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Synthesis of new stereoregular 2,4,6,8-tetraphenylcyclotetrasiloxanes with mesogenic groups and the influence of spatial isomerism on the phase state of individual isomers and their mixtures

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The hydrosilylation of four isomers of tetra(dimethylsiloxy)tetraphenylcyclotetrasiloxane with (4´-cyanobiphenyl-4-yl)undec-10-enoate in the presence of a platinum catalyst afforded four liquid-crystalline stereoisomers of phenylcyclotetrasiloxane with mesogenic cyanobiphenyl groups. The reaction was performed for the first time. The influence of the spatial structure of the stereoisomers of tetraphenylcyclotetrasiloxanes with mesogenic groups on the formation of the liquid-crystalline state by thermooptical, X-ray diffraction, and calorimetric methods. The temperatures and enthalpies of phase transitions were determined, and their reversibility was shown. Differences in both the textures of melts formed on cooling and the phase state and in interplanar distances were found by optical microscopy and X-ray diffraction methods. Based on these data, the spatial structure of the isomers was concluded to affect the phase composition and type of packing in the liquid-crystalline state.

Key words: stereoregular organocyclosiloxanes, liquid-crystalline compounds, phase transitions, hydrosilylation.

Data on the influence of the structure of stereoisomers of cyclosiloxanes on the properties and type of packing in the liquid-crystalline (LC) state are lacking in literature. This is related, first of all, to the fact that methyl(hydrido)cyclosiloxanes used for the synthesis of LC compounds usually represent mixtures of isomers (regardless of the cycle size). The influence of the flexibility of the central core and spacer on the type of the forming LC phase has been revealed[1,2] to the present time by computer simulation. Weak interactions between mesogens, a sufficiently long spacer, and a flexible core favor the formation of nematic phases, whereas discotic molecules with a rigid core, a short spacer, and strongly interacting mesogenic groups form smectic or columnar phases. For example, studying methylcyclosiloxanes, the authors assumed the existence of several types of packing: cylindrical,[3—5] sheaf-like, and disk-like.[6] Since several stereoisomers of methylcyclosiloxanes can exist, the types of packing in the LC state for the *cis*-isomer and *r*-2,*t*-4,*t*-6,*t*-8-isomer should differ due to different intramolecular interactions of mesogenic groups. Unfortunately, none of the published works discusses the influence of the spatial structure of stereoisomers or the composition of a mixture of isomers of methylcyclosiloxanes on the type of packing in the LC state.[3—10]

We earlier[11] attempted to study this influence for cyclohexasiloxane. It was found that methylcyclosiloxanes enriched in the *trans*-isomer form different LC textures on cooling of the isotropic melt.[11] *cis*-Isomers of cyclotetra- and cyclohexasiloxanes with the same mesogenic groups also form different types of packing in the LC state.[12]

The purpose of this work is to synthesize structural isomers of cyclosiloxanes with a certain position of mesogenic cyanobiphenyl groups and to identify phase transitions and the type of packing in the LC state.

Results and Discussion

Synthesis of LC stereoisomers of tetraphenylcyclotetrasiloxanes with cyanobiphenyl mesogenic groups. Although many cyclic organosilicon compounds (including

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cyclosiloxanes) with reactive groups are known, the number of cyclosiloxanes promising for the isolation of individual stereoisomers is limited. For example, noncentrosymmetric isomers of cyclopentasiloxane do not crystallize, and for the cycles with six SiO units and more the number of possible isomers increases, which creates difficulties for their isolation.

