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F. Barbarin[a]; M. Dugay[a]; A. Piovesan[a]; H. Fadel[b]; D. Guillon[b]; A. Skoulios[b]
[a] Laboratoire d'Electronique et Résonance Magnétique, Université de Clermont, Aubière, France [b] Institut Charles Sadron (CRM-EAHP), ULP-CNRS, Strasbourg Cedex, France

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Structural study of the smectic phases of several 4-cyanoalkoxybenzylidene-4′-alkylanilines

by F. BARBARIN, M. DUGAY and A. PIOVESAN
Laboratoire d'Electronique et Résonance Magnétique, Université de Clermont,
24, Avenue des Landais, 63170 Aubière, France

and H. FADEL, D. GUILLON and A. SKOULIOS
Institut Charles Sadron (CRM-EAHP), ULP-CNRS, 6, rue Boussingault,
67083 Strasbourg Cedex, France

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A series of 4-cyanoalkoxybenzylidene-4′-alkylanilines (CN-nO.m; n = 3, 4, 6 and m = 4, 5, 8) have been synthesized. Their thermotropic liquid-crystalline polymorphism has been investigated using optical microscopy, differential scanning calorimetry and dilatometry. Nematic, smectic A and smectic B mesophases have been identified. The structure of the smectic phases has been studied with X-ray diffraction. Depending upon the compound and the temperature, the smectic layers have been found to be either single (A_1) or double (A_2) layers of molecules. Unexpected from a simple comparison with the well-known behaviour of the very similar nO.m smectogens, which belong to the class of the so-called symmetric and therefore exhibit single-layered smectics only, this structural behaviour has been interpreted to mean the importance of the dipole interactions of the terminal cyano groups. For CN-6O.8, a transition has been detected at 64°C between the single and double layered structure.

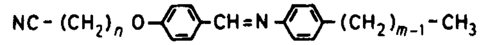
1. Introduction

The layered structure of smectic mesophases is now a matter of common knowledge. When the smectogenic rod-like molecules are symmetric, that is when the two aliphatic chains carried by their central rigid aromatic core are of equal length, the layer thickness, d, is comparable to the length, L, of the molecules in the fully extended conformation [1]. The smectic layers are made of single layers of molecules set side by side and oriented upright or at an angle θ with respect to the layer normal ($d/L \simeq \cos\theta$). In fair lateral register with one another, the aromatic cores point up and down randomly, and the hydrocarbon chains are disordered. The same single layer arrangement also occurs when the two aliphatic chains are of unequal lengths [2]; these are then mixed efficiently within the aliphatic sublayers on a molecular level [3].

When the smectogenic molecules are dissymmetric, that is when they carry a single aliphatic chain on one end of the aromatic core and a highly polar group on the other, the smectic behaviour is more complex [4, 5]. The smectic layers may be single layers of molecules oriented antiparallel to one another (antiferro or paraelectric lateral packing of the molecules) as in smectic A_1 where $d/L \# 1$, or be bilayers of molecules associated head to head through their polar endgroups as in smectic A_2 where $d/L \# 2$, or else partial bilayers of molecules incompletely associated head to head as in smectic A_d where $1 < d/L < 2$ [5].

The highly polar smectogenic molecules reported so far in the literature have their polar endgroup directly, and therefore rigidly, attached to the aromatic core. In order to study the smectic behaviour of dipolar smectogenic molecules containing a highly dipolar endgroup mechanically and electronically decoupled from the rigid moiety, 4-cyanobutoxybenzylidene-4′-octylaniline was recently studied [6]. The first observations made suggested a bilayer structure for the smectic A and smectic B mesophases observed. This behaviour could not have been expected, since the molecules contain two aliphatic chains and, consequently, could reasonably be considered to belong to the class of the so-called symmetric mesogens.

