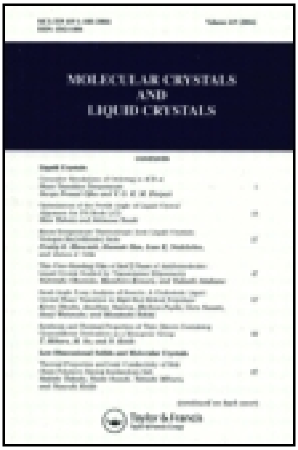


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Reentrant Phases of Four-Ring Aromatic Esters

R. Dabrowski [a], K. Pyc [a], J. Przedmojski [b] & B. Pura [b]

[a] Military Technical Academy, Warsaw, Poland
[b] Institute of Physics, Warsaw Technical University, Warsaw, Poland

Version of record first published: 07 Mar 2011.

To cite this article: R. Dabrowski, K. Pyc, J. Przedmojski & B. Pura (1985): Reentrant Phases of Four-Ring Aromatic Esters, Molecular Crystals and Liquid Crystals, 129:1-3, 169-190

To link to this article: http://dx.doi.org/10.1080/15421408408084173

Mol. Cryst. Liq. Cryst., 1985, Vol. 129, pp. 169–190
0026-8941/85/1293-0169/$25.00/0

Printed in the United States of America

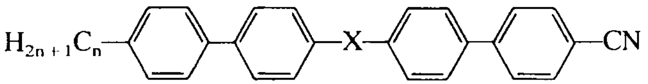
Reentrant Phases of Four-Ring Aromatic Esters†

R. DABROWSKI,‡ K. PYC,‡ J. PRZEDMOJSKI§ and B. PURA§

‡*Military Technical Academy, 00-908 Warsaw, Poland.*
§*Institute of Physics, Warsaw Technical University, Koszykowa 75, 00-662 Warsaw, Poland.*

(*Received July 19, 1984*)

The results are described of microscopic, calorimetric and X-ray diffraction investigations of compounds of the general formula **1**



1

where X = —COO— **1a**, —N=N— **1b**, $-\underset{\underset{O}{\downarrow}}{N}=N-$ **1c**, and n = 5 to 9.

Compounds **1a** have $S_{A_1} \rightarrow N \rightarrow I$ phases for n = 5 , 6 and 7 and $S_{A_1} \rightarrow N_{re} \rightarrow S_{A_d} \rightarrow N \rightarrow I$ for n = 8 and 9.

Compounds **1b** show the following sequence of phases: $S_E \rightarrow S_B \rightarrow S_{A_1} \rightarrow N \rightarrow I$.

Compounds **1c** have the same smectic phases as compounds **1b** but the S_A phase is observed up to the decomposition temperature of the compound.

Many binary mixtures containing compounds **1a** have been examined and their phase diagrams are discussed. X-ray diffraction results are presented for these compounds.

---

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

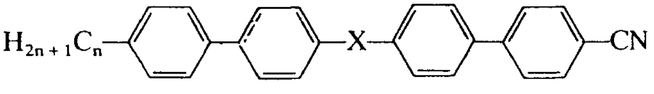
---

†The authors are indepted to Dr. J. Baran for calculating the molecular lengths.

INTRODUCTION

Liquid crystal compounds are in ever more frequent use; in addition to their applications in displays, they are valuable in chromatographic analysis as highly selective stationary phases enabling efficient separation of many mixtures, especially those consisting of geometric isomers.[1]

Our interest in liquid crystal stationary phases (see refs in [1]) prompted the synthesis and examination of the mesomorphic properties of the four-nuclear compounds of the general formula **1**



1

where X = —COO— (**1a**), —N=N— (**1b**), $-\underset{\underset{0}{\downarrow}}{N}=N-$ (**1c**) and n = 5 to 9. Some of the esters of this series have already been described by Gray[2] (for n = 5 and 7). Repeateding the investigation of these esters with a greater number of members has lead us to the discover of some unexpected properties.

We found that compounds **1a** show an abnormal sequence of phases: for n = 8 and 9 one observes a nematic "reentrant" phase, and for n = 8 a smectic A reentrant phase in addition. The phenomenon of reentrant phases, since its discovery by Cladis, has been of great interest. The French researchers, who synthesized many new series of compounds, have contributed largely to the better knowledge of the nature of this phenomenon.[4-6] The trinuclear esters described by these authors which reveal enantiotropic $S_{A_{rc}}$ and N_{rc} phases are at present the most convenient examples for studying reentrant phase phenomena. Compounds **1**, whose molecular and dipole structures are simpler than those of the above mentioned compounds (as they have only two polar groups, the central group —COO— and the terminal —CN), may present even more convenient material for such studies. With this in mind, we decided to study in greater detail the liquid crystal properties of these compounds.

In the present work we describe the results obtained by optical microscopy, scanning calorimetry and X-ray diffraction methods and discuss the analysis of the phase diagrams.

EXPERIMENTAL

The method of synthesizing and purifying compounds of series **1** has been described in detail in our earlier work.[7]

The phase transition temperatures were determined by two methods:

(i) The change of texture in polarized light was observed of samples placed between microscope slides on the heated stage of a VEB Analytik (Dresden) PHMK apparatus for measuring the melting point. The phase transitions Cr → S → N → I were observed in the heating and cooling cycles, care being taken to ensure that thermal equilibrium was achieved between the sample and the stage in the phase transition temperature; this was done by short alternations of heating and cooling.

(ii) The thermal effects of the phase transitions were observed under nitrogen by means of a Du Pont 910 differential scanning calorimeter. The heating rate was held constant over the transition region ($\pm 15°$) at 1 deg/min. The transition temperatures were obtained from the position of the maximum of the transition heat effect peak.

The liquid crystal phases were identified on the basis of the phase diagrams obtained for a large number of weighed-out samples of binary mixtures and by X-ray diffraction.

The molecular lengths used in the discussion were calculated using the additivity of bonds and assuming that the alkyl chain has a *trans* conformation (ℓ_{max}) or that it assumes the direction of the rigid core axis (ℓ_{min}).†

RESULTS

Esters—series 1a

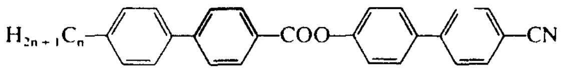
Temperatures and enthalpies of the phase transitions

The phase transition temperatures and molar enthalpies are summarized for the esters **1a** in Table 1.

