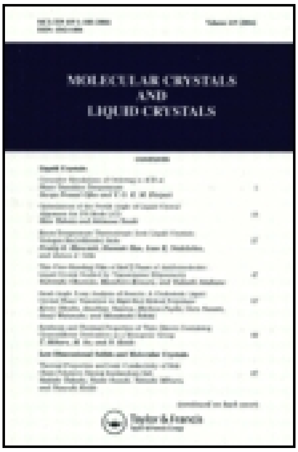

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Synthesis and Mesomorphic Properties of Novel Ferroelectric Liquid Crystals with a Trifluoromethyl Group at the Chiral Center

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To cite this article: A. Sakaigawa , Y. Tashiro , Y. Aoki & H. Nohira (1991): Synthesis and Mesomorphic Properties of Novel Ferroelectric Liquid Crystals with a Trifluoromethyl Group at the Chiral Center, Molecular Crystals and Liquid Crystals, 206:1, 147-157

To link to this article: http://dx.doi.org/10.1080/00268949108037727

Mol. Cryst. Liq. Cryst., 1991, Vol. 206, pp. 147–157
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Printed in the United States of America

Synthesis and Mesomorphic Properties of Novel Ferroelectric Liquid Crystals with a Trifluoromethyl Group at the Chiral Center

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(Received January 22, 1991; in final form April 15, 1991)

A variety of ferroelectric liquid crystals with a trifluoromethyl group at the chiral center were newly synthesized utilizing optically active 3-trifluoromethylalkanoic acids prepared by optical resolution procedures. Some homologous compounds having a various length of the alkyl chain or the kind of the spacer group between the core and the chiral center were synthesized and their physical properties, particularly concerning phase behavior, spontaneous polarization, optic tilt angle and response time were evaluated. Most of these compounds exhibited chiral smectic C phase in a wide temperature range including room temperature and were found to possess a large spontaneous polarization value.

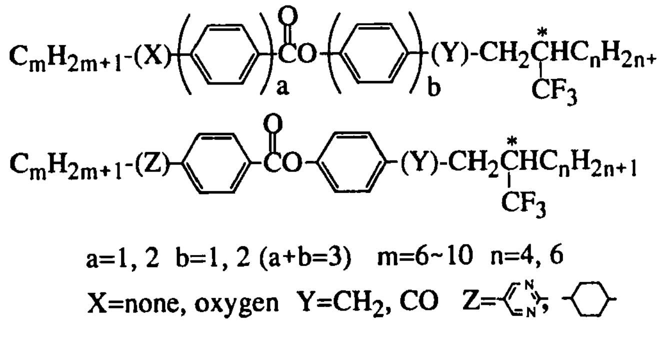
INTRODUCTION

Ferroelectric liquid crystals have been currently studied with great interest in the field of material synthesis because of their highly potential applicability for display devices, initially proposed by Clark and Lagerwall.[1]

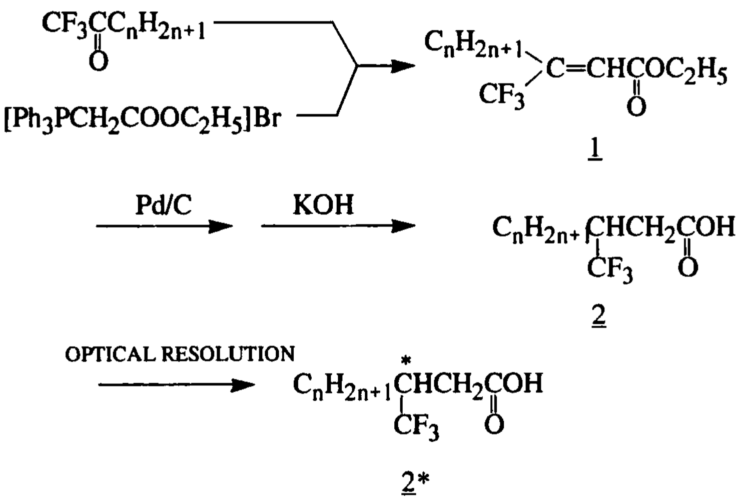
Most ferroelectric liquid crystals so far synthesized have been oriented for having a wide temperature range of the chiral smectic C phase, a large spontaneous polarization, and a quick response. However, there are few compounds prepared to have satisfactory mesomorphic properties for practical use. Usually, several liquid crystal compounds are practically mixed to achieve effective properties.

