

Polymers from multifunctional isocyanates: 7. Synthesis and phase behaviour of liquid-crystalline triad ester-group-containing diisocyanates

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A number of novel triaromatic diisocyanates based on *para*-linked ester mesogens (1,4-phenylene dibenzoate, diphenyl terephthalate, diphenyl *trans*-1,4-cyclohexanedicarboxylate and *trans*-dicyclohexyl *trans*-1,4-cyclohexanedicarboxylate) are described. One series was synthesized by reaction of 4-trimethylsilyloxyphenyl or cyclohexyl isocyanate with terephthaloyl chloride or *trans*-1,4-cyclohexanedicarbonyl chloride, and the other from a 4-isocyanatobenzoyl chloride with a 1,4-bis(trimethylsilyloxy)benzene (trimethylsilyl-protected hydroquinone). Acidic and basic catalysts were used in this reaction. The influence of substituents in various positions of the mesogenic cores on the phase transitions was also investigated. All liquid-crystalline diisocyanates have a nematic mesophase.

(Keywords: diisocyanates; liquid crystals; synthesis; phase behaviour)

INTRODUCTION

Our studies of the manufacture and properties of thermotropic polyurethanes were initially based on those made from diaromatic mesogenic diisocyanates¹. The main emphasis in the field of diisocyanates was on those having ester linking groups², since semirigid polyesters are one of the best-investigated classes of liquid-crystalline main-chain polymers³. A general synthesis of ester-group-containing isocyanates starting from mono-isocyanate precursors enables us to design isocyanates within this framework, to introduce substituents in various positions of the mesogens, and to study their influence on the mesomorphic properties^{2,4}. Diad *para*-linked aromatic diisocyanato esters and polyurethanes made therefrom have been described in previous papers of this series. The isocyanates showed liquid-crystalline properties⁵; the polyurethanes, however, had at maximum a monotropic nematic mesophase, indicating that the aspect ratio of the mesogen was too low⁶.

Hence we were unable to reach our final goal: the synthesis and investigation of segmented thermoplastic polyurethane elastomers with a nematic hard-segment phase. These are expected to have an improved rate and a higher degree of phase separation after processing by injection moulding, thus giving better mechanical properties. Finally these materials could be the basis of melt-spun polyurethane fibres.

Enlargement of the aspect ratio can be achieved by going from diaromatic 'diad' mesogens to triaromatic 'triad' mesogenic diisocyanates, which are also accessible from monoisocyanate precursors and allow a systematic variation of composition and substitution pattern. The unsubstituted parent compounds have melting points of approximately 180°C and clearing transitions around 300°C accompanied by decomposition². Polyurethanes from these isocyanates melted too high for any structural investigation and identification of possible mesophases. Substituents will therefore be necessary to depress the melting transitions below the decomposition temperature.

An in-depth investigation of mesogenic diisocyanates will be useful for the study of liquid-crystalline polyurethanes. Apart from making polyurethanes, isocyanates can be used for the synthesis of a number of other polymers by step polyaddition and polycondensation reactions:

(i) The reaction with amines to give poly(urea)s is the basis of the fast cure in the reaction injection moulding (r.i.m.) process⁷.

(ii) Cyclotrimerization results in networks through the formation of triazinetriones (isocyanurates) – another important reaction⁸.

(iii) The cycloaddition reaction of isocyanates with oxiranes, a linear step addition reaction, yields thermostable oxazolidones⁹. In combination with cyclotrimerization, less tightly crosslinked polymers can be obtained.

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(iv) Poly(amide)s, poly(imide)s and poly(amide-imide)s are also made from isocyanates by reaction with dicarboxylic acids or dianhydrides¹⁰.

Apart from our work, diurethanes from mesogenic diisocyanates with different cores have been described by Kosfeld and coworkers¹¹.

In this paper we report on the synthesis and properties of a series of triaromatic diisocyanato esters, in which the structure and the substitution pattern have been varied in a systematic manner in order to study the dependence of the thermal transitions on the structure of the mesogens. The efficiency of different types of catalysts has also been studied.

RESULTS AND DISCUSSION

Synthesis of mesogenic diisocyanato esters

Two series of triad diisocyanato esters were synthesized, one by reaction of appropriate 4-isocyanatobenzoyl chlorides with 1,4-bis(trimethylsiloxy)benzenes (1-7) and the other (8-10) by reaction of 4-trimethylsiloxyphenyl isocyanates with terephthaloyl chlorides as outlined in *Scheme 1*. The two aromatic series differ only in the direction (inversion) of the ester group. Partly or fully cycloaliphatic diisocyanates (11-13) were made with *trans*-4-trimethylsilyloxycyclohexyl isocyanate or *trans*-1,4-cyclohexanedioic acid chloride.

