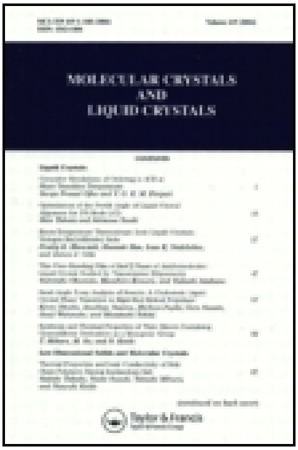

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Cyano and Nitrobenzyloxy Derivatives: New Polymorphism Aspects

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Cyano and Nitrobenzyloxy Derivatives: New Polymorphism Aspects†

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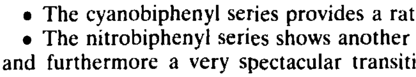
Several polar molecules with three benzene rings and having the general formula:


with X = —, —OCO—, or —N = CH—
and Z = CN or NO_2

have been synthesized. All these compounds are built with the flexible —CH_2O— linkage and provide rather low temperature mesomorphic phases easily accessible for physical investigations.

The striking features of these six series are:

- The cyanobiphenyl series provides a rather classical polymorphism.
- The nitrobiphenyl series shows another example of the re-entrant nematic phase and furthermore a very spectacular transition $N_{re} \rightarrow S_{G \text{ or } H}$ with complex spatial structuring.
- The cyanobenzoate series provides examples of the so-called S_{A_1}, A_{A_d}, S_{A_2}, $S_{\tilde{C}}$ phases and also an *interesting* S_{A_d}–S_{A_2} transition directly observable under the microscope.
- The nitrobenzoate series not only exhibits a classical re-entrant nematic phase, but also the inverted sequence $K\ N\ S_A\ I$ in a pure compound.
- The cyano-Schiff's base series presents the first example of a S_B hexatic phase in polar systems.
- The nitro-Shiff's base series not only exhibits a new enantiotropic re-entrant sequence $K\ S_F\ S_C\ N_{re}\ S_A\ N\ I$, but also the first example of the S_F phase in polar compounds and the inverted sequence $K\ S_F\ S_C\ N\ S_A\ I$.

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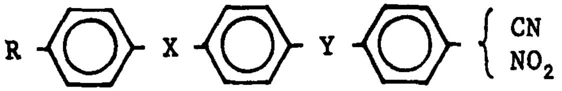
†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

INTRODUCTION

It is now well established that polar molecules with three phenyl rings belonging to the general formula:



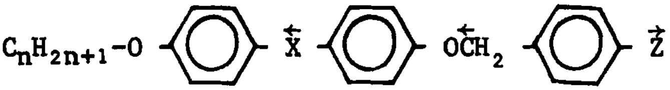
lead to a rich polymorphism with a number of re-entrant sequences and new fluid smectic modifications (S_{A_1}, S_{A_d}, S_{A_2}, S_{C_2}, $S_{\tilde{C}}$. . .).[1]

A systematic study of the influence of the relative longitudinal dipolar moment of the central groups (X and Y) on these phenomena[2] was performed and showed the compounds to be more interesting when the X and Y longitudinal dipolar moments are in the opposite direction to that of the cyano- or nitro-group. For these series, the X and Y (—COO—, —CH = N, —CH = CH— . . .) central linkages are rather rigid so that the T_{NI} temperatures are too high for several physical investigations. On the other hand, with rigid molecules such as:

[3]

the temperature range of the higher nematic phase is larger than that of the re-entrant phase. In order to provide more accessible materials for physical measurements and in the hope of obtaining an inverted sequence, we have explored the more flexible —CH_2—O— linkage.

Here we report on six homologous series having the general formula:



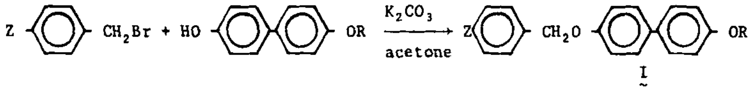
where X = single bond (I), —OCO— (II), —N = CH— (III)

Z = CN (A) or NO_2 (B)

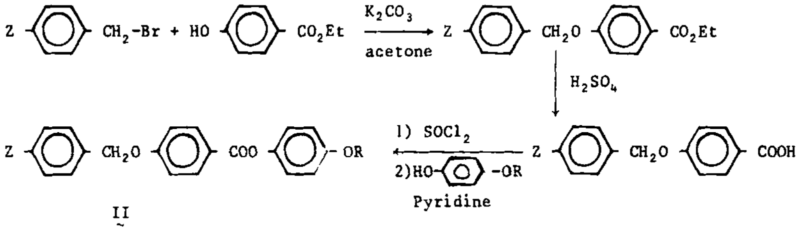
n = 1 → 14

RESULTS AND DISCUSSION

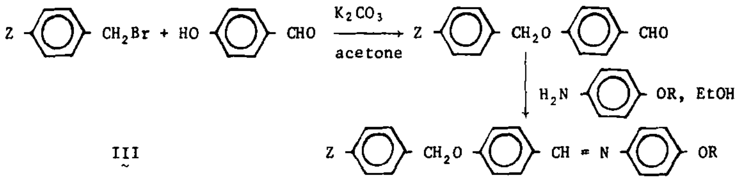
Compounds of these series were prepared according to schemes I, II and III.



Scheme I



Scheme II



Scheme III

They were purified by chromatography on silica gel eluted with benzene or by repeated recrystallization from ethanol. Phase transitions were studied both by polarization microscopy (using a Mettler FP5) and by differential scanning calorimetry (Dupont 990).

- *Cyanobiphenyl series* (IA) This series (Table I) does not present the re-entrant phenomenon, but it exhibits, in addition to classical nematic and S_A phases, several tilted smectic phases (S_C, S_G, S_H). However, the re-entrant nematic phase was observed in a binary mixture. For example, with 63.5 wt% of the octyloxy derivative and 36.5 wt% of the nonyloxy derivative, the following sequence was observed.

$$K\ 126\quad (S_G\ 116)\quad (N_{re}\ 117)\quad S_{A_d}\ 145\quad N\ 170\ I$$

TABLE I

Transition temperatures (°C) of compounds of the series

IA

n	K	S_H	S_G	S_C	S_A	N	I
4	. 155	—	—	—	. 158	. 189	.
5	. 139	(. 132)	(. 135.5)	—	. 146.5	. 180	.
6	. 138	(. 116)	(. 130)	—	(. 137)	. 179	.
7	. 130	(. 124)	(. 126)	(. 127)	—	. 173	.
8	. 129	—	(. 119)	—	—	. 171	.
9	. 128	—	—	—	. 162	. 168	.
10	. 127	—	—	—	. 167	—	.
11	. 124	—	—	—	. 167	—	.
12	. 124	—	—	—	. 168	—	.