To study further the mesomorphic behaviour of this new class of symmetric and yet highly polar mesogens, we describe in the present work the structure of a series of cyanoalkoxybenzylidene-alkylanilines (symbolically abbreviated to CN-nO.m) with various lengths of aliphatic chains (n = 3, 4, 6; m = 4, 5, 8):



2. Thermotropic polymorphism

The thermotropic liquid-crystalline behaviour of CN-nO.m was first studied by optical polarizing microscopy. The textures observed are the usual focal conic and schlieren textures which are indicative of smectic and nematic mesophases, respectively. Upon heating, the crystal has been found to transform into a smectic A mesophase only when m = 8, whereas it transforms directly into an isotropic liquid when m = 4, 5. On cooling, however, the isotropic liquid has been found to produce a nematic followed by smectic mesophases for m = 4, 5, whereas it produces directly smectic mesophases for m = 8. It is of interest to note that, on cooling, within their thermal stability domain, the focal conic textures exhibit temporary striations in a narrow temperature range, typical of a smectic A to smectic B phase transition [7].

Differential scanning calorimetry was then used to specify better the transitions observed and to determine their temperatures and enthalpies. Heating and cooling scans have fully confirmed the existence of the mesophases detected by optical microscopy and also their enantiotropic and monotropic character. The experimental observations and measurements are summarized in the following polymorphic schemes. They show that the nature and the thermal stability of the mesophases obtained are influenced much more by the length (n, m) of the flexible chains in the CN-nO.m series than in the non-polar nO.m series.

CN-3O·8

$$\begin{tikzcd}
K \arrow[r, "36{\cdot}4^\circ C", "45{\cdot}8\ kJ/mol"'] & S_B \arrow[r, leftrightarrow, "49{\cdot}0^\circ C", "1{\cdot}8\ kJ/mol"'] & S_A \arrow[r, leftrightarrow, "94{\cdot}0^\circ C", "7{\cdot}1\ kJ/mol"'] & I
\end{tikzcd}$$

CN-4O·8

$$\begin{tikzcd}
K \arrow[rr, "79{\cdot}5^\circ C", "36{\cdot}8\ kJ/mol"'] & & S_A \arrow[r, leftrightarrow, "85{\cdot}3^\circ C", "6{\cdot}3\ kJ/mol"'] \arrow[dl, leftrightarrow, "59{\cdot}3^\circ C", "2{\cdot}1\ kJ/mol"'] & I \\
& S_B \arrow[ul, "(39{\cdot}6^\circ C)"] & &
\end{tikzcd}$$

CN-6O·8

$$\begin{tikzcd}
K \arrow[rr, "66{\cdot}3^\circ C", "39{\cdot}1\ kJ/mol"'] & & S_{A1} \arrow[r, leftrightarrow, "72{\cdot}9^\circ C", "4{\cdot}9\ kJ/mol"'] & I \\
S_B \arrow[u, "(34{\cdot}9^\circ C)"] & S_{A2} \arrow[l, leftrightarrow, "47{\cdot}7^\circ C"', "1{\cdot}7\ kJ/mol"] \arrow[ur, leftrightarrow, "64^\circ C", "<0{\cdot}04\ kJ/mol"'] & &
\end{tikzcd}$$

CN-6O·4

$$\begin{tikzcd}
K \arrow[rrr, "63{\cdot}7^{\circ}C", "41{\cdot}5\,\mathrm{kJ/mol}"'] & & & I \\
 & S_A \arrow[ul, "(57{\cdot}2^{\circ}C)"'] \arrow[r, leftrightarrow, "58{\cdot}0^{\circ}C", "2{\cdot}9\,\mathrm{kJ/mol}"'] & N \arrow[ur, leftrightarrow, "61.4^{\circ}C", "0{\cdot}8\,\mathrm{kJ/mol}"'] &
\end{tikzcd}$$

CN-4O·4

$$\begin{tikzcd}
K \arrow[rrr, "77{\cdot}4^{\circ}C", "39{\cdot}1\,\mathrm{kJ/mol}"'] & & & I \\
 & S_A \arrow[ul, "(53{\cdot}2^{\circ}C)"'] \arrow[r, leftrightarrow, "57{\cdot}0^{\circ}C", "2{\cdot}2\,\mathrm{kJ/mol}"'] & N \arrow[ur, leftrightarrow, "60.1^{\circ}C", "0{\cdot}5\,\mathrm{kJ/mol}"'] &
\end{tikzcd}$$