Ferroelectric liquid crystals inevitably have an asymmetric frame-work and a lateral dipole associated with the chiral center that causes a spontaneous polarization, so that the compound having a substituent with a large dipole at the chiral center consequently could be expected to show a large spontaneous polarization.[2,3]

We have recently reported ferroelectric liquid crystals with a fluorinated asymmetric framework possessing a large spontaneous polarization and a quick response.[4] In this paper, we will report new ferroelectric liquid crystals with a trifluoromethyl group at the chiral center, Scheme I, prepared from optically active 3-trifluoro-methylalkanoic acid, and describe their unique mesomorphic properties.



SCHEME I



SCHEME II

RESULTS AND DISCUSSION

Synthesis of 3-Trifluoromethyl Alkanoic Acid (2)

The series of racemic 3-trifluoromethyl alkanoic acids (2) were substantially prepared by the following method (Scheme II). 1,1,1-trifluoro-2-alkanone were treated with carboethoxymethyl-triphenylphosphonium bromide to give ethyl 3-trifluoromethyl-2-alkenoate (1). The hydrogenation of (1) in the presence of palladium-carbon followed by the hydrolysis gave (2) in good yields.

Optical Resolution of (±)-(2)

Optically active 3-trifluoromethylalkanoic acids (2)* were prepared by the diastereoisomeric salt formation method using optically active amines as resolving agents (Scheme II). Thus 3-trifluoromethylheptanoic acid (n = 4) was resolved by optically active α-methylbenzylamine (abbreviated as MBA), while 3-trifluoromethylnonanoic acid (n = 6) was resolved by optically active 1-(1-naphthyl)ethylamine (abbreviated as NEA). The results and properties of optically active 3-trifluoromethylalkanoic acid (2)* are shown in Table I.

Synthesis of Intermediates (3) ~ (6)

Optically active 3-trifluoromethylalkanoic acids (2)* were converted to the corresponding acid chlorides which were treated with anisole in the presence of aluminum chloride to give 4-(3-trifluoromethylalkanoyl) anisoles (3, b = 1) with a 70% yields. In a similar way, 4-methoxy-4′-(3-trifluoromethylalkanoyl)biphenyls (4, b = 2) were derived from 4-methoxybiphenyl with a 30% yield. These compounds (3) and (4) were demethylated with hydrobromic acid to give the corresponding phenol (5) and 4-hydroxybiphenyl (6).

On the other hand, reduction of (3) with lithium aluminum hydride and aluminum chloride,[5] and successive demethylation of the methyl group by the treatment with HBr gave (7) (Scheme III).

Synthesis of Liquid Crystals (8) ~ (11)

New types of liquid crystals (8) ~ (11) were readily synthesized as shown in Scheme IV. The phenols (5) and (7) were treated with 4-alkyl- or 4-alkyloxy-4′-biphenylcarboxylic acid chloride to give liquid crystals (8) and (10) respectively, while (6) was treated with a 4-alkyloxybenzoic acid chloride to give (9). The different types of liquid crystals (11) were similarly prepared from the phenol (7) with the corresponding 4-substituted benzoic acid chloride.