The meanings of the signs used in this table and in the following Tables are: K: crystalline phase; N: nematic phase; S: smectic phases A, C . . ., smectic phases S_A, S_C; N_{re}: re-entrant nematic phase; I: isotropic phase; .: the phase exists; —: the phase does not exist; ( ): monotropic phase

We must point out that the corresponding esters (note that the —COO— linkage is more rigid than —CH_2O—) are also devoid of any re-entrant behaviour for the pure compounds but they do exhibit the new smectic $S_{\tilde{C}}$ phase:

n = 8 K 128 ($S_{\tilde{C}}$ 123) S_{A_1} 159 N 236 I

n = 9 K 126 $S_{\tilde{C}}$ 142 S_{A_d} 208 N 229 I

- *Nitrobiphenyl series* IB (Table II)

Like the cyano-series IA, the nitro-derivatives IB exhibit below the classical nematic and smectic A phases some tilted ordered smectic G and H phases. In the C_8 and C_9 homologues the enantiotropic re-entrant nematic (N_{re}) phase was observed. Furthermore in these two compounds a very spectacular transition ($N_{re} \rightarrow S_G$) with complex spatial structuring occurred over three degrees (3°C)[4] (Figure 1a, b). We must point out that the heptyloxy derivative presents the normal transition $N \rightarrow S_G$ without spatial structuring. This seems to indicate

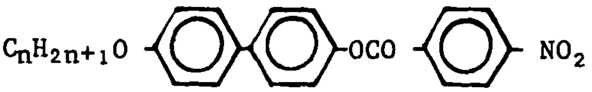
TABLE II

Transition temperatures (°C) of compounds of the series

IB

n	K	$S_{H?}$	$S_{G?}$	N_{re}	S_A		N	I
4	. 137	—	—	—	—		. 172	.
5	. 116	(. 114.5)	(. 114.7)	—	(. 115)		. 167	.
6	. 108	. 107	. 114	—	—		. 166	.
7	. 112	. 109	. 115	—	—		. 162	.
8	. 108	—	. 114	. 124	.	154	. 162	.
9	. 112	—	. 114	. 126	.	154.5	. 161	.
10	. 113	—	—	—	.	161.5	. 161.8	.
11	. 113	(. 110)	—	—	.	162	—	.
12	. 90	. 108	—	—	.	163	—	.

some specific difference between the N_{re} and N phases. This N_{re} phase was not observed for any pure compound in the series:



$n = 7$ K 124 S_{A_1} 146 N 223 I

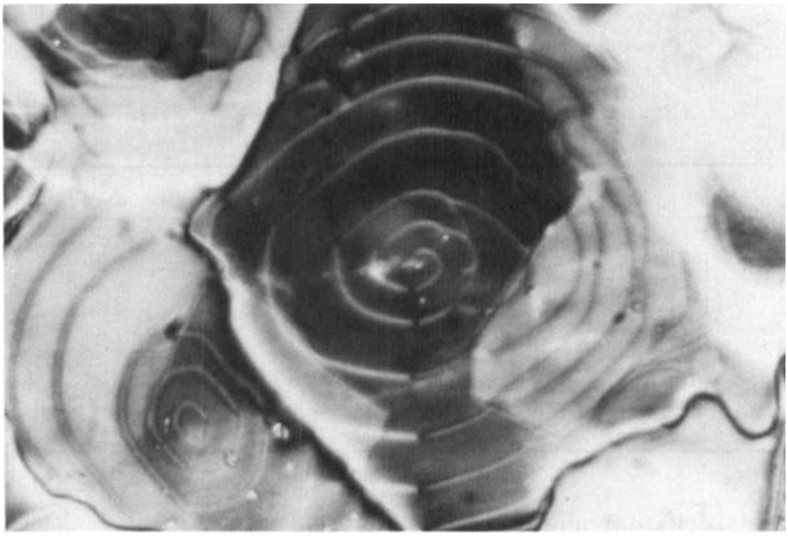
$n = 8$ K 123.5 S_{A_d} 197 N 221 I

However, a 53.33 wt% of C_8 and 46.67 wt% of C_7 binary mixture shows the doubly re-entrant phenomenon:

K 120 S_{A_1} 145.5 N_{re} 149 S_{A_d} 178 N 222 I

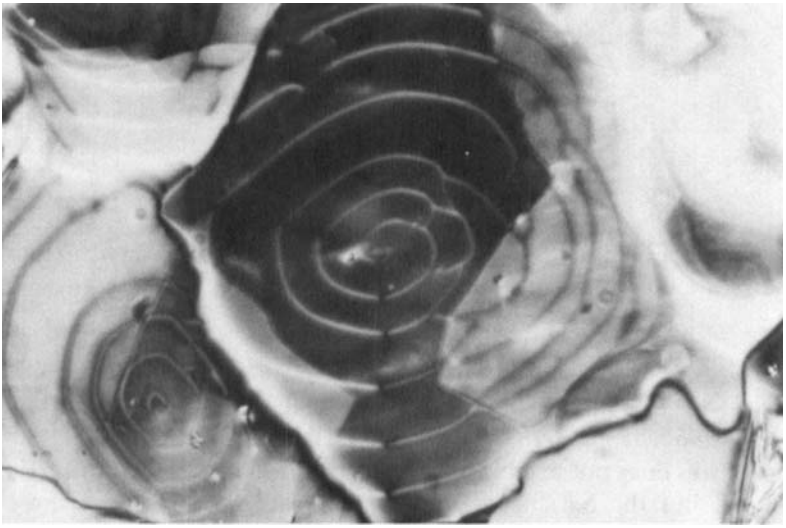
- *Cyanobenzoate series* IIA (Table III)[5]

This series does not exhibit the tilted smectic phases shown by series IA, IB, but the $S_{\bar{C}}$ smectic modification is given. The first three compounds (n = 5, 6, 7) give S_A and N phases. This S_A phase is a monolayered smectic A phase[6] (S_{A_1}) which persists until n = 9. We must point out that the T_{NA}/T_{NI} ratios calculated for these compounds are equal to or higher than McMILLAN's number (≈ 0.87) with the exception of the S_{A_1} phase of the n = 5 derivative which is very



(a)

See Color Plate XIII, located in the final volume of these conference proceedings.



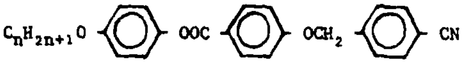
(b)

See Color Plate XIV, located in the final volume of these conference proceedings.

FIGURE 1 Moving spirals observed at the $N_{re} \rightarrow S_G$ transition on cooling at 0.2° mn^{-1} (*a*) at 124°C; (*b*) two seconds later.

TABLE III

Transition temperatures (°C) of compounds of the series



IIA

n	K	S_{A_2}	$S_{\bar{C}}$	S_{A_1}	S_{A_d}	N	I
5	. 135	—	—	(. 111)	—	. 174	.
6	. 115	—	—	. 116	—	. 173	.
7	. 106	—	—	. 118.5	—	. 168	.
8	. 114.5	—	(. 110.5)	. 122	—	. 167	.
9	. 116	(. 114.5)	. 122.5	. 123.7	—	. 163	.
10	. 102	. 124	. 125	—	. 141	. 162	.
11	. 106	. 127	—	—	. 155	. 160	.
12	104	—	—	—	. 158	—	.

metastable (T_{NA} and T_{NI} are respectively the temperatures in Kelvin of the S_A–N transition and the N–I transition), whereas, in the series with re-entrant nematic behaviour, this ratio is largely lower than 0.87

n	5	6	7	8	9	10	11	12
T_{NA}/T_{NI}	0.86	0.87	0.89	0.90	0.91	0.95	0.99	—

From the derivative $n = 10$, the partially bilayered S_A phase (S_{A_d}) appears, while the S_{A_1} disappears. The layer spacing of the S_{A_d}[6] phase increases as the temperature decreases: as an example, for the decyloxy derivative, the ratio d/L (d: the layer thickness and L: the molecular length in the most extended conformation) varies from 1.4 to 1.55 when the temperature decreases from 140 to 120°C. The re-entrant nematic phase was also obtained with a mixture of the $n = 9$ and $n = 10$ derivatives. In this series, the S_{A_d}–S_{A_1} system is quite distinct and the S_{A_d}–S_{A_2} phase boundary is easily revealed (Figure 2). The undecyloxy derivative exhibits a direct transition S_{A_d}–S_{A_2} providing a new example of a directly observable S_{A_d}–S_{A_2} phase transition;[7] as a matter of fact, a clear textural change is observed under microscope, and correlatively the entropy change (0.91 mcal. g^{-1} K^{-1}) (Table IV) and the layer spacing are strongly enhanced at this transition (Figure 3*a*, *b*).

