Influence of a Nitro Side Group on Liquid Crystalline Properties of Trimellitimides

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Two series of ester imides from trimellitic anhydride as well as 6-nitrotrimellitic anhydride (4-carboxy-6-nitrophthalic anhydride) have been synthesized. Their thermotropic properties have been compared. Only one nitro compound, *N*-dodecyl-4-[(4'-decyloxybiphenyl-4-yl)oxycarbonyl]-6-nitrophthalimide has shown liquid crystalline properties.

Key words: Trimellitimides, Nitro Side Group, Liquid Crystals

Introduction

A wide range of lateral groups have been incorporated into many liquid crystal systems. Initially, it may be thought that they disrupt molecular packing and reduce liquid crystal phase stability. Indeed such destabilisation often occurs through lateral substituents. On the other hand, in many cases, this disruption may be also advantageous for mesomorphism as well as properties required for technical use. Such groups like -CN, -NO$_2$ or -F nearly always reduce the stability of the smectic phase more than of the nematic one. In general, the depression of the nematic-isotropic transition is proportional to the size of the substituent irrespective of its polarity. For smectic phases, the lamellar packing is destabilised by an increase in size but enhanced by an increase in polarity of side groups [1]. The lateral groups mentioned above introduce strong side dipole moments altering intermolecular forces. Similar interactions have been observed also for liquid crystalline thioimides [2, 3].

The nitro group often appears as a lateral substituent in structures of liquid crystals. A comprehensive review concerning the effect of terminal and side NO$_2$ groups in calamitic liquid crystals on the physicochemical properties has been published by Petrov and Shimizu [4]. These authors have shown that the introduction of a nitro group into the liquid crystalline system usually leads to a decrease of the clearing temperatures and nematic ranges, but there were also cases where the same substituent increased the melting points. This influence obviously depends on the molecular structure of the liquid crystalline compounds. Examples are given in Fig. 1 [5 – 7].

For the banana-shaped liquid crystal type the influence of the nitro group at the central phenyl ring on the thermal behaviour was also examined. In this case the rare B_7 phase has been found [8]. Systematic studies on liquid crystalline ester imides have been carried out since 1993 [9]. The central moiety, in these compounds, was derived only from trimellitic imides. The general formula of such ester imides is given in Fig. 2.

Biphenylyl or cholesteryl derivatives were used most often as mesogenic units. The influence of several parts of the structure of ester imides on the liquid crystalline behaviour was studied in detail [10, 11]. It has been found that the phthalimide core itself does not favour the formation of ordered phases due to a non-coplanar conformation of the phenylene ring and the *N*-substituents which hinder molecular packing. On the other hand, substituents X (CN, OC$_n$H$_{2n+1}$), R (C$_n$H$_{2n+1}$, CH$_2$COOCH$_3$,) as well as mesogenic units (biphenylyl or cholesteryl moiety) connected with an ester imide moiety increase the potential of mesophase formation.

The aim of the present paper was to obtain new group of low molecular ester imides having -NO$_2$ substituents, and to investigate the influence of this side group in the imide core on thermotropic properties of the trimellitimides. Therefore we have synthesized six ester imides with different biphenyl mesogens and as well as their nitro analogues derived from 6-nitrotrimellitic anhydride (4-carboxy-6-nitrophthalic anhydride). The general syn-
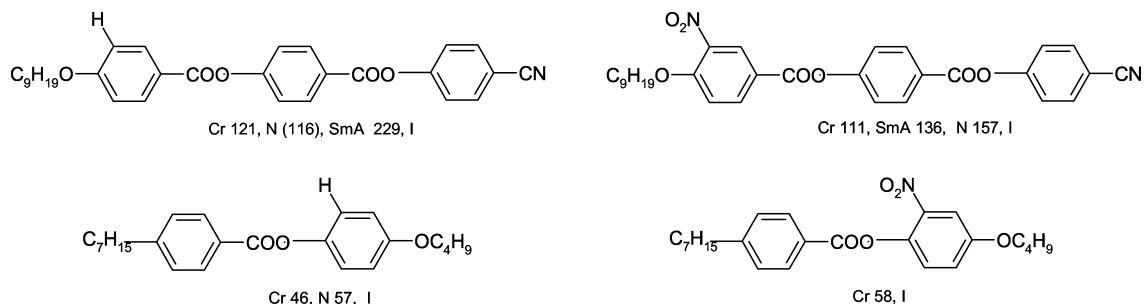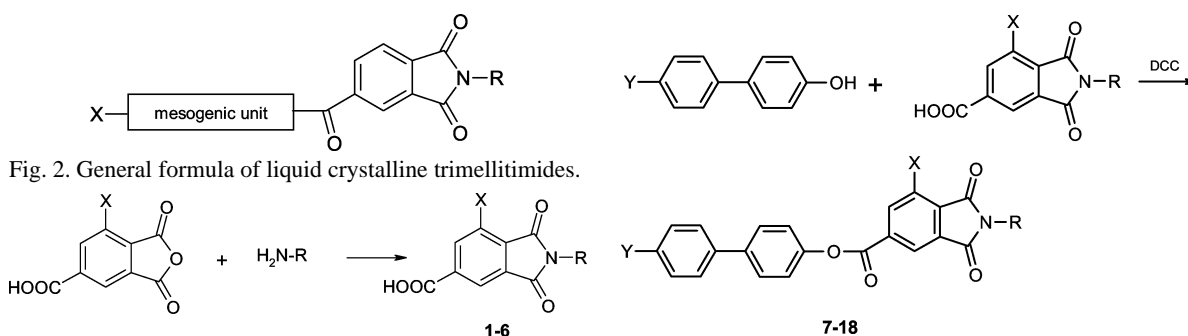
Fig. 1. Influence of the nitro side group on the liquid crystalline behaviour of 4-substituted benzoates. Cr = crystal phase, SmA = smectic A phase, N = nematic phase, Iso = isotropic phase.