Phase Behavior of Liquid Crystals

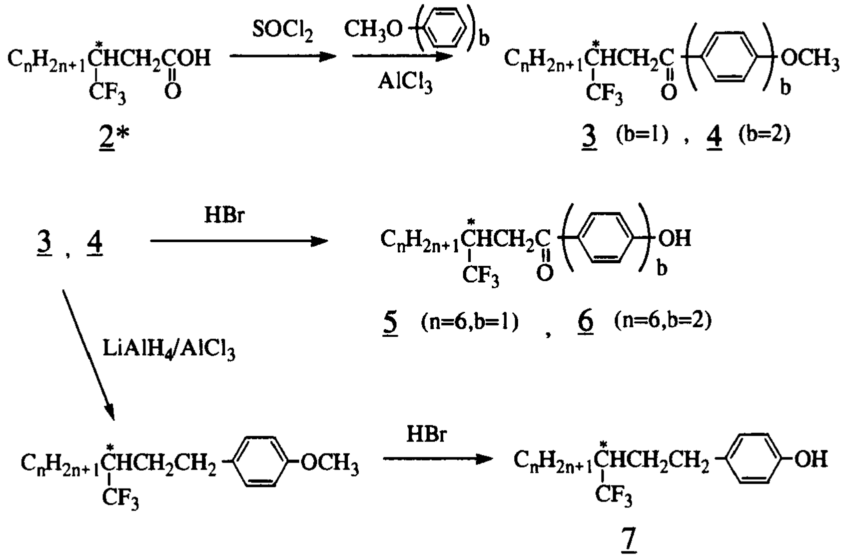
The sequence of phases and the transition temperatures of (8) and (9) were properly determined, as shown in Table II. These compounds revealed a chiral smectic C

TABLE I

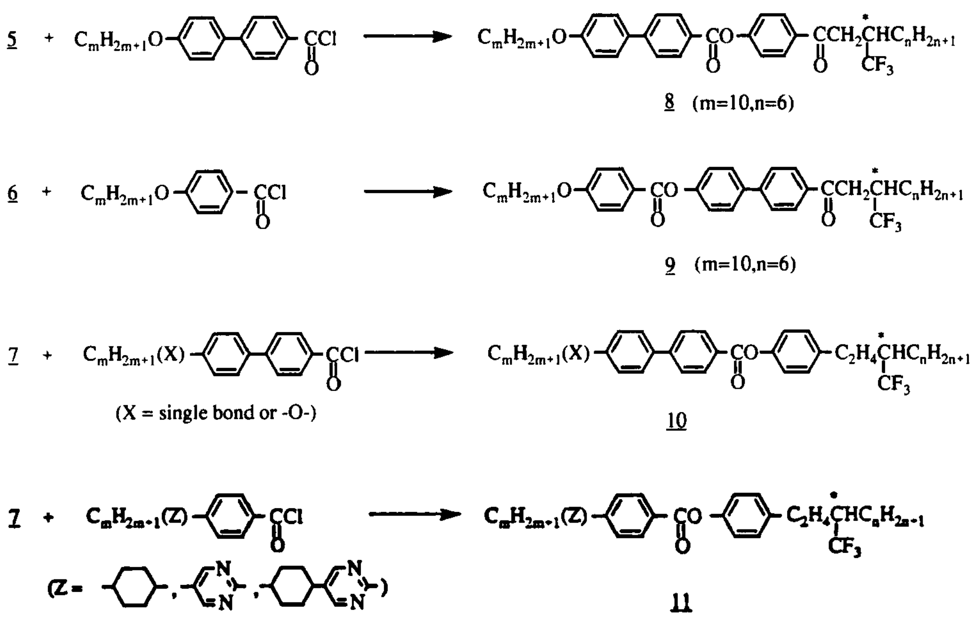
Optical resolution of 2

n	resolving agent	number of recrystallization	salt $[\alpha]_D$	free acid $[\alpha]_D$	bp (°C/mmHg)	yield1) (%)
4	(+)-MBA	3	+5.6° (c2,MeOH)	-4.5° (c2,CHCl$_3$)	140/35	25.6
6	(+)-NEA	3	+5.0° (c3.5,CHCl$_3$)	-5.5° (c4,CHCl$_3$)	170/32	22.1

1) The yield was calculated based on half the amount of racemic 2



SCHEME III



SCHEME IV

phase in a wide temperature range, and smectic A phase as well. The compound (8) showed an unidentified ferroelectric smectic phase (S_3^*) below the Sc* phase.

