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Advances in Synthesis and the Role of Molecular Geometry in Liquid Crystallinity

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Advances in Synthesis and the Role of Molecular Geometry in Liquid Crystallinity

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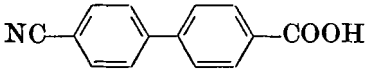
Abstract—Although publications concerning advances in synthesis and the role of molecular geometry in liquid crystallinity have not been numerous since the last conference in 1965, I have nevertheless had to be somewhat selective in the material which I have chosen to review in the available time. Broadly speaking, I have selected those areas of study which have given rise to new results which can be logically related to past experience in the field of molecular structure and the properties of liquid crystals. To this end, I have divided the lecture into three parts, of which the first is largely introductory.

Introduction

Kast's lists of liquid crystalline systems published in Landolt-Börnstein[1] illustrate clearly the diversity of structure of liquid crystalline compounds, and the situation today is that the synthesis of a new liquid crystalline compound is no longer of great significance unless the structure is unique or the behavior of the system teaches us something new about liquid crystals. Whether a substance will be liquid crystalline or not can be predicted with reasonable certainty, and indeed chemists are beginning to use liquid crystalline behavior as evidence in structure elucidation. I will do no more than quote a simple illustration of this, since Dr. Kelker will tell us more of this in relation to naphthalene chemistry in the first paper this afternoon.

If we react benzonitrile with the diazonium salt of methyl *p*-aminobenzoate, three isomeric cyanobiphenyl-4-carboxylic esters are obtained. These or the acids derived from the esters by hydrolysis are readily enough separated. Although it is not a difficult task to assign structures to the esters or the acids using modern techniques, it certainly was of assistance to us in the early stages of the work to note that one of the acids was liquid crystalline. This allowed us to assign to this acid the structure below.



Structure/liquid crystal correlations can therefore be of use to the organic chemist.

In the last fifteen years, a considerable body of qualitative information has accumulated concerning liquid crystal thermal stability in relation to molecular structure. Much of the basic work has been done in fact, and the need is for a quantitative approach to interpreting the existing information.

For these reasons therefore, publications describing the synthesis of liquid crystalline systems and the effects of structure change on liquid crystalline behavior have decreased, and research since 1965 has concentrated on physical studies of liquid crystals. In this area it is encouraging to see that systems other than *p*-azoxyanisole are more frequently being studied; for this we should thank the chemical companies which are making a wider range of pure liquid crystalline compounds commercially available.

A problem of physical studies has always been the necessity to operate with the sample at temperatures in excess of room temperature. A valuable commodity indeed would be a trinity of substances each exhibiting one of the three main types of liquid crystal at room temperature. We may hear of success in this direction at this meeting. About this I am uncertain, for the discovery of such compounds would probably involve patent rights which may lead to delays in publication. However, I think

that it is worth reviewing briefly some of the established findings connected with room temperature liquid crystals, and outlining what the problems are.

The alkane-2,4-dienoic acids (Table 1) reported by Markau and Maier[2] are examples of compounds which exhibit enantiotropic nematic liquid crystals at around room temperature. Unfortunately, these compounds are unstable, since they undergo spontaneous Diels Alder coupling yielding dimeric and polymeric products. They are not therefore such attractive systems as they appear at first sight.

TABLE 1 Transition Temperatures for Alkane-2,4-dienoic acids (R—CH=CH—CH=CH—COOH)

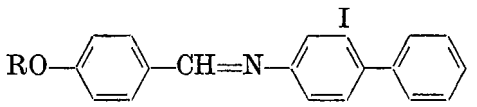
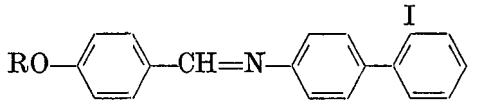
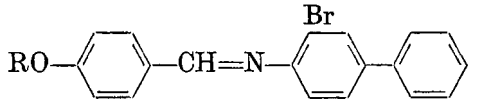
R	C_2H_5	n-C_4H_9	n-C_6H_{13}
Crystal-nematic	44	23	32 °C
Nematic-isotropic	46	53.5	62.5 °C

Markau, K. and Maier, W., *Ber.* **95**, 889 (1962)

To obtain nematic-isotropic transitions at around room temperature is in fact no problem. As shown in Table 2, the iodo-compounds[3] (R = n-heptyl-n-decyl) give nematic-isotropic transition temperatures covering the range *ca.* 0–30°. However, these nematic states are monotropic and occur only in the supercooled isotropic liquid, i.e., below the melting points of the crystals. Two of the bromo-compounds[3] (R = n-nonyl and n-decyl) in Table 2 do however give enantiotropic nematic states, not at such competitive temperatures as the dienoic acids, but nevertheless at lower temperatures than p-azoxyanisole. These bromo-anils are easily prepared, and moreover the compounds are quite stable.

