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Liquid Crystals

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The influence of structural changes of the *N*-substituent on liquid crystalline behaviour of ester imides

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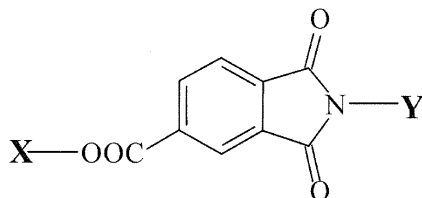
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Several new ester imide derivatives with different *N*-substituents in the imide ring were synthesized and their mesogenic properties investigated by thermal analysis, optical microscopy and X-ray diffraction. All the esters of *N*-4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid and aliphatic alcohols exhibited monolayer SmA and SmC phases. In addition, for the ethyl and propyl esters a monotropic hexatic (F or I) phase was observed. The introduction of additional substituents at the carbon atom in the methylenemethoxycarbonyl group (in the vicinity of the nitrogen atom) substantially influenced liquid crystalline properties: the compounds with a flexible chain exhibited monotropic SmA–SmB dimorphism, but liquid crystalline properties vanished for the substituent containing the more rigid phenyl ring.

1. Introduction

Studies of the liquid crystalline (LC) derivatives of trimellitic acid imide have shown that, although the imide group does not necessarily endow mesogenic properties, it can strongly influence the mesomorphism of appropriate ester imides by its strong polar character [1]. This effect can be compared with the influence of two other highly polar substituents, namely, nitro and cyano groups. In contrast to nitro or cyano substituents, which can only play the role of terminal groups, the esterimide core allows for a greater diversity of modifications in molecular structure, since substituents can be attached to the ester group (X) as well as to the nitrogen atom (Y), incorporating this highly polar group inside the molecular structure (see scheme 1).



Structure 1. General structure of ester imides.

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Among many LC compounds containing the ester imide moiety synthesized by ourselves in recent years, two compounds with $X=C_{10}H_{21}O-C_6H_4-C_6H_4-$ have been found to show extremely interesting properties, concluding the modulated smectic \tilde{C} phase (antiphase) formation [2]. These are the methyl esters of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid ($Y=CH_2COOCH_3$) and 2-[(4'-decyloxybiphenyl-4-yl)-oxycarbonyl]phthalimide}propanoic acid $Y=CH(CH_3)COOCH_3$). It was shown that for ester imides containing a methoxycarbonyl group in the *N*-substituent, the modulated smectic \tilde{C} phase appeared when only one carbon atom separated this group from the imide ring [2]; if the methoxycarbonyl group ($COOCH_3$) was separated by more than one methylene group the antiphase disappeared [3]. This type of mesophase has been observed for the compounds with cyano or nitro substituents [4, 5]. In such LC compounds the polymorphism and frustrated smectic phase behaviour occurs primarily due to the dipole–dipole and dipole-induced dipole interactions between polar molecules [6], but modulated smectic phases arising from steric effects have been also observed for mesogens with fluorinated terminal chains [7].

The aim of this work was to investigate the influence of other changes in the chemical constitution of ester imides with $X=C_{10}H_{21}O-C_6H_4-C_6H_4-$ on their mesomorphic properties. It must be pointed out that the

compounds investigated were chosen on the basis that the only difference lies in the geometrical anisotropy and the polarity of the *N*-substituent. We have introduced several modifications in the basic methylenemethoxycarbonyl group. Compounds **Iam** and **Iiab**, which retained the methyleneoxycarbonyl substituent ($-\text{CH}_2\text{COO}-$) at the nitrogen atom, had different alkoxy or phenoxy groups at the ester linkages (see scheme 2). In the structure of compound **IIIa** we introduced the methyl group at the carbon atom of the methylene group in the vicinity of the imide ring (table 1). We also introduced some larger substituents in the methylenemethoxycarbonyl group, i.e. 3-(methylthio)propyl, 2-methylpropyl and benzyl. These structural changes were chosen in respect of the synthesis of the imide ring via the imidization with methyl ester of the appropriate natural aminoacids: (L)-methionine (**IVa**), (L)-leucine (**IVb**) and (L)-phenylalanine (**IVc**) (scheme 2). Some comparisons with ester imides described earlier by ourselves are also made.

2. Experimental

2.1. Instrumentation

All product structures were confirmed by FTIR, ^1H NMR and ^{13}C NMR spectroscopy. The infrared spectra (in CH_2Cl_2) were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrans 2000 software, and the NMR spectra (in CDCl_3) were recorded using a Varian Gemini 200 MHz spectrometer. The structures

were also confirmed by elemental analysis (within $\pm 0.4\%$ of theoretical values). All the chemicals used were analytical grade commercial products (Aldrich) and were applied without further purification. The purity of all compounds obtained was checked by TLC using SiO_2 plates with UV indicator and chloroform/methanol mixture as an eluent.

The phase transitions were observed using a polarizing microscope, Nikon Optiphot 2-Pol, equipped with Mettler hot stage FE82/80HT. DSC measurements were carried out at the rate of 5°C min^{-1} using a Perkin-Elmer 7 calorimeter. The X-ray diffraction measurements of powder samples were carried out using an X' Pert PRO Philips diffractometer with CuK_α radiation. The molecular lengths were calculated with the Hyperchem 6 workpackage.

