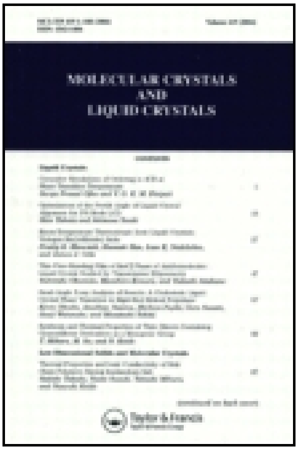

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Synthesis and Properties of Optically Active (+)-p′-2-methyl-butoxyphenyl p-(p″-alkoxybenzoyloxy)-benzoates

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Synthesis and Properties of Optically Active (+)-*p*′-2-methyl-butoxyphenyl *p*-(*p*″-alkoxybenzoyloxy)-benzoates

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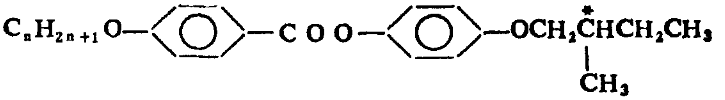
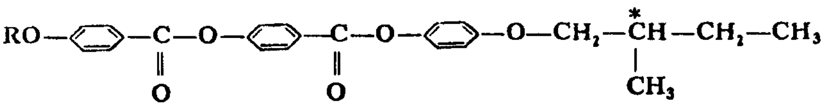
Ten compounds of the title series represented by (*d*)AmPABOB were synthesized and their mesomorphic properties evaluated by DSC and optical microscopy. All the compounds have liquid crystal phases and three out of ten have a smectic C* phase. Measurements of the molecular tilt angle and the pitch were presented. Investigation on textures of mesophases revealed some anomalous phenomena.

INTRODUCTION

In recent years ferroelectric liquid crystals have attracted much attention because of their potential applicability to a wide variety of electro-optical devices.[1–3] In view of the practical application, it is necessary to synthesize the ferroelectric liquid crystals with the following characteristics: broad-band room temperature range, high spontaneous polarization, chemical stability etc. Several years ago we once synthesized a series of compounds (some of them have also been synthesized and examined by other researchers, e.g. Loseva *et al.*[4] and Ostrovskii *et al.*[5]), i.e. the esters of (+)-*p*-2-methylbutyloxy-phenyl-*p*-alkyloxy benzoic acid represented by (*d*)AmPAB (series I), which have the following formula[6]:



where $n = 4 - 12$. In this series of compounds five out of nine exhibit the enantiotropic smectic C* phase. These compounds are stable, but the temperature range of the smectic C* phase is too narrow, especially in heating. Considering that the temperature range might be widened by increasing the length of the rigid part of the molecule, therefore, we synthesized a new series of compounds represented by (*d*)AmPABOB (series II). Their molecular formula is as follows:



where R = CH_3, C_2H_5, n-C_3H_7 to n-$C_{10}H_{21}$. In this paper some preliminary experimental results are reported and discussed.

SYNTHESIS

1. (+)-2-methylbutyl bromide

Phosphorus tribromide (298 g, 1.1 mol) was added dropwise to a stirred (−)-2-methylbut-1-ol (264 g, 3 mol). The temperature during the addition was kept below 0°C in an ice-salt bath. The solution was stirred in a hot-water bath for 3–5 hrs, then the crude product was washed with: water (twice), 5% sodium carbonate, water, concentrated sulphuric acid, water, 5% sodium bicarbonate and water. After drying (M_gSO_4), the crude bromide was distilled to give (+)-2-methyl butyl bromide, 375.6 g, b.p. 119–121°C, 82.9%, n_D^{22} = 1.4460, (lit. n_D^{20} = 1.4451), $[\alpha]_D^{20}$ = +3.64, (lit. $[\alpha]_D^{20}$ = +3.68).

