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Liquid Crystals

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Preliminary Communication

Liquid crystalline phase transitions in cyclotriphosphazenes with different mesogenic moieties in the side chains

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New cyclophosphazene derivatives incorporating five different mesogenic moieties have been synthesized and their liquid crystalline behaviour has been studied by DSC and polarizing optical microscopy. Smectic A and unclassified smectic 1 phases have been found for the first time in these cyclotriphosphazene derivatives. The relatively good thermal stability of the smectic phases of the mesomorphic cyclotriphosphazenes was interpreted in terms of the peculiar molecular shape of the cyclotriphosphazenes.

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Aryloxycyclotriphosphazenes are cyclic compounds of the general formula $(PN(OR)_2)_3$, in which four-coordinated phosphorus atoms alternate regularly with nitrogen atoms in a ring as shown in figure 1.

Much attention has been concentrated on the syntheses of cyclotriphosphazenes with different side chains in order to bestow functional properties on the compounds [1–3]. Liquid crystalline cyclotriphosphazenes have been synthesized as precursors of polyphosphazenes [4–6]. However, they have long alkyl ether chains from the oxygen to the phosphorus in the cyclotriphosphazene. Such compounds can easily form typical liquid crystals because of the relatively high mobility of the mesogenic side groups.

Recently, we have studied liquid crystalline phase transitions in cyclotriphosphazene derivatives with biphenyl mesogenic groups without spacers, since we considered that the attachment of such mesogenic units direct to the cyclotriphosphazene ring via phosphoether linkages creates a new group of liquid crystals, because movement of the mesogenic group is limited by the P–O bond and the packing of the molecules. We have already found N, S_C and S_C^* phases in such compounds [7–11].

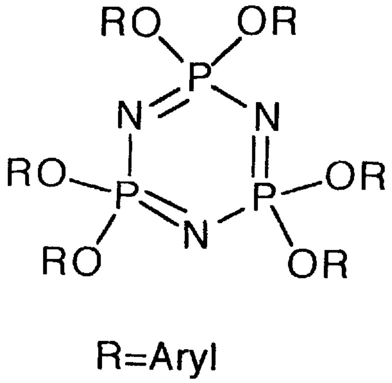

Figure 1. Structure of aryloxycyclotriphosphazenes.

In this paper, we consider how different mesogenic side chain groups in cyclotriphosphazenes affect the nature of the liquid crystalline phase transitions in cyclotriphosphazenes. To do this we synthesized five different cyclotriphosphazenes having different structural units in the rigid cores of the mesogenic moieties and similar flexible tails in the side chains, and studied the relation between their mesogenicity and the different mesogenic side groups by polarizing optical microscopy and differential scanning calorimetry (DSC).

Compounds **1**, **2**, **3** and **4** (see the table) were synthesized from the corresponding phenoxide and hexachlorocyclotriphosphazene (HCCP) in THF. The phenoxide was synthesized from the corresponding phenol and sodium hydride. The phenolic ethers were synthesized from dodecyloxy bromide, the dihydroxy compounds with different mesogenic, rigid central groups, and KOH in ethanol. Compound **5** was synthesized from 4-dodecyloxyaniline and hexakis(4-formylphenoxy)phosphazene, prepared from the sodium salt of 4-hydroxybenzaldehyde and HCCP in THF. The crude compounds **1–4** were purified chromatographically on a silica gel column (developing solvent; chloroform).The compounds **1–5** were recrystallized from hexane, THF–cyclohexane (1 : 1), ethyl acetate, ethanol and absolute THF, respectively. The structures of all the compounds were confirmed

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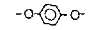
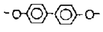
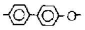
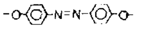
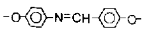
Liquid crystalline phase transitions and ^{31}P NMR chemical shifts for the compounds $[C_{12}H_{25}\text{-}X\text{-})_{1}PN]_{3}$.

Compound	*X*	Phase transition temperature/K									^{31}P NMR chemical shift/ppm
		Cr		S_1		S_C		S_A		I	
1		●	346							●	11·1
2		●	425			●	453			●	10·6
3		●	406			●	424	●	426	●	10·6
4		●	416			●	443			●	9·7
5		●	435	●	452	●	486	●	500	●	9·7

by IR, and ^1H and ^{31}P NMR. The compounds were judged to be thoroughly pure by TLC, IR, ^1H and ^{31}P NMR and elemental analysis.

