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MOLECULAR ASPECT : STRUCTURES AND DYNAMICS.

STRUCTURE OF LIQUID CRYSTALS, ESPECIALLY ORDER IN TWO DIMENSIONS

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Résumé. — Une revue des phases liquide-cristalline et de leurs structures est présentée en insistant sur les propriétés de symétrie. En particulier les phases smectiques ordonnées sont classées suivant les 17 groupes spatiaux à deux dimensions.

Abstract. — Liquid-crystalline phases and their structures, as known today, are briefly reviewed. Emphasis is on symmetry properties. Smectic ordered phases are assigned to some of the 17 two-dimensional space groups.

1. **Introduction.** — In 1922 G. Friedel [1] gave the first classification of liquid crystals in terms of structure : he distinguished nematic, cholesteric, and smectic mesophases. Later it became increasingly clear that there is a variety of smectic phases. Sackmann and Demus began to classify those by capital letters. Ten years ago the three phases A, B, and C could be reliably identified by the method of continuous miscibility. A fourth, D, had just been found [2], but as it is optically isotropic it is probably not a liquid crystal in the proper sense. Since then several new smectic phases have been discovered and investigated. Reading the abundant literature one may feel that about ten years ago a new hunt or, depending on one's mood, Pandora's box was opened.

We will not try here to give a comprehensive review of recently discovered smectic phases, but only cite examples. After a brief summary of liquid crystalline states and their structures, as known and accepted today, a fairly abstract approach is taken. We apply to liquid crystals the theory of two-dimensional crystal lattices of which there are 17 symmetry types or space groups, listed in the International Tables for X-Ray Crystallography [3].

The two-dimensional order in the layers is doubtless the most important characteristic of smectic mesophases. Two dimensional analysis may also prove useful to classify liquid crystals, recently discovered by Chandrasekhar and coworkers [4], in which the molecules are arranged in parallel columns instead of layers. Looking for a suitable designation, we might call the latter *columnar* liquid crystals.

A classification in terms of two-dimensional space groups seems reasonable, to a first approximation, even if certain smectic phases are three-dimensional crystals, as has been repeatedly claimed for smectics

with crystalline order in the layers. However, we prefer the view that they are liquid rather than plastic crystals and will present some supportive arguments. It appears desirable in the long run that the name *smectic* be reserved for true liquid crystals, i.e. mesophases permitting at least one component of simple shear flow $\partial v_i / \partial x_j$, $i \neq j$.

This paper is devoted to thermotropic or non-amphiphilic liquid crystals. The general ideas should be transferable to lyotropic or amphiphilic liquid crystals formed by a solute and a solvent, e.g. an amphiphile in water. However, these systems are quite complex. Our aim is to assign the known non-amphiphilic smectic phases as best as possible to the various two-dimensional space groups.

2. Summary of established liquid-crystalline phases.

— Nematic liquid crystals are three-dimensional fluids made up of elongated molecules with a preferred (apolar) axis of orientation. Their order is essentially quadrupolar and may be described by the order parameter

$$\langle P_2(\theta) \rangle = \frac{3}{2} \langle \cos^2 \theta - \frac{1}{3} \rangle$$

where θ is the angle made by the long molecular axis (often not too well defined) with the unique or preferred axis and P_2 the second Legendre polynomial. They are uniaxial bodies of the highest possible symmetry : ∞ -fold rotational symmetry and reflection planes perpendicular and parallel to the axis at any point in space. The molecules forming liquid crystals are in general not only elongated but also lath-like. Theoretically there is a possibility of biaxial nematics [5] whose order has to be described by a full second-rank traceless symmetric tensor.

In the last decade cholesteric liquid crystals (N^*) have come to be considered a special case of the nematic phase (N). They differ from nematics only by a spontaneous twist of the unique axis along an orthogonal helical axis, the pitch being always very large as compared with molecular dimensions. The cholesteric character is brought about by chiral molecules. The phase is fluid perpendicular to the helical axis, it has a period of translation parallel to this axis. There are two-fold axes of rotation parallel to the local unique axis, to the helical axis, and perpendicular to the two at any point in space, but because of chirality no reflection planes. Being layered structures like smectics, cholesterics share some symmetries with the latter.

In smectic liquid crystals the elongated molecules are arranged in molecular layers, the preferred axis being parallel to the layer normal or tilted. S_A , the smectic phase of highest symmetry is made up of disordered and, thus, fluid layers. It is uniaxial and permits reflection planes parallel to the unique axis at any point. In contrast to nematics, reflection planes perpendicular to the unique axis may be placed only in the middle of a layer or between two layers which give rise to a period of translation. Disordered smectics and cholesterics are sometimes called one-dimensional crystals and our symmetry considerations are based on that concept. This seems correct from a topological point of view, but one has to bear in mind that the vertical fluctuations of these layers diverge logarithmically with the size of the sample [6].

Also well-known are disordered smectics in which the elongated molecules are collectively tilted away from the layer normal. These S_C phases are called biaxial and, in fact, many of their anisotropies (e.g. magnetic, dielectric) are those of a hypothetical biaxial nematic. However, their name derives from

the fact that there is an axis of preferred molecular alignment besides the axis of the layer normal. All planes subtended by the two defining axes are reflection planes. The only symmetry axes of two-fold rotation are perpendicular to the two defining axes in the middle of the layers or between them.

Smectic C phases are spontaneously twisted (C^*) if they contain chiral molecules. The lack of reflection symmetry makes them ferroelectric [7], at least in principle and with dipolar molecules, the local polarization being perpendicular to the two defining axes. Apart from the translational freedom associated with the fluidity within the layers, the only symmetry operations left are the two-fold rotations of S_C .