2. (+)-*p*-2-methylbutoxyphenol

Hydroquinone (110 g, 1 mol), ethanol (150 ml) and (+)-2-methyl-butyl bromide (75 g, 0.5 mol) were stirred and refluxed. A solution of potassium hydroxide (28 g, 0.5 mol) in ethanol (100 ml) was added dropwise during 2 hrs. The reaction was continuously stirred and refluxed for 10 hrs. After cooling, the mixture was acidified with concentrated chlorhydric acid and extracted with ligroin twice. The combined ligroin layers were extracted several times with 10% solution of potassium hydroxide. The combined aqueous layers were acidified with sulphuric acid. After cooling, a crystalline precipitate formed. It was filtered off and washed with water. After drying, the crude product was recrystallized from light petroleum several times to give pure product 22.5 g, 25%, m.p. 40–41°C.

3. *p*-2-methyl butoxyphenyl *p*′-hydroxybenzoate

The reaction mixture of *p*-2-methylbutoxyphenol (18 g, 0.1 mol), *p*-hydroxybenzoic acid (10.5 g, 0.075 mol), boric acid (0.232 g, 3.75 mmol), concentrated sulphuric acid (0.375 g, 3.75 mmol), in toluene (250 ml), was heated and refluxed for 24 hrs under a Dean-Starp. Then, the solvent was removed, and the crude product was recrystallized from aqueous solution of ethanol to give 17.8 g of pure product, yield 79%, m.p. 168–170°C.

4. (+)-*p*′-2-methylbutoxyphenyl *p*-(*p*″-alkoxybenzoyloxy)-benzoates

The solution of *p*-alkoxybenzoic acid (0.01 mol), thionyl chloride (4.8 g, 0.04 mol), and benzene (30 ml), was heated and stirred for 3 hrs. Then, the solvent was removed. *p*-2-methylbutoxyphenyl *p*′-hydroxybenzoate (3 g, 0.01 mol), pyridine (2 ml), toluene (75 ml) were added. The mixture was refluxed and stirred for 12 hrs. After cooling, it was washed with 2N chlorhydric acid, water, 5% potassium hydroxide, water. After drying (M_gSO_4), the solvent was removed. The residue was recrystallized from ethyl acetate to give pure product.

RESULTS AND DISCUSSION

1. Transition temperatures and enthalpies

The list of compounds and their phase temperatures as well as enthalpies measured by DSC (with a heating rate of 10°C/min) and optical microscopy are summarized in Table I. The relationship between transition temperatures and the number *n* of carbon atoms in alkyloxy chain is shown in Figure 1. With increase of *n*, we can note the following phenomena:

i) The melting points drop down, and show the odd-even fluctuation. In addition, the melting points with even *n* are lower than the corresponding odd ones.

ii) The clearing points first increase then drop down, and the odd-even fluctuation is not obvious.

TABLE I

Transition temperatures and enthalpies for the homologues (d)AmPABOB.

n	C	S_C^*	S_A	Ch	I
1	. 104.5(13.4)	—	—	. 220.0(0.60)	.
2	. 96.0(22.1)	—	—	. 231.0(0.65)	.
3	. 103.0(28.8)	—	—	. 242.0(0.95)	.
4	. 95.0(17.2)	—	. 113.0	. 206.5(0.81)	.
5	. 99.0(24.6)	—	. 134.0	. 196.0(0.63)	.
6	. 94.0(23.2)	—	. 147.0(0.49)	. 194.5(0.65)	.
7	. 96.0(21.7)	—	. 153.0(0.83)	. 187.5(0.80)	.
8	. 91.0(22.2)	. 95.0	. 158.5(1.03)	. 186.5(0.85)	.
9	. 93.5(31.1)	. 120.5	. 160.0(0.73)	. 185.0(0.89)	.
10	. 92.0(27.1)	. 128.5	. 168.0(1.08)	. 190.0(0.90)	.

