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A new family of chiral smectic liquid crystals

Synthesis and properties of liquid crystals bearing a pyridine heterocycle

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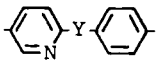
A new family of chiral smectic liquid-crystalline compounds having a core structure of  (Y = C≡C or CH_2CH_2) have been synthesized and their thermal stabilities have been examined systematically in terms of influences of the linkage between the benzene ring and the pyridine ring, and the chain length of the terminal alkyl group.

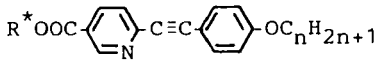
1. Introduction

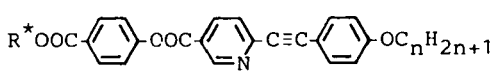
Although a large number of liquid-crystalline compounds forming chiral smectic C (S_C^*) are known, relatively few examples bearing heterocycles have appeared in the literature [1]. Especially, there have been few studies on S_C^* liquid-crystalline compounds bearing a pyridine heterocycle. The reason may be attributable to less attention to the core structure of ferroelectric liquid crystals and to lack of methods applicable to preparing pyridine derivatives, which have a structure required for ferroelectric liquid-crystalline compounds. Based on the molecular shape and polarity it is supposed that a 2,5-substituted pyridine unit is suitable for a principal unit in the core of S_C liquid-crystalline compounds [2]. We have elaborated a strategy to construct the core by adopting the palladium-catalysed coupling reaction [3] between a halopyridine and an ethynyl compound either of which possesses a chiral moiety.

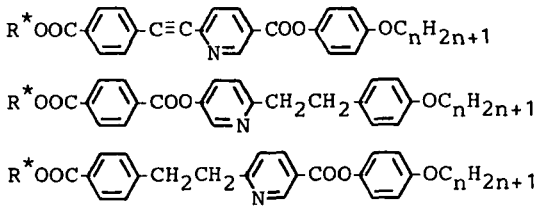
In this study, we report on the synthesis and properties of S_C^* liquid-crystalline compounds bearing a pyridine heterocycle.

2. Synthesis

We chose compounds **I–V** as target molecules which have a 2,5-disubstituted pyridine ring as the principal unit in the core.

 **Ia–d**

 **IIa,b**



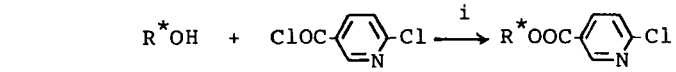
IIIa,b

IVa,b

Va,b

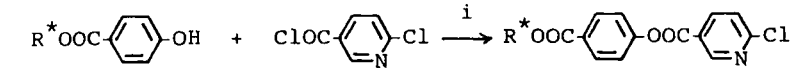
a, R* = (S)-$C_2H_5(CH_3)CHCH_2$–; **b**, R* = (R)-$C_6H_{13}(CH_3)CH$–;
c, R* = (S)-$C_2H_5(CH_3)CH(CH_2)_3$–; **d**, R* = (S)-$C_2H_5(CH_3)CH(CH_2)_5$–.

The chiral groups of **I–V** are linked to the core through an ester group. The cores consist of a pyridine ring, a benzene ring, an ester, and an acetylenic or a methylene linkage. Compounds **I–III** were synthesized starting from chloronicotinic acid by esterification and coupling reaction, and compounds **IV** and **V** by hydrogenation of **II** and **III**, respectively. The synthetic pathway is illustrated in scheme 1.



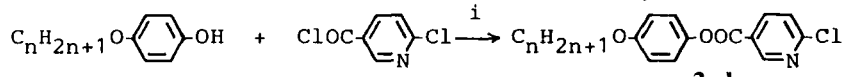
(1)

1a–d



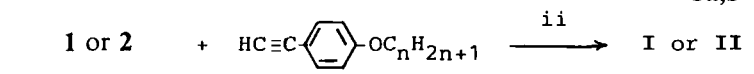
(2)

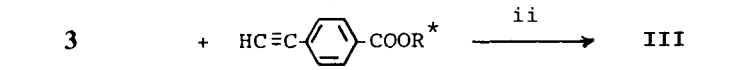
2a,b



(3)

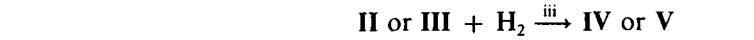
3a,b





4

5



i, pyridine; ii, $(Ph_3P)_2PdCl_2$, CuI, NEt_3; iii, 5 per cent Pd/C, AcOEt.

