9.0	c,e,f
2.55	2	t	7.0	g
2.45	2	t	7.0	b
2.0-0.52	2n + 1,2m + 1	m	---	a,h

Z = O

8.19	2	d	9.0	d
7.18	2	d	9.0	c
7.00	2	d	9.0	e
6.79	2	d	9.0	f
3.90	2	t	6.0	g
2.50	2	t	7.0	b
2.10-0.50	2n + 1,2m + 1	m	---	a,h

of the chemical shift values for these protons in the acyloxy acid, aldehyde and other acyloxy esters/thioesters with those on the alkylphenolic end of the esters indicates that the *g* protons have a slightly larger δ value than the *b* protons giving the assignment shown in Table II. A similar comparison with the thioesters gives the assignments for *4a*. In the thioester, *4b*, the slant of the doublet aromatic peaks gives the assignment for the *c* and *e* protons. When there is a difference in δ for protons *ortho* to C, S, and O atoms, the values are in the order of

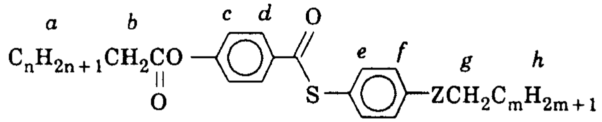


$$-\mathrm{C}\begin{matrix}{}^{/\!/\mathrm{O}}\\ {}_{\backslash\,\mathrm{O(S)}}\end{matrix} > -\mathrm{SCOA_2} > -\mathrm{OCOR} > \mathrm{OCOA_2} > \mathrm{C} > \mathrm{OR}$$

An additional observation when both types of α-CH_2 groups are present ($ArOCH_2$ and $ArCH_2$) is that the one attached to the benzene

TABLE II

(*continued*)



Z = nothing

8.11	2	d	9.0	d
7.39	2	d	9.0	f
7.14	4	d*	9.0	c,e
2.62	2	t	7.0	g
2.50	2	t	7.0	b
2.10-0.50	2n + 1,2m + 1	m	---	a,h

Z = O

8.01	2	d	9.0	d
7.32	2	d	9.0	e
7.12	2	d	9.0	c
6.85	2	d	9.0	f
3.89	2	t	6.0	g
2.48	2	t	7.0	b
2.27-0.3	2n + 1,2m + 1	m	---	a,h

***2 overlapping doublets which appear as a doublet.**

ring via an oxygen atom has a higher chemical shift by ~1 ppm and a smaller coupling constant (6.0 Hz) than one attached *via* a carbon atom with J = 7.0 Hz.† This was reported earlier,[4] but it is interesting to observe that the $ArOCOCH_2$ group also has a J value of 7.0 Hz.

Additional information on the experimental methods employed can be found in the Experimental Section.

MESOMORPHIC PROPERTIES

Phase transition temperatures for the esters (Table III) and thioesters (Table IV) prepared were determined using hot stage polarizing mi-

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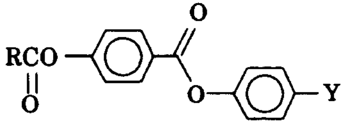
†This difference is, however, within the error of experimental measurement so that it is not always detected.

TABLE III

Transition temperatures (°C) for



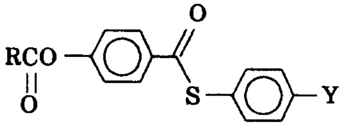
R	Y	C	S_B	S_C	S_A	N	I
C_7	C_5	81.7		86.7-87.8	---	90.0-91.1	99.6-100.7
	C_{10}	46		53.6-56.7	---	58.0-58.6	67.1-67.9
	C_{12}	41.3	58.2-59.1	60.0-63.7	---	64.5-64.7	80.0-81.0
C_9	C_3	78.4	---	---	---	---	84.0-85.3
	C_5	21.3	(45.8-46.7)	(51.5-51.7)	59.0-59.4	60.9-61.0	67.0-67.4
	C_8	34.2	(48.0-48.4)	56.8-57.5	67.2-67.4	71.0-71.7	71.7-74.4
	C_{10}	39.5	(50.1-50.7)	57.6-58.8	70.9-71.2	---	72.3-74.1
	C_{12}	52.3	(54.3-54.4)	62.0-62.9	70.1-72.1	---	74.1-75.0
C_{11}	C_3	30.3	(55.3-58.2)	---	64.4-64.7	64.7-65.2	66.3-67.5
	C_5	a	(62.2-63.2)	---	65.4-66.5	---	70.3-71.9
	C_8	40 [b]	59.4-59.9	60.3-60.7	---	---	73.3-75.4

a. a crystallization temperature could not be determined. b. estimated from a DSC scan.

