Dimesogenic liquid crystalline organosiloxanes

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Liquid crystalline (LC) organosiloxanes with two terminal cyanobiphenylyl groups attached to a linear or cyclic siloxane center through an aliphatic spacer $(CH_2)_n$ with n = 10 were synthesized. The ability of compounds to pass into the LC state was confirmed by thermooptical, X-ray diffraction, and calorimetric measurements. The temperatures and the enthalpies of phase transitions were determined. The types of LC structures and the capability of one compound for polymesomorphism to form the chiral S_mC^* phase without a chiral center in the mesogenic group were established. The temperatures and the enthalpies of the reversible phase transitions, crystal $\rightleftharpoons S_mC \rightleftharpoons S_mA \rightleftharpoons$ melt and crystal $\rightleftharpoons S_mA \rightleftharpoons$ melt, for linear and cyclic LC organosiloxanes, respectively, were determined. Models of molecular packing in the S_mA and S_mC^* phases were proposed based on X-ray diffraction data. A specific feature of the S_mA phases of new LC organosiloxanes is a negative gradient of the temperature dependence of the interlayer spacing.

Key words: disiloxanes, cyclosiloxanes, liquid crystalline compounds, mesogen, phase transitions, spatial isomers.

During the last three decades, syntheses of comb-like liquid crystalline (LC) polyorganosiloxanes have been performed and their phase behavior has been comprehensively studied depending on the chemical structure of the mesogen and the length of spacers.¹ The number of publications dealing with monomeric LC siloxanes is much smaller; these studies consider compounds with linear siloxane and cyclotetrasiloxane centers and with variable structure of mesogenic groups.²⁻⁵ It was found that an increase in the length of siloxane units in dimesogenic α,ω -dimethyloligosiloxanes entails a decrease in the temperatures of phase transitions.^{3,4} Dimesogenic compounds with a hexamethyldisiloxane center and chiral groups exhibit enantiotropic mesomosphism, S_mA-S_mC* (S_mA and S_mC are smectic A and C phases) with a change in the interlayer spacing.² Spontaneous polarization was found in dimesogenic hexadecamethylheptasiloxanes with a chiral center in the terminal group.⁴

This study is devoted to the structure of linear and cyclic siloxane centers of molecules with a particular spatial position of terminal cyanobiphenylyl mesogenic groups connected to the core by an aliphatic $(CH_2)_n$ spacer with n = 10. The purpose of the study was to elucidate the influence of the structure of the central siloxane core on phase transition temperatures and on the type of LC structures formed.

Results and Discussion

Synthesis of liquid-crystalline organosiloxanes. We synthesized dimesogenic compounds with different structures of the siloxane center. Linear tetramethyldisiloxane **1** (Scheme 1) and cyclic decamethylcyclohexasiloxane **2** (Scheme 2) were used as central cores. The mesogenic group for compounds **1** and **2** was chosen resorting to published data, ¹ stating that the use of an aliphatic spacer with n > 8 decreases the effects related to the odd-andeven structure of the uncoupling; simultaneously, this creates an additional dipole moment.

Disiloxane 1 was prepared⁵ by hydrosilylation of unsaturated ester 3 with chlorodimethylsilane in the presence of a Pt catalyst (the Carsted catalyst) followed by hydrolysis if the resulting chlorosilane 4 in the presence of NaHCO₃ (see Scheme 1).

Dimesogenic compound 2 with the central cyclohexasiloxane fragment was prepared by the reaction of *trans*-2,8-dihydroxy-2,4,4,6,6,8,10,10,12,12-decamethylcyclohexasiloxane (5) ⁶ with chlorosilane 4 (see Scheme 2).

The choice of cyclic cyclohexasiloxane 5 as a core for an LC monomer is due to the presence of two tetramethyldisiloxane groups between two $MeSiO_3$ centers connected to the mesogenic group. Within this group, the

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Si—O—Si angle can vary from 148° to 178° (the four Si atoms lie in one plane), which provides a hypothetical possibility of the formation of LC packings of different types.

The structures and purity of compounds **1** and **2** were confirmed by TLC, ¹H and ²⁹Si NMR and IR spectroscopy, and elemental analysis.

