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Synthesis and mesogenic properties of diaromatic cyanates and isocyanates – monomers for liquid crystalline thermosets†

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Five pairs of mesogens with identical cores having either a cyanate or an isocyanate reactive terminal group have been synthesized. The monofunctional mesogens have a *n*-butoxy or a methoxy substituent as the second terminal group. The influence of the two isomeric OCN moieties on the formation of a mesophase and on the thermal transitions has been investigated. The mesophases observed were identified as nematic. A tremendous difference in the mesogenic power (stabilizing effect on a mesophase) has been found for the two reactive terminal groups. The isocyanates have lower melting points than the isostructural cyanates and clearing points which are approximately 30°C higher per isocyanate group, as compared to a cyanate moiety.

1. Introduction

Networks with chemical fixing of the liquid crystal organization have been studied by several research groups [1–3]. No general picture, however, can be drawn from the experimental results up to now, since these studies to a large extent have no systematic character. Ober and co-workers have however made important contributions in the field of liquid crystal epoxy and cyanurate networks [4, 5]. The dicyanates used in their study were mixtures of isomeric triad bis(4-cyanato methylphenyl) terephthalates which melted to an isotropic phase. Epoxy resins, which have been the most intensely studied as liquid crystal thermosets, are not ideally suited in terms of relating mesophase formation to the curing kinetics and network build up, since a number of side reactions occur apart from the main curing reaction, regardless of whether chain polymerization or curing with amines, anhydrides or other agents is chosen [6].

A systematic investigation of liquid crystal thermosets has to answer a number of questions: What is the influence of the reactive terminal groups on the mesogenic properties of the monomers? What is the contribution of the structural element formed by the crosslinking reaction (the crosslink) to the mesomorphic properties? What are the contributions of the monomer and of the curing agent? How does the isotropization temperature vary with conversion? What is the influence of mesophase formation on the network properties and vice versa?

Highly pure monomers with adjustable mesogenic properties are of prime importance for a study of these features. Network build up must proceed by one clean reaction, which gives only one type of crosslink and allows, for example, prediction of oligomer distribution as a function of conversion. A precise spectroscopic method should be available to monitor conversion and relate phase transitions to conversion and network parameters. Isocyanates and cyanate esters fulfil these requirements [7]. They react by cyclotrimerization to *s*-triazines (isocyanurates, cyanurates) with virtually no by-products, the reaction rate can be adjusted with catalysts, and the functional groups have infrared absorptions of sufficient intensity, which do not overlap with other bands. In previous papers we investigated the mesogenic properties of the isocyanate terminal group [8, 9].

The present paper deals with the synthesis and characterization of some novel mono- and di-functional cyanate esters, which are compared with the isostructural isocyanates. Other questions raised above will be discussed in forthcoming publications.

2. Results and discussion

2.1. *Synthesis of mesogenic cyanate esters and isocyanates*

The influence of the two isomeric OCN terminal groups was studied with monofunctional compounds based on phenyl benzoate as a mesogenic core. The second terminal group was either a methyl or a butoxy group. In the case of the butoxy terminal group, both isomers (involving interchange of the terminal groups) were prepared in order

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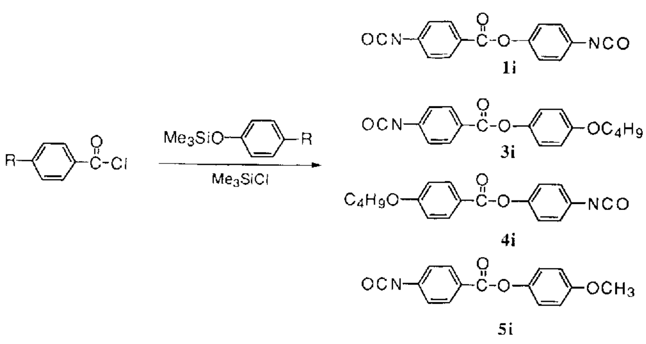
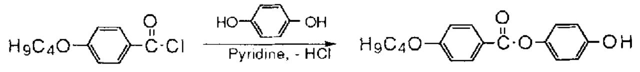
to obtain information on the influence of the orientation of the ester group on the mesomorphic properties. Two difunctional compounds, 4-cyanatophenyl 4-cyanatobenzoate (**1 c**), and 4,4′-diacyanatobiphenyl (**2 c**) were also synthesized, since they were expected to be suitable monomers for liquid crystalline thermosets, and the comparable isocyanates exhibit enantiotropic nematic mesophases.

