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CHEMICAL CHARACTERISTICS, STRUCTURE, AND PROPERTIES OF LIQUID CRYSTAL

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1. Introduction 495
2. Chemical characteristics of molecules 497
3. X-Ray diffraction by liquid crystals 502
4. Some properties of liquid crystals 505

1. INTRODUCTION

Some organic compounds, heated below their melting point, can form a structure whose properties are intermediate between those of true solid crystals and those of true liquids [1,2]. Liquid crystals combine properties of liquids (fluidity, drop formation, etc.) with properties of solid crystalline materials (anisotropy, electrical, optical, and other properties).

Heating is not the only method of preparing liquid crystals: dissolution of solid crystals of certain substances in specific solvents can also give rise to liquid crystals.

The nature of liquid crystals has been the object of many investigations. The problem has been reviewed by Vul'f [3], Lehmann [4], Friedel [5], Mauguin [6], Vorländer [7], Tsvetkov [8], Weygand [9], Brown and Shaw [10], and Chistyakov [11]. The most comprehensive survey, by Brown and Shaw, cites 475 original papers. The properties of liquid crystals have been discussed at symposia in Germany [12], held in 1931, and in England [13,14], held in 1933 and in 1958.

The last few years have witnessed a renewal of interest in liquid crystals, due above all to their practical importance [15]. Liquid crystals play an important part in the metabolism of living organisms [16-19], and their study is of interest in medicine and biology. Because many wetting agents and detergents, dyes, and polymers can form liquid crystals, their study is of great importance to chemical technology. Shubnikov has pointed out [15] that the remarkable properties of liquid crystals (very large specific rotation of the plane of polarisation, strong pleochroism, electrical and magnetic properties) can be utilised by preparing these materials in a glassy form.

Lehmann [4] distinguished two types of liquid crystals, of widely different viscosities, which he called, respectively, liquid crystals ["Flüssige Kristalle" (Ed. of Translation)] (viscosity of the order of 10^{-2} P) and flowing crystals ["Fliessende Kristalle" (Ed. of Translation)] (viscosity approximately 10 times higher).

Friedel [5] showed that the most essential characteristic of liquid crystals is not their viscosity, but their internal structure, which is intermediate between the three-dimensional lattice of solid crystals and the structureless, amorphous liquid state. Friedel introduced the concept of a mesomorphic state, and distinguished two types of mesomorphs, the nematic and the smectic, corresponding respectively to Lehmann's liquid and flowing crystals.

States of matter can be classified as follows from the point of view of their internal structure:

1. Amorphous state. This is characterised by a completely disordered distribution of molecular position and motions. Molecular rotation is possible about three mutually perpendicular axes.

2. Nematic state. The centres of gravity of the chain-like molecules of which the liquid crystal is composed are randomly distributed, but the chains themselves are oriented along a strictly defined direction. The centres of gravity of the molecules can move in all three dimensions, and molecular rotation is possible about the long axis (Fig. 1*a*).

Compounds which form nematic liquid crystals include *p*-azoxyanisole (t_1 = 116°, t_2 = 133°) and anisaldazine (t_1 = 160°, t_2 = 180°). Throughout the present article, t_1 is used for the melting point of the solid crystal to the liquid-crystalline state and t_2 for the melting point of the liquid crystal to the isotropic liquid state.

3. Smectic state. The centres of gravity (and the chain ends) of the molecules are located on equidistant planes. The centres of gravity can move in two directions (on their plane); molecular rotation is possible about one axis (Fig. 1*b*).

Smectic liquid crystals are formed, for example, by ammonium oleate (at room temperature) and by ethyl *p*-azoxybenzoate (t_1 = 114°, t_2 = 120°).

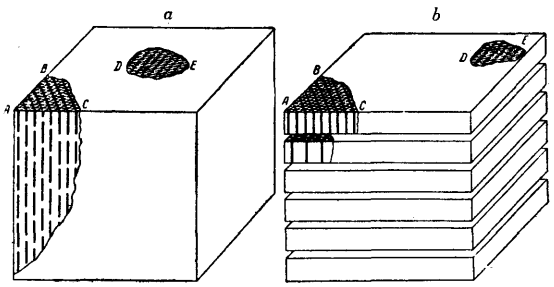


Fig. 1. *a*) schematic arrangement of molecules in the nematic state; *b*) schematic arrangement of molecules in the smectic state.

TABLE 1. Symmetry of the states of aggregation.

Substance	Dimensions of symmetry group	Number of groups
Amorphous	0	—
Nematic	1	∞
Smectic	2	80
Crystalline	3	230

TABLE 2. Possible translation types and corresponding X-ray diffraction patterns.

Brown and Shaw's number	Hermann's number	Translation type	Number of statistical translations	Sets of planes	X-Ray diffraction patterns
1	1	*SSS*	3	—	no sharp rings
2	3-*a*	SSP_2	2	—	ditto
3	3-*b*	SSP_1	2	—	»
4	3-*c*	SSP_0	2	—	»
5	3	*SSD*	2		»
6	2	*SSR*	2	1	one set of sharp rings
7	4-*a*	$SS(SP_1)$	2	1	ditto
8	4-*b*	$SSRP_0$	2	1	»
9	4	$SS(RD)$	2	1	»
10	5-*a*	SP_1R	1	1	»
11	5-*b*	SP_0R	1	1	»
12	5	*SDR*	1	1	»
13	7-*b*	P_1P_0R	—	1	»
14	7-*c*	P_0P_0R	—	1	»
15	7-*a*	P_0DR	—	1	»
16	7	*DDR*	—	1	»
17	6	*DRR*	—	2	at least two sets of sharp rings
18	8-*a*	$DR(RP_0)$	—	2	ditto
19	8	$DR(RD)$	—	2	»
20	9	$(RD)(RD)(RD)$	—	many	many sharp rings

4. Crystalline state. The positions of the molecules are fixed in a three-dimensional crystal lattice. Molecular rotation can be: (a) permitted about one or more axes, or (b) absent.

The distinguishing feature of liquid crystals, therefore, is their internal structure, which can be described by considerations of symmetry. According to Shubnikov[20,21], smectic liquid crystals show space semicontinuum microsymmetry of the first kind, arising from parallel translation of a given plane *A* (two-dimensional continuum) along the translation axis *C* (perpendicular to the plane *A*). The symmetry symbol in this case is given as $C:A$.

Nematic liquid crystals have space semicontinuum microsymmetry of the second kind, associated with infinitely small displacements of the ornament *B* [*sic*. (Ed. of Translation)]. The symmetry symbol is now $C^1:B$, where C^1 is the axis of infinitely small translations and *B* is the ornament symbol [*sic*. (Ed. of Translation)].

Thus the symmetry of nematic liquid crystals is described by continuous, linear symmetry groups, whilst the symmetry of smectic liquid crystals corresponds to planar continuous symmetry groups.

Alexander and Herrmann[22] classify the states of matter, from the point of view of their symmetry, as shown in Table 1. In the nematic state, molecules are arranged in filamentary formations described by one-dimensional space groups, whilst in the smectic state we find ordered layers with true planar space groups.

An article by Neronova and Belov[23] gives a comprehensive discussion of black–white and classical symmetry groups, including those needed to describe liquid crystals.

Hermann[24] approached the symmetry problem from a different angle. He discusses the symmetry groups of amorphous phases and liquid crystals in terms of statistical translation groups, and introduces the concepts of statistical translations (*S*), direct translations (*D*), pseudo-translations (*P*), and reciprocal translations (*R*).

In amorphous substances the translation group is statistical in three dimensions (*SSS*), whilst solid crystals are given the symbol $(RD),(RD),(RD)$ because in these materials direct and reciprocal translations are possible in all three dimensions. Between these extremes we find 18 possible translation types for the liquid-crystalline state. Hermann's twenty translation types are arranged in Table 2 so that each succeeding triplet represents a higher order than the preceding; also included is the X-ray diffraction pattern proposed by Hermann for each type. This arrangement does not appear in the original article by Hermann, and is due to Brown and Shaw[10]. The translation types (SSD), $(SSS)C_{00}$, and (P_1P_0R) correspond to the classical types of nematic, smectic, and cholesteric liquid crystals respectively.