Scheme 1. Route to a new family of liquid-crystalline compounds.

The esters of 6-chloronicotinic acid, **1**, **2** and **3**, were prepared by the reaction of 6-chloronicotinyl chloride with a chiral alcohol or phenol and/or a normal alkyloxy phenol in dry benzene containing pyridine [4]. The compounds **I**, **II** and **III** were successfully synthesized in good yields by coupling the esters with corresponding 4-alkyloxyphenylacetylenes (**4**) or chiral alkoxycarbonylphenylacetylenes (**5**) [5]. Analogous series **IV** and **V** were obtained by the hydrogenation of compounds **II** and **III** in ethyl acetate with molecular hydrogen in the presence of a 5 per cent Pd/C catalyst. The final products were purified by silica-gel column chromatography, followed by recrystallization from hexane.

3. Phase behaviour

Series **I** showed quite low thermal stabilities of S phases, and monotropic S_C^* phases were observed only for compounds **Ic** and **Id** in which the bulky lateral

Table 1. Phase transition temperatures for compounds of series **I**.

Compound	R*	*n*	Transition temperatures/°C						
			M.p.	S_C^*		S_A			I
Ia	2M4	5	75						●
Ia	2M4	7	80						●
Ia	2M4	8	79						●
Ia	2M4	10	71						●
Ia	2M4	12	76						●
Ib	1M7	10	69						●
Ic	4M6	10	63	●	(56)	●	(58)		●
Id	6M8	10	51	●	(60)				●

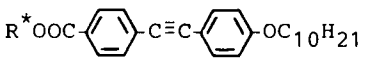
M.p., melting point; S_C^*, chiral smectic C; S_A: smectic A; I, isotropic liquid phases; ( ), monotropic transition; 2M4, (*S*)-2-methylbutyl; 4M6, (*S*)-4-methylhexyl; 6M8, (*S*)-6-methyloctyl; 1M7, 1-methylheptyl.

Table 2. Phase transition temperatures for compounds of series **II**.

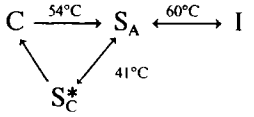
Compound	R*	*n*	Transition temperatures/°C								
			M.p.	S_C^*		S_A		N*		I	
IIa	2M4	8	102	●	137	●	165	●	176	●	
IIa	2M4	9	95	●	142	●	166	●	173	●	
IIa	2M4	10	94	●	144	●	164	●	171	●	
IIb	1M7	6	99			●	134			●	
IIb	1M7	7	100	●	(91)	●	128			●	
IIb	1M7	8	82	●	103	●	128			●	
IIb	1M7	9	85	●	111	●	120			●	
IIb	1M7	10	92	●	115					●	
IIb	1M7	11	99	●	110					●	
IIb	1M7	12	95	●	111					●	

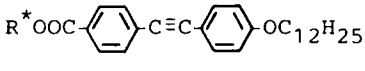
See table 1 for abbreviations.

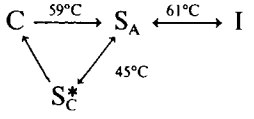
group is kept away from the core by long spacer methylene units. The compounds having a bulky group like 2-methylbutyl or 1-methylheptyl in the neighbourhood of the core did not form any S phases. They differ from analogous compounds **VIa** [5], homocyclic systems, in the phase behaviour.



Phase sequence







VIa

R* = (S)-$C_2H_5(CH_3)CHCH_2$-

In comparison with **I**, homologous series **II**, **III**, **IV** and **V** exhibited high thermal stabilities of mesophases because they have a structure composed of three aromatic

Table 3. Phase transition temperatures for compounds of series **III**.