The isocyanates were synthesized by reaction of a suitable 4-isocyanato- or 4-butoxy-benzoyl chloride with the corresponding silylated 4-butoxy-, 4-methoxy-, or 4-isocyanato-phenol according to procedures which have been previously described [10] (cf. scheme 1). 4,4′-Diisocyanatobiphenyl (**2 i**) was obtained by reaction of the corresponding diamine with phosgene [11].



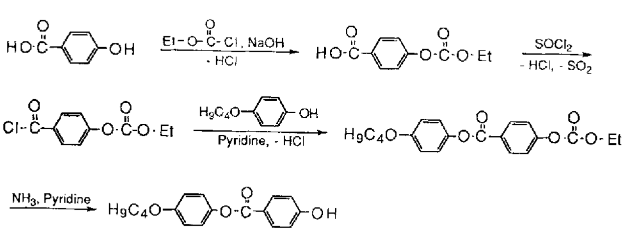
Scheme 1.

Cyanate esters cannot be prepared from monofunctional precursor molecules. 4-Hydroxyphenyl 4-butoxybenzoate was synthesized by a straightforward reaction from 4-butoxybenzoyl chloride and hydroquinone in pyridine [12] (see scheme 2), while the inverse compound 4-butoxyphenyl 4-hydroxybenzoate required a multi-step reaction sequence (see scheme 3).



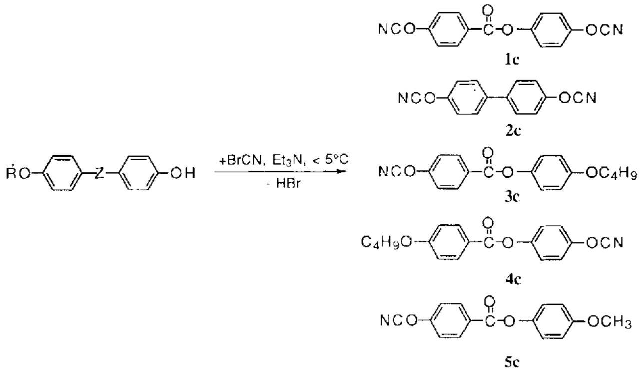
Scheme 2.

First the hydroxy group of 4-hydroybenzoic acid was protected by reaction with ethyl chlorocarbonate. Then the carboxy group was interacted with thionyl chloride to give 4-ethoxycarbonyloxybenzoyl chloride, which underwent esterification with 4-butoxyphenol to yield 4-butoxyphenyl 4-ethoxycarbonyloxybenzoate. Deprotection of the hydroxy group was achieved by reaction of the carbonate ester with ammonia in pyridine at room temperature [12] (see scheme 3).



Scheme 3.

The mesogenic phenols were converted into the cyanate esters **1 c–5 c** by reaction with cyanogen bromide in the presence of an acid acceptor as shown in scheme 4.



Scheme 4.

Based on these reactions, the isocyanates and cyanate esters were obtained in high yields. The isocyanates were purified by short path distillation in a Büchi Kugelrohr apparatus, while the cyanate esters could be purified by flash chromatography on silica gel or by recrystallization. All new compounds were characterized by their IR and NMR spectra and by elemental analysis. The analytical data for the cyanate esters are summarized in table 1 and those for the isocynates in table 2.