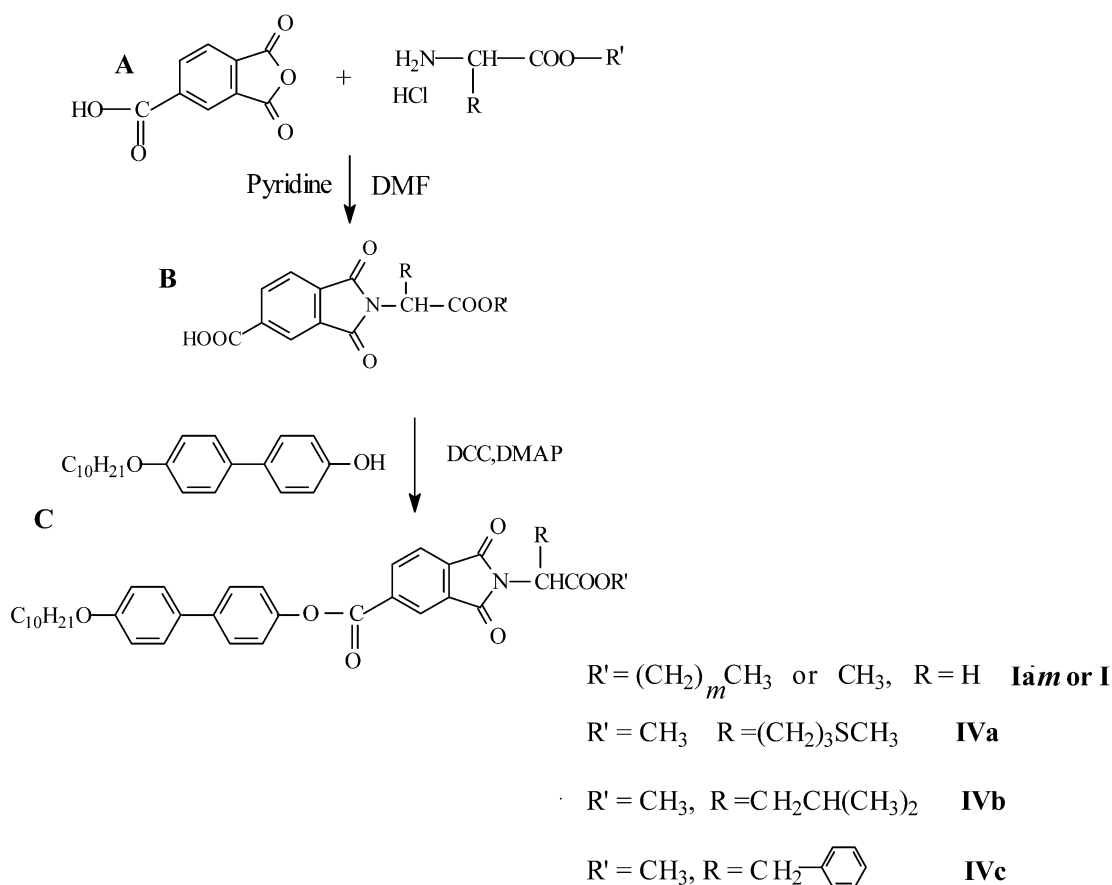
2.2. Synthesis

The esterimides **Ia1–5** and **IVa–c** were synthesized according to scheme 1. The phenyl esters **Iia,b** were obtained via direct esterification of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonylphthalimide]acetic acid (scheme 2). Only the chiral compound **IIIa**, because of low yield in this method, was obtained from butyl lactate via the Mitsunobu reaction [8] according to scheme 3. Typical experimental procedures and some spectroscopic data are described below.

2.2.1. *N*-substituted trimellitimidides, **B**. Stoichiometric amounts (0.05 mol) of benzene-1,2,4-tricarboxylic

Table 1. Structures of the ester imides under investigation. For the sake of comparison, the structures of esterimides from earlier studies are included.

Compound	<i>n</i>	<i>R</i>	<i>R'</i>	Ref.
I	1	H	CH_3	2
series Iam	1	H	$(\text{CH}_2)_m\text{CH}_3$, $m=1, 2, 3, 4, 5$,	—
series I bn	2, 3, 5	H	CH_3	2, 3
II a	1	H		—
II b	1	H		—
III	1	CH_3	CH_3	2
III a	1	CH_3	$(\text{CH}_2)_3\text{CH}_3$	—
IV a	1	$(\text{CH}_2)_3\text{SCH}_3$	CH_3	—
IV b	1	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	CH_3	—
IV c	1		CH_3	—



