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# Some Cholesteric Derivatives of S-(+)-4-(2′-Methylbutyl) Phenol

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# Some Cholesteric Derivatives of S-(+)-4-(2′-Methylbutyl)Phenol

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A facile synthesis of S-(+)-4-(2′-methylbutyl)phenol and its interaction with a number of different acids are used to provide a wide variety of new chiral nematic liquid crystals. These new cholesterogens display a range of liquid crystal and other physical properties, and are potentially useful for application in display device and other technologies. Of particular interest in this respect are the materials containing two chiral centres and which therefore have very small helical pitch lengths—as low as 0.1 μm.

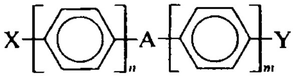
## INTRODUCTION

The continued escalation of research on cholesterogens is a clear indication of the increasing interest in the application of the unique colour reflecting properties of the cholesteric phase in display devices and other technologies. The extended awareness of the technological potential of the cholesteric phase has been the result of the organic chemists' ability to synthesise chiral nematogens which are *not* derived from sterols, but which give cholesteric phases with pitch lengths analogous to those of, for example, the cholesteryl esters. This has been achieved by the simple expedient of incorporating in the structures of well proven nematic liquid crystalline materials, alkyl groups derived from S-(−)-2-methylbutan-1-ol, which is a readily available material of high optical purity.

The organic chemists' efforts[2–7] were initially directed by a commercial desire to find cholesteric liquid crystal additives suitable for use in twisted nematic and cholesteric-nematic phase change electro-optical display devices. The only requirements expected of such an additive were that it should be at least as electrochemically, chemically and photochemically stable as the host nematogen. The results of this work made available a wide structural variety of cholesteric liquid crystals (chiral nematics) which could not have been achieved with derivatives of cholesterol. Furthermore, these new cholesterogens embodied for the first time many of the physical properties, such as dielectric anisotropy, birefringence, viscosity, etc, which were found to be advantageous in the commercial application of electro-optical display devices using the analogous nematogens. However, while gaining in general structural versatility of the molecular core, the new cholesteric liquid crystals do not lend themselves to the normal variation in liquid crystalline properties that can be obtained by progressing along a homologous series. This is particularly so for nematogens containing only one chiral alkyl group and a cyano group introduced in order to achieve materials with a high positive dielectric anisotropy. For instance, in the case of the nematogenic 4-*n*-alkyl- and 4-*n*-alkoxy-4′-cyanobiphenyls, a number of useful low-melting eutectic mixtures[1] can be made by incorporating the various homologues. However, essentially only one *tight* twisting cholesterogen, S-(+)-4-(2″-methylbutyl)-4′-cyanobiphenyl,[2] may be prepared with this type of structure. Of course, differences in liquid crystal thermal stabilities (transition temperatures) can be obtained by altering the position of the asymmetric centre by employing homologues of the S-(+)-2-methylbutyl group, eg, the S-(+)-3-methylpentyl or S-(+)-4-methylhexyl groups. While such changes do allow certain variations in the liquid crystal transition temperatures to be achieved, they also affect the cholesteric helical pitch sense and considerably reduce its size.[3] In this context, the S-(+)-2-methylbutyl group has been established as a very effective twisting group and therefor one which is highly desirable in any non-steryl cholesterogen.

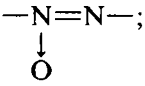
## RESULTS AND DISCUSSION

Many previous studies of liquid crystals have been carried out on compounds of the type (I) below:



(I)

where X = alkyl or alkoxy
Y = alkyl or alkoxy
*n* or *m* = 1 or 2
A = —CH=N—; —N=N—;



$\underset{\underset{\displaystyle O}{\downarrow}}{—N{=}N—}$; or
—CO·O—

With two alkyl groups in such a structure, both end groups may be varied to produce a great number of homologous series. Also the chiral analogues of these materials (azo-methines,[4] azo-compounds,[5] azoxy-compounds[5] and esters[6,7]) may be prepared to give some useful series of cholesterogens with negative or weakly positive dielectric anisotropies. Of these types, the esters are the most desirable for commercial application, since they are relatively stable materials and are colourless. The inclusion of the S-(+)-2-methylbutyl group into the acid moiety of esters of the above structure (where A = —CO·O—) has provided many useful cholesterogens with a wide variety of liquid crystal and other physical properties.

