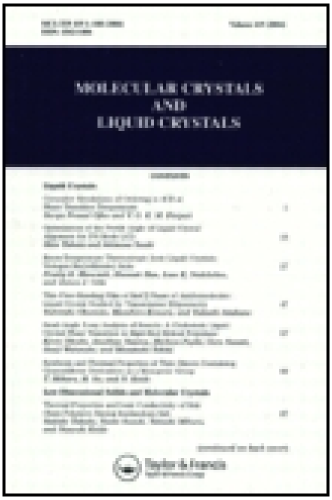

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Synthesis and Mesomorphic Properties of the Homologous Series of 4-Alkyl or Alkoxy-4′-Bromo or Cyanotolanes

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Synthesis and Mesomorphic Properties of the Homologous Series of 4-Alkyl or Alkoxy-4′-Bromo or Cyanotolanes†

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A homologous series of 4-alkyl or alkoxy-4′-bromo or cyanotolanes in which the alkyl group is $C_4 \rightarrow C_{10}$ and the alkoxy group is $C_1 \rightarrow C_{12}$, has been prepared. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot stage microscopy and differential scanning calorimeter. The bromo compounds have a smectic polymorphism. Three pure products of cyano derivatives with the chains $C_9H_{19}O$, $C_{10}H_{21}O$ and $C_{10}H_{21}$ present an enantiotropic or monotropic reentrant nematic phase at atmospheric pressure. The reentrant phenomenon itself will be discussed as well as the absence of correlation between T_{NA}/T_{NI} McMillan parameter and the heat of transition. A plot of the nematic isotropic transition temperatures against the number of carbon atoms in the alkoxy chain shows the usual odd even effect.

INTRODUCTION

Some reentrant nematic phases have been described in binary mixtures at atmospheric pressure[1] or in pure materials but at high pressure.[2] After the first observations of enantiotropic reentrant nematic phases at atmospheric pressure in pure compounds of two series: 4-*n*-alkoxybenzoyloxy-4′-cyano stilbenes[3–5] and then, the 4-*n*-alkoxybenzoyloxy-4′-cyanobiphenyls,[6] we have carried on the systematic study of such series with three phenyl rings

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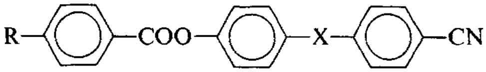
† Presented at the third Liquid Crystal Conference of Socialist countries, Budapest, Hungary, August 1979.

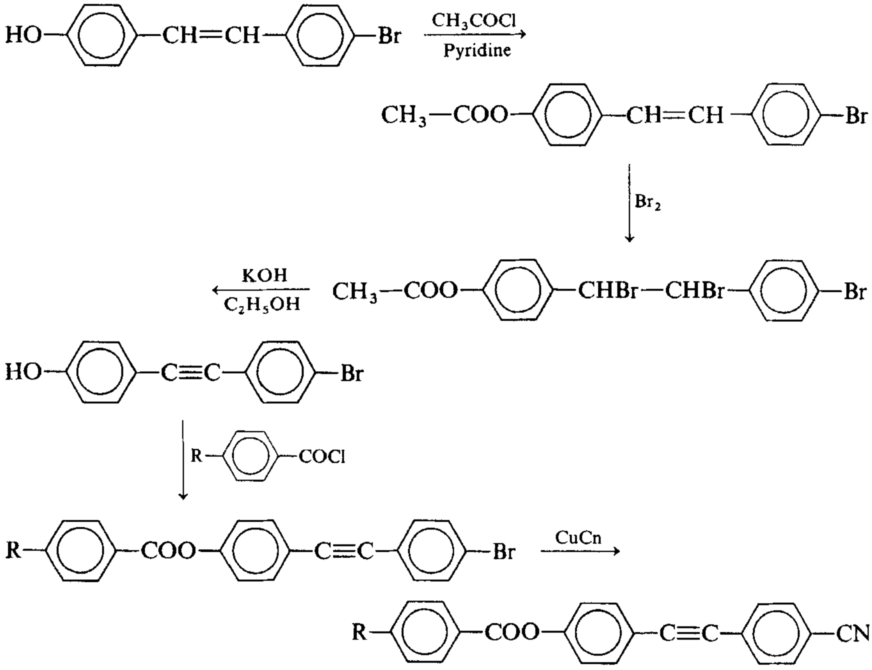
in the rigid core and a cyano end group. All these compounds present the same general formula.