Vainshtein has recently pointed out[164] that the symmetry perturbations which occur in real liquid crystals must be taken into consideration. If we take a cross-section normal to the long axes of the molecules we reveal a lattice with two translation axes, t' and t''. This lattice is ordered in a sufficiently small region surrounding any given point, but it does not possess long-range order.

The perturbation of the lattice is described by a distribution function $f(t't'')$, which shows a definite periodicity within any small region surrounding the origin but becomes damped and approaches a constant value at larger distances from the origin. Under these conditions, a group of finite translations $t't''$ becomes a group of continuous displacements $\tau'\tau''$. The symmetry symbol of nematic liquid crystals is $\tau f(t't'')$, that for smectic liquid crystals is $tf(t't'')$.

Five types of $t't''$ lattice are possible for liquid crystals. Relatively large volumes (several mm^3) of liquid crystals have the appearance of a turbid liquid. This is because the specimen consists of a multitude of small regions within which the molecules have their optic axes

parallel. These regions (or "swarms") are birefringent, electrically polarisable, and diamagnetically anisotropic. Each swarm contains 10^4–10^5 molecules[25,26].

There are also other theories of the liquid-crystalline state in which the medium is treated as highly continuous and the concept of swarms is abandoned. The orientation of the molecules in the liquid crystal is considered to vary gradually from point to point along some well-defined directions. These theories include the nematic threaded texture ["structure à fils" (Ed. of Translation)] and the smectic focal-conic texture of related ellipses and hyperbolas[27-29].

More detailed discussions of the various theories of the liquid-crystalline state can be found in a number of review articles[25-33].

2. CHEMICAL CHARACTERISTICS OF MOLECULES

Up to the time of writing, approximately 3000 compounds all of them organic, have been found to exist in the liquid-crystal state. There have been some reports of inorganic liquid crystals, but they have been few and usually not very convincing. Thus, liquid crystals of silver iodide and other monohalides of silver and thallium have been described[2], but it is now generally believed that these materials are highly plastic aggregates of ordinary crystals rather than true liquid crystals.

Perhaps the most interesting claim to have observed liquid crystals in an inorganic system (in this case, metallic bismuth) is that of Donat and Stierstand[34]. These workers placed a single crystal of bismuth in a mould which was specially shaped so as to minimise the relative displacement of adjacent volume elements produced by the volume change on melting. The crystal was melted and on cooling a single crystal of the same orientation as the original charge was obtained provided the melt had not been superheated by more than 10° above the melting point. The authors suggested, therefore, that bismuth can exist in the liquid crystal state.

There is, of course, no fundamental reason why inorganic substances should not form liquid crystals. The new inorganic polymers would seem to open definite possibilities in this direction.

The most important studies of the chemical properties associated with the liquid-crystalline state are due to Vorländer[7] and to Weygand and Gabler[9,35]. According to Vorländer[7], the ability to form liquid crystals depends first and foremost on the shape of the molecule.

There can be no doubt that substances capable of forming liquid crystals must have elongated, relatively straight molecules. Molecular branching and side-chains tend to inhibit the formation of liquid crystals. However, rod-shaped molecules do not invariably form liquid crystals.

Formation of liquid crystals cannot yet be reliably predicted from a knowledge of the chemical formula of the material.

Both aliphatic and aromatic compounds can form the liquid-crystal state, but the vast majority of known liquid crystals belong to the aromatic series. This is due obviously to the relative lack of rigidity of long aliphatic chains and their consequent inability to retain a linear configuration in the liquid state.

Vorländer[7] pointed out that all aliphatic mesomorphic compounds are salts. Salts have a much greater tendency to orientation owing to the equivalence of the oxygen atoms of the carboxyl groups, which affects the rigidity of the chain.

Some aliphatic mesomorphs which are not salts are known already, but they are very few. Those most studied are aliphatic monocarboxylic acids; there is some information about alcohols and esters[36,37].

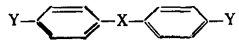
Typical aliphatic compounds that can exist in a liquid-crystalline state are 2,4-nonadienoic acid ($t_1 = 23°$, $t_2 = 49°$), 2,4-undecadienoic acid ($t_1 = 32°$, $t_2 = 58°$), and the sodium salts of monocarboxylic acids listed in Table 14.

Vold and coworkers[38] showed that sodium palmitate and stearate pass through several liquid-crystalline modifications when the crystals are heated to the liquid; this phenomenon has been studied by other workers[39-41].

The present writers have described a thermographic method[42-45] which identifies unambiguously the nature and the number of liquid-crystalline modifications.

Additional information on the properties of aliphatic compounds with a liquid-crystalline modification is given in Brown and Shaw's review[10].

Aromatic molecules, according to Bernal and Crowfoot[46], must possess the following structure in order to show mesomorphism: (1) the molecule must be geometrically anisotropic and either rod-shaped, flat, or lath-shaped; (2) there must not be more than one group in the molecule with a high dipole moment. Brown and Shaw[10] interpret Bernal and Crowfoot's requirements in terms of the following basic structure for aromatic compounds with a liquid-crystalline modification:



Tables 3 and 4 list a series of compounds of this type, divided into symmetrical and unsymmetrical molecular structures (after Brown and Shaw).

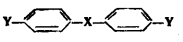
It is pointed out that aromatic substances which exist in a liquid-crystalline modification and contain a single aromatic ring invariably have a substituent in the *para*-position, which makes the molecule elongated. When the substituent is in the *ortho*- or the *meta*-position, liquid crystals are no longer formed. Typical of this type of compound is *p*-methoxycinnamic acid.

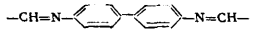
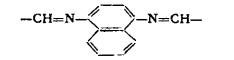
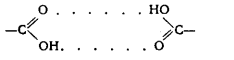
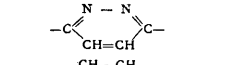
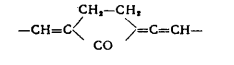
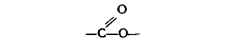
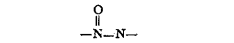
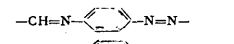
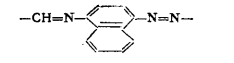
In general, the presence of carboxyl groups in aromatic compounds favours the formation of liquid crystals, but the effect is even more marked when the acid is converted into a salt. Evidently, salt formation from aromatic acids, just as from aliphatic acids, gives rise to additional orientating forces which favour the formation of liquid crystals. For example, sodium benzoate gives liquid crystals over the wide temperature range 410°–430°.

Many compounds known to exist in a liquid-crystalline state contain two or more aromatic nuclei. The nuclei are invariably joined in the *para*-position, and the terminal nuclei are also frequently *para*-substituted.

The tendency to form liquid crystals increases with the number of aromatic nuclei in the molecule. With four benzene rings (quaterphenyl), elongated substituents in the *para*-positions of the end nuclei are no longer necessary, nitro- or amino-groups being sufficient to induce mesomorphism.

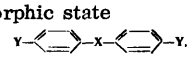
TABLE 3. Composition of central group in aromatic type molecules giving liquid crystals of general formula



X = central group	Type	Typical example
Symmetrical molecules		
—CH=CH—	*trans*-diphenylethylene	*p,p'*-diacetoxystilbene
—N=N—	*trans*-azobenzene	*p*-(*p*-acetoxyazo)benzoic acid
—C≡C—	diphenylacetylene	*p,p'*-diacetoxydiphenylacetylene
—CH=CH—CH=CH—	diphenylbutadiene	*p,p'*-dimethoxydibenzalbutadiene
—CH=N—N=CH—	dibenzalazine	*p,p'*-dimethoxybenzalazine
	dibenzaldiphenyldiamine	dibenzalbenzidine
	dibenzalnaphthalenediamine	*p,p'*-dimethoxydibenzal-1,4-naphthalenediamine
	carboxylic acids* (double molecule)	*p*-butylbenzoic acid (double molecule)
	diphenylpyridazine	*p,p'*-butyldiphenylpyridazine
	dibenzalcyclopentanone	*p,p'*-diethoxybenzalcyclopentanone
Unsymmetrical molecules		
—CH=N—	benzalaniline	*p*-(*p*-cyanobenzal)-anisidine
	phenyl esters of benzoic acid	*p*-(*p*-methoxybenzoxy)-benzoic acid
	azoxybenzene	*p*-azoxyanisole
	benzal-*p*-aminoazobenzene	anisal-*p*-aminoazobenzene
	benzal-1-aminonaphthalene-4-azobenzene	anisal-1-naphthylamino-4-azobenzene

* Other workers, *e.g.* Bennett and Jones[47], are also of the opinion that these molecules are dimeric.