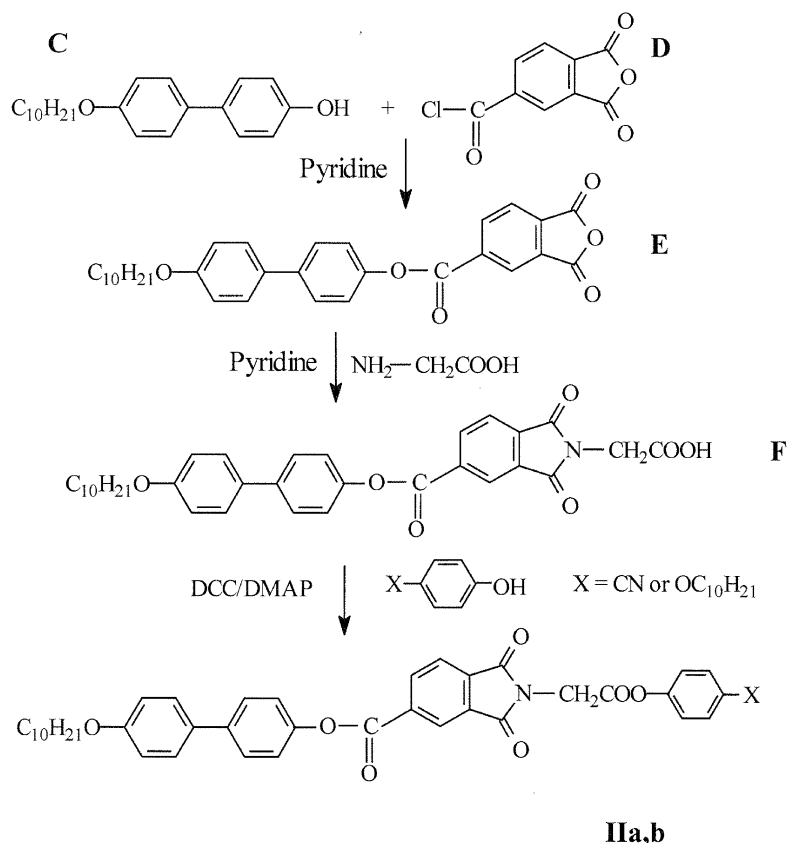
Scheme 1. Synthesis of esterimides, derivatives of natural aminoacids (glycine **I** and **Ia**, methionone **IVa**, leucine **IVb** and phenylalanine **IVc**)

anhydride (trimellitic anhydride, **A**, scheme 1), pyridine and appropriate glycine ester hydrochloride (0.05mol), L-methionine methyl ester hydrochloride (0.05 mol), L-leucine methyl ester hydrochloride (0.05 mol), or L-phenylalanine methyl ester hydrochloride (0.05 mol), were dissolved in 50 ml of DMF and heated under reflux for 4 h. The mixtures were diluted with 5% HCl and cooled. The crude products were collected by suction, thoroughly dried and used without further purification.

2.2.2. 4-Decyloxy-4'-hydroxybiphenol, C. A flask equipped with a magnetic stirrer was charged with 9.3 g (0.05 mol) of 4,4'-dihydroxybiphenyl and 50 ml of freshly distilled DMSO. The 4,4'-dihydroxybiphenyl dissolved during stirring, and 8.5 g (0.15 mol) of KOH powder was added. Next 11.65 g (0.05 mol) of *n*-decyl bromide was added at such a rate that room temperature was maintained. During the reaction the suspension turned yellow and slowly became denser because of the KBr precipitate. The product began to separate as a white solid. When the mixture became very dense (after about 30 min) 25 ml of freshly distilled

DMSO was added; the course of the reaction was followed by TLC. 200 ml of cold water and 13 ml of conc. HCl were then added to the mixture to neutralize KOH and convert the product to the acid form. The product was filtered off, washed with 200 ml of cold water, and twice crystallised from methanol; yield 70%, m.p. 151°C.

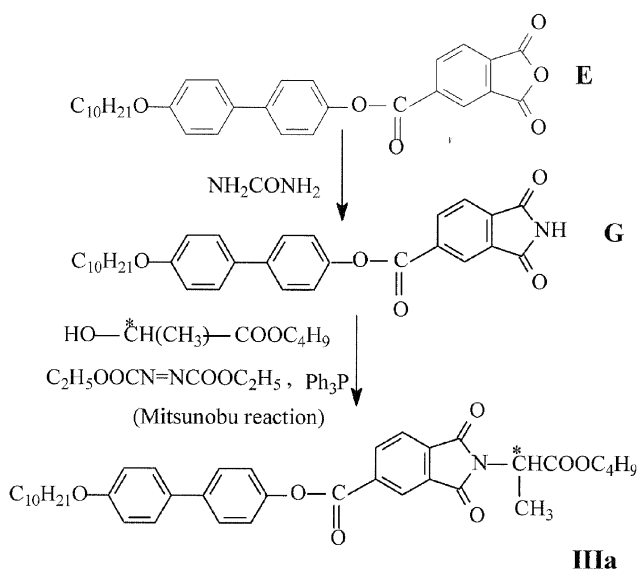
2.2.3. *N*-substituted 4-[(4'-decyloxybiphenyl-4-yl)oxy-carbonyl]phthalimideacetates Ia1-5 and IV a-c. To 0.001 mol of *N*-substituted the trimellitimidides, 0.31 g (0.001 mol) of 4-decyloxy-4'-hydroxybiphenyl in 25 ml of dry CH_2Cl_2 , 0.23 g (0.0011 mol) of DCC and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added. The reaction mixtures were stirred for 24 h, then *N,N*-dicyclohexylurea was filtered off. The mixtures were washed twice with 20 ml of 5% HCl and then with 20 ml of water. The mixtures were dried over MgSO_4 and the solvent evaporated. The crude glycine ester derivatives were crystallized twice from ethanol. Products were purified by column chromatography (SiO_2) using $\text{CHCl}_3/\text{MeOH}$ (50/1) as eluant: yield *c*.