The sequence of phases and the transition temperatures of compounds of type (10) are summarized in Table III. The transition temperatures in general tend to shift lower and ranges of the Sc* phase were expanded towards low temperatures by replacing the carbonyl group at the spacer group between the core and the

TABLE II

Phase transition temperature of 8, 9

	C	S_3*	S_C*	S_A	I
8	· 56	· 98	· 132	· 145	·
9	· 49	—	· 104	· 135	·

All values are measured at the cooling time
C:Crystal Phase , S_3*:Unidentified ferroelectric smectic phase
S_C*:Chiral Smectic C Phase , S_A:Smectic A Phase
I:Isotropic Liquid

TABLE III

Phase transition temperature of 10

X	m	n	C	(S_4)	S_3	Sc*	S_A	I
—	7	4	·	(· 31)	· 69	—	· 114	·
O	6	4	· 43	—	· 44	—	· 104	·
O	8	4	· 17	—	—	(· 20)	· 89	·
O	10	4	· -22	—	—	· 47	· 86	·
O	12	4	· -10	—	—	· 46	· 81	·
O	16	4	· 25	—	—	(· 35)	· 73	·
—	7	6	·	—	(· 25)	—	· 104	·
O	6	6	· 49	—	—	—	· 90	·
O	8	6	· 17	—	· 39	· 82	· 132	·
O	9	6	· -0.8	—	· 46	· 90	· 123	·
O	10	6	· 14	—	· 36	· 90	· 121	·
O	12	6	· 40	—	—	· 97	· 115	·
O	16	6	· 22	—	—	—	· 50	·

The values in parenthesis are monotropic phase transitions

chiral center with a methylene group. Especially, it should be noted that the same compounds having a suitable length of the alkyl chain, e.g. (m, n) = (12, 4), (10, 4), (10, 6), (9, 6), (8, 6), exhibited the Sc* phase below or close to room temperature. However, other compounds, different in the length of the terminal alkyl chain m, in either a case of too long or too short, showed the Sc* phase quite briefly or almost vacantly. In compounds (10), appearance of Sc* phase was sensitive to the length of terminal alkyl chain. On the other hand, reduction of carbonyl in the spacer group to methylene was apparently affected lowering the temperature of the Sc* phase and, moreover, largely expanding its temperature range. The temperature showing the Sc* phase shifted lower and its range was extremely expanded.

Table IV collects phase transition temperature of various compounds having different core structures. In those compounds, no Sc* phase was observed. In any case, smectic phases observed were identified as smectic A by microscopic texture.

Spontaneous Polarization, Optic Tilt Angle and Response Time

The spontaneous polarizations of (8) ~ (10) were determined as a function of the standardized temperature, as shown in Figure 1. The temperature dependence of spontaneous polarization is known to be described by the following expression: $Ps = Po(Tc - T)^{\alpha}$.[6] In this study, the value of α was found to be 0.5 ~ 0.85.

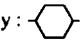
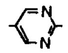
The compounds (10) showed approximately the same value of 40 nC/cm^2 at the temperature of $Tc - T = 10$, although compounds (8) and (9) showed a smaller value by one tenth. It would be interested in the fact that reduction of the carbonyl group that carries large lateral dipole led to the large spontaneous polarization. It might be largely due to a mutual cancellation of the dipoles between the carbonyl and the trifluoromethyl group in the framework. Reduction of the carbonyl group should consequently raise the dipole originated with a trifluoromethyl group.

The optic tilt angles θ of compound (10) were also determined as a function of standardized temperatures, as shown in Figure 2. The temperature dependence of the tilt angles is also known to be defined by the following expression: $\theta = \theta_0(Tc - T)^{\beta}$.[7] In this study the value of β was 0.3 ~ 0.4. The value of the optic tilt angles θ increased with the lengthening of the terminal alkyl chain.[8] Thus the compounds $(m, n) = (12, 4)$ and $(12, 6)$ of (10) were found to possess tilt angles larger than 28 degrees at the temperature of $Tc - T = 30$. The response times of compounds (8) ~ (10) are shown in Table V. The value of (8), measured at 10 V/μm is more than twice as large as that of (9) $(m, n) = (10, 6)$, measured at 4 V/μm. It would be accounted for in terms of the different structures in their core parts; the core moiety of (8), bearing the chiral chain, is a phenol derivative, while

TABLE IV

Phase transition temperature of 11

Z	m	n	C		S_3		S_A		I
Cy	8	4	·	16	(·	62)	·	86	·
Cy	8	6	·	5	(·	43)	·	64	·
Py	7	4	·	80	—		·	118	·
Py	7	6	·	58	—		·	103	·
Cy-Py	7	6	·	33	—		·	225	·

