Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthetic Chemistry Related to Liquid Crystals

G. W. Gray [a]

[a] Department of Chemistry, The University of Hull, Yorkshire, England

Version of record first published: 21 Mar 2007.

To cite this article: G. W. Gray (1973): Synthetic Chemistry Related to Liquid Crystals, Molecular Crystals and Liquid Crystals, 21:1-2, 161-186

To link to this article: http://dx.doi.org/10.1080/15421407308083317

Molecular Crystals and Liquid Crystals. 1973. Vol. 21, pp. 161–186

Synthetic Chemistry Related to Liquid Crystals†

G. W. GRAY

Department of Chemistry
The University of Hull
Yorkshire, England

Received September 22, 1972

Abstract—Because of the continued escalation of interest in liquid crystals and in their applications in display devices, the efforts of organic chemists have recently been concentrated on the synthesis of better mesogens for technological exploitation. Therefore, although the stability of available liquid crystal materials, their electrical properties and their applications will provide topics for other sections of this meeting, I feel that a review of those factors which have motivated synthetic chemists over the last two years must be given now even though some overlap may in consequence arise. I will therefore survey briefly some electro-optical effects now under active consideration with the aim of illustrating why the attention of the chemist is directed towards particular types of mesogen with particular characteristics. Whereas at one time the aim was simply to produce nematogens giving nematic mesophases in the room temperature range so that their dynamic scattering characteristics could be studied, the need is now for a wider range of mesogens with different physical properties. The reasons are that dynamic scattering, once the most widely studied electro-optical effect, is now realized to have some drawbacks, and this has led to the development of other electro-optical effects of potential and real value in display devices.

I will consider five electro-optical effects:

1. The Fréedericksz Effect (F.E.)
2. The Dynamic Scattering Effect (D.S.E.)
3. The Twisted Nematic Effect (T.N.E.)
4. The Cholesteric Memory Effect (C.M.E.)
5. The Cholesteric–Nematic Phase Change Effect (P.C.E.)

1. The Fréedericksz Effect (F.E.)

Although claims have been laid to the discovery of this effect quite recently, the effect is based essentially on experimental observations made by Fréedericksz over forty years ago, and it seems fitting to

---

† Plenary Lecture presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

describe the effect by his name. For this effect, we might have the lath-like molecules oriented perpendicular to the conducting surfaces of the cell and make these turn through 90° on applying the field (Fig. 1).

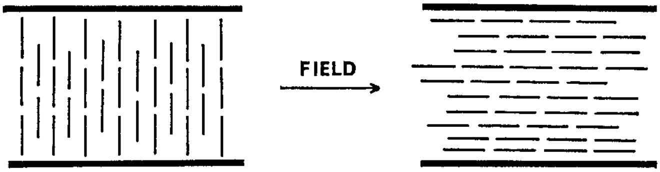


Figure 1. Fréedericksz Effect: long molecular axes turned through 90° on application of the field ($\epsilon_{\parallel} - \epsilon_{\perp}$ = negative).

The dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) required is therefore negative, the driving force is the field, and the effect is made visible using polarizers. Naturally, the opposite effect could be achieved, i.e., going from right to left in Fig. 1 on applying the field, starting with an alignment of the molecules parallel to the surfaces and material of positive dielectric anisotropy. In both cases, a nematic liquid crystal is of course involved.

2. **The Dynamic Scattering Effect** (D.S.E.)

This well known effect was first discussed in detail by Heilmeier(1) in 1968. In the relaxed state the lath-like molecules in thin films of a nematic liquid crystal lie statistically in parallel alignment in localized areas, and thin films up to a few hundred microns in thickness are quite transparent. Transparency is further improved if the nematogen is oriented with respect to the surfaces, e.g., with the long molecular axes perpendicular to the surfaces as in Fig. 1. (left). If the nematogen is of negative dielectric anisotropy, although this should not be too high, and conducting (with a resistivity of less than say 10^{10} ohm cm) continued application of a field across such a film gives a strong turbulence forming a large number of scattering centres. This turbulence arises through conductance by the nematic phase and the mechanism and the role of ions and space charge have been discussed by several investigators.(2,3,4) The practical outcome is that the cell changes from a clear OFF state to a cloudy ON state.

Materials of high resistivity can be doped to achieve a suitable conductivity for dynamic scattering.

3. The Twisted Nematic Effect (T.N.E.)

This now familiar effect was first reported by Schadt and Helfrich(5) and used by Fergason in his Ilixco Cell. The cell is constructed so that the long molecular axes of the nematogen are oriented parallel to the conducting glass surfaces, the orientation at one plate being perpendicular to that at the other. The director therefore turns continuously through 90° across the sample thickness. With molecules of positive dielectric anisotropy, the long axes turn round on application of the field so that they lie perpendicular to the plates. The effect of the twisted film on plane polarized light is therefore changed in the ON state which is essentially homeotropic and extinct between crossed polarizers.

4. The Cholesteric Memory Effect(6) (C.M.E.)

For this a conducting cholesteric liquid crystal of negative dielectric anisotropy is required. The OFF state consists of the relatively transparent plane texture of the cholesteric mesophase, with

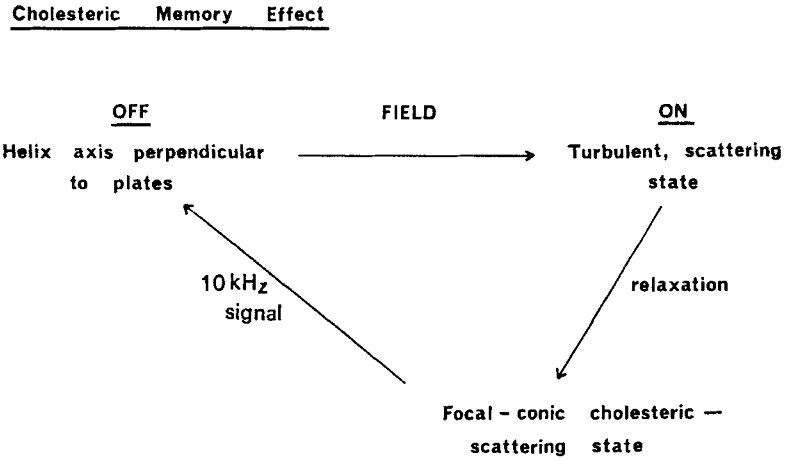


Figure 2. A summary of the changes involved for the cholesteric memory effect.

the helix axis perpendicular to the conducting surfaces and to the molecular long axes. Regarding this effect as the cholesteric analogue of dynamic scattering, conduction produces a turbulent, scattering ON state (Fig. 2) which on switching off the current relaxes to the opaque scattering, " focal-conic " texture of the cholesteric phase. This reverts only slowly—hence the memory effect—to the transparent plane texture, unless the phase is disturbed by a movement of one of the supporting surfaces or by say a 10 kHz signal. Thus, we require material of negative dielectric anisotropy which is conducting, i.e., the resistivity must not be too high (say $< 10^{10}$ ohm cm), and this may be achieved by doping high resistivity materials.

