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The structural study of liquid crystals

P M Zorkii, T V Timofeeva, A P Polishchuk
Moscow State University
Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow
Institute of Physics, Ukrainian SSR Academy of Sciences, Kiev

ABSTRACT. Structural (mainly X-ray diffraction) studies of thermotropic liquid-crystalline mesophases have been reviewed. The classification of mesophases has been examined and refined. The discussion deals mainly with the structure of liquid crystals formed by rod-shaped molecules (calamitic mesophases). Mesophases of a new type, containing columnar associates of molecules joined by hydrogen bonds, have also been described.

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I. Introduction

The study of liquid crystals (LC) began as early as last century,[1,2] and its hundredth anniversary has already passed. It now covers a remarkable scale, but the increase in the number and range of these studies has not been smooth. It was only about 25 years ago that it became clear that LC do not represent an exotic phenomenon; they are widely encountered in living and non-living nature, and have found a large number of practical applications in technology and medicine, and in recent years in chemistry (as orienting solvents in the study of NMR spectra and for carrying out topochemical reactions). The intensive study of LC has also led to the development of theoretical ideas which make up an integral and important part of present-day physical chemistry.

As in other fields of chemistry, structural data have here been extremely important. In structural chemistry, an independent branch referred to as "the structure of mesophases" has been distinguished.†

Even in the early stages of the study of LC, they were classified according to the degree and nature of the ordering as nematic, smectic, and cholesteric.[2] Thus structural studies from the beginning have played an important role in the investigation of LC, although in many cases the descriptions of the structure suffered from lack of clarity and specificity, and sometimes contradicted physicochemical data and the principle of close packing of molecules. Since like liquids they retain a considerable degree of disorder, liquid-crystalline phases naturally cannot be characterised structurally in the same detail as solid crystals. The statistical nature of their structure, however, reflects objective reality, so that in principle it should in each specific case be described in completely definite fashion, albeit in statistical language. Compared with liquids, experimental diffraction methods in this case give much more information, although, as in the case of liquid phases, the details of the structure of individual molecules remain out of reach.

The present review gives a systematic analysis of the structural aspects of studies of LC, carried out mainly in the last 25 years. Liquid-crystalline phases can be classified as thermotropic (produced from liquids or crystals by change in temperature) and lyotropic (formed in solution). Only the former are considered in the present review.

For a long time it was considered that the role of mesogens, that is compounds capable of existing in the thermotropic liquid-crystalline state, was played only by substances with rod-shaped molecules (so-called calamitic mesophases). In 1977, however, LC formed by disc-shaped molecules were reported,[4] and in 1987, liquid-crystalline phases consisting of cup-shaped molecules were described.[5] There is no doubt that, other types of mesogen will be detected. Usually, however, when LC are mentioned, it is calamitic mesophases that are meant. The present review also deals mainly with these LC (it is proposed to devote a separate review to the structure of disc-shaped mesophases).

In a rod-shaped molecule it is possible to distinguish a long axis, denoted L. The vector indicating the average direction of these axes is called the director (this concept is most useful for nematic mesophases). A calamitic mesophase can apparently be defined as a liquid crystal whose structure is regarded as sufficiently fully characterised if the arrangements of the molecular axes L are described (with allowance for statistics). This definition corresponds to the picture of molecules as cylinders with a circular cross-section. In some important cases (for flattened molecules), however, this description of the structure cannot be regarded as sufficient, and it is necessary to represent the molecules as cylinders with an elliptical cross-section. It is then necessary to add to the structural parameters the angles characterising the orientation of the ellipses perpendicular to the axes L.

† The term "mesophase" is now often used as a synonym for "liquid crystal"; this use of these concepts has also proved convenient in the present review. It should be borne in mind, however, that the concept of "mesophase" is sometimes given a more general meaning, to include various partly disordered (and partly ordered) phases occupying an intermediate position between ideal crystals and isotropic liquids.[3]

Liquid crystals are practically always molecular compounds, but liquid-crystalline phases show a number of distinctive features, compared with molecular crystals. In addition to the appreciably statistical nature of the structure, a domain structure is highly characteristic of LC. Domains with coherent boundaries apparently are also fairly frequently present in solid molecular crystals (more frequently than is usually assumed[6]). Nevertheless, this is not typical of solid crystals, whereas in LC domains are observed as the rule. They are readily rearranged and change their orientation under the influence of external factors, in particular electric and magnetic fields.

In a liquid-crystalline material, the domains are often arranged completely randomly. In an electric or magnetic field, they are ordered, leading to the formation of so-called oriented mesophases. It is these phases that are usually studied by X-ray diffraction. For solid crystals, the influence of an external field (and even temperature) on the structure is studied comparatively rarely (studies of this kind are only beginning to develop on a large scale), whereas for LC the study of structure as a function of field intensity and temperature has been customary for a long time.

In the study of the structure of LC it is important to bear in mind that their structure is dynamic. The problem in principle is to give a specific description of not only the average arrangement of the molecules, preserved for a more or less long time, but also the dynamics of the structure, that is the vibrational and rotational movements of the molecules, and also their diffusion and transfer from one molecular agglomerate to another. The information at present available, however, relates mainly to the averaged static structure of LC; this information is obtained by optical, dilatometric, and other physicochemical studies, but the main source of structural information is diffraction, in particular optical modelling of the diffraction pattern. Information on molecular dynamics is also provided by NMR and experiments on quasi-elastic neutron scattering.‡

II. The structural classification of calamitic mesophases

The first classification of LC having a structural basis was proposed in 1922 by Friedel,[2] who classified the 42 liquid-crystalline substances known to him as nematic, smectic, and cholesteric. The distinctive feature of nematic LC is that the molecules in them are arranged in approximately parallel fashion, that is they are characterised by approximately parallel orientation of the long axes. In smectic LC, the molecules again are approximately parallel, but in addition they are arranged in parallel layers. The local structure of a cholesteric mesophase is analogous to the structure of a nematic, on the other hand, cholesteric LC are characterised by a gradual change in the orientation of the vector L in space, leading to a spiral arrangement, as a result of which these crystals are optically active.

Subsequent studies showed that there is considerable variety in the properties and structures of smectic phases. This led to the classification of smectics as types A, B, C, D, E, F, and G by Sackmann and Demus.[8] This classification was based on experimental data on the miscibility of the mesophases, but it was already known at that time from X-ray diffraction studies[9] that the miscibility criterion corresponds to definite structural characteristics. Subsequently, X-ray diffraction studies made it possible to characterise specifically each of the types $A-G$, and also to add the types H, I, J, and K.

Generally speaking, the picture of the molecules as rods with cylindrical symmetry is inadequate for the description of these types of structure. A more adequate model is that of a cylinder with an elliptical cross-section, or a ribbon, and in some cases it is also necessary to take into account the non-equivalence of the two sides of this ribbon. In the simplest version, the structure of smectics of different types is usually described without taking into account the polarity of the molecules and the possibility of dimer formation. It is also assumed that the smectic phase consists of "monolayers", in that the centres of gravity of the molecules forming the layer lie approximately in the same plane, and that the thickness of the layer d is determined by the length of the molecule l ($d = l\cos\varphi$, where φ is the angle between the axis L and the normal to the layer).

In the description and classification of the structure "monolayer" smectics, account is usually taken of the nature of the packing of the molecules in the layer, whether or not the molecules lie at an angle to the normal to the layer ($\varphi = 0$ or $\varphi \neq 0$), and the presence or absence of correlation in the superposition of the layers. Four types of packing of the molecules in the layer are distinguished: 1) disordered, 2) "hexatic" (having only short-range order), 3) hexagonal, and 4) herring-bone. According to Goodby and Gray,[10] who summarised structural data on smectic phases, this gives the following classification of known smectics (the notation of the phases in which there is a correlation in the superposition of the layers is underlined):

Packing in the layer	$\varphi=0$	$\varphi'\neq0$	$\varphi''\neq0$
Disordered	*SmA*	*SmC*	
"Hexatic"	*SmB*$_h$	*SmI*	*SmF*
Hexagonal	*SmB*	*SmJ*(*G'*)	*SmG*
Herring-bone	*SmE*	*SmK*(*H'*)	*SmH*

This Table corresponds to Fig. 1, taken from Goodby and Gray,[10] which shows schematically the packing of the molecules in the smectic layers. Here, the circles denote vertically arranged molecules, whose effective symmetry is cylindrical as a result of the statistical character of the azimuthal orientations (or because of the domain structure of the layer, discussed below). The triangles denote sloping molecules with cylindrical symmetry (in the case of molecules with an elliptical effective cross-section, the slope of their long axes is indicated by arrows). Two versions of the slope of the molecules relative to the section of the layer are distinguished (φ' and φ''), giving two series of "sloping" smectics ($I-J-K$ and $F-G-H$). Fig. 2 gives a clearer picture of the arrangement of the molecules in the bulk of some smectics.

It should be emphasised that the representations of the structure of the layers in the hexatic phases in Fig. 1 are highly arbitrary. In fact, the following is understood. In contrast to hexagonal and herring-bone packing, in which the arrangement of the centres of gravity of the molecules is characterised by long-range positional order (although not so perfect as in true crystals), hexatic phases show only short-range positional order, and the molecular coordination number 6 is the most probable; the symmetry of the immediate environment of a molecule in the layer is therefore hexagonal or pseudo-hexagonal. At the same time, in these phases there is bond-orientational order, in which all the coordination hexagons are oriented in approximately the same way. Analogous

‡ This method detected the diffusion of molecules in a direction perpendicular to the smectic layers.[7]

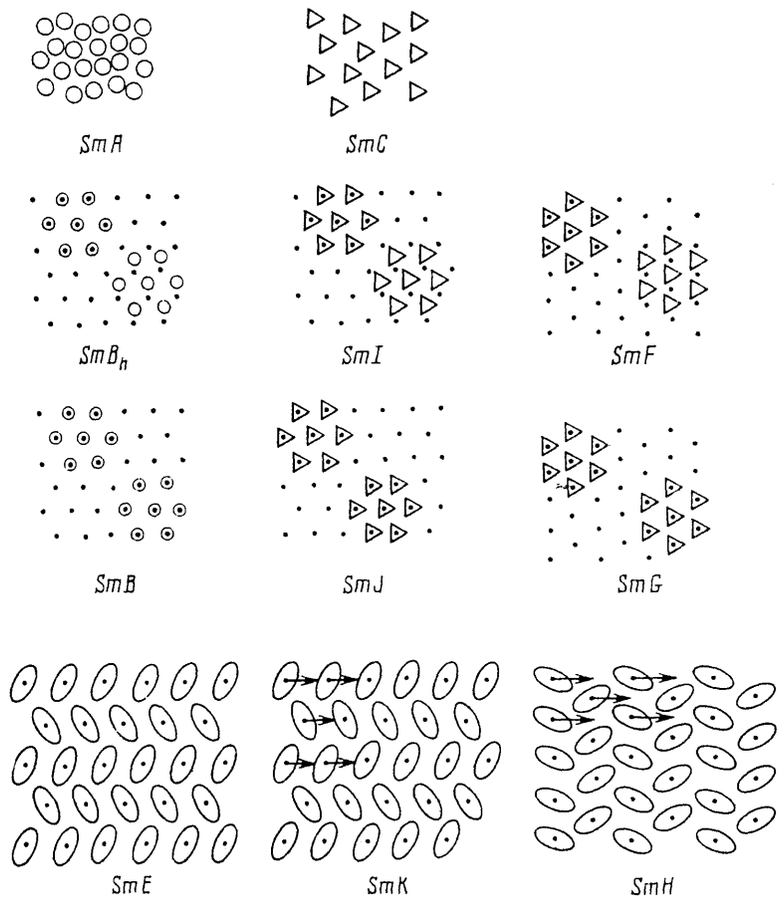


Figure 1. Arrangements of the molecules in smectic layers.[10]

phases with short-range order of a different type ("tetratic", etc.) are possible in principle, but these phases have not been reported in X-ray studies

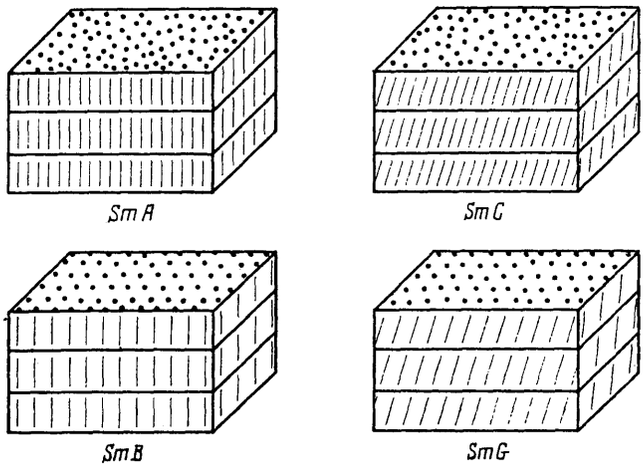


Figure 2. Schematic representation of the arrangement of the molecules in various smectics.

This classification gives a satisfactory description of experimental data on the structure of smectic mesophases. There is however some indeterminacy in the structural characterisation of *SmI* (this question will be examined later in section V). It should also be noted that the structural description sometimes contradicts experimental data on the miscibility of liquid-crystalline phases. The miscibility or immiscibility of two smectics apparently does not always indicate unambiguously a similarity or difference between their structures. A final conclusion can be reached only from special structural studies.

An unsatisfactory feature of the above systematisation is that it only reproduces the experimentally observed picture of the structure of smectics (more accurately, a set of models which has been used to interpret the experimental data); there is no possibility of predicting structures which are possible in principle but which have not yet been discovered.

A more *a priori* systematisation is that of de Vries,[11] which has been extended to lyotropic mesophases.[12] Here, the herring-bone arrangement of the molecules, denoted by the symbol "2", as taken as the basis of the structure of the smectic layers, but account is also taken of the possible production, at sufficiently high temperatures, of dynamic structures in which there is a spontaneous cooperative change in the azimuthal orientation, as a result of which the structure represented schematically in Fig. 3*a* is converted into the structure shown in Fig. 3*b*, and conversely. X-Ray diffraction records the

overall statistical structure (Fig. 3*c*), which is denoted by the symbol *m*. Moreover, according to de Vries it is possible to have a structure with three interconvertible azimuthal orientations of the molecules (Fig. 4), effectively having hexagonal symmetry (symbol "6"). To this is added a statistical structure with a non-fixed azimuthal orientation of the molecules, denoted by the symbol ∞.

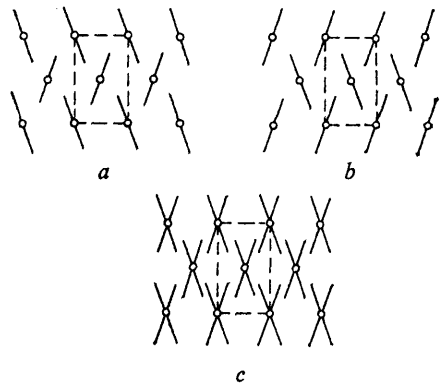


Figure 3. Structure of the layers 2 and *m* according to de Vries:[11] *a*, *b*, two equivalent herring-bone patterns; *c*, overall structure (detected by X-ray diffraction) in which versions *a* and *b* are equally probable.

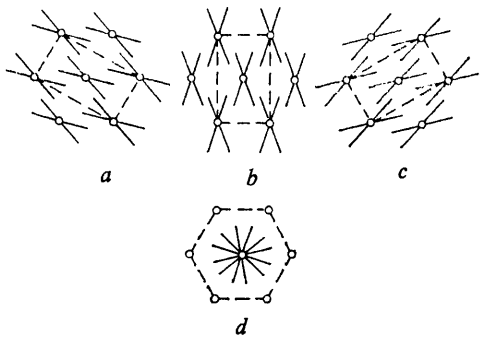


Figure 4. The formation of statistical layers according to de Vries:[11] *a*, *b*, *c*, three equivalent orientations of the layers *m*; *d*, overall structure.

