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Studies on the liquid crystalline behaviour of novel *N*-alkyl-substituted ester imides

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Three new series of *N*-alkyl-substituted ester imide derivatives, which differ in the polarity of their mesogenic groups; specifically, either cholesteryl, 4′-undecyloxybiphenyl or 4′-cyanobiphenyl, have been synthesized. For the *N*-alkyl-[4-(cholesteryloxycarbonyl)]phthalimides the chiral nematic N* phase and the monolayer SmA_1 phase have been observed up to the dodecyl homologue. The pentadecyl and octadecyl members of this series show only the SmA_1 phase. The monolayer smectic A_1 phase was also observed for all members of the *N*-alkyl-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide series while the longer homologues (with $n>5$) exhibited SmA–SmC dimorphism. In the case of the *N*-alkyl-4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]phthalimides, the short homologues exhibited only a nematic phase, while for the butyl homologue in addition to the nematic phase the bilayered SmA_2 phase was observed. The smectic phase vanished for the pentyl and hexyl members but reappeared as a partially bilayered smectic A_d phase for the longer homologues.

1. Introduction

Although there are many liquid crystalline polymeric materials containing ester imide groups [1], low molar mass ester imides are uncommon mesogenic compounds. The imide group is of high polarity and therefore can be compared to cyano or nitro terminal substituents. By contrast to monovalent cyano or nitro groups, however, the ester imide core creates more synthetic possibilities because it enables substituents to be introduced into the ester as well as into the imide systems. The imide group incorporated into the mesogenic moieties can be critical in terms of liquid crystalline properties; for example, the replacement of an ester group by an ester imide promotes the mesogenic properties of some monomeric and dimeric cholesteryl derivatives [2].

In this paper we continue studies on low molar mass LC ester imides [3–7]. We have described previously the synthesis of homologous series of ester imides containing the cholesteryl group and an alkyl or oxyethylene chain connected via a methyleneoxycarbonyl spacer to the imide nitrogen. For these materials a strong tendency towards the microsegregation of the polar and non-polar parts of the molecules was observed, resulting either in the bilayered smectic C_2 phase [6, 7] or modulated SmC phase [3].

The aim of the present work was to investigate the

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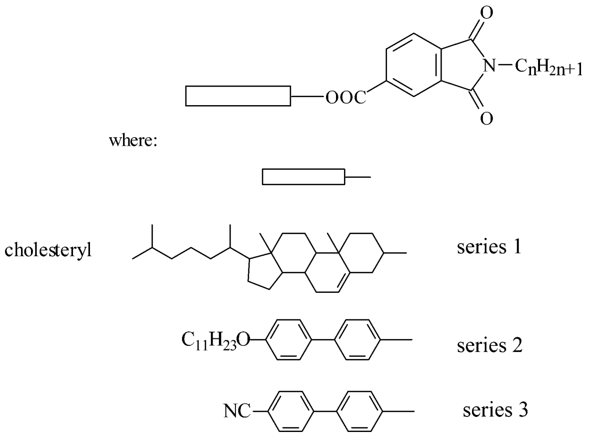
influence of different mesogenic moieties on the liquid crystalline properties of *N*-alkyl ester imide derivatives. We have chosen mesogenic groups of different character, and specifically either the non-polar cholesteryl and 4-undecyloxybiphenyl groups or the highly polar 4-cyanobiphenyl group (series 1–3, respectively). The trimellitimides (the IUPAC name for trimellitimide is 5-carboxy-2,3-dihydro-1*H*-isoindole-1,3-dione) used to obtain these three series, were substituted at the *N*-position with the similar alkyl groups C_nH_{2n+1} and *n*-varied from 1 to 18. The mesogenic properties of these compounds, see scheme 1, have been studied as a function of the length of the alkyl substituent at the imide nitrogen atom. The general synthetic routes to obtain these new compounds are shown in schemes 2 and 3.

2. Experimental

2.1. *Instrumentation*

All product structures were confirmed by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. The infrared spectra (in CH_2Cl_2) were recorded on a Perkin–Elmer 2000 spectrometer equipped with Pegrams 2000 software; the NMR spectra (in $CDCl_3$) were recorded using a Varian Gemini 200 MHz spectrometer. The structures were confirmed by elemental analysis and the data symbols were within $\pm 0.4\%$ of theoretical values. The phase transitions were observed using a polarizing microscope, Nikon Optiphot 2-Pol, equipped with a Mettler hot stage FE82/80HT. DSC measurements were carried out at $5^{\circ}\mathrm{C\,min^{-1}}$ using a Perkin-Elmer 7 differential scanning calorimeter. The X-ray measurements on powder samples were carried out using an X' Pert PRO Philips diffractometer with CuK$_\alpha$ radiation. The molecular structures were calculated with HyperChem 6 software using the semi-empirical AM1 method.