CN-4O·5

$$\begin{tikzcd}
K \arrow[rrr, "80{\cdot}9^{\circ}C", "40{\cdot}9\,\mathrm{kJ/mol}"'] & & & I \\
S_B \arrow[u, "(41{\cdot}9^{\circ}C)"'] \arrow[r, leftrightarrow, "(45{\cdot}0^{\circ}C)", "1{\cdot}7\,\mathrm{kJ/mol}"'] & S_A \arrow[r, leftrightarrow, "67{\cdot}7^{\circ}C", "1{\cdot}9\,\mathrm{kJ/mol}"'] & N \arrow[r, leftrightarrow, "71{\cdot}9^{\circ}C", "0{\cdot}8\,\mathrm{kJ/mol}"'] & \arrow[u]
\end{tikzcd}$$

In the particular case of CN-4O. 5, the thermotropic liquid-crystalline behaviour has also been investigated using dilatometry. Figure 1 shows the temperature dependence of the molar volume upon heating and cooling. The transition from the crystal to the isotropic liquid gives rise to an abrupt and important increase in the volume of about 10 per cent ($\Delta V = 32{\cdot}0\,\mathrm{cm^3/mol}$). On the other hand, the transition from the isotropic liquid to the nematic, then to the smectic A mesophase, as usual gives rise to abrupt, but much smaller volume jumps of $-0{\cdot}2$ per cent ($\Delta V = -0{\cdot}7\,\mathrm{cm^3/mol}$) and $-0{\cdot}5$ per cent ($\Delta V = -1{\cdot}6\,\mathrm{cm^3/mol}$), respectively. The molar volume measured at 67·0° C for the smectic A mesophase was found to be equal to $355{\cdot}0\,\mathrm{cm^3}$. The thermal expansion coefficients, $1/V(\delta V/\delta T)$, were found to equal $2 \times 10^{-4}\,\mathrm{K^{-1}}$,

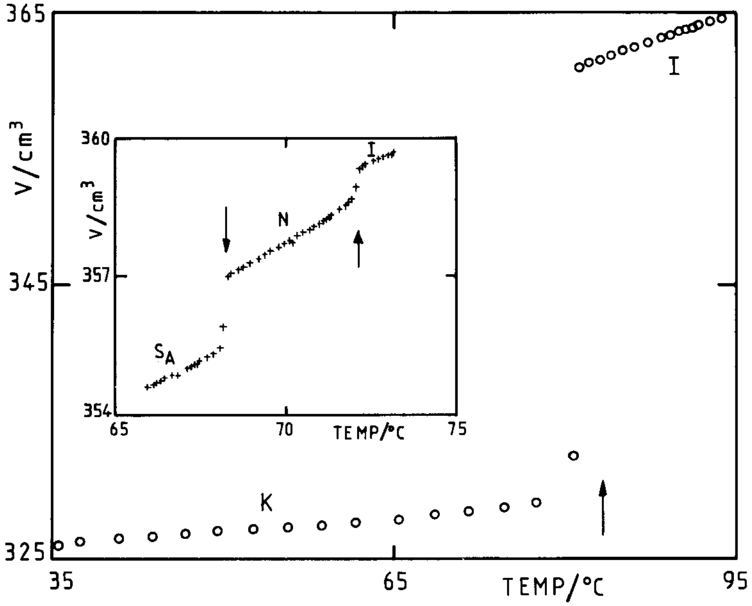


Figure 1. Temperature dependence of the molar volume of CN-4O. 5 upon heating (○) and cooling (+). Arrows indicate the transition temperatures determined by differential scanning calorimetry and optical microscopy.

$9{\cdot}3 \times 10^{-4}K^{-1}$, $12 \times 10^{-4}K^{-1}$ and $8{\cdot}6 \times 10^{-4}K^{-1}$ for the crystal, the smectic A, the nematic and the isotropic liquid phases respectively.

