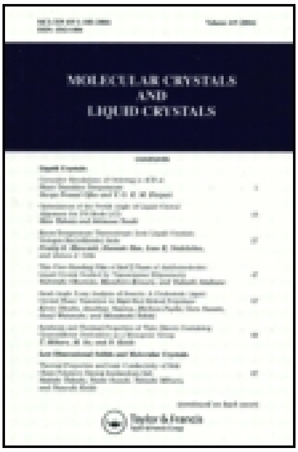

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Liquid Crystalline 4′-(2,3 Dihydroxypropoxy) Diphenyl 4-n-Alcoxy Acids

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Liquid Crystalline 4′-(2,3 Dihydroxypropoxy) Diphenyl 4-n-Alcoxy Acids

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4′-(2,3 Dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid have been synthesized and analyzed by IR and NMR experiments. The liquid crystalline character and the phase transitions of these two acids have been studied by differential scanning calorimetry (DSC) and variable temperature X-ray diffraction (VTXRD). These two liquid crystalline monomers are designed to be flexible, rigid and polyfunctional, so that they can be used in the synthesis of new macromolecules with side chain liquid crystals.

Keywords Dihydroxypropoxy diphenyl 4-n-alcoxy acids; liquid crystalline diol-acid monomers

Introduction

Biphenyl derivatives have been extensively studied owing to their application in liquid crystal displays [1] and because they are able to undergo functionalization reactions, providing access to a variety of interesting compounds in different research fields [2, 3].

One of these fields is their use for obtaining liquid crystalline polymers with mesogenic side chains, which have attracted special interest because of the possible applications in the fields of non-linear optics, optical storage and electro-optic displays [4]. These polymers can be obtained either by chemical modification of a prepolymer with a functionalized liquid crystal or by polymerization of a liquid crystal monomer.

Among the different functionalities, diol-acid compounds are important in both supramolecular chemistry [5] and polymer chemistry [6, 7]. In the present work, 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid (see structures in Fig. 1) were prepared and their properties are

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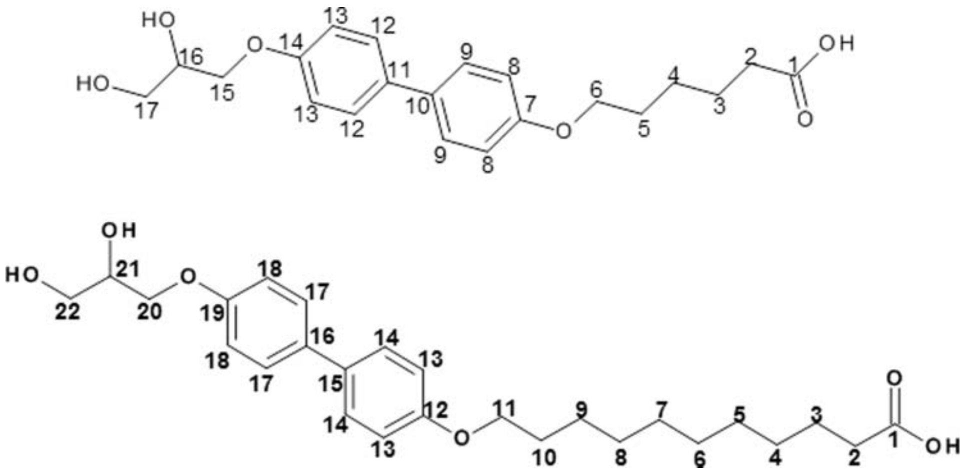


Figure 1. Structure formulae of the 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid monomers.

being investigated for the first time. The title compounds are potential monomers which may form liquid crystals polymers. The phase transitions of these two acids have been studied by differential scanning calorimetry (DSC). The mesomorphic behavior of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic is analyzed by variable-temperature X-ray diffraction (VTXRD). The corresponding analysis for 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid is more complicated, due to the overlapping of the different transitions, as will be shown below, so that its mesomorphic behavior will be reported in due course.

Experimental

Materials

The following reagents were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted: 4,4′-dihydroxybiphenyl, 6-bromohexanoic acid, 11-bromoundecanoic acid, 6-bromohexanoyl chloride, 4-chloromethyl-2,2-dimethyl-1,3-dioxolane, thionyl chloride and KOH.