R	Y	C	S_B	S_C	S_A	N	I
C_9	OC_3	71.4				71.5-72.8	78.7-79.0
	OC_5	56.9		66.6-67.3	- - -	67.7-67.9	83.4-83.7
	OC_8	58.9		66.5-67.5	- - -	82.2-82.3	89.3-89.4
	OC_{10}	65.1		74.5-74.7	- - -	86.4-87.3	89.0-90.3
C_{11}	OC_3	72.9		- - -	- - -	73.5-75.8	79.7-80.0
	OC_8	59.6	(67.0-67.4)	71.8-72.3	- - -	89.6-90.3	90.4-91.0
	OC_{10}	68.9		77.1-77.8	- - -	- - -	92.2-93.3

TABLE IV

Transition temperatures (°C) for



R	Y	C	S	S_B	S_C	N	I
C_7	C_5	31.2				57.6-59.2	89.6-93.2
	C_{12}	41.3		(57.9-57.6)	60.0-63.7	64.5-64.7	80.0-81.0
C_9	C_5	33.5		(51.8-52.4)	(59.4-59.7)	61.5-62.2	78.6-79.5
	C_8	28.4		52.7-52.2	61.2-61.8	69.3-69.9	79.1-79.5
	C_{10}	42.8		59.5-60.0	69.3-69.6	77.7-77.9	81.3-81.5
	C_{12}	45.5	(63.7)*	64.6-65.8	74.6-74.9	80.1-80.4	81.1-81.4
	OC_5	42.6		(44.4-44.6)	(58.1-58.5)	74.2-74.8	92.5-92.7
	OC_7	24.0		(43.4-43.8)	59.1-59.3	70.9-71.2	95.7-96.0
	OC_8	30.9		(45.5-45.7)	54.6-54.9	74.9-75.5	93.6-96.1
	OC_{10}	38.6		(51.4-51.6)	71.0-71.3	84.8-85.1	101.9-102.5

* See text.

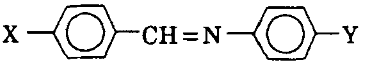
croscopy. The N, S_A, and S_C phases were identified by comparison with known textures for these phases. Conoscopic studies were used to determine whether the mesophases were uniaxial or biaxial. The S_B phases were not always so easy to identify, especially in the thioesters. Transition bars seemed to be present in all the $S_B \rightarrow S_A$ or S_C transitions, although they were not always obvious. Thus, these S_B phases are probably crystalline rather than hexatic. When doubt existed, mixture studies with the S_B phase in the known ester, *1* ($X = C_9O$, $Y = OC_4$) were done using the contact method with total miscibility being observed. However, X-ray studies are needed to confirm this identification. In the thioester, *4*, with $R = C_9$ and $Y = C_{12}$, a change in the S_B fans was observed at ~64°. The clear fans acquired more texture and the phase seemed to become more biaxial. This might also occur in some of the other homologs but could only be convincingly observed in this one. The S_B phase in the thioesters has previously been reported to be more complex than a normal S_B phase,[5] so we are not certain at this time whether this is an additional smectic phase or just changes within the S_B phase.

In some of these compounds showing S_B phases, crystallization was very slow and did not show an obvious change in texture as it usually does. In one ester, *3a* ($R = C_{11}$, $Y = C_5$), this temperature could not be determined either by microscopy or DSC. The sample was allowed to set overnight and then reheated to obtain the melting temperature.

In the esters, *3a*, with $Y = R'$; N, S_A, S_C, and S_B phases were all observed, whereas no S_A phase was found when $Y = OR$ (*3b*). This was also true in both thioester series, *4*. In both the esters and thioesters, the clearing transition was not always sharp. This could be due to the problem we had obtaining pure materials, but we could not sharpen this transition by further purification. These compounds gave good NMR spectra and showed only one spot by TLC. The nematic phase often seemed to have a low viscosity, as it tended to run towards the edge of the slide. Most transition temperatures were below 100°, as would be expected for these simple esters.

DISCUSSION

Mesomorphic properties of a few acyloxy esters of the type, *3*, were reported earlier,[6] but not enough of the longer homologs were studied to give an accurate indication of the smectic trends which occur in this series. Additionally, we needed the same homologs for our comparisons with other series. Data are also available for a series of acyloxy anils, *9b*:[7]



9a X = RO, *b* X = $\mathrm{R}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O}$

Y = R′, OR′

Since anils tend to give more mesophases at mid-chain lengths than the esters, the homologs studied probably give a better indication of the trends in this series. A comparison of the data for these two series[8] in which the same number of carbon atoms in X are compared (Table V) shows that fewer mesophases occur in the acyloxy series. Interestingly, when Y = OR′ in the acyloxy ester series, *1b*, the N phase seems more favored; longer homologs were not reported so the number of smectic phases cannot be compared.

A comparison of clearing and melting temperatures of the acyloxy esters/thioesters with those for the alkoxy esters (Table VI) indicates a small decrease in the clearing temperatures but fluctuating values for the melting temperatures. Consideration of only the effect an added carbonyl group would have on the electronic contribution of the alkoxy group on the resonance structures of the acid end, lower temperatures would be expected, as this carbonyl group would tend to attract electrons away from the benzene ring. The increased flow of electrons from the alkoxy oxygen atom is generally thought to be the reason alkoxy substituted compounds have higher transition temperatures than the alkyl ones.