To study the influence of the structure of the isomers on the LC phase type, we chose 2,4,6,8-tetrahydroxy(tetraphenyl)cyclotetrasiloxane (**1**) as the starting cyclosiloxane. It is known that this compound can exist as four stereoisomers,[13] providing thus a wide scope of intra- and intermolecular interactions (compared to LC methylcyclosiloxane[11] for which only two isomers are possible). However, in acidic media compound **1** usually isomerizes rapidly with equilibration. It is experimentally proved that the *cis*-isomer of compound **1** isomerizes in the presence of HCl to form all four isomers, which were separated by TLC, and their structure was confirmed by X-ray diffraction analysis of single crystals of tricyclosiloxane derivatives.[14] Note that TLC used for identifying isomers of compound **1** [14] is necessary but insufficient, because the difference in R_f for two isomers is very low. Therefore, to identify the isomers and isomeric composition of their mixtures, we used ^{29}Si NMR for the first time. According to the ^{29}Si NMR spectral data, the presence of 5—7% admixture of any isomer **1b—d** in compound **1a** can easily be determined. The TLC method with UV detection for a mixture of stereoisomers of compound **1a—d** under the specially found conditions turned out to be insufficiently sensitive despite a good difference in R_f. A comparison of the ^{29}Si NMR spectra of the reaction products of the hydrolytic polycondensation of trichlorophenylsilane obtained with changes in the pH of the medium and reaction time using a known procedure[13] shows that the isolated powders are characterized by different numbers of signals with different ratios between them. Stereoisomers **1a—d** were isolated by the fractional crystallization of compound **1**, and their purity was confirmed by TLC data, R_f, and chemical shifts in the ^{29}Si NMR spectra. The absolute chemical shifts (δ) in the ^{29}Si NMR spectra for stereoisomers **1a—d** change, depending on the concentration and composition of the isomers, but the difference (Δδ) between three singlets of isomers **1a,c,d** is constant (Table 1). The Δδ values in the ^{29}Si NMR spectra were necessary additional data to establish the composition of two stereoisomers with close R_f. To check the assignment of the chemical shifts in the ^{29}Si NMR spectra of stereoisomers of compound **1a—d**, we prepared solutions of pure isomers **1a**, **1b**, and **1d** in $(CD_3)_2CO$ and their mixtures in a ratio of 1.0 : 2.5 : 1.0. The obtained spectral data confirmed the assignment on Δδ. The chosen ratio is related to nonequivalent silicon atoms in isomer **1b**. The reconstructed ^{29}Si NMR spectrum of the isomers of compound **1a—d**, obtained by the successive addition of preliminarily prepared solutions of isomers **1a** + **1d** + **1b** with different percentage concentrations, is presented in Fig. 1. Thus, based on the number of signals, their integral intensity, and Δδ, one can determine the isomeric composition of the starting compounds used for the synthesis of LC phenylcyclosiloxanes.

Table 1. Chemical shifts in the ^{29}Si NMR spectra of stereoisomers of compounds **1a—d** and their mixtures

Compound	$\Delta\delta_{Si}$					
1a	−69.79	—	—	—	—	—
1b	—	—	−70.08	−70.12	−70.31	—
1c	—	−69.94	—	—	—	—
1d	—	—	—	—	—	−70.52
1a + **1d**	−69.65	—	—	—	—	−70.44
1a + **1b** + **1d**	−69.59	−69.95	−70.04	−70.20	−70.38*	—

* In mixture **1a** + **1b** + **1d**, one of the signals of compound **1b** coincides with the signal from isomer **1d**, which is confirmed by an increase in the integral intensity.

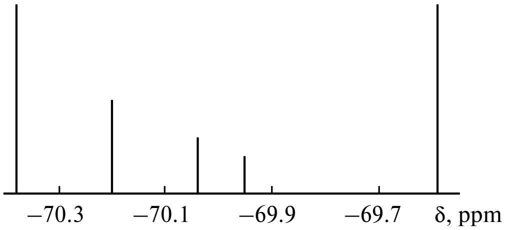


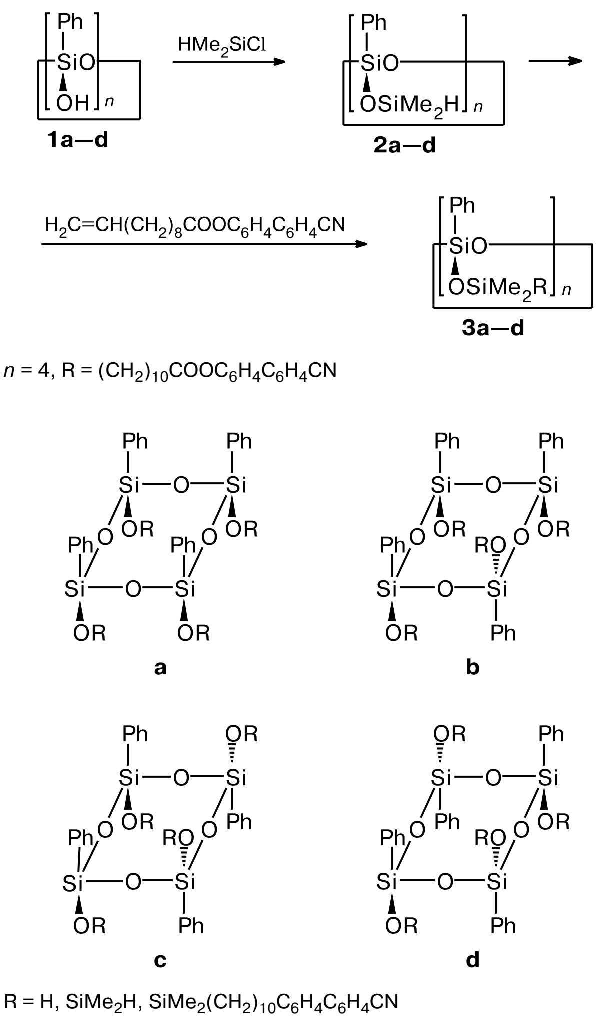
Fig. 1. Reconstruction of the ^{29}Si NMR spectrum of a mixture of spatial isomers of compound **1a—d**.