The following structural changes and their influence on properties should be studied:

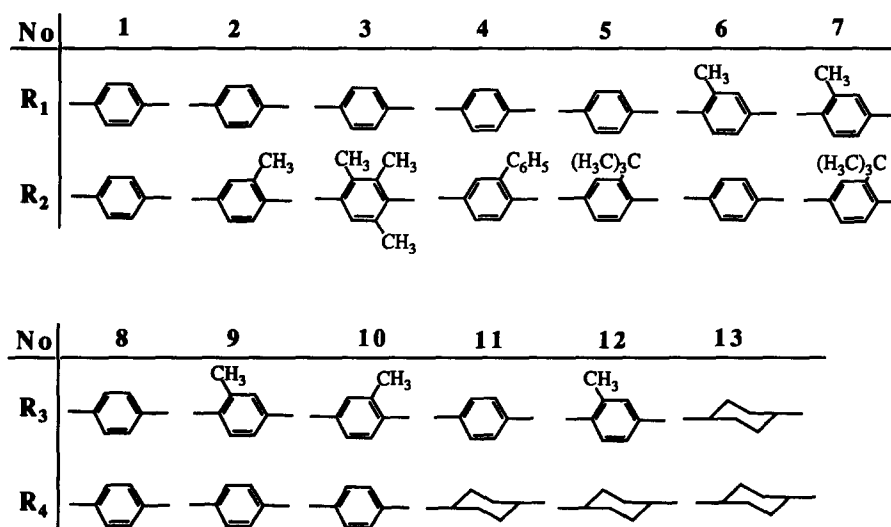
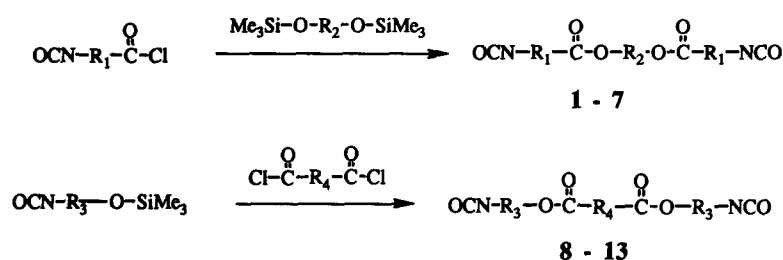
(i) Inversion of the ester group, which influences the dipole moment of the molecule and the reactivity of the isocyanate groups.

(ii) Exchange of the planar rigid phenyl rings by cyclohexyl rings, which renders the mesogenic core more flexible and in addition lowers the reactivity of the isocyanates attached to it.

(iii) Introduction of substituents in the mesogen and variation of the substitution pattern to study their influence on the phase behaviour.

The influence of the substitution pattern was studied with the methyl group since it is not too bulky and non-reactive. From *Scheme 1* it follows that substituents can be introduced simultaneously in both of the outer rings, in the middle ring only, or in all three rings. In addition to the substitution pattern, we were interested in the influence of substituents of varying bulkiness in the central aromatic ring. In this series we chose methyl, phenyl and *t*-butyl groups and in addition a trimethyl-substituted hydroquinone.

The trimethylsiloxy-group-containing isocyanates used in this study were synthesized from suitable aminohydroxy compounds (aminophenols, aminocyclohexanol, aminobenzoic acids), which were converted into the trimethylsiloxyamines by reaction with hexamethyldisilazane¹². The aminotrimethylsiloxy compounds were reacted with excess high-boiling isocyanate (4,4'-diisocyanatodiphenylmethane, MDI) to give the desired trimethylsiloxy isocyanates¹³. This synthesis involves formation and cleavage of ureas and the equilibrium is shifted towards the desired products by continuous distillation. The trimethylsiloxy isocyanates are identical to those used in the synthesis of diad diisocyanato esters⁶. Details of the synthesis and analytical properties of both trimethylsiloxy-group-containing amines and isocyanates have been reported in previous papers^{2,6,13}.



Scheme 1

Isocyanatobenzoyl chlorides were obtained from the corresponding amino acids either by phosgenation¹⁴ or by reaction of the isocyanatosilyl ester with thionyl chloride. Again the preparation and analytical properties have been reported elsewhere⁶.

Substituted hydroquinones were silylated with 20% excess of hexamethyldisilazane and isolated by distillation under reduced pressure. *trans*-1,4-Cyclohexanedicarbonyl chloride was obtained as described by Kricheldorf from the acid having 90% *trans* content by conversion into the trimethylsilyl ester, which was purified by fractional crystallization and subsequently reacted with thionyl chloride to give the pure dicarbonyl chloride¹⁵.