where X is: —CH=CH=,[3–5] single bound,[6] —CH=N—,[7] —COO—,[8] —N=N—,[9] we present here the results obtained with X = —C≡C— for which preliminary results have been published.[10]

RESULTS AND DISCUSSION

Compounds of these series are prepared according to the scheme below:



$R = C_nH_{2n+1}$ with $n = 4 \rightarrow 10$

or

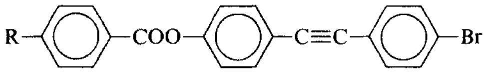
C_nH_{2n+1} with $n = 1 \rightarrow 12$

The 4-bromo-4′-hydroxystilbene was prepared according to Ref. [11].

The mesophases of the prepared compounds were observed by means of a polarizing microscope equipped with a heating and cooling stage (Mettler

TABLE I

Transition temperatures and enthalpies of fusion of compounds with formula



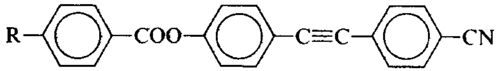
R		K		S		S_B		S_A		N		I	ΔHf Kcal/mole
$C_nH_{2n+1}O$	n												
	1	.	164	—		—		—		.	275	.	3.94
	2	.	146	—		—		—		.	271	.	8.6
	3	.	158	—		—		—		.	262.5	.	3.2
	4	.	158.5	—		—		—		.	259	.	7.47
	5	.	123	—		—		—		.	239	.	3.70
	6	.	111	—		—		—	192	.	211	.	4.15
	7	.	128	—		—		—	163	.	225	.	8.12
	8	.	122	—		—		—	182	.	221	.	4.10
	9	.	117	—		—		.	182	.	211	.	7.07
	10	.	110	—		—		.	188	.	210	.	6.8
	11	.	114	—		—		.	189	.	202	.	10.8
	12	.	106	—		—		.	189	.	196	.	10.4
C_nH_{2n+1}	n												
	3	.	131	—		—		—		.	237	.	5.05
	4	.	128	—		—		.	(118.5)	.	224.6	.	5.87
	5	.	107	—		.	(79)	.	119.5	.	218.4	.	6.3
	6	.	97.6	.	(78)	.	(84.3)	.	141	.	205	.	5.5
	7	.	103.4	.	(79.6)	.	(101)	.	167	.	206	.	6.5
	8	.	85	—		.	(84.1)	.	163	.	195	.	5.2

The meanings of the signs used in this table and in the following are: K: crystalline phase; S: smectic phase (s); S_A, S_B . . . smectic phases A, B . . .; N: nematic phase; I: isotropic phase; . : the phase exists; — ; the phase does not exist.

The temperatures are given in Celsius degrees. Metastable transitions are indicated between bracked.

TABLE II

Transition temperatures and enthalpies of fusion of compounds with formula



R		K		S_A		N		S_A		N		I	ΔHf Kcal/mole
$C_nH_{2n+1}O$	n												
	5	.	107	.	(105)	—		—		.	276	.	5.8
	6	.	113	.	(107)	—		—		.	268	.	9.3
	7	.	102	.	108	—		—		.	256	.	8.6
	8	.	86	.	96	—		—		.	248	.	7.6
	9	.	90	.	(75.7)	.	141	.	183	.	239	.	12
	10	.	84	—		.	102	.	208	.	233.5	.	9.8
	11	.	85	—		—		.	213	.	227	.	7
	12	.	92.5	—		—		.	216	.	223	.	9.9
C_nH_{2n+1}	n												
	5	.	115	—		—		—		.	258	.	4.9
	6	.	100	.	(78.5)	—		—		.	242	.	4.1
	7	.	87	.	(63)	—		—		.	234	.	5.8
	8	.	78	.	(53)	—		—		.	228	.	5.95
	9	.	71	.	(44.5)	—		—		.	227	.	5.8
	10	.	65	—			(62)	.	188	.	217	.	7.25

The notations are that of Table I.