Scheme 1. Structures of the new ester imides.

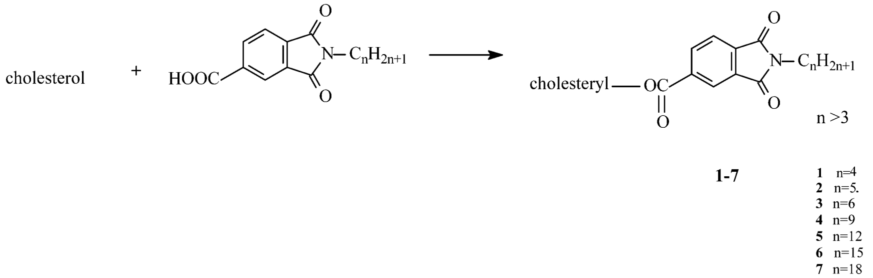
2.2. *Synthesis*

All the chemicals used were analytical grade commercial products (Aldrich) and were used without further purification. *N*-Alkyltrimellitimides with butyl and longer substituents were synthesized according to the well known and patented method from trimellitic anhydride and appropriate amines in dry refluxing DMF [5, 8]. The purity of all compounds obtained was checked by TLC using SiO_2 plates with UV indicator and a chloroform/methanol mixture as an eluant.

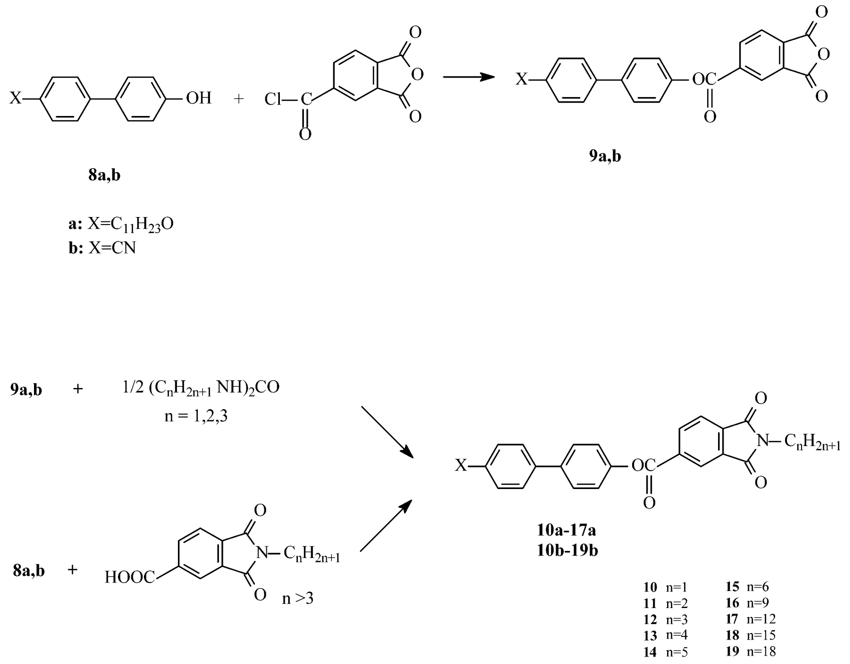
2.2.1. *N-Alkyl-[4-(cholesteryloxycarbonyl)]phthalimides (1–7)*

The synthesis was carried out from cholesterol and the appropriate *N*-alkyltrimellitimide in methylene chloride using dicyclohexylcarbodiimide (DCC) according to the method described previously [3–7]. The crude products were crystallized from benzene/methanol mixture and the crystals purified further by means of flash-column chromatography (SiO_2) using chloroform/methanol (20/1) as eluant. Typical characterization results are given for compound **1**.

