

acids by slightly modifying synthetic procedures described in the literature (2). In a typical procedure 6.9 g (0.3 mol) sodium was dissolved in 250 ml absolute ethanol under nitrogen. Sodium dithionite (0.1 g) was added to the solution to prevent oxidation of reactants and products. Hydroquinone, 33 g (0.3mol), was added, and the flask was equipped with a magnetic stirrer and a reflux condenser. 0.3 mol of α -bromo-n-alkanoic acid ethyl ester was slowly added. The reaction mixture was refluxed overnight. Most of the solvent was then removed by distillation. Water (100 ml) was added to replace the ethanol and distillation was continued to near dryness. The mixture was then cooled to room temperature and dissolved in 200 ml of cold 30% aqueous sodium hydroxide, and washed with two 50 ml portions of ether to remove the disubstituted products. The aqueous solution was then refluxed for 2 h under nitrogen to hydrolyse the ester. The reaction mixture was acidified by dropwise addition of concentrated hydrochloric acid and the crude product was filtered off. The crude product was purified by dissolution in 100 ml ether and extraction with 3x100 ml of 10% aqueous sodium bicarbonate. The aqueous phase was acidified and filtered to isolate the hydroxyphenoxy acid. The yields after recrystallization from ethyl acetate/petroleum ether were around 50 %.

Characterization.

The synthetic products and intermediates were characterized by infrared spectroscopy (Perkin-Elmer 457 and Nicolet FT IR 205), NMR spectroscopy (Varian Gemini 2000), mass spectrometry (Jeol SX 102), differential scanning calorimetry (Perkin-Elmer DSC 7) and by polarizing optical microscopy (Leitz equipped with a hot stage with regulating unit Mettler FP81 and FP800).

Characteristics of compounds 1 n=1: Commercial 4-hydroxyphenoxy acetic acid (Johnson & Matthew) was used as received.

n=2: mp 167-168°C (lit. 173°C (3), 169.5-170.5°C (2)). IR/cm⁻¹: 3350(s); 3200-2500(broad); 1710(s); 1510(s); 1350-1030 (several,s); 920(m) acid dimer; 840(m) and 810(m). ¹HNMR (acetone-D₆/ppm): 2.8 (t, 2H); 4.2(t, 2H); 6.8(m, 4H).

n=3: mp 118°C (lit. 120°C (3), 121-122°C (2)). IR/cm⁻¹: 3350(s); 2950-2860(several,m); 3200-2500(broad); 1700(s); 1510(s); 1430(m); 1350-1030(several,s); 940(m); 830(m) and 810(m). ¹HNMR (acetone-D₆/ppm): 2.1 (m); 2.5 (t, 2H); 4.0 (t, 2H); 6.8 (m, 4H).

n=4: mp 141-142°C (lit. 142-145°C (4)). IR/cm⁻¹: 3350(s); 3200-2500(broad); 2950-2850(several,m); 1700(s); 1510(s); 1430(m); 1350-1030(several,s); 830(m) and 810(m). ¹HNMR (acetone-D₆/ppm): 1.8 (m, 4H); 2.4 (t, 2H); 3.95 (t, 2H); 6.8 (m, 4H).

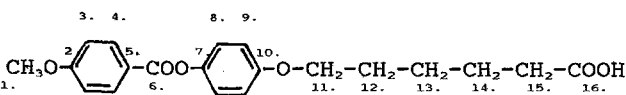
n=5: mp 103-104°C. IR/cm⁻¹: 3150(s); 3200-2500(broad); 2950-2860(several, m); 1696(s); 1600(w) and 1511(s); 1470(m); 1300-1030(several,s); 962(w) acid dimer; 825(m). ¹H1NMR (methanol-D₄, ppm): 1.5-1-8 (m, 6H); 2.4 (t, 2H); 3.9 (t, 2H); 6.7 (m, 4H).

Syntheses of compounds 2. The 4- ω -carboxyalkoxyphenyl-4'-methoxybenzoates **2** were prepared from the corresponding compounds **1** and 4-anisoyl chloride in a Schotten-Baumann esterification reaction. Typically, 0.05 mol of compound **1** and 0.3 g of sodium dithionite were dissolved in 85 ml of 10% aqueous potassium hydroxide in a 200 ml flask, placed in an ice bath. The flask was equipped with a mechanical stirrer and nitrogen inlet. A solution of 8.53 g (0.05 mol) anisoyl chloride in 10 ml of ether was added from a dropping funnel. Mixing was continued for 2 h. The reaction mixture was then acidified with 3 M hydrochloric acid, and the crude product was obtained by filtration. The crude product was purified by recrystallization from a mixture of ethanol, acetic acid and water (5/1/1). The yields after recrystallization were around 70%.

