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Synthesis and Mesomorphic Properties of Diisocyanatobenzoates

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A number of novel ester group containing aromatic and cycloaliphatic diisocyanates: 4,4′-diisocyanatophenyl benzoate, 4,4′-diisocyanato-trans-cyclohexyl benzoate and several derivatives containing lateral substituents were synthesized by reaction of appropriate trimethylsiloxy phenyl or cyclohexyl isocyanates with isocyanatobenzoyl chlorides. They form nematic liquid crystalline phases. The isocyanate group greatly stabilizes the mesophase with regard to other three atom terminal groups. The influence of lateral methyl substituents in various positions on the thermal transitions was studied. They reduce the nematic range. 4-Isocyanatophenyl 4-methoxybenzoate and the corresponding diazetidinedione (dimer with a higher aspect ratio) were also synthesized. The pure dimer gives an isotropic melt due to a cycloreversion to the monomer. When present as impurities diazetidinediones decrease the melting point and increase the clearing temperature of the parent isocyanate.

Keywords: Diisocyanatobenzoates, nematic, transition temperatures, enthalpies, 1,3-diazetidinedione formation, influence

INTRODUCTION

Low molecular weight mesomorphic compounds usually contain non reactive terminal groups, since one of the criteria for phase stability is chemical stability. Mesogens with one reactive terminal group have been described as monomers in the synthesis of liquid crystalline side chain polymers.[1]

Intermediates for main chain LC polymers, which are normally made by step growth polymerization reactions, are either non mesogenic precursors or reactive mesogens. These can have high reactivity (low stability), e.g. azoxy-4,4′-bischloroformylbenzene[2] or low reactivity (high stability), e.g. hydroquinone bis(4-acetoxy)benzoates.[3]

Mesogenic diisocyanates are of interest as starting materials for liquid crystalline polyurethanes, which have not been systematically investigated up to now.[4] The only liquid crystalline diisocyanate described in the literature so far, to our knowledge, is 4,4′-diisocyanatophenyl benzoate,[5] which, however, only recently has been recognized as a nematogen.[6]

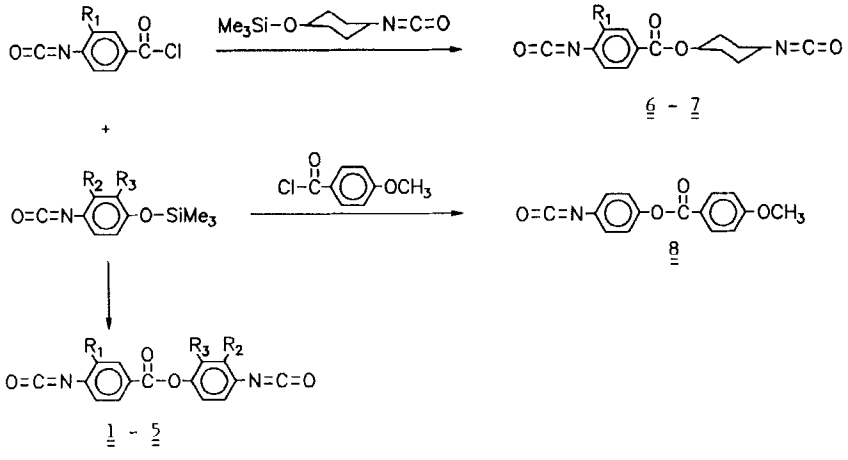
In the course of our work on liquid crystalline polyurethanes we were interested in a general synthesis of mesogenic diisocyanates enabling the systematic introduction of substituents in various positions of the mesogens. The central core of the molecules was chosen to consist of 1,4-phenylene or 1,4-trans-cyclohexanediyl moieties with ester bridging groups.

This paper reports on the synthesis and mesomorphic properties of a number of novel diad 4,4′-diisocyanatophenyl benzoates and 4,4′-diisocyanato-trans-cyclohexyl benzoates.

RESULTS AND DISCUSSION

Synthesis of mesogenic diisocyanatoesters

The diisocyanatoesters were prepared by reaction of a trimethylsiloxy group containing isocyanate with an isocyanatobenzoyl chloride in 1,2-dichlorobenzene at elevated temperatures as outlined in Scheme 1.