3. Structural behaviour

3.1. *Crystalline phase*

X-ray diffraction has, finally, been used to ascertain the nature of the various phases observed and to determine their structural parameters. The powder diffraction patterns measured at low temperatures for the K phases are typical of rod-like mesogenic compounds in the crystalline state. They contain a large number of sharp Bragg reflections located in the wide angle region, characteristic of the three-dimensional ordering of the molecules. A series of several equidistant sharp reflections, located in the small angle region, indicate the lamellar structure of the system. The stacking period, *d*, measured experimentally (table 1), is significantly smaller than the molecular length, and so it is clear that the molecules must be set in single layers and tilted with respect to the layer normal.

Table 1. Lamellar thickness of CN-*n*O.*m* in the crystalline state.

Mesogen	*L*/Å	*d*/Å	*T*/°C
CN-3O.8	27·7	23·1	20
CN-4O.8	29·0	23·3	25
CN-6O.8	31·5	22·5	20
CN-6O.4	26·5	18·1	21
CN-4O.4	23·9	19·6	20
CN-4O.5	25·2	20·8	40

3.2. *Smectic A phases*

The X-ray powder patterns of the S_A phases contain one or two equidistant, sharp Bragg reflections in the small angle region, indicating the smectic layering of the molecules. A broad diffraction band, located at a spacing of about 4·5 Å, is evidence for the liquid-like arrangement of the molecules within the smectic layers. The measured stacking periods, *d*, are reported in table 2. When $m = 4$ or 5, the periodicity, *d*, is close to the molecular length. This indicates a single layer arrangement of molecules randomly oriented up and down and perpendicular to the layers, as commonly observed with symmetric smectogenic molecules exhibiting the conventional smectic A_1 mesophase. In the special case of CN-4O.5, where the molar volume *V* at 67°C is available, we can determine the lateral packing density by calculating the molecular area $S = V/Nd$ where *N* is the Avogadro constant. The value found (24.1 Å^2) is in agreement with the usual values reported in the literature.

Table 2. Stacking period of CN-*n*O.*m* in the smectic A state.

Mesogen	*L*/Å	*d*/Å	*T*/°C
CN-3O.8	27·7	51·4	60
CN-4O.8	29·0	54·6	65
CN-6O.8	31·5	61·1	61
CN-6O.4	26·5	25·7	58
CN-4O.4	23·9	23·2	56
CN-4O.5	25·2	24·5	65

It is of special interest to stress that, when $m = 8$, the spacing d is unexpectedly close to two molecular lengths, indicative of a double-layer arrangement analogous to that observed for smectic A_2 mesophases. This behaviour is unexpected, for the molecules carry two aliphatic chains at their two ends and, as a result, have a symmetric form. This is, no doubt, related to the presence of the cyano endgroups which tend to associate themselves in a head to head configuration (cf. figure 2 (*a*)) due to their electrostatic interactions [8]. However, we must take care not to concur immediately with this very simple picture of double-layered ordering without considering other possible structural models which are in equal agreement with the experimental evidence.

The X-ray diffraction patterns, measured for the S_A when $m = 8$, contain two sharp small angle reflections whose intensities depend upon the sample under consideration. Generally, the second harmonic is unusually intense, frequently even more intense than the first order reflection, despite the strong longitudinal thermal diffusion of the molecules, classically observed for smectic A mesophases. This is due simply to the electron density distribution along the layer normals, which presents a pseudo-period of one molecular length as a result of the stacking of the aromatic sublayers. The first harmonic, which is indicative of the double layer ordering, is closely associated with the presence of a cyano group at only one extremity of the molecules. When the molecules are arranged as shown in figure 2 (a), the electron density distribution presents, indeed, a period of two molecular lengths: the cyano and the methyl endgroups introduce an excess [8] and a deficiency of electron density, respectively, while the difference in length of the two aliphatic chains introduces a difference in the thickness of the two aliphatic sublayers within each molecular bilayer.

