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New mesogens with cubic phases: hydrogen-bonded bipyridines and siloxane-containing benzoic acids
I. Preparation and phase behaviour

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Several 4-(oligodimethylsiloxyl)alkoxybenzoic acids and their hydrogen-bonded complexes with 4,4′-dipyridyl or 1,2-bis(4-pyridyl)ethane were prepared and their phase behaviour studied by DSC and polarized optical microscopy. The neat acids showed no liquid crystalline phases. The 4,4′-dipyridyl complex of 4-(*n*-heptamethyltrisiloxyl)hexyloxybenzoic acid (Si_3C_6BA) exhibits an optically isotropic, highly viscous liquid crystalline phase below a smectic A phase. The 1,2-bis(4-pyridyl)ethane complex of Si_3C_6BA also shows an optically isotropic liquid crystalline phase above its smectic C phase. Its behaviour is similar to that of the well known cubic D phase found in 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids. In the hydrogen-bonded mesogens studied herein, the cubic phase appears to assemble spontaneously in order to take account of the chemical incompatibility between the siloxane moiety terminating the H-bonded complex and the stiff aromatic cores. The transition temperatures of the cubic phases in these materials is around 100°C, hence they are amenable to a variety of physical measurements.

1. Introduction

Cubic thermotropic liquid crystalline phases have recently attracted much attention, although such optically isotropic, highly viscous mesophases were first reported more than four decades ago. A homologous series of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (abbreviated ANBC-*n*, where *n* is the number of carbon atoms in the alkoxy chain) were shown to be optically isotropic by Gray *et al.* in 1957 and identified as having cubic symmetry by Demus *et al.* in 1968 [1–3]. Intensive investigations have been carried out to elucidate the detailed supramolecular structure in the cubic phase and the origin of this isotropic thermotropic phase. These studies included X-ray diffraction investigations by Diele *et al.* and Levelut *et al.* [4, 5], ^{1}H NMR by Ukleja *et al.* [6], ^{14}N NMR by Tansho *et al.* [7], viscoelastic studies by Kutsumizu *et al.* [8], electron microscopy by Bruce *et al.* [9], and thermal measurements by Sorai *et al.* [10].

As a result of studies carried out primarily on the ANBC-*n* series, the detailed structure of the cubic phase—the so-called 'D phase' in the literature—for the ANBC-*n* mesogens seems to converge to a class of supramolecular structural models. In particular the interpenetrating jointed-rod model proposed first by Tardieu and Billard figures prominently. There is less support for the spherical micelle model by Diele *et al.* and the unconnected, infinite-rod model by Etherington *et al.* [3, 4, 11, 12]. However the origin of such a highly organized cubic structure, and more generally the reason for the existence of the D phase in a temperature range between stratified smectic A and smectic C phases, remain open questions. On the other hand several new compounds showing an isotropic cubic phase have been found in the last decade, and these materials help to define the chemical structural prerequisites for a thermotropic cubic phase—usually a H-bonded dimeric structure comprising a stiff mesogenic core with long, terminal alkyl chains [13–16]. In order to obtain a more general understanding of the cubic phase, detailed physical studies on compounds other than the ANBC-*n* series are necessary. However, as the cubic phase is observed primarily at relatively high temperatures, such studies become difficult due to partial thermal decomposition of the components. Therefore materials showing a cubic phase over a moderate temperature range are desired for a more comprehensive investigation of this phenomenon.

By considering the proposed supramolecular models of extant D phase materials along with the chemical structures of those mesogens we concluded that one

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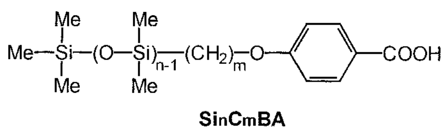
of the important factors for thermotropic cubic phase formation is nanophase separation of chemically distinct parts of the mesogens. In the case of the ANBC-n series, the nitrobiphenylbenzoic acid moiety (which dimerizes through hydrogen bonding) leads to a highly polar core while the alkyl chain termini (which should be longer than $n = 15$) are nonpolar [17]. These two distinct chemical moieties tend to segregate from each other forming a nanophase-separated supramolecular structure. The interpenetrating, jointed-rod model of Tardieu and Billard proposed for amphiphiles in water is one such structure that takes account of nanophase separation. And recent calorimetric studies have suggested that the alkyl chains in D phase materials might behave analogously to the solvent in lyotropic liquid crystals [18]. Hence by focusing on the chemical incompatibility aspect of extant cubic materials, we decided to synthesize the new series of H-bonded materials shown in figure 1. We reasoned that such complex mesogens might show nanophase separation into supramolecular structures with cubic symmetry.