The ¹H NMR spectra of compounds 1 and 2 exhibit high-field signals for the protons of the alkyl substituents. The singlet with δ 0.021 in the spectrum of compound **1** refers to the two methyl groups at the silicon atom. The spectrum of compound 2 contains signals with δ 0.02 and 0.04 (3 H) for the MeSiO₃ methyl groups corresponding to *trans*- and *cis*-isomers with the intensity ratio *trans* : $cis \approx 3$: 1. The signals of compound 5 in different solvents ((CD₃)₂CO, CDCl₃-CCl₄, C₆D₆-CCl₄) were assigned to cis- and trans-isomers on the basis of previously published data.⁶ Other methyl-group protons related to Me₂SiO in cyclosiloxane and to Me₂SiCH₂ are responsible for singlets with $\delta 0.06$ (12 H) and 0.09 (6 H), respectively. In this case, the nonequivalence of the methyl protons in cis- and trans-isomers is not observed. The proton signals of the mesogenic group in compounds 1 and 2 are identical.

The ²⁹Si NMR spectrum of compound **1** contains only one signal at δ 7.15, *i.e.*, in the region characteristic of Me₂SiCH₂ groups. However, in the case of compound **2**, this spectral region contains two signals δ 7.92 and 7.27, with an intensity ratio of ~3 : 1, while the region from δ -66.0 to -67.0, typical of the methylsilsesquioxane group, exhibits two signals at δ -66.47 and -66.73 with an intensity ratio of ~3 : 1, which points to the presence of *cis*- and *trans*-isomers in compound **2**. A difference between the chemical shifts, $\Delta \delta \approx 0.20$, has been found for MeSiO₃ groups in the same region for bifunctional monomers and cyclolinear polymers; however, the non-equivalence of silicon in the Me₂SiO groups of cyclosiloxane isomers was not manifested.⁷

Since the starting cyclosiloxane 5 was a pure *trans*isomer according to a previous publication,⁶ the results we obtained attest to partial inversion of one silicon atom during the formation of compound 2.

The IR spectra of compounds **1** and **2** exhibit absorption bands typical of SiMe₂ groups (791 cm⁻¹); Si–O (1070 cm⁻¹), Si–CH₂CH₂ (1135 cm⁻¹), CH₂O–C (1172 cm⁻¹), and Si–Me (1255 cm⁻¹) bonds; C₆H₄ groups (1495, 1607 cm⁻¹); and C=O (1759 cm⁻¹) and C=N (2235 cm⁻¹) bonds. Absorption bands corresponding to asymmetric and symmetric stretching vibrations of the C–H bonds in methyl and methylene groups are observed in the 2845–2920 cm⁻¹ region. The bands corresponding to asymmetric and symmetric bending vibrations of these groups occur at about 1460 and 1390 cm⁻¹.

Phase behavior. Comparative study of the phase behaviors of compounds **1** and **2** was carried out by DSC. Figure 1 shows the DSC curves recorded at the heating rate $V = 10 \,^{\circ}\text{C} \,^{\min^{-1}}$. It can be seen from these data that compound **1** undergoes at least two phase transitions at 56 and 116 $^{\circ}\text{C}$, unlike compound **2**, where only one diffuse transition can be detected. The enthalpy of isotropization $\Delta H_i = 11.0 \,\text{J g}^{-1}$ for compound **1** is close to published data for siloxane polymers with alkoxycyanobiphenylyl side groups and the (CH₂)_n alkyl spacer with $n = 11 \, (\Delta H_i = 9.2 \, \text{J g}^{-1})$, which form the S_mA phase with a parallel pack-



Fig. 1. DSC curves for compounds **1** (*a*) and **2** (*b*) at a heating and cooling rate of 10 °C min⁻¹: (1, 2) are the heating and cooling curves, respectively.

ing of backbone sections.⁸ The lower isotropization temperature T_i found for 2 is probably due to both the greater number of tetramethyldisiloxane groups in molecule 2 compared to that in 1 and the fact that compound 2 is a mixture of two spatial isomers present in ~3 : 1 ratio.*

During cooling of compound 1, DSC measurements (see Fig. 1, curve 2) show two transitions at 113.0 and 8.0 °C, while in the case of compound 2, only one exotherm with a poorly resolved maximum is observed. The overall enthalpy of phase transitions in compound 2 is much lower than that for compound 1.