The diisocyanato esters 1–13 were made according to Scheme 1 in 1,2-dichlorobenzene to ensure a homogeneous mixture throughout the course of the reaction in the presence of a suitable catalyst. This was sulphuric acid in the case of aromatic compounds and 4-dimethylaminopyridine (DMAP) for cycloaliphatic compounds

in order to avoid elimination of a silanol and isomerization of the cyclohexane moiety (Table 1). A 10% excess of the monoisocyanates was used to ensure complete formation of the triad compounds since the former did not separate from the reaction mixture, thus causing no trouble in the work-up procedure. The reaction temperatures were 165 and 110°C with cycloaliphatic diisocyanato esters (11–13), again in order to avoid *cis*–*trans* isomerization. The reactions were controlled by infra-red spectroscopy and the amount of trimethylchlorosilane formed. The crude diisocyanates separated from the mixture upon cooling, and were purified by repeated recrystallization and extraction with a non-polar solvent. The yields varied from 45 and 85%. Losses were due to purification.

The diisocyanato esters are colourless crystalline materials at room temperature. They were characterized by i.r. and n.m.r. spectroscopy and elemental analyses. The i.r. spectra show the characteristic absorptions of

Table 1 Analytical properties of diisocyanato diesters

No.	Yield (%)	Purification ^a	¹ H n.m.r. (ppm)	Molecular formula (mol. mass)	El. anal. (%)		
					C calc. found	H calc. found	N calc. found
2	85	R: ODCB ^b E: Benzene	2.25 (s, 3H); 7.0–7.3 (m, 3H); 7.1–8.3 (AA'XX', 8H)	C ₂₃ H ₁₄ N ₂ O ₆ (414.4)	66.67 66.4	3.41 3.29	6.76 6.80
3	50	R: ODCB	2.1 (s, 6H); 2.2 (s, 3H); 6.9 (s, 1H); 7.1–8.3 (AA'XX', 8H)	C ₂₅ H ₁₈ N ₂ O ₆ (442.42)	67.8 67.4	4.1 4.3	6.33 6.4
4	81	R: ODCB E: Benzene/ cyclohexane	7.0–8.3 (2 AA'XX', 8H); 7.2–7.6 (m, 5H)	C ₂₈ H ₁₆ N ₂ O ₆ (476.44)	70.59 70.44	3.39 3.42	5.88 5.86
5	54	R: Toluene E: Cyclohexane	1.37 (s, 9H); 7.1–8.3 (AA'XX', 8H and m, 3H)	C ₂₆ H ₂₀ N ₂ O ₆ (456.45)	68.42 68.6	4.42 4.45	6.13 6.05
6	74	E: ODCB	2.4 (s, 6H); 7.1–8.1 (m, 6H and s, 4H)	C ₂₄ H ₁₆ N ₂ O ₆ (428.4)	67.29 67.06	3.76 3.8	6.54 6.45
7	82	R: Toluene/ cyclohexane	1.38 (s, 9H); 2.43 (s, 6H); 7.0–8.1 (m, 9H)	C ₂₈ H ₂₄ N ₂ O ₆ (484.5)	69.41 69.7	5.0 5.15	5.78 5.7
9	55	R: Toluene	2.42 (s, 6H); 6.9–7.3 (m, 6H); 8.3 (s, 4H)	C ₂₄ H ₁₆ N ₂ O ₆ (428.4)	67.29 67.6	3.76 3.75	6.54 6.65
10	54	R: ODCB	2.23 (s, 6H); 6.9–7.2 (m, 6H); 8.35 (s, 4H)	C ₂₄ H ₁₆ N ₂ O ₆ (428.4)	67.29 67.2	3.76 4.0	6.54 6.65
11	48	R: Toluene	1.4–2.8 (m, 10H); 6.9–7.3 (m, 8H)	C ₂₂ H ₁₈ N ₂ O ₆ (406.39)	65.02 65.05	4.46 4.55	6.89 7.0
12	52	R: Toluene	1.4–2.8 (m, 10H); 2.35 (s, 6H); 6.8–7.7 (m, 6H)	C ₂₄ H ₂₂ N ₂ O ₆ (434.44)	66.35 66.42	5.10 5.25	6.46 6.4
13	75	R: ODCB	1.2–2.4 (m, 26H); 3.55 (m, 2H); 4.8 (m, 2H)	C ₂₂ H ₃₀ N ₂ O ₆ (418.48)	63.14 63.19	7.23 7.25	6.69 6.77

11 ¹³C: 27.8, 42.35, 122.6, 124.7, 125.5, 128.14, 130.87, 148.1, 173.48 ppm

12 ¹³C: 18.3, 27.8, 42.3, 119.9, 123.46, 124.5, 125.6, 129.8, 134.1, 148.0, 173.57 ppm