The structure of a smectic phase as a whole is described by de Vries by means of a three-position symbol, where the type of packing of the molecules in the layer (2, *m*, 6, or ∞) is given by the first position, whether or not the director lies at a slope to the plane of the layer (∞ or *m*) is given by the second position, and the presence or absence of a correlation in the superposition of the layers (0 or 1) is given by the third position. This gives the 14 types of smectic structure shown in Table 1. De Vries identifies nine of them with types of smectic described in the literature; two types [*SmX* and *Sm*(*X*)] are said[11] to have been identified be de Vries and co-workers; and three types (6*m*1, 2∞0, 2*m*0) have apparently not yet been identified.

Table 1. Types of smectic mesophase (according to de Vries).

Type of packing of the molecules in the layer	Smectic mesophases			
	upright layers (∞)		sloping layers (*m*)	
	0	1	0	1
∞	∞∞0 (*SmA*)	—	∞*m*0 (*SmC*)	—
6	6∞0 (*SmB*)	6∞1 (*Sm*(*B*))	6*m*0 (*SmF*)	6*m*1 —
m	*m*∞0 (*SmX*)	*m*∞1 (*Sm*(*X*))	*mm*0 (*SmI*)	*mm*1 (*SmG*)
2	2∞0 —	2∞1 (*SmE*)	2*m*0 —	2*m*1 (*SmH*)

It should however be noted that there are discrepancies between de Vries' treatment and the structural systematisation of smectic phases described above.[10] This applies primarily to hexatic structures, which according to de Vries represent a fifth version of the packing of the molecules in the layer, so that they should be regarded as supplementing the 14 types listed in Table 1. At the same time, in de Vries' monograph,[10] the types *SmB*, *SmI*, and *SmF* are treated as hexatic phases (see also section V). Correspondingly, the interpretation of the types *SmI* and *SmG* as phases with structures corresponding to the symbols *mm*0 and *mm*1 differs from the description of these phases in de Vries' monograph.[10] In addition, de Vries' systematisation does not reflect different relations of the slope of the molecules to the section of the layer.

Moreover, the production of two or three spontaneously interconvertible orientations, proposed by de Vries, contradicts the principle of close packing, which should apparently be applicable not only to crystals but also to the liquid-crystalline state. A more probable model of the layers denoted by the symbols 6 and *m* is a domain structure (see Fig. 27) in which the boundaries of the domains can migrate either spontaneously or under the influence of external factors; there coexist three orientations of the domains in a layer of type 6, and two orientations in a layer of type *m*.

Another feature which apparently must be taken into account in an *a priori* systematisation of smectic phases is the following. It is known from organic crystal chemistry[13,14] that the characteristic packing of molecules includes not only the herring-bone pattern (layers with symmetry P_l2_1, P_lc, and P_l2_1/c) but also primitive packing with an oblique-angled cell (layers with symmetry P_l1 or $P_l\bar{1}$). If this mode of packing of the molecules in the layer is denoted by the symbol "1" and, following de Vries, the possible versions of the structure of a smectic with an oblique-angled planar cell are examined, then another four types of smectic phase are obtained: 1∞0, 1*m*0, 1∞1, and 1*m*1. Smectic phases of this type have not yet been detected by X-ray diffraction. This however is apparently due not to the fact that they do not exist in the systems studied but to the fact that the more symmetrical models used in the interpretation of the X-ray diffraction patterns have been fairly consistent with the experimental data. With increase in the accuracy

of X-ray diffraction studies, however, phases will possibly be found, whose X-ray diffraction patterns can be interpreted satisfactorily only on the basis of an oblique-angled structure of the smectic layers.

It is appropriate to supplement the above classification schemes by a parametric description of different types of liquid-crystalline structures. This description will make it possible to list structural parameters whose fixed values define the type of liquid-crystalline phase. An advantage of this approach is not only that it is quantitatively specific but also it makes it possible to regard polymorphic transformations of liquid-crystalline phases as the "de-freezing" (or "freezing") of individual degrees of freedom of the molecules. This opens up the way to a quantitative energetic analysis of mesomorphism.

The parameters characterising the structure of a calamitic LC include: 1) the angles φ, ψ, and θ describing the position of the long axis of the molecule and its azimuthal orientation (Fig. 5), 2) the distance between the axes of adjacent molecules D, and 3) for smectic phases, the thickness of the layer d. In the case of highly ordered smectics, the distances between the molecules are determined by the parameters of the two-dimensional lattice a and b (for hexatic phases by the parameters of the immediate environment a' and b'); for smectics with three-dimensional order, which in the literature are sometimes provisionally called "crystalline", the thickness of the layers is defined by the period c. Table 2 lists for each type of LC the parameters which make it possible to describe the principal features of the structure.

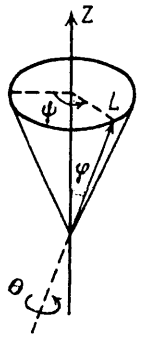


Figure 5. Angles characterising the orientation of a rod-shaped molecule.

For a more detailed characterisation of the structure, it is necessary to take account of the actual conformation and to indicate the way in which the axis L is selected. Moreover, in the study of the structure of specific mesophases, the formation of dimeric molecular agglomerates (they are often called "dimers", although they do not correspond to dimers in the chemical sense of the term) and "bilayer" structures are often encountered. (These questions will be examined later.)

It is also necessary to take account of the characteristics of the structure of LC arising in sloping ($\varphi \neq 0$) smectics in connection with the chirality of the molecules.[15] In this case, optically active mesophases *SmC**, *SmI**, and *SmF** are formed, in which the superposition of the layers of chiral molecules leads to spiral twisting, together with mesophases *SmI**, *SmG**, *SmK**, and *SmH**, in which this twisting does not take place[10] (the optical activity of the substance is due to the chirality of the molecules).

Table 2. Characteristic structural parameters of mesophases of different types.

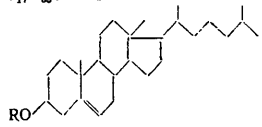
Type of mesophase	Notation	Fixed parameters
Nematics	*N*	$\varphi=0$, *D*
Smectics	*SmA*	$\varphi=0$, *D*, *d*
disordered	SmA_C	φ, *D*, *d*
	SmC	φ, ψ, *D*, *d*
hexatic	SmB_h	$\varphi=0$, $a'=b'$, $\gamma=120°$, *d*
	SmI	φ, $\psi=0$, $a'=b'$, $\gamma=120°$, *d*
	SmF	φ, $\psi=90°$, $a'=b'$, $\gamma=120°$, *d*
with three-dimensional order	*SmB*	$\varphi=0$, $a=b$, *c*, $\gamma=120°$
	SmG	φ, $\psi=0$, $a=b$, *c*, $\gamma=120°$
	SmI	φ, $\psi=90°$, $a=b$, *c*, $\gamma=120°$
	SmE	$\varphi=0$, $\theta=0$, 180°, *a*, *b*, *c*
	SmK	φ, $\psi=0$, $\theta=0$, 180°, *a*, *b*, *c*
	SmH	φ, $\psi=90°$, $\theta=0$, 180°, *a*, *b*, *c*

The calamitic mesogens for which X-ray diffraction data are available are listed in Table 3. They are arranged in a definite sequence (according to their chemical characteristics). Table 3 also gives the names of the compounds or groups of homologues, and the corresponding structural formulae. In some cases, letter abbreviations for the compounds, encountered in the literature, are given.

Table 3. List of calamitic mesogens studied by X-ray diffraction.

Compound	Name, abbreviation	Formula*
I	4-n-Octyl-4′-cyano-biphenyl	$C_8H_{17}—C_6H_4—C_6H_4—CN$
II	Alkoxycyanobiphenyl	$RO—C_6H_4—C_6H_4—CN$
III	n-Alkyl 4′-n-alkoxybiphenyl-4-carboxylate	$R'O—C_6H_4—C_6H_4—COOR$
IV	1α-Pentyl-4α-*p*-cyano-phenylbicyclo[2.2.3]octane	$C_5H_{11}—C_8H_{12}—C_6H_4—CN$
V	4′-n-Alkoxy-3′-nitrobiphenylcarboxylic acid	$RO—(NO_2)C_6H_3—C_6H_4—COOH$
VI	4′-n-Alkoxy-3′-cyanobiphenylcarboxylic acid	$RO—(CN)C_6H_3—C_6H_4—COOH$
VII	Alkylcyanotriphenyl	$R—C_6H_4—C_6H_4—C_6H_4—CN$
VIII	1-n-Heptyl-4-cyanobiphenyl-cyclohexane	$C_7H_{15}—C_6H_{10}—C_6H_4—C_6H_4—CN$
IX	1-n-Pentyl-4-ethylbiphenyl-cyclohexane	$C_5H_{11}—C_6H_{10}—C_6H_4—C_6H_4—C_2H_5$
X	1-n-Pentyl-4-X-biphenylcyclo-hexane	$C_5H_{11}—C_6H_{10}—C_6H_4—C_6H_4—X$, X = Cl, Br, CN, C_2H_5
XI	Cyanobiphenylpentylbicyclo-octane	$C_5H_{11}—C_8H_{12}—C_6H_4—C_6H_4—CN$
XII	4-Alkoxybenzylidene-4′-alkylaniline	$RO—C_6H_4—CH=N—C_6H_4—R'$
XIII	N-4-Cyanobenzylidene-4′-alkylaniline	$CN—C_6H_4—CH=N—C_6H_4—R$
XIV	N-4-Cyanobenzylidene-4′-octyloxyaniline	$CN—C_6H_4—CH=N—C_6H_4—OC_8H_{17}$
XV	2-Methylbutyl N-(4-n-decyloxybenzyl-idene)-4′-aminocinnamate	$C_{10}H_{21}O—C_6H_4—CH=N—C_6H_4—CH=CH—COO—CH_2—CH(CH_3)—C_2H_5$
XVI	n-Pentyl 4-phenylbenzylidene-4′-aminocinnamate	$C_6H_5—C_6H_4—CH=N—C_6H_4—CH=CH—COO—C_5H_{11}$
XVII	2-Chloropropyl 4-hexyloxybenzylidene-4′-aminocinnamate	$C_6H_{13}O—C_6H_4—CH=N—C_6H_4—CH=CH—COO—CH_2—CHCl—CH_3$

Table 3 (cont'd)

Compound	Name, abbreviation	Formula*
XVIII	4-(4-n-Alkoxybenzylidene-amino)-4′-cyanobiphenyl (n = 7, HOBACB; n = 8, OOBACB)	RO—C_6H_4—CH=N—C_6H_4—C_6H_4—CN
XIX	4-Nitrophenyl 4′-octyloxybenzoate	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_4—NO_2
XX	4-Cyanophenyl 4′-octylbenzoate	C_8H_{17}—C_6H_4—CO—O—C_6H_4—CN
XXI	4-Butoxyphenyl 4′-decyloxybenzoate	$C_{10}H_{21}O$—C_6H_4—CO—O—C_6H_4—OC_4H_9
XXII	4-Cyanobiphenyl 4′-heptylphenylbenzoate	C_7H_{15}—C_6H_4—C_6H_4—CO—O—C_6H_4—C_6H_4—CN
XXIII	4-Pentoxyphenyl 4′-octyloxyphenylbenzoate	$C_8H_{17}O$—C_6H_4—C_6H_4—CO—O—C_6H_4—OC_5H_{11}
XXIV	4-Isopentylphenyl 4′-octyloxyphenylbenzoate	$C_8H_{17}O$—C_6H_4—C_6H_4—CO—O—C_6H_4—$CH_2CH(CH_3)C_2H_5$
XXV	p-Alkoxyazoxybenzene (n = 1, PAA)	RO—C_6H_4—N(O)=N—C_6H_4—OR
XXVI	Ethyl azoxybenzene-p-dicarboxylate	C_2H_5O—CO—C_6H_4—N(O)=N—C_6H_4—CO—OC_2H_5
XXVII	1-Heptyl-4-p-cyanophenoxy-methylcyclohexane	C_7H_{15}—C_6H_{10}—CH_2—O—C_6H_4—CN
XXVIII	4-n-Pentylphenyl 4′-n-tetradecyloxythio-benzoate	C_5H_{11}—C_6H_4—S—CO—C_6H_4—O—$C_{14}H_{29}$
XXIX	4-Alkyl-4′-cyanostilbene	R—C_6H_4—CH=CH—C_6H_4—CN
XXX	4-Acetyl-4′-n-alkanoyloxy-azobenzene	R′—CO—C_6H_4—N=N—C_6H_4—O—CO—R
XXXI	Ethyl p-anisolamino-cinnamate	CH_3O—C_6H_4—NH—C_6H_4—CH=CH—COO—C_2H_5
XXXII	Bis-(4-n-hexyloxyphenyl)-mercury	$C_6H_{13}O$—C_6H_4—Hg—C_6H_4—OC_6H_{13}
XXXIII	1,2-Bis-(4-n-alkoxybenzoyl)-hydrazine	RO—C_6H_4—CO—NH—NH—CO—C_6H_4—OR
XXXIV	4-Nitrophenyl 4′-nonyloxy-benzoyloxybenzoate	$C_9H_{19}O$—C_6H_4—CO—O—C_6H_4—O—CO—C_6H_4—NO_2
XXXV	4-Cyanophenyl 4′-hexyl-benzoyloxybenzoate	C_6H_{13}—C_6H_4—CO—O—C_6H_4—O—CO—C_6H_4—CN
XXXVI	*trans*-1,4-Di-(n-octyloxy-benzoyloxy)cyclohexane	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_{10}—O—CO—C_6H_4—OC_8H_{17}
XXXVII	2-Alkyl-1,4-di-(4′-n-octyloxy-benzoyloxy)benzene	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_3R—O—CO—C_6H_4—OC_8H_{17}
XXXVIII	Terephthalylidene bis-4-n-alkylaniline (n = 4, TBBA; n = 5, TBPA; n = 10, TBDA)	R—C_6H_4—N=CH—C_6H_4—CH=N—C_6H_4—R
XXXIX	Bis-(4′-n-alkoxybenzylidene)-1,4-phenylenediamine	RO—C_6H_4—CH=N—C_6H_4—N=CH—C_6H_4—OR
XL	α-Phenylazo-(methoxybenzyl-idene-α′-naphthylamine)	C_6H_5—N=N—$C_{10}H_6$—N=CH—C_6H_4—OCH_3
XLI	Bis-(4′-n-alkoxyphenyl)-2-chloro-1,4-phenylene-diamine	RO—C_6H_4—NH—C_6H_3Cl—NH—C_6H_4—OR
XLII	4-n-Octyloxybenzoyloxy-4′-cyanostilbene	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_4—CH=CH—C_6H_4—CN
XLIII	4-n-Alkoxybenzoyloxy-4′-cyanoazobenzene	RO—C_6H_4—CO—O—C_6H_4—N=N—C_6H_4—CN
XLIV	Thallium stearate	$C_{17}H_{35}COO^-Tl^+$
XLV	Cholesteryl alkanoate	

*Here, R = C_nH_{2n+1}, R' = C_mH_{2m+1}.

Calamitic mesogenic molecules usually contain the following characteristic fragments: a) rigid rings (benzene, cyclohexane, adamantane, and heterocycle residues); b) bridges joining these rings [—CH=N—, CO—O—, —CH=CH—, —N(O)=N—, etc.]; c) groups joined to the rings (most frequently, alkyl or alkoxy groups). In Table 3, the compounds are arranged in the following order: 1) molecules not containing bridges (one-ring, two-ring, etc.) (I—XI); 2) molecules with one bridge (two-ring, three-ring, etc.) (XII—XXXIII); 3) molecules with two bridges (XXXIV—XLIII); 4) others (XILIV, XILV).

III. Nematic mesophases

Since the arrangement of the domains in non-oriented nematics is random, their X-ray diffraction patterns differ little from those of liquids. An oriented mesophase usually gives an X-ray diffraction pattern similar to that shown in Fig. 6. X-Ray diffraction patterns of this kind were obtained for compound XXV (n = 1, PAA) by Kast[16] (in an alternating electric field) and later by Kosterin and Chistyakov[17,18] (in direct and alternating fields). Here, equatorial and meridional reflections are observed. The former are usually represented by one or two pairs of intense crescent-shaped arcs, and are due to the approximately parallel orientation of the long axes of the molecules (L). The position of the equatorial reflections on the X-ray diffraction pattern makes it possible to determine the average distance between the long axes of neighbouring parallel molecules (D). The meridional reflections indicate the existence of a period a in the arrangement of the centres of gravity of the molecules along the direction of the direction **n**. This means that the nematic mesophase contains cylindrical rows of molecules (strings),[19] extending along **n** (Fig. 7). With the parallel orientation of the axes L this arrangement is the natural expression of the tendency to adopt a compact packing. The strings naturally exist only within certain molecular clusters (bundles). The width of the meridional reflections is determined by the average number of molecules in the string.