Compound	R*	*n*	Transition temperatures/°C							
			M.p.	S_C^*		S_A		N*		I
IIIa	2M4	8	105	●	139	●	156	●	167	●
IIIa	2M4	9	106	●	135	●	156	●	172	●
IIIa	2M4	10	105	●	138	●	156	●	167	●
IIIb	1M7	6	65			●	122			●
IIIb	1M7	7	73	●	87	●	117			●
IIIb	1M7	8	75	●	92	●	117			●
IIIb	1M7	9	80	●	106	●	111			●
IIIb	1M7	10	80	●	109					●
IIIb	1M7	11	86	●	106					●
IIIb	1M7	12	87	●	106					●

N*, cholesteric phases; see table 1 for the other abbreviations.

Table 4. Phase transition temperatures for compounds of series **VI**.

Compound	R*	*n*	Transition temperatures/°C					
			M.p.	S_C^*		S_A		I
VIa	2M4	8	63	●	88	●	121	●
VIa	2M4	9	59	●	96	●	121	●
VIa	2M4	10	41	●	93	●	119	●
VIb	1M7	6	57			●	94	●
VIb	1M7	7	51	●	63	●	89	●
VIb	1M7	8	53	●	73	●	88	●
VIb	1M7	9	51	●	80	●	86	●
VIb	1M7	10	50	●	83	●	86	●
VIb	1M7	11	52	●	83·5	●	84	●
VIb	1M7	12	44	●	84			●

See table 1 for abbreviations.

Table 5. Phase transition temperatures for compounds of series **V**.

Compound	R*	*n*	Transition temperatures/°C					
			M.p.	S_C^*		S_A		I
Va	2M4	8	50	●	97	●	122	●
Va	2M4	9	57	●	97	●	121	●
Va	2M4	10	51	●	96	●	121	●
Vb	1M7	6	62	●	(43)	●	90	●
Vb	1M7	7	57	●	72	●	86	●
Vb	1M7	8	44	●	77	●	86	●
Vb	1M7	9	61	●	80	●	84	●
Vb	1M7	10	63	●	80	●	83	●
Vb	1M7	11	66	●	82	●	83	●
Vb	1M7	12	59	●	83			●

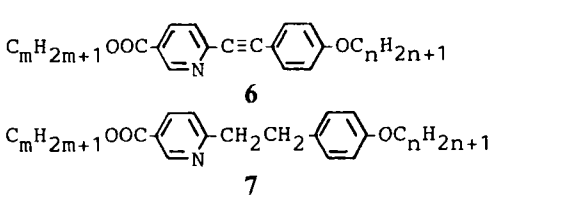
See table 1 for abbreviations.

rings. The homologous series **II** and **III** exhibit phase sequences of C–S_C^*–S_A–N*–I (n = 8–10) when the chiral group R* is (*S*)-2-methylbutyl, and of C–S_A–I (n = 7–9) or C–S_C^*–S_A–I (n = 10–12) when R* is (R)-1-methylheptyl. The homologous series **IV** and **V** have those of C–S_C^*–S_A–I when R* is (*S*)-2-methylbutyl, and of C–S_C^*–S_A–I (n = 7–11 for **IV**; n = 6–11 for **V**). Except for homologue **V**, the compounds having the alkyloxy group n = 6 did not form the S_C^* phase. When the every homologous series has a different binding mode of three aromatic rings, i.e. Ph–C≡C–Py–COO–Ph for series **II** and Ph–OOC–Py–C≡C–Ph for **III**, they show almost the same thermal stabilities and phase sequences of the S_A, S_C^* and N* phases. The same tendencies exist for the relationship between the homologous series **IV** and **V**.

Difference in the stability of mesophases was observed for the N* phases; series **IIa** and **IIIa** form stable N* phases, whereas series **IVa** and **Va** do not have N* phases. Series **II** and **III** show higher melting points and form more thermally stable S phases than series **IV** and **V**.

4. Discussion

The figure shows the melting points and the range of S_C^* phases for the compounds of **II**, **III**, **IV** and **V** with the alkyl group of n = 10. In order to estimate the influence of linking groups on the melting points and the stabilities of mesophases, we prepared compounds **6** and **7** as models, which have the same molecular structure except for the linking group. Their melting points and transition enthalpies (ΔH) are summarized in table 6.

