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SYNTHESES AND MESOMORPHIC PROPERTIES OF NEW LATERALLY ATTACHED MESOGENIC DIMERS

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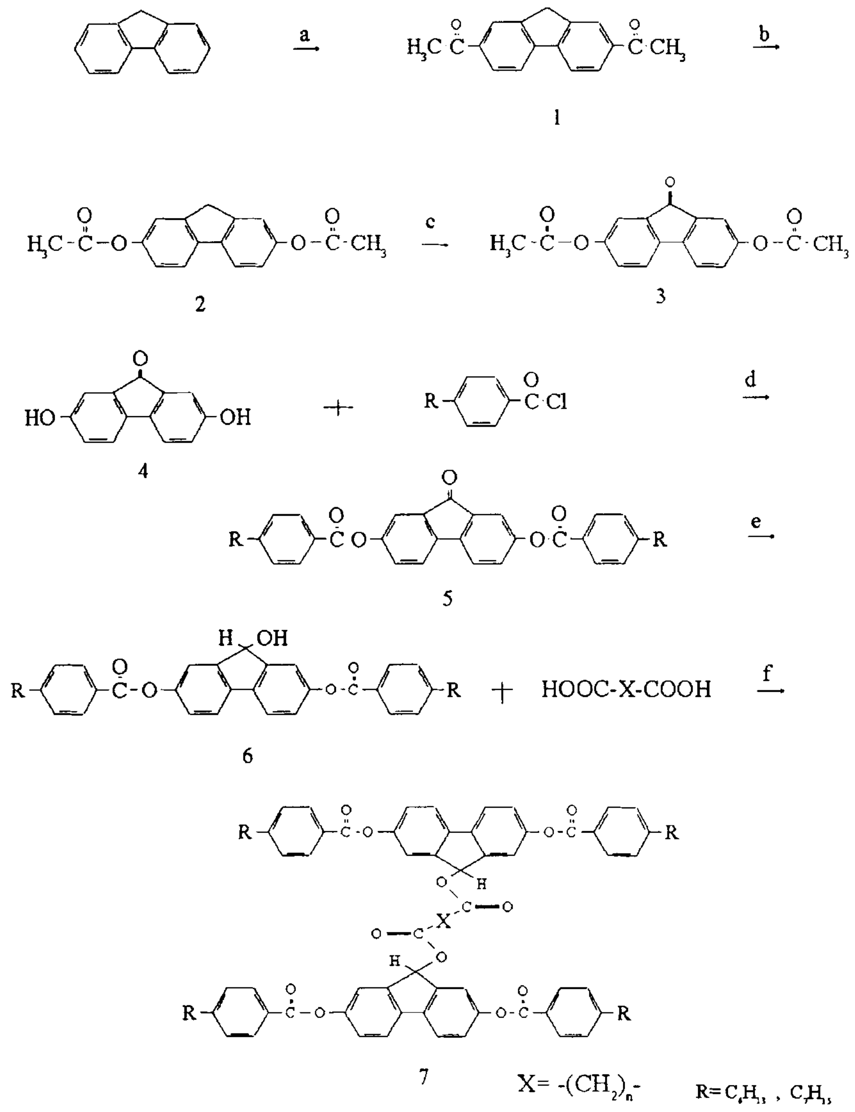
Abstract The syntheses and mesomorphic properties of novel laterally attached non-chiral and chiral dimers have been reported. The reported non-chiral dimers showed monotropic nematic phase and the chiral dimers showed monotropic cholesteric phase.

INTRODUCTION

Liquid crystalline dimers, trimers and oligomers are intermediates between low molecular mass liquid crystal materials and liquid crystalline polymers. The interest in dimeric mesogens, in particular, stems not only from their ability to act as model compounds for liquid crystalline polymers but also from their quite different properties to conventional low mass liquid crystals[1]. For instance, the transitional properties of dimers are known to be dependent on the length and the parity of the flexible spacer, *i.e.* the members of the series with an even number of atoms in the spacer have significantly higher nematic-isotropic transition temperatures than those members with an odd number of atoms. Several terminally attached liquid crystalline dimers have been investigated[2-4] extensively in recent years. Very few laterally attached dimers have been reported in literature as compared to terminally attached dimers. We report here the syntheses and mesomorphic properties of new laterally attached liquid crystalline dimers incorporating a 2,7-disubstituted fluorine as the monomer unit.

