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Some three-ring esters containing a pyrazine ring
A comparison of their liquid crystal properties

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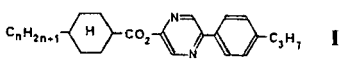
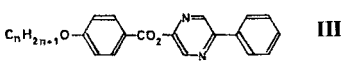
Two novel series of pyrazine-containing esters, together with an analogous phenyl system have been prepared, and their liquid crystalline phase behaviour compared in order to establish how the replacement of a phenyl ring by a pyrazine ring affects the liquid crystal behaviour of these esters. Both of the heterocyclic-containing ester series show significant suppression of the smectic phases, and some suppression of the nematic phase, when compared with the non-heterocyclic series.

1. Introduction

Some mesogenic compounds containing the pyrazine ring have been reported previously and their liquid crystal properties studied [1–3]. However, little systematic comparative work has been carried out on pyrazine ester systems. In this paper we report the synthesis of homologues series of two novel pyrazine-containing ester systems and an analogous all phenyl system—see **I**, **II** and **III**. These compounds were prepared in order to carry out an initial investigation into the properties of pyrazine-containing liquid crystal materials and to assess the potential of pyrazine liquid crystals for high birefringence applications such as polymer dispersed liquid crystals. The liquid crystal behaviour of the homologous ester series **I**, **II** and **III** is reported, and a comparison of the liquid crystal transition temperatures of series **I** with **II** and of **III** with the previously reported [4] all phenyl system **IV** is made. The measurement of viscosity and birefringence for these ester systems was attempted, but met with limited success because of their poor solubility in room temperature liquid crystal mixtures. However, the viscosity and birefringence measurements for one of the pyrazine compounds were made and are reported. An



I



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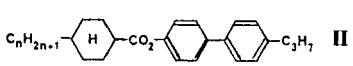

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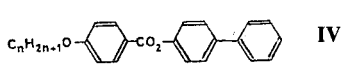

IV

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interesting range of liquid crystal behaviours is shown by these compounds. Transition temperatures for members of the different series (**I, II** and **III**) are shown plotted against the number of carbon atoms (n) in the terminal alkyl chain in figures 1–3 and are listed in the corresponding tables. Liquid crystal phase types were identified from the optical textures observed during thermal microscopy.

2. Results and discussion

2.1. *Esters of type I and II*

The liquid crystal transition temperatures (see table 1). of the 5-(4-*n*-propylphenyl)pyrazin-2-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates **I** are plotted against n, the number of carbon atoms in the alkyl chain in figure 1. The T_{N-I} values show the expected alternation, with the points for even n members lying on a rising curve situated below a falling curve for the odd n members. The homologues where $n=2$–4 show an as yet unidentified S_1 phase for which the N–S_1 transition temperatures lie on a smoothly falling curve; the optical texture is fern-like which settles on standing to a large mosaic with bright coloured and dark platelets, and is

