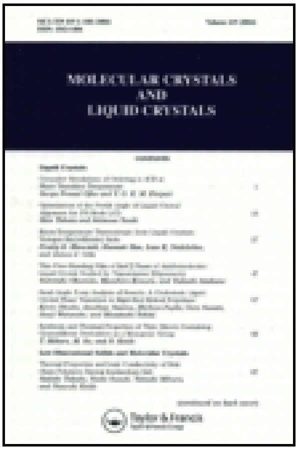

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The Mesomorphic Behaviour of Bisalkyl 4,4′-(Terephthaloyldioxy)dibenzoates as Models of Thermotropic Polyesters

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The Mesomorphic Behaviour of Bisalkyl 4,4′-(Terephthaloyldioxy)dibenzoates as Models of Thermotropic Polyesters

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The thermotropic liquid-crystalline behaviour of fifteen bisalkyl 4,4′-(terephthaloyldioxy)dibenzoates, as possible model compounds of corresponding polyesters, was studied by DSC and polarizing microscopy. The flexible tails included linear or branched alkyl groups, aryl alkyl groups, or oxygen-containing groups. Depending on the structure of the flexible tails, smectic A, smectic C, nematic or cholesteric phases were observed. The X-ray diffraction study of the homologues with linear alkyl chains showed the existence of a smectic A phase for alkyl groups constituted by 4 to 8 carbon atoms, and both smectic A and C phases for samples with alkyl tails with 9 and 10 carbon atoms. The influence on the nature of the flexible chains on the thermotropic behaviour of the compounds is discussed, in relation to the behaviour of corresponding structurally analogous polyesters.

Keywords: bisalkyl 4,4′-(terephthaloyldioxy)dibenzoate, smectic phases, thermotropic polyesters, model compounds

INTRODUCTION

Within the framework of the definition of structure-property relationships in thermotropic liquid-crystalline polymers, low molar mass model compounds appear well suited to the scope as they assume under mesophase conditions well defined structures and undergo phase transitions sharper than the corresponding high molecular weight analogues. In particular, they obviously allow to rule out any side influence on structural and thermodynamic parameters dependent on molecular weight and polydispersity of the polymers.

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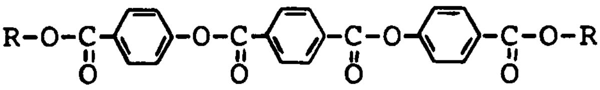
There exist basically two types of model compounds, which comprise mesogens consisting alternatively of a sequence of rigid-flexible-rigid elements ("twin" models) or of a succession of flexible-rigid-flexible elements. The compounds of the former class are at present receiving much attention[1-6] and may be considered as oligomer models having chemical structures intermediate between those of low molar mass liquid crystals and polymeric liquid crystals. However, we have obtained valuable information by using compounds of the latter kind as models of thermotropic polyesters in respect of the study of, e.g., their liquid crystal behaviour,[6-9] dynamic-mechanical properties[10] and chiroptical properties in dilute solutions.[11,12]

In the present paper we describe the mesomorphic behaviour as studied by thermal analysis (DSC), polarizing microscopy and X-ray diffraction of fifteen low molar mass model compounds **1a–1o** based on the 4,4′-(terephthaloyldioxy)dibenzoyl (HTH) mesogenic core:



1

	1a	**1b ÷ 1i**	**1j**	**1k**
R:	C_2H_5	$n - C_3H_7 \div n - C_{10}H_{21}$	$n - C_{12}H_{23}$	$\overset{*}{C}H(CH_3)CH_2CH_2CH_3$
	1l	**1m**	**1n**	**1o**
R:	$CH_2\overset{*}{C}H(CH_3)C_2H_5$	$CH_2CH_2OCH_3$	$(CH_2CH_2O)_2CH_3$	$CH_2C_6H_5$

The substituents R may be purely alkyl groups, linear (*R* = ethyl to *n*-dodecyl, **1a–1j**) or branched, either preferentially chiral (**R** = (*S*)-2-methylbutyl, **1l**) or racemic (**R** = (*R*)(*S*)-1-methylbutyl, **1k**); in a few cases the substituent **R** is an aryl alkyl group (**1o**) or contains oxygen atoms (**1m**, **1n**).

