Synthesis and Thermal Properties of Twin Compounds, Alkanediacids 4-(4′-Cyano)-biphenyl Diesters

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Alkanediacids 4-(4′-Cyano)-biphenyl Diesters, Twin Mesogens

Four twin mesogens from the homologous series of alkanediacids 4-(4′-cyano)-biphenyl diesters (n = 4, 6, 8, 10) have been synthesized and their thermal properties have been studied. Assignment of the phases has been made by means of polarizing microscopy and DSC measurements. It has been found, that the increase of the spacer length causes the lowering of the mesophase temperature range and influences other thermodynamic parameters of the compounds investigated.

I. Introduction

Recently, dimeric liquid crystalline compounds formed through rigid mesogen – flexible spacer – rigid mesogen sequences ("twins") have been the object of the interest of many research workers. In many scientific papers [1–10] twins comprising two calamitic units connected via their terminal chains have been reported. This class of mesogens is very interesting because they are often regarded as model compounds for thermotropic liquid crystalline semi-flexible main chain polymers on one hand and for the conformational study of alkyl or alkoxy chains on the other. Moreover, many liquid crystalline dimers possess quite different properties in comparison with conventional low molecular mass mesogens. Some of them can form very rare liquid crystalline phases.

This paper is intended to describe the synthesis and liquid crystalline properties of symmetric diesters connected via linear aliphatic alkyl groups.

To the best of our knowledge, liquid crystalline dimers of such type had not been previously reported.

II. Materials and Methods

Synthesis

The four diesters were prepared from the diacids HOOC(CH₂)ₙCOOH (n = 4, 6, 8, 10) and 4-cyano-4'-hydroxybiphenol:

\[ 2 \text{NC} \equiv \text{O} + \text{HOOC} \equiv \text{C}(\text{CH}_2)_n \equiv \text{COOH} \rightarrow \text{NC} \equiv \text{O} \equiv \text{OOC} \equiv \text{C}(\text{CH}_2)_n \equiv \text{COO} \equiv \text{CN} \]

All chemicals were of commercial origin (Aldrich). In a typical esterification procedure the 1,6-hexanedicarboxylic (suberic, n = 6) acid (0.435 g, 0.0025 mol) and 4-cyano-4'-hydroxybiphenol (0.975 g, 0.005 mol) were dissolved in 15 cm³ of dry methylene chloride and 1.24 g (~ 0.006 mol) of N,N-dicyclohexylcarbodiimide and a catalytic amount of 4-dimethyl-aminopyridine were added. The reaction mixture was stirred for 24 h, then N,N-dicyclo-hexylurea was filtered off and, after removal of solvent, the crude product was purified by column chromatography (silicagel, CHC₃) in comparison with conventional low molecular mass mesogens. Some of them can form very rare liquid crystalline phases.

The analogous procedure was used in the synthesis of other diesters with almost the same yield. The structure of all final products were confirmed by means of IR and 'H NMR spectra, mass spectrometry and elemental analysis.

Apparatus

Infrared spectra were obtained by using FT-IR Perkin Elmer 2000 spectrophotometer, whereas...
\( ^1H \) NMR spectra were recorded by means of Varian Gemini 200 spectrometer. Mass spectrometry was done on Fimigan MAT 8200 mass spectrometer. Differential scanning calorimetry (DSC) measurements were carried out on Perkin-Elmer DSC-2 calorimeter, calibrated with indium and zinc standards. Samples of the mass between 5–7 mg were scanned with the rate of 5 °C/min. Transition enthalpies were determined with the accuracy of 5%. Polarizing microscope observations were performed with Leitz Orthoplan microscope equipped with Mettler hot stage FP82. Isotropic melts of samples were placed between clean glass plates and then they were cooled down to the desired temperatures.