5. The Cholesteric-Nematic Phase Change Effect(7) (P.C.E.)

The required conditions here are that the helix axes lie at least approximately parallel to the conducting surfaces. The orientation need not be uniform as shown diagrammatically in Fig. 3 and the " focal-conic " texture of a cholesteric phase will suffice. The film is then opaque or scattering. If the cholesterogen is of positive dielectric anisotropy and of high resistivity, an applied field will turn the molecular long axes perpendicular to the glass surfaces, effectively unwinding the helix. The cholesteric phase therefore changes to nematic. In the OFF state, relaxation gives the scattering " focal-

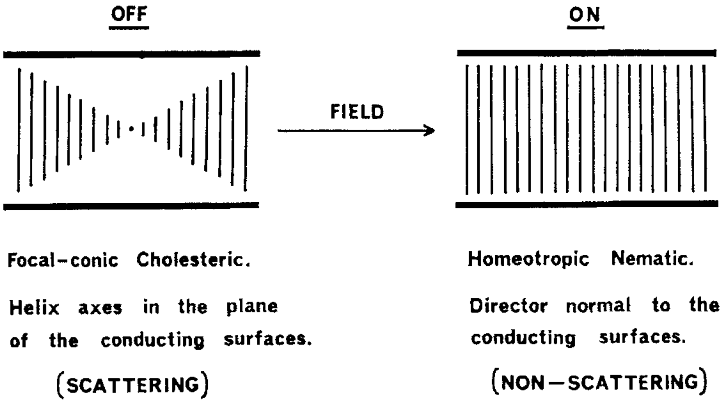


Figure 3. Operation of cholesteric-nematic phase change effect—($\epsilon_{\parallel} - \epsilon_{\perp}$ = positive).

conic " cholesteric state. The effect is a field effect and visibility is because of the change from a scattering to a clear ON state.

The essential factors emerging from these considerations are summarized in Table 1. The first three lines relate to the dielectric anisotropy of the material, the driving force for the effect and the reasons for its visibility. The fourth line relates to factors that determine lifetime in D.C. operation, and the next two lines give some typical rise and decay times, although considerable variation arises in the values reported in the literature for these two characteristics.

This table shows that for these electro-optical effects we require:

(a) Both nematogens and cholesterogens.

(b) Cholesterogens of TWO types:
  (i) $\epsilon_{\parallel} - \epsilon_{\perp}$ should be negative for the Cholesteric Memory Effect, for which conductance is needed. Therefore materials of fairly low resistivity are needed or preferably pure materials to which dopants have been added
  (ii) $\epsilon_{\parallel} - \epsilon_{\perp}$ should be positive and the resistivity high for the Phase Change Effect.

(c) Nematogens of TWO types:
  (i) $\epsilon_{\parallel} - \epsilon_{\perp}$ should be negative and the material should be of high resistivity for the Fréedericksz Effect. For the Dynamic Scattering Effect, $\epsilon_{\parallel} - \epsilon_{\perp}$ should again be negative, but conductance is required, so that low resistivity materials or pure materials with added dopants are needed.
  (ii) $\epsilon_{\parallel} - \epsilon_{\perp}$ should be positive and the material should be of high resistivity for the Twisted Nematic Effect.

Although I do not presume to give any comparative assessment of the merits of these various electro-optical effects, considering the situation in this way does help to focus the attention of the chemist on several important characteristics that are required of the mesogens. However, we must remember that other requirements are also essential if the mesogens are to be of real practical value in devices.

Other requirements for mesogens: The mesogens must be

(a) *low melting.* The C—N temperature should be −20 °C or lower and the nematic/cholesteric phase should persist until at least 65 °C.

Table 1. Summary of Requirements for Some Electro-optical Effects

MESOPHASE:	NEMATIC			CHOLESTERIC		
Effect	F.E.	D. S. E.	T. N. E.	C. M. E.		P. C. E.
				Write	Erase	
Driving force	Field	Current (doping)	Field	Current (doping)	Field	Field
$\varepsilon_{\parallel} - \varepsilon_{\perp}$	Neg.	Neg.	Pos.	Neg.		Pos.
Visibility	Polarising	Scattering	Polarising	Scattering		Scattering
D. C. life	Surface alignment	Material	Surface alignment	Material		Material
Rise time	> 10ms	> 10ms	>100 μs	> 10 ms	—	> 30 μs
Decay time	> 100ms	> 50ms	> 100 ms	—	> 100 ms	> 50 μs

(b) *chemically stable* to hydrolysis, oxidation etc.

(c) *photochemically stable*—resisting photochemical polymerization, rearrangement, and racemization in the case of cholesterogens.

(d) *electrochemically stable.*

(e) *safe chemicals* that do not constitute a health hazard to those handling them during manufacture or repair of cells.

These add up to a formidable specification for the ideal mesogens for device fabrication, and it is not surprising that seemingly no materials are yet satisfactory in all respects.

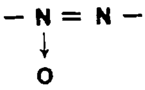
The approach to the main problem of achieving the required low melting point has been the obvious one of preparing compounds with simple structures that are also consistent with mesomorphic properties. Since, with the exception of the cholesteryl *n*-alkanoates and related esters, no aliphatic compounds have useful liquid crystal properties, and no nematic/cholesteric compounds contain only one *p*-phenylene ring (the *p*-*n*-alkoxybenzoic acids are dimers), attention has been centred on compounds containing two *p*-phenylene rings linked through a central group A—B which often involves a double or a triple bond to preserve the rigidity and linearity of the molecules—examples are shown below:

e.g., X = n-alkyl and Y = n-alkoxy or <u>vice versa</u>;

X and Y = n-alkyl

A — B = —CH=N— **Azomethines**

—N=N— **Azo-compounds**



$-\underset{\downarrow \atop O}{N}=N-$ **Azoxy-compounds**

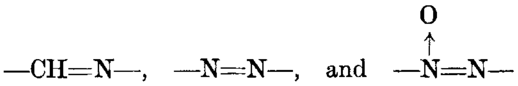
—CH=CH— **Stilbenes**

—C≡C— **Tolanes**

The *p*-substituents X and Y may vary in nature considerably, but the lowest C—N temperatures have been achieved with

X = *n*-alkyl and Y = *n*-alkoxy or *vice versa*, or
X and Y = *n*-alkyl groups.

For the central groups



$$\text{—CH=N—},\quad \text{—N=N—},\quad \text{and}\quad \text{—}\overset{\overset{\displaystyle O}{\uparrow}}{\text{N}}\text{=N—}$$

the position regarding the thermal ranges of the nematic phases has been assessed very thoroughly by van der Veen and de Jeu of the Phillips Research Laboratories at Eindhoven.(8,9,10) With constant end groups X and Y, the N—I temperatures change in the order

$$\begin{array}{ccccc} \text{azoxy} & > & \text{azo} & \approx & \text{azomethine} \\ \text{(slightly twisted)} & & \text{(planar)} & & \text{(twisted)} \end{array}$$

This is attributed to a combination of effects involving primarily the changes in anisotropy of molecular polarisability and in stereochemistry along the series.