The mesomorphic properties of some members of the series were previously known[8,13-16] but details were not given on the sequences and structures of the different mesophases.[16]

Results and discussion

The reported compounds **1** were typically synthesized by reacting 4,4′-(terephthaloyldioxy)dibenzoyl chloride with the alcohol of choice, according to.[7,12] The same procedure is also used for the preparation of corresponding polyesters from different diols.[12,16-18] Alternatively, samples **1a**, **1k**, **1l**, and **1o** were synthesized by coupling terephthaloyl chloride with the preformed alkyl 4-hydroxybenzoates.[8,10]

Thermal analysis

The phase transition temperatures of compounds **1a–1o** are summarized in Table 1, while those of the homologous series **1a–1j** are also reported in Figure 1 as a

TABLE 1

Phase transition temperatures for model compounds **1**

Compound	*R*	Phase transition temperature (in *K*)[a]							
		K_I–K_{II}	K–S_C	K–S_A	S_C–S_A	S_A–N	S_A–I	N–I	K–I
1a	ethyl			465		478		512	
1b	*n*-propyl			395		478.5		492	
1c	*n*-butyl	367.5		405.5			457.5		
1d	*n*-pentyl			418			461		
1e	*n*-hexyl	350.5		419			451		
1f	*n*-heptyl			416	(409)		446		
1g	*n*-octyl	352		416	(416)		439		
1h	*n*-nonyl	344	413		418		435		
1i	*n*-decyl	366	410		422		428		
1j	*n*-dodecyl		412		419.5		422		
1k	(*R*)(*S*)-1-methylbutyl								400
1l	(*S*)-2-methylbutyl			408.5	(408)	418		432[b]	
1m	3-oxybutyl			404	409	416		422	
1n	3,6-dioxyheptyl								385
1o	benzyl								462

[a] K: crystalline; S_C: smectic C; S_A: smectic A; N: nematic (or cholesteric); I: isotropic. Monotropic transitions in parentheses.

[b] Blue phase at 431.5 K.

function of the number *n* of carbon atoms in the alkyl tails. Generally, the liquid crystal-isotropic liquid temperatures undergo a marked depression for the lower homologues ($n = 3,4$) and then decrease more gradually, as the series is ascended. However, the melting temperatures show a more dramatic decrease in going from **1a** ($n = 2$) to **1c** ($n = 4$) and afterwards reach a sort of plateau, being in all cases comprised between 410 and 420 K. This dual behaviour results in a very broad mesophasic range at $n = 3$ (97 K), tending to narrow with increasing *n* and reaching a minimum (10 K) at $n = 12$. The lower homologues ($n = 2, 3$) show enantiotropic smectic A and nematic phases. The S_A–N transition temperature is not affected be lengthening the alkyl substituents, whereas the N-I temperature is much depressed, thus resulting in a little expanded nematic range for **1b**. For **1c** ($n = 4$) the nematic properties are extinguished and the compound becomes purely smectic. In the higher homologues, the S_A–I transition temperatures gradually decrease in a weakly alternating fashion, the members with odd values of *n* lying on an upper curve. For samples with $n \geq 7$, a smectic C phase is observed. For **1f** ($n = 7$) and **1g** ($n = 8$) such a phase is monotropic, but it becomes enantiotropic on lengthening the alkyl tails ($n \geq 9$). The S_A–S_C temperatures again lay on two slightly separated curves, but the sense of alternation is opposite to that for the S_A–I temperatures. The curve for the even members reaches a maximum at $n = 10$. Odd-even alternations of transition temperatures, particularly for the N–I and S_A–I temperatures, are well established in liquid crystals and polymeric liquid crystals.[19]

Compounds **1c**, **1k**, **1l**, and **1m** are comparable in terms of the length of the alkyl chain, but are characterized by differences either in the position of side substituents or in the presence of an oxygen atom. The introduction of a methyl branching in