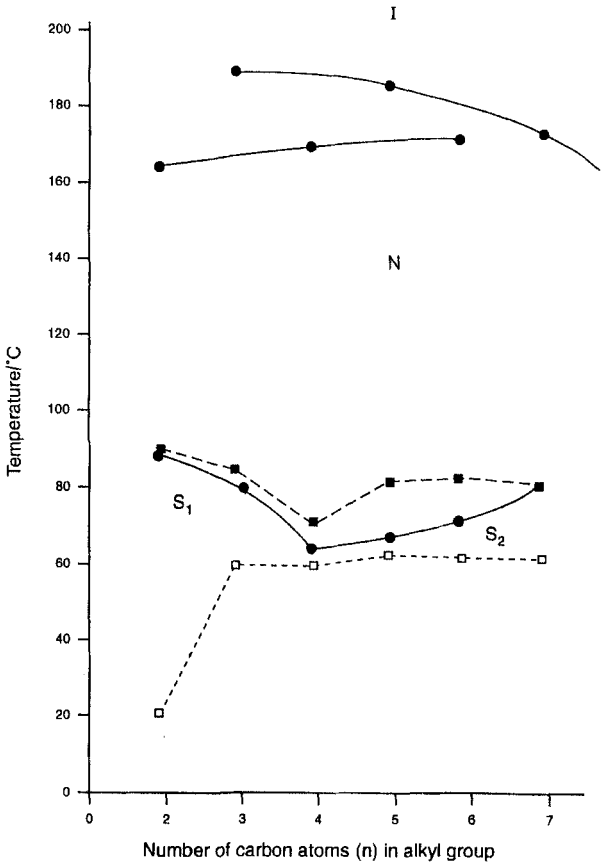


Figure 1. Plot of transition temperatures (°C) against alkyl chain length (n) for the 5-(4-*n*-propylphenyl)pyrazin-2-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates **I**. ●, N–I, S_1/S_2–N; ■, C–N; □, S_1/S_2–C.

similar to a G phase. Homologues with $n=5$–7 show a S_2 phase which exhibits a mosaic texture and is similar to a smectic B phase; the N–S_2 transition temperatures lie on a rising curve. X-ray techniques are being used to investigate these phases and the results will be reported at a later date. The birefringence and viscosity measured (see Experimental section) for 5-(4-*n*-propylphenyl)pyrazin-2-yl *trans*-4-*n*-propylcyclohexan-1-carboxylate are $\Delta n=0{\cdot}1938$ and 41·4 cSt, respectively.

For the 4-*n*-propylbiphenyl-4′-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates **II**—see figure 2 and table 2—the plot of the $T_{N\text{-}I}$ values against n shows similar characteristics to series **I** except that the curves for odd n and even n compounds merge at $n=4$ instead of $n=7$. This series exhibits a G phase when $n=2$, 3, 4 and an additional H phase when $n=4$. The homologues where $n=5$, 6 and 7 show a smectic A and a smectic B phase for which the transition temperatures lie on smoothly rising curves.

A comparison of the N–I thermal stability shows that the average N–I transition ($n=4$, 5, 6, 7) for series **I** is 174·7°C, whereas comparable data ($n=4$, 5, 6, 7) for series **II** give 193·5°C. This indicates a drop in N–I thermal stability of about 20°C for the pyrazine-containing system. The average S_2–N transition ($n=5$, 6, 7) for pyrazine series **I** is 74·2°C whereas for the analogous phenyl series **II** the value, in this case for S_A–N, is 139·5°C. This is a large drop in smectic phase stability of 65·3°C, but of course different phases are being compared. It is noted that there is a drop in overall smectic phase stability of 25·6°C for the pyrazine containing series when the more ordered phases of the homologues where $n=2$, 3, 4 are considered.

2.2. *Esters of type III and IV*

For the 5-phenylpyrazin-2-yl 4-*n*-alkoxybenzoates **III** the plot of the $T_{N\text{-}I}$ values (see figure 3, table 3) against n gives the expected alternation with the points for the odd n members lying on an initially rising curve and then almost horizontal curve situated below a falling curve for the even n members. The curves would seem to merge at $n=12$ and there is no evidence of any smectic phases.

The biphenyl-4-yl 4-*n*-alkoxybenzoates **IV** are known materials [4] and the plot of $T_{N\text{-}I}$ against n shows the usual odd–even alternation with the curves merging at $n=11$. This series exhibits a smectic A phase for which the $T_{S_A\text{-}N}$ values lie on a smoothly rising curve for $n\geqslant 8$. The transition temperatures are reproduced in table 4.

The average N–I transition ($n=4$, 5, 6, 7) for the pyrazine based series **III** is 118·5°C. For series **IV** ($n=4, 5, 6, 7$) it is 135·6°C. There is a drop of about 17°C in

Table 1. Transition temperatures (°C) for the 5-(4-*n*-proplyphenyl)pyrazin-2-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates **I**.

R	C–N	N–I	S_1–N	S_2–N	S_1†/S_2‡–C
n-C_2H_5	90	164·8	(89·0)	—	20†
n-C_3H_7	88	188·9	(80·9)	—	60†
n-C_4H_9	71	168·9	(63·8)	—	60†
n-C_5H_{11}	83	185·5	—	(69·0)	63‡
n-C_6H_{13}	81	171·0	—	72·0	62‡
n-C_7H_{15}	82	173·4	—	81·5	62‡

Brackets denote a monotropic transition.