The problem is not therefore one of producing a system which gives a low nematic-isotropic transition temperature, but of foreseeing what the rather unpredictable melting point of the compound will be. However, these examples illustrate that a stable nematic system giving an enantiotropic liquid crystal at room

TABLE 2 Transition Temperatures for Some Systems giving Low Liquid Crystal to Isotropic Transition Temperatures

	R	Crystal-nematic or -isotropic	Nematic-isotropic‡
	*n*-Heptyl	69.5 °C	(3.5) °C
	n-Octyl	60.5	(17.5)
	n-Nonyl	73.5	(16)
	n-Decyl	62.5	(22.5)
	*n*-Heptyl	79	(10.5)
	n-Octyl	59.5	(22)
	n-Nonyl	64	(22.5)
	n-Decyl	61	(29.5)
	*n*-Heptyl	91	(82)
	n-Octyl	96	(85)
	n-Nonyl	59	83.5
	n-Decyl	63	85
		Crystal-smectic	smectic-isotropic
Vinyl oleate		– 45	– 18

‡ Temperatures in parentheses are for monotropic transitions.

temperature should be achievable, and it would be no surprise to learn that this has been done.

The great need for such a system has to some extent been alleviated by the availability of mixtures of different liquid crystalline systems, which, through melting point depression, are liquid crystalline at room temperature. Such mixtures[4,5] are extremely valuable provided that the particular study does not require the use of a single component system.

Mixtures of compounds yielding smectic states are also useful, but it should be remembered that it is not uncommon to find for these a depression of melting point and an elevation of the smectic-isotropic transition temperature. A recent paper by Schroeder and Schroeder[6] proposes some interesting ideas as to why such enhancements should occur. Single component systems can however yield smectic states at low temperatures, as shown by the example of vinyl oleate[7] (Table 2) which is smectic below 0°; the ester is however prone to polymerise.

Finally, we should not forget the valuable mixtures of cholesteric compounds[8–11] studied mainly by Fergason and yielding cholesteric states at room temperature. We all know the commercial interest and value of these systems today.

There is still much however that the organic chemist can contribute by planned studies of structure or geometry change of the molecule on liquid crystal properties, and I would like to review two areas of study in this connection for the remainder of this lecture.

The Effect of Polyfluorination of Some Organic Systems

The first of these concerns the work of Goldmacher and Barton[12] on the effects of polyfluorination of some organic systems. This work shows that polyfluorination along the sides (polylateral substitution) of an elongated molecule leads to more highly thermally stable liquid crystals than might have been expected. In some cases the liquid crystals are more thermally stable than those of the unsubstituted system, and smectic properties are particularly enhanced.

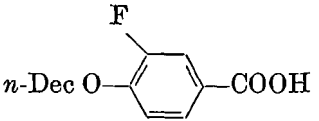
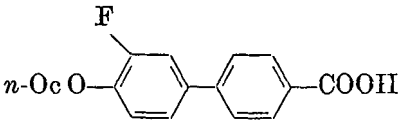
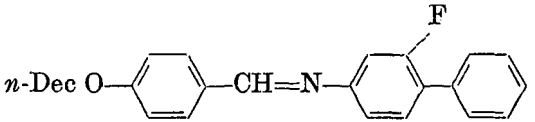
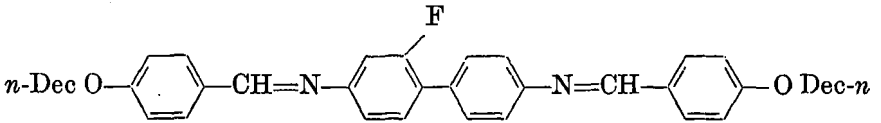
The effects of lateral substitution of liquid crystalline systems have been fully published[13] and reviewed.[14,15] I will simply summarise the essential points and then evaluate the results for these polyfluoro-compounds in terms of previous observations.

The first two examples in Table 3 show the effect of a single fluoro-substituent which broadens the system and forces the axes of the molecules apart, an effect which is to some extent counteracted by the dipole of the C—F bond. The broadening effect predominates, the intermolecular attractions are lowered and the transition temperatures for both smectic and nematic liquid crystals are decreased. This is a general effect for monosubstitution which broadens a molecule, i.e., a reduction in nematic thermal stability (mainly a function of substituent *size*), and a reduction in smectic thermal stability (a function of both substituent *size* and *dipole*). The fluoro-substituent is quite small, and the temperature decreases from the unsubstituted systems are not large. Note too that the magnitude of the effect varies with the system—the effect in the longer biphenyl acids is less marked than that in the shorter benzoic acids.

The next two examples in Table 3 show that the same substituent has a much more dramatic effect if it imposes a steric effect on the system. Rotation of parts of the molecule out of the plane has severe repercussions on the close packing of the rod-like molecules, giving rise to marked decreases in liquid crystal thermal stability.

However, there are cases in which lateral monosubstitution *enhances* liquid crystal thermal stability. Consider the 5-substituted 6-*n*-alkoxy-2-naphthoic acids.[16] Fig. 1 represents the unsubstituted alkoxy acid as a dimer, and the perimeter of the molecule is represented by the dashed lines A—A′ and B—B′ (the alkyl chains are considered flexible). A substituent such as chloro- or bromo- can be accommodated at the 5-position without noticeably broadening the molecule. Because of this feature of molecular shape which prevents any breadth increase, the dipole of the 5-substituent may act to increase the intermolecular attractions and enhance the liquid crystal transition temperatures. The results in Table 4 show that this is the case.