Knaak, Rosenberg and Servé(11) have also reviewed statistically the N—I temperatures in the literature for a large number of azo- and azoxy- compounds and azomethines, and have been able to assign different parameters for the effects of various central groups on the N—I temperatures, relative to the azo-group. The parameters are:

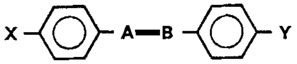
azoxy (+21), azo (0), azomethine (−9)

The azoxy compounds are therefore best, giving the most thermally stable nematic phases. It should however be noted that N—I temperatures quoted for unsymmetrically disubstituted azoxy compounds often relate to the mixture of isomers formed from the substituted aniline on oxidation with H_2O_2, but, in cases where both isomers have been isolated,(12,13) the N—I temperatures are similar to one another and also to that for the eutectic mixture.

Attempts to correlate C—N temperatures with structure for these systems and many others have had a notable lack of success, and only qualitative observations that a terminal group such as *n*-butyl, *n*-pentyl or n-hexyl often results in low melting points have emerged. The results in Table 2 show that the trends discussed above for N—I temperatures are followed, but that no clear trends for C—N temperatures occur.

It is noted again that when mixtures of two unsymmetrically disubstituted azoxy-compounds are under consideration, much lower C—N temperatures are involved than those for the pure isomers. This can lead to confusion. Thus a mixture of the isomeric azoxy compounds given in lines 1 and 2 of Table 2 has C—N, 16° and N—I, 76 °C. Failure to detect smectic phases also leads to erroneous conclusions based on literature melting points. This is particularly true for azomethines, e.g., the compound with X = *n*-butyl and Y = *n*-butyl is quoted⁽¹⁰⁾ as having a m.p. of 7 °C, but the phase formed is smectic.⁽¹⁴⁾

Table 2. Melting Points and N-I Temperatures for some Mesogens



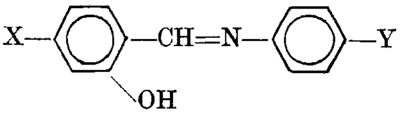
	A—B	$-N{=}N-$		$-\underset{\overset{\downarrow}{O}}{N}{=}N$		$-CH{=}N-$	
X	Y	C–N or I	N–I	C–N	N–I	C–N or I	N–I
CH_3O	C_4H_9	32	48	42	77	20	47*
C_4H_9	OCH_3	32	48	41	74	46	49
C_2H_5O	OCH_3	134	[131]	96	154	123	[121]
C_4H_9	C_4H_9	26	-	14	28	-	-
C_5H_{11}	C_5H_{11}	49	[38]	22	65	-	-
C_6H_{13}	C_6H_{13}	38	[18]	22	50	-	-

All transition temperatures are in °C.
Values in parenthesis are for monotropic transitions.
Data for the first three compounds are from ref. 11.
Data for the last three compounds are from ref. 10.
* More usually quoted as C-N, 22 and N-I, 47.5°C.

However, because azoxy compounds give the highest N—I temperatures of the three types of compound being considered, alkyl groups may be used for both X and Y, whilst preserving nematic properties. With X = Y = alkyl, the problem of isomers does not arise, and useful single component, purely nematic systems are obtained. Thus (Table 2) with X and Y = *n*-pentyl or *n*-hexyl, compounds with C—N temperatures as low as that usually quoted for MBBA are obtained. With X and Y = *n*-butyl, the C—N temperature is still lower, but the N—I temperature is also well down.

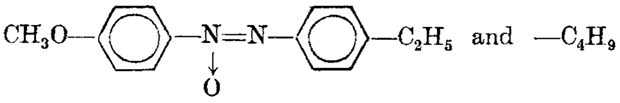
The azo- compounds appear to be the least satisfactory, having the lowest N—I temperatures and being highly coloured, unstable to oxidation and prone to isomerize. The azomethines are less coloured, of negative dielectric anisotropy and very readily prepared. Moreover, when mixed with other mesogens, lower melting nematogenic mixtures are easily attained. Thus, mixtures of MBBA and EBBA feature in several experimental and commercial dynamic scattering devices. However, Schiff's bases have several disadvantages. They are unstable to oxidation and hydrolysis, they may polymerize and aromatic amines (potentially toxic materials) are amongst their decomposition products. Further, mixtures of two differently disubstituted azomethines, in the presence of traces of moisture, will, through breakdown and recombination, give an equilibrium mixture of the four Schiff's bases possible. The composition of such a mixture will therefore be liable to change with change in conditions. Furthermore, though easy to make, azomethines are not easy to purify because of their chemical instability. In this connection it must be appreciated that the ability of azomethines to give dynamic scattering is dependent on their purity (resistivity). Thus, impure azomethines dynamic scatter well, but do so only because uncontrolled amounts of variable impurities are present. Only now that pure, high resistivity azomethines are available which do not dynamic scatter unless controlled quantities of known dopants are added, can consistent data be expected on dynamic scattering behaviour. MBBA can readily be purified by crystallization and drying over P_2O_5 to a resistivity of 1.6×10^{11} ohm cm. This dynamic scatters only weakly, but if the resistivity is raised to 2×10^{11} (e.g., that of MBBA supplied by the Vari-Light Corp.) dynamic scattering does not occur. Techniques such as electrodialysis, molecular distillation, zone refining and azeotropic distillation of impurities may be used to further purify azomethines.

It is noted that azomethines with an *ortho*-hydroxy group, e.g., of the type studied by Labes *et al.*,⁽²⁰⁾

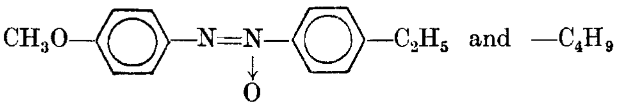


are more chemically stable and more is to be said on such systems at this meeting.

However, azomethines in general do have real faults, and azoxy-compounds, being more stable, are superior except in so far as they are quite coloured. This problem has been neatly reduced in seriousness by Merck, who by the use of suitable additives to their Merck Phase V, a eutectic quaternary mixture of



C—N, -5 °C; N—I, 75 °C

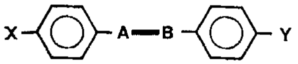


have produced a chemically stable, room temperature nematic (Merck Phase VI) that spontaneously adopts a homeotropic alignment on glass and thus gives a clear and much less coloured film. The dielectric anisotropy is -0.6 and the phase dynamic scatters well. Although doubts have been expressed⁽¹⁵⁾ about the photochemical stability of azoxy compounds, Merck appear by this elegant method to have largely overcome the problem of colour and so have promoted azoxy compounds to a superior position above azo-compounds and azomethines for dynamic scattering device fabrication.

Earlier than this, attempts were made to overcome the problems of the chemical instability of Schiff's bases and of colour by investigating the use of other central groups, A—B. The use of —CH=CH— and —C≡C— functions (see Table 3) should be mentioned. The tolanes were investigated by Malthète, Leclerq, Gabard, Billard and Jacques⁽¹⁵⁾ and the stilbenes by Young, Aviram and Cox.⁽¹⁶⁾ Such compounds are colourless, and with the tolanes (Table 3) quite low

C—N temperatures and reasonable nematic ranges were obtained. A eutectic mixture of the two tolanes listed in Table 3 had C—N, 13°; N—I, 64 °C. These tolanes have positive dielectric anisotropy and are claimed to be stable, although it is not clear whether this refers to chemical or photochemical stability or to both.