Characteristics of compounds 2. n=1: mp 180°C. IR/cm⁻¹: 3100-2500; 2960-2850(m); 1730(s); 1700(m, shoulder); 1610(s) and 1510(s); 1420(m); 1290-1030(s, several); 840(m) and 820(w). ¹HNMR (DMSO-D₆, ppm): 4.7 (s, 2H); 6.9-7.3 (m, 6H); 8.1 (d, 2H). MS: m+, z/e=302.0797, deviation from calculated mass for C₁₆H₁₄O₆ = 0.6 mmu.

n=2: mp 140-141°C. IR/cm⁻¹: 3100-2500(broad); 2960-2850(m); 1729(s); 1702(m, shoulder); 1609(s) and 1510(s); 1420(m); 1300-1030(s, several); 840(m) and 820(w). ¹HNMR (CDCl₃, ppm): 2.9 (t, 2H); 3.9 (s, 3H); 4.9 (t, 2H); 6.9-7.1 (m, 6H); 8.1 (d, 2H). MS: m+ z/e=316.0953, deviation from calculated mass for C₁₇H₁₆O₆ = 0.6 mmu.

Table 1. ¹³CNMR chemical shifts for compounds **2** n.



	n = 1	n = 2	n = 3	n = 4	n = 5
1.	57.4	55.4	55.4	55.2	56.2
2.	165.5	163.7	163.8	163.9	164.3
3.	116.1	113.9	113.7	113.2	114.4
4.	131.8	132.1	132.1	132.0	132.6
5.	120.8	121.8	121.9	121.8	121.8
6.	164.3	165.5	165	165	165.2
7.	144.2	144.6	144.5	144.0	144.6
8.	122.6	122.5	122.4	122.0	123.0
9.	114.9	115.2	114.9	114.2	115.6
10.	157.2	156.0	156.2	156.2	157.0
11.	64.6	63.8	66.8	67.2	68.4
12.	-	24.2	28.2	29.1	34.6
13.	-	-	30.3	20.6	24.9
14.	-	-	-	32.8	25.8
15.	-	-	-	-	34.3
16.	169.9	171.7	178	179	179.3

n=3: IR/cm⁻¹: 3100-2500(broad); 2960-2850(m); 1730(s); 1690(s); 1600(s) and 1500(s); 1420(m); 1300-1030(s,several); 840(m) and 820(m). ¹HNMR (CDCl₃, ppm): 2.1 (t, 2H); 2.6 (t, 2H); 3,9 (s, 3H); 4.1 (t, 2H); 6.8-7.1 (m, 6H); 8.1 (d, 2H). MS: m+, z/e=330.1102, deviation from calculated mass for C₁₈H₁₈O₆ = 0.2 mmu.

n=4: mp 126.5°C. IR/cm⁻¹: 3200-2500(broad); 2960-2850(m); 1726(s); 1708(s); 1604(s) and 1511(s); 1420(m); 1270-1015(s, several); 939(m, broad); 845(m) and 819(w). ¹HNMR (CDCl₃, ppm): 2.8 (m, 4H); 2.5 (t, 2H); 3,9 (s, 3H); 4.0 (t, 2H); 6.8-7.1 (m, 6H); 8.1 (d, 2H). MS: m+, z/e=344.1243, deviation from calculated mass for C₁₉H₂₀O₆ = 1.7 mmu.

n=5: IR/cm⁻¹: 3200-2500(broad); 2960-2850(m); 1719(s); 1708(s); 1605(s) and 1510(s); 1420(m); 1280-1070(s,several); 935(m,broad); 840(m) and 820(w). ¹HNMR (CDCl₃, ppm): 1.5-1.9 (m, 6H); 2.4 (t, 2H); 3,9 (s, 3H); 4.0 (t, 2H); 6.8-7.1 (m, 6H); 8.1 (d, 2H). MS: m+, z/e=330.1102, deviation from calculated mass for C₂₀H₂₂O₆ = 0.5 mmu.