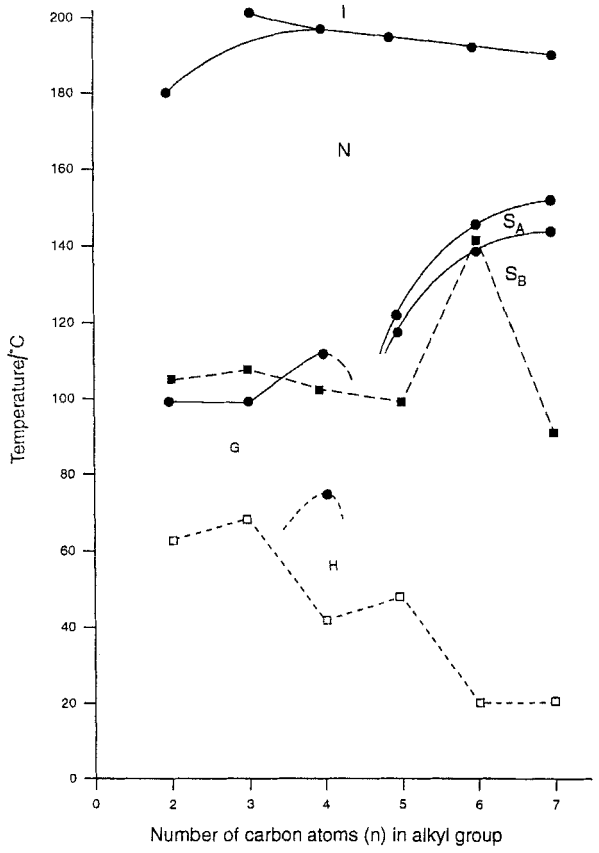


Figure 2. Plot of transition temperatures (°C) against alkyl chain length (*n*) for the 4-*n*-propylbiphenyl-4-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates **II**. ●, N–I, S_A/G–N, S_B–S_A, H–G; ■, C–N/S_A/S_B/G; □, S_A/S_B/H–C.

Table 2. Transition temperatures (°C) for the 4-*n*-propylbiphenyl-4-yl *trans*-4-*n*-alkyl cyclohexan-1-carboxylates **II**.

R	C–N/S_A†/ S_B‡/G§	H–G	G–N	S_A–N	S_B–S_A	N–I	G§/H¶/ S_B‡–C
n-C_2H_5	105	—	(99·0)	—	—	182·0	64§
n-C_3H_7	108–9	—	(99·0)	—	—	201·5	71§
n-C_4H_9	103§	(75·2)	112·4	—	—	197·4	42¶
n-C_5H_{11}	99–100§	—	—	122·5	120·7	194·0	48‡
n-C_6H_{13}	140–1†	—	—	145·0	139·0	192·4	20‡
n-C_7H_{15}	90‡	—	—	151·0	141·7	190·0	20‡

Brackets denote a monotropic transition.