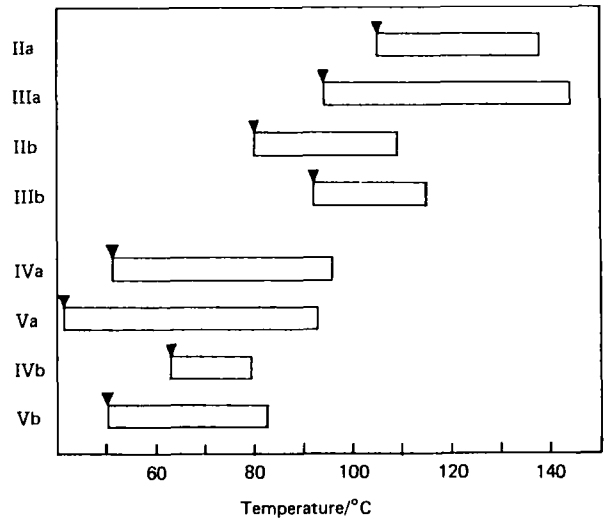


Phase sequence

C ⟶ I

S_C

C ⟷ I



The chiral smectic C ranges and melting points for series **II**–**V** (n = 10). ▼, melting point.

Table 6. ΔH values for compounds **6** and **7**.

Compound **6** (m,n)	m.p./°C	ΔH/kJ/mol	Compound **7** (m,n)	m.p./°C	ΔH/kJ/mol
(10, 10)	80	48	(10, 10)	51	55
(10, 12)	82	50	(10, 12)	56	56
(12, 10)	82	53	(12, 10)	55	57
(12, 12)	85	53	(12, 12)	61	67

By changing the $-C\equiv C-$ linkage for $-CH_2CH_2-$, the melting points become lower similar to the result when the series **II** and **III** are converted into the series **IV** and **V**, respectively. The difference of the average melting point between **6** and **7** is about 31°C, while the values of ΔH become higher and the average ΔH is 51 kJ/mol for **6** and 59 kJ/mol for **7**. Thus, change of the linking group from $-C\equiv C-$ to $-CH_2CH_2-$ results in an increase of the entropy in the liquid state. These model studies imply that compounds **IV** and **V** are more flexible and have stronger intermolecular forces than compounds **II** and **III**. The flexibility of **IV** and **V** may lower melting points and decrease thermal stabilities of mesophases, whereas it arises from, in comparison with **IIa** and **IIIa**, the increase of the intermolecular forces that **IVa** and **Va** do not form the N* phase, but only the smectic phase.

5. Conclusion

Although compound **I** of the two-ring system exhibits only monotropic S_C^* phases, most of **II**, **III**, **IV** and **V** composed of pyridine and two aromatic rings show thermodynamically stable S_C^* phases. The S_A–S_C^* transition temperatures are almost independent of the chain length of the terminal alkoxy group.

The transformation of the $-C\equiv C-$ linkage to the $-CH_2CH_2-$ results in the lowering of the S_A–S_C^* transition temperature, but the S_C^* range is approximately retained since the melting points are also lowered. This trend is good for practical applications.

6. Experimental

IR spectra were obtained with a HITACHI-270-30 infrared spectrophotometer and ^{1}H-NMR spectra were recorded with a JEOL JNM-PX60. Transition temperatures were measured, and mesomorphic properties were observed, using a Nikon OPTIPHOT-POL polarizing microscope connected with Mettler FP 82 heating stage and a Shimazu DT-308 differential scanning calorimeter. The rate of heating or cooling was fixed to 5°C/min.

6-Chloronicotinates (**1**, **2** *and* **3**)

To a suspension of 6-chloronicotinic acid (21·5 g, 136 mmol) in 1,2-dichloroethane (210 ml) containing DMF (200 mg), 1·1 equiv. of thionyl chloride was added, and the suspension was heated under reflux until the mixture became a homogeneous solution. The solution was then evaporated to dryness under reduced pressure, and the resultant liquid of acid chloride was dissolved again in dry toluene (50 ml). A solution of chiral alcohol (150 mmol) or chiral phenol (136 mmol) in dry pyridene (40 ml) was cooled in an ice-bath, to which the toluene solution of acyl chloride was added. The mixture was stirred for 18 hours, being allowed to reach room temperature

as the ice melted. It was then heated at 60°C for 1 hour. After cooling, the precipitate formed was filtered off, and the filtrate was evaporated under reduced pressure. The residue was chromatographed on a column (SiO_2, CH_2Cl_2) to yield 6-chloronicotinates, which were purified by recrystallization from hexane or by vacuum distillation.