( )	transition enthalpy
n	number of carbon atoms in alkyloxy chain
C	crystal
S_C^*	smectic C* phase
S_A	smectic A phase
Ch	cholesteric phase
I	isotropic phase

The transition temperatures are given in degree centigrade, and the enthalpies in KJ/mol.

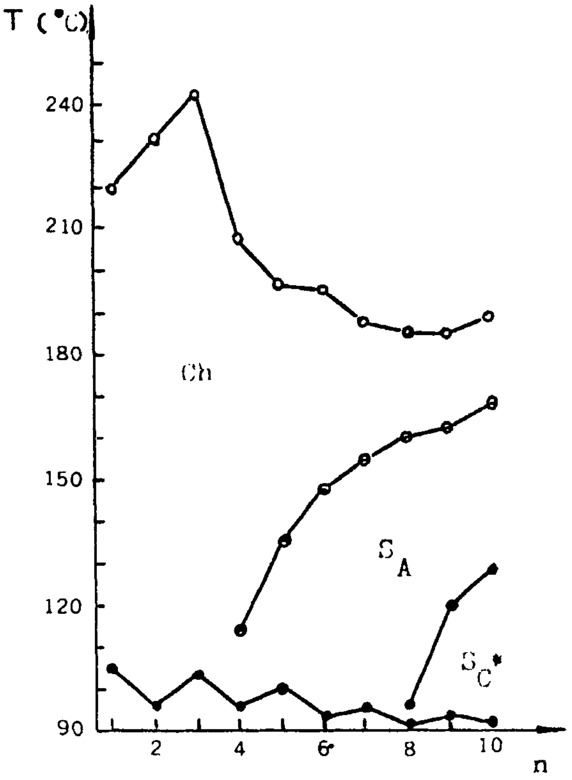


FIGURE 1 Schematic representation of the phase transition temperatures of the homologues (d)AmPABOB.

iii) The temperature range of cholesteric phase becomes narrow. When $n \geq 4$, i.e. for compounds C_4–C_{10}, the smectic A phase can form. When $n \geq 8$, i.e. for compounds C_8–C_{10}, they exhibit the smectic C* phase if further cooling from the smectic A phase. It is expected that some homologues of $n \geq 11$ will still show the smectic C* phase.

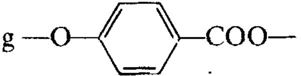
Now let us make a comparison between series I and series II. For convenience, here we give full mesomorphic data on series I as shown in Table II. We notice that the molecules for series II is longer than those for series I (The former corresponds to inserting  into the later.), and this gives rise to the following effects. Because of longer rigid part of molecules for series II, both the melting and clearing points are higher, and the temperature range of mesophases are widened, especially, the temperature range of cholesteric phase for C_1–C_3 are very wide ($\Delta T \sim 110$–$140°C$). Meanwhile, due to the increase of molecular length and the ratio of molecular length to width, all homologues for series II have enantiotropic mesophases, while for series I, only the homologues with $n \geq 6$ can show the enantiotropic mesophases. Besides, although the smectic C* phase exists in the homologues with $n \geq 8$ for both series, its temperature ranges are different.

TABLE II

Transition temperatures for the homologues (d)AmPAB.

n	C	S_C^*	S_A	Ch	I
4	. 77.4	—	—	—	.
5	. 58.5	—	—	—	.
6	. (46.0)	—	—	. 54.0	.
7	. (37.0)	. 48.5	—	. 52.5	.
8	. 40.0 (27.0)	. 42.6	. 58.5	—	.
9	. 45.5 (34.5)	. 47.6	. 59.2	—	.
10	. 44.0 (37.0)	. 51.5	. 63.5	—	.
11	. 50.5 (39.0)	. 51.5	. 64.5	—	.
12	. 50.4 (37.0)	. 52.4	. 65.5	—	.

n	number of carbon atoms in alkyloxy chain
C	crystal
S_C^*	smectic C* phase
S_A	smectic A phase
Ch	cholesteric phase
I	isotropic phase

The transition temperature are given in degree centigrade and temperature in the parentheses refers to the cooling cycle.

