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Ferroelectric liquid crystals
VI. Chiral 5-alkyl-2-phenylpyrimidines

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Over 50 variously substituted 5-alkyl-2-phenylpyrimidines have been synthesized. The effect of the presence of an additional olefinic double bond in the terminal position of the alkoxy chain or of a trans-1,4-disubstituted cyclohexane ring on the liquid crystal transition temperatures of these systems has been studied in detail. All of the phenyl-pyrimidines studied possess an optically active centre at the point of methyl branching of one of the terminal carbon chains. The dependence of the transition temperatures of these systems on the position of the chiral centre has also been investigated. The effect of chain length has also been studied for various homologous series of mesogens. Almost all of the 5-alkyl-2-phenylpyrimides prepared exhibit enantiotropic chiral smectic C and cholesteric mesophases, some at and just above room temperature.

1. Introduction

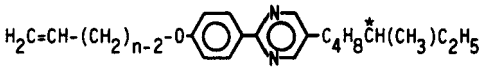
The effects of introducing an additional trans-1,4-disubstituted cyclohexane ring [1, 2] or an olefinic double bond [3] into various phenyl benzoates exhibiting smectic C or chiral smectic C mesophases have been reported recently [1–3]. Significant improvements in the liquid transition temperatures were observed. Ferroelectric liquid crystal mixtures containing some of these new modified phenyl benzoates are being investigated for commercial applications. These investigations have now been extended to include substituted 5-alkly-2-phenylpyrimidines [4]; a substantial number of such compounds have recently been reported to exhibit chiral smectic C mesophases [5].

Many of the reaction intermediates and starting materials used in the earlier investigations [1–3] could be used to prepare a wide range of new compounds containing the 5-alkyl-2-phenylpyrimidine moiety. The 5-alkly-2-phenylpyrimidine intermediates were synthesized according to literature methods [6]. The starting materials and reaction intermediates incorporating the olefinic double bond were also prepared as described elsewhere [2, 3]. The 4-alkoxybenzoic acids were commercially available, whereas the trans-4-alkylcyclohexane-1-carboxylic acids had to be prepared according to modified literature methods [7]. The chiral branched chain 4-alkoxybenzoic acids and 4-alkoxyphenols could be prepared using methods described elsewhere [2, 3].

2. Results

The liquid crystal transition temperatures and enthalpies of fusion of the 2-(4-alkenyloxy)phenyl)-5-[(S)-5-methylheptyl]pyrimidines (**I**) are listed in table 1. The melting points (C–*S_C,C–Ch) fall below room temperature for compounds having

Table 1. The liquid crystal transition temperatures and enthalpies of fusion for the 2-(4-(alkenyloxy)phenyl)-5-((S)-5-methylheptylpyrimidines (I). Parentheses indicate a monotropic transition.

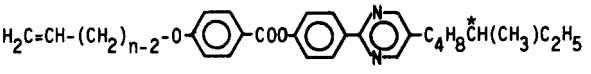


n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	30	—	31	7·9
7	35	(29)	46	—
8	29	(28)	40	11·4
9	16	35	48	10·4
10	17	34	44	14·2
11	20	40	49	11·1
12	35	40	47	27·1

intermediate chain lengths (n = 9–11). The chiral smectic C–cholesteric transition temperature (*S_C–Ch) and the clearing point (Ch–I) increase with increasing chain length and are still rising for the longest chains studied. Thus the ethers (I) exhibit enantiotropic chiral smectic C mesophases at and above room temperature. This is most unusual because there are few reports [3, 5] of such a chiral smectic C phase at this temperature for a single component system. The enthalpies of fusion of the ethers (I) are remarkably low for several homologues. These properties are advantageous for the preparation of commercial mixtures exhibiting a ferroelectric chiral smectic C mesophase for electro-optic display devices [8].

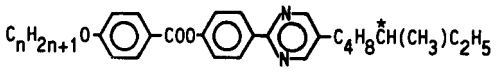
The liquid crystal transition temperatures and enthalpies of fusion of the 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenyl 4-alkenyloxy)benzoates (II) are listed in table 2. The presence of an additional ester function and a 1,4-disubstituted phenyl ring relative to the ethers (I) results in surprisingly small increases in the transition temperatures. The melting points (C–*S_C, C–Ch) and the chiral smectic C–cholesteric transition temperatures(*S_C–Ch) are increased by almost the same amount; namely,

Table 2. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-(methylheptyl)-2-pyrimidinyl)phenyl 4-(alkenyloxy)benzoates (II); parentheses indicate a monotropic transition.



n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	8	(51)	143	28·2
7	44	48	149	20·7
8	56	58	141	—
9	62	(61)	142	25·2
10	68	71	136	—
11	67	75	136	34·7
12	68	81	131	31·3

Table 3. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenyl 4-alkoxybenzoates (**III**); parentheses indicate a monotropic transition.



