Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Yongmao, Sun , Liangyu, Wang , Hongping, Yu , Huimin, Zhao and Shouyi, Xu(1993) 'The properties of phenyl cyclohexyl ferroelectric liquid crystals', Liquid Crystals, 13: 5, 701 — 710
To link to this Article: DOI: 10.1080/02678299308026342
URL: http://dx.doi.org/10.1080/02678299308026342

LIQUID CRYSTALS, 1993, VOL. 13, NO. 5, 701–710

The properties of phenyl cyclohexyl ferroelectric liquid crystals

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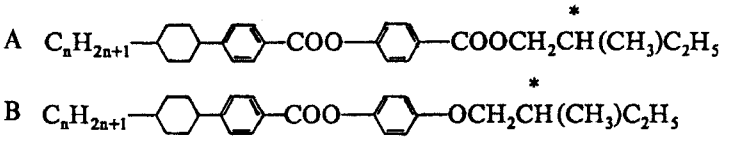
(*Received 29 April 1992, accepted 25 November 1992*)

To continue the search for novel series of ferroelectric liquid crystals, an additional two series of compounds, C *S*(+)-4-[(2-methylbutyl)phenyl]4′-(4″-*trans*-*n*-alkylcyclohexyl) benzoates and D *S*(+)-4-[(4-methylhexanoyl)phenyl]4′-(4″-*trans*-*n*-alkylcyclohexyl) benzoates, where alkyl = C_5–C_6 are reported in this paper. Their mesomorphic properties have been characterized by optical textural observations and DSC. Some of these compounds show a C–S_C^*–S_A–N*–I phase transition sequence. The effects of the alkyl chains on transition temperatures and optically active terminal groups on phase behaviour are discussed.

1. Introduction

In our earlier paper [1], the following homologous series have been studied:



where $n = 5$–10. All these compounds were demonstrated to be ferroelectric.

Since the discovery of bistable switching in surface stabilized ferroelectric liquid crystals by Clark and Lagerwall [2], chemists have been working hard to develop ferroelectric mixtures. In the beginning, the important characteristics of mixtures usable for display application were unknown. Today all the suppliers of FLC mixtures follow some general rules for the preparation of adapted materials: up to date FLC mixtures have been developed using the following major specifications [3]:

(i) The use of chemically, photochemically, thermally and electrically stable compounds;
(ii) The use of materials with low vapour pressure and no absorption in the visible region;
(iii) A wide S_C^* temperature range;
(iv) A S_C^*–S_A–N*–I sequence to give good sequence alignment;

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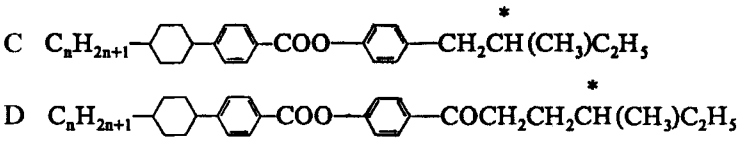
0267–8292/93 $10·00

(v) A short response time in order to operate at video frame rate;
(vi) A low rational viscosity;
(vii) A spontaneous polarization value which is not too large.

All the requirements mentioned above can only be fulfilled with multi-component mixtures. It is well-known that the introduction of a *trans*-1, 4-disubstituted cyclohexane ring into liquid crystal molecules has remarkable effects on their LC transition temperatures and other physical properties [4–6]. These findings prompted us to investigate the new homologous series C and D:



2. Results and discussion

The mesomorphic properties were determined using a differential scanning calorimeter Du Pont 990. Optical studies were carried out on an Olympus polarizing microscope in conjunction with an Olympus photomicrographic system PM-10AD and a Newport hot stage model 871.

2.1. *Thermal properties*

The mesomorphic properties of the titled compounds are summarized in tables 1 and 2. Figure 1 shows a plot of the melting points (C–S_C^*), S_C^*–S_A, S_A–N* and N*–I transition temperature values as a function of the alkyl chain length (n) of series C. Four curves are obtained, the trend of the melting points (C–S_C^*) and the S_A temperature range show little variation with increasing alkyl chain length. The values of S_C^*–S_A and S_A–N* transition temperatures, as well as the S_C^* temperature range, increase generally as the alkyl chain length lengthens, whereas the N*–I transition temperature curve shows a general tendency to descend from $n=5$ to $n=10$.