Fig. 2. General formula of liquid crystalline trimellitimides.

Compound	X	R
1	H	$CH_2CH(CH_3)C_2H_5$
2	NO_2	$CH_2CH(CH_3)C_2H_5$
3	H	$(CH_2)_{11}$-CH_3
4	NO_2	$(CH_2)_{11}$-CH_3
5	H	CH_2COOCH_3
6	NO_2	CH_2COOCH_3

thetic pathway to obtain these compounds is shown in Scheme 1.

Results and Discussion

The use of 6-nitromellitic anhydride for the synthesis of ester imides **1**–**6** allowed us to obtain the new compounds **7**–**18** with a modified central imide unit. Their liquid crystalline properties have been compared with analogues without the nitro side group. The transition temperatures, as well as the enthalpies taken from DSC traces, are collected in Table 1.

As can be seen the majority of the nitroimides do not form liquid crystals. The introduction of a large and polar side group into the phthalimide core effects liquid crystalline disordering while non-substituted compounds **7**, **11**, **13**, **15** and **17** show thermotropic properties. Only in the case of the pair **9** and **10**, both compounds are liquid crystals. Two long aliphatic tails attached to the oppositive sides of molecule **9** strongly

Compound	Y	X	R
7	$OC_{10}H_{23}$	H	$CH_2CH(CH_3)C_2H_5$
8	$OC_{10}H_{23}$	NO_2	$CH_2CH(CH_3)C_2H_5$
9	$OC_{10}H_{23}$	H	$(CH_2)_{11}$-CH_3
10	$OC_{10}H_{23}$	NO_2	$(CH_2)_{11}$-CH_3
11	$OC_{10}H_{23}$	H	CH_2COOCH_3
12	$OC_{10}H_{23}$	NO_2	CH_2COOCH_3
13	$OC_{10}H_{21}$	H	$(CH_2)_{11}$-CH_3
14	$OC_{10}H_{21}$	NO_2	$(CH_2)_{11}$-CH_3
15	Br	H	$(CH_2)_{11}$-CH_3
16	Br	NO_2	$(CH_2)_{11}$-CH_3
17	CN	H	$(CH_2)_{11}$-CH_3
18	CN	NO_2	$(CH_2)_{11}$-CH_3

Scheme 1. Synthesis of trimellitimides and their nitro analogues.

stabilise smectic C and A phases. The lateral group –NO_2 in **10** insignificantly disrupts molecular packing. For this compound only the tilted phase disappears, but the orthogonal smectic order is saved. On the other hand, the compounds with the short polar end groups –CN, –Br or –CH_2COOCH_3 lose their liquid crystal properties when substituted by the equally strong polar side –NO_2 group. These phenomena might be explained when the dipole moments of the compounds are compared. The resultant dipole moments and their components calculated by means of the AM1 semi-empirical method are given in Table 2.

| Compound | Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in parentheses) | | | | | | |
	Cr		SmC		SmA		Iso
7[a]	●	105.9 (27.7)	●	146.8 (0.126)*	●	179.1 (6.99)	●
8	●	115.1 (33.5)					●
9	●	131.3 (51.76)	●	170.1 (0.05)	●	175.9 (5.62)	●
10	●	132.5 (21.0)			●	156.2 (10.8)	●
11[b]	●	114.0 (22.2)	●	[90.1][d] (14.2)	●	155.4 (4.9)	●
12	●	95.0 (44.1)					●
13	●	124.0 (33.2)	●	171.5 (0.11)	●	175.0 (4.40)	●
14	●	170.3 (40.0)					●
15	●	152.6 (35.0)			●	174.4 (10.1)	●
16	●	99.9 (42.2)					●
17[c]	●	130.0 (33.24)			●	177.2 (4.86)	●
18	●	112.0, (38.9)					●

Table 1. The liquid crystalline properties of trimellitimides and their nitro analogues.

