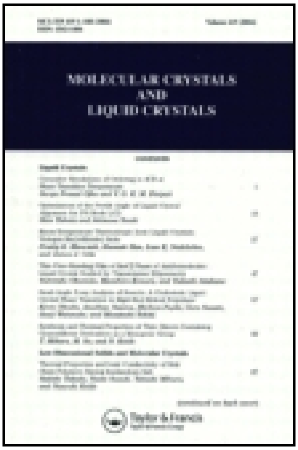

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Synthesis and Mesomorphic Properties of New T- Shaped Dimesogens

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Synthesis and Mesomorphic Properties of New T- Shaped Dimesogens

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Several new T- shaped liquid crystalline dimesogenic compounds were synthesized and their LC properties were characterized. These T-shaped dimesogens consist of substituted fluorene and substituted biphenyl units connected by flexible spacer units of varying lengths. The compounds were characterized for their liquid crystallinity by differential scanning calorimetry (DSC) and polarizing microscopy. All the compounds were found to exhibit enantiotropic nematic phase.

Keywords: dimesogens; synthesis; nematic phase

INTRODUCTION

Liquid crystalline dimers and oligomers are intermediates between low molecular mass liquid crystals and liquid crystalline polymers. The interest in phase transitions and mesomorphic properties of dimesogens consisting of similar or dissimilar mesogenic units connected by a flexible spacers have been growing in recent years. The interest in this types of materials[1-14] stems not only from their ability to act as model compounds for main chain liquid crystalline polymers but also from their quite different properties to conventional low mass liquid crystals. Liquid crystalline dimesogens in which the monomer units are attached laterally by flexible spacers have also been reported. Recently a few liquid crystalline dimesogens in which the monomer units are attached laterally to give a T- shaped geometry have been reported

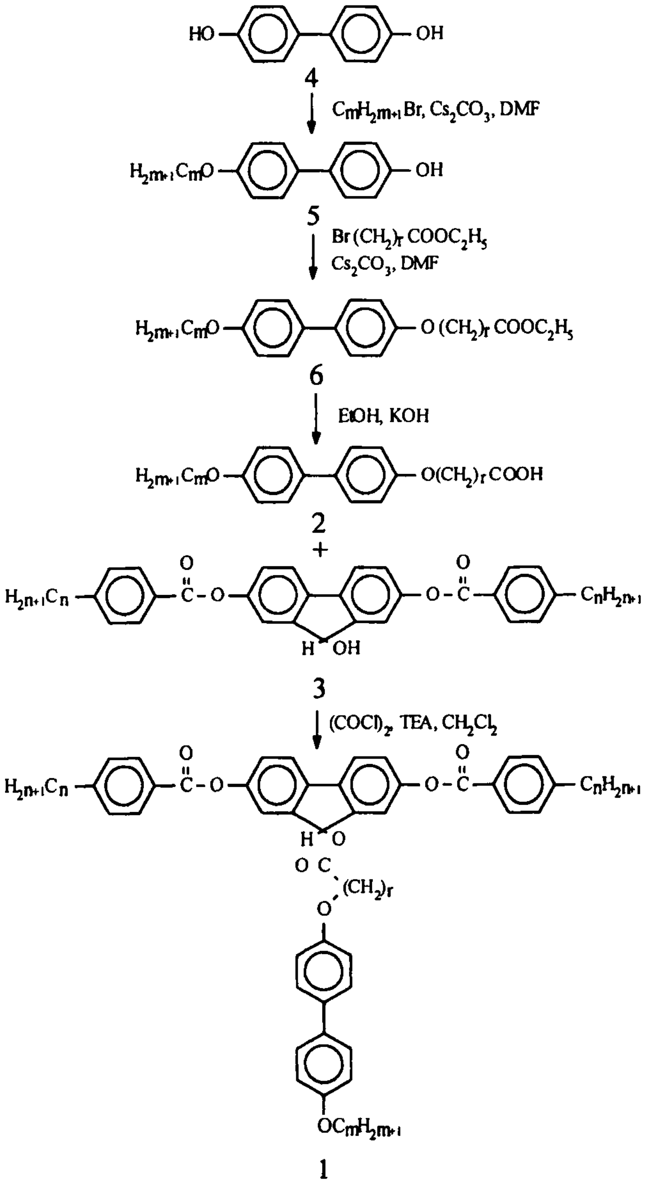
[17,18]. These materials form uniaxial nematic phase enantiotropically. The synthesis and mesomorphic properties of new T-shaped dimesogens incorporating a substituted fluorene unit and a substituted biphenyl moiety are reported here.