Consequently, we have developed a facile method of incorporating the chiral S-(+)-2-methylbutyl group into the phenol moiety of such esters, thereby providing a wide number of new cholesterogens of which examples are now quoted.

A) S-(+)-4-(2′-Methylbutyl)phenyl 4-substituted benzoates and S-(+)-4-(2′-methylbutyl)phenyl trans-4-alkylcyclohexane-1-carboxylates

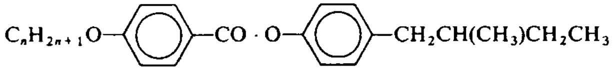
The physical constants for some of these esters derived from 4-*n*-alkoxybenzoic acids are given in Table I.

The lower homologues of this particular series have been reported recently by Hsu, *et al.*,[8] who have assigned their materials the absolute configuration *R*. However, we feel that this assignment should be S, since we have already shown, in a previous publication,[3] that ester derivatives of S-(+)-4-(2′-methylbutyl)phenol, synthesised from S-(−)-2-methylbutan-1-ol are also S, with cholesteric pitch senses that are dextro.

A comparison of these compounds with the analogous benzoate esters (Table II) of the type reported by Klanderman, *et al.*,[6] but where the chiral alkyl group is in the acid moiety, shows a change in the thermodynamic properties.

TABLE I

Physical constants for the compounds (II)



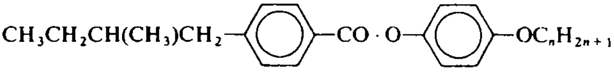
(II)

| *n* | C-$S_A$/I (°C) | $S_A$-Ch (°C) | Ch-I (°C) | Pitch (μm) |
|---|---|---|---|---|
| 6 | 38.0 | — | (36.7) | 0.23 |
| 7 | 45.5 | — | (36.3) | 0.23 |
| 8 | 47.5 | — | (42.0) | 0.23 |
| 9 | 49.5 | (37.2) | (42.7) | 0.23 |
| 10 | 41.8 | 42.2 | 45.3 | 0.23 |

C = crystal; $S_A$ = smectic A; Ch = cholesteric; I = isotropic liquid. ( ) = monotropic transition. Pitch—see experimental section—second method.

TABLE II

Physical constants for the compounds (III)



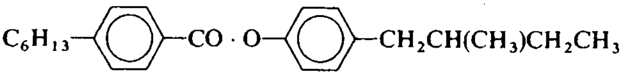
$CH_3CH_2CH(CH_3)CH_2-C_6H_4-CO\cdot O-C_6H_4-OC_nH_{2n+1}$

(III)

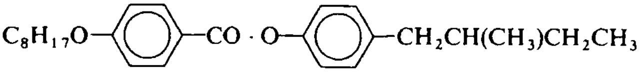
| $n$ | C-I (°C) | Ch-I (°C) | Pitch (μm) |
|---|---|---|---|
| 6 | 22.0 | (17) | 0.23 |
| 10 | 36.0 | (32) | 0.23 |

C = crystal; Ch = cholesteric; I = isotropic liquid. ( ) = monotropic transition. Pitch = see experimental section—first method and extrapolation.

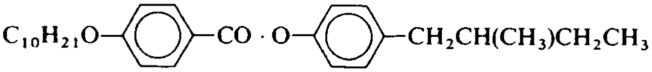
It is obvious that the liquid crystal thermal stabilities are enhanced in the compounds (II), particularly those of the smectic phase. This is useful, because pretransitional effects associated with the onset of the smectic A phase cause a sudden change in the cholesteric helical pitch length near the cholesteric to smectic transition.[9] Therefore mixtures of these materials can be made that are very colour sensitive to changes in temperature in the body temperature range. One typical example of a mixture which may be prepared is given below.