[a] Ref. [12]; [b] ref. [9]; [c] ref. [8]; Cr = crystal phase, Sm = smectic phase, Iso = isotropic phase; ● presence of mesophase; [d] monotropic smectic $\tilde{C}$ phase; * chiral smectic C phase.

Table 2. The total dipole moments μ and μ_x, μ_y, μ_z components (in D) of compounds studied.

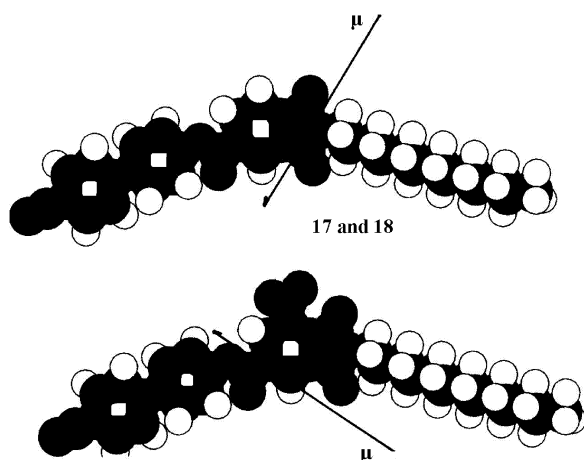| Compound	μ	μ_x	μ_y	μ_z
7	3.75	−2.25	2.55	−1.58
8	3.25	1.82	2.69	0.08
9	3.75	−2.30	2.55	−1.55
10	3.35	1.82	2.81	0.10
11	4.13	−3.14	2.67	−0.22
12	3.51	0.54	2.09	2.18
13	3.77	−2.51	2.43	−1.40
14	3.28	1.78	2.80	0.06
15	1.34	−1.17	−0.61	0.19
16	3.39	3.09	−0.33	1.36
17	3.50	−2.46	−2.19	−1.21
18	2.66	1.76	−1.97	0.31

Fig. 3. Molecular structures of N-dodecyl-4-[(4-cyanobiphenyl-4'-yl)oxycarbonyl]phthalimide (**17**) and N-dodecyl-4-[(4-cyanobiphenyl-4'-yl)oxycarbonyl]-6-nitrophthalimide (**18**) as obtained by semiempirical AM1 calculations.

The introduction of the nitro group into the phthalimide ring changes the total dipole moment values μ as well as the sense of their μ_x and μ_z components. It should be noticed that for the pair **9** and **10** these differences are much smaller than for the other ester imides. This result may explain why thermotropic properties appear only in the case of the nitroimide **10**.

As examples, in Fig. 3 the models of the molecular structures of the cyanobiphenylyl derivatives **17** and **18** and their resultant dipole moments are shown.

The shapes of the ester imides and their nitro derivatives are almost the same but the directions of the total dipole moments μ and their μ_x and μ_z components are completely different. We suppose that these data explain the changes in molecular ordering and liquid crystalline properties. It should be noted that all ester nitroimides exhibit lower melting points or clearing points than their non-substituted analogues.

Experimental Section

Instrumentation: The infrared spectra (in CH_2Cl_2) were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrams 2000 software, and the NMR spectra (in $CDCl_3$) were recorded using a Varian Gemini 200 MHz spectrometer. The compositions were confirmed by elemental analysis. The data indicated by symbols were within ±0.4% of the theoretical values.

The phase transitions were observed using a polarising microscope BIOLAR equipped with a LINKAM heating stage THMs 600. Temperatures and enthalpies were measured by means of a DSC 141 SETARAM microcalorimeter. The measurements were made in both heating and cooling cycles at the rate of 1 K min^{-1}. The sample quantity was about 30 mg and special aluminium crucibles, with good thermal contact, were used. The hermetically sealed crucibles with the samples were heated to the sample clearing temperature and then cooled to the crystallisation temperatures. After this procedure, the DSC measurement was started. The values of temperature and enthalpy were read directly from the calorimeter integration curves after preliminary calibration using standards. The accuracy of phase transition temperature measurements was about ±0.1 K.

Molecular modelling was performed using the semi-empirical method AM1 (HyperChem software).

Synthesis: All chemicals used were analytical grade commercial products (Aldrich) and were applied without further purification. *N*-Substituted trimellitimides were synthesized according to the well known and patented method from trimellitic or 6-nitrotrimellitic anhydride and the amines in dry boiling DMF [2, 3, 13]. The purity of all compounds was checked by TLC using SiO_2 plates with an UV indicator and a chloroform/methanol mixture as eluent.

