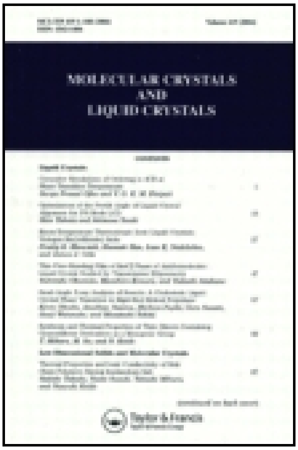

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Synthesis and Liquid Crystal Properties of Chiral Alkyl-Cyano-Biphenyls (and -p-Terphenyls) and of Some Related Chiral Compounds Derived from Biphenyl

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Synthesis and Liquid Crystal Properties of Chiral Alkyl-Cyano-Biphenyls (and -*p*-Terphenyls) and of Some Related Chiral Compounds Derived from Biphenyl†

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(*Received August 23, 1976*)

Using only (−)-2-methylbutan-1-ol as an optically active starting material, other chiral aliphatic materials have been derived by synthetic procedures which preserve the optical activity, and a number of chiral mesogens incorporating the biphenyl (or *p*-terphenyl) ring system have been prepared. The new cholesterogens give a wide range of physical properties—melting points, cholesteric–isotropic liquid transition temperatures and pitch values. The twisting powers of the individual materials, i.e., the cholesteric pitch values, are related to the proximity of the chiral centre of the alkyl group to the ring system in which it is a substituent. Many of the compounds exhibit only cholesteric mesophases but some give additional smectic phases. The physical properties of the mesogens are assessed with particular reference to their applications in electro-optical displays or in surface thermography. In the latter case, the compounds provide a range of cholesterogens of good chemical/photochemical stabilities from which mixtures with thermochromic properties can be made. Examples are given of mixtures; with such materials, the sensitivity of colour play for a given mixture composition can be manipulated in a way which is not practical with sterol-type cholesterogens. With regard to the smectic properties exhibited by some of the compounds, of particular interest are those chiral smectic C phases which, as thin films in the planar texture, show iridescence colours through selective, temperature dependent reflection of light in the visible wavelength range.

INTRODUCTION

During the last few years, the unique properties of cholesteric liquid crystals have found many new applications in display devices and in medical and other technologies.[1] Cholesterogens used in electro-optical display devices

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† Presented at the Sixth International Liquid Crystal Conference, Kent State University, Kent, Ohio, USA, August, 1976.

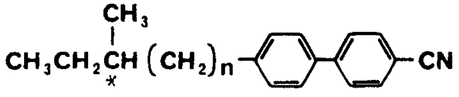
have two important functions as additives to nematic liquid crystals of positive dielectric anisotropy: (a) at low concentrations to prevent areas of reverse twist in twisted nematic displays and (b) at higher concentrations to give long pitch cholesterics suitable for the cholesteric-nematic phase-change display. Due to their unique colour properties, certain cholesteric phases can also be used to measure surface temperatures or by utilising colour differences to indicate the temperature variations over a surface. This particular property has many medical applications in the thermal mapping of the human skin and the consequent diagnosis of, for example, vascular diseases or breast cancer. Cholesterogens based on cholesterol have usually been used in the development of such devices mainly because of the low cost and ready availability of the materials. However, because of the inherent instability of these materials, their continued use and serious commercial application have been somewhat limited, particularly in the area of surface thermography. Consequently there is a desire for cholesterogens of high photochemical/chemical stability with similar helical twisting powers to those of sterol-type cholesterogens. Some suitable materials have already been reported by us[2,6] and other workers,[4] and we wish now to report the preparation of a wider range of new materials which give cholesteric liquid crystals possessing a combination of the physical properties required for the applications outlined above and also high chemical stability.

RESULTS AND DISCUSSION

Two cholesterogens of high chemical/photochemical stability that were already available have the structures II (with $n = 1$) and III (with $n = 3$). The first of these compounds, the alkoxy-cyanobiphenyl, had some interest for electro-optical displays, but because of its low, virtual cholesteric-isotropic liquid transition temperature, this restricted the *upper* working temperature ranges of its mixtures. The second of the compounds, the alkyl-cyano-*p*-terphenyl was more useful, but its high melting point (120°C) imposed some restrictions on the *lower* limits of melting of its mixtures.

We have therefore prepared some new cholesterogens by the incorporation of a chiral centre in the alkyl group of the well reported[5] 4-*n*-alkyl-4′-cyanobiphenyls. This has provided us with a series of low melting materials[6] with the general structure I. The asymmetric centre is asterisked and *n* has the values 1, 2 or 3. The members of the series vary not only in alkyl chain length, but also in the location of the asymmetric centre with respect to the ring system. From the thermodynamic data given in Table I, it can be seen that the materials are all low melting and give monotropic cholesteric and smectic A phases, but because of the low enthalpies of fusion (ΔH), all three compounds exist

I



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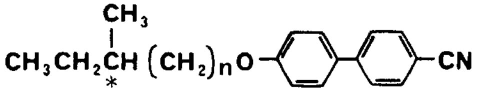
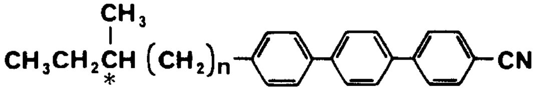
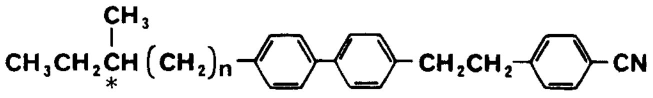


III



IV



n is usually from 1 to 3

for indefinite periods as isotropic liquids at room temperature. The smectic phase of each of the materials was found to be A in type by showing that each phase was separately miscible at all concentrations with the known S_A phase of cholesteryl myristate.[7] Together with their high twisting powers, particularly when $n = 1$ or 2, the physical characteristics of these materials and their strong positive dielectric anisotropies make them most suitable for use in electro-optical display devices. The cholesteric-nematic phase change

TABLE I

Physical constants for compounds I and II

Structure	n	C-I °C	I-Ch °C	Ch-S_A °C	ΔH kcal mol^{-1}	Pitch* μm
I	1	4	(−30)	(−54)	1.5	0.2
I	2	9	(−14)	(−22)	3.2	0.3
I	3	28	(−10)	(−20)	6.0	0.4
II	1	53.5	(9) ± 3[a]	–	3.5	1.5
II	3	57.5	(35) ± 3[a]	–	7.2	1.0

C = crystal; S_A = smectic A; Ch = cholesteric; I = isotropic liquid

ΔH = enthalpy of fusion of the most stable solid

Pitch* = values for cholesteric phases extrapolated from measurements on 10% solutions in 5CB

5CB = 4-*n*-pentyl-4′-cyanobiphenyl

( ) = monotropic transition

[a] virtual transition

device requires low melting, wide range cholesteric mixtures of strong positive dielectric anisotropy, with pitch lengths in the region 2.0–3.0 μm. Hence these chiral 4-alkyl-4′-cyanobiphenyls are very satisfactory materials for use in conjunction with nematic mixtures of the already commercially successful[8] 4-*n*-alky-4′-cyanobiphenyls and 4-*n*-alkyl-4″-cyano-*p*-terphenyls for phase-change displays and also for twisted nematic displays free from problems of reverse twist.

