

Synthesis and properties of thermotropic compounds with two terminal mesogenic units and a central spacer

Homologous series of polymethylene

- α , ω -bis[4-(4'-n-hexyloxybenzoyloxy)benzoate]

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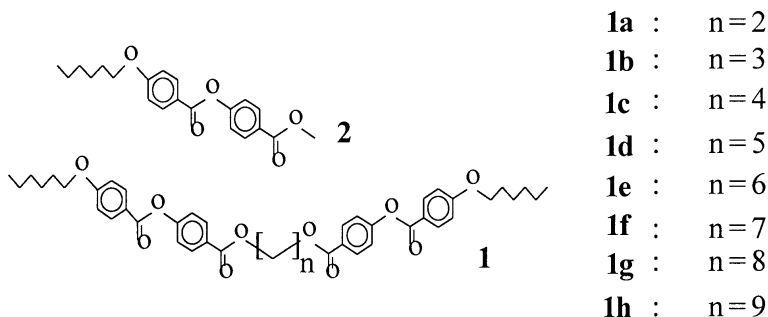
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SUMMARY

A new series of aromatic esters with two terminal mesogenic units and a central spacer **1** together with the free rodlike mesogenic ester unit **2**, was synthesized and studied. The mesogenic properties of these compounds were investigated by differential scanning calorimetry, polarizing microscopy and X-ray diffraction.

INTRODUCTION

Typical mesogenic groups linked by flexible spacers or twins have been studied as precursor models of main chain mesogenic units linked by flexible spacer polymers. Character and length of spacers, as well as character of mesogen groups have been reported [1 - 11]. The anisotropic structures formation trend increases as spacer length does, appearing first nematic and later smectic mesophases. Alternant behaviour for transition temperatures, enthalpy and entropy depending even or odd atom number on spacer main chain has been observed. [12-16]. This effect has been explained based on molecular geometry considerations. Here we offer a more deep sight of phenomena thanks to X-ray diffraction of oriented mesophases and scale molecular models.



EXPERIMENTAL

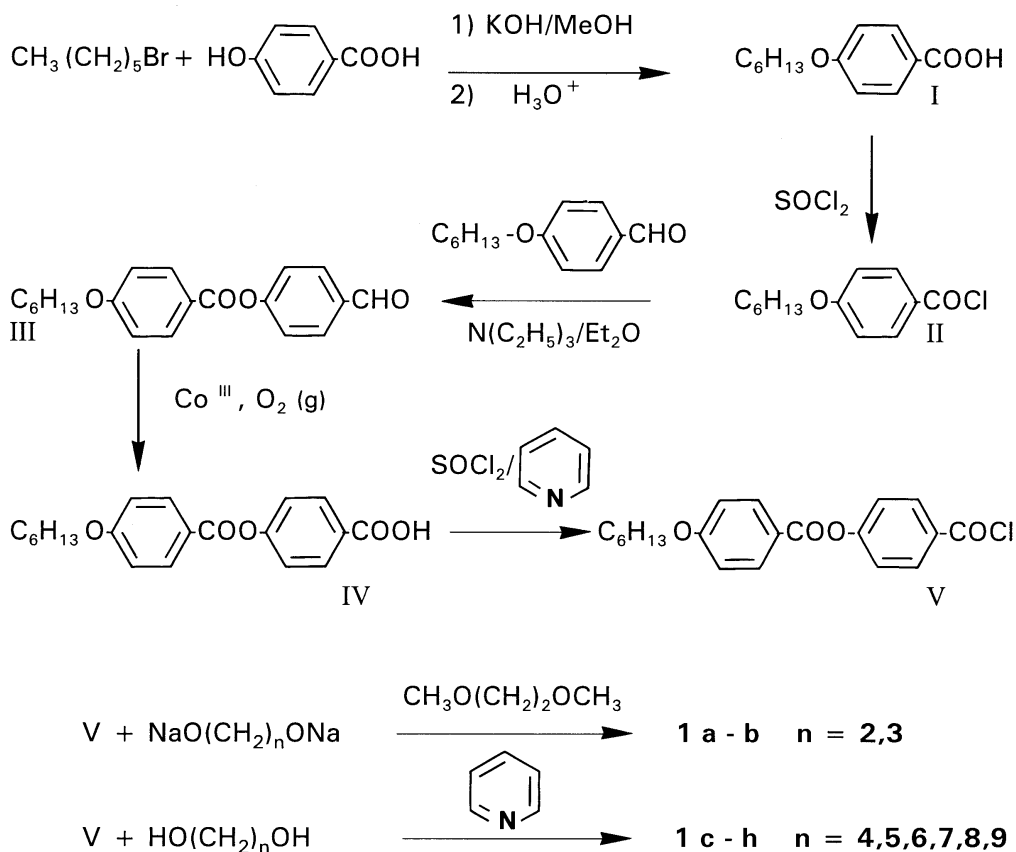
Materials

Aldrich and Merck reagents were used without further purification. Analytical TLC was conducted on precoated silica gel fluorescent plates and UV lamp was used as detector. Ethylacetate was used as mobile phase.