(S)-2-Methylbutyl 6-chloronicotinate **1a**

^{1}H NMR ($CDCl_3$) δ = 0·7–2·1 (m, 9 H), 4·2 (d, J = 6 Hz, 2 H), 7·4 (d, J = 8 Hz, 1 H), 8·2 (dd, J = 2 and 8 Hz, 1 H), 8·9 (d, J = 2 Hz, 1 H). IR (KBr film): 2964 (CH); 1720, 1290 (COO); 1588, 1460, 768 (Ar) cm^{-1}. $[\alpha]_D^{25}$ = +4·9 (c 5, $CHCl_3$); b.p. = 92–94°C/0·13 torr.

(R)-1-Methylheptyl 6-chloronicotinate **1b**

^{1} NMR ($CDCl_3$) δ = 0·7–2·2 (m, 15·7 H), 5·1 (m, 1 H), 7·4 (d, J = 8 Hz, 1 H), 8·2 (dd, J = 2 and 8 Hz, 1 H), 8·9 (d, J = 2 Hz, 1 H). IR (KBr film): 2932, 2860 (CH); 1722, 1290 (COO); 1588, 1456, 768 (Ar) cm^{-1}. $[\alpha]_D^{25}$ = −34·8 (c 5, $CHCl_3$); b.p. = 105–107°C/0·13 torr.

1c: $[\alpha]_D^{25}$ = +5·7 (c 5, $CHCl_3$); b.p. = 99–101°C/0·18 torr.

1d: $[\alpha]_D^{25}$ = +4·6 (c 5, $CHCl_3$); b.p. = 109–111°C/0·15 torr.

(S)-4-(2-Methylbutoxycarbonyl)phenyl 6-chloronicotinate **2a**

^{1}H NMR ($CDCl_3$) δ = 0·8–2·2 (m, 9 H), 4·2 (d, J = 6 Hz, 2 H), 7·2–7·5 (m, 3 H), 8·1 (d, J = 8 Hz, 2 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·1 (d, J = 2 Hz, 1 H). IR (KBr disc): 2960 (CH); 1746, 1712, 1278 (COO); 1586, 1504, 1458, 886, 756. 744 (Ar) cm^{-1}. $[\alpha]^{25}$ = +3·2 (c 5, $CHCl_3$); m.p. = 72·4–73·3°C.

(R)-4-(1-Methylheptyloxycarbonyl)phenyl 6-chloronicotinate **2b**

^{1}H NMR ($CDCl_3$) δ = 0·6–2·1 (m, 16 H), 5·1 (m, 1 H), 7·1–7·5 (m, 3 H), 8·0 (d, J = 8 Hz, 2 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·0 (d, J = 2 Hz, 1 H). IR (KBr disc): 2928, 2856 (CH); 1732, 1712, 1276 (COO); 1586, 1504, 1462, 876, 850, 760 (Ar) cm^{-1}. $[\alpha]_D^{25}$ = −24·8 (c 5, $CHCl_3$); m.p. = 44·5–45·3°C.

4-Alkoxyphenyl 6-chloronicotinate **3**

^{1}H NMR ($CDCl_3$) δ = 0·7–2·1 (m, 2n–1 H), 4·0 (t, J = 6 Hz, 2 H), 6·9 (d, J = 9 Hz, 2 H), 7·1 (d, J = 9 Hz, 2 H), 7·4 (d, J = 8 Hz, 1 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·1 (d, J = 2 Hz, 1 H). IR (KBr disc): 2920, 2852 (CH); 1738, 1210 (COO); 1590, 1510, 1462, 872, 816, 758, (Ar) cm^{-1}; m.p. = 85·5–85·6 (n = 6), 91·6–92·3 (n = 7), 93·5–93·8 (n = 8), 100 (n = 9), 95·4 (n = 10), 101 (n = 11), 98·1–98·4 (n = 12)°C.