A comparison of the number of mesophases observed for the acyloxy esters, *3*, with the alkoxy esters *1* (X = RO),† indicates that when Y is an alkyl group (R′) more mesophases occur in the acyloxy series (Figure 1), but the reverse is true when Y is an alkoxy group (OR′) (Figure 2). A reversal also occurs in the thioesters, *4*, but in the opposite direction (Figures 3 and 4). When Y = R′, fewer mesophases are present in the acyloxy series with the S_A phase disappearing (Figure 3), whereas when Y = OR′ more mesophases occur with the addition of a S_B phase (Figure 4). Try using these trends to predict mesomorphic properties in a new series!

The trends observed in the types of mesophases which occur seems more ordered (Table VII). The acyloxy group on the acid end favors the N phase, as shown by the longer phase length in most of the

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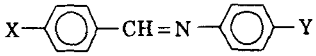
*X with the total number of carbon atoms in the chain being the same is used.

TABLE V

Transition Temperatures (°C) for

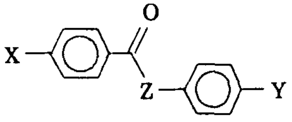


R	Y	S_B	S_C	S_A	N	I
C_7O	C_4[a]	31.5	62.5	63.6	73	75.5
C_6CO_2	C_4[b]			(68.0)	(76.0)	96.0
C_8O	C_4	39.5	66	69.5	- - -	83.5
C_7CO_2	C_4	(71.0)			(74.5)	76.0
C_7O	OC_2[c]				100.5	118
C_6CO_2	OC_2[d]				94	120

a. data for $X = RO$, $Y = R'$ is from Ref. 6
b. data for $X = RCO_2$, $Y = R'$ is from Ref. 7
c. data from Ref. 6
d. data from Ref. 8

TABLE VI

Comparison of Melting and Clearing Temperatures for



with $X = C_9CO_2$ as compared to $X = C_{10}O$[a]

Z	Y	Δmp[b]	Δclp[b]
O	C_{10}	-2.9	-2.1
	C_{12}	-21.4	-1.2
	OC_{10}	3.2	-0.2
S	C_5	1.9	-6.1
	C_8	-4.5	-6.4
	C_{10}	2.8	-5.3
	OC_5	0.3	-3.7
	OC_7	-12.1	-2.8
	OC_8	-10.9	-4.0
	OC_{10}	+ 16.6	-4.2

a. data from References 4,6,10, and 11
b. transition temperatures for $X = C_9CO_2$-$C_{10}O$

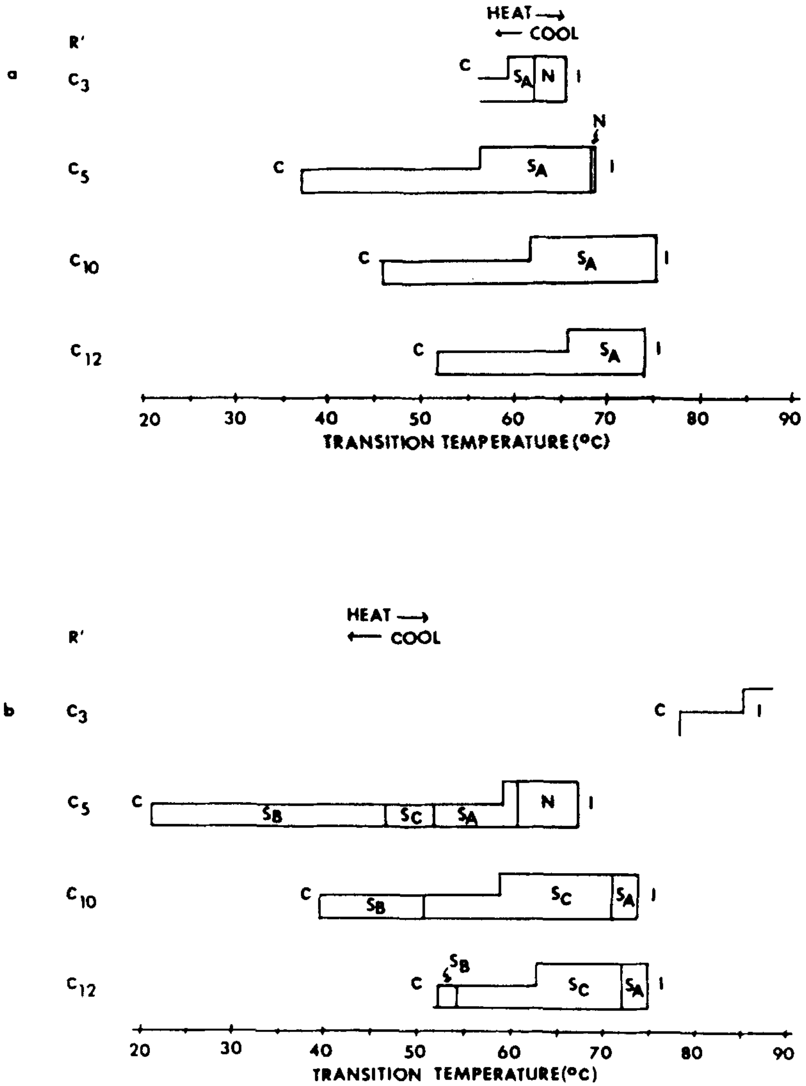
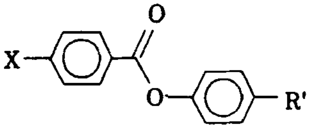


FIGURE 1 Comparison of Mesomorphic Properties for



where X = $C_{10}H_{21}O$ (a, data from reference 9) and $C_9H_{19}CO_2$(b).