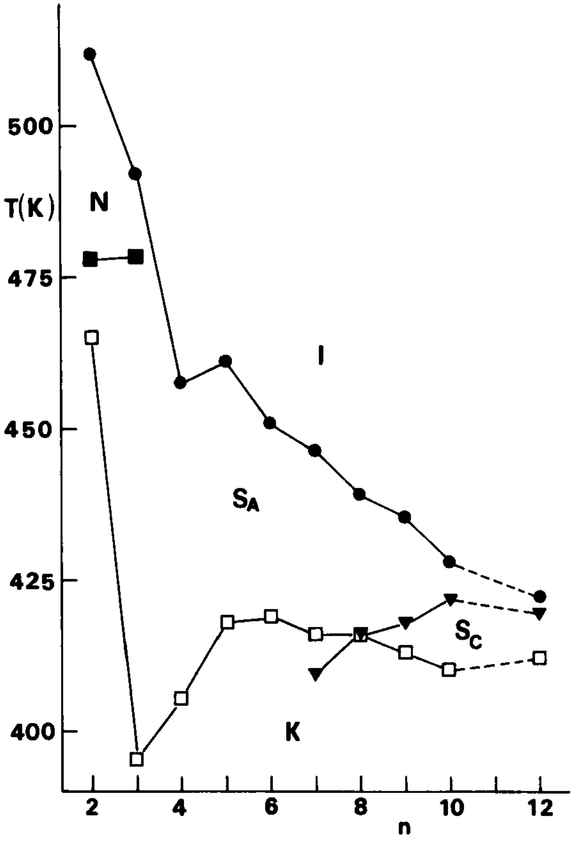


FIGURE 1 Phase transition temperatures for homologues **1a–1j** as function of the number *n* of carbon atoms in the linear alkyl chains: (●) N or S_A–I; (■) S_A–N; (▼)S_C–S_A; (□) K–S_A or S_C.

the alkyl tail of **1k** and **1l** greatly disfavours[20] the overall mesogenic tendency relative to unsubstituted **1c**. When the lateral group is on the C_1 of the ester alkyl chain (**1k**), the sample does not show mesogenic properties, even in the highly supercooled states, whereas when that is moved to the C_2 atom (**1l**) a comparatively small decrease of the mesomorphic range (23.5 K) is observed (Table 1). However, the smectic tendency is more depressed, and a cholesteric phase appears at 418 K accompanied by a monotropic S_A–S_C transition at 408 K. A blue phase occurs at 431.5 K ($\Delta H \simeq 0.13$ kJ/mol). The replacement of a methylene group by an oxygen atom in **1m** (R = 3-oxybutyl) causes analogous depressing effects on the mesophase stability and S and N phases are encountered with limited persistence, 12 K and 6 K respectively. The insertion of a second oxygen atom in **1n** (R = 3,6-dioxyheptyl) suppresses any liquid-crystalline properties relative to **1f** (R = *n*-heptyl). All these compounds have comparable melting points and the remarkable narrowing of the mesophasic range is due solely to depressing effects on the isotropization temperature. Finally, the high-melting compound **1o** (R = benzyl) is not mesogenic, whereas a N–I temperature of 670 K was estimated for the inferior homologue diphenyl 4,4'-(terephthaloyldioxy)dibenzoate (*R* = phenyl).[16] Depending on the length of the ω-phenylalkyl substituent, the bulky aromatic ring can be accommodated alternately in and out of line with the rest of the molecule, thus determining dramatic alternations of the mesomorphic behaviour.[21] The phase transition enthalpies of the prepared samples are summarized in Table 2. The melting enthalpies are high and vary with chemical structure in an irregular manner. In each case, the melting enthalpy is greater than the corresponding, low temperature crystal-crystal transition enthalpy. The heats connected with the S_A–S_C transitions are rather low and could not be generally detected, probably due to the second order character of the transition.[22–24] The S_A–I enthalpies and entropies (Table 2) were significantly greater than those of any other observed mesophase transition, as expected. The trends of the S_A–I enthalpies and entropies as function of the length of the flexible tails of the homologous members **1c–1j** are illustrated in Figure 2. Both parameters increase in a monotonous fashion, with no appreciable odd-even alternations, thus suggesting the occurrence of a progressive, increasing contribution from the alkyl substituents. With successive additions of methylene units, intermolecular attractive forces increase more in the more ordered smectic phase relative to the isotropic phase, thus resulting in an increase in ΔH_{SI}. ΔS_{SI} also increases as chain extension contributes additional (conformational) order to the smectic phase relative to the open molecular arrangement of the isotropic liquid. The S–I temperatures decrease with increasing length of the alkyl group (Figure 1), and accordingly the variation of ΔS_{SI} vs. alkyl length overwhelms the corresponding ΔH_{SI} trend, thus confirming the expectation of the predominance of entropy factors with increasing molecular complexity (Figure 2).