SYNTHESIS

The T-shaped dimesogenic compounds were prepared following the reaction sequence shown in scheme 1. 4,4′-dihydroxybiphenyl **4** was monoalkylated at ambient temperature using *n*-alkyl halide in the presence of cesium carbonate [16] in dimethylformamide. The resulting monoalkylated compound **5** was alkylated using ethyl ω-bromo-*n*-alkanoate in the presence of cesium carbonate in dimethylformamide to give the dialkylated compound **6**. The dialkylated compound **6** was subjected to alkaline hydrolysis to give the acid **2**. The substituted fluorene intermediate **3** required for the synthesis of compound **1** was prepared according to the procedure reported in our earlier publication [15]. The acid **2** was converted to its acid chloride and reacted with fluorenol **3** using TEA as the HCl acceptor to give the T-shaped dimesogenic compound **1**. A description of a representative synthetic procedure for the preparation of the compound **1 (n=6, m=6, r=10)** is given.

PROPERTIES

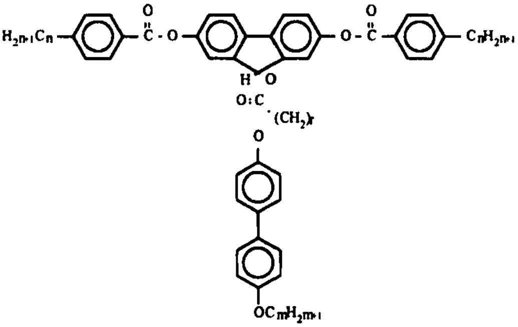
The phase transition temperature and the enthalpy of transition for the T-shaped dimesogenic compounds are given in table 1. All the dimesogenic compounds form enantiotropic nematic phase. The nematic phase was assigned by the marble optical texture which flashed when subjected to mechanical stress, combined with high mobility of the phase. Small enthalpy of nematic - isotropic transition (<4KJmol^{-1}) further substantiated the phase assignment. The melting transition and the nematic–isotropic transition temperatures decreased with increasing methylene spacer length(r). All the compounds reveal peaks corresponding to mesophase–isotropic transition on both heating


HO
OH
4
$C_mH_{2m+1}Br, Cs_2CO_3, DMF$
$H_{2m+1}C_mO$
OH
5
$Br(CH_2)_rCOOC_2H_5$
Cs_2CO_3, DMF
$H_{2m+1}C_mO$
$O(CH_2)_rCOOC_2H_5$
6
EtOH, KOH
$H_{2m+1}C_mO$
$O(CH_2)_rCOOH$
2
+
$H_{2n+1}C_n$
O
C-O
O-C
O
C_nH_{2n+1}
H
OH
3
$(COCl)_2$, TEA, CH_2Cl_2
$H_{2n+1}C_n$
O
C-O
O-C
O
C_nH_{2n+1}
H
O
O C
$(CH_2)_r$
O
OC_mH_{2m+1}
1

SCHEME 1

TABLE 1

Transition temperatures(°) for:



#	n	r	m	K	N	I
1	6	4	6	● 139.8 [64.4]	● 157.6 [1.65]	●
2	6	4	7	● 136.6 [57.6]	● 154.1 [1.43]	●
3	6	4	8	● 133.4 [58.6]	● 154.2 [1.74]	●
4	7	4	6	● 146.7 [61.0]	● 157.4 [2.10]	●
5	7	4	7	● 142.0 [63.4]	● 155.2 [2.11]	●
6	7	4	8	● 141.6 [63.0]	● 154.9 [2.83]	●
7	6	5	6	● 123.9 [54.0]	● 140.0 [2.39]	●
8	6	5	7	● 115.2 [47.7]	● 136.6 [1.86]	●
9	6	5	8	● 106.8 [50.5]	● 136.5 [1.81]	●
10	7	5	6	● 118.34 [59.1]	● 139.3 [2.22]	●
11	7	5	7	● 120.4 [60.9]	● 134.7 [3.21]	●
12	7	5	8	● 120.9 [61.3]	● 137.7 [3.93]	●
13	6	10	6	● 77.83 [41.9]	● 125.17 [2.65]	●
14	6	10	7	● 76.6 [43.5]	● 121.6 [2.52]	●
15	6	10	8	● 76.3 [43.6]	● 121.5 [2.64]	●
16	7	10	6	● 84.9 [47.0]	● 126.8 [2.95]	●
17	7	10	7	● 86.1 [46.4]	● 124.3 [2.58]	●
18	7	10	8	● 86.0 [47.1]	● 123.3 [2.35]	●

[ ] $KJmol^{-1}$

and cooling cycles. However, the larger peaks corresponding to the crystal-mesophase transition i.e. the melting transition, were observed only during the heating cycle in DSC for the compounds with longer spacers(r=10). The nematic phase exhibited by these compounds indicates that the two different mesogenic units are more or less parallel to each other. This suggests a bent conformation of the flexible spacer unit to facilitate nearly parallel arrangement of the different mesogenic units in these T-shaped dimesogenic compounds.