Scheme 2. Synthesis of *p*-substituted phenyl 4-[(4'-decyloxybiphenyl-4-yl)-oxycarbonyl]phthalimideacetates (series II a,b)

30%. Typical characterization results are given for compounds **Ia2** and **IV a-c**.

Ia2: FTIR (cm^{-1}) 1727($\text{C}=\text{O}_{\text{imide}}$), 1742 ($\text{C}=\text{O}_{\text{ester}}$), 1784($\text{C}=\text{O}_{\text{imide}}$). ^1H NMR, δ (ppm) 0.85–0.98 (m, 6H, $2 \times \text{CH}_3$), 1.28–1.63 (m, 14H, $(\text{CH}_2)_7$), 1.63–1.84 (m, 4H, $\text{CH}_2\text{CH}_2\text{O}$, $\text{COOCH}_2\text{CH}_2\text{CH}_3$), 4.06 (t, 2H, CH_2O), 4.18, (t, 2H, COOCH_2), 4.49 (s, 2H, NCH_2), 7.00–8.72 (m, 11 H, CH_{arom}). **IVa**: FTIR (cm^{-1}) 1726($\text{C}=\text{O}_{\text{imide}}$), 1742 ($\text{C}=\text{O}_{\text{ester}}$), 1783($\text{C}=\text{O}_{\text{imide}}$). ^1H NMR, δ (ppm) 0.88 (t, 3H, CH_3), 1.41–1.61 (m, 16H, $(\text{CH}_2)_8$), 1.74–1.94 (m, 4H, $\text{CH}_2\text{CH}_2\text{O}$, NCHCH_2), 2.09 (s, 3H, CH_3S), 3.76 (s, 3H, COOCH_3) 4.00 (t, 2H, CH_2O), 5.15 (m, 1H, N-CH), 7.00–8.70 (m, 11 H, CH_{arom}). **IVb**: FTIR (cm^{-1}) 1723($\text{C}=\text{O}_{\text{imide}}$), 1743 ($\text{C}=\text{O}_{\text{ester}}$), 1780($\text{C}=\text{O}_{\text{imide}}$). ^1H NMR, δ (ppm) 0.8–1.00 (m, 9H, $3 \times \text{CH}_3$), 1.21–1.43 (m, 15H, $(\text{CH}_2)_7$, $\text{CH}_2\text{-CH}$), 1.74–2.07 (m, 4H, $\text{CH}_2\text{CH}_2\text{O}$, NCHCH_2), 3.70 (s, 3H, COOCH_3) 4.00 (t, 2H, CH_2O), 5.02 (m, 1H, N-CH), 7.00–8.70 (m, 11 H, CH_{arom}). **IVc**: FTIR (cm^{-1}) 1725($\text{C}=\text{O}_{\text{imide}}$), 1744 ($\text{C}=\text{O}_{\text{ester}}$), 1781($\text{C}=\text{O}_{\text{imide}}$). ^1H NMR, δ (ppm) 0.88 (t, 3H, CH_3), 1.25–1.74 (m, 14H, $(\text{CH}_2)_7$), 1.84–2.05 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 3.64 (d, 2H, NCHCH_2), 3.89 (s, 3H, COOCH_3) 4.05 (t, 2H, CH_2O), 5.28 (t, 1H, N-CH), 7.03–8.68 (m, 16 H, CH_{arom}).



Scheme 3. Synthesis of *(R)*-2-[4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide] propanoic acid butyl ester (**IIIa**)

2.2.4. 4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalic anhydride, E. To 5.5 g (0.016 mol) of 4-decyloxy-4'-hydroxybiphenol (**C**) in 65 ml of dry pyridine, 3.55 g (0.016 mol) of trimellitanhydride chloride (**D** scheme 2) was added. The reaction mixture was stirred for 1 h at room temperature and then heated under reflux for 30 min. After cooling to room temperature pyridine was evaporated, and the crude product was purified by crystallization from toluene; yield 65%.

2.2.5. 4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide]acetic acid, F. 4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalic anhydride (10 g, 0.020 mol) was added to 1.5 (0.020 mol) of aminoacetic acid suspended in a mixture of acetic acid (75 ml) and pyridine (50 ml). The reaction mixture was boiled for 1 h, 5 ml of acetic anhydride was added and the mixture heated under reflux for 30 min. After cooling to room temperature the precipitate was filtered off, washed with cold methanol and crystallized from THF; yield 80%, m.p. 160°C.

2.2.6. 4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide]acetic acid phenyl esters, compounds IIa, IIb. To 0.60 g (0.001 mol) of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide]acetic acid, 0.25 g (0.001 mol) of 4-decyloxyphenol or 0.12 g (0.001 mol) of 4-cyanophenol in 30 ml of dry CH₂Cl₂, 0.23 g (0.0011 mol) of DCC and a catalytic amount of DMAP were added. The reaction mixture was stirred for 24 h, and *N,N*-dicyclohexylurea was filtered off. The mixture was washed with 20 ml of 5% HCl twice and then with 20 ml of water; it was dried

over MgSO₄ and the solvent evaporated. The products were purified by column chromatography (SiO₂) using CHCl₃/MeOH (50/1) as eluent: yield *c.* 30%.