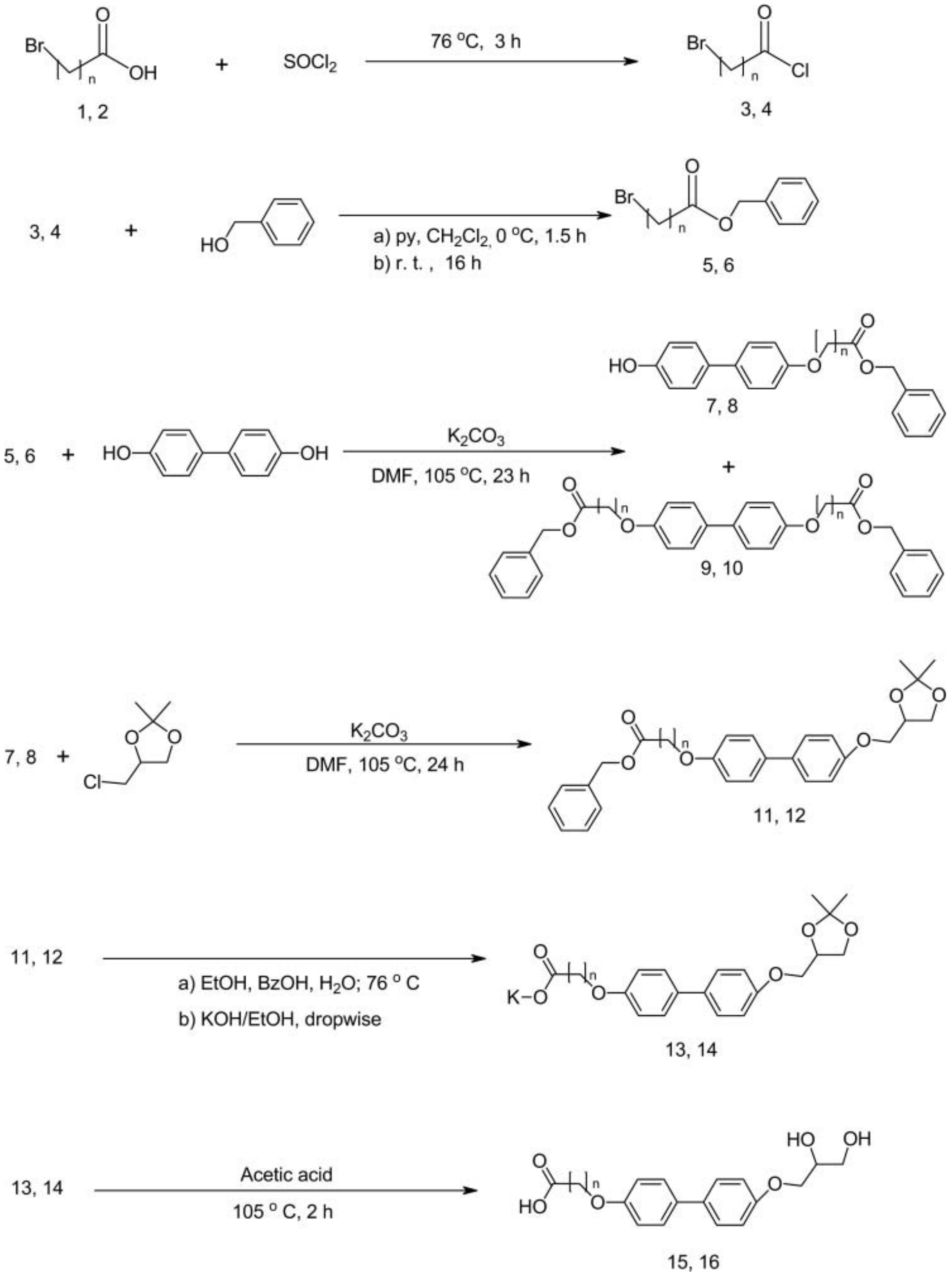
Benzyl alcohol, pyridine and DMF were also obtained from Aldrich and distilled from CaH_2 prior to use. Reagent grade dichloromethane was distilled from CaH_2 under argon.

Acetic acid, ethanol, hexane and K_2CO_3 were purchased from JT. Beaker (reagent grade) and were used without further purification.

For column chromatography we used a MN Kieselgel 60(0.063-0.2mm). The eluents are given at the individual compounds.