In this homologous series we observe a large diversity of properties in terms of polymorphic changes in the solid phase and the phase transitions between mesophases. The esters, **1a**, with the exception of the $n = 7$ compound, reveal two phase changes in the solid below the melting point. Compounds with $n = 5$ and 6, have a high enthalpy, while compounds with $n = 8$ and 9 the enthalpies of both polymorphic changes are low. In compounds with $n = 5$, 8 and 9 the second polymorphic change ($Cr_2 \rightarrow Cr_3$) lies up to a dozen or so degrees

TABLE I

The phase transition temperatures (°C) and enthalpies ($kJmole^{-1}$) for esters:



1a

Those transitions which are visible by microscopy are given on the upper lines and those observed by DSC on the lower lines.

n	Cr_1		Cr_2		Cr_3		S_{A1}		N_{re}		S_{Ad}		N		I
5	•	X	•	134	•	139	•	166.5	—		—		•		•
	•	103.5	•	134	•	139	•	X	—		—		•	380	•
		2.3		14.1		11.6							•	1.1	•
					•	140	•	166[a]	—		•			280	
6	•	X	•	X	•	140.5	•	158	—		—		•		
	•	80	•	100	•	141	•	X	—		—		•	360	•
		14.4		1.0		21.7								1.3	
7	—		—		•	126	•	141	—		—		•		•
	—		—		•	127	•	X	—		—		•	352	•
						21.1								1.4	
						125		131[b]							
8	•	X	•	X	•	118	•	/108.5/	•	160.5	•	298	•		•
	•	56.5	•	103	•	119	•	X	•	X	•	X	•	343	•
		2.9		2.0		20.0								1.3	
9	•		•	111	•	116	•	100	•	127	•	312	•		•
	•	82	•	110	•	116	•	X	•	X	•	313	•	338	•
		1.5		3.2		20.7	•					0.25		1.8	

According to refs (2) -a, (8) -b,

— the phase is absent,

• the phase is present,

X the transition was not observed by microscopy or DSC.

below the melting point. Above the temperature of the $Cr_2 \rightarrow Cr_3$ change the solid becomes plastic and readily deforms under light pressure.

Compounds **1a** with $n \leq 7$ melt to the smectic A_1 phase which has been identified, on the basis of measurements of the layer spacing (d_1) which is approximately equal to the length of a single molecule (ℓ) (see Table II). The phase transition $S_{A_1} \rightarrow N$ was not observed by the DSC method since its enthalpy is smaller than the sensitivity of the calorimeter used. This transition must have therefore a very small or even zero enthalpy.

The temperatures of all the observed phase transitions in compounds **1a**:

$$Cr \rightleftarrows S_{A_1} \rightleftarrows N \leftrightarrows I$$

decrease as n increases from 5 to 7.

A pattern of phase transitions is observed for the esters with $n = 8$ and 9. These compounds on melting, pass immediately to the nematic phase, which at higher temperatures changes into the A_d smectic phase (the layer spacing is $d_2 > \ell$) which in turn changes at higher temperature again to the nematic phase. Thus in these two compounds the nematic phase exists twice: once before and once after the A_d smectic phase. In accordance with the accepted convention the low-temperature nematic phase is termed reentrant. In compounds **1a** with $n = 8$, on cooling we observe a transition at 108.5° from the N_{re} phase to the S_{A_1} phase. The latter phase has only a small stability range and crystallizes directly after the $N_{re} \rightarrow S_{A_1}$ transition.

In the case of compound **1a** with $n = 9$, crystallization takes place before the $N_{re} \rightarrow S_{A_1}$ phase transition. The temperature of the virtual $N_{re} \rightarrow S_{A_1}$ transition can be extrapolated from the phase diagrams (Figure 2) as ca. 100°. In the case of compounds **1a** with $n = 8$ and 9 the observed sequence of mesomorphic transitions is:

$$\begin{tikzcd}
Cr \arrow[r, shift left] & N_{re} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift right] & S_{A_d} \arrow[l, shift left] \arrow[r, shift left] & N \arrow[l, shift left] \arrow[r, shift left] & I \arrow[l, shift left] \\
& S_{A_1} \arrow[u, shift right] \arrow[ul] & & &
\end{tikzcd}$$

The enthalpies of the phase transitions $S_{A_1} \rightleftarrows N_{re} \rightleftarrows S_{A_d} \rightleftarrows N$ are very small (below the sensitivity of our calorimeter). In the case of the ester with $n = 9$ only the enthalpy of the $S_{A_d} \rightleftarrows N$ transition is greater and amounts to ca. 0.25 $kJ/mole^{-1}$. Some differences are observed in the microscopic picture of the nematic reentrant phase between the esters **1a** with $n = 8$ and $n = 9$. In the compound with n = 8, the $N_{re} \leftrightarrows S_{A_d}$ phase transition is sharp and very distinct whereas in the case of compound with n = 9 it is diffuse and indistinct—the two phase region extends over a wider temperature range. If we observe the N_{re} phase of the ester with n = 9, flowing between two microscope slides, caused by tilting the stage, then we see distinctly that it contains regions of lower and higher viscosity. The compound behaves as if it were a mixture of the nematic and smectic phases. In this phase there are probably large domains of a structure close to that of the A_d smectic.

Diagrams of binary mixtures

In binary mixtures obtained from a compound with the normal nematic phase (n = 5 or 6 or 7) and a compound with the reentrant phase (n = 8 or 9) the normal nematic phase and the reentrant nematic phase combine in a continuous way (Figures 1 and 2). The region of existence of the high-temperature smectic phase A_d is limited in the binary mixture, to a small concentration range. The concentration range over which the phase S_{A_d} exists in the mixture is greatest for a mixture consisting of the compound with the reentrant phase and the compound preceding it (n = 7), and decreases as the lengths of the alkyl chains of the two components differ more widely. The phase diagrams of mixtures of compounds belonging to the series, **1a** are similar to those encountered by the French groups: Sigand, Nguyen Hun Tinh, Hardouin and Gasparoux[5-7] or Gobl-Wunsch et al.[9]

We observed a somewhat surprising course of the boundary line separating the smectic phase A_d from the phase N_{re} for the mixture of compounds with n = 8 and n = 9 (Figure 3). The transition temperatures of phases $S_{A_d} \rightarrow N_{re}$ do not lie on the line connecting $S_{A_d} \rightarrow N_{re}$ phase transition temperatures of the pure compounds, but over the major part of the concentration range (up to 50% wt. of the compound with n = 9) they lie instead on the straight line connecting the point corresponding to the $S_{A_d} \rightarrow N_{re}$ transition of compound n = 8 with the point corresponding to the virtual $S_{A_1} \rightarrow N_{re}$ transition for the compound with n = 9. This seems to point to the partial miscibility of the smectic phase S_{A_d} of compound with n = 8 with the smectic phase A_1 of compound with n = 9. This is probably due to the fairly small difference between the spacings of the smectic layers of the two phases. The spacing of the S_{A_d} smectic layer of compound with n = 8 is 4.1 nm and the estimated spacing of the S_{A_1} smectic layer for the compound with n = 9 is ca. 3.35 nm. The