For compounds C_6 and C_7, when heating the sample, the crystals will directly transform to the isotropic phase, and the corresponding transition temperatures are 61.5° and 52.5°C respectively.

For example, the temperature range of the smectic C* phase for series I (n = 10) is only 7.5°C, but for series II (n = 10) it is 36.5°C. Therefore, the temperature range of the smectic C* phase can be indeed widened by increasing the length of the rigid part of the molecules.

2. Textures

The classification of the phases was made in the light of the results of texture observation. The textures were investigated using a Leitz polarizing microscope (ORTHOPLAN-POL) equipped with a hot stage.

All compounds exhibit the cholesteric phase at high temperature. When the sample is heated for the first time from the crystal up to the cholesteric phase, the typical texture with oily streaks can be observed (Figure 2). It is worth noticing that when the sample is continuously heated to the isotropic liquid and then cools down to the cholesteric phase, two different cases should be distinguished.

i) The sample consists of two glass plates only cleaned by sulphurchromic acid

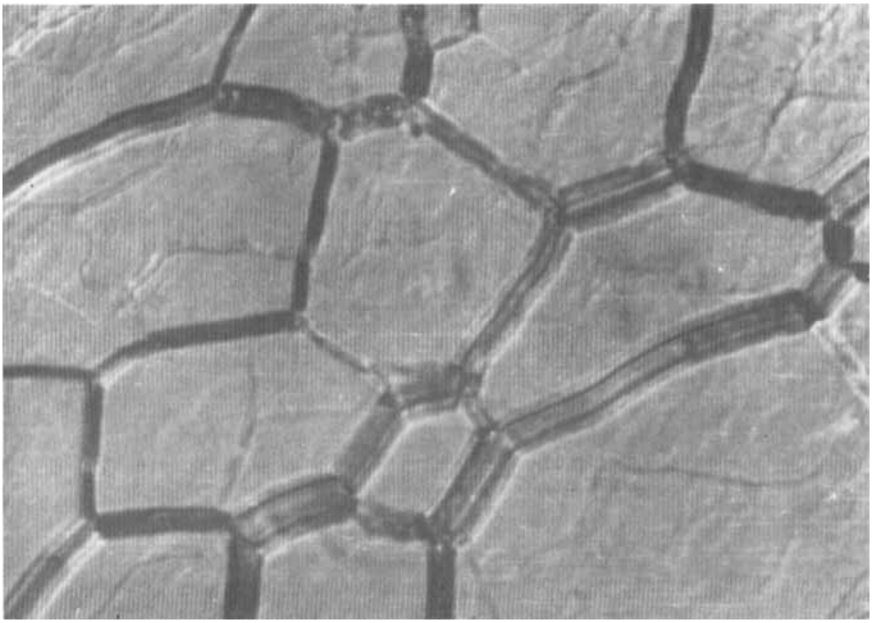


FIGURE 2 Cholesteric texture with oily streaks, C_9, 170°C, ×200.

with or without spacers (If with spacers, the distance between the two parallel spacers must not be too narrow, i.e. wider than 5 mm.).

Under such condition, the texture of the cholesteric phase is fan-shaped (Figure 3). With drop in temperature, the color of the texture continues to change, which characterises the intrinsic property of cholesteric phase. When the samples for C_4–C_{10} further cool, the smectic A phase with the homeotropic texture forms. According to the ordinary opinion, if we wish to form a smectic A phase with the homeotropic texture, we have to treat the glass plates in advance by some special techniques. However, here the smectic A phase shows the homeotropic texture spontaneously without any treatment of plates. The formation mechanism has not yet been clear. Maybe it is related to the fact that the central part of the molecule is relatively longer, which leads to the stronger lateral force. So the homeotropic texture can form spontaneously much easier.