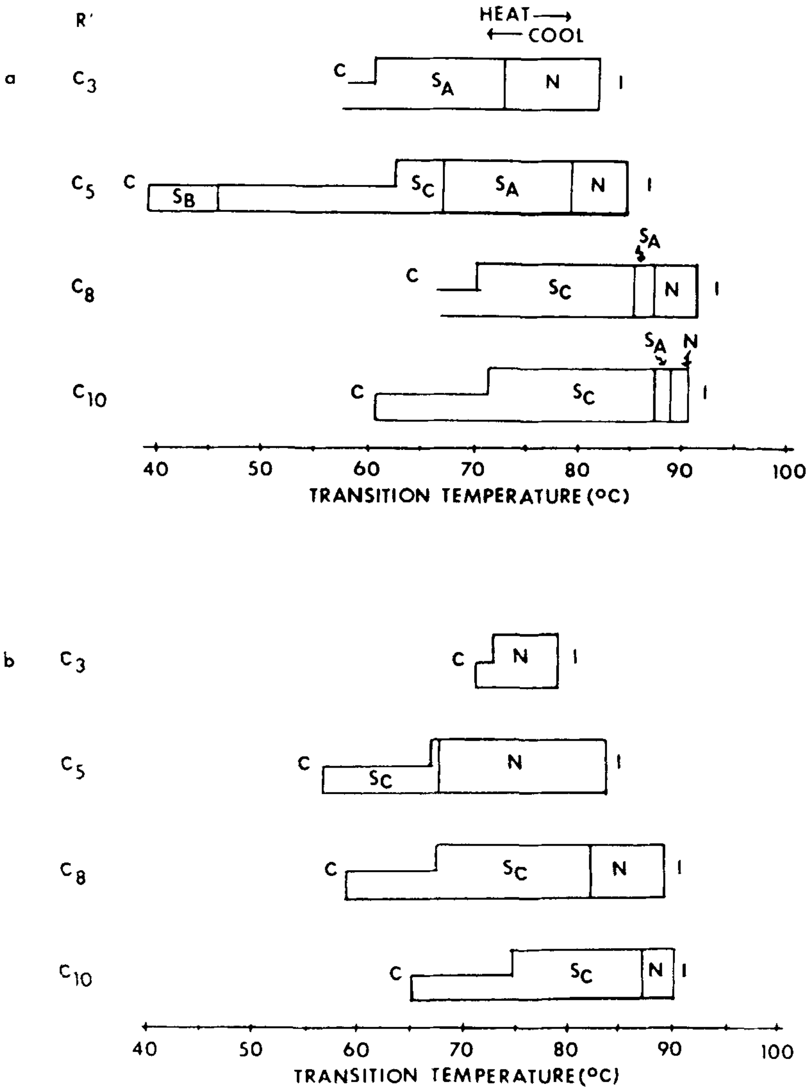
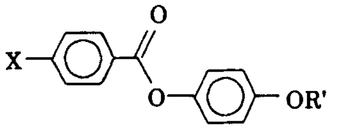


FIGURE 2 Comparison of Mesomorphic Properties for



where X = $C_{10}H_{21}O$ (a, data from references 4 and 6) and $C_9H_{19}CO_2$(b).

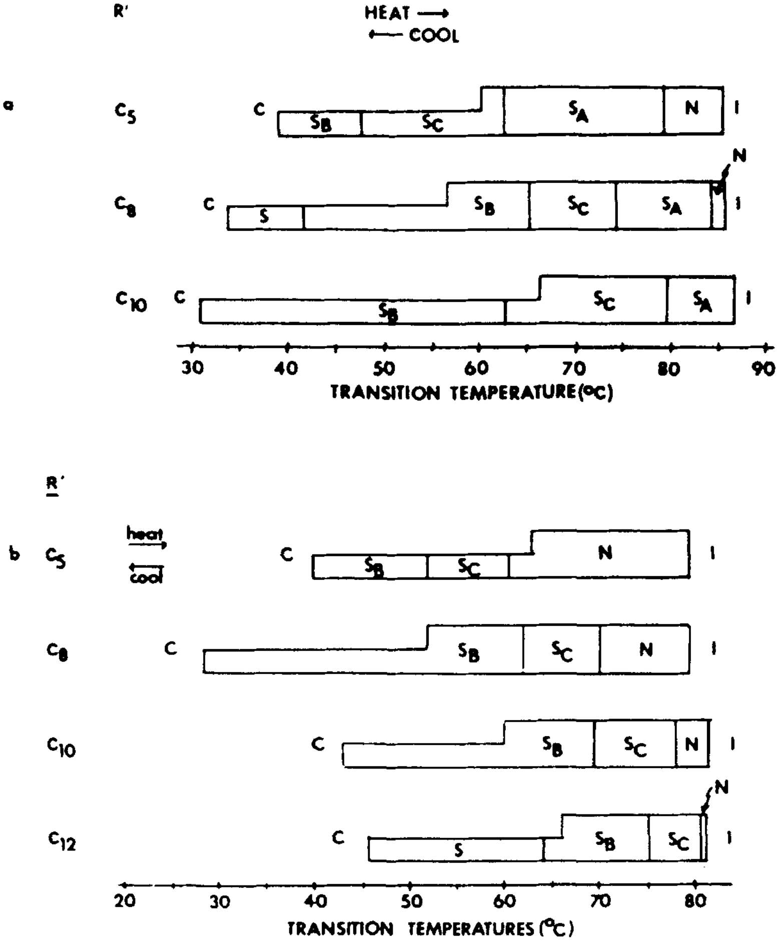
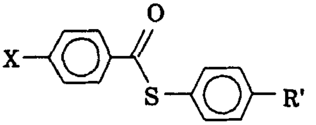