Table 1. Transition temperatures (°C) for series C.

Compound	R	C–S_C^*	S_C^*–S_A	S_A–N*	N*–I
5C	C_5H_{11}	81	85	109·5	147·5
6C	C_6H_{13}	79	93	115	141
7C	C_7H_{15}	82	101	122	142
8C	C_8H_{17}	81	103	121·5	135·5
9C	C_9H_{19}	79	105	120	130
10C	$C_{10}H_{21}$	76	104·5	120·5	129·5

Table 2. Transition temperatures (°C) for series D.

Compound	R	C–S_A	S_A–N* or I	N*–I
5D	C_5H_{11}	118	158	165·5
6D	C_6H_{13}	116	160	163
7D	C_7H_{15}	116·5	163·5	165
8D	C_8H_{17}	110·5	148	—
9D	C_9H_{19}	104	155	—
10D	$C_{10}H_{21}$	105	156	—

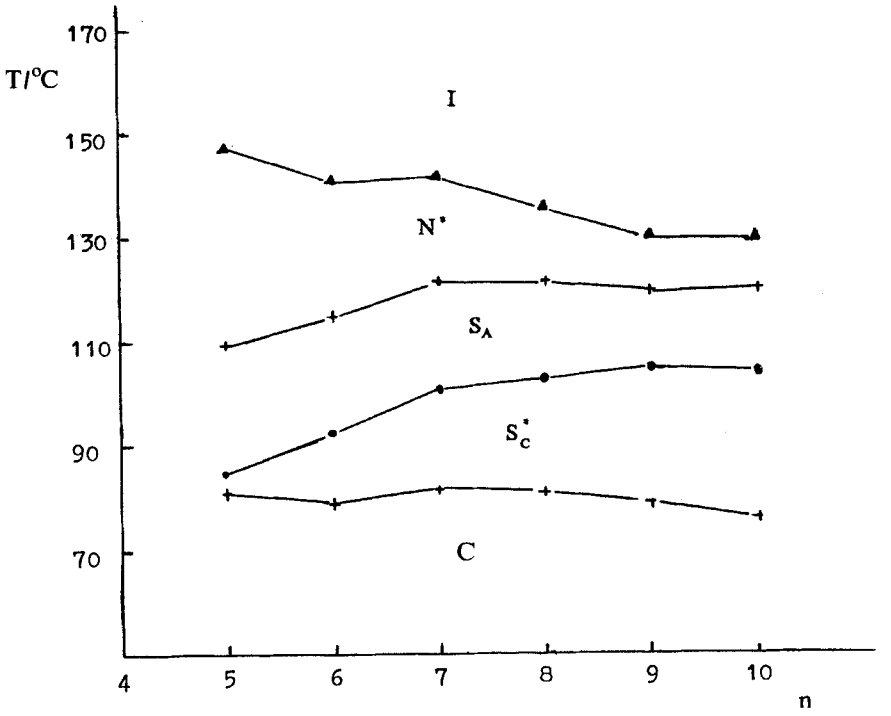


Figure 1. Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain for series C.