TABLE 2

Phase transition enthalpies and isotropization entropies for model compounds **1**

	Enthalpy (kJ/mol)						Entropy (J/mol·K)	
Compound	K–K	Melting	S_C–S_A	S_A–N	S_A–I	N–I	S_A–I	N–I
1a		42		0.8		0.3		0.6
1b		30[a]		1.5		0.5		1.0
1c	14	32			4.1		9.0	
1d		21			4.8		10.4	
1e	16	40			5.5		12.2	
1f		40	nd[b]		6.0		13.5	
1g	28	45	nd[b]		6.3		14.4	
1h	26	41	0.3		6.6		15.2	
1i	22	25[a]	nd[b]		6.7		15.6	
1j		57	0.3		7.4		17.6	
1k		39[a]						
1l		35	0.1	0.3		0.3		0.7
1m		43	nd[b]	1.3		0.2		0.5
1n		40						
1o		55						

[a] Complex melting endotherms at DSC.
[b] Not detectable with reliability.

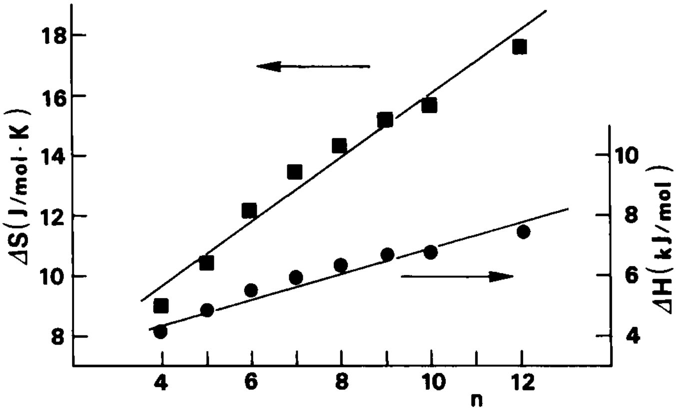


FIGURE 2 Thermodynamic parameters for the S_A–I transition of homologues **1c–1j** as function of the number *n* of carbon atoms in the alkyl chains: (●) enthalpy; (■) entropy.

Optical polarizing microscopy

On cooling the isotropic liquid, the nematic phase of **1a**, **1b** and **1m** separated in small droplets that afterwards coalesced to give a schlieren texture characterized by shimmering motion. At the N–S_A transition, familiar striations or batonnets were formed that, on further cooling, developed a focal-conic fan texture. The S_A phase separated from the isotropic phase (**1c–1j**) as batonnets that, with decreasing temperature, coalesced to give the typical texture with fans (Figure 3). Small regions

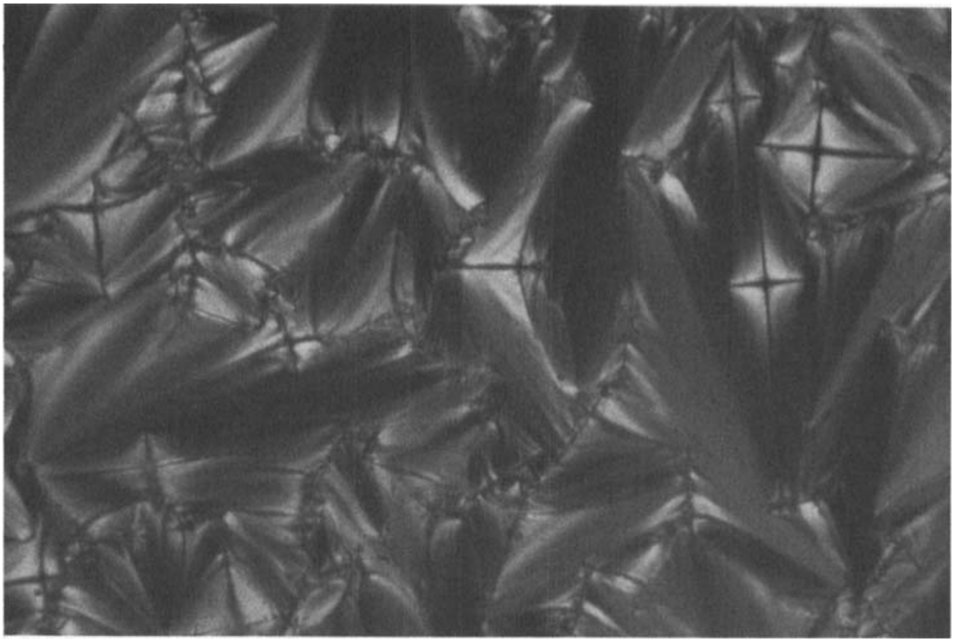


FIGURE 3 Focal-conic texture with fans of the S_A phase of compound **1h** at 425 K.