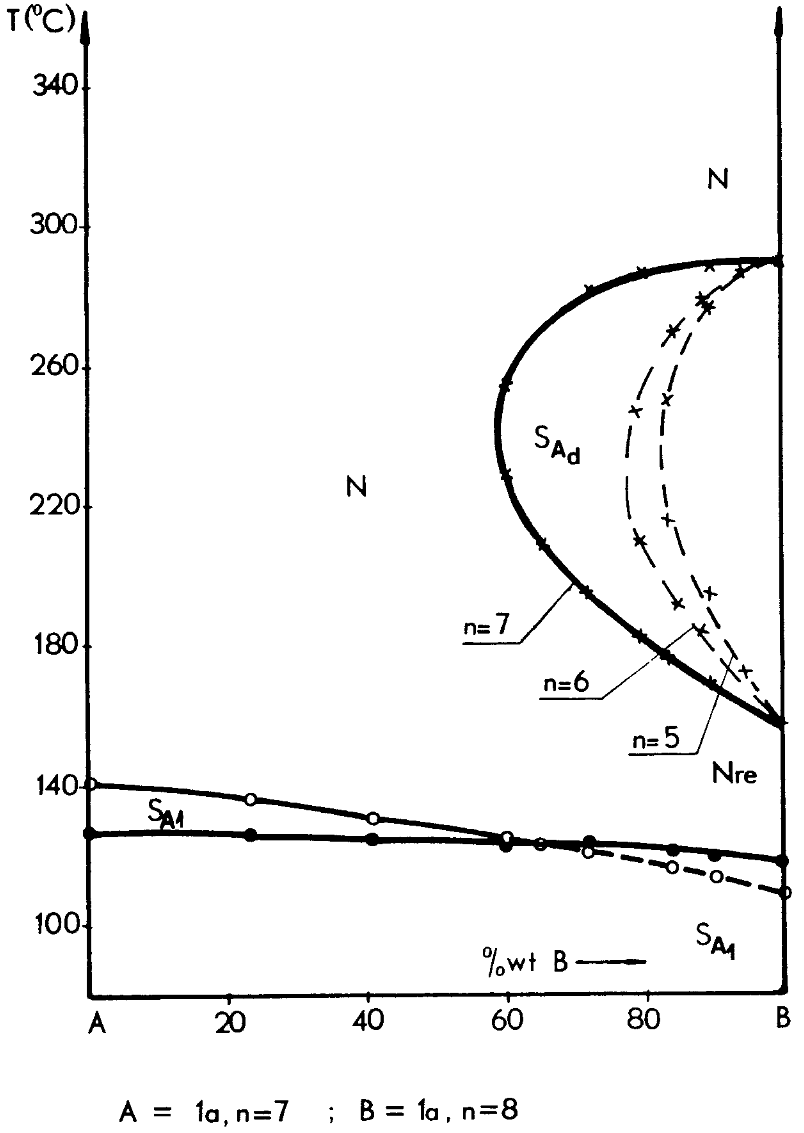


FIGURE 1 Binary phase diagram showing isomorphism of the N and N_{re} and S_{A1} phases of the **1a** compound with n = 8, with the N and S_{A1} phases of the same series of compounds with values of n of 5, 6 and 7. ● melting point, S_{A1}—N transition, ○ S_{A1}—N transition.

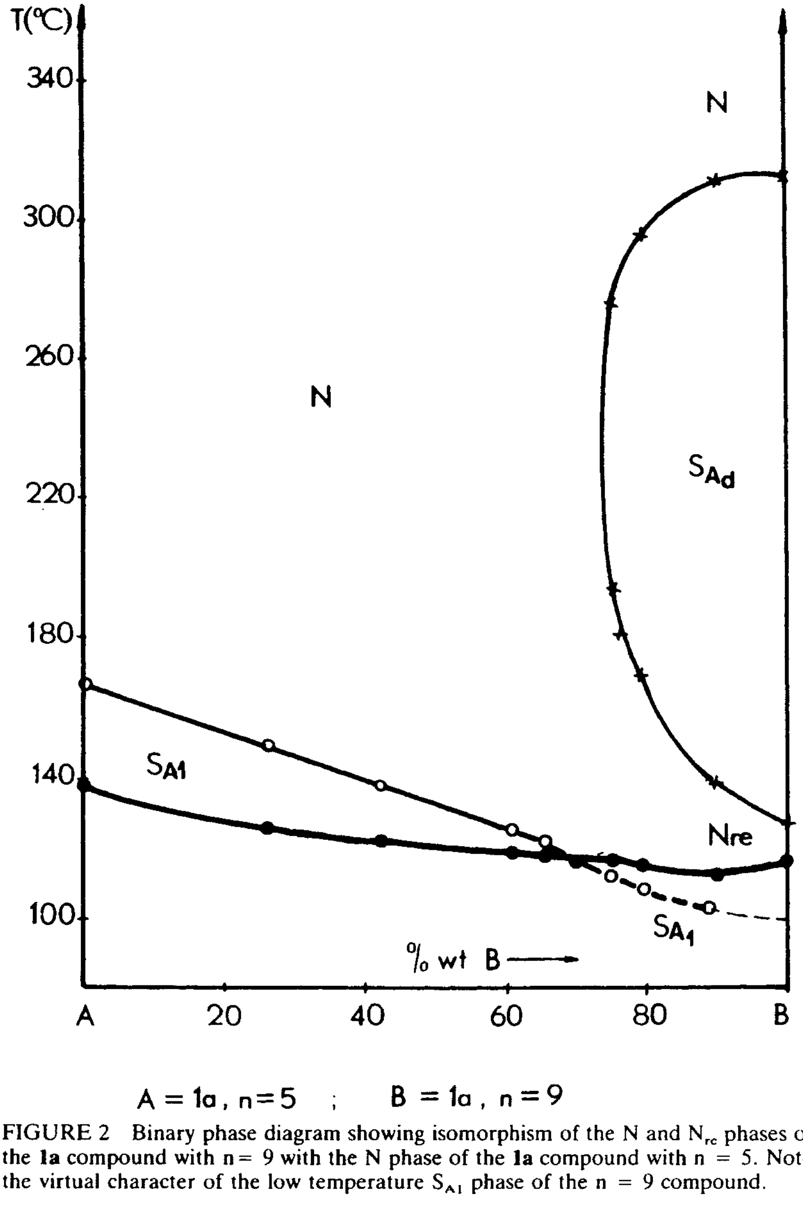


FIGURE 2 Binary phase diagram showing isomorphism of the N and N_{rc} phases of the **1a** compound with n = 9 with the N phase of the **1a** compound with n = 5. Note the virtual character of the low temperature S_{A1} phase of the n = 9 compound.