Synthesis

The synthesis of 4′-(2,3 dihydroxypropoxy) diphenyl 4-n-alcoxy acids involved a protection deprotection method [8]. The synthetic route for these acids is illustrated in Scheme 1, involving several steps, as follows: *Step 1)* Protection of the carboxylic acid of



Scheme 1. Synthetic route for 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid monomers.

6-bromohexanoic acid with benzyl alcohol to yield Benzyl 6-bromo hexanoate (**5**). Using the commercial available acyl chloride or preparing it by the well known reaction of thionyl chloride [9] with the benzyl alcohol; *Step 2)* Preparation of (**7**) by etherification of 4,4′-dihydroxybiphenyl with the chain extender benzyl 6-bromohexanoate using standard procedures for a Williamson ether synthesis; *Step 3)* Etherification of 4-chloromethyl-2,2-dimethyl-1,3-dioxolane with compound **7** using standard procedures for a Williamson ether synthesis, and *Step 4)* Cleavage of the benzylic ester (**11**) and 1,3-dioxolane with acetic acid to afford the diol-acid monomer **15** or **16**.

The synthesis of the 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid monomers follows the same technique. The synthetic procedure for the preparation of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid is given as an example.

The particular conditions for any of these steps are given below.

Preparation of the acyl chlorides (3, 4): They were be prepared by treating 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid or 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid with an excess of thionyl chloride. The excess thionyl chloride is distilled off to give, as the residue, the corresponding acyl chloride.

Preparation of the benzyl esters (5): Esterification of 6-bromohexanoyl chloride with benzyl alcohol. The crude acid chloride **3** (2.2 g, 10×10^{-3} mol) was dissolved in dry dichloromethane (20 ml) and added to a mixture of benzyl alcohol (2.2 g, 20×10^{-3} mol), dry pyridine (0.98 mL) in dry dichloromethane (70 mL). The reaction mixture was stirred for 18 hrs and then acidified with 2% aq. HCl. The organic layer was separated and washed with water until it become neutral. The solvent was removed and the residue was dried under a vacuum overnight. The crude product was subsequently purified by column chromatography on silica gel with dichloromethane and hexane. The pure product **5** (2.25 g, 7.89×10^{-3} mol, 77.5%) was obtained as a pale yellow liquid from vacuum distillation.

IR: ν (C=O), 1732 cm^{-1}; ν (C—O), 1253 cm^{-1}; ν (C_{Ar}—H), 3034 cm^{-1}; ν (C_{sp3}—H), 2940 cm^{-1}; ν (C-Br), 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.38 ppm (CH_2-Br, $2H_1$); 1.81 ppm (CH_2, $2H_2$); 1.46 ppm (CH_2, $2H_3$); 1.87 ppm (CH_2, $2H_4$); 2.37 ppm (CH_2, $2H_5$); 5.12 ppm (CH_2-Φ, $2H_7$), 7.35 ppm (C-H_{Ar}, $5H_{9\text{-}11}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): $C_{1,}$33.03 ppm; C_2 33.45 ppm; C_3, 27.60 ppm; C_4, 24.05 ppm; C_5, 34.03 ppm; C_6, 173.23 ppm; C_7, 66.16 ppm; C_8, 136.00 ppm; C_9, 127.76 ppm; C_{10}, 128.55 ppm; C_{11}, 128.21 ppm.

Preparation of the intermediate 7: It was synthesized from **5** and 4,4′-dihydroxybiphenyl using a typical Williamson ether reaction conditions. After 23 hr reaction, the suspension was allowed to cool. The KCO_3 was filtered off and the solvent was evaporated to dryness in vacuo. The residue of the reaction mixture was dissolved in dichloromethane and cooled to 0°C. The resulting unreacted crystals of 4,4′-dihydroxybiphenyl were filtered and the dichloromethane was removed by evaporation. The residue was further purified by column chromatography on silica gel with dichloromethane/ethyl acetate 9:1, and again with CH_2Cl_2. Crystallization from dichloromethane/hexane 3:1 gave (**7**) as a white solid and the yield is 66%. *Elem. anal.* calculated for $C_{25}H_{26}O_4$ (theory/experimental):%C 76.92/75.69;%H 6.67/6.46;%O 16.41/16.85.

Preparation of compound 11: The title compound was synthesized from **7** and 4-chloromethyl-2,2-dimethyl-1,3-dioxolane using a typical Williamson ether reaction conditions. The product was isolated and purified as mentioned above. However, column chromatography on silica gel with dichloromethane/ethyl acetate was not realized. The yield is 49% (**11**). *Elem. anal.* Calcd for $C_{31}H_{36}O_6$ (theory/experimental):%C 73.81/73.88;%H 7.14/6.64;%O 19.05/19.48.