1: FTIR (cm^{-1}) 2930 and 2856 (C–H$_{\mathrm{aliph.}}$), 1775 (C=O$_{\mathrm{imide}}$), 1717 (C=O$_{\mathrm{imide,ester}}$); ^{1}H NMR (ppm) 0.69–2.06 (m, 41H, C–H$_{\mathrm{chol.}}$ + 7H, C–H$_{\mathrm{alk.}}$), 2.47 (d, 2H, H$_{\mathrm{chol.}}$-4), 3.70 (t, 2H, CH$_2$–N), 4.90 (m, 1H, H$_{\mathrm{chol.}}$-3), 5.43 (m, 1H, H$_{\mathrm{chol.}}$-6), 7.90 (dd, 1H, H$_{\mathrm{ar.}}$), 8.39 (dd, 1H, H$_{\mathrm{ar.}}$), 8.47 (dd, 1H, H$_{\mathrm{ar.}}$); yield 46%.



Scheme 2. Synthesis of cholesteryl ester imides.



Scheme 3. Synthesis of alkoxy- and cyano-biphenyl derivatives.

2.2.2. *4′-Undecyloxy-4-hydroxybiphenyl (**8a**)*

This compound was obtained as described previously in dry DMSO on solid KOH, at room temperature; m.p. 153°C [9].

2.2.3. *4-[(4′-Undecyloxybiphenyl-4-yl)oxycarbonyl]-phthalic anhydride (**9a**)*

This compound was synthesized according to the method published previously [10]. Yield 58 % (3 g); m.p. 174°C.

2.2.4. *4-[(4′-Cyanobiphenyl-4-yl)oxycarbonyl]phthalic anhydride (**9b**)*

Compound **9b** was obtained according the same procedure as **9a**. Yield 70% (3.2 g); FTIR (cm^{-1}) 2229 (CN), 1867 ($C{=}O_{anh}$), 1785 ($C{=}O_{anh}$), 1741 ($C{=}O_{ester}$); m.p. 204–206°C.

2.2.5. *N-Alkyl-4-[(4′-undecyloxybiphenyl-4-yl)-oxycarbonyl]phthalimides (**10a–12a**) and N-alkyl- 4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]-phthalimides (**10b–12b**)*

A mixture of 2 mmol (1.28 g) of **9a** or **9b** and 1 mmol (60 mg) of 1,3-dialkylureas, was carefully melted for 5 min. The resulting mixtures were powdered and crystallized from benzene/methanol. The crystals were further purified by flash-column chromatography (SiO_2) using chloroform/methanol (20/1) as eluant. Typical characterization results are given for compounds **10a** and **10b**.

10a: FTIR (cm^{-1}) 2930 and 2858 ($C{-}H_{aliph.}$), 1775 ($C{=}O_{imide}$), 1741 ($C{=}O_{ester}$), 1716 ($C{=}O_{imide}$); ^1H NMR (ppm) 0.88 (t, 3H, CH_3), 1.28–1.81 (m, 18H, $(CH_2)_9$), 3.25 (s, 3H, $CH_3{-}N$), 4.00 (t, 2H, $CH_2{-}O$), 6.96–8.68 (m, 11H, $C{-}H_{ar.}$); yield 54%.

10b: FTIR (cm^{-1}) 2934 and 2860 ($C{-}H_{aliph.}$), 2229 (CN), 1775 ($C{=}O_{imide}$), 1743 ($C{=}O_{ester}$), 1716 ($C{=}O_{imide}$); ^1H NMR (ppm) 3.25 (s, 3H, $CH_3{-}N$), 7.39–8.87 (m, 11H, $C{-}H_{ar.}$); yield 59%.

2.2.6. *N-Alkyl-4-[(4′-undecyloxybiphenyl-4-yl)-oxycarbonyl]phthalimides (**13a–17a**) and N-alkyl- 4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]-phthalimides (**13b–19b**)*

General procedures for the synthesis of compounds **13a–17a** and **13b–19b** have been published [2–7]. The synthesises were carried out from 4′-substituted 4-hydroxybiphenyls **8a,b** and the appropriate *N*-alkyl-trimellitimides in methylene chloride using DCC and 4-(dimethylamino)pyridine (DMAP) as catalyst. The crude products were crystallized from benzene/methanol mixture and, if necessary, the crystals were purified by means of flash-column chromatography (SiO_2) using chloroform/methanol (20/1) as eluant. Typical characterization results are given for compounds **13a** and **13b**.