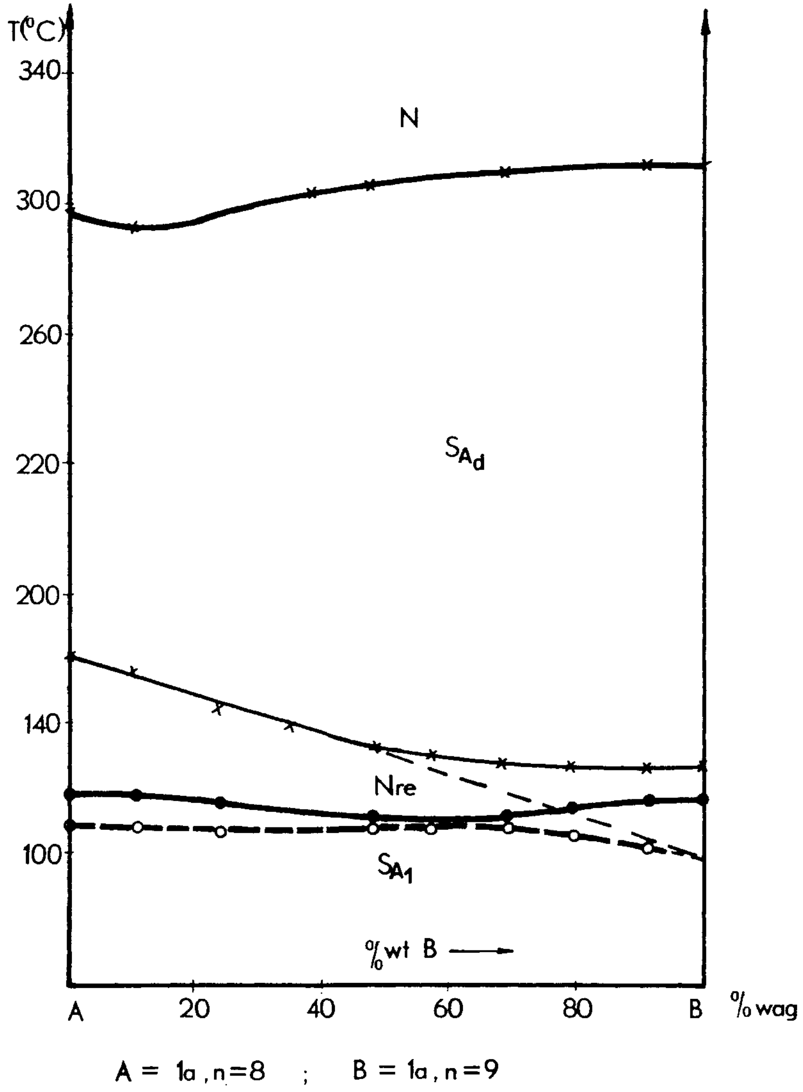
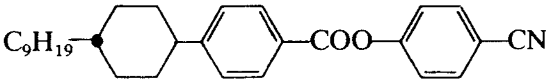


FIGURE 3 Binary phase diagram showing the isomorphism of the mesophases of the **1a** compounds with n = 8 and n = 9.

ratio of the spacings of these smectic layers $d_2/d_1 \approx 1.22$ is smaller than that required for preventing the miscibility of the two S_A phases.[10] The results presented in Figures 4 and 5 relating to mixtures of esters **1a** with n = 5 or n = 8 with the ester



2

reveal the significant effect of the smectic layer spacing ratio on the character of the phase diagram. Ester **2** gives an A_d type smectic phase with a spacing d_2 = 4.0 nm[10] and molecular length ℓ = 2.94 nm. Compound **1a** with n = 5 which has only the A_1 smectic phase with spacing d_1 = 2.75 nm reveals a high incommensurability of this spacing with that of compound **2** (d_2), which is confirmed by the ratio d_2/d_1 = 1.45. As a result, the smectic A phases of the pure components are not miscible and are separated by a nematic region (Figure 4). In this binary mixture the stability of the ester **1a** smectic phase of A_1 type decreases rapidly and that of ester **2** (of A_d type) much more slowly. In addition, the border of $S_{A_d} \rightarrow I$ bends forming a parabola and as a result the nematic phase is observed twice, at higher and lower temperatures, over the concentration range of ester **2** from 60 to 80%. This characteristic of the phase diagram confirms our suggestion that occurrence of the reentrant phases phenomenon as a function of temperature and the appearance of nematic gaps as a function of concentration have a common cause. In particular, the compound **1a** with n = 8, which also has an A_d smectic phase of spacing close to that observed for **2**, exhibits excellent miscibility of its A_d phase with the A_d smectic phase of ester **2** over the whole concentration range (Figure 5). It is very interesting that ester **2** in a mixture with compound **1a** with n = 8 strongly destabilizes the reentrant nematic phase. The latter phase in this binary mixture is limited to a very narrow compound **2** concentration interval (less than 5% in the mixture). In the mixture of compound **1a** with n = 8 containing 5% of compound **2** we observed the reentrant nematic phase in an interval as narrow as 118–104° and below this interval crystallization of the mixture occurred without the earlier appearance of the S_{A_1} phase. One can believe that the presence of compound **2** strongly destabilizes the smectic phase A_1. This conclusion follows even more directly from Figure 4.

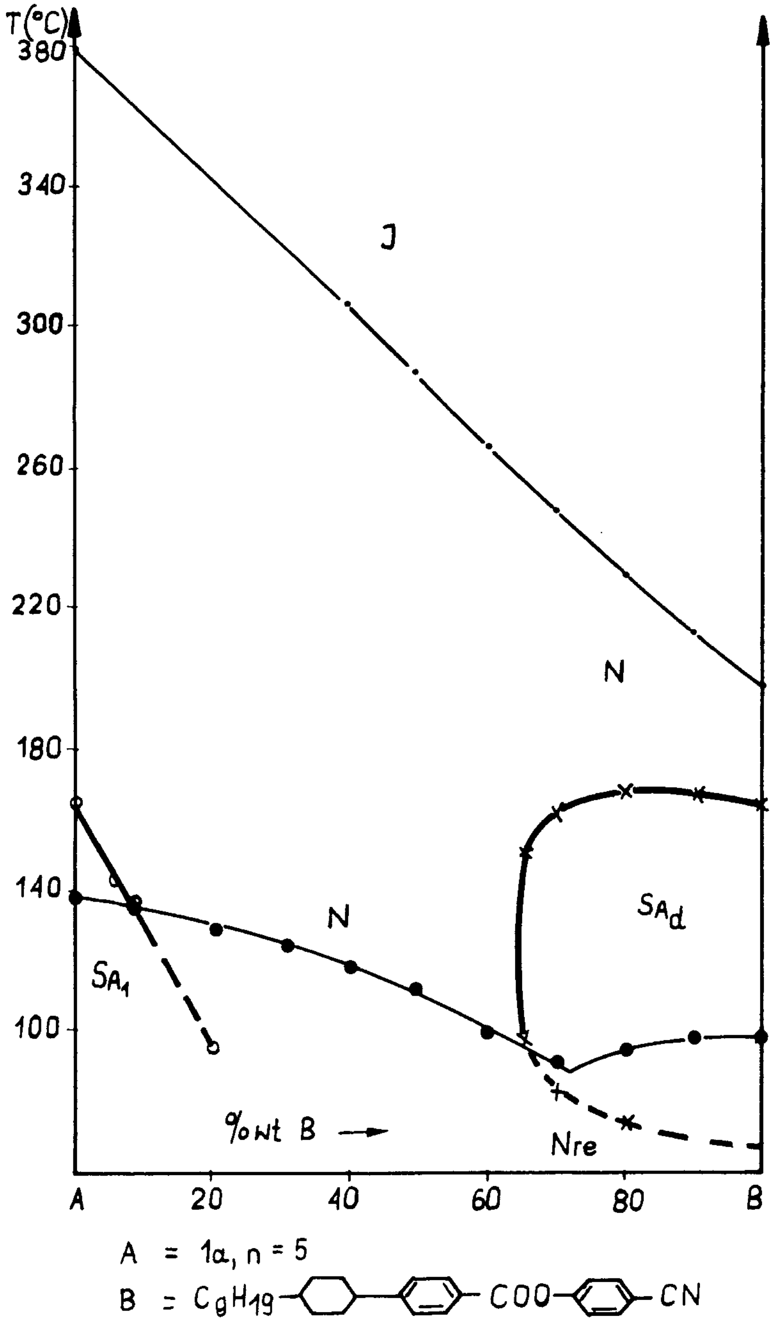


FIGURE 4 Binary phase diagram illustrating the non-miscibility of the S_A phases of compounds A and B.