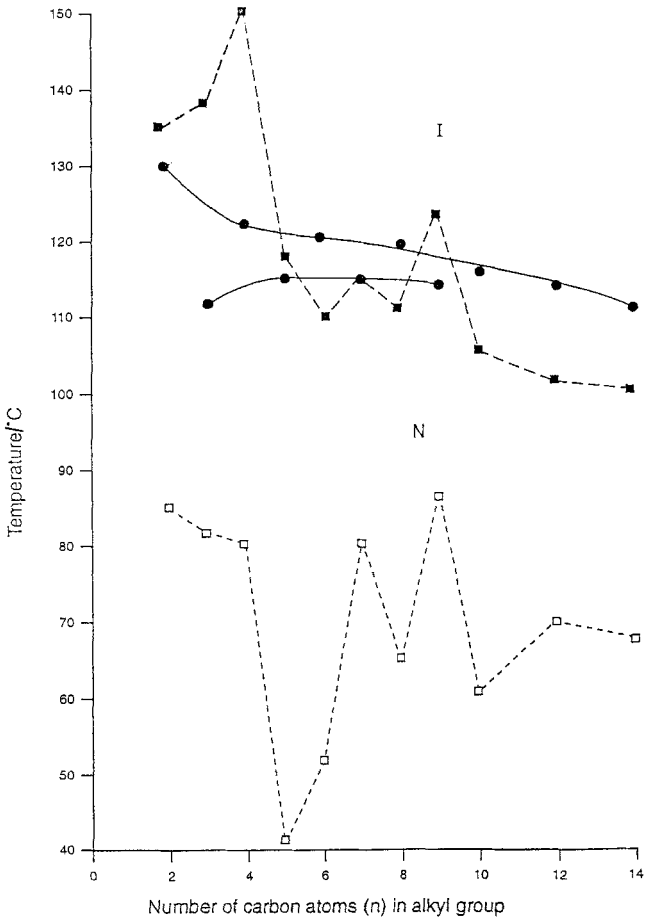


Figure 3. Plot of transition temperatures (°C) against alkyl chain length (*n*) for the 5-phenylpyrazin-2-yl 4-*n*-alkoxybenzoates **III**. ●, N–I; ■, C–I/N; □, N–C.

Table 3. Transition temperatures (°C) for the 5-phenylpyrazin-2-yl, 4-*n*-alkoxybenzoates **III**.

R	C–I	C–N	N–I	N–C
C_2H_5	135	—	(130·5)	85
C_3H_7	138	—	(112·1)	82
C_4H_9	150	—	(122·9)	81
C_5H_{11}	118	—	(115·8)	41
C_6H_{13}	—	109·7	120·5	52
C_7H_{15}	116	—	(114·8)	81
C_8H_{17}	—	111·6	120·4	65
C_9H_{19}	124	—	(113·6)	87
$C_{10}H_{21}$	—	106·3	115·7	61
$C_{12}H_{25}$	—	102·0	114·1	70
$C_{14}H_{29}$	101	—	112·0	68

Brackets denote a monotropic transition.

the nematic thermal stability of the pyrazine containing system, and no evidence of any smectic phases. The depression of nematic thermal stability and lack of, or suppression of smectic phases in both pyrazine containing systems may arise from an effective increase in molecular breadth due to the lone pairs of the nitrogen atoms and some twisting about interannular bonds. The single example of viscosity and birefringence obtained indicates that these pyrazine containing esters may have a reasonably low viscosity and high birefringence, but, a recent paper [5] using model compounds has cast some doubt on the potential of pyrazine containing liquid crystal systems for commercial applications because of possible poor light stability. Further work on pyrazine based liquid crystals is however in progress and will be reported in due course.

3. Experimental

Thermal optical microscopy was carried out using a Nikon Optiphot-2 polarizing microscope in conjunction with a Linkam THMS 600 hot-stage and TMS 91 control unit. IR spectra were recorded (KBr discs) using a Perkin–Elmer 782 infrared spectrophotometer, and ^{1}H NMR spectra were measured with tetramethylsilane as internal standard using a Perkin–Elmer R 32 90 MHz spectrometer. Mass spectra were determined using a VG Trio-2 quadrupole mass spectrometer. The purity of all liquid crystal materials was confirmed by satisfactory elemental analysis or by HPLC (>99·8 per cent) using a C_{18} reverse phase column, a Perkin–Elmer LC 235 diode array detector and acetonitrile as eluent. Birefringence and viscosity measurements were made at 20°C using a 10 wt % solution of the ester in ZLI 13086, using an Abbé refractometer at 589 nm for birefringence, and by the capillary flow method for viscosity.

3.1. *Preparation of materials*

3.1.1. *Synthesis of Pyrazine containing esters*

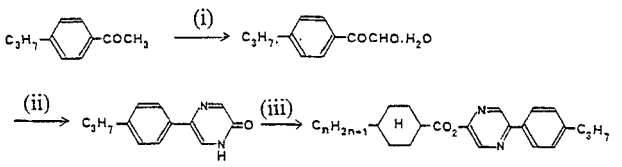
The routes used to synthesize the two series of esters containing a pyrazine ring are summarized in schemes 1 and 2 below.