Preparation of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid ($C_{21}H_{26}O_6$) 15: Compound **11** (2.14 g, mol) was dissolved at 76°C in a stirred mixture of 120 mL ethanol, 20 mL benzyl alcohol, and 3 mL water. A solution of KOH

(20 mL) in ethanol/water was then added slowly. The reaction mixture was stirred for one hour. After cooling to room temperature the resulting white solid was filtered to yield the potassium carboxylate **13**, which was used without further purification. The potassium salt (0.18 g, 0.39×10^{-3} mol) was refluxed in acetic acid (20 mL) with stirring at 105°C for 2h. The resulting clear solution was allowed to cool and then poured into water (5 × 20 mL). The diol-acid (**15**) formed was collected by filtration, washed with copious amount of water and dried under vacuum at 80°C for 15 hours. Yield: 0.095 g, 68%.

IR: ν (br, O—H), 3383 cm^{-1}; ν (C—H sp^3), 2938 cm^{-1}; ν (Φ-H), 3037 cm^{-1}; ν (C=C),1606 cm^{-1}; ν (C—O),1243 cm^{-1}; ν (Φ-disust.), 807 cm^{-1}; (C=O acid), 1691 cm^{-1}.

^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): $C_{1,}$175.21 ppm; C_2 34.29 ppm; C_3, 24.97 ppm; C_4, 25.85 ppm; C_5, 29.15 ppm; C_6, 67.99 ppm; C_7, 158.40 ppm; C_8, 115.44 ppm; C_9, 127.85 ppm; C_{10}, 132.89 ppm; C_{11}, 132.82 ppm; C_{12}, 127.85 ppm; C_{13}, 115.49 ppm; C_{14}, 158.40 ppm; C_{15}, 70.29 ppm; C_{16}, 70.62 ppm; C_{17}, 66.38 ppm.

4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid (16): *IR:* ν (br, O—H), 3383 cm^{-1}; ν (C-H sp^3), 2916 cm^{-1}; ν (Φ-H), 3037 cm^{-1}; ν (C=C),1606 cm^{-1}; ν (C—O), 1242 cm^{-1}; ν (Φ-disust.), 807 cm^{-1}; (C=O acid), 1710 cm^{-1}. *^{13}C NMR* (100 MHz, DMSO-d_6) δ (ppm): $C_{1,}$175.27 ppm; C_2 34.57 ppm; C_3, 25.2 ppm; C_4, 29.16 ppm; C_5, 29.25 ppm; C_6, 29.30 ppm; C_7, 29.35 ppm; C_8, 29.35 ppm; C_9, 26.11 ppm; C_{10}, 29.47 ppm;; C_{11}, 68.43 ppm; C_{12}, 158.57 ppm; C_{13}, 115.79 ppm; C_{14}, 127.86 ppm; C_{15}, 133.20 ppm; C_{16}, 132.96 ppm; C_{17}, 127.86 ppm; C_{18}, 115.70 ppm; C_{19}, 158.57 ppm; C_{20}, 70.56 ppm; C_{21}, 70.77 ppm; C_{22}, 63.53 ppm.

Instrumentation and Measurements

The chemical structures of intermediates and products were confirmed by a combination of nuclear magnetic resonance (NMR) spectroscopy (Varian 400 MHz spectrometer), Infrared (IR) spectroscopy (Perkin-Elmer Paragon 500 spectrometer) or elemental analysis. FTIR analyses were performed on a Perkin–Elmer Paragon 500 spectrometer, which was equipped with a diamond crystal (attenuated total reflection (ATR) crystal). ^{1}H-NMR and ^{13}C-NMR spectra were acquired with a Varian (400 MHz) spectrometer. The NMR samples were prepared as 10–20% (w/v) solutions in $CDCl_3$ or DMSO-d_6. Spectra were usually recorded at room temperature. Elemental analysis was performed by the Microanalytical Laboratory of the Universidad Autónoma de Hidalgo (UAEH), México, on a Perkin Elmer 2400 analyzer.