TABLE 4. Composition of end groups in aromatic molecules showing the liquid-crystalline mesomorphic state



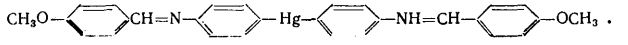
Y = end group	Type
$CH_3(CH_2)_n$—	normal alkyl
$(CH_3)_2CH(CH_2)_n$—	branched alkyl
$CH_3(CH_2)_nO$—	alkoxy
Cl, Br, I	halogen
$CH_3(CH_2)_nCOO$—	carboxylic acid ester
—CN	cyano
$-NO_2$	nitro
$-NH_2$	amino

Most of the aromatic compounds for which evidence of liquid-crystal formation has been obtained contain only benzene rings, but liquid crystals with naphthalene rings are also known. In the latter, however, the tendency towards formation of liquid crystals is much less marked than in benzene derivatives. The liquid-crystalline phases of naphthalene derivatives are often unstable and difficult to study.

In addition to the above, there is another class of these compounds containing the cyclopentylperhydrophenanthrene group with a long side-chain (cholesteryl esters).

The molecular structure of substances which form liquid crystals is often found to consist of two or more benzene nuclei joined by chains of two (or a multiple of two) atoms. Compounds in which the benzene rings are joined by a single atom, or by a chain containing an odd number of atoms, show a negligible tendency to form liquid crystals. Examples of this type of behaviour are provided by the derivatives of diphenylamine, diphenylmethane, diphenylthioether, and diphenyl oxide.

Vorländer explains this effect by pointing out[7] that the bond angles of the atoms linking the nuclei are appreciably different from 180°, and can distort the linearity of the molecule. Nevertheless, the condensation products of aromatic aldehydes with di(*p*-aminophenyl)mercury show mesomorphic properties, *e.g.*



This led Vorländer to propose a linear configuration for the two bonds between the mercury atom and the benzene rings.

Groups joining aromatic nuclei into chains are also of great importance. The following groupings were shown to be particularly effective:

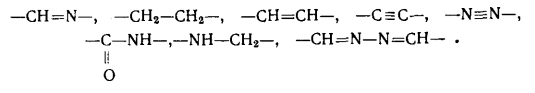
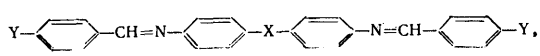


Table 5 gives examples of relatively simple compounds which contain these central groups and readily form liquid crystals.

Table 6, taken from Brown and Shaw's article[10], illustrates the effect of rearranging the end groups in unsymmetrical molecules, and of the change of arrangement of the central group, on the t_1 and t_2 transformation temperatures. Replacement of a methoxy-group by a non-polar phenyl group has relatively little effect on t_2, but the exchange of two polar groups changes it by as much as 20°. The polarity and disposition of the central grouping also affect t_2. If the molecule contains a strong central dipole, such as the azoxy-group, re-orientation of the central group does not appreciably affect t_2, but in the case of a weaker dipole, such as the azo-group, a change in the arrangement of the central grouping gives a large change in t_2 (up to 40°). Further experimental work may, of course, alter the picture.

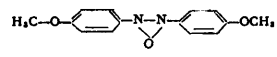
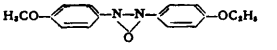
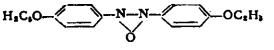
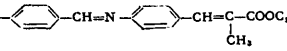
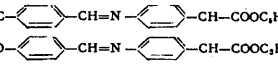
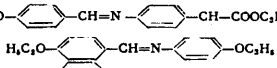
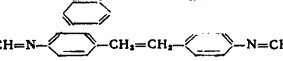
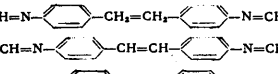
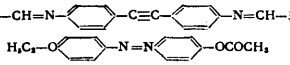
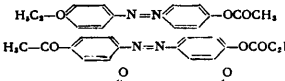
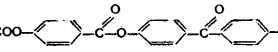
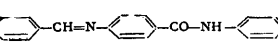
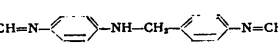
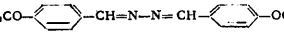
Fig. 2 summarises (after Brown and Shaw) the effect of the central and the end groups on temperature t_2 for a series of compounds having the basic structure:



where X is the central group and Y an end group. Non-polar ($-CH_3$) and polar ($-NO_2$) end groups are considered separately.

These data exemplify the general rule that for any given basic molecular structure, and for a given central group, an increase in the polarity of the end groups decreases t_2.

TABLE 5.

Bond type	Typical compound
	
or 	
	
—CH=N— aldimines	
	
	
	
—CH_2—CH_2—	
—CH=CH—	
—C≡C—	
—N=N—	
	
—O—C— ‖ O	
—C—NH— ‖ O	
—NH—CH_2—	
—CH=N—N=CH—	

An exception to this rule is found in the case where the central group is a carboxyl group. The effect of the nature of the central group on the t_2 temperature is also clearly shown by Fig. 2.

Table 7, compiled by Brown and Shaw, illustrates the effect of the central group on the phase transformation

TABLE 6. Effects of the arrangement of the end groups and of the central group on the t_1 and t_2 temperatures.

Compound	t_1, °C	t_2, °C
Change in arrangement of unsymmetrical end groups		
$C_6H_5C_6H_4CH{=}NC_6H_4OCH_3$	176	186
$CH_3OC_6H_4CH{=}NC_6H_4C_6H_5$	161	177
$CH_3COOC_6H_4CH{=}NC_6H_4OCH_3$	112	128
$CH_3OC_6H_4CH{=}NC_6H_4OCOCH_3$	81.5	108
$CNC_6H_4CH{=}NC_6H_4OC_2H_5$	115	132
$C_2H_5OC_6H_4CH{=}NC_6H_4CN$	105	124
Change in arrangement of central group		
$CH_3OC_6H_4CH{=}NC_6H_4N{=}N(\rightarrow O)\rightarrow O{-}C_6H_4N{=}CHC_6H_4CH_3$	185	292
$CH_3OC_6H_4N{=}CHC_6H_4N{=}N(\rightarrow O)\rightarrow O{-}C_6H_4CH{=}NC_6H_4OCH_3$	226	295
$CH_3C_6H_4CH{=}NC_6H_4N{=}NC_6H_4N{=}CHC_6H_4CH_3$	190	285
$CH_3C_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4CH_3$	228	297
$CH_3OC_6H_4CH{=}NC_6H_4N{=}NC_6H_4N{=}CHC_6H_4OCH_3$	220	300
$CH_3OC_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4OCH_3$	257	340

temperatures for the homologues of a series [10,35,48]. It is clearly seen that the differences in the t_2 values decrease with increase in molecular weight. The maximum differences in the t_2 points are observed with the lower-molecular-weight compounds.

Vorländer [7] studied the change in the transformation temperatures with a change in the central grouping for a series of substituted dianisalbenzidines, and found some very large effects (Table 8). He also made a comparative study [49] of derivatives of the type

$$C_6H_5CH = NC_6H_4 - X - C_6H_4N = CHC_6H_5,$$

and showed that the behaviour of analogous central groupings in the two structures was very similar.