In the case of ordered smectic liquid crystals it becomes even more dangerous to use three-dimensional symmetry considerations, if the two-dimensional crystals formed by the layers can, in fact, slide upon each other. For the positional fluctuations within the plane of a two-dimensional lattice are well-known to diverge logarithmically with the diameter of the area. Whether the vertical fluctuations diverge does not seem so clear with crystalline layers. In any event, from a topological point of view, it appears permissible in discussing symmetry to disregard the logarithmic divergences of positional fluctuations and to regard the layers as flat and well-behaved two-dimensional crystals.

It is generally assumed that in ordered smectics, as in disordered smectics and nematics, the long axes of the molecules point as often up as down, so that there is no polarity parallel to the layer normal. In other words, the molecules are taken to be free to flip end over. (This allows for bilayers made up of polar monolayers and does not rule out ferroelectricity in tilted smectics.) The assumption is indispensable in reducing flat monolayers to truly

TABLE I

Self-explanatory scheme of established non-amphiphilic liquid-crystalline phases and their structures. The symbols O and Z are introduced here for convenience. The dashed lines indicate the absence of a phase boundary

	Solid crystals	Plastic crystals	Smectic liquid crystals			Nematic liq. crystal	Isotropic fluid
			ordered		disordered		
			herringbone	hexagonal pseudo			
Upright (orthogonal)	K		E	B	A		
Tilted	K		G	H	C	N	I
Chiral (twisted)					C*	N* (= cholesteric)	

rising temperature \rightarrow

Additional phases and their neighbors in temperature :

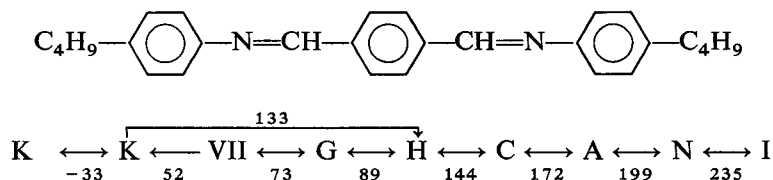
undefined tilted smectic F	H-F-C	} probably not liquid-crystalline but solid mesophases.
columnar (discotic) phase Z	K-Z-I	
optically isotropic phase D	C-D-N	
blue phase O	N*-O-I	

two-dimensional structures that can be analyzed in terms of two-dimensional space groups. Physically, the restriction is quite reasonable as layers polar in this sense could display spontaneous curvature destroying the smectic order.

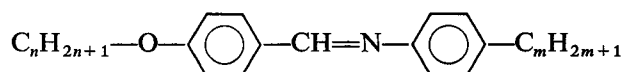
The structures of the four established ordered smectic phases [8, 9, 10, 11] B, H, E, and G are given

in the self-explanatory scheme of table I. The assignment of these letters to certain structures has not been universal and unambiguous until very recently (and, perhaps, will not long remain so). A few compounds used in current work are given here together with their structural formulas and phase sequences. (Reference is made to recent work, not to discovery.)

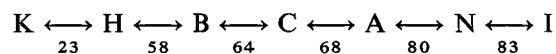
TBBA = terephthal-bis-[4-n-butyl-aniline] [12, 13]



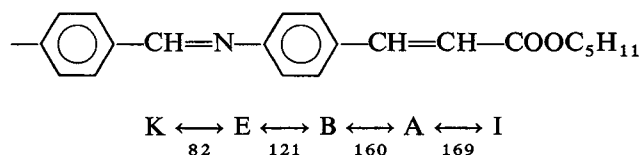
$n0.m$ = N-(alkoxy-benzylidene)-p-n-alkylaniline [10, 14]



e.g. 70.5

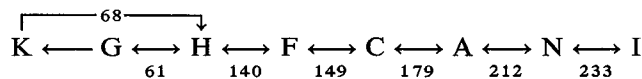


PBAPC = p-phenyl-benzylidene-p-amino-n-pentyl-cinnamate [15, 16]

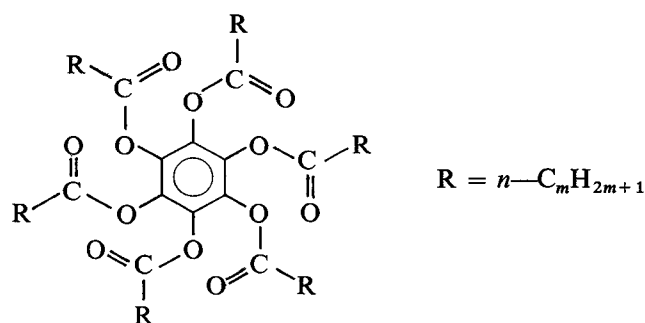


The numbers are the approximate transition temperatures in °C. Phase VII of TBBA is probably a further smectic phase (see below).