For compounds C_8–C_{10}, when cooling from the homeotropic smectic A phase, the samples exhibit the smectic C* phase. In the smectic C* phase the tilt molecules form a helical structure and the tilt directions average out to zero. Therefore, the texture is not true homeotropic but pseudo-homeotropic. It is true that we did observe a black cross by conoscopy, but it is more blurred than that in the true homeotropic texture of the nematic or smectic A phase. It is strange that the schlieren texture, the typical texture of the smectic C phase, also co-exists with the pseudo-homeotropic one in the sample (Figure 4). Gray *et al.* once pointed out that the pseudo-homeotropic texture (C*) can coexist quite naturally in contact preparations with the schlieren texture (C) and showed a photograph to demon-

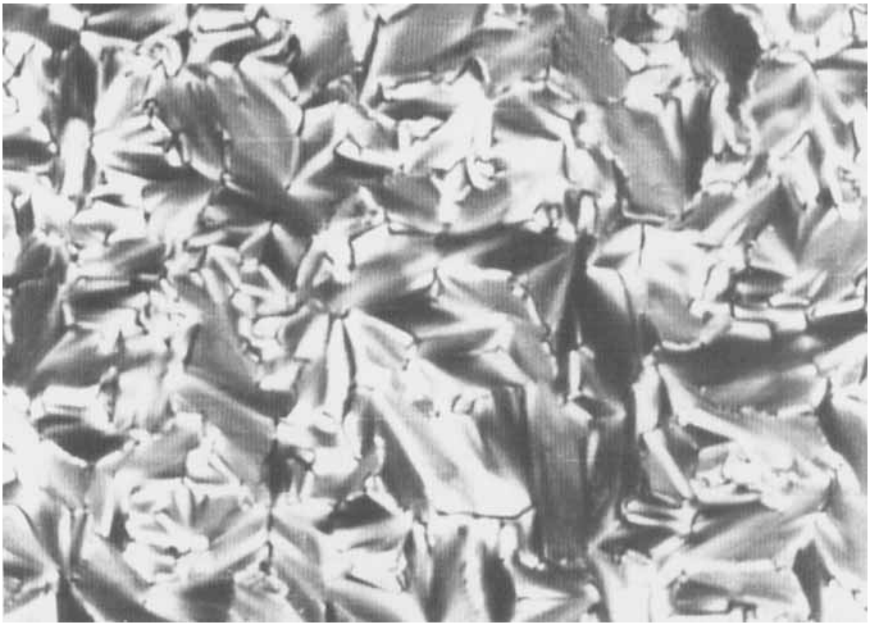


FIGURE 3 Cholesteric fan-shaped texture, C_9, 170°C, ×200.