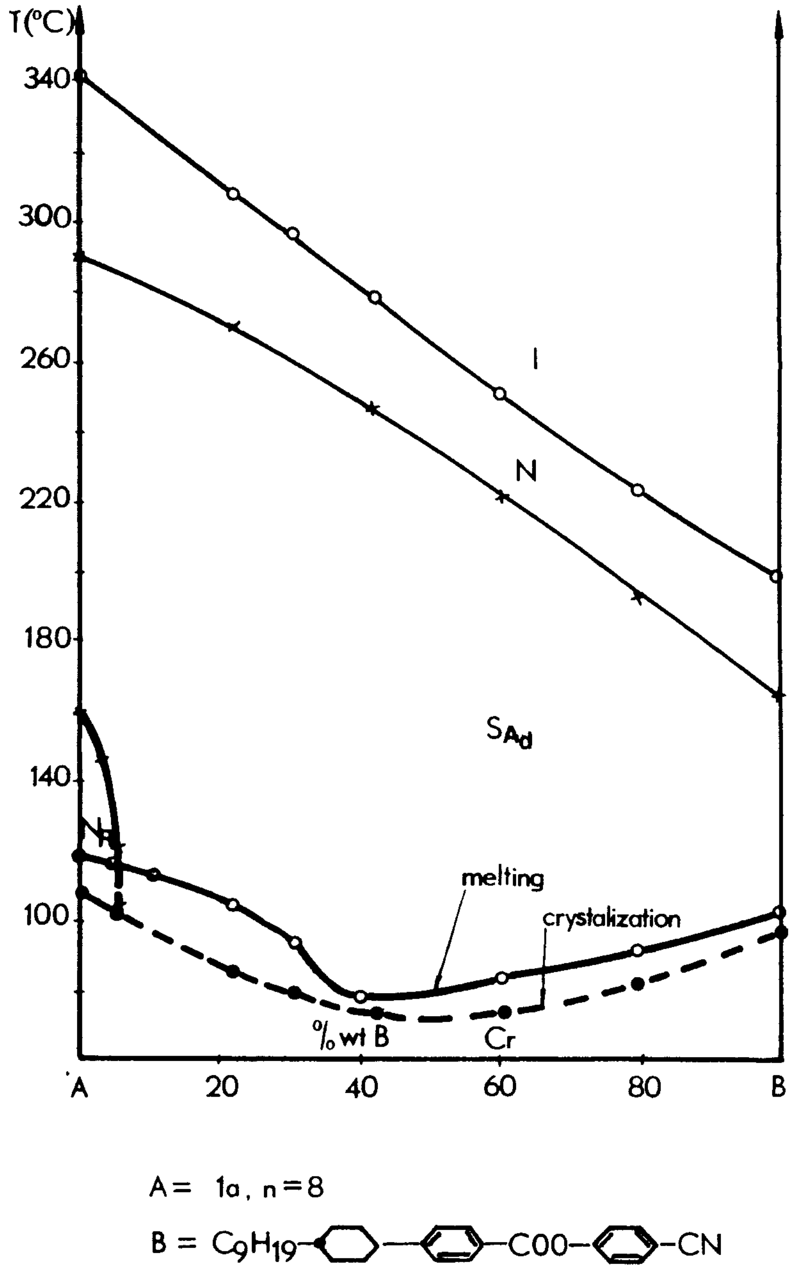


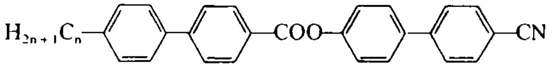
FIGURE 5 Binary phase diagram demonstrating the isomorphism of the S_A phase of compound A with the high temperature S_{A_d} phase of compound B.

x-Ray diffraction

The measured spacings of smectic layer have been compared with the calculated molecular lengths and the results are presented in Table II. In compounds **la** with n = 5 , 6 and 7 the smectic layer spacing is insignificantly smaller than the calculated molecule lengths ℓ_{min}. This has been observed in the case of other smectics A_1.[5] It can be explained by partial penetration of the molecules of adjacent smectic layers or by some tilting of the molecules. In compounds **la** with n = 8 to 9 the spacing of smectic layers of the high temperature smectic phase is larger than the molecule length d_2/ℓ = 1.34 and 1.35 for n = 8 and n = 9, respectively. In the reentrant nematic phase of compound **la** with n = 8 two reflections with low angle are observed. The splitting of these reflections is best seen near the transition point $N_{re} \rightarrow Cr$ Figure 6 shows this effect at 110°. The outer reflection in Figure 6a is connected with the d_1 = 3.05 nm interplanar distance, while the interplanar distance of the inner reflection is d_2 = 4.1 nm; d_2/d_1 = 1.34. The position of the d_1 peak was found to be constant, whereas the position of the d_2 peak varied slightly with temperature (Figure 7) except for a temperature close to the crystallization point, at which d_2 decreases rapidly to the value of 3.85 nm. In contrast, the intensity of d_1 and d_2 peak reflections change markedly with temperature. The intensity of the d_1 peak decreases so this reflection would not be observed at the temperature of about 150°. The intensity of the d_2 reflection increases with temperature.