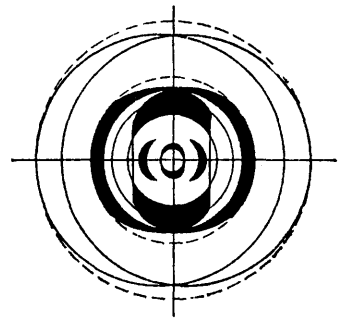


Figure 6. Diagram showing the positions of the reflections on the X-ray diffraction pattern of PAA (field intensity 4000 V cm^{-1}, temperature 123 °C).[17]

The PAA molecule shows negative dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp} < 0$ (the minimum value of ε in the direction of the long axis of the molecule with dipole moment forming an angle of 57° with this axis[20]). Thus in an electric field these molecules tend to be arranged in such a way that their axes L are perpendicular to the intensity vector (**n** ⊥ **E**). At the same time, in an electric field, a flux of the impurity ions usually present in the substance is produced; this flux also has an orienting influence, but it leads to the parallel arrangement of the axes L along the field lines (**n**||**E**).[21,22] The final result is determined by the competition between these two factors, and depends on the magnitude of the field strength. A published[17] set of X-ray diffraction patterns of a PAA mesophase at different direct field intensities shows that at E = 50 V cm^{-1}, only the orienting action of the field is felt (**n** ⊥ **E**), whereas at E > 10 V cm^{-1}, the

orienting action of the flux predominates (**n**||**E**). Similar X-ray diffraction patterns were obtained[23] for nematic specimens of compound XL.

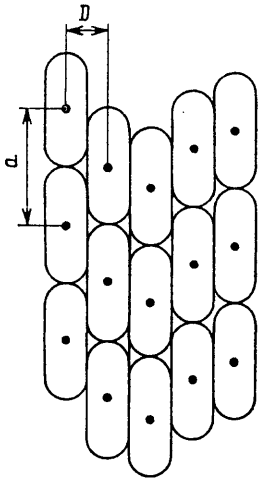


Figure 7. Arrangement of the molecules in a nematic mesophase.

Naturally, Fig. 7 gives a highly idealised picture of the structure of nematic mesophases. The relatively low intensities of the meridional reflections indicates that not all the molecules form periodic strings, and the weakness and vertical broadening of the equatorial reflections indicate that the orientation of the long axes of the molecules deviates from the strictly parallel. Distribution functions of the molecules with respect to orientation, and radial distribution functions of the atoms in the direction of the director, have been constructed.[17,18,23] The authors of these studies also report that they detected three preferred modes of relative azimuthal orientation of the molecules, corresponding to different values of D (D_1—the benzene rings of neighbouring molecules lie in the same plane, and their ends touch; D_2—the touching benzene rings are perpendicular to one another; and D_3—the benzene rings of neighbouring molecules are parallel). For PAA, these values were 6.2, 5.4, and 3.6 Å in a field with a strength of 200 V cm^{-1}, and 7.0, 5.3, and 3.6 Å in a field with a strength of 400 V cm^{-1}. Similar results were obtained for the nematic phase of compound XL. These data indicate that the effective shape of the molecule deviates from cylindrical.

A diffraction pattern similar to that described above is also obtained for cholesteric phases, in which the immediate environment of the molecules is approximately the same as in a nematic phase. In particular, this has been observed for specimens of derivatives of cholesterol (XLV, n = 8 and 13) which had not been subjected to special orienting treatment, but which evidently showed a considerable degree of orientation,[24] and for specimens oriented by a constant shear deformation (specimen in contact with a rotating rod).[25]

A more complex diffraction pattern was obtained for oriented nematic mesophases of homologues of compounds XXV and XLI.[26–28] An X-ray diffraction pattern typical of these phases is shown in Fig. 8. Here, the first meridional reflection has the form of a dumbbell, and the second meridional reflection is split. This type of meridional reflection indicates the appearance of order in a direction not coinciding with the director. To explain this pattern, de Vries[29] proposed the existence of so-called skewed cybotactic groups (Fig. 9), in which the molecules are arranged in layers § as in the smectic *C*.



Figure 8. Schematic representation of the X-ray diffraction pattern of a nematic with splitting of the meridional reflections.[38]

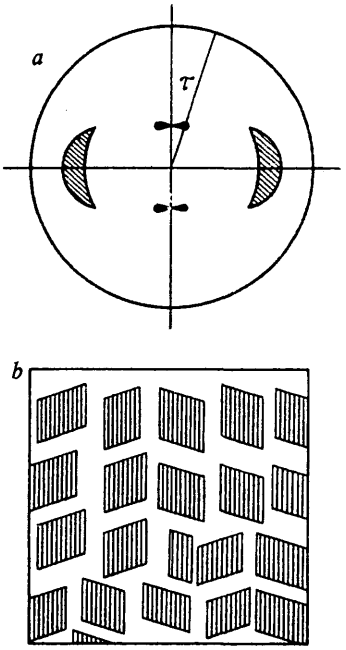


Figure 9. X-Ray diffraction pattern (*a*) and structure (*b*) of a nematic phase with cybotactic groups.

According to de Vries,[29] the angle τ on the X-ray diffraction pattern (Fig. 9*a*) is equal to the average value of the angle between the long axes of the molecules and the normal to the plane of the

§ The presence in liquid phases of cybotactic groups of molecules (that is molecular aggregates with definite spatial order) was first postulated by Stewart,[30] who later pointed out[31] that these groups apparently play an important role in nematic mesophases.

layer. This X-ray diffraction pattern also makes it possible to determine the average thickness of the layer d and the average distance D between the long axes of the molecules. The temperature dependence of these parameters and the intensity of the reflections was determined[32] for nematic phases of compound XLI (homologues with n = 6, 8, 10, 12) oriented in a magnetic field. Some of the numerical data are given in Table 4. With increase in temperature, the values of D and d increase, the former linearly, and the latter non-linearly. The angle τ also undergoes a corresponding non-linear change; with increase in temperature from the point of the transition into the nematic phase (T_N) to the point of the transition into the isotropic liquid (T_I), the value of τ decreases by $\sim 10°$. With increase in temperature, the intensities of the reflections naturally decrease, but for the homologues with n = 6 and 8 at high temperatures the intensity of the meridional reflections remains almost constant (including the range of existence of the isotropic liquid). The last feature was attributed[32] to the preservation of the cybotactic groups in the isotropic liquid phase.¶

Table 4. Geometric characteristics of the nematic phases of homologues of compound XLI.

n	T_N, K	T_I, K	d, Å at T_N	d, Å at 420 K	D, Å at 420 K	$(\Delta D/\Delta T)\times$ $\times 10^{-3}$, Å K^{-1}
6	371.9	471.5	24.05	26.54	5.015	2.60
8	334.0	453.7	27.04	30.30	5.066	2.80
10	384.9	440.9	32.16	35.92	5.066	2.53
12	406.7	432.7	36.32	37.46	5.090	3.14

De Vries[36] also studied the liquid and nematic phases of compound XII (homologues with n = 5–7). The value of D in the mesophase was determined from the equatorial reflections (the outer diffuse ring), and the value of a in the liquid phase was obtained from the meridional reflections (the inner diffuse ring). The presence of the inner ring on the X-ray diffraction pattern of the isotropic phase itself indicates the preferred orientation of at least some of the molecules; in the present case this orientation was evidently due entirely to the orienting action of the walls of the capillary. An increase in a was observed with decrease in the temperature of the liquid. Extrapolation of this relationship from the point of the liquid–nematic transition gave the value of a corresponding to the limiting elongated conformation of the molecule. For all three homologues, this value was found to be close to that obtained for a model in which the *trans*-conformation was assumed for the alkyl chains, and the chains were assumed to be coplanar with the benzene rings. The decrease in a with increase in temperature indicates that this conformation is lost, although the broadening of the inner ring may also be due to a decrease in the orientational order. In the nematic phases, with increase in temperature, a linear decrease in D from 4.94 Å to 5.03 Å was observed, as in the nematic phases described above.[32]

¶ Calculations carried out by the methods of molecular dynamics[33–35] also indicate the existence, in the instantaneous structure of the nematic phase, of molecular clusters, that is regions with higher orientational and translational order. These molecular clusters can apparently be identified with the cybotactic groups.

The layer associates (cybotactic groups) are usually present in nematics which on cooling form smectic phases. An exception is provided by the homologues of compound XXXVII with n = 0, 1, 3, 5, 9, 12, and 16, where n is the number of carbon atoms in the side chain, which does not lie along the axis of the ring in the molecule. In this series, with increase in n from 0 to 6, the angle of slope of the central aromatic fragment within the layers increases, and then decreases.[37] The explanation put forward by the authors cited[37] is that the short lateral "tail" hinders the parallel orientation of the molecules, but with increase in its length it becomes more flexible and can be arranged parallel to the long axis of the molecule.

According to Azaroff,[38] the explanation for the observed[26,27] broadening of the meridional reflections in a direction perpendicular to the meridian is that in the oriented nematic mesophase, the periodic strings of rigid molecules form layers (Fig. 10), and periodicity is also produced in a direction perpendicular to the strings. In the stack of parallel layers there is no periodicity along any direction not lying in the plane of the layer; at the same time, the stacks are arranged regularly in space. Azaroff considers that this model basically explains the intensity distribution on the X-ray diffraction patterns obtained,[26,27] although a real nematic phase also contains randomly arranged (non-correlating) molecular strings. On heating, the number and size of the stacks decrease, and the number of non-correlating strings increases, leading to splitting of the reflection, which acquires the form of a dumbbell.

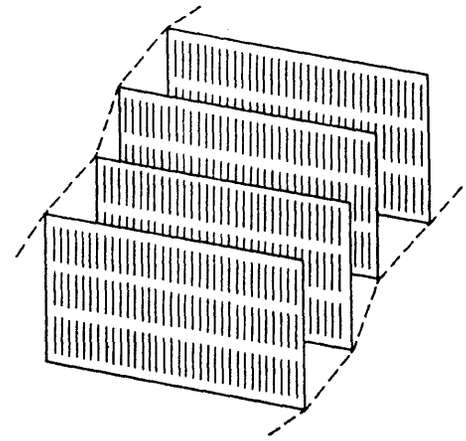


Figure 10. Stacks of parallel molecular layers in a nematic phase.[38]

Azaroff's model is criticised in a brief review by de Vries,[39] analysing published data on the structure of "cybotactic" nematics. The main argument against this model is that the existence of "planar layers" is not revealed in any properties of the nematic phase. According to de Vries, it is more probable that within this phase there are blocks of molecules with structures similar to those of the fragments of layers of the type *SmA* or *SmC*, whose appearance corresponds to the nucleation of the smectic layer order.

Optical modelling of diffraction on planar models of different molecular packings lead to similar conclusions about the structure of "cybotactic" nematics (Fig. 11).[40] In the opinion of the author cited, however, the value of the angle τ (see Fig. 9) is determined not by the slope of the molecules in the cybotactic groups (blocks) but by the average distance between these groups and their dimensions.

It is therefore suggested, in contrast to the work cited above,[32] that with increase in temperature the size of the blocks decreases.

Another possible increase in the complexity of the structure of the nematic phase may be due to the presence of dimeric associates of molecules, leading to the formation of molecular strings whose period is appreciably greater than the length of the molecule. This is apparently the situation in the cyanophenyl derivatives studied by Leadbetter and co-workers.[41–43] For these compounds, the ratio $a/l > 1$ and depends on the length of the aliphatic chains; at the same time, the period of the string a changes little with change in the central aromatic part of the molecule.

This last feature indicated to the authors cited a form of packing of the molecules in which their aromatic parts overlap (come into contact). The structure of the string is given approximately by the diagram in Fig. 12 (proposed by the present authors). The authors cited[41–43] talk about "bilayer" packing, but in the opinion of the present authors, when discussing the nematic phase, it is better to say that the string contains molecules oriented in antiparallel fashion, or that the strings are formed by dimers, which in the present case are most probably stable associates of molecules. These dimers are stabilised, in particular, by electrostatic interaction, since the molecules have an appreciable dipole moment (3.5–4.0 D).

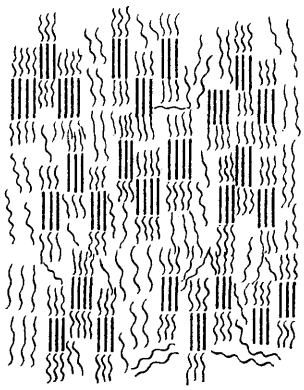


Figure 11. Model of the structure of a "cybotactic nematic", obtained by optical modelling.[40]

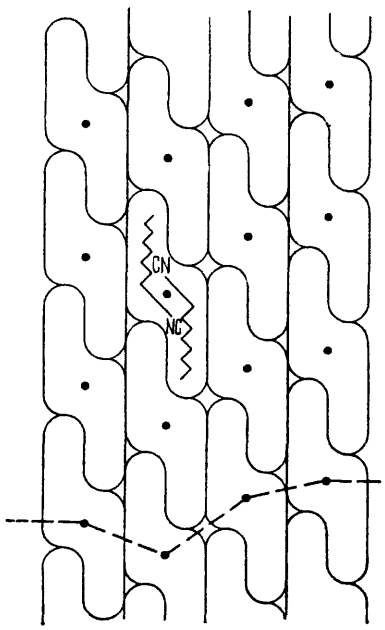


Figure 12. Structure of a nematic phase made up of dimers (for the case of cyano-derivatives).

Table 5 gives the values of l and a for a series of cyano-derivatives.[43] An interesting feature is that for compounds IV, VII, and XI, in addition to the reflectance given by the period a corresponding to the dimeric organisation of the strings, additional reflections indicating the existence of a period $a_2 < l$ are observed. This indicates the presence of strings in which dimers are not observed, and the molecules possibly do not have the most elongated conformation. The temperature dependence of the intensity of the reflections shows that strings with the period a_2 predominate at low temperatures, and strings with the period a_1 predominate at high temperatures.

A picture similar to that described above is also observed for a number of other compounds, for example compounds XXIX and X.[44,45] In the last case, the ratio a/l shows a marked dependence on the substituent, having the value ~1.4 for the cyano-derivatives, and ~1.1 for the halogeno-derivatives.

Table 5. Comparison of the lengths of the molecules (l) and the periods (a_1 and a_2) in the nematic phases of cyano-derivatives.

Compound	l*, Å	a_1, Å	a_2, Å
(II, n=6)	20.5	27.7	—
(IV)	19	24.9	13.2
(VII)	22	30.9	20.4
(XI)	23.5	30.7	18
(XX)	24	31.7	—
(XXVII)	22.2	32.2	—

* l is the maximum length of the molecule for the most elongated conformation.

IV. Smectic *A* and *C* phases

The X-ray diffraction patterns of a smectic mesophase oriented in an electric or magnetic field often have the form shown schematically in Fig. 13*a*. X-Ray diffraction patterns of this type have been obtained[46] for compound XXXI, and also in other studies.[47–52] In contrast to the X-ray diffraction patterns of nematics, in this case the meridional reflections have the form of fairly distinct spots. According to the simplest treatment, this type of X-ray diffraction pattern corresponds to an ideal smectic *A*, in which the molecular axes L are perpendicular to the layers ($\varphi = 0$); if however the axes L lie at a slope to the plane of the layer ($\varphi \neq 0$), that is in the case of an ideal smectic *C*, the straight line passing through the centres of the meridional reflections should make an angle ω with the equator (Fig. 13*b*). This picture has been observed fairly infrequently, however, and only for single-domain specimens. The distance between the meriodional reflections is determined by the thickness of the layer d, and the position of the equatorial reflections, as in the case of nematics, can be used to calculate the value of D.

In fact, smectics have a more complex structure. In particular, the condition $\varphi = 0$ for smectics *A* is usually satisfied only statistically.