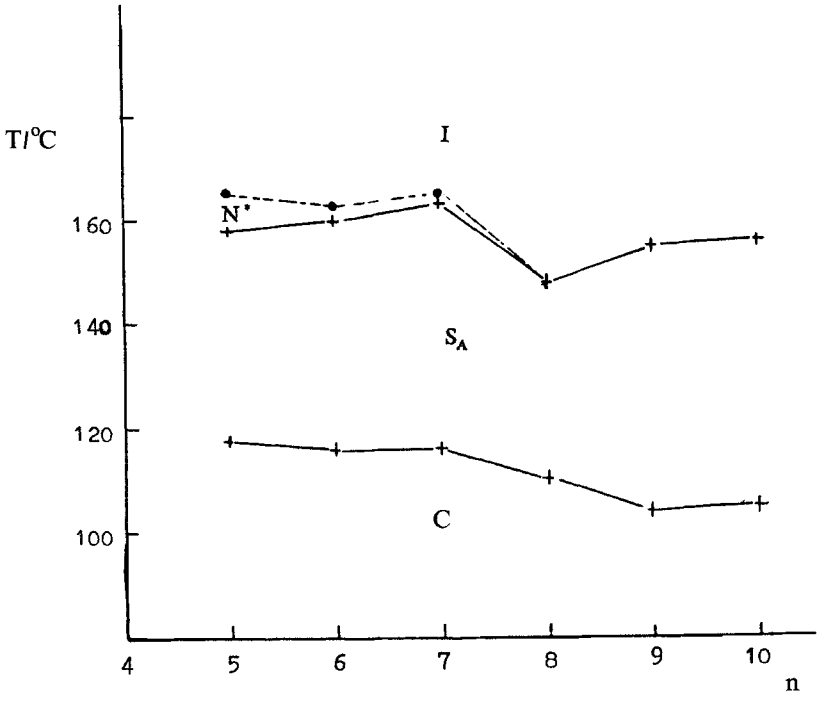


Figure 2. Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain for series D.

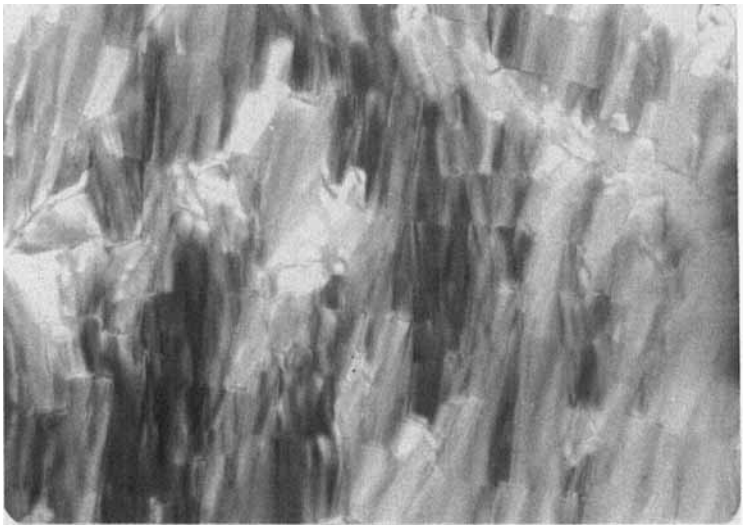


Figure 3. S_C^*, broken fan-shaped texture. Crossed polarizers, 80·1°C, ×400, on cooling 5C.

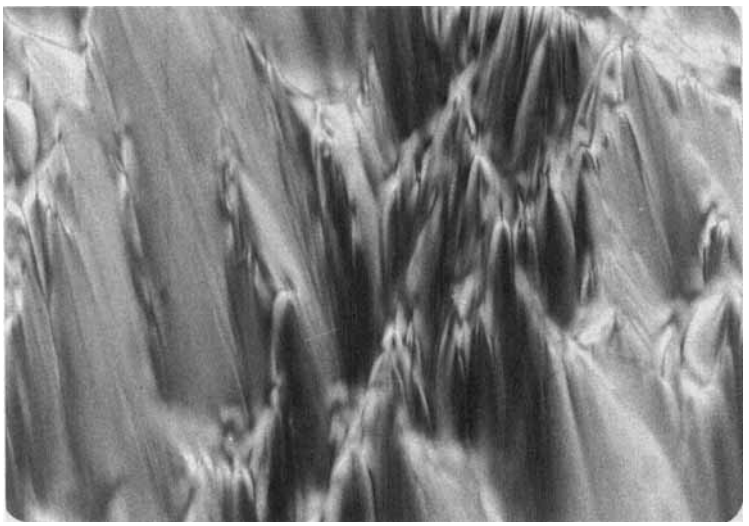


Figure 4. S_A, fan-shaped texture. Crossed polarizers. 106·5°C, ×400, on heating 5C.