SCHEME 1

4-Isocyanatophenyl 4-methoxybenzoate **8** was prepared for reasons of comparison and as a suitable monoisocyanate for the synthesis of a 1,3-diazetidine-2,4-dione **9** which has a more favourable aspect ratio.

The novel diisocyanato esters were characterized by Ir-, ^{1}H-NMR spectroscopy and elemental analyses, and the cycloaliphatic compounds in addition by ^{13}C-NMR spectra in order to make sure that no isomerization of the desired trans isomers occurred during the reactions.[7] Details of the synthesis and analytical properties of the diisocyanato esters will be published separately.[8]

Mesomorphic properties

The phase behaviour of the diisocyanato esters was studied by optical polarizing microscopy and differential scanning calorimetry. The mesomorphic phases of all

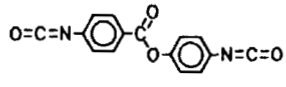
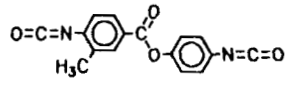
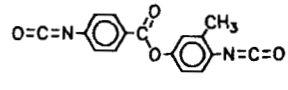
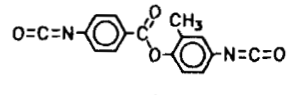
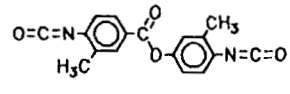
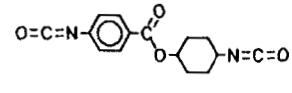
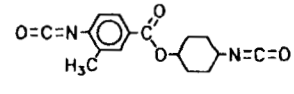
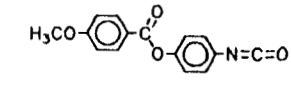
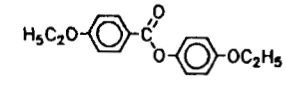
liquid crystalline compounds as far as they could be identified were nematic. The transition temperatures and enthalpies are summarized in Table I.

The high reactivity of the aromatic isocyanates makes it difficult to characterize the mesomorphic phases. In the solid state, especially close to the melting point, [2+2] cycloaddition occurs. Therefore microscopic investigation was made with the preheated hot stage.

The unsubstituted parent compound **1** melts at 118°C forming a nematic phase with a clearing temperature of 148°C. The rigid isocyanate group dramatically stabilizes the nematic range of the diisocyanato esters as compared to other three atom end groups though the melting points are almost uneffected. The corresponding 4,4′-diethoxyphenyl benzoate **10**, for example, has the same melt temperature

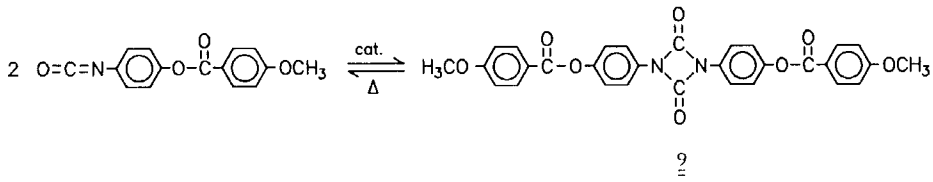
TABLE I

Thermal properties of diisocyanatobenzoates

No.		T_m °C		T_c °C	ΔH_{kn} kJ/mol	ΔH_{ni} kJ/mol
1		118.0	n	148.0	34.2	0.82
2		83.0		n (74)	32.4	0.94
3		73.0		n (72)	28.5	0.74
4		103.0		n (56)	31.8	0.47
5		70.0		-	23.2	-
6		60.0		(14)	26.2	-
7		75.0		-	21.7	-
8		91.3		n 94.2	32.2	1.00
9	Dimer	234.0		-	120.0	-
10		118.0		119.5	-	-

but a clearing point of only 119.5°C (Table 1). Compound **8** with one isocyanate and one methoxy group melts at 91.3°C and has a clearing point of 94.2°C.