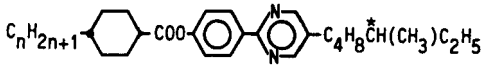
n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	56	(54)	152	18·5
7	64	65	148	—
8	71	(70)	142	25·4
9	78	(77)	142	28·6
10	74	82	141	—
11	78	85	136	31·2
12	83	88	133	32·0

about 35°C and 30°C, respectively. Thus enantiotropic chiral smectic C mesophases exist over a narrow temperature range or monotropic behaviour is observed. The clearing point (Ch–I) is increased by a much larger extent, 97°C on average, although this is significantly less than would have been expected on the basis of previous results [3]. Thus, a cholesteric phase is observed over a wide temperature range. No other smectic mesophases were observed and this is quite unusual for three ring systems of this kind.

The result of effectively hydrogenating the olefinic double bond of the terminal carbon chain of the esters (**II**) to produce the corresponding 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenyl 4-alkoxybenzoates (**III**) can be elucidated by a comparison of the transition temperatures given in tables 2 and 3. The clearing points (Ch–I) of both systems are almost identical and on average are 140°C and 142°C, respectively. The melting points (C–*S_C, C–Ch) and the chiral smectic C–cholesteric transition temperatures of the saturated esters (**III**) are marginally higher by, on average, 9°C and 10°C, respectively.

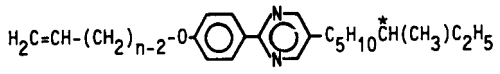
Table 4 gives the liquid crystal transition temperatures and the enthalpies of fusion of the 4-(5-((S)-methylheptyl)-2-pyrimidinyl)phenyl trans-4-alkylcyclohexane-1-carboxylates (**IV**); no smectic polymorphism was observed. The melting points

Table 4. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenyl trans-4-alkylcyclohexane-1-carboxylates (**IV**).



n	C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
3	119	153	13·8
5	132	154	15·4
7	114	165	13·8
9	104	141	18·7

Table 5. The liquid crystal transition temperatures and enthalpies of fusion for the 2-(4-(alkenyloxy)phenyl)-5-((S)-6-methyloctyl)pyrimidines (**V**).



n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	13	—	21	9·8
7	7	19	39	9·7
8	4	15	32	—
9	−1	28	42	9·1
10	12	27	38	21·7
11	17	36	45	19·1
12	33	37	43	27·9

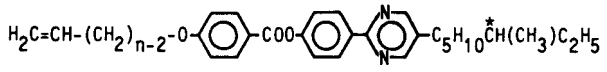
(C–Ch) and clearing points (Ch–I) are moderately high. For a three-ring system the temperature range of the cholesteric phase is not particularly broad. The absence of smectic polymorphism may be attributed to the lower degree of aromaticity and the lower concentration of lateral dipoles in the esters (**IV**) as compared with the esters (**II**) and (**III**) [9].

The addition of an extra methylene unit to the ethers (**I**) to produce the 2-(4-(alkenyloxy)phenyl)-5-((S)-6-methyloctyl)pyrimidines (**V**) changes the liquid crystal transition temperatures significantly as comparison of the data in tables 1 and 5 shows. All the transition temperatures of the ethers (**V**) are lower than those of the analogous ethers (**I**). However, the melting point (C–*S_C, C–Ch) is decreased much more, 16°C on average, than either the chiral smectic C–cholesteric transition temperature, 7°C on average, or the clearing point, 6°C on average. This results in a broadening of the temperature range of the observed chiral smectic C mesophase. A minimum in the melting point is again observed for intermediate chain lengths (m = 9). The trends in the transition temperatures are almost identical for both homologous series (**I**) and (**V**). The enthalpy of fusion is exceptionally low for several homologues.

