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

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Version of record first published: 20 Apr 2011.

To cite this article: Teruo Kitamura , Akio Mukoh , Masato Isogai , Takashi Inukai , Kenji Furukawa & Kanetsugu Terashima (1986): Synthesis and Some Properties of Low Melting Ferroelectric Liquid Crystals of Benzylidene Anilines, Molecular Crystals and Liquid Crystals, 136:2-4, 167-173

To link to this article: http://dx.doi.org/10.1080/00268948608074725

Mol. Cryst. Liq. Cryst., 1986, Vol. 136, pp. 167–173
0026-8941/86/1364–0167/$15.00/0

Printed in the United States of America

Synthesis and Some Properties of Low Melting Ferroelectric Liquid Crystals of Benzylidene Anilines

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(*Received October 12, 1985; in final form January 10, 1986*)

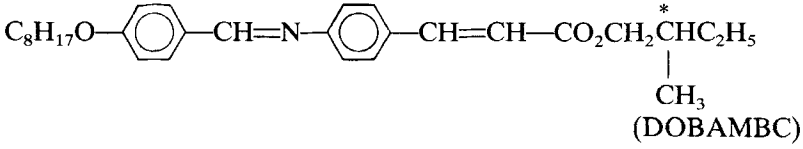
A series of chiral benzylidene-aniline compounds, 4-alkoxybenzylidene 4′-(2-methylbutyloxycarbonyl)anilines, have been synthesized and their mesomorphic properties are examined. They showed a monotropic chiral smectic C phase in conjunction with enantiotropic smectic A phase, and their chiral smectic C–smectic A phase transition temperatures are around room temperatures. Their spontaneous polarization values are moderately higher than those of DOBAMBC "4-decyloxybenzylidene 4′-amino-(2-methylbutyl)cinnamate".

Keywords: ferroelectric liquid crystal, chiral smectic C phase, benzylidene-aniline, mesomorphic range, low melting

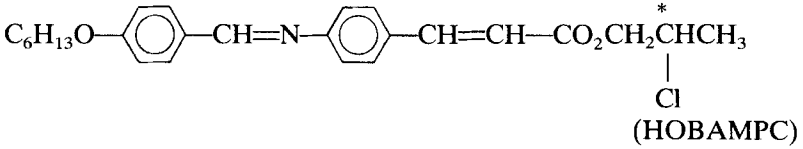
INTRODUCTION

Since the demonstration[1] of the electrooptic effect on ferroelectric liquid crystals, interest in the display devices using them has increased considerably. At the same time, much attention has been given to the synthesis of ferroelectric liquid crystal materials which exhibit chiral smectic C phase (S_C^*), and many materials have been prepared up to now.[2–5] However, the number of S_C^* materials available for these applications is limited, particularly those which exhibit S_C^* phase

at room temperature and sufficiently high spontaneous polarization values are few. Although DOBAMBC[6] and HOBAMPC,[7] showing a high value of spontaneous polarization, melt around 70°C, these S_C^* materials were used exclusively for experimental investigations on electrooptical devices.



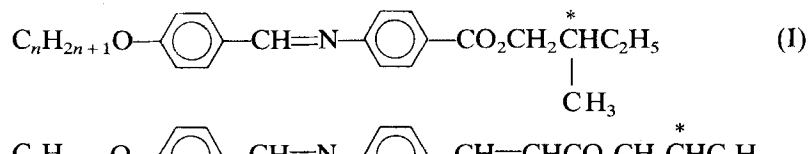
(DOBAMBC)



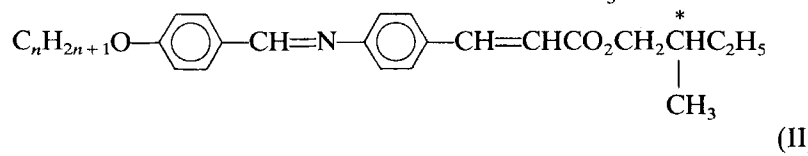
(HOBAMPC)

The aim of this work is, therefore, to prepare a new series of ferroelectric liquid crystal materials which exhibit S_C^* phase at room temperature or close to room temperatures and which have high spontaneous polarization values.