SUMMARY

Several new T-shaped liquid crystalline dimesogens incorporating substituted fluorene units and substituted biphenyl units were synthesized. All the compounds exhibited enantiotropic nematic phase.

EXPERIMENTAL

TLC data were collected from Anal-Tech silica gel GHLF uniplates and UV light as the detector. Flash chromatography was done on E Merck silica gel(230-400 mesh) under nitrogen(10-15 psi). IR spectra were obtained using a Pye Unicam 3-200 instrument and NMR spectra were run in $CDCl_3$ with TMS as the internal standard using Varian Gemini 200 MHz instrument. Transition temperatures (^{0}) and enthalpy of transitions were determined using DSC. The mesophases were identified using a Nikon polarizing microscope fitted with a Mettler FP 82 HT hot stage and a Mettler FP 80 central processor. DSC scans were run using Perkin Elmer DSC 4 at a heating rate of 5° / minute.

4-Hexyloxy-4′-hydroxybiphenyl, 5 (m=6)

Cesium carbonate(4.8g, 14.77mmol) was added to a stirred solution of 4,4′-dihydroxybiphenyl, **4** (3.7g, 20mmol) in dry DMF(40mL) under nitrogen and stirring was continued for 24 hr. at ambient temperature. The reaction mixture was added to distilled water(100mL) and acidified with aqueous 1N HCl. The precipitated solid was filtered, washed with water, dried, and extracted with boiling toluene(100mL). The solid obtained after evaporation of toluene under reduced pressure was purified by flash chromatography on silica gel using methylene chloride as the eluent. First few fractions contained the diether(0.6g) and the latter fractions contained the monoether. The fractions containing the monoalkylated product were combined and the solvent was evaporated under reduced pressure to give the compound **5 (m=6)** 1.83g (31.0%), mp. 158-9°, TLC(CH_2Cl_2), R_f = 0.4, IR(nujol), 3400(phenolic OH), 1450, 1390, 1275, 1050, and 840cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.8-1.0 (t, 3H, CH_3), 1.2-1.7(m, 8H, methylene H), 1.7-1.85 (m, 2H, $OCH_2\underline{CH_2}$), 3.9-4.1 (t, 2H, Ar-$O\underline{CH_2}$), 4.8(s, 1H, br, phenolic H), 6.8-7.0 (m, 4H, ArH), and 7.4-7.5 (m, 4H, ArH).

Ethyl 11-(4-*n*-hexyloxybiphenyloxy)-undecanoate, 6 (m=6, r=10)

Cesium carbonate(0.98g, 3mmol) was added at ambient temperature to a stirred solution of 4-hexyloxy-4′-hydroxybiphenyl, **5 (m=6)** (0.6g, 2mmol) in dry DMF(20mL) under nitrogen and stirred for 24 hr. The reaction mixture was added to distilled water(150mL) and acidified with aqueous 1N HCl. The precipitated solid was filtered, washed with water, dried, and recrystallized from ethanol to give the compound **6 (m=6, r=10)** 0.8g (80.0), mp 102-3° TLC($CHCl_3$: hexane, 2:1) 0.78, IR(nujol) 1720(ester carbonyl), 1500, 1465, 1180, 1280, 1260, 1180, 1030, 840, and 820cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.9(t, 3H, CH_3), 1.1-1.9(m, 16H, methylene H), 2.3(t, 2H, $\underline{CH_2}COOEt$), 3.93-3.98(t, 4H, Ar-$O\underline{CH_2}$), 4.0(q, 2H, $COO\underline{CH_2}$), 6.9-6.95(t, 4H, ArH), and 7.41-7.47(m, 4H, ArH).

11-(4-*n*-Hexyloxybiphenyloxy)-undecanoic acid 2 (m=6, r=10)

A solution of potassium hydroxide (0.5g, 12mmol) in water (1ml) was added to a boiling solution of ester **6 (m=6, r=10)** (0.6g, 1.24mmol) in ethanol (25ml) and the mixture was heated under reflux for 4 hr. The cooled reaction mixture was added to cold water(100ml) and acidified with 1N HCl.. The solid was filtered, washed with water, dried, and recrystallized from acetic acid to give the white crystalline compound **2,** 4g, (80%), mp. 148-9°, IR (nujol) 1690(acid carbonyl) 1510, 1485, 1260, 1040, 840, and 810 cm^{-1}; The NMR data could not be obtained due to poor solubility of the material in $CDCl_3$, acetone, and DMSO.