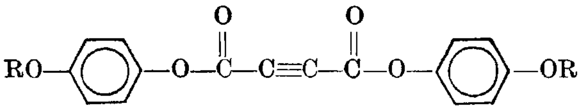
Table 3. Melting Points and N–I Temperatures for some Tolanes and Stilbenes



A—B	X	Y	C–N or I (°C)	N–I (°C)
$-C\equiv C-$	CH_3O	C_7H_{15}	39	54
	C_2H_5O	C_8H_{17}	47.5	73.5
$-CH=CH-$	C_3H_7O	C_3H_7O	198	-
	CH_3O	C_3H_7O	177	[161]
	CH_3O	$C_8H_{17}O$	151	[146]
$-CH=\underset{\underset{Cl}{\mid}}{C}-$	C_2H_5O	C_4H_9	29 (31)*	58 (58)*
	C_2H_5O	C_8H_{17}	32 (34)*	61 (62.5)*

Temperatures in square brackets are for monotropic transitions.
* Results obtained by Young, Aviram and Cox[16] are followed in round brackets by results obtained at Hull University.[18]

More recently,⁽¹⁷⁾ derivatives of acetylene of the following type have been examined, where R = *n*-alkyl.



None is particularly low melting, but the materials are said to dynamic scatter and are presumably negative in dielectric anisotropy.

Stilbenes (without α- or β- or *o*-substituents) are planar molecules, and, as shown by the data in Table 3 for some 4,4′-dialkoxy-trans-stilbenes, they have fairly high C—N temperatures and tend to give monotropic nematic phases. Young, Aviram and Cox,⁽¹⁶⁾ reasoning that α-, β- or *o*-substituents would twist the molecules, prepared a range of such substituted stilbenes. Included in Table 3 are the two lowest melting nematogens that they reported; a eutectic mixture of 60: 23 mole % of the butyl and octyl stilbenes gave C—N, 8°; N—I, 59 °C. Preparation of these α-chlorostilbenes involves some relatively low yield steps, and as reported by Young *et al.*, column chromatography is essential for purification of the compounds. The final low temperature crystallization procedure (light petroleum, b.p. 60–80 °C at − 78 °C) they report is an excellent purification step. As can be seen, we have fully corroborated the results of Young *et al.* The resistivities obtained were excellent (10^{13} ohm cm) and dynamic scattering did not occur without dopants. The compounds do have excellent chemical stability, but in sunlight or UV light, the resistivities fall quickly. We find that light of <400 nm causes this problem, and even exposure of the nematic melts to fluorescent light caused them to turn red. Thus the problem is photochemical not electrochemical instability. Cells using α-chlorostilbenes would apparently have to use glass opaque to light <400 nm, but the use of say yellow glass would negate the value of the compounds being colourless.†

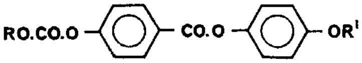
Earlier still, Castellano, McCaffrey and Goldmacher(19) approached these general problems of colour and stability by using the more flexible bridging group —CO.O— in 4,4′-disubstituted phenyl benzoates.

Reflecting the greater flexibility of this bridging group, Knaak, Rosenberg and Servé assign the parameter − 35 to the —CO.O— function relative to —N═N— = 0 (see Table 2). Thus, Castellano *et al.* found that one *n*-alkyloxycarbonyloxy terminal group was desirable. In Table 4 are given the lowest melting nematogens which they made together with results we obtained at Hull during studies of the merits of these systems.

Quite significant discrepancies occur between the two sets of data. There is no problem over the C—N temperatures of compound 2, which is dimorphic. We always obtained a predominance of the higher melting form. The other discrepancies might be explained, as suggested to me by Dr. Steinstrasser, if the esters of Castellano *et al.* contained some *diesters* arising from contamination of the

† It was subsequently pointed out that an alternative to a yellow glass filter is provided by a film of relatively colourless polymer opaque to light of 400 nm, thus restoring the advantage of the colourless nature of α-chlorostilbenes.

Table 4. Melting Points and N—I Temperatures for 4,4'-Disubstituted Phenyl Benzoates



where R and R' are n-alkyl groups

			Castellano et al.[19]		Gray et al.[18]	
No	R	R'	C-N (°C)	N-I (°C)	C-N (°C)	N-I (°C)
1	C_6H_{13}	C_6H_{13}	43	84	45	73.5
2	C_6H_{13}	C_7H_{15}	36	54	36 or 45.5	73
3	C_5H_{11}	C_5H_{11}	45	85	49	69.5
4	C_5H_{11}	C_6H_{13}	42	76	45.5	73.5
5	C_5H_{11}	C_7H_{15}	47	72	48.5	72
1:2	40:60		27	73	38-41	73-73.5
3:4:5	20:40:40		24	76	28-32	72-72.5

intermediate quinol half ethers with quinol itself. This could explain the lower C—N temperatures and the substantially higher N—I temperatures obtained in some cases. We found chromatographic purification of the esters was essential and obtained excellent analytical, spectroscopic and mass spectrometric corroboration of the structure and purity of our compounds. We were interested solely in preparing the binary and ternary eutectic mixtures given in Table 4, and it should be noted that these are the only compounds of the very large number studied by Castellano *et al.* that we have examined. As can be seen, higher melting and less interesting eutectic mixtures are given using our compounds.

Finally, with respect to these compounds, Fig. 4 reproduces plots of the N—I temperatures against alkyl chain length for two of the series worked on by Castellano *et al.* Superimposed as full points are the N—I temperatures we have obtained. It seems clear that better approximations to regular alternations of the temperatures are obtained using our results, and this lends support to these new values.

Despite the low parameter(11) for the —CO.O— function, we have examined a few more simply disubstituted phenyl benzoates with the results given in Table 5.