The smectic F phase is tilted, but it is an open question whether it is disordered or ordered. All available information thereon is contained in three papers [16, 17, 18]. As an example we mention TBPA [18] which differs from TBBA only by a pentyl group replacing the butyl group. The sequence of phases is



The compounds on which the columnar phase was discovered by Chandrasekhar *et al.* [4] are benzene-hexa-n-alkanoates



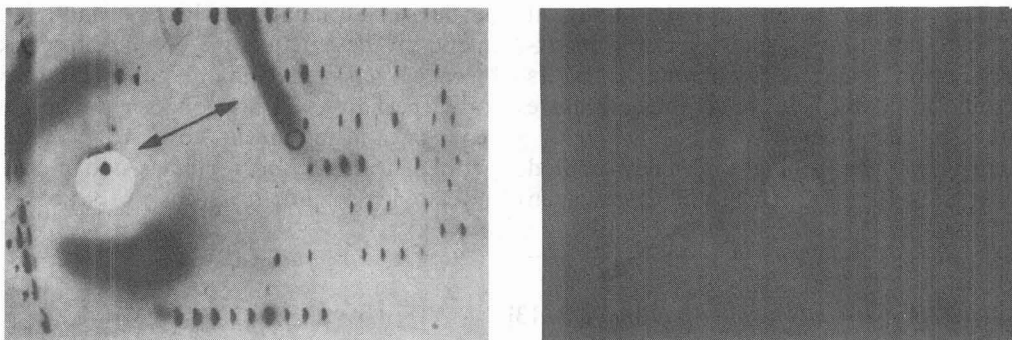
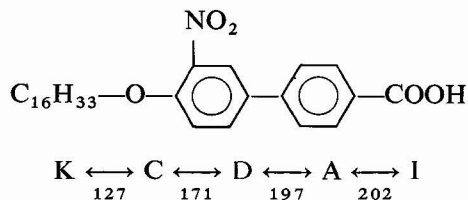


FIG. 1. — X-ray diffraction patterns of TBBA at 20 °C in the solid phase (a) and at 125 °C in the smectic H phase (b). The monodomain sample was oriented so that the molecules, indicated by arrows, were in the plane of the photographs (from ref. [25]).

The material with $m = 6$ became mesomorphic at 69 °C and isotropically fluid at 86 °C. The parallel columns of disk-like molecules are arranged hexagonally and seem to be free to flow along each other. Du Bois *et al.* [19] have found another type of flat compounds which form a columnar or, as they call it, discotic phase.

The optically isotropic phase D has as yet been seen in just two very similar compounds [20]. One of them is 4'-n-hexadecyloxy-3'-nitrodiphenyl-4-carboxylic acid



X-ray analysis [21] indicates a body-centered cubic lattice of micellar rods, space group $Ia\bar{3}d$, which also occurs in some amphiphilic structures.

A phase that has been known for a long time but only lately explained [22], at least in principle, is the blue phase, a name coined by Gray [23]. It appears, if at all, in a small temperature interval of the order of 1 °C between the cholesteric and isotropic phases. In contrast to a uniformly twisted cholesteric, the blue phase permits at the same time local uniaxiality and twist. The resulting decrease in free energy is partially compensated by the unavoidable formation of defects, possibly parallel disclinations arranged in a hexagonal array [24].

3. Are ordered smectics solid or liquid crystals ? —

In the case of TBBA it is possible to compare X-ray diffraction patterns of S_H with those of an unequivocally solid phase. Back in 1971 Levelut and Lambert [25] published the monodomain spectra shown in figure 1. The Debye-Scherrer spectra of figure 2 were presented by Doucet, Levelut and Lambert [12] in 1974. Evidently, the solid phase gives many more points and rings than do S_H and the

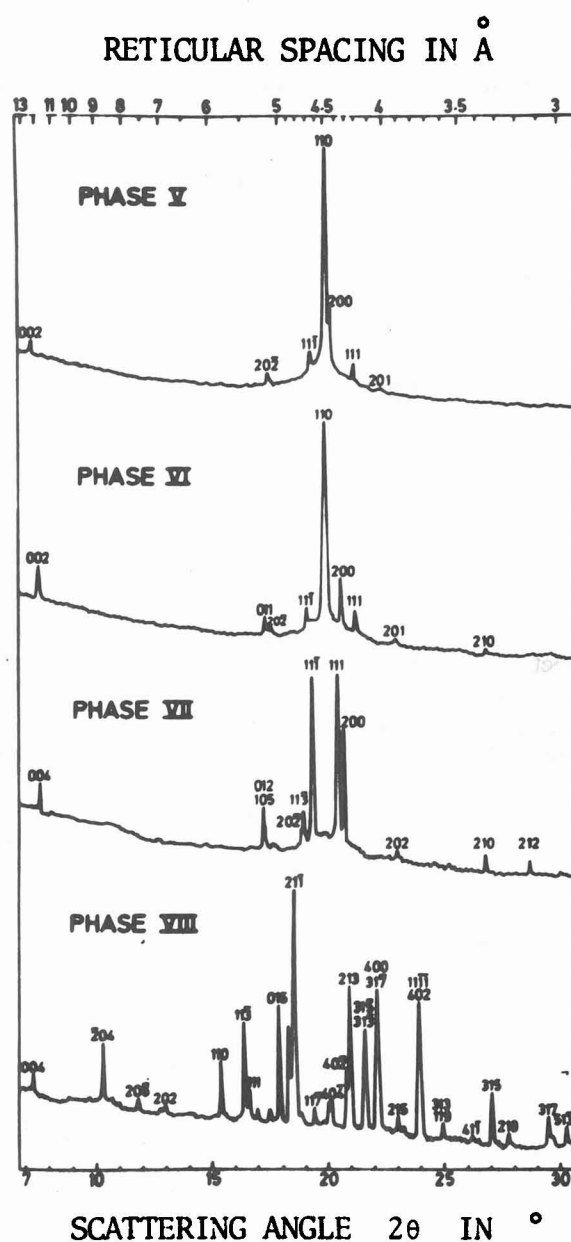


FIG. 2. — Debye-Scherrer patterns of TBBA in various phases (V = H, VI = G, VII = bilayer smectic, VIII = K) (from ref. [12]).

other liquid-crystalline phases. This by itself is a strong argument for an essential difference between ordinary solids and ordered smectics. Extensive X-ray diffraction studies were also carried out on the $n0.m$'s [11, 14]. There is general agreement that the two-dimensional lattice axes and, if it exists, the tilt have the same directions in each layer of an ordered smectic (except for ferro-electric ones, see below).

