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Smectic polymorphism of the 4-butyl-4′-alkoxyazobenzenes and 4-pentyl-4′-alkoxyazobenzenes

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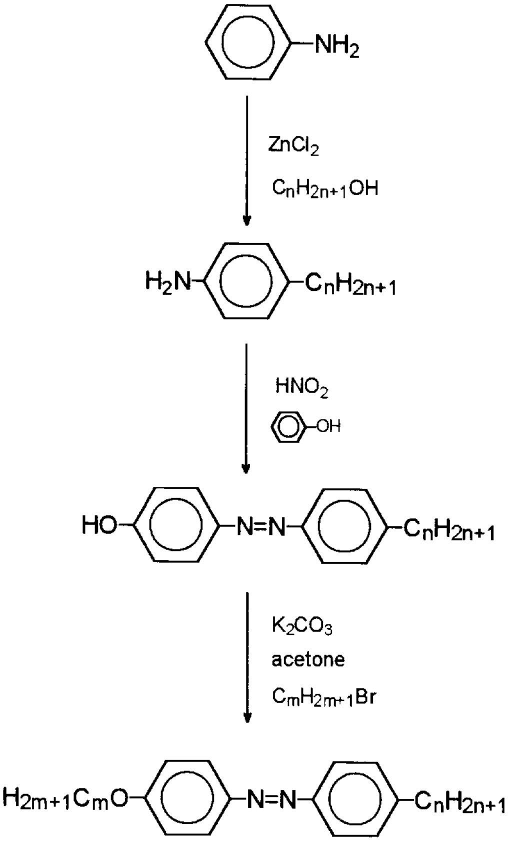
Two families of liquid crystalline compounds have been synthesised, the 4-butyl-4′-alkoxyazobenzenes and the 4-pentyl-4′-alkoxyazobenzenes; for the second family results are presented for the first time for alkoxy chains longer than butyl. The results for both families have been obtained up to the octadecyl homologues. In both families, on the basis of DSC, polarizing microscopy and thermo-optical analysis, a rich polymorphism has been detected (maximum tetramorphism). The smectic properties start with the hexyl derivative (for the butyl family) and with the heptyl derivative (for the pentyl family). Strong odd–even effects for the temperatures of clearing in both groups of compounds were detected. Our results are compared with those of de Jeu *et al.* and of Adomenas *et al.* for the 4-butyl-4′-alkoxyazobenzenes, for which only one smectic modification was described.

1. Introduction

The azobenzenes were among the first ten liquid crystalline compounds to be synthesized [1], but at that time only the compounds with methyl and ethyl carbon chains were investigated. A long list of 4-alkyl-4′-alkoxyazobenzenes with short alkyl chains (up to hexyl) was described in 1971 by Steinsträsser *et al.* [2] from the point of view of a search for room temperature nematic compounds. The substances investigated were indeed only nematogenic, but their applications were limited because of optical instability. More detailed investigations, connected with a study of the dependence of polymorphism on the length of the alkoxy chain, were made by de Jeu *et al.* [3] and Adomenas *et al.* [4] for the 4-butyl-4′-alkoxyazobenzenes. Nematic mesophases were detected for the derivatives from methoxy up to heptyloxy, and from octyloxy an extra smectic A phase was found. They investigated this family up to the decyloxy member. In the similar 4-alkyl-4′-alkoxy Schiff's bases, a rich polymorphism was well known [5]. Analogously, Peltz *et al.* [6] investigated smectic polymorphism in 4-nonyl-4′-alkoxyazobenzenes with long alkoxy chains (from octyloxy up to octadecyloxy). On the basis of X-ray and miscibility studies, they found five mesophases: nematic, smectic A, smectic C, smectic I and smectic G.

There is still great interest concerning the influence of alkyl and alkoxy chain lengths on the smectic phase modification and stabilization. It is a widely known fact



Scheme.

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[7] that the 4-4′-bis(alkyl)azobenzenes have only smectic A mesophases and the 4-4′-bis(alkoxy)azobenzenes have only smectic C mesophases. The subtle balance between alkyl and alkoxy chains can very differently affect mesophase topology.

The main goals of this work were: (1) the synthesis of two groups of liquid crystalline compounds, the 4-butyl-4′-alkoxyazobenzenes and the 4-pentyl-4′-alkoxyazobenzenes, for which in the first family the derivatives from undecyl up to octadecyl and in the second from butyl up to octadecyl are presented for the first time; (2) a full report of the influence of the alkoxy chain length on the smectic polymorphism; (3) a discussion of the values of the phase transition entropies between the smectic phases.

2. Experimental

2.1. *Synthesis*

The compounds were synthesized according to the following scheme:

4-Alkylanilines were prepared using a small modification of the literature method [8, 9].