2.2.7. 4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide, G. A mixture of 3 g (6 mmol) of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalic anhydride and 0.18 g (3 mmol) of urea was carefully melted for 5 min, (scheme 3). The cooled product was powdered and crystallized from dry THF; yield 77%.

2.2.8. (R)-2-{4-[(4'-Decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide}propanoic acid butyl ester, IIIa. A solution of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide (0.472 g, 1 mmol), (*S*)-butyl lactate (0.150 g, 1 mmol), triphenylphosphine (0.270 g, 1 mmol) and diethylazadicarboxylate (0.180 g, 1 mmol) in THF (25 ml) was stirred at room temperature for 24 h. The THF was evaporated and MeOH added to dissolve triphenylphosphine oxide. The residue was filtered off. The crude product was purified by column chromatography (SiO₂) using CHCl₃/MeOH (50/1) as eluent: yield 70%. FTIR (cm⁻¹) 1721(C=O_{imide}), 1741 (C=O_{ester}), 1780(C=O_{imide}). ¹H NMR, δ (ppm) 0.85–0.93 (m, 6H, 2 × CH₃), 1.2–1.80 (m, 23H, (CH₂), N-CH(CH₃)), 4.03 (t 2H, CH₂O), 4.17, (t, 2H, COOCH₂), 5.03 (q, 1H, NCH), 7.00–8.70 (m, 11 H, CH_{arom}).

3. Results and discussion

The LC properties of the synthesized compounds are collected in table 2. The data for the methyl ester of

Table 2. The liquid crystalline properties of alkyl or *p*-substituted phenyl 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide]acetates (series **Iam** and **IIa,b**), methyl ω-{4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide}alkanoates (series **Ibn**) and *N*-{4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide}alkanoic acid esters (**IIIa** and **IVa,b,c**), see table 1: [] indicates monotropic transition, Δ*T* is the mesophase temperature range.

Compound	Phase transition temperatures (°C) and enthalpies (kJ mol ⁻¹ in parentheses)	Δ <i>T</i>	Ref.
I	Cr ₁ 63.5(10.25), Cr ₂ 114.0(22.23), SmC̄[90.1](-0.14), SmA 155.4(4.92), I	41.4	[2]
Ia1	Cr ₁ 75.3(16.25), Cr ₂ 122.1(20.91), SmX[97.3](-0.06), SmC 142.7(0.08), SmA 163.4(5.12), I	41.3	—
Ia2	Cr ₁ 75.8(14.21), Cr ₂ 94.1(27.21), SmX[86.8](0.07), SmC 144.0(0.14), SmA 155.2.(6.08), I	61.1	—
Ia3	Cr ₁ 66.4(15.09), Cr ₂ 84.8(14.27), SmC 147.1[0.31], SmA 156.3(4.90), I	71.5	—
Ia4	Cr ₁ 68.8(34.92), SmC 145.6(0.53), SmA 151.7(5.35), I	82.9	—
Ia5	Cr ₁ 60.28(14.26), Cr ₂ 72.7(17.11), SmC 134.0(0.08), SmA 139.5(7.63), I	66.8	—
Ib1	Cr ₁ 167.3(10.9), SmA 185.2(7.55), I	17.9	[3]
Ib2	Cr ₁ 134.9(8.82), Cr ₂ 147.9 (34.4), SmA 167.2(6.30, I	19.3	[3]
Ib4	Cr ₁ 30.3(51.39), SmC 136.6(0.17), SmA 154.5(6.03), I,	24.2	[2]
IIa	Cr 183.5, I	—	—
IIb	Cr 163.5, I	—	—
III	Cr ₁ 66.3 (15.56), Cr ₂ 89.2(7.48), SmC̄[84.5](-0.15), SmC 103.5 (0.28), SmA 120.2 (4.53), I	31.0	[2]
IIIa	Cr 93.2 (28.50), SmC 107.5 (0.65), SmA 118.7 (5.05), I	25.5	—
IVa	SmB[64.4](-11.60), SmA[70.8](-5.05), Cr ₁ 81.9(52.46), I	[17.5]	—
IVb	SmB[52.3](-5.91), SmA[67.9](-2.92)Cr ₁ 71.6 (30.72), I	[19.3]	—
IVc	Cr 75, I	—	—

4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid (**I**), 2-[[4-(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimidepropanoic acid (**III**) [2] and a series of methyl esters of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimidealkanoic acids (**Ibn**) [3] are added to allow comparisons to be made. The transition temperatures were taken from the DSC traces and corresponds to the onset points of the enthalpy peaks.

Optical microscopy observations revealed that all the compounds from series **Iam** exhibited enantiotropic SmC (schlieren texture) and SmA (focal-conic texture) phases. This was confirmed by the temperature dependence of the smectic layer spacing d shown for compound **Ia1** in figure 1. The thickness of the smectic layer increased with increasing temperature in the smectic C phase, corresponding to a decrease of the tilt angle of the director.

The smectic layer spacings d are compared with the calculated lengths of the molecules l in their most extended conformations. The tilt angle varied from 14° ($d/l \approx 0.97$) to 29° ($d/l \approx 0.92$). Then, in the smectic A range the interlayer distance became more or less constant; the d/l ratio was typical for the monolayer SmA₁ phase (about 0.98). In the case of other smectic C mesophases the d/l distances measured at 130°C oscillated in the range 0.94–0.88.

