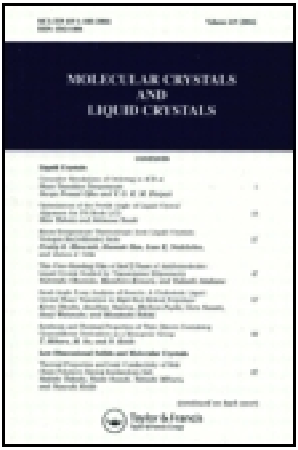


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Some Novel Cholesteric Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring

G. W. Gray [a] & S. M. Kelly [a b]
[a] Department of Chemistry, University of Hull, HULL, HU6 7RX, England
[b] Brown Boveri Research Centre, CH-5405, Baden-Dattwil, Switzerland

To cite this article: G. W. Gray & S. M. Kelly (1983): Some Novel Cholesteric Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring, Molecular Crystals and Liquid Crystals, 95:1-2, 101-116

To link to this article: http://dx.doi.org/10.1080/00268948308072412

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 101–116
0026-8941/83/9502-0101/$18.50/0

Printed in the United States of America

Some Novel Cholesteric Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring

G. W. GRAY and S. M. KELLY[†]

Department of Chemistry, University of Hull, HULL, HU6 7RX, England

(Received February 2, 1983)

A chiral center has been introduced into different positions of one of the terminal alkyl chains of the known 4-alkylphenyl, 4-alkoxyphenyl and 4-alkyl-2-fluorophenyl 4-alkylbicyclo(2.2.2)octane-1-carboxylates[1,2] to produce seven homologous series of esters possessing cholesteric phases. Several of the esters exhibit enantiotropic cholesteric phases of tight pitch at and above room temperature, whilst others exhibit longer pitch enantiotropic cholesteric phases (sometimes at room temperature) which reflect light in the visible region of the electro-magnetic spectrum and are thermochromic.

INTRODUCTION

In the last few years, many materials exhibiting cholesteric phases, often at or above room temperature, have been prepared.[3-9] Although many of these cholesterogens are sterol derivatives that are of questionable stability even if they are rigidly purified, *e.g.*, carbonate esters of cholesterol,[9] others *are* stable, nonsterol systems.[3,4] However, the majority of these stable cholesterogens either exhibit cholesteric phases which are strongly monotropic or have relatively high melting points.[3,4]

Cholesteric materials are of considerable commercial interest for use in both twisted nematic (*TN*) and guest-host (*GH*) electro-optic displays, and also for many thermographic applications.[10,11,12] Recent intensified commercial interest in the *GH* display,[10] in compensated cholesteric mixtures for multiplexed *TN* and *GH* displays,[11] and in thermographic applications

---

[†] Present address: Brown Boveri Research Centre, CH-5405 Baden-Dattwil, Switzerland.

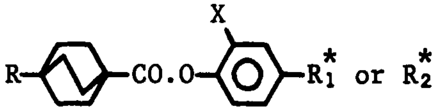
(particularly in the medical area)[12] serves to refocus attention on the limitations in the range of stable cholesteric materials that are commercially available.[13,14]

It was against this background that it was decided to incorporate an optically active (chiral) center into various positions in the alkyl chains of the known 4-*n*-alkylphenyl, 4-*n*-alkoxyphenyl and 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates.[1,2] Branching of the terminal alkyl chains of nematogens is known to depress strongly the clearing points of the parent, unsubstituted materials.[3,4] However, it was considered that the higher clearing points of the bicyclo-octane esters and the ability of the bicyclo-octane ring to shield lateral substituents in the phenolic moiety of such esters offered the possibility of producing several new series of cholesteric materials which might have reasonable clearing points, and possibly also, moderately low melting points. The decision was made to use the S-(+)-2-methylbutyl and the S-(+)-3-methylpentyl groups in the esters, because it has been clearly demonstrated that the closer the chiral center is to the rigid core of the molecules, then the smaller is the pitch of the resultant cholesteric phase.[3,4]

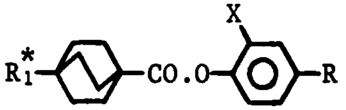
RESULTS AND DISCUSSION

Several homologous series [(I) to (VII)] of novel esters incorporating the 1,4-disubstituted bicyclo(2.2.2)octane ring and either an S-(+)-2-methylbutyl or an S-(+)-3-methylpentyl group have been prepared.

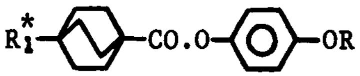
The liquid crystal transition temperatures of the esters



((I) - (IV))



((V), (VI))



(VII)

where R = n-alkyl

R_1^* = S-(+)-2-methylbutyl

R_2^* = S-(+)-3-methylpentyl

X = H or F

[(I) to (VII)] are recorded in Tables I, II, III, and IV and some plots of the liquid crystal transition temperatures against the number (*n*) of carbon atoms in the *n*-alkyl chain are shown in Figures 1–4.