2.1.1. *4-Pentylaniline*

A mixture of aniline (168 g, 1·8 mol), aniline hydrochloride (52 g, 0·4 mol) and anhydrous $ZnCl_2$ (178 g, 0·4 mol) was heated under reflux at 210°C. *n*-Pentyl alcohol (176 g, 2 mol) was added dropwise in such a manner that the temperature remained above 200°C. The reaction mixture was then cooled and treated with a solution of NaOH (160 g, 4 mol) in 500 ml of water. The organic layer was dried over anhydrous $CaCl_2$ and filtered the next day. The crude product was vacuum distilled to give 147 ml (yield: 45%) of 4-pentylaniline as a colourless liquid: b.p. 102°C (1 mm Hg), ^1H NMR ($CDCl_3$), δ: 0·89(3H, t, CH_3), 1·34(4H, m, CH_2), 1·58(2H, m, CH_2), 2·5(2H, t, CH_2), 3·53(2H, s, NH_2), 6·62(2H, d, Ph–H), 6·98(2H, d, Ph–H).

2.1.2. *4-Pentyl-4′-hydroxyazobenzene*

A well stirred mixture of 4-pentylaniline (82 g, 0·5 mol) and 16% HCl (300 ml) was cooled below 5°C and a solution of $NaNO_2$ (35·2 g, 0·51 mol) in water (100 ml) was added dropwise in such a way that the temperature of the mixture was in the range 0–5°C. The cold, dark

Table 1. Phase transition temperatures and enthalpies of 4-butyl-4′-alkoxy-azobenzenes. In round brackets—monotropic phase transition; in square brackets—entropies of phase transition in J mol^{-1} K^{-1}.

n	Melting	Freezing	SmI		SmC		SmA		N		I
1	32·52 [55·11]	18·2 [53·96]							●	48·6 [1·04]	●
2	43·28 [46·73]	36·66 [46·64]							●	78·1 [2·27]	●
3	65·5 [54·35]	54·8 [52·87]							●	(57·1) [a]	●
4	64·95 [44·29]	56·75 [41·55]							●	74·54 [1·87]	●
5	42·48 [36·64]	39·04 [36·33]							●	65·41 [1·83]	●
6	42·77 [72·11]	27·86 [60·24]					●	(30·69) [4·50]	●	73·3 [2·56]	●
7	52·96 [86·71]	32·85 [71·08]					●	(42·55) [4·92]	●	70·14 [2·09]	●
8	55·09 [100·31]	32·87 [88·27]	●	(39·03) [1·50]	●	(54·63) —	●	57·99 [2·42]	●	75·83 [3·19]	●
9	61·38 [110·01]	50·67 [101·97]			●	(59·35) —	●	63·75 [5·08]	●	73·27 [2·94]	●
10	54·17 [82·38]	41·26 [71·91]	●	(52·46) [4·65]	●	64·03 —	●	70·86 [9·58]	●	76·41 [5·25]	●
11	65·58 [101·5]	53·42 [84·59]	●	(57·51) [6·32]	●	67·24 —	●	74·42 [12·93]	●	76·3 [6·43]	●
12	63·82 [97·15]	45·89 [78·45]	●	(61·14) [7·83]	●	67·9 —	●	76·3 [22·48]	●	76·7 [a]	●
14	61·4 [85·70]	46·89 [80·51]	●	(56·86) [7·13]	●	70·12 [23·07]					●
16	70·88 [103·38]	49·82 [89·00]	●	(68·92) [19·32]	●	76·35 [31·80]					●
18	69·63 [173·75]	59·63 [134·30]	●	70·31 [41·00]							●

[a] Phase transition detected by optical microscopy method.

solution was added dropwise to a cold mixture of phenol (47 g, 0·5 mol), NaOH (100 g, 2·5 mol) and water (150 ml). The temperature of the mixture was kept below 5°C. Acidification with aqueous HCl gave the crude precipitate which was filtered off, dried and recrystallized several times from hexane to give yellow crystals (100 g, 0·4 mol, 79% yield): m.p. 86°C, ^{1}H NMR ($CDCl_3$), δ: 0·9(3H, t, CH_3), 1·36(4H, m, CH_2), 1·67(2H, m, CH_2), 2·68(2H, t, Ph–CH_2), 5·8(1H, s, OH), 6·94(2H, d, Ph–H), 7·31(2H, d, Ph–H), 7·81(2H, d, Ph–H), 7·86(2H, d, Ph–H).