Synthesis

4-n-hexyloxybenzoic acid **I** was obtained by Jones B.method [17]. 4-(4'-n-hexyloxybenzoyloxy) benzaldehyde **III** was prepared by Sandler and Karo method [18]. 4-(4'-n-hexyloxybenzoyloxy)benzoic acid **IV** was obtained by a Co^{III} homogenous catalized oxidation whose mechanistic aspects are presented by Masters C.[19].

4-(4'-n-hexyloxybenzoyloxy)benzoic acid **IV** was synthesized by entirely avoiding anhydride formation and in a different way from that reported by Young, Haller and Green [20]. The twins are purified by successive crystallization's with methanol or ethanol.



Scheme 1. The synthetic route of twin molecules

Synthesis of Polymethylene - α,ω - bis [4-(4'-n-hexyloxybenzoyloxy) benzoate](1a - h) : 0.004 mol of 4 - (4'-n-hexyloxybenzoyloxy) benzoyl chloride was added dropwise to the corresponding sodium dialkoxialkanes and 25 ml ethylenglycol dimethylether for **1 a - b** derivatives and the corresponding α,ω - dihydroxyalkanes and 50 ml of pyridine for **1 c-h** derivatives. The systems were smoothly heated in an air bath until white precipitates appeared. These precipitates were separated by filtration. The solvents are rotary evaporator removed from filtrates and white crude products are obtained. These crude products are crystallized from methanol. Yielding 20-50 per cent of pure TLC final products.

The NMR signals from inserted mesogen structures are essentially the same than those from compound **2**. The signals (ppm) from polymethylene spacer are the following:

n = 2: 52.22; n = 3: 52.42, 22.65; n = 4: 64.78, 25.60; n = 5: 65.02, 25.72, 28.42; n = 6: 65.28, 25.88, 28.73; n = 7: 65.37, 26.05, 28.74, 29.10; n = 8: 65.43, 26.07, 28.77, 29.28
n = 9: 65.33, 26.16, 28.88, 29.34, 29.54

IR (KBr)

The signals from these compounds are the same than those described for compound **2**. Microanalysis agreed well with the calculated and found C, H and O per cent values.

4-(4'-n-hexyloxybenzoyloxy) methylbenzoate (2.) In a 0.1 l round bottom flask provided with reflux condenser and CaCl₂ guard - tube, 0.005 mol (1.71 g) of 4-(4' - n-hexyloxybenzoyloxy)benzoic acid were converted in the corresponding acid chloride by means of thionyl chloride and pyridine as catalyzer. Thionyl chloride and pyridine excess was removed in vacuum rotary evaporator. 0.005 mol (0.27 g) of sodium methoxide dissolved in 40 ml of ethylenglycol previously dried with sodium shaving were added. The system was smoothly heated in an air bath until a white precipitate appeared. This precipitate was separated by filtration. The solvent was rotary evaporated from filtrate and a white crude product was obtained. This crude was crystallized from methanol. Yielding 70 per cent of pure TLC final product.

¹³ C-NMR (CDCl₂-(CDCl₂) δ : 163.35 (s, COOAr); 161.34 (s, COOAr); 160.74 (s, C-OR, Ar.); 151.80 (s, C-O-COAr, Ar.); 129.35, 127.92, 118.80, 111.36 (4 d. Ar.); 124.53, 118.02 (2s, C-CO, Ar.); 65.33 (t, -CH₂-O); 49.12 (q, CO-OCH₃); 28.51, 26.02, 22.62, 19.55 (4 t, -CH₂-); 10.98 (q, -CH₃). IR (KBr) cm⁻¹ : 2950 (m, C-H. (-CH₃); 2855 (m, -CH₂); 1720 (s, C = O ester Ar); 1600 (m, C= C Ar) ,1500 (w, C= C-Ar); 1435 (w, C-H C-CH₃); 1420 (w, C-H -CH₂-); 1385 (w, C-H C-CH₃); 1275 (s, C-O ester Ar); 1215 (m, C-H Ar); 1160 (m, C-O ether Ar); 1110 (m, C - O ester Ar.); 1100 (w, C-H Ar); 1072 (m, C-O ether alif.); 1018 (w, C-H Ar), 1005 (w, C-H Ar); 845 (m, C-H Ar); 765 (m, C-H -CH₂-); 690 (m, C-H Ar.), 510 (w C-H Ar.). Anal. Calcd. For C₂₁ H₂₄ O₅ : C, 70.76; H, 6.78; O, 22.44; Found : C, 70.17; H, 7.06; O, 22.27.