2,7-Di-(4-*n*-hexylphenylcarbonyloxy)-fluoren-9-ol, 3 (n=6)

The detailed synthetic procedure for the preparation of this compound **3 (n=6)** has been described in our earlier publication [15].

2,7-Di-(4-*n*-hexyl-4-carbonyloxyphenyl)-9-[10-(4-*n*-hexyloxy biphenyloxy)-decylcarbonyloxy]-fluorene, 1 (n=6, m=6, r=10)

The carboxylic acid **2 (m=6, r=10)** (0.15g, 33mmol), oxalyl chloride (0.5ml) and a drop of DMF was stirred at ambient temperature for half an hour and the solvents were removed under reduced pressure to give the crude acid chloride. The solution of the crude acid chloride in methylene chloride was added to a stirred solution of compound **2 (n=6)** (0.195g, 0.33mmol) in dry methylene chloride (20ml) and TEA (0.5ml) at ~ 4°. The mixture was stirred at ambient temperature for 24 hr., washed with water, dried, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography using 1:1 mixture of chloroform and hexane as the eluent. The material was crystallized using a mixture of ethanol and chloroform to give the compound **1 (n=6, m=6, r=10)**, 0.18g (60%) mp. 77-8°, TLC ($CHCl_3$: hexane, 2:1) R_f =0.69, IR (nujol) 1740 (ester carbonyls)1500, 1480, 1380, 1280, 1260, 1220, 1200, 1180, 1150, 1080, 1000 and 960 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.9 (t, 9H, methyl H), 1.1 –1.9 (m, 40, methylene H), 2.4 (s, 2H, $\underline{CH_2}COO$), 2.5 (t, 4H, Ar-$\underline{CH_2}$), 3.95 (m, 4H, Ar-O$\underline{CH_2}$), 6.8(s, 1H, Fluorene H9), 6.95-7.0 (m, 4H, ArH), 7.2-7.45 (m, 12H, ArH), 7.7 (d, 2h, ArH), and 8.1 (d, 4H, ArH).

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References

[1] A.C. Griffin and T.R. Britt, *J. Am. Chem. Soc.*, **103**, 4957 (1986).

[2] R.W. Date, C.T. Imrie, G.R. Luckhurst, and J.M. Seddon, *Liq. Cryst.*, **12**, 203 (1992).
[3] G.S. Attard, R.W. Date, C.T. Imrie, G.R. Luckhurst, S.J. Roskilly, J.M. Seddon, and L. Taylor, *Liq. Cryst.*, **16**, 529 (1994).
[4] A.E. Blatch and G.R. Luckhurst, *Liq. Cryst.*, **27**, 775 (2000).
[5] F. Hardouin, M.F. Achard, J-I. Jin., J.-W. Shin, and Y.-K. Yun, *J. Phys. II Fr.*, **4**, 627 (1994).
[6] T.M. Antonius, A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudholter, *Liq. Cryst.*, **16**, 843 (1995).
[7] P.J. Barnes, A.G. Douglass, S.K. Heeks, and G.R. Luckhurst, *Liq. Cryst.*, **13**, 603 (1993).
[8] F. Hardouin and M.F. Achard, *Liq. Cryst.*, **14**, 971 (1993).
[9] A.C. Griffin and S.R. Vaidya, *Liq. Cryst.*, **3**, 1275 (1988).
[10] F. Hardouin, M.F. Achard, J.-I. Jin, and Y.-K. Yun, *J. Phys. II Fr.*, **5**, 927 (1995).
[11] F. Hardouin, M.F. Achard, J.-I. Jin, and S.-J. Chung, *Eur. Phys. J.*, **1**, 47 (1998).
[12] S.M. Huh and J.-I. Jin, *Liq. Cryst.*, **25**, 285 (1998).
[13] V. Surendranath, *Mol. Cryst. Liq. Cryst.*, **332**, 135 (1999).
[14] V. Surendranath and D.L. Johnson., *Mol. Cryst. Liq. Cryst.*, **303**, 305 (1997).
[15] J.P. Parrish, B. Sudaresan, and K.W. Jung, *Synth. Commun.*, **29**, 4423 (1999).
[16] J.-I. Jin, J.-S. Kim, Y.-K. Yun, and W.-C. Zin, *Mol. Cryst. Liq. Cryst.*, **308**, 99 (1997).
[17] J.-W. Lee, X.L. Piao, Y.-K. Yun, J.-I. Jin, Y.-S. Kang, and W. C. Zin, *Liq. Cryst.*, **26**, 1671 (1999).