TABLE 3 The Effects of Monofluorination on Liquid Crystal Thermal Stability

	Decrease in thermal stability from unsubstituted system to fluoro-compound	
	Smectic	Nematic
	10 °C	25.5 °C
	0.5	9
	57.5	44.5
	58.5	29.5

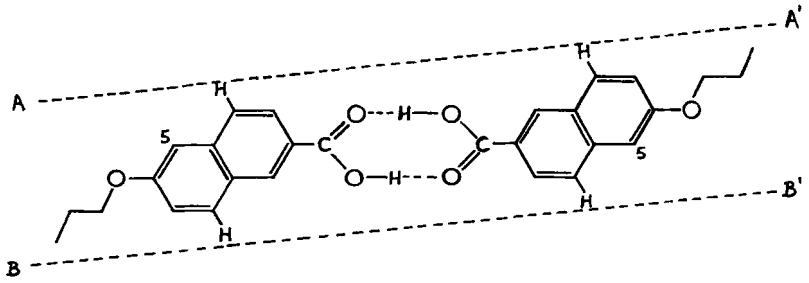


Figure 1. Structural representation of the dimer of a 6-*n*-alkoxy-2-naphthoic acid.

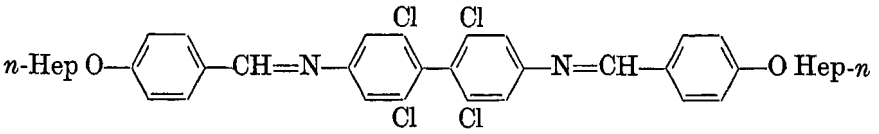
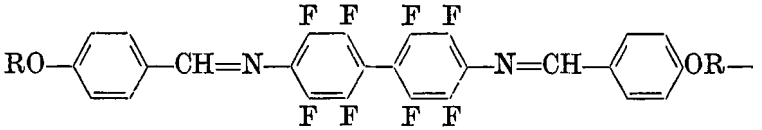
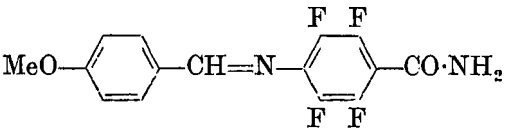
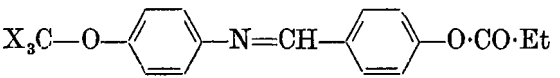
TABLE 4 Transition Temperatures for 5-substituted 6-*n*-nonyloxy-2-naphthoic Acids

Substituent	Smectic-nematic (°C)	Nematic–isotropic (°C)
None	140	183.5
Cl	185.5	194.5
Br	180	192.5
I	157.5	182

The 5-chloro- and 5-bromo-substituents enhance the smectic and nematic thermal stabilities, the smectic state being more affected, as we would expect, because the cross dipole associated with the 5-substituent will enhance the lateral attractions and the thermal stability of a layer system. The iodo-substituent does increase the molecular breadth. As a consequence, the nematic–isotropic temperature is slightly lower and the smectic–nematic temperature is much less enhanced. The dipole moments of the C—Cl and C—Br bonds being about the same, these substituents enhance the smectic thermal stability by 40–45° and the nematic thermal stability by about 10°. Corresponding 5-fluoro-derivatives have not been studied, but the fluoro-substituent being smaller, and the C—F dipole about the same, we might anticipate similar increases in smectic and nematic thermal stabilities for these compounds relative to the unsubstituted system.

Substituents of this kind are therefore filling gaps between molecules, improving intermolecular contact, and increasing attractive forces. For the tetrachloro-compound[17] shown in Table 5, the situation is different. *Each* of the *four* chloro-substituents increases intermolecular separation, because the biphenyl ring system is twisted about the 1,1′-bond, the planes of the benzene rings making an angle of about 90° to one another. The estimated decrease in nematic thermal stability from the unsubstituted compound was *ca.* 282° *i.e.*, a nematic–isotropic transition temperature of *ca.* 61° was predicted. The melting point of the compound was however 89°, and the isotropic liquid underwent very little supercooling. No liquid crystal was therefore observed, and we can only say that decreases of $> 201°$ and $> 253.5°$ occurred for the smectic and nematic states, respectively. At this time, I suggested[14] that the tetrafluoro-compound might be liquid crystalline, but that it was doubtful and would depend on the melting point of the crystals. In pointing out that the related octafluoro-compounds in Table 5 are liquid crystalline, Goldmacher and Barton[12] refer to this statement. However, the comparison is not quite simple, as four of the fluoro-substituents (those in the 3, 3′, 5 and 5′-positions) are now acting as gap fillers, increasing intermolecular attractions. Consequently, smaller decreases in nematic and particularly smectic thermal stability would be expected compared with the tetrafluoro-compounds. The true situation is unfortunately not easy to assess, as Goldmacher and Barton chose as alkyl groups R = Me and R = *n*-Pr, and for these, the nematic–isotropic transition temperatures for the unsubstituted compounds have not been assessed as better than $> 390°$.[15] Consequently, the decreases in nematic thermal stability from unsubstituted compound to octafluoro-compound cannot be estimated more exactly than $> 20°$ for R = Me and $> 75°$ for R = *n*-Pr. However, the occurrence of a smectic state when R = *n*-Pr is interesting, suggesting an enhancement of smectic properties arising from the additional four fluoro-substituents. The parallel between these compounds and the naphthoic acids is therefore quite close.