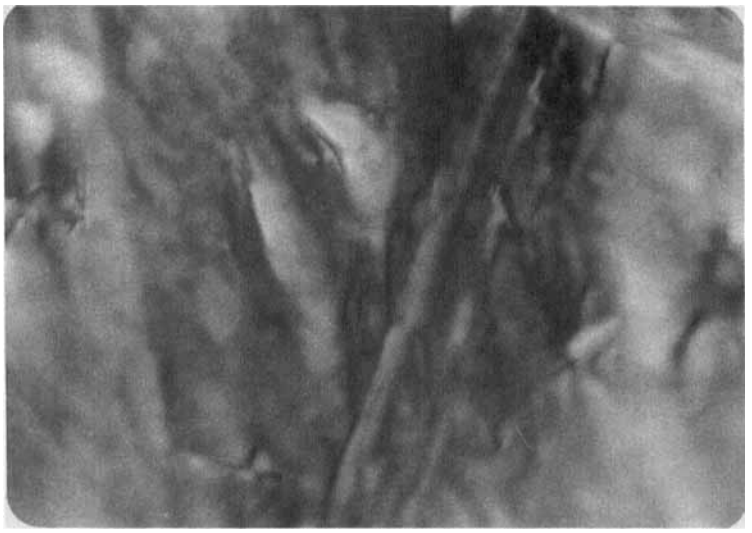


Figure 5. N*, schlieren texture. Crossed polarizers, 122·7°C, ×400, on heating 5C.

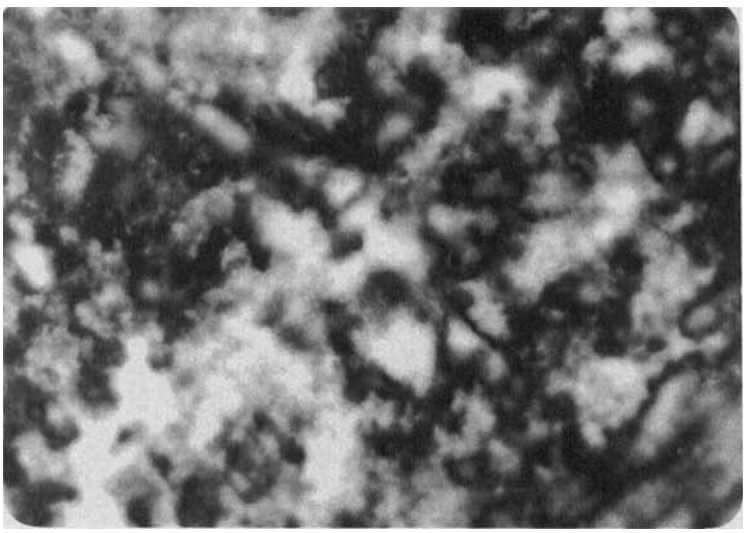


Figure 6. N*, schlieren texture. Crossed polarizers, 147·2°C, ×400, on heating 5C.

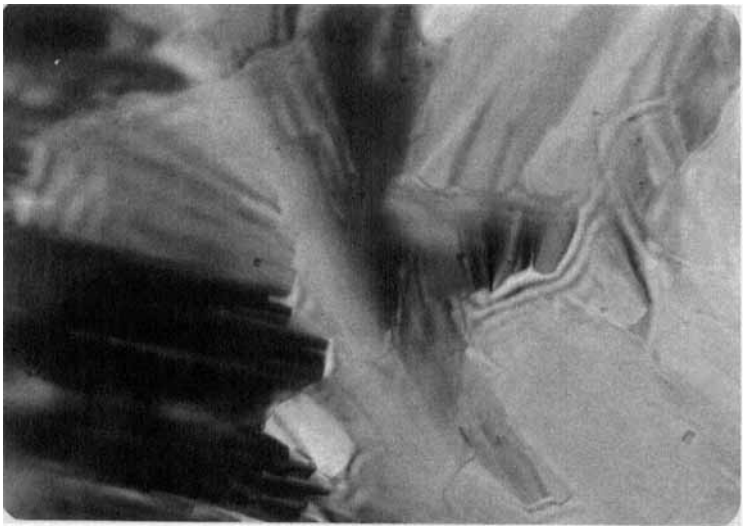


Figure 7. S_C^*, broken fan-shaped texture with scaly pattern. Crossed polarizers, 94·6°C, × 400, on heating 7C.

