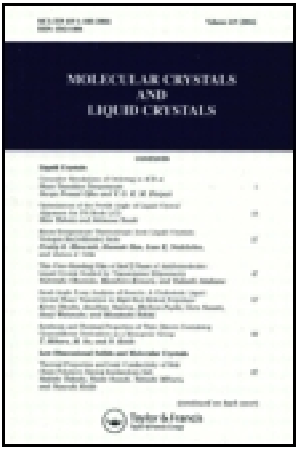

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Synthesis and Thermal Properties of Liquid Crystalline Compounds Containing Carbazolyl Group

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Synthesis and Thermal Properties of Liquid Crystalline Compounds Containing Carbazolyl Group

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New liquid crystalline compounds containing carbazolyl moiety as part of the mesogenic group were synthesized. 2-(9-Methylcarbazolyl)-4-alkoxybenzoate and 2-(9-methylcarbazolyl)-4-trifluoromethylbenzoate did not show any textures by polarizing optical microscopy (POM) measurement. However, 2-(9-methylcarbazolyl)-4-cyanobenzoate and 2-(9-metylcarbazolyl)-4-alkanecarboxybenzoate show schlieren texture. 2-(9-methylcarbazolyl)-4-cyanobenzoate has two phase transition temperatures on both heating and cooling process. By X-ray diffraction measurement of this compound, only one weak broad peak was detected at the mesomorphic temperature in the wide-angle region. Therefore, the LC phase of the compound was assigned to a nematic. 2-(9-Methylcarbazolyl)-4-pentynylcarboxybenzoate shows only one phase transition on heating process. However, the compound shows two phase transition temperatures on cooling processes. By X-ray diffraction measurement, the compound indicates two broad peaks at around 4.5 and 19.0 degree. These LC phases would be assigned to a cybotactic nematic phase based on the shorten molecular length of the calculated value and the optical texture.

Keywords: carbazole; liquid crystalline compound; nematic phase; carbazolyl derivatives

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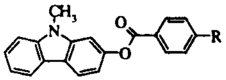
INTRODUCTION

Carbazole is one of the single multifunctional chromophore with photoconductivity, hole-transporting properties and so on.[1-4] Therefore, carbazolyl derivatives have in recent years attracted much attention in various fields. For example, polycarbazoles have extensively studied for electroluminescence (EL) devices because of their good hole-transporting and luminescent properties.[4-7] Carbazole has also been the study target as photorefractive (PR) materials.[1,2,8,9] The two-dimensional charge transfer chromophore can be formed by introducing electron accepter groups at 3,6-positions of carbazole molecule (*para*-positons to the nitrogen atom). It presents not only photoconductive, but also nonlinear optical (NLO) properties.

The enhancement of these properties is expected by the orientation of molecules. As the PR material, improvement of the diffraction efficiency with low intensity of recording beam is expected by highly ordered molecules being realized.[8] This situation is caused by the effect of orientational enhancement. As the EL devices, the improvement of the rate of carrier mobility is expected.[4]

It is well known that liquid crystal can be organized by itself without application of external fields. In this study, we synthesized liquid crystalline compounds containing carbazolyl group and investigated thermal properties of them. Figure 1 indicates the structure of synthesized carbazolyl derivatives. Carbazole was introduced to the part of mesogenic group.



COMPOUND	R
6OBCzMe	$-O(CH_2)_{11}CH_3$
12OBCzMe	$-O(CH_2)_5CH_3$
NCBCzMe	$-CN$
F_3CBCzMe	$-CF_3$
2MBOCzMe	$-OCH_2CH(CH_3)CH_2CH_3$
AcOBCzMe	$-OCOCH_3$
5COOBCzMe	$-OCO(CH_2)_4CH_3$
F_3CBBCzMe	-OCO ⬡ CF_3
NCBBCzMe	-OCO ⬡ CN

FIGURE 1 Structure of carbazolyl derivatives

RESULT AND DISCUSSION

Figure 2 shows the path for synthesis of the carbazolyl derivatives, which exhibit liquid crystalline phase. The synthesis route of the carbazolyl derivatives, which do not exhibit a liquid crystalline phase is deleted. The products in each reaction step were confirmed by ^{1}H-NMR and IR measurements.

