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Some novel liquid crystalline derivatives of 4-carboxyphthalimide

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Some novel liquid crystalline derivatives of 4-carboxyphthalimide

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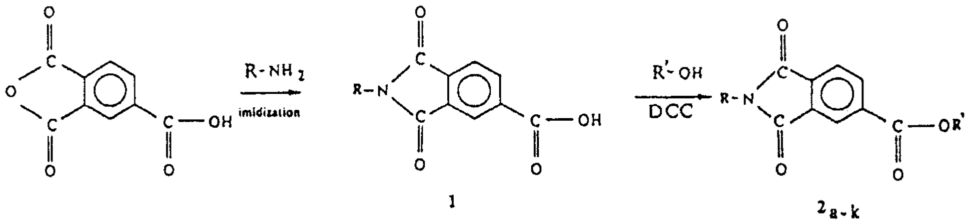
A series of novel esters of 4-carboxyphthalimides has been prepared. Differential scanning calorimetry and polarizing optical microscopy studies reveal that *N*-substituted 4-cholesteryloxycarboxyphthalimides exhibit a chiral nematic (cholesteric) phase in the range 120–205°C. Unexpectedly, esters containing well-known mesogenic groups such as 4-cyano- or 4-methoxy-phenyl do not form liquid crystal phases.

Trimellitic anhydride (4-carboxyphthalic anhydride) is a very useful monomer in the synthesis of poly(ester imide)s. Some of them have liquid crystalline properties [1–5]. It was suggested that imide monomeric units of poly(ester imide)s, especially those derived from *N*-phenylcarboxyphthalimide, would be good mesogens.

The purpose of this work was to check the possibility of synthesizing low molecular mass liquid crystal derivatives of *N*-substituted 4-carboxyphthalimides (trimellitic imides) (2) and assess the mesogenic potential of the imide ring.

A general pathway of synthesis of ester imides is shown in the scheme:



Synthesis of 4-carboxyphthalimides (**1**) was carried out according to procedures described earlier [6, 7].

Esters (**2 a–k**) were synthesized from the acids (**1**) and appropriate phenols or cholesterol by standard procedures, using DCC (1,3-dicyclohexylcarbodiimide) and DMAP (4-*N*, *N*-dimethylaminopyridine) as catalyst. The products were crystallized from ethanol and purified by column chromatography (SiO_2, $CHCl_3$).

All compounds had satisfactory elemental analyses; the presence of functional groups (ester and imide) was confirmed by IR spectroscopy. Their purity was also checked by TLC.

The phase transition temperatures of the esters of the 4-carboxyphthalimides obtained are listed in the table. DSC investigations and polarized optical microscopy revealed that all the *N*-substituted cholesteryl esters have liquid crystalline properties.

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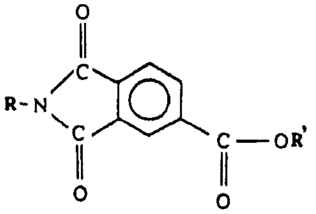
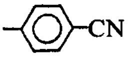
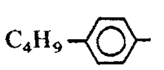
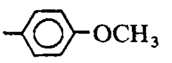
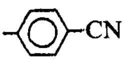
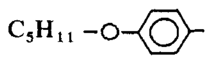
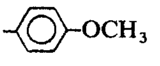
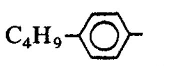
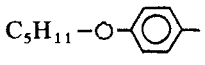
They form a chiral nematic (cholesteric) phase at 120·5–184·7°C depending on the kind of substituent attached to the nitrogen of the imide group. The isotropization temperatures varied from 131·6 to 204·5°C. In the DSC thermograms of 4-cholesteryloxycarbonyl-*N*-allylphthalimide (see figure 1) and 4-cholesteryloxycarbonyl-*N* (4′-butylphenyl)phthalimide, additional endothermal peaks are observed at 124·5°C and 135°C, respectively. These correspond to polymorphic transition in the crystalline state.