It was found by polarization microscopy that compounds **1** and **2** are crystalline at 20 °C; they exhibit enantiotropic LC mesomorphism and undergo isotropization upon temperature rise to 120 and 100 °C, respectively. During cooling of an isotropic melt, the liquid crystalline isotropic state is retained down to -70 °C with a cooling rate of 3-10 °C min⁻¹. The crystal structure is completely restored after 2 days at 20 °C.

Figure 2, *a* shows the texture of compound 1 at 116.5 °C during cooling the isotropic melt from 120 °C. As the temperature decreases in the case of compound 1, the texture of the S_mA phase disappears and a new texture typical of the chiral S_mC phase appears instead (see Fig. 2, *c*). Similar textures for the S_mA and S_mC phases

were observed for polyacrylates with alkoxycyanobiphenylyl groups and the $(CH_2)_n$ spacer with n = 11.9 The cooling rate (V) affects appreciably the temperature of the S_mA \rightarrow S_mC transition. Indeed, for $V = 3 \circ C \min^{-1}$ it is equal to 28 °C, while for $V = 0.5 \circ C \min^{-1}$, to 45–52 °C. Figure 2, b shows the texture of compound 1 during the S_mA \rightarrow S_mC transition at 52 °C. The lowest phase transition temperature $T_{S_mA\rightarrow S_mC} = 8.0 \circ C$ was determined by DSC at $V = 10 \circ C \min^{-1}$. Figure 2, c shows the texture of the S_mC phase of compound 1 at 26 °C. The temperature range of existence of the LC state for compound 1 is twice as wide as that for the initial mesogen 3.⁵

Figure 3, *a* shows the texture of the rod-shaped liquidcrystalline nuclei obtained on cooling of compound **2** from an isotropic melt at 90 °C. The shape of the nuclei indicates that the growth rate in the axial direction is greater than that in the radial direction. When compound **2** is cooled at a rate of V = 0.5 °C min⁻¹ to 80 °C, the background field is filled with the focal conic texture of the S_mA phase, which remains unchanged down to 20 °C (see Fig. 3, *b*). The texture of the S_mA phase predominates for compound **2**. However, on further cooling of compound **2**, an additional texture looking as crosses without disruption of each branch was found to appear in the remaining isotropic melt (in the black field) (see Fig. 3, *c*). This is probably due to formation of the texture of the *cis*-isomer of **2**.

Figure 4 shows the X-ray diffraction patterns of ester **3** used to prepare compounds **1** and **2**. One can see that the mesogen is crystalline at 20 °C. Compound **3** is known to pass to the S_mA phase at 50 °C.⁵ The X-ray diffraction pattern for the S_mA phase of compound **3** recorded at 54 °C (see Fig. 4, curve 2) contains only one narrow reflection at $2\theta = 2.14^{\circ}$ ($d_1 = 41.23$ Å) with the half-width $\Delta_{1/2} = 0.27^{\circ}$ and a broad nearly symmetrical amorphous halo at $2\theta_a = 19.83^{\circ}$ ($d_a = 4.47$ Å) with $\Delta_{1/2} = 6.0^{\circ}$. According to previous data,⁵ the S_mA phase exists over a narrow temperature range ($\Delta T_{S_mA} = 50.0-67.5^{\circ}$ C). The X-ray diffraction pattern of ester **3** recorded above T_i , at 105 °C, contains only a symmetrical amorphous halo with a maximum at $2\theta_a = 19.0^{\circ}$ ($d_a = 4.67$ Å, $\Delta_{1/2} = 6.8^{\circ}$).