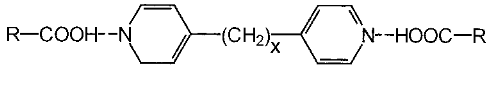
The stoichiometric mixtures of 4-(oligodimethylsiloxyl)-alkoxybenzoic acids and bipyridines form H-bonded complex mesogens that have siloxane termini which are highly incompatible with the benzoic acid/bipyridine mesogenic cores. In recent years the incompatibility between siloxane components and hydrocarbon mesogenic cores was investigated in low molecular mass liquid crystals [19] and polymer liquid crystals [20]. Generally, nanophase separation was shown to stabilize lamellar supramolecular architectures. Moreover, due in part to the bulkiness and flexibility of siloxane units that affect the packing efficiency in the solid state, the phase transition temperatures are reduced [19]. Therefore it was expected that the new series of compounds described herein could exhibit mesophases at lower temperatures than those of corresponding alkyl chain analogues. More importantly, if a thermotropic cubic phase did form, it would exist within a moderate temperature range and thus make the cubic phase amenable to physical characterization by a variety of techniques. In this paper the synthesis and phase behaviour of hydrogen-bonded complexes of 4-(oligodimethylsiloxyl)alkoxybenzoic acids with 4,4′-dipyridyl and 1,2-bis(4-pyridyl)ethane are described. We have found a thermotropic cubic phase below a temperature of 100°C.

4-(Oligodimethylsiloxyl)alkoxybenzoic acid (R-COOH)



SinCmBA

Hydrogen-bonded complexes



X = 0 (**DiPy**)
X = 2 (**BisPy**)

Figure 1. Structural formula of 4-(oligodimethylsiloxyl)-alkoxybenzoic acid (Si_nC_mBA).

2. Experimental

2.1. *Synthesis*

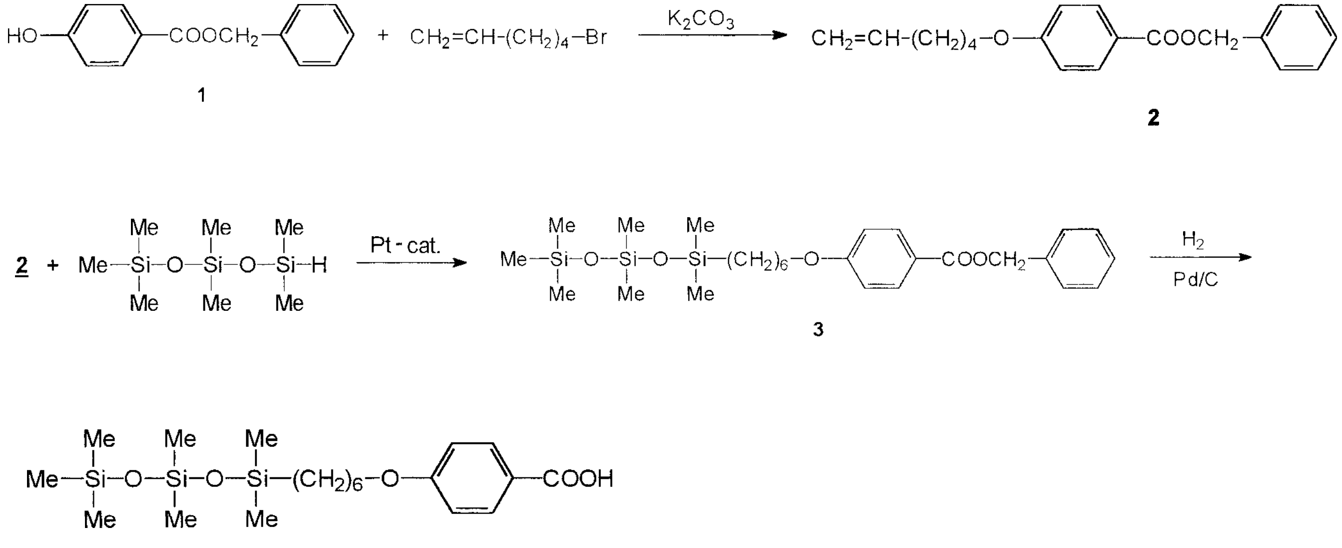
The three 4-(oligodimethylsiloxyl)alkoxybenzoic acids Si_3C_3BA, Si_2C_6BA and Si_3C_6BA (see figure 1) were synthesized by the same route as shown in the case of Si_3C_6BA (see the scheme) using the corresponding alkenyl bromide and siloxane; compounds Si_2C_6BA and Si_3C_6BA were prepared previously [20]. Starting from benzyl 4-hydroxybenzoate and alkenyl bromide, benzyl 4-alkenyloxybenzoate is obtained by Williamson's method; this is followed by hydrosilylation and then deprotection of the benzyl group using hydrogen in the presence of palladium on carbon. In the following sections the synthesis of Si_3C_6BA is described in detail, and the preparation of the hydrogen-bonded complexes of the acids with 4,4′-dipyridyl or 1,2-bis(4-pyridyl)ethane is outlined. The synthesis of other acids will be described elsewhere.