$C_6H_{13}-C_6H_4-CO\cdot O-C_6H_4-CH_2CH(CH_3)CH_2CH_3$ 59% w/w



$C_8H_{17}O-C_6H_4-CO\cdot O-C_6H_4-CH_2CH(CH_3)CH_2CH_3$ 18% w/w



$C_{10}H_{21}O-C_6H_4-CO\cdot O-C_6H_4-CH_2CH(CH_3)CH_2CH_3$ 23% w/w

$S_A$-Ch, 24.5°C; Ch-I, 39°C

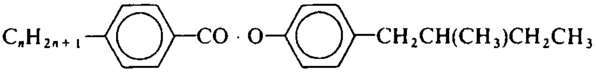
| Selective Reflection | Temperature (°C) |
|---|---|
| Red | 24.5 |
| Yellow | 24.6 |
| Green | 24.7 |
| Turquoise | 24.9 |
| Blue | 25.2 |
| Isotropic liquid | 39.0 |

This mixture, which is not a eutectic composition, has nevertheless shown no sign of segregation since its preparation several months ago. Microscope slide preparations with a cover glass were left exposed to direct sunlight and a normal laboratory atmosphere for the same period without any apparent changes in the colour brightness or sensitivity to temperature change.

As would be expected (see Table III), the alkyl derivatives corresponding to the alkoxy esters (II) have lower mesomorphic transition temperatures, because of the reduction in the polarisability of the molecules.

TABLE III

Physical constants for the compounds (IV)



(IV)

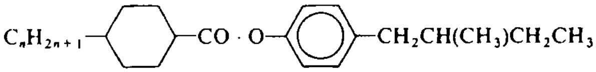
| $n$ | C-I (°C) | Virtual Ch-I (°C) | Pitch (μm) |
|---|---|---|---|
| 5 | 5-6 | (−1) | 0.23 |
| 8 | 17 | (−3) | 0.23 |

C = crystal; Virtual Ch = virtual cholesteric; I = isotropic liquid. ( ) = virtual transition temperature determined by extrapolation. Pitch—see experimental section— first method and extrapolation.

Further structural changes may be made to this basic cholesteric structure. For instance, it is known from work by Demus, *et. al.*[10] on the cyclohexane analogues of the simple 4-alkylphenyl 4-alkylbenzoates that the nematic thermal stabilities of the cyclohexyl compounds are increased. The cyclohexyl analogues of the cholesteric materials in Table II should therefore embody the same characteristics, and provide a further series of cholesteric materials derived from the same optically active phenol, but having significantly different physical properties (see Table IV).

TABLE IV

Physical constants for the compounds (V)



(V)

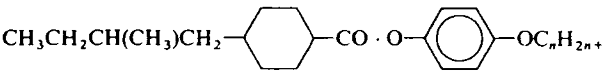
| $n$ | C-I (°C) | Virtual Ch-I (°C) | Pitch (μm) |
|---|---|---|---|
| 2 | 2.0 | (−33) | 0.23 |
| 3 | 24.0 | (1) | 0.23 |
| 4 | 22.0 | (−14) | 0.23 |
| 5 | 17.0 | (7) | 0.23 |

Pitch—see experimental section—first method and extrapolation.

A comparison of the two sets of data in Tables 3 and 4 for the compounds (IV) and (V) with $n = 5$ shows that the liquid crystal thermal stability has been increased by 8°C. One would also expect that these cyclohexyl materials would have lower viscosities than their aromatic counterparts (IV), and it would appear that their isotropic melts are more fluid. However, whether this would hold for the cholesteric phases requires experimental verification. Furthermore, it is interesting to note that the only way of introducing a cyclohexane ring into the benzoate ester structure while retaining reasonable cholesteric liquid crystal stability and a small pitch length is by using S-(+)-4-(2'-methylbutylphenol with trans-4-*n*-alkylcyclohexane-1-carboxylic acids. Esters derived from trans-4-*n*-alkylcyclohexan-1-ols and S-(+)-4-(2'-methylbutyl) benzoic acid are not liquid crystalline,[16] possibly because the molecular structure is not sufficiently linear. A more linear structure is obtained with esters derived from S-(+)-trans-4-(2'-methylbutyl)cyclohexane-1-carboxylic acid and 4-*n*-alkylphenols, but much of the effectiveness of the S-(+)-2-methylbutyl group is lost. This point is demonstrated by the pitch lengths given in Table V for the compounds (VI).