Non-cholesteryl esters containing 4-cyano- or 4-methoxy-phenyl substituents (compounds **2a**–**2d**) and an alkyl chain or an even 4-alkyl- or 4-alkoxy-phenyl substituent in the imide group exhibit only crystalline and isotropic phases, despite the good mesogenic properties of these groups in many other systems. It should be noted that the unsubstituted imide, 4-cholesteryloxycarbonylphthalimide (compound **2e**), does not form a liquid crystal phase, although simple esters of cholesterol (for example cholesteryl benzoate) are well-known mesomorphic compounds. These observations

Structures and phase transitions of esters of 4-carboxyphthalimides (**2a**–**k**).



Structure	*R*	*R′*	Transition temperatures†/°C
2a	$CH_2{=}CHCH_2-$		C, 110·0, I
2b			C, 260·4, I
2c	$C_8H_{17}-$		C, 100·1, I
2d			C, 210·1, I
2e	H–	Cholesteryl	C, 132·4, I
2f	$CH_2{=}CHCH_2-$	Cholesteryl	C, 139·6‡, N*, 170·5, I
2g	CH_3OCOCH_2-	Cholesteryl	C, 120·5, N*, 145·0, I
2h	C_4H_9-	Cholesteryl	C, 124·5, N*, 131·6, I
2i	$C_8H_{17}-$	Cholesteryl	C, 184·7, N*, 204·5, I
2j		Cholesteryl	C, 135·5‡, N*, 186·4, I
2k		Cholesteryl	C, 161·7, N*, 200·5, I

† C, crystal phase: N*, chiral nematic: I, isotropic phase.

‡ Compound shows additional polymorphic crystal–crystal transition: compound **2f** at 124·5°C and compound **2j** at 127°C.

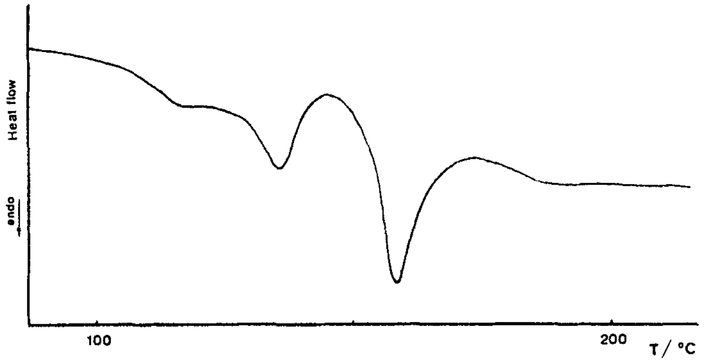


Figure 1. DSC scan at a heating rate of 10°C min^{-1} for 4-cholesteryloxycarbonyl-*N*-allylphthalimide (**2f**).

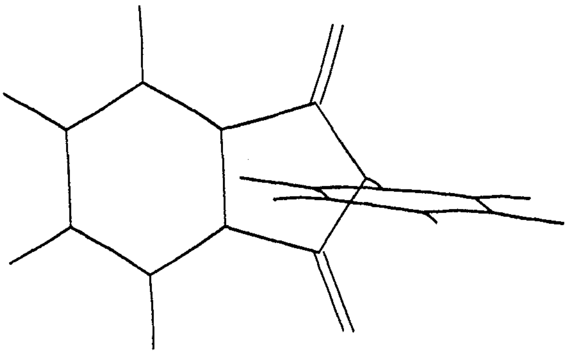


Figure 2. Computer picture of the molecule of *N*-phenylphthalimide.

lead us to suppose that at least in low molecular mass compounds an imide ring does not favour an ordered structure.

For a better understanding of the geometrical parameters of the compounds studied, a simple molecule, *N*-phenylphthalimide was examined by computer molecular modelling, using the Alchemy II program. The computer picture of *N*-phenylphthalimide is presented in figure 2. The conformation shown corresponds to the minimum internal energy of the imide under consideration. One can see that the *N*-substituent of phthalimide is twisted and almost perpendicular to the plane of the imide ring. The hybridization of the nitrogen atom (close to sp^3) is responsible for the angle between the imide ring and N–C bond. (Geometrical parameters of different kinds of imide rings have been calculated in our previous paper [7].)

These results are in good agreement with Lenz's study on polyesters of *N*-(4′-carboxyphenyl)-4-carboxyphthalimide. It was found that the non-planar conformation between the phenylene ring and the imide group hinders molecular packing [5]. The results also agree with our findings that the degree of crystallinity of poly(ester imide)s decreases with increase in the concentration of imide units in the copolymer chain [8].

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