The novel smectic phase made of ribbons, $S_{\bar{C}}$, is present in the

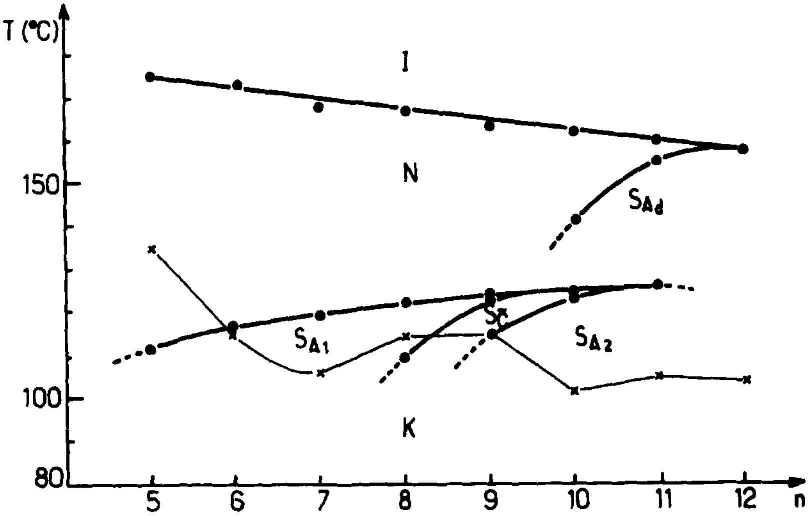
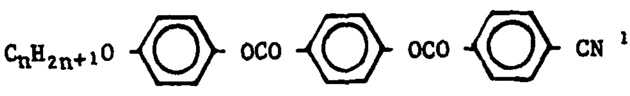


FIGURE 2 Plot of transition temperatures against *n* for series IIA.

three derivatives $n = 8 \rightarrow 10$. This phase is very difficult to observe under the microscope when the higher temperature smectic phase is S_{A_1} ($n = 8$ and 9), whereas it appears highly birefringent when it originates from a S_{A_d} phase ($n = 10$). This behaviour may be correlated with the corresponding entropies of the S_{A_1}–$S_{\tilde{C}}$ transition (18 and 33 mcal. g^{-1} K^{-1} respectively in the $n = 8$ and 9 derivatives) and the S_{A_d}–$S_{\tilde{C}}$ transition (61 mcal. g^{-1} K^{-1} in the derivative $n = 10$) (Table IV). As a probable consequence of the existence of both S_{A_1} and S_{A_d} phases, this $S_{\tilde{C}}$ phase represents a necessary step toward the S_{A_2} condensation. However, if there is no S_{A_1}, the $S_{\tilde{C}}$ phase does not appear. With the homologous diester series:



1 (Table V)

we obtained only the S_{A_d} and S_{A_2} phases, but no S_{A_1} and $S_{\tilde{C}}$ phases.

- *Nitrobenzoate series* IIB (Table VI, Figure 4)

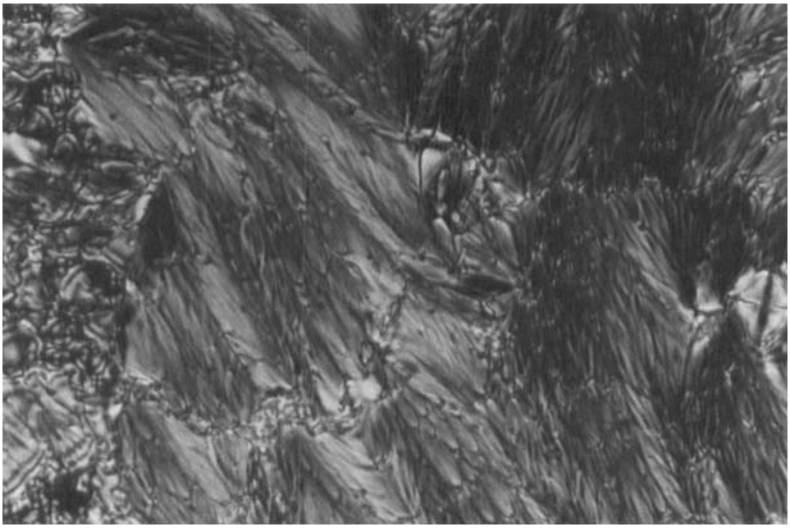
For this series, it is very surprising to observe in the first *eleven* compounds ($n = 1 \rightarrow 11$) only the classical nematic phase. The S_{A_d} phase appears from the dodecyloxy derivative simultaneously with a

TABLE IV

Transition enthalpies and entropies of compounds IIA

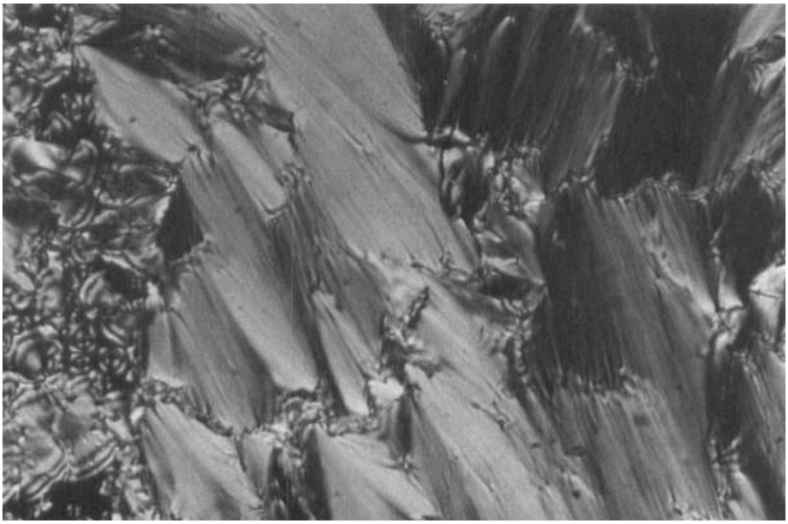
(ΔH in cal. g^{-1} and ΔS in cal. g^{-1} K^{-1})

n	K	S_{A_2}	$S_{\tilde{C}}$	S_{A_1}	S_{A_d}	N	I
6 ΔH	. 16.6	—	—	. 47×10^{-3}	—	. 872×10^{-3}	.
ΔS	*0.043*			0.12×10^{-3}		1.96×10^{-3}	
7 ΔH	. 19	—	—	. 43×10^{-3}		. 873×10^{-3}	.
ΔS	*0.051*			0.11×10^{-3}		1.98×10^{-3}	
8 ΔH	. 16.33	—	. $(.15 \times 10^{-3})$	. 51×10^{-3}		. 840×10^{-3}	.
ΔS	*0.042*		(0.04×10^{-3})	0.13×10^{-3}		1.91×10^{-3}	
9 ΔH	. 18.32	. $(.58 \times 10^{-3})$	. 27×10^{-3}	. 77×10^{-3}		. 836×10^{-3}	.
ΔS	*0.046*	(0.15×10^{-3})	0.07×10^{-3}	. 0.19×10^{-3}		1.92×10^{-3}	
10 ΔH	. 16.85	. 54×10^{-3}	. 108×10^{-3}	—	. 20×10^{-3}	. 1090×10^{-3}	.
ΔS	*0.044*	0.14×10^{-3}	0.27×10^{-3}		0.05×10^{-3}	2.51×10^{-3}	
11 ΔH	. 20.8	. 360×10^{-3}	—	—	. 50×10^{-3}	. 966×10^{-3}	.
ΔS	*0.055*	0.91×10^{-3}			0.12×10^{-3}	2.24×10^{-3}	
12 ΔH	. 20.9	—	—	—	. 1513×10^{-3}	—	.
ΔS	*0.053*				3.54×10^{-3}		



a

See Color Plate XV, located in the final volume of these conference proceedings.