TABLE 5 The Effects of Polyhalogenation on Liquid Crystal Thermal Stability

	Decrease in thermal stability from unchlorinated system		
	Smectic > 201	Nematic > 253.5 °C	
	*Octafluoro-*		
	R = Me	N—I 370 °C (d)	
	R = *n*-Pr	S—N 210; N—I 315 °C	
	Unsubstituted		
	R = Me	N—I > 390 °C	
	R = *n*-Pr	N—I > 390 °C	
	*Tetrafluoro-*	S—I	268 °C
	Unsubstituted	S—I	195 °C
	Terminal —OCH_3	N—I	118 °C
	Terminal —OCF_3	S—I	136 °C

Key: N = nematic S = smectic I = isotropic

The next example in Table 5 is more striking, the smectic–isotropic transition temperature of the amide being enhanced by 73° on tetrafluorination. Two of the fluoro-substituents (one on either side) will act to decrease the smectic thermal stability as in the fluoro-substituted benzoic acids and biphenyl-4-carboxylic acids (Table 3). A decrease of between 1 and 20° in smectic thermal stability would therefore be anticipated. Basing our arguments on the naphthoic acids, the other two fluoro-substituents (gap fillers) might increase the smectic thermal stability by 80–90°, i.e., the smectic-isotropic transition temperature for the tetrafluoro-amide could lie between 255 and 284°. The observed value was 268°. This is a striking example of polar substitution enhancing smectic thermal stability when the molecular breadth increase accompanying substitution is limited in its extent.

The last example in Table 5 is also interesting, and shows that a change from C—H to C—F bonds in the terminal —OCX_3 group changes the system from nematic to smectic, and enhances the liquid crystal-isotropic transition temperature. Compared with —OCH_3, the —OCF_3 group gives a much stronger dipole acting across the long molecular axis. In the —OCF_3 group we therefore have a useful smectic-producing terminal substituent to add to groups such as —$CO{\cdot}NH_2$ (also stemming from the work of Goldmacher and Barton) and —CO·OR.

Finally, I would like to discuss:

The Influence of Molecular Structure on the Thermal Stability of Cholesteric Liquid Crystals

The most common examples of cholesteric liquid crystals are provided by derivatives of cholesterol itself, e.g., cholesteryl halides and cholesteryl esters, $R{\cdot}CO{\cdot}O{\cdot}C_{27}H_{45}$, including alkyl cholesteryl carbonates. One way of studying structure effect on liquid crystal thermal stability would be to modify the sterol skeleton. Wiegand[19] studied a number of benzoate esters derived from cholesterol, cholestanol, and epicholestanol. He also studied the effect of changing the position of the double bond in cholesterol

and of the two double bonds in a cholestadienol. The cholesteric–isotropic transition temperatures were appreciably affected, and in some cases the esters were not liquid crystalline. Interpretation of results is however difficult, because we are dealing with a complex, fused alicyclic ring system, and quite minor structural changes are capable of bringing about substantial changes in the stereochemistry of the system.

The sensitivity of cholesteric properties of sterol systems to structure change is also shown by the more recent work[20–22] on stigmasteryl esters. These compounds are in fact smectic, whilst the corresponding cholesteryl esters are cholesteric. The change here involves only the side chain—the introduction of a double bond at C_{22}—C_{23} and of an ethyl substituent at C_{24}.

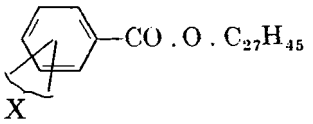
Bearing in mind also the difficulties of a synthetic kind associated with making tailored changes to the sterol skeleton, it is natural to look for alternative means of studying structure effects on cholesteric properties. For example, we could modify the group R in $R \cdot CO \cdot O \cdot C_{27}H_{45}$.

R = *n*–alkyl

This provides the homologous series of cholesteryl *n*-alkanoates,[23] and a study of these compounds shows that short alkyl chains favor cholesteric behavior and longer alkyl chains give additional smectic properties; chain branching lowers the transition temperatures.[24]

R = X—C_6H_4

Studies of substituted benzoate esters of cholesterol (see below) are more informative. *o*- or *m*-Substitution[19,25] decreases the



cholesteric-isotropic transition temperatures, and *p*-substitution enhances the cholesteric-isotropic transition temperatures. Using

results from the earlier literature, the group efficiency order for *p*-substituents is:

$$Ph^{19} > NO_2{}^{25} > NH_2{}^{25} > Me^{19} > MeO^{19} > H$$
$$290 \qquad 265 \qquad 250 \qquad 241 \qquad 236 \quad 178.5\,°C$$

These cholesteric-isotropic transition temperatures will be referred to later, but the efficiency order does suggest a similarity between the cholesteric and nematic states.

A difficulty with the benzoate esters of cholesterol is that the transition temperatures are high, and decomposition becomes an important factor at such elevated temperatures.

Because of this, I felt it would be useful to study some of the cholesteric systems provided by condensing (—)2-methylbutyl *p*-aminocinnamate (the active amyl ester) with *p*-substituted benzaldehydes. The compounds formed are:

(—)2-*Methylbutyl* 4-(*p-substituted benzylideneamino*)*cinnamates*

(Fig. 2), and it is useful to abbreviate this name to SBAC.