The liquid crystal transition temperatures of the 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)phenyl 4-(alkenyloxy)benzoates (**VI**), given in table 6, are almost identical with those of the corresponding esters (**II**) with one less methylene unit in the chiral terminal chain. The trends in the transition temperatures with respect to chain length are also very similar. A small difference between the two series is the slightly higher values of the enthalpy of fusion for the esters (**VI**). This similarity of behaviour is not surprising considering the relatively minor difference in chemical structure between these two homologous series of three-ring esters. The temperature range of the chiral smectic C mesophase is still somewhat narrow for three-ring esters [3, 9] although it increases significantly with increasing chain length.

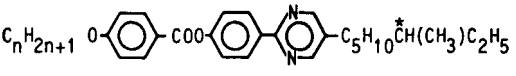
The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)phenyl 4-alkoxybenzoates (**VII**) are listed in table 7. Almost exactly the same differences between the average transition temperatures for the esters (**III**) and (**VII**) are observed as for those discussed for the corresponding alkenyloxy esters (**II**) and (**VI**); this is shown in tables 2 and 6, and tables 3 and 7, respectively. A similar small increase in the enthalpy of fusion is also observed for the esters (**VII**) with respect to the esters (**III**). However, in contrast to the corresponding

Table 6. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)phenyl 4-(alkenyloxy)benzoates (**VI**). Parenthesis indicate a monotropic transition.



n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	66	(44)	139	29·4
7	45	48	144	32·3
8	50	60	137	33·3
9	53	67	139	27·2
10	67	75	133	35·5
11	61	80	132	34·9
12	65	84	127	37·2

Table 7. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)phenyl 4-alkoxybenzoates (**VII**), parenthesis indicate a monotropic transition.



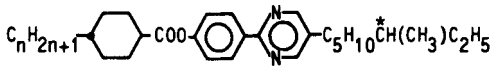
n	C–*S_C/Ch/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
6	72	(50)	148	—
7	56	64	144	33·9
8	56	72	142	33·6
9	68	80	138	34·9
10	86	(84)	137	—
11	83	90	132	35·8
12	69	94	132	30·0

alkenyloxy-substituted esters (**VI**), only one homologue (n = 12) exhibits an enantiotropic chiral smectic C mesophase over a reasonably wide temperature range (25°C).

If the ester linkage in the decyl homologue of the series (**VII**) is inverted to yield 4-decycloxyyphenyl 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)benzoate there is only a small change in the observed transition temperatures (C–Ch, 88°C; *S_C–Ch 84°C; Ch–I, 133° C).

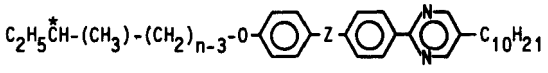
The 4-(5-((S)-6-methyloctyl)-2-pyrimidynyl)phenyl trans-4-alkylcyclohexane-1-carboxylates (**VIII**) exhibit liquid crystal transition temperatures and enthalpies of fusion given in table 8. The melting points (C–S_B, C–Ch) and clearing points (Ch–I) are substantially lower, 18°C and 12°C, respectively, than those of the corresponding esters (**IV**) listed in table 4. In contrast to the esters (**IV**), the nonyl homologue of the esters (**VIII**) possesses an enantiotropic, narrow-range chiral smectic C mesophase above an enantiotropic smectic B mesophase. This is the first example of smectic polymorphism observed for the esters investigated so far (**I–VIII**). The presence of a trans-1, 4-disubstituted cyclohexane ring is known to support strongly the appearance of smectic B phases [9], although there are some important exceptions to this [1, 2].

Table 8. The liquid crystal transition temperatures and enthalpies of fusion for the 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)phenyl trans-4-alkylcyclohexane-1-carboxylates (**VIII**).



n	C–S_B/Ch/°C	S_B–S_C/°C	*S_C–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
3	98	—	—	141	12·1
5	110	—	—	147	31·0
7	105	—	—	141	17·1
9	82	87	92	136	19·3

Table 9. The liquid crystal transition temperatures and enthalpies of fusion for the esters of structure; parentheses indicate a monotropic transition.



n	Z	C–*S_C/S_A/Ch/°C	*S_C–S_A/Ch/°C	S_A–Ch/°C	Ch–I/°C	ΔH kJ mol^{-1}
4	COO	94	—	—	130	26·8
6	COO	70	78	—	140	29·8
8	COO	62	99	—	142	—
4	OOC	109	(99)	137	138	34·8
6	OOC	100	111	138	145	24·3
8	OOC	78	109	142	146	27·7