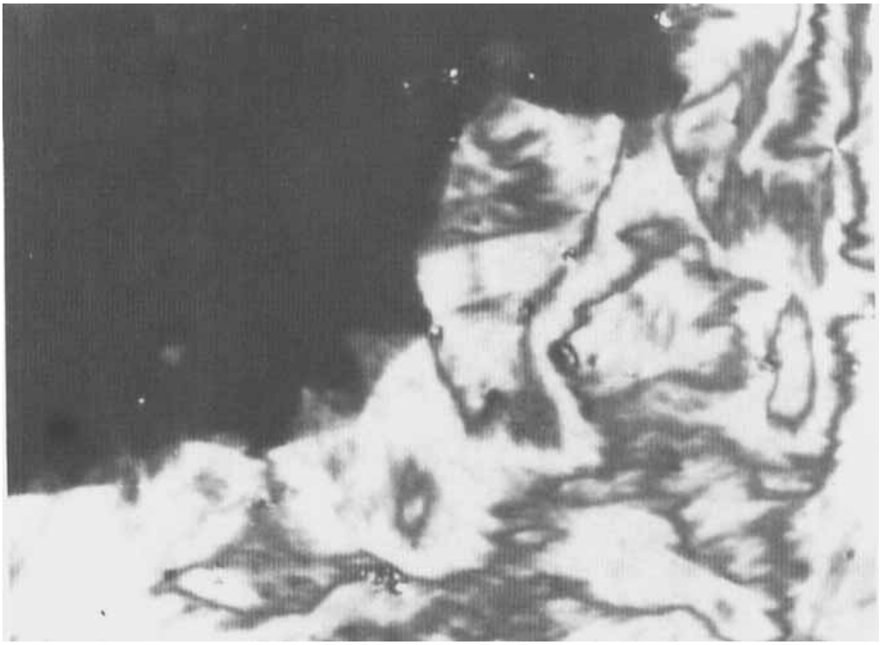


FIGURE 4 Co-existence of pseudo-homeotropic and Schlieren texture in the smectic C* phase, C_9, 120°C, ×200.

strate this.[7] We notice that Figure 4 is very similar to this photograph (Plate 23 in Reference (7)). However, Gray *et al.* observed this phenomenon only in a racemic mixture of the two optically active isomers, while we find such co-existence of two textures in the pure compounds.

(ii) The sample consists of two glass plates with spacers of definite thickness (e.g. 50 μm) and the distance between the two spacers is narrow enough (less than 3 mm).

When the sample cools from the isotropic state to the cholesteric phase, both oily streak and fan-shaped textures can be observed. For compounds C_4–C_{10}, the cooling will lead to form the smectic A phase with the typical fan-shaped texture. For C_8–C_{10}, when the temperature drops further, the smectic C* phase appears, in which we can see the ordinary pitch fringes (Figure 5). Here, no schlieren texture can be found, which indicates that these compounds don't have smectic C phase. On the other hand, we see that the molecular alignment shown in Figure 5 is planar (the smectic layers are perpendicular to the plates.), different from that in case (i), which shows that the boundary conditions can strongly affect the texture.

In case (i) we also found another new interesting phenomenon in smectic A—cholesteric transition. When the sample heated from the homeotropic smectic A phase to the smectic A—cholesteric phase transition temperature, the cholesteric phase appears in the smectic A phase and grows into the smectics. The front of the new phase shows thin and sharp stripes which moves into the old phase steadily and quickly (Figure 6). The whole interface displays a chaotic form reminiscent of

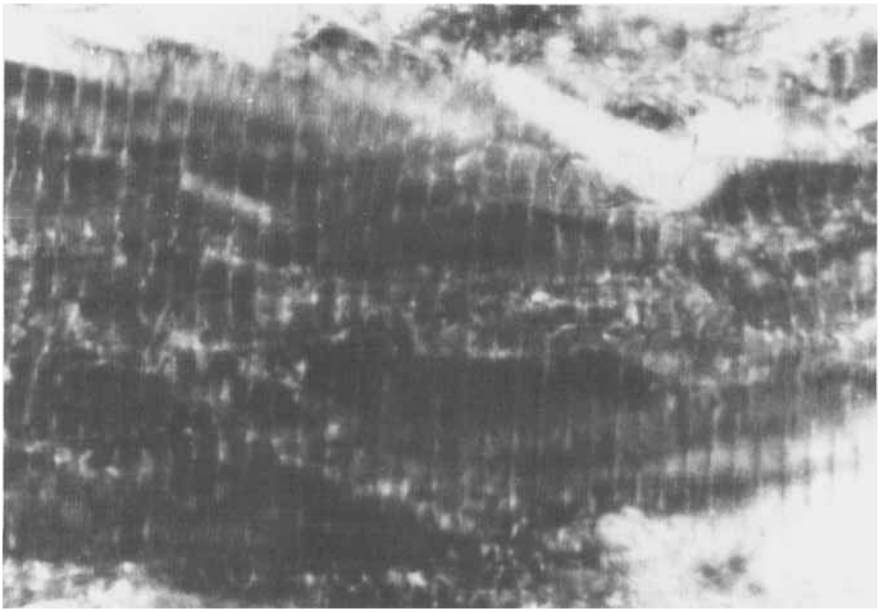


FIGURE 5 The pitch fringes in the smectic C* phase, C_9, 110°C, ×200.