2.2. *Mesomorphic properties*

The mesophase behaviour of the new compounds was investigated by polarized light microscopy and thermal analysis (differential scanning calorimetry). The thermal transitions together with the corresponding enthalpies are given in table 3. Each entry gives the properties of the cyanate ester on the left hand side and those of the isostructural isocyanates on the right hand side. All mesophases that could be identified on the basis of the textures exhibited between crossed polarizers in the microscope were of the nematic type.

One striking result can be seen immediately from table 3. Regardless of the mesogenic core, the isocyanate group, obviously, is much better suited to stabilize a liquid

Table 1. Yields, purification, analytical data, and spectroscopic properties of mesogenic cyanates.

Compound	^{1}H NMR ($CDCl_3$) δ/ppm	Molecular formula (M_w)	Elemental analysis/per cent calculated (found)			T_m/°C	Yield/per cent (purification)
			C	H	N		
1 c	7·38–7·58 (m, 6 H), 8·33 (d, ^{3}J = 9·2 Hz, 2 H)	$C_{15}H_8N_2O_4$ (280·24)	64·3 (64·5)	2·9 (3·0)	10·0 (9·9)	139	80 (Flash chrom. CH_2Cl_2)
2 c	7·40 (d, ^{3}J = 7·3 Hz, 4 H), 7·65 (d, ^{3}J = 7·3 Hz, 4 H)	$C_{14}H_8N_2O_2$ (236·23)	71·2 (71·1)	3·4 (3·5)	11·9 (11·9)	138	74 (from acetone)
3 c	1·00 (t, ^{3}J = 6·7 Hz, 3 H), 1·52 (m, ^{3}J = 6·7 Hz, 2 H), 1·80 (m, ^{3}J = 6·7 Hz, 2 H), 4·00 (t, ^{3}J = 6·6 Hz, 2 H), 6·95 (d, ^{3}J = 7·3 Hz, 2 H), 7·13 (d, ^{3}J = 8·7 Hz, 2 H), 7·48 (d, ^{3}J = 7·3 Hz, 2 H), 8·35 (d, ^{3}J = 8·7 Hz, 2 H)	$C_{18}H_{17}NO_4$ (311·34)	69·4 (69·3)	5·5 (5·4)	4·5 (4·2)	72	76 (from hexane)
4 c	1·00 (t, ^{3}J = 6·7 Hz, 3 H), 1·51 (m, ^{3}J = 7·3 Hz, 2 H), 1·85 (m, ^{3}J = 7·3 Hz, 2 H), 4·08 (t, ^{3}J = 6·7 Hz, 2 H), 6·78 (d, ^{3}J = 8·7 Hz, 2 H), 7·00 (m, 4 H), 8·18 (d, ^{3}J = 8·0 Hz, 2 H)	$C_{18}H_{17}NO_4$ (311·34)	69·4 (69·5)	5·5 (5·5)	4·5 (4·3)	75	84 (from hexane)
5 c	3·84(s, 3 H), 8·40–6·92 (m, 8 H)	$C_{15}H_{11}NO_4$ (269·26)	66·9 (66·7)	4·1 (4·0)	5·2 (5·1)	97	93 (from toluene)

IR all compounds –C≡N 2282–2232 cm^{-1}, –C=O 1746–1736 cm^{-1} (ester).

Table 2. Yields, analytical data, and spectroscopic properties of mesogenic isocyanates.