The synthesis of 4-*n*-propylbiphenyl-4-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates was carried out according to scheme 3.

Table 4. Transition temperatures (°C) for the biphenyl-4-yl 4-*n*-alkoxybenzoates [4] **IV**.

R	C–I	C–S_A	C–N	S_A–N	N–I
CH_3	155	—	—	—	(148)
C_2H_5	160	—	—	—	(157)
C_3H_7	145	—	—	—	(139)
C_4H_9	153	—	—	—	(143)
C_5H_{11}	153·5	—	—	—	(133·5)
C_6H_{13}	—	—	132·5	—	136·5
C_7H_{15}	—	—	126	—	129·5
C_8H_{17}	—	—	119	(97·5)	130·5
$C_{10}H_{21}$	—	—	110	(106·5)	127
$C_{12}H_{25}$	—	108·5	—	112	123
$C_{14}H_{29}$	—	114	—	116·5	121·5

Brackets denote a monotropic transition.



Scheme 1. (i) SeO_2/EtOH/H_2O; (ii) Glycinamide HCl; (iii) $RC_6H_{10}CO_2H$/TFAA.

The *trans*-4-*n*-alkylcyclohexyl carboxylic acids were supplied by Merck Ltd., and the 4-*n*-alkoxybenzoic acids were either obtained commercially or prepared by literature methods [4].

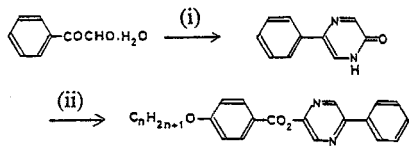
3.1.2. *4-*n*-Propylphenylglyoxal monohydrate*

4-*n*-Propylacetophenone (25·0 g, 0·15 mol) was added to a solution of selenium dioxide (17·1 g, 0·15 mol) in 95 per cent aqueous ethanol (100 ml), and heated at reflux for 4 h. Upon cooling, the selenium was filtered off and the solvent removed under reduced pressure. The resultant orange oil was purified by vacuum distillation (kugelrohr) to yield 25·7 g (95 per cent) of 4-*n*-propylphenylglyoxal, b.p. 130–135°C/0·5 mm. A stable hydrate was formed by stirring the oil in water (100 ml) for 24 h to give 28·4 g of the monohydrate as a yellow crystalline solid, m.p. 76–81°C.

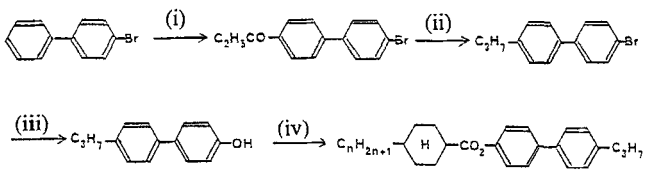
ν_{max} (KBr), 3400 (OH), 2920 (C–H), 1690 (C=O), 1600 (C=C, Ar) cm^{-1}; NMR δ_H(DMSO-d_6), 0·8–1·1 (3 H, t, CH_3), 1·4–2·0 (2 H, m, CH_2), 2·5–2·9 (2 H, t, CH_2), 5·6–5·9 (1 H, t, ArCOC<u>H</u>$(OH)_2$ collapses to singlet upon D_2O shake), 6·6–6·8 (2 H, d, ArCOCH(O<u>H</u>$)_2$ disappears on D_2O shake), 7·3–8·2 (4 H, 2d, ArH); m/z = 176 (M^+–18).