Cy :  , Py : 

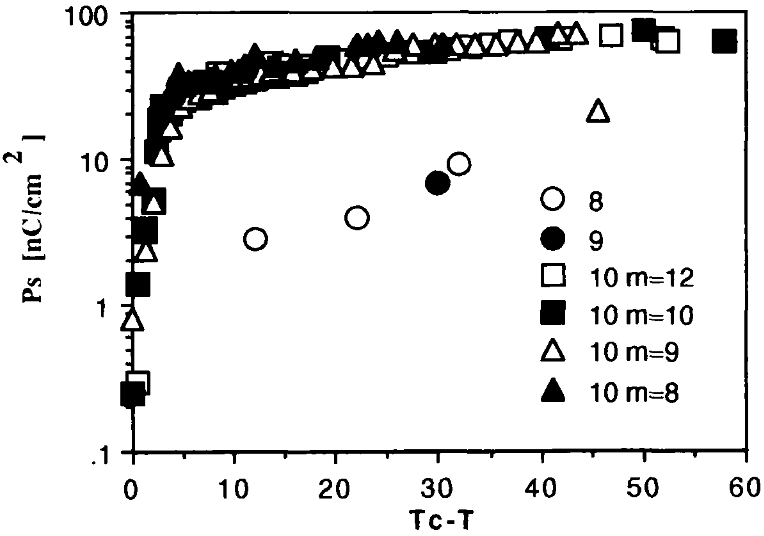


FIGURE 1 Spontaneous polarization of 8, 9 and 10 (n = 6, X = 0).

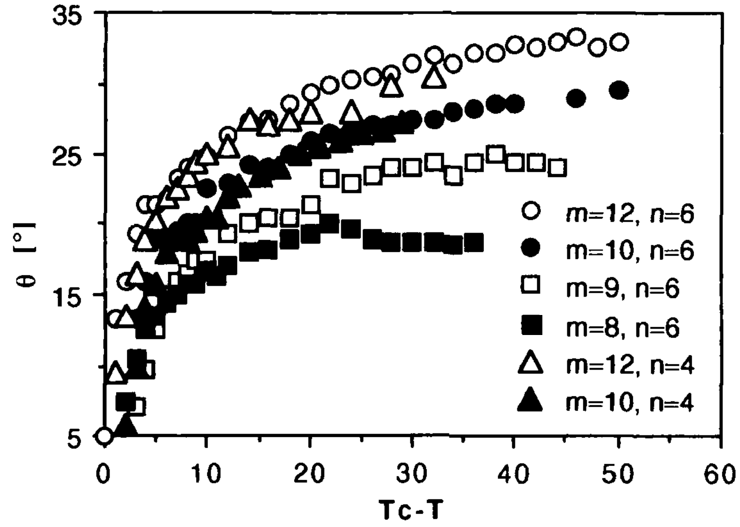


FIGURE 2 Tilt angle θ of 10 (X = 0).

that of (9) is a biphenyl derivative. On the other hand, the response time of (10) (m, n) = (10, 6), which has methylene group, is the same as that of (8). In the homologous series (n = 6) of compound (10), the value of response time slightly increases with the lengthening of the terminal alkyl chain. However, it should be noted that the compound (m, n) = (10, 4) showed a value more than ten times larger than that of the compound (m, n) = (10, 6). This means the rotational viscosity should be quite sensitive to the alkyl chain outside of the chiral center.

TABLE V

Response time τ of 8, 9 and 10

	m	n	τ (μsec)	Tc-T(°C)
8[1]	10	6	45.6	12
9[1]	10	6	40.5	10
10[2]	10	4	1090	12
	12	4	1450	12
	8	6	30.2	12
	9	6	36.2	12
	10	6	50.4	15
	12	6	70.8	12

1)Condition of measurement : 8V/μm

2)Condition of measurement : 4V/μm

Experimental. All products prepared were identified mainly by the spectroscopic methods, the ^{1}H-NMR(JEOL PMX-60SI and BRUKER AM-400), and IR(PERKIN ELMER FT-1640). The specific rotation was measured on JASCO DIP-360 digitalpolarimeter.