Preparation of target compounds **I–III**: *a general procedure for the coupling of acetylenes* **4** *and* **5** *with 6-chloronicotinates* **1–3**

6-Chloronicotinate (5 mmol) and 4-substituted phenylacetylene (5 mmol) were dissolved in triethylamine (30 ml) under an atmosphere of nitrogen. Copper(I) iodide (6 mg), triphenylphosphine (100 mg) and dichloribis(triphenylphosphine)palladium (50 mg) were added to the stirred solution. The solution was heated at 80°C for

16 hours. After cooling, the precipitate formed were filtered off, and the triethylamine was removed by rotary evaporation. Ether was added to the residue, and the solution was washed with water and brine, and then dried. After filtration the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, $CHCl_3$) and recrystallization from hexane. Pale yellow crystalline powders were obtained in 48–64 per cent yields.

Physical data of compound **Ia** (n = 10). ^{1}H NMR ($CDCl_3$) δ = 0·7–2·1 (m, 28 H), 4·0 (t, J = 6 Hz, 2 H), 4·2 (d, J = 6 Hz, 2 H), 6·9 (d, J = 9 Hz, 2 H), 7·5–7·6 (m, 3 H), 8·2 (dd, J = 2 and 8 Hz, 1 H), 9·2 (bs, 1 H). IR (KBr disc): 2928, 2852 (CH); 2220 (C–C); 1710, 1290 (COO); 1588, 1510, 1470, 834, 778 (Ar) cm^{-1}. Anal. Calcd for $C_{29}H_{39}NO_3$: C, 77·47; H, 8·74; N, 3·12 per cent. Found: C, 77·68; H, 8·48; N, 3·12 per cent. $[\alpha]_D^{25}$ = +3·4 (c 5, $CHCl_3$).

Physical data of compound **Ib** (n = 10). ^{1}H NMR ($CDCl_3$) δ = 0·7–2·2 (m, 35 H), 4·0 (t, J = 6 Hz, 2 H), 5·2 (m, 1 H), 6·9 (d, J = 9 Hz, 2 H), 7·5–7·6 (m, 3 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·2 (bs, 1 H). IR (KBr disc): 2924, 2856 (CH); 2220 (C≡C); 1714, 1284 (COO); 1588, 1514, 1468, 840, 780 (Ar) cm^{-1}. Anal. Calcd for $C_{32}H_{45}NO_3$: C, 78·17; H, 9·22; N, 2·85 per cent. Found: C, 78·12; H, 8·99; N, 2·97 per cent. $[\alpha]_D^{25}$ = −34·8 (c 5, $CHCl_3$).

Physical data of compound **Id** (n = 10). ^{1}H NMR ($CDCl_3$) δ = 0·5–2·2 (m, 36 H), 4·0 (t, J = 6 Hz, 2 H), 6·9 (d, J = 9 Hz, 2 H), 4·4 (t, J = 6 Hz, 2 H), 6·9 (d, J = 9 Hz, 2 H), 7·5–7·6 (m, 3 H), 8·2 (dd, J = 2 Hz, 1 H), 9·2 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{34}H_{47}NO_3$: C, 78·37; H, 9·37; N, 2·77 per cent. Found: C, 78·28; H, 9·27; N, 2·82 per cent. $[\alpha]_D^{25}$ = +2·9 (c 5, $CHCl_3$).

Physical data of compound **IIa** (n = 10). ^{1} NMR ($CDCl_3$) δ = 0·6–2·1 (m, 28), 4·0 (t, J = 6 Hz, 2 H), 4·2 (d, J = 6 Hz, 2 H), 6·9 (d, J = 9 Hz, 2 H), 7·3–7·7 (m, 5 H), 8·1 (d, J = 9 Hz, 2 H), 8·4 (dd, J = 2 and 8 Hz, 1 H), 9·3 (bs, 1 H). IR (KBr disc): 2924, 2852, (CH); 2216 (C≡C); 1736, 1720, 1274 (COO); 1588, 1512, 1470, 834, 776 (Ar) cm^{-1}. Anal. Calcd for $C_{36}H_{43}NO_5$: C, 75·89; H, 7·61; N, 2·46 per cent. Found: C, 76·11; H, 7·40; N, 2·52 per cent. $[\alpha]_D^{25}$ = +2·4 (c 5, $CHCl_3$).