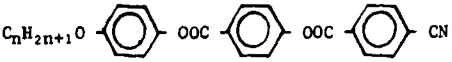
b

See Color Plate XVI, located in the final volume of these conference proceedings.

FIGURE 3 Optical textures of the compound $\underset{\sim}{\text{IIA}}$ ($n = 11$) (*a*) S_{A_d} smectic phase at 128°C; (*b*) S_{A_2} smectic phase at 126°C.

TABLE V

Transition temperatures (°C) of compounds of the series



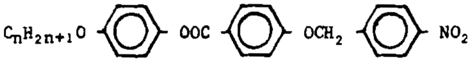
n	K	S_C	S_{A_2}	S_{A_d}	N	I
6	. 131	—	. 166	—	. 255.5	.
7	. 130.5	—	. 174	. 181	. 246	.
8	. 129	—	—	. 199	. 241	.
9	. 132	(. 111)	—	. 213	. 232	.

N_{re} re-entrant nematic phase. Let us point out that the temperature range of the high temperature nematic phase is very small (3°C), and surprisingly is smaller than that of the low temperature one (>10°C). Consequently, on increasing the chain length (n = 13), the first phase completely disappears and gives a new example of an *inverted sequence* in a pure rod-like mesogen. We obtained for the tridecyloxy derivative the following sequence:

$$K\ 112\quad (N\ 106)\quad S_{A_d}\ 158\ I$$

TABLE VI

Transition temperatures (°C) of compounds of the series



IIB

n	K	N_{re}	S_A	N	I
1	. 169	—	—	. 178	.
2	. 166	—	—	. 182	.
3	. 155	—	—	. 176	.
4	. 143	—	—	. 169	.
5	. 124	—	—	. 165.5	.
6	. 120	—	—	. 164	.
7	. 116	—	—	. 162	.
8	. 117	—	—	. 161	.
9	. 155.5	—	—	. 159.5	.
10	. 115	—	—	. 158.5	.
11	. 112.5	—	—	. 158	.
12	. 115	. 125.5	. 154.5	. 157	.
13	. 112.5	(. 106)	. 158	—	.
14	. 112	—	. 156	—	.

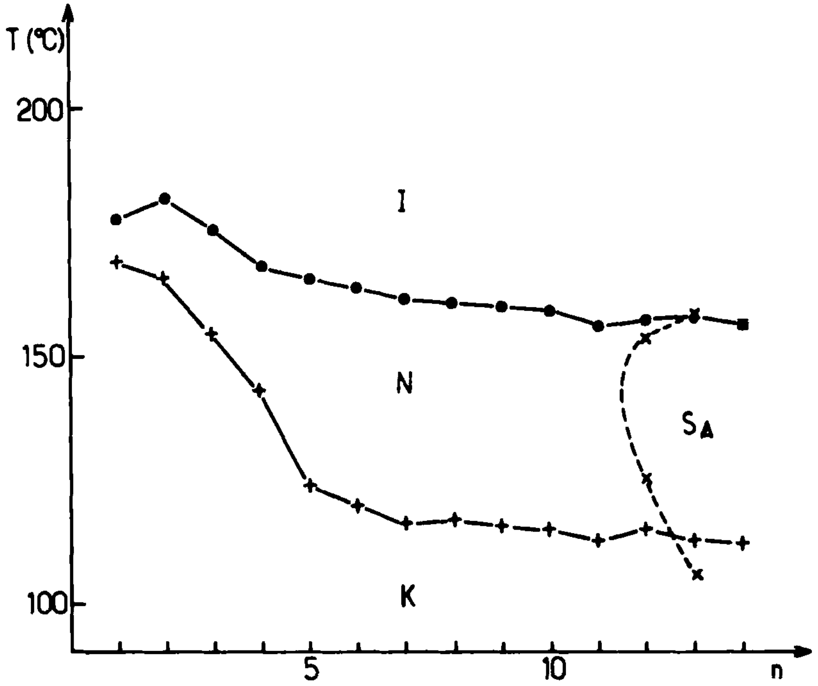
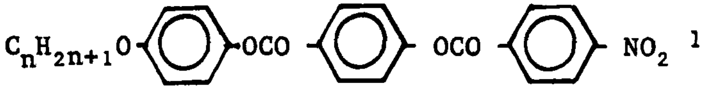


FIGURE 4 Plot of transition temperatures against *n* for series II$\underset{\sim}{\mathrm{B}}$.

This inverted sequence is also obtained in binary mixures of the dodecyloxy and tetradecyloxy derivatives. With the absence of the S_{A_1} phase, this series does not exhibit the $S_{\tilde{C}}$ phase which is observed in the homologous ester series:



[1,3]

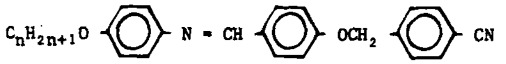
Actually this latter series is the only one exhibiting the triply reentrant phenomenon with the nonyloxy derivative.

- *Cyano Shiff base series* (III$\underset{\sim}{\mathrm{A}}$) (Table VII, Figure 5)

The first two compounds ($n = 1, 2$) present only the nematic phase. In the next five homologues ($n = 3 \rightarrow 7$), we could detect both S_A and S_B phases. On cooling the S_A phase, transition bars appear at the $S_A \rightarrow S_B$ transition. The bars cross the fans at the start of the transition, widen and disappear. In this case, the smectic S_B phase formed shows an almost truncated focal-conic texture.

TABLE VII

Transition temperatures (°C) of compounds of the series


IIIA

n	K	S_B	S_{Bhex}	$S_{\bar{C}}$	S_C	S_A	N	I
1	. 170.5	—	—	—	—	—	. 221	.
2	. 173.5	—	—	—	—	—	. 228	.
3	. 142	(. 120)	—	—	—	(. 134)	. 213	.
4	. 131	(. 120)	—	—	—	. 142	. 212	.
5	. 118	. 118.5	—	—	—	. 142	. 201	.
6	. 113	. 123.4	—	—	—	. 143	. 199	.
7	. 112	. 123	—	—	—	. 140	. 193	.
8	. 112	. 122	. 124	—	—	. 138	. 191	.
9	. 115	. 120.5	—	. 129	. 130.5	. 132	. 187	.
10	. 114	(. 113)	—	. 128	—	. 177	. 185	.
11	. 118	(. 105)	—	. 121	—	. 182.5	. 182.7	.
12	. 116	—	—	(. 101)	—	. 182	—	.
13	. 118	—	—	—	(. 107)	. 182	—	.
14	. 116.5	—	—	—	(. 110)	. 182	—	.