Liquid crystalline phases were identified by observation of the textures with a polarizing microscope (OLYMPUS model-POS) equipped with a heating stage and transition temperatures were determined with a DSC(SEIKO I & E DSC-20). Spontaneous polarizations were measured by the triangular-wave method reported by Miyasato *et al.*[9] Optic tilt angles were measured with a polarizing microscope equipped with a Photomultiplier (HAMAMATU R2228).

Response times were measured by the field reversal method of Skarp *et al.*[10] cells of different thickness were used to conform; 20 μm thick cells were used at the phase identification, measurements of spontaneous polarizations and response times, while 1.3 μm thick cells were used for the measurement of optic tilt angles. Applied voltage was 4 Vpp/μm in regular measurement. Optically active (1-(1-naphthyl)ethylamine (NEA) and α-methylbenzylamine (MBA) as the optically resolving agent produced by Yamakawa Chemical Industry Co. Ltd., were utilized without purification.

Preparation of Ethyl 3-Trifluoromethyl-2-nonenoate (1) (*n* = 6)

In a 1 liter round flask, 5.85 g (254 mmole) of metallic sodium was added and enough of dry ethanol to solve the sodium was added to give sodium ethoxide. Then, 500 ml of dry dichloromethane solution containing 109 g (254 mmole) of carboethoxytriphenylphosphoniumbromide was added and stirred for an hour at room temperature. Into the resulting solution, 23.2 g (127 mmole) of 1,1,1-trifluoro-

2-octanone was added and the mixture stirred for 80 hours at room temperature. After evaporating the solvent, 600 ml of water was added to it and the product was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated, then the deposited triphenylphosphine oxide was filtrated and washed thoroughly with hexane. The filtrate and washings were distilled under reduced pressure to give ethyl 3-trifluoromethyl-2-nonenoate ($\underline{1}$). The yield was 26.0 g (103.6 mmole) with a 81.6%, bp 101°C/20 mmHg.

Preparation of 3-Trifluoromethylnonanoic Acid (TNA) ($\underline{2}$) (*n* = 6)

A mixture of 23.0 g (91.3 mmole) of ethyl 3-trifluoromethyl-2-nonenoate, and 230 ml of dry methanol was added to 2.3 g of 5% palladium-carbon. Catalytic hydrogenation under atmospheric pressure was carried out by stirring. When the absorption of hydrogen reached saturation, the palladium carbon was filtrated. Sodium hydroxide 33.3 g dissolved in 40 ml of water was poured in the filtrate and the mixture was refluxed for 2 hours, then acidified (PH < 2) with 6 M hydrochloric acid. Product was extracted with dichloromethane and dried over anhydrous sodium sulfate. Distillation under reduced pressure gave 3-trifluoromethylnonanoic acid ($\underline{2}$). The yield was 17.2 g (76.1 mmole) with a 83.4%, bp 142°C/20 mmHg.

Optical Resolution of 3-Trifluoromethylnonanoic Acid (*n* = 6)

Into a 100 ml of hexane solution of racemic 3-trifluoromethylnonanoic acid ($\underline{2}$) 29.54 g (130.7 mmole), was added 22.2 g (130.7 mmole) of (+) 1-(1-naphthyl)ethylamine (NEA) and the mixture stirred for a while at room temperature. The resulting insoluble diastereomer salt was filtered and recrystallized twice from hexane. To the purified salt was added 2M sodium hydroxide solution to liberate the NEA. After the amine was extracted with ether, 3-trifluoromethylnonanoic acid was liberated from the water layer by acidifying with 2M hydrochloric acid. The liberated acid was extracted with ether, and ($\underline{2}$)* was purified by distillation under reduced pressure, bp 170°C/32 mmHg. The yield was 3.22 g (14.3 mmole) with a 21.8%.†

Specific rotation

(+)-1-(1-naphthyl)ethylamine	$[\alpha]_D$ + 61.4° (c7.8, MeOH)
(+)-NEA(−)-TNA salt	$[\alpha]_D$ + 5.0° (c3.5, $CHCl_3$)
(−)-3-trifluoromethylnonanoic acid	$[\alpha]_D$ − 5.5° (c4.1, $CHCl_3$)