SYNTHESIS

The synthesis of monomers and the laterally attached dimers was accomplished following the reaction sequence shown in scheme1.The reactive intermediate 4 required for the preparation of the monomers was synthesized starting from readily available fluorene. Synthesis of this material has been reported by Hornor *et.al*[5] and it involves several steps. We describe here an alternative synthesis involving a fewer number of steps. Fluorene was diacetylated using acetyl chloride and aluminum chloride and the resulting 2,7-diacetylfluorene was subjected to Bayer-Villiger



a) CH_3COCl / $AlCl_3$ b) MCPB / $CHCl_3$ c) $Na_2Cr_2O_7$ / CH_3COOH

d) PYRIDINE e) $NaBH_4$ / EtOH f) DCCI / DMAP

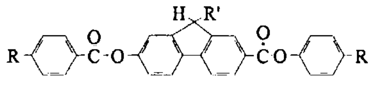
SCHEME-1

oxidation to give 2,7-diacetoxy fluorene. Oxidation of the diacetoxy compound using sodium dichromate and subsequent alkaline hydrolysis provided the desired intermediate 4. 2,7-Dhydroxyfluorenone 4 was esterified with 4-n-alkylbenzoyl chloride in pyridine and the resulting keto diester was reduced with sodium borohydride. The liquid crystalline dimers were prepared by reacting the hydroxy compound 6 with aliphatic dicarboxylic acids in the presence of dicyclohexyl cabodiimide and dimethylaminopyridine. All the compounds were purified by crystallization and flash chromatography until they showed a single spot on TLC and the NMR indicated the absence of impurities. As a typical example the synthesis of Bis [9 (2,7-di-n-hexylphenylcarbonyloxy) fluorenyl] glutarate is described in detail.

PROPERTIES

The phase transition temperatures of the monomers and the dimers are given in tables 1 and 2 respectively. The monomers with lateral hydroxyl substituent showed nematic phase. The acetyl derivative is nonmesomorphic. The non-chiral dimers showed monotropic nematic phase and the chiral dimers showed monotropic cholesteric phase. The isotropic to nematic phase transition enthalpy (0.3-0.6cal/g) is consistent with N-I transition. The transition enthalpy of nematic to cholesteric transition is also small (0.3-0.45 cal/g). The transition temperature of the terminally attached dimers are known to depend on the length and parity of the spacer. The change in the spacer length gave only the monotropic nematic phase. The appearance of the nematic phase for the dimer (x=$(CH_2)_5$) a few degrees below the melting temperature indicates that longer spacers could induce enantiotropic mesophase. The melting temperatures are also appreciably affected by the spacer length. The melting temperature of the dimer decreases with an increase in the chain length at the terminal ends of the monomer unit. In the case of terminally attached

Table 1
Transition temperatures(°) for

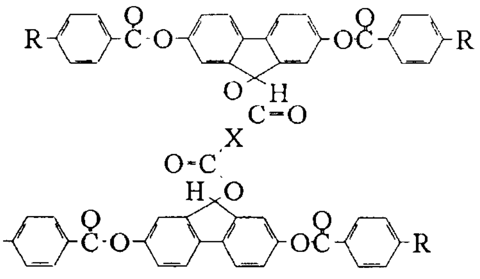


R	R'	K		N		I
C_6H_{13}	OH	.	181.8	.	191.8	.
C_7H_{15}	OH	.	173.7	.	210.5	.
C_6H_{13}	OAc	.	115.9			.

dimers it has been observed that the compounds become smectogenic when the alkyl chain length is increased. Studies are underway to understand similar effects in the case of laterally attached dimers reported here.

Table2

Transition temperatures(^{0})for



R	X	K		N	I
C_6H_{13}	$(CH_2)_2$	.	178.0	[.87.0]	.
C_6H_{13}	$(CH_2)_3$	.	143.0	[.105.0]	.
C_6H_{13}	$(CH_2)_4$	.	162.8	[.129.8]	.
C_7H_{15}	$(CH_2)_3$	.	128.5	[.105.0]	.
C_7H_{15}	$(CH_2)_4$	.	145.0	[.128.0]	
C_7H_{15}	$(CH_2)_5$	.	135.2	[.131.3]	.
		K		CH	I
C_6H_{13}	$CH_2C{*}H(CH_3)CH_2$	.	152.9	[.118.0]	.
C_7H_{15}	$CH_2C{*}H(CH_3)CH_2$	.	121.2	. [.119.1]	.