The effect of chain length, n, and the position of the chiral centre, as well as the direction of the central ester linkage (Z), on the liquid crystal transition temperatures of the parent isomers (**IX**) and (**X**) is clearly shown by the data in table 9. The melting points (C–*S_C, C–Ch) of the esters (**IX**), (Z = COO), decrease with increasing chain length, whereas the chiral smectic C transition temperatures (*S_C–Ch) and the clearing points (Ch–I) increase. No other smectic mesophases were observed. This is consistent with the data given in tables 3 and 7 for the similar esters (**III**) and (**VII**) in which the chiral centre is incorporated in the other terminal carbon chain. Inversion of the ester linkage, Z = OOC, to produce the esters (**X**) results in large changes in the transition temperatures and also the appearance of a smectic A mesophase at elevated temperatures. The melting point (C–*S_C), chiral smectic C transition temperature (*S_C–S_A) and the clearing point (Ch–I) are substantially higher by an average 21°C, 31°C and 6°C, respectively for the esters (**X**). This is consistent with previous results [1–3, 9].

3. Conclusions

A significant number of 5-alkyl-2-phenylpyrimidines have been prepared which exhibit moderately wide-range, enantiotropic chiral smectic C mesophases at and just above room temperature. A variety of aromatic three-ring esters have also been

synthesized which possess enantiotropic chiral smectic C and cholesteric mesophases at reasonably elevated temperatures. The transition temperatures and the appearance of a smectic A phase depends upon the direction of the ester linkage (*Z*). The presence of a trans-1,4-disubstituted cylcohexane ring does not exclude the possibility of a chiral smectic C phase, but it is also associated with a smectic B phase at elevated temperatures. The presence of an olefinic double bond in a terminal position of the carbon chain leads to a general lowering of the liquid crystal transition temperatures in examples for which valid comparisons may be made. In several cases, the temperature range of the chiral smectic C mesophase is significantly broader for the alkenyloxy-substituted compounds as compared with that of the corresponding alkoxy-substituted materials.

4. Experimental

The structural and thermal characterization of these compounds (**I–X**) was performed using methods described in detail elsewhere [2, 3].

2-(4-(9-Decenyloxy)phenyl)-5-((S)-5-methylheptyl)pyrimidine. A mixture of 9-decenyl-tosylate [2] (0·7 g, 0·0021 mol), (S)-4-(5-(5-methylheptyl)-2-pyrimidinyl) phenol (0·5 g, 0·0018 mol), anhydrous potassium carbonate (1·0 g, 0·0070 mol) and anhydrous butanone (50 ml) was refluxed overnight. The cooled reaction mixture was poured into water (500 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with water (2 × 500 ml) and dried over anhydrous magnesium sulphate. The solvent was removed under slightly reduced pressure; purification of the crude product was performed using column chromatography on silica gel with toluene as eluent followed by distillation using Kugel–Rohr apparatus. Tables 1 and 5 list the liquid crystal transition temperatures of this compound and the other homologues prepared by this method.

4-(5-((S)-5-Methylheptyl)-2-pyrimidinyl)phenyl 4-(9-decenyloxy)benzoate. A solution of 4-(9-decenyloxy)benzoic acid [2] (0·30 g, 0·0011 mol), 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenol (0·31 g, 0·0011 mol), dicyclohexylcarbodiimide (0·27 g, 0·0013 mol), 4-(dimethylamino)pyridine (0·04 g) and anhydrous dichloromethane (40 ml) was stirred at room temperature overnight. After filtration to remove precipitated material, the filtrate was evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent followed by recrystallization from alcohol until the transition temperatures remained constant. Tables 2–4 and 6–9 give the liquid crystal transition temperatures and enthalpies of fusion for this ester and the other esters prepared using this general procedure.

4-(5-((S)-5-Methylheptyl)-2-pyrimidinyl)phenol. A solution of tetrachlorotitanium (22·5 ml, 0·205 mol) and anhydrous dichloromethane (125 ml) was added dropwise over 1 hour to a solution of 2-(4-isopropoxyphenyl-5-((S)-5-methylheptyl)pyrimidine (22·7 g, 0·069 mol) and anhdyrous dichloromethane (300 ml) under anhydrous conditions and cooled using an ice bath. The reaction solution was maintained at this temperature for a further 45 min and then stirred overnight at room temperature. The reaction mixture was added to water (1500 ml) and the organic layer was separated off. The aqueous layer was extracted using dichloromethane (2 × 200 ml) and the combined organic layers were washed with water (2 × 1000 ml) and dried over

anhydrous sodium sulphate. After filtration, the solvent was removed by evacuation and the crude phenol was recrystallized from hexane (yield 80 per cent; m.p. 49–50°C).