Also in addition to (+)-4-(4‴-methylhexyl)-4″-cyano-*p*-terphenyl, structure III, $n = 3$, we have prepared (+)-4-(3‴-methylpentyl)-4″-cyano-*p*-terphenyl, structure III, $n = 2$. The properties of this compound are given in Table II. These compounds offer the possibility of composing phase-change eutectic mixtures in conjunction with the cholesteric biphenyls (I), such that a high cholesteric thermal stability is maintained without detriment to the helical pitch length.

As well as providing large pitch cholesteric mixtures for display devices, the compounds with structures I and III may be used in mixtures with each other to give tight pitch cholesterics which exhibit thermochromism.[9] This means that the helical pitch lengths of their molecular formations are such that thin films of the phases in the Grandjean plane texture will rotate the plane of polarisation of incident polarised light and will reflect elliptically polarised light of specific wavelengths (according to conditions) when illuminated by ordinary light.

Examples of such mixtures (neither is claimed to be a eutectic composition) are given below, together with their transition temperatures and the colours of selective light reflection at particular temperatures.

Mixture 1

14 wt % of (+)-4-(3‴-methylpentyl)-4″-cyano-*p*-terphenyl (III, $n = 2$).
86 wt % of (+)-4-(3″-methylpentyl)-4′-cyanobiphenyl (I, $n = 2$).
Transition temperatures: S_A–Ch, 4.8°C; Ch–I, 17.5°C

Selective Reflection	Temperature (°C)
Red	5
Yellow	8
Green	9
Turquoise	12
Blue	14
Isotropic liquid (clear)	17.5

Mixture 2

14 wt % of (+)-4-(2″-methylbutyl)-4′-cyanobiphenyl (I, $n = 1$)
74 wt % of (+)-4-(4″-methylhexyl)-4′-cyanobiphenyl (I, $n = 3$)

12 wt % of (+)-4-(4‴-methylhexyl)-4″-cyano-*p*-terphenyl (III, $n = 3$)
Transition temperatures: S_A–Ch, −13°C; Ch–I, +4°C

Selective Reflection	Temperature (°C)
Pink	−12
Yellow	−11.5
Green	−10
Turquoise	−8.5
Blue	−6
Isotropic liquid (clear)	+4

Both these mixtures (neither has yet been otained as a solid) have remained stable, without segregation, over a period of a year, and have shown decreases of <1°C in the Ch–I transition temperatures and no changes in colour intensity of reflected light when ordinary microscope slide preparations with a cover glass were left in the normal laboratory atmosphere for the same period of time.

Besides the advantages of the greater stability of these non-sterol cholesterogens compared with sterol cholesterogens, the racemic, nematic analogues of these materials may be synthesised; this is not practicable with cholesterol and other sterol derivatives. Thus the sensitivity of colour play for a mixture can be manipulated without altering the actual relative amounts of its constituents—see Mixture 5 for an example. By comparing the data for the compounds in Table I, it can be been that firstly, the chiral alkyl compounds are superior to the chiral alkoxy compounds, and that secondly, the (+)-2-methylbutyl group appears to be the most effective in producing tight pitch cholesterics. Hence, in the remaining examples, this group is used extensively in direct linkage with the ring system.

(+)-4′-Substituted 4-(β-4″-substituted-phenylethyl)biphenyls (Structure IV) The 4′-*n*-alkyl and 4′-*n*-alkoxy analogues of the present chiral 4′-alkyl 4-(β-4″-substituted-phenylethyl)biphenyls have already been reported[10] on and shown to be possible nematogenic substitutes for 4-*n*-alkyl-4″-cyano-*p*-terphenyls[11] in eutectic mixtures with the 4-*n*-alkyl-4′-cyanobiphenyls, without the loss of any of the excellent stability properties of these mixtures. Therefore, we have prepared the cholesterogens of structure IV with $n = 1$ or 2 as possible alternatives to the chiral 4-alkyl-4″-cyano-*p*-terphenyls for use in phase-change eutectic mixtures. The physical constants for these materials—alternatively named (+)-1,2-[4′-(4″-substituted-biphenylyl)-4‴-substituted-phenyl]ethanes—are given in Table II.

Of most significance is the compound IV with $n = 1$, which gives a cholesteric phase of small pitch length. This material may be used in conjunction with (+)-4-(2″-methylbutyl)-4′-cyanobiphenyl (I, $n = 1$) to obtain wide range cholesteric mixtures, with pitch lengths of the order 1–2 μm, for display

TABLE II

Physical constants for compounds III and IV

Structure	n	C-S$_A$/Ch °C	S$_A$-Ch °C	Ch-I °C	ΔH kcal mol^{-1}	Pitch 10% in 5CB μm
III	2	157	—	202	3.7	3.7
III	3	120	163	186	3.3	2.8
IV	1	91.7	—	103.4	5.6	1.5
IV	2	91.6	—	110.8	6.1	4.5

C = crystal; S$_A$ = smectic A; Ch = cholesteric; I = isotropic liquid
ΔH = enthalpy of fusion of the most stable solid
5CB = 4-*n*-pentyl-4′-cyanobiphenyl

device application. Although the Ch–I transition temperatures of the chiral disubstituted-phenylethylbiphenyls are lower than those of the analogous *p*-terphenyls and their solubilities in the 4-*n*-alkyl-4′-cyanobiphenyls are of the same order, they do enable the preparation of eutectic compositions with quite high Ch–I transition temperatures and with lower melting points than those containing only chiral terphenyl additives.

The (+)-1,2-[4′-(4″-alkylbiphenylyl)-4‴-cyanophenyl]ethanes also extend the range of possible thermochromic mixtures with other cholesteric materials. An example of such a mixture is shown below.

Mixture 3

20 wt% of (+)-1,2-[4′-{4″-(2⁗-methylbutyl)biphenylyl}-4‴-cyanophenyl] ethane (IV, $n = 1$)
80 wt % of (+)-4-(4″-methylhexyl)-4′-cyanobiphenyl (I, $n = 3$)
Transition temperatures: S$_A$-Ch, −3°C; Ch-I, 15°C

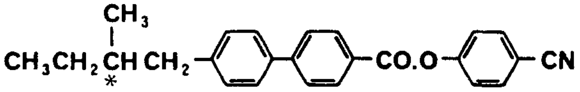
Selective Reflection	Temperature (°C)
Red	−3
Yellow	−2.5
Green	−2.0
Turquoise	−1.5
Blue	−1.0
Isotropic liquid (clear)	15

This particular example demonstrates that very narrow temperature ranges for selective reflection of light covering the visible spectrum can be achieved with these new cholesterogens.

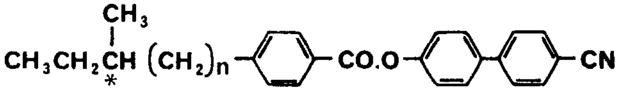
Esters

Since esters are relatively stable systems and are readily accessible, we felt that a suitable selection of such materials would provide useful results for a comparison of the effects of chiral substituents in different cholesterogens. The selected products, compounds V–VIII, would also provide further non-sterol cholesterogens for technological uses.

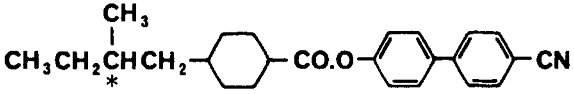
V



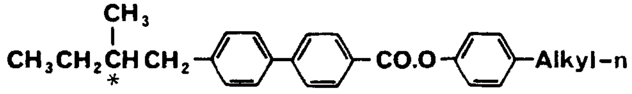
VI



VII



VIII



n is usually from 1 to 3

Compounds V–VII have positive dielectric anisotropies and some physical constants for these materials are given in Table III.