CONCLUSIONS

The synthesis and mesomorphic properties of new laterally attached dimers have been reported. The non-chiral dimers showed a monotropic nematic phase and the chiral dimers showed a monotropic cholesteric phase.

EXPERIMENTAL

The n-alkylbenzoyl chloride and (R)-(+)-3-methyladipic acid were purchased from Aldrich Chemical Co. TLC data were collected from Anal-Tech silica gel GHLF Uniplates and UV light as detector. Flash chromatography[6] 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 and mesophase identification were determined using Leitz polarizing microscope fitted with a modified FP-2 heating stage. DSC scans were run using a Perkin Elmer DSC4 at a heating rate of 5^0 per minute.

2,7-Dacetylfluorene, 1

To a stirred suspension of fluorene (8.3g, 0.05mol) and $AlCl_3$ (14.6g , 0.11mol) in anhyd carbon disulfide at 0^0 was added dropwise a solution of acetyl chloride (8.66g, 0.11mol) in carbon disulfide (20ml). The reaction mixture was stirred at ambient temperature for 24hr, and heated under reflux for 1hr. The solvent was removed under reduced pressure and poured into a mixture of conc HCl (50ml) and ice-water (100ml) and stirred for 4hr. The precipitated solid was filtered washed with water repeatedly , dried and purified by crystallization from EtOH to give the diacetyl compound 1: 8.5g (68%), mp. 180-2 , TLC (CH_2Cl_2) R_f=0.16, IR (nujol) ,1680, 1660, (ketone) , 1600, 1250, 870 and 810cm^{-1} and ^{1}H NMR ($CDCl_3$) δ 2.65 (s. 6, CO$\underline{CH_3}$) , 3.95 (s , 2, $-CH_2$) ,7.8(d,2, J=8.1Hz , ArH), 8.05 (m, 2, ArH) , and 8.15(s, 2, ArH).

2,7-Diacetoxyfluorene, 2

To a stirred solution of diacetyl fluorene 1, (2.5g , 0.01mol) in $CHCl_3$ (50ml) at 0^0 and protected from light was added in small portions m-chloroperbenzoic acid (4.52g , 0.026mol) and the mixture was stirred at ambient temperature for three days. The resulting suspension was washed repeatedly with 5% aq $NaHCO_3$, water, dried over anhyd Na_2SO_4 and filtered and the filtrate was rotovaped to give the crude product. Recrystallization of the material gave diacetoxy fluorene 2: 1.9g (68-70%)mp. 165-6, TLC (CH_2Cl_2) R_f=0.42 and IR (nujol) 1740 (s, ester C=O), 1460, 1210, 1110, 1010, 900 and 830 cm^{-1}and ^{1}H NMR ($CDCl_3$) δ 2.34 (s ,6 , $OCOCH_3$), 3.84 (s , 2 $-CH_2$) , 7.1 (m , 2, ArH), 7.3 (s , 2, ArH) 7.7 (d , 2 , j=8Hz, ArH).

2,7-Diacetoxyfluoren-9-One, 3

Finely powdered sodium dichromate (2.5g) was added in small portions to a boiling solution of diacetoxy compound 2 (0.5g , 1.8mmol) in glacial acetic acid (25ml) and the reaction mixture was heated under reflux for 1hr after the addition was complete. The cooled reaction mixture was added to ice-cold water (200ml), stirred for 1hr , filtered, and the solid was washed with water. Recrystallization of the dried yellow solid from EtOH/$CHCl_3$ gave the ketone 3: 0.25g (48-50%) mp. 228-30, TLC (CH_2Cl_2) 0.16 and IR (nujol) 1750 (s , ketone), 1730 (s , ester), 1450, 1200, 1010, 930, 900, and 840 cm^{-1}. The solubility of compound 3 in $CHCl_3$ acetone, and DMSO was very poor for obtaining NMR data.

2,7-Dih ydroxyfluoren-9-one , 4

A mixture of diactoxyfluorenone 3 (0.5g, 1.69mmol), KOH (0.2g ,3.5mmol) in EtOH (20ml) and water (4ml) was heated under reflux for 2hr. The cooled reaction mixture was added to water (50ml) and acidified with dil HCl and the precipitated solid was washed with water repeatedly to give the crude phenolic compound. Recrystallization from aq EtOH gave the ketone 4: 0.28g (78%), mp.235-7(dec) IR (nujol) , 3400(ArOH),and 1740 (ketone) and ^{1}H NMR ($CDCl_3$/ DMSO-D6) δ 6.8-7.2(m ,6 , ArH) and 9.45 (b , ArOH).