According to X-ray diffraction data, compound **1** is crystalline at 20 °C (Fig. 5, *a*). In the X-ray diffraction pattern, transition to the S_mA phase was detected at 54 °C (see Fig. 5, *b*). The X-ray diffraction pattern of the S_mA phase exhibits one narrow intense reflection at $2\theta = 1.98^{\circ}$ ($d_1 = 44.57$ Å, $\Delta_{1/2} = 0.26^{\circ}$) and a broad amorphous halo. The position of the halo maximum, $2\theta_a = 19.9^{\circ}$, is virtually identical to the corresponding value for the mesogen.³ Thus, the amorphous maximum at $2\theta_a$ is mainly due to scattering on mesogenic groups. The X-ray diffraction pattern of the melt of compound **1** measured at 120 °C (see Fig. 5, *c*) contains only one amorphous halo with a maximum at $2\theta_a = 16.47^{\circ}$ ($\Delta_{1/2} = 4.1^{\circ}$). The average intermolecular distance in the melt calculated for com-

^{*} The introduction of Me₂SiO units in LC compounds is known to result in a sharp decrease in $T_{i}^{.3,4}$



Fig. 2*. Optical photomicrographs of the textures of compound **1** at 116.5 °C in the S_mA phase (cooling rate 1.0 °C min⁻¹) (*a*), in the instant of the S_mA \implies S_mC transition at 52 °C (cooling rate 0.5 °C min⁻¹) (*b*), and in the S_mC phase at 26 °C (cooling rate 3.0 °C min⁻¹) (*c*).

pound 1, $d_a = 5.38$ Å, is substantially greater that the corresponding value for mesogen 3 for which $d_a = 4.67$ Å. This is indicative of changes introduced by the siloxane center to the statistics of intra- and intermolecular distances. Comparison of the $2\theta_a$ values for the S_mA phase and the isotropic melt suggests the possibility of micro-







Fig. 3*. Optical photomicrographs of the textures of compound 2 in the S_mA phase at 90 (*a*) and 80 °C (*b*) (cooling rate 0.5 °C min⁻¹) and in the S_mA phase at 20 °C (cooling rate 1.0 °C min⁻¹) (*c*).

b

^{*} Figures 2 and 3 are available in full color in the on-line version of the journal (http://www.wkap.nl/journalhome.htm/1066-5285) and on the web site of the journal (http://rcb.ioc.ac.ru).



Fig. 4. X-Ray diffraction patterns of compound 3 at 20 °C (a) and 54 (1) and 105 °C (2) (b).

phase separation between mesogenic groups and the siloxane core in the LC phase.

According to X-ray diffraction data, compound 1 does not crystallize immediately after cooling from 120 to 20 °C; crystallization is very slow, the crystal structure being completely restored only after 48 h at 20 °C.

As noted above, $S_mA \rightarrow S_mC$ transition taking place on cooling of an isotropic melt was found for compound **1** using polarization microscopy. X-Ray diffraction analysis

did not show a stepwise change in the d_1 parameter on cooling of compound **1** in the temperature range of existence of the LC phase. This is probably due to the close positions of the melting point and the $S_mC \rightarrow S_mA$ transition found by DSC (see Fig. 1). It should be emphasized that the gradient of the $d_1(T)$ dependence was negative. On cooling of the melt, the small-angle reflection from the LC phase gradually shifted to smaller angles, pointing to an increase in the parameter d_1 with a decrease in temperature (Fig. 6). In the 40–50 °C region correspond-



Fig. 5. X-Ray diffraction patterns of compound 1 at 20 (*a*), 54 (*b*), and 120 °C (*c*).

ing to the $S_mA \rightarrow S_mC$ transition, the parameter d_1 was noted to decrease (by ~1.5 Å).

Compound **2** is partially crystalline at 20 °C (Fig. 7, curve *I*), the fraction of the crystalline phase being small. On heating to 30 °C, this compound completely transforms in the S_mA phase (curve 2). The X-ray diffraction pattern obtained at 30 °C (curve 2) shows one intense



Fig. 6. X-Ray diffraction characteristics of compound 1 in the liquid-crystalline state: (*a*) fragments of X-ray diffraction patterns obtained by cooling of a melt at 110 (*1*), 92 (*2*), 86 (*3*), 74 (*4*), 54 (*5*), and 20 °C (*6*); (*b*) the temperature dependence of the interlayer spacing d_1 .

reflection at $2\theta = 3.07^{\circ}$ (d = 28.74 Å) with the half-width $\Delta_{1/2} = 0.23^{\circ}$ and amorphous scattering. The distribution curve for the intensity of amorphous scattering has a complex shape. However, it is possible to distinguish two maxima at $2\theta_{a_1} = 10.08^{\circ}$ ($d_{a_1} = 8.75$ Å) and $2\theta_{a_2} = 20.36^{\circ}$ ($d_{a_2} = 4.36$ Å) located in the third, very broad halo at



Fig. 7. X-Ray diffraction patterns of compound 2 at 20 (1), 30 (2), 81 (3), and 105 °C (4).