Of special interest are the diffuse parallel lines that go through the diffraction points characteristic of the smectic layer spacing, as seen in figure 1 and, exceptionally well resolved, in figure 3 [26]. They are interpreted by the authors [27] as being due to an uncorrelated motion of strings of parallel molecules through the layers, which would imply strong correlation between the two-dimensional lattices. We propose here a slightly modified interpretation: no inter-layer correlation is required, but the diffuse lines are ascribed to smectic undulations [6]. The length of the diffuse lines indicates that undulation wave

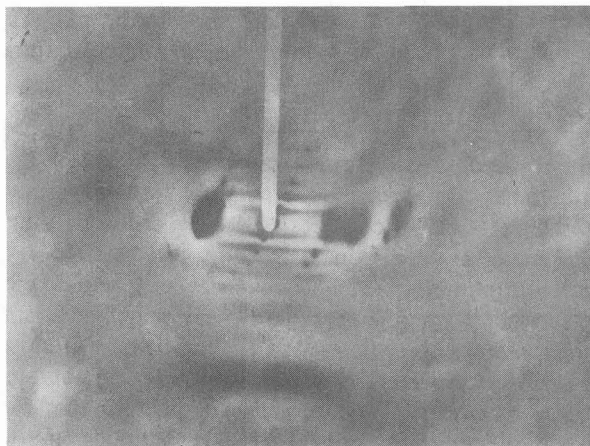


FIG. 3. — X-ray diffraction pattern of monodomain of 4-n-butyl-oxybenzal-4'-ethylaniline in phase S_H . The smectic planes were parallel to the incident beam (from ref. [26]).

vectors up to the cutoff limit are involved. The strongest undulations should be those whose wave vector is perpendicular to the long molecular axes, for any compression or dilation along this direction requires larger energies than layer curvature. Undulations with only curvature to a first approximation are sketched for upright and tilted smectics in figure 4. The elongated molecules are thought to be parallel to the lines cutting the layers. Contrary to continuum theory [6] it is assumed here that the alignment of the molecules does not follow the curvature. This hypothesis is essential only for tilted layers; it appears reasonable as only very short wavelengths have to be considered in the present context. Both interpretations, the old and the new, can explain why with tilted smectics the diffuse lines are perpendicular to the long molecular axes while the sequence of the

