Synthesis and Mesomorphic Properties of Polymethylene-α,ω-bis [2-thio-5-(4',4''n-alcoxybenzoyloxy)phenyl]-1,3,4-oxadiazole

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Three homologous series of polymethylene-α,ω-bis[2-thio-5(4',4"n-alkoxybenzoyloxy)-phenyl]-1,3,4-oxadiazole (series **5 a, b, c**), are reported.The compounds have identical mesogenic units at both ends of a spacer (*i.e.* they are twins). These twins possess a spacer of 6, 8 and 10 carbon atoms joined directly to the oxadiazole ring through sulphur atoms. The lateral alkylic chains vary between 6 and 10 carbon atoms.The presence of enantiotropic and monotropic nematic phase is related to the length of the spacer group.

The influence of molecular structure on the mesomorphic properties has been studied. Mesomorphic properties and phase transitions have been determined using polarizing hot-stage microscopy and differential scanning calorimetry.

Introduction

The investigation of the relationship between molecular structure and properties in liquid-crystalline twins compounds is of great interest.

During the last decades these compounds had obtained great attention [1 - 5]. The twins may be considered as liquid crystal prepolymers which are well suited for theoretical modelling. Lately twins are considered in numerous publications as model compounds for main chain polymers [6 - 7]. In addition, they are used for conformational analysis by means of ^{2}H NMR spectroscopy in compounds with deuteriated spacers [8 - 9].

Besides of the chemical structure and the geometrical shape of the mesogenic units, the nature of their linking and the length of the spacer have a remarkable influence on the mesomorphic behaviour [10 - 14].

In this paper we describe the synthesis and mesomorphic properties of three new homologous series of twins liquid crystals containing the 1,3,4-oxadiazole heterocycle with a flexible polymethylenic spacer joined to the mesogen by means of sulphur atoms **5(a, b, c)**.

Results and Discussion

Three homologous series of polymethylene -α,ω-bis([2-thio - 5(4',4 "n-alkoxybenzoyloxy)phenyl])-1,3,4-oxadiazole (series **5 a, b, c**) were prepared according to Scheme 1.

5 (a,b,c)
5a x = 6
5b x = 8
5c x = 10
R = C_nH_{2n+1}, n = 6 -10

The homologous series **5** was synthesized by using 4-hydroxyphenyl-hydrazide **1** as a precursor [15]. The treatment of **1** with carbon disulfide in basic medium produces thiones **2**, according to the procedure reported in reference [16 - 17]. In the following sequences, the selective S-alkylation of **2** leads to the homologous series of the oxadiazoles **3**.By esterification of **3** with p-n-alkoxybenzoyl chlorides previously synthesized **4**, the homologous series **5(a, b. c)** were obtained after purification by recrystallization from dimethylformamide/water.

All the homologue of series **5a** present a crystal-crystal transition and a nematogenic enantiotropic behaviour with exception of the monotropic compound with n = 10.

The homologue of series **5b** with n = 7 and 8 present a crystal-crystal transition, those with n = 6

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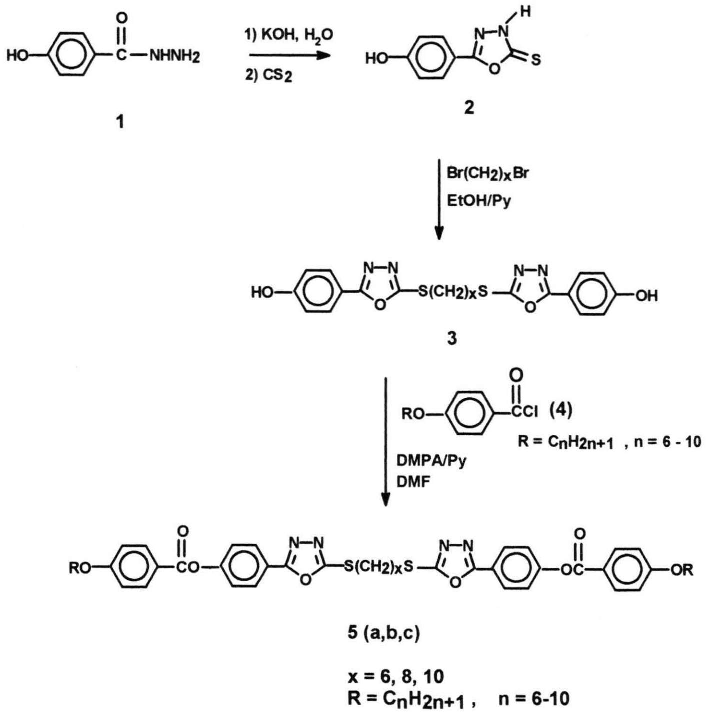

Scheme 1. Synthetic routes for twin mesogens.