 $2\theta_{a_3} = 17.74^\circ$. Comparison of the X-ray diffraction patterns obtained at 30 and 81 °C (see Fig. 7, curves 2 and 3) shows that the angle position of the first amorphous maximum depends only slightly on the temperature, unlike that of the second maximum, which is highly sensitive to temperature changes. This indicates that the maxima at $2\theta_{a_1}$ and $2\theta_{a_2}$ are due to scattering on different molecular fragments.

The d_{a_1} value is close to the thickness of the siloxane cyclic fragment, which is 7.8 Å.* Hence, the arrangement of cyclic fragments within the layer is subject to a short-range order, the strictest correlation being observed along the direction normal to the plane of the rings. The angle position of the second amorphous halo, $2\theta_{a_2}$, virtually coincides with the $2\theta_a$ value for mesogen **3** ($d_a = 4.47$ Å). Therefore, it is most likely that the second amorphous halo at $2\theta_{a_2}$ reflects scattering on mesogenic groups.

A temperature rise results in a substantial shift of $2\theta_{a_2}$ toward smaller scattering angles, indicating an increase in the average distance between mesogenic groups. Mean-while, the $2\theta_{a_1}$ value depends only slightly on the temperature, *i.e.*, the correlation in the mutual arrangement of cyclic fragments is retained. The high gradient for the $2\theta_{a_2}(T)$ dependence found for the temperature range of existence of the S_mA phase may attest to the lack of complete overlap of the mesogenic groups at the intermolecular level.

According to X-ray diffraction data, isotropization of compound **2** takes place at 90 °C, which is consistent with the DSC and optical microscopy data. The X-ray diffraction pattern of the melt of compound **2** (see Fig. 7, curve 4) contains only an amorphous halo of a complex shape. The intensity distribution curve for the amorphous scattering for the melt of compound **2** differs appreciably from the diffraction patterns of the melts of mesogen **3** and compound **1** by the presence of a clear maximum at $2\theta_{a_1} = 10.0^\circ$ corresponding to scattering on the siloxane rings. Thus, the microphase separation between the siloxane centers and organic mesogens noted previously for the S_mA phase is retained in the isotropic melt. The scattering curve from the melt has a maximum at $2\theta_{a_2} = 17.40^\circ$.

The obtained data imply the following sequence of phase transformations for mesogen 3 and compounds 1 and 2:



To summarize the data obtained for mesogen 3 and compounds 1 and 2, the following conclusions can be drawn:

(1) the introduction of the cyclic siloxane core between two mesogenic groups decreases the thermal stability of the crystal phase, thus extending the temperature range of existence of the S_mA phase;

(2) the presence of the linear siloxane core has no influence on the thermal stability of the crystal phase and leads to pronounced supercooling of the LC phase, giving rise to the S_mC phase in the absence of chiral centers. The presence of siloxane cores increases the thermal stability of the mesomorphic state due to additional interactions caused by microphase separation between the siloxane and mesogenic organic fragments (the substantial broadening of the isotropization region of cyclic LC organosiloxane is due to the presence of *cis*-isomers).

The interlayer spacing for the linear LC siloxane near T_i ($d_1 = 41.62$ Å) is close to the analogous parameter for mesogen **3** ($d_1 = 41.23$ Å). As the temperature decreases, the interlayer spacing in the S_mA phase of linear LC siloxane increases, reaches the maximum value, $d_1 = 44.79$ Å, near the S_mA \Rightarrow S_mC transition at 54 °C, and decreases to $d_1 = 43.04$ Å in the S_mC phase. Figure 8 shows the

^{*} A similar value has been found for the mesophases of cyclolinear polymethylsiloxanes containing decamethylcyclohexasiloxane fragments.¹⁰



Fig. 8. Model of molecular packing for compound 1 in the S_mA phase. (In the smectic C phase, the mesogenic groups are arranged at an angle of ~15° relative to the director.)