13a: FTIR (cm^{-1}) 2929 and 2857 ($C{-}H_{aliph.}$), 1774 ($C{=}O_{imide}$), 1741 ($C{=}O_{ester}$), 1716 ($C{=}O_{imide}$); ^1H NMR (ppm) 0.89–1.76 (m, 28H, $(CH_2)_9$, $(CH_2)_2$, 2x CH_3) 3.72 (t, 2H, CH_2–N), 4.00 (t, 2H, CH_2–O), 6.96–8.67 (m, 11H, C–$H_{ar.}$); yield 62%.

13b: FTIR (cm^{-1}) 2932 and 2860 (C–$H_{aliph.}$), 2230 (CN), 1775 (C=O_{imide}), 1743 (C=O_{ester}), 1716 (C=O_{imide}); ^1H NMR (ppm) 0.87 (t, 3H, CH_3), 1.26–1.84 (m, 4H, $(CH_2)_2$), 3.75 (t, 2H, CH_2–N), 7.40–8.87 (m, 11H, C–$H_{ar.}$); yield 68%.

3. Results and discussion

The liquid crystalline properties of the new compounds are collected in tables 1–3. The transition temperatures were taken from the DSC traces and correspond to the onset points of the enthalpy peaks. The smectic layer spacings *d* are compared with the calculated lengths of the molecules *l* in their most extended conformations in each table. The intensity profiles of the X-ray diffraction patterns of the smectic phases showed a first, and in some cases a second, order Bragg reflection in the low angle region and a diffuse wide angle maximum characteristic of a liquid-like arrangement of molecules within the smectic layer, typical for smectic A or C phases.

Table 1 lists the data for the ester imides containing a cholesteryl mesogenic moiety, **1**–**7**. The layer spacing *d* depends only weakly on temperature (figure 1). The

Table 1. The liquid crystalline properties of the *N*-alkyl-[4-(cholesteryloxycarbonyl))phthalimides (series 1).

Compound	n^a	Phase transition temperatures/°C and enthalpies /kJ mol^{-1} (in parentheses)	*d*/nm at 150°C	*d*/*l*
1	4	Cr112.7(14.29), SmA167.3(0.87), N* 199.9(0.63), I	2.90	1.15
2	5	Cr126.2(15.48), SmA185.7(1.83), N*202.4(0.50), I	2.92	1.06
3	6	$Cr_1$114.2(6.30), $K_2$133.6(14.12), SmA191.0(4.00), N*196.1(0.47), I	3.21	1.11
4	9	Cr99.3(17.20), SmA 175.0(5.34), N*203.0(0.14), I	3.63	1.11
5	12	$Cr_1$90.7(26.52), $K_2$96.2(5.29), SmA177.9(6.10), N*196.5 (0.10), I	3.78	1.04
6	15	Cr111.2(25.62), SmA 171.9(5.46), I	4.16	1.04
7	18	Cr112.4(29.22), SmA158.3(5.39), I	4.20	0.96

[a] *n* = number of carbon atoms in alkyl chain.

Table 2. The liquid crystalline properties of the *N*-alkyl-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimides (series 2).

Compound	n^a	Phase transition temperatures/°C, and enthalpies /kJ mol^{-1} (in parentheses)	*d*/nm at 150°C	*d*/*l*
10a	1	Cr145.6(47,88), SmA214.4(6.36), I	3.34	1.02
11a	2	Cr145.7(45.99), SmA198.0(7.61), I	3.40	1.00
12a	3	Cr138.2(47.61), SmA199.6(8.35), I	3.46	0.99
13a	4	Cr141.0(32.93), SmA194.1(7.88), I	3.59	0.99
14a	5	Cr141.77(41.73), SmC161.9(0.10), SmA 196.9(8.88), I	3.48	0.93
15a	6	Cr131.8(43.71), SmC167.6(0.17), SmA186.2(7.39), I	3.47	0.90
16a	9	Cr129.6(55.70), SmC 170.1 SmA[b], 175.9(5.62), I	3.67	0.87
17a	12	Cr131.3(51.76), SmC176.5 SmA[b]181.2(7.43), I	3.48	0.74

[a] *n* = number of carbon atoms in alkyl chain.

[b] The SmA phase range is too narrow to resolve the SmC–SmA–I transitions in the calorimetric measurements. Phase transition temperatures taken from microscopic observation.

Table 3. The liquid crystalline properties of the *N*-alkyl- 4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]phthalimides (series 3).