TABLE V

Physical constants for the compounds (VI)



(VI)

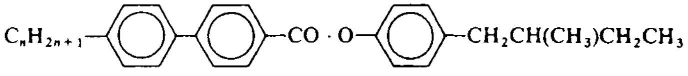
| $n$ | C-I (°C) | $S_A$-Ch (°C) | Ch-I (°C) | Pitch (μm) |
|---|---|---|---|---|
| 6 | 50.0 | — | (29.5) | 0.43 |
| 10 | 49.0 | (41.8) | (45.4) | 0.43 |

C = crystal; $S_A$ = smectic A; Ch = cholesteric; I = isotropic liquid. ( ) = monotropic transition. Pitch—see experimental section—first method and extrapolation.

None of the cholesterogens so far mentioned is cholesteric at room temperature, although a room temperature mesophase may be produced by mixing some of the materials together. However, using many of these compounds, particularly those with low mesophase transition temperatures, the upper working temperature ranges of the mixtures are restricted. In order to achieve compounds with higher transition temperatures, we prepared some esters derived from 4'-*n*-alkyl- and 4'-*n*-alkoxy-biphenyl-4-carboxylic acids and S-(+)-4-(2'-methylbutyl)phenol.

TABLE VI

Physical constants for compounds (VII)



(VII)

| $n$ | C-$S_B$ (°C) | $S_B$-$S_A$ (°C) | $S_A$-Ch (°C) | Ch-I (°C) | Pitch ($\mu$m) |
|---|---|---|---|---|---|
| 5 | 66.0 | 77.3 | 133.9 | 156.0 | 0.23 |
| 6 | 81.0 | 71.0 | 132.6 | 146.2 | 0.23 |
| 7 | 74.6 | 75.0 | 138.4 | 147.6 | 0.23 |

C = crystal; $S_B$ = smectic B; $S_A$ = smectic A; Ch = cholesteric; I = isotropic liquid. Pitch—see experimental section—first method and extrapolation.

B) S-(+)-4-(2′-Methylbutyl)phenyl 4′-substituted biphenyl-4-carboxylates.

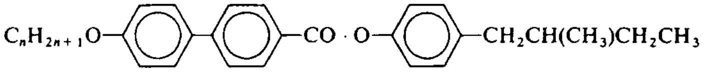
The physical constants for some of these materials are given in Tables VI and VII.

These compounds are similar in structure to those (Tables VIII and IX) reported in a previous publication,[7] except that the chiral alkyl group has been moved to the opposite end of the molecule with quite marked effects on the physical properties.

On comparing the two sets of data, the most striking feature is the greatly enhanced smectic thermal stability of the new materials (structures (VII)

TABLE VII

Physical constants for the compounds (VIII)



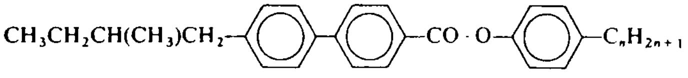
(VIII)

| $n$ | C-$S_3$ (°C) | $S_3$-$S_C$ (°C) | $S_C$-$S_A$ (°C) | $S_A$-Ch (°C) | Ch-I (°C) | Pitch ($\mu$m) |
|---|---|---|---|---|---|---|
| 8 | 78.0 | 80.0 | 128.3 | 171.0 | 174.2 | 0.23 |
| 9 | 72.0 | 77.6 | 132.0 | 168.0 | 170.0 | 0.23 |

C = crystal; $S_3$ = uncharacterised enantiotropic smectic phase; $S_C$ = smectic C; $S_A$ = smectic A; Ch = cholesteric; I = isotropic liquid. Pitch—see experimental section—first method and extrapolation.