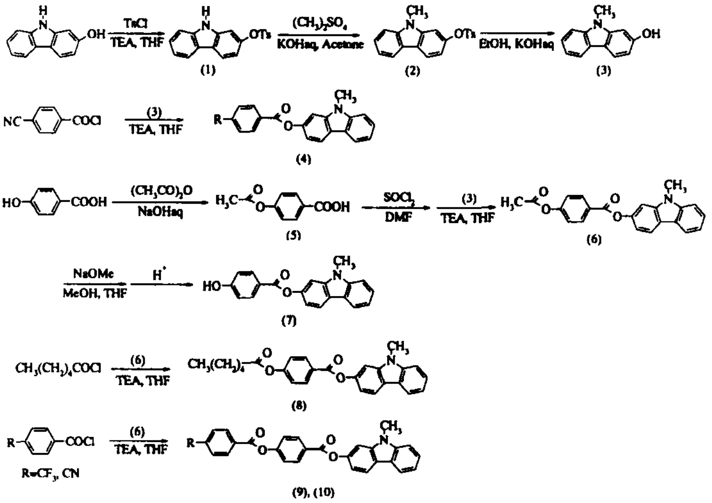


FIGURE 2 Synthesis of carbazolyl derivatives

The phase transition temperatures of carbazolyl derivatives were shown in Table 1. By differential scanning calorimetry (DSC) measurement, 6OBCzMe and 12OBCzMe connecting ether bond between the mesogen and alkyl spacer, have two phase transitions. However, mesomorphic temperature ranges are too narrow to analyze the structures of these compounds by X-ray diffraction measurement. By POM measurement, they do not show any textures, which relate to the liquid crystal.

2MBOCzMe containing asymmetric carbon atom in an alkyl spacer, do not show any texture, either. It is confirmed that no phase transition temperatures related to the mesomorphic phase are existed.

TABLE 1 Phase transition temperatures of carbazolyl derivatives

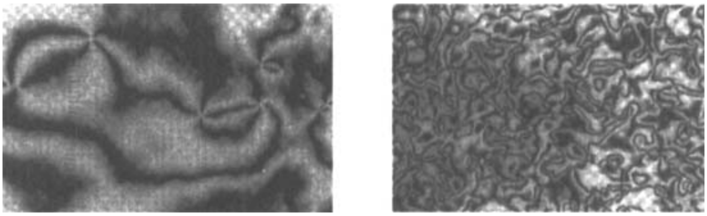
compounds	phase transition temperatures
6OBCzMe	$\mathrm{Cr} \xrightarrow{131.3} \mathrm{I} \xrightarrow{110.9} \mathrm{M} \xrightarrow{110.3} \mathrm{Cr}$
12OBCzMe	$\mathrm{Cr} \xrightarrow{157.5} \mathrm{I} \xrightarrow{118.6} \mathrm{M} \xrightarrow{117.1} \mathrm{Cr}$
NCBCzMe	$\mathrm{Cr} \xrightleftharpoons[117.0]{179.8} \mathrm{N} \xrightleftharpoons[128.4]{182.9} \mathrm{I}$
F_3CBCzMe	$\mathrm{Cr} \xrightleftharpoons[166.1]{183.3} \mathrm{I}$
2MBOCzMe	$\mathrm{Cr} \xrightleftharpoons[130.1]{158.5} \mathrm{I}$
AcOBCzMe	$\mathrm{Cr} \xrightarrow{137.9} \mathrm{Cr'} \xrightarrow{176.1} \mathrm{I} \xrightarrow{133.6} \mathrm{N} \xrightarrow{71.2} \mathrm{Cr}$
5COOBCzMe	$\mathrm{Cr} \xrightarrow{136.0} \mathrm{I} \xrightarrow{135.9} \mathrm{N} \xrightarrow{101.6} \mathrm{Cr'} \xrightarrow{98.0} \mathrm{Cr}$
F_3CBBCzMe	$\mathrm{Cr} \xrightleftharpoons[195.2]{234.3} \mathrm{N} \xrightleftharpoons[273.6]{273.8} \mathrm{I}$
NCBBCzMe	$\mathrm{Cr} \xrightarrow{206.2} \mathrm{N} \xrightarrow{280.0} \mathrm{Decom.}$