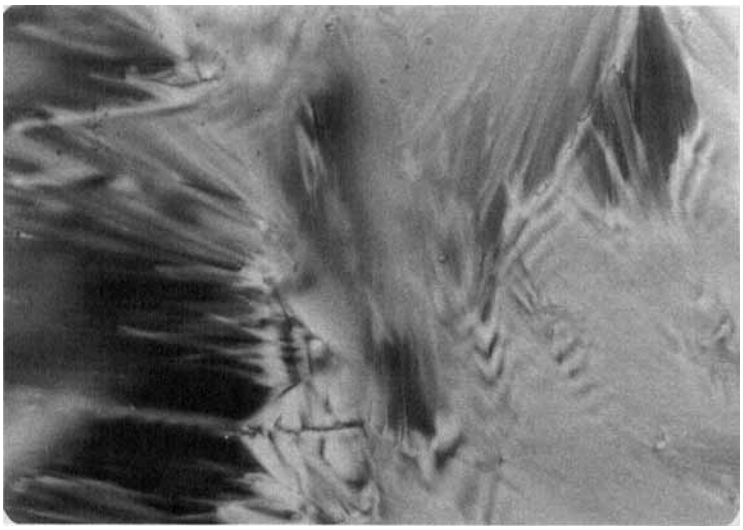


Figure 8. S_A, simple fan-shaped texture. Crossed polarizers, 112·9°C, × 400, on heating 7C.

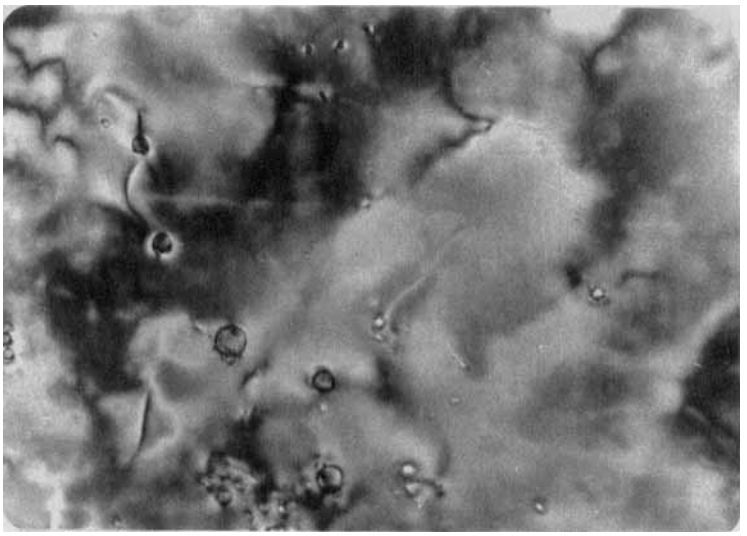


Figure 9. N*, schlieren texture. Crossed polarizers, 129·7°C, ×400, on heating 7C.

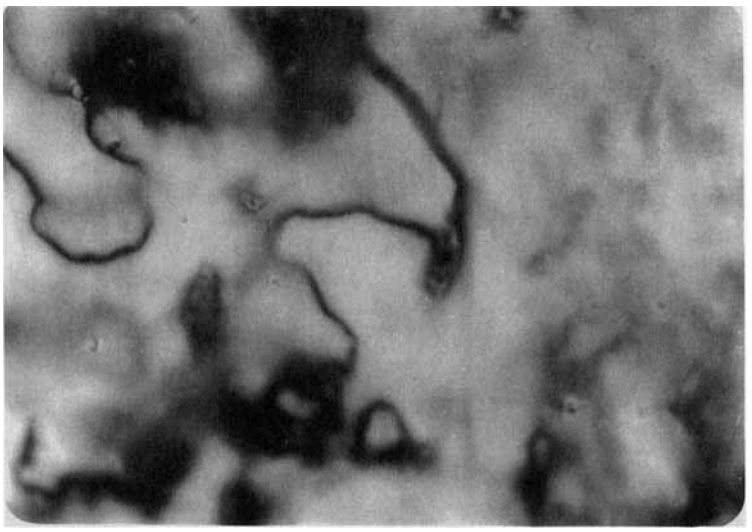


Figure 10. N*, schlieren texture. Crossed polarizers, 122·9°C, ×400, on cooling 7C.