A Perkin-Elmer Calorimeter equipped with an auto-cool accessory and Thermal Analysis Data Station was employed for DSC studies; transition temperatures were collected during heating and cooling scans, under N_2 atmosphere, at a rate of 10°C/min. The temperature calibration was performed with high-purity standards of n-dodecane, Indium and Zinc, while the enthalpy calibration was also performed with Indium ($\Delta H = 28.45$ J/g). Estimated errors are the following: ± 0.2°C in temperature and 1 J/g in enthalpy.

X-Ray Diffraction (XRD) powder patterns were recorded in the reflection mode by using a Bruker D8 Advance diffractometer provided with a PSD Vantec detector (from Bruker, Madison, Wisconsin). Cu Kα radiation ($\lambda = 0.1542$ nm) was used, operating at 40 kV and 40 mA. The parallel beam optics was adjusted by a parabolic Göbel mirror with horizontal grazing incidence Soller slit of 0.12° and LiF monochromator. The equipment was calibrated with different standards. A step scanning mode was employed for the detector. The diffraction scans were collected with a 2θ step of 0.024° and 0.2 s per step.

Variable-temperature experiments (VTXRD) were performed by using as temperature controller an Anton-Paar TTK-450 chamber, provided with a liquid nitrogen regulator and a vacuum pump. A step-temperature acquisition mode was used: the temperature was raised or lowered to the desired value, and after 5 min for temperature equilibration the diffractograms were acquired.

Results and Discussion

All compounds had IR, ^{1}H and ^{13}C NMR spectroscopic data and/or elemental analysis data, as shown above, in accordance with their assigned structures.

Phase Transitions

The phase transitions of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid **(15)** and 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid **(16)** were studied by thermal analysis. The DSC curves of the acid **(15)** are presented in Fig. 2 for the first melting, subsequent cooling and second melting. Two intense transitions, with peak temperatures at 120.5 and 175.9°C, are observed in the first melting of the sample, both comprising a relatively high enthalpy: 31.6 and 57.8 J/g, respectively, which, in principle, are indicative of highly ordered phases: most probably 3-dimensional crystals. On the contrary, the cooling from the isotropic melt exhibits two transitions, at 170.2 and 127.6°C, involving now considerably smaller enthalpies: 8.1 and 16.2 J/g, respectively, which may indicate that mesophases are involved.

The subsequent melting presents again two main transitions (151.9°C, 13.5 J/g and 176.9°C, 9.4 J/g) but also a small one is observed at around 163°C, with an enthalpy of only 1 J/g.

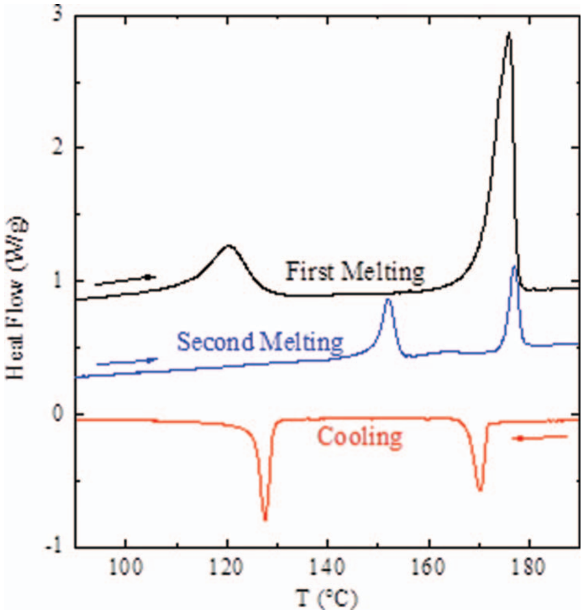


Figure 2. DSC curves for 4′-(2,3-dihydroxypropoxy) diphenyl 4-oxy hexanoic acid (**15**).

Table 1. Parameters of the Phase Transitions for the Acid **15** in the First DSC Heating Run, Cooling from the Isotropic Melt, and Second Melting.

	First melting: T, °C (ΔH, J/g)	Cooling: T, °C (ΔH, J/g)	Second melting: T, °C (ΔH, J/g)
	120.5 (31.6)	170.2 (8.1)	151.9 (13.5)
	175.9 (57.8)	127.6 (16.2)	163.0 (1.0)
			176.9 (9.4)
Total ΔH, J/g	(89.4)	(24.3)	(23.9)

The different transitions are collected in Table 1, where it is evident that the enthalpy is not recovered after the first melting, since the total enthalpy was originally of 89.4 J/g and it is only around 24 J/g for the subsequent cooling and second melting.