Cr : crystal, I : isotropic phase, M : mesophase, N : nematic phase
Decom. : thermal decompositon

NCBCzMe containing the cyano group as the polar moiety has two phase transitions on both heating and cooling run and shows a schlieren texture at the mesomorphic temperature ranges. By X-ray diffraction measurement, it indicates only one weak broad peak at the mesomorphic temperature in the wide-angle region shown in Figure 4 (A). The d-spacing of NCBCzMe is around 4.6Å, which corresponds to the distance between the molecules. Therefore, the liquid crystalline phase would be assigned the nematic phase.

F_3CBCzMe containing trifluoromethyl group as the polar moiety like the cyano group, does not exhibit any liquid crystalline phase.

AcOBCzMe and 5COOBCzMe connecting ester bond between the

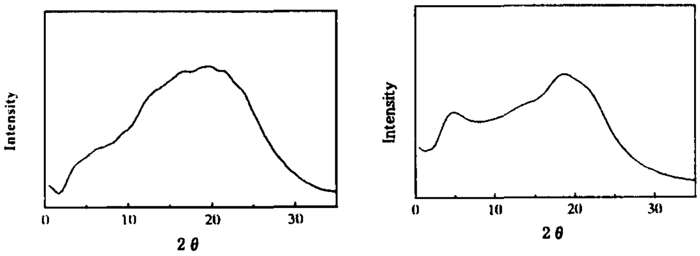


(A) (B)

FIGURE 3 Photomicrographs of carbazolylderivatives
(A) NCBCzMe (B) 5COOBCzMe

mesogen and alkyl spacer shows a schlieren texture on cooling run only. Therefore, they are assigned to the monotropic liquid crystal. By X-ray diffraction measurement, 5COOBCzMe indicates two broad peaks at around 4.5 and 19.0 degree, as shown in Figure 4 (B). One in the small-angle region was weaker than the other one. That peak would arise from the layer structure in the part of a nematic phase. Therefore, the LC phase would be assigned a cybotactic nematic phase. An appearance of a cybotactic nematic phase would be caused by an interaction of alkyl spacer.

F_3CBBCzMe, which has two phase transitions on both heating and cooling run and shows a schlieren texture at mesomorphic temperature ranges. Therefore, it is an enantiotropic liquid crystal.



(A) (B)

FIGURE 4 X-ray diffraction pattern of carbazolyl derivatives
(A) NCBCzMe (B) 5COOBCzMe

NCBBCzMe shows a schlieren texture at the mesomorphic temperature range. However, thermal decomposition is occurred at 280.0℃.

CONCLUSION

The compounds connecting ester bond between the mesogen and alkyl spacer and the compound containing cyano group exhibit liquid crystalline phase. However, the compounds connecting ether bond between mesogen and alkyl spacer, and the compound containing trifluoromethyl group do not exhibit. LC phases of NCBCzMe and 5COOBCzMe would be assigned to the nematic phase and the cybotactic-nematic phase, respectively. X-ray diffraction patterns supported these results.

EXPERIMENTAL

Characterization

^{1}H-NMR is obtained by JNM-LA400 and JNM-LA500 spectrometer using $CDCl_3$ or DMSO as a solvent. Infrared (IR) spectra were taken on JEOL JIR7000 type spectrometer. DSC measurements were conducted with Mettler DSC821^e. Heating and cooling rates were 5℃/min in all cases. Optical microscopy was performed on a Nikon polarizing optical microscopy, OPTI PHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. X-ray diffraction experiments on liquid crystal phase of the compounds were recorded with a RIGAKU RINT 2500 series. The samples in glass capillaries were held in a temperature-controlled cell.