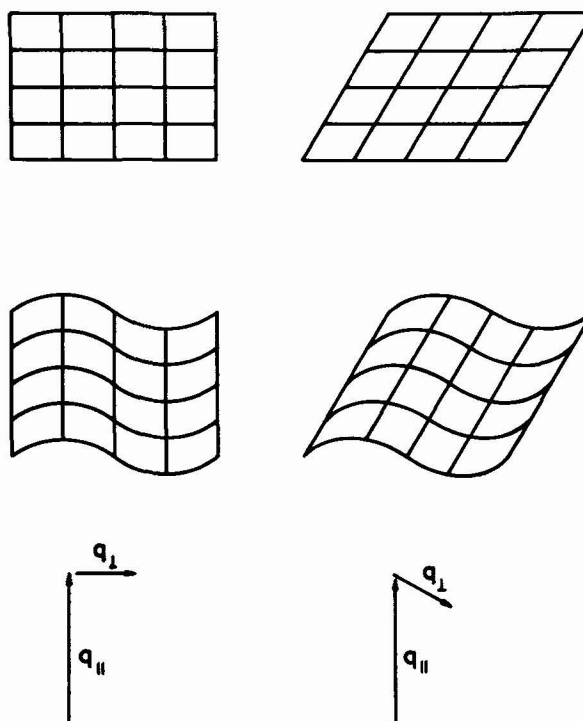
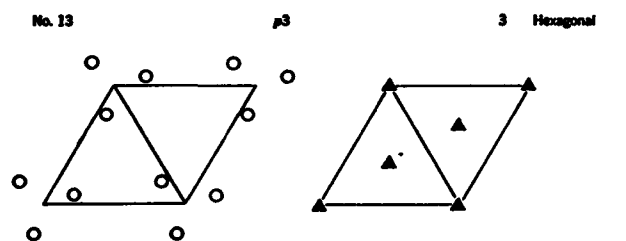
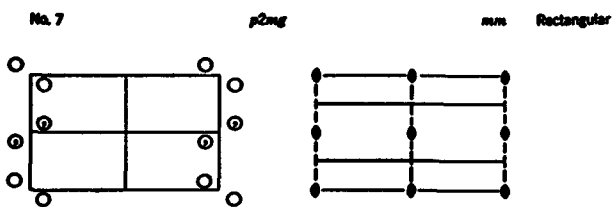
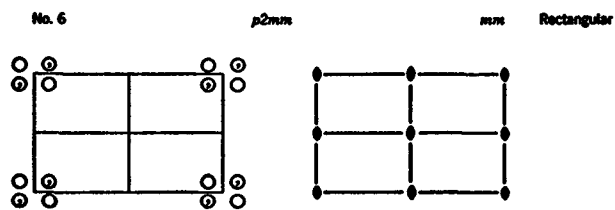
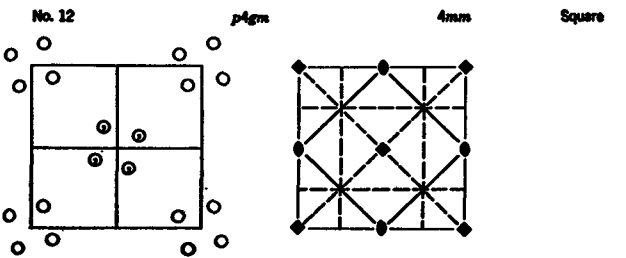
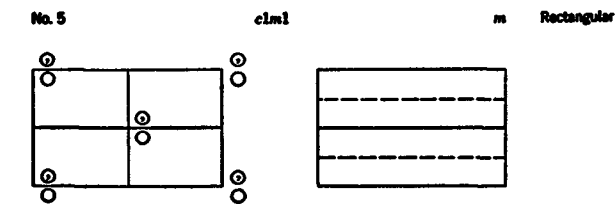
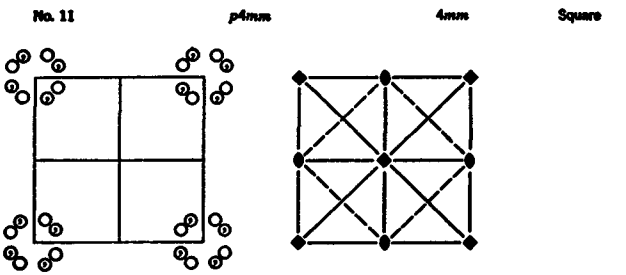
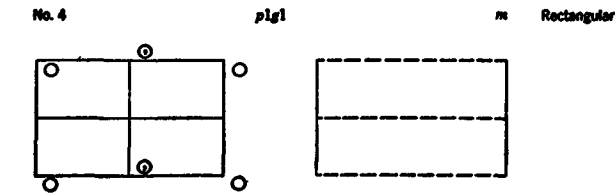
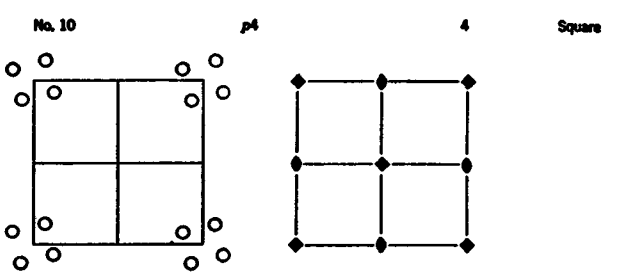
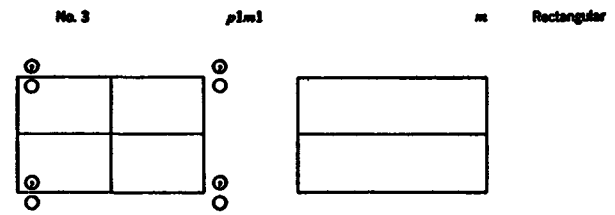
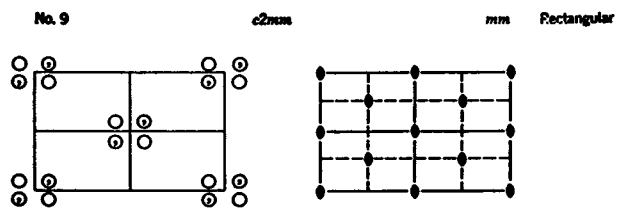
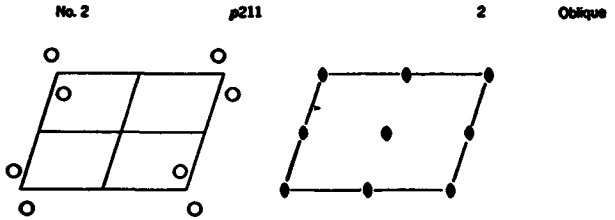
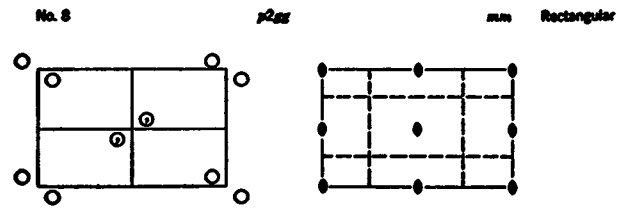
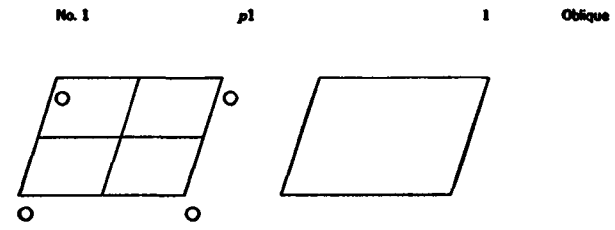


FIG. 4. — Schematic diagram of the most prominent undulation modes in upright and tilted smectics. The scattering wave vector is the sum of q_{\parallel} and q_{\perp} .

diffraction points due to the layered structure is normal to the layers. The interpretation in terms of undulations is compatible with the concept of layer sliding without excluding a certain positional correlation of the two-dimensional lattices.

Very recently, the ordered smectic phases of TBBA were studied by inelastic coherent neutron scattering [28] and those of PBAPC and other materials by transverse ultrasonic waves [29]. In both cases, the authors come to the conclusion that their data are insufficient to decide whether or not the smectic layers are locked to each other. Apparently, it is not enough to investigate these materials at large wave vectors or high frequencies. Rather old-fashioned mechanical experiments, e.g. a search for shear flow at very low frequencies, would appear more promising. The only work of this kind known to us was done by Meiboom and Hewitt [30]: They studied a torsional pendulum containing TBBA in a magnetic field and found viscous effects in all liquid-crystalline phases, possibly including Sm VII, but not in the truly solid state. The authors attribute the apparent viscosity of the ordered, smectic phases to migrating dislocations. Independently of the exact mechanism, we think that their observations indicate a certain fluidity which may be related to a viscous sliding of the smectic layers.