FIGURE 6 The morphology of interface in smectic A-cholesteric transition, C_9, 160°C, ×200.

the fireworks, which sensitively depends on the temperature and initial condition. The detailed experiment will be reported in a separate paper.

3. Tilt angle and pitch

In the smectic C* phase the molecular tilt angle and the pitch are the fundamental structure parameters. The tilt angle can be determined by X-ray diffraction using the relation $\theta = \cos^{-1}(d_C^*/d_A)$, where d_A and d_C^* are the smectic interlayer distance in the A and C* phases respectively. It has been found out that for a series of compounds the tilt angle presents the same temperature dependence with about the same absolute values because of the chemical similarity.[8,9] Figure 7 shows the results of tilt angle determinations in the smectic C* phase of compound C_9, measured versus temperature using X-ray diffraction. The experimental set-up and method have been described in detail in Reference (9). As shown in Figure 7, the large tilt is $\theta \sim 15°$, for $T - T_C \sim -10°C$, and the curve $\theta(T)$ is similar to that for the compounds of series I presented in Reference (9). According to this fact it seems that the molecular length doesn't affect the tilt angle obviously.

The pitch can be measured by observing the fringes of the helical structure in the planar sample with an ocular micrometer attached to the polarizing microscope. The measurement of the pitch has been described in detail in Reference (8). For compound C_9, the pitch is approximately 9 μm at $T = 115°C$ (Figure 5), which is larger than that for DOBAMBC. This experiment confirms that if the distance between the liquid crystal core and the asymmetric carbon is greater, the pitch will increase, as pointed out by Decobert *et al.*[10]

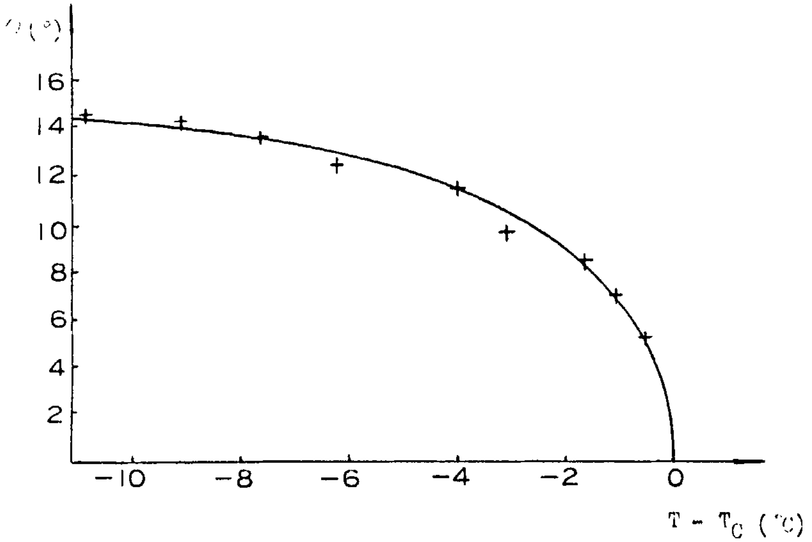


FIGURE 7 The tilt angle as a function of temperature for compound C_9 as determined by X-ray diffraction.

CONCLUSION

In this study we report the synthesis of a series of chiral compounds and their mesomorphic properties. We have demonstrated that the temperature range of the smectic C* phase can be widened by increasing the length of the rigid part of the molecule. As can be seen from Table I, the three ring compounds show the smectic C* phase with relatively high transition temperatures. It makes these compounds suitable for mixtures and for doping. On the other hand, we note that the compounds C_1–C_4 have the cholesteric phase with very wide temperature range ($\Delta T \sim 90$–$140°C$), so they are very useful as mixture components. Furthermore, they are stable chemically, therefore, they can replace the derivatives of cholesterol and be applied to the color display due to the temperature effect.

Acknowledgments

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