Oriented liquid-crystalline specimens of compounds XXVI, XXXII, and XLIV, obtained on freshly split mica plates, have been studied by X-ray diffraction.[53] The X-ray diffraction patterns had the form corresponding to the type *SmA* (Fig. 13*a*), but the best agreement with experiment was given by a model in which the molecules were displaced relative to one another along their long axes by 5–6 Å, and their slope to the normal to the layer was 30° and 43° for compounds XXVI and XLIV respectively (for compound XXXII, a structural model corresponding to the experimental diffraction data could not be obtained). The structural analysis carried out in this study was based on an examination of the width and intensity of the meridional reflections as functions of the order of diffraction; these relationships should be different for different trial models, of which the following were considered: 1) monolayer *SmA*, 2) bilayer *SmA*, and 3) bilayer *SmC* (with allowance for the degree of disorder of the para-crystalline type). The best model was found to be the third model, which was constructed using X-ray diffraction data obtained for single crystals of these compounds or their analogues. Thus the order of the type *SmA* ($\varphi = 0$) is here achieved only effectively, as a result of averaging of the orientations with respect to the para-crystalline domains and with respect to the thickness of the specimen. Estimation of the linear dimensions of the crystallites gave the value ~400–800 Å.

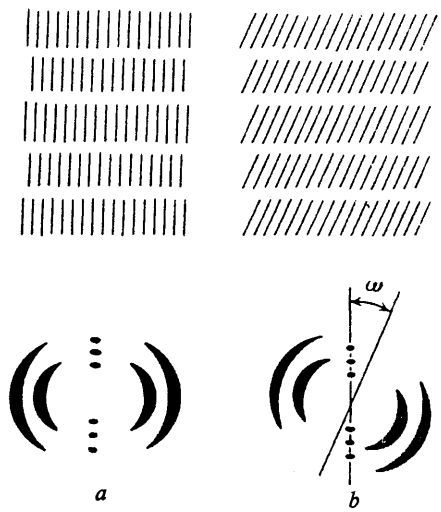


Figure 13. Arrangement of the molecules in upright (*a*) and sloping (*b*) smectic mesophases, and a schematic representation of the corresponding X-ray diffraction patterns.

For a deeper structural analysis of LC it is necessary to take into account the fact that the form of the molecules often differs significantly from cylindrical; this applies particularly to molecules containing long terminal aliphatic chains, which may extend in a direction which differs considerably from the direction in which the rigid central part extends.

The X-ray diffraction pattern obtained[54] for the smectic phase of compound XXXIX ($n = 6$) in a magnetic field had the form represented schematically in Fig. 14 ($\omega = 43°$). Assuming that the molecules retain the conformation found in the crystalline substance (the angle between the straight line passing through the centres of the benzene rings and the direction in which the aliphatic chains extend is 59°), the authors cited constructed a multi-domain model of this smectic. One of the two orientations of the layers represented in Fig. 15 is produced in each domain. Within the layer, the axes of the central parts of the molecules are arranged in sloping fashion, and make an angle of 47° with the plane of the layer, whereas the aliphatic chains are almost perpendicular to the plane of the layer (~74°). The proposed structure was confirmed by optical modelling. Here, a definite analogy with the structure of a nematic containing cybotactic groups is observed (Fig. 9). The smectic phase differs in that in it the layers are much more extensive than the cybotactic groups, and extend to the boundaries of each domain.

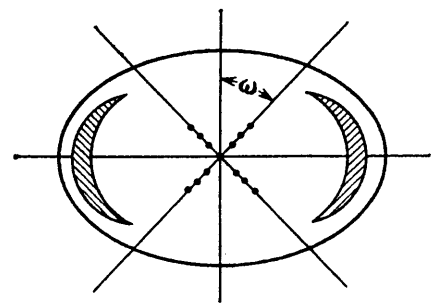


Figure 14. Schematic representation of the X-ray diffraction pattern compound XXXIX ($n = 6$).[54]

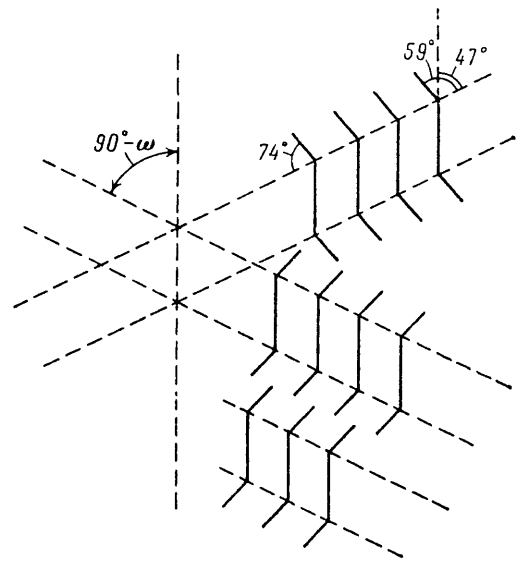


Figure 15. Polydomain model of the smectic phase of compound XXXIX ($n = 6$).[54]

The example given shows that allowance for the non-linearity of the molecules (an attempt to make this allowance was also undertaken in the work cited above[53]) blurs the classical structural representations of the calamitic phases *SmA* and *SmC*. To this must be added the possible sinusoidal corrugation of the layers, allowance for which, for example, gives best agreement with experiment in the optical modelling of the diffraction pattern of the smectic mesophase of compound XXV (n = 7).[55] The authors cited proposed the examination of various hypothetical layer structures formed from rod-shaped and zigzag molecules to explain the extended (parallel to the equator) form of the meridional reflections. The best model was found to be the model of type *SmÃ* discussed below.

Recent studies have shown that in many cases, smectic phases have a bilayer structure. This important feature of their structure is usually related to the non-linear configuration and polarity of the molecules.

One of the first investigations in which the bilayer structure of a smectic mesophase was detected involved an X-ray diffraction and dilatometric study of compound I at different temperatures.[56] The proposed structural model, constructed with allowance for the angular configuration of the molecules, is shown in Fig. 16.

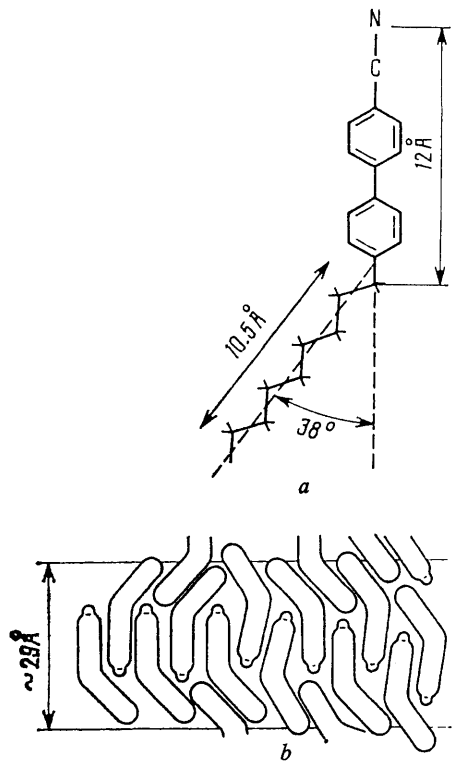


Figure 16. Structure of the molecule of compound I (*a*) and the packing of the molecules in the smectic phase (*b*).[56]

Dilatometric and X-ray diffraction data[57,58] were also combined in a study of the structure of the mesophases of compound XXX, of the type *SmA*. Two homologous series (m = 0 and 1) were studied, in each of which the central aromatic part remained unchanged, and the aliphatic chain joined to the ester group was varied (n = 1–16). The dilatometric study gave the molar volume, and the X-ray diffraction study gave the layer thickness (d) throughout the temperature range of existence of the mesophase. In the opinion of the authors cited, the experimental data show best agreement with the "bilayer" model (Fig. 17). The central part of the "bilayer" consists of the aromatic sub-layer, which contains practically no aliphatic "tails" and is therefore comparatively rigid and highly ordered. On both sides of the aromatic sub-layer there are much less ordered sub-layers consisting of aliphatic chains. The axes of the aromatic fragments of the molecules of the lower homologues of the series with m = 0 make an angle of 70–75° with the average plane of the layer, but are arranged approximately at right angles for the higher homologues and for all members of the series with m = 1. The thickness of the aromatic sub-layer for m = 0 and n = 2 is 16.7 Å, and for m = 0 and n = 14 it reaches 18.0 Å, which is practically equal to the length of the aromatic part, found from the model of the molecule; on going from one homologue to another, the total thickness of the layer increases by an average of 1.51 Å (m = 0) and 1.35 Å (m = 1), although according to model representations the increment in the length corresponding to a CH_2 group is 1.27 Å. This last feature is due to the specific structure of the bilayer. For m = 0, the thickness of the aliphatic part of the layer is determined by the average slope of the chains to the plane of the layer, which is equal to ~40°; for m = 1, the thickness of this part of the layer decreases, and the degree of order also decreases. With increase in temperature, the thickness of the bilayer increases slightly, according to a linear law. Using the X-ray diffraction patterns and the data on the structure of smectics described above, the authors cited tried to obtain information on the structure of the layers in the crystalline forms of the smectogens XXX being considered.[59] Unambiguous results could not be obtained, however (in principle, both bilayer and monolayer packings of the molecules are possible).

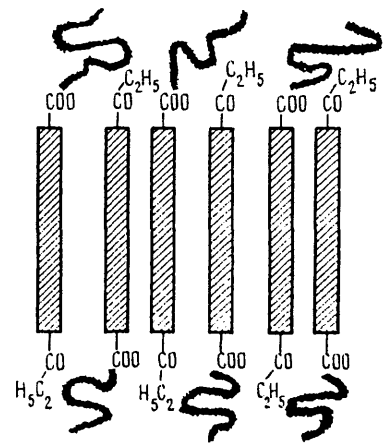


Figure 17. Structure of a smectic "bilayer".[57]

Similarly, a small-angle X-ray diffraction study[60] detected a "bilayer" structure in the phase of type *SmA* formed by compound VIII (the nematic phase of this substance contains molecular dimers, represented schematically in Fig. 12).

In addition to the nematic phases described in the previous section, smectics of the cyano-derivatives II (n = 10, 13, 16, 18), VII (n = 8), and XXII have been studied.[41–43] Here, three features are noteworthy. Firstly, for the phase *SmA* of compound XXII, decrease in temperature leads to the appearance of dumbbell-shaped reflections, indicating the production of skewed cybotactic groups, and the lines drawn through the centres of gravity of the molecules making up the cybotactic group make an angle of 27° with the *SmA* layers. Secondly, in this case also, bilayers in which the molecules are arranged in antiparallel orientations and are apparently joined to form dimers are also observed. Thirdly, and finally, in the smectic phase† of compound VII (n = 8), as in the nematic phase, a double periodicity is observed ($d_1 \simeq 1.4l$, $d_2 \lesssim l$). This apparently indicates the coexistence of bilayers and monolayers in which the molecules on the average have the parallel orientation.

Double periodicity of the smectic phase has also been observed[50] for compound XIX. In the weakly oriented state of the mesophase, splitting of the meridional reflections is observed; instead of the period 24.9 Å, periods of 32.5 Å and 26.6 Å appear for orientation in an electric field, and of 31.6 Å and 21.3 Å for orientation in a magnetic field. The authors cited pointed out, however, that both the existence of double periodicity in the packing of the layers and the presence of domains in which the smectic layers have the form of coaxial cylinders are possible in this case. According to Mineev,[51] the diffraction of X-rays on cylindrical smectic layers should lead to the observed splitting of the reflections.

The general picture of the bilayer structure of smectics, the phenomenon of double periodicity, and the reflection of these effects on the X-ray diffraction patterns were examined by Hardouin and co-workers.[61–63] According to the authors cited, there are three sub-types of mesophases *SmA* (Fig. 18) constructed from polar molecules: 1) the smectic A_1, consisting of non-polar monolayers (in a special case, the molecules in this layer may be joined to form dimers); in this smectic, $d \simeq l$; 2) the smectic A_2, consisting of double layers, each of which includes two polar monolayers; in this case, $d \simeq 2l$; and 3) the smectic A_d, formed by bilayers, where $l < d < 2l$. To this must be added the phase of type $Sm\tilde{A}$ with periodic modulation.[61]

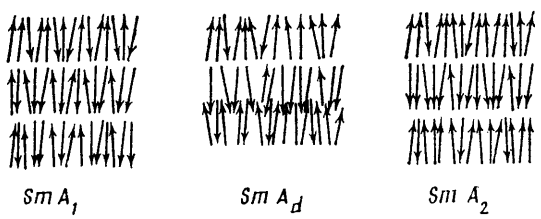


Figure 18. Structure of mesophases *SmA* belonging to different sub-types.

Fig. 19 compares the diffraction patterns (meridional reflections) characteristic of these three types of smectic with that for the nematic mesophase. The two diffuse haloes on the X-ray diffraction pattern of the nematic are characterised by the wave vectors $\mathbf{q}_2 = (2\pi/l)\mathbf{n}$ and $\mathbf{q}_1 > (2\pi/2l)\mathbf{n}$, where $\mathbf{n}$ is a vector showing the direction of the director; the vector $\mathbf{q}_1$ is due to the periodicity of the strings formed by individual molecules, and the vector $\mathbf{q}_2$ is due to the periodicity of the strings consisting of dimers. The smectic A_2 gives two Bragg peaks, corresponding to the polar monolayers and the double layers. For the smectic A_d, two Bragg peaks are observed, corresponding to the first and second order of diffraction from the bilayers. Here, however, a diffuse halo is usually observed in the region corresponding to the wave vector $\mathbf{q}_2 = (2\pi/l)\mathbf{n}$; this is due to the fact that the bilayer structure generally contains regions having a monolayer structure (see Fig. 23). For the smectic A_1, a Bragg peak corresponding to monolayer packing is observed, together with a diffuse halo, which indicates that this smectic is usually impregnated with the bilayer structure. The modulation of the layers, characteristic of smectic *A*, leads to doubling of the meridional reflection. If this modulation is sinusoidal, the reflection may be not split, but elongated along the equator.

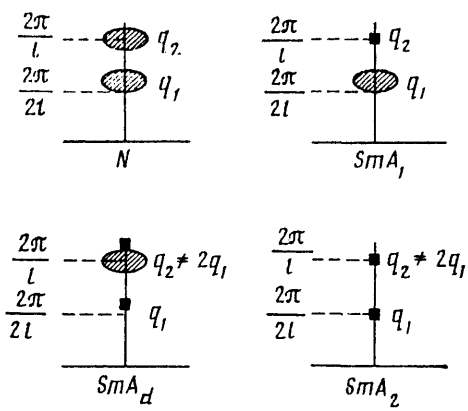


Figure 19. Schematic representation of the X-ray diffraction patterns of a nematic and of mesophases *SmA* belonging to different sub-types.[63] The black points denote the Bragg peaks corresponding to highly ordered elements of the structure; the hatched regions represent the diffuse peaks corresponding to structural features with a low degree of order.

These characteristics of the X-ray diffraction patterns can be established and studied systematically only by highly accurate measurements, examples of which have been published.[63] Thus compound XXXV in a narrow temperature range is converted from the nematic to the smectic phase SmA_d, and then to SmA_2. A mixture of compounds XXXV and XXXVIII (n = 4) with decrease in temperature passes through stages involving the formation of a nematic and then the successive phases SmA_1 and SmA_2. A study of the temperature dependence of the thickness of the smectic layer, carried out[64] for individual compounds and mixtures, showed that in the transformation $SmA_d \rightarrow SmA_2$ the value of d increases smoothly and continuously, indicating, in the opinion of the authors cited, that this transformation is not a phase transformation. Examples of mixtures of mesogens whose structure corresponds to the type $Sm\tilde{A}$ have been given.[61]

† This phase is a phase of the type *SmE*; these smectics are described in section V.