Physical data of compound **IIb** (n = 10). ^{1}H NMR ($CDCl_3$) δ = 0·6–2·1 (m, 35 H), 4·0 (t, J = 6 Hz, 2 H), 5·2 (m, 1 H), 6·9 (d, J = 9 Hz, 2 H), 7·3–7·7 (m, 5 H), 8·1 (d, J = 9 Hz, 2 H), 8·4 (dd, J = 2 and 8 Hz, 1 H), 9·3 (bs, 1 H). IR (KBr disc): 2924, 2852 (CH); 2216 (C≡C); 1736, 1714, 1276 (COO); 1588, 1512, 1468, 834, 774, 762, (Ar) cm^{-1}. Anal. Calcd for $C_{39}N_{49}NO_5$: C, 76·56; H, 8·07; N, 2·29. Found: C, 76·77; H, 8·06; N, 2·48. $[\alpha]_D^{25}$ = −19·3 (c 5, $CHCl_3$).

Physical data of compound **IIIa** (n = 10). ^{1}NMR ($CDCl_3$) δ = 0·7–2·2 (m, 28 H), 3·9 (t, J = 6 Hz, 2 H), 4·2 (d, J = 6 Hz, 2 H), 6·8 (d, J = 9 Hz, 2 H), 7·1 (d, J = 9 Hz, 2 H), 7·5–7·6 (m, 3 H), 7·9 (d, J = 8 Hz, 2 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·2 (bs, 1 H). IR (KBr disc): 2920, 2852 (CH); 2216 (C≡C); 1730, 1710 (COO); 1588, 1508, 1470, 856, 822, 774 (Ar) cm^{-1}. Anal. Calcd for $C_{36}H_{43}NO_5$: C, 75, 89; H,

7·61; N, 2·46 per cent. Found: C, 76·04; H, 7·32; N, 2·66 per cent. $[\alpha]_D^{25} = +2·3$ (c 5, $CHCl_3$).

Physical data of compound **IIIb** (*n = 10*). ^{1}H NMR ($CDCl_3$) δ = 0·7–2·2 (m, 35 H), 3·9 (t, J = 6 Hz, 2 H), 5·1 (m, 1 H), 6·8 (d, J = 9 Hz, 2 H), 7·1 (d, J = 9 Hz, 2 H), 7·5–7·6 (m, 3 H), 7·9 (d, J = 8 Hz, 2 H), 8·3 (dd, J = 2 and 8 Hz, 1 H), 9·2 (d, J = 2 Hz, 1 H). IR (KBr disc): 2920, 2852 (CH); 2216 (C≡C); 1732, 1714, 1704, 1308 (COO); 1590, 1508, 1470, 856, 768 (Ar) cm^{-1}. Anal. Calcd for $C_{39}H_{49}NO_5$: C, 76·56; H, 8·07; N, 2·29 per cent. Found: C, 76·62; H, 7·86, N, 2·53 per cent. $[\alpha]_D^{25} = -28·0$ (c 5, $CHCl_3$).

Preparation of target compounds **IV** *and* **V**: *a general procedure for the hydrogenation of compounds* **II** *and* **III**

To a suspension of 5 per cent palladium–carbon (200 mg) in ethyl acetate (20 ml), a benzene solution of compound **II** or **III** (2·0 mmol) was added, and then the mixture was stirred under atmospheric pressure of hydrogen. The reaction temperature was kept at 25 ± 5°C. The reaction was traced by TLC (SiO_2, CH_2Cl_2), and the complete reaction required about 2 hours. The catalyst was filtered off, and the filtrate was evaporated under reduced pressure, and the resultant residue was purified by column chromatography (SiO_2, $CHCl_3$) and recrystallization from hexane. White crystalline powders were obtained in 87–94 per cent yields.

Physical data of compound **VIa** (*n = 10*). ^{1}H NMR ($CDCl_3$) δ = 0·7–2·2 (m, 28 H), 3·1 (bs, 4 H), 3·9 (t, J = 6 Hz, 2 H), 4·2 (d, J = 6 Hz, 2 H), 6·7–7·4 (m, 7 H), 8·1–8·4 (m, 3 H), 9·3 (d, J = 2 Hz, 1 H). IR (KBr disc): 2290, 2852 (CH); 1740, 1724, 1274 (COO); 1598, 1516, 1468, 880, 814, 758 (Ar) cm^{-1}. Anal. Calcd for $C_{36}H_{47}NO_5$: C, 75·36; H, 8·26; N, 2·44 per cent. Found: C, 75·46; H, 8·60; N, 2·44 per cent. $[\alpha]_D^{25} = +2·0$ (c 5, $CHCl_3$).