13 ¹³C: 28.05, 28.10, 31.09, 42.72, 52.03, 70.20, 122.63, 174.59 ppm

I.r. absorptions (all isocyanates): 2320–2270 cm⁻¹ (NCO), 1750–1725 cm⁻¹ (COO)

^aR = Recrystallization

E = Extraction

^b*o*-Dichlorobenzene

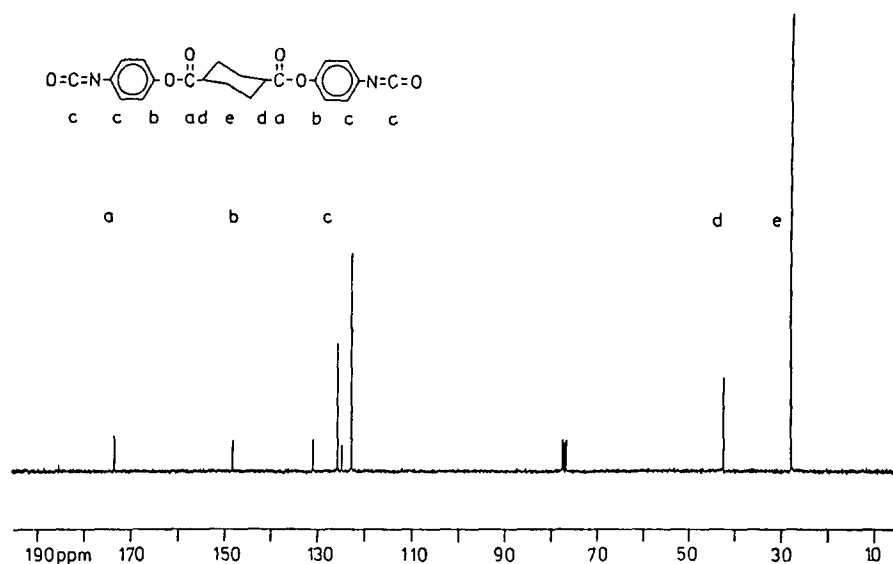


Figure 1 ^{13}C n.m.r. spectrum of bis(4-isocyanatophenyl)-*trans*-1,4-cyclohexanedicarboxylate (11)

the isocyanate group (from 2320 to 2270 cm^{-1}), the ester carbonyl group (1745 to 1725 cm^{-1}) and aromatic double bonds. The properties of the diisocyanato esters are given in Table 1. The unsubstituted 1,4-phenylenebis-(4-isocyanatobenzoate) **1** and bis(4-isocyanatophenyl) terephthalate **8** have been described previously².

^{13}C n.m.r. spectra of the cycloaliphatic compounds were recorded in order to ensure that no isomerization of the desired *trans* isomers occurred during the reactions. Figure 1 shows the ^{13}C n.m.r. spectrum of **11**. The purity was estimated from the chemical shifts of the carbon atoms in the cyclohexyl ring as reported by Kricheldorf¹⁵. The presence of the *cis* isomer would be indicated by additional signals about 1–2 ppm downfield from the absorptions of the corresponding carbon atoms in the *trans* configuration.

Catalysis of the esterification reaction

The esterification of benzoyl chlorides with trimethylsiloxyarenes does not proceed in the absence of catalysts if very pure starting materials are used. Kricheldorf found that up to 300°C no reaction took place¹⁶. There are, however, several ways to catalyse this reaction:

(1) Increase of the electrophilicity of the carbonyl carbon with electrophilic agents like proton or Lewis acids.

(2) Increase of the nucleophilicity of the trimethylsiloxy group by conversion into the phenoxy group.

According to Kricheldorf, chloride ions present as impurities or added deliberately form chlorotrimethylsilane and the phenolate ion, which adds to the acid chloride and regenerates the chloride ion. A particularly high catalytic effect is observed with soluble naked chloride as in potassium chloride–crown ether complexes or tetraalkylammonium chlorides¹⁶.

(3) Acylation catalysts like DMAP. These react with e.g. benzoyl chloride in an equilibrium to give *N*-benzoyl-4-(dimethylamino)pyridinium chloride, which acts as acylating agent¹⁷. The chloride ion, in addition, may activate the trimethylsiloxy compound as described above.

Catalysts of the three types mentioned were investigated with benzoyl chloride (anisoyl chloride) and trimethyl-

siloxylbenzene to find optimum conditions. These were sulphuric acid, benzyltriethylammonium chloride, KCl–crown ether complex and DMAP. Special care was taken in these experiments to exclude impurities and humidity, which would result in acidic impurities and chloride ions. The reactions were monitored by n.m.r. spectroscopy, since the protons of the trimethylsiloxy group had chemical shifts sufficiently different from those of chlorotrimethylsilane to allow separate peak integration. The amounts of unreacted trimethylsiloxybenzene plotted against the reaction time gives an impression of the catalytic activity of the different compounds. It is shown in Figure 2.