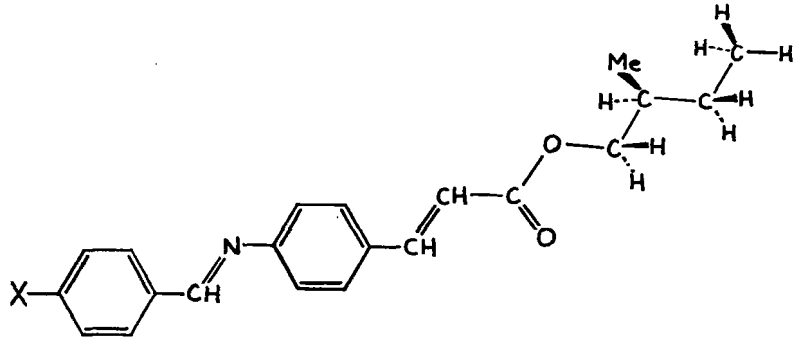


Figure 2. 2-Methylbutyl 4-(*p*-substituted benzylideneamino)cinnamates (SBAC).

We first examined the effect of having different alkoxy groups as the substituent X, and examined the homologous series where X = —OMe to —O*n*Octyl. Table 6 summarises the constants for these systems, the transition temperatures being determined

TABLE 6 Transition Temperatures for (—)2-methylbutyl 4-(*p*-*n*-alkoxybenzylideneamino)cinnamates

n-Alkoxy group	Temperature of transition (°C) C—S	S—Ch	S or Ch—I
MeO	54	76.5	98
EtO	75.5	—	124.5
PrO	86.5	—	120.5
BuO	84	—	126.5
PnO	64	—	120
HxO	60.5	—	122.5
HpO	74	—	117
OcO	73.5	—	118
Literature data:	C—S	S—N	N—I
MeO[25,26]	49	73	95
EtO[25,26]	68	114	125

Key: C = crystalline solid S = smectic Ch = cholesteric N = nematic I = isotropic liquid

using a sample contained in a melting point capillary. Of the compounds listed, two, X = —OMe and —OEt, are known from the early literature,[25,26] where they are listed as smectic and nematic in behavior. Our compound with X = —OMe has about the same constants as those in the literature, but the compound shows smectic and cholesteric properties. In our hands, the compound having X = —OEt is purely smectic, as are also the other six homologues studied.

It is more instructive to consider a plot of these transition temperatures against alkyl chain length. It is clear from Fig. 3 that the smectic–isotropic temperatures and the smectic–cholesteric temperature for X = —OMe alternate, giving two curves which rise to a maximum and then fall.

The direction of the dotted line in Fig. 3 is quite arbitrary, and seeks only to illustrate the narrow range of cholesteric properties for the series. However, this line must cut a line joining the smectic–cholesteric temperature for X = —OMe and the smectic–isotropic temperature for X = —OEt, since the latter compound is purely smectic. We learn from this series that cholesteric

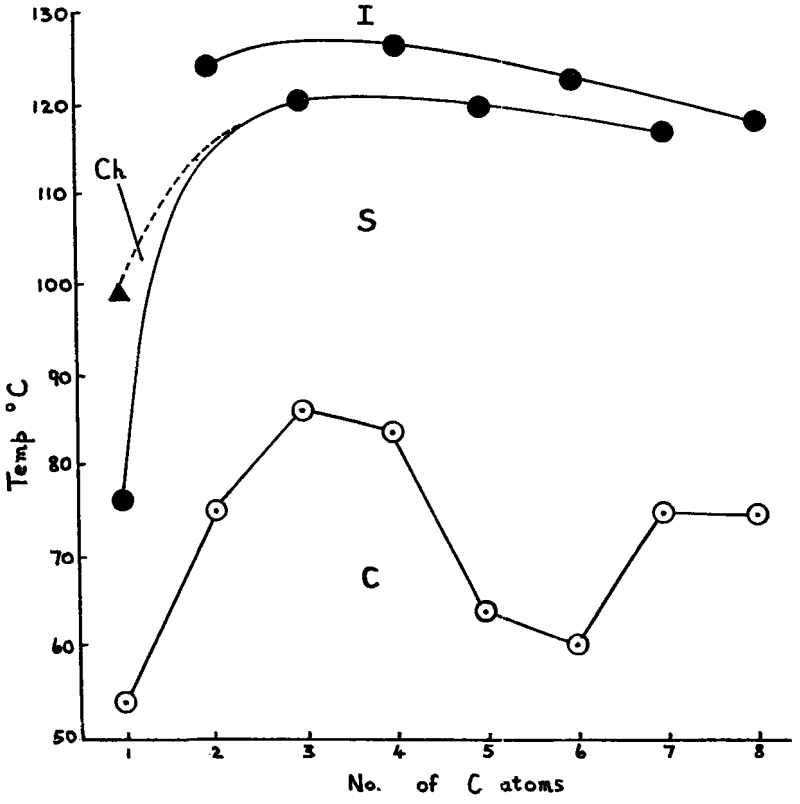


Figure 3. Plot of transition temperatures for 2-methylbutyl 4-(*p*-*n*-alkoxybenzylideneamino)cinnamates against number of carbons in the alkyl chain.

● = smectic-cholesteric or isotropic (S—Ch or I)
○ = crystal-smectic (C—S)
▲ = cholesteric-isotropic (Ch—I)

properties are favored by only the shortest of alkyl chains. Again this relates the cholesteric and the nematic states, because for the non-cholesteric *ethyl* esters corresponding to this homologous series, nematic properties are extinguished in favor of purely smectic properties very early in the series.

We next turned to SBAC systems carrying other substituents X.