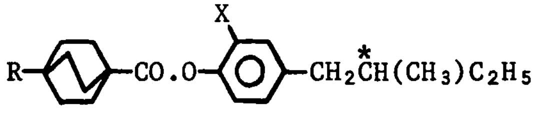
Thermal and optical properties of the cholesteric phases

The known 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acid chlorides[1] were esterified in the usual way[1] with S-(+)-4-(2′-methylbutyl)phenol or S-(+)-2-fluoro-4-(2′-methylbutyl)phenol to yield the esters [(I) and (II), respectively]—see Table I and Figure 1.

The clearing points for both series alternate, but rise generally from relatively low values for the members with short alkyl chains (*n* = 3 and 4); the melting points tend to fall somewhat irregularly as the alkyl chains lengthen. This results in the formation of enantiotropic cholesteric mesophases at or around room temperature for the esters with relatively long alkyl chains [(I); *n* = 7; C-Ch, 16°; Ch-I, 35.5°; *n* = 8; C-Ch, 19°; Ch-I, 36.5°: (II); *n* = 8; C-Ch, 22°; Ch-I, 36.5°]. The liquid crystal transition temperatures for the ester series [(I) and (II)] are similar, and the average

TABLE I

Data for compounds of structure (I), X = H and (II), X = F



n-R	X	Transition temperatures (°C) C-Ch or I	Ch-I
C_3H_7	H	31.5	(18.5)
C_4H_9	H	34	[7]
C_5H_{11}	H	28.5	(27.5)
C_6H_{13}	H	27	(25)
C_7H_{15}	H	16	35.5
C_8H_{17}	H	19	36.5
C_3H_7	F	36	(14)
C_4H_9	F	27	[2]
C_5H_{11}	F	43.5	(27.5)
C_6H_{13}	F	31	(22)
C_7H_{15}	F	32.5	34.5
C_8H_{17}	F	22	36.5

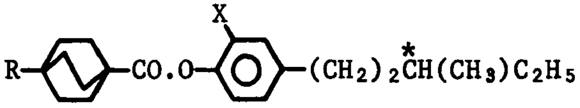
*represents the chiral center.

( ) denotes a monotropic transition temperature.

[ ] denotes a virtual transition temperature obtained by extrapolation of data derived from mixtures.

TABLE II

Data for compounds of structure [(III) and (IV)]



n-R	X	Transition temperatures (°C)		
		C–S_B, Ch or I	S_B–Ch or I	Ch–I
C_3H_7	H	34	—	[−4]
C_4H_9	H	45	—	[−8]
C_5H_{11}	H	46.5	(27)	(31.5)
C_6H_{13}	H	49.5	(36.5)	—
C_7H_{15}	H	45	(40)	—
C_8H_{17}	H	48	(41.5)	—
C_3H_7	F	32.5	—	(10.5)
C_4H_9	F	30.5	—	(−3)
C_5H_{11}	F	22.5	—	23.5
C_6H_{13}	F	13.5	—	16.5
C_7H_{15}	F	24	—	32.5
C_8H_{17}	F	21.5	—	32.5

*represents the chiral center.

( ) denotes a monotropic transition temperature.

[ ] denotes a virtual transition temperature obtained by extrapolation of data derived from mixtures.

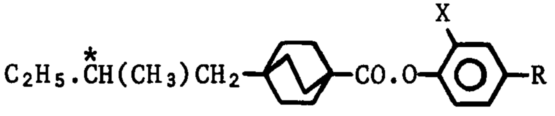
differences between the melting points (8°) and the clearing points (2°) are therefore small; the melting points of the fluoro-substituted esters (II) are however generally higher than those of the unsubstituted esters (I), while their clearing points are lower (see Table I). Thus the cholesteric phase range of the fluoro-esters is on average smaller. Despite substantial supercooling (to $<-20°$), no smectic phases could be observed.

The esters [(I); *n* = 7 and 8: (II); n = 8] represent useful new materials which are stable and exhibit—as single component systems—enantiotropic cholesteric phases at room temperature. This facilitates physical studies of their cholesteric phases as well as of their associated blue phases.

The Grandjean plane textures of the cholesteric phases of the esters reflect light in the ultra-violet region of the spectrum ($\lambda_{20°}$, 305 nm) and the wavelength changes very little over the relatively narrow temperature ranges of the phases ($\lambda_{35°}$, 312 nm). The pitch values of the cholesteric phases of the bicyclo-octane esters [(I) and (II)] are approximately the same (ca. 0.2 μm) as those of the corresponding esters ($P_{20°}$, 0.23 μm)[4] where the bicyclo-octane ring has been replaced by either a 1,4-disubstituted benzene ring or a *trans*-1,4-disubstituted cyclohexane ring.[4]

TABLE III

Data for compounds of structure [(V) and (VI)]



n-R	X	Transition temperatures (°C) C-S_B, Ch or I	S_B-I	Ch-I
C_3H_7	H	19	—	[−40]
C_4H_9	H	26	—	[−115]
C_5H_{11}	H	49	—	[22]
C_6H_{13}	H	22	—	[−55]
C_7H_{15}	H	25	—	(15)
C_8H_{17}	H	4	20.5	—
C_3H_7	F	19	—	[−45]
C_4H_9	F	15	—	[−100]
C_5H_{11}	F	2.5	—	[−5]
C_6H_{13}	F	3	—	[−30]
C_7H_{15}	F	3.5	—	9.5
C_8H_{17}	F	13	—	(6)

*represents the chiral center.