FIGURE 3 Comparison of Mesomorphic Properties for



where X = $C_{10}H_{21}O$ (a, data from reference 10) and $C_9H_{19}CO_2$(b).

acyloxy esters/thioesters. This is opposite the trend observed for this phase in the acyloxy anils. The S_A phase is definitely not favored occurring only in the esters *3a* (Y = R'). An enhancement of the S_C phase occurs in the acyloxy esters, but a slight decrease is present in the thioesters. All the acyloxy series except the esters with Y = OR'

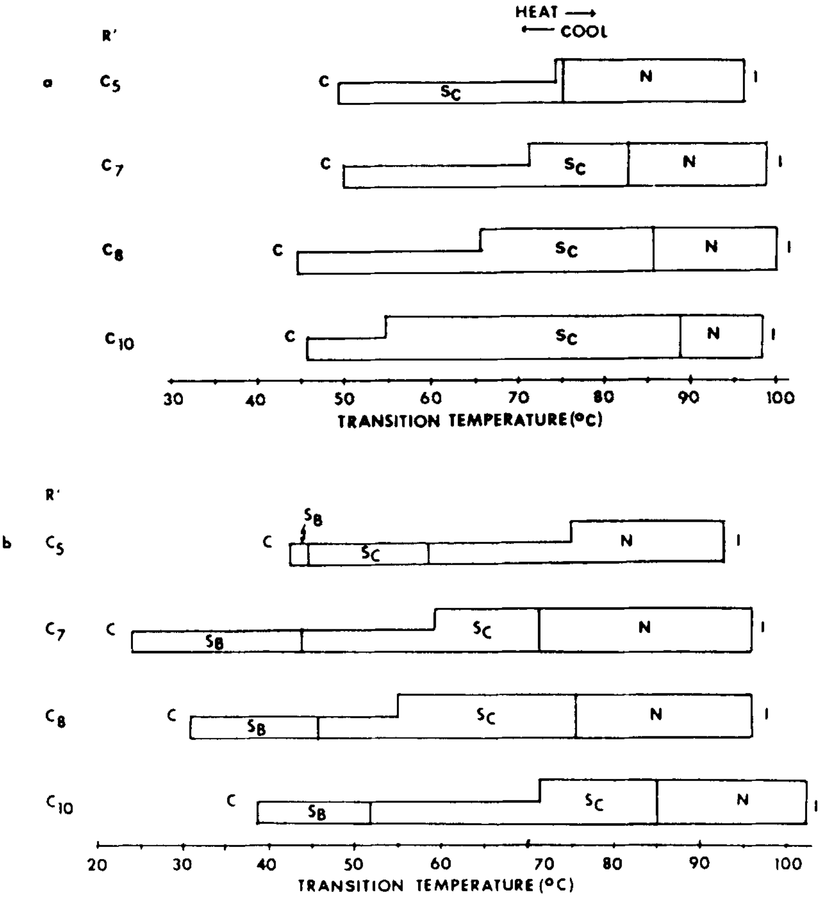
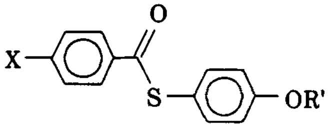


FIGURE 4 Comparison of Mesomorphic Properties for

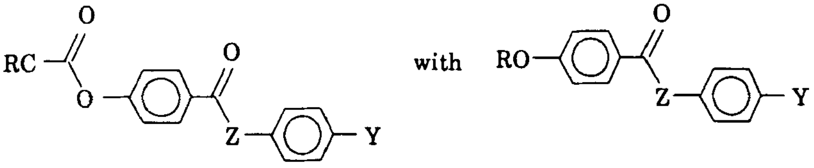


where X = $C_{10}H_{21}O$ (a, data from reference 11) and $C_9H_{19}CO_2$(b).