Fig. 9. Putative models for the packing of compound 2 in the S_mA phase (the smectic layers are arranged vertically): (*a*) packing with full overlap of mesogen groups; (*b*) layered packing.

The results of X-ray diffraction measurements may imply two variants of molecular packing for compound 2 in the S_mA phase. First, with known interlayer spacing calculated from the angle position of the small-angle reflection (d = 28.8 Å) and the length of the mesogenic group (L = 27.8 Å), one can construct the model of molecular packing with full overlap of the mesogenic groups (Fig. 9, a). However, within the bounds of this model, it is difficult to interpret a number of features inherent in the X-ray diffraction patterns of compound 2 in the S_mA phase, in particular, the complex pattern of amorphous scattering and the negative gradient of the $d_1(T)$ dependence. It follows from X-ray diffraction data that the layer packing with $d = 2d_{002} = 57.44$ Å shown in Fig. 9, b is most probable for compound 2. Indeed, the presence of amorphous diffraction in the X-ray diffraction pattern caused by scattering on the siloxane rings attests to an increase in the electron density in the center of the layer. This should result in a decrease in the intensity of odd reflection orders responsible for interlayer periodicity. Therefore, an index of 002 should be ascribed to the registered interlayer reflection with $2\theta = 3.07^{\circ}$, assuming that the <001> direction coincides with the normal to the plane of the layer.

The presence of these features in the X-ray diffraction characteristics in the case of compound **2** and their lack for compound **1** is due to a substantial increase in the volume fraction of the siloxane moiety upon replacement of the linear central fragment by a cyclic one. The calculation showed that the ratios of the sums of the increments of the van der Waals volumes of atoms incorporated in the siloxane and mesogenic fragments, $\Sigma \Delta V_i^{Si} / \Sigma \Delta V_i^{m}$ are 178.3/689.4 \approx 0.26 and 671.2/689.4 \approx 0.97 for compounds **1** and **2**, respectively.¹¹

Thus, in relation to two liquid crystalline organosilicon compounds with linear and cyclic siloxane centers with the predominant *trans*-position of the terminal cyanobiphenylyl mesogenic groups connected to the core by an aliphatic $(CH_2)_n$ spacer (n = 10), it was shown that the type of packing in the LC state depends on the structure of the siloxane core. The cyclosiloxane core stabilizes the layer type of packing in the LC state, while the linear core in the absence of a chiral center in the mesogenic group creates conditions for the formation of the S_mC chiral phase with a maximum interlayer distance in the region of the $S_mA \rightleftharpoons S_mC$ transition. Irrespective of the structure of the siloxane center, the synthesized liquid-crystalline methylsiloxanes are characterized by a negative gradient of the temperature dependence of the interlayer spacing in the S_mA phase.

Experimental

¹H and ²⁹Si NMR spectra were recorded on a Bruker AMX-400 spectrometer at 20 °C in a CDCl₃—CCl₄ mixture and the IR spectra were measured on a Specord M-82 spectrometer in KBr pellets. The temperatures and enthalpies of phase transitions in the compounds were determined by differential scanning calorimetry on a Perkin-Elmer DSC-7 instrument at a heating rate of 2, 5, or 10 °C min⁻¹. The X-ray diffraction measurements were carried out on a Dron-3M diffractometer. Prior to the measurements, the samples were maintained at a constant temperature, to within ± 1 °C, for 20 min. The phase state was determined by optical polarization microscopy using an Axiolab Pol microscope (Zeiss). A Linkam controlled hot stage was used.