The materials have quite high melting points and high cholesteric to isotropic liquid transition temperatures. The (+)-2-methylbutyl group is as effective a twisting group in either compound V or VI, with $n = 1$, but not in compound VII. This is possibly due to the loss of rigidity in the molecule due to the cyclohexylene ring.

TABLE III

Physical constants for coupounds V, VI and VII

Structure	n	C-S_A/Ch °C	S_A-Ch °C	Ch-I °C	ΔH kcal mol^{-1}	Pitch 10% in 5CB μm
V	–	99.5	–	195.9	7.1	1.6
VI	1	96	–	210	5.2	1.6
VI	2	99.2	–	205	4.5	4.7
VII	–	77.6	138	190.4	4.6	4.7

C = crystal; S_A = smectic A; Ch = cholesteric; I = isotropic liquid
ΔH = enthalpy of fusion of the most stable solid
5CB = 4-*n*-pentyl-4′-cyanobiphenyl

The racemic analogue of compound VI, with $n = 1$, was also prepared and found to have a melting point (105°C) which is higher than that of the optically active material. This may possibly be due to the formation of a more thermodynamically stable crystal in the form of a racemic compound.

Mixtures 4 and 5 demonstrate the use of 4-(4′-cyanobiphenylyl) 4-(2′-methylbutyl)benzoate in mixtures. The pure optically active isomer is used in mixture 4, but in mixture 5 some of the racemic modification is used, and its effect in widening the temperature range for reflection of light covering the visible spectrum is clearly demonstrated.

Mixture 4

20 wt % of (+)-4-(4′-cyanobiphenylyl) 4-(2′-methylbutyl)benzoate (VI, $n = 1$)
80 wt % of (+)-4-(4″-methylhexyl)-4′-cyanobiphenyl (I, $n = 3$)
Transition temperatures: S_A–Ch, −10°C; Ch–I, +19°C

Selective Reflection	Temperature (°C)
Red	−10
Green	−9
Turquoise	−8
Blue	−7
Isotropic liquid (clear)	+19

Mixture 5

12 wt % of (+)-4-(4′-cyanobiphenylyl) 4-(2′-methylbutyl)benzoate (VI, $n = 1$)
8 wt % of (∓)-4-(4′-cyanobiphenylyl) 4-(2′-methylbutyl)benzoate (VI, $n = 1$)
80 wt % of (+)-4-(4″-methylhexyl)-4′-cyanobiphenyl (I, $n = 3$)
Transition temperatures: S_A–Ch, −10°C; Ch–I, +19°C

Selective Reflection	Temperature (°C)
Red	−10.0
Orange	−9.5
Yellow	−8.5
Green	−7.0
Turquoise	−3.0
Blue	+16
Isotropic liquid (clear)	+19

Although the transition temperatures for the two mixtures have remained constant, the full range of selective reflection of light from red to blue occurring over 3°C for mixture 4 has been expanded to 26°C for mixture 5 by the addition of the racemate.

A comparison of the liquid crystalline properties of 4-*n*-alkylbenzoic acids and trans-4-*n*-alkylcyclohexane-1-carboxylic acids[12,13] showed that the cyclohexane acids had lower melting points, enhanced smectic thermal stabilities, and slightly lower N–I transition temperatures. Therefore we prepared (+)-4-(4′-cyanobiphenylyl) trans-4-(2′-methylbutyl)cyclohexane-1-carboxylate (VII) in order to gain some improvement, by way of a lowering of the melting point, in the properties of (+)-4-(4-cyanobiphenylyl) 4-(2′-methylbutyl)benzoate. However, although a lowering in melting point was obtained much of the effectiveness of the (+)-2-methylbutyl group in producing a tight pitch was lost.

In order to obtain a lowering in the melting point of compound V, without any loss in twisting power, the cyano group was replaced by a *n*-alkyl group to give an homologous series of compounds of general structure VIII. Physical constants for these cholesteric (+)-4-*n*-alkylphenyl 4″-(2‴-methylbutyl)biphenyl-4′-carboxylates are given in Table IV.

TABLE IV

Physical constants for compounds VIII

n-Alkyl	C–Ch °C	Ch–I °C	ΔH kcal mol^{-1}	Pitch* μm
C_2H_5	81.3	141.1	5.7	ca. 0.2
C_3H_7	81.5	151.3	5.6	
C_4H_9	65.6	127.5	4.4	
C_5H_{11}	63.6	138.2	4.1	
C_6H_{13}	60.3	132.3	6.5	

C = crystal; Ch = cholesteric; I = isotropic liquid
ΔH = enthalpy of fusion for the most stable solid
Pitch* = actual pitch values measured for the cholesteric phases at 120°

These lower melting compounds have negative dielectric anisotropies and small pitch lengths and provide a useful homologous series of non-sterol cholesterogens for study. None of the materials exhibits a smectic phase, but miscibility studies with cholesteryl myristate show that they have latent S_A properties.

Although a complete analysis of the "handedness" of the cholesteric phases of new cholesterogens described in this paper has not been made, it can be said, from qualitative observations made when mixing the various materials, that the sign of rotation of the cholesteric helices of the compounds VIII is opposite to the sign of the helices for some† of the compounds I–VII. The handedness of the compounds VIII has been determined by examining microscopically various mixtures of the individual members of the series with cholesteryl chloride, which is right-handed (type: dextro) and with cholesteryl myristate, which is left-handed (type: laevo). The mixtures with cholesteryl

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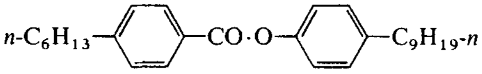
† Added in proof: I, III, IV, VI, $n = 2$ and II, $n = 1$ or 3.

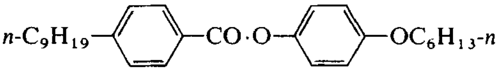
myristate at approx. 50/50 composition are nematic, but with cholesteryl chloride, they are cholesteric. Therefore the materials VIII are right-handed cholesterogens (type: dextro).

Chiral esters exhibiting S_C phases

By comparison of the properties of the two terminally disubstituted phenyl benzoates[14,15] shown below, the effect of the alkoxy group is seen, as expected, to enhance the liquid crystal thermal stability; moreover, the monotropic smectic phase of the alkoxy compound is S_C in type.



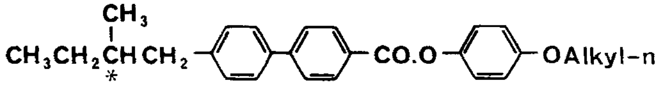
Transition temperatures: C–I, 33°C; (N–I, 28°C)



Transition temperatures: C–N, 43°C; (S_C–N, 34°C); N–I, 62°C

We reasoned therefore that the esters of Structure IX derived from 4-*n*-alkoxyphenols and (+)-4-(2″-methylbutyl)biphenyl-4′-carboxylic acid, would exhibit similar mesophases to the 4-*n*-alkoxyphenyl benzoate ester with the additional property of being optically active. The corresponding mesophases would then be chiral smectic C and cholesteric, and the helical pitch lengths should be of the order 0.2 μm. The melting points and mesomorphic transition temperatures for these (+)-4-*n*-alkoxyphenyl 4-(2″-methylbutyl)biphenyl-4′-carboxylates are given in Table V.