TABLE II

Comparison of the interplanar distance, d obtained from X-pattern with molecular lengths (l) for esters:



la

n	l_{min} (nm)	l_{max} (nm)	d in mesomorphic state (nm)			Temp. (°C)
			S_A	N_{re}	Cr	
5	2.94	2.97	2.75			150
6	3.00	3.06	2.85			150
7	3.15	3.21	3.00			130
	3.1*					
8	3.21	3.29			3.05;3.85	100
				3.05;4.1		110
			4.05			170
9	3.36	3.44		4.65		120
			4.0			170

*according to ref. (8)

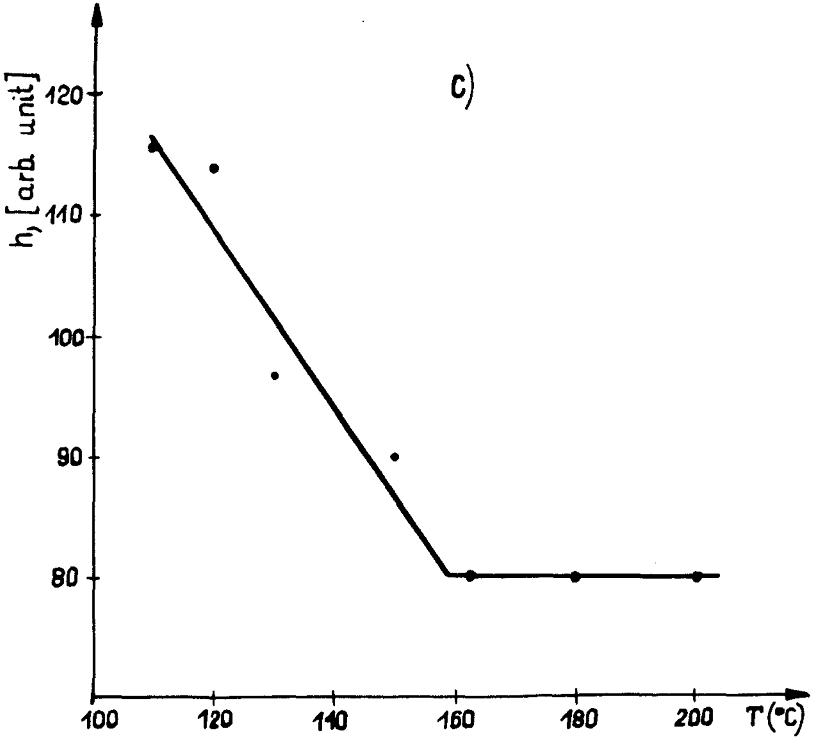


FIGURE 6 X-ray diffraction patterns of the mesophases of the **1a** compounds with n = 8. (a) the reentrant nematic phase at 115°, (b) the smectic S_{Ad} phase at 165°. Figure (c) shows the variation of the line width of the inner reflection (d_2 = 4.1 nm) with temperature.

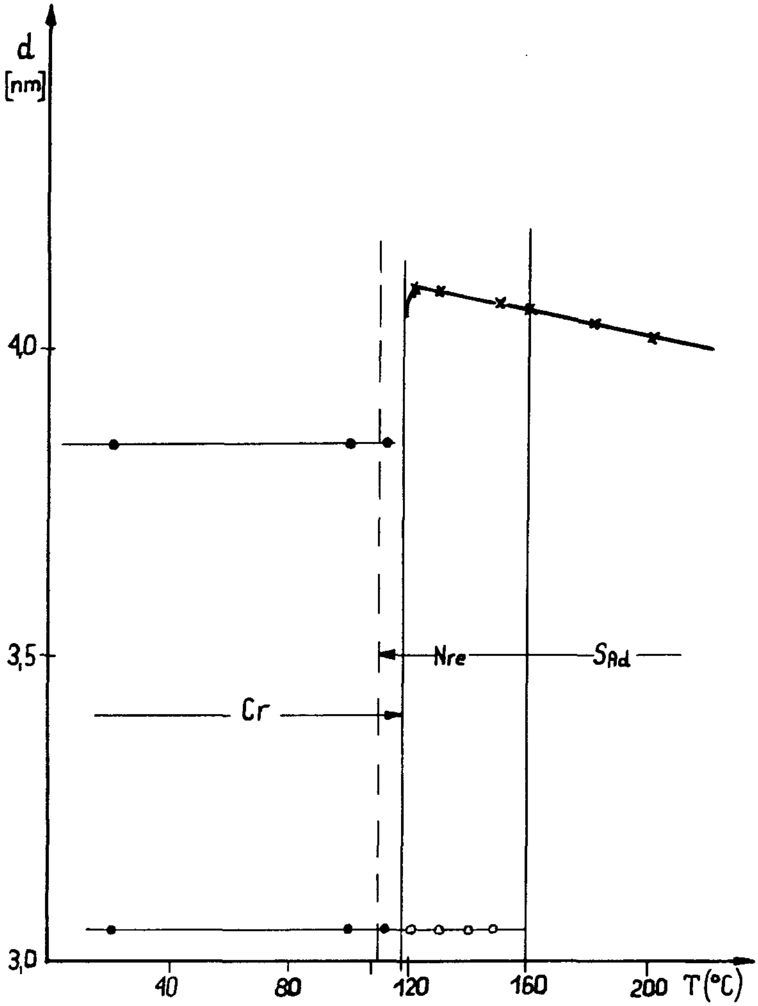


FIGURE 7 The variation of the d-spacing of crystalline solid and mesophases of the **1a** compound with n = 8, with temperature.

In the reentrant nematic phase of compound **1a** with n = 8, one more characteristic phenomenon has been noted. At low temperature, about 110°, the reflections described above have an elongated linear shape in the direction perpendicular to the director (Figure 6a). Their heights in this direction decrease with the increase of temperature, reaching the usually observed shape above 160°, i.e. for the smectic A phase (Figure 6b). The variation of the line width of the reflection $d_2 = 4.10$ nm is presented in Figure 6c. It is characteristic of the compound **1a** with n = 8 that two reflections were also observed in the crystalline phase where the interplanar distances are $d_2 = 3.85$ nm and $d_1 = 3.05$ nm and the $d_2/d_1 = 1.26$ ratio is lower than that determined for the nematic reentrant phase. The $d_1 = 3.05$ nm peak is strictly related to the reflection in the low-temperature (ca.120°) reentrant nematic phase.

The X-ray patterns of both reentrant and crystalline phases mentioned above suggest that the presence of two reflections in the reentrant phase might be connected with the fluctuation of the crystalline phase in the nematic phase on the one hand, and the fluctuation of the high-temperature smectic phase with antiparallel molecules in clusters on the other hand.

The linear shape of the reflections d_1, d_2 in the reentrant nematic phase (Figure 6a,b) could be explained in two ways:

(i) There are skew cybotactic groups in the nematic phase with a tilt angle which changes continuously from zero to some angle α (this angle characterizes the linear shape of the reflection and depends on temperature). This interpretation is based on the concept of de Vries regarding cybotactic groups.[11]

(ii) Some molecules are tilted in the smectic layer and some are normal—this means that the thickness of the smectic layer is not constant. When the magnetic field is applied such a layer must be modified. It can be shown that this gives the difraction peak a linear shape. In the reentrant phase of the compound **1a** with n = 9 the magnetic field used, (ca. 8 kG) was insufficient to give parallel alignment of the sample. This made it impossible to obtain more detailed information about the structure of this phase.

The azo compounds

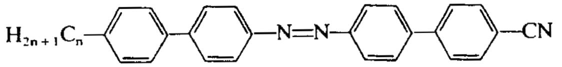
Table III summarizes the phase transition temperatures and enthalpies of the azo compounds **1b**. In the homologous series of azo compounds, **1b** with n = 5 to 8 the following sequence of phase transitions is observed:

$$\mathrm{Cr} \rightarrow S_E \rightarrow S_B \rightarrow S_A \rightarrow N \rightarrow I$$

The clearing temperatures of these compounds are high—above 400°—and they cannot be determined because decomposition of the compound takes place. It was found for the samples of all compounds tested that the phases S_A and S_B often assumed a homeotropic texture.