1.3-Bis[10-(4'-cyanobiphenyl-4-ylcarbonyloxy)decyl]tetramethyldisiloxane (1). A solution of chlorosilane 4 (1.9 g, 4.1 mmol) in 10 mL of an Et₂O-toluene mixture (1 : 1) was added over a period of 30 min to a mixture of H_2O (0.07 g, 3.9 mmol) and NaHCO₃ (0.34 g, 4.0 mmol) in 5 mL of Et_2O . The mixture was heated for 2 h on a water bath. The precipitate was filtered off and the upper layer was washed with water and dried with Na2SO4. The solvents were evaporated in vacuo. Fractional crystallization from hot EtOH and subsequent recrystallization from Et₂O gave 1.40 g (78.6%) of compound 1 with T_i 108-110 °C. Found (%): C, 72.70; H, 7.75; N, 3.20; Si, 6.78. C₅₂H₆₈N₂OSi₂. Calculated (%): C, 72.90; H, 7.24; N, 3.27; Si, 6.54. ¹H (δ: 0.02 (s, 6 H, MeSi); 0.48 (m, 2 H, CH₂Si); 1.28 (m, 12 H, $CH_2CH_2CH_2$; 1.39 (quint., 2 H, $CH_2CH_2CH_2$, $^3J =$ 7.6 Hz); 1.76 (quint, 2 H, C(O)CH₂CH₂, J = 7.6 Hz); 2.55 (t, 2 H, C(O)C \underline{H}_2 CH₂, ³J = 7.6 Hz); 7.15 (d, 2 H, C \underline{H} CCN, C_6H_4CN , ${}^3J = 8.4$ Hz); 7.53 (d, 2 H, C<u>H</u>CHCCN, C_6H_4CN , ${}^{3}J = 8.4$ Hz); 7.61 (d, 2 H, C<u>H</u>CHCO, ${}^{3}J = 8.4$ Hz); 7.68 (d, 2 H, CHCHCO, C₆H₄O, ${}^{3}J$ = 8.4 Hz). ²⁹Si NMR, δ: 7.15 (s, CH₂SiMe₂O).

2,8-Bis[10-(4'-cyanobiphenyl-4-yloxycarbonyl)decyl(dimethyl)silyloxy]-2,4,4,6,6,8,10,10,12,12-decamethylcyclohexasiloxane (2). A solution of chlorosilane 4 (0.16 g, 3.58 mmol) in 2 mL of toluene was placed into an argon-filled flask equipped with a reflux condenser, a dropping funnel, and a thermometer. At 20 °C, a mixture of cyclohexasiloxane 5 (0.06 g, 0.145 mmol) and 0.4 mL of Et₃N in 6 mL of toluene was added from a dropping funnel with stirring over a period of 0.5 h and the resulting mixture was heated for 12 h at 50 °C. The precipitate was filtered off, the solution was washed many times with water and dried with CaCl₂, and the solvent was evaporated. The residue was purified on a column with silica gel (elution with toluene—acetone, 5:1) to give 0.06 g (32%) of compound 2 with T_i 87–89 °C. Found (%): C, 57.60; H, 7.58; N, 2.05; Si, 17.61. C₆₂H₉₈N₂O₁₂Si₈. Calculated (%): C, 57.78; H, 7.65; N, 2.17; Si, 17.43. ¹H NMR, δ: 0.02, 0.04 (both s, 3 H each, cis and trans MeSiO₃); 0.06 (s, 24 H, Me₂SiO₂); 0.09 (s, 6 H, CH₂(CH₃)₂SiO); 0.51 (m, 2 H, CH₂Si); 1.28 (m, 12 H, $CH_2CH_2CH_2$); 1.40 (quint, 2 H, $CH_2CH_2CH_2$, ${}^{3}J = 7.6$ Hz); 1.76 (quint, 2 H, C(O)CH₂C<u>H₂</u>, J = 7.6 Hz); 2.56 (t, 2 H, $C(O)CH_2CH_2$, ${}^{3}J = 7.6$ Hz); 7.16 (d, 2 H, CHCCN, C₆H₄CN, ${}^{3}J = 8.4$ Hz); 7.55 (d, 2 H, C<u>H</u>CHCCN, C₆H₄CN, ${}^{3}J =$ 8.4 Hz); 7.64 (d, 2 H, C<u>H</u>CHCO, ${}^{3}J = 8.4$ Hz); 7.71 (d, 2 H, CHC<u>H</u>CO, C₆H₄, ${}^{3}J$ = 8.4 Hz). ²⁹Si NMR, δ : 7.92

(s, *trans* CH₂SiMe₂O); 7.27 (s, *cis* CH₂SiMe₂O) (intensity ratio, *trans* : *cis* \approx 3 : 1); -22.26 (s, Me₂SiO₂); -66.47 (s, *trans* MeSiO₃); -67.73 (s, *cis* MeSiO₃) (intensity ratio, *trans* : *cis* \approx 3 : 1)).