IX



Chiral Smectic C – Iridescence colours

All the compounds exhibit enantiotropic cholesteric phases which show blue/violet iridescence in the Grandjean plane texture, corresponding to pitch lengths of *ca.* 0.2 μm at temperatures of about 120°C. The wavelength of the reflected light shifts towards the red end of the spectrum as the temperature falls, and underlying the cholesteric phases, the compounds with $n = 5$–10 exhibit chiral S_C phases. Figure 1 shows the plot of the transition temperatures against the number of carbon atoms in the alkyl chain for this series; this reveals no unusual features. When the compounds which give enantiotropic S_C phases are heated they melt to give a focal-conic texture (Plate 1) for this

TABLE V

Thermodynamic data for compounds IX

n-Alkyl	C–S_C/Ch °C	S_C–Ch °C	Ch–I °C	ΔH kcal mol^{-1}
C_4H_9	81.7	—	169.3	5.0
C_5H_{11}	79.8	(70)	164.5	6.9
C_6H_{13}	68.8	80.2	163.5	6.1
C_7H_{15}	80.4	87.3	157.7	7.2
C_8H_{17}	76	88.6	155.4	10.7
C_9H_{19}	79	89.5	147	10.2
$C_{10}H_{21}$	76.8	93.4	148.5	11.5

C = crystal; S_C = chiral smectic C; Ch = cholesteric; I = isotropic liquid

ΔH = enthalpy of fusion of the most stable solid

( ) = monotropic transition

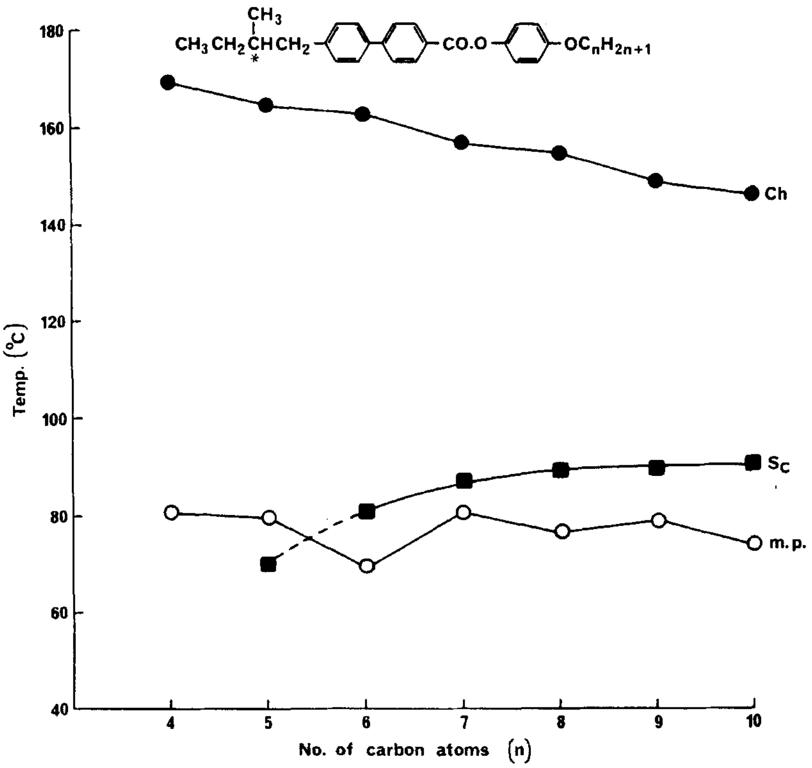


FIGURE 1 Plot of transition temperatures against the number of carbon atoms in the ether alkyl chain for the 4-*n*-alkoxyphenyl esters of 4′-(2″-methylbutyl)biphenyl-4-carboxylic acid.

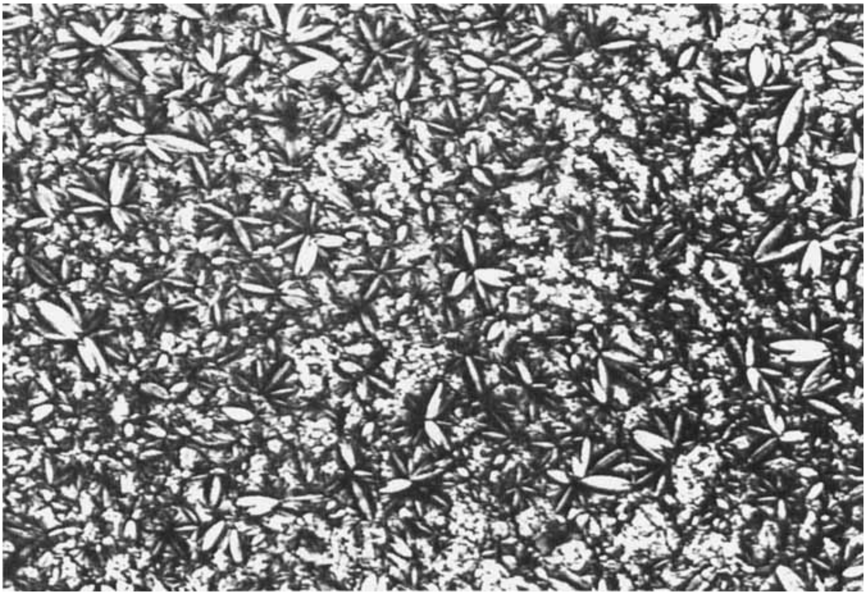


PLATE 1 Focal-conic texture of the chiral smectic C phase of compound IX with $n = 6$. (× 200)

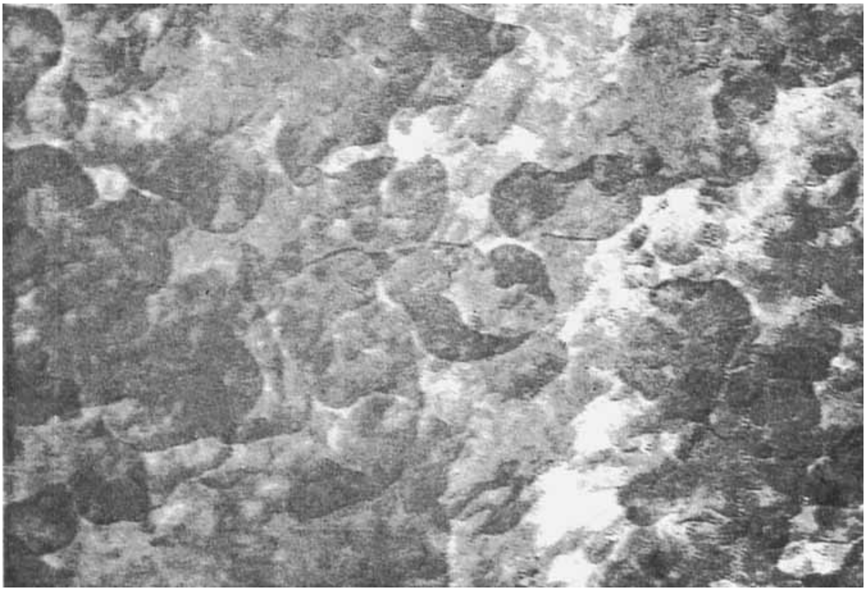


PLATE 2 Planar texture of the chiral smectic C phase of compound IX with $n = 6$ (× 200)—see also plate 3.