(*3b*) favor the S_B phase. This contrasts with the alkoxy esters with the acyloxy group on the phenolic end (*1*, X = RO, Y = OCOR') where the S_B phase is enhanced compared to when Y = OR'. This is the only difference in the mesophase trends observed for these two isomeric acyloxy series. Again, these smectic trends are opposite those reported in the acyloxy anils which seem to favor fewer smectic phases, at least in the shorter homologs.

TABLE VII

Comparison of Mesophases Observed



Z	Y	S_B	S_C	S_A	N
O	R′	+	A	-	+ +
O	OR′	-	+	D	+ +
S	R′	+	-	D	+ +
S	OR′	A	-	O	+ +

+,-	slight increase or decrease
+ + or --	larger increase or decrease
A	phase appears
D	phase disappears

One would expect that putting an acyloxy group on the acid end of these esters would have a greater effect than on the phenolic end since the alkoxy group on the phenol does not enhance polarization through resonance as it does on the acid end. However, the transition temperatures generally do not vary appreciably from the alkoxy compounds in either series nor do the types of mesophases which occur (Figure 5). In fact, the effect of an acyloxy group on the phenolic end with X = RO seems greater since it tends to lower the crystallization temperature allowing for the observance of more S_B phases. However, a comparison of these two series with the other substituent being an alkyl group shows better mesomorphic properties when the acyloxy group is on the acid end (Figure 6). This could be due to the need for a strong dipole on the acid end to obtain good mesomorphic properties.

What is it about the acyloxy group that causes an enhancement of the N and S_B phases but a disliking for the S_A phase? An increasing number of alkoxy substituents on these types of compounds seems to favor S_C over S_A phases.[12] However, if the added carbonyl in the acyloxy group is decreasing the polarizability of this group, one would expect a slight increased favor for the S_A phase, whereas there is a strong decrease. At this time, we have no explanation to offer for these trends.

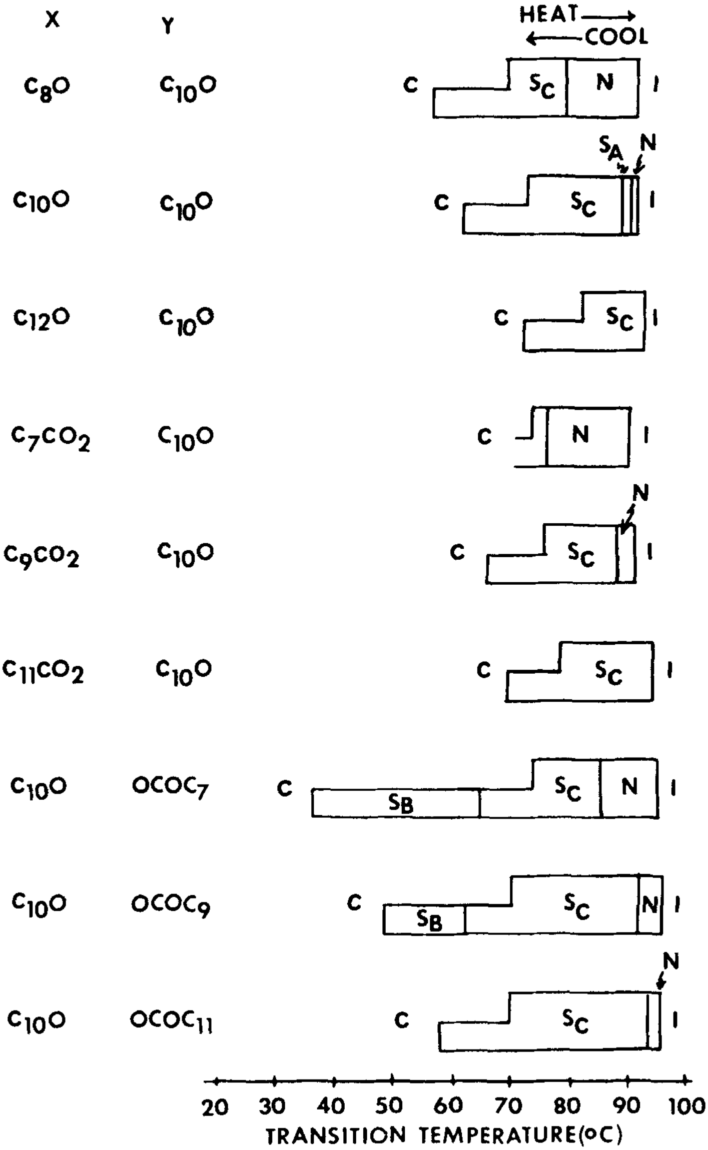
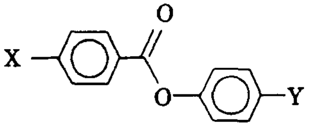