TABLE VIII

Physical constants for the compounds (IX)



(IX)

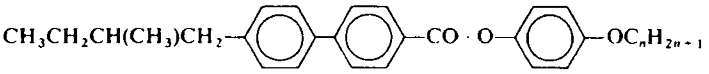
| $n$ | C-Ch (°C) | Ch-I (°C) | Pitch (μm) |
|---|---|---|---|
| 5 | 63.6 | 138.2 | 0.23 |
| 6 | 60.3 | 132.0 | 0.23 |
| 7 | 61.0 | 133.4 | 0.23 |

C = crystal; Ch = cholesteric; I = isotropic liquid. Pitch—see experimental section—second method.

and (VIII)); this was also the case with the analogous benzoate esters. The $S_C$ phases of the compounds (VIII) are not however iridescent as are those of the compounds (X). Therefore the helical pitch lengths of the $S_C$ phases of the former compounds are greater than those of the latter. Since the cholesteric phases for both types of ester have the same pitch lengths, this suggests that the tilt angle of the molecules in the $S_C$ layers of the compounds (VIII) is less than that for the compound (X).

TABLE IX

Physical constants for the compounds (X)



(X)

| $n$ | C-$S_C$ (°C) | $S_C$-Ch (°C) | Ch-I (°C) | Pitch (μm) |
|---|---|---|---|---|
| 8 | 76.0 | 88.6 | 155.4 | 0.23 |
| 9 | 79.0 | 89.5 | 147.0 | 0.23 |

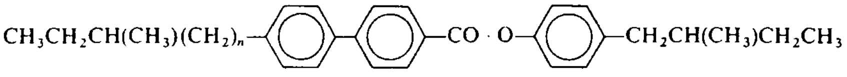
C = crystal; $S_C$ = smectic C; Ch = cholesteric; I = isotropic liquid. Pitch—see experimental section— second method.

### C) Esters containing two chiral groups

The optically active phenol also provides a convenient method of having two points of chirality in the general structure (I) (where both X and Y are branched alkyl groups), by interacting it with optically active acids. Two examples are given in Table X.

TABLE X

Physical constants for the compounds (XI)



(XI)

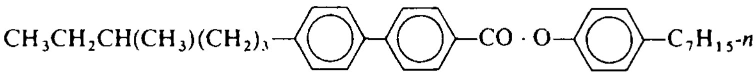
| $n$ | C-Ch (°C) | $S_C$-$S_A$ (°C) | $S_A$-Ch (°C) | Ch-I (°C) | Pitch* (μm) |
|---|---|---|---|---|---|
| 1 | 103 | — | — | 115.5 | 1.9 |
| 3 | 83.4 | (74.3) | (81.0) | 113.5 | 3.0 |

C = crystal; $S_C$ = smectic C; $S_A$ = smectic A; Ch = cholesteric; I = isotropic liquid. ( ) = monotropic transition. Pitch* — Pitch values are those actually recorded spectrophotometrically using 5% w/w solutions in 4-*n*-pentyl-4′-cyanobiphenyl.

The effect of two such chiral centres, provided that both, if considered independently, would induce the same sense of helical rotation in the cholesteric phase, is approximately additive.[3] Thus compound (XI) with $n = 1$, in its Grandjean plane texture, selectively reflects in the ultra-violet at a value corresponding to a pitch length as low as 0.1 μm. This is approximately half the value for the previously mentioned esters containing only one S-(+)-2-methylbutyl group.

The same effect is observed for compound (XI) with $n = 3$, where one of the chiral groups is S-(+)-4-methylhexyl and the other is S-(+)-2-methylbutyl. Both these groups induce the formation of right-handed helices; consequently the helical pitch length is intermediate between the values of 0.23 μm and 0.1 μm.

An example of an ester containing only the S-(+)-4-methylhexyl group is given below



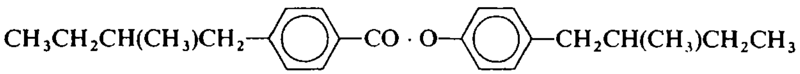
(XII)

C-$S_C$, 91.5°C; $S_C$-$S_A$, 93°C; $S_A$-Ch, 112°C; Ch-I, 131°C

The helical pitch length of the cholesteric phase of this material is 0.43 μm and its helical sense is dextro.