X = NMe_2, Me, CN, NO_2, Cl, Br, F

The transition temperatures for these systems are given in Table 7, and it is at once obvious that not all of these compounds are cholesteric, although all are *active* esters.

TABLE 7 Transition Temperatures for (—)2-methylbutyl 4-(*p*-substituted benzylideneamino)cinnamates (SBAC)

X	Temperature of transition‡ (°C) C—S	C—Ch	S—Ch	S—I	Ch—I
NMe_2	96	—	—	125	—
Me	78	—	—	84	—
MeO	54	—	76.5	—	98

	C—I		C—Ch	Ch—I
CN	—		93.5	108
NO_2	—		82.5	84
Cl	80	——or——	66.5	69.5
Br	84.5		—	64.5§
F	72		—	⩽45§
H	56.5		—	—

‡ Symbols used are defined in the key to Table 6.
§ Monotropic cholesteric states.

The following points are noteworthy:

(a) X = H—not liquid crystalline;
(b) X = NMe_2 and Me—purely smectic;
(c) X = OMe—smectic and cholesteric;
(d) X = CN and NO_2—enantiotropic liquid crystals are exhibited having all the characteristic properties of the cholesteric state, and reflecting colored light which changes from red to blue on cooling.
(e) X = Cl—a dimorphic compound. Using C_1 and C_2 to denote the two different crystal forms and the other symbols summarized in the key to Table 6, the observations made were:

C_1, on fairly rapid heating, passed to Ch at 66.5° and Ch changed to I at 69.5°. If heating was continued, the isotropic liquid would either persist or crystallize, giving C_2 which melted at 80°, i.e., C_2 changed to I at 80°. On cooling the isotropic liquid, the change, I to Ch, occurred

at 69.5°. If the crystals C_1 were heated slowly, they changed to crystal form C_2 at a temperature below 66.5°. C_2 then passed to the isotropic liquid at 80°, without forming a liquid crystal. The cholesteric state is therefore enantiotropic with respect to C_1 and monotropic with respect to C_2.

(f) X = Br and F—monotropic cholesteric states were exhibited. For X = F, the cholesteric liquid crystal was observed only on very rapid chilling of the isotropic liquid, and then it was seen only as a flash of color preceding the crystals. The transition, I to Ch, must lie much below 45°.

The liquid crystalline properties of the SBAC systems are therefore very sensitive to the nature of the terminal substituent X, both with regard to the nature of the liquid crystal and its thermal stability.

These results may now be considered in terms of the terminal group efficiency order. Using data[15] for two systems (1) and (2), we obtain the nematic terminal group efficiency orders shown in Table 8. From these orders we can derive an average nematic

TABLE 8 Terminal Group Efficiency Orders for Some Liquid Crystal Systems

Nematic	MeO > NO_2 > Cl > Br > H	(1)
	CN > MeO > Cl > H	(2)
Average Nematic Order	CN > MeO > NO_2 > Cl > Br > H	
Cholesteric	CN > MeO > NO_2 > Cl > Br > H	(3)
Smectic	Br > Cl > H > NO_2 > MeO	(4)

(1) 4-(*p*-substituted benzylideneamino)-4′-methoxybiphenyls.
(2) 4′-substituted biphenyl-4-carboxylic acids.
(3) SBAC.
(4) 4-(*p*-substituted benzylideneamino)-4′-*n*-octyloxybiphenyls.

terminal group efficiency order, which can then be compared with the cholesteric group efficiency order obtained using the results in Table 7 for the SBAC systems. The two efficiency orders are identical, providing convincing evidence of the close relationship between cholesteric and nematic liquid crystals, since the thermal stabilities of both liquid crystals are determined by the same

factors associated with the terminal substituent. The smectic terminal group efficiency order is quite different, and as shown in Table 8, terminal MeO and NO_2 groups depress the smectic thermal stability relative to the unsubstituted system.

Two further points may be noted.

(1) The SBAC system with X = Ph has been reported[1] as nematic. Assuming that the compound is really cholesteric, the cholesteric terminal group efficiency order in Table 8 may be extended to:

$$\text{Ph} \gg \text{CN} > \text{MeO} > \text{NO}_2 > \text{Cl} > \text{Br} > \text{H}$$

Moreover, for system (2) in Table 8, Ph > CN.

(2) The cholesteric terminal group efficiency order mentioned earlier for the *p*-substituted benzoate esters of cholesterol is different from that for the SBAC systems. As long ago as 1962, I pointed out[14] that some of the literature constants for the *p*-substituted benzoate esters of cholesterol were suspect. Two of these were the *p*-nitro- and *p*-methoxy-benzoate esters, and the more recent constants for these esters together with the earlier literature constants are given below.

p-NO_2	Ch—I	258–9°(d)	Lit. 265°
p-MeO	Ch—I	258.5° (d)	Lit. 236°

At that time, we also prepared cholesteryl *p*-chlorobenzoate and observed a cholesteric to isotropic transition at 245–6°. Using these results, we obtain the modified terminal group efficiency order for the cholesteric states of cholesteryl *p*-substituted benzoates shown below:

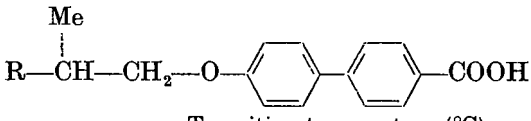
$$\text{Ph} \gg \text{MeO} \approx \text{NO}_2 > \text{Cl} > \text{Me} > \text{H}$$

This order is now closely similar to the order for the SBAC systems.