Synthesis

2-Carbazolyl-4-toluensulfonate (1)
To a flask cooled with an ice water bath containing a solution of 2-hydroxycarbazole (15.0g, 81.9mmol) and triethylamine (17.1ml, 122.7mmol) in dry THF (150ml) was added dropwise a solution of p-toluensulfonyl chloride (15.6g, 81.9mmol) and 120ml of dry THF. The mixture was stirred under N_2 for 12h at room temperature. The

solvent was evaporated to dryness. The residue was washed with dilute KOHaq and water for several times. The yellow-brown powder was gained.

2-(9-Methylcarbazolyl)-4-toluensulfonate (2)
Dimethylsulfate (27.0g, 214mmol) was added dropwise into a mixture of 2-carbazolyl-4-toluensulfonate, KOHaq (12.9g (230mmol) of KOH in 30ml of water), and acetone (400ml), and stirred at room temperature for 30min. The solvent was evaporated and $CHCl_3$ was added. The organic phase was separated and washed with water and dilute K_2CO_3aq, and dried with $MgSO_4$. Upon distillation of the solvent, the light yellow-brown powder was gained.

2-Hydroxy-9-methylcarbazole (3)
A mixture of 2-(9-methylcarbazolyl)-4-toluensulfonate, KOHaq (27.8g (230mmol) of KOH in 30ml of water), and EtOH (500ml) was refluxed for 2h. The solvent was evaporated and diethylether was added. The organic phase was separated and washed with water and dilute HClaq, and dried with $MgSO_4$. The solvent was distilled and then the light yellow-brown powder was gained. The product was purified by column chromatography (silica gel, $CHCl_3$) to yield 4.2g (26% from 2-Hydroxycarbazole).
^{1}H-NMR ($CDCl_3$, δ ppm) : 3.75 (s, 3H), 4.96 (s, 1H), 6.71-7.99 (m, 7H)
IR (Nujol, cm^{-1}) : 3200-3600, 1598.72, 1581.36, 1488.79, 1359.59

2-(9-Methylcarbazolyl)-4-cyanobenzoate (4)
To a flask cooled with an ice water bath containing a solution of 2-hydroxy-9-methylcarbazole (1.2g, 6.32mmol), triethylamine (1.9g, 18.7mmol) in dry THF (100ml) was added dropwise a solution of 4-cyanobenzoyl chloride (1.1g, 6.64mmol) and 30ml of dry THF. The mixture was stirred under N_2 for 11h at room temperature. The solvent was evaporated to dryness. The residue was washed with dilute HClaq and water for several times, and then washed with MeOH. The product was recrystallized from MeOH/$CDCl_3$ to yield 1.0g (54.7%).
^{1}H-NMR ($CDCl_3$, δ ppm) : 3.80 (s, 3H), 7.05-7.50 (m, 5H), 7.75 (d, 2H), 8.10 (q, 2H), 8.35 (d, 2H)
IR (Nujol, cm^{-1}) : 1737.57, 1600.65

p-Acetoxybenzoic Acid (5)
A mixture of p-hydroxybenzoic acid (20g, 163mmol), NaOHaq (19.7g (493mmol) of NaOH in 300ml of water), and anhydrous acetic acid

(33.4g, 327mmol) was stirred for 1h in ice water bath. HClaq was added in the solution to precipitate the product. The precipitate was washed with water and recrystallized from MeOH to yield 16.94g (63.0%).