Measurements: NMR¹³C spectra were recorded on a Bruker 300 MHz spectrometer, chemical shifts are given in ppm, (§ TMS = 0) using as an internal reference in CDCl₂-CDCl₂. All products were identified through their elemental analysis. IR spectra were recorded on a Perkin Elmer 577 spectrometer. The thermal properties of the synthesized compounds were studied using differential scanning calorimetry, DSC measurements were performed at 5 °C min⁻¹ heating and cooling rate. Samples and aluminum capsules were weighed on a Perkin Elmer autobalance AD-2 Processor. The Lc textures were studied using a polarizing microscope and ordenator Ortho - Lux POL BK II, with Mettler FP 84 TA Microscopy Cell, Mettler FP 80 and Central Mettler FP 84. Thin samples were observed between two untreated cover slips of ordinary glass at 5 °C heating and cooling rate. X-ray diffraction of magnetically oriented mesophases were obtained from powder samples in 1 mm diameter Lindemann capillary glass. Isotropic melts were cooled at 1 °C h⁻¹ immersed in 1.5 Tesla magnetic field parallel to capillar axe in thermally controlled furnace. These samples were irradiated with Cu K α =1.5405 Å from Philips PN 1140. The length between the sample and the photographic plate was determined on tg2 q = 0.5641 basis from calcite, and the molecular model, were Ealing CPK Atomic Models.

Results and discussion

The thermal phase behaviour of **2** and **1 a-h** compounds is shown in Figure 1. Polarized light microscopy textures (Figure 2.) and X - ray diagrams of well aligned samples (Figure 3.) revealed nematic (N) and Smectic A (S_A) mesophases besides solid (K) and isotropic (I) phases.

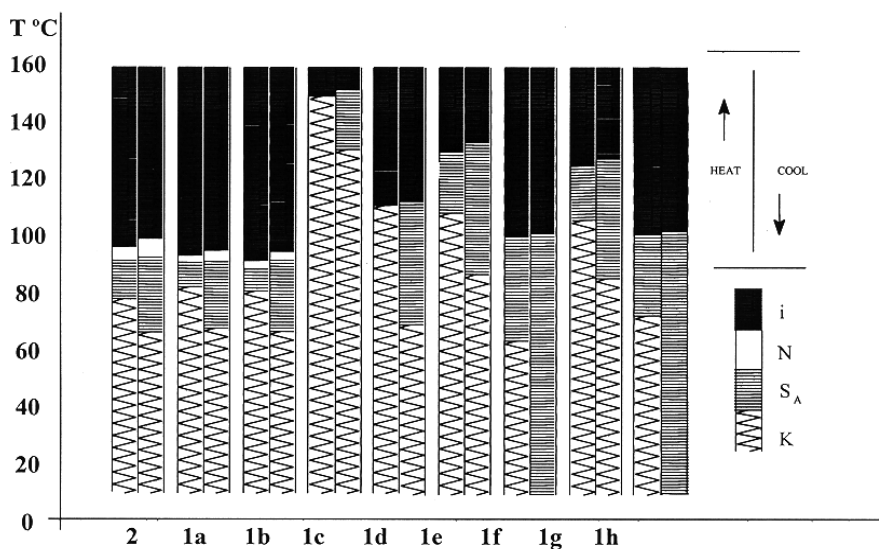


Figure 1. Mesomorphic properties of **2** and **1 a-h** derivatives

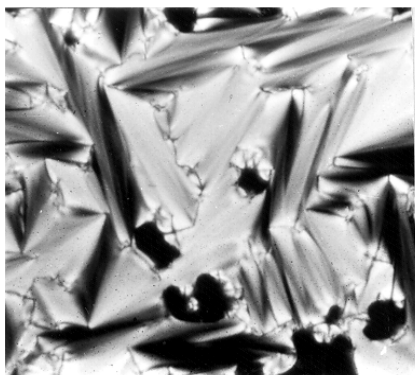


Figure 2. Fan shaped textures; S_A Dimethylen bis [4-(4'-n-hexyloxybenzoyloxy) benzoate](75 °C), **2**.