On the basis of these four esters only, the parameter of −35 would

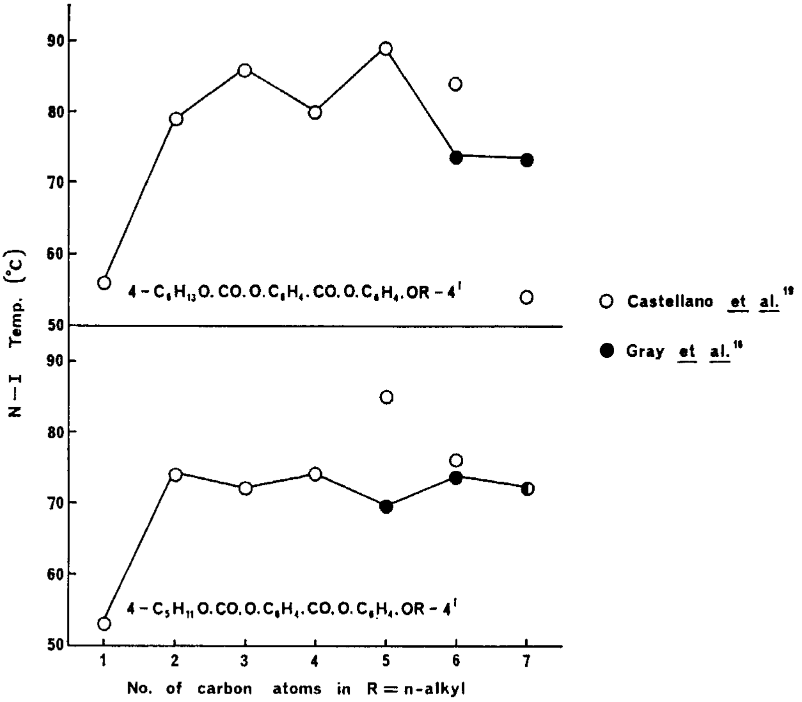
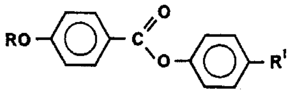


Figure 4. Plots of N—I temperatures against alkyl chain length for the carbonate esters indicated.

Table 5. Melting Points and N-I Temperatures for some 4,4'-Disubstituted Phenyl Benzoates



n-Alkyl R	R'	C-S, N or I (°C)	S-N (°C)	N-I (°C)
CH_3	C_3H_7	63	-	[40]
CH_3	C_4H_9	41.5	-	[25]
C_7H_{15}	C_3H_7	64.5	-	[<60.5 *]
$C_{10}H_{21}$	C_3H_7	59.5	62.5	66

Temperatures in parenthesis are for monotropic transitions.

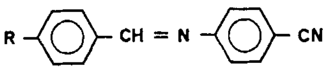
* Exhibits a nematic phase, but supercooling of the amorphous melt was insufficient for an accurate I—N temperature to be measured.

seem to be on the high side (numerically), but it should be emphasized that this value was derived statistically from a much wider range of esters. At any rate, the results show that such simple esters are capable of giving nematic melts; these dynamic scatter and the dielectric anisotropy is negative. These investigations have not been pursued further since we learned some months ago that Steinstrasser(21) has worked more extensively on such systems and I believe will present a paper at this meeting describing interesting eutectic mixtures prepared from these and other closely related compounds. A recent report by Young, Haller and Green(39) has also appeared on ring-methylated phenyl benzoyloxybenzoates.

Cyano-substituted Mesogens

Materials of the types discussed so far, dependent on their dielectric anisotropies are suitable mainly for devices based on the D.S.E. or the F.E. A stronger, positive dielectric anisotropy is required for the T.N.E. as provided by compounds of the type shown in Table 6 and first patented by Castellano.(38) Schadt and Helfrich(5) employed a 1:1:1 molar ratio of the azomethines with R = n-$C_6H_{13}O$—, n-C_4H_9O— and n-$C_7H_{15}CO.O$— having C—N *ca.* 20° and N—I, 94 °C. With reference to their preparation, these Schiff's bases do not form readily from 4-aminobenzonitrile in boiling ethanol. We have found boiling propan-2-ol is an excellent reaction medium in which complete Schiff's base formation occurs in 20 minutes without

Table 6. Physical Data for some Cyano-substituted Schiff's Bases



R	C–N (°C)	N–I (°C)	ΔH(kcal mol^{-1}) C–N	ΔH(kcal mol^{-1}) N–I	Resistivity** (ohm cm)
n-$C_6H_{13}O$*	56.5 & 61.5 (56.5)	102 (101.5)	5.32	0.14	1.6 x 10^{10}
n-C_4H_9O	65 (64.5)	108 (108.5)	8.02	0.15	1.7 x 10^{9}
n-$C_7H_{15}CO.O$*	53 & 60 (54)	96.5 (98)	8.18	0.18	10^{10}

* These compounds may exist in two crystal forms with different C–N transition temperatures.

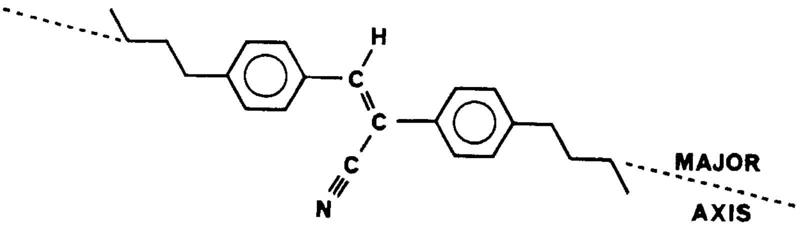
** Measured at 65-70°C; equivalent to resistivities of 1.7 x 10^{10} - 1.6 x 10^{11} ohm cm at 25°C.

Temperatures in round brackets are those obtained by Scherrer.[23]

acid catalysis. Like most Schiff's bases, the compounds are difficult to obtain of really high resistivity and purity by crystallization alone; the results in Table 6 are those obtained at Hull.(22)

Mixtures of such cyano-azomethines with other low melting mesogens (even though these are of negative dielectric anisotropy) may be used to obtain lower melting mixtures than that referred to above. With a suitable concentration of cyano- compound, these give the T.N.E. These compounds of course suffer from the inherent disadvantages of azomethines, although, since the effect is a field effect, materials of the highest attainable resistivity may be used. Thus, without the need for dopants to produce conduction, the risks of cell breakdown through chemical failure are probably smaller. Details of better materials of positive dielectric anisotropy will however no doubt soon be published.

The cyano group may also be used to obtain a *negative* dielectric anisotropy. Thus in the α-cyano-stilbenes, we have shown by



n-$C_6H_{13}O$	C—N, 60·5 °C N—I, 70 °C	OCH_3

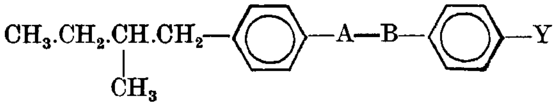
N.M.R. that the two phenyl groups are trans, so that the cyano-group contributes to the component of the molecular polarizability acting at right angles approximately to the major molecular axis.(24) As shown by the one example quoted above, quite low melting compounds may be achieved, suggesting that the twisting effect proposed by Young *et al.* acts here also. Compounds of this kind seem worth exploring, but again some overlap of thinking has occurred, as I believe that van der Veen will present a paper on α-cyanosubstituted azomethines at this meeting.

Heterocyclic Mesogens

The search for information on the effects of molecular structural change on liquid crystal properties of mesogens has led inevitably to studies of the effects of replacing benzenoid rings by various heterocyclic rings; these replacements have been made both for terminal and central rings in the molecules. Following earlier work by Young, Haller and Aviram(25) and Schubert,(26) results obtained for Schiff's bases containing nitrogen heterocycles have appeared recently.(27,28) At Hull we have been examining the effects of introducing heterocyclic rings not only into Schiff's bases, but also into stilbenes and esters. Since we are presenting a paper(29) on this work at this meeting and as Professor Schubert is also to speak on heterocyclic mesogens, I feel it is unnecessary for this area to be reviewed here.