2-(9-Methylcarbazolyl)-4-acetoxybenzoate (6)

A mixture of p-acetoxybenzoic acid (1.0g, 5.50mmol), thionyl chloride(40ml), and small amount of N,N-dimethylformamide was stirred at 70℃ under N_2 for 5h. Thionyl chloride was evaporated under reduced pressure, and then the residue was dissolved in dry THF. The product was added dropwise into a solution of 2-Hydroxy-9-methylcarbazole (1.0g, 5.07mmol), triethylamine (1.5g, 14.8mmol), and dry THF (150ml). The mixture was stirred under N_2 at room temperature for 11h. The solvent was evaporated to dryness. The residue was washed with dilute HClaq and water for several times, and then washed with MeOH. The product was recrystallized from MeOH/$CDCl_3$ to yield 1.0g (50.3%).

^{1}H-NMR ($CDCl_3$, δ ppm) : 2.45 (s, 3H), 3.80 (s, 3H), 7.00-7.50 (m, 7H), 8.05-8.25 (m, 4H)

IR (Nujol, cm^{-1}) : 1756.85, 1726.00, 1598.72

2-(9-Methylcarbazolyl)-4-hydroxybenzoate (7)

2-(9-Methylcarbazolyl)-4-acetoxybenzoate (1.0g, 2.78mmol) was dissolved in THF (10ml). Sodium methylate (28% in MeOH) was added into the solution, and stirred at room temperature for 3min. The solution was poured into dilute HClaq (500ml) to precipitate the product. The precipitate was washed with water and filtered out to yield 0.5g (56.8%).

^{1}H-NMR (DMSO, δ ppm) : 3.85 (s, 3H), 6.90-7.55 (m, 7H), 8.00-8.20 (m, 4H)

IR (Nujol, cm^{-1}) : 3403.79, 1691.29, 1606.43

2-(9-Methylcarbazolyl)-4-pentynylcarboxybenzoate (8)

To a flask cooled with an ice water bath containing a solution of 2-(9-methylcarbazolyl)-4-hydroxybenzoate (0.4g, 1.26mmol) and triethylamine (0.38g, 3.78mmol) in dry THF (150ml) was added dropwise a solution of n-caproyl chloride (0.49g, 3.64mmol), and dry THF (30ml). The mixture was stirred under N_2 at room temperature for 11h. The solvent was evaporated to dryness. The residue was washed with dilute HClaq and water for several times, and then washed with MeOH. The product was recrystallized from MeOH/$CDCl_3$ to yield 0.2g (40.0%).

^{1}H-NMR ($CDCl_3$, δ ppm) : 0.95 (t, 3H), 1.37-1.54 (m, 4H), 1.77 (t, 2H), 2.62 (t, 2H), 3.86 (s, 2H), 7.05-7.50 (m, 7H), 8.10 (t, 2H), 8.25 (d, 2H)
IR (Nujol, cm^{-1}) : 1768.43, 1731.78, 1600.65

2-(9-Methylcarbazolyl)-4-(4-trifluoromethylbenzoyloxy)-benzoate (9)
This compound was synthesized in a procedure similar to that used for 2-(9-methylcarbazolyl)-4-pentynylcarboxybenzoate. A yield of 0.5g (54.0%) was obtained.
^{1}H-NMR ($CDCl_3$, δ ppm) : 3.86 (s, 3H), 7.08 (d, 2H), 7.10-7.30 (m, 3H), 7.40-7.51 (m, 4H), 7.82 (m, 2H), 8.11 (t, 2H), 8.35-8.39 (t, 4H)
IR (Nujol, cm^{-1}) : 1733.71, 1631.50, 1600.65

2-(9-Methylcarbazolyl)-4-(4-cyanobenzoyloxy)-benzoate (10)
This compound was synthesized in a procedure similar to that used for 2-(9-methylcarbazolyl)-4-pentynylcarboxybenzoate. A yield of 0.4g (45.3%) was obtained.
^{1}H-NMR ($CDCl_3$, δ ppm) : 3.84 (s, 3H), 7.08 (d, 1H), 7.24-7.29 (m, 3H), 7.82 (m, 2H), 8.11 (t, 2H), 8.35-8.39 (t, 4H)
IR (Nujol, cm^{-1}) : 2229.33, 1743.36, 1726.00, 1629.57, 1598.72

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