DSC and microscopy also revealed the presence of a smectic hexatic X phase (F or I) on cooling the ethyl (**Ia1**) and propyl (**Ia2**) esters from the smectic C phase (see figure 2). On cooling to the hexatic phase the schlieren texture inherited from the SmC phase is

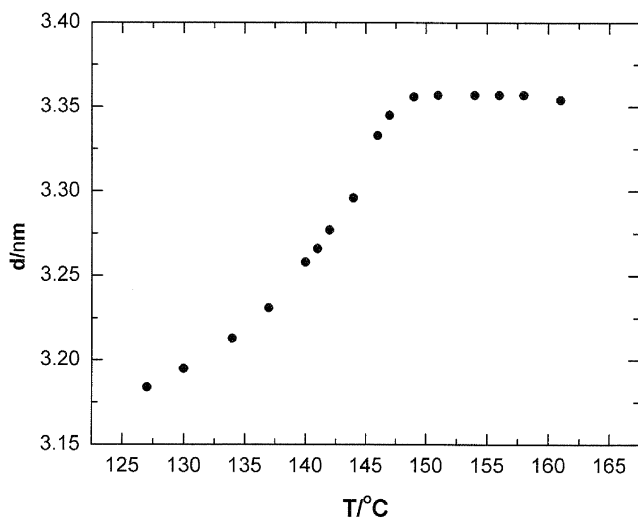
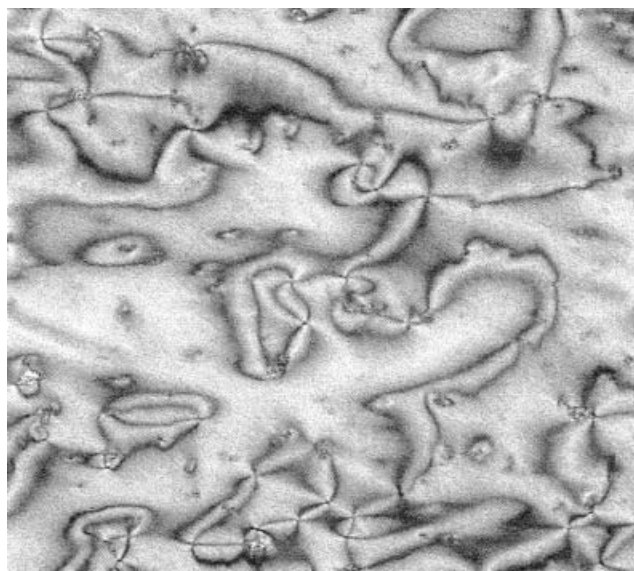
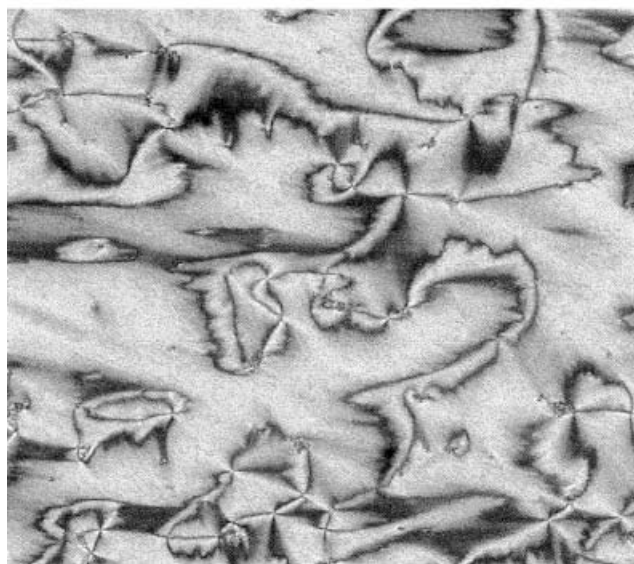


Figure 1. Temperature dependence of smectic layer d for 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid ethyl ester (**Ia1**).



(a)



(b)

Figure 2. Photomicrographs of compound **Ia1**: (a) the schlieren texture of the smectic C phase at 144°C and (b) the texture of the smectic hexatic X phase at 144°C formed on cooling the schlieren texture of SmC, the same area as (a).

preserved; only the dark brushes formed around the $+/-$ defects become slightly sharper.

The characteristic feature of these compounds is the strong permanent dipole of the planar phthalimide group, with the longitudinal component equal to 2.42D [3]. The additional polar ester group at the N -substituent plays an important role in the stability of the mesophase: its dipole moment having longitudinal and transverse components leads to delocalization of

dipole–dipole interactions and destabilizes the mesomorphic properties. This effect is clearly visible in comparison of the clearing and melting temperatures of the series **Iam** with the those of the *N*-alkyl-substituted ester imides (series 2 in [1]). Despite some slight differences in the length of the alkyl substituents in the biphenyl moiety, higher melting (130–140°C) and clearing (*c.* 200°C) temperatures seem to be characteristic of the compounds having an alkyl substituent at the nitrogen atom. Therefore it may be concluded that the ester group in the terminal substitution destabilizes the LC properties of ester imides.