A comparison of the relative efficiency of heterocumulene type (isocyanate-, isothiocyanate-) and cyano groups in promoting LC properties would be of interest. No data were available from the literature for the isothiocyanato- and cyano compounds corresponding to **1** or **8**. Comparison with the n-butoxy derivatives, however, which have been described (J. van der Veen, J. Phys. (Fr.) Supp., No. **6**, **37** C3-13 (1976)) would be missleading because of the influence of the butyl group as compared to the methyl group of **8**.



SCHEME 2

In a German patent[10] a clearing point of 173°C is given for **1**. We observed a similar temperature for a sample kept in the molten state over a longer period. The IR-spectrum of this sample showed an additional absorption at 1770 wavenumbers obviously due to a [2 + 2] cycloaddition of the isocyanate groups (formation of oligomers containing the 1,3-diazetidine-2,4-dione moiety). Heating this sample on a hot stage to 220°C and quenching gave almost the correct phase transitions.

This behaviour is in agreement with the results obtained from the [2 + 2] cycloaddition product of 4-isocyanatophenyl 4-methoxybenzoate, which was prepared as a pure compound. It melts at 234°C and simultaneously is cleaved to the monomer which can be seen from the extremely high "melt energy" (120 kJ/mol), as compared to the other diisocyanato esters (about 30 kJ/mol), and from the infrared spectrum of a quenched sample which shows the strong isocyanate absorption at 2280 cm^{-1} and besides a very weak band at 1700 wavenumbers, only the carbonyl absorption of the ester group (Figure 1). The thermal instability of the diazetidinedione moiety explains why the melt is isotropic though, according to the structure, the dimer should be a better mesogen than the monomer (more favourable length to breadth ratio). On second heating a quenched sample showed transitions almost identical with those of the monomeric compound (Figure 2). The melting point is slightly decreased while the clearing point increases due to the higher virtual clearing temperature of the dimer.

Broadening of mesogens

Due to the big positive nematic range it was possible to study the influence of methyl substituents in various positions of the aromatic rings. Introduction of lateral methyl substituents in the ortho position to either of the isocyanate groups lowers the melting points of diisocyanato esters by 40 to 50°C with regard to the parent compound (**2** and **3**). The clearing temperatures are lowered even more and mon-

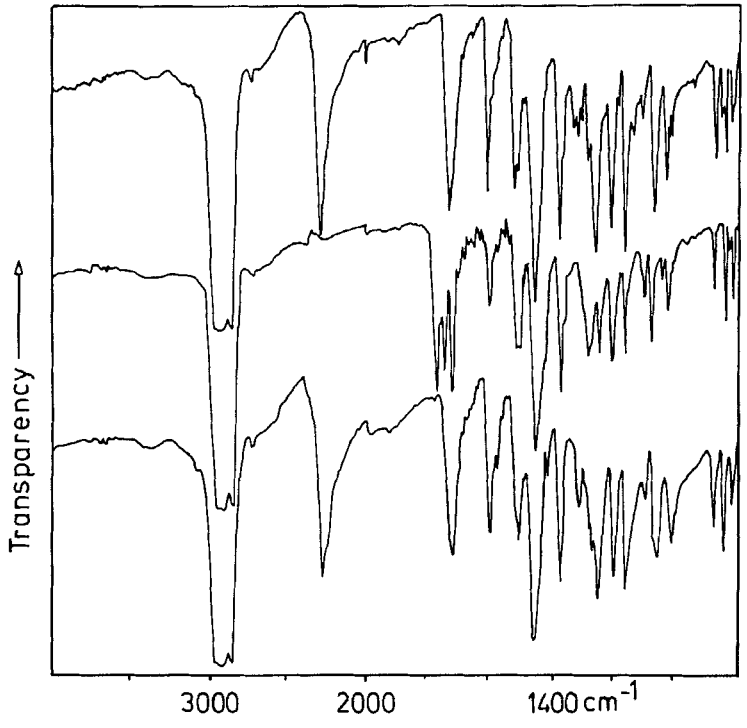


FIGURE 1 Ir-spectra of pure 4-isocyanatophenyl 4-methoxybenzoate **8** (upper curve), 1,3-bis[4-(4'-methoxybenzoyloxy)-phenyl]-diazetidine-2,4-dione **9** (middle curve) and quenched sample of molten **9** (lower curve).