FP 5). The transition temperatures and enthalpies of fusion were determined by means of a differential scanning calorimeter (Dupont 990). The results are listed in Tables I and II.

The structures of the smectic phases were identified using the contact method by their isomorphy with a known reference compound.[12]

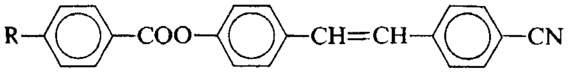
1 p-bromo substituted compounds

When $R = C_nH_{2n+1}O$, the first five compounds ($n = 1 \rightarrow 5$) are only nematic. From the hexyloxy, the compounds exhibit a smectic A phase in addition to the nematic phase. We point out that the stability range of the smectic A phase for even n is about 82°C and for odd n about 65°C. The nematic existence range becomes smaller while the smectic A range becomes larger. The odd even effect on the clearing point is rather well followed, except for the compound with $n = 6$ (Figure 1). At first, we thought it was a problem of purity of the sample but repeated careful purifications lead to the same transition temperatures. In fact, we have to point out that this compound is the first in this homologous series where the S_A phase is observed. The same results have been obtained on our series with $X = CH_2{-}CH_2$.[13]

When $R = C_nH_{2n+1}$, the compound with $n = 3$ is only nematic, the butyl derivative has a monotropic S_A phase. The hexyl and heptyl compounds exhibit in addition, two monotropic smectic phases S and S_B. The textures of the S_A and S_B phases are either focal conics or homeotropic, the textures of the S phase are striated focal conics.

2 p-cyano substituted compounds

These are colourless, stable materials having wide thermal range of mesomorphism (Table II). When $R = C_nH_{2n+1}O$, the two derivatives ($n = 5, 6$) exhibit an enantiotropic nematic phase and a monotropic S_A phase. The enantiotropic S_A phase appears from $n = 7$. The nonyloxy derivative presents a stable reentrant nematic phase; below this nematic phase and from 75.7°C, another smectic A phase is observed. It is the third compound having a tetramorphism N S_A H S_A. The two others are the octyloxy and the nonyloxy of the series.



4.5

9

Another compound with such tetramorphism was then reported. The decyloxytolane derivative presents three enantiotropic phases with increasing temperature N, S_A, N. From the undecyloxy derivative the

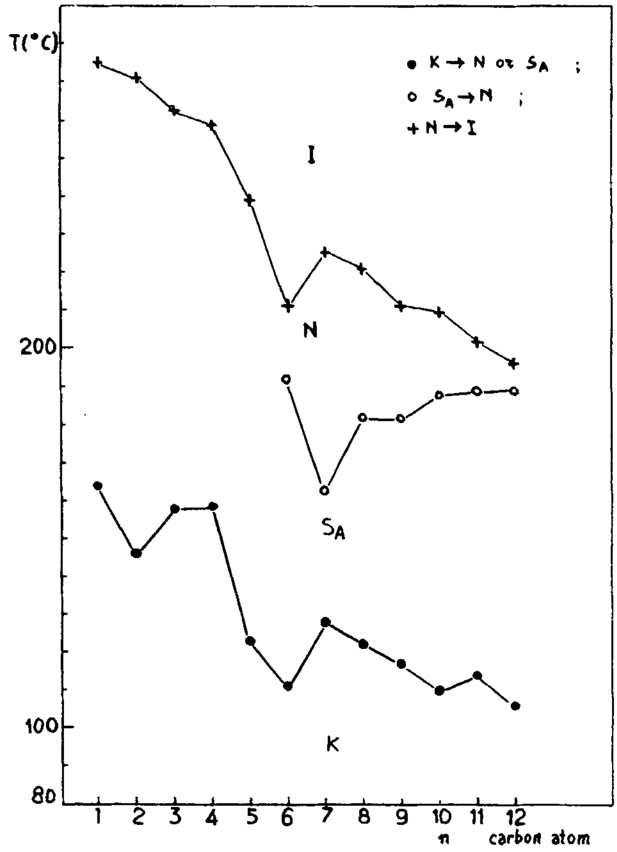
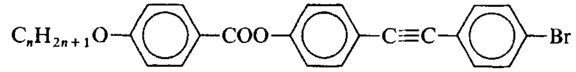
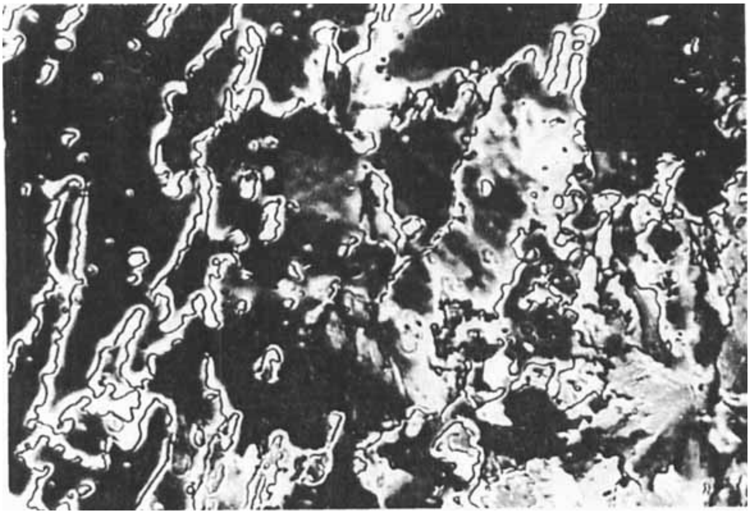