The compound (XI), with $n = 3$ and compound (XII) are also interesting since they exhibit $S_C$ phases, despite the fact that their molecular structures do not conform with requirements laid down in certain theories relating to the existence of that phase.[10]

The simple benzoate ester (XIII) analogous to compound (XI), with $n = 1$, is an oil, which has not as yet been obtained solid; the virtual Ch-I is −53°C.



(XIII)

The pitch length of this cholesteric phase, estimated from measurements made on chiral nematic mixtures with E8 (BDH commercial eutectic mixture of 4-*n*-alkyl- and 4-*n*-alkoxy-4′-cyanobiphenyls with a 4-*n*-alkyl-4″-cyano-*p*-terphenyl) corresponds to that of compound (XI), with $n = 1$, ie, about 0.1 μm.

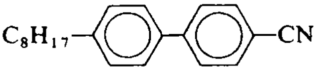
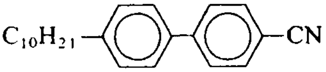
Provided that other properties are suitable, these compounds, with their small cholesteric helical pitch lengths, can be used in quite low concentrations in nematic eutectic mixtures to produce cholesteric mixtures with pitch lengths of about 1.0 μm for use in the cholesteric to nematic phase change device. Typical examples of such mixtures are given below.

| | | |
|---|---|---|
| *Mixture 1* | | |
| | 88% w/w of E8 | Ch-I, 57°C |
| | 12% w/w of (XIII) | Pitch, 0.7 μm |
| *Mixture 2* | | |
| | 92% w/w of E8 | Ch-I, 62°C |
| | 8% w/w of (XIII) | Pitch, 1.1 μm |
| *Mixture 3* | | |
| | 91% w/w of E8<br>5% w/w of (XIII)<br>4% w/w of (XI), $n = 1$ | Ch-I, 67.5°C<br>Pitch, 1.0 μm |

The various cholesterogens now reported may therefore be used to provide a variety of mixtures with wide range cholesteric phases for use in electro-optical and other display devices.

In relation to surface thermography and thermochromism generally, the esters with high helical twisting power are particularly useful, since only 25–35% of the twisting power of these materials needs to be used to produce pitch lengths in the visible spectral region. Therefore mixtures based largely on nematic materials may be prepared and yet display a selective reflection of coloured light which is temperature dependent. An example of such a mixture is given below.

*Mixture 4*

| | |
|---|---|
|  | 45% w/w |
|  | 21% w/w |
| Compound (XIII) | 14% w/w |
| Compound (XI), $n = 1$ | 20% w/w |

$S_A$-Ch, 18.5°C; Ch-I, 43.0°C

| Selective reflection | Temperature (°C) |
|---|---|
| Red | 23.5 |
| Yellow | 25.5 |
| Green | 26.6 |
| Turquoise | 33.0 |
| Blue | 35.0 |
| Isotropic liquid | 43.0 |

The obvious advantage of this type of thermochromic mixture is that it capitalises on the great variety of established nematic liquid crystals developed for use in electro-optical display devices and makes them suitable for commercial application in the field of surface thermography. In this respect, the cost of materials is important, because of the relatively large amounts of material that thermochromic devices contain compared with those for electro-optical display devices.

## CONCLUSION

The very useful phenol, S-(+)-4(2′-methylbutyl)phenol, can therefore be used to produce a number of cholesterogens with a diverse range of liquid crystal and other physical properties. Although these new materials are esters, they are chemically reasonably stable molecules and can readily be prepared with high specifications of chemical purity. This is important in guaranteeing the reproducibility of thermodynamic and other physical properties which is necessary in the commercial application of liquid crystals for display devices.

## EXPERIMENTAL

### Physical measurements and purity of materials

Transition temperatures were measured using either a Nikon L-Ke polarising microscope fitted with a Mettler FP 52 heating stage and FP5 control unit or, when the values occurred at low temperatures, a polarising microscope with a cold stage (C. Reichert, Optische Werke AG, Wien, Austria).