Compound	n^a	Phase transition temperatures/°C, and enthalpies /kJ mol^{-1} (in parentheses)	*d*/nm at 150°C	*d*/*l*
10b	1	Cr242.6(40.73), N289.2(1.18), I	—	—
11b	2	Cr163.4(16.53), N229.3(0.60), I	—	—
12b	3	Cr177.6(32.35), N228.3(0.63), I	—	—
13b	4	Cr135.1(29.24), SmA 155.3(0.15), N 183.1(0.58), I	4.92	2.2
14b	5	Cr135.5(29.94), N 209.8(0.64), I	—	—
15b	6	Cr131.3(28.97), N188.7(0.47), I	—	—
16b	9	Cr135.6(32.42), SmA166.3(0.53), N178.2(0.58), I	5.03	1.72
17b	12	Cr130.0(33.24), SmA177.2(4.86), I	5.62	1.74
18b	15	Cr125.1(32.70), [SmC122.0][b], SmA177.2(5.24), I	5.86	1.64
19b	18	Cr126.8(39.70), [SmC126.0][b], SmA178,8(7.35), I	6.19	1.58

[a] *n* = number of carbon atoms in alkyl chain.

[b] Monotropic phase transition taken from microscopic observation.

small increase in layer spacing with decreasing temperature may be attributed to a stiffening of the mesogenic groups due to a reduction in thermal motions. The smectic A phase was observed for all imide-cholesteryl derivatives of series 1. The ratio $d/l \sim 1$ indicates the presence of a monolayer smectic A_1 phase. Chiral nematic–smectic dimorphism was observed for shorter homologues with $n \leqslant 12$ (compounds **1**–**5** of series 1). For compounds **4**–**7**, increasing the length of the hydrocarbon substituent gradually decreases the stability of the mesophases by lowering the clearing temperatures. It should be noted, that for the previously described cholesteryl ester imides with a methyleneoxycarbonyl substituent at the nitrogen atom, the clearing temperatures were ~200°C and the smectic A_1 and chiral nematic N* phases were observed for all members of the homologous series up to $n = 21$ [7].

In series 2 (**10a**–**17a**) and 3 (**10b**–**19b**) we replaced the cholesteryl group with a 4,4′-biphenyl moiety containing either a long undecyloxy non-polar substituent or a strongly polar cyano group at the 4′-biphenyl position. The data for compounds **10a**–**17a** with a 4′-undecyloxybiphenyl unit are collected in table 2 and shown in figure 2.

Optical microscopy observations revealed that all these compounds formed a smectic A phase as indicated by the homeotropic texture observed. The d/l ratio for compounds **10a**–**13a** is approximately 1 and indicates the presence of a SmA_1 phase. The smectic C phase characterized by the observation of a schlieren texture was seen for homologues with $n \geqslant 5$. The temperature dependence of the smectic layer-spacing d for *N*-hexyl-4-[(4′-undecyloxybiphenyl-4-yl)-oxycarbonyl]phthalimide **15a** (figure 3) indicates that the SmC–SmA transition is a weakly first order transition. This was confirmed by optical studies in which at the phase transition a sudden change of light transmission is observed between crossed polarizers for a homeotropically aligned sample. The thickness of the smectic layer (figure 3) of **15a** increased with increasing temperature in the smectic C phase corresponding to a decrease of the tilt angle of the director. The tilt angle calculated from the layer spacing is 23° for **14a** and 47° for **17a** (at 150°C). However, this temperature

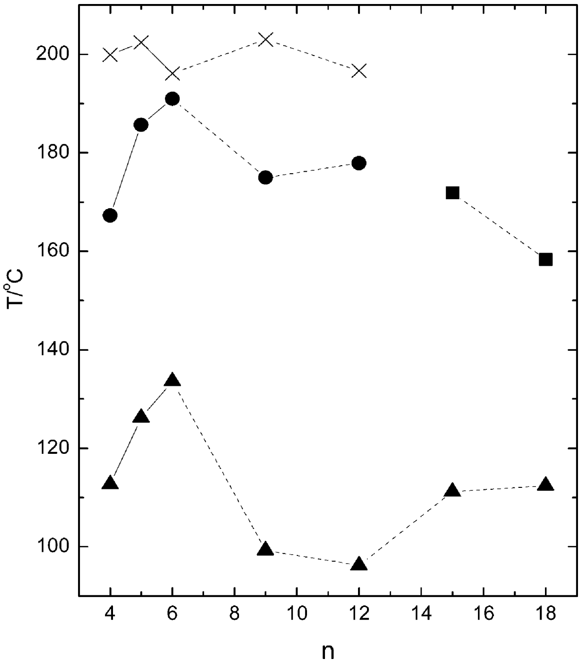


Figure 2. Dependence of transition temperature on the number of carbon atoms n in the alkyl chain for *N*-alkyl[4-(cholesteryloxycarbonyl)]phtalimides. Cr–SmA (▲), SmA–I (■), SmA–N* (●), N*–I (×).