Results and discussion

Optical observations of compounds 2 n at the polarizing microscope suggest the occurrence of liquid-crystalline phases when n=3 or 5. The calorimetric analysis supports this assumption. In figure 1 the DSC traces of 2 n=3, 4 and 5 are seen. In the heating run the endothermic peaks for 2 n=3 are separated by only a few degrees and not very well resolved, but the exothermic peak at the isotropization temperature is clearly seen on cooling. The liquid crystalline region is much broader in 2 n=5 and the endothermic peaks are well resolved. The shoulder at 107°C on the melting endotherm of this compound is probably due to cold crystallization. The transition temperatures and the thermodynamic data are collected in table 2.

Table 2. Thermodynamic data for mesomorphic compounds 2.

n	T _m	ΔH	ΔS	T _i	ΔH	ΔS
	/°C	/kJ mol ⁻¹	/kJ mol ⁻¹ K ⁻¹	/°C	/kJ mol ⁻¹	/kJ mol ⁻¹ K ⁻¹
3	141	37.5	0.090	146	3.3	0.0079
5	110	30.4	0.081	134.5	5.9	0.0145

The mesophase-isotropic phase transitions are almost reversible, while a marked supercooling is observed for the solid-mesophase and the solid-isotropic transitions. Such behaviour is typical for many types of low molar mass thermotropic liquid crystals (5). The mesophases showed schlieren textures and droplets typical of nematic phases under the polarizing microscope, and the mesophases are therefore identified as nematic phases.

The molar isotropization enthalpies and entropies for the compounds investigated are rather high, closer to values

measured for smectics than for nematics (5). On the other hand it is reasonable to assume that compounds 2 $n=3$ and $n=5$ form dimers by hydrogen bonding, and therefore resemble nematogenic compounds with rigid terminal groups and flexible cores. The scarce data available for such compounds (6, 7, 8) seem to indicate high values of enthalpy and entropy of isotropization as well as for crystal-nematic transitions in such systems.

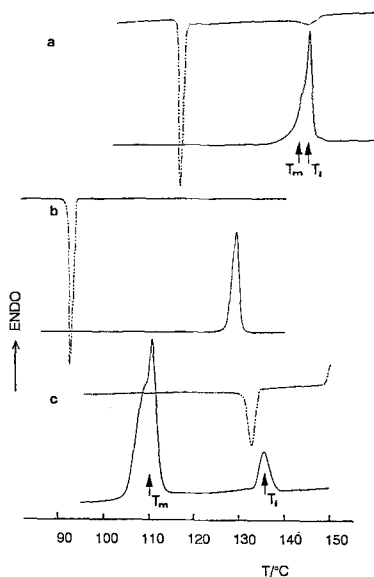


Figure 1. The DSC traces of compounds a) 2 $n=3$, b) 2 $n=4$, and c) 2 $n=5$. Heating and cooling rate $10^{\circ}\text{C min}^{-1}$.

The ratio $\delta S(\text{nematic-isotropic})/\delta S(\text{total})$ has been used as an indirect measure of the degree of order of a nematic phase. For a large number of low molar mass nematics this ratio ranges between 0.02 and 0.04, evaluated from calorimetric measurements.(5) Calculated values for semiflexible polymers range between 0.07 and 0.17 (9, 10). For the compounds under investigation the values for the entropic ratio are 0.08 for 2 $n=3$ and 0.15 for 2 $n=5$ thus showing that spacers of conformational mobility do not decouple the interaction between the aromatic rings in the dimer.

The reason why compound 2 with $n=4$ does not form a liquid-crystalline phase is not very clear. Several series of compounds with similar behaviour have been reported, however. Krone and Ringsdorf (11) report two cases of dimers with interconnecting flexible spacers where the spacer contains an odd number of methylene groups and the compounds do not form liquid-crystalline phases, whereas dimers with even membered spacers do. Similar odd-even behaviour has been observed in other cases (8, 12). In the compounds under investigation the

spacer in 2 $n=3$ contains four atoms, in 2 $n=5$ six atoms, but in 2 $n=4$ the spacer contains five atoms.

Compounds of type 2 are currently used in our laboratory as side-chains for liquid-crystalline polymers.

Acknowledgements

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