3.1.3. *5-(4-*n*-Propylphenyl)-2-pyrazinol*

(Note the pyrazinols are formally pyrazinones, but for consistency have been named as 'pyrazinols', irrespective of the predominant tautomeric form of these compounds.) 4-*n*-Propylphenylglyoxal monohydrate (15·0 g, 0·08 mol) was dissolved in methanol (50 ml), cooled to −40°C and dry powdered glycinamide hydrochloride (8·5 g, 0·08 mol) was added to the stirred solution. The temperature was allowed to rise to −30°C and sodium hydroxide (7·7 g, 0·19 mol in 25 ml water) was added, dropwise. The reaction mixture was maintained at −30°C overnight and allowed to warm to room temperature over 5 h. After cooling to 0°C, the pH was adjusted to 5·0 with concentrated hydrochloric acid, when an orange precipitate formed which was collected and washed with water. Purification of the crude product was carried out by dissolving it in dichloromethane (100 ml) and shaking with M sodium hydroxide (150 ml). The aqueous layer was washed with dichloromethane



Scheme 2. (i) Glycinamide HCl; (ii) $ROC_6H_4CO_2H$/TFAA.



Scheme 3. (i) $C_2H_5COCl/AlCl_3$; (ii) $(Et)_3SiH$; (iii) $Mg/(MeO)_3B/H_2O_2$; (iv) $RC_6H_{10}CO_2H$/TFAA.

(2 × 50 ml). The pH of the aqueous layer was adjusted to 5·0 with concentrated hydrochloric acid and the solid precipitate filtered off and washed with water until the washings were neutral. (In some preparations the purification process was repeated.) The yield of beige solid was, 9·4 g (57 per cent), which was 5-(4-*n*-propylphenyl)-2-pyrazinol, m.p. 150–1°C. ν_{max} (KBr), 2800–3000 (C–H), 1700 (C=O), 1500 (C=C, Ar) cm^{-1}; NMR δ_H(DMSO-d_6), 0·85–1·0 (3H, t, CH_3), 1·4–1·8 (2H, m, CH_2), 2·5–2·7 (2H, t, CH_2), 7·0–7·9 (4H, 2d, ArH), 8·0–8·2 (2H, 2s, pyrazine ArH), 12·5 (1H, broad s, NH disappears on D_2O shake); $m/z = 214$ (M^+).

3.1.4. *5-(4-*n*-Propylphenyl)pyrazin-2-yl* trans-*4-*n*-alkylcyclohexan-1-carboxylates*

5-(4-*n*-Propylphenyl)-2-pyrazinol (1·0 g, 0·0047 mol) was added to a stirred solution of the appropriate *trans*-4-*n*-alkylcyclohexan-1-carboxylic acid (0·0047 mol) and trifluoroacetic anhydride (1·18 g, 0·0056 mol) in dry methylene chloride (100 ml) in a flask fitted with a calcium chloride guard tube. After 4 h the reaction mixture was washed with M sodium hydroxide solution (2 × 100 ml), water (100 ml), and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a white crystalline solid which was purified by column chromatography on silica gel, eluting with toluene. The esters were recrystallized from *n*-hexane until the melting points and mesomorphic transitions were constant after successive recrystallizations. Yields were of the order of 30 per cent; melting points and mesomorphic transition temperatures for these compounds are given in table 1. Spectroscopic characteristics of the esters are broadly similar and the following data for the *n*-pentyl homologue are typical of the series. ν_{max} (KBr), 2900 (C–H, alkane), 1750 (C=O, ester), 1600 (C=C, Ar) cm^{-1}; NMR δ_H($CDCl_3$), 0·7–2·9 (28H, m, alkyl CH_2CH_3), 7·2–8·1 (4H, 2d, ArH), 8·4–8·9 (2H, 2s, pyrazine, ArH); $m/z = 394$ (M^+); purity (hplc) > 99·8 per cent.

3.1.5. *5-Phenyl-2-pyrazinol*

This was prepared in an analagous manner to 5-(4-*n*-propylphenyl)-2-pyrazinol using phenylglyoxal hydrate instead of 4-*n*-propylphenylglyoxal monohydrate. The product was a beige crystalline solid (67 per cent yield), m.p. 213–4°C (Lit. m.p. 212–4°C [6]).