Systems in which so-called reverse mesomorphism is detected have been studied.[65,66] The term denotes the existence of a nematic mesophase at lower temperatures or at higher pressures than the temperature and pressure corresponding to the range of existence of the smectic phase. The compounds XIV and XIII (n = 8, 9), in which the high-temperature nematic phase $N(1)$ with increase in pressure was converted first into the smectic phase *SmA* and then into the nematic phase $N(2)$, were studied.[65,66] The authors cited[66] point out that no differences were detected in the macroscopic properties of the nematics $N(1)$ and $N(2)$; from preliminary X-ray diffraction studies it was assumed that they were microscopically identical. More complete X-ray diffraction data have not been published by the authors cited, however, and the structural identity of the phases $N(1)$ and $N(2)$ remains unproved and appears unlikely.

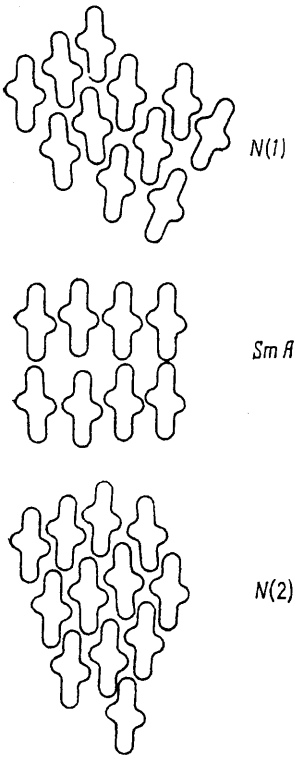


Figure 20. Structure of the mesophases $N(1)$, *SmA*, and $N(2)$ of compounds XIV and XIII (n = 8, 9).[66]

Comparison of the thickness of the smectic layer with the maximum length of the molecule enabled the authors cited[65,66] to put forward the following models of the structure of these phases. In their opinion, all the mesophases contain dimers, in which the aromatic rings of the molecules with alkyl chains extending from them in opposite directions‡ are superimposed in antiparallel fashion on one another ("overlap"). The transformation $N(1) \rightarrow SmA$ is accompanied by the appearance of a lateral interaction of the aromatic parts of the molecules, relating to different dimers (Fig. 20). The smectic layers produced, however, have a comparatively low density. Increase in pressure therefore leads to the formation of the more compact nematic $N(2)$, in which there is lateral interaction of the aromatic rings and the alkyl chains. This interpretation of the transformations $N(1) \rightarrow SmA \rightarrow N(2)$ might seem to indicate the nature of the structural differences between the nematics $N(1)$ and $N(2)$. The schematic representations of the structures $N(1)$ and $N(2)$ given in the work cited[66] (Fig. 20), however, are in fact identical. Another unsatisfactory feature of these representations, in the opinion of the present authors, is that they do not reflect the nematic nature of the phases $N(1)$ and $N(2)$; in both cases, sloping smectic layers are clearly visible.

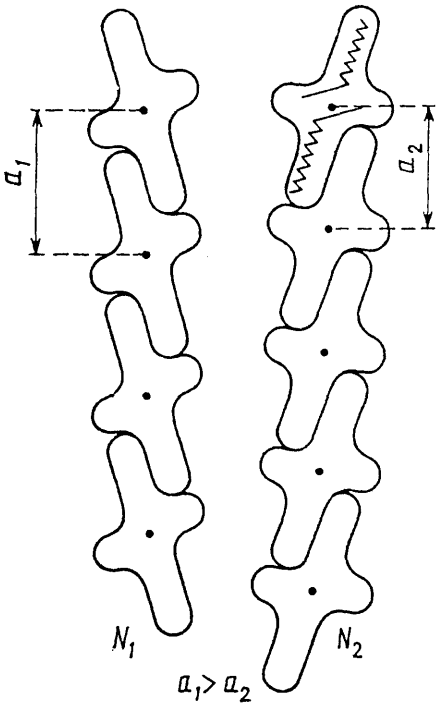


Figure 21. Hypothetical model of the structure of the strings in nematics $N(1)$ and $N(2)$.

Another structural interpretation of these transformations can be proposed. It is represented in Fig. 21, constructed on the same lines as Fig. 12 above. It can be seen that the difference between the

‡ The phases $N(1)$ and *SmA* of compound XIV were also studied by Jha and co-workers[67] (at atmospheric pressure). The authors cited consider that these phases have a "bilayer structure" (in the case of the nematic this apparently indicates the presence of dimers). The change in the value of D under the influence of a magnetic field was also studied; with increase in the field intensity, the value of D at first decreases sharply, and then remains constant.

phases $N(1)$ and $N(2)$ reduces to a difference in the structures of the strings, which have a larger period in the first case. The lateral interaction of these strings in the regions of the equilibrium diagram corresponding to the nematic mesophases is insufficient for their relative displacement to be detected. When the nematic is converted into the smectic phase, a rearrangement takes place, as a result of which the layer structure is detected.

The structural interpretation of the transformations proposed by Cladis and co-workers,[66] and also the model represented in Fig. 21, apparently have an arbitrary element; the existence of dimers is assumed *a priori*, although in fact they may not be present in some of the phases examined. In one of their papers,[65] the authors cited also took account of the possibility of rearrangement (or breakdown) of the dimers in the phase transformation, but this alternative does not appear in their subsequent paper.[66]

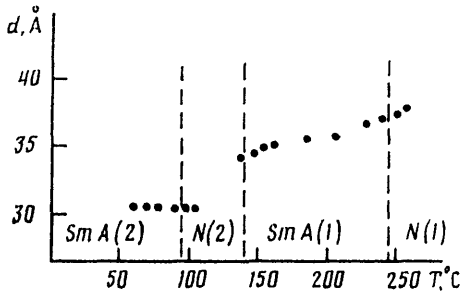


Figure 22. Temperature dependence of the thickness of the smectic layers of compound XLII.[69]

A completely different interpretation of the reverse mesomorphism observed for compound XLII was given by other workers.[68,69] In this case the following chain of thermotropic transformations was detected:

$$C \overset{95\,^\circ C}{\longleftrightarrow} SmA\,(2) \overset{96\,^\circ C}{\longleftrightarrow} N\,(2) \overset{138.9\,^\circ C}{\longleftrightarrow} SmA\,(1) \overset{247\,^\circ C}{\longleftrightarrow} N\,(1) \longleftrightarrow I,$$

where C represents the crystal, and I the isotropic liquid. The thickness of the layer in the phase $SmA(2)$ in fact is independent of temperature and approximately equal to the length of the molecules (31.4 Å), whereas in the phase $SmA(1)$ the thickness of the layer increases considerably with increase in temperature (Fig. 22). The diagram in Fig. 22 confirms the difference in the periods of the strings in the nematics $N(1)$ and $N(2)$ mentioned above. The authors cited[68,69] also measured the average distances between the long axes of the molecules D for all the phases:

Phase	Temperature, °C	d, Å
$N(1)$	263	5.3
$SmA(1)$	150	5.1
$N(2)$	115	5.0
$SmA(2)$	75	4.85

They consider that the structure $SmA(2)$ is a monolayer structure, and that $SmA(1)$ is predominantly bilayer. At the same time, with decrease in temperature, the X-ray diffraction patterns of the phase $SmA(1)$ show an additional periodicity, corresponding approximately to four times the length of the molecules (~120 Å). This last feature was attributed to the appearance of monolayer regions. A schematic representation of the structure of the mesophase assumed by the authors cited in this temperature range is shown in Fig. 23, which explains the modulation with a period of ~120 Å. A study of the diffuse spots corresponding to small angles of scattering on the X-ray diffraction patterns of the phase $N(2)$ indicated the presence of cybotactic groups, which are similar to the monolayers of the phase $SmA(2)$ in the lower part of the temperature range, and similar to the bilayers of the phase $SmA(1)$ in the upper part; in the middle of this range, both types of group are observed.

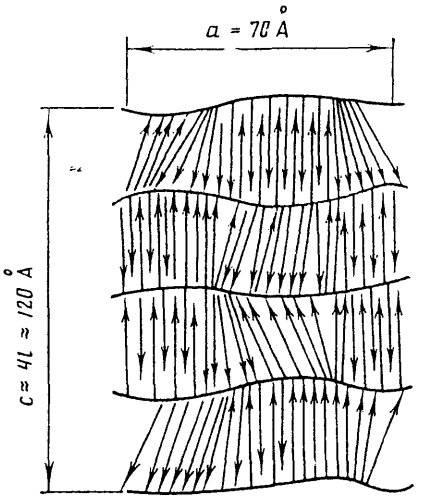


Figure 23. Structure of the mesophase of compound XLIII.[69]

Similar results were obtained[7] for the compound XLIII (n = 9), which differs from the compound XLII studied by Hardouin and co-workers[68,69] only in the bridging group: the group $-CH=CH-$ is replaced by the group $-N=N-$. Here, the following phase transformations are observed:

$$C \xrightarrow{94.0\,^\circ C} N\,(2) \xrightarrow{116.0\,^\circ C} SmA\,(1) \xrightarrow{212.4\,^\circ C} N\,(1) \xrightarrow{242.9\,^\circ C} I.$$
$$\searrow SmA\,(2) \swarrow 70.9\,^\circ C$$

The temperature dependence of the value of d for specimens oriented in a magnetic field is analogous to that represented in Fig. 22, but in this case it was also possible to measure the change in the period of the strings in the range corresponding to the reverse nematic $N(2)$. Here, the interpretation of the results is similar; it is considered that the phase $SmA(2)$ consists of monolayers, the phase $SmA(1)$ is partly bilayer, and in the range of existence of the phase $N(2)$ there is a gradual change from the first to the second structure.

The same compound XLIII (n = 9) and its homologue with n = 8 has been studied at a high pressure.[71] For the homologue with n = 8, reverse mesomorphism was not observed; the change in the temperature of the transformation of the monolayer phase $SmA(1)$ into the nematic phase was linear (Fig. 24*a*). A fundamentally different result was obtained for the bilayer reverse phase $SmA(1)$ of the homologue with n = 9 (Fig. 24*b*). In the last case the phase boundary is represented by a symmetrical curved line; at a pressure of 0.51 kbar the bilayer phase $SmA(1)$ disappears. Thus pressure

stabilises the monolayer structure and destabilises the bilayer structure, converting the latter into a nematic structure (the authors cited point out that their interpretation of the results was based on the model proposed by Cladis and co-workers[65,66]).

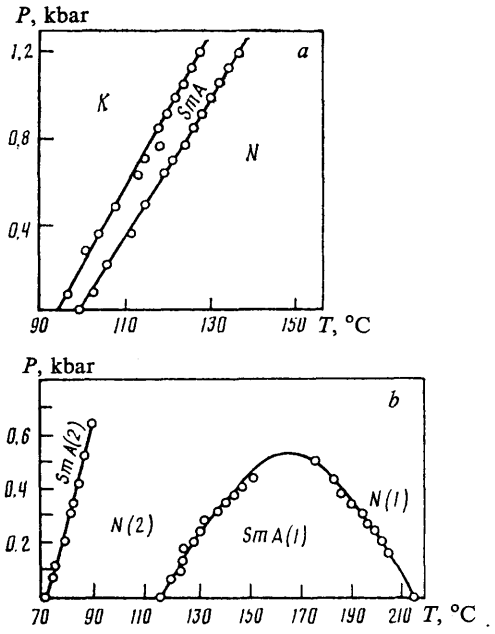


Figure 24. Equilibrium diagrams of homologues of compound XLIII:[71] *a*, homologue with $n = 8$; *b*, homologue with $n = 9$.

In a recent paper[72] it was shown that the number of smectic–nematic reverse phase transformations observed in a single system may be fairly large. Thus for compound XXXIV the following sequence of mesomorphic phases (in the notation of the authors cited) is observed; the types of phase were confirmed by X-ray diffraction data:

$$I \xrightarrow{224\ ^\circ C} N \xrightarrow{195\ ^\circ C} Sm(\text{bilayer}) \xrightarrow{156\ ^\circ C} N(1R) \xrightarrow{138.5\ ^\circ C} Sm(\text{bilayer})$$
$$\xrightarrow{124\ ^\circ C} N\ (2R) \xrightarrow{121\ ^\circ C} SmA\ (1) \xrightarrow{119\ ^\circ C} SmC \xrightarrow{100\ ^\circ C} SmA\ (2) \xrightarrow{96\ ^\circ C} SmC\ (2).$$

The authors cited relate this variety of phases, firstly to the change with change in temperature in the conformational mobility of the terminal alkyl chains, leading to a change in the effective length of the molecule, and secondly to the possible formation or breakdown of dimers.

Before considering papers dealing with the study of smectics of type *C*, it may be noted that X-ray diffraction data on these mesophases are fairly sparse. The tilt angle φ of the molecules in the phase *SmC* is determined in different ways: 1) from the position of the reflections on the X-ray diffraction patterns, 2) from the ratio of the length of the thicknesses of the layers in the phases *SmC* and *SmA* of a given compound. These estimates are clearly always more or less approximate, since they involve the assumption that the molecules have a cylindrical form, or (and) other approximations.

For compound XXV ($n = 7, 8$), the phase *SmC* is formed directly from the nematic, and the angle φ (~30°) changes little compared with the angle of slope of the molecules in the cybotactic groups of the nematic phase.[73] For a typical representative of smectics of type *C*, namely compound XXXVIII (TBBA), the classical sequence of phase transformations $N \rightarrow SmA \rightarrow SmC$ is observed on cooling. The transformation $SmA \rightarrow SmC$ is accompanied by an increase in the angle φ from 0 to 25 °C, and the results of the direct measurement of φ from the X-ray diffraction patterns (the value φ_P) and its calculation from the thickness of the smectic layers ($\cos\varphi_X = d_C/d_A$) show good agreement.[74]

The temperature dependence of the angle φ in *SmC* has been studied[37] for compound XXI; with increase in temperature, the angle φ increases, and φ_P and φ_X diverge. The authors cited attribute this last feature to the zigzag form of the molecules, and suggest that the thickness of the smectic layer be described by the expression

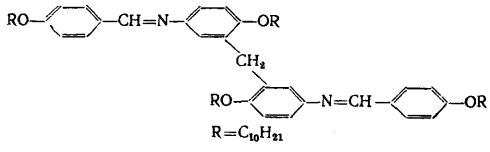
$$d = a_0 \cos\varphi_1 + (l_1 + l_2)\cos\varphi_2,$$

where a_0, l_1, and l_2 are the lengths of the central aromatic part and the terminal fragments of the molecule, and φ_1 and φ_2 the angles of slope of the aromatic ring and the "tails" to the plane of the layer ($\varphi_1 = \varphi_P$). It was found that in the substance studied, the terminal chains are arranged almost at right angles to the layer, and the aromatic rings are sloping.

The thickness of the smectic layer of the phase *SmC* of compound XXV ($n = 7$) has been measured at different pressures up to 1.5 kbar [75] and up to 3.8 kbar,[76] and the angle of slope of the molecules to the plane of the layer determined. For $d = 23.5$ Å, atmospheric pressure, and a molecule length of 32.1 Å (found from the model), $\varphi = 43°$. An interesting feature is that with increase in pressure, the value of *d* and hence the angle of slope remain practically unchanged. The authors cited[76] point out that the nature of the change in the structure with the smectic *C* is compressed is still not clear. The *P*–*T* diagram shows a triple point at a pressure of 6.67 kbar and a temperature of 164 °C. Above this pressure, the solid phase is converted directly into the nematic phase.

A characteristic feature of the smectic phase of the chiral compound XV [75] is its spiral character (type *SmC**). This phase is produced from the phase *SmA* with increase in pressure, and the thickness of the layer, which in *SmA* was independent of pressure, decreases considerably in *SmC** (the slope of the molecules increases) (Fig. 25); the substance is then converted into *SmI**. The authors cited compared the behaviour of this substance with that of compound XXV ($n = 7$); in the last case the phase *SmC* is formed directly from the nematic phase (the stage *SmA* is not observed), and the thickness of the sloping smectic layer is practically independent of temperature and pressure. An attempt to relate the difference described to the structures of the molecules of the compounds being compared was unsuccessful, however.