4. Two-dimensional space groups and ordered smectics. — There are 17 types of two-dimensional crystals represented by 17 different space groups. This is



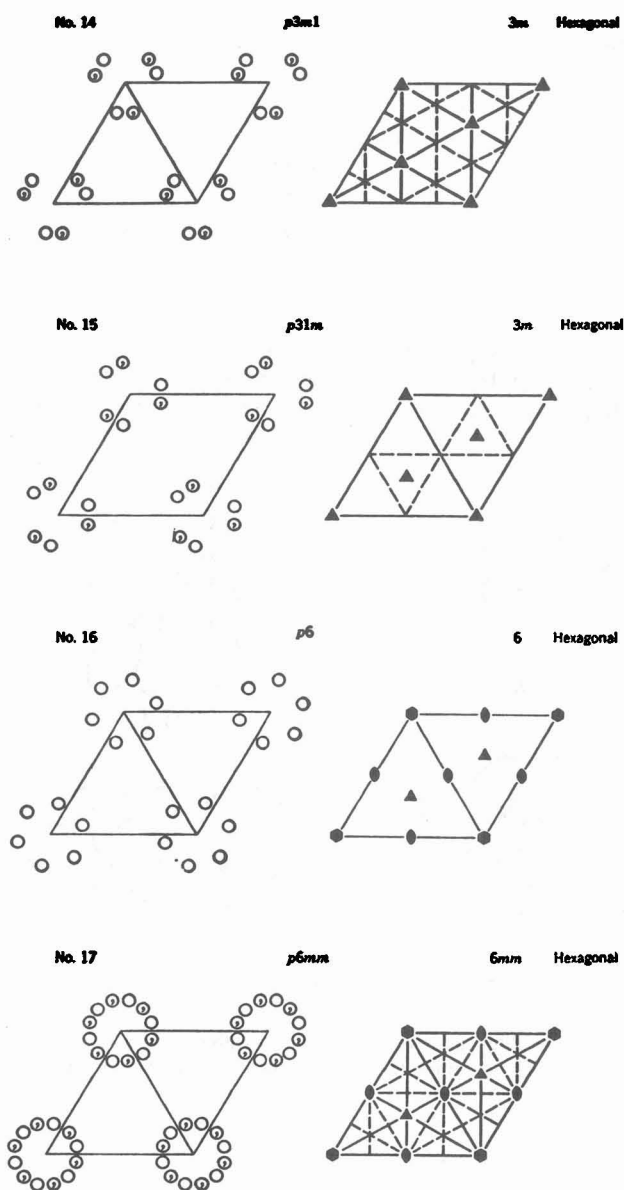


FIG. 5. — The complete set of two-dimensional space groups or crystal types. Points marked \odot are in a mirror relationship to points marked \circ . See text for additional explanations (from ref. [3]).

little in comparison with the 230 space groups conceivable in three dimensions, but it is still much more than the known number of ordered smectic liquid crystals. Although none of the 17 groups can be rigorously excluded, only a few of them have apparently been observed to date, while several others will be seen to be more or less unlikely to be found in smectics. However, there are also space groups as yet unknown that do not seem out of reach. We hope the following discussion will help to realize them, if possible.

The 17 space groups are depicted in figure 5 as taken from the International Tables for X-Ray Crystallography [3]. Each group has its number,

its long and short denotations, and its lattice type. Rectangular lattices can be either centered or primitive. The diagrams on the left are the well-established simple representations of the molecules or groups of molecules forming the identical building blocks of the crystal. The lattice points also have a meaning and we could mark the crossings of the lattice lines with heavy bars along the lines to make this clearer. The diagrams on the right indicate all the symmetry operations transforming the crystal into itself. Two-, three-, four-, and six-fold axes of rotational symmetry are denoted by simple symbols at the points, where these operations (called point groups) are permitted. Heavy lines denote planes (or lines) of reflection symmetry and dashed lines are glide lines. The latter symmetry operation consists in a translation along the line by half its period and a subsequent reflection at the line.

Inspection of the space groups shows that there is a relation between the symmetry of the building blocks or molecules and that of the lattice. Scalene triangles form oblique lattices with the possible exception of singularities, e.g. at a certain temperature where the otherwise oblique angle passes 90° . Molecules possessing reflection symmetry are needed to form rectangular lattices. Square lattices, if not at a singularity, require quadratic building blocks. Triangular, hexagonal or, of course, circular building blocks will be necessary to obtain hexagonal lattices. It should be noted, however, that the symmetry of the lattice can be lower than that of the building blocks, at least in principle.

Most mesogenic molecules consist of a fairly rigid core and one or two hydrocarbon chains. At room temperature they are quite flexible, i.e. there are many bonds which permit some thermal rotation of one side of the molecule relative to the other. Often the energy as a function of rotation angle has more than one minimum, which further increases flexibility. From a snapshot of such a molecule at a given moment one could infer that these highly asymmetric structures will give rise to an oblique lattice, i.e. to a crystal of space group No. 1.

However, in plastic or fluid phases internal and rotational thermal motion may render, in effect, a molecule more symmetric than it is in one of its states of lowest energy. We now extend to ordered smectic layers our earlier postulate that the elongated molecules of the liquid crystal are free to flip end over. Let us first consider upright phases. If the elongated and lath-like molecules are also free to flip side over, they are, in effect, rectangular or elliptical. Therefore, we would expect rectangular lattices of the space groups nos. 6, 7, 8 and 9. In the case of tilted phases we may represent the molecules by two-dimensional objects possessing just one reflection plane, e.g. by triangles of two equal sides, even if they are free to flip side over as before. We can then assign to the tilted phases the rectangular lattices of space

groups nos. 3, 4, and 5. Expressing tilt in three dimensions by polarity in two dimensions appears permissible as long as we do not consider smectic liquid crystals with physical polarity.