2.1.3. *4-pentyl-4′-nonyloxyazobenzene*

A mixture of 4-pentyl-4′-hydroxyazobenzene (5 g), bromononane (10 g) and anhydrous K_2CO_3 (30 g) in acetone (50 ml) was heated under reflux for 48 h. The reaction mixture was filtered and the acetone distilled off from the filtrate to give a crude yellow precipitate, which was recrystallized several times from methanol and acetone. The final product was purified twice by flash column chromatography (Fluka silica gel 60 mesh, $CHCl_3$ as eluent), recrystallized from acetone and melted a few times under vacuum (90% yield): ^{1}H NMR ($CDCl_3$) δ: 0·9(6H, m, CH_3), 1·29–1·36(16H, m, CH_2), 1·65(2H, m, CH_2), 1·83(2H, m, CH_2), 2·67(2H, t, Ph–CH_2), 4·05(2H, t, OCH_2), 7·01(2H, d, Ph–H), 7·31(2H, d, Ph–H), 7·81(2H, d, Ph–H), 7·9(2H, d, Ph–H).

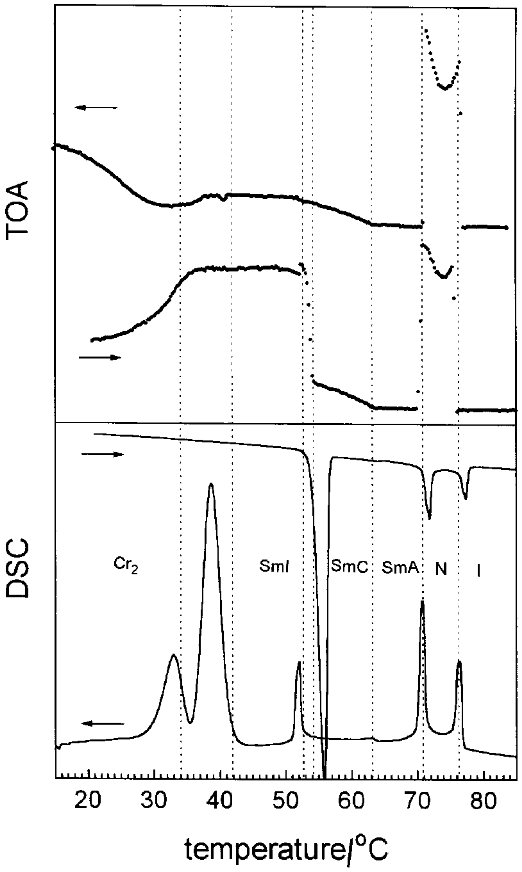

Figure 1. Thermo-optic (TOA) and DSC scans of 4-butyl-4′-decyloxyazobenzene.

2.2. *Characterization*

Confirmation of the structure of all intermediates and products was obtained by ^{1}H NMR spectroscopy (Bruker AMX 300 MHz) and using a HP 5890II gas chromatograph with mass selective detector HP5974A. Microanalyses were performed using a Perkin Elmer 2400 CHN Elemental Analyser.

Transition temperatures were measured using a Linkam THMS 600 hot stage and TMS 93 control unit in conjunction with an Olympus BX60P polarizing microscope, and were confirmed using differential scanning calorimetry (Perkin Elmer DSC7). DSC scans were made at 5 K min^{-1} and indium was used as the enthalpy standard. The thermo-optic set-up has been described elsewhere [10].

3. Results and discussion

Each member of the families investigated was liquid crystalline.

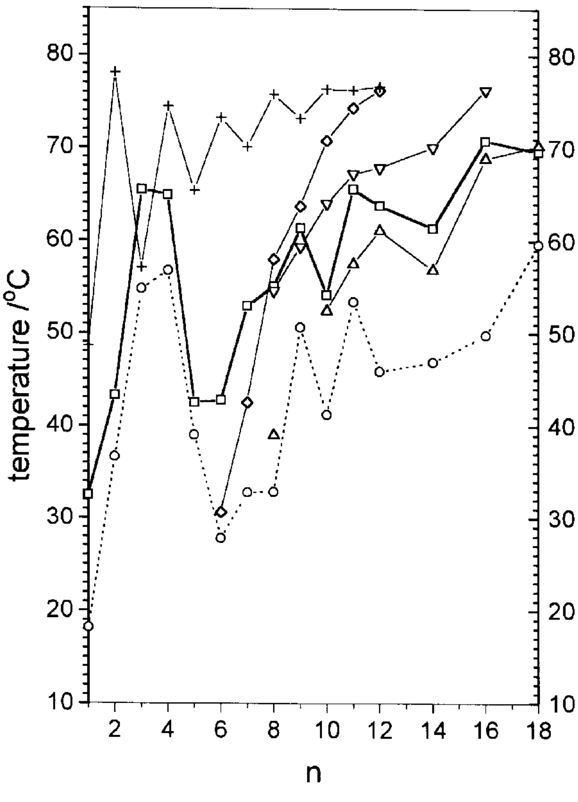

Figure 2. Phase diagram of the 4-butyl-4′-alkoxyazobenzenes: melting (□), freezing (○), SmI–SmC or I (△), SmC–SmA or I (▽), N–I (+).