For many LC compounds the increase in length of the alkyl chain in the terminal group for a given homologous series promotes smectic behaviour [9]. Therefore it is of interest to consider, first, the effect of increase of the alkyl chain length in the series **Iam** on mesomorphic properties. As can be seen in table 2 and figure 3, the addition of a (CH₂) group in the substituent results in the decrease of the melting temperature and the increase of the mesophase range. This effect may be accounted for by the increase of the flexibility of the end group as well as the increase of the lateral interactions leading to a higher degree of ordering in the mesomorphic state.

Comparing the ester imides containing the methylenealkoxycarbonyl group (series **Iam**) with those containing poli(methylene)methoxycarbonyl substituents

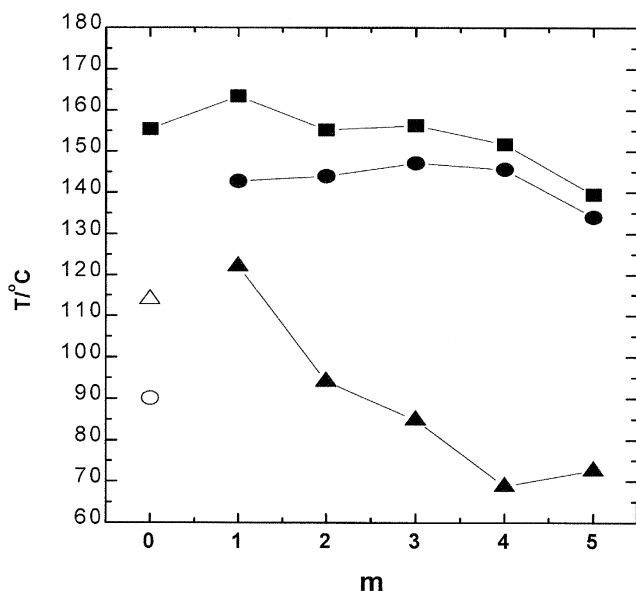


Figure 3. Dependence of transition temperature on the number of carbon atoms m in the $\text{COO}(\text{CH}_2)_m\text{CH}_3$ group for 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid esters (series **Ia**), Cr–SmC (Δ), SmC–SmA (\circ), Cr–SmC (\blacktriangle), SmC–SmA (\bullet), SmA–I (\blacksquare).

(series **Ibn**, table 1) we noticed that an increase in the distance between the polar imide ring and the ester group results in a considerable decrease of the mesophase range due to delocalization of the dipole moment of the molecule. It should also be noted that, in contrast to compounds **Ia1** and **Ia2**, the analogues from series **Ibn** did not form the smectic C phase. Our observations seem to support the van der Meer and Vertogen model of the smectic C phase [10]. According to this model the mesophase stability is dependent mainly on the intermolecular interactions, in which the location of an acentral dipole, and particularly an acentral transverse dipole, plays an important role. In contrast to the behaviour of the alkyl esters (series **Iam**) the cyanophenyl and decyloxyphenyl derivatives (compounds **Ila** and **Ilb**) did not show liquid crystalline phases.

The effect of small changes in molecular structure on the smectogenic properties of a compound has been studied by many authors (see for example [11–13]). The mesophase stability [12] and the smectic A polymorphism [13] were mainly considered in terms of the changes of the polarity and/or polarizability of the mesogenic part of the molecule. It was shown, however, that the smectic A polymorphism, dependent on the orientation of the ester linkages, cannot be interpreted only in terms of dipole–dipole interactions, but a geometrical factor must also be taken into consideration [13].

To investigate the effect of steric factors on the mesomorphic properties of ester imides modifications involving the branching of the chain at the carbon atom in the methyleneoxycarbonyl group were made in compounds **IIIa** and **IV a, b, c**. We have already shown [2], that the replacement of one hydrogen atom in the methyleneoxycarbonyl group by a methyl substituent in the methyl ester of 4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimideacetic acid (**I**→**III**), results in SmC formation, which confirms the observation in [11]. Compound **IIIa**, i.e. the butyl ester of 2-[[4'-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide} propanoic acid exhibits SmA–SmC dimorphism (see figure 4); its mesomorphic behaviour was similar to the methylenemethoxycarbonyl analogue **Ia3**, although the phase transition temperatures and mesophase ranges of the latter were lower than those of the former because of the branching of the *N*-substituent.

As can be seen from table 2, two methyl ester imides (**IVa, b**) show monotropic LC smectic A and CrB phases (see figure 5). Observing the texture in a homogeneously aligned cell, an increase of birefringence (from $\Delta n=0.13$ to 0.15) at the SmA–CrB phase transition was detected, implying the increase of the