Cholesteric Mesogens

For the last two electro-optical effects listed in Table 1 (C.M.E. and P.C.E.) cholesterogens are required. If a single component cholesteric mesophase is needed, then a pure optical enantiomer of a nematogen must be used. Apart from using suitable derivatives of optically active alcohols such as cholesterol and other sterols, one may achieve this end by having an asymmetric carbon in a suitably branched alkyl chain present say as a terminal substituent in the molecule, e.g.,

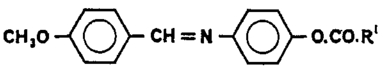


If the racemic modification of the compound is a nematogen with good properties, e.g., low melting point, high N—I temperature, high resistivity and a given sign of anisotropy of the molecular polarizability, then each diastereoisomer will have the same characteristics but will give a cholesteric phase.

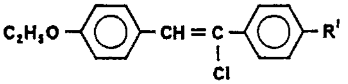
For this reason amongst others, the effects of chain branching of terminal alkyl groups have been fairly extensively studied in the last two years.(16,30,31,32) Though the detailed effects of chain branching are known to vary dependent upon whether the alkyl group is part of a terminal alkoxy group or a terminal carboalkoxy group, it is generally agreed that N—I temperatures are decreased by a methyl branch, the effect usually diminishing as the branching point is moved towards the extremities of the chain. The effects are illustrated by the results (from Refs. 16 and 32) in Table 7, which also show that chain branching affects C—N temperatures rather variably. None the less, diastereoisomers of compounds such as these containing an asymmetric carbon would provide quite low melting cholesterogens from which even lower melting eutectic mixtures could be formed.

Table 7. Melting Points and N–I Temperatures for some Mesogens with Branched Alkyl Chains

I



II



System	R'	C–N or I (°C)	N–I (°C)
I	$CH_2CH_2CH_2CH_3$	55	100
	$CH(CH_3)CH_2CH_2CH_3$	32 - 33	-
	$CH_2CH(CH_3)CH_2CH_3$	35 - 36	78
	$CH_2CH_2CH_2CH_2CH_3$	82	100
	$CH_2CH(CH_3)CH_2CH_2CH_3$	48 - 49	78
II	$CH_2CH_2CH_2CH_3$	29	58
	$CH_2CH(CH_3)CH_2CH_3$	29 & 32*	34
	$CH_2CH_2CH(CH_3)_2$	40	[35]
	$CH_2CH_2CH_2CH_2CH_2CH_3$	34	59
	$CH_2CH(CH_3)CH_2CH_2CH_2CH_3$	22	35

The temperature in parenthesis is for a monotropic transition.

* The compound gives two crystal forms with different C–N temperatures.

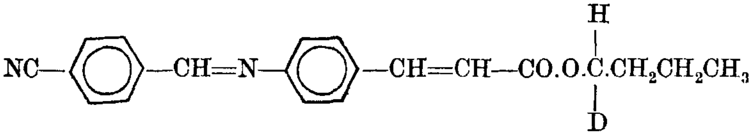
An alternative approach to obtaining low melting cholesteric systems is of course to induce cholesteric properties in nematic materials by adding comparatively small quantities of an optically active solute which may be a cholesterogen or a non-mesogen. If this is done with a room temperature nematic, a room temperature cholesteric is obtained.

Thus, MBBA + EBBA + a cholesteryl ester would give a room temperature cholesterogen with $\epsilon_{\parallel} - \epsilon_{\perp}$ negative, and with high purity materials, dopants would give a conductance suitable for the C.M.E.

Similarly, a cyano-substituted Schiff's base added to a room temperature cholesteric would give a cholesteric with $\epsilon_{\parallel} - \epsilon_{\perp}$ positive and suitable for the cholesteric–nematic P.C.E.

An optically active deuterio-compound

Remaining on the subject of cholesterics, but leaving the subject of materials for devices, I would like to mention that at Hull we have prepared the compound



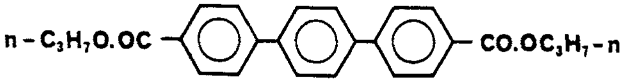
(Active)

which contains an asymmetric carbon atom by virtue of the deuterio-substituent. Optically active butan-ld-l-ol, $[\alpha]_D^{22} + 0.208°$ was synthesized and used to prepare the ester of *p*-nitrocinnamic acid which was then reduced to the active amino-ester, $[\alpha]_D^{22} - 0.308°$. This was then used for condensation with *p*-cyanobenzaldehyde to obtain the active Schiff's base ester. The ordinary *n*-butyl ester and the racemic but-ld-yl ester of the Schiff's base were also prepared. Each compound gave two crystal forms with distinct C-mesophase temperatures, 90° or 108.5 °C, at which a mesophase was formed which became isotropic (amorphous) at 133 °C. The *n*-butyl ester and the racemic but-ld-yl ester gave nematic phases which when viewed microscopically between crossed polarizers showed small homogeneous areas of varying birefringence and containing black, thread-like lines. The phase of the active but-ld-yl ester was consistently different; it was of a more uniform birefringence and contained both thread-like lines and ribbons which approached in their appearance the alignment discontinuities typical of cholesteric plane textures. The phase did not reflect coloured light, but in a cleavage wedge of mica, well defined Grandjean terraces were visible. The phase is therefore cholesteric. These observations cast considerable doubt on the validity of statements that have appeared in the literature to the effect that the twist in a cholesteric phase is induced mechanically by steric interactions involving substituents present in the asymmetric, right or left handed molecules. There is little effective difference in size between a C—D and a C—H unit that can produce a steric effect, and the twist must develop through a weighting either to the left or the right of the statistical parallel orientation of the lath-like molecules because of the asymmetry of the force fields to which they give rise. A detailed description of this work is in the course of publication.(33)

New Smectogens

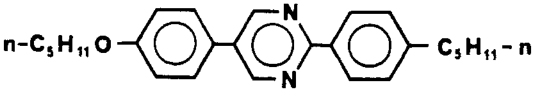
Another area which has recently commanded the chemist's interest concerns the synthesis of new mesogens giving novel polymorphic smectic modifications. Much more will certainly be said on this subject at this meeting, but I would like to draw attention to important recent developments.

The first of the compounds shown below -di-*n*-propyl *p*-terphenyl-4,4″-dicarboxylate was examined by Diele, Brand and Sackmann(34) and is one of four compounds which give a S_E phase. The second compound,



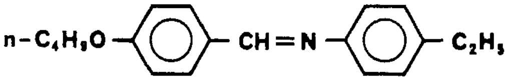
$C - S_E$, 122° ; $S_E - S_A$, 137·1° ;

$S_A - I$, 239·2°C.



$C - S_G$, 79° ; $S_G - S_F$, 102·7° ; $S_F - S_C$, 113·8° ;

$S_C - S_A$, 144° ; $S_A - I$, 210°C.