In the mixture without added catalyst, no reaction occurred within 24 h. Potassium chloride–crown ether complex had little catalytic activity. This may be due to the *in situ* preparation of the complex in order to avoid humidity and active hydrogen-containing compounds, which can hardly be excluded when the complex is made in methanol and isolated by evaporation of the solvent. *N*-Benzyl-*N,N,N*-triethylammonium chloride shows higher activity, probably as a result of its better

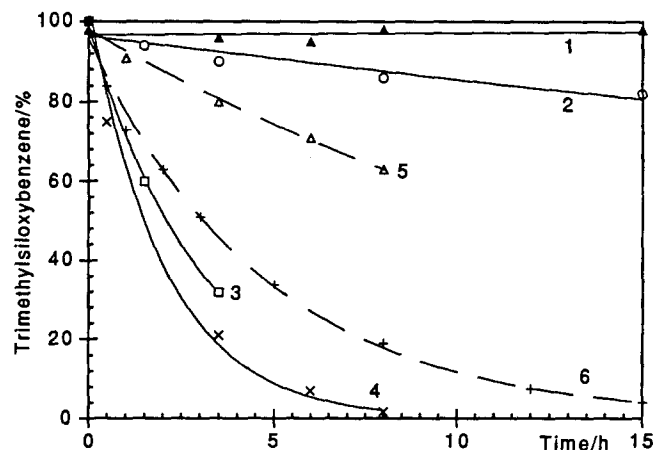


Figure 2 Activity of different catalysts in the reaction of trimethylsiloxybenzene with benzoyl chloride: (1) no catalyst, (2) KCl–dibenzo-18-crown-6, (3) sulphuric acid, (4) DMAP; and with 4-methoxybenzoyl chloride: (5) benzyltriethylammonium chloride, (6) DMAP

solubility. In this case, however, 4-methoxybenzoyl chloride was used, so that for benzoyl chloride a higher rate close to that of sulphuric acid could be expected. The highest catalytic activity was for DMAP. After 3.5 h, 75% and after 6 h, 93% conversion is observed.

Comparison of DMAP and *N*-benzyl-*N,N,N*-triethylammonium chloride in the system 4-methoxybenzoyl chloride/trimethylsilyloxybenzene (curves 5 and 6 in Figure 2) shows that DMAP has four times the efficiency of the latter. The half-lives are 3.2 h and 12.7 h respectively.

The electronic effect of substituents in the acid chloride on the rate of the esterification reaction can be estimated by comparing benzoyl chloride and 4-methoxybenzoyl chloride. It will be reported together with that of the phenol part in a separate paper.

Mesomorphic properties of triad diisocyanato esters

Thermal and phase behaviour of the novel diisocyanates was studied by thermal analysis and microscopy under polarized light. If samples were heated slowly from room temperature to the melting temperature, no clear melt was obtained, which could arise either from reaction of the highly reactive isocyanate groups with traces of humidity or because of [2 + 2] cycloaddition reaction of the isocyanates to give oligomers containing the 1,3-diazetidinedione ring, which has been observed in the diad series. Above 250°C gas bubbles were observed under the microscope, probably due to the formation of carbodiimides, which is known to proceed under these conditions. In order to reduce these side-reactions, d.s.c. investigation was performed with heating rates of 20 K min⁻¹ and microscopic investigation under polarized light was made with a preheated hot stage. Reproducible data of the thermal transitions could thus be obtained. The melting and clearing transitions of the diisocyanato esters are given in Table 2. It is worth mentioning that, unlike 4,4'-diisocyanatodiphenylmethane (MDI), none of the diad nor triad diisocyanato esters have a tendency to form diazetidinediones by [2 + 2] cycloaddition in the solid phase at room temperature. This may be due to a somewhat different crystal structure and to the higher rigidity of the ester group as compared to the methylene group.

The unsubstituted diisocyanato esters **1** and **8** have melting points of 185°C, which is almost 70°C higher than that of the corresponding diad compound, and clearing points of 300°C – more than 150°C above that of 4,4'-diisocyanatophenylbenzoate. At these temperatures decomposition of **1** and **8** occurs and reproduction of the transitions by cooling and second heating is not possible. These data also demonstrate the beneficial effect of a longer mesogenic unit on the liquid-crystalline range.

