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THERMOTROPIC COMPOUNDS WITH TWO IDENTICAL TERMINAL MESOGENIC UNITS AND A CENTRAL SPACER

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ABSTRACT

Five molecules, having both rigid extremities separated by a central flexible backbone composed of aliphatic chains with 6, 12 and 22 methylene groups, were synthesised with the aim of studying the effect of the length of the central chain on the mesomorphic behaviour. The molecule with 6 central methylene groups showed a single, nematic monotropic phase while a smectic, ordered phase was observed for molecules with 22 central methylene groups. The latter showed a tilt of the molecules in the smectic layer of about 50°.

INTRODUCTION

Most liquid crystal molecules giving rise to smectic and nematic mesophases are formed by a central rigid core with one or two aliphatic end chains. Recent results, on molecules having a flexible spacer and two identical terminal mesogenic moieties, show that these molecules are able to produce nematic phases [1–4]. When the two mesogenic moieties are different in nature, smectic phases are also observed [5]. These symmetrical dimeric molecules were synthesised on the one hand, as interesting new liquid crystal compounds and, on the other, as intermediates between monomeric and polymeric materials [6,7] in order to better understand the monomer → oligomer → polymer sequence.

In all the results reported in the literature, the maximum length of the central spacer was limited to 12 methylene groups. In this paper, we report preliminary results on the synthesis and thermal behaviour of such a compound containing a longer aliphatic spacer (22 methylene groups). In comparison with previous results concerning compounds of the same homologous series but with shorter spacers, the occurrence and nature of the mesomorphic phases observed is discussed as a function of the length of the spacer and of the possible conformations of the molecules. In addition, we report the thermal and structural behaviour of other compounds in which the central spacer is formed by a linear aliphatic chain containing six and twelve methylene groups.

EXPERIMENTAL

The general chemical formula of the compounds studied in the present work is

$X-C_6H_4-CO-O-C_6H_4-O-(CH_2)_n-O-C_6H_4-O-CO-C_6H_4-X$

$X = NO_2$, $n = 22$ (abbreviated as C22NO2)

$X = C_4H_9$, $n = 6$ and 12 (abbreviated as PBC6 and PBC12 respectively)

$X = C_8H_{17}$, $n = 6$ and 12 (abbreviated as POC6 and POC12 respectively)

Synthesis

The 4,4′-dihydroxy-α,ω-diphenoxyalkane intermediates were prepared following the method described in ref. 6 (the reaction was kept under nitrogen). They were recrystallised several times in a mixture of water and ethanol. Then their condensation with the corresponding acid chloride was performed in pyridine. The final products were recrystallised, first in a mixture of ethanol and toluene, then in pure toluene. The corresponding elemental analyses are given in Table 1.

X-ray diffraction experiments have been performed on the samples. The patterns were recorded photographically as a function of temperature, using either a Guinier focusing camera equipped with a bent quartz monochromator (Cu $K\alpha_1$ radiation from a Philips PW-1009 generator) and an electrical oven, or a Searle camera with toroidal optics (Ni-filtered Cu radiation from

TABLE 1

Elemental analyses of the compounds

	%C	%H	%N	%O
C22NO2	69.60 (69.88)	7.59 (7.33)	3.33 (3.39)	19.65 (19.39)
PBC6	77.15 (77.14)	7.28 (7.44)		15.63 (15.41)
PBC12	78.36 (78.15)	8.34 (8.27)		13.71 (13.58)
POC6	78.56 (78.44)	8.50 (8.50)		13.06 (13.06)
POC12	79.57 (79.17)	9.03 (9.10)		12.18 (11.72)

The theoretical values are given in parentheses.

an Elliot GX20 rotating anode generator) and an electronically controlled oven.

Differential scanning calorimetry (DSC) studies were carried out with a Perkin–Elmer DSC2 instrument. Measurements were systematically made with a heating or cooling rate of 2.5 K min^{-1}.

Molecular modelisation was performed with an Evans and Sutherland graphics station, using the Sybyl commercial program from Tripos.

RESULTS AND DISCUSSION

The POC6, POC12, PBC6 and PBC12 compounds do not exhibit any enantiotropic liquid crystalline behaviour. On heating, the lamellar crystalline phase (as found by X-ray diffraction) transforms directly into an isotropic phase (all the thermal and structural parameters of the compounds are listed in Table 2). A monotropic nematic phase is observed only with POC6 in a narrow temperature range below 147 °C (see the corresponding DSC diagram represented in Fig. 1). These results should be compared with those already reported by Griffin and Britt [1] on a similar homologous series where $n = 10$ and X is an alkoxy paraffinic chain, instead of an alkyl chain in the present work. Whatever the length of the alkoxy chain, only nematic phases were found by these authors. All these observations clearly show that the presence of a central aliphatic spacer does not favour the occurrence of smectic mesomorphism. Nevertheless, it should be noted that the terminal alkoxy chain length contributes, at least, to the occurrence of a nematic phase, this being due, presumably, to the larger flexibility of the alkoxy chain compared to the alkyl chain.