Square lattices seem difficult to realize because they require molecules (or groups of molecules) whose effective symmetry is characterized by a four-fold rotation axis. Perhaps the least likely space groups are the hexagonal lattices whose building blocks are trigonal, i.e. possess a three-fold axis of rotational symmetry. Elongated molecules whose cross section is hexagonal are also difficult to imagine.

However, the very last space group, No. 17, is privileged for two reasons. It comprises the case of full rotational symmetry around the long molecular axis which has the highest rotational entropy. Furthermore, the cross-section of many mesogenic molecules, if approximated by an ellipse, is such that the lattice formed by the molecular centers in a rectangular herringbone pattern is fairly close to a hexagonal lattice. Levelut [31] was the first to point out this similarity, sketched in figure 6, to explain the transition $S_G \rightarrow S_H$ (and $S_E \rightarrow S_B$) as a break-up of the herringbone order into herringbone clusters.

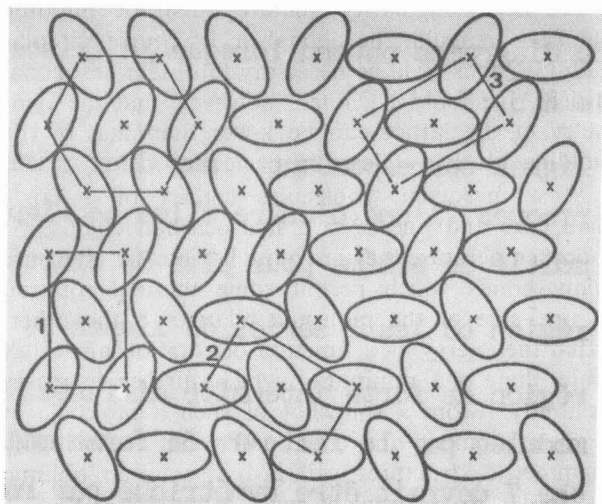


FIG. 6. — Schematic diagram of arrangement of molecules in S_B and S_H . The rectangles indicate the three possible orientations of herringbone clusters (from ref. [31]).

On the basis of the cited literature the well-known ordered smectic phases may be assigned to two-dimensional space groups as follows.

Smectic phase	Space group no.
B	17
E	8
H	5
G	4

Some obvious rules for smooth transitions from upright to tilted :

- 17 \rightarrow 5
- 9 \rightarrow 5
- 8 \rightarrow 4
- 7 \rightarrow 3 or 4
- 6 \rightarrow 3

It remains to explain why the other rectangular space groups have apparently not yet been observed. Part of the explanation for the upright phases may be read from figure 7 which shows ellipses packed as closely as possible in the relevant lattice types.

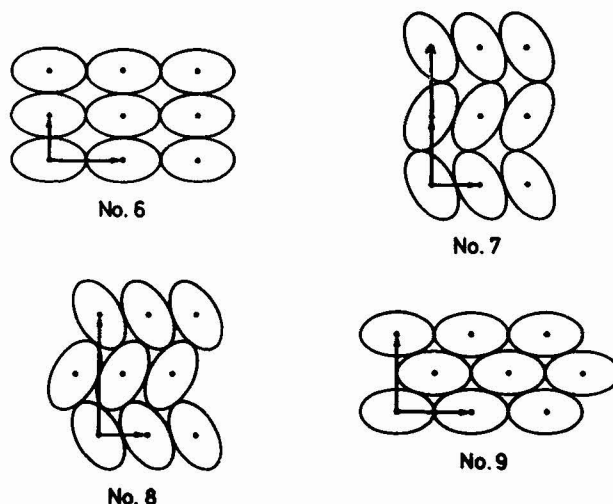


FIG. 7. — Elliptical molecules in contact with each other, arranged according to the indicated space groups. Basic translation vectors are shown.

Assuming van der Waals interaction between molecules and comparing packing densities, one may expect space groups nos. 6 and 7 to be poor candidates. They have, it seems, not yet been reported. However, space group no. 9 may be a serious competitor of no. 8 (S_E) and a search for it could be worth-while. Of the space groups associated with tilt, only no. 3 has apparently not been found and this can again be attributed to poor packing.

The phases n° 6 to 9 and 17 can tilt along two non-equivalent axes. The two types of tilt have, in fact, been found [32], though in different compounds, and distinguished by the numbers I and II. However, even a single phase may display both types of tilt, depending e.g. on temperature. Hypothetical phase diagrams of binary mixtures are depicted in figure 8. The miscibility of types I and II can be continuous, with a transition through a tilted square lattice, but there could also be a first-order phase boundary, perhaps even a critical point.

