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Biforked mesogens with ester linkages, derived from 3-(3,4-dialkoxyphenyl)-propanoic acid

C. Alstermark[a]; M. Eriksson[a]; M. Nilsson[a]; C. Destrade[b]; H. T. Nguyen[b]
[a] Department of Organic Chemistry, Chalmers University of Technology, Göteborg, Sweden [b] Centre de Recherche Paul Pascal, Domain Universitaire, Talence Cedex, France

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Biforked mesogens with ester linkages, derived from 3-(3,4-dialkoxyphenyl)-propanoic acid

by C. ALSTERMARK, M. ERIKSSON and M. NILSSON,
Chalmers University of Technology, Department of Organic Chemistry,
S-412 96 Göteborg, Sweden

C. DESTRADE and H. T. NGUYEN
Centre de Recherche Paul Pascal, Domain Universitaire, F-33405 Talence Cedex,
France

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Biforked or polycatenar mesogens derived from 3-(3,4-dialkoxyphenyl)-propanoic acid and with ester bridges between all of the aromatic rings are described. These derivatives exhibit both lamellar, columnar and cubic mesophases. One example of reversed phase order is found (when the sample is cooled from the isotropic liquid as compared to when it is heated from the crystal) which is demonstrated by DSC measurements and microscopy. The relationships between molecular structure and polymorphism are discussed.

1. Introduction

Biforked mesogens [1–3] or, more generally, polycatenar mesogens, are interesting compounds because of their unusual polymorphism which can comprise lamellar and columnar as well as nematic, cubic or rhombohedral mesophases [3]. Here the phrase polycatenar mesogens is intended to denote rod-like mesogens with more than two aliphatic substituents. This type of compound fills the gap between the traditional rod-like and disc-like molecules which exhibit either lamellar or columnar mesophases but never both. Compare, however, thermotropic mesophases of alkali metal soaps, which exhibit both lamellar and columnar mesophases.

X-ray measurements and dilatomeric studies [4] have resulted in a model in which groups of three molecules are packed with their aromatic cores approximately parallel to one another and surrounded by their paraffinic chains. The aromatic cores are not entirely parallel since the terminal phenyl groups of the two outer molecules in the discs are bent out (see [4], figure 5). These disc-like clusters are aggregated one over another as in classic columnar mesophases. This model emphasizes the importance of molecular associations, which govern the rich polymorphism in polycatenar thermotropic mesogens because of the amphiphilic structure of the molecules (i.e. segregation of the aromatic and aliphatic parts).

In a previous paper [3] we described four new series of type I (see figure 1). In this work we studied the influence of the flexibility of X, the number of aromatic rings (five or six) and the length of the alkyl chain on the mesomorphic behaviour. In one of the series we found the new rhombohedral (ϕ_{Rh} and $\phi_{\mathrm{Rh'}}$) mesophases with R3C symmetry and in two series the new compact hexagonal mesophase which has a three-dimensional lattice and P63mc symmetry [3, 5]. Three of the series exhibited both lamellar and columnar mesophases. Here the symbol ϕ is used for the hexagonal columnar (ϕ_h), the ribbon-like oblique (ϕ_{Ob}) and the rhombohedral (ϕ_{Rh} and $\phi_{Rh'}$) mesophases to indicate the peculiar shape of the polycatenar moieties which generates these phases. This symbol was first introduced by Malthête *et al.* for phasmidic compounds [6]. So, if the nomenclature D_h (used normally for a hexagonal columnar phase) and ϕ_h corresponds strictly to the same columnar arrangement, the local molecular arrangements for the two cases are rather different.

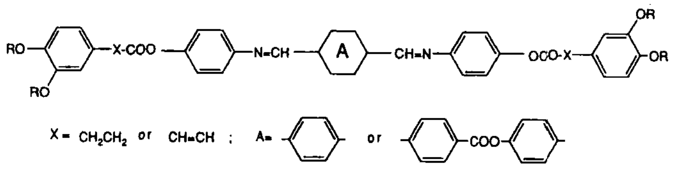


Figure 1. Schematic representation of the compounds of type I.

In the present work we have prepared a new series of type II (see figure 2). In this series (II) we studied the influence of exchanging the imine bridges for ester bridges, and thus also the decreased conjugation between the three central aromatic rings. These mesogens can be compared to compounds in the corresponding series of type I described previously (which are built up of 3-(3,4-dialkoxyphenyl)-propanoic acid and contain five aromatic rings).