Table I. Transition temperatures (°C), transition enthalpies (kJ/mol) and yields (%), data for the series **5a**.

n	K		K₁		N		I	Yields
6	.	134	.	174 (33,9)	.	185 (3,8)	.	7
7	.	130	.	152 (31,8)	.	172 (3,2)	.	21
8	.	135	.	155 (78,5)	.	173 (0,94)	.	35
9	.	119	.	167 (36,9)	.	174 (4,2)	.	25
10	.	112	.	162 (29,1)	.	160*	.	4

K = crystal; K_1 = crystal-crystal; N = nematic; I = isotropic; ( ) = ΔH (kJ/mol); * = transition monotropic.

Table II. Transition temperatures (°C), transition enthalpies (kJ/mol) and yields (%), data for the series **5b**.

n	K		K₁		N		I	Yields
6	.	-	.	157 (43,2)	.	181 (4,7)	.	24
7	.	108	.	151 (33,7)	.	161 (3,6)	.	35
8	.	131	.	142 (66,0)	.	133*	.	18
9	.	-	.	140 (58,4)	.	138*	.	36
10	.	-	.	137 (75,1)	.	131*	.	32

K = crystal; K_1 = crystal-crystal; N = nematic; I = isotropic; ( ) = ΔH (kJ/mol); * = transition monotropic.

and 7 a nematogenic enantiotropic behaviour, and the compounds with n= 8 - 10 are monotropic.

In the homologous series **5c** the compounds with n = 7 present a crystal-crystal transition and those with n = 6-8 present a nematogenic monotropic behaviour, those with n = 9 and n = 10 do not present liquid crystalline properties.

The temperatures and transtion enthalpies are shown in Tables I, II and III, respectively. The phase transition temperatures versus the number of carbon atoms of the alkylic chain (n) are plotted in Fig. 1.

The homologous series **5 (a, b, c)** presents a regular decrease of the transition temperature from nematic to isotropic with an increase of both spacer size and of the alkylic chains. The even-odd number effect where the mesophase of the compounds having even-numbered polymethylene units is of a higher degree order at the transition temperature

Table III. Transition temperatures (°C), transition enthalpies (kJ/mol) and yields (%), data for the series **5c**.

n	K		K_1		N		I	Yields
6	.	-	.	145 (77,2)	.	128*	.	6
7	.	143	.	153 (81,3)	.	143*	.	30
8	.	144	.	152 (81,6)	.	142*	.	33
9	.	-	.	151 (96,8)	.	-	.	35
10	.	-	.	153 (67,1)	.	-	.	28

K = crystal; K_1 = crystal-crystal; N = nematic; I= isotropic; ( ) = ΔH (kJ/mol); * = transition monotropic.

than the one with odd-numbered, is not observed, confirming that this behaviour is not always valid [18].

The mesophases present a low mesomorphic range. The nematic mesophase is favored, but it possesses low stability. This could be related to the deviation from linearity due to the presence of the oxadiazole heterocycle [16].

Mesophase texture were observed through a polarized light microscope and compared with the literature [19]. The nematic mesophase presented a marbled and schlieren type texture.

The transition temperatures and enthalpies were determined by DSC.

Experimental

The structure of the synthesized compounds were confirmed by FT-IR spectroscopy (Nicolet, Magna-IR^{TM}550), ^{1}H and ^{13}C NMR spectroscopy (Bruker AC-250).

The liquid crystalline properties were studied with an Ortholux Pol-BK-II polarizing microscope with Mettler FP 82 hot stage and Mettler FP 80 central processor.Measurements of temperatures and enthalpies of transition were carried out using a DSC (STA 625), differential scanning calorimeter with a heating and cooling rate of 10°c/min, calibrated with Indium (99.99%) and operated under nitrogen.