Further results [10,50] illustrating the effect of the end groups on the transformation points are summarised in Table 9. They show that if the alkyl of the alkoxy-group in

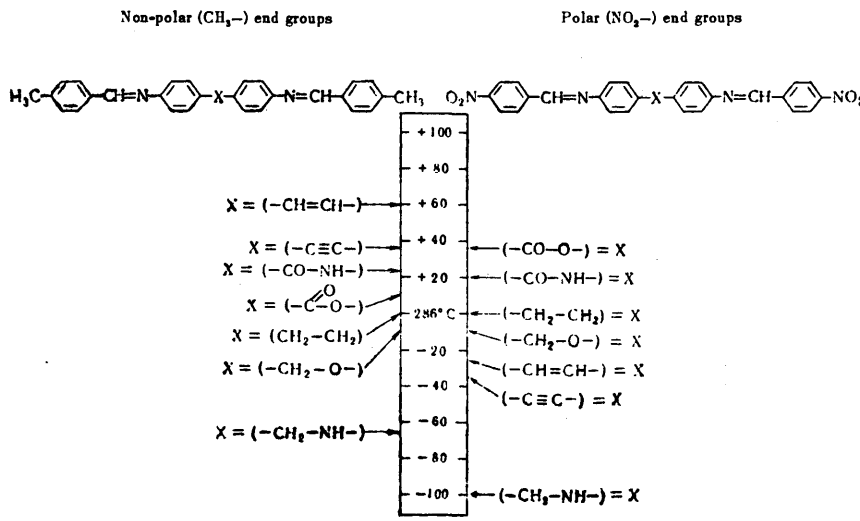


Fig. 2. Effect of end groups and of central group on the melting point of liquid crystals.

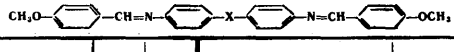
TABLE 7. Transformation points for the azoxyphenol, azophenol, and azomethinephenol ethers*.

Length of side-chain**	Azoxyphenol ethers, °C			Azophenol ethers, °C			Azomethinephenol ethers	
	t_1	t_2	t_3	t_1	t_2	t_3	t_1	t_2
2	116	134	—	165	(110)	—	146	99
3	134	168	—	159	150	—	149	143
4	116	122	—	146	(112)	—	133	(107)
5	107	134	—	135	124	—	125	121
6	82	119	—	113	108	—	113	103
7	81	127	72	102	114	—		
8	74	122.5	92	102	109	97		
9	76	124.5	106	98	—	—		
10	77	121	113	103	107	99		
11	78	123	119.5	106	—	107		
12	78	—	120.5	—	—	—		
13	82	—	122					

* t_1 is the solid→liquid crystal-transformation temperature; t_2 is the temperature of the transformation from nematic liquid crystals to the isotropic liquid; t_3 is the temperature of the transformation from the smectic modification to the nematic or to the isotropic liquid.

** Length of side-chain: 2 = methoxy; 3 = ethoxy; 4 = propoxy, etc.

TABLE 8. Effect of change of the central group of dianisalbenzidine on t_1 and t_2.



X	t_1	t_2	X	t_1	t_2
No central group	253	>345	—OCH_2—CH_2O—	209	298
—CH_2—	not liquid crystalline		—$NHCH_2CH_2NH$—	187	241
			—$COOCH_2CH_2OCO$—	183	197
			—$OCOCH_2CH_2COO$—	183	266
—CH_2—CH_2—	171	312	—C_6H_4—	290	320
—CH_2—CH_2—CH_2—	not liquid crystalline		—O—	not liquid crystalline	
—CH_2—CH_2—CH_2—CH_2—	156	270	—S—	not liquid crystalline	
—CH_2—CH_2—CH_2—CH_2—CH_2—	very small liquid crystallinity		—NH—	239	<239
—CH=CH—	230	>360	—Hg—	209	285
—C≡C—	235	251			
—CH_2O—	209	298			
—C(=O)—O—					
	206	>310			

TABLE 9. Transformation temperatures of some compounds of the *p*-alkoxybenzal-*p'*-alkylaniline type*.

Compound	Temperature, °C			
	t_1	t_2	t_3	t_4
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_3$	73	74	70	76
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_2CH_3$	65	77	74	—
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4OCH_3$	108	—	—	96
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_2CH_2CH_3$	51	84	79	—
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	101.5	84	79	115
n-$C_7H_{17}OC_6H_4CH$=$NC_6H_4OC_7H_7$-n	133	—	—	107
$CH_3OCH_2OC_6H_4CH$=$NC_6H_4OCH_2OCH_3$	47	—	—	—
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	105.5	—	—	129.5
$CH_3CH_2OCH_2OC_6H_4CH$=$NC_6H_4OCH_2OCH_2CH_3$	64	—	—	—
n-$C_7H_{15}OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	125	—	—	123.5
$CH_3OCH_2OC_6H_4CH$=$NC_6H_4OCH_2CH_2CH_3$	80.5	—	—	—

* t_1 is the temperature of the transformation from solid crystal to liquid crystal; t_2 and t_3 are temperatures for transformations between different liquid-crystalline modifications; t_4 is the temperature of the transformation from liquid crystal to isotropic liquid.

p-alkoxybenzal-*p*-alkoxyanilines is replaced with an ether (*i.e.* RCH_2CH_2O– with $ROCH_2O$– or $ROCH_2CH_2OCH_2$–) the temperature of the transformation from nematic phase to isotropic liquid will be lowered, or the liquid-crystalline structure will disappear altogether.

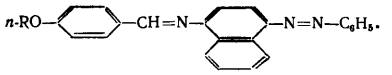
Wiegand's work[51] on dianisalbenzidine and its derivatives illustrates the effect of substituents in different positions of the biphenyl portion of the molecule (Table 10).

Gray and Jones[52,53] have made a similar study of substituted alkoxybenzoic acids and alkoxynaphthoic acids. Their results are set out in Table 11.

The alkoxybenzoic acids and the alkylbenzoic acids afford an interesting series of compounds for comparison of the effect of change of t_1 and t_2 temperatures in a homologous series. These series of compounds give both smectic and nematic structures. In Fig. 3 transformation points are plotted against the chain length of the alkyl or alkoxy-group[10].

It can be seen from Fig. 3 that for the lower-molecular-weight members of the series the smectic and nematic curves show a very similar type of periodicity†, and that the curves tend to flatten out as the length of the molecules increases. The general slope of curves *1* and *3* is negative, that of curve *2* is positive. This type of behaviour is representative of most of the homologous series which have been studied.

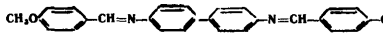
In homologous series exhibiting a distinct periodicity[54], the melting point of the liquid crystals depends on the length of the end chain. An example is the benzalnaphthylamino-azobenzene compounds:



In this system the nematic → isotropic liquid transformation points alternate regularly and strongly between 85° and 100°.

The position of the substituent groups also determines whether the compounds shall form liquid crystals, as work on dianisylnaphthyldiamines has shown[55]. Table 12, after

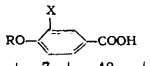
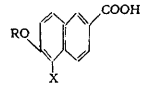
TABLE 10. Effect of substituents on the nature of the liquid-crystalline state of dianisalbenzidine derivatives



Compound	Temperature, °C	
	t_1	t_2
Dianisalbenzidine	252–253	>345
2,2′-Dichlorodianisalbenzidine	215–216	320–321
3,3′-Dichlorodianisalbenzidine	148–149	>340
2,2′,6,6′-Tetrachlorodianisalbenzidine	217–219 (m.p.)	no liquid-crystalline state
2,2′-Dimethyldianisalbenzidine	172–173	307–308
3,3′-Dimethyldianisalbenzidine	180–181	353
2,2′,6,6′-Tetramethyldianisalbenzidine	212–213 (m.p.)	no liquid-crystalline state

† This statement is not consistent with the description of the curves in the caption to Fig. 3 (Ed. of Translation).

TABLE 11. Influence of substituents on the nature of the liquid-crystalline state of alkoxybenzoic acids and alkoxynaphthoic acids. n = number of carbon atoms in alkoxy--side-chain.

X	Value of n at first appearance of: nematic structure	smectic structure	smectic structure only	Value of n at max. phase interval	Maximum phase interval, °C
Alkoxybenzoic acids					
					
H	3	7	18	10	57
F	8	9	16	16	16
Cl	8	8	—	16	4.5
6-Alkoxy-2-naphthoic acids					
					
Cl	3	6	16 and 18	6	42
Br	3	7	16 and 18	7	40
I	4	8	16 and 18	8	25
NO_2	9	12	—	10	1.5

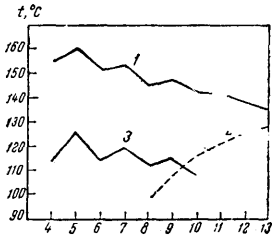


Fig. 3. Transformation points of alkylbenzoic and alkoxybenzoic acids as a function of side-chain length and substituents:
1) nematic → isotropic liquid temperatures for *p*-n-alkoxybenzoic acids;
2) smectic → nematic temperatures for *p*-n-alkoxybenzoic acids;
3) nematic → isotropic liquid temperatures for *p*-n-alkoxybenzoic acids [*p*-n-alkylbenzoic acids (Ed. of Translation)].