2.1.1. *Benzyl 4-hexenylbenzoates* **2**

A solution of hexenyl bromide (3 g, 18.4 mmol), benzyl 4-hydroxybenzoate **1** (4.2 g, 18.4 mmol) and anhydrous potassium carbonate (7.5 g, 3 eq.) in acetone (100 ml) was stirred under reflux for 2 days. The solvent was removed by rotary evaporation, and then ether (150 ml) was added to the residue. The insoluble material was filtered off, and the filtrate washed with 10% aqueous NaOH and sat. NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography using silica gel as the stationary phase and hexanes/ethyl acetate (8 : 1) as the eluent to yield 4.5 g (79%) of the benzyl 4-hexenylbenzoate **2** as a white solid. ^{1}H NMR in $CDCl_3$ (δ ppm): 1.5–2.1 (m, $-CH_2CH_2CH_2-$), 4 (t, $-OCH_2-$), 5 (t, $=CH_2$), 5.3 (s, $-OCH_2Ph$), 5.8 (m, $=CH-$), 6.91 (d, 2 aromatic H *ortho* to OCH_2), 7.4 (m, 5 aromatic H of benzyl ring), 8.02 (d, 2 aromatic H *ortho* to COO).

2.1.2. *Benzyl 4-(heptamethyltrisiloxyl)hexyloxybenzoate* **3**

A trace amount of dicyclopentadienyl platinum dichloride was added to a solution of benzyl 4-(n-hexenyloxy)benzoate **2** (1 g, 3.2 mmol) and 1,1,1,3,3,5,5-heptamethyltrisiloxane (1 g, 1.4 eq.) in dry toluene (3 ml). The solution was held at 45°C for 20 h, then the solvent was



Si_3C_6BA

Scheme. Synthesis route to 4-(heptamethyltrisiloxyl)hexaoxybenzoic acid (Si_3C_6BA) and hydrogen-bonded complexes.

removed and the residue purified by column chromatography (eluent: hexanes/ethyl acetate = 9/1) to yield 1.3 g (75%) of benzyl 4-(heptamethyltrisiloxyl)hexyloxybenzoate **3** as a colourless viscous liquid. ^{1}H NMR in $CDCl_3$ (δ ppm): 0–1 (m, $-SiCH_3$, 21H), 0.5 (t, $-CH_2Si-$, 2H), 1.3–1.5 (m, $SiCH_2\underline{CH_2CH_2CH_2}-$, 6H), 1.75 (m, $-OCH_2CH_2-$, 2H), 3.95 (t, OCH_2-, 2H), 5.3 (s, OCH_2Ph, 2H), 6.9 (d, 2 aromatic H *ortho* to OCH_2), 7.4 (m, 5 aromatic H of benzyl ring), 8.05 (d, 2 aromatic H *ortho* to –COO–).