( ) denotes a monotropic transition temperature.

[ ] denotes a virtual transition temperature obtained by extrapolation of data derived from mixtures.

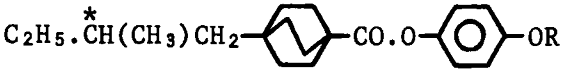
The liquid crystal transition temperatures of the bicyclo-octane esters (I); *e.g.*, $n = 5$; C-Ch, 28.5°; Ch-I, (27.5°), are higher than those of the corresponding cyclohexane esters, $n = 5$; C-Ch, 17°; Ch-I, (7°) and the analogous benzoate esters, $n = 5$; C-Ch, 6°; Ch-I, (−1°). Thus the order of decreasing clearing point of the esters is that expected on the basis of earlier experimental data:[15]

Bicyclo-octane > Cyclohexane > Benzene

The clearing points of the esters [(I) and (II)] derived from S-(+)-4-(2′-methylbutyl)phenol are always lower (ca. 15–30°) than those of the corresponding unbranched esters derived[1,2] from 4-butylphenol. This is consistent with the observed effect of branching the terminal alkyl chain of a nematogen.[3,4] However, the depression in the clearing point for these esters is much smaller than would normally be expected and this may well be attributed to the 'shielding-effect' of the bicyclo-octane ring[2] which is also considered to be the reason for the small decrease in clearing point associated with a lateral fluoro-substituent in the bicyclo-octane esters.

TABLE IV

Data for compounds of structure (VII)



n-R	C-Ch or I	Ch-I
C_2H_5	42	47.5
C_3H_7	47	[−15]
C_4H_9	52	(45.5)
C_5H_{11}	50.5	[29]
C_6H_{13}	43	50
C_7H_{15}	48.5	49
C_8H_{17}	50.5	55

*represents the chiral center.

( ) denotes a monotropic transition temperature.

[ ] denotes a virtual transition temperature obtained by extrapolation of data derived from mixtures.

The 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids were also interacted with S-(+)-4-(3′-methylpentyl)phenol and S-(+)-2-fluoro-(3′-methylpentyl)phenol to produce the esters [(III) and (IV)] listed in Table II with their liquid crystal transition temperatures. Figure 2 depicts one plot of the liquid crystal transition temperatures against the number of carbon

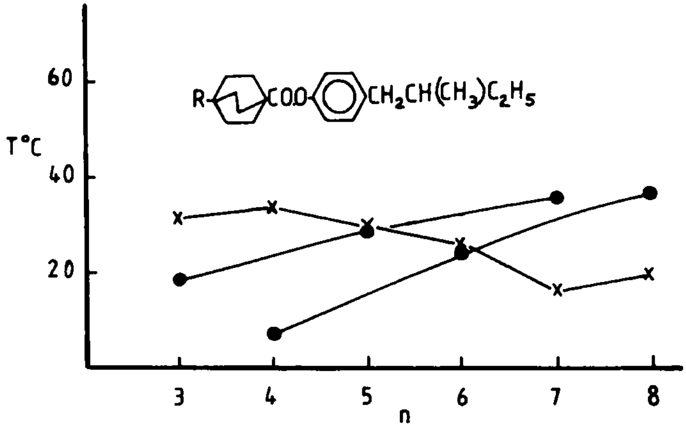


FIGURE 1 Transition temperatures (X, C-Ch or I; ●, Ch-I) for the 4-(2′-methylbutyl)phenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates plotted against number of carbon atoms (*n*) in the *n*-alkyl chain (*R*).