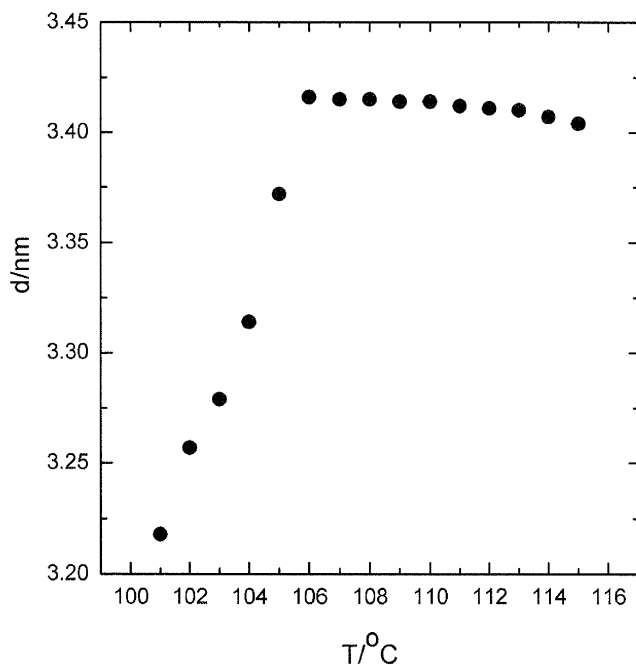


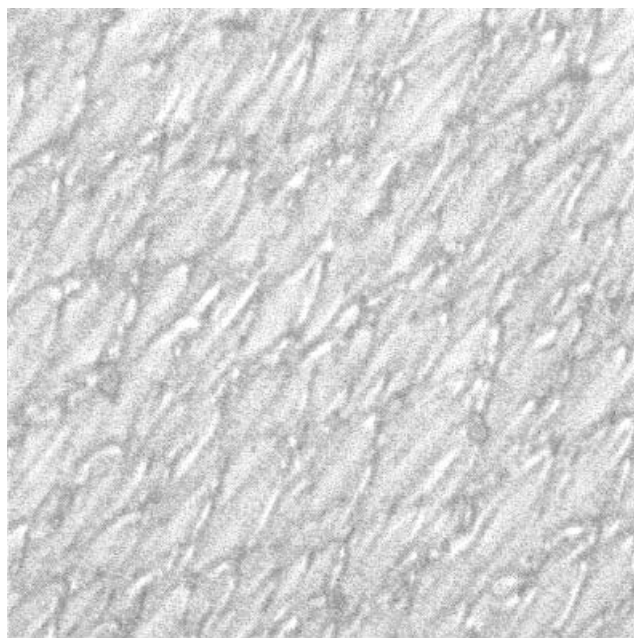
Figure 4. Temperature dependence of smectic layer d for 2-[4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl] phthalimide]propanoic acid methyl ester (**IIIa**).

order parameter at the CrB transition. At the phase transition there was also a decrease in the number of focal-conic defects, indicating that the CrB phase is less susceptible to elastic deformation. The changes in the texture are stepwise, consistent with a first order transition.

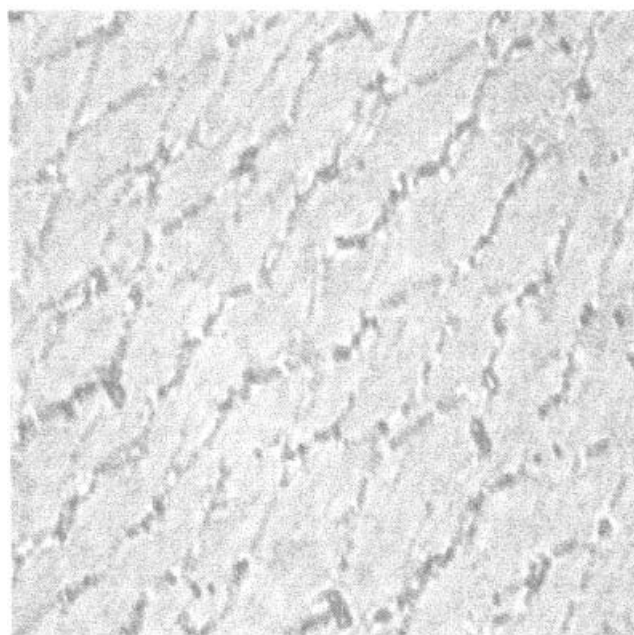
Compounds **IVa,b** had lower mesogenic tendencies than compounds **I** and **III**, as a consequence of the branching in the methyleneoxycarbonyl group. All the phase transition temperatures were lowered by the additional branching in the case of the 2-methylpropyl substituent (**IVb**) as compared with the thiomethylpropyl substituent (**IVa**). The most bulky and rigid benzyl substituent (**IVc**), which increased the breadth of the molecule and thus reduced the lateral intermolecular interactions, inhibits mesophase formation. It is noteworthy that the same effect by the presence of the phenyl ring was observed for compounds of series **IIa** and **IIb**, but in the latter case it should be attributed to the increase of the melting point of the ester imide containing the phenyl ring non-conjugated with the mesogenic rigid core instead of a methyl group.

4. Conclusions

In earlier work [3] we showed that the distance between the imide ring and the ester group situated in the substituent nitrogen atom is crucial in terms of the



(a)



(b)

Figure 5. Photomicrographs of compound **IVa**: (a) the focal conic texture of the smectic A phase at 61°C and (b) the texture of the smectic B phase at 58°C ; the same area as (a) observed in a $6\mu\text{m}$ cell with planar alignment.

smectic $\tilde{\text{C}}$ antiphase formation. The present investigations confirmed the important role of the distribution of partial dipoles in stabilization of the mesogenic properties of ester imides. We have shown that even small changes in the immediate vicinity of the polar imide ring

(i.e. in substituents situated on the nitrogen atom), realized by the elongation of the alkyl chain in the ester group, substantially influence the mesomorphic properties of ester imides. These results underline the fundamental role of the dipole–dipole interactions. Furthermore, it was shown, with the aid of the introduction of branching in the *N*-substituent, that steric considerations are also substantial.

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