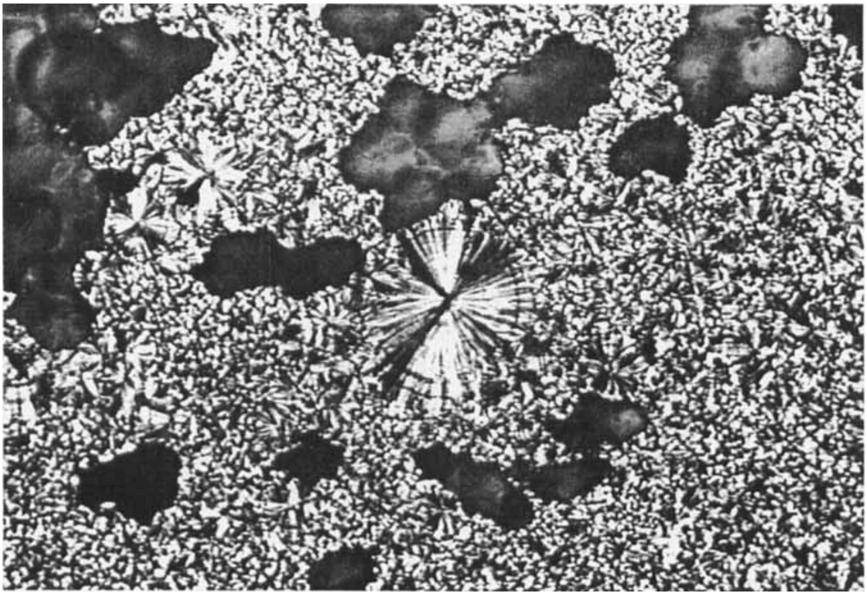


PLATE 3 Photomicrograph showing focal-conic and planar regions of the chiral smectic C phase of compound IX with $n = 6$. (× 200)

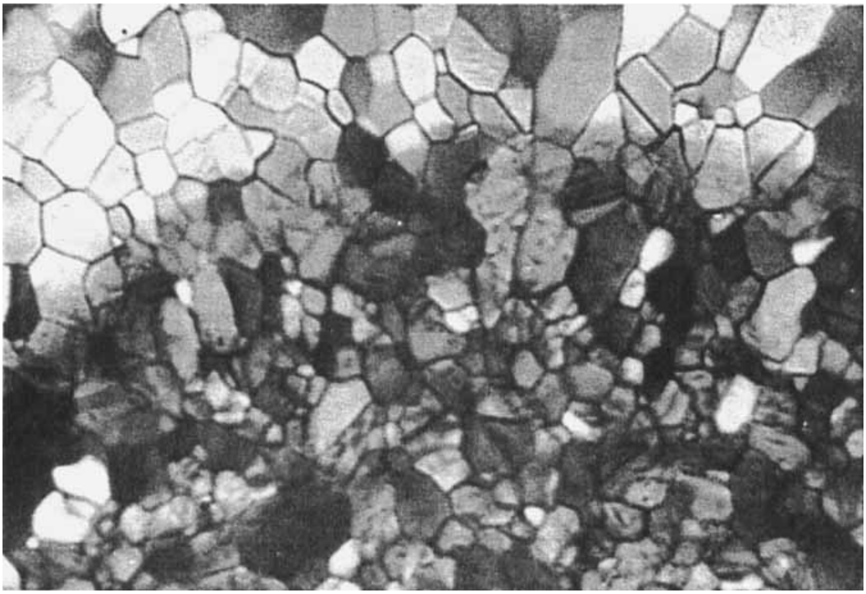


PLATE 4 Platelets of the cholesteric "blue phase" of compound VI with $n = 1$. The upper region shows the clear platelets and the lower region the wrinkled platelets separated by a well defined curved front. (× 200)

phase. Thin films of these chiral S_C phases in the focal-conic texture may be pressed out to form a planar texture (Plate 2), which is the equivalent of the schlieren texture of a non-chiral S_C phase. The focal-conic S_C texture is also formed if the "focal-conic" or Grandjean plane cholesteric texture is cooled below the Ch–S_C transition temperature.

Previous[16] examples of compounds exhibiting chiral S_C phases have such long pitch lengths that the light reflected from their planar textures is not in the visible range. Figure 2 shows a temperature against pitch length plot for the compound IX, with $n = 6$. On heating, the pitch length of the chiral S_C phase increases. Therefore, the selectively reflected light changes from the blue to the red end of the visible spectrum, the wavelength passing into the infra-red at the S_C–Ch transition; on further heating, the wavelength then shifts in the opposite direction for the cholesteric phase, which first reflects red and finally blue-violet light nearer to the Ch–I transition.

Although the single compounds have not got particularly wide range, chiral S_C phases, lower melting mixtures of the compounds with each other

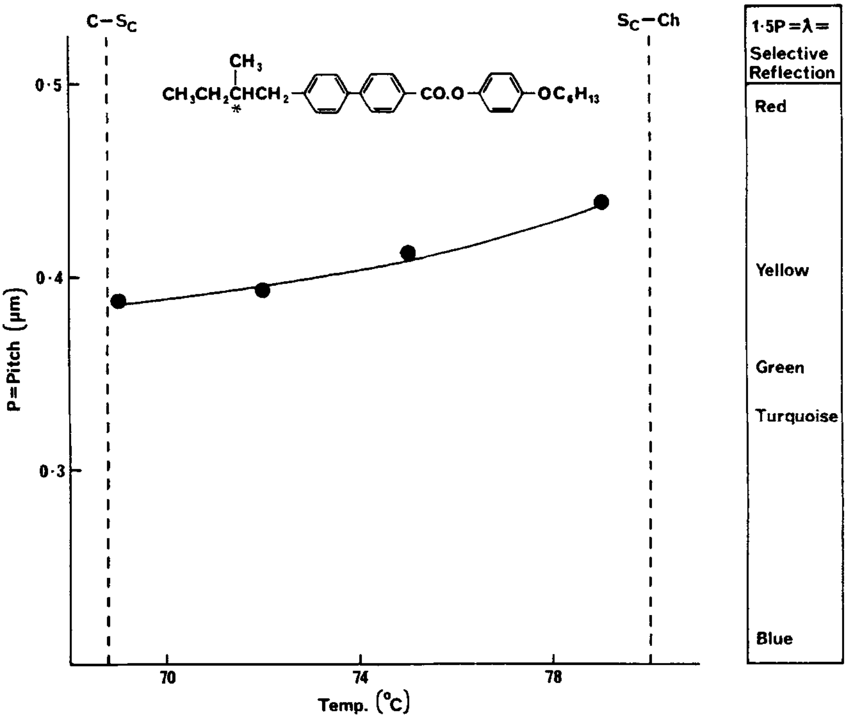


FIGURE 2 Plot of pitch against temperature covering the range of the chiral S_C phase of the compound IX with $n = 6$.

or with other compatible materials can be obtained and do exhibit wider range thermochromic S_C and also Ch phases.

The results for two such mixtures are given below: neither mixture is claimed to correspond to a eutectic composition.

Mixture 6

40 mole % of compound IX, with $n = 4$
31 mole % of compound IX, with $n = 5$
29 mole % of compound IX, with $n = 7$
Transition temperatures: C-S_C, 49°C; S_C-Ch, 72°C; Ch-I, 163.3°C

Selective Reflection	Temperature (°C)
Blue	50.0
Turquoise	57.0
Green	59.0
Yellow	66.5
Orange	67.2
Red	68.2
Transition to cholesteric	72.0
Red	72.5
Yellow	72.8
Green	74.0
Turquoise	83.0
Blue	84.5
Blue/violet	92.0
Transition to isotropic liquid	163.3

The colours for the above mixture, as for mixture 7—see Figure 3—were seen on viewing a thin film of the planar texture of this mixture in a direction at right angles to the film.