FIGURE 5 Comparison of Mesomorphic Properties for



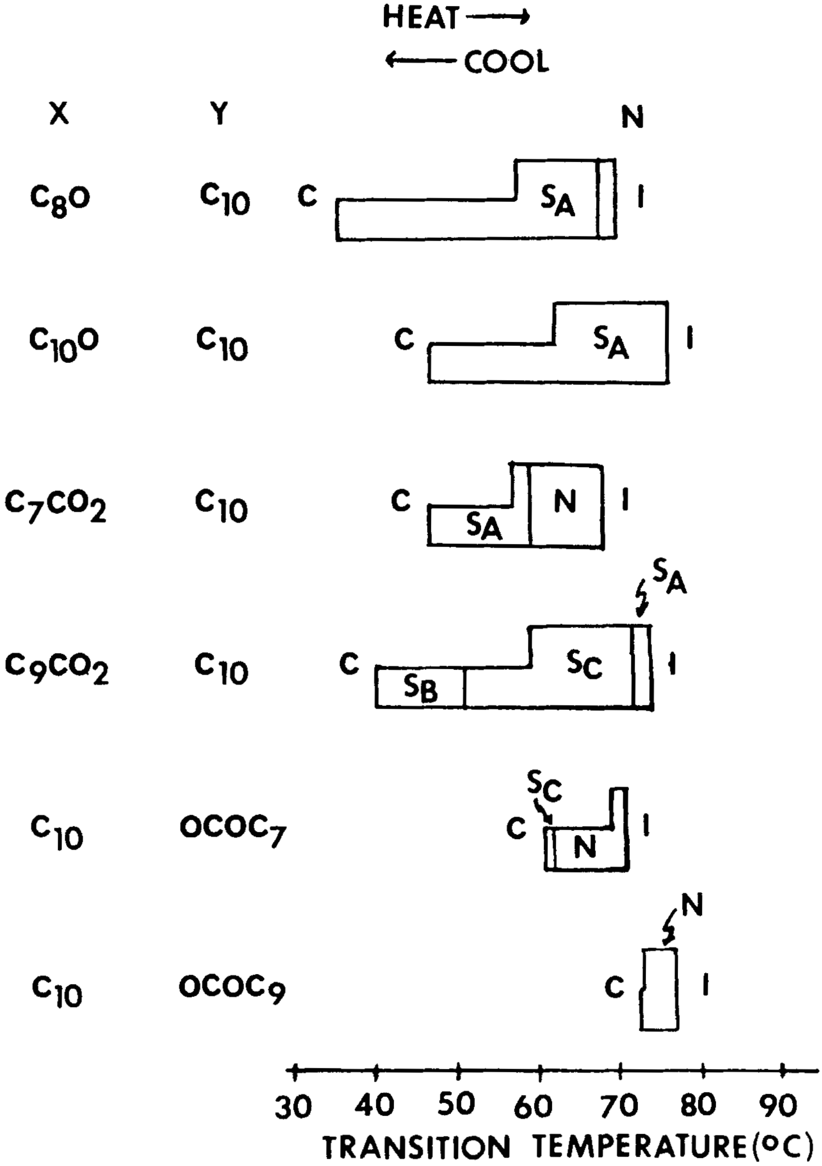
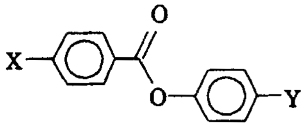


FIGURE 6 Comparison of Mesomorphic Properties for



EXPERIMENTAL

Known methods were used to prepare the 4-alkyl-[13,14] and alkoxy[15] phenols and 4-alkylbenzene thiols.[13] The synthesis of 4-alkoxybenzene thiols is described in Ref. 11. Anhyd Na_2SO_4 was used to dry all organic extracts.

TLC data were obtained using Anal-Tech silica gel GHLF-Uniplates with $CHCl_3$ as the solvent and UV light as the detector. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus, unless otherwise noted and are corrected. IR spectra were obtained using a Pye Unicam 3-200 instrument. NMR spectra were determined in CCl_4 with TMS as an internal standard on a Varian EM 360 instrument, unless otherwise noted. Typical NMR data are presented in Table II.

Transition temperatures (°C) were determined using a Leitz Ortholux or Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min, as described in Reference 16. Contact mixture studies were done using the method described in Ref. 17. Abbreviations used for phases are C = crystal, M = mesophase, S = smectic, S_G = smectic G, S_F = smectic F, S_B = smectic B, S_C = smectic C, S_A = smectic A, N = nematic, and I = isotropic liquid. Monotropic phases are indicated in tables by parentheses. Samples were cooled until they crystallized so no monotropic phases before this temperature were missed.

4-*n*-Heptanoyloxybenzoic Acid, 5 (R = C_7H_{15})

To a soln of 50 g (0.36 mole) of 4-hydroxybenzoic acid in 500 ml CH_2Cl_2 containing 57 ml Et_3N was added dropwise 59.0 g (0.36 mole) of undecanoyl chloride. The rxn mixture was stirred for 1 hr at RT and then washed with H_2O. The organic layer was dried, filtered, and the filtrate rotovaped. The residue was air dried to give 90.1 g (94.2%) of the crude acid. Recrystallization of this material from abs EtOH gave 41.4 g (43.3%) of the purified acid, *5* (R = C_7H_{15}): m.p. in Table I. IR ($CHCl_3$) 3400–2400 (br acid OH), 1755 (str CO_2R), 1690 (str CO_2H), and 1600 cm^{-1} (str Ar).