TABLE 12. Effect of molecular structure on the liquid-crystalline state.

Compound	Temperature, °C: t_1	t_2
Dianisal-1,4-naphthylenediamine	182.5–184	262–263
Dianisal-1,5-naphthylenediamine	196	282.5
Dianisal-2,6-naphthylenediamine	188.5–189.5	354–356
Dianisal-1,7-naphthylenediamine	142–143 (m.p.)	no liquid-crystalline state
Dianisal-2,5-naphthylenediamine	133–134 (m.p.)	ditto
Dianisal-2,7-naphthylenediamine	204–206 (m.p.)	»

Wiegand, illustrates this effect. Molecules that are rod--shaped, or nearly rod-shaped, can form liquid crystals, whilst molecules lacking a linear structure do not.

Work on the *p*-alkoxycinnamic acids and their halogen derivatives[56,57] gave very similar results. Only the *trans*--form was found to exist in the liquid-crystal state.

Many colloidal systems form structures similar to nematic or smectic liquid crystals. Typical of these are a number of aqueous systems with soap[58,59], the tobacco mosaic virus and other viruses[19], 10-bromophenanthrene--sulphonic acids[60], and some dyestuffs[61,63]. Lawrence[59] classifies these structures as *lyotropic* liquid crystals, since they are formed during dissolution of the solid crystals.

The solvent weakens the intermolecular cohesive forces which hold the crystal lattice together. On dilution, initially these forces are destroyed in one direction only and the substance acquires the properties of a smectic liquid crystal. Increase in dilution causes bond breaking in two dimensions, and the substance becomes nematic. Eventually, at the highest dilutions, the solution becomes isotropic.

The equilibrium diagram of the potassium palmitate–water system, reproduced in Fig. 4, illustrates these lyotropic phase transformations.

It is interesting to consider the formation of these crystals in three-component systems[64–66]. Some organic materials which are insoluble in water are known to dissolve in aqueous soap solutions. These three-component systems (soap–water–insoluble substance) show a liquid--crystal field over some region of the equilibrium diagram. For example, cholesterol melts at 148.5°, but it can exist in a stable liquid-crystalline state at room temperature when mixed with one equivalent of soap solution[66].

Some compounds exhibit several liquid-crystalline modifications[35,67–69]: for example, the dianil obtained from ethyl *p*-aminocinnamate and terephthalaldehyde has four liquid-crystalline modifications, and undergoes the following transformations:

$$\text{IL} \rightleftharpoons \text{LC}_1 \rightleftharpoons \text{LC}_2 \rightleftharpoons \text{LC}_3 \rightleftharpoons \text{LC}_4 \rightleftharpoons \text{SC}.$$

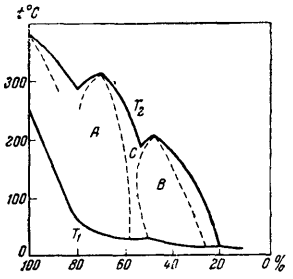
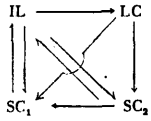


Fig. 4. Equilibrium diagram for the potassium palmitate–water system. The lower curve (T_1) forms the boundary of the region of gels and coagels. The isotropic solution is stable above T_2. The region between T_1 and T_2 defines the liquid-crystalline state.

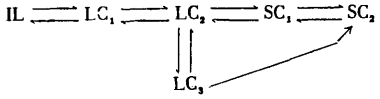
IL is the isotropic liquid, LC the liquid crystals, and SC the solid crystal. The arrows show that the phase transformations can occur in either direction. Consequently, the liquid crystals exhibit *polymorphism*.

In some compounds the liquid-crystalline state is monotropic with respect to the solid state. Thus, cholesteryl acetate never forms liquid crystals when the solid crystals are heated[70,71], but melts at 114° to give an isotropic liquid. On cooling this liquid, however, metastable liquid crystals are formed. At large enough supercooling the liquid crystals are converted into beautiful spherulites (the SC_2 modification), which are themselves monotropic with respect to the stable SC_1 solid modification.

The transformations of cholesteryl acetate are summarised in the following diagram:



Phenyl *p*-azoxyphenetolebenzoate gives this series of transformations:

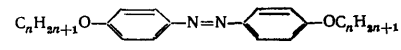


The third liquid-crystalline modification appears only during cooling.

According to Shubnikov[21], the complexity of the conversion scheme and the number of possible modifications increase with the number of thermodynamic variables and can, therefore, be infinitely large.

Small additions of isomorphous impurities can significantly extend the region of existence ($t_1 - t_2$) of liquid crystals. There is a clear analogy between this phenomenon and the formation of crystalline solid solutions: the impurity affects the properties of the liquid crystals as well as the temperature limits of their existence[72].

Arnold and Sackmann[73,74] discuss, with a comprehensive list of references, the isomorphism of liquid-crystalline phases, and point out that mixtures of liquid-crystalline phases should provide examples of both complete and partial miscibility. Two-component systems consisting of pairs of homologues of the series



(4,4′-di-*p*-alkoxyazobenzenes; n = 2, 3, 4, 8, 9, 10, 12) have been studied microscopically. Complete miscibility was observed for mixtures of isomorphous phases (smectic–smectic, or nematic–nematic), and for mixtures of the isotropic liquids, but mixtures of different liquid-crystalline phases or of solid phases did not form a continuous series of solutions.

These observations led to the suggestion that miscibility might be used as a criterion for isomorphism, but further experimental work is needed.

Studies of the factors which determine the miscibility of liquid crystals of a single (or of more than one) class are, unfortunately, only just beginning. The approach is to explore the stability limits of the phases under study by varying the size and shape of the molecules without disturbing the type (or the intensity) of molecular interactions.

3. X-RAY DIFFRACTION BY LIQUID CRYSTALS

Liquid crystals were examined by *X-ray structural analysis* shortly after the discovery of X-ray diffraction. Van der Lingen[75] obtained Laue patterns from *p*-azoxyanisole and *p*-azoxyphenetole, but could only conclude that liquid crystals lack a three-dimensional lattice, since the X-ray diffraction patterns were similar to those of ordinary amorphous liquids.

Hückel[76] confirmed the absence of a crystal lattice after examining the diffraction patterns of *p*-azoxyanisole, *p*-azoxyphenetole, dianisaldazine, cholesteryl propionate, and cholesteryl benzoate. More advanced X-ray techniques, however, enabled Kast to show[77] that the plot of intensity *versus* diffraction angle for the nematic state is slightly displaced relatively to that for the isotropic liquid.

A large proportion of the X-ray work on nematic liquid crystals was done in a magnetic field. According to Kast[78], each swarm gives two interference maxima at right angles to the long axis of the molecules, but since the swarms are randomly oriented the diffraction pattern contains one broad, diffuse ring, as in the case of amorphous liquids. In the presence of a magnetic field the swarms take up an orientation parallel to the magnetic lines of force, and the diffuse ring splits into two crescents corresponding to two interference maxima at right angles to the direction of the field.

Stewart[79–82], using molybdenum $K\alpha$ radiation, found that the diffraction-intensity curves of nematic *p*-azoxyanisole and of the corresponding isotropic liquid differ slightly at the principal maximum, which is approximately 10% higher for the nematic than for the liquid structure. The curvature, and the sharpness of the peak, are also slightly more pronounced in the nematic state. Stewart concludes that the swarms in the liquid crystals are much larger than any similar aggregates in the isotropic liquid. If the latter are assumed to comprise 100–1000 molecules, the swarms in liquid crystals must be thought to contain at least 10^6 molecules.

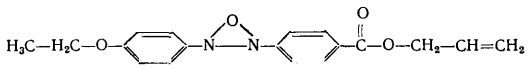
Glamann *et al.*[83] examined *p*-azoxyanisole by X-ray diffraction. Two diffraction rings were found with copper $K\alpha$ radiation, while three rings were obtained with molybdenum $K\alpha$ radiation. In a magnetic field the two diffraction rings obtained using the copper radiation split into crescents.