Compound	^{1}H NMR ($CDCl_3$) δ/ppm	Molecular formula (M_w)	Elemental analysis/per cent calculated (found)			T_m/°C	Yield/per cent
			C	H	N		
3 i	1·00 (t, 3 H), 1·50–4·00 (m, 6 H), 6·80–8·30 (m, 8 H)	$C_{18}H_{17}NO_4$ (311·34)	69·4 (69·6)	5·5 (5·3)	4·5 (4·5)	78	62
4 i	1·00 (t, 3 H), 1·50–4·05 (m, 6 H), 6·15–8·20 (m, 8 H)	$C_{18}H_{17}NO_4$ (311·34)	69·4 (69·3)	5·5 (5·7)	4·5 (4·7)	75	77
5 i	3·90 (s, 3 H), 6·90–8·35 (m, 8 H)	$C_{15}H_{11}NO_4$ (269·26)	66·9 (66·9)	4·1 (4·1)	5·2 (5·3)	97	50

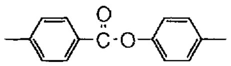
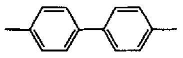
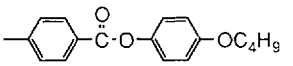
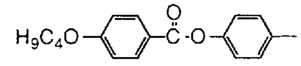
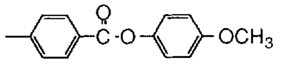
IR all compounds –N=C=O 2265–2275 cm^{-1}, –C=O 1746–1736 cm^{-1} (ester).

crystalline phase than the isomeric cyanate group. Thus all the isocyanates have an enantiotropic nematic mesophase, with the exception of **4 i** which has a monotropic nematic phase with a clearing point 8°C below the melting point. The phases were assigned on the basis of their typical textures and additionally confirmed by the enthalpies of isotropization, which are well in the range of nematic compounds [13]. The cyanate group, instead, has little tendency to stabilize a mesophase. No textures could be observed for either of the dicyanates and no phase transition apart from recrystallization was found from the DSC traces, which are shown for the two biphenyl based compounds **2 c** and **2 i** in figure 1.

Therefore, an attempt was made to determine the virtual clearing transitions of both dicyanates (**1 c** and **2 c**) from mixtures with the nematogen 1,4-bis(4-methoxybenzoyloxy) chlorobenzene. Due to recrystallization of the dicyanates, clearing points could be measured only from mixtures containing approximately 50 per cent of the dicyanates (see figure 2). Although there is a significant error margin due to the large range of the extrapolation, the virtual clearing points are quite reliable, because the clearing points of the mixtures lie almost perfectly on straight line extrapolations.

The two liquid crystalline di-isocyanates (**1 i** and **2 i**) have melting points in the range of 120°C and exhibit enantiotropic nematic mesophases with clearing points points of 148 and 137°C, respectively, while the melting

Table 3. Thermal transitions, enthalpies and phase behaviour of mesogenic cyanates and isostructural isocyanates.

	Cyanate (–O–C≡N)						Isocyanate (–N=C=O)			
Compound	T_m/ °C	$T_{N\text{-}I}$/ °C	ΔH_m/ kJ mol^{-1}	$\Delta H_{N\text{-}I}$/ kJ mol^{-1}	Mesogenic core	Compound	T_m/ °C	$T_{N\text{-}I}$/ °C	ΔH_m/ kJ mol^{-1}	$\Delta H_{N\text{-}I}$/ kJ mol^{-1}
1c	139	virtual (80)	32·8	—		**1i**	118	148	34·2	0·52
2c	138	virtual (54)	31·4	—		**2i**	107	131	28·1	0·52
3c	72	(58)	25·3	—		**3i**	78	102	32·1	0·52
4c	75	(48)	35·5	—		**4i**	97	(89)	34·7	0·55
5c	97	—	22·1	—		**5i**	90	96	22·9	0·13

Parentheses denote a monotropic transition.

points of the isostructural cyanates are roughly 20°C higher and the (virtual) clearing transitions almost 80°C lower. A similar tendency was found for the mono-isocyanates and the isostructural cyanates. Clearing points around 90°C, which were close to the melting points, were found for the isocyanates (**3i** and **4i**), while monotropic nematic mesophases with clearing temperatures around 50°C were observed for the butoxy substituted cyanates (**3c** and **4c**). The 4-methoxyphenyl 4-(iso)cyanatobenzoates (**5i** and **5c**) show once more the different mesogenic power of the isomeric OCN groups very dramatically. Again, the isocyanate has an enantiotropic mesophase, while no liquid crystalline properties could be observed for the corresponding cyanate.