Influence of substituents and substitution pattern

Introduction of substituents in the two outer rings of the diisocyanato diesters has little effect on the melting point, which can be attributed to the still symmetric shape of the mesogens (**6**, **9**). Moving the methyl groups further towards the centre of the molecules (**10**) (methyl substituents in the *ortho* position to the ester group) surprisingly results in an increase in melting temperature of almost 40°C, which is reproducible but cannot be explained at present. Substituents in the central ring should have a stronger influence on the melting transition

since they impart dissymmetry of the molecules. This is true for the methyl and phenyl substituents (**2** and **4**), where a depression of 30°C is observed. The trimethyl-substituted **3** melts at 175°C, almost 25°C higher than **2** and 10°C lower than **1**. This can be explained by the assumption that the molecules are arranged in an antiparallel fashion with the single methyl group of one molecule filling the gap of the other. Unexpected is the rather high melting point (189°C) of **6** with the bulky *t*-butyl substituent, which is slightly higher than that of the unsubstituted **1**.

The biggest effect in lowering the melting points of the triad diisocyanato esters is due to the exchange of a phenyl ring by the more flexible cyclohexane ring (**11–13**). The melting points are close to 140°C regardless of whether only the central (**11**) or all three rings (**13**) are cycloaliphatic. Additional methyl substituents in the 3'-positions of the outer rings (**12**) have no effect on the melting behaviour. Gain in entropy obviously contributes more to the decrease of melting points than packing effects.

With the exception of the highly substituted diisocyanate **7** and the only flexible cyclohexane rings containing **13**, all triad diisocyanates have a nematic mesophase. Figure 3 shows the d.s.c. traces of some representative diisocyanato esters while Figure 4 shows optical micrographs of **2**, **6** and **11** with the textures typical of nematic phases. The influence of substituents can be explained best by looking at the aspect ratio (length over diameter of a cylinder or ellipsoid formed by rotation of the mesogens around the long axis of the mesogens). Absolute numbers of the aspect ratio can be derived only from scattering experiments in the mesophase; however, it is possible to compare them in a qualitative manner.

The isotropization temperature of the unsubstituted diisocyanato esters **1** and **8** are above 300°C. Methyl groups in the *ortho* position to the isocyanates give clearing points 60–80°C lower (**6**, **9**). Moving the methyl

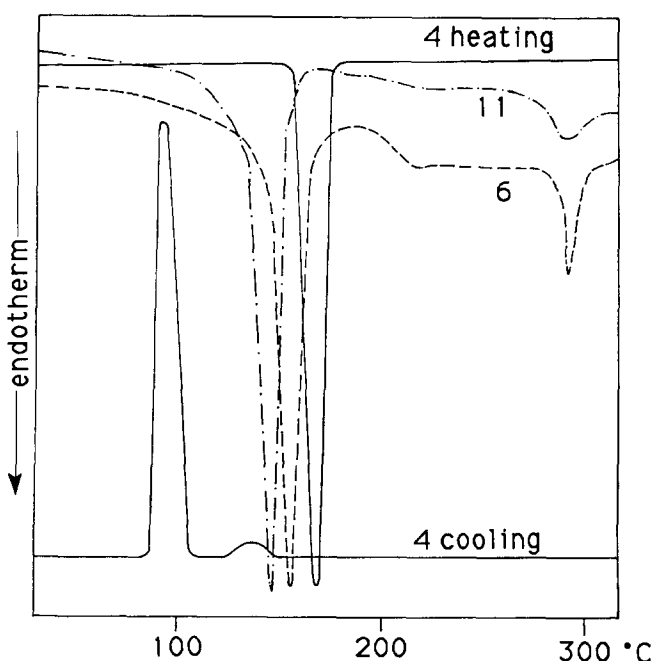


Figure 3 D.s.c. traces of diisocyanates **4**, **6** and **11** (heating rate 20 K min⁻¹)

Table 2 Thermal properties of diisocyanato esters

No.	Structure	Thermal properties (K)				
		T_m		T_i	Range	
1		k	185	n	300(d)	115
2		k	151	n	300(d) i	149
3		k	175	n	>300(d)	125
4		k	166	n	135 i	-
5		k	189	n	178 i	-
6		k	174	n	243 i	69
7		k	164		i	-
8		k	186	n	300(d) i	124
9		k	179	n	218(d) i	39
10		k	223	n	230 ^b i	7
11		k	144	n	291 i	147
12		k	144	n	139 ^a i	-
13		k	141		i	-

(d) Decomposition

^aFrom d.s.c. in cooling mode

^bObtained by microscopy

groups towards the centre (9 → 10) increases the clearing point by 10°C. The influence of substituents in the central ring is very useful for the liquid-crystalline range of the diisocyanato esters. Although they caused a big decrease of the melting point, the clearing transition is almost unaffected, thus giving a liquid-crystalline range of 150°C for 2. Bulkier substituents 4 and 5 lower the clearing points even below the melting points and monotropic mesophases result. Substituents in all three rings further decrease the isotropization temperature, and no mesophase can be observed.