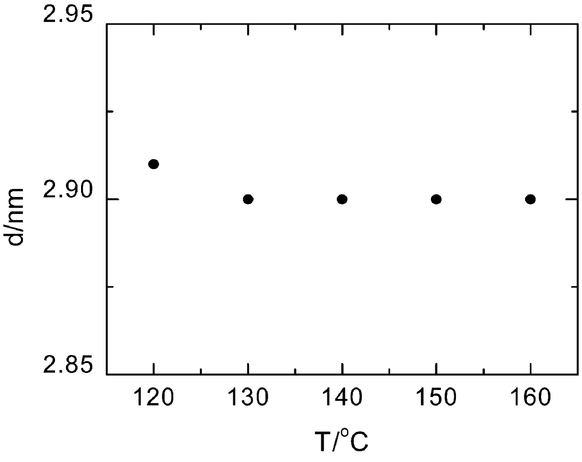


Figure 1. Temperature dependence of the smectic layer spacing d for *N*-butyl[4-(cholesteryloxycarbonyl)]phthalimide **1**.

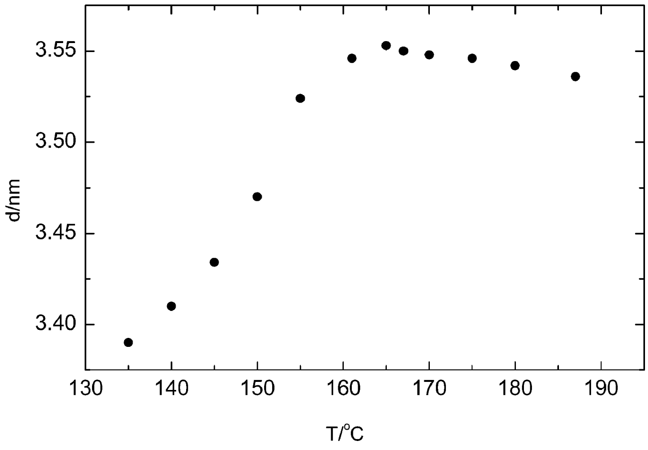


Figure 3. Temperature dependence of the smectic layer spacing d for *N*-hexyl-4-[(4′-undecyloxybiphenyl-4-yl)-oxycarbonyl]phthalimide **15a**.

dependence of the *d*/*l* ratio is also probably associated with a shortening of the molecular length due to the change of the conformations of the two long terminal alkyl chains. This effect is much more pronounced in this series than the *N*-alkyl[4-(cholesteryloxycarbonyl)]-phthalimide series due to the flexibility of both alkyl tails, while the cholesteryl substituent is rigid. For the first six members of series 2, the SmA–I transition temperatures are higher for homologues with an odd number of carbon atoms in the alkyl chain than for those compounds with a even membered chains (see figure 4).

This odd-even effect observed for liquid crystals with alkyl chains has been interpreted by Gray and Goodby [11], Marcelja [12] and Dowell [13]. The calculations performed in the latter paper showed that intrachain constraints (as opposed to intermolecular constraints) were the major factors responsible for odd–even effects.

The most interesting results we have found are for the *N*-alkyl-4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]-phthalimides, series 3 (see table 3 and figure 5). The compounds with shorter alkyl chains (**10b**–**12b** and **14b**, **15b**) form exclusively a nematic phase. Such behaviour is typical for cyanobiphenyl compounds containing a rather short alkyl substituent [14]. The only exception is the *N*-butyl-substituted imide **13b**, which forms a smectic A phase as well as a nematic. The measured *d*/*l* ratio ~2.2 (table 3) indicates a bilayered SmA_2 phase. The longer homologues of series 3 ($n=9$–18) exhibit only smectic phases. The smectic layer spacings of **16b**–**19b** are between one and two molecular lengths indicating a partially bilayered smectic A_d phase. In addition to the smectic A phase characterized by a focal-conic texture, a monotropic smectic C phase with broken focal-conic texture was observed for **18b** and **19b**.