Recent work by Falgueirettes[84] has shown that nematic *p*-azoxyanisole, oriented in a magnetic field or by contact with mica leaves prepared by Chatelain's method, gives three pairs of crescents in copper $K\alpha_1\alpha_2$ radiation. One pair of crescents is parallel to the optic axis, and is ascribed to intermolecular interference. The two remaining pairs are weaker, perpendicular to the optic axis of the nematic single crystal, and they are produced by intramolecular interferences. Falgueirettes calculated the molecular distribution in the nematic single crystal, $f(\theta)$ as a function of θ, by a microphotometric study of the variation of intensity along the diffraction rings.

Crescent-shaped interference maxima are also found in the diffraction patterns of nematic liquid crystals oriented by an electric field[85]. However, in contrast to the crescents observed in a magnetic field, these can be oriented either parallel or perpendicular to the direction of the electric field. The effect depends on the orientation of the long axes of the molecules, which is determined by the molecular structure[8].

When liquid crystals of *p*-azoxyanisole are placed in a low-frequency a.c. electric field the diffuse ring of the diffraction pattern splits into two crescents whose axes are oriented parallel to the field, showing that the molecules themselves have taken up this orientation. Increase in frequency to 300 c/s destroys the sickle-shaped pattern and restores the diffuse ring, but at still higher frequencies the crescent shape once again appears, with its axis at right angles to the initial direction. Kast[86] accounts for this phenomenon in terms of frictional dispersion: the swarms cannot align themselves with the field once the period of the applied a.c. becomes shorter than the relaxation time involved. The relaxation time of the swarms, evaluated by this method, was found to be 10^{-5} sec, as compared with 10^{-11} sec for a typical isolated molecule.

Numerous X-ray studies[87-89] have confirmed the layer structure of smectic liquid crystals. Herrmann[90] examined a series of cinnamic and of benzoic esters which can give both nematic and smectic liquid crystals. His tabulated results show that the first three compounds exhibit a new kind of interference (immediately above the liquid crystal–solid crystal transformation point) whose origin is ascribed to hexagonal cylindrical packing of the molecules within the smectic layers. Herrmann and Krummacher[91] examined allyl *p*-phenetoleazoxybenzoate



(a compound which can exist in nematic and smectic mesophases), and reported the following transformation points: solid crystal $\underset{66°}{\rightleftharpoons}$ smectic liquid crystal $\underset{77°}{\rightleftharpoons}$ nematic liquid crystal $\underset{95°}{\rightleftharpoons}$ isotropic liquid.

These workers also found that in a magnetic field of 8600 G the diffraction patterns of the smectic and the nematic liquid crystals are practically indistinguishable, and consist of two pairs of crescents. However, the molecules appear to be better aligned in the smectic phase, since the diffraction ring is more sharply resolved into crescents. The results are summarised in Table 13.

The diameter of the outer ring varies with temperature, and therefore also with the amount of intermolecular interference. Herrmann and Krummacher arrived at similar conclusions in their work[92] on the X-ray diffraction of anisal-1,5-diaminonaphthalene.

TABLE 13. X-Ray data on allyl phenetole-azoxybenzoate.

Temperature, °C	Structure	Diameter of outer ring	θ/2	d, Å
	Radiation: Cu Kα (*H* = magnetic field)			
100	liquid, no *H*	32	8°47′	5.0
88	nematic, with *H*	34	9°18′	4.8
79.5	nematic, with *H*	34	9°18′	4.8
75.5	smectic, with *H*	35	9°33′	4.6
72	smectic, with *H*	35	9°33′	4.6
	Radiation: Mo Kα (*H* = magnetic field)			
94	nematic, with *H*	34.4	9°26′	2.16
82	nematic, with *H*	36.5	9°56′	2.04
70	smectic, with *H*	38	10°19′	1.96

Many papers on the X-ray analysis of liquid crystals include diffraction patterns of the same materials in the solid crystalline state. Bernal and Crowfoot's paper[46] on the structure of six crystalline solids able to form liquid crystals is among the most informative.

It is found that molecules with a single active terminal group (or two symmetrical terminal groups) have a tendency to crystallise in layer structures, which yield smectic liquid crystals when the solid crystals are heated. Compounds of this type (*e.g.* ammonium oleate or ethyl *p*-azoxybenzoate) are termed "smectogenic". On the other hand, molecules having central active groups tend to form "nematogenic" solid crystals. These materials (*e.g.* *p*-azoxyanisole or *p*-azoxyphenetole) give nematic liquid crystals on heating.

X-Ray diffraction and other methods of investigation have established the existence of five allotropic liquid-crystalline phases in anhydrous sodium soaps[93,94]. The results of this work are summarised in Table 14.

Many diffraction lines (sometimes more than 20) are found in the centre of the diffraction pattern of each liquid-crystalline phase. Further out, there are diffuse rings with a fine structure which sharpens up when the temperature is lowered.

The first four phases have a two-dimensional, face-centred, rectangular lattice. The structure consists of parallel bands of polar end groups packed in a rectangular lattice, with liquid-like hydrocarbon chains (Fig. 5). The cell dimensions (*a* and *b*) depend on the soap and on the phase (Table 14). The fifth (or "neat") phase has a lamellar structure (Fig. 6*a*).

The X-ray pattern of the isotropic phase a few degrees above the melting point contains two or three fairly sharp rings, confirming that the structure of a melt close to the transformation temperature is not very dissimilar from the structure which is stable below the transformation point.

TABLE 14.*

Structure	*t*	Sodium laurate	*t*	Sodium myristate	*t*	Sodium palmitate	*t*	Sodium stearate
Two-dimensional rectangular	100		107		117		118	
Two-dimensional rectangular	141	*a*=75.2 *b*=30.9 at 166°	141	*a*=80.0, *b*=34.5 at 155°	135	*a*=86.6, *b*=38.3 at 152°	132	*a*=80.0, *b*=40.3 at 140°
Two-dimensional rectangular	182	*a*=68.5, *b*=30.3 at 195°	176	*a*=69.0 *b*=33.6 at 195°	172	*a*=74.2 *b*=36.8 at 195°	167	*a*=72.5 *b*=37.9 at 198°
Two-dimensional rectangular	220	*a*=49.8 *b*=27.0 at 234°	217	*a*=53.8 *b*=29.1 at 233°	208	*a*=56.2 *b*=30.6 at 236°	198	*a*=62.4 *b*=34.4 at 238°
Lamellar	255	*d*=25.3 at 290°	245	*d*=27.5 at 271°	253	*d*=29.1 at 278°	257	*d*=30.6 at 285°
Isotropic melt	336		310		295		298	

* *t* is the phase transformation temperature, *a* and *b* the dimensions of the unit cell in Å, *d* the interplanar spacing.

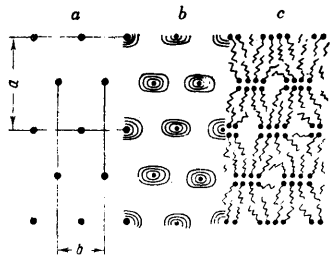


Fig. 5. *a*) Two-dimensional, centred rectangular lattice; *b*) electron density projection along {001}; *c*) schematic of the rectangular phase structure.

A recent paper[94] points out that sodium laurate can form, between the "superwaxy" and the "subneat" phases, yet another new phase with a three-dimensional, face-centred, orthorhombic lattice (lattice constants a = 55.5, b = 28.3, c = 32.7 Å).

Complete conversion of the sample from one form to another takes several hours. This may account for some disagreement between different research groups[93-95].

Many X-ray investigations of lyotropic liquid crystals of soaps and detergents have been published[96-100]. Recent work[101-102] has shown that phase *A* (Fig. 4) takes the form of smectic double layers of soap molecules. The surfaces of each layer contain the polar ends of the molecules, and the "liquid" hydrocarbon chains are pointed inwards (Fig. 6*a*). At higher soap concentrations the layers of soap molecules become thicker, whilst the intervening water layers become thinner.

Phase *B* is formed as a hexagonal array of long cylinders (Fig. 6*b*) whose diameter is not a function of concentration at constant temperature.