It is known that the molecular structures of terminal groups and ring systems, such as a hard-rod core, have a significant effect on the mesomorphic properties. In nematic liquid crystals, mesogens having amino-cinnamate moiety show higher melting points than those having amino-benzoate moiety.[8] Thus the ring systems affect its melting properties and the elimination of the double bond (—CH=CH—) brings about a decrease of melting points. In the area of S_C^* liquid crystal materials, it is presumed that similar phenomena are noticed. Therefore, 4-alkoxybenzylidene 4′-(2-methylbutyloxycarbonyl)-anilines (I) are prepared and examined and their mesomorphic properties are compared with 4-alkoxybenzylidene 4′-amino(2-methylbutyl)cinnamate (II).



(I)



(II)

MATERIALS

The benzylidene-aniline compounds (I) were prepared as shown in Figure 1. The optically active precursor to 4-(2-methylbutyloxycarbonyl)aniline is (S)-2-methylbutanol. Chiral alcohol was esterified with 4-nitrobenzoic acid, and the reduction of this ester compound gave an optically active 4-(2-methylbutyloxycarbonyl)aniline. Finally, the benzylidene-aniline compounds were prepared from equimolar amounts of the above aniline and commercially available 4-alkoxybenzaldehyde in refluxing benzene.

The compounds were recrystallized from ethylalcohol until constant transition temperatures were obtained. The molecular structures of all compounds were established by analysis of ir, nmr and mass spectroscopy and the purity of each compound was checked by glc.

The transition temperatures were determined by optical microscopy with a polarizer and heating stage and by a differential scanning calorie meter.

RESULTS AND DISCUSSION

The transition temperatures of 4-alkoxybenzylidene-4′-(2-methylbutyloxycarbonyl)anilines were shown in Table I. They all exhibit enantiotropic smectic A (S_A) phase. And when the *n*-number is between 7 and 14, they exhibit monotropic chiral smectic C (S_C^*) phase. Although the values for *n* were increased, they did not exhibit enantiotropic S_C^* phase and, unfortunately, at $n = 16$ the S_C^* phase disappeared. Additionally, when the *n*-number is below 6, these compounds did not exhibit S_C^* phase. This indicates that the *n*-numbers which exhibit S_C^* phase are limited in the region between 7 and 14.

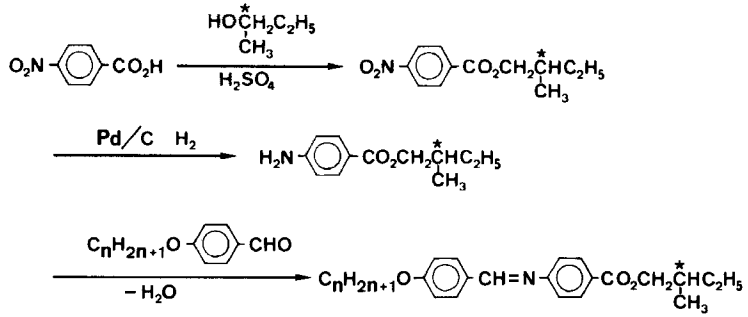
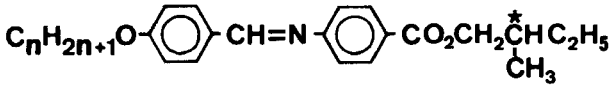


FIGURE 1 Route of synthesis for 4-alkoxybenzylidene 4′-(2-methylbutyloxycarbonyl)anilines. The stars above the carbon given indicate the asymmetric carbon atom.