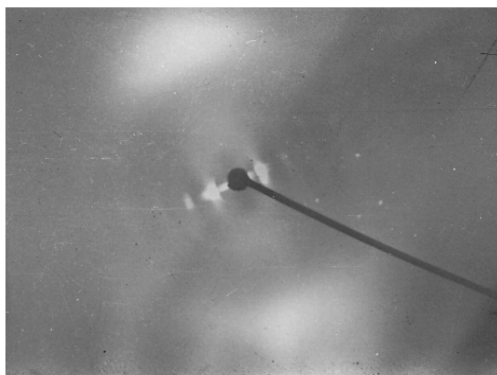


Figure 3. X-ray diffraction patterns of smectic A phase with preferred alignment. Hexamethylen bis [4 - (4'-n-hexyloxybenzoyloxy) benzoate] (130 °C), **1e**.

Transition temperatures, enthalpies and entropies changes for these compounds are shown in Table 1.

A decrease of the capacity to form nematic phases and an enlargement of the smectic ones such as the length of the spacer, were observed. Both K - S_A and S_A - I transition temperatures did not show ascending or descending trend as the length of the spacer changes. However, these transition temperatures showed high and low alternating values depending on even or odd methylene groups number in the spacer, respectively.

Transition entropies K - S_A and S_A - I increased with the spacer length in agreement with the higher number of the molecular conformational possibilities. Entropies and enthalpies, also showed high or low alternating values depending on even or odd methylene group numbers in the spacer, respectively. This phenomenon has been explained [3] in virtue of higher order or molecular linearity in trans, respect even methylene group spacer, mesogen groups.

Table 1. Transition temperatures, Enthalpy and Entropy changes for **2** and **1 a-h** compounds

Compound	Transition	T /°C	ΔH/ kJ mol ⁻¹	ΔS/ J mol ⁻¹
2	K - S _A	78.3	17.5	49.6
	S _A - N	91.8	4.3	11.7
	N - I	97.0	1.3	3.4
1a (n = 2)	K - S _A	82.6	42.6	132.0
	S _A - N	91.7	9.2	21.1
	N - I	93.5	4.4	12.0
1b (n = 3)	K - S _A	81.1	40.5	114.0
	S _A - N	88.8	9.5	26.0
	N - I	92.1	3.1	8.4
1c (n = 4)	K - I	149.8	73.5	173.0
	I - S _A	(149.0)	-17.7	-41.6
	S _A - K	(130.8)	-46.1	-114.0
1d (n = 5)	K - I	111.5	55.6	144.0
	I - S _A	(111.0)	-13.2	-34.2
	S _A - K	(69.6)	-29.8	-87.0
1e (n = 6)	K - S _A	109.0	27.8	72.8
	S _A - I	130.2	13.9	34.5
1f (n = 7)	K - S _A	64.0	14.9	44.3
	S _A - I	100.5	12.6	33.6
1g (n = 8)	K - S _A	106.5	54.9	144.0
	S _A - I	125.4	18.4	46.0
1h (n = 9)	K - S _A	73.0	40.1	115.0
	S _A - I	101.4	13.3	35.3

Heat and cooling rate 5 °C min⁻¹ (DSC)

K = Crystal; N = Nematic; I = Isotropic; () = Transition Monotropic.

X- ray interplanar spacings for **2** and **1 a-h** mesophases were determined according De Vries [21] $l_N \sin 2\theta = \lambda$ for nematic phases and $2 l_s \sin \theta = n\lambda$ and $2D \sin\theta = 1.1547\lambda$ for smectic phases. The results are presented in Table 2. (See also Experimental section).

Table 2. Intermolecular spacings for **2** and **1 a-h** mesophases. (a)

Compound	$l_N/\text{Å}^\circ$	$T_{X\text{-RAY}}/^\circ\text{C}$ (b)	$l_s/\text{Å}^\circ$	$D/\text{Å}^\circ$	$T_{X\text{RAY}}/^\circ\text{C}$ (b)
2	21.7	95 Exo	23.3	5.03	85 Exo
1a (n = 2)	23.5	94 “	23.5	5.21	83 “
1b (n = 3)	23.5	95 “	23.0	5.23	87 “
1c (n = 4)			22.8	5.22	150 “
1d (n = 5)			21.7	5.24	110 “
1e (n = 6)			23.9	5.17	130 “
1f (n = 7)			22.3	5.21	101 “
1g (n = 8)			25.2	5.20	124 “
1h (n = 9)			24.0	5.22	99 “

(a) These results refer X - ray diffraction measurements.