Isolated stereoisomers **1a—d** were used as the starting compounds for the synthesis of stereoisomers of tetraphenylcyclotetrasiloxanes with reactive hydrido(dimethyl)siloxy groups of compound **2a—d**. The use of the reactive hydridodimethylsiloxy groups in (tetraphenyl)cyclotetrasiloxane warrants the addition of unsaturated aliphatic moieties, which were added to mesogens by hydrosilylation in the presence of Karstedt´s catalyst at four Si—H bonds.[12] Tetrakis(dimethylsiloxy)(tetraphenyl)cyclotetrasiloxane stereoisomers of compound **2a—d** were obtained *via* Scheme 1.

The completion of the reaction was monitored by a decrease in the absorption band of the Si—OH bond at 3300—3700 cm^{-1} in the IR spectrum until it disappeared and by the disappearance of signals in the ^{29}Si NMR spectra at δ (−69.80)—(−70.60) ppm characteristic of the (OH)PhSiO units.

Isolated compounds **2a—d** were identified by ^{1}H and ^{29}Si NMR, IR spectroscopy, and elemental analysis. The chemical shifts in the ^{1}H and ^{29}Si NMR spectra of compounds **2a—d** and their mixtures are presented in Table 2. As can be seen, the ^{1}H NMR spectrum of isomer **2b**

Scheme 1



1a—d **2a—d** **3a—d**

$n = 4$, R = $(CH_2)_{10}COOC_6H_4C_6H_4CN$

R = H, $SiMe_2H$, $SiMe_2(CH_2)_{10}C_6H_4C_6H_4CN$

contains three septets of hydride protons and three signals of methyl protons, and the difference between the signals of the hydride protons in the HMe_2SiO group is $\Delta\delta$ = 0.07—0.28 and that for the methyl protons is 0.06—0.39 ppm. The constant $\Delta\delta$ value is observed for the corresponding protons of the HMe_2SiO groups in isomers **2a** and **2c,d**: 0.20 and 0.28 ppm for the hydride protons and 0.08 and 0.25 ppm for the methyl protons. In addition, as can be seen from the data in Table 2, isomer **2b** contains more than 3% isomers **1a** and **1d** and about 7% isomer **1c**. For isomer **2b** and the mixtures studied, the number of signals in the ^{29}Si NMR spectra corresponded to the calculated value but the ratio between integral intensities was not fulfilled rigidly (deviation ~15%). The IR spectra of compounds **2a—d** exhibited absorption bands at ν 791 cm^{-1} characteristic of the $Si(CH_3)_2$ groups; at ν_{as} 1063 cm^{-1} of stretching asymmetric vibrations of the Si—O—Si bond; at 760, 1131, and 1430 cm^{-1} of the Si—Ph bond; 897 and 1242 cm^{-1} of the Si—Me bond; 2132 cm^{-1} of the Si—H bond. Absorption bands for the SiOH groups (free and bonded through intra- and intermolecular hydrogen bonds) in a region of 3400—3690 cm^{-1} were absent.

Stereoisomers of tetraphenylcyclotetrasiloxanes with [4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethylsiloxy) mesogenic groups of compound **3a—d** were obtained by the hydrosilylation of compounds **2a—d** with (4´-cyanobiphenyl-4-yl)undec-10-enoate (**4**) in excess **4** in the presence of Karstedt´s catalyst *via* Scheme 1. The completion of the reaction was monitored by IR spectroscopy by a decrease in the intensity of the band at 2138 cm^{-1}, characteristic of the Si—H bond, until the band disappeared.

Compounds **3a—d** were isolated by the preliminary removal of platinum using column chromatography on silica gel followed by separation using preparative TLC on Silufol plates (size 20×20 cm) (eluent toluene—hexane—ethyl acetate) or triple precipitation from a benzene—methanol solution.