On the other hand, the DSC first melting curve for 4′-(2,3-dihydroxypropoxy) diphenyl 4-oxy undecanoic acid **(16)** is presented in Fig. 3. Multiple transitions are now observed, with a high degree of overlapping, involving a total enthalpy of melting of 137 J/g. All of them appear in the interval from around 120 to 180°C, i.e. rather similar to acid **15**, but now the deconvolution into different transitions is rather difficult.

Analysis of the Phase Structure

Figure 4 shows the diffractograms, acquired at room temperature, of the original powders of the two acids. Multiple and narrow diffractions are observed in both cases, indicating, most probably, the presence of highly-ordered 3-dimensional crystals.

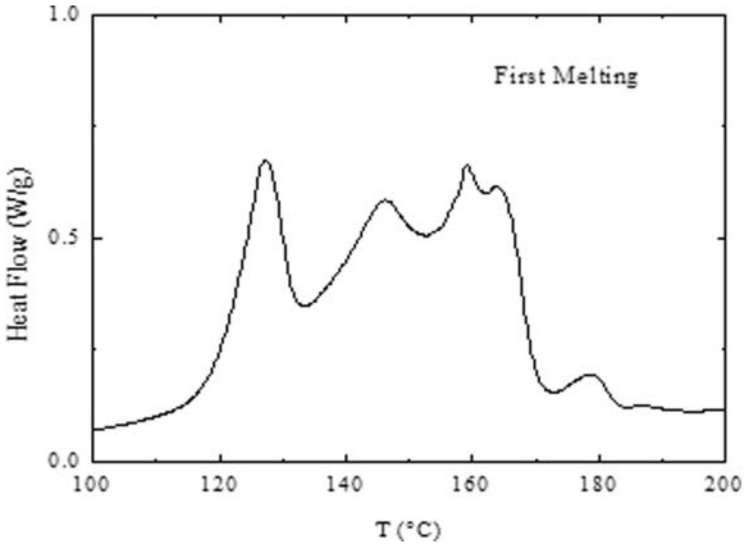


Figure 3. DSC first melting curve for 4′-(2,3-dihydroxypropoxy) diphenyl 4-oxy undecanoic acid (**16**).

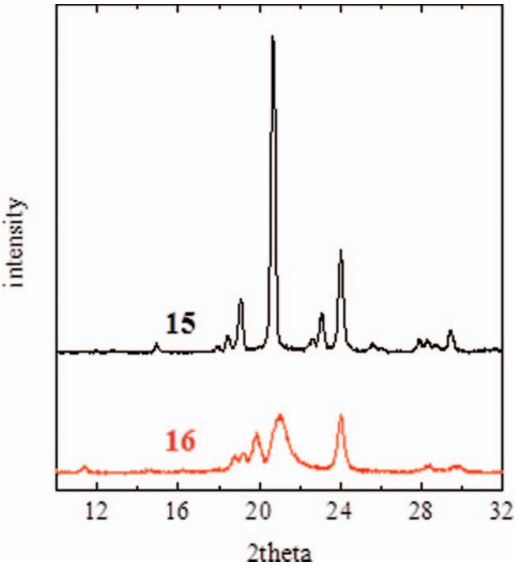


Figure 4. Room-temperature X-ray diffractograms of the original powders of the two acids.

The nature of the phases involved in the different transitions observed by DSC has been studied by variable temperature X-ray diffraction (VTXRD). Thus, Fig. 5 shows the successive diffraction patterns obtained: a) upon heating 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid to 180°C, b) on cooling it from the isotropic melt, and c) during the subsequent second melting.