Preparation of (+)-4-(3-Trifluoromethylnonanoyl)anisole ($\underline{4}$) (*b* = 1)

A mixture of 0.23 g (1.0 mmole) of (−)-3-trifluoromethylnonanoic acid ($\underline{3}$) and 1.5 ml of thionyl chloride was heated at 80°C by stirring. After 1.5 hours, the excess thionyl chloride was removed by evaporation. To this acid chloride, 2 ml

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† The yield was calculated based on half the amount of racemic ($\underline{2}$).

of carbondisulfide and 0.1 g (0.93 mmole) of anisole were added by stirring. To this mixture was carefully added 0.16 g (1.2 mmole) of smashed aluminum chloride, and the mixture was refluxed for an hour. After cooling it with an ice bath 1M hydrochloric acid and cooled water were added dropwise by stirring. The product was extracted with ether and washed with saturated sodium hydrogen carbonate solution. The organic layer was dried over anhydrous sodium sulfate. Distillation under reduced pressure gave a purified product (4), bp 230°C/15 mmHg. The yield was 0.216 g (0.68 mmole) with a 79.5%. (4); $[\alpha]_D$ + 20.0° (c2.1, $CHCl_3$).

Preparation of (+)-4-(3-trifluoromethylnonyl)phenol (7)

To a mixture of 0.07 g (1.8 mmole) of lithium aluminum hydride and 0.24 g (1.8 mmole) of smashed aluminum chloride in 7 ml of dry ether was added dropwise 0.5 g (1.6 mmole) of (+)-4-(3-trifluoromethylnonanoil)anisole (4) in dry ether by stirring under nitrogen replaced atmosphere and then the mixture was heated under reflux for 40 minutes. After cooling, 1M sulfuric acid was added dropwise to collapse any excess of lithium aluminum hydride. The product was extracted with ether. After the ether was removed, a mixture of 20 ml of acetic acid and 4 ml of 47% hydrobromic acid was added to the residue and the mixture was refluxed for 13 hours by stirring. A large quantity of cold water was added and the product was extracted with ether. The organic layer was thoroughly washed with saturated sodium hydrogen carbonate solution and dried over anhydrous sodium sulfate. (7) was purified by distillation under reduced pressure, bp 183°C/0.3 mmHg. The yield was 0.30 g (1.05 mmole) with a 65.6%. (7); $[\alpha]_D$ + 2.4° (c1.36, $CHCl_3$).

Preparation of (+)-4-(3-Trifluoromethylnonyl)phenyl = 4-octyloxybiphenyl-4'-carboxylate (10) (m = 8, X = 0)

A mixture of 0.25 g (0.78 mmole) of 4-octyloxybiphenyl-4'-carboxylic acid and 1.5 ml of thionyl chloride was heated at 80°C by stirring for 3 hours to give the acid chloride. After the excess thionyl chloride was evaporated, 0.15 g (0.52 mmole) of (+)-4-(3-trifluoromethylnonyl)phenol (7), 3 ml of dry benzene, and 0.2 g (1.6 mmole) of 1,4-diazabicyclo[2.2.2]octane in dry benzene were added to the acid chloride. The mixture was heated at 50°C by stirring for 3 hours. After cooling, 38 mg (0.95 mmole) of 60% sodium hydride in oil was added, and the reaction mixture was stirred over night at room temperature and then refluxed for 5 hours. After cooling, 5 ml of 1M hydrochloric acid and 20 ml of water were added. The product was extracted with benzene and the benzene layer was washed with saturated sodium hydrogen carbonate solution, then dried over anhydrous sodium sulfate. Purification by thin layer chromatography on silica gel using benzene as the eluent and the following recrystallization from 99% ethanol gave pure (10). The yield was 0.257 g (0.431 mmole) with a 82.9%. (10); $[\alpha]_D$ + 1.7° (c1.03, $CHCl_3$).

Acknowledgments

We thank Canon Inc. for their support and discussion of the physical measurements of mesomorphic properties. We also thank Yamakawa Chemical Industry Co. Ltd. for their supply of the optical resolving agents.

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