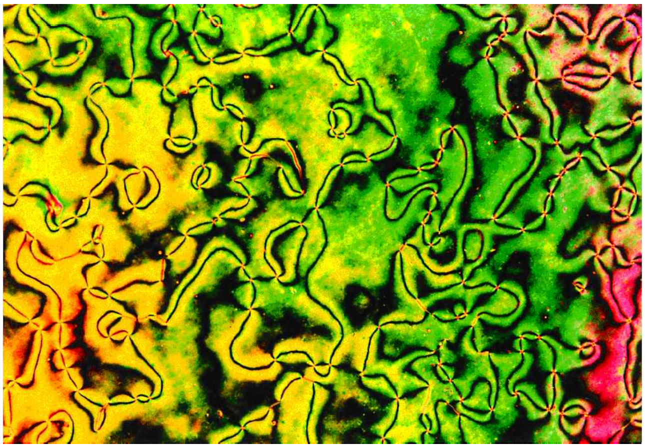

Figure 3. Optical micrograph (× 125) of 4-butyl-4′-decyloxyazobenzene in the nematic phase at 72·9°C.

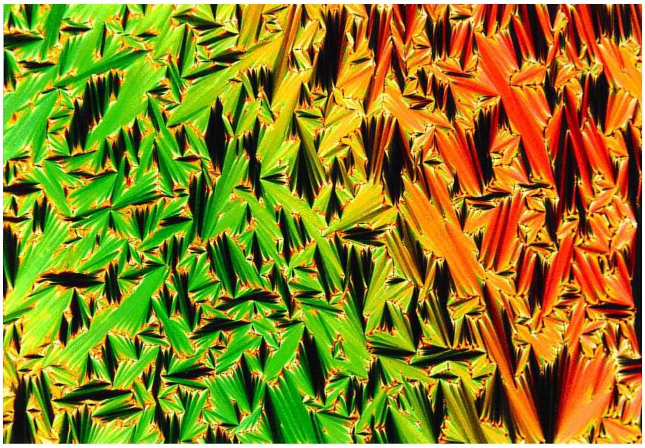

Figure 4. Optical micrograph (× 125) of 4-butyl-4′-decyloxyazobenzene in the smectic A phase at 68·7°C.

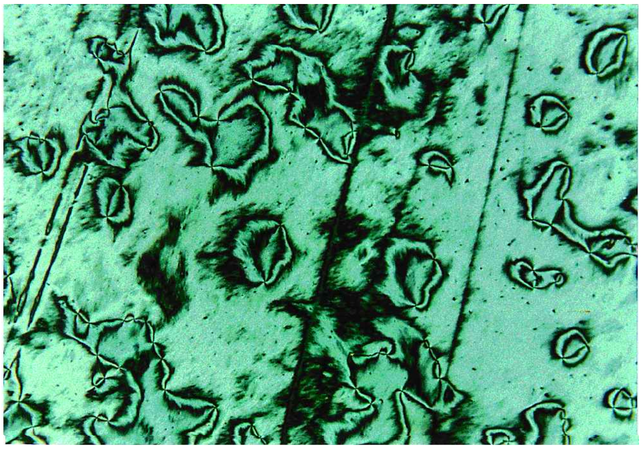

Figure 5. Optical micrograph (× 125) of 4-butyl-4′-decyloxyazobenzene in the smectic C phase at 59·0°C.

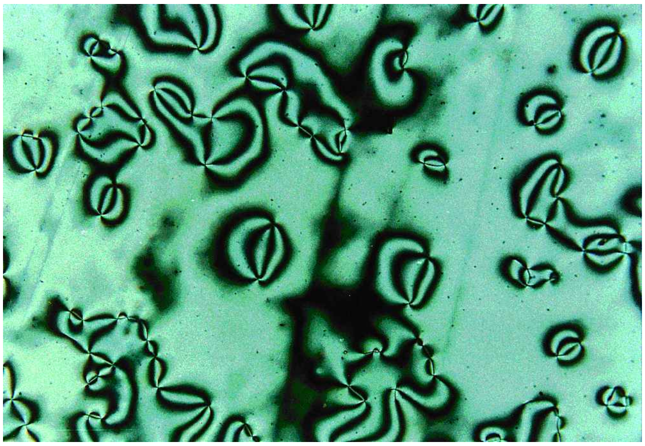

Figure 6. Optical micrograph (× 125) of 4-butyl-4′-decyloxyazobenzene in the smectic I phase at 52·0°C.