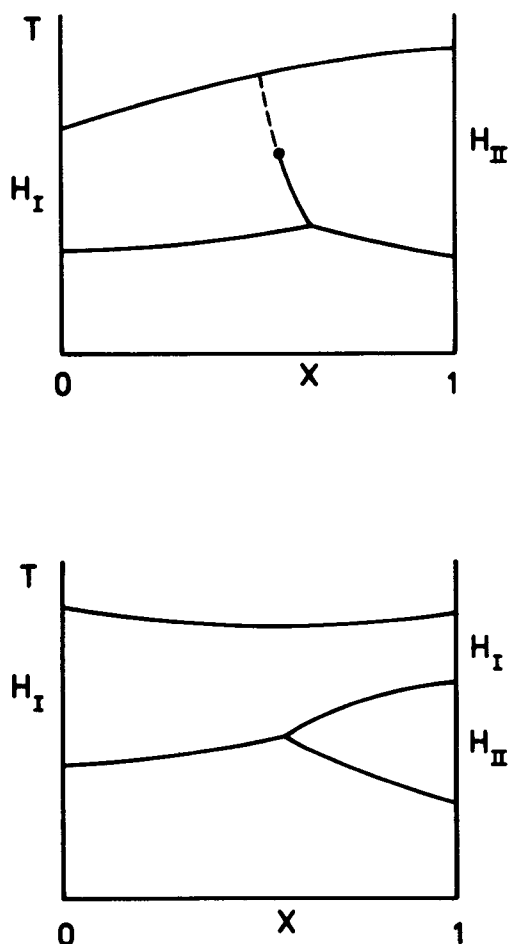


FIG. 8. — Hypothetical phase diagrams of binary mixtures, showing possible phase transition within the phase S_H . The upper diagram contains a critical point. The dotted line is without thermodynamic significance; it could represent a square lattice of tilted molecules.

5. Concluding remarks. — The classification of ordered smectic liquid crystals in terms of two-dimensional space groups may be helpful in the search of further phases. Eventually, it should be extended to mesophases consisting of symmetric bilayers. It may be noted that the phase VII of TBBA is thought to be an ordered smectic phase made up of bilayers [12]. Bilayers or rather interdigitated monolayers have been observed and studied [34] on disordered non-amphiphilic smectics.

Two ferroelectric ordered smectic phases have just been investigated by Doucet *et al.* [32] on HOBACPC = (R⁻)chloro-2-propyl-p-

-hexyloxy-benzylidene-p'-cinnamate

and other compounds. Their phases III and IV are possibly related to H and G in a similar manner as C* to C. The high-temperature phase is indeed twisted as may be expected in the case of uncoupled layer lattices. The low-temperature phase is not

and this could be used as a proof of lattice locking. To defend the standpoint of smectic fluidity, it might be argued that the herringbone phase G permits shear flow only along the parallel lines connecting adjacent molecules of equal orientation. In a defect model of the solid- S_G phase transition [33] this would imply that only the interlayer dislocations associated with the shortest Burgers vectors have blown up into infinite loops in S_G . The pair of shortest Burgers vectors is indicated in figure 9. Other models explaining the absence or weakness of twist in SmIV seem also possible, e.g. bilayer formation. Strictly speaking, ferroelectric ordered smectics have scalene molecules in our scheme based on two-dimensional space groups. This is because of their physical polarity. Inspection shows that at least ferroelectric S_G should deform into an oblique lattice (which was not observed for SmIV).

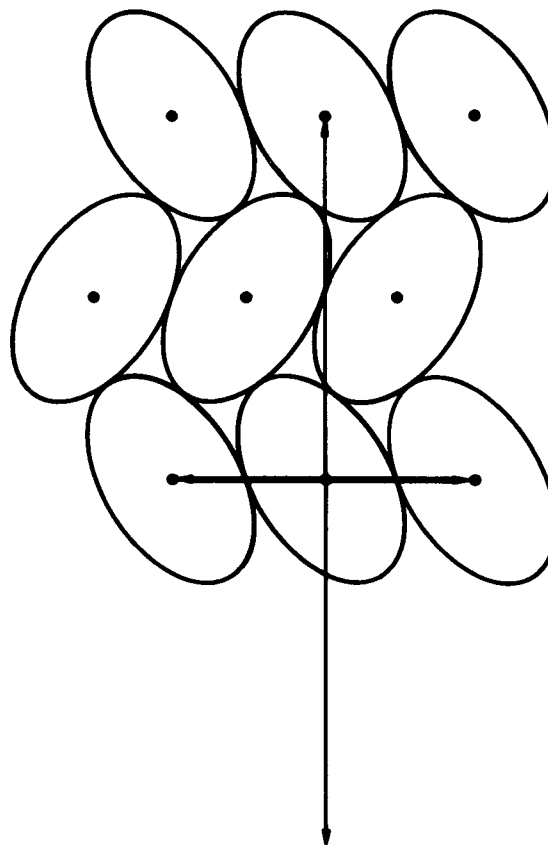


FIG. 9. — Some short Burgers vector in S_E or S_G (tilt is not shown).

There appears to be no room for S_F in our assignment of ordered smectic phases to space groups. The unspecified tilted smectic phase F could be a high-temperature modification of S_H , but this is unlikely, especially in view of the recent studies of Gray and coworkers [17, 18, 35]. A very interesting theoretical possibility is the following: The well-defined lattice of S_H may melt in such a way as to

form a two-dimensional liquid crystal. The melting could be regarded, according to Kosterlitz [36], as a breakup of lattice order by the dissociation of pairs of point dislocations in the two-dimensional lattice. This process does not directly lead to a two-dimensional fluid. Depending on whether some or all of the basic Burgers vectors are involved, each layer could become a two-dimensional smectic or nematic before it finally melts completely by another process. However, more experimental data and a thorough theoretical treatment are needed to check this speculation.

Finally, we would like to recall that our classification of ordered smectics is based on the premise that they are *liquid* crystals. In other words, the smectic layers are supposed to slide upon each other in viscous shear flow in at least one direction. Experiments to check this hypothesis seem highly desirable. The validity of the classification would have to be re-examined, if all or some ordered smectics turned out to be three-dimensional crystals. Even unidirectional fluidity poses new problems. For instance, there could be two types of E and G phases differing by the number of permitted shear flow components.

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