4-*n*-Nonanoyloxybenzaldehyde, 8 (R = C_9H_9)

To a soln of 10.0 g (82.0 mmoles) of *p*-hydroxybenzaldehyde in 100 ml CH_2Cl_2 containing 12 ml Et_3N was added dropwise 15.6 g (82.0 mmoles) of decanoyl chloride and the mixture refluxed for 30 min.

The cooled reaction mixture was extracted with H_2O, 5% aq KOH and H_2O. The organic layer was dried, filtered, and the filtrate rotovaped to give 25.4 g (100%) of the crude aldehyde. Distillation of this material at 155–160° (0.5 mm) gave 20.3 g (89.3%) of the purified aldehyde, *8* (R = C_9H_9): TLC: R_f = 0.36 (R_f for starting material = 0.10), IR (film) 2860 (wk aldehyde CH), 1760 (str CO_2R), 1700 (str CHO) and 1600 cm^{-1} (Ar). The C_7 aldehyde was prepared in the same manner in a purified yield of 85.6%, bp 165° (0.5 mm).

4-*n*-Nonanoyloxybenzoic Acid, *8* (R = C_9H_{19})

A soln of 38.5 g (0.24 mole) of $KMnO_4$ in 400 ml of a 1:1 mixture of $Me_2CO—H_2O$ was added gradually to a stirred soln of 40.0 g (0.16 mole) of the above aldehyde in 400 ml Me_2CO and the mixture stirred at RT for 12 hr. TLC of an aliquot from this reaction indicated it was complete after this time. A satd soln of aq $NaHSO_3$ (600 ml) was added and the pH adjusted from 8.5 to 5 with 3 *N* HCl. The resulting precipitate was removed by filtration, washed with H_2O and air dried to give 39.6 g (93.2%) of the crude acid. Recrystallization of this material from $CHCl_3$–EtOH gave 31.2 g (72.8%) of the purified acid, *8* (R = C_9H_{19}).

Two new esters, *3*, were also prepared. Their transition temperatures are as follows: X = C_8O, Y = C_{10}; 54.1–56.4 (C—S_A), 67.2–67.4 (S_A–N), 68.4–69.1 (N–I), 34.9 (S_A–C), and X = C_8O, Y = OC_{10}; 67.0–67.7 (C–S_C), 77.9–78.0 (S_C–N), 90.0–90.2 (N–I), 55.1 (S_C–C).

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References

1. M. E. Neubert, F. C. Herlinger, M. R. Jirousek and A. de Vries, *Mol. Cryst. Liq. Cryst.*, **139**, 299 (1986).
2. M. E. Neubert, P. J. Wildman, M. J. Zawaski, C. A. Hanlon, T. L. Benyo and A. de Vries, *Mol. Cryst. Liq. Cryst.*, **145**, 111 (1987).
3. T. R. Criswell, B. H. Klanderman and D. C. Batesky, *Mol. Cryst. Liq. Cryst.*, **22**, 211 (1973).

4. M. E. Neubert, M. R. Jirousek and C. A. Hanlon, *Mol. Cryst. Liq. Cryst.*, **133**, 223 (1986).
5. P. A. C. Gane, A. J. Leadbetter, P. A. Tucker, G. W. Gray and A. R. Tajbakhsh, *J. Chem. Phys.*, **77**, 6215 (1982).
6. D. Demus, H. Demus and H. Zashke, *Flüssige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974).
7. D. L. Fishel and P. R. Patel, *Mol. Cryst. Liq. Cryst.*, **17**, 139 (1972).
8. D. Demus and H. Zaschke, *Flüssige Kristalle in Tabellen II* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1984).
9. M. E. Neubert, L. T. Carlino, D. L. Fishel and R. M. D'Sidocky, *Mol. Cryst. Liq. Cryst.*, **59**, 253 (1980).
10. M. E. Neubert, R. E. Cline, M. J. Zawaski, P. J. Wildman and A. Ekachai, *Mol. Cryst. Liq. Cryst.*, **77**, 43 (1981).
11. M. E. Neubert, B. Ziemnicka-Merchant, M. R. Jirousek, S. J. Laskos, Jr., D. Leonhardt and R. B. Sharma, *Mol. Cryst. Liq. Cryst.*, 1987, accepted for publication.
12. W. H. de Jeu, *J. Phys.* (*Paris*), **38**, 1265 (1977).
13. M. E. Neubert, S. J. Laskos, Jr., R. F. Griffith, M. E. Stahl and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **54**, 221 (1979).
14. M. E. Neubert, M. E. Stahl and R. E. Cline, *Mol. Cryst. Liq. Cryst.*, **89**, 93 (1982).
15. M. E. Neubert, S. J. Laskos, Jr., L. J. Maurer, L. T. Carlino and J. P. Ferrato, *Mol. Cryst. Liq. Cryst.*, **44**, 197 (1978).
16. M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **43**, 313 (1977).
17. M. E. Neubert, K. Leung and W. A. Saupe, *Mol. Cryst. Liq. Cryst.*, **35**, 283 (1986).