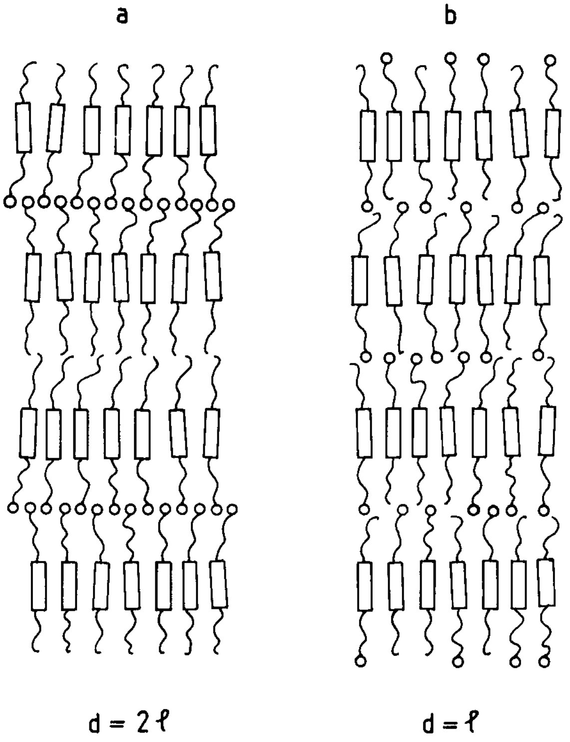


Figure 2. Schematic view of double layer and single layer arrangement of molecules: circles represent the cyano endgroups, and rectangles the aromatic cores.

However, as already pointed out in our previous preliminary paper [6], the presence of this first Bragg harmonic does not necessarily imply the formation of a perfect double layered structure with complete segregation of the cyano and the methyl endgroups into distinct interfacial regions of the system. In fact, within each monolayer (half of the double layer), the molecules can easily come together either in such a way as to reject all (or nearly all) of the cyano groups on the same side of the aromatic sublayer (i.e. a ferroelectric intralamellar arrangement), or so as to orient themselves randomly up and down (i.e. a paraelectric intralamellar arrangement), or else in such a way as to alternately point up and down in as regular a fashion as possible (i.e. a frustrated antiferroelectric intralamellar arrangement) [10]. It is clear that whatever their stacking, when the monolayers correspond to a paraelectric intralamellar arrangement of the molecules, they can only lead to the formation of A_1 single-layered smectic systems (cf. figure 2(*b*)). When the monolayers correspond to a (partially) ferroelectric intralamellar arrangement of the molecules, they can stack either over one another in a ferroelectric or a paraelectric manner to form A_1 single layered smectic systems, or else stack in an antiferroelectric manner to form A_2 double layered smectic systems. Finally, when the monolayers correspond to a frustrated antiferroelectric intralamellar arrangement of the molecules, or when fluctuations can exist in the intralamellar or the interlamellar ordering, the structure is much more complex to analyse, for it requires all possible local couplings and interactions (clusters, files, . . .) to be taken into account.

To return to the first Bragg harmonic observed in the X-ray patterns, its existence cannot imply, therefore, a perfect double layered structure, but only eliminate the macroscopically non-polarized monolayers (para and antiferroelectric intralamellar arrangement). In other words, it can only indicate the existence of a certain ferroelectric intralamellar ordering of the molecules with an antiferroelectric interlamellar stacking of the monolayers, but it cannot give any information about their spatial extension. Although this structure is not necessarily perfectly double layered, it will nevertheless be referred to in the following as a smectic A_2 structure.

3.3. *Smectic $A_1 \leftrightarrow$ smectic A_2 transition*

For each of the CN-*n*O . *m* compounds studied here, the X-ray diffraction patterns of the smectic A phases have so far been measured only at a few temperatures. It has been possible therefore to show that the structure is of the A_1 or of the A_2 type depending whether $m = 4, 5$ or $m = 8$, respectively. However, for CN-6O . 8, both A_1 and A_2 structures have been observed at distinct temperatures. This led us to undertake a systematic X-ray diffraction study of this specific compound as a function of temperature.

Figure 3 shows the temperature dependence of the reciprocal spacings, using X-ray patterns measured photographically. It is clear that the smectic A_1 structure occurs at temperatures above 64°C, while the smectic A_2 structure appears at temperatures below 64°C. The transition between the two structures is reversible. Moreover, it seems to be discontinuous, as the Bragg reflection corresponding to $d \# 2L$ either is observable or not. Close inspection of the X-ray patterns shows, however, that this reflection fades out rapidly in a narrow temperature range. In fact, the transition is not strictly second order, since careful differential scanning calorimetry measurements give evidence of an extremely weak transition at 64°C ($\Delta H <$ 0·04 kJ/mol). At any rate, this phenomenon suggests that the spatial extension of the double layering is finite, as it changes with temperature.

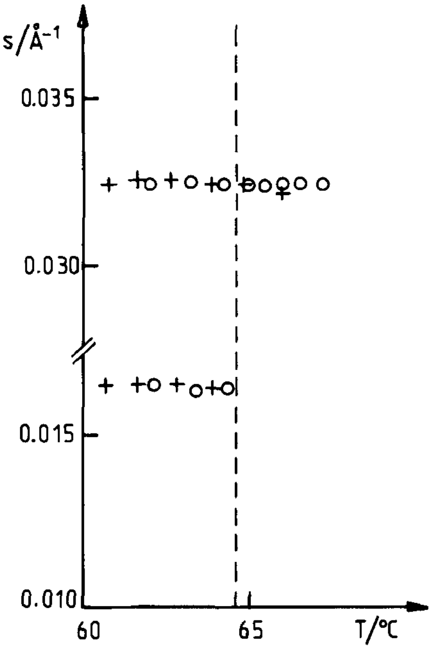


Figure 3. Temperature dependence of the reciprocal spacings (2 sin θ/λ) of the Bragg reflections observed for the smectic A phases of the CN-6O.8 upon heating (○) and cooling (+).

3.4. *Smectic B phase*

The X-ray powder patterns of the S_B phase have only been recorded for CN-3O.8 and CN-4O.8, the thermal stability of the monotropic S_B phases being much too short for the other derivatives. They contain one sharp reflection at $D = 4{\cdot}4$ Å typical of the well-known hexagonal, lateral ordered packing of the molecules in the smectic B state. The molecular area deduced, $S = 2D^2/\sqrt{3} = 22{\cdot}3$ Å^2, is slightly smaller, as usual, than that observed in the S_A state, and comparable to that generally found with conventional smectic B phases.

The X-ray patterns also contain up to three sharp Bragg reflections located in the small angle region. The corresponding reciprocal spacings are in the ratio 1 : 2 : 4, indicating the lamellar stacking of the system. The stacking periods found (cf. table 3) are equal to exactly twice the molecular lengths, revealing the double layered nature of the structure (B_2). The intensities of the first two harmonics are comparable, while that of the fourth is very weak. Although the first harmonic is here more intense than for the smectic A_2 phase, it is still impossible, as for the A_2, to analyse precisely the perfection of the double layering and to specify the spatial extension of the ferroelectric intralamellar ordering of the molecules and of the antiferroelectric interlamellar stacking of the monolayers.

Table 3. Stacking period of CN-*n*O.*m* in the smectic B state.

Mesogen	*L*/Å	*d*/Å	*T*/°C
CN-3O.8	27·7	52·8	38
CN-4O.8	29·0	56·1	45

4. Conclusion

In conclusion, it is worth noting that the most important result of the present work is to show that double layered smectic structures (A_2 and B_2) can indeed be obtained with smectogenic molecules with two aliphatic chains at their ends, despite their symmetrical chemical architecture. This new behaviour is all the more interesting as the behaviour of the well-known *n*O.*m* compounds, which are CN-*n*O.*m* compounds deprived of the cyano group, is completely different; in the latter case, the smectic layers are always single layers of molecules [2]. No doubt, the difference in behaviour is due to the strong dipole interactions of the cyano endgroups; these tend to associate themselves in an antiparallel fashion, although they are mechanically decoupled from the rigid aromatic cores through the quite flexible aliphatic chains and thereby are expected to be free to move throughout the aliphatic sublayers.

It is also worthwhile to recall another important result of our work, showing the existence of a transition between the single and the double layered smectic A structures as a function of temperature. Such a transition has already been observed in mixtures of two smectogens [11]; but, to our knowledge, this is the first time it is observed with pure compounds. The exact nature of the transition is still to be understood: is it a true thermodynamic transition and if so, is it a first or a second order transition? An answer to these questions will, we hope, be given by a systematic study, actually under progress, of the relative intensities of the two first Bragg harmonics in the X-ray patterns as a function of temperature.

5. Experimental

The chemical synthesis of the CN-*n*O.*m* compounds studied here was performed in two stages. The 4-cyano-alkoxy-p-benzaldehydes were first synthesized [12], and then reacted [13] with the corresponding *p*-alkylanilines. The products were purified by successive recrystallizations in hexane. Their chemical composition determined by elemental analysis is reported in table 4.

The optical microscopy observations were carried out with a Leitz polarizing microscope equipped with a Mettler FP82 hot stage. The differential scanning calorimetry measurements were made using a Perkin-Elmer DSC-4 apparatus, with a heating or cooling rate of 2·5 K/min. The dilatometric experiments have been performed following the Bekkedahl method already described in the literature [14]. The X-ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically using monochromatic copper $K\alpha_1$ radiation and a Guinier focusing camera equipped with a bent quartz monochromator and an electrical oven.

Table 4. Elemental analysis.

	Percentage C		Percentage H		Percentage N		Percentage O	
Mesogen	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
CN-3O.8	79·76	79·74	8·70	8·57	7·35	7·44	4·32	4·25
CN-4O.8	80·06	79·96	8·88	8·77	7·03	7·17	4·22	4·10
CN-6O.8	80·26	80·33	9·15	9·15	6·48	6·69	3·98	3·82
CN-6O.4	79·67	79·52	8·52	8·34	7·64	7·73	4·35	4.41
CN-4O.4	79·19	79·00	7·95	7·83	8·30	8·37	4·82	4·78
CN-4O.5	79·50	79·27	8·25	8·10	7·98	8·04	4·34	4·59

References

[1] GRAY, G. W., and GOODBY, J. W. G., 1984, *Smectic Liquid Crystals* (Leonard Hill).

[2] LEADBETTER, A. J., MAZID, M. A., and RICHARDSON, R. M., 1980, *Liquid Crystals*, edited by S. Chandrasekhar (Heyden), p. 65. DOUCET, J., 1978, Ph.D. Dissertation, University of Orsay.

[3] BARBARIN, F., CHAUSSE, J. P., FABRE, C., GERMAIN, J. P., DELOCHE, B., and CHARVOLIN, J., 1983, *J. Phys., Paris*, **44**, 45.

[4] HARDOUIN, F., LEVELUT, A. M., ACHARD, M. F., and SIGAUD, G., 1983, *J. Chim. phys.*, **80**, 53.

[5] GUILLON, D., and SKOULIOS, A., 1984, *J. Phys., Paris*, **45**, 607.

[6] BARBARIN, F., DUGAY, M., GUILLON, D., and SKOULIOS, A., 1986, *J. Phys., Paris*, **47**, 931.

[7] GOODBY, J. W., and PINDAK, R., 1981, *Molec. Crystals liq. Crystals*, **75**, 233.

[8] As suggested in [5] (see footnote 2), and as actually demonstrated in [9] (see figure 3), the dipole interactions lead to an antiparallel side-by-side arrangement of the cyano end-groups with a lateral approach distance of about 3·5 Å, corresponding to a molecular area of about 10 Å^2, i.e. half the molecular area of the smectogenic molecules. The electron density in the cyano regions should, therefore, be twice as large in the surrounding aliphatic regions.

[9] HAASE, W., PAULUS, H., and MULLER, H. T., 1983, *Molec. Crystals liq. Crystals*, **97**, 131.

[10] The antiferroelectric ordering of molecules is not possible in two dimensional systems of any symmetry.

[11] HARDOUIN, F., LEVELUT, A. M., BENATTAR, J. J., and SIGAUD, G., 1980, *Solid St. Commun.*, **33**, 337.

[12] GRAY, G. W., and JONES, G., 1954, *J. chem. Soc.*, p. 1467.

[13] KELLER, P., and LIEBERT, L., 1978, *Solid State Physics*, Suppl. 14, *Liquid Crystals*, edited by L. Liébert (Academic Press).

[14] BEKKEDAHL, N., 1949, *J. Res. natn. Bur. Strand.*, **42**, 145.