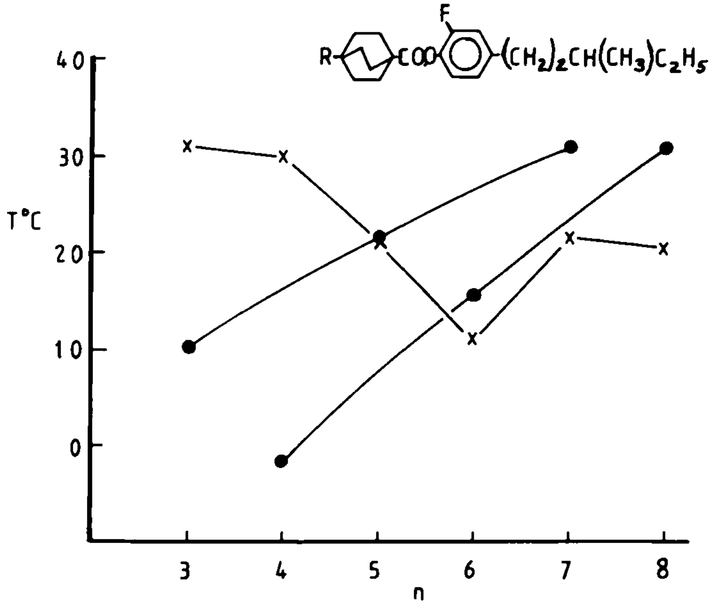


FIGURE 2 Transition temperatures (X, C-Ch or I; ●, Ch-I) for the 2-fluoro-4-(3′-methylpentyl)phenyl 4-*n*-alkylbicyclo(2.2.2) octane-1-carboxylates plotted against number of carbon atoms (*n*) in the *n*-alkyl chain (*R*).

atoms (*n*) in the terminal alkyl chain attached to the bicyclo-octane ring. The transition temperatures and the shapes of the plots are rather similar to those for the esters [(I) and (II)], but the clearing points of the esters [(III) and (IV)] with shorter alkyl chains are significantly lower (although the accuracy of virtual values obtained by extrapolation must be taken into account — see the Experimental Section).

The esters (III) demonstrate strong smectic tendencies, the higher homologues exhibiting no cholesteric phases. This is consistent with the generally observed pattern of increasing smectic character with increasing chain length. The increase in smectic character is also accompanied by generally rather higher melting points than those for the other ester series [(I), (II) and (IV)]. However, incorporation of a lateral 2-fluoro-substituent in the phenolic moiety giving the esters (IV) not only results in several significant decreases in melting point (four members of the series melt below 25°), but also completely removes the smectic phases. This agrees with results obtained for several other series[2] and confirms the efficiency of a lateral fluorine in this position in eliminating even strong smectic tendencies.

It is known that moving the chiral center from the second to the third carbon atom of the alkyl chain results in an increase in the magnitude of the

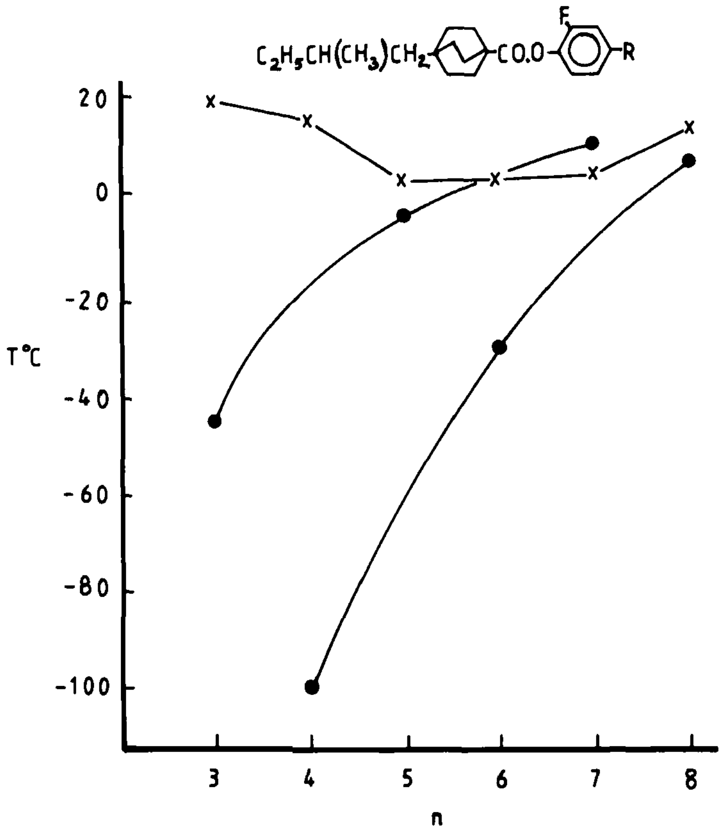


FIGURE 3 Transition temperatures (X, C-Ch or I; ●, Ch-I) for the 4-*n*-alkyl-2-fluorophenyl 4-(2′-methylbutyl)bicyclo(2.2.2) octane-1-carboxylates plotted against number of carbon atoms (*n*) in the *n*-alkyl chain (*R*).

pitch.[3,4] Whereas, the corresponding esters [(I) and (II)] containing the S-(+)-2-methylbutyl group reflect ultra-violet light from the Grandjean plane textures, the cholesteric phases of the esters [(III) and (IV)] now reflect light in the visible region of the spectrum and are also thermochromic. Only one homologue of the unsubstituted series [(III); $n = 5$] exhibits an observable cholesteric phase. However, just above the smectic phase (S_B-Ch, 27°), the Grandjean texture reflects red light and as the temperature is increased the color changes from red, through orange, until green light is reflected just beneath $T_{\text{Ch-I}}$ at 31.5°. The fluoro-substituted esters (IV) all exhibit thermochromic cholesteric Grandjean textures. For example, one homologue ($n = 8$) reflects red light at room temperature and green light just below the cholesteric-isotropic liquid transition