exhibited the homeotropic or pseudoisotropic texture. The S_C phase (**1f–1j**) developed either a broken fan texture from the S_A fan texture (Figure 4), or a schlieren pattern from the S_A homeotropic texture. On cooling the isotropic phase of **1l**, a blue phase appeared with a blue-green platelet texture from which the focal-conic pattern of the cholesteric phase generated. The cholesteric phase could also be observed in a planar texture with oily streaks that reflected the visible light. The sample, when observed with perpendicularly incident light, showed a violet iridescence at 152–148°C, blue at 148–147°C, green at 146°C, and yellow at 145.5°C. The maximum wavelength of reflected light is proportional to the pitch length of the cholesteric helix,[25] and our results are consistent with a progressively greater unwinding of the helical array with decreasing temperature down to the cholesteric-smectic transition.[26]

X-ray diffraction

Model compounds **1c**, **1e–1i** (n = 4, 6–10) were studied by X-ray diffraction on heating between 298 and 450 K. The X-ray diagrams obtained as function of the temperature can be classified in two families, corresponding to the crystalline and smectic phases respectively. The crystalline polymorphism is complex and depends upon the thermal history of the sample. Therefore, only the crystalline phase found at temperatures higher than approximately 380 K and the smectic phases were studied.

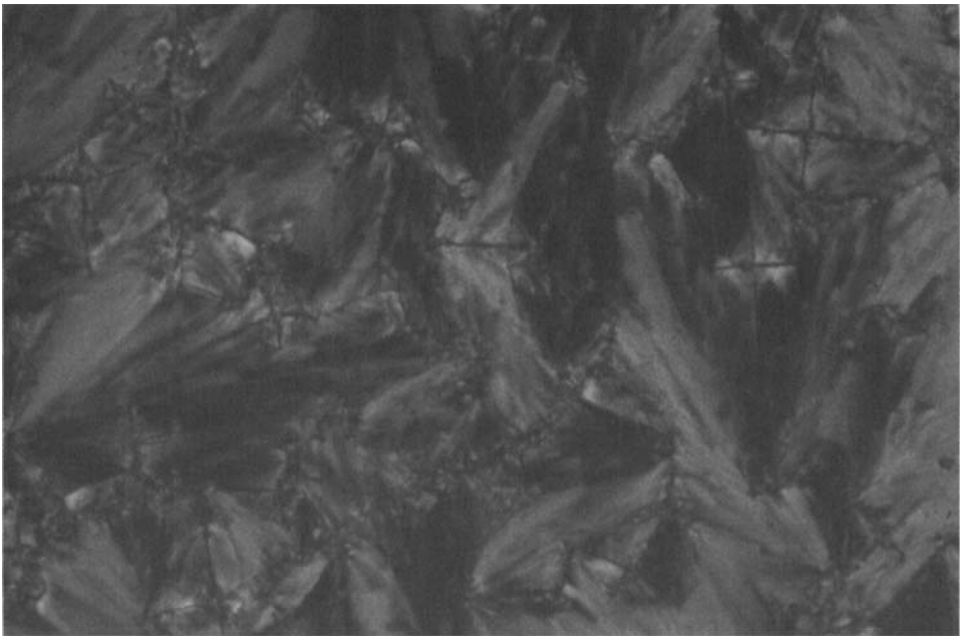


FIGURE 4 Focal-conic texture with broken fans of the S_C phase of compound **1h** at 415 K.

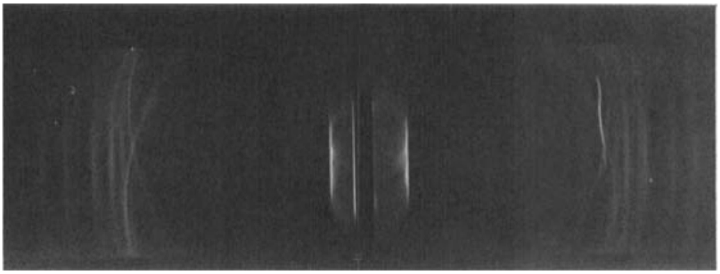


FIGURE 5 X-ray diffraction pattern of the lamellar crystalline structure of compound **1e** at 393 K.