The effect of a cyclohexane ring depends on the structure of the rest of the molecules. Changing the central benzene ring to cyclohexane (8 → 11) causes only a small decrease in isotropization temperature, and

together with the low melting point gives the second largest nematic range (145°C). The two adjacent benzene rings obviously stabilize the chair conformation. Methyl substituents (12) decrease this stabilization and lower the clearing point by 150°C, whereas a fully cycloaliphatic compound (13) is too flexible to show a mesophase.

Influence of inversion of ester groups

The direction of the ester group also has an influence on the thermal behaviour. 1,4-Phenylene dibenzoates (1, 6) have lower melting and higher clearing points than the inverse diphenyl terephthalates (8, 9). Similar behaviour has been observed with these mesogenic cores having different terminal groups. We think that the polarity of the phenylene dibenzoates is higher than that

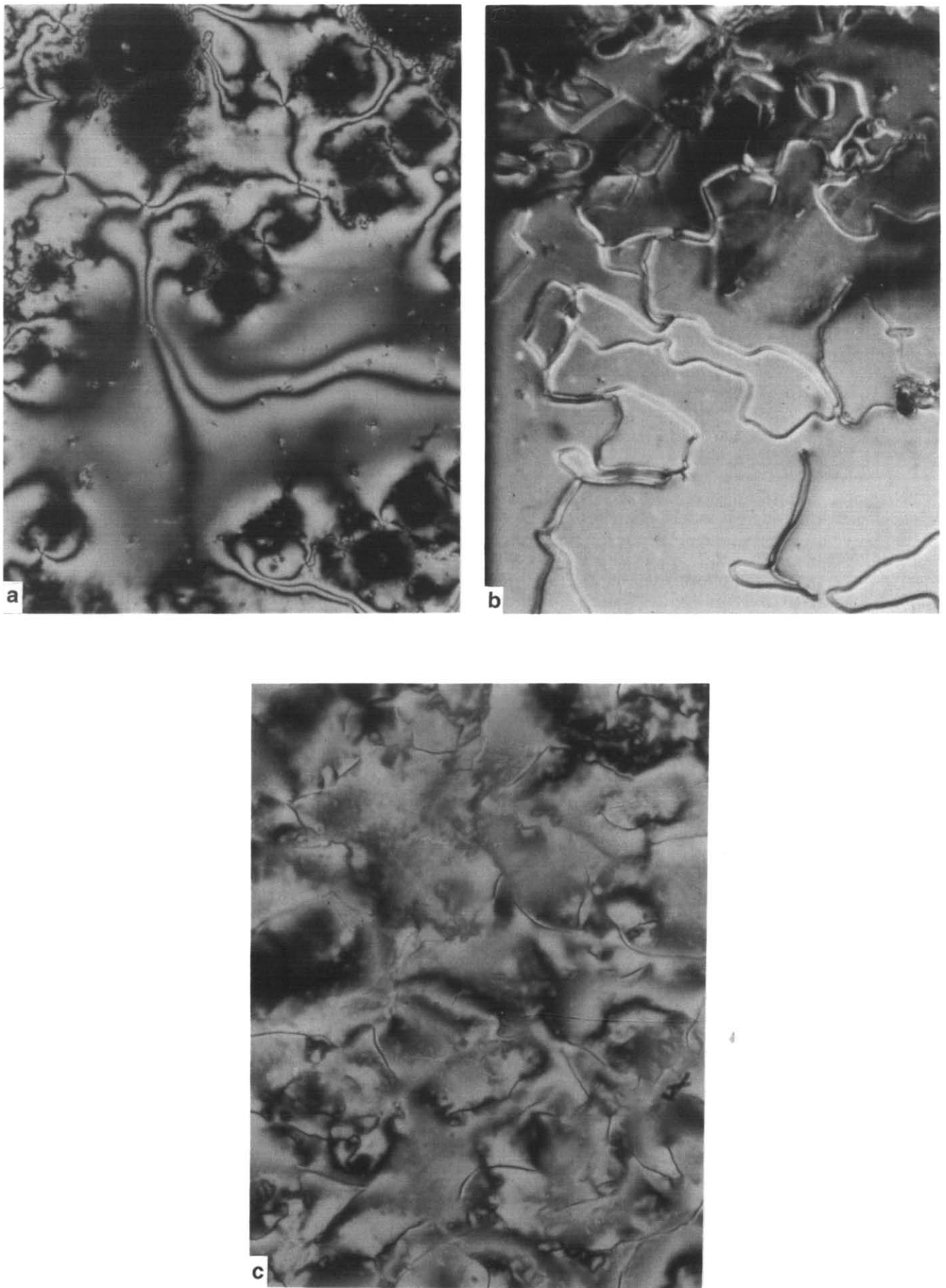


Figure 4 Optical micrographs of diisocyanates (a) **2** (200°C), (b) **6** (230°C) and (c) **11** (264°C); original magnification 200 \times , reduced to 98% in printing