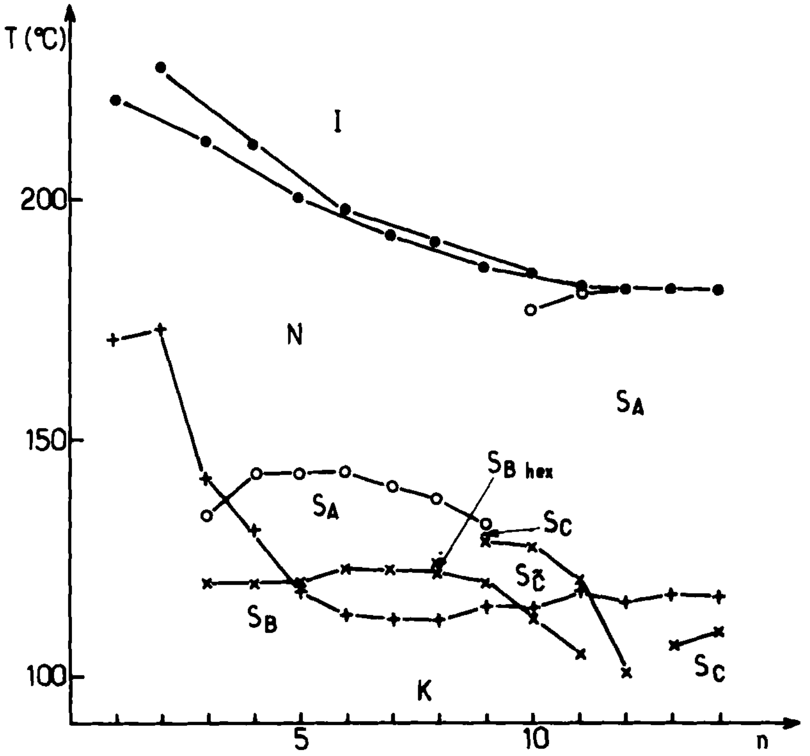


FIGURE 5 Plot of transition temperatures against n for series IIIA.

The octyloxy derivative is more interesting. It also exhibits the *nematic and smectic* S_A phases. On cooling from the S_A phase with the focal-conic texture, we could observe a transition at 123°C, but could not detect the transition bars. X-ray measurements[8] show two phases below the S_A phase: the S_B hexatic and crystal S_B phases.[9] So the octyloxy derivative is the first strongly polar compound which exhibits the S_B hexatic phase. The sequence observed is:

$$K\ 112\quad S_B\ 122\quad S_{Bhex}\ 124\quad S_{A_1}\ 138\quad N\ 191\ I$$

In the C_9 homologue, below the N and S_{A_1} phases, three smectic phases: S_C (probably monolayered), $S_{\tilde{C}}$, and S_B, could be observed. So we have the new sequence:

$$K\ 115\quad S_B\ 120.5\quad S_{\tilde{C}}\ 129\quad S_C\ 130.5\quad S_{A_1}\ 132\quad N\ 187\ I$$

From the decyloxy derivative, the S_{A_1} phase disappears and the other S_{A_d} phase is observed.

The binary isobaric phase diagram (Figure 6) for the nonyloxy and decyloxy derivatives shows for the 90.15 wt% of C_9 and 9.85 wt% of C_{10} mixture the new re-entrant sequence:

$$K\ 113\quad S_B\ 120.3\quad S_{\tilde{C}}\ 131.2\quad N_{re}\ 136\quad S_A\ 139\quad N\ 186.5\quad I$$

In this diagram, the S_{A_d}–S_{A_1} systems are distinct and the latter entirely disappears with the 92.00 wt% of C_9 mixture, and we cannot observe the doubly re-entrant phenomenon. This series is more interesting than that for the homologous diester for which the more complex sequence is as follows:[2]

$$K\ 124\quad (S_{C_2}\ 114)\quad S_{\tilde{C}}\ 142\quad S_A\ 236\quad N\ 252\quad I\qquad (\text{for } n = 10)$$

- *Nitro-Schiff's base series* (IIIB) (Table VIII, Figure 7)[10]

The first five derivatives ($n = 1 \rightarrow 5$) exhibit only the nematic phase. From the hexyloxy to tetradecyloxy derivatives, all the compounds exhibit the S_C phase with a maximum stability temperature with $n = 9$. The five derivatives ($n = 6 \rightarrow 10$) present the three phase N, S_C, and $S_{H?}$. The undecyloxy derivative exhibits for the first time the re-entrant sequence $I\ N\ S_A\ N_{re}\ S_C\ S_F\ S_{H?}\ K$ (Figure 8*a*–*f*). On cooling

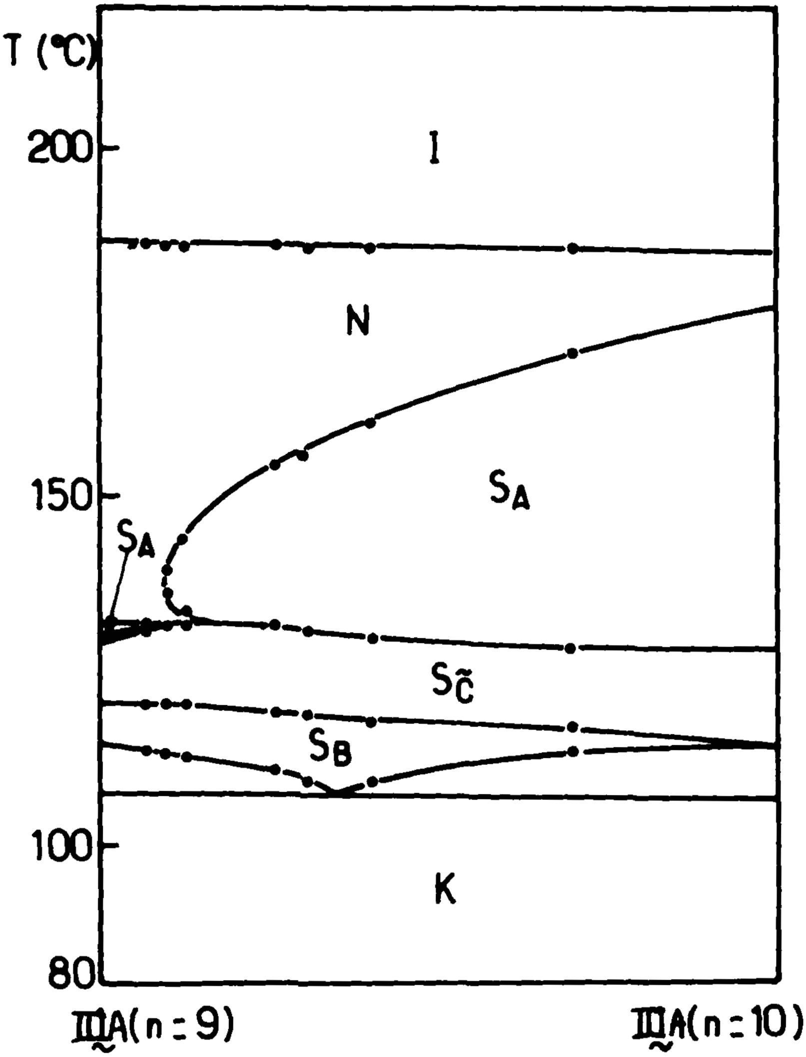
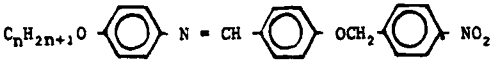


FIGURE 6 Isobaric diagram of state for mixtures of IIḬA (n = 9) (on left) and IIḬA (n = 10) (on right).

the isotropic liquid of this compound, one can observe the nematic phase with a thread like or marbled texture. Below this nematic phase, the smectic *A* phase with focal-conic and homeotropic textures appears. On further cooling, one can observe the re-entrant nematic phase with a thread like or paramorphic fan-shaped texture. On cool-

TABLE VIII

Transition temperatures (°C) of compounds of the series



IIIB

n	*K*	$S_{H?}$	S_F	S_C	N_{re}	S_A	*N*	*I*
1	. 159	—	—	—	—	—	. 207	.
2	. 151	—	—	—	—	—	. 213	.
3	. 143	—	—	—	—	—	. 198	.
4	. 120	—	—	—	—	—	. 197	.
5	. 123	—	—	—	—	—	. 189	.
6	. 113	(. 104)	—	. 114	—	—	. 188	.
7	. 96	. 109	—	. 119.4	—	—	. 184	.
8	. 86	. 109	—	. 120.5	—	—	. 183	.
9	. 98	. 110	—	. 121.8	—	—	. 181	.
10	. 95	. 107	—	. 120	—	—	. 180	.
11	. 105	(. 95)	(. 105)	. 118	. 135	. 177	. 179	.
12	. 103	—	(. 101)	. 118	. 121.5	. 178.3	—	.
13	. 104	—	(. 94)	. 108.5	—	. 178	—	.
14	. 106	—	(. 94)	. 106.5	—	. 178	—	.