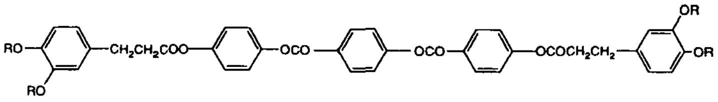
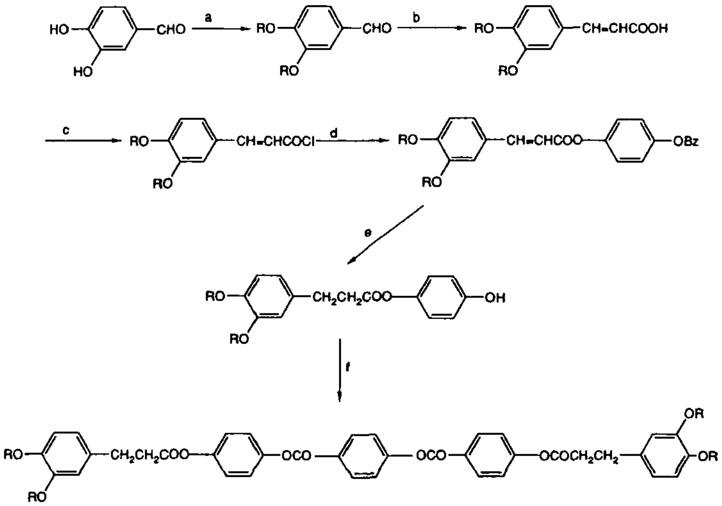


Figure 2. The compounds of type II.

2. Synthesis

All compounds of type II were prepared starting with alkylation of 3,4-dihydroxybenzaldehyde. Knoevenagel condensation of the aldehydes with malonic acid,



Scheme. a, RBr, K_2CO_3, DMF; b, malonic acid, pyridine piperidine; c, oxalyl chloride, toluene; d, *p*-benzyloxyphenol, pyridine, RT; e, H_2, Pd/C, HOAc, RT; f, terephthaloyl dichloride, pyridine.

treatment of the cinnamic acids with oxalyl chloride and condensation of the acid chlorides with 4-benzyloxyphenol furnished 4-benzyloxyphenyl 3,4-dialkoxycinnamates. Treatment with hydrogen over palladium on charcoal cleaved the benzyl ether and reduced the double bond affording phenols in 42–82 per cent yields after recrystallization from ethanol (once) and hexane (once). Condensation of the phenols with terephthaloyl dichloride afforded the target esters in 34–76 per cent yields after chromatography on silica gel with dichloromethane and recrystallization from ethanol/benzene.

The synthetic route is outlined in the scheme and full details are given in the experimental section.

3. Results and discussion

Phase transitions were studied with polarizing microscopy and with differential scanning calorimetry. The tentative identification of the mesophases is based on observation of textures and comparison with the equivalent phases described in [3].

The mesomorphism of the compounds of type II are in accord with previous results [1–3]. Both lamellar (S_C) and columnar mesophases can be found as well as a cubic phase. The table lists the transition temperatures and enthalpies of transition for the mesophases. As is normal for biforked mesogens, where long chains lead to strong curvature of the paraffinic extremities and short chains lead to a weak curvature, the longer homologues ($R = C_{12}$ to C_{14}) show columnar phases while the shorter homologues ($R = C_7$ and C_8) exhibit a lamellar phase.

An unusual mesomorphic behaviour is found for the C_8 derivative which exhibits a reversed phase order upon heating as compared to cooling. This behaviour was

Phase transitions (°C) for compounds of type II; C = crystal; I = isotropic liquid; S_C = smectic C mesophase; ϕ_{Ob} = oblique ribbon mesophase; ϕ_h = hexagonal columnar mesophase; Cub = cubic mesophase; ( ) = transition enthalpies (ΔH) in kJ/mol;