Pitch measurements were made spectrophotometrically either with solutions of the cholesterogens in 4-*n*-pentyl-4′-cyanobiphenyl by using an SP 200 spectrometer, or with the pure materials (in a heated cell) by 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 tlc and their structures confirmed by mass spectrometry. In addition, satisfactory elemental analysis results were obtained for all the materials, and further structural checks were carried out wherever desirable using a Jeol JNM-4H 100 MHz instrument for nmr results and a PE 457 instrument for infra-red spectra.

## Preparation of materials

*S-(+)-4-(2′-Methylbutyl)-1-methoxybenzene* Under anhydrous conditions, 4-bromoanisole (0.49 mole) dissolved in sodium dried ether (250 ml) was added to magnesium turnings (0.5 g atom) covered with sodium dried ether (100 ml). A small volume (30 ml) of the solution was first added to the magnesium, and a single crystal of iodine was used to initiate the reaction. Once the reaction had begun, the remaining solution of 4-bromoanisole was added in drops, so as to maintain the reaction at a steady rate. When addition was complete, the reaction mixture was heated under reflux and stirred for one hour.

The Grignard solution was then cooled in an ice-bath and a solution of iron (III) chloride (0.005 mole) in ether (5 ml) was added dropwise, followed immediately by a solution of S-(+)-2-methylbutyl bromide[7] (0.49 mole) in sodium dried ether (100 ml), at such a rate that the temperature of the mixture did not rise above 5°C. The mixture was then left to stir at room temperature for 24 hours, and finally heated under reflux for 12 hours.

On cooling, the mixture was poured into a 10% hydrochloric acid solution (1.5 l) at 0°C and stirred for 1 hour. The product was extracted into ether (3 × 200 ml) and the combined ether extracts were washed with water (3 × 200 ml) and dried ($Na_2SO_4$). The ether was removed by rotary evaporation and the oily residue distilled, collecting the fraction boiling at 120°C at a reduced pressure of *ca* 12–15 mm Hg.

*S-(+)-4-(2′-Methylbutyl)phenol* *S*-(+)-4-(2′-Methylbutyl)-1-methoxybenzene (0.12 mole), constant boiling hydrogen bromide in water (96 ml) and 45% w/w hydrogen bromide in acetic acid (140 ml) were heated under reflux for 6 hours.

On cooling, the mixture was poured into water (1 l) and stirred for 0.5 hour. The product was extracted into ether and the combined extracts were washed with water and dried ($Na_2SO_4$). The ether was removed by rotary evaporation and the residue distilled collecting the fraction boiling at 120°C at a pressure of 0.1 mm Hg.

4-*Alkoxybenzoic acids* These known materials were prepared by alkylating[11] 4-hydroxybenzoic acid.

4-*Alkylbenzoic acids* These known materials were prepared by Friedel-Crafts acylation[12] of alkylbenzenes, followed by hypobromite oxidation[11] of the 4-alkylacetophenones to the corresponding acids.

*Trans*-4-*n*-*alkylcyclohexane*-1-*carboxylic acids* A solution of 4-*n*-alkylbenzoic acid (0.2 mole) in sodium hydroxide (0.205 mole) dissolved in water (160 ml) was hydrogenated in the presence of Raney nickel catalyst (10 g) in an autoclave (1 l) at 190°C and at a pressure of 170 atm for 30 hours. On cooling, the catalyst was filtered off and the filtrate washed with ether. The aqueous layer was separated and acidified. The precipitated acids were extracted into ether and the ether extracts were washed with water and dried ($Na_2SO_4$). The ether was distilled off giving a mixture of the cis- and trans-acids.

The mixture of acids was dissolved in methanol (225 ml). Solid thiourea (45 g) was dissolved with heating in the solution obtained. Upon cooling, the inclusion compound of trans-4-*n*-alkylcyclohexane-1-carboxylic acid crystallised from solution in the form of fine white needles. These were filtered off and dried.