4-(5-((S)-6-Methyloctyl)-2-pyrimidinyl)phenyl. (m.p. 70–71°C) was prepared in a 95 per cent yield using the method described for 4-(5-((S)-5-methylheptyl)-2-pyrimidinyl)phenol.

4-(5-Decyl-2-pyrimidinyl)phenol. A solution of borontribromide (5·3 g, 0·0212 mol) in absolute dichloromethane (50 ml) was added dropwise to a solution of 5-decyl-2-(isopropyloxyphenyl)pyrimidine (5·0 g, 0·0141 mol) in absolute dichloromethane (50 ml) under anhydrous conditions and cooled using an ice bath. The reaction solution was stirred at 0°C for about 1 hour and then poured carefully into an ice/water mixture. The organic layer was separated off and the aqueous layer shaken with dichloromethane (50 ml). The combined organic layers were washed with 2 N sodium carbonate solution (50 ml) and water (2 × 500 ml) and then dried over anhydrous magnesium sulphate. The drying agent and solvent were removed, and the residue was purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent. Recrystallization from hexane gave the pure phenol (yield 3·0 g, 68 per cent); m.p. 61–62°C).

2-(4-Isopropoxyphenyl)-5-((S)-5-methylheptyl)pyrimidine. A 5 per cent (mol per cent) of sodium methoxide in methanol (80 ml) was added dropwise to a mixture of (S)-2-(methoxymethylidene)-7-methylnonanal (23 g, 0·116 mol), 4-isopropoxybenzamidine-hydrochloride (20·1 g, 0·094 mol) and anhydrous methanol (250 ml); during this addition the temperature was kept below 10° C. The reaction mixture was stirred at room temperature overnight. Concentrated hydrochlorid acid was added (pH 4–5) and the inorganic material was filtered off. The filtrate was concentrated under reduced pressure, dichloromethane (500 ml) was added and the resultant solution washed with water (2 × 500 ml) and dried over anhydrous sodium sulphate. Column chromatography on silica gel using a 19 : 1 hexane/ethyl acetate mixture as eluent recrystallization from methanol gave the pure product (yield 21·0 g, 68 per cent; m.p. 47–48°C).

2-(4-Isopropoxyphenyl)-5-((S)-6-methyloctyl)pyrimidine (yield 55 per cent; m.p. 35–35·5°C) and *5-decyl-2-(4-isopropoxyphenyl)pyrimidine* (yield 65 per cent; m.p. 54–55°C) were prepared using the method described for 2-(4-isopropoxyphenyl)-5-((S)-5-methylheptyl) pyrimidine.

(S)-2-(Methoxymethylidene)-7-methylnonanal. A mixture of 2-((S)-5-methylheptyl)malonaldehyde-tetramethylacetal (27 g, 0·097 mol), 4-toluene-sulphonic acid-mono hydrate (0·2 g) and water (2 ml) was heated at 70–80° C for 2 hours. Sodium bicarbonate (0·6 g) was added to the cooled solution. The resultant mixture was stirred for about 5 min and then filtered to remove the inorganic material; the residue was washed with small amounts of methanol. The filtered methanolic solution of the aldehyde was used immediately in the next reaction assuming a quantitative yield.

(S)-2-(Methoxymethylidene)-8-methyldecanal and *2-(methoxymethylidene)dodecanal* were prepared using the method described for (S)-2-(methoxymethylidene)-7-methylnonanal.

2-((S)-5-Methylheptyl)malonic aldehyde-tetramethyl acetal. (S)-1-methoxy-7-methyl-1-nonene (19 g, 0·111 mol) was added dropwise to a freshly prepared solution of trimethyl orthoformate (73 ml, 0·66 mol) and boron trifluoride diethyl ether (1 ml) cooled using an ice bath. The reaction solution was stirred for a further 4 hours at 0°C and then neutralized using triethylamine (4 ml) before being concentrated under reduced pressure. The liquid residue was taken up in diethyl ether (500 ml) and washed with concentrated sodium carbonate solution and with water (2 × 150 ml), and then dried over anhydrous sodium sulphate. Filtration to remove the drying agent and removal of the solvent under reduced pressure yielded the crude product (yield 29·2 g, 96 per cent).