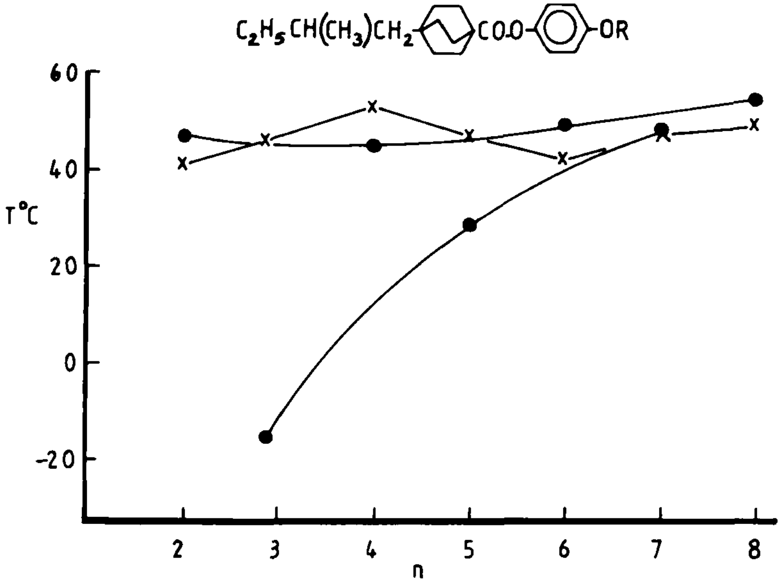


FIGURE 4 Transition temperatures (X, C-Ch or I; ●, Ch-I) for the 4-*n*-alkoxyphenyl 4-(2′-methylbutyl)bicyclo(2.2.2)octane-1-carboxylates plotted against number of carbon atoms (*n*) in the *n*-alkyl chain (*R*).

(ca. 31°). The latter ester appears to represent the first pure non-sterol derivative to exhibit an enantiotropic cholesteric phase at room temperature that selectively reflects incident light in the visible region of the electromagnetic spectrum.

Two esters produced by the interaction of a 4-*n*-alkylbicyclo(2.2.2)-octane-1-carboxylic acid with S-(+)-4-(2-methylbutyl*oxy*)-phenol possessed higher clearing points [*n* = 5; Ch-I, (54°); *n* = 7; Ch-I, 59°], but also much higher melting points (*n* = 5; C-I, 62.5°; *n* = 7; C-Ch, 57°) and higher smectic tendencies [(*n* = 7; S_B-Ch, (53°)] than the esters [(I) - (IV)]. The wavelengths of light reflected by the Grandjean textures of the cholesteric phases of the S-(+)-4-(2-methylbutyloxy) derivatives are also longer (i.e., in the infra-red region of spectrum) than those for the corresponding alkyl substituted materials. This is again consistent with previous results obtained for other (non-ester) systems.[3]

S-(+)-4-(2-Methylbutyl)bicyclo(2.2.2)octane-1-carboxylic acid was then esterified in the usual way with 4-*n*-alkyl-, 4-*n*-alkyl-2-fluoro-, and 4-*n*-alkoxy-phenols to yield the esters [(V), (VI), and (VII)]. The liquid crystal transition temperatures of these esters are listed in Tables III and IV and plotted against the number of carbon atoms in the terminal alkyl chain attached to the phenol moiety for two of the three series in Figures 3 and 4.

The melting points and clearing points of the dialkyl esters [(V) and (VI)], see Table III, are significantly lower than those of the corresponding dialkyl esters [(I) and (II)], where the chiral center is located in the alkyl chain of the phenolic part of the molecule (see Table I). The liquid crystal transition temperatures of the fluoro-substituted esters (VI) are generally lower than those of the unsubstituted esters (V). However, a most striking effect is the decrease in $T_{\mathrm{Ch\text{-}I}}$ on passing from ester type (I) to (V) and from ester type (II) to (VI). Apparently the shielding effect of the bicyclo-octane ring is less effective against the depressing effect of chain branching on clearing point when the branched chain is directly attached to the bicyclo-octane ring.

The plots of the cholesteric-isotropic transition temperatures against the length of the terminal alkyl chain rise sharply from very low values (obtained by extrapolation of data derived from mixtures with cholesteryl oleyl carbonate — see the Experimental Section) for both series, but hardly reach room temperature for the longest chains studied. The highest homologue of the series (V) is smectic (S_B-I, 20.5°), whereas, as might be expected, the corresponding homologue of the fluoro-substituted series (VI) is purely cholesteric (Ch-I, 6°).