FIGURE 1 Plot of transition temperatures against *n*, the number of carbon atoms in the alkoxy chain of

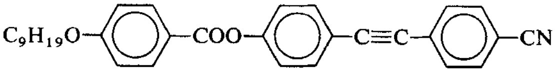


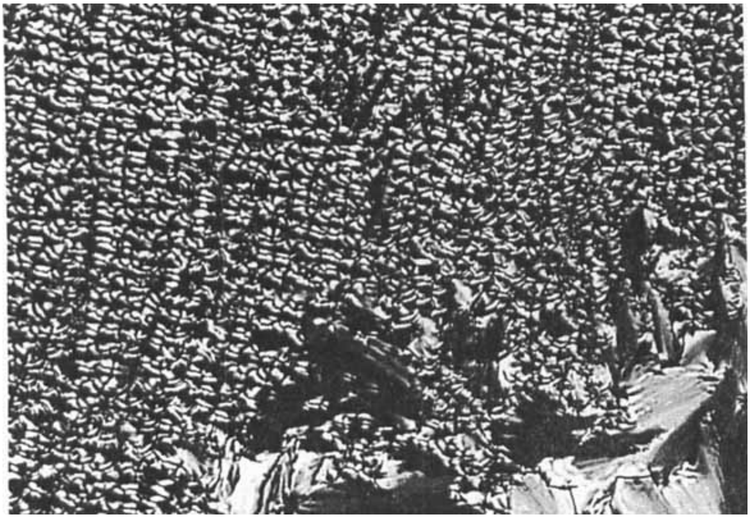
reentrant nematic phase disappears. On cooling the isotropic liquid of the nonyloxy derivative one can observe the nematic phase with a classical schlieren textures (Figure 2a). Below this nematic phase, the smectic A phase with a focal conic or homeotrope texture appears (Figure 2b). On further cooling another schlieren is observed (Figure 2c) followed by a focal conic or homeotropic texture (Figure 2d). The identification of the tetramorphism N, S_A, N, S_A, of the nonyloxy derivative has been made by the miscibility method with the four corresponding phases of the 4-cyano-4′-octyloxybenzoyloxystilbene (Figure 3). The odd even effect on the clearing point is rather well followed (Figure 4, Table II).



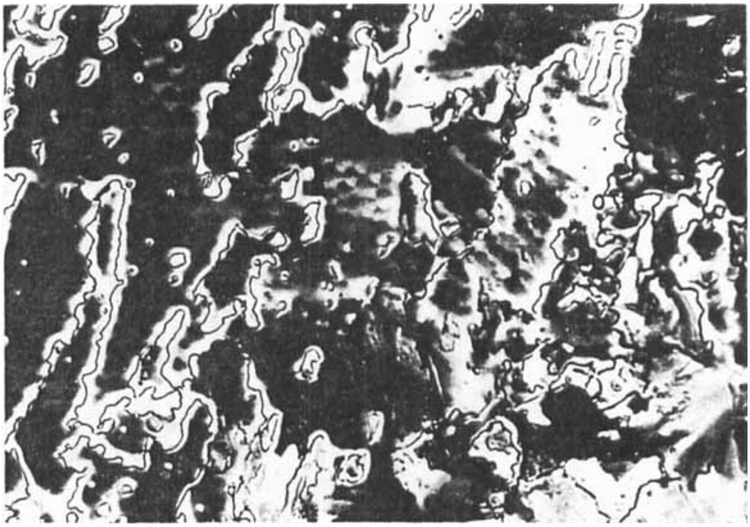
a) Nematic phase at 189°C;