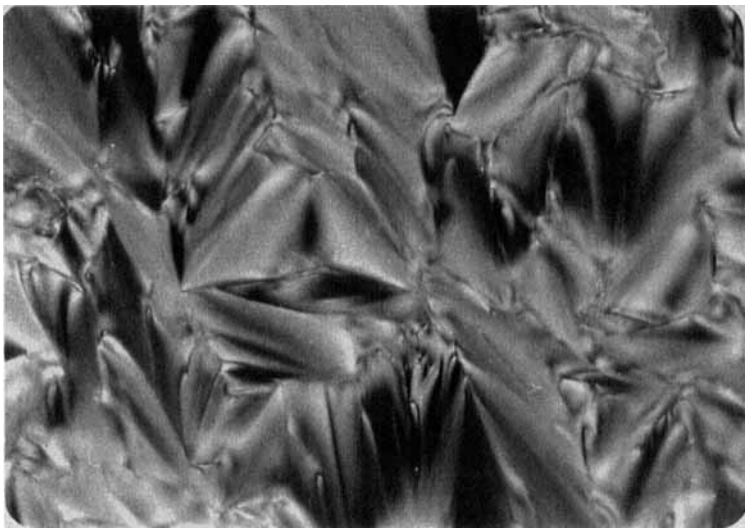


Figure 11. S_A, fan-shaped texture. Crossed polarizers 147·1°C, ×400, on cooling 5D.

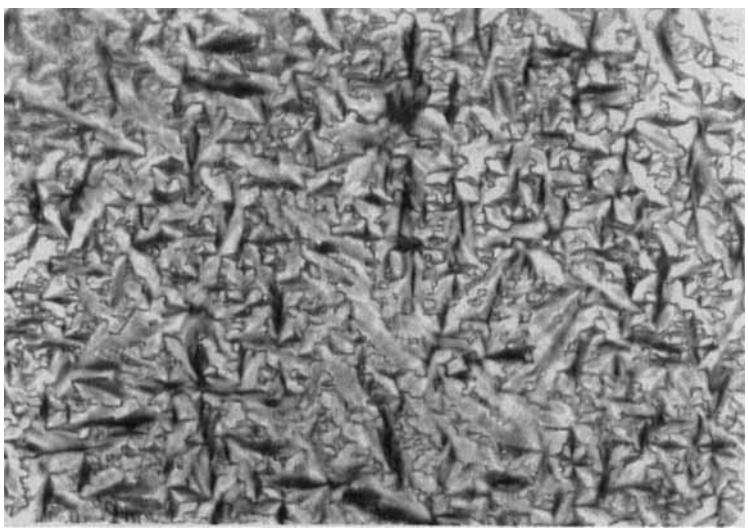


Figure 12. N*, cholesteric fan-like texture. Crossed polarizers, 165·2°C, ×400, on heating 5D.

For series D, the results in table 2 are plotted against the number of carbon atoms in the alkyl chain in figure 2. There were no regular trends for the C–S_A and S_A–N* or I transition temperatures, when the alkyl chain length increases. It is noted that the N* mesophase disappears with $n=8$. This effect is due to the intermolecular interaction: with the increase of the alkyl chain length, the closer molecular packing arrangement may be responsible for depressing the formation of the N* phase. A similar phenomenon was observed for series B [1].