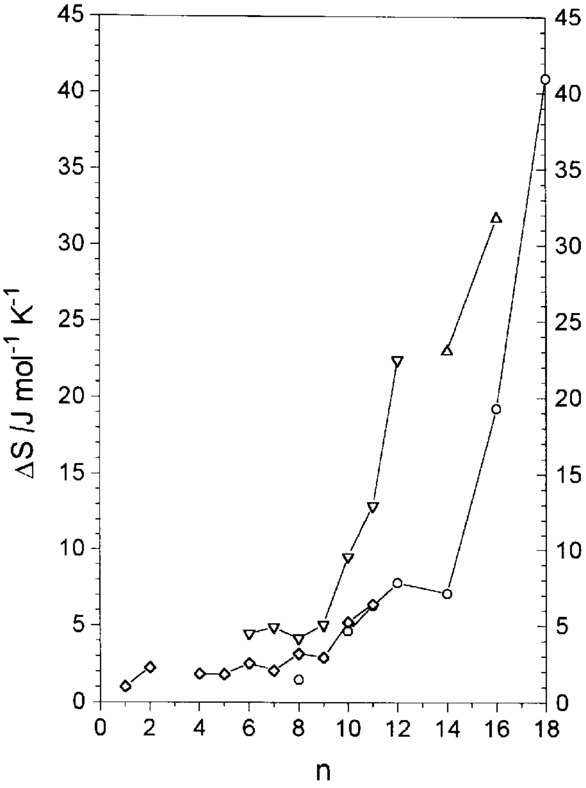

Figure 7. Phase transition entropies of the 4-butyl-4′-alkoxyazobenzenes: SmI–SmC or I (○), SmC–I (△), SmA–N or I (▽), N–I (◇).

3.1. *The 4-butyl-4′-alkoxyazobenzenes*

These exhibit nematic mesophases for alkoxy chains from methoxy up to dodecyloxy. Only the propyl derivative has a monotropic nematic phase; the others are enantiotropic. Smectic modifications started from the hexyl derivative. (See table 1).

All phase transitions, temperatures and enthalpies were detected by DSC and TOA scans. An example of these measurements is given in figure 1. Both types of scan, at the same speed of 5 K min^{-1}, were carried out. Especially important is the possibility of identifying second order and quasi first order phase transitions by these two complementary methods (for example, smectic A→smectic C).

The even–odd effect of the clearing temperatures is very significant. The biggest difference in clearing temperature, 30 K, was found for the methoxy and ethoxy members. This value decreases with alkoxy chain length and is almost unchanged from the decyloxy members. The smectic A mesophase appears for the first time in the hexyl derivative and very rapidly increases from 30 to 75°C in the dodecyl derivative (the last compound to be smectic A). Smectic C phases were identified in derivatives from octyl up to hexadecyl. The increase in smectic A–smectic C phase transition temperature is smaller than that for smectic A–nematic. In this family an extra smectic I mesophase was found. This appears in the derivatives from octyl up to octadecyl, with the exclusion of the nonyl member. This fact is connected with the high recrystallization temperature which exceeds that of the expected smectic C–smectic I transition temperature. The fall in the clearing temperature for the smectic I–isotropic phase transition of the octadecyl homologue is unusual and interesting.

The full phase diagram is presented for the butyl family in figure 2. Significant is the high temperature of melting for the propyl and butyl derivatives. Mesophases were classified on the basis of texture observations and the similarity to the 4-nonyl-4′-alkoxyazobenzenes [9] (figures 3, 4, 5 and 6).

The family of 4-butyl-4′-alkoxyazobenzenes was previously partly described by de Jeu *et al.* [1] and Adomenas *et al.* [2]. They found only nematic and smectic A phases (in investigations of derivatives from methoxy up to decyloxy). In our measurements, extra smectic C and smectic I phases have been found for the same octyl and decyl derivatives. The temperatures of melting, smectic A–nematic transition and clearing significantly agree very well with the results of Steinsträsser *et al.* [4], de Jeu *et al.* [1] and Adomenas *et al.* [2]. There are small differences in melting temperatures associated with the samples. Our samples were purified twice with the help of flash column chromatography and then melted in a vacuum several times in order to remove

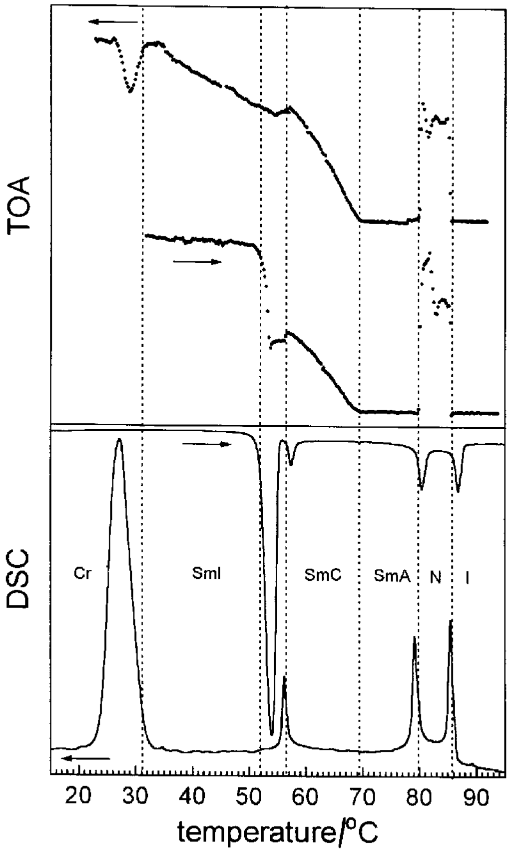

Figure 8. Thermo-optic (TOA) and DSC scans of 4-pentyl-4′-decyloxyazobenzene.