The 'direction' of the ester group in the mesogens also has a remarkable influence on the thermal transitions. If the OCN moiety is attached to the benzoic acid part of the mesogen, the melting point is lower and the clearing transition is higher than in those cases where it is in the phenolic part of the mesogen. In the former case, the OCN is in conjugation with an electron withdrawing substituent (phenoxycarbonyl), while in the isomeric compounds the OCN is in conjugation with a more electron releasing substituent (benzoyloxy).

The different mesogenic powers of the isomeric OCN terminal groups and the influence of the direction of the ester group on the isotropization temperature can be explained in terms of geometrical and polar effects. The bond angle between the cyanate group and the aromatic carbon is 109° at the oxygen, which has sp^3 hybridization. It can be increased to 120° for sp^2 hybridization, for

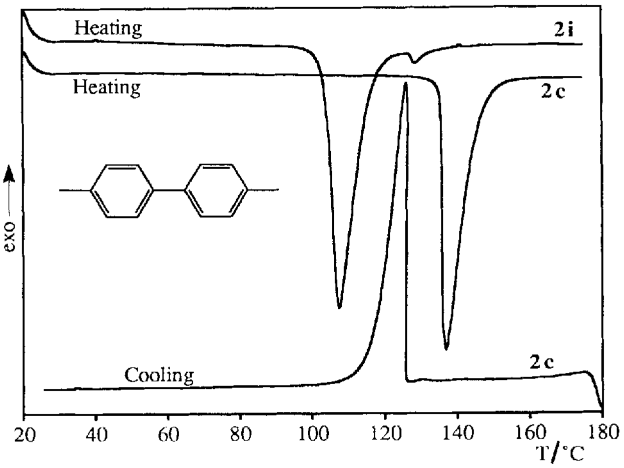


Figure 1. DSC traces of 4,4′-di-isocyanatobiphenyl (**2i**) (heating) and of the isomeric 4,4′-dicyanatobiphenyl (**2c**) (heating and cooling).

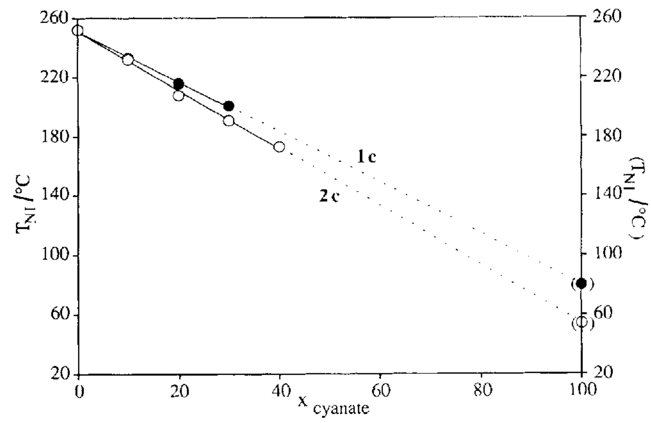


Figure 2. Virtual clearing points of dicyanates **1c** and **2c** by extrapolation of clearing points from mixtures with 1,4-bis(4-methoxybenzoyloxy)chlorobenzene.