FIGURE 2 Textures of the compound

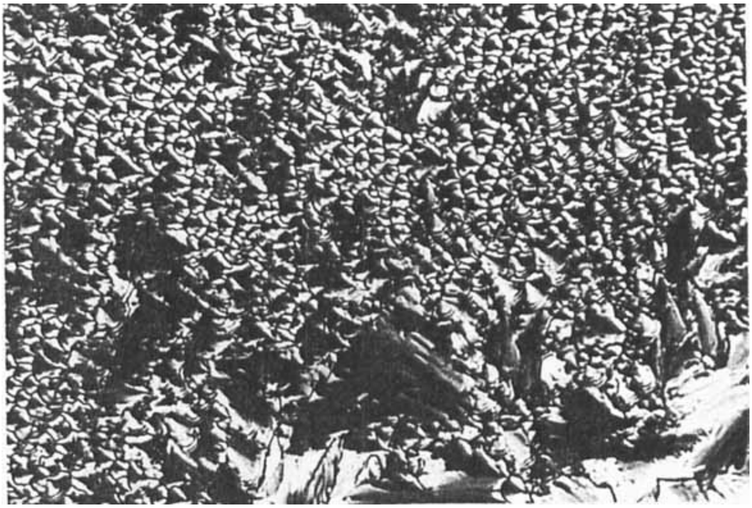




b) Smectic A phase at 160°C:



c) Reentrant nematic phase at 130°C;



d) Reentrant smectic phase A at 74°C.

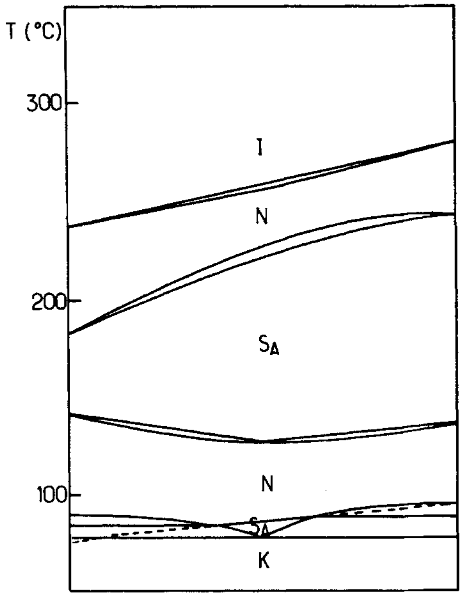
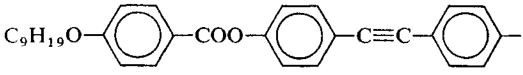
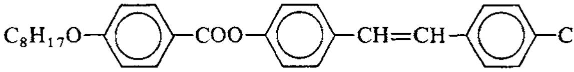


FIGURE 3 Diagram of isobaric state for the mixture of



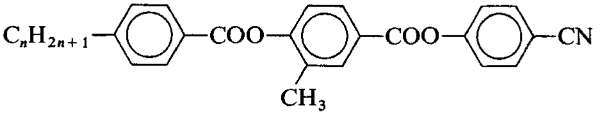
(on left)

with



(on right)

When $R = C_nH_{2n+1}$, the pentyl compound is only nematic. From the hexyl to the nonyl, these compounds have, in addition, a monotropic S_A phase. The decyl derivative exhibit a monotropic reentrant nematic phase. This enantiotropic S_A phase and this monotropic reentrant nematic phase have been checked by miscibility with the corresponding phases of the decyloxy derivative (Figure 5). This last alkyl derivative exhibits a wide S_A range (123°C) and has the lowest melting point (65°C). This phenomenon with an alkyl chain is recently observed by Madhusudana *et al.*[14] in the series:



$n = 11, 12$

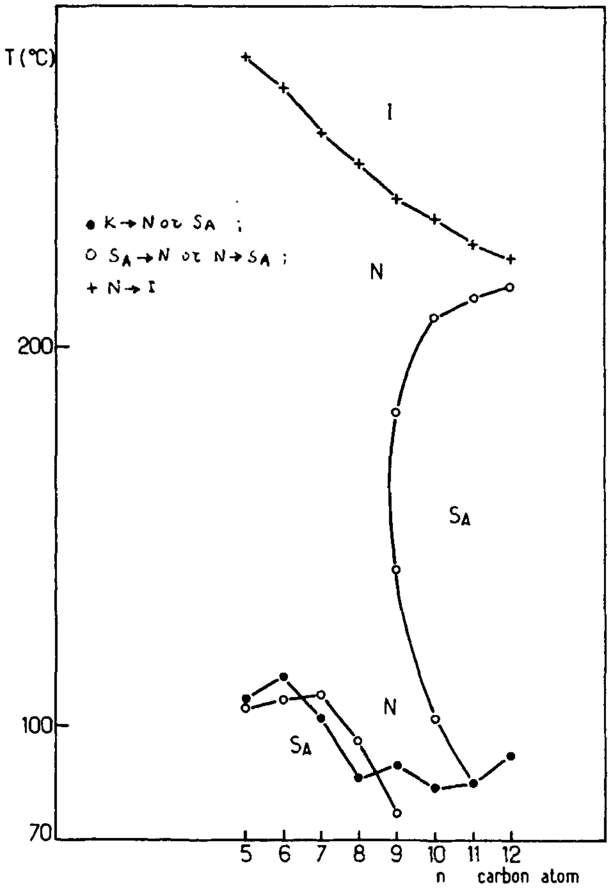
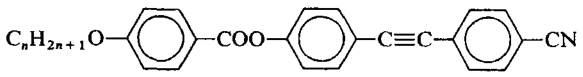


FIGURE 4 Plot of transition temperatures against *n*, the number of carbon atoms in the alkoxy chain of



In the series of the cyanotolanes, another remarkable fact is the evolution of the T_{NA}/T_{NI} ratio calculated for each compound in Table III.

T_{NA}, T_{NI} are respectively the temperature in Kelvin of the smectic A-nematic transition at the highest temperature and the nematic-isotropic transition. As in the series of 4-alkoxy-benzoyloxy-4'-cyanostilbenes recently discussed,[5] this parameter is almost constant and largely inferior to the McMillan's number[15] ($\simeq 0.87$) up to octyloxy and nonyl and changes abruptly for nonyloxy and decyl. From the nonyloxy the evolution of this parameter with the

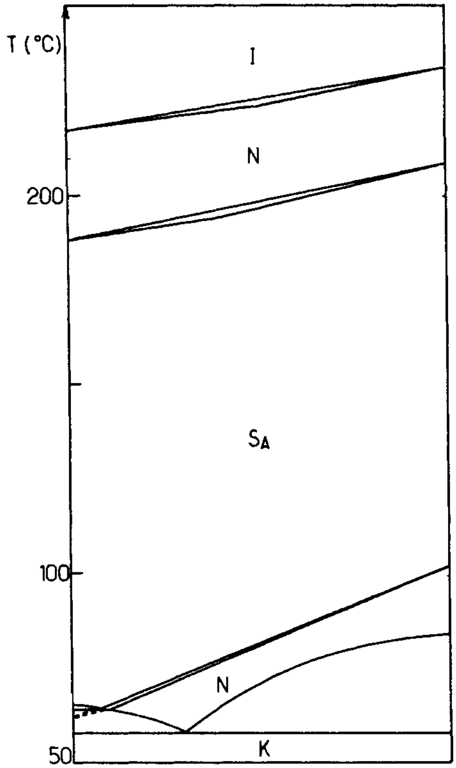
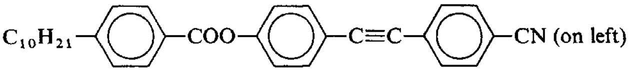
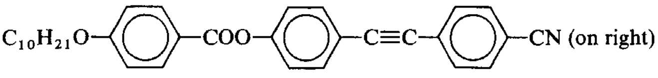


FIGURE 5 Diagram of isobaric state for the mixture of

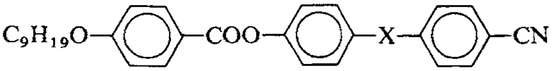


with



highest T_{NA} seems to agree with the McMillan's theory. It seems that there is a close relation between this parameter and the existence of the reentrant nematic and smectic A phases at low temperature.