Synthesis of polymethylene bis-α(ω-2-thio-5(p-hydroxy)-phenyl-1,3,4-oxadiazole 3(a,b,c)

General method [16]: The series **3** were synthesized according to the procedure given in [17, 18]. 13.0 mmol (1.32 g, 1.80 ml) of pyridine and 13.0 mmol of a,w-dibromoalkanes were added drop by drop to a stirred solution of 52.0 mmol (10.0 g) of **2** in 26 ml of absolute ethanol. The mixture was refluxed for 8 h, filtered and the precipitate was crystallized from DMF/water (4:1). Fusion temperature: 21°C, yield 24%.

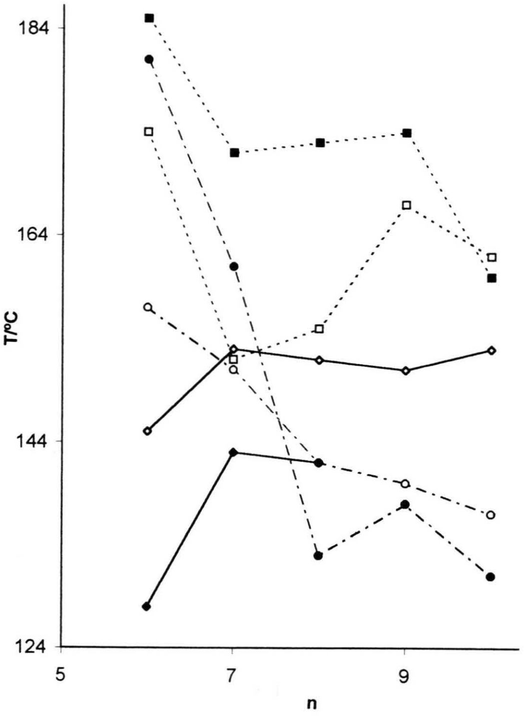

Fig. 1. The phase transition temperatures of the series **5a** (□, ■); **5b** (○, ●); **5c** (◇ ,◆); □, ○ K_1-N; ■, ● N-I; ◇ K_1-I ; ◆ I-N (n is the number of C-atoms in the substituent R).

Spectroscopy characterization of the homologue **3b** *with n = 8*

^{1}H NMR (d_6-DMSO, TMS, 250 MHz): δ(ppm) = 10.37 (2H, 2OH); 7.85 (d, J = 8.7 Hz, 4H C_6H_4); 7.05 (d, J = 8.7 Hz, 4H C_6H_4); 3.34 (t, J = 7.2 Hz, 4H, $2SCH_2$); 1.82 (m, 4H, $2CH_2$); 1.40 (m, 8H, $4CH_2$).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) = 165.22; 162.62; 160.72; 128.27; 116.12; 113.82 (C arom.); 32.90; 28.90; 28.14; 27.66 (aliphatic carbons)

Synthesis of polymethylen bis - α,ω -[2-thio-5(4',4''-n-alkoxy benzoiloxy) phenyl]-1,3,4-oxadiazole 5(a,b,c)

General method [16-17]: To a solution containing 1.06 mmol (0.5 g) of **3**, 0.011 g of 4-dimethylamonopyridine (DMPA) and 0.2 ml of dry pyridine in 10 ml of dry dimethylformamide,was added 2.34 mmol (0.56 g) of *p*-n-alkoxybenzoyl chlorides (**4**). The mixture was stirred for 24 h at room temperature, filtered and the white precipitate was crystallized from ethanol. The transition temperatures, enthalpies and the yields are given in Tables I, II and III.

Spectroscopic characterization of the homologue **5b** *with* $n = 7$

^{1}HNMR ($CDCl_3$, TMS, 250 MHz): δ(ppm) = 8.15 (d, J = 8.85, 4H C_6H_4) ; 8.05 (d, J = 8.85, 4H, C_6H_4); 7.40 (d, J = 8.83, 4H, ring joined to 1,3,4-oxadiazole); 7.00 (d, J = 8.83, 4H, ring joined to 1,3,4-oxadiazole); 4.05 (t, J = 6.53, 4H, $2OCH_2$); 3.30 (t, J = 7.28, 4H,$2SCH_2$); 1.85 (m, 8H, $4CH_2$); 1.40 (m, 24H, $12CH_2$); 0.90 (t, J = 6.61, 6H, $2CH_3$)

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ (ppm) = 174.01 (C=O, ester); 165.09; 164.687; 164.375; 163.79; 153.65; 132.34 ; 127.99; 122.61; 120.33; 114.39 (C arom.); 68.35; 32.57; 31.70; 29.08; 28.87; 28.40; 25.89; 22.56; 14.01 (alkyl chain carbons)

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