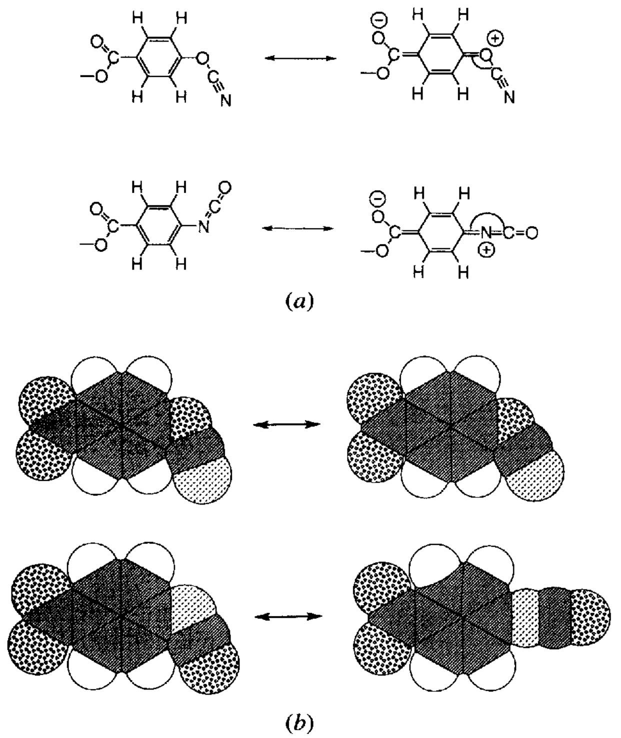


Figure 3. (*a*) Increase in bond angle and change in hybridization by the introduction of an electron accepting substituent in the *para*-position. (*b*) Space filling models of **1 c**-upper (sp^2 hybridization of the cyanate oxygen) and **1 i**-lower (sp hybridization of the isocyanate nitrogen).

example, with strong electron withdrawing substituents in the *p*-position. The equivalent atom in the isocyanate is the nitrogen which already has sp^2 hybridization corresponding to a bond angle of 120°. An electron accepting substituent in the *p*-position will change the hybridization towards sp and increase the bond angle towards 180° as demonstrated in figure 3 (*a*). An ester oxygen in the *p*-position is an electron releasing substituent rather than electron withdrawing, and hence the expected bond angles are close to those with the higher hybridization (the structures on the left in figure 3).

Space filling models of the structures from figure 3 (*a*) are shown in figure 3 (*b*). Molecular models demonstrate that there is no increase in the diameter of the rotational cylinder (5·55 Å). Its length, however, is affected particularly in the case of the isocyanate terminal group (16·97 Å for the diisocyanate **1 i** with sp hybridization of the nitrogen and 14·94 Å for the dicyanate **1 c** with sp^2 hybridization of the oxygen). The resulting aspect ratios are 3·1 and 2·7 respectively.

A similar effect results from the partial dipole moments of the mesogens. As can be seen from figure 3 (*a*), a cyanate or an isocyanate group in conjugation with the phenoxycarbonyl moiety causes a partial dipole moment.

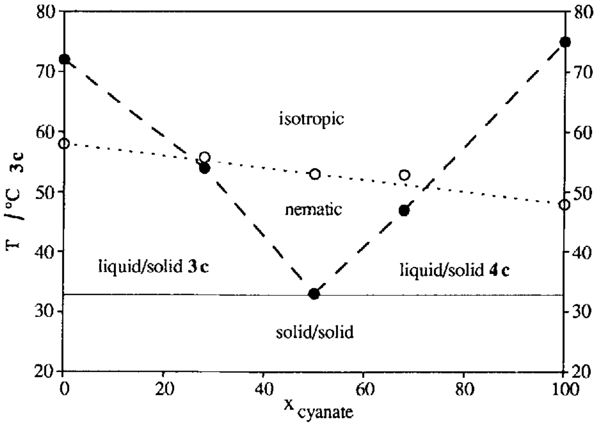


Figure 4. Binary phase diagram of the two isomeric cyanates **3 c** and **4 c**.

The same groups in conjugation with the benzoyloxy moiety—both have a − I and a + M electronic effect—results in an almost zero overall dipole moment. To what extent either of these effects is responsible cannot be answered at present. Geometric reasons seem to be predominant, since phenylcyanate has a dipole moment of 3·93 Debye [14] whereas 2·29 Debye has been found for phenylisocyanate [15]. A final proof may be obtained from X-ray analysis.