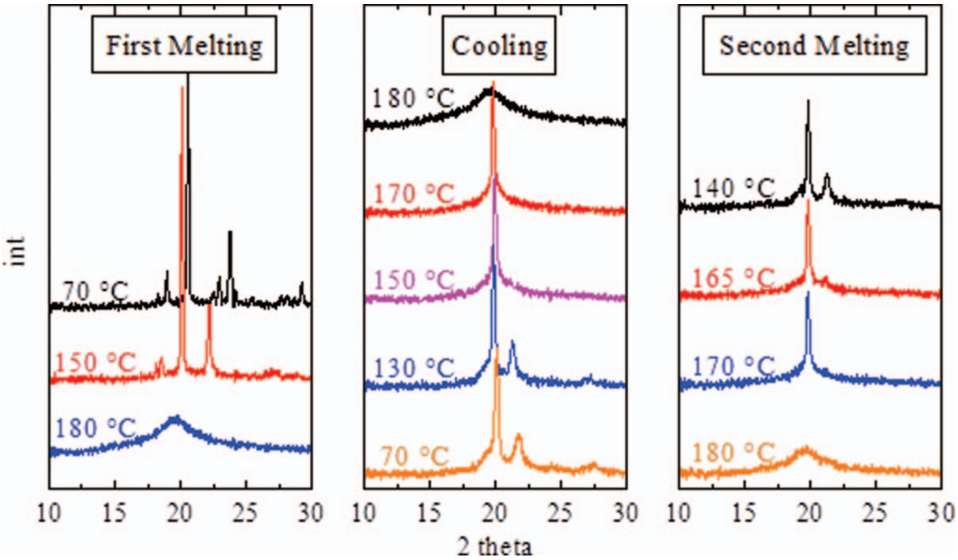


Figure 5. VTXRD patterns for 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid (**15**) on the first melting of the original powder (left), cooling from the isotropic melt (middle) and subsequent second melting (right).

It was observed, first, that the initial diffractogram at room temperature in Fig. 4 is maintained up to around 110°C (see diffractogram at 70°C). Afterwards, and coinciding with the first DSC melting peak, the diffractogram changes, but keeping multiple and narrow diffractions (pattern at 150°C). Finally, the isotropization of the sample is attained, and only a broad amorphous peak is obtained (diffractogram at 180°C). With this information and from that in the corresponding DSC melting curve, it can be deduced that the first DSC peak at around 120°C should correspond to a solid-solid transition involving two different crystalline forms, and the DSC transition at around 175°C corresponds to the melting of the second crystalline form directly to the isotropic melt. Therefore, no mesophases seem to be involved during the first melting of the acid **15**.

The diffraction patterns during the cooling from the isotropic melt are presented in the middle frame of Fig. 5. At 170°C, a well different diffractogram is obtained, characterized by a single diffraction with a relatively broad base. This pattern is maintained down to around 130°C, when the diffractogram changes to a well different one, involving two main, relatively narrow, diffractions. This diffractogram does not change at lower temperatures down to ambient conditions (see diffractogram at 70°C in the middle frame of Fig. 5), except, evidently for the displacement of the diffractions due to temperature changes. From these patterns and by comparison with other similar systems [2], it seems that the first exotherm in Fig. 3, at around 170°C, may correspond to the formation of a smectic mesophase of intermediate order, most probably of SmB type. The second exotherm may correspond to the transformation into a smectic crystal of the type SE.

It is important to mention that no transformation of this SE phase is obtained even after several hours at room temperature. Therefore, none of the two crystal forms observed in the first melting are recovered, at least in a reasonable time. They seem to be obtained only after crystallization from solution.

The second melting of **15** (right frame in Fig. 5) indicates a reverse behavior in relation to the former cooling, since the low-temperature phase (assigned to a SE phase) transforms into the smectic SmB mesophase at around 170°C, prior to its final isotropization. However, it is not clear the nature of the small transition centered at around 163°C in the DSC second melting curve. We plan to perform real-time variable-temperature experiments employing synchrotron radiation in order to ascertain this aspect and the former conclusions.

Regarding the phase transition in the acid **16**, the fact that all of them appear very much overlapped precludes the analysis by VTXRD in our diffractometer, so that it will be also studied by using synchrotron techniques.

Conclusion

Two new monomers, derivatives of 4,4′-dihydroxybiphenyl, have been prepared by a protection/deprotection method. Structures were confirmed by IR, NMR and elemental analysis.

This method is useful for the construction of several functionalized biphenol derivatives with one alcoxy acid and diol terminal chains. These terminal groups enhance the polarity of the compounds, leading to the appearance of mesomorphic properties. The DSC and variable-temperature X-ray diffractograms of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-hexanoic acid indicate the appearance, after the first melting, of several LC phases, probably of the type SmB and SE. In the case of 4′-(2,3 dihydroxypropoxy) diphenyl 4-oxy-undecanoic acid, the DSC transitions are very much overlapped, and further studies are needed.

Anyway, it is expected that these acids may be used as liquid crystals monomers, and for obtaining new liquid crystal macromolecules.

Acknowledgments

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