### III. Results and Discussion

The results of elemental analysis are listed in Table I. The data confirm the suggested molecular formulae. The spectral data of the compounds 1–4 give almost identical values of IR absorption maxima and \( ^1H \) NMR resonance. As an example the results for compound 2 are given as follows:

- IR (CH\(_2\)Cl\(_2\)): 2229.8 cm\(^{-1}\) (CN), 1756.2 cm\(^{-1}\) (\(>\text{C}=\text{O}\));

- \( ^1H \) NMR (200 MHz, CDCl\(_3\)) \(\delta\) ppm:
  - 1.45–1.54 (m, 4H, \(-\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^{-}\)),
  - 1.78–1.82 (m, 4H, \(-\text{CH}_3\text{CH}_2\text{COO}^{-}\)),
  - 2.58–2.63 (t, 4H, \(-\text{CH}_2\text{COO}^{-}\)),
  - 7.18–7.23 (m, 4H, aromatic protons),
  - 7.57–7.75 (m, 12H, aromatic protons).

The results of the mass spectrometry (for compound 2) are as follows: \(m/z\): 529 (m+1), 528, 334, 264, 236, 196.

Phase identifications for compounds 1–4 were performed using polarizing microscopy. Between crystalline and isotropic phases, only one enantiotropic liquid crystalline phase was found, which was recognized as nematic one. This phase was assigned from its schlieren or hemototropic textures, which flashed with slight pressing on the glass plates. The transition temperatures determined from the microscope observations were in good agreement with those obtained by DSC, deviations being less than 1 °C. The fundamental thermodynamic properties related to the transitions obtained from DSC measurements are collected in Table II. The data given in parenthesis were obtained during cooling of the sample. Fig. 1 presents DSC thermograms of compound 4 as an example, recorded both by heating and cooling.

### Table II. Transition temperatures \(T\) and enthalpies of transition \(\Delta H\) for alkanediacids 4-(4'-cyano)-biphenyl diesters.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>(n)</th>
<th>(T) [°C]</th>
<th>(\Delta H) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>202(160)</td>
<td>252(–) 31.4 11.1</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>197(181)</td>
<td>225(223) 36.7 8.3</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>138(–)</td>
<td>150(131) 199(197) 40.9 7.3</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>145(120)</td>
<td>185(183) 42.1 7.2</td>
</tr>
</tbody>
</table>

**Fig. 1.** DSC heating and cooling scans for compound 4.

### Table I. Elemental analysis data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(n)</th>
<th>Formula</th>
<th>Calculated [%]</th>
<th>Found [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>C(<em>{32})H(</em>{24})O(_4)N(_2)</td>
<td>C 76.78 H 4.83 N 5.59</td>
<td>C 76.71 H 4.88 N 5.52</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>C(<em>{34})H(</em>{28})O(_4)N(_2)</td>
<td>C 77.25 H 5.34 N 5.30</td>
<td>C 77.13 H 5.30 N 5.24</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>C(<em>{36})H(</em>{32})O(_4)N(_2)</td>
<td>C 77.68 H 5.79 N 5.03</td>
<td>C 77.76 H 5.85 N 5.11</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>C(<em>{38})H(</em>{36})O(_4)N(_2)</td>
<td>C 78.06 H 6.21 N 4.79</td>
<td>C 78.14 H 6.26 N 4.86</td>
</tr>
</tbody>
</table>
The results presented in Table II indicate on the influence of the spacer length on some thermal properties of the compounds investigated. The increase of the spacer length leads to a decrease of the clearing point and then the isotropization enthalpy. Such an effect had been found previously [1, 2, 4, 7, 8] for many dimeric mesogens. The behaviour of the crystal-nematic transition temperature is more complicated. The tendency to lower the melting point with the elongation of the spacer has been observed, but when the samples have been slowly cooled from the isotropic melt down, the supercooling effect has occurred, which has not showed any regularity along the series. The greatest difference between the mesophase range obtained during heating and that recorded during cooling has been observed for the compound 1. By heating of the compound 3, two various crystalline phases have been distinguished which have, however, not been recognized during cooling, probably because of supercooling effect. The enthalpy of the crystal-nematic phase transition has increased as the length of the spacer rose and, within the experimental uncertainty, it has had the same value for both ways of the temperature changes.

Finally, it should be noted that the chemical structure of the dimers under investigation is symmetric and not very complicated, the dimers are characterized by good chemical and thermal stability. Therefore, they can be treated in many cases as low molar mass model compounds in the field of polymer science.

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