(4'-Cyanobiphenyl-4'-yl)undec-10-enoate (3) was prepared by a known procedure⁵ by acylation of 4-cyanobiphenyl-4-ol with undec-10-enoyl chloride (m.p. 49.5 °C)⁵ in dry THF in the presence of Et₃N. The yield of compound **3** was 80% after two recrystallizations from EtOH, m.p. 49.5 °C; the temperature of the nematic phase (N)->isotropic melt (I) transition, $T_{N\rightarrow I} = 75$ °C.

4'-Cyanobiphenyl-4-yl 11-(dimethylchlorosilyl)undecanoate (4). Ether 3 (3.5 g, 9.7 mmol), dimethylchlorosilane (2.2 mL, 10.0 mmol), and the Carsted catalyst PCO72 (Aldrich) (3 µL) were placed into an argon-filled tube equipped with a magnetic stirrer and a reflux condenser. The course of the reaction was monitored by ¹H NMR spectroscopy. The reaction mixture was heated on a water bath for 9 h at 60 °C and evacuated for 4 h at 3 Torr to give 4.4 g (95.0%) of crystalline compound 4, T_i 80 °C. Found (%): C, 68.20; H, 7.45; N, 2.90; Cl, 7.60; Si, 6.40. C₂₆H₃₄NClO₂Si. Calculated (%): C, 68.46; H, 7.51; N, 3.07; Cl, 7.78; Si, 6.14. IR, v/cm⁻¹: 725, 792, 833, 923, 1073, 1140, 1170, 1210, 1254, 1495, 1565, 1608, 1759. ¹H NMR, δ: 0.38 (s, 6 H, MeSi); 0.79 (m, 2 H, CH₂Si); 1.30 (m, 12 H, CH₂CH₂CH₂); 1.39 (quint, 2 H, $CH_2CH_2CH_2$, ${}^{3}J = 7.6$ Hz); 1.76 (quint, 2 H, $C(O)CH_2CH_2CH_2$, ${}^{3}J = 7.6$ Hz); 2.56 (t, 2 H, $C(O)CH_2CH_2$, ${}^{3}J = 7.6$ Hz), 7.17 (d, 2 H, C<u>H</u>CCN, C₆H₄CN, ${}^{3}J = 8.4$ Hz); 7.64 (d, 2 H, CHCHCO, J = 8.4 Hz); 7.70 (d, 2 H, CHCHCO, C_6H_4O , ${}^3J = 8.4$ Hz).

trans-2,8-Dihydroxy-2,4,4,6,6,8,10,10,12,12-decamethylcyclohexasiloxane (5) was synthesized by a known procedure,⁶ m.p. 97-98 °C. This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32585).

References

- 1. *Side Chain Liquid Crystal Polymers*, Ed. C. B. McArdle, Chapman and Hall, New York, 1989.
- 2. A. Kaeding and P. Zugenmaier, Liq. Cryst., 1998, 25, 449.
- 3. S. Aquilera and L. Bernal, Polymer Bull., 1984, 12, 383.
- H. Poths, E. Wischerhoff, R. Zentel, A. Schönfeld, G. Henn, and F. Kremer, *Liq. Cryst.*, 1995, 18, 811.
- 5. B. Krucke, M. Schlossarek, and H. Zaschke, *Acta Polymer.*, 1988, **39**, 607.
- N. N. Makarova and B. D Lavrukhin, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1985, 1114 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, 34, 1017 (Engl. Transl.)].
- B. D. Lavrukhin, N. N. Makarova, and I. M. Petrova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1460 [*Russ. Chem. Bull.*, 1993, 42 (Engl. Transl.)].
- S. G. Kostromin, and V. P. Shibaev, Vysokomolekulyar. soedineniya, Ser. A, 1999, 41, 1854 [Polym. Sci., Ser. A, 1999, 41 (Engl. Transl.)].
- S. G. Kostromin, V. V. Sinitsyn, R. V. Tal'roze, and V. P. Shibaev, *Vysokomolekulyar. soedineniya, Ser. A*, 1984, 26, 335 [*Polym. Sci. USSR, Ser. A*, 1984, 26 (Engl. Transl.)].

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