A further amount of solid thiourea (35 g) was dissolved in the solution. Again on cooling, more inclusion compound and some thiourea crystals came out of solution. These were filtered off and dried.

The filtrate was concentrated to about half its volume and left to cool. Again the crystals were filtered off and dried.

The combined crystallisates of inclusion compound and thiourea were dissolved in 5% aqueous potassium hydroxide (*ca* 150 ml).

The pure trans-acid, liberated upon acidification with concentrated hydrochloric acid, was taken up in ether, after which the ethereal solution was dried over anhydrous magnesium sulphate.

The ether was distilled off and the crude trans-acid crystallised from approximately the same volume of acetone (*ca* 30 ml), cooling to −25°C.

Trans-4-ethylcyclohexane-1-carboxylic acid, mp 49°; N-I, 47.5°;
Trans-4-*n*-propylcyclohexane-1-carboxylic acid, mp 99°C;

Trans-4-*n*-butylcyclohexane-1-carboxylic acid, mp 40.5°C; N-I, 93.5°C;
Trans-4-*n*-pentylcyclohexane-1-carboxylic acid, mp 53.5°C; N-I, 101°C.

*4-n-Alkylbiphenyl-4'-carboxylic acids* These known[13] materials were prepared by the alkaline hydrolysis of the corresponding commercially available 4-*n*-alkyl-4'-cyanobiphenyls.[14]

*4-n-Alkoxybiphenyl-4'-carboxylic acids* These known[15] materials were prepared by the alkaline hydrolysis of the corresponding commercially available 4-*n*-alkoxy-4'-cyanobiphenyls.[14]

*S-(+)-4-(2'-Methylbutyl)benzoic acid, S-(+)-trans-4-(2'-methylbutyl)cyclohexane-1-carboxylic acid and S-(+)-4-(2"-methylbutyl)biphenyl-4'-carboxylic acid* were prepared as described previously.[7]

*S-(+)-4-(4'-Methylhexyl)biphenyl-4"-carboxylic acid* This was prepared by the alkaline hydrolysis of S-(+)-4-(4'-methylhexyl)-4"-cyanobiphenyl, which is a known material.[2,7]

$$\text{C-S}_\text{C}, 175.4°\text{C}; \text{S}_\text{C}\text{-Ch}, 219.1°\text{C}; \text{Ch-I}, 235.8°\text{C}$$

*Preparation of esters* 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 which was eluted with chloroform. The combined fractions of ester were, in the case of solids, crystallised to constant melting point from either hexane or methanol/ethanol, where appropriate, or in the case of oils, distilled at 0.1 mm Hg.

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## References

1. K. J. Harrison, D. S. Hulme, and E. P. Raynes, *J. C. S. Chem. Comm*, 1549 (1974).
2. G. W. Gray and D. G. McDonnell, *Electron. Lett.*, **11**, 556 (1975).
3. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 211 (1977).
4. D. Dolphin, Z. Muljiani, J. Cheng, and R. B. Meyer, *J. Chem. Phys.*, **58**, 413 (1973).
5. M. Tsukamoto, T. Ohtsuka, K. Morimoto, and Y. Murakawi, *Jap. J. Appl. Phys*, **14**, 9 (1975).
6. B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **97**, 1585 (1975).

7. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1976).
8. Y. Y. Hsu and D. Dolphin, *Mol. Cryst. Liq. Cryst.*, **42**, 319 (1977).
9. R. S. Pindak, C. Huang, and J. T. Ho, *Phys. Rev. Lett.*, **32**, 2 (1974).
10. J. W. Goodby, G. W. Gray, and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 183 (1977).
11. G. W. Gray and B. Jones, *J. Chem. Soc.*, 678 (1954).
12. G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).
13. Unpublished results, Liquid Crystal Group, Department of Chemistry, The University, Hull, England.
14. B. D. H. Publication, *Liquid Crystals*, 1975; B. D. H. Chemicals Limited, Broom Road, Poole, England.
15. G. W. Gray, J. B. Hartley, and B. Jones, *J. Chem. Soc.*, 1412 (1955).
16. D. G. McDonnell, unpublished results.