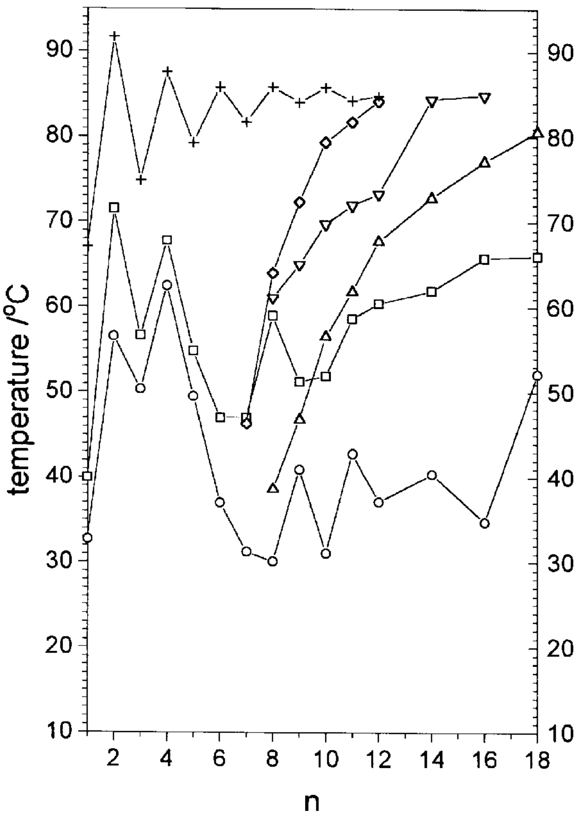

Figure 9. Phase diagram of 4-pentyl-4′-alkoxyazobenzenes: melting (□), freezing (○), SmI–SmC or I (△), SmC–SmA or I (▽), SmA–N (◇), N–I (+).

any solvent. Small differences may also be connected with the influence of light on the temperatures of phase transition during microscopic observations (especially for the nematic–isotropic phase transition). Photo-induced *cis-trans*-isomerization of these compounds is a well known fact [11]; in our experiments a red filter was applied.

In the butyl family there is an interesting balance between the different influences of the alkyl and alkoxy chains on the phase modifications. The smectic A phase was detected for derivatives from hexyl up to dodecyl and the smectic C phase from octyl up to hexadecyl. This means that longer alkoxy chains stabilize the smectic C phase more and shorter alkoxy chains the smectic A phase. Entropies of phase transition for the 4-butyl-4′-alkoxyazobenzenes are presented in figure 7. These entropy values can help in phase identification [11]. The entropy of the nematic–isotropic phase transition is small, $\sim 2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and increases with alkyloxy chain length, especially for the longest chains. The entropy of the nematic–smectic A transition is bigger, $\sim 5\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and very sharply increases from the nonyloxy derivative. The entropy of transition for the more ordered smectic I phase is, as expected, the largest.

3.2. *The 4-pentyl-4′-alkoxyazobenzenes*

The same methods of purification and identification of phases and transitions were applied in the study of this second family (see table 2). Typical DSC and TOA scans are given in figure 8; figure 9 shows the full phase diagram for the 4-pentyl-4′-alkoxyazobenzenes. The same kinds of mesophases were found. Very interesting is the even–odd effect for the clearing temperatures, which have average values 10 K higher than for the 4-butyl-4′-alkoxyazobenzenes. The biggest difference in clearing temperature is 23 K between the methoxy and ethoxy derivatives. The highest melting temperatures were detected for the ethoxy and butyloxy derivatives. The smectic A appears for the first time in the heptyl member (monotropic smectic A). The temperature of the smectic A–nematic phase transition rises sharply up to the dodecyl derivative. The smectic C phase was found for members from octyl up to hexadecyl. Finally, the

Table 2. Phase transition temperatures and enthalpies of 4-pentyl-4′-alkoxyazobenzenes. In round brackets—monotropic phase transition; in square brackets—entropies of phase transition in J mol^{-1} K^{-1}.