3.1.6. *5-Phenylpyrazin-2-yl 4-*n*-alkoxybenzoates*

These were prepared from 5-phenyl-2-pyrazinol and the appropriate 4-*n*-alkoxybenzoic acid using an identical method to that utilized to prepare 5-(4-*n*-propylphenyl)pyrazin-2-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates. The products were white crystalline solids obtained in yields of the order of 40 per cent. Melting points and mesomorphic transition temperatures are given in table 3. Spectroscopic characteristics of these esters are broadly similar, and the following data for the *n*-pentyloxy homologue are typical of the series. $C_{22}H_{22}N_2O_3$: required, C, 72·9;

H, 6·1; N, 7·7. Found, C, 72·7; H, 6·1; N, 7·6 per cent; ν_{max} (KBr), 2950 (C–H, alkane), 1730 (C=O, ester), 1600 (C=C, Ar), 1570 (C=C, Ar); NMR δ_H($CDCl_3$), 0·9–1·1 (3H, t, CH_3), 1·2–1·9 (6H, m, CH_2), 3·9–4·1 (2H, t, CH_2O), 6·9–8·3 (9H, m, ArH), 8·7–8·9 (2H, 2s, pyrazine ArH); $m/z = 362$ (M^+).

Steps (i) and (ii) in scheme 3 involve known procedures and are well documented in the literature.

3.1.7. *4-Hydroxy-4'*-n-*propylbiphenyl*

4-Bromo-4'-*n*-propylbiphenyl (8·0 g, 0·029 mol) was dissolved in dry tetrahydrofuran (40 ml) and added slowly to magnesium (0·78 g, 0·032 mol) under an atmosphere of nitrogen. The reaction was initiated by heat and the addition of an iodine crystal. On completion of the addition, the reaction mixture was heated at reflux for 1 h and then cooled to −78°C. Trimethyl borate (4·80 g, 0·046 mol) was slowly added to give a cream coloured precipitate and stirring continued for a further 2 h. The reaction mixture was cooled to −10°C, and chilled glacial acetic acid (2·4 g, 0·04 mol) was added in one portion, followed by the addition of 30 per cent hydrogen peroxide (2·5 ml) over 15 min. The reaction mixture was stirred vigorously and the temperature maintained below 0°C, whereupon the solid dissolved. After warming to room temperature, the reaction mixture was stirred for a further 20 min, saturated aqueous iron (II) sulphate (50 ml) was added and stirring continued for 15 min. The reaction mixture was shaken with dichloromethane (3 × 50 ml); the extract was washed with water (2 × 100 ml), dried ($MgSO_4$) and the solvent removed to give a yellow solid which was recrystallized from ethyl acetate–light petroleum (b.p. 60–80) yielding 4·7 g (76 per cent), m.p. 151–3°C, ν_{max} (KBr), 3600–4000 (OH), 2900 (C–H, alkane), 1600 (C=C, Ar), 1500 (C=C, Ar), 800 (C–H, Ar) cm^{-1}; NMR δ_H(DMSO-d_6), 0·8–1·1 (3H, t, CH_3), 1·3–1·9 (2H, m, CH_2), 2·5–2·9 (2H, t, CH_2), 7·1–7·8 (8H, m, ArH), 9·4 (1H, s, OH); m/z 212 (M^+).

3.1.8. 4-n-*propylbiphenyl-4'-yl* trans-4-n-*alkylcyclohexan-1-carboxylates*

These were prepared from 4-hydroxy-4'-*n*-propylbiphenyl and the appropriate *trans*-4-*n*-cyclohexan-1-carboxylic acids in an identical manner to that used to prepare 5-(4-*n*-propylphenyl)pyrazin-2-yl *trans*-4-*n*-alkylcyclohexan-1-carboxylates. The products were white crystalline solids, and yields were in the order of 55 per cent. Melting points and mesomorphic transition temperatures are given in table 2. The spectroscopic characteristics of these esters are broadly similar and the following data for the *n*-pentyl homologue are typical of the series: $C_{27}H_{36}O_2$: required, C, 82·6; H, 9·3. Found, C, 82·8; H, 9·5 per cent; ν_{max} (KBr), 2800–3000 (C–H, alkane), 1750 (C=O, ester); NMR δ_H($CDCl_3$), 0·8–2·8 (28H, m, alkyl and cyclohexyl, C–H), 7·0–7·8 (8H, m, ArH); m/z 392 (M^+).

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