The esters [(V) and (VI)] in their Grandjean plane textures reflect light in the visible region of the electro-magnetic spectrum. For example, one material [(VI), $n = 7$] reflects violet light just below the clearing point (ca. 8.5°); then the range of spectral colors is seen as the temperature decreases, until red light (at ca. −20°), and eventually infra-red light, is reflected. A cholesteric "blue-phase" was particularly clearly observed just below the clearing point of this ester.

Comparison of the esters (I) and (V) and of the esters (II) and (VI) shows that the twisting power of the 2-methylbutyl group is greater when it is attached to the aromatic ring of the phenolic moiety than it is when it is attached to the bicyclo-octane ring at the other extremity of the ester molecule.

The clearing points of the alkoxy esters [(VIII), see Table IV], are considerably higher (ca. 50–80°) than those of the corresponding dialkyl esters [(V) and (VI), see Table III], although the melting points are also somewhat higher ($\leqslant$30°). Thus the tendency to exhibit cholesteric phases is much stronger for these alkoxy esters. The series studied contains four esters which give enantiotropic cholesteric phases and one which gives a weakly monotropic phase. The plot of the cholesteric-isotropic transition temperature against the number of carbon atoms in the alkoxy chain of the phenolic moiety rises steeply from low values (again extrapolated) for the homologues with an odd number of carbon atoms ($n = 3, 5, 7$) and almost joins the plot for the esters with an even number of carbon atoms ($n = 2, 4, 6, 8$) which falls at first and then rises gently, see Figure 4. The liquid crystal transition temperatures of the alkoxy-esters (VIII) are generally lower (ca. 10–20°) than those of the corresponding esters, in which the chiral center is attached to the phenolic part of the molecule (see earlier). However, no smectic phases have been observed for the esters (VII) despite the large degree of super-cooling ($\leqslant 20°$) that occurs below the melting points.

All of the Grandjean textures of the observable cholesteric phases of the alkoxy esters (VII) are thermochromic. For example, one homologue ($n = 6$) reflects blue light just beneath the clearing point (ca. 50°); then the wavelength of reflected light passes through the visible region on cooling and finally, at room temperature, red light is reflected.

Other physical properties of the esters

Although no systematic study was made of them, narrow-range, cholesteric "blue-phases" ($<0.5°$) could be observed for many of the esters. These "blue-phases" could be detected by microscopy using reflected light at temperatures just below the final transition of the cholesteric phase to the isotropic liquid.

The birefringence of the cholesteric phases of the esters [(I) and (II)] was found to be low ($\Delta n_{20°}$, 0.07), and the Δn values for all the other esters [(III) – (VII)] would be expected to be very similar.

The ester derivatives [(I) and (II)] of S-(+)-4-(2-methylbutyl)phenol are dextro-rotatory (10% w/v in chloroform; $[\alpha]_D^{20}$, +0.45°) and consistent with the empirical SOL/SED rule[16] have right-handed cholesteric helices. The derivatives [(III) and (IV)]* of S-(+)-4-(3′-methylpentyl)phenol are therefore expected to have left-handed helices[4] and this has been confirmed by observing the contact region between the cholesteric phases of the esters [(I) and (III)]. The contact zone is a narrow nematic ribbon where the two esters have mixed and given a compensated nematic.[4]

Other physical properties of the esters [(I) – (VII)] are expected to be very similar to those of the parent, unbranched esters,[1,2] except that their macroscopic viscosity is expected to be greater.

---

*10% w/v solutions in chloroform gave very small positive $[\alpha]_D^{20}$ values (0.1 – 0.2°).

EXPERIMENTAL

Structure and purity of materials

Infra-red, ^{1}H nmr, and mass spectra of S-(+)-4-(2-methylbutyl)bicyclo(2.2.2)octane-1-carboxylic acid were obtained and found to be consistent with the required structure. Where relevant, the spectral data were compared with those of the corresponding known 4-*n*-alkylbicyclo(2.2.2)-octane-1-carboxylic acids;[1] the results were identical in all essential aspects. Similar comparisons between the spectra of the esters [(I) − (VII)] and the corresponding 4-*n*-alkylphenyl, 4-*n*-alkyl-2-fluorophenyl, and 4-*n*-alkoxyphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates[1] were also made. The spectra were again identical in all essential details, and the data were entirely consistent with the desired structures. Each ester gave a "single spot" on analysis by thin layer chromatography (tlc) and analysis of the esters by gas-liquid chromatography (glc) revealed purities of at least 99%.

Spectral analysis

Infra-red, ^{1}H nmr, and mass spectra were determined using, respectively, a Perkin Elmer 457 spectrometer, a Jeol JNM-4H 100 Mz spectrometer, and an AEI MS 902 mass spectrometer.

Pitch determinations

Pitch determinations were made using a Perkin Elmer 550 spectrometer with a modified, thermostatted cell compartment.

Polarimetry

Specific rotations, $[\alpha]_D^{20}$ values, were determined for 10% w/v solutions in chloroform, utilizing a Bendix-NPL Automatic Polarimeter Type 143A.