2.1.3. *4-(Heptamethyltrisiloxyl)hexyloxybenzoic acid Si_3C_6BA*

To a solution of benzyl 4-(heptamethyltrisiloxyl)-hexyloxybenzoate (4 g, 7.5 mmol) in ethanol (60 ml) and ethyl acetate (80 ml), Pd/C (0.4 g) was added, and the mixture vigorously stirred under a slight pressure of H_2 at room temperature overnight. The insoluble material was filtered off using celite, and the filtrate concentrated. The white residue was purified by recrystallization from methanol/water (5 : 1) to yield 2 g (60%) of 4-(heptamethyltrisiloxyl)hexyloxybenzoic acid Si_3C_6BA as a white solid. ^{1}H NMR in $CDCl_3$ (δ ppm): 0–1 (m, $-SiCH_3$, 21H), 0.5 (t, $-CH_2Si-$, 2H), 1.3–1.5 (m, $SiCH_2\underline{CH_2CH_2CH_2}-$, 6H), 1.75 (m, $-OCH_2CH_2-$, 2H), 4.05 (t, OCH_2-, 2H), 6.95 (d, 2 aromatic H *ortho* to OCH_2), 8.05 (d, 2 aromatic H *ortho* to –COO–).

2.1.4. *Hydrogen bonded complexes*

In the general procedure used to prepare the hydrogen bonded complexes, a 2 : 1 molar ratio of a 4-(oligodimethylsiloxyl)alkoxybenzoic acid and 4,4′-dipyridyl or 1,2-bis(4-pyridyl)ethane was dissolved in diethyl ether; the solvent was removed by heating at 50°C and the residue was further heated at 120–130°C to yield the complex.

2.2. *Characterization*

The differential scanning calorimetry data were recorded with a Seiko Denshi DSC-220 at a heating/cooling rate of 5 K min^{-1}. The observation of textures was performed using a Nikon Microphot-FX microscope equipped with a Mettler FP-82HT (or a Linkam TMS-90) hot stage and a Sony CCD-IRIS video camera.

3. Results and discussion

The phase behaviour of the 4-(oligodimethylsiloxyl)-alkoxybenzoic acids Si_3C_3BA, Si_2C_6BA and Si_3C_6BA (see figure 1) and their hydrogen-bonded complexes with 4,4′-dipyridyl (DiPy) or 1,2-bis(4-pyridyl)ethane (BisPy) are summarized in the table. The transition temperatures were determined by DSC and optical microscopy. All of the neat siloxane-containing benzoic acids form an elongated dimeric structure through cyclic hydrogen bonding, but show no liquid crystalline (LC) phases with the exception of Si_3C_3BA wherein a transient LC phase is observed by optical microscopy at 64°C on cooling the melt. On comparing the fusion of Si_3C_6BA with Si_2C_6BA the mere increase of one dimethylsiloxane unit decreases the melting temperature by 40 K. On the other hand Si_3C_6BA melts about 20 K lower than Si_3C_3BA, showing that the transition temperatures are also sensitive to the length of the alkyl chain ‘spacer’ connecting the siloxane moiety to benzoic acid. This result clearly shows that the reduced packing efficiency associated with the increased bulkiness and flexibility of

Table. Phase behaviour of Si_nC_mBA homologues and their 4,4′-dipyridyl and 1,2-bis(4-pyridyl)ethane complexes. The phase transformation temperatures (°C) were obtained from DSC data in the first cooling process at the rate of $5\,K\,min^{-1}$. Cr_1, Cr_2 = crystalline; Sm = smectic; SmC = smectic C; SmA = smectic A; I, I_1, I_2 = isotropic, D = cubic.