R	C		S_C		ϕ_{Ob}		ϕ_h		Cub		I
C_7H_{15}	●	125 (60·7)	●		–		–		–	137 (4·8)	●
C_8H_{17}†	●	121 (54·8)	●	127·5 (0·29)	–		–		●	135 (4·8)	●
C_9H_{19}	●	123 (70·8)	–		–		●	(132·5) (−3·3)	●	137·5 (5·6)	●
$C_{10}H_{21}$	●	122 (77·9)	–		●	(134) (−4·2)	–		●	137 (5·4)	●
$C_{11}H_{23}$	●	122 (82·3)	–		●	137 (5·3)	–		–		●
$C_{12}H_{25}$	●	121 (89·7)	–		●	135 (0·13)	●	138 (5·8)	–		●
$C_{13}H_{27}$	●	121·5 (96·9)	–		●	134·5	●	139 (6·5)	–		●
$C_{14}H_{29}$	●	121 (106·5)	–		–		●	139·5 (7·3)	–		●

†Reversed phase order is found upon heating as compared to cooling

C_8H_{17} (cooling): I 132 S_C 126 Cub 114 C
(−3·7) (0·35) (−54·9)

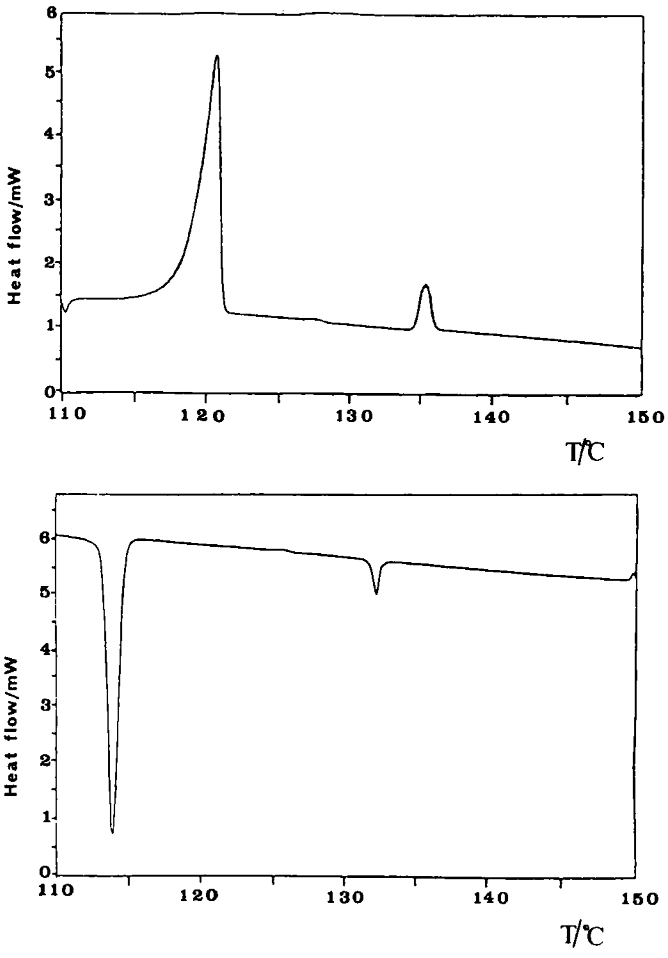


Figure 3. DSC curves for the C_8 compound of type II on heating and cooling.

confirmed both by microscopy and DSC measurements (see figure 3). According to the DSC measurement represented in figure 3, the transitions upon heating are:

$$\text{C} \quad 121 \quad \text{S}_\text{C} \quad 128 \quad \text{Cub} \quad 135 \quad \text{I},$$

and upon cooling:

$$\text{I} \quad 132 \quad \text{S}_\text{C} \quad 126 \quad \text{Cub} \quad 114 \quad \text{C}.$$

However, the transition S_C-cubic does not occur at a specific temperature, but can occur at any temperature once the S_C phase is formed. More thorough microscopy revealed that the cubic phase is stable within the whole temperature interval and that the S_C phase is metastable. It seems, however, as if the cubic phase can not be formed directly, either from the crystalline or from the isotropic liquid states, but must nucleate from a preceding S_C phase. The DSC curves obtained for the two cases show that the transition S_C to Cub is endothermic and weakly first order.

For the C_9 derivative a monotropic hexagonal columnar mesophase (ϕ_h) is found upon cooling, in addition to the cubic phase. The ϕ_h phase is metastable and not formed upon heating. A similar metastable phase appears for the C_{10} derivative which has an oblique ribbon mesophase in addition to the cubic phase.