Transition temperatures

The liquid crystal transition temperatures of the esters recorded in the tables were determined by optical microscopy using either a Nikon L-Ke polarizing microscope or a Vickers M72c polarizing microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit. The Mettler stage could be cooled (to $<-20°$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage. In those cases when it was not possible to observe the transition directly, "virtual" cholesteric-isotropic liquid (Ch-I) transition temperatures were determined in the usual way using mixtures with cholesteryl oleyl carbonate [COC, C-Ch, 26.4°; S_A-Ch, (20.8°); Ch-I, 35.7°][9] supplied by Croda Chemicals Limited (Goole), North Humberside. Transition temperatures, particularly crystal to smectic transition temperatures were checked using a Perkin-Elmer DSC-2C differential scanning calorimeter.

Preparation of materials

The esters were prepared by a standard literature procedure[1] involving interaction of the appropriate phenols with acid chlorides of the known 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids[1] and of S-(+)-4-(2′-methylbutyl)bicyclo(2.2.2)octane-1-carboxylic acid; the latter acid was prepared by a modified literature method.[1,17,18] The necessary S-(+)-2-fluoro-4-(2′-methylbutyl)-and S-(+)-4-(2′-methylbutyl)-phenols and S-(+)-2-fluoro-4-(3′-methylpentyl)- and S-(+)-4-(3′-methylpentyl)-phenols were supplied by BDH Chemicals Limited (Poole), Dorset under a Ministry of Defence Supply Contract. The S-(+)-4-(2′-methylbutyloxy)-phenol was prepared by the monoalkylation of hydroquinone in the normal way. The esters were purified in the usual fashion by column-chromatography using silica-gel as the stationary phase and a 1.5:1 mixture of chloroform and light petroleum (bp 40–60°) as eluent, followed by distillation or crystallization, until constant liquid crystal transition temperatures were observed.

Experimental details

S-(+)-3-Acetyl-3-(2′-methylbutyl)-1,5-dicyanopentane Cyanoethylene (146 g, 2.8 mol) was added dropwise to a stirred solution of S-(+)-5-methylheptan-2-one (176.5 g, 1.4 mol) and a 40% w/v solution of benzyltrimethylammonium hydroxide in methanol (10 cm^3) in 2-methylpropan-2-ol (300 cm^3), while the temperature of the solution was maintained between 10 and 15°. The solution was stirred overnight and allowed to reattain room temperature. Crystallization of the crude product from methanol yielded S-(+)-3-acetyl-3-(2′-methylbutyl)-1,5-dicyanopentane, 176 g (52.6%), mp 74–75°, m/e, 234.

S-(+)-3-Acetyl-3-(2′-methylbutyl)pentane-1,5-dicarboxylic acid A mixture of S-(+)-3-acetyl-3-(2′-methylbutyl)-1,5-dicyanopentane (176 g, 0.75 mol), sodium hydroxide (90 g, 2.26 mol), and water (300 cm^3) was stirred and heated under reflux until the evolution of ammonia had ceased

(10 h) and all of the organic material had gone into solution. Concentrated hydrochloric acid was added cautiously to the cooled solution (Congo Red) and the precipitated crude product was collected by filtration, washed several times with small volumes of water, and pressed dry. The product was taken up in boiling ethanol and hot-filtered to remove any residual inorganic material. The product, which crystallized out on cooling, was collected to yield S-(+)-3-acetyl-3-(2′-methylbutyl)pentane-1,5-dicarboxylic acid, 129 g (62.5%), mp 131–132°, m/e, 272.

S-(+)-4-Acetyl-4-(2′-methylbutyl)cyclohexanone A solution of S-(+)-3-acetyl-3-(2′-methylbutyl)pentane-1,5-dicarboxylic acid (130 g, 0.078 mol), anhydrous potassium acetate (0.94 g, 0.009 mol) and acetic anhydride (200 cm^3) was heated under reflux (2 h). The residual acetic anhydride was removed by distillation at water pump pressure and the residue was distilled under reduced pressure to yield S-(+)-4-acetyl-4-(2′-methylbutyl)cyclohexanone, 79 g (79%), bp 130° at 0.8 mm Hg, m/e, 210.

S-(+)-1-(2′-Methylbutyl)-4-methoxybicyclo(2.2.2)octan-2-one[17] S-(+)-4-Acetyl-4-(2′-methylbutyl)cyclohexanone (78 g, 0.37 mol) and trimethylorthoformate (134 g, 1.11 mol) were added to a saturated solution of hydrogen chloride in sieve-dried methanol (500 cm^3), and the resultant solution was heated under reflux for 40 min. Residual trimethylorthoformate and methanol were distilled off under reduced pressure (water pump) and the crude product was distilled under reduced pressure to yield S-(+)-1-(2′-methylbutyl)-4-methoxybicyclo(2.2.2)octan-2-one, 77 g (92.5%), bp 86° at 0.1 mm Hg, m/e, 224.