Acid	Base	Phase transitions
Si_3C_3BA	—	Cr 89 I
Si_3C_3BA	DiPy	Cr 110 I
Si_3C_3BA	BisPy	Cr_1 95 Cr_2 121 I
Si_2C_6BA	—	Cr 107 I
Si_2C_6BA	DiPy	Cr 124 I
Si_2C_6BA	BisPy	Cr 87 Sm_1 108 Sm_2 123 I
Si_3C_6BA	—	Cr_1 33 Cr_2 67 I
Si_3C_6BA	DiPy[c]	Cr_1 42 Cr_2 96 D 100[1] SmA 103 I_1 115 I_2
Si_3C_6BA	BisPy	Cr_1 27 Cr_2 72 Sm 81 SmC 91[b] D 104 I_1 116 I_2

[a] The smectic A phase is observed only on cooling.

[b] This phase transformation temperature was determined by polarized optical microscopy.

[c] The stability of the smectic A phase depends on the excess amount of DiPy.

the siloxane moiety is much more significant than the methylene spacer. In these neat, H-bonded acids, mesophase formation might be precluded in part by the bulkiness and flexibility of the siloxane moiety in conjunction with the relatively small dimeric acid core. By elongating the core and thereby enhancing the excluded volume interactions between cores of these complexes, a mesophase might be realized. To this end, the acid–base H-bonded complexes of the 4-(oligodimethylsiloxyl)-alkoxybenzoic acids with 4,4′-dipyridyl (DiPy) or 1,2-bis-(4-pyridyl)ethane (BisPy) were prepared. Neither the DiPy nor the BisPy complex of Si_3C_3BA shows a mesophase. The DiPy complex of Si_2C_6BA melts to an isotropic liquid directly, but the BisPy complex shows highly ordered smectic phases. The detailed nature of these smectic phases has not been completely ascertained.

We observed interesting phase behaviour for the DiPy and the BisPy complexes of Si_3C_6BA. The textures observed by polarized optical microscopy are reported in figures 2 and 3. In case of the DiPy complex of Si_3C_6BA, the focal conic texture characteristic of a smectic A phase is observed on cooling at 100°C, figure 2(*a*). However this texture is not stable. Simultaneously, under crossed polarizers completely dark areas start developing in the smectic A texture, figure 2(*b*), and the entire observed field eventually becomes dark, figure 2(*c*). On

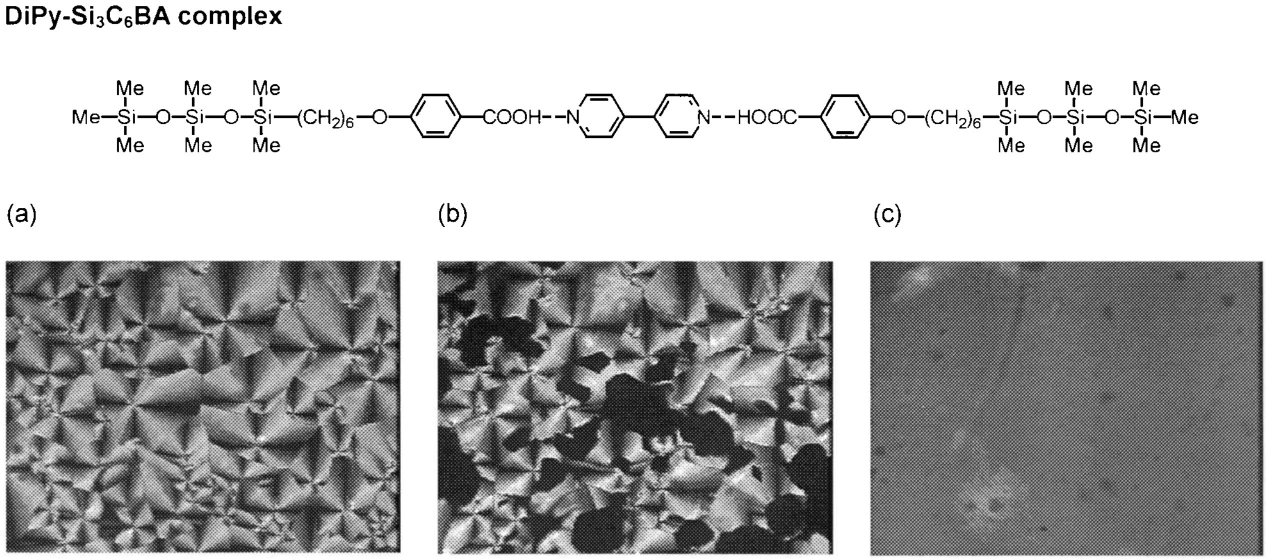
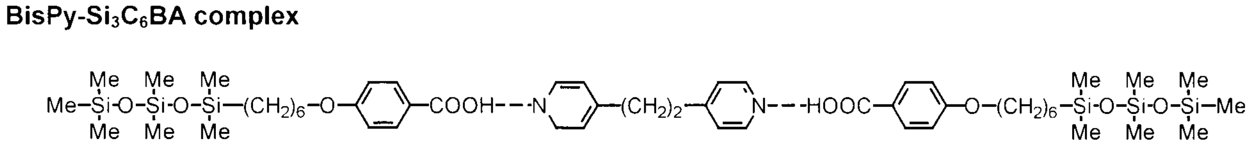