TABLE III

The phase transition temperatures (°C) and enthalpies (kJmole⁻¹) for the azo compounds:



1b

n	Cr		S_E		S_B		S_A		N		I
5	•	138	•	210	•	217	•	280	•	>400	•
		5.7		2.8		3.7		0.5			
6	•	112	•	217	•	223	•	276	•	>400	•
		6.5		2.9		4.2		0.8			
7	•	97	•	221	•	224	•	266	•	>400	•
		9.0		2.8		4.2		0.5			
8	•	92	•	227	•	229	•	259	•	>400	•
		11.2		2.7		4.8		0.5			

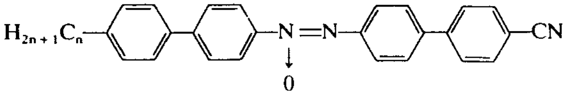
The transition from the homeotropically ordered B phase to an E phase was accompanied by the generation of a colored, strongly scattering, texture with irregular borders to the domains. The DSC plots show that the phase transitions E → B and B → A occur over a narrow temperature interval, while the melting and S_A—N transition peaks are much wider. The smectic phases E and A are observed over a wide temperature range, but the smectic phase B—over a range of only a few degrees. The smectic phase A_1 shows high thermal stability, which decreases slightly with the increase of the alkyl length. Thus, in this series of compounds we should not expect the occurrence of the nematic reentrant phase for compounds with alkyl chains longer than those of the compounds tested.

The azoxy compounds

Table IV summarizes the phase transition temperatures and enthalpies for the azoxy compounds **1c**. In the series of azoxy compounds **1c** for n = 5 and 6 we observed initially the same order of smectic phases as in the azo compounds **1b**, viz.: Cr → S_E → S_B → S_A. Thermal decomposition of these compounds takes place before the S_A → N transition is observed. In this series, the phases E and B have a low thermal stability, whereas the phase S_A is observed over a very wide range of temperatures. Compounds **1c** are mixtures of position isomers which probably hinders the ordering of molecules in the smectic phase, and hence the phases E and B exist in a narrow temperature interval. In compounds with n = 7 or 8 a larger number of phase transitions was observed. The DSC peaks for these com-

TABLE IV

The phase transition temperatures (°C) and enthalpies for the azoxy compounds:



Ic

(mixture of the position isomers)

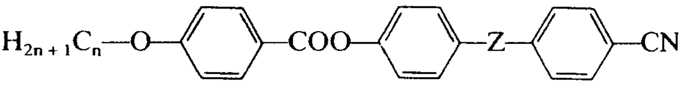
n	Cr		S_E		S_B		S_A		N	
5	•	86 17.1	•	102 2.2	•	111 0.2	•	>350	•	decomp.
6	•	71 11.2	•	104 2.3	•	120 0.4	•	>350	•	decomp.

pounds are broad, which may point to their unsatisfactory level of purity. Therefore we have not quoted the phase transition temperatures for these compounds.

DISCUSSION

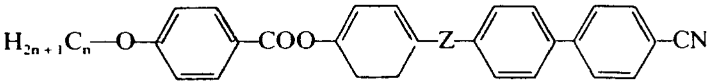
The esters **Ia** described in the present work are the first compounds that exhibit the phenomenon of reentrant nematic and smectic phases with four benzene rings in the rigid core of the molecule.

It has been found on the basis of the properties of the series of compounds so far tested, that the most advantageous molecular structure for the appearance of the reentrant nematic and smectic phases is possessed by the trinuclear compounds with two bridging groups of the general formula **3** which have been synthesized by the French researchers from the Centre de Recherche Paul Pascal:[4-6]



3

where: Z = —CH=CH—, —C≡C—, —N=N—, —O—CO—, —COO—, —CH=N, —N=CH—. The extension of the molecule rigid core of compounds **3** by an additional benzene ring (formation of the compound of formula **4**) results in the disappearance of the reentrant phase phenomenon[4,12]

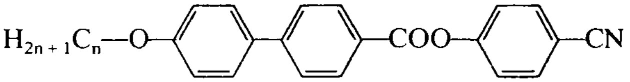


4

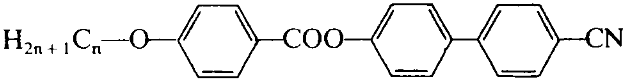
where Z = —COO— or —CH=N—

The removal of one bridging group from the molecule of compound

3 (giving compounds of formulae **5** or **6**) also decreases the tendency of the compounds to yield reentrant phases



5

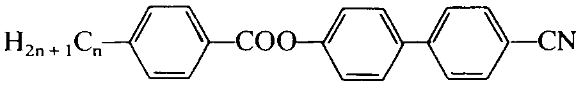


6

In esters **5** we do not observe reentrant phases, but they do appear in mixtures with other compounds which allow us to estimate the temperature of the virtual transition $S_{A_d} \rightarrow N_{re}$.[4]

The isomeric esters **6** have a nematic reentrant phase, but no member of the series revealed the smectic phase A_1.[13]

Substitution in esters **6** of the alkoxy group by an alkyl group results in the disappearance of the reentrant nematic phase, however, in mixture with compound **7** with n = 7 or 8

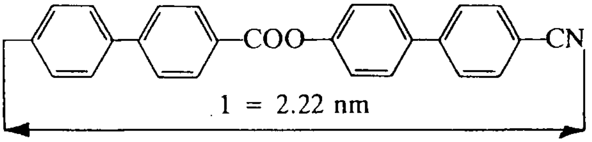


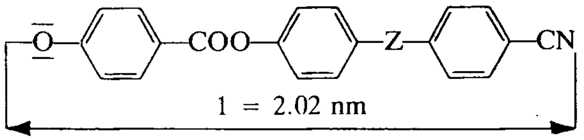
7

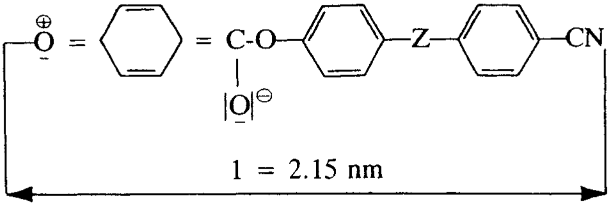
this phase is observed.

From the examples given above it follows that the removal from the molecule of compounds **3** of one bridging group or the replacement of the alkoxy group by an alkyl group or extension of the molecule by one benzene ring hinders the phenomenon of reentrant phases.

If we consider, however, the results obtained by us for **la** esters it does not seem convincing that the presence in the molecule of the two bridging groups and the alkoxy group is decisive for the existence or absence of the reentrant phases. Esters **la** having the alkyl group in the terminal position and only one bridging group reveal properties very similar to those of compounds **3**. It seems that a common feature of the molecules of compounds **la** and **3** is the similar length of the rigid cores of 2.22 nm and 2.02 nm, respectively.