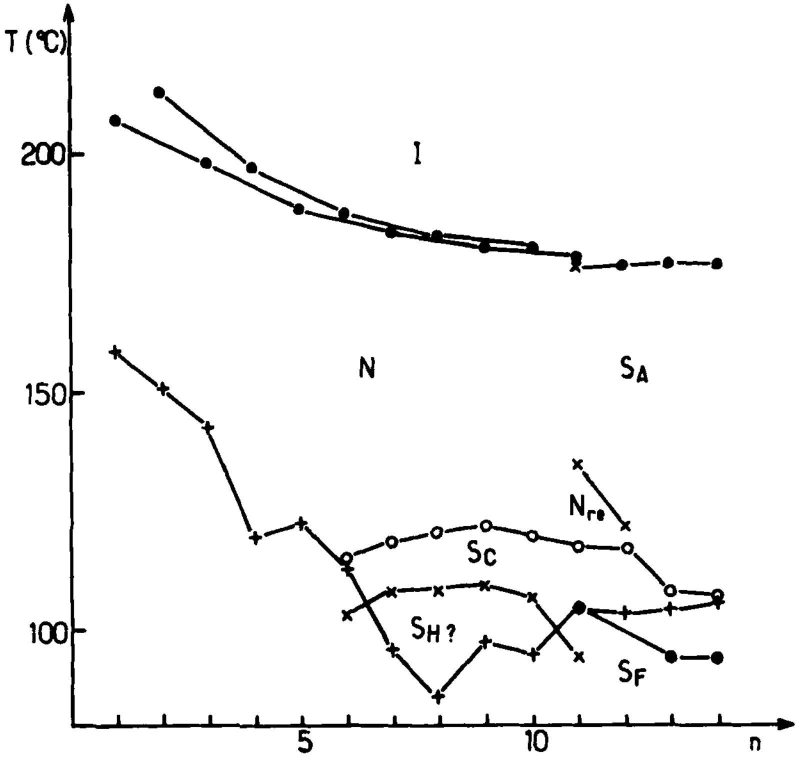
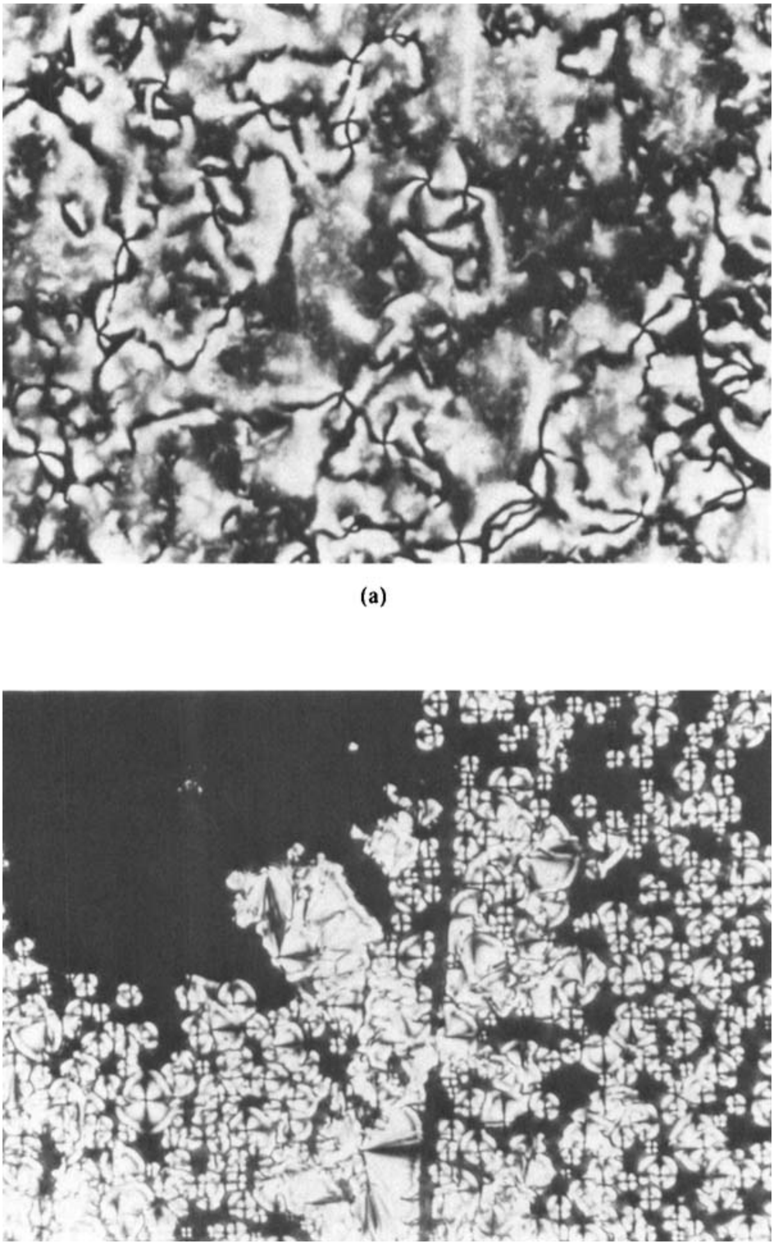


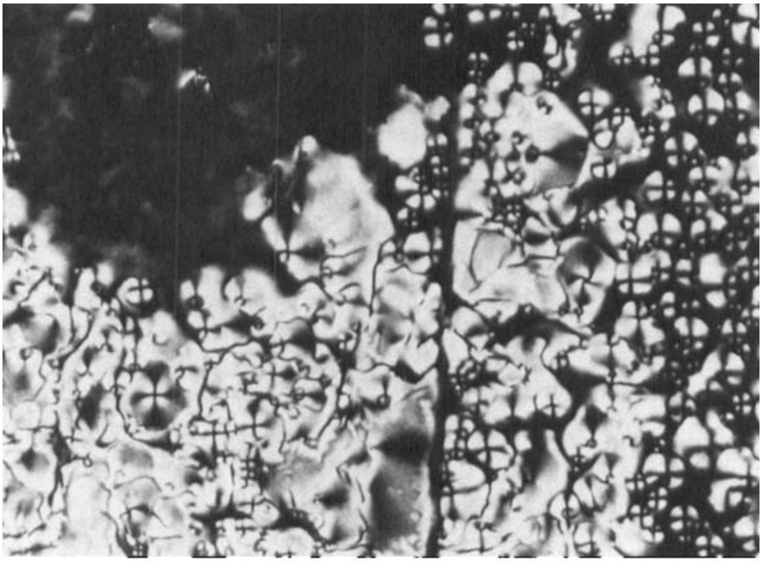
FIGURE 7 Plot of transition temperatures against *n* for series IIIB.