n	Melting	Freezing	SmI		SmC		SmA		N		I
1	40·00 [59·62]	32·74 [59·33]							●	67·10 [2·257]	●
2	71·53 [39·98]	56·61 [39·70]							●	91·70 [2·354]	●
3	56·65 [48·79]	50·35 [48·33]							●	74·87 [2·720]	●
4	67·84 [44·93]	62·54 [44·87]							●	87·59 [2·995]	●
5	54·87 [42·47]	49·51 [42·01]							●	79·30 [2·943]	●
6	47·04 [65·00]	37·00 [58·99]							●	85·81 [3·323]	●
7	47·04 [67·59]	31·31 [57·96]					●	(46·37) [1·881]	●	81·75 [3·453]	●
8	59·01 [107·0]	30·11 [90·73]	●	(38·60) [0·952]	●	61·14 —	●	64·09 [2·698]	●	85·84 [5·491]	●
9	51·28 [77·15]	40·99 [67·74]	●	(46·83) [1·455]	●	65·06 —	●	72·40 [4·651]	●	84·03 [5·764]	●
10	51·90 [73·73]	31·07 [75·10]	●	56·57 [3·507]	●	69·79 —	●	79·43 [7·382]	●	85·79 [6·994]	●
11	58·65 [75·86]	42·85 [79·80]	●	61·88 [4·680]	●	72·03 —	●	81·80 [9·569]	●	84·24 [6·789]	●
12	60·44 [82·81]	37·11 [70·59]	●	67·77 [8·672]	●	73·30 —	●	84·22 [23·50]	●	84·80 [a]	●
14	61·97 [86·90]	40·41 [70·57]	●	72·85 [13·19]	●	84·39 [29·54]					●
16	65·81 [83·48]	34·76 [84·75]	●	77·15 [11·87]	●	84·88 [25·01]					●
18	66·09 [111·0]	52·21 [108·9]	●	80·63 [44·26]							●

[a] Phase transition detected by optical microscopy method.

smectic I phase is the last mesophase to appear on cooling the derivatives, from octyl up to hexadecyl. It is also the phase formed direct from the isotropic melt on cooling the octadecyl member. Again in this series, the clearing temperature falls from hexadecyl to octadecyl.

For full phase identification, the Sackmann–Demus miscibility method [13] was used in the case of 4-pentyl-4′-decyloxyazobenzene. As standard I, 4,4′-bis(terephthalylidene)-n-pentylaniline (TPPA) [5] and as standard II, 4-heptyloxybenzylidene-4′-pentylaniline were used. The two phase diagrams are given in figures 10 and 11. From the first diagram, the first three phases are easily identified as nematic, smectic A and smectic C. Smectic I is in equilibrium with smectic F and CrG, with two triple points. The fourth phase, CrG, was found in solutions very low in 4-pentyl-4′-decyloxyazobenzene, but was not found in the pure sample. CrH was detected as the lowest phase in each investigated mixture, but not in the pure 4-pentyl-4′-decyloxyazobenzene. This phase interpretation agrees with molecular models for smectic mesophases, where smectic F and smectic I have the same orientational disorder and differ only in direction of tilting [14]. The second phase diagram (figure 11) involves the second standard material, which has mesophases in similar temperature ranges to 4-pentyl-4′-decyloxyazobenzene. The first three mesophases were identified as nematic, smectic A and smectic C. Very interesting is the problem of the fourth mesophase, which for the standard II is smectic B and for the compound investigated, is smectic I. There was found a critical molar ratio of 2: 1 at which the smectic B phase changes into smectic I. Below the smectic B, CrG was detected, but below the smectic I, only solid was observed. In terms of molecular models of the smectic I phase as a tilted smectic B, these results are understandable [14]. Moreover, these phase diagrams confirm our phase identifications on the basis of texture observations and agree with the X-ray investigations on the similar family of 4-nonyl-4′-alkoxyazobenzenes [6].

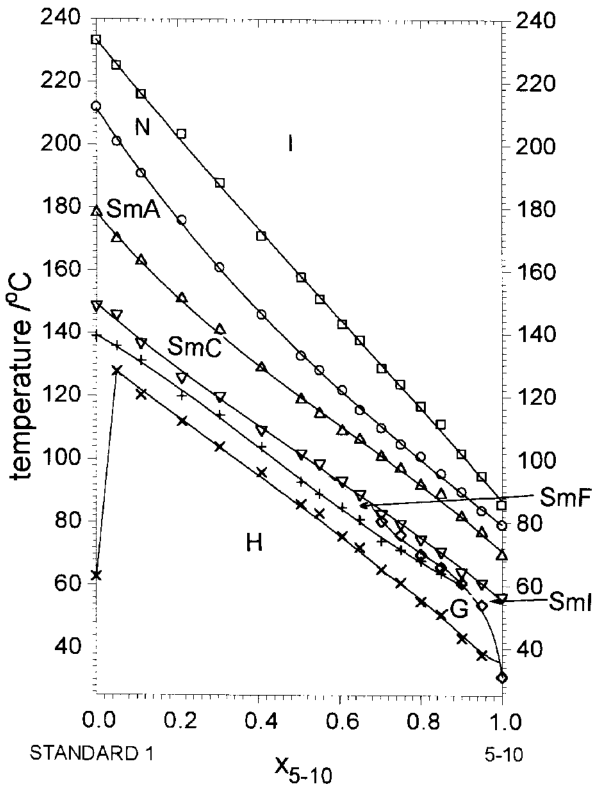

Figure 10. Phase diagram of 4-pentyl-4′-decyloxyazobenzene with 4,4′-bis(terephthalylidene)-n-pentylaniline.