The longer homologues ($R = C_{12}$ to C_{14}) seem to have both ϕ_{ob} and ϕ_h mesophases. For $R = C_{12}$ the transition is confirmed both with microscopy and DSC measurements and both phases are enantiotropic. The enthalpy change for the transition is 0·13 kJ/mol. For the C_{13} compound the transition can be observed with microscopy but the corresponding DSC curve shows no enthalpy change. The longest homologue ($R = C_{14}$) showed an enthalpy change on the DSC curve but the transition could not be confirmed by microscopy.

The compounds thus show an increased tendency to give columnar mesophases with increased chain lengths. This fits the structural model given by Levelut *et al.* [7] on how columnar phases are built up by biforked mesogens. Long alkyl chains with high flexibility are more likely to favour the association of molecules in discs which build up the columnar mesophases.

4. Experimental

The chemicals used in the synthesis were purchased from Fluka, Janssen, Aldrich and Merck. Toluene and tetrahydrofuran (THF) were distilled over sodium. Pyridine was distilled over potassium hydroxide and *N,N*-dimethyl formamide (DMF) was distilled over calcium hydride. Ethyl acetate and dichloromethane used for chromatography and recrystallizations were distilled before use. The proton NMR spectra were recorded on a Bruker WH 270 spectrometer. Phase transitions and melting points were determined on a Perkin–Elmer DSC 7 apparatus and texture observations were made using an Olympus BHA polarizing microscope in connection with a Mettler FP 52 hot stage and FP 5 control unit.

3,4-Dialkoxycinnamoyl chlorides were prepared following the procedure described in [3].

General procedure for preparation of 4-benzyloxyphenyl 3,4-dialkoxycinnamates. 3,4-Dialkoxycinnamoyl chloride (5 mmol) was dissolved in dry pyridine (25 ml). 4-Benzyloxyphenol (5 mmol, 1·0 g) was added and the mixture was stirred at room temperature for 15–20 hours and then poured into ice/conc. sulphuric acid. The brownish-yellow crystals were filtered off and carefully washed with water. Recrystallization from ethyl acetate furnished the product as slightly yellow crystals in 57–89 per cent yield. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7·77 (d, 1 H, J = 16 Hz), 7·29–7·45 (m, 5 H), 7·05–7·13 (m, 4 H), 6·95–7·00 (m, 2 H), 6·84–6·89 (m, 1 H), 6·45 (d, 1 H, J = 16 Hz), 5·06 (s, 2 H), 3·99–4·06 (m, 4 H), 1·78–1·89 (m, 4 H), 1·19–1·56 (m, 16–44 H), 0·85–0·93 (m, 6 H).

General procedure for preparation of 4-hydroxyphenyl 3-(3,4-dialkoxyphenyl)-propanoates. 4-Benzyloxyphenyl 3,4-dialkoxy-cinnamate (4·79 mmol) was dissolved in acetic acid (35 ml) and THF (15 ml). Palladium on charcoal (0·5 g, 10 per cent) was added and the mixture was stirred under hydrogen for 3 hours. After filtration the solvent was evaporated and the product was recrystallized from light petroleum (60–70°C) affording the product as white crystals in 42–82 per cent yield. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6·71–6·92 (m, 7 H), 3·91–4·02 (m, 4 H), 2·79–3·03 (m, 4 H), 1·73–1·86 (m, 4 H), 1·19–1·53 (m, 16–44 H), 0·83–0·92 (m, 6 H), 4·9 (s, broad, 1 H)

General procedure for preparation of bias 4-(3-(3,4-dialkoxy-phenyl)propanoyloxy)phenyl terephthalates. 4-Hydroxyphenyl 3-(3,4-dialkoxyphenyl)propanoate (2·34 mmol) was dissolved in dry pyridine (3 ml). Powdered terephthaloyl dichloride (1 mmol) was added in small portions and dissolved gradually at 60°C. After stirring at 60°C for 2 hours the solution was slowly cooled to room temperature. The reaction mixture was poured into ice/conc. sulphuric acid. The greyish crystals were filtered off, dried and recrystallized from benzene. Chromatography on silica gel (230–400 mesh) with dichloromethane afforded the target compounds in 34–76 per cent yields. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8·32 (s, 4 H), 7·08–7·29 (m, 8 H), 6·74–6·88 (m, 6 H), 3·94–4·04 (m, 8 H), 2·75–3·07 (m, 8 H), 1·74–1·89 (m, 8 H), 1·23–1·56 (m, 32–88 H), 0·84–0·92 (m, 12 H).

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