Figure 2. Texture of the DiPy-Si_3C_6BA complex observed by polarized optical microscopy: (*a*) the smectic A phase, (*b*) the cubic phase growing into a field of the smectic A phase, (*c*) the cubic phase.



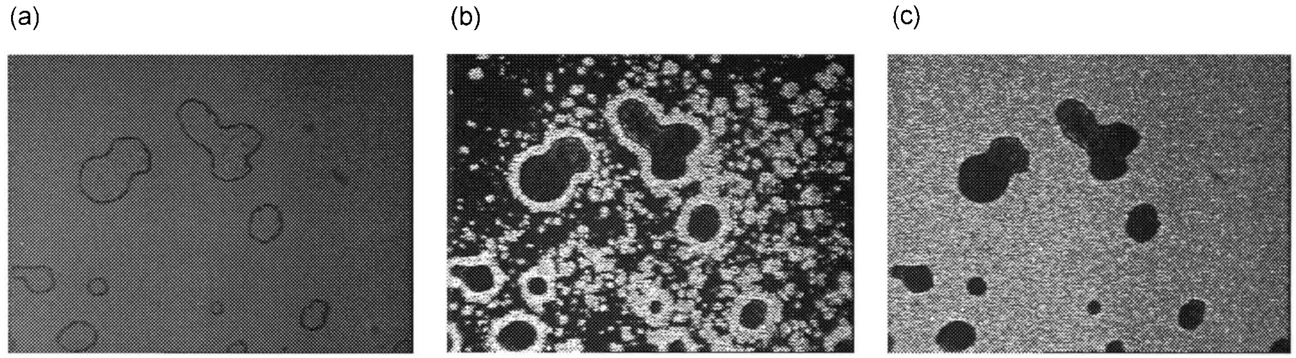


Figure 3. Texture of the BisPy-Si_3C_6BA complex: (*a*) the cubic phase, (*b*) the smectic C phase growing in the cubic phase, (*c*) the smectic C phase.

further cooling crystallization takes place. Upon heating, the crystal melts at 96°C into an optically isotropic, highly viscous phase, and then the phase transforms into a low viscosity, isotropic phase at 103°C without forming the smectic A phase. The observed high viscosity in an optically isotropic fluid found on cooling below a mesophase exhibiting a conventional smectic texture suggests that there is supramolecular structure present in the optically isotropic mesophase; and, that this mesophase of the DiPy-Si_3C_6BA complex has cubic symmetry similar to the well-known cubic D phases in the ANBC-*n* series. A 'cubic phase' is also observed for the BisPy complex of Si_3C_6BA: on cooling, the phase transformation from an isotropic liquid to a cubic phase takes place at 95°C with an enthalpy change of 2 J g^{-1}. As shown in figure 3 (*a*) the high viscosity of the cubic phase prevents the deformed air bubbles from assuming circular shapes. On further cooling, a birefringent, smectic C-like phase begins growing into the black areas of the cubic phase, figure 3 (*b*), and it develops completely throughout the field of view, figure 3 (*c*). Then there is a phase transformation from the smectic C-like phase to another smectic phase at 70°C, which in turn is followed by crystallization. On heating, the same phase sequence is observed: the melting to a smectic phase occurs at 72°C, then the low temperature smectic transforms into a smectic C phase at 81°C. The cubic phase starts appearing at 91°C, and finally the transition into a low viscosity isotropic phase takes place at 104°C.