TABLE 2

The thermal and structural parameters of the compounds

	Transition	T (°C)	ΔH (kcal mol^{-1})	d (Å)	
POC6	K K_1	69.5	12.37	27.1	(30 °C)
	K_1 I	147.0	19.83		
	I N^{m} [a]	145.3	3.16		
POC12	K I	123.3	23.50	14.8	(30 °C)
PBC6	K I	160.5	22.80	20.9	(57 °C)
PBC12	K K_1	87.3	3.43	44.3	(30 °C)
	K_1 I	128.5	25.75		
C22NO2	K K_1	106 [b]			
	K_1 S	127 [b]			
	S I	132	12.56		

[a] m, Monotropic phase.

[b] Values deduced from DSC curves.

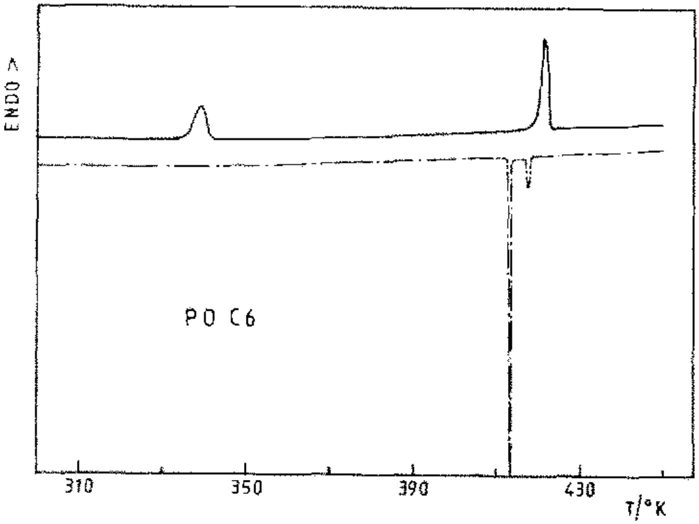

Fig. 1. Heating and cooling thermogram of POC6.

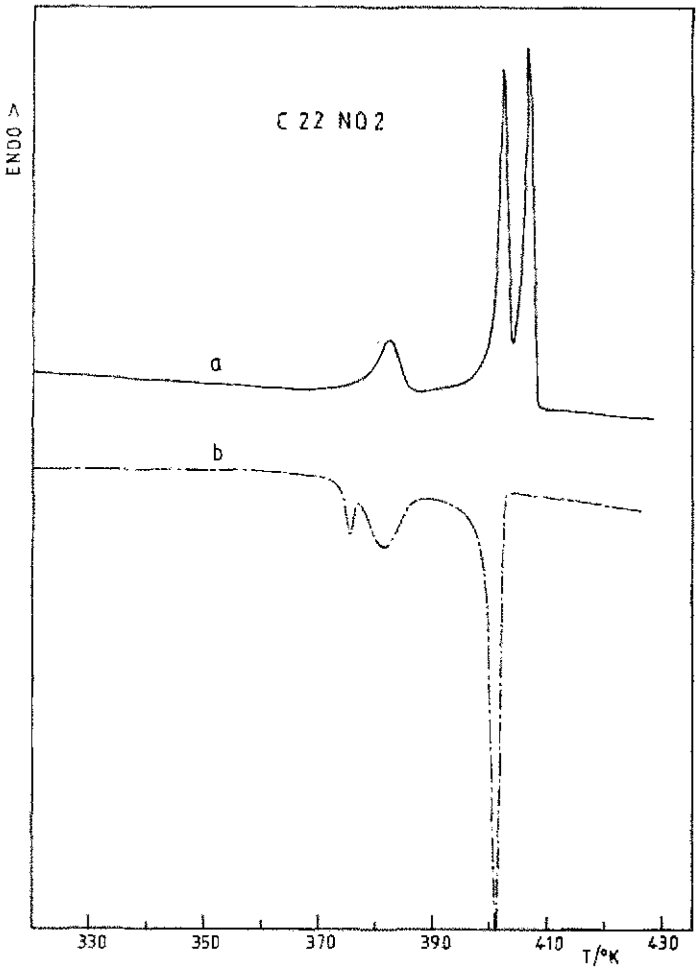

Fig. 2. Heating and cooling thermogram of C22NO2.

Fig. 3. The smectic phase of C22NO2 formed on cooling from isotropic liquid. Crossed polarisers, magnification 77 ×.