of the terephthalates because the isocyanate group acts as electron donor to the electron-accepting ester carbonyl group and hence gives two dipoles with the positive end in the isocyanate groups. The isocyanate group is a weak inductive electron acceptor and a resonance donor, as is the phenol oxygen, which prevents the formation of a dipole in the terephthalate series (Scheme 1).

EXPERIMENTAL

Materials

4-Hydroxyaniline, 4-hydroxy-3-methylaniline, 4-hydroxy-2-methylaniline, 4-aminobenzoic acid, 3-methyl-4-aminobenzoic acid, hydroquinone, methylhydroquinone, t-butylhydroquinone, trimethylhydroquinone and 2,5-dihydroxybiphenyl were purchased from Janssen. *trans*-4-Aminocyclohexanol was purchased from Aldrich, and *trans*-1,4-cyclohexanedicarboxylic acid was a gift from Bayer AG.

The catalysts used were 4-dimethylaminopyridine, dibenzo-18-crown-6 and benzyltriethylammonium chloride (Janssen).

Methods of characterization

I.r. spectra were recorded on a Bruker IFS48 FTi.r. spectrometer using films or Nujol mulls between NaCl plates. ¹H n.m.r. spectra were obtained on a Bruker WP 80, and ¹³C n.m.r. spectra on a Bruker WH 400 (100 MHz) in deuteriochloroform using tetramethylsilane (TMS) or CHCl₃ as internal standard. Thermal properties were investigated with a Mettler TA 4000 system with DSC 30 and TG 50 equipment. Heating rates were 20 K min⁻¹. The birefringent textures were observed with a Leitz Ortholux 12 polarizing microscope equipped with FP 82 hot stage (Mettler).

All reactions were carried out in flame-dried glass equipment in an argon atmosphere.

Evaluation of catalytic activity

Some 2–3 g of the benzoyl chloride were distilled from CaH₂ into a 25 ml nitrogen flask, and the equivalent amount of trimethylsilyloxybenzene and 1% of the catalyst (DMAP, KCl–dibenzo-18-crown-6, sulphuric acid, benzyltriethylammonium chloride) added. The flask was equipped with a microdistillation apparatus and the chlorotrimethylsilane formed removed at 300 mbar. Samples for n.m.r. were taken at appropriate times, and the intensity of the trimethylsilyl absorption relative to that of the protons of the benzoyl chloride was plotted as a function of time.

Diisocyanato esters 2–7: general procedure

In a 25 ml nitrogen flask equipped with magnetic bar and a microdistillation apparatus, 25 mmol of 4-isocyanatobenzoyl chloride and 12 mmol of 4-trimethylsilyloxyphenyl isocyanate, together with 20 mg of catalyst in 6 ml 1,2-dichlorobenzene, were heated to 165°C while trimethylchlorosilane was removed at 500 mbar. The reactions were monitored by i.r. spectroscopy and stopped when the absorption of the chloroformyl group had disappeared (6–10 h). The diisocyanato esters precipitated directly or after removal of the solvent as colourless solids. They were collected by filtration and purified by recrystallization or solvent extraction. For yields, i.r. absorptions, n.m.r. data and elemental analyses, see Table 1.

Diisocyanato diesters 9–13: general procedure

First, 25 mmol of the trimethylsilyloxyphenyl isocyanate (trimethylsilylocyclohexyl isocyanate) and 12 mmol of the dicarboxylic acid chloride were treated as described above (11–13 reaction temperature 110°C, reaction time 30 h). When the reaction was complete, the solvent was removed and the residue recrystallized. Purification, yields, i.r. absorptions, n.m.r. data and elemental analyses are given in Table 1.

CONCLUSIONS

The synthesis and systematic variation of substituents and substitution pattern of triad diisocyanato esters has shown that melting and clearing points can be designed and varied over a broad temperature range. Substituents in the outer rings have a moderate influence on the melting points and a strongly decreasing effect on the clearing transition. Methyl groups and probably other not-too-bulky substituents in the central ring give the biggest decrease of melting points and leave the isotropization temperatures almost unaffected. The validity of the structure–property relationships derived will be checked with polyurethanes and other polymers made from these diisocyanates. First encouraging results have been obtained with diurethanes and oligourethanes from diisocyanato esters with substituents in the central ring¹⁸.

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