Figure 4 shows the DSC trace of the BisPy-Si_3C_6BA complex recorded at heating/cooling rates of 5 K min^{-1}. Besides the phase transitions described above, a broad isotropic-to-isotropic phase transformation around 110°C is obvious. This unique I-to-I phase transition is also characteristic of the ANBC-*n* series mesogens [17] and probably indicates the assembly of the H-bonded complex mesogens into aggregates. Interestingly, the phase transformation between the cubic and the smectic C phase was not clearly detected by DSC; it might be second order. Here it should be noted that the stability of the smectic A phase of the DiPy-Si_3C_6BA complex is a sensitive function of the excess 4,4′-dipyridyl in the mixtures. The stoichiometric complex was prepared from a 2:1 Si_3C_6BA:DiPy mol ratio mixture. However by using a small excess of DiPy (for instance, a 2 mol % excess) the smectic A phase was destabilized, changing immediately to the cubic phase while observed. By contrast, the smectic A phase was stabilized when the complex was prepared using a small excess amount of

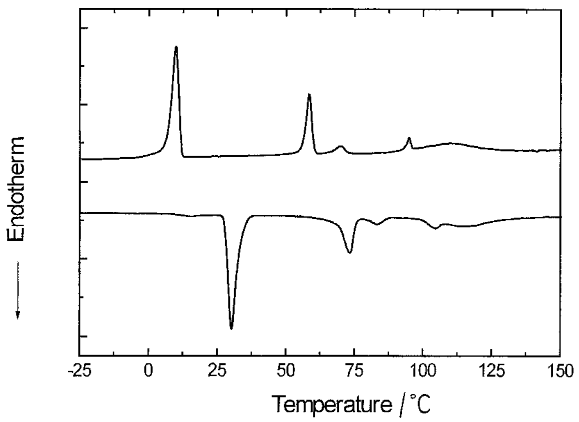


Figure 4. DSC traces (heating/cooling rates of 5 K min^{-1}) of the BisPy-Si_3C_6BA complex.

acid. In that case, only after annealing for several hours did the cubic phase begin to develop and it did so gradually. At present we do not understand the origins of the variable transition kinetics for the phase transformation between the smectic A phase and the cubic phase in the off-stoichiometry, H-bonded mesogens.

4. Conclusions

We have found a new class of materials exhibiting a cubic thermotropic liquid crystalline phase. These materials have characteristic chemical structural similarities to other known compounds showing a cubic 'D' phase. That is, they possess a dimeric structure with a stiff and elongated polar core that has flexible long tail terminal groups. However, probably the most important feature of our H-bonded complexes is the combination of highly incompatible parts in the same mesogen: the polar, rectilinear aromatic core lengthened through hydrogen bonding, and the bulky, flexible, nonpolar siloxane tails. Inherent chemical incompatibilty within the mesogen structure could promote nanophase-separated supramolecular structures and be crucial for the formation of the cubic phases we observed. This hypothesis is reinforced by the observation that neither of the DiPy and BisPy complexes of 4-dodecyloxybenzoic acid show cubic phases, even though they have similar molecular dimensions and architecture. But these totally hydrocarbon H-bonded complexes are more chemically homogeneous—they possess long alkoxy tail groups instead of siloxane tails [21]—and their tendency to nanophase separation might not be strong enough to assemble a cubic supramolecular arrangement. In the case of the ANBC-*n* series, the polar nitro group plays a significant role in the formation of the D phase, presumably by enhancing the incompatibility between the polar aromatic core and the non-polar alkoxy tails.

Lastly, the siloxane-based complexes investigated exhibit cubic phases over a moderate temperature range (under 100°C), which is ideal for performing physical measurements. We are currently examining the cubic structures in more detail with NMR and X-ray diffraction measurements. Some of our findings are reported in a companion paper [22].

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