4-Carboxy-6-nitrophthalic anhydride (6-nitrotrimellitic anhydride): The synthetic rout was based on earlier prescription [12]. Trimellitic anhydride (30.0 g, 0.16 mol) was dissolved in H_2SO_4 (97%, 230 cm^3). KNO_3 (80 g, 0.68 mol) was added in portions with vigorous shaking over a period of 2 h at 65 – 100 °C. The mixture was heated at 120 °C for 20 h. Another portion of KNO_3 (30 g, 0.25 mol) was added and heated for 6 h. After final portion of KNO_3 (30 g, 0.25 mol) had been added, the mixture was heated for 16 hours, and then poured on ice, end extracted with ether. After evaporation of solvent the crude residue was refluxed with acetic anhydride over 30 minutes. After cooling the product crystallized and then crystals were dried under vacuum. Yield 22.5 g (59.1%). The melting point was conformable to the literature data (237 – 239 °C).

N-Substituted trimellitimides and 6-nitrotrimellitimides **1 – 6**: The synthesis was carried out from trimellitic anhydride or 6-nitrotrimellitic anhydride according to the method described previously [13, 14]. Typical characterisation results are given here for *N*-dodecyl-6-nitrotrimellitimide (**4**), (IUPAC name: 2-dodecyl-7-nitro-1,3-dioxo-2,3-dihydro-1*H*-isoindole-5-carboxylic acid): M. p. 115 – 120 °C. – FTIR (CH$_2$Cl$_2$): $v = 3600 – 2500$ (COOH), 2928 and 2856 (C-H$_{aliph.}$), 1788 (C=O$_{imide}$) 1726 (C=O$_{acid,imide}$), 1550 (NO$_2$) cm^{-1}. – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 0.89$ (t, 3H, CH$_3$), 1.22 – 1.78 (m, 20H), 3.79 (t, 2H, NCH$_2$), 8.85 (s, 1H$_{ar}$), 8.88 (s, 1H$_{ar}$). – C$_{21}$H$_{29}$NO$_4$ (359.47): calcd. C 70.17, H 8.13, N 3.90; found C 70.11, H 8.10, N 3.85.

Ester imides and ester nitroimides **7 – 18**: These compounds were synthesized according to the method published previously [10, 11]. Typical characterization results are given for ester imide **9** and its nitro derivative **10**.

N-Dodecyl-4-[(4-decyloxybiphenyl-4'-yl)oxycarbonyl] phthalimide (**9**): Yield 66%. FTIR (CH$_2$Cl$_2$): $v = 2929$ and 2856 (C-H$_{aliph.}$), 1775 (C=O$_{imide}$) 1744 (C=O$_{ester}$), 1725 (C=O$_{acid,imide}$) cm^{-1}. – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 0.86 – 0.92$ (m, 6H), 1.27 – 1.30 (m, 31H), 1.57 – 1.85 (m, 4H), 3.74 (t, 2H, NCH$_2$), 4.04 (t, 2H, OCH$_2$), 7.00 (d, 2H$_{ar}$), 7.29 (d, 2H$_{ar}$), 7.52 (d, 2H$_{ar}$), 7.62 (d, 2H$_{ar}$), 7.98 (d, 1H$_{ar}$), 8.61 (d, 1H$_{ar}$), 8.68 (s, 1H$_{ar}$). – C$_{43}$H$_{57}$NO$_5$ (667.94): calcd. C 77.32, H 8.60, N 2.10; found C 77.40, H 8.77, N 2.05.

N-Dodecyl-4-[(4-decyloxybiphenyl-4'-yl)oxycarbonyl]-6-nitrophthalimide (**10**): Yield 45%. – FTIR (CH$_2$Cl$_2$): $v = 2929$ and 2856 (C-H$_{aliph.}$), 1785 (C=O$_{imide}$) 1748 (C=O$_{ester}$), 1725 (C=O$_{acid,imide}$), 1552 (NO$_2$); – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 0.86 – 0.92$ (m, 6H), 1.27 – 1.29 (m, 31H), 1.57 – 1.85 (m, 4H), 3.76 (t, 2H, NCH$_2$), 4.03 (t, 2H, OCH$_2$), 6.96 (d, 2H$_{ar}$), 7.29 (d, 2H$_{ar}$), 7.52 (d, 2H$_{ar}$), 7.63 (d, 2H$_{ar}$), 7.98 (d, 1H$_{ar}$), 8.86 (m, 2H$_{ar}$). – C$_{43}$H$_{56}$N$_2$O$_7$ (712.93): calcd. C 72.44, H 7.92, N 3.93; found C 72.41, H 7.98, N 3.88.

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