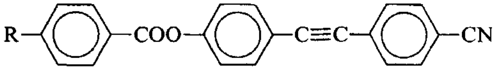
We can also compare compounds having the same general formula:



with various linkage X = —CH=CH—, —C≡C—, single bond, —COO—, —CH=N—, —N=N—. All these compounds exhibit a

TABLE III

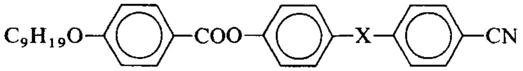
T_{NA}/T_{NI} ratio of compounds with formula



*R = $C_nH_{2n+1}O$								
n	5	6	7	8	9	10	11	12
T_{NA}/T_{NI}	0.69	0.70	0.72	0.70	0.89	0.95	0.97	0.98
*R = C_nH_{2n+1}								
n	6	7	8	9	10			
T_{NA}/T_{NI}	0.68	0.66	0.65	0.64	0.94			

TABLE IV

Transition temperatures of compounds with formula



—X—	K		S_A		N		S_A		N		I
—CH=CH—	.	97	.	(63)	.	(93.7)	.	261	.	275.3	.
single bond	.	96	—		.	(71)	.	217	.	232	.
—C≡C—	.	90	.	(75.7)	.	141	.	183	.	239	.
—COO—	.	121	—		.	(116)	.	198	.	228.5	.
—CH=N—	.	96	—		.	(92)	.	228	.	251	.
—N=N—	.	90	.	(72)	.	118	.	214	.	253	.

reentrant nematic phase (Table IV), have a highly polar cyano group attached to one end of the molecule which results in strong antiparallel correlations between neighbouring molecules.[16] This leads to a formation of a bilayer structure with interdigitated molecules in each bilayer.[17] As the temperature is varied the structure is slightly modified and this change is favourable for the occurrence of the reentrant nematic phase.[27]

CONCLUSION

We show that 4-alkyl or alkoxy benzoyloxy-4′-cyanotolanes exhibit another example of pure substances with a stable nematic reentrant phase at atmospheric pressure. Our results show that these new materials have the same general feature than the previous ones.

Now, we must point out several new interesting facts:

— the alkoxy series is the first one which presents two stable reentrant nematic phases. One of them exhibit a tetramorphism N, S_A, N, S_A

— the alkyl series present also a monotropic reentrant nematic phase

— the bromo derivatives do not present a reentrant nematic phase but give a polymorphism smectic.

EXPERIMENTAL

The infrared spectra have been recorded using a Perkin Elmer 225 spectrophotometer and the NMR ones with a Bruker 270 MHz.

p-Alkoxybenzoic acids They were prepared from the *p*-hydroxybenzoic-acid and the selected alkyl bromide following the method of Gray *et al.*[18]

p-Alkylbenzoic acid chlorides They were prepared from the alkylbenzene and the oxalyl chloride following the method of Reynolds *et al.*[19]

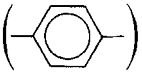
4-Acetyloxy-4'-bromostilbene The acetyl chloride (8.6 g, 0.11 mole) was added dropwise to a mixture of the 4-bromo-4'-hydroxystilbene[11] (27.5 g, 0.1 mole) in anhydrous pyridine (200 ml). The mixture stirred magnetically at 0°C for five hours and at room temperature for 20 hours. The reaction mixture was poured onto a mixture of crushed ice (400 g) and concentrated hydrochloric acid (200 ml) and stirred for half hour. It was filtered off, washed with water, 10% aqueous sodium hydroxide solution, water. The product was recrystallized from a mixture of solvents $CHCH_3 + C_2H_5—OH$ (1:2) into white needles: yield, 80%, m.p. 159°C.