S-(+)-1-Methoxy-4-(2′-methylbutyl)bicyclo(2.2.2)octane A mixture of S-(+)-1-(2′-methylbutyl)-4-methoxybicyclo(2.2.2)octan-2-one (76 g, 0.34 mol) and 98–100% hydrazine hydrate (425 cm^3) was heated under reflux (5 h). Potassium hydroxide (57 g, 1.02 mol) and diethylene glycol (400 cm^3) were added to the cooled mixture and the temperature of the solution was raised to 210°, in the process distilling off the excess of hydrazine hydrate. The solution was then heated at this temperature until the evolution of nitrogen had ceased (2.5 h). The cooled mixture was added to water (1,500 cm^3) and the resultant mixture shaken with diethyl ether (3 × 300 cm^3). The combined organic extracts were washed with 15% hydrochloric acid (2 × 300 cm^3), with brine (2 × 1,000 cm^3), and dried ($MgSO_4$). The crude product was distilled under reduced pressure to yield S-(+)-1-methoxy-4-(2′-methylbutyl)bicyclo(2.2.2)-octane, 55.4 g (77.8%), bp 98–99° at 1.0 mm Hg, m/e, 210.

S-(+)-4-(2′-Methylbutyl)bicyclo(2.2.2)octane-1-carboxylic acid[18] Concentrated formic acid (98/100%, 20 cm^3) was added dropwise (2 h) to a vigorously stirred mixture of S-(+)-4-methoxy-1-(2′-methylbutyl)bicyclo(2.2.2)octane (5.0 g, 0.024 mol) and concentrated sulfuric acid (200 cm^3) initially cooled in an ice-salt bath and maintained under anhydrous conditions. The resultant solution was allowed to reattain room temperature and stirred for a further 2 h. The reaction mixture was then poured onto ice and the resultant precipitate collected by filtration, washed with small volumes of water, pressed dry, and crystallized from a water/methanol mixture to yield S-(+)-4-(2′-methylbutyl)-bicyclo-(2.2.2)octane-1-carboxylic acid, 3.2 g (60%), mp 117–118°, m/e, 224.

CONCLUSION

Seven homologous series of novel bicyclo-octane esters containing a chiral center have been prepared. Several members of the series represent the first stable, non-sterol materials to exhibit enantiotropic cholesteric phases as single component systems at room temperature. The pitch values of the cholesteric phases of two of the ester series [(I) and (II)] are small (ca. 0.2 μm) and relatively insensitive to temperature. These esters are, thus, of significant interest for both the TN and GH effects. Five of the ester series [(III) - (VII)] contain homologues whose cholesteric phases, in their Grandjean textures, selectively reflect incident light in the visible region of the electro-magnetic spectrum. The cholesteric phases of these esters are thermochromic, often at and above room temperature. Thus these esters are of interest for thermographic applications.

Acknowledgments

This work was carried out under a contract from the Ministry of Defence (UK), and the authors gratefully acknowledge the research grant associated with this contract. The authors also thank Mr. J. Jenner and Dr. I. Sage of BDH Chemicals Limited (POOLE) for the supply of the appropriate optically-active starting materials. Mr. A. J. Cole is also thanked for the pitch measurements and Dr. A. Tajbakhsh for DSC checks on several of the esters. This paper is published by permission of the Director HMSO.

References

1. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **75**, 95 (1981).
2. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **75**, 109 (1981).
3. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1976).
4. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **48**, 37 (1978); **34**, 211 (1977).

5. D. Dolphin, Z. Muljiani, J. Cheng and R. B. Meyer, *J Chem. Phys.*, **58**, 413 (1973).
6. M. Tsukamoto, T. Ohtsuka, K. Morimoto and Y. Murakami, *Jap. J. Appl. Phys.*, **14**, 1309 (1975).
7. B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **97**, 1585 (1975).
8. Y. Y. Hsu and D. Dolphin, *Mol. Cryst. Liq. Cryst.*, **42**, 319 (1977).
9. G. W. Gray and M. Hannant, *Mol. Cryst. Liq. Cryst.*, **53**, 263 (1979).
10. D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
11. A. Gõbl-Wunsch, G. Heppke and F. Oestreicher, *J. Phys. (Paris)*, **40**, 773 (1979).
12. O. S. Selawry, H. S. Selawry and J. F. Holland, *Mol. Cryst. Liq. Cryst.*, **1**, 495 (1966).
13. 'Liquid Crystals', Catalogue, BDH Chemicals Limited (Poole) Dorset, GB.
14. Licristal Data Sheets, E Merck Limited (Darmstadt) BRD.
15. G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **63**, 3 (1981).
16. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 221 (1977).
17. H. E. Zimmerman and R. D. McKelvey, *J. Amer. Chem. Soc.*, **93**, 3638 (1971), and references cited therein.
18. G. W. Gray, N. A. Langley and K. J. Toyne, to be published.