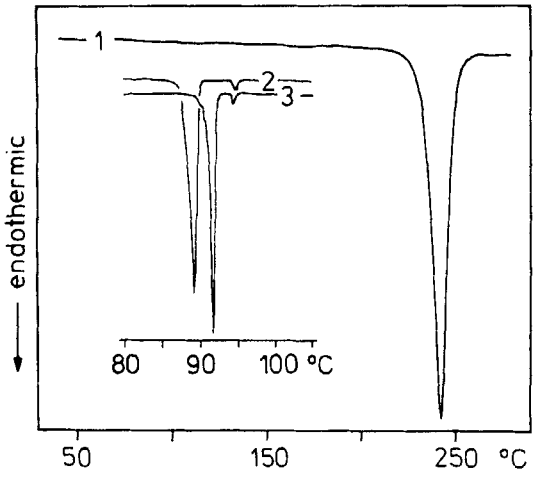


FIGURE 2 DSC traces of 1,3-bis[4-(4'-methoxybenzoyloxy)-phenyl]-diazetidine-2,4-dione **9** (upper curve), a quenched sample of molten **9** (middle curve) and of pure 4-isocyanatophenyl 4-methoxybenzoate **8** (lower curve).

otropic liquid crystalline compounds result. A methyl group in the meta position of the isocyanate in the phenol part (**4**) reduces the melting point less (15°C) and the clearing point more as compared to the o-methyl substituent. Introduction of a trans-4-isocyanatocyclohexyl-instead of the 4-isocyanatophenyl group lowers the melting point by 60°C and the clearing temperature by as much as 130°C (**6**)! This is known from other cyclohexyl benzoates[11] though the magnitude of the effect seems to be surprising.

A methyl substituent in both the 3 and 3′ positions of the phenyl-benzoate (**5**) leads to the loss of liquid crystalline properties, which is also observed with one methyl group in the acid part of the cyclohexyl benzoate (**7**).

The transition enthalpies are well in the usual range of low molecular weight nematics[12] (Table I).

CONCLUSIONS

A new series of reactive thermotropic liquid crystals: diisocyanatophenyl and diisocyanato-trans-cyclohexyl benzoates has been described and the influence of the isocyanate group as well as of lateral methyl substituents on the phase transitions has been studied. The results should lead to a better understanding of the phase behaviour of polyurethanes made from these isocyanates which are currently under investigation.

Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

EXPERIMENTAL PART

Methods of characterization: ^{1}H-NMR spectra were obtained on a Bruker WP 80 in deuterochloroform using tetramethylsilane (TMS) or $CHCl_3$ as internal standard. The thermal properties were investigated with a Mettler TC 10 with DSC 30 equipment. Heating rates were 5 or 20 K/min. The birefringent textures were observed with a Leitz Ortholux 12 polarizing microscope equipped with an FP 82 hot stage (Mettler).

Materials: The synthesis and characterization of the isocyanatobenzoyl chlorides, 4-trimethylsiloxyphenyl and cyclohexyl isocyanates and diisocyanatobenzoates will be described elsewhere.[8]

4-Isocyanatophenyl 4-methoxybenzoate **8**. 25 mmol of 4-methoxybenzoyl chloride and of 4-trimethylsiloxyphenyl isocyanate,[13] together with 20 mg of sulfuric acid catalyst in 6 ml 1,2-dichlorobenzene, were heated to 165°C while trimethylchlorosilane was removed at 500 mbar. The reaction was stopped when the absorption of the chloroformyl group had disappeared. The resulting ester isocyanate was purified by short path vacuum distillation in a Büchi glass tube oven.

1,3-Bis[4-(4′-methoxybenzoyloxy)-phenyl]-diazetidine-2,4-dione **9**. 1 g of 4-isocyanatophenyl 4-methoxybenzoate, 5 ml of dry toluene and 3 drops of tribu-

tylphosphine were heated to 80°C over night. The white precipitate formed was isolated by filtration washed several times with toluene and dried.

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