Polarizing optical microscopy was carried out using a Nikon Optiphoto-pol XTP-11 with a Mettler hot stage FP-82 at a heating/cooling rate of 5 K min^{-1} from 300 K to above the clearing point. DSC measurements were made using a Seiko Electronics DSC 210 from 300 K to over the clearing point at a heating/cooling rate of 5 K min^{-1}. ^1H and ^{31}P NMR spectra were obtained using a JEOL JNM-GX 270 spectrometer and $CDCl_3$ solutions with an internal standard of TMS and THF solutions locked externally by D_2O with H_3PO_4 as standard, respectively.

The chemical structures of the rigid cores of the mesogenic groups in the cyclotriphosphazene derivatives are shown in the table, together with the phase transition temperatures obtained in the second DSC heating process and the chemical shifts in the ^{31}P NMR. All ^{31}P NMR spectra of these samples showed only one singlet, indicating that the chlorine atoms of the HCCP had been completely substituted with the chosen side chains. The ^{31}P NMR chemical shifts are different in the cyclotriphosphazenes having different mesogenic side chains suggesting that they have different electronic environments.

For compound **1**, the melting point is lower than for the other cyclotriphosphazene derivatives and no phase transition except that for melting to the liquid was observed by polarizing microscopy. This result shows that the 4-dodecyloxyphenyl side chains are too short to produce a liquid crystalline phase in the cyclotriphosphazene. In compound **2**, between 425 and 453 K, a schlieren texture with $s = \pm 1$ disclination lines and simultaneous broken-fans was observed, showing the existence of an enantiotropic smectic C [8]. In compound **3**, between 406 and 424 K, a schlieren texture with $s = \pm 1$ disclination lines and simultaneous broken-fans, was again observed, and between 424 and 426 K, a fan-like texture was found, showing the existence of smectic C and smectic A phases, respectively. In compound **4**, a texture similar to that of compound **2** was observed between 416 and 443 K, again showing the existence of an enantiotropic smectic C phase. In compound **5**, enantiotropic smectic 1, C and A phases were observed in the ranges 435 and 452, 452 and 486, and 486 and 500 K, respectively. S_1 was a biaxial, higher order smectic liquid crystal phase as confirmed by polarizing microscopy, but its type is not certain at present. Compound **5**, which has benzylideneaniline side groups, possesses a high melting point and a wide liquid crystalline temperature range compared with compounds **2** and **3**, both of which contain biphenyl containing groups in the side chain. This result may be due to the fact that benzylideneaniline groups have a dipole moment in the lateral direction. Comparing the compounds having alkyl and alkyloxy groups at the ends of the side chains, alkyloxy compound **2** has more than 20 K higher melting and clearing points than alkyl compound **3**. This result is commonly found for a wide variety of normal mesogenic compounds [12]. Compound **4**, which has phenylazobenzene mesogenic groups in the side chain, forms its enantiotropic smectic C phase with a different schlieren texture to the other compounds between 416 and 443 K, as shown in figure 2. The reason for the different optical texture may be the high viscosity, but the cause must be studied more thoroughly.

The order of mesophase thermal stability for cyclotriphosphazenes **2**, **4** and **5** is benzylideneaniline > biphenyl > phenylazobenzene, the order of thermal stability usually found for liquid crystal material having single mesogenic groups as the core [13]. These mesomorphic cyclotriphosphazenes all have smectic phases, indicating the relatively good stability of the smectic state in cyclotriphosphazenes. One reason for the smectic stability is that the cyclotriphosphazenes have relatively large interactions in the lateral directions of the molecules, because the side chains connected to the P atoms of the

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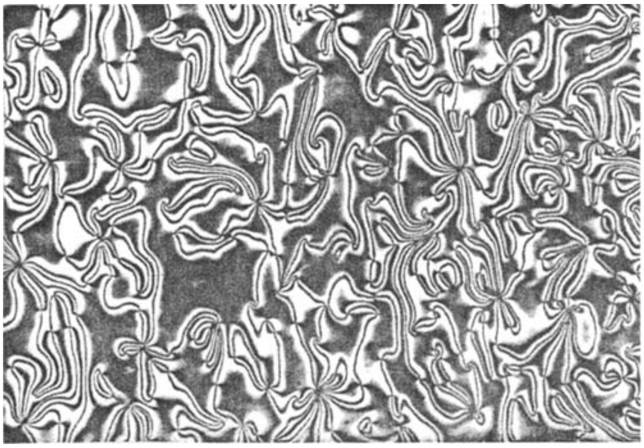

Figure 2. Polarizing microscope photograph of the schlieren texture of compound **4** at 449 K in the first cooling process.

cyclotriphosphazene ring are arranged three up and three down, perpendicularly to the cyclotriphosphazene ring plane [14].

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