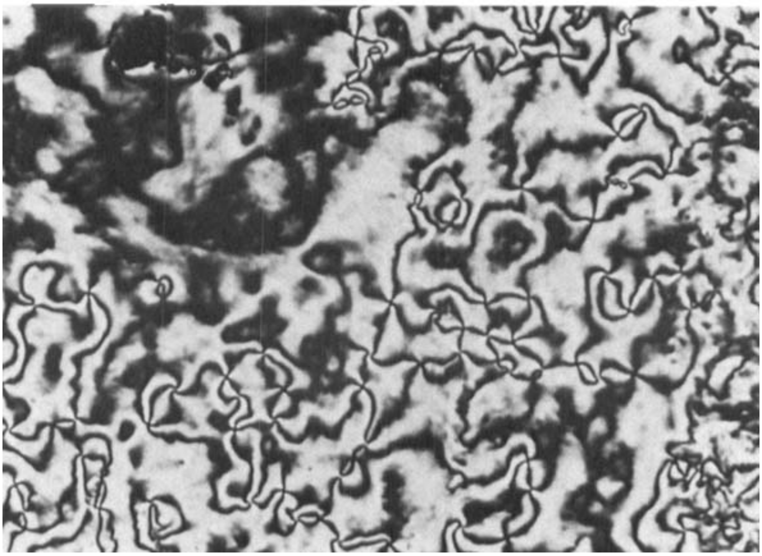
(a)

(b)

FIGURE 8 Optical textures of the compounds IIIB ($n = 11$). (*a*) *N* nematic phase at 178°C; (*b*) S_A smectic *A* phase at 170°C; (*c*) N_{re} reentrant nematic phase at 138°C; (*d*) S_C smectic *C* phase at 120°C; (*e*) S_F smectic *F* phase at 104°C; (*f*) $S_{H?}$ smectic phase at 95°C.

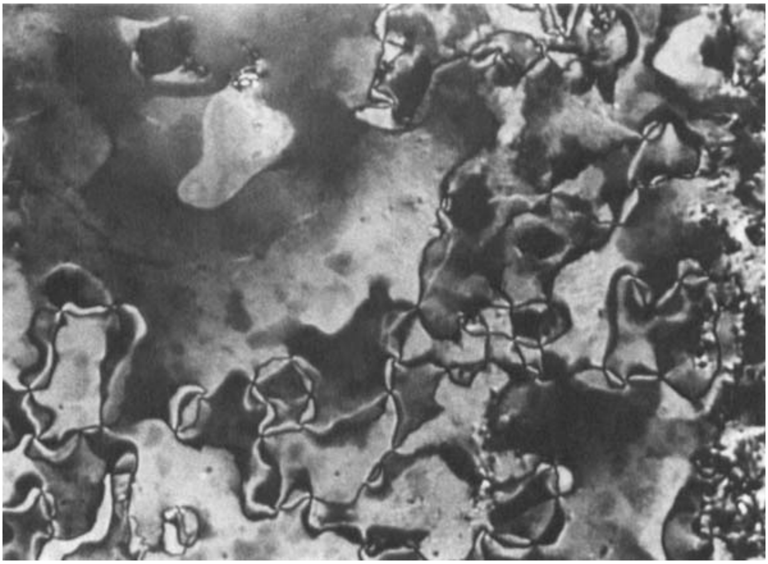


(c)

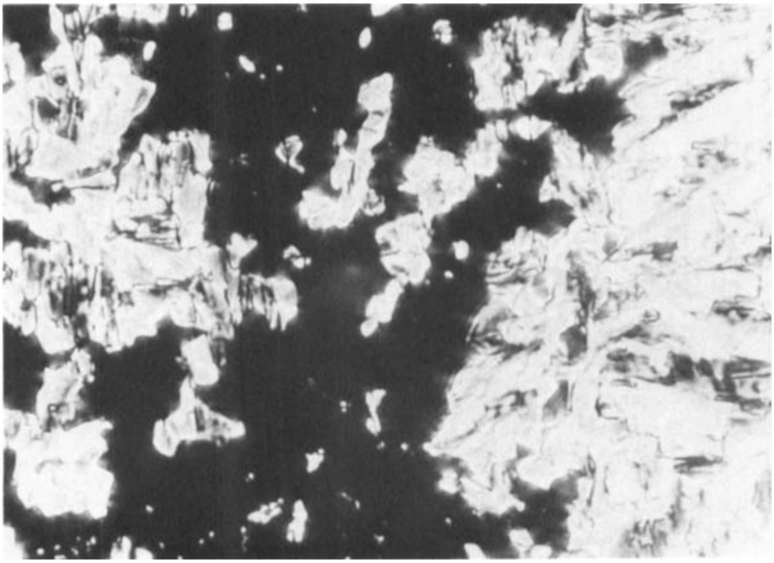


(d)

FIGURE 8 (*Continued*)



(e)



(f)

FIGURE 8 (*Continued*)

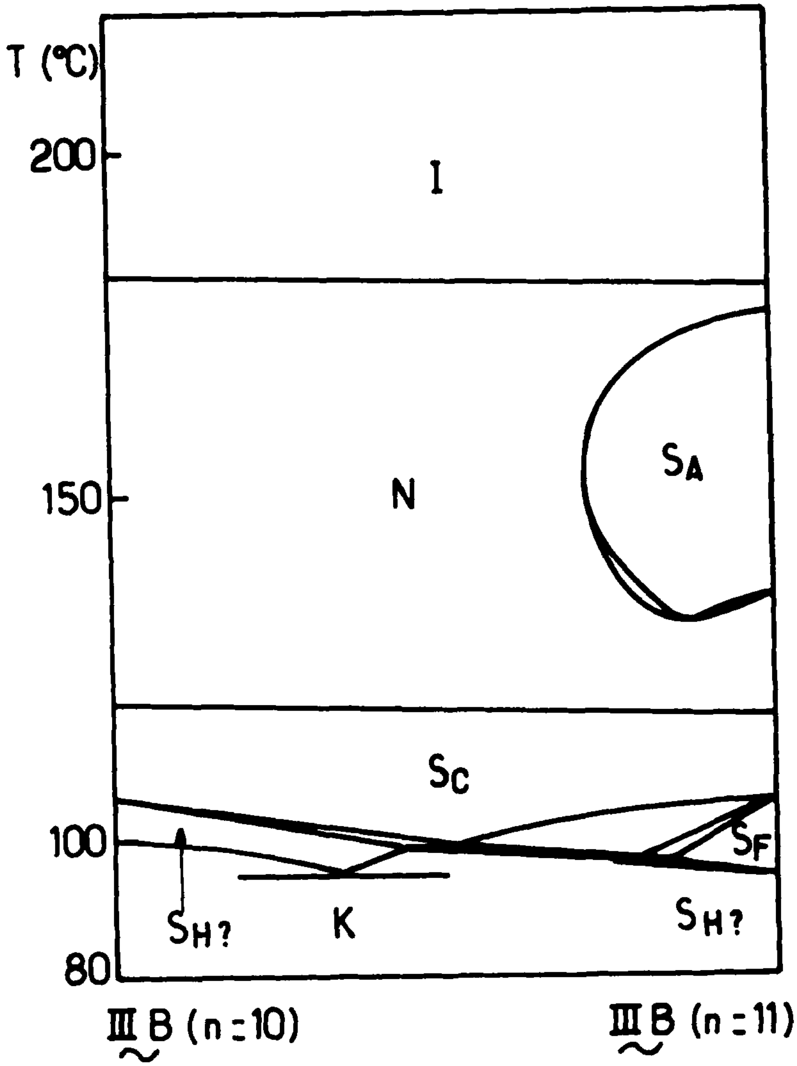
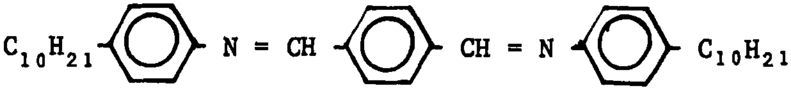