The DSC diagram obtained on heating C22NO2 (Fig. 2) shows two main transitions close to each other at 127 and 132 ° C. On cooling, the higher transition is reversible within 1 ° C, whereas there is a large supercooling effect for the lower transition. This indicates that the phase occurring between 127 and 132 ° C is a mesomorphic phase. The texture observed under the polarising microscope (Fig. 3) does not reveal any specific feature of the classical mesomorphic phases [8], but is strongly birefringent and seems to correspond to an ordered smectic phase.

The X-ray diffraction patterns registered as a function of temperature show the existence of three distinct stability domains: at room temperature, two coexisting solid lamellar phases with layer spacings of 47 and 44 Å; at temperatures between 100 and 125 ° C, a unique ordered system witb a lamellar spacing of 34 Å; finally, at temperatures above 130 ° C and below the isotropic phase, an ordered smectic phase, characterised by a layer thickness of 29 Å. It was not possible to properly index the reflections in the wide-angle region of the X-ray diffraction pattern in order to determine the two-dimensional lattice of the smectic ordering, nor has it been possible to register X-ray diffraction patterns on oriented samples as no nematic phase occurs when the temperature increases. However, we can discuss how the molecules can fit within the smectic layers.

The molecular model corresponding to C22NO2 is represented in Fig. 4. The most interesting result from the conformational study of the molecule is that C22NO2 cannot adopt a very stretched conformation; this is essentially due to the presence of the ester group. The conformational study was performed by defining the rotatable bonds as shown in Fig. 5, and the energy of each possible conformer has been calculated by taking into account the electrostatic interactions. The lowest energy found for one isolated molecule is − 7.84 kcal and corresponds to the conformer illustrated in Fig. 4. (Of course, g-conformers can also exist in the smectic phase.) The

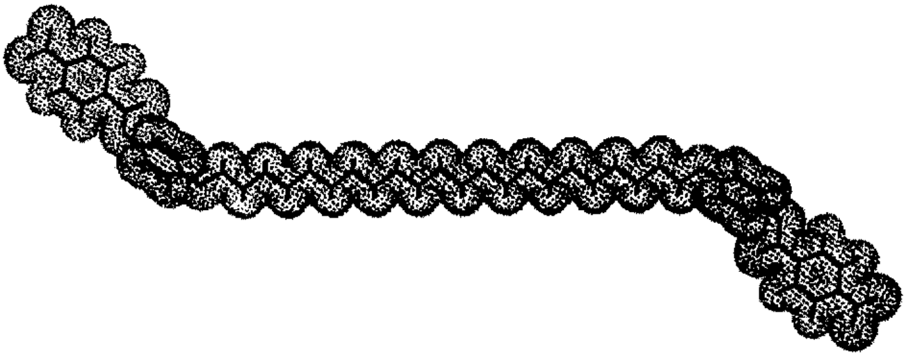

Fig. 4. Molecular modeling of C22NO2. The dots simulate the van der Waals volume of the different atoms.

packing of C22NO2 molecules, illustrated in Fig. 6, corresponds to the best lateral register of the rigid aromatic parts, on the one hand, and of the aliphatic chains, on the other, so that the amphipathic character [9] of the molecules is well satisfied. Because the average molecular length is 50 Å (as measured along the molecular axis), it is clear that the molecules are tilted within the layers. By comparison with the layer thickness, the tilt angle can be estimated to be about 50°.

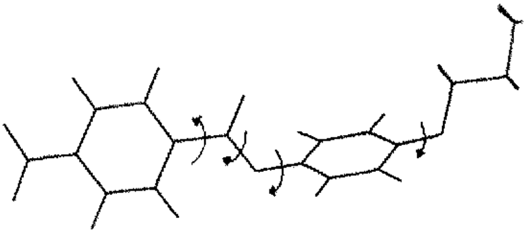

Fig. 5. Definition of the bonds allowed to rotate in the conformational study of C22NO2.

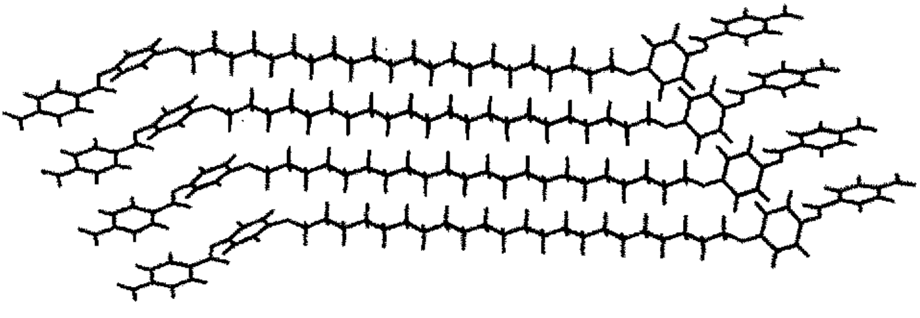

Fig. 6. Lateral packing of the C22NO2 molecules within the smectic layers.

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