(b) The diffractograms were obtained nearly mesophase formation by cooling.

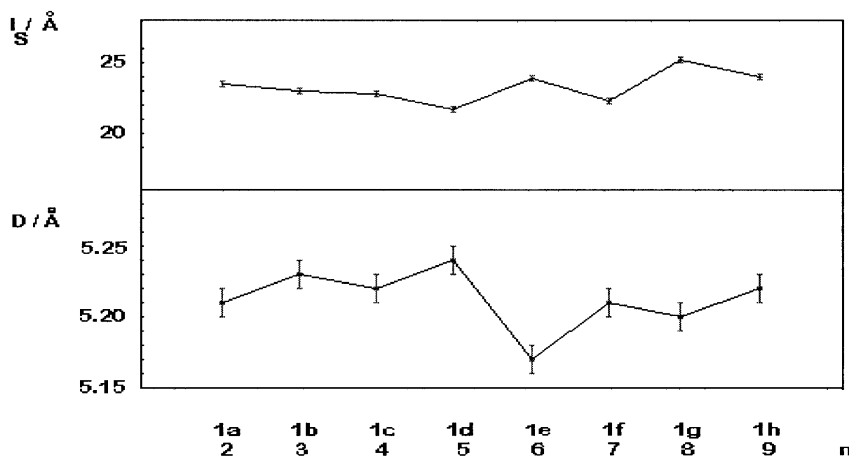
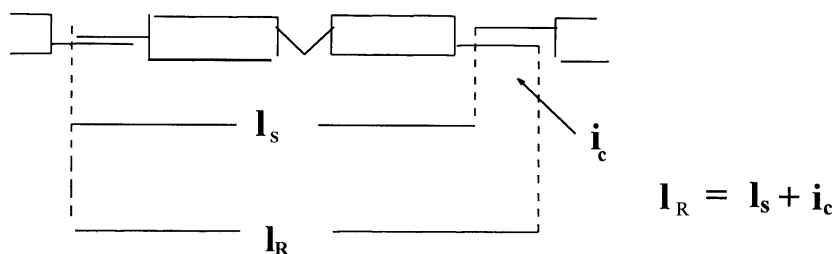


Figure 4. l_s and D spacings. Smectic S_A mesophases. Homologous series of α,ω - bis [4 - (4'-n-hexyloxybenzoyloxy)benzoate]alkanes.

An alternant and reciprocally inverse variation for l_s and D spacings for smectic S_A bimesogenic structures is observed notwithstanding ± 0.2 and ± 0.01 Å° uncertainties on l_s and D values respectively. For even number of methylene units on spacer, greater l_s and smaller D values are registered. For odd number of methylene units on spacer, smaller l_s and greater D values are registered. (Fig.4). With respect to bimesogenic smectic A mesophases, molecular models and l_s and D spacings values show:



If l_R is real length of bimesogen molecule, l_s is spacing between layers, i_c is interdigitating length of alcoxyl chains then; $l_R = l_s + i_c$. If l_M is the length of extended (more stable conformation) bimesogen molecule according molecular model, then $l_M - l_R$ is a measure of deviation from more stable conformation. If $l_M - l_R = 0$ for $n = 2$ (no spacer deviation). Then $i_c = 4.5 \text{ \AA}$. This i_c value is assumed in all cases.

n	l_s	i_c	l_R	l_M	$l_M - l_R (\text{Å})$
2	23.5	4.5	28.0	28.0	0
3	23.0	4.5	27.5	28.5	1.0
4	22.8	4.5	27.3	29.0	1.7
5	21.7	4.5	26.2	29.5	3.3
6	23.9	4.5	28.4	30.0	1.6
7	22.3	4.5	26.8	31.0	4.2
8	25.2	4.5	29.7	31.5	1.8
9	24.0	4.5	28.5	32.0	3.5

Higher values of $l_M - l_R$ for odd n values with respect to even n value are observed. This circumstance could be explained by a certain twisted character that the spacer (n odd) adopts to satisfy global molecular linearity. These twisted conformations or deviations from the more stable conformation also explain higher D values.

Smectic S_A phase of free mesogen **2**, according molecular models, l_s and D spacings agrees antiparallel bilayer structure. In this manner polar ester ends are founded in good interaction as interdigitated apolar alcoxyl chains ends also are.

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