Liquid-crystalline compounds **3a—d** were identified from the data of ^1H and ^{29}Si NMR, IR spectroscopy, elemental analysis, and TLC. The chemical shifts in the ^1H and ^{29}Si NMR spectra of compounds **3a—d**

Table 2. Chemical shifts (ppm) in the ^1H and ^{29}Si NMR spectra of compounds **2a—d** and their mixtures

Compound	δ_H												δ_{Si}	
	$\underline{H}Me_2Si$						$H\underline{Me}_2Si$						HMe_2Si	$PhSiO_{3/2}$
2a			4.88 m						0.30				−3.92	−78.35
2b	4.90;	4.84;	4.77;	4.70;	4.62;	4.56	0.32;	0.24;	0.16;	0.09;	−0.01;	−0.07	−3.84	−78.02; −78.20;
	(>3.0)	(22.0)	(44.0)	(7.0%)	(>3.0)	(21.0)	>3.0;	22.0;	45.0;	7.0;	>3.0;	20.0		−78.34
	a	**b**	**b**	**c**	**d**	**b**	**a**	**b**	**b**	**c**	**d**	**b**		
2c				4.64 m					0.08				−3.86	−78.23
2d				4.59 m					−0.03				−3.78	−78.23
2a+2b	4.90;	4.84;	4.76;	—	—	4.56	0.31;	0.23;	0.16;	−0.08	—	—	−3.85	−78.02; −78.19;
	(73.0)	(7.0)	(14.0)			(6.0)	(70.0);	(12.0);	(26.0);	(10.0)			−3.91	−78.28; −78.34
	a	**b**	**b**			**b**	**a**	**b**	**b**	**b**			−3.95	
2a+2d	4.89;			4.60			0.31;			−0.03			—	—

Table 3. Chemical shifts (ppm) in the ^{1}H and ^{29}Si NMR spectra of compounds **3a—d** and their mixtures

Compound	δ_H						δ_{Si}							
							Me_2SiO				$PhSiO_{3/2}$			
3a			0.17					10.73				−79.70		
3b	0.160;	0.085;	0.007;	0.068;	-0.160;	-0.203		10.27			−79.50;	−79.63;	−79.73	
	4.0	23.0	41.0	8.0	3.0	21.0					**b**	**b**	**b**	
	a	**b**	**b**	**c**	**d**	**b**								
3c			0.07 s					10.50				−79.50		
3d			−0.15 s					10.27				−79.63		
3a+3b	0.24;	0.19;	0.08;	—	—	−0.126	10.766;	10.716;	10.533;	10.30	−79.34;	−79.43;	−79.54;	−79.58
	a	**b**	**b**			**b**	68.0	10.0	22.0	8.0	**b**	**b**	**a**	**b**
							a	**b**	**b**	**b**				
3a+3d	0.18;	—	—	—	−0.15	—	10.30;	—	—	10.70	—	−79.53;	—	−79.60
							d			**a**		**a**		**d**
3a+3c+3d	0.18;	0.07;	−0.15	—	—	—	10.27;	10.46;	—	10.69;	—	−79.42;	79.51;	−79.60
	a	**c**	**d**				**d**	**c**		**a**		**c**	**a**	**d**

are presented in Table 3. The ^{29}Si NMR spectra of the isomers of compounds **3a—d** contain signals at (+10.76)—(+10.27) ppm and (−79.34)—(−79.63) ppm characteristic of the $—CH_2Me_2SiO—$ and $PhSiO_{3/2}$ moieties. The absolute chemical shifts of protons in compounds **3a—d** depend insignificantly on their concentration in the solution in a deuterated solvent. The data for mixtures of isomers **3a** + **3b** и **3a** + **3d** are also presented in Table 3. They show that the ^{1}H and ^{29}Si NMR spectra contain a necessary number of signals and $\Delta\delta$ between the signals is constant (both between the singlets for stereoisomers **3a**,**c**,**d** and between the signals for isomer **3b**). Thus, it can be stated that the presence of any isomer in the obtained mixture of LC compounds **3** can easily be established from the values of chemical shifts and their difference ($\Delta\delta$) in the ^{1}H and ^{29}Si NMR spectra.

The IR spectra of compounds **3a—d** exhibit absorption bands characteristic of the $Si(CH_3)_2$ group (ν 842 cm^{-1}), $(CH_2)O—C$ bond (1178 cm^{-1}), C_6H_4 group (1492, 1611 cm^{-1}), C=O bond (1758 cm^{-1}), and C≡N group at C_6H_4 (2234 cm^{-1}). For compounds **3a—d**, bands corresponding to stretching asymmetric and symmetric vibrations of the C—H bonds of the methyl and methylene groups are observed at ν 2845—2920 cm^{-1}. Bands characteristic of asymmetric and symmetric bending vibrations of these groups are present at ν 1460 and 1390 cm^{-1}.