FIGURE 9 Isobaric diagram of state for mixtures of IIIB (n = 10) (on left) and IIIB (n = 11) (on right).

ing the N_{re} phase, the smectic S_C phase becomes visible through a *schlieren* or broken fan-shaped texture. Below this S_C phase, a smectic phase appears with a mosaic texture which is identified by X-ray investigation as a smectic S_F phase.[8] Below this phase, a supercooled smectic phase occurs which is miscible with the $S_{H?}$ phase of the decyloxy derivative (Figure 9). This is the first example of a S_F phase found with strongly polar mesogen; it is not miscible with that of the compound:[11]



K 75 S_G 115 S_F 149 S_I 156 S_C 198 N 199 I

The more interesting compound is the dodecyloxy derivative which exhibits the new inverted sequence:

$$K\ S_F\ S_C\ N\ S_A\ I$$

The sequence $I\ S_A\ N\ S_C$ was first observed by G. Pelzl *et al.*[12] in binary systems. The existence of a nematic phase below a S_A phase without a nematic at high temperature has already been predicted by Prost[13] and Heppke *et al.*[14] The above sequence was also observed in binary mixtures of the $n = 11$ and $n = 12$ derivatives (Figure 10) or of the $n = 11$ and $n = 13$ derivatives.

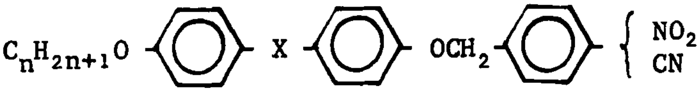
This N phase below the S_A phase totally disappears from $n = 13$.

Table IX gives the transition enthalpies and entropies of some compounds of series IIḬB. It shows that the N–I transition enthalpies increase with chain length and that the S_C–S_F transition enthalpies are weaker than those for the S_C–$S_{H?}$ transition.

Once more this series is more interesting than the homologous diester series which only exhibits nematic and S_A phases.

CONCLUSION

Substitution of the —COO— linkage by the more flexible —CH_2O— linkage in polar compounds with three phenyl rings having the general formula



where X = — single bond, —OCO—, —N = CH—, reveals several interesting results:

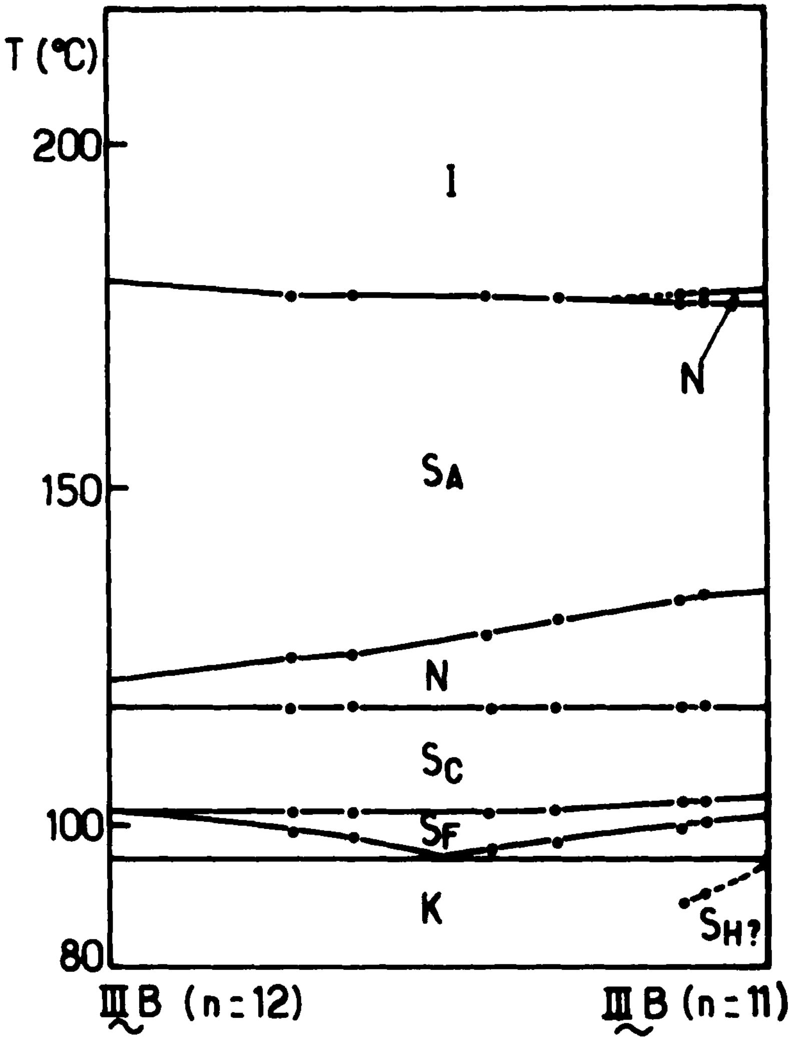


FIGURE 10 Isobaric diagram of state for mixtures of IIIB (n = 12) (on left) and IIIB (n = 11) (on right).

- The transition temperatures (T_{NI}) of the latter compounds are much lower than those of the former (by about 70°C); they are therefore more amenable to physical investigations.
- These compounds also give a rather rich polymorphism involving the so-called S_{A_1}, S_{A_d}, S_{A_2}, and $S_{\tilde{C}}$ smectic modifications and a reentrant phenomenon. However, they also exhibit some new phenom-

TABLE IX

Transition enthalpies and entropies of compounds $\underset{\sim}{\text{IIIB}}$

(ΔH in Kcal.mol^{-1} and ΔS in cal.mol.$^{-1}$ K^{-1})

n		K	$S_{H?}$	S_F	S_C	N_{re}	S_A	N	I
8	ΔH	. 6.68	. 0.71	—	. 0.09	—	—	. 0.40	.
	ΔS	*18.6*	*1.86*		*0.23*			*0.88*	
9	ΔH	. 6.80	. 0.86	—	. 0.10	—	—	. 0.49	.
	ΔS	*18.3*	*2.24*		*0.25*			*1.08*	
10	ΔH	. 6.01	. 0.54	—	. 0.08	—	—	. 0.50	.
	ΔS	*16.2*	*1.42*		*0.20*			*1.1*	
11	ΔH	. 6.87	.	. 0.39	. 0.19	. 0.01	. 0.11	. 0.63	.
	ΔS	*18.2*		*1.03*	*0.49*	*0.03*	*0.24*	*1.4*	
12	ΔH	. 8.30	.	(. 0.36)	. 0.05	. 0.03	. 1.18	—	.
	ΔS	*22.*		*0.96*	*0.13*	*0.08*	*2.6*		
13	ΔH	. 7.10	.	.	. 0.14	—	. 1.24	—	.
	ΔS	*18.8*	.		*0.37*		*2.75*		

ena and sequences, e.g., the first $S_{B_{hex}}$ and S_F phases in a pure *polar* compound, the inverted sequence, and finally, a spectacular N_{re}–S_G transition.

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