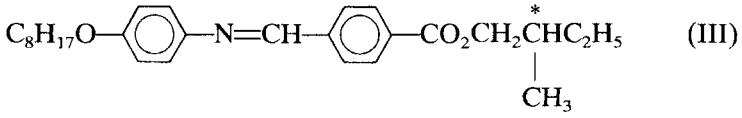
n	K	S_C^*	S_A	I
4	• 60.4	-	• 63.0	•
5	• 45.6	-	• 58.3	•
6	• 46.5	-	• 61.4	•
7	• 46.1	(• 35.2)	• 61.4	•
8	• 41.3	(• 39.3)	• 66.0	•
9	• 59.8	(• 41.6)	• 66.0	•
10	• 52.0	(• 42.2)	• 68.0	•
11	• 52.7	(• 41.2)	• 66.7	•
12	• 47.5	(• 40.6)	• 68.5	•
14	• 53.5	(• 36.8)	• 67.8	•
16	• 54.8	-	• 67.2	•
18	• 63.8	-	• 65.6	•

TABLE 1 Single compounds with their phase transition temperatures in degree centigrade, solid-smectic A phase transition, chiral smectic C–smectic A phase transition and smectic A–isotropic liquid phase transition. The abbreviations mean respectively, K solid phase; S_C^* chiral smectic C phase; S_A smectic A phase and I isotropic liquid phase. The points beneath the symbols given indicate the existence of the phase concerned, and the absence of the phase is indicated by a dash (-). Transitions which only appear in an unstable area—usually called "monotropic"—have been placed in brackets.

This limitation for the *n*-number will be affected, of course, by the ring systems of the hard-rod core.

The members of series (I) generally showed lower transition temperatures, with the S_A–S_C^* phase transition temperatures below 42°C. And their S_C^* phase can be readily supercooled to a state of 25°C and crystallization does not occur after one hour at 25°C.

A reversal of the central linkage of series (I) gave similar mesomorphic properties. For example, with material for the octyloxy homologue (III)



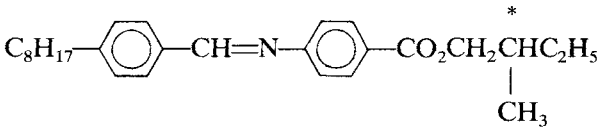
(III)

the following phase sequence is observed:

$$\text{Iso} \xrightarrow[74]{} S_A \xrightarrow[49]{} S_C^* \qquad \underset{53}{\text{m.p.}} \qquad (°C)$$

The compound (III) exhibited a enantiotropic S_A phase and monotropic S_C^* phase, and the phase transition temperatures are similar to those of series (I).

But the displacement of alkoxy groups by alkyl groups brings about the disappearance of mesophases. The following compound



exhibits no mesophases. Alkyl groups, as terminal groups of smectic mesogens, favor forming no mesophases.

The examples shown in Figure 2 illustrate the differences of phase transition temperatures between series (I) and series (II). The series (II) are homologues of DOBAMBC. From Figure 2, it is noticed that the S_A–S_C^* phase transition temperatures of series (I) are lower (by about 50°C) than those of series (II). Additionally, Iso-S_A transition temperatures of series (I) are lower (by 60°C) than those of series (II). Thus, the elimination of the carbon-carbon double bond (CH=CH) brings about the decrease of transition temperatures. It is known that in the nematic mesogens eliminations of double bonds brought about the decrease of clearing points (Iso-nematic phase transition temperatures). The effect of the elimination of double bonds in the smectic mesogens is similar to that of nematic mesogens.

The elimination of double bonds brought about a little increase in spontaneous polarization. Figure 3 shows the value of spontaneous polarization of the series (I) compared with that of DOBAMBC (series II). These values were determined by using the Sowyer-Tower