In addition to these two phases, three intermediate phases have been identified in region *C* of Fig. 4. These include a complex hexagonal phase (Fig. 6*c*), a distorted variant of phase *B* showing an orthorhombic lattice, and a cubic (isotropic) phase in which the hydrocarbon chains are arranged in spheres separated by water molecules.

The diffraction patterns of lyotropic liquid crystals of tobacco mosaic virus in water[103,104] have four sharp equatorial spots, which justify the belief that the particles are arranged in a two-dimensional hexagonal lattice (Fig. 7).

The cholesteric lyotropic liquid crystals formed by certain polypeptides have been shown[105] to have a structure similar to that of Fig. 7, but with some additional coiling along the Z axis.

Diffraction studies of aqueous desoxyribonucleic acid and nucleoprotein systems[106,107] have identified a number of phases, including some which are liquid crystalline. Haemoglobin, α-keratin, and many other biologically important substances are able to form liquid crystals.

The theory of X-ray diffraction in similar biological systems has been developed by Hosemann[108,109] [the "ideal paracrystal" model of liquid crystallinity (Ed. of Translation)].

The *nuclear magnetic resonance* (NMR) of liquid crystals has been discussed in a number of recent papers[110-117]. The isotropic melt of *p*-azoxyanisole in a magnetic field of 7300 G has a resonance line[110] of width 0.1 G. When the temperature is lowered to 135.8° and the specimen is converted into the liquid-crystalline state, the amplitude of the signal decreases and the line is resolved into three components. The separation between the two satallite peaks is approximately 3.3 G; the intensity ratio is 2 : 3 : 2. The NMR line loses its structure when the specimen is converted into the solid-crystalline state.

Comparative NMR results for three compounds are given in Fig. 8 (after Jain *et al.*[112]). The investigation, which was concerned with the effect of temperature on the NMR spectrum of three compounds, established that the NMR signal of 4,4'-dimethoxyazoxybenzene (*p*-azoxyanisole, PAA) is fairly independent of temperature within the limits of the liquid-crystalline state, but that the peak separation decreases with increasing temperature.

4,4'-Dimethoxy-D_3-azoxybenzene (DPAA) differs from PAA in having the hydrogen atoms of the end groups replaced by deuterium, so that the protons attached to the benzene rings are the only possible source of NMR signals. The signal in this case consists of a strong doublet with a relatively weak central component. Again, the shape of the signal is fairly independent of temperature over the

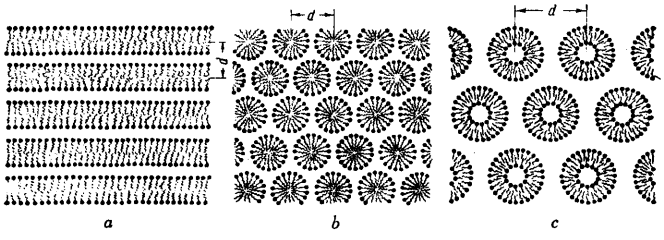


Fig. 6. Structure of the soap–water liquid-crystalline system. *a*) Phase *A* (see Fig. 4); *b*) phase *B*; *c*) complex hexagonal phase *C*. The spaces between the soap micelles are filled with water.

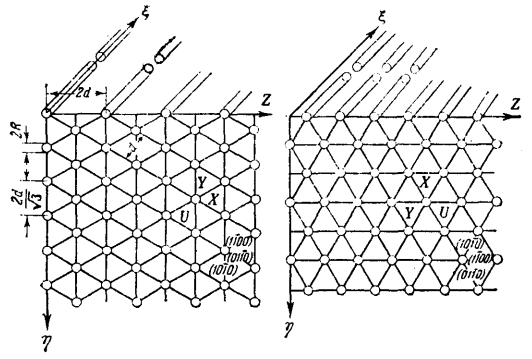


Fig. 7. Structure of the tobacco mosaic virus. *XYZU* are the crystallographic axes, $\eta\xi$ are the molecular axes.

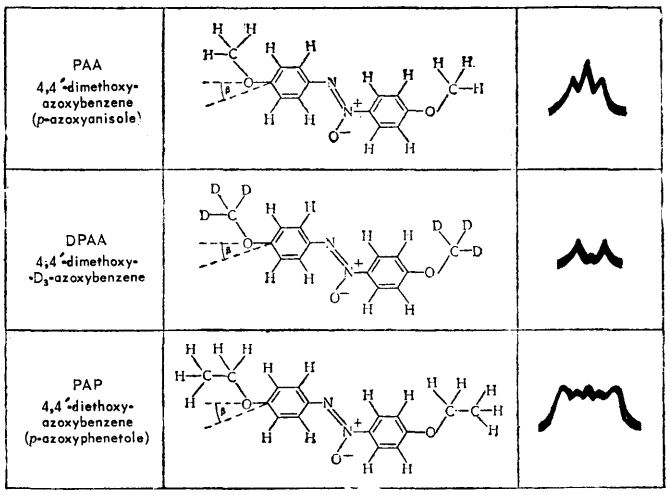


Fig. 8. Molecular structure and shape of proton magnetic resonance signals.

entire liquid-crystalline region, but the peak separation decreases at higher temperatures. However, within 0.5° of the liquid crystal → isotropic liquid transformation point the central component begins to increase rapidly and reaches an amplitude 1.5 times that of the satellite peaks. At the transformation point the satellite peaks disappear and a single narrow line remains.

The NMR line of *p*-azoxyphenetole (PAP) is similar, at the highest temperatures, to that of PAA (Fig. 8). At lower temperatures, however, the central peak begins to shrink and two additional peaks appear (Fig. 8, bottom). This justifies the conclusion that the replacement of methyl groups (PAA) by ethyl groups (PAP) produces a more highly oriented liquid-crystalline phase.

4,4'-Propoxyazobenzene and anisaldazine behave like PAA. Smectic substances, like sodium oleate and sodium stearate, give simple lines of average width at all temperatures between the isotropic-liquid and the solid-crystalline phase [112].

NMR has been used to study transition phenomena in many substances [113]. It has been shown that these phenomena are not symmetrical about the transformation point, and that they depend on the thermal history of the specimen. Frenkel's theory of fluctuations in heterogeneous phases can account for these results if contamination by the thermal decomposition products of the material is considered.

The newest developments in the NMR study of smectic and nematic liquid crystals are due to Lippman [115–117], who has also produced a comprehensive review of the theoretical and experimental aspects of the application of NMR to liquid crystals.

Another recent review article, by Saupe and Maier [118], deals with the methods (including NMR) of studying the degree of ordering in nematic crystals.

4. SOME PROPERTIES OF LIQUID CRYSTALS

Smectic crystals are always uniaxial and positive. A smectic substance, pressed between a microscope glass slide and cover slip, can form large homogeneous areas within each of which the optic axes of the molecules are uniformly oriented (homeotropic texture). Each of these areas is effectively a liquid single crystal.

At temperatures close to the smectic → isotropic liquid transformation point, differences in the strength of attachment of the molecules to the glass surface may cause the smectic layers to move or become disturbed, giving a focal-conic texture (Fig. 9). A discussion of focal-conic textures can be found in the literature [5,119].

When the isotropic melt of a smectogenic compound is cooled, the liquid crystals adopt the shape of elongated rods ["bâtonnets" (Ed. of Translation)] which coalesce at the points of contact, producing spherical bulges at the points of coalescence of a small rod with a larger one (Fig. 10).



Fig. 9. Focal-conic texture. Ethyl *p*-azoxybenzoate. Crossed Nicols.



Fig. 10. Smectic rods of cholesteryl palmitate. Crossed Nicols.

The lack of sphericity of these smectic droplets suggests that their surface tension is anisotropic. On further cooling the rods coalesce completely to form the focal-conic texture.

Smectic liquid crystals produced lyotropically give rise to the same textures. The liquid-crystalline texture shown in Fig. 11, for example, was produced by evaporation of an aqueous alcoholic solution of potassium oleate. It was shown to be stable only between definite limits of concentration and temperature: at higher soap concentrations the texture begins to separate into layers, and gives a slightly different type of focal-conic texture[120] (Fig. 12).