Physical data of compound **IVb** (*n = 10*). ^{1}NMR ($CDCl_3$) δ = 0·7–2·2 (m, 35 H), 3·1 (bs, 4 H), 3·9 (t, J = 6 Hz, 2 H), 5·2 (m, 1 H), 6·7–7·4 (m, 7 H), 8·1–8·4 (m, 3 H), 9·3 (d, J = 2 Hz, 1 H). IR (KBr disc): 2290, 2852, (CH); 1738, 1722, 1282 (COO); 1598, 1516, 1468, 880, 814, 758, (Ar) cm^{-1}. Anal. Calcd for $C_{39}H_{53}NO_5$: C, 76·06; H, 8·67; N, 2·27 per cent. Found: C, 76·36; H, 8·89; N, 2·48 per cent. $[\alpha]_D^{25} = -17·1$ (c 5, $CHCl_3$).

Physical data of compound **Va** (*n = 10*). ^{1}H NMR ($CDCl_3$) δ = 0·7–2·1 (m, 28 H), 3·2 (bs, 4 H), 3·9 (t, J = 6 Hz, 2 H), 4·2 (d, J = 6 Hz, 2 H), 6·7–7·2 (m, 8 H), 7·8 (d, J = 8 Hz, 2 H), 8·2 (dd, J = 2 and 8 Hz, 1 H), 9·2 (d, J = 2 Hz, 1 H). IR (KBr disc): 2920, 2852, (CH); 1740, 1712, 1276 (COO); 1600, 1510, 1468, 870, 856, 776 (Ar) cm^{-1}. Anal. Calcd for $C_{36}H_{47}NO_5$: C, 75·36; H, 8·26; N, 2·44 per cent. Found: C, 75·51; H, 8·16; N, 2·56 per cent. $[\alpha]_D^{25} = +2·0$ (c 5, $CHCl_3$).

Physical data of compound **Vb** (*n = 10*). ^{1}NMR ($CDCl_3$) δ = 0·7–2·1 (m, 35 H), 3·2 (bs, 4 H), 3·9 (t, J = 6 Hz, 2 H), 5·1 (m, 1 H), 6·7–7·2 (m, 8 H), 7·8 (d, J = 8 Hz, 2 H), 8·2 (dd, J = 2 Hz, 8 Mz, 1 H), 9·2 (d, J = 2 Hz, 1 H). IR (KBr

disc): 2924, 2852 (CH); 1730, 1712, 1278 (COO); 1596, 1506, 1478, 852, 822, 770 (Ar) cm^{-1}. Anal. Calcd for $C_{39}H_{53}NO_5$: C, 76·06, H, 8·67, N, 2·27. Found: C, 76·28; H, 8·48; N, 2·43. $[\alpha]_D^{25} = -15{\cdot}4$ (c 5, $CHCl_3$).

References

[1] MOHR, K., KOHLER, S., WORM, K., PELZL, G., DIELE, S., ZASCHKE, H., and DEMUS, D., 1987, *Molec. Crystals liq. Crystals*, **146**, 151. TAGUCHI, M., HARADA, T., and SUENAGA, H., *Jap. Kokai Tokkyo Koho*, JP 60/260564.

[2] ZASCHKE, H., ISENBERG, A., and VORBRODT, H.-M., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum Press), p. 75.

[3] TAKAHASHI, S., KUROYAMA, K., SONOGASHIRA, K., and HAGIHARA, N., 1990, *Synthesis*, p. 627.

[4] GRAY, G. W., and GOODBY, J. W., 1976, *Molec. Crystals liq. Crystals*, **37**, 157.

[5] SETO, K., SHIMOJITOSYO, H., IMAZAKI, H., MATSUBARA, H., and TAKAHASHI, H., 1990, *Bull. chem. Soc. Japan*, **63**, 1020.