Mixture 7

24 mole % of compound IX, with $n = 4$
16 mole % of compound IX, with $n = 5$
32 mole % of compound IX, with $n = 6$
15 mole % of compound IX, with $n = 7$
7 mole % of compound IX, with $n = 8$
6 mole % of compound IX, with $n = 10$
Transition temperatures: C-S_C, 39.4°C; S_C-Ch, 74.3°C; Ch-I, 162.2°C

Figure 3 shows the variation of pitch length and of colour of selectively reflected light with temperature for mixture 7. This shows clearly that the variation of colour with temperature for the chiral S_C phase is the reverse of that for the cholesteric phase. When a thin film of such a material is cooled as

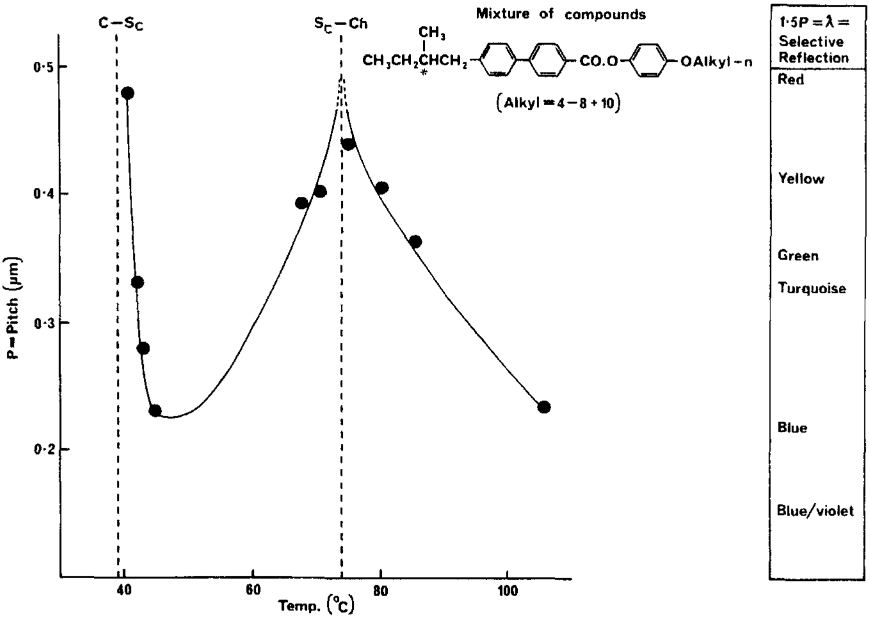


FIGURE 3 Plot of pitch against temperature covering the entire range of the chiral S_C phase and part of the cholesteric phase range for a mixture of esters (compound IX, n = 4–8 + 10).

the Grandjean plane texture, the colour of the cholesteric phase (initially violet) changes from blue-violet to red over a range of about 30°C above the Ch–S_C transition. Just above this transition, the wavelength of light reflected passes into the infra-red. If the S_C phase is then converted mechanically into the planar texture, the wavelength of the light reflected is found to have shifted back into the red end of the visible spectrum. Over a range of cooling of about 20°C, the colour changes back to blue. On rapid cooling of a thin film, two fairly narrow rainbows of opposite colour sequence are therefore seen on either side of the S_C–Ch transition temperature. A third rainbow is in fact observed just before crystallisation occurs. This may possibly be caused by the buildup of cybotactic groups of a second smectic phase which is not seen because it induces crystallisation. In support of this possibility, it is noted that the degree of supercooling for the mixture is slight—crystallisation occurs consistently at close to 36°.

Amorphous liquid-cholesteric liquid crystal transitions

We have examined microscopically the Ch–I transitions for all these new cholesterogens and found that their associated pretransitional effects provide further examples of the categories described by Coates and Gray.[17,18] For the majority of the examples (compounds I, III, V, VI, VII, VIII and IX), on heating the "focal-conic" cholesteric textures, platelet textures are given at a temperature denoted T°C; a typical example of the platelets (which constitute the blue phase or blue apparition, seen by eye) is shown in Plate 4. At a temperature T_1°C, the amorphous liquid forms, and on cooling, this gives the reappearance of the platelets at T_1°C, followed, just below T°C, by the "focal-conic" texture.

The colours of the platelets vary from sample to sample, but all show the typical feature of becoming wrinkled and veiled reversibly as shown in Plate 4, with rising or falling temperature. These features therefore correspond to Type 2 for non-steryl cholesterogens. The platelets for compound I are not easily seen in transmitted light, but can be seen more easily in reflected light.

Typically, the blue phases persisted over 0.2–1.0°C, and no particular extension of this range was observed for any of the cholesteric mixtures. The platelets for the cyclohexyl cholesterogen (VII) were comparatively much slower to form than those of the other cholesterics.

Compounds of structure IV; with $n = 1$ and 2, showed no pretransitional features microscopically or by the naked eye, and thereby correspond to Type 1 for non-steryl cholesterogens.

CONCLUSION

We hope that the potential of these new, stable materials stimulates a wider interest in the practical application of cholesteric liquid crystals for uses other than as novelty thermometers. Besides the mixtures quoted, we have prepared many others and feel confident that, with further development work, thermochromic mixtures can be tailor-made to suit any desired specification. Those we have looked at so far could readily be developed for sensitive measurement in the freezing- or body-temperature regions. Other mixtures could be devised for less obvious applications, for instance, in the possible development of an electro-optic colour display device incorporating an iridescent, chiral smectic C liquid crystal.

EXPERIMENTAL

Transition temperatures were measured by optical microscopy using either a Nikon L-Ke polarising microscope fitted with a Mettler FP 52 heating state and FP 5 control unit or, at low temperatures, a polarising microscope with a cold stage (C. Reichert, Optische Werke AG, Wien, Austria). Enthalpies of fusion for the most stable crystal forms of the mesogens were measured using a Stanton Redcroft (Model 671) low temperature differential thermal analyser.

Specific rotations, $[\alpha]_D^{20}$ values, were measured with 10% w/v solutions in chloroform, using a Bendix–NPL Automatic Polarimeter (Type 143A).

Pitch measurements were made spectrophotometically either with solutions of the cholesterogens in 4-*n*-pentyl-4′-cyanobiphenyl using an SP 200 spectrometer or with the pure materials (in a heated cell) using an SP 700 spectrometer.

The purities of all the final products synthesised and of all those reaction intermediates which were isolated were carefully checked by t.l.c. and mass spectrometry. In addition, satisfactory elemental analysis results were obtained for all the materials, and structural checks were carried out wherever desirable using a Jeo LCO JNM–4H 100 MH3 instrument for n.m.r. results and a P.E. 457 instrument for infra-red spectra.

Preparation of materials

(+)-2-*Methylbutyl bromide*. To a stirred solution of commercially available (−)-2-methylbutan-1-ol (0.34 mol) in dry pyridine (0.12 mol) was added dropwise phosphorus tribromide (0.136 mol). The temperature during the addition was maintained below 15° by cooling the mixture in an ice bath. The white emulsion which formed was stirred at room temperature for 2 hr. After this time, the crude bromide was distilled from the emulsion under reduced pressure (300 mmHg) until the mixture turned orange and "seethed." The crude distillate was taken up in petroleum ether (b.p. 40–60°; 100 ml) and was washed with:

a) 5% sodium hydroxide solution (3 × 50 ml);
b) water (3 × 50 ml);
c) 10% sulphuric acid (2 × 50 ml);
d) concentrated sulphuric acid (100 ml);
e) water (2 × 100 ml).