2,7-Di- (4-n-hexylphenylcarbonyloxy) fluoren-9-one , 5

4-n-Hexylbenzoyl chloride (0.67g ,3mmol) was added to a stirred solution of fluorenone 4 (0.3g ,1.4mmol) in pyridine at 0^0 and the stirring was continued for 24hr at ambient temperature. The reaction mixture was poured into ice-cold water (200ml) , stirred for 1hr and the precipitated yellow material was washed with water repeatedly and dried to give the crude ester. Recrystallization of the crude product from EtOH/$CHCl_3$ gave the pure diester 5: mp. 191-2 , TLC ($CHCl_3$) , R_f=0.48 and IR (nujol) 1750 (s , ketone), 1730 (s , ester C=O) ,1460, 1270, 1060, 850 and 800cm^{-1} and ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 6, -CH_2CH_3) , 1.3 (m ,12 , methylene H) 1.5-1.7 (m ,6 , methylene H) , 2.7 (t, 4 , j=8.0Hz ,$ArCH_2$) , 7.5-7.7 (m , 3 ,ArH,Fluorine ring), 8.15 (d , 4 , j=8.0Hz , ArH).

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

Sodium borohydride (0.25g ,0.68 mmol) was added to a stirred solution of fluorenone 5 (0.4g , 0.68 mmol) in EtOH (10ml) and CH_2CL_2 (10ml) and the stirring continued until the yellow color of the solution disappeared. The reaction mixture was diluted with water (50ml), and extracted with CH_2Cl_2 (3x25ml). The CH_2Cl_2 extract was washed with water, dried over anhyd Na_2SO_4, filtered, and rotovaped to give the crude product. Recrystallization from EtOH/ $CHCl_3$ gave the pure compound 6: mp. 181-2, TLC (CH_2Cl_2) R_f=0.23 and IR (nujol) 3480 (ArOH) , 1635 (s , ester C=O) , 1610, 1380 , 1290, 1210, and 1180 cm^{-1} and ^{1}H NMR ($CDCl_3$) δ 0.86-0.9 (t, 6 , -CH_2CH_3) , 1.2-1.7 (m , 16 , methylene H) 2.68 (d, 1 , j=10Hz , O-H) , 2.7 (t, 4 , J=7.9Hz), 5.55 (d, 1, J=10Hz , 9H in the fluorine ring) , 7.15-7.35 (m, 6 , ArH) , 7.45 (s , 1 , 1H in fluorine ring), 7.65 (d, 2 , J=8Hz ArH , ortho to alkyl chain) and 8.15 (d, 4 , J=8.0Hz , ArH , ortho to ester in fluorine ring).

Bis[9(2,7-dihexylphenylcarbonyloxy)fluorenyl] glutarate , 7

To a solution of fluorenol 6 (0.2g, 0.29mmol), glutaric acid (0.13g, 0.08mmol) and DMAP (0.13, 0.1mmol) in CH_2Cl_2 (10ml) was added DCC (0.041g ,0.1mmol). The resulting solution was stirred for three days. After removal of solvent by evaporation, the residue was washed with EtOH and the product was purified by flash chromatography on silica gel with 1% EtOAc in CH_2Cl_2 as the eluent.

Crystallization from EtOH/$CHCl_3$ gave the pure dimer 7: 0.1g (47%), TLC (CH_2Cl_2) R_f=0.27, IR (nujol) 1730 (s, ester), 1460, 1250, 1200, 1080, and 1010 cm^{-1} and ^1H NMR ($CDCl_3$) δ 0.88 (t, 6, CH_2CH_3), 1.2-1.4 (m, methylene H), 1.52-1.62 (m, methylene H) 2.1 (m, 2, $\underline{CH_2}CH_2COO$), 2.55 (t, 2, $\underline{CH_2}COO$), 2.7 (t, 8, J=8.0Hz, $ArCH_2$), 6.75 (s, 1, 9H in fluorene ring), 7.15-7.3 (m, 12, ArH), 7.65 (d, 2, J=8.0Hz, ArH ortho to alkyl chain) and 8.15 (d, 8, ArH in phenyl ring ortho to ester).

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