The closeness of the connection between cholesteric and nematic liquid crystals has recently been emphasized by the work of Cano[27,28] and of Leclerq, Billard, and Jacques.[29]

The work of the latter group on racemic and optically active ethers of 4′-hydroxybiphenyl-4-carboxylic acid is summarized in Table 9. With reference to Table 9, it should be noted that when R = Et, the alkyl group is the same active amyl or 2-methylbutyl group used in the SBAC systems. In all cases, the active compounds were cholesteric and the racemates were nematic. In certain cases, polymorphism of the liquid crystals was noted, but for the present discussion, the important point is that the crystal to liquid crystal transition temperatures for the racemic and active forms of each compound and the N—I and Ch—I temperatures for the racemic and active forms of two of the compounds are the same. Only for R = *n*-Bu are different liquid crystal to isotropic transition temperatures recorded for the optically active and racemic forms. Furthermore, when the enthalpies of the transitions were measured, the values were virtually identical in each of the two cases in which the racemate and the active form had identical liquid crystal to isotropic transition temperatures. From this we can conclude that the nematic and cholesteric states are so closely related that the same energy factors are involved in passing from either state to the isotropic liquid. A structurally similar situation must therefore exist in the two liquid crystals.

TABLE 9 Data by Leclerq, Billard, and Jacques[29] for 4′-alkoxybiphenyl-4-carboxylic acids



R			Transition temperature (°C)			$[\alpha]_{578}^{22}$
C_2H_5	Racemate	C—N	238–9	N—I	249	
	Active	C—Ch	238–9	Ch—I	249	+ 10.8°
n-C_4H_9	Racemate	C—N	171	N—I	245	
	Active	C—Ch	171	Ch—I	229	+ 7.9°
$PhCH_2$	Racemate	C—N	205.5	N—I	241	
	Active	C—Ch	205.5	Ch—I	241	+ 50°
Ph	Racemate not liquid crystalline					

Earlier, Cano had reported that the active and racemic forms of the SBAC system where X = CN were cholesteric and nematic, respectively. Independently, we had also examined the racemic system with X = CN and also that with X = NO_2. The findings are summarized in Table 10. The active and the racemic 2-methylbutyl esters of *p*-aminocinnamic acid were prepared from the alcohol and *p*-aminocinnamic acid, and condensed with either *p*-cyano- or *p*-nitro-benzaldehyde. Data relating to the optical rotations of the starting alcohol and the intermediate amino-ester are given in Table 10. The racemic Schiff's bases are virtually inactive. Values for the specific rotations of the Schiff's bases of $< 0.4°$ and $< 0.2°$ are quoted for the following reason. Only limited concentrations of the Schiff's bases in chloroform could be obtained, and using these solutions, the polarimeter gave no detectable rotation. However, zero rotation cannot be distinguished from a rotation of 0.001°, and the specific rotations have been calculated assuming that zero rotation was in fact $< 0.001°$. The specific rotations of the active Schiff's bases are numerically comparable with those for the starting active alcohol and the intermediate amino-ester.

TABLE 10 Data for 2-methylbutyl 4-(*p*-substituted benzylideneamino)-cinnamates (SBAC)

Substituent		Transition temperature (°C)				$[\alpha]_D^{24}$
CN	Racemate	C—N	93.5	N—I	108	$< +0.4°$
	Active	C—Ch	93.5	Ch—I	108	$+4.3°$
NO_2	Racemate	C—N	82.5	N—I	84	$< +0.2°$
	Active	C—Ch	82.5	Ch—I	84	$+3.6°$

Intermediates in the synthesis of active Schiff's bases:
(—)2-Methylbutanol $[\alpha]_D^{25} = -5.73°$
(—)2-Methylbutyl *p*-aminocinnamate $[\alpha]_D^{25} = +6.8°$
High concentrations of the racemic alcohol and ester gave no measurable rotations.

Again therefore, the active forms are cholesteric and the racemates are nematic, and in both cases, the melting temperatures and liquid crystal to isotropic temperatures give identical

pairs, confirming the findings of Cano and of Leclerq, Billard, and Jacques, and emphasizing the similar natures of the two types of liquid crystal.

As an extension of this work, we prepared the systems shown in Table 11. We have already seen that the SBAC system with X = NMe_2 is smectic even although the ester is active. Thus, the NMe_2 group is not a good group for promoting cholesteric properties, despite the fact that the system contains a center of asymmetry and is optically active. As expected therefore, the racemic form of this system is also smectic and gives the same C—S and S—I transition temperatures.

TABLE 11 Data for Some Alkyl 4-(*p*-substituted benzylideneamino)-cinnamates

Alkyl	Substituent	Transition temperature (°C)			
2-Methylbutyl (racemate)	NMe_2	C—S	96	S—I	125
2-Methylbutyl (active)	NMe_2	C—S	96	S—I	125
3-Methylbutyl	NMe_2	C—S	111.5	S—I	134
3-Methylbutyl	CN	C—N	101	N—I	107
3-Methylbutyl	NO_2	C—I	101	N—I	88.5‡

‡ Monotropic nematic liquid crystal.