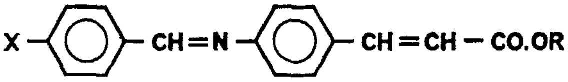


$C - S_H$, 40·5° ; $S_H - N$, 51° ; $N - I$, 65·5°C.

2-(*p*-*n*-pentylphenyl)5-(*p*-*n*-pentyloxyphenyl)pyrimidine was studied by Demus, Diele, Klapperstuck, Link and Zaschke(35) and gives four smectic modifications including S_F and S_G. A new smecitc polymorph,

S_H, has been discovered by de Vries and Fishel(36) for the third compound, 4-*n*-butoxybenzylidene-4-ethyl-aniline. X-ray studies have been made on these compounds and the various smectic modifications all appear to have layer structures. Consequently, the cubic S_D phase of 3′-nitro-4′-*n*-hexadecyloxy- and -octadecyloxybiphenyl-4-carboxylic acids remains distinct from other smectic polymorphs so far discovered. In addition to these findings, further information on homologues of the Schiff's base studied by de Vries and Fishel(36) will be discussed by Smith(14) at this meeting. He has found up to five different smectic forms in individual compounds of this kind.

In discussing new smectogenic systems, reference may be made in passing to our own work at Hull on esters of 4-*p*-substituted-benzylideneaminocinnamic acid of the type shown below:



X = CH_3O, CN, NO_2, $CH_3CO.O$ and Ph

R = n-Alkyl, branched alkyl, phenyl and ω-phenylalkyl

The results of full microscopic and DTA studies of these esters were discussed at a recent Faraday Society Symposium on Liquid Crystals held in London.(31) Several of the esters exhibit a smectic modification which we call S_3 (possibly S_E) and which we will discuss more fully in a paper at this meeting. An interesting structural point which emerged from these studies was the effect on the liquid crystal properties of ascending homologous series of ω-isopropylalkyl and ω-phenylalkyl esters. With nematogens, a very high degree of alteration of N—I temperatures characterizes the series as shown in Fig. 5 for the ω-phenylalkyl 4-*p*-cyanobenzylideneaminocinnamates. A similar, but less marked alternation is shown by the analogous ω-isopropylalkyl esters. When smectic phases are involved, however, the alternation of smectic thermal stabilities is quite small, so that, as shown in Fig. 6 for the series of ω-isopropylalkyl 4-*p*-acetoxy-benzylideneaminocinnamates, an alternation between purely smectic

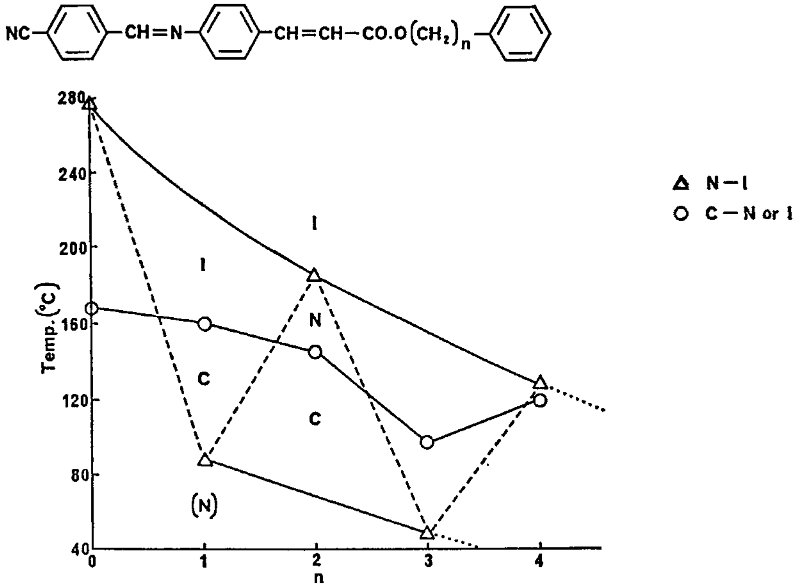


Figure 5. Plot of transition temperatures against number of methylene groups groups in the alkylene chain for ω-phenylalkyl 4-*p*-cyanobenzylideneamino-cinnamates.

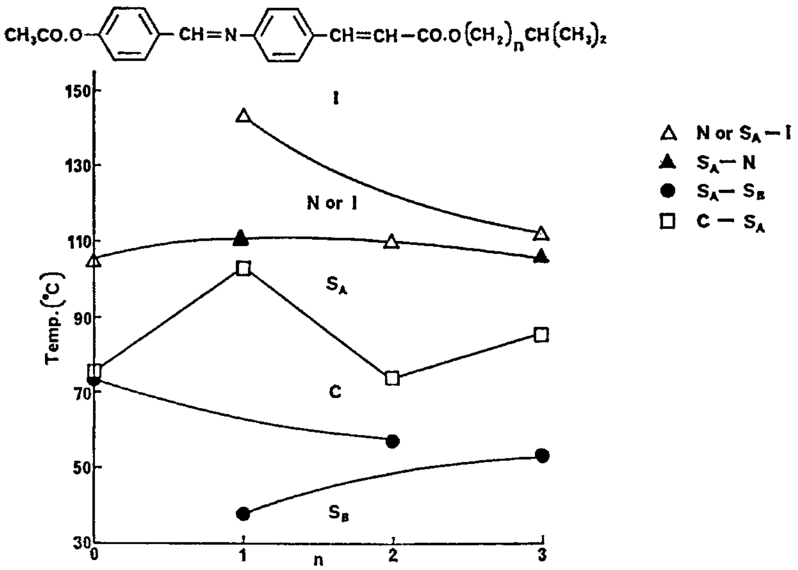


Figure 6. Plot of transition temperatures against number of methylene groups in the alkylene chain for ω-isopropylalkyl 4-*p*-acetoxybenzylidene-aminocinnamates.

and smectic + nematic properties occurs along the series. This is shown in Fig. 6 by the alternation from S_A—I to S_A—N and N—I transitions along the series.

Fig. 7 for the ω-isopropylalkyl 4-*p*-phenylbenzylideneaminocinnamates shows the same effect; in this case nematic properties occur for only one member because the smectogenic tendencies of the system are much higher. This series shows the S_3 phase referred to earlier and the regular trends in the S_3—S_B temperatures.