The *nematic* type of liquid crystals can be classified‡ into *true nematic* and *cholesteric* forms. In true nematic liquid crystals dark filaments are visible. If the threads are arranged normally to the slide and coverslip they appear as dark spots, nuclei from which dark lines are seen to radiate when the specimen is viewed between crossed Nicols in a polarising microscope (see Fig. 13*a*). By analogy with dislocations in crystals, these threads can be called dislocation lines, since the orientation of the molecules suffers a sharp discontinuity at these features.

Nematic liquid crystals are uniaxial and positive. They do not rotate the plane of polarisation, but optical activity can be induced by mechanical distortion of the liquid-crystalline specimen.

The cholesteric liquid crystals are thus named because derivatives of cholesterol are this type (Fig. 13*b*). Cholesteryl benzoate, in which liquid crystals were first observed[1], gives cholesteric liquid crystals with $t_1 = 146°$ and $t_2 = 178.5°$.

Amyl cyanobenzalaminocinnamate ($t_1 = 95°$, $t_2 = 105°$) is an example of a cholesteric compound not chemically related to cholesterol.

Cholesteric liquid crystals are uniaxial, negative, and strongly optically active (up to 200 complete rotations of the plane of polarisation per 1 mm thickness). These properties stem from the structure of the liquid crystals, which is twisted in a direction perpendicular to the long axes of the molecules, thus permitting some measure of stratification, which ultimately leads to a focal-conic texture. The pitch of the twisted structure (equal to the thickness of the resulting layers) is of the order of 1000 Å.

The optical properties of liquid crystals can be studied only if the specimens are suitably oriented. Chatelain[121-125] has worked out a simple and reliable method of producing nematic single crystals, by melting the sample between a slide and cover slip previously rubbed with a sheet of paper in a definite direction. This treatment produces a single crystal with its optic axis in the direction of rubbing.

Chatelain and his coworkers used this technique to study the scattering of light by nematic structures, and also the refractive index. Measurements of the refractive index of PAA, summarised in Table 15, show that the enormous birefringence of the liquid crystal decreases gradually on raising the temperature towards the point of transformation

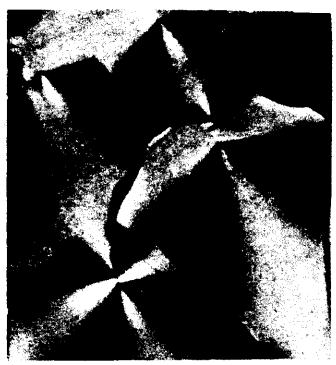


Fig. 11. Liquid-crystalline texture of potassium oleate between slide and cover slip. Crossed Nicols.



Fig. 12. Liquid-crystalline texture obtained by disrupting the texture of Fig. 11. Crossed Nicols.



Fig. 13. *a*) *p*-Azoxyanisole in the liquid-crystalline state. Crossed Nicols. *b*) Cholesteryl cinnamate, showing the focal-conic texture. Crossed Nicols.

‡ The assignment of cholesteric mesophases to the general nematic type, originally due to Friedel[5], is far from universally accepted (Ed. of Translation).

TABLE 15. Refractive indices of liquid crystals of *p*-azoxyanisole. n_0 = ordinary refractive index; n_e = extraordinary refractive index.

Temperature, °C	589 mμ		546 mμ		Temperature, °C	589 mμ		546 mμ	
	n_0	n_e	n_0	n_e		n_0	n_e	n_0	n_e
105	1.558	1.875	1.568	1.907	122	1.564	1.836	1.574	1.872
110	1.559	1.865	1.569	1.898	125	1.566	1.825	1.576	1.862
114	1.560	1.856	1.570	1.890	128	1.569	1.814	1.578	1.850
117	1.561	1.849	1.571	1.884	130	1.571	1.806	1.581	1.843
120	1.563	1.842	1.572	1.877	132	1.576	1.795	1.584	1.833

into isotropic liquid, and suddenly drops to zero at the transformation point.

Studies of the *absorption spectra* of PAA liquid crystals revealed a closer similarity to the solid state than to the isotropic liquid state. The solid and the liquid crystals have an absorption band at 1247 cm^{-1} which is not observed in the isotropic liquid. Differences in the absorption spectra of the solid, liquid-crystalline, and isotropic liquid states [126-128] have been reported also for a number of other substances, both in the visible [126-128] and in the infrared [129-131] and ultraviolet [132] regions of the spectrum.

An anomalous change in *viscosity* has been observed [133-136] near the point of transformation from liquid crystal to isotropic liquid (Fig. 14). Bose [137] ascribes this phenomenon to anisotropy of the viscosity of the liquid-crystalline particles.

Kast and Becherer [138] measured the viscosity of PAA, and reported a linear variation of viscosity with temperature in the liquid-crystalline and the isotropic liquid states, with a sudden discontinuity from 0.0317 to 0.0254 C.G.S. units at the transformation point.

Owing to the anisotropy of viscosity, the rate of flow of liquid crystals through capillaries can be altered by applying an electric or magnetic field [139-143]. Measurements of the anisotropic viscosity of PAA liquid crystals, flowing through a capillary in the presence of a magnetic field and at 122°, gave the following values [139]: $\eta_1 = 0.024$ (molecules parallel to the flow direction); $\eta_2 = 0.092$ (molecules parallel to the velocity gradient); $\eta_3 = 0.034$ (molecules perpendicular to the velocity gradient).

The application of a magnetic field in the same direction as the electric current has been shown [144,145] to increase the electrical conductivity of liquid crystals. It follows that the *electrical conductivity* of a substance in the liquid-crystalline state is anisotropic, with a maximum in the direction of the long axes of the molecules.

Anisotropy of the electrical conductivity has recently been observed, and widely studied, in lyotropic liquid crystals (anisotropic soap solutions) oriented between a fixed and a rotating cylinder [146-149].

Kast [150] showed that the dielectric constant of liquid crystals is affected by a magnetic field, and made a quantitative study of the effect. Several investigators have discussed the dielectric constant [8,150,155]. Typical changes in dielectric constant and dielectric anisotropy are plotted in Fig. 15. [156]

Foix and Royer [157] reported that PAA is diamagnetic, and that the liquid crystals are more weakly diamagnetic than either the solid crystals or the isotropic liquid. The molecules therefore show *anisotropic diamagnetism*. The magnetic susceptibility at constant magnetic field [158] is plotted against temperature in Fig. 16.



Fig. 14. Anomalous change in viscosity at the temperature of the transformation between isotropic liquid and liquid crystals (after Vorländer).

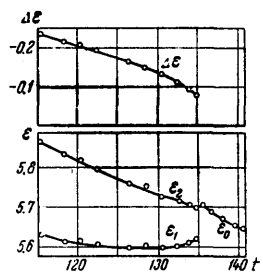


Fig. 15. Temperature dependence of the dielectric constants ϵ_1 and ϵ_2, and of the dielectric anisotropy $\Delta\epsilon$, for *p*-azoxyanisole. The ϵ_0 curve refers to the isotropic melt.

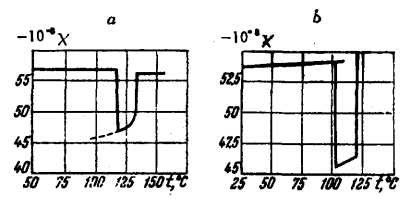


Fig. 16. Effect of temperature on the magnetic susceptibility in a constant magnetic field for: *a*) *p*-azoxyanisole (nematogenic); *b*) ethyl *p*-azoxybenzoate cooled from the isotropic melt (smectogenic).

Systematic studies of the electrical and magnetic properties of liquid crystals, and of their molecular structure, were carried out in Leningrad by Frederiks and his team of physicists [159-163]. More detailed treatments of the properties of liquid crystals are given in the previously mentioned reviews [3-11].

In conclusion, it can truly be said that transformation into the liquid-crystalline state causes important changes in the physical properties of a system.

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VIBRATIONAL SPECTRA OF COMPOUNDS CONTAINING ELEMENTS OF THE CARBON SUBGROUP

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CONTENTS

I. Introduction 510

II. Compounds containing an E–H bond (E = Si, Ge, Sn) 510

1. Compounds of the type EH_4 (E = C, Si, Ge) 510

2. The E–H bond in halogeno-derivatives (E = C, Si, Ge) 511

3. Alkyl, alkenyl, and alkenylalkyl derivatives containing an E–H bond (E = Si, Ge, Sn) 511