Thus, a comparison of the ^{29}Si NMR spectra for three series of isomers **a—d** of compounds **1—3** shows that the maximum difference $\Delta\delta$ between the signals of isomers of compounds **1a—d** achieves 0.79 ppm, while for isomers of compounds **2a—d** $\Delta\delta$ is 0.30, and for compounds **3a—d** it is 0.20 ppm. The minimum $\Delta\delta$ value between isomers of compounds **1—3** ranges from 0.40 for isomers **1a** and **1c** to 0.05 ppm for isomers **3b** and **3c**, *i.e.*, the shielding effects of the substituents equalize with an increase in the size of the organic substituent at the silicon atom in cyclosiloxane.

Some properties of LC stereoisomers of compounds 3a—d. Pure stereoisomers **3a—d** and their mixtures **3a** + **3b**, **3a** + **3d** were characterized by differential scanning calorimetry (DSC), optical microscopy, and X-ray diffraction analysis. On cooling from a melt, the DSC curves of almost all stereoisomers, except for isomer **3a**, exhibit one pronounced exotherm corresponding to the transition from the isotropic (I) to LC state. The resulting characteristic are collected in Table 4. The heat of formation of the LC state (isotropization) is 7—11 J g^{-1}, which is characteristic of this transition. The highest enthalpy of phase transition $\Delta H_{LC/I}$ was observed for *cis*-isomer **3a**, which is likely related to a stronger cooperative character of both intra- and intermolecular interactions between the mesogenic groups. This is also indicated by an additional LC—crystal transition in compound **3a**. However,

Table 4. Temperatures and enthalpies of phase transitions of LC compounds **3a—d** and their mixtures

Compound	DSC			Optical microscopy	
	$T_{g.t}$	$T_{LC/I}$	$\Delta H_{LC/I}$ /J g^{-1}	$T_{LC/I}$	T*
	°C			°C	
3a**	−4	66	11.5	77	62
3b	−2	67	6.3	53	30
3c	−4	78	10.0	78	65
3d	−2	77	7.0	79	72
3a+3b	−9	74	6.6	78	60
3a+3d	—	—	—	85	70

* Temperature at which texture formation is completed.

** The temperature of the phase transition $T_{C/LC}$ for compound **3a** is 58 °C.

note that the glass transition ($T_{g.t}$) and isotropization (T_I) temperatures of compounds **3a**—**3d** and their mixtures **3a** + **3b** and **3a** + **3d** are close.

It is found by optical microscopy that the textures formed on cooling of an isotropic melt of compounds **3a**—**d** and their mixtures **3a** + **3b** and **3a** + **3d** are different. The textures of LC compounds **3a**—**d** are presented in Fig. 2. Compounds **3c**,**d** form primary billets in the form of rods (see Fig. 2, *c*, *d*), whereas compounds **3a**,**b** and mixtures **3a** + **3b** and **3a** + **3d** form pseudofocal-conic or drop-like textures over the whole field (see Fig. 2, *a*, *b*). Similar textures were observed for several compounds with different architectures of the center forming different LC phases: for example, hexahydro-1,3,5-triazine derivatives form a columnar phase,[14] a trisubstituted 1,4,7-triazacyclononane metal complex with carbonyl groups form a columnar phase of the pyramid-like type,[15] and compounds with a tricycloquinazoline core form a discotic phase.[16] The filling of the whole field with the texture in compounds **3a**—**d** depends on the cooling rate and exposure time in an isothermal regime. The crystal structure recovered slowly only in isomer **3a**, and other isomers did not crystallize for a month.

The crystal and LC structures of the compounds under study were characterized by X-ray diffraction analysis. It was found that the three-dimensional crystal range develops, in fact, in compound **3a**, which is indicated by many narrow reflections in its high-angle X-ray diffraction pattern at room temperature (Fig. 3). The diffraction patterns of samples **3b** and **3d** exhibit only two broad diffuse haloes with maxima at 8.4° and 19.9°. As established by molecular simulation, the first maximum can be related to the mutual packing of the cyclosiloxane rings, and the second maximum is probably associated with the packing of the mesogenic groups.

The X-ray diffraction pattern of a mixture of compounds **3a** + **3b** contains weak crystalline reflections, whose positions coincide with those of reflections of sample **3a** (these reflections are emphasized by vertical lines in Fig. 3) against the amorphous halo characteristic of sample **3b**. Thus, we can conclude that this sample has no complete mixing of stereoisomers at the molecular