4-Acetyloxy-4'-bromostilbene dibromide Bromine (29 g, 0.18 mole) was added to a solution of 4-acetyloxy-4'-bromostilbene (25.3 g, 0.08 mole) in chloroform (600 ml). This solution was stirred for 3 hours. The excess of bromine was destroyed by the addition of an aqueous solution of sodium metabisulfite. The product was isolated by filtration. It was recrystallized from ethanol. Yield: 76%, m.p. 220°C (dec.)

4-Bromo-4'-hydroxytolane The stilbene dibromide (29.5 g) was added to a hot solution of potassium hydroxyde (84 g) in absolute ethanol (180 ml).[20] The reaction mixture was stirred, heated in oil bath at 140°C for 24 hours and allowed to cool. It was poured onto mixture of crushed ice (180 g) and concentrated hydrochloric acid (150 ml) and stirred for half hour. It was filtered off, washed with water and recrystallized from a mixture of solvents: CH_2Cl_2 + hexane (30:70). This procedure gave 4.4 g (26 %) of the required product m.p. 182°C.

4-Bromo or cyano-4′-alkyl or alkoxybenzoyloxytolane All the alkyl and alkoxy have been prepared following the same general procedure. We give only the example of the preparation of the octyloxy derivatives.

4-Bromo-4′-octyloxy benzoyloxy tolane A mixture of 4-octyloxy-benzoic acid (0.55 g, 21 mmol) and thionyl chloride (2 ml) was refluxed for 2 hours and the excess thionyl chloride was removed under reduced pressure. The acid chloride was added to a solution of 4-bromo-4′-hydroxytolane (0.5 g, 1.8 mmol) in anhydrous pyridine (4 ml). The mixture was stirred magnetically at room temperature for 24 hours and poured onto a stirred mixture of crushed ice and concentrated hydrochloric acid. The product was filtered off, washed with water and air dried. It was chromatographed on silica gel and eluted with the mixture benzene-hexane (1:1) and the finally recrystallized from ethanol. Yield 0.6 g (65 %), K 117 S_A 199 N 231 I

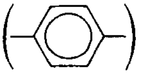
I.R. (Nujol = 1730 cm^{-1} (COO stretching) 840 cm^{-1} 

pmr ($CDCL_3$): δ: 0.905 (*t*-3, CH_3 of $-C_8H_{17}$),1.3–2.06 (m-12, six $-CH_2$),
4.05 (*t*-2 CH_2O), 6.96–8.16 (six *d*-12 aromatic)

Calculated ($C_{29}H_{29}O_3Br$): C % 68.91; H %, 5.74; Br %, 15.84
Found : C %, 69.08; H %, 5.85; Br %, 16.09

4-Cyano-4′-octyloxybenzoyloxytolane Cuprous cyanide (0.27 g, 3 mmole) was added to a solution of 4-bromo-4′-octyloxybenzoyloxytolane (0.51 g, 1 mmole) in *N*-methyl-2-pyrolidone (1 ml). This mixture was stirred and heated in an oil bath at 200°C for 2 hours. The cooled reaction mixture was poured onto a solution of ferric chloride (0.8 g) in water (15 ml and concentrated hydrochloric acid (0.4 ml) and heated at 60°C for 30 min. The organic product was extracted into ether. The etheral solution was washed with water, dried (anhydrous sodium sulfate) and then evaporated to dryness. It was chromatographed on silica gel and eluted with benzene and finally recrystallized from ethanol. Yield 0.25 g (53 %) K 86 S_A 96 N 248 I

I.R. (Nujol) 2240 cm^{-1} (C≡N stretching), 1740 cm^{-1} (COO stretching)

830 cm^{-1} 

pmr ($CDCL_3$)δ(ppm) 0.905 (t. 3 CH_3 of C_8H_{17}), 1.308–2.005 (m-12, six CH_2)

4.056 (*t*-2, CH_2O), 6.97–8.16 (six *d*-12, aromatic)

Calculated: ($C_{30}H_{29}O_3N$): C %, 79.82; H %, 6.43; N %, 3.10

Found : C %, 79.68; H %, 6.50; N %, 3.15

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