The solution was dried (Na_2SO_4) and the solvent evaporated off. The residue was distilled and the fraction boiling at 121° collected (96.5% by g.l.c.); $[\alpha]_D^{20}$, 3.9°.

(+)-3-*Methylpentanoic acid*. This was prepared from (+)-2-methylbutyl bromide by an adaptation of the method of Gilman and Kirby.[19] The product distilled at 136° at a pressure of 450 mmHg; $[\alpha]_D^{20}$, 4.7°.

(+)-4-*Methylhexanoic acid*. This was prepared from (+)-2-methylbutyl bromide by the method of Vogler and Chopard-dit-Jean[20] giving the required product boiling at 134° at 25 mmHg; $[\alpha]_D^{20}$, 9.4°.

(+)-4-*Methylhexane*-1-*ol*. This was prepared from the methyl ester of (+)-4-methylhexanoic acid by reduction with lithium aluminium hydride.[21] The product had b.p. 108° at 20 mmHg; $[\alpha]_D^{20}$, 7.6°.

(+)-4-*Methylhexyl bromide*. This was prepared by a standard literature[21] method, by treating the alcohol with bromine over red phosphorus. The final product was distilled at 170°; $[\alpha]_D^{20}$, 7.6°.

(+)-4-(2′-*Methylbutyl*)*biphenyl*. (+)-2-Methylbutyl bromide (0.07 mol) was added, in dry tetrahydrofuran (20 ml), to magnesium turnings (0.2 g atom) in dry tetrahydrofuran (20 ml) and the mixture stirred for 0.5 hr. The reaction was initiated by a crystal of iodine and then controlled by adding the alkyl bromide dropwise.

4-Bromobiphenyl (0.13 mol) in dry tetrahydrofuran (20 ml) was then added dropwise to the Grignard entrainer at such a rate as to maintain a steady reflux. When addition was completed, the mixture was stirred and heated under reflux for 4 hr.

The solution of the Grignard reagent was cooled in an ice bath and with vigorous stirring, a solution of iron III chloride (0.005 mol) in dry tetrahydrofuran (1.5 ml) was added followed by solution of (+)-2-methylbutyl bromide (0.2 mol) in dry tetrahydrofuran (20 ml). The mixture was stirred for 12 hr, then stirred and heated under reflux for 12 hr. After cooling, the mixture was poured into cold dilute (15%) hydrochloric acid solution (600 ml) and stirred for 0.5 hr.

The aqueous mixture was shaken with ether (4 × 200 ml) and the combined extracts were washed with water (3 × 100 ml) before drying over anhydrous sodium sulphate. The solvent was removed and the crude oily product was purified by chromatography, using a silica gel column eluted with petroleum ether (b.p. 40–60°), followed by distillation at 0.1 mmHg. The product had m.p. 25.5°; $[\alpha]_D^{20}$, 11.0°.

(+)-4-(2″-*Methylbutyl*)-4′-*bromobiphenyl*. Under anhydrous conditions, a solution of bromine (0.5 ml) in dry chloroform (5 ml) was added to (+)-4-(2′-methylbutyl)biphenyl (0.04 mol), dissolved in dry chloroform (10 ml). The reaction mixture was kept at 0° throughout the reaction time and light was excluded from the reaction vessel.

After 18 hr and 36 hr, two further additions (2 × 4 ml) of the chloroform solution of bromine (10% v/v) were added. Eighteen hours after the second addition, the mixture was poured into a sodium metabisulphite solution (150 ml). The aqueous solution was shaken with ether (3 × 80 ml). The combined extracts were washed with water (3 × 50 ml), dried over anhydrous sodium sulphate and the solvent was evaporated off. The crude solid was crystallised from ethanol to a constant melting point of 75°; $[\alpha]_D^{20}$, 9.0°.

(+)-4-(2″-*Methylbutyl*)-4′-*cyanobiphenyl.* This was prepared by the method described by Gray *et al.*;[3] $[\alpha]_D^{20}$, 11.8°.

(+)-4-(3″-*Methylpentyl*)-4′-*cyanobiphenyl*, $[\alpha]_D^{20}$, 16.1°; (+)-4-(4″-*Methylhexyl*)-4′-*cyanobiphenyl*, $[\alpha]_D^{20}$, 10.0°; *and* (+)-4-(3‴-*Methylpentyl*)-4″-*cyano-p-terphenyl*, $[\alpha]_D^{20}$, 11.7°. These were prepared by Friedel Crafts acylation, reduction and finally cyanation as described[3] for the 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkyl-4″-cyano-*p*-terphenyls. The m.p.s. for the intermediates are given below.

(+)-4-(3″-Methylpentanoyl)-4′-bromobiphenyl, m.p. 97°; $[\alpha]_D^{20}$, 8.5°;

(+)-4-(4″-Methylhexanoyl)-4′-bromobiphenyl, m.p. 55.7°; $[\alpha]_D^{20}$, 7.4°;

(+)-4-(3‴-Methylpentanoyl)-4″-bromo-*p*-terphenyl, m.p. 196.1°, giving a cholesteric phase until 197.8°; $[\alpha]_D^{20}$, 13.4°;

(+)-4-(3″-Methylpentyl)-4′-bromobiphenyl, m.p. 99°; $[\alpha]_D^{20}$, 12.6°;

(+)-4-(4″-Methylhexyl)-4′-bromobiphenyl, m.p. 88°; $[\alpha]_D^{20}$, 6.9°;

(+)-4-(3‴-Methylpentyl)-4″-bromo-*p*-terphenyl, m.p. 256°; solubility in chloroform is too low to allow a meaningful $[\alpha]_D^{20}$, value to be measured.

(+)-4-(4″-*Methylhexyloxy*)-4′-*bromobiphenyl.* Commercially available 4-bromo-4′-benzenesulphonyloxybiphenyl (0.012 mol) was heated under reflux for 2 hr with a mixture of water (24 ml), dioxan (48 ml) and sodium hydroxide (1.5 g). (+)-4-Methylhexyl bromide (0.01 mol) was added to the solution and the mixture heated under reflux for a further 4 hr. The reaction mixture was poured into water (600 ml) and the precipitated product removed by filtration. The solid was recrystallised from ethanol to constant melting point (128°); $[\alpha]_D^{20}$, 4.4°.

(+)-4-(4″-*Methylhexyloxy*)-4′-*cyanobiphenyl.* This was prepared by the method of Gray *et al.*,[3] for the 4-*n*-alkoxy-4′-cyanobiphenyls; $[\alpha]_D^{20}$, 5.3°.

(+)-1,2-{4′-[4″-(2⁗-*Methylbutyl*)*biphenylyl*]-4‴-*cyanophenyl*}*ethane*, $[\alpha]_D^{20}$, 7.6° *and* (+)-1,2-{4′-[4″-(3⁗-*Methylpentyl*)*biphenylyl*]-4‴-*cyanophenyl*} *ethane*, $[\alpha]_D^{20}$, 9.6. These were prepared by analogous methods to those described by Coates and Gray[10] for the *n*-alkyl homologues. The m.p.s. for (+)-4-[4′-(2‴-*methylbutyl*)*biphenylyl*] 4″-*bromophenylmethyl ketone* and (+)-4-[4′-(3‴-*methylpentyl*)*biphenylyl*] 4″-*bromophenylmethyl ketone* were 154° and 148.5°, respectively.