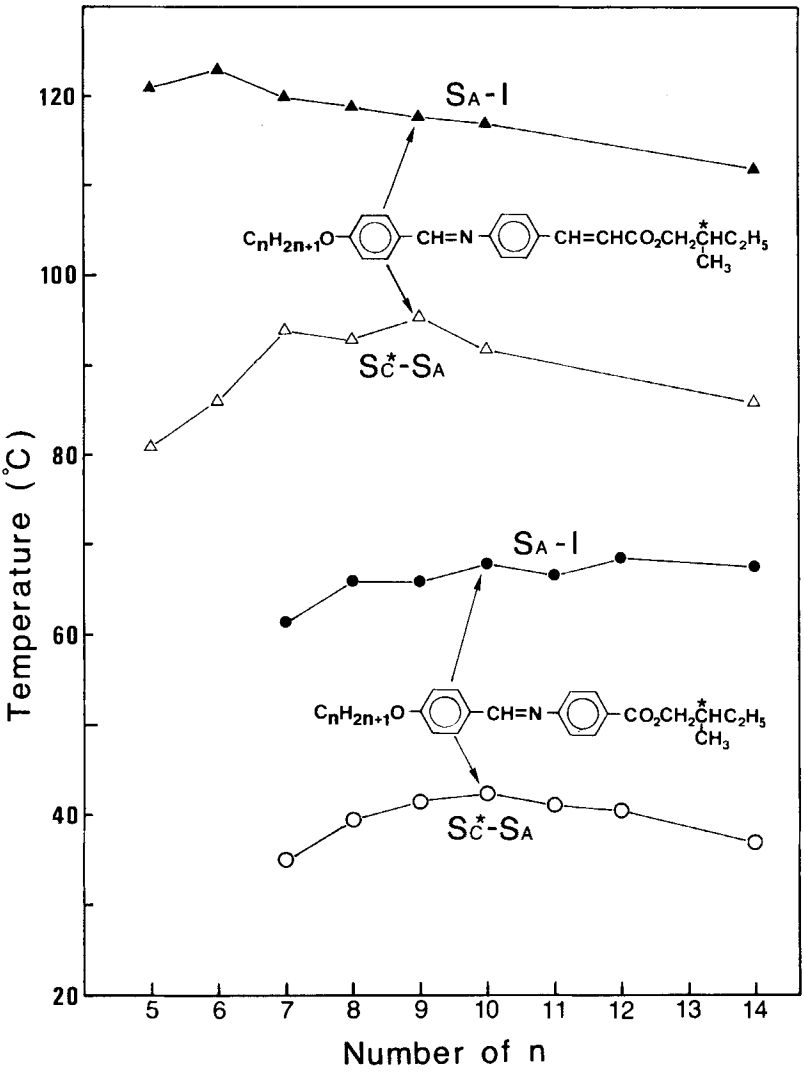


FIGURE 2 Smectic phase transition temperatures versus *n*-number of alkoxy chain in the compounds which are illustrated in the Figure.

method and were measured under the supercooled state. It is noticed that the value of spontaneous polarization of series (I) is a little higher than that of DOBAMBC. Additionally, there is no clear dependence of the value of spontaneous polarization on the length of the terminal chain length (*n*-number) in the series (I).

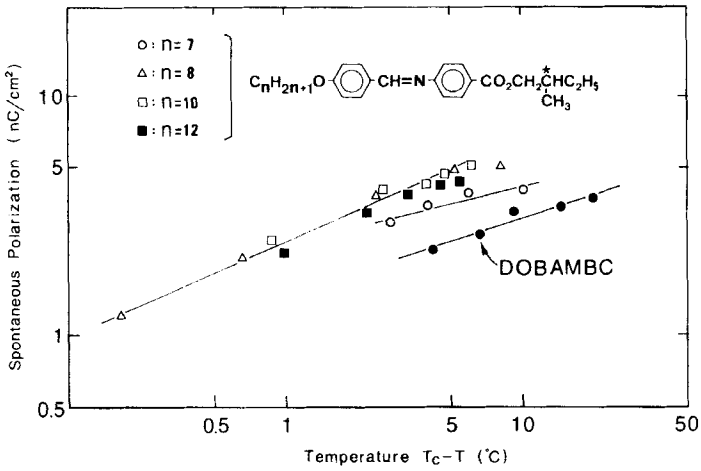


FIGURE 3 Temperature dependences of spontaneous polarizations of compounds (I) and DOBAMBC. The temperature (T_c-T) indicates the difference in the temperatures between $S_C^*-S_A$ phase transition temperatures (T_c) and the temperatures at which the measurement was made (T).

From the above results, it was concluded that the elimination of the carbon-carbon double bond shows remarkable effects on its properties. These effects were the lowering transition temperatures and the small increase of spontaneous polarization.

Acknowledgments

The authors wish to express their grateful acknowledgments to their colleagues for preparing the materials and measuring the value of transition temperatures and spontaneous polarizations.

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