Therefore, if we choose terminal NMe_2, CN, and NO_2 groups for the SBAC system and use as the ester alkyl group a group similar to 2-methylbutyl, but one which contains no asymmetric center, e.g., 3-methylbutyl, then X = NMe_2 should give a smectic system and X = CN or NO_2 should give a nematic system. As shown in Table 11, this is in fact the case, showing again, in an indirect way, that the cholesteric and nematic states are closely related. Thus, optical asymmetry will confer cholesteric properties on a nematogenic system, but not on a smectogenic system. The nematogenic character of a compound is as important for the manifestation of cholesteric properties as is the function in the molecule which confers upon the system the property of optical activity.

Finally, let us consider why the various terminal groups should act as they do in promoting

(a) smectic properties when X = Me, NMe_2, and OEt to O*n*Oc,
(b) smectic and cholesteric properties when X = OMe, and
(c) cholesteric properties, or nematic properties if the system is not optically active, when X = NO_2, CN or halogen.

A clear answer is not obvious. When X = NO_2, CN, or halogen, a strong dipole operates straight out from the *p*-position of the benzal grouping. Such a dipole may act either by attracting the ester groupings of neighbouring terminally situated molecules, or by repelling like dipoles in neighbouring molecules lying in a layer arrangement of a smectic kind.[15] In either case, a smectic arrangement will be less likely than a cholesteric/nematic arrangement, i.e., the ratio of the lateral to the terminal attractions will be low. Presumably, a highly polarizable, as distinct from a polar terminal substituent, e.g., X = Ph, can also lead to enhanced terminal attractions. That enhancement of terminal attractions is probably the most important issue is suggested by the behavior of SBAC systems carrying terminal alkoxy groups. When X = OMe, the dipole acts at an angle across the long molecular axis and could be considered to enhance either lateral or terminal attractions. However, it may be implied that the dipole contributes mainly to terminal attractions because the higher homologues are smectic and not cholesteric. The function of the lengthening alkyl chain would be to provide "terminal insulation" between terminal dipoles of neighbouring molecules arranged in an end to end manner, i.e., to lower terminal attractions. Furthermore, a terminal Me group is of low dipolarity and not likely to contribute greatly to terminal attractions; we have seen that when X = Me the system is purely smectic. The substituent NMe_2 is more difficult to discuss. The dipole moment (Fig. 4)

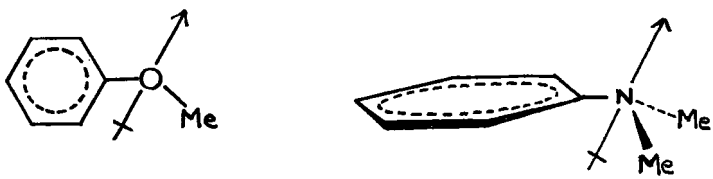


Figure 4. Orientation of dipoles for terminal —OMe and —NMe_2 groups.

will make a similar angle to the long axis of the molecule as in the case when X = OMe, but the dipole will in this case be directed in a plane at right angles to the plane of the ring. Why this should favor smectic rather than cholesteric/nematic properties cannot be explained qualitatively.

We should also remember that when NMe_2 or Me groups occupy terminal positions in other systems, e.g., in the 4-(*p*-substituted benzylideneamino)-4′-methoxybiphenyls, they in fact favor nematic properties compared with the unsubstituted system Thus, dependent upon the system in which the terminal group occurs, we can have a cut off of nematic properties at different points of the terminal group efficiency order. For the methoxy anils, the system is strongly nematogenic and any substituept enhances the nematic properties relative to X = H. Thus, the cut off of nematic properties is to the right of H (Fig. 5). For the SBAC system, the molecular structure is less favorable to liquid crystalline properties, and no liquid crystals are exhibited by the unsubstituted system. Moreover, the system must be less nematogenic, since only those terminal substituents which most strongly favor nematic behavior give rise to nematic states in the racemic forms and cholesteric states in the optically active forms (Fig. 5).

	$MeO > NO_2 > Cl > Br$	$> NMe_2 > Me$	$> H$
For SBAC systems	Cholesteric or nematic	Smectic	Not liquid crystalline

Figure 5. Terminal group efficiency order for the *nematic* states of 4-(*p*-substituted benzylideneamino)-4′-methoxybiphenyls and the behavior of SBAC systems with the same terminal substituents.

The lower nematogenic character or higher smectogenic character of the SBAC systems is consistent with the fact that the compounds are esters. Note too, that a terminal Me group favors cholesteric properties in the cholesteryl *p*-substituted benzoates. These systems are therefore more nematogenic/cholesterogenic than the SBAC systems, and are in fact more similar to the methoxy anils, with a cut off to the right of H. The effects of terminal substituents

on liquid crystal properties must therefore be considered in relation to the nature of the system in which they occur.

Conclusions

The great weight of evidence now suggests strongly that cholesteric and nematic liquid crystals are very closely related. Until this evidence accumulated in the last three years, I preferred to consider the cholesteric liquid crystal as a third distinct type of liquid crystal, and indeed, some of the properties of cholesteric liquid crystals are still difficult to rationalize in terms of a nematic system, e.g., the apparent focal-conic texture of the cholesteric state. However, it now seems preferable to regard the cholesteric state as closely akin to the nematic state, but exhibiting additional and unique optical properties stemming from the optical asymmetry of the molecules. The general conclusions reached by Friedel[30] about the cholesteric state seem therefore to be vindicated by these results obtained some 45 years later.

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