The complex polymorphism observed in series 3 seems to be a result of a competition between dispersive and dipolar interactions together with steric repulsions [15, 16]. The occurrence of the bilayered smectic A phase for **13b** probably results from a superposition of two opposing factors. One of these is the tendency towards a microphase segregation between the polar parts of the molecule and the hydrocarbon chains; the other is the shape of the molecule. Calculations of molecular geometry performed using the HyperChem program have shown that ester imides are slightly bent-shaped. This results from the presence of a carboxylic substituent at the 4-position of the phthalimide ring. As can be seen from figure 6, the symmetry axes of the

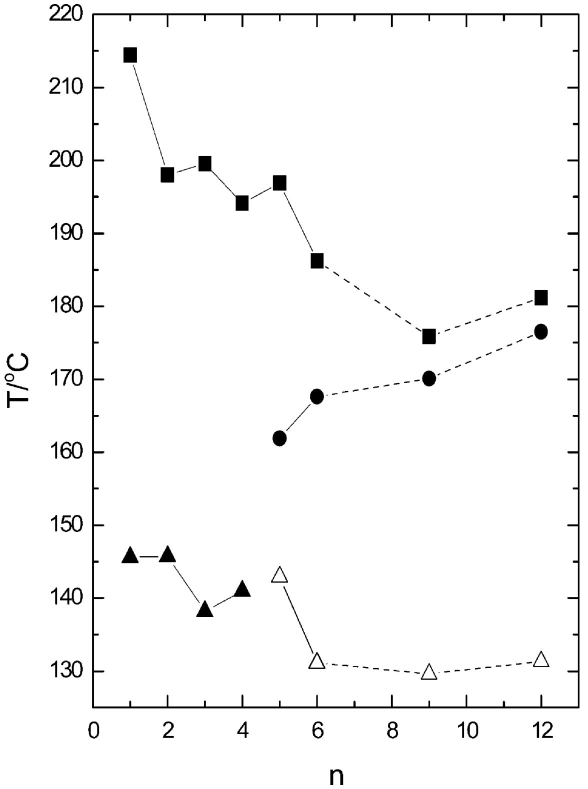


Figure 4. Dependence of transition temperature on the number of carbon atoms *n* in the alkyl chain for *N*-alkyl-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimides. Cr–SmA (▲), Cr–SmC (Δ), SmC–SmA (●), SmA–I (■).

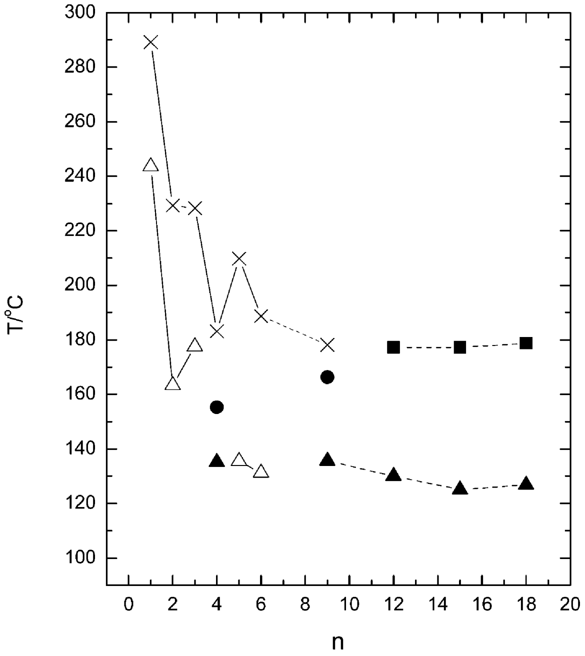


Figure 5. Dependence of transition temperature on the number of carbon atoms *n* in the alkyl chain for *N*-alkyl-4-[(4′-cyanobiphenyl-4-yl) oxycarbonyl]phthalimides. Cr–N (Δ), Cr–SmA (▲), SmA–I (■), SmA–N (●), N–I (×).

biphenyl ring (A) and the phthalimide group (B) form an angle of ~30°.