2.2. *Optical microscope observations*

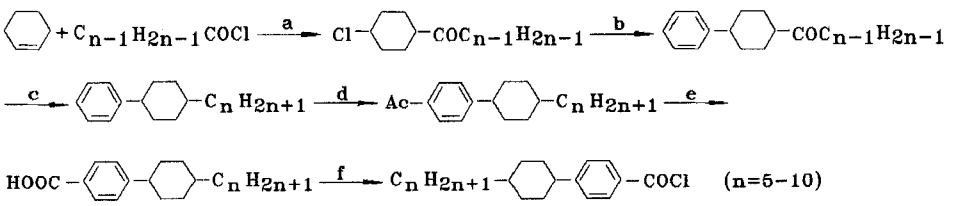
Phase identification was achieved by comparing the observed textures with those found in the literature [7, 8]. Figures 3–6 show the textures of *S*(+)-4-[(2-methylbutyl) phenyl]4′-(*trans*-4′-*n*-pentylcyclohexyl) benzoate, 5C. Figures 7–10 give the textures of *S*−(+)-4-[(2-methylbutyl) phenyl]4′-(*trans*-4″-*n*-heptylcyclohexyl) benzoate, 7C. Figures 11 and 12 are the textures of *S*(+)-4-[(4-methylhexanoyl)phenyl]4′-*trans*-4″-*n*-pentylcyclohexyl) benzoate, 5D.

3. Conclusions

Comparison of the data in tables 1 and 2 reveals that the presence of the carbonyl group in the optically active alkyl chain changes the liquid crystal transition temperatures and phase states to a large extent: the melting points of series D have been increased by 40°C (on average) and their clearing points have been increased by 20°C (on average). A chiral smectic C and a chiral nematic, as well as a smectic A, are observed for series C. Series D exhibits only S_A and N* mesophases.

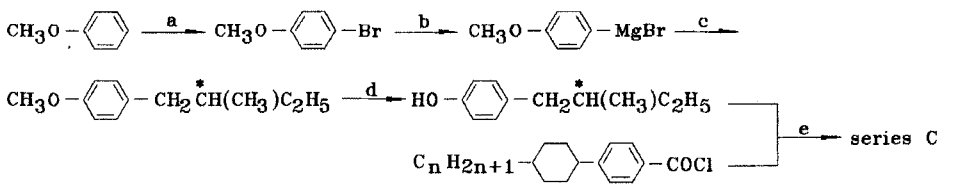
4. Experimental

Two new series C and D were prepared by fairly standard procedures. Full synthetic details are illustrated in schemes 1, 2 and 3 and other physical data are available in [9].



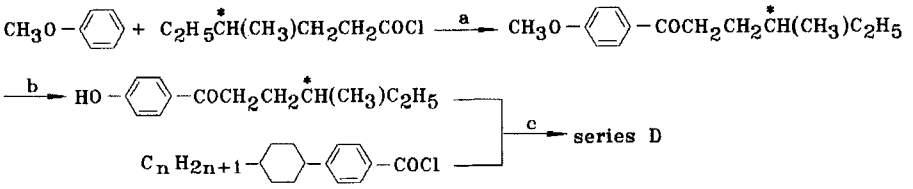
(*a*) $AlCl_3$, CH_2Cl_2; (*b*) benzene, $AlCl_3$; (*c*) $NH_2NH_2 \cdot H_2O$, KOH, diethylene glycol; (*d*) acetyl chloride, $AlCl_3$, CH_2Cl_2; (*e*) Br_2, NaOH, dioxan; (*f*) $SOCl_2$, benzene.

Scheme 1. Synthetic route for the intermediate 4-(*trans*-4′-*n*-alkylcyclohexyl) benzoyl chlorides.



(*a*) Br_2, acetic acid; (*b*) THF, Mg; (*c*) THF, $BrCH_2\overset{*}{C}H(CH_3)C_2H_5$; (*d*) HI, acetic acid; (*e*) Pyridine, benzene.

Scheme 2. Synthetic route for series C.



(*a*) $AlCl_3$; (*b*) HI, acetic acid; (*c*) Pyridine, benzene.

Scheme 3. Synthetic route for series D.

The authors are grateful to Professors Liao Songsheng, and Yao Naiyan for many helpful suggestions. We thank also Mrs Don Shuzhen for the DSC measurements. This work was supported by the National Natural Science Foundation of China under Grant No. 29070056.

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