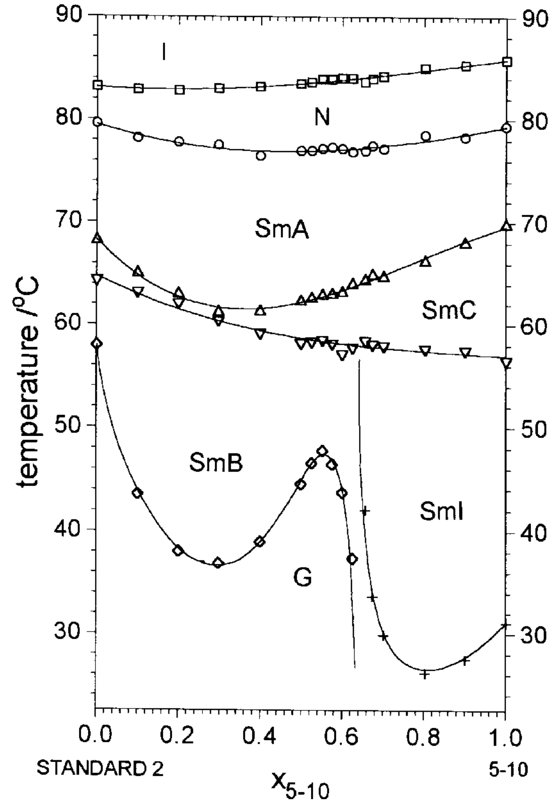

Figure 11. Phase diagram of 4-pentyl-4′-decyloxyazobenzene with 4-heptyloxybenzylidene-4′-pentylaniline.

In both investigated families, the lowest members are only nematogenic, up to the hexyloxy derivatives. The derivatives with longer alkoxy chains have both smectic A and smectic C phases as the balance changes between the influence of the alkyl and alkoxy chains. Below the smectic C phase the more oriented smectic I appears as the tilted modification of smectic B (hexatic). The entropies of phase transition are presented in figure 12 for the pentyl family; these entropy values agree with those for the 4-butyl-4′-alkoxyazobenzenes and confirm the interpretation of phase sequence.

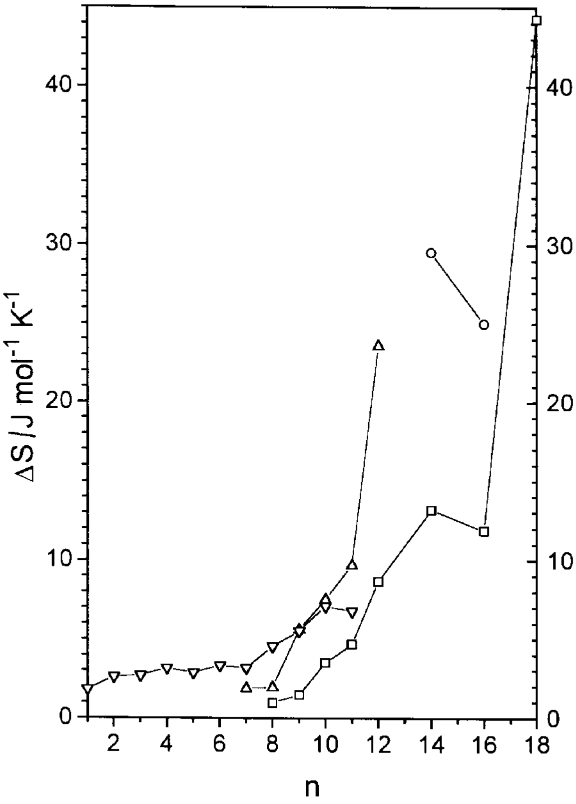

Figure 12. Phase transition entropies of 4-pentyl-4′-alkoxyazobenzenes: SmI–SmC or I (□), SmC–I (○), SmA–N or I (△), N–I (▽).

4. Conclusions

The two families investigated have a rich and interesting liquid crystalline polymorphism (maximum tetramorphism). They are of potential interest as readily soluble dyes with their own liquid crystalline properties or for non-linear optics because of their interesting optical properties (high optical anisotropy, photoinduced *cis-trans*-isomerization) combined with a rich polymorphism.

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