An analysis of the structure of mesophases of the type *SmC* for the compound



proved to be extremely complicated, because of the conformational non-rigidity of the molecules and the possible coexistence of completely different conformers in the same mesophase. Three

specimens (obtained in different ways) of this compound, called "Siamese twins", were studied.[77] Specimen *A*, obtained by crystallising from a solvent, in both the crystalline (28 °C) and the smectic (122 °C) phases gave a diffraction maximum indicating the presence of layers with d = 23 Å. Specimen *B*, obtained by cooling the melt, at the same temperatures in both the crystalline and smectic phases gave a maximum corresponding to layers with d = 32 Å. Finally, for specimen *C*, obtained by rapid heating to 125 °C, a diffraction pattern with two maxima (d = 23 Å and 32 Å) was observed. The authors cited consider that the phases *A* and *B* are formed by different conformers (*a* and *b*) (this naturally leads to the production of layers with different structure and thickness), and that the phase *C* is a mixture of the conformers and contains two types of smectic domain. In the interpretation of the results, the conformers *a* and *b* were assigned structures in which the $C_{10}H_{21}O-C_6H_4-CH=N-C_6H_3(OC_{10}H_{21})$ chains are directed in different directions in one case, and in the same direction in the other. It was also noted that the smectic phase of the compound $C_{10}H_{21}O-C_6H_4-CH=N-C_6H_4-O-C_{10}H_{21}$ (corresponding approximately to half of the "twins" molecule) also give a diffraction maximum corresponding to a layer with d = 32 Å. (This obviously means that in specimens *A* and *B* the extended parts of the molecules are oriented in different ways relative to the planes of the smectic layers.) It is clear, however, that the interpretation of the diffraction data given in the work cited is indefinite. Such complex molecules have an extremely wide range of conformational possibilities; these molecules can also be arranged in layers in different ways.

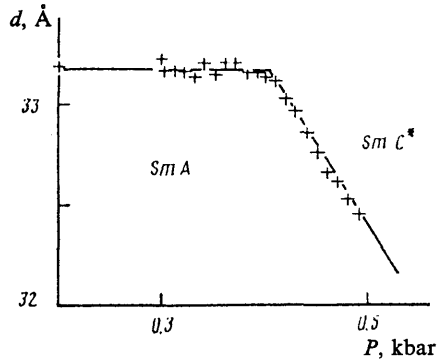


Figure 25. Pressure dependence of the thickness of the smectic layer in compound XV.[75]

Like the smectic phases of the *SmA* type, the sloping smectics show monolayer structures (SmC_1) and structures with double layers (SmC_2).[61] Cases of modulation of the layers are known,[78,79] giving the sub-type *SmC*; here, sinusoidal modulation is replaced by corrugation of the layers, "like the teeth of a saw".[78]

V. Smectic phases with a high degree of ordering

This section is devoted to a systematic examination of X-ray diffraction studies of "crystalline" smectics (the two lowest rows in Fig. 1), and then the less ordered hexatic smectics (second row in Fig. 1). This sequence of presentation is dictated by the chronology: the first detailed studies of the structure of "crystalline" LC preceded slightly the detailed study of hexatic phases.

It should be emphasised that the term "crystalline smectic" indicates the possibility of the experimental determination of the three parameters of a statistical lattice, but does not imply the three-dimensional periodicity characteristic of solid crystals. In addition to local breakdown of the order (for example, faults in the orientation due to the isometric character of the molecules in certain directions), considerable dispersion of the orientational and positional parameters is usually observed in this case, and domain structures of different types are often encountered, together with structural modulations which do not correspond to the effective period. In this case the dynamic parameters naturally have values appreciably higher than those characteristic of solid crystals. It is also important to emphasise that many liquid-crystalline systems are sufficiently ordered (suitable for structural studies) only under special conditions (for example in an electric or magnetic field).

A significant contribution to the study of highly ordered smectic phases was made by Doucet, who summarised his work in a review.[80] In particular, "crystalline" smectics of the compound XXXVIII (n = 4) (TBBA) were studied by X-ray diffraction;[81] the following transformations were observed between the large number of mesomorphic phases:

$$C(9) \xrightarrow{-33\,^\circ C} C(8) \xrightarrow{113\,^\circ C} (SmG)\,(5) \xrightarrow{144\,^\circ C} SmC\,(4) \xrightarrow{172\,^\circ C}$$
$$52\,^\circ C \uparrow \qquad \uparrow 84\,^\circ C$$
$$(7) \xrightarrow[68\,^\circ C]{} (6)$$
$$\longrightarrow SmA\,(3) \xrightarrow{200\,^\circ C} N\,(2) \xrightarrow{236\,^\circ C} I\,(1).$$

A "single crystal" of phase (5), obtained by melting the single crystal (8) without applying an external field, gave two types of X-ray diffraction pattern. These X-ray diffraction patterns, and the arrangements of the molecules deduced from them are shown in Fig. 26. When the X-ray beam is perpendicular to the long molecular axes *L*, the diffraction pattern (Fig. 26*a*) consists of a series of parallel diffuse bands (layer lines), the distances between which are proportional to the reciprocal of the length of the molecule (1/29 Å). This indicates the presence of molecular string along the *c* axis. The thickness of the diffuse layer lines depends on the extent of the ordered section of the string; in the present case it is close to 200 Å, which corresponds to approximately seven molecules. The length of the diffuse bands can be used to find the mean-square deviations of individual molecules from the direction of the string (2°) and the mean-square displacements of the molecules along the string (2.5 Å). Unlike the diffuse bands given by nematics, the diffuse bands in the present case are not curved, indicating that there is little departure from the parallel arrangement of the strings. The intense spots forming a regular row on the layer lines are produced by the smectic layers. The angle between the long molecular axes and the normal to the plane of the layer is 32° at 115 °C (it can be measured directly on the X-ray diffraction pattern). Strings are formed when the layers are superimposed.

The other X-ray diffraction pattern (Fig. 26*b*) corresponds to the equatorial plane *ab*, which is perpendicular to the long axes of the molecules. The 6 Bragg reflections observed in this case indicate two-dimensional translational ordering of the smectic layers (a pseudo-hexagonal lattice). This X-ray diffraction pattern also contains diffuse spots, which can be grouped into three sets of four, lying at an angle of 120 ° to one another. This last feature was interpreted as corresponding to three orientations of the domains. Doucet[80] constructed a scheme for the coherent coupling of

domains oriented in different ways (Fig. 27). Within each domain the cell is monoclinic. The X-ray diffraction patterns described, and also the "powder diagrams", were used to determine the parameters of this cell (at 125 °C):

$$a=10.10(5),\ b=5.18(2),\ c=28.3(2)\ \text{Å},\ \beta=119.0(5)^\circ.$$

According to the current structural classification of smectics (see section II), this structure of the domain corresponds to the type *SmH*. The coexistence of three orientations of the domains, leading to the pseudo-hexagonal nature of the layers, makes it possible to assign the mesophase described to the type *SmG*. In the works cited,[80,81] this mesophase was first regarded as a representative of the smectics of type *SmB* (from the miscibility criterion). Having established the sloping arrangement of the molecules relative to the layers, Doucet suggested that the smectics of type *B* be sub-divided into "upright" (B_A) and "sloping" (B_C). In his review,[80] however, he points out that the X-ray diffraction data show that the phases classified as *SmG* according to the miscibility criterion are identical to phases of the type SmB_C.

In the model described for the structure of the phase (5) of TBBA, the question of the nature of the azimuthal disorder remains open; it may be static (there are no reorientational movements of the molecules involving rotation of the molecules about their long axes) or dynamic (reorientational movements take place, so that the orientation of the domains is constantly changing). Inelastic neutron scattering has shown[82] that the molecules in the phase being considered change their orientation, by rotating through 60°. This is consistent with the proposed model (Fig. 27) if it is assumed that the molecules situated at the vertices of the cell and at its centre are rotated through 60° relative to one another and that they change their orientation in synchronous fashion.

The degree of crystallinity, revealed in the correlation of the relative arrangement of the smectic layers, can be estimated by analysing the profile of the diffuse spots surrounding the Bragg reflections (Fig. 28). An analysis of the phonons generating these diffuse spots at different temperatures was carried out.[80] The intensity profile of the diffuse scattering is described by the function $I(q) = I/q^\alpha$, where q is the distance from the centre of the reflection in reciprocal space, and α the crystallinity criterion. If there is no correlation between the layers of the smectic phase, then, as shown by de Gennes and Sarma,[83] $\alpha < 2$. On the contrary, for phase (5) close to the point corresponding to its formation from the crystal, the value of α is close to 2, indicating a high degree of crystallinity.

A similarity is observed between the structures of the phase (5) and the crystals (8). According to X-ray diffraction data,[84] the crystals (8) contain molecular layers parallel to the plane *ab*, and also strings extending along the *c* axis. The lattice parameters are: $a = 17.56$, $b = 5.75$, $c = 53.2$ Å, $\beta = 115.47°$, structural class $C2/c$, $Z = 8(1)$. Thus the structures of the layers in the mesophase (5) and in the crystalline substance (8) differ considerably, but the

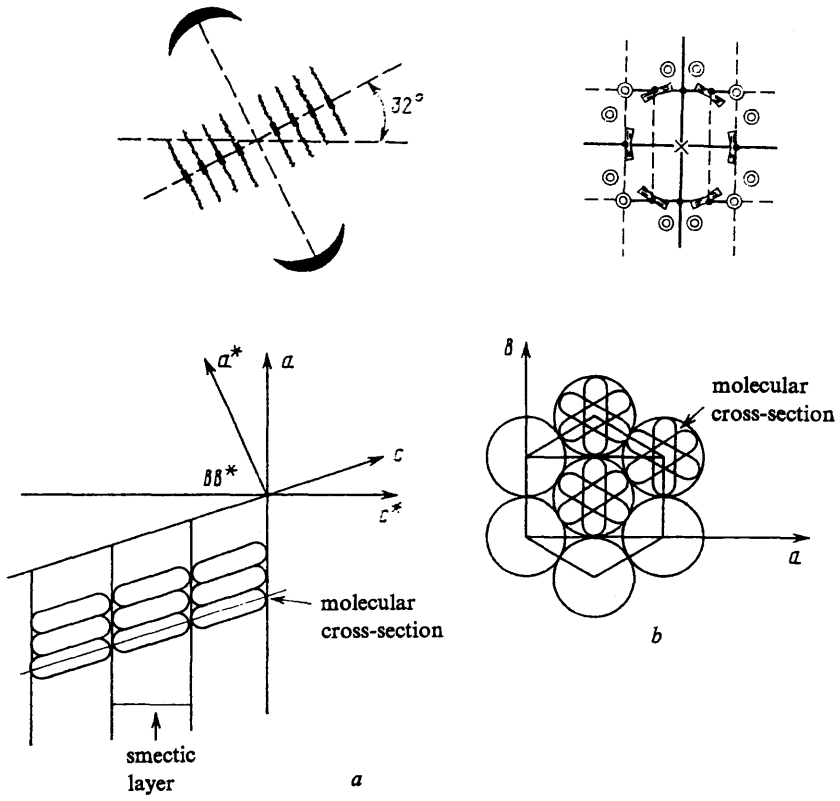


Figure 26. X-Ray diffraction patterns (schematic representations) and arrangement of the molecules in the highly ordered smectic phase of the compound TBBA:[80] *a*, projection perpendicular to the axis *L*; *b*, projection along the axis *L*.

angle between the long axes of the molecules and the normal to the plane of the layer in the crystals is 35°, that is it is close to the corresponding value found for the smectic phase (5). Disorder is observed in the arrangement of the terminal methyl groups, and there is extremely little penetration of the butyl chains into adjacent layers. These two factors weaken considerably the cohesion of the layers, enabling the latter, on fusion of the crystal, to be converted into the smectic phase with comparatively little rearrangement.

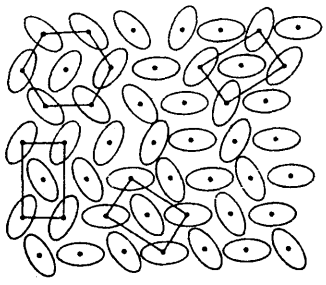


Figure 27. Arrangement of the molecules in the smectic layer of the highly ordered mesophase of compound XXXVIII;[80] three orientations of the cell of the layer are shown.

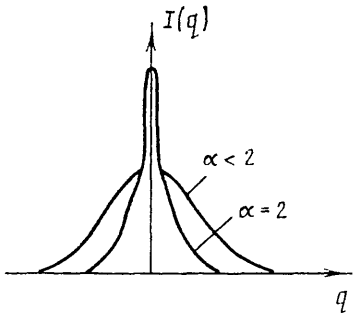


Figure 28. Profile of a Bragg peak surrounded by a background of diffuse scattering.

The conversion of the phase (5) into the crystalline state takes place with the formation of the intermediate mesophases (6) and (7), which are also highly ordered smectics. The X-ray diffraction patterns of phase (6) are similar to those of phase (5), but differ in that only four diffuse spots, that is one orientation of the domains, is observed. Thus the phase (6) can be classified as type *SmH*. In this case the monoclinic cell parameters are: a = 10.38, b = 5.24, c = 28.31 Å, β = 123°. The disorder apparently involves mainly rotation of the molecules through 180° about their long axes (statistical distribution in two azimuthal orientations), in agreement with neutron scattering data.[85] In the phase (7), doubling of the period along the long molecular axes is observed (cell parameters: a = 10.17, b = 5.27, c = 55.24 Å, β = 122.3°). According to the current classification, the phase (7) is evidently a bilayer smectic of the same type.

The X-ray diffraction data[80,85] indicate that the structures of the phases (5) and (6) of TBBA are similar to those of the phases *SmB* and *SmE* of compound XVI (n = 5). The latter undergoes the following mesomorphic transformations:

$$C \overset{92\,^\circ C}{\longleftrightarrow} SmE \overset{101.5\,^\circ C}{\longleftrightarrow} SmB \overset{168\,^\circ C}{\longleftrightarrow} SmA \overset{204\,^\circ C}{\longleftrightarrow} I.$$

The phases *SmB* and *SmE* of compound XVI (n = 5) differ from the phases (5) and (6) of TBBA in that the molecules are approximately perpendicular to the plane of the layer. The X-ray diffraction patterns of the phase *SmB* of this compound do not contain rings with index l equal to 1, indicating a decrease in the correlation of the layers in the transformation *SmE* → *SmB*. Doucet[80] points out that this is not a property typical of all smectics of type *B*; in other compounds, phases of type *B* give reflections with l = 1.§ In the phase *SmB* the azimuthal disorder is such that all the molecules behave as translationally equivalent; this evidently corresponds to the existence of three orientations of the domains with the "herring-bone" arrangement of the molecules. In the phase *SmE* the disorder corresponds to reorientational rotations of the molecules round their long axes through 180°. Neutron diffraction data[87] indicate that this disorder is dynamic.

The phase *SmE* of the homologue of compound XVI with n = 4 has been studied.[88,89] In contrast to the work of Doucet and co-workers,[80,86] it was established that the smectic is "bilayer" (in this case this term apparently means that in a period perpendicular to the plane of the layers *ab* there are two "sub-layers", whose thickness (26.8 Å) is slightly greater than the length of the molecule (25.3 Å); each "sub-layer" is displaced by a distance $a/2$ relative to its neighbour, as shown by X-ray diffraction data for the crystalline phase). The conversion of the crystals into the mesophase *SmE* is accompanied by a marked change in entropy (70% of the entropy effect of the conversion of the crystal into the isotropic liquid). This corresponds to an appreciable structural rearrangement; the angle between the long axis of the molecules and the normal to the layer decreases from ~40° to a value close to 0°.[89] In the specimens obtained by melting the crystal, domains with six different orientations are observed. Incoherent quasi-elastic neutron scattering showed that the relaxation time of the azimuthal rotation of the molecules does not exceed 10^{-10} s, and this rotation is not free (height of the barrier ~10 kT).

"Bilayer" packing of the molecules in a smectic of type *SmE* was also found for compound XVIII (n = 7).[90] X-Ray diffraction showed that the phase *SmE* has an orthogonal cell with parameters a = 8.29, b = 5.17, c = 58.0 Å. By making use of the nature of the absences, which indicates the presence of a glide plane of reflection n, and also by constructing close packing from three-dimensional models of the molecules (with length L = 29.5 Å), the authors cited obtained a model of the structure of the meso-phase (Fig. 29). In their opinion, the unfavourable contact between the CN groups of molecules belonging to different layers (Fig. 29*a*) is compensated by the close packing in the layers, where the benzene rings are in contact with the alkyl chains.