In compounds **10b**–**12b** the alkyl chain is too short to drive the microphase separation. For compounds **14b** and **15b** the hydrocarbon part may be long enough for phase separation, but due to the bent-shaped molecule, a parallel arrangement in the smectic phase is impossible. The case of compound **13b** is special because the alkyl chain is sufficiently long to enable phase separation while also being sufficiently short to afford the possibility for lamellar arrangement of the molecules.

The smectic A_d phase occurs in the case of molecules containing long hydrocarbon chains and two phenyl rings with a polar substituent. The polarized molecules tend to be arranged in such a way that the opposite charges are located at a minimum distance. A typical example of the partially bilayered smectic A is 4-octyloxy-4′-cyanobiphenyl [17]. The layer spacing *d* is approximately 1.4 times the molecular length estimated with the alkyl chain in its fully extended all-*trans*-conformation. This ratio indicates complete overlap of the polar cyanobiphenyl parts of the molecules. In the case of ester imides, the polar mesogenic rigid core consists not only of cyanobiphenyl, but also of the ester imide part. The value of the *d*/*l* ratio of about 1.6–1.7 suggests that interdigitation involves only the cyanobiphenyl fragments, although the whole mesogenic rigid core is of a polar character. The characteristic feature of the ester imides studied here is that they are composed of several polar groups possessing dipole moments of different directions [4]. The transverse dipole moment of an ester group and the longitudinal moment of an imide group, which have opposite directions to that of the cyano group, makes the complete interdigitation of the rigid cores impossible.

A similar smectic polymorphism was observed for some other series of compounds, and particularly for the non-symmetrical dimeric compounds of general formula (acronym CBO*n*O*m*) [18]:

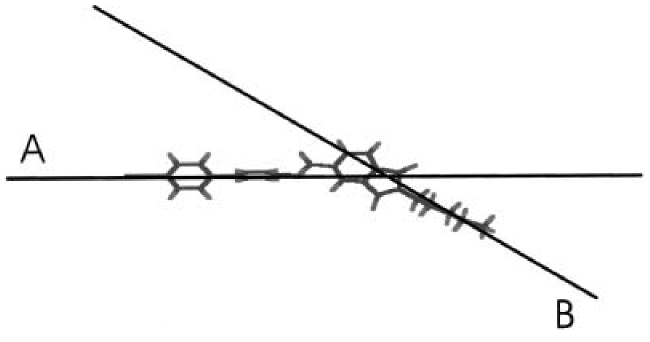
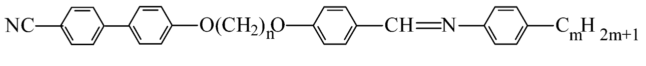


Figure 6. The optimized molecular geometry of *N*-pentyl-4-[(4′-cyanobiphenyl-4-yl)oxycarbonyl]phthalimide **14b**.



The CBO*n*O*m* series exhibits nematic, intercalated (SmA_c) or interdigitated (SmA_d) smectic phases depending on the number (*n*) of the methylene groups in the flexible spacer and carbon atoms (*m*) in the terminal substituent. For example, in the case of the CBO*n*O10 series, for short spacers the SmA_d phase was observed while compounds with longer spacers exhibited only the SmA_c phase. For the intermediate chain lengths only nematic behaviour was observed. This was interpreted in terms of polar and steric interactions. Thus, the intercalated SmA phase occured if there was sufficient space between the mesogenic cores (i.e. a sufficiently long spacer) to accommodate the terminal chains. In the case of shorter spacers, only the A_d phase could exist, which is stabilized by electrostatic interactions between polar cyano groups.

4. Conclusions

The liquid crystalline behaviour of three series of new *N*-alkyl-substituted ester imides containing cholesteryl as well as biphenyl mesogenic moieties has been studied. It was seen that the clearing temperatures for the three series do not differ significantly. It was found, that compounds with a cholesteryl substituent form chiral nematic and monolayer smectic A_1 phases. The replacement of the cholesteryl mesogen by 4-undecyloxybiphenyl promotes smectic behaviour and the smectic A_1 phase was observed for all members of this series. In addition, the longer homologues (with $n > 5$) exhibit SmA_1–SmC dimorphism. Replacing the undecyloxy group by a polar cyano group reduces the smectogenic properties. A complex polymorphism (N, SmA_d, and SmA_2 phases) was observed for the series with the 4-cyanobiphenyl substituent. Such behaviour can be considered as a result of an interplay between polar and steric interactions.

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