The X-ray diagrams obtained at temperatures between 380 K and T_m are characteristic of a lamellar crystalline structure. They exhibit in the wide angle region several intense reflections that were not indexed, and in the low angle region a sharp reflection, the Bragg spacing of which is related to the thickness d_k of the lamellae (Figure 5). In order to determine whether the molecules are perpendicular to the plane of the lamellae or tilted, we compared the thickness d_k with the length L of the molecules in the fully extended all-trans conformation as calculated from known bond angles and distances[27] (Table 3).

For all the samples studied, L is much longer than d_k indicating that the molecules are tilted, but the angle of tilt is practically the same (θ_k = 21.2 ± 1°) for all the models, within the limits of accuracy of the experiments. The variation of the thickness of the crystalline lamellae is plotted in Figure 6 as a function of the number n of carbon atoms of the flexible alkyl tails.

TABLE 3

Structural parameters of the crystalline and smectic structures of some model compounds **1** with linear alkyl tails of n carbon atoms.

		Crystalline			Smectic	
Compound	n	L (Å)[a]	d_K (Å)[b]	θ_K (deg)[c]	d_{S_C} (Å)[d]	d_{S_A} (Å)[e]
1c	4	30.16	28.2	20.8		33.6
1e	6	35.24	33.0	20.5		37.3
1f	7	37.78	35.1	21.7		39.1
1g	8	40.32	37.5	21.6		40.9
1h	9	42.86	39.7	22.1	42.3[f]	43.1
1i	10	45.40	42.5	20.6	44.7[g]	45.5

[a] Calculated length of the molecule in the fully extended all-trans conformation.

[b] Interlayer spacing ±0.4 Å in the lamellar crystalline structure at $T >$ 380 K.

[c] Angle of tilt of the molecules in the lamellar crystalline structure at T > 380 K.

[d] Interlayer spacing ±0.3 Å in the smectic C phase.

[e] Interlayer spacing ±0.3 Å in the smectic A phase.

[f] At 415 K.

[g] At 413 K.

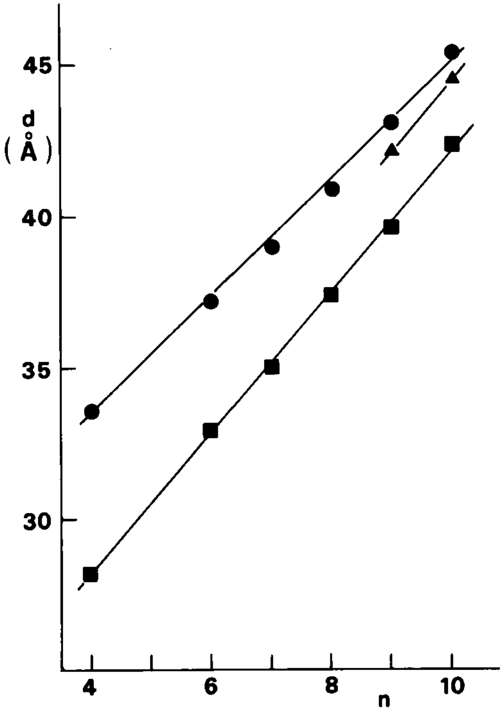


FIGURE 6 Variation of the intersheet layer spacing *d* for homologues **1c**, **1e–1i** as a function of the number *n* of carbon atoms in the alkyl chains: (■) lamellar crystalline structure; (▲) smectic C structure; (●) smectic A structure.

At T_m the X-ray patterns change substantially. In the low angle region, the sharp reflection shifts to lower angles, and for any given sample the relevant Bragg spacing corresponds to a higher layer thickness than that observed in the lamellar crystalline structure (Table 3). In the wide angle region, the reflections are replaced by a diffuse band characteristic of disordered smectics (A or C) (Figure 7). The average intermolecular distance *D* is in all cases 4.8 ± 0.2 Å. The values of the smectic interlayer distances *d* are plotted in Figure 6 as function of the number *n* of carbon atoms in the alkyl tails *R*, and suggest that each addition of a methylene unit