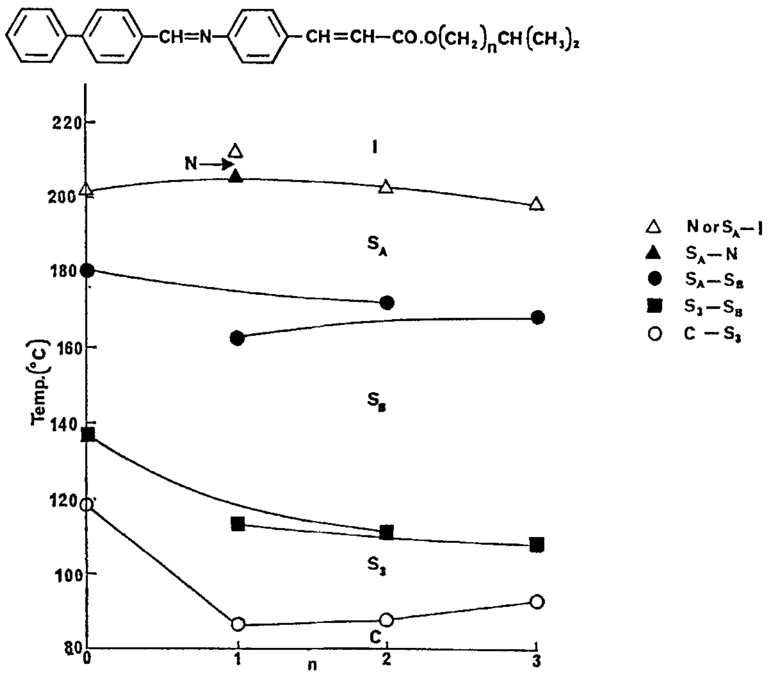
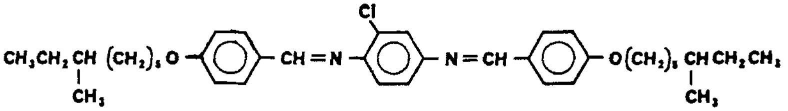


Figure 7. Plot of transition temperatures against number of methylene groups in the alkylene chain for ω-isopropylalkyl 4-*p*-phenylbenzylideneaminocinnamates.

Finally, bridging the topics of smectic and cholesteric mesophases, it is important to remember the work of Helfrich and Oh⁽³⁷⁾ who have studied the following optically active compound that forms a smectic mesophase at 29 °C followed by a cholesteric mesophase.



The lower temperature phase, like the cholesteric mesophase, was highly optically active (23,000°/mm at 4500 Å). This smectic phase would appear therefore to have a twisted structure, the molecules being inclined at an angle <90° to the layer planes, and the twist axis being at right angles to these layer planes, i.e., there is a progressive rotation of the layers over one another.

Concluding Remarks

In a review of this nature, with a time limit on its presentation, it has not of course been possible to mention specifically all the contributions which organic chemists have made to studies of liquid crystals. It is hoped however that the selection of topics presented has been a fair one which will provide both the chemist and the non-chemist involved in liquid crystal research with a useful synopsis of synthetic developments over the last 2–3 years.

REFERENCES

1. Heilmeier, G. H., Zanoni, L. A. and Barton, L. A., *Proc. IEEE* **56,** 1162 (1968).
2. Felici, N., *Rev. Gen. Elect.* **78,** 717 (1969).
3. Orsay Liquid Crystal Group, *Phys. Rev. Lett.* **25,** 1642 (1970).
4. Helfrich, W., *J. Chem. Phys.* **51,** 4092 (1969); Carr, E. F., *Mol. Cryst. and Liq. Cryst.* **7,** 253 (1969).
5. Schadt, M. and Helfrich, W., *Appl. Phys. Lett.* **18,** 127 (1971).
6. Heilmeier, G. H. and Goldmacher, J. E., *Proc. IEEE* **57,** 34 (1969).
7. Jakeman, E. and Raynes, E. P., *Phys. Lett.* **39A,** 69 (1972).
8. van der Veen, J. and Grobben, A. H., *Mol. Cryst. and Liq. Cryst.* **15,** 239 (1971).
9. van der Veen, J., de Jeu, W. H., Grobben, A. H. and Boven, J., *Mol. Cryst. and Liq. Cryst.* **17,** 291 (1972).
10. de Jeu, W. H. and van der Veen, J., *Phillips Res. Rept.* **27,** 172 (1972).
11. Knaak, L. E., Rosenberg, H. M. and Servé, M. P., *Mol. Cryst. and Liq. Cryst.* **17,** 171 (1972).
12. Kelker, H., Scheurle, B., Matz, R. and Bartsch, W., *Angew. Chem.* **82,** 984 (1970).

13. Vorländer, D. and Frohlich, A., *Ber.* **67**, 1556 (1934).
14. Smith, G. W., personal communication.
15. Malthète, J., Leclerq, M., Gabard, J., Billard, J. and Jacques, J., *Compt. rend. Acad. Sci., Paris* **273**, 265 (1971).
16. Young, W. R., Aviram, A. and Cox, J., *IBM Res. Rept.* RC3559 (1971), and *Angew. Chem.* **83**, 399 (1971).
17. Verbit, L. and Tuggey, R. L., *Mol. Cryst. and Liq. Cryst.* **17**, 49 (1972).
18. Gray, G. W., Harrison, K. J. and Nash, J. A., hitherto unpublished results.
19. Castellano, J. A., McCaffrey, M. T. and Goldmacher, J. E., *Mol. Cryst. and Liq. Cryst.* **12**, 345 (1971).
20. Teucher, I., Palios, C. M. and Labes, M. M., *Mol. Cryst. and Liq. Cryst.* **11**, 187 (1970).
21. Steinstrasser, R. paper presented at 4th Int. Liq. Cryst. Conf., Kent State University, Kent, Ohio, U.S.A., August 1972.
22. Gray, G. W. and Harrison, K. J., hitherto unpublished results.
23. Scherrer, H., personal communication.
24. Gray, G. W. and Nash, J. A., hitherto unpublished results.
25. Young, W. R., Haller, I. and Williams, L., *Liquid Crystals and Ordered Fluids* (edited by J. F. Johnson and R. S. Porter), Plenum Press, New York and London (1970), p. 383.
26. Schubert, H., *Wiss. Z. Univ. Halle* **XIX**, 5, 1 (1970).
27. Champa, R. A., *Mol. Cryst. and Liq. Cryst.* **16**, 175 (1972).
28. Fishel, D. L. and Patel, P. R., *Mol. Cryst. and Liq. Cryst.* **17**, 139 (1972).
29. Nash, J. A. and Gray, G. W. paper presented at 4th Int. Liq. Cryst. Conf., Kent State University, Kent, Ohio, U.S.A., August 1972.
30. Gray, G. W. and Harrison, K. J., *Mol. Cryst. and Liq. Cryst.* **13**, 37 (1971).
31. Gray, G. W. and Harrison, K. J., *Symposium of the Chemical Society Faraday Division* **5**, 54 (1971).
32. Goldmacher, J. E., German Patent 2026280 (1970).
33. Coates, D. and Gray, G. W. (to be published).
34. Diele, S., Brand, P. and Sackmann, H., *Mol. Cryst. and Liq. Cryst.* **17**, 163 (1972).
35. Demus, D., Diele, S., Klapperstuck, M., Link, V. and Zuschke, H., *Mol. Cryst. and Liq. Cryst.* **15**, 161 (1971).
36. De Vries, A. and Fishel, D. L., *Mol. Cryst. and Liq. Cryst.* **16**, 311 (1972).
37. Helfrich, W. and Oh, C. S., *Mol. Cryst. and Liq. Cryst.* **14**, 289 (1971).
38. Castellano, J. A., U.S. Patent 1928003 (1970).
39. Young, W. R., Haller, L. and Green, D. C., *IBM Res. Rept.* RC3827 (1972); *J. Org. Chem.*, in press.