The m.p.s. for (+)-1,2-{4′-[4″-(2″″-*methylbutyl)biphenylyl*]-4‴-*bromophenyl*}*ethane* and (+)-1,2-{4′-[4″-(3″″-*methylpentyl)biphenylyl*]-4‴-*bromophenyl*}*ethane* were 127° and 136.3°, respectively.

(+)-2-*Methylbutylbenzene*, b.p. 120° *at* 20 mmHg; $[\alpha]_D^{20}$, 5.6° *and* (+)-3-*methylpentylbenzene*, b.p. 108° *at* 20 mmHg; $[\alpha]_D^{20}$, 14.3°. These were prepared by the interaction of (+)-2-methylbutyl bromide and the Grignard reagents of bromobenzene and benzyl chloride, respectively, according to the method of Vavon and Mottez.[22]

(+)-4-(2′-*Methylbutyl)benzoic acid*, m.p. 132°, $[\alpha]_D^{20}$, 13.1° *and* (+)-4-(3′-*methylpentyl)benzoic acid*, m.p. 121°, $[\alpha]_D^{20}$, 16.4°. These were prepared by the conversion of the corresponding alkyl benzenes to the acetophenones, by Friedel Crafts acylation,[23] followed by hypobromite oxidation to give the free acids. The oily intermediate acetophenones were purified by reduced pressure (0.1 mmHg) distillations.

(+)-4-(2″-*Methylbutyl)biphenyl*-4′-*carboxylic acid*. (+)-4-(2″-Methylbutyl-4′-cyanobiphenyl (0.015 mol) was dissolved in methanol (50 ml) and added to a mixture of potassium hydroxide (0.54 mol) and sodium hydroxide (0.75 mol) in methanol (40 ml) and water (20 ml). The solution was heated under reflux until evolution of ammonia ceased (*ca.* 72 hr). The mixture was diluted with water (1000 ml) and acidified with concentrated hydrochloric acid. The precipitated product was filtered off and crystallised twice from ethanol: C-Ch, 224°; Ch-I, 247.4°.

(+)-*Trans*-4-(2′-*methylbutyl)cyclohexane*-1-*carboxylic acid*. A solution of (+)-4-(2′-methylbutyl)benzoic acid (0.2 mol) in sodium hydroxide (0.02 mol) dissolved in water (160 ml) was hydrogenated in the presence of Raney Nickel catalyst (10 g) in an autoclave (1000 ml) at 195° and a pressure of 170 atm of hydrogen for 30 hr.

On cooling, the catalyst was filtered off and the filtrate washed with ether. The aqueous layer was acidified and the precipitated acids were extracted into ether, washed with water and dried (Na_2SO_4). The ether was distilled off and the acids were taken up in methanol (200 ml); the solution was treated successively with 40 g and 30 g of thiourea. After each treatment with thiourea, the crystallisate was filtered from the methanol. The combined crystallisates were dissolved in a 5% potassium hydroxide solution (800 ml), which was then acidified and the (+)-trans-4-(2′methylbutyl)cyclohexane-1-carboxylic acid precipitated was extracted into ether; the extract was washed with water and dried (Na_2SO_4).

The ether was evaporated off and the acid crystallised from acetone to a constant melting point of 50.3°; $[\alpha]_D^{20}$, 11.5°.

4′-*Cyano*-4-*hydroxybiphenyl*, m.p. 198°. This was prepared by the method of Gray *et al.*[3]

4-*Alkylphenols*. These were either commercially available or were prepared by standard methods such as those described by Van der Veen, de Jeu, Grobben and Boven[24] for the preparation of 4-alkylanilines, followed by diazotisation of the amines and hydrolysis of the diazonium sulphates.

4-*Alkoxyphenols*. These were prepared by the mono-alkylation of *p*-quinol using the method of Neubert, Carlino, D'Sidocky and Fishel.[25] The colourless products were purified by column chromatography and crystallisation from hexane.

Esters V–IX. These were prepared by interacting the relevant acid chlorides and phenols in pyridine solution. Purification was achieved by dissolving the residue left, after evaporating off the solvent under reduced pressure, in a minimum volume of chloroform and using chromatography on a silica gel column eluted with chloroform. The combined fractions of ester were recrystallised to constant melting points from either hexane or methanol/ethanol, where appropriate.

Acknowledgement

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References

1. G. Meier, E. Sackmann, and J. G. Grabmaier, *Application of Liquid Crystals* (Springer Verlag, Berlin, Heidelberg, New York, 1975).
2. G. W. Gray, K. J. Harrison, J. A. Nash, and E. P. Raynes, *Electron. Lett.*, **9**, 616 (1973).
3. G. W. Gray, *Proc. Vth Int. Conf. on Liquid Crystals*, Stockholm, June, 1974; *J. Phys. Paris*, **36**, 337 (1975).
4. B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **97**, 1585 (1975).
5. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, *Liquid Crystals and Ordered Fluids*, ed. by J. F. Johnson and R. S. Porter (Plenum Press, New York, 1974), p. 617.
6. G. W. Gray and D. G. McDonnell, *Electron. Lett.*, **11**, 556 (1975).
7. D. Coates and G. W. Gray, *J. C. S. Chem. Comm.*, 101 (1974).
8. B.D.H. Publication, *Liquid Crystals*, 1975; B.D.H. Chemicals Limited, Broom Road, Poole, England.
9. G. W. Gray, *Liquid Crystals and Plastic Crystals*, Vol. 1, ed. by G. W. Gray and P. A. Winsor (Ellis Horwood Limited, Chichester, 1974), Chap. 7.1, p. 327.
10. D. Coates and G. W. Gray, *J. C. S. Perkin II*, 863 (1976).

11. G. W. Gray, K. J. Harrison, and J. A. Nash, *J. C. S. Chem. Comm.*, 431 (1974).
12. G. W. Gray and D. G. McDonnell, to be published.
13. H. Schubert, R. Dehne, and V. Uhlig, *Z. Chem.*, **12**, 219 (1974).
14. D. Demus, H. Demus, and H. Zaschke, *Flüssige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974).
15. R. Steinsträsser, *Z. Naturforsch.*, **27b**, 774 (1972).
16. D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst. Letters*, **34**, 1 (1976).
17. D. Coates and G. W. Gray, *Phys. Lett.*, **45A**, 115 (1973).
18. D. Coates and G. W. Gray, *Phys. Lett.*, **51A**, 335 (1975).
19. H. Gilman and R. H. Kirby, *Org. Syn.*, Coll. Vol. 1, p. 879.
20. K. Vogler and L. H. Chopard-dit-Jean, *Helv. Chim. Acta.*, **43**, 279 (1960).
21. A. I. Vogel, *Practical Organic Chemistry* (Longman Group Limited, London, 1970), 3rd edition.
22. G. Vavon and P. Mottez, *Compt. Rend.*, **218**, 557 (1944).
23. G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).
24. J. Van der Veen, W. H. de Jeu, A. H. Grobben and J. Boven, *Mol. Cryst. Liq. Cryst.*, **17**, 291 (1972).
25. M. E. Neubert, L. T. Carlino, R. D'Sidocky and D. L. Fishel, *Liquid Crystals and Ordered Fluids*, Vol. 2, ed. by J. F. Johnson and R. S. Porter (Plenum Press, New York, 1974), p. 293.