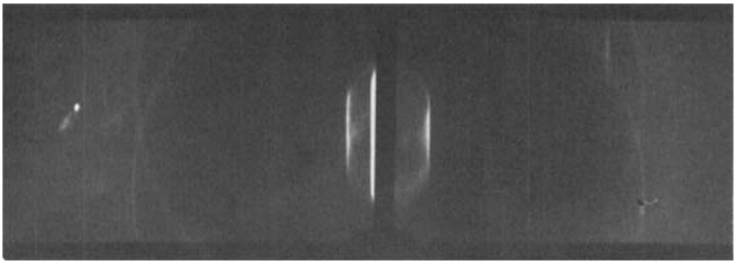


FIGURE 7 X-ray diffraction pattern of the smectic A phase of compound **1c** at 423 K.

implements regularly the smectic spacing without exhibiting any odd-even effect of the end segments.

For samples with $n = 4, 6, 7$, or 8, d is slightly longer than L and independent of temperature, so the structure may be considered of the orthogonal S_A type. For **1h** ($n = 9$), d increases gradually from 42.3 to 43.1 Å as temperature increases from 415 to 428 K. As $L = 42.9$ Å, it appears that a tilted S_C phase with a tilt angle $\theta_C \simeq 9°$, progressively transforms into a S_A phase with increasing temperature. For **1i** ($n = 10$), L is slightly longer than d and the structure may be considered as a S_C with a tilt angle $\theta_C \simeq 10°$. However, the small range of stability of this smectic phase made it difficult to evaluate with reliability the influence of temperature on the geometrical parameters.

Conclusions

Among the fifteen ester compounds with a 4,4′-(terephthaloydioxy)dibenzoyl (HTH) mesogenic core, twelve exhibit liquid-crystalline phases whose existence, nature and number are related with the nature and the length of the flexible chains. All the mesomorphic samples present at least a smectic phase, that is accompanied by a nematic phase in the inferior homologues. In the case of linear chains, when $n \geq 7$ two different smectic phases (C and A) are observed. The first is monotropic for $n = 7$ and 8, and enantiotropic for $n = 9$, 10, and 12. Two smectic phases are also observed for the optically active compounds with a 5 carbon atom alkyl group, but in that case the S_A phase is followed by a cholesteric phase. Such a behaviour demonstrates the high smectogenic power of the HTH core, which is enhanced on lengthening the flexible chains. The thermal persistence of different smectic types is extremely sensitive to minor changes in the molecular framework of **1**.

It is not surprising that smectic A or C phases can also be found in thermotropic polyesters based on the same mesogenic HTH core and flexible alkylene spacers with 9, 10, or 12 methylene groups.[10,28] However, polyesters with the same mesogenic unit but dipropyleneglycol spacers show, with increasing temperature, more ordered smectic phases (E or H) before the onset of smectic C or A phases.[18] The incorporation of optically active residues into the polymer backbone can result in the establishment in HTH polyesters of chiral twisted mesophases.[17,29] The prepared compounds can also be used as suitable precursors[30] of thermotropic liquid crystalline polyesters achievable by transesterification procedures.

Experimental

Synthesis: The syntheses of some individual model compounds of the series have been already described,[7,8,10,12] and the same procedures were adopted here. The prepared models were purified by repeated crystallizations using ethyl acetate for **1g–1i**, 95% ethanol for **1m**, ethyl acetate/ethanol (1:1 vol:vol) for **1a**, **1b**, and **1d–1f**, ethyl acetate/ethanol (1:2 vol:vol) for **1c** and **1k**, ethyl acetate/ethanol (1:3 vol:vol) for **1n**, and dimethylsulfoxide/water (6:1 vol:vol) for **1l**.

Physicochemical measurements: Calorimetric analysis was carried out with a Perkin-Elmer DSC-2 apparatus at heating/cooling rate of 2.5 K/min under dry nitrogen flow. Experiments of supercooling of the melts were carried out with cooling rates of 10–40 K/min. Indium standards were employed for temperature calibration and evaluation of enthalpy changes. Optical microscopy observation was performed with a Reichert Polyvar polarizing microscope equipped with a Mettler FP52 programmable heating stage. Photomicrographs were taken between crossed polarizers at the original magnification of 300x.

X-ray diffraction was performed under vacuum with a Guinier-type focusing camera equipped with a bent quartz monochromator giving a linear collimation of strictly monochromatic X-rays ($CuK_{\alpha I}$) and a device for recording the diffraction patterns from samples at various temperatures between 20 and 200°C with an accuracy of ±1°C.

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