Another surprising effect of the ester group and its direction is demonstrated in figure 4, which shows a binary phase diagram of the two isomeric cyanates **3 c** and **4 c**. Again the isotropization temperatures are a linear function of composition, while a strong depression of the melting points is observed. The eutectic is found for the 1 : 1 mixture with a melting temperature of 33°C, which is almost 40°C below those of the pure compounds. Such behaviour can be favourable for the synthesis of liquid crystal thermosets, since it offers the possibility of curing at rather low temperatures in the liquid crystalline phase, without the problem of crystallization of monomers.

3. Conclusions

From a comparative investigation of the mesogenic power of the cyanate and the isocyanate terminal group, it has been shown that rigid linear three atom terminal groups can give liquid crystals with a broad range of mesophase stability, if they have a heterocumulene structure. The single bond/triple bond combination is not favourable although the dipole moment is higher in this case. Electron withdrawing substituents in conjugation with either of the isomeric (iso)cyanate groups lower the melting point and increase the clearing transition. Finally, the isocyanate terminal group is far more capable of stabilizing a mesophase than the cyanate moiety. In a forthcoming paper we will report on the effect of the two isomeric *s*-triazine rings formed by the cyclotrimerization reaction of the two OCN groups.

4. Experimental

4.1. *Materials*

Hydroquinone, 4-methoxyphenol, and 4-butoxyphenol were purchased from Janssen, 4-Butoxybenzoyl chloride, cyanogen bromide, and ethyl chloroformate were purchased from Aldrich. 4-Hydroxybenzoic acid and 4,4′-dihydroxybiphenyl were a gift from Bayer AG, Leverkusen. Pyridine was distilled from potassium hydroxide, dimethylformamide (DMF) from phosphorus(V) oxide and collected over 4 Å molecular sieves. Thionyl chloride was distilled prior to use. Flash chromatography was performed on Merck silica gel 60/40–63.

4.2. *Methods of characterization*

Infrared spectra were recorded on a Bruker IFS48 FT-IR for films between NaCl plates. Solid samples were either dissolved in an appropriate solvent or prepared as nujol mulls. NMR spectra were obtained using a Bruker AC-200, deuteriochloroform as solvent and TMS as internal standard. Thermal transitions were investigated with a Nikon Optiphot 2 polarizing microscope equipped with a Mettler FP 82 hot stage and FP 80 processing unit. Transition enthalpies and temperatures were recorded with a Mettler DSC/30 TC 11 system (heating rate $20\,\mathrm{K\,min^{-1}}$).

Elemental analyses were made by Bayer, Leverkusen or Mikroanalytisches Labor Beller, Göttingen.

4-Ethoxycarbonyloxybenzoic acid, 4-ethoxycarbonyloxybenzoyl chloride, 4-methoxyphenyl 4-ethoxycarbonyloxybenzoate, and 4-methoxyphenyl 4-hydroxybenzoate were synthesized according to literature methods [12].

4.3. *Synthesis of 4-butoxyphenyl 4-ethoxycarbonyloxybenzoate*

To a solution of 6·88 g (30·1 mmol) of 4-ethoxycarbonyloxybenzoyl chloride in 50 ml of dry pyridine a solution of 5·00 g (30·1 mmol) of 4-butoxyphenol in 30 ml of anhydrous pyridine was added dropwise at room temperature during 1 h. After the addition, the reaction mixture was poured into 100 ml of diluted hydrochloric acid. The precipitate was filtered off, dried in *in vacuo*, and recrystallized from 50 ml of ethanol to give a yield of 60 per cent.

Elemental analysis. Found (calculated for $C_{20}H_{22}O_6$): C 67·10 (67·03), H 6·10 (6·19) per cent. IR, ν cm^{-1}, NaCl: 1756 (carbonyloxy), 1730 (ester). ^{1}H NMR, δ ppm, 0·98 (t, 3 H), 1·41 (t, 3 H), 1·50 (m, 2 H), 1·78 (m, 2 H), 3·96 (t, 2 H), 4·28 (q, 2 H), 8·28–6·85 (AA′ XX′, 8 H).