The lengths of the rigid cores of both series of compounds, **1a** and **3**, are even closer if we consider the oxygen atom of the alkoxy group to be an element of the rigid core (since its free electron pair may couple with the π electrons of the neighbouring ring).

Nguyen Hun Tinh postulates that the length of the rigid core optimal for the existence of the reentrant phases is approximately 2.0 nm.[6] Our results support this suggestion.

Undoubtedly, however, another very important factor is the character of the group linking the rings in the rigid core. It seems that the —COO— group is particularly suitable for this purpose, since its substitution by the azo or azoxy group leads to compounds **1b** or **1c** which do not reveal reentrant phases.

Enantiotropic reentrant phases in compounds with one bridging group other than —COO— have been observed so far only in the 4-n-alkoxybenzylidene-amino-4'cyanobiphenyl homologous series.[14]

The close similarity of the properties of compounds **1a** and **3** is apparent not only as regards the members with the reentrant phase but also as regards the whole homologous series.

Figure 8 shows the variation of phase transition temperatures of compounds **1a** with the length of the alkyl chain. In this series of compounds, as in the analogous series **3**, the compounds with alkyl chains with $n \leq 7$ give only the A_1 smectic phase and the nematic phase, the stability of the A_1 smectic phase decreasing for $n > 5$. For $n \geq 8$ the generation of the high-temperature smectic phase A_d is observed in both series.

The low-temperature smectic phases A_1 in both series **1a** and **3** have monolayers of parallel molecules. With the increase of temperature and length of the alkyl chain this type of ordering in the layers disappears in favour of the structure with an antiparallel arrangement of the molecules. Possibly the change of equilibrium between the dispersion forces due to the alkyl chains and rings and the forces due to dipoles and transfer of charges between the rings and the —CN group is responsible for the change of ordering from parallel to antiparallel.

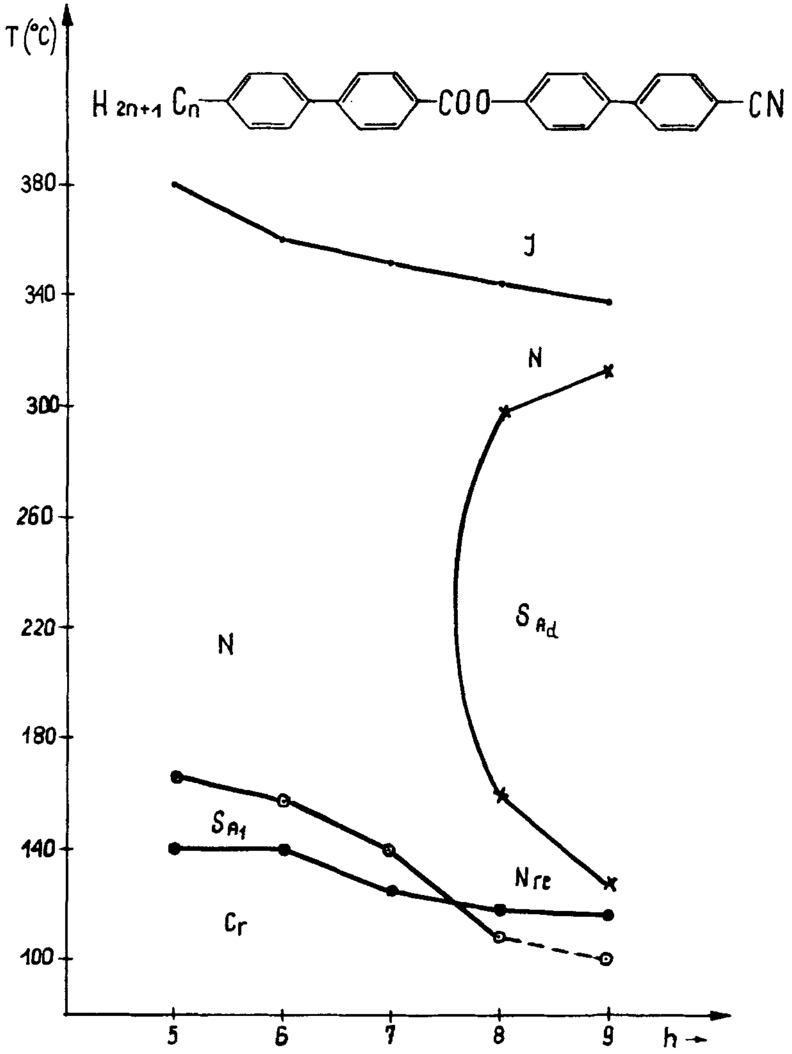


FIGURE 8 The variation of the phase transition temperatures of the **Ia** esters with the alkyl chain length.

At low temperatures, when the alkyl chains are rigid, the dispersive forces between the methylene groups and rings contribute largely to the stabilization of the monomolecular smectic layers. If the temperature rises, the alkyl chains "melt" yielding flexible forms which destabilize the smectic phase A_1. The arrangement of the rigid cores is then more advantageous since the repulsion forces due to parallel dipoles disappear and stabilization becomes possible through charge transfer forces. The observation that S_{A_d} phases are formed at a certain length of the alkyl chain may be explained in terms of the decrease of the dielectric constant of the mesophase in compounds with longer alkyl chains. This in turn favours the increase of the charge transfer energy which is inversely proportional to the dielectric constant of the medium which follows from the Coulomb term (W) in that interaction: $W = e^2/\epsilon \cdot r$.

References

1. Z. Witkiewicz, *J. Chrom.*, **261**, 311 (1982).
2. D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **37**, 249 (1976).
3. P. E. Cladis, *Phys. Rev. Lett.*, **35** 48 (1975).
4. G. Sigaud, Nguyen Huu Tinh, F. Hardouin and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **69**, 81 (1981).
5. F. Hardouin, A. M. Levelut and H. F. Achord, G. Sigaud, *J. Chim. Phys.*, **80**, 53 (1983).
6. Nguyen Huu Tinh, *J. Chim. Phys.*, **80**, 83 (1983).
7. K. Pyc and R. Dabrowski, *Biul. Wojsk. Akad. Tech.*, (1985) in press.
8. G. J. Brownsey and A. J. Leadbetter, *Phys. Rev. Lett.*, **44**, 1608 (1980).
9. A. Göbl-Wunsch, G. Heppke and R. Hopf, *Z. Naturforsch.*, **36a**, 213 (1981).
10. R. Dabrowski and J. Szulc, J. Phys (Fr), **45**, 1213 (1984).
11. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
12. W. Weissflog, G. Pelzl and D. Demus, *Mol. Cryst. Liq. Cryst.*, **76**, 261 (1981).
13. F. Hardouin, A. M. Levelut, Nguyen Huu Tinh and G. Sigaud, *Mol. Cryst. Liq. Cryst., Lett.*, **56**, 35 (1979).
14. D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, *Mol. Cryst. Liq. Cryst., Lett.*, **56**, 289 (1980).