2-((S)-6-Methyloctyl)malonic aldehyde-tetramethyl acetal (yield 97 per cent) and *2-decylmalonic aldehyde-tetramethyl acetal* (yield 96 per cent) were prepared using the method described for 2-((S)-5-methylheptyl)malonic aldehyde-tetramethyl acetal.

(S)-*1-Methoxy-7-methyl-1-nonene.* A solution of (S)-6-methyloctanone (31 g, 0·219 mol) and diethly ether (100 ml) was added dropwise over about 30 min to a mixture of methoxymethyl-triphenylphosphoniumchloride (105 g, 0·306 mol), potassium tert. butylate (34·3 g, 0·306 mol) and diethyl ether (500 ml) under anhydrous conditions and cooled using an ice bath. The reaction mixture was stirred at room temperature for a further 4 hours and then added to a 0·8 N sodium bicarbonate solution (160 ml). The aqueous layer was separated off and shaken with ether (3 × 100 ml). The combined organic layers are washed with water (2 × 100 ml) and dried over anhydrous sodium sulphate. The filtered solution was concentrated under slightly reduced pressure, pentane (800 ml) was added and the resultant mixture cooled to 0°C. The precipitated triphenylphosphoniumoxide was filtered off and the filtrate concentrated again under slightly reduced pressure. The liquid residue was distilled under reduced pressure to give the pure product (yield 30·2 g, 81 per cent; b.p. 83–89°C/11 Torr).

(*S*)-*1-Methoxy-8-methyl-1-decene* (yield 79 per cent; b.p. 96–105°C/11 Torr) and *1-methoxy-1-dodecene* (yield 75 per cent; b.p. 122–124° C/11 Torr) were prepared using the method described for (S)-1-methoxy-7-methyl-1-nonene.

(*S*)-*7-Methylnonanal.* A solution of (S)-1-methoxy-7-methyl-1-nonene (32·5 g, 0·191 mol), 2 N hydrochloric acid (100 ml) and tetrahydrofuran (400 ml) was refluxed for about 1 hour. The cooled reaction solution was added to water (1200 ml) and shaken with ether (4 × 250 ml). The combined organic layers were washed with water (3 × 200 ml) and dried over anhydrous sodium sulphate. The drying agent was removed by filtration and the solvent evaporated off under slightly reduced pressure; the crude product obtained was used directly in the next reaction without further purification.

4-(5-((S)-6-Methyloctyl)-2-pyrimidinyl)benzamide. A solution of freshly prepared sodium methoxide (1·8 g sodium and 25 ml methanol) was added dropwise to a solution of 4-carbamylbenzamidine-hydrochloride (10·5 g, 0·053 mol), (S)-2-(methoxymethylidene)-8-methyldecanal (10·7 g, 0·050 mol) and methanol (125 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred at room temperature overnight and then acidified (pH 3–4) with concentrated hydrochloric acid. The

precipitate was filtered off, washed with portions of water and methanol, pressed dry and then dried under vacuum to give the crude product (yield 10·8 g, 66 per cent) *4-(5-Decyl-2-pyrimidinyl)benzamide* (yield 87 per cent) was prepared in a similar fashion.

4-(5-(S)-6-Methyloctyl)-2-pyrimidinyl)benzoic acid. A solution of 4-(5-((S)-6-methyloctyl)-2-pyrimidinyl)benzamide (10·8 g, 0·033 mol), potassium hydroxide (7·6 g, 0·136 mol) and ethylene glycol (200 ml) was heated at 160° C for 3·5 hours. The cooled reaction mixture was poured into water (300 ml) and acidified (pH 1) with 3 N hydrochloric acid. The precipitate was filtered off and dissolved in ether; the resultant solution was washed with water (2 × 500 ml) and dried over anhydrous sodium sulphate. The solvent was removed by evaporation under reduced pressure to give the pure acid (yield 10·6 g, 98 per cent; m.p. 216–218°C).

4-(5-Decyl-2-pyrimidinyl)benzoic acid. A solution of 4-(5-decyl-2-pyrimidinyl) benzamide (10 g, 0·0295 mol), concentrated sulphuric acid (30 ml), water (30 ml) and glacial acetic acid (100 ml) was heated at 120° C overnight. The cooled reaction solution was poured into an ice/water mixture (200 ml). The resultant precipitate was filtered off, washed with small amounts of water, pressed dry and then recrystallized from ethanol to give the pure acid (yield 7·5 g, 75 per cent; C–S_2, 52°C, S_2–S_B, 192°C, S_B–I, 206°C).

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