4.4. *Synthesis of 4-butoxyphenyl 4-hydroxybenzoate*

6·30 g (17·6 mmol) of 4-butoxyphenyl 4-ethoxycarbonyloxybenzoate was stirred at room temperature for 20 h in a solution of 20 ml of pyridine, 40 ml of acetone, 20 ml of water, and 2·6 ml of 25 per cent aqueous ammonia. The solution was acidified with hydrochloric acid, and the white precipitate was filtered off, washed twice with water, and recrystallized from a mixture of water/acetone (8/1). 4-Butoxyphenyl 4-hydroxybenzoate was obtained in a yield of 83 per cent.

Elemental analysis. Found (calculated for $C_{17}H_{18}O_4$): C 71·10 (71·31), H 6·30 (6·34) per cent. IR, ν cm^{-1}, NaCl: 3336 (hydroxyl), 1730 (ester). ^{1}H NMR, δ ppm, 0·96 (t, 3 H), 1·50 (m, 2 H), 1·78 (m, 2 H), 3·94 (t, 2 H), 6·05 (s, 1 H), 6·95–8·10 (AA′ XX′, 8 H).

4.5. *Synthesis of 4-butoxy 4-hydroxyphenylbenzoate*

To a solution of 137·5 g (1·25 mol) of hydroquinone in 250 ml of dry pyridine, 53·2 g (0·25 mol) of 4-butoxybenzoyl chloride were added in five portions. The mixture was stirred for 24 h at room temperature. After pouring the mixture into 1·1 l of 2 M hydrochloric acid, the precipitate was filtered off, washed with water, and stirred for 1 h with aqueous sodium hydrogen carbonate. After filtration and drying, the product was recrystallized from a mixture of water/ethanol (1/1). The yield was 87 per cent.

Elemental analysis. Found (calculated for $C_{17}H_{18}O_4$): C 71·40 (71·31), H 6·40 (6·34) per cent. IR, ν cm^{-1}, NaCl: 3233 (hydroxyl), 1734 (ester). ^{1}H NMR, δ ppm, 1·00 (t, 3 H), 1·51 (m, 2 H), 1·85 (m, 2 H), 4·08 (t, 2 H), 4·80 (s, 1 H), 6·78–8·18 (AA′ XX′, 8 H).

4.6. *Cyanate esters (**1c–5c**) general procedure*

To a stirred solution of a (bis)phenol containing 0·10 equivalent of phenolic groups and 0·105 mol of cyanogen bromide in anhydrous DMF or acetone, 0·10 mol of triethylamine was added dropwise, keeping the temperature at 0–5°C. After the addition was complete, the reaction mixture was stirred for a further 10 min at 0–5°C, poured on to ice/water and the resultant precipate filtered off, washed with water, and dried *in vacuo*. The crude product was stirred with ethanol or isopropanol and purified as mentioned in table 1. For yields, analytical results and physical properties see table 1.

4.7. *Synthesis of isocyanatophenyl benzoates (**1 i, 3 i–5 i**) general procedure*

25 mmol of a 4-substituted benzoyl chloride and 25 mmol of a 4-substituted trimethylsiloxybenzene, together with 20 mg of catalyst (sulphuric acid, DMAP) were dissolved in 6 ml of 1,2-dichlorobenzene, and heated to 165°C while trimethylchlorosilane was removed at 500 mbar. The reactions were monitored by IR spectroscopy and stopped when the absorption of chloroformyl

group had disappeared (6–9 h). The resulting (di)isocyanatophenyl benzoates were purified by short-path distillation in a Büchi glass tube oven. Yields, analytical data, and spectroscopic data are given in table 2.

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