For compound XVIII (n = 7), the following sequence of mesomorphic transformations was observed:

$$C(II) \overset{65\,^\circ C}{\longleftrightarrow} C(I) \overset{73\,^\circ C}{\longleftrightarrow} SmE \overset{95\,^\circ C}{\longleftrightarrow} SmB \overset{111\,^\circ C}{\longleftrightarrow} N_1 \overset{140\,^\circ C}{\longleftrightarrow}$$
$$\underset{51\,^\circ C}{\overset{\uparrow}{\underset{\downarrow}{S_X}}}$$
$$\rightarrow SmA \overset{222\,^\circ C}{\longleftrightarrow} N_2 \overset{273\,^\circ C}{\longleftrightarrow} I.$$

§ According to the ideas presented in section II, the phase *SmB* of compound XVI (n = 5) is to some extent hexatic (*SmB*$_h$).

It is suggested that the transformation *SmE* → *SmB* is accompanied by a relative displacement of the layers, which acquire a hexagonal structure as a result of the orientational disorder, by the magnitude of the vector 1/6*a* + 1/2*b* to give packing of the type ...*ABAB*... With further increase in temperature, on formation of the phases N_1 and *SmA*, adjacent molecules are displaced relative to one another to give "dimers" in which the aromatic parts of the molecules are in contact; this produces a "bilayer" structure with $d/L > 1$ (layer thickness 41.5 Å). At the same time, a non-matching density wave with a period of 34.5 Å is produced. This is interpreted as due to the coexistence of dimers and monomers. The packing of the paired molecules ("dimers" with a bulky central region) in the smectic layers leads to the production of cavities between the alkyl chains. These cavities are occupied by monomers (the ratio of the numbers of dimers and monomers is 1 : 1).

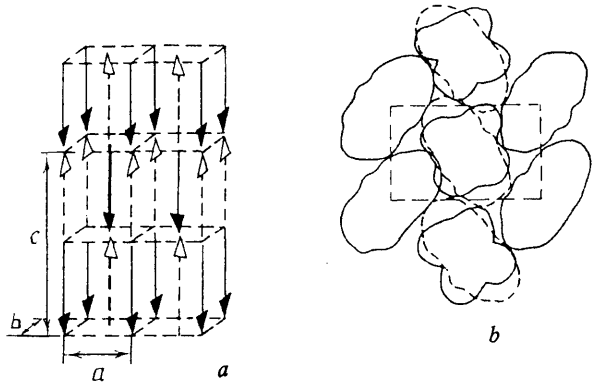


Figure 29. Structure of the phase *SmE* of compound XVIII: *a*, arrangement of the molecules in the volume; the arrows indicate the positions of the CN groups; *b*, section perpendicular to the long axes of the molecules.[90]

A number of detailed studies of the structure and transformations of smectics of type *B* have been carried out in recent years.

Thus Pershan and co-workers[91] studied the phase *SmB* of compound XII ($n = 4$, $m = 8$), which undergoes the following mesomorphic transformations:

$$C \overset{33\,^\circ C}{\longleftrightarrow} SmB \overset{49.6\,^\circ C}{\longleftrightarrow} SmA \overset{63.6\,^\circ C}{\longleftrightarrow} N \overset{78.8\,^\circ C}{\longleftrightarrow} I.$$

Specimens oriented by a magnetic field were studied on a three-circle diffractometer. It was established that the phase *SmB* has three-dimensional long-range positional order. At the same time, an appreciable contribution is made by diffuse scattering. Fig. 30 gives a diagram showing the arrangement of the molecules in the layer and the way in which the layers are superimposed; the packing of the layers is of the type ...*ABAB*... The correlation length is close to 1.4 μm (1.4×10^4 Å) in the plane of the layers, and about 0.14 μm in the perpendicular direction. In the phase *SmA* the correlation length in the plane of the layer is ~20 Å. Thus the conversion of *SmB* into *SmA* is accompanied by very considerable disordering.

The phase *SmB* of this compound was also studied with a higher resolution (synchrotron radiation).[92] The specimens consisted of suspended films, so that it was possible to study the orientational structure of the layers. Sufficiently thick films (number of layers $N = 100$) showed the existence of three-dimensional long-range order. With decrease in the thickness of the film, the inter-layer correlation decreased. In thin films ($N = 4$), which are actually two-dimensional crystals, a correlation length of more than 800 Å was observed, indicating long-range positional order within the layers.

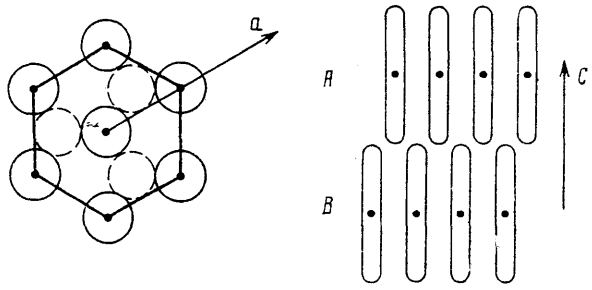


Figure 30. Schematic representation of the superposition of the layers in the smectic phase *B*.

Strong diffuse scattering, not characteristic of ordinary crystals, was also observed for this phase.[82] This scattering was attributed to the existence of a soft displacement mode of the molecular vibrations, due to the weakness of the interaction of the layers. The weakness of this interaction is confirmed by the fact that compound XII ($n = 4$, $m = 8$) in the range 27–5 °C undergoes three structural phase transformations involving a change in the way in which the layers are superimposed. This last feature indicates that the potential energy of the interaction of the layers depends little on their relative displacement.

Similar studies of the phase *SmB* of the compounds XII ($n = m = 4$) and XXXVI established in these cases also the existence of long-range positional order in all three dimensions.[93]

A new and effective method for obtaining oriented single-domain specimens on a hydrophobised support[94] has been used[95,96] to study the mesophases of compound XVIII ($n = 7$), which are formed in the following sequence:

$$X - SmE - SmB - N_{reverse} - SmA - N.$$

The phase originally denoted *X* was found to be a reverse smectic of type *SmB*. This is the first case of the detection of a phase *SmB* below the temperature of the existence of the phase *SmE*.

The structure of the smectic phase of the type *SmG*, and the change in the structure of the LC in the *SmB* → *SmG* transformation, were studied[97–99] for compound XII ($n = 5$, $m = 7$), for which the following phase transformations are observed (°C):

$$C \overset{15\,^\circ C}{\longleftrightarrow} SmG \overset{36\,^\circ C}{\longleftrightarrow} SmB \overset{51\,^\circ C}{\longleftrightarrow} SmC \overset{54\,^\circ C}{\longleftrightarrow} SmA \overset{64\,^\circ C}{\longleftrightarrow} N \overset{78\,^\circ C}{\longleftrightarrow} I.$$

The smectic *SmG* has a monoclinic base-centred (*C*) cell with parameters: $a = 9.54$, $b = 5.02$, $c = 27.9$ Å, $\beta = 114.8°$. The period *c* is approximately equal to the length of the molecule; from this it

follows that the long axes of the molecules form an angle of ~25° with the normal to the plane of the layer. The hexagonal phase *SmB* has a cell with parameters: a = 5.07 Å, c = 28.4 Å.

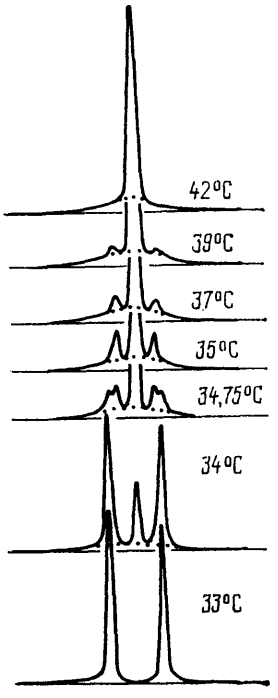


Figure 31. Temperature dependence of the profile of the meridional reflections (l = 1) in the region of the transformation *SmB* → *SmG* for compound XII (n = 5, m = 7).[97]

On the X-ray diffraction pattern of the phase *SmB*, the meridional reflections are extensively broadened and contain a pair of satellite spots, which become stronger and more isolated with decrease in temperature (Fig. 31). The transformation *SmB* → *SmG* leads to doubling of the meridional reflections (only the satellite spots remain). This transformation is preceded by the production of sinusoidal modulation (parallel to the layers) with a wavelength of ~78 ± 3 Å, which is approximately 17 times the period a of the hexagonal lattice. This last result follows from an analysis[98] of the evolution of the satellite spots with change in temperature. The authors cited consider that these spots are produced by the modulated displacement of the molecules at right angles to the layers with an amplitude H, and that the intensity of the satellites is proportional to H^2. The broadening of the meridional reflections is due to the bending of the layers, and the discrete satellite reflections are generated by the wave character of these bends. The amplitude of the modulation increases regularly with decrease in temperature, and reaches a maximum value (4 Å) at 35.5. °C, when the phase *SmG* is produced. There is an abrupt change in the orientation of the long axes of the molecules, which make an angle of 25° with the normal.

The corrugated character of the layers in the phase *SmB* of compound XII (n = 5, m = 7) is confirmed by a study[100] using optical modelling. In the opinion of the authors cited, the diffraction pattern shows best agreement with a model containing, between the layers, cavities separated from one another by an average of 80 Å (Fig. 32). It is suggested that this model is dynamic—the cavities migrate along the layers. The fluidity of this phase was attributed to this migration.

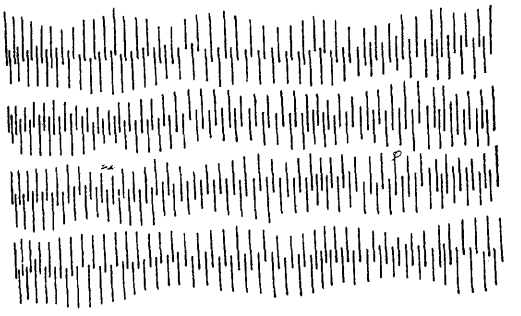


Figure 32. Schematic representation of the arrangement of the molecules in the phase *SmB* of compound XII (n = 5, m = 7), from optical modelling data.[100]

The dynamics of the mesophase of this compound were studied by neutron diffraction. Incoherent quasi-elastic neutron scattering showed[101] that the constant characterising the reorientation of the molecules round their long axes is 1.8 × 10^{11} rad^2 s^{-1} for the phase *SmB* and 1.7 × 10^{11} rad^2 s^{-1} for the phase *SmG*. In the second of these phases, two azimuthal orientations of the molecules, differing by rotation through 180°, predominate. Movement in the direction of the long axes of the molecules is observed in both phases, with a mean-square displacement of 1.4 Å in *SmB* and 1.1 Å in *SmG*. The relaxation time of this movement is comparable with the rotation time of the molecule round its long axis (~5 × 10^{11} s).

The coherent inelastic scattering of neutrons on a completely deuteriated specimen oriented in a magnetic field showed[102] that the relaxation time associated with the modulation of the phase *SmB* is close to 10^{-7} s. Since the longitudinal displacements of the molecules (1.4 Å) takes place in ~5 × 10^{-11} s, the authors cited[102] conclude that the modulation of the phase *SmB* is static (for dynamic modulation the relaxation time should be close to 5 × 10^{-11} s). Thus increase in the amplitude of the modulation with decrease in temperature ensures a minimum value of the free energy; simultaneously, in the opinion of the authors cited, synchronisation of the wave distortion of the layers takes place (more accurately, the displacement with respect to phase for adjacent layers tends to zero), leading to the phase transformation *SmB* → *SmG*.

The description of smectics ordered in three dimensions can be concluded by considering the phases *SmJ*(*SmG'*) and *SmK*(*SmH'*), detected for compound XXXIX (n = 7):[103]

$$C \xrightarrow{127\ ^\circ C} C_1 \xrightarrow{130\ ^\circ C} C_2 \xrightarrow{146\ ^\circ C} SmH' \xrightarrow{154\ ^\circ C} SmG' \xrightarrow{157\ ^\circ C} SmI \xrightarrow{164\ ^\circ C} \rightarrow SmC \xrightarrow{197\ ^\circ C} N \xrightarrow{241\ ^\circ C} I.$$

These phases, however, were also encountered earlier for compounds XVII (the phase *SmG'*) [104] and XXIV (the phases *SmG'* and *SmH'*).[105] The phase *SmX* has been reported[106] for compound XXVIII, whose structural characteristics can be obtained from Table 1. The existence of these phases was not confirmed in subsequent papers, however.

Hexatic phases were predicted in theoretical studies,[107,108] and aroused considerable interest because of an important specific characteristic: with no inter-layer correlations and with only short-range positional order within the layers in these phases, it was suggested that there is long-range order in the orientation of the vectors connecting the centres of gravity of the molecules (bond-orientational order). According to the theoretical hypotheses,[109–111] these phases should be produced by the step-wise fusion of solids. Hexatic character was apparently first established for the smectics *F*. Here, however, the phases of type *B* will be considered first, since they represent the most characteristic hexatic structure, which has also been the subject of a theoretical analysis.

As already noted, different degrees of correlation of the layers in the phases *SmB* have been detected in a number of studies (in particular, temperature-dependent inter-layer correlations have been studied[101]). In addition to the phases *SmB* with crystalline order described above, phases in which there is no inter-layer correlation have been detected.[112] The X-ray diffraction patterns of these phases showed extended rods of scattering with a length of $\sim \pm C^*$, parallel to c^* and centred at sites of the reciprocal lattice *hkl* of low order. Compound XXIII, which exists in the form of a phase *SmB* in the temperature range 107–119 °C, has been studied.[103] The complete absence of reflections *hkl* indicated disordered superposition of the layers. An analysis of the profile of the reflections gave the value of the correlation length within the layer; this was found to be $\gtrsim 350$ Å, which apparently indicates the existence of only short-range order in the layers.

An X-ray diffraction study of freely suspended films of compound III in the phase *SmB*[93] with a thickness of 4 molecular layers established definitely that this phase is hexatic. In this case, analysis of the profile of the peak gave the correlation length $\xi = 150$ Å. At the same time, the very broad form of the maximum for the inter-layer correlations indicates that the latter extend to only one layer.

Smectic phases of the type *F* were first detected in experiments on miscibility in the 1970's; they were later studied by X-ray diffraction[101,103,105,113,114,115,116] in the compounds XXXVIII ($n = 5$) (TBPA) and XXXVIII ($n = 10$) (TBDA), for which the following sequence of phase transformations is observed:

$$C \xrightarrow{68\,^\circ C} SmG \xrightarrow{140\,^\circ C} SmF \xrightarrow{149\,^\circ C} SmC \xrightarrow{179\,^\circ C} SmA \xrightarrow{212\,^\circ C} N \xrightarrow{233\,^\circ C} I$$
$$\nwarrow SmH \swarrow 61\,^\circ C$$

$$C \xrightarrow{73\,^\circ C} SmG \xrightarrow{120\,^\circ C} SmF \xrightarrow{150\,^\circ C} SmI \xrightarrow{158\,^\circ C} SmC \xrightarrow{160.8\,^\circ C} SmA \xrightarrow{192.4\,^\circ C} I.$$

Single-domain specimens obtained by slowly melting single crystals or by cooling the isotropic liquid (with a transition through the phase *SmA*), and a polycrystalline (polydomain) specimen, placed in a capillary subjected to a strong magnetic field, and then cooled in the absence of the field to the temperature corresponding to the formation of the phase *SmF*, were studied.[116]

X-Ray diffraction patterns of two types were examined. In the first case the primary beam was directed parallel to the smectic layers. In this case, sharp 00*l* ($l = 1, 2$) reflections were observed, indicating a layer structure (similar to the phase *SmG*). The *hk*0 reflections (in contrast to those observed for the phase *SmG*) were elongated along the c^* axis, that is along the normal to the layers, and *hkl* reflections with $l \neq 0$ were not observed at all. These features indicate the absence of three-dimensional order. The elongated *hk*0 reflections, which had the form of rods, correspond to the two-dimensional lattice of the layer.

The X-ray diffraction patterns of the second type were obtained with the beam directed parallel to the long molecular axes. Here, six diffuse *hk*0 reflections were observed, indicating (as in the case of the phase *SmG*) a pseudo-hexagonal arrangement of the axes *L* (no signs of herring-bone packing of the molecules were detected).

The X-ray diffraction patterns of polydomain specimens gave the following values of the parameters of the monoclinic *C*-centred cell (Fig. 33): for TBPA at 132 °C, $a = 9.62$, $b = 5.14$, $c \simeq 31.2$ Å, $\beta = 114°$; for TBDA at ~120 °C, $a = 9.64$, $b = 5.22$, $\beta \simeq 112°$ (the angle $180° - \beta$ characterises the slope of the axes *L* to the plane of the layer).

Thus the structure of the phase *SmF* is extremely similar to that of the phase *SmG*. The main differences are that in the phase *SmF* there is almost no inter-layer correlation and, apparently, no elements of the herring-bone pattern in the layers (isotropic rotation or *pseudorotation* of the molecules about the axes *L*).¶

The general features of the X-ray diffraction patterns obtained for the phase *SmI* of compound XXXVIII ($n = 10$) are similar to those for the phase *SmF*; here, however, instead of the rods with indices 200, an extended reflection with indices 020 appears (Fig. 33). This last feature is due to a change in the direction of the axis *L* relative to the lattice of the layer. At 152 °C, the lattice parameters of the phase *SmI* have the values: $a \simeq 5.57$, $b \simeq 9.0$, $c \simeq 42$ Å, $\beta \simeq 116°$. As in the case of *SmF*, the angle $180° - \beta$ is equal to the angle of slope of the axis *L* to the plane of the layer, but in this case the axis *L* forms this angle not with the long period but with the short period of the orthogonal lattice of the layer (Fig. 33). Here, as in *SmF*, the molecules are most probably in a state of rotation or pseudo-rotation about their long axes.

The mechanism of the *SmF* → *SmI* transformation assuming the existence of a phase boundary along which molecules with coordination 5 and 7 alternate in the layer (Fig. 34)[116] is of considerable interest. The displacement of this boundary leaves the positions of the axes *L* unchanged, but rotates the lattice of the layer through 30°. In the opinion of the authors cited,[116] however, an alternative interpretation of the transformation as a collective change in the direction of the axes *L* is possible.

An important part of the works cited[103,116,117] was the analysis of the profile of the diffraction maxima. It was established that the profile of the diffuse "rods" in the direction perpendicular to c^* is described by a Lorenzian curve with correlation length $\xi > 50$ Å for *SmF* and $\xi > 180$ Å for *SmI*. Thus the degree of ordering of the molecules is greater in the layers *SmI* than in the layers *SmF*, although the phase *SmI* is produced at a higher temperature. This is confirmed by the X-ray diffraction patterns of the "polycrystalline" specimens, where the half-width of the diffuse *hk*0 rings for *SmI* is one quarter of that for *SmF*.

Finally, mention may be made of one of the latest practical applications of highly-ordered smectics, closely related to their structure, namely the use of LC as orienting solvents in organic synthesis.[118–120] An example is provided by the isomerisation of benzenesulphonates.

¶ Interestingly, the transformation *SmG* → *SmF* is of first order for TBPA and of second order for TBDA.

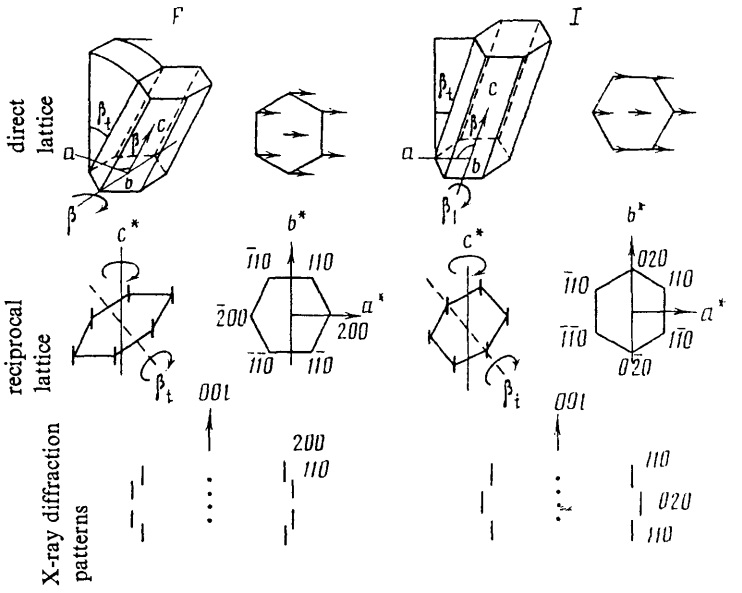
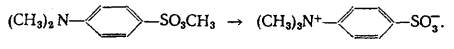
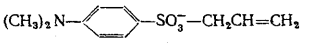


Figure 33. Real and reciprocal lattices and X-ray diffraction patterns of the phases *SmF* and *SmI*, obtained by recording along the layers (specimens oriented in a magnetic field);[103] the arrows indicate the direction of slope of the axes *L*.

Thus the isomerisation of methyl *p*-(dimethylamino)benzenesulphonate, involving the intermolecular migration of a methyl group:



has been studied in detail.[118,121,122] At room temperature, this reaction takes place in the crystal, where the arrangement of the molecules is convenient for this (antiparallel), but does not take place in solution (this question has been examined in detail[123]). The isomerisation of the related compound



does not take place either in solution or in the crystal. Both of these benzenesulphonates isomerise, however, when dissolved in the smectic phase of compound IX,[118] for which the following phase transformations have been detected:

$$C \xleftrightarrow{34.4\,^{\circ}C} SmB \xleftrightarrow{146.4\,^{\circ}C} N \xleftrightarrow{164.7\,^{\circ}C} I$$

An interesting feature is that the isomerisation takes place only in the temperature range of existence of the phase *SmB*. X-Ray diffraction data[121,122] indicate that this phase is highly ordered. The distances between the molecules in the layer (5.50 ± 0.03 Å) differ little from the distances *D* in the nematic phase (5.52 ± 0.06 Å). The thickness of the layer (21.4 ± 0.2 Å) is close to the length of the molecule (23.5 ± 0.5 Å), indicating a perpendicular arrangement of the molecules. Rigid aromatic sub-layers situated between less rigid aliphatic layers are distinguished. Benzenesulphonate molecules have almost no influence on the geometic characteristics of the phase *SmB*. It is suggested that clusters (dimers or larger agglomerates) of the benzenesulphonate molecules are inserted in "head to tail" fashion into the aromatic sub-layer of the phase SmB. This creates conditions for the migration of the methyl groups from one molecule to another for both benzenesulphonates studied. The influence of the molecular packing on the isomerisation is proved by the sharp decrease in its rate on going to the nematic phase of the solvent.

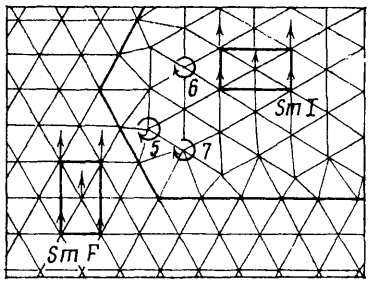


Figure 34. Structure of the boundary separating the phases *SmF* and *SmI*, consisting of 5-, 6-, and 7-coordinate molecules;[116] the arrows indicate the slope of the axes *L*.

VI. Cubic phases

A unique place among calamitic mesophases is occupied by the LC called smectics *D*, although it will be seen that this name does not give a correct picture of their structure. The first homologous series of compounds for which mesophases of this type were found as synthesised in 1957 [124] (compounds V, VI, and XXXIII in Table 3). The homologues of compound V with $n = 16$ and 18

undergo the following phase transformations, detected by differential scanning calorimetry:[125]

$$n=16: C \xleftrightarrow{126.8\,^\circ C} SmC \xleftrightarrow{171.0\,^\circ C} SmD \xleftrightarrow{197.2\,^\circ C} SmA \xleftrightarrow{201.9\,^\circ C} I,$$

$$n=18: C \xleftrightarrow{124.6\,^\circ C} SmC \xleftrightarrow{158.9\,^\circ C} SmD \xleftrightarrow{195.0\,^\circ C} I.$$

X-Ray diffraction showed[126] that the phases *D* do not have the layer arrangement of the molecules characteristic of smectics. Here, the X-ray diffraction patterns of polycrystalline specimens revealed a cubic lattice (space group $Ia3d$) with parameter a = 102 Å and $Z \simeq 1150$ molecules per cell.

A sufficiently well-founded model of the arrangement of the molecules in this mesophase has not yet been constructed. It is considered that in this case, as a result of hydrogen bond formation (or other sufficiently strong intermolecular interactions), the molecules are joined in stable associates as spherical or rod-shaped micellar formations similar to the supermolecular formations in lyotropic LC. (These micelles form a cubic lattice.) The important role of specific intermolecular interactions in the formation of the phase *D* is indicated by the fact that the replacement of the nitro-group in compound V by Cl, Br, or CH_3 leads to the disappearance of this phase.

A cubic phase is also formed by the acid VI (n = 16, 18), which is similar to compound V, but in which the NO_2 group has been replaced by CN. A recent study[127] of the homologue of this compound with n = 18 detected a primitive cubic lattice with symmetry $P23$ or $Pm3$ and parameter a = 86 Å.

The study of the phases *D* is made difficult by the fact that they are formed by only a limited number of compounds. Examples are the hydrazine derivatives XXXIII, which undergo the following sequence of phase transformations:

$$C \rightarrow SmD \rightarrow SmC \rightarrow I.$$

The homologues of compound XXXIII with n = 8, 9, and 10 have cubic lattices with parameters a = 45.7, 48.8, and 51.7 Å respectively.[128] In this case it is considered that intermolecular H-bonds between the NH and CO groups are responsible for the formation of the cubic phase. The polymorphic forms of the compound with similar structure containing the $-CH=N-$ group instead of the $-CO-NH-$ group (which excludes the formation of H-bonds) do not form a cubic phase (the phase *SmC* of this compound with n = 10 has the usual structure for LC of this type).

Another type of mesophase with a cubic lattice is the so-called cholesteric "blue" phase, which exists in a narrow temperature range (less than 1 K) between the ordinary cholesteric phases, which have a one-dimensional spiral structure, the blue phase shows three-dimensional spatial periodicity. This phase has been studied mainly by the optical methods, the use of which in this case is analogous to X-ray diffraction studies, since here the parameter of the cubic lattice is commensurate with the wavelength of visible light.

The present state of structural studies of the blue phases has been reviewed.[129,130]† Several possible models are discussed, including: 1) a three-dimensional lattice of disclinations, and 2) an emulsion model, which assumed that the isotropic liquid is disseminated in the cholesteric structure. None of these models has yet been reliably established, however.

† Since the present manuscipt was prepared, another review has been published: H Stegemeyer, T Blümel, K Hiltrop, et al. *Liq. Cryst.*, 1986, **1** 1

VII. Phases with columnar H-associates

The previous sections dealt with mesophases formed by rod-shaped molecules. The liquid-crystalline state is also often observed for compounds whose molecules have a quite different shape. These include primarily the disc-like mesophases, which have been intensively studied in recent years and are the subject of a number of reviews.[131–133] They are formed by molecules containing a rigid disc-shaped nucleus (benzene, triphenylene, truxene, etc.) with alkoxy or alkanoyl substituents attached. The most characteristic forms of discotic is the columnar mesophase, in which the molecules are arranged in periodic or aperiodic stacks. It has recently been found, however, that thermotropic columnar LC may be formed by molecules with shapes completely different from discs. In this case the construction of the columns involves the formation of a system of hydrogen bonds. Examples of these compounds are described below.

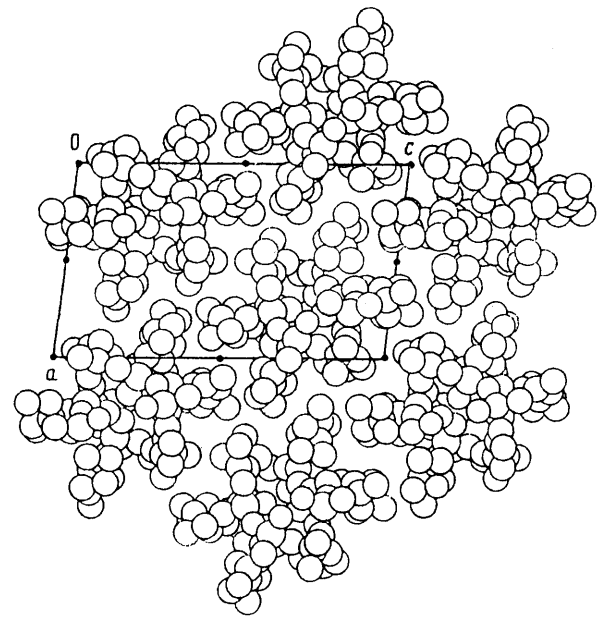
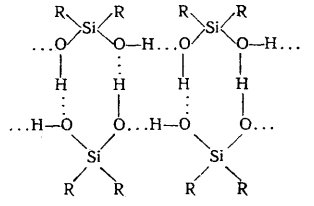


Figure 35. Projection of the crystal structure of $[(n\text{-}Pr)_2Si(OH)]_2O$ on the (010) plane, perpendicular to the axes of the columns.[140]

As early as the 1950s it was noted that a mesophase is formed by the silanol $R_2Si(OH)_2$ with R = iso-Bu, whereas other members of the series (R = Me, Et, Ph, iso-Pr, t-Bu) did not show mesomorphism.[134,135] At the time, this mesophase was characterised as smectic, but it was later established[136] that the optical texture of the mesophase of $(iso\text{-}Bu)_2Si(OH)_2$ is similar to that of discotics (in addition, unlimited miscibility of this substance with the classical discotic benzenehexa-n-heptanoate was observed). In the opinion of the authors cited,[136] the similarity in the heats of the phase transformations $C \rightarrow$ LC and LC $\rightarrow I$ (7.6 kJ mol^{-1} and 7.2 kJ mol^{-1} respectively) indicates that each of these transformations involves the rupture of a certain fraction of the H-bonds present in the crystal.

An X-ray diffraction study of single crystals of this compound could not be carried out. An X-ray diffraction study of close homologues of this compound (R = iso-Pr, t-Bu) showed,[137,138] however, that the crystals are made up of infinite H-associates containing cyclic dimers:

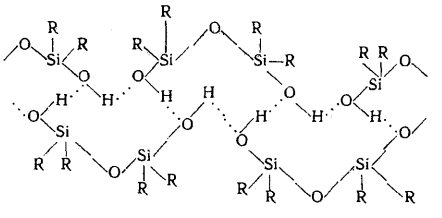


The silanediol with R = iso-Bu should apparently have a similar structure. The authors cited[136] liken this associate to a discotic column, where the role of the discs is played by "platforms" approximately perpendicular to the ribbon and each containing two SiR_2 groups.

Similar phase transformations were also observed for various dihydroxysiloxanes. The most extensively studied $[(n\text{-}Pr)_2Si(OH)]_2O$ undergoes the following transformations:[139]

$$C \xrightarrow[29.3\ kJ\ mol^{-1}]{43\ ^\circ C} LC \xrightarrow[20\ kJ\ mol^{-1}]{69\ ^\circ C} I.$$

An X-ray diffraction study[140] of a single crystal of this siloxane grown in a capillary directly from the mesophase showed that in the crystal the molecules are joined in columns (Fig. 35). The outer layer of the columns is formed by the aliphatic substituents, and the core of the column consists of a cooperative system of H-bonds:



The packing of the columns is pseudohexagonal (the crystal belongs to the triclinic system); the averaged parameter of the pseudo-hexagonal two-dimensional lattice is a = 12.66 Å. A planar hexagonal lattice with a = 12.58 Å was also detected in the mesophase of this compound. This suggests that cylindrical columnar H-associates similar to those found in the crystal are preserved in the mesophase. This is confirmed by the similarity in the spectral characteristics of the crystal and the mesophase.

The number of examples of this kind should apparently increase considerably in the near future. It will then be possible to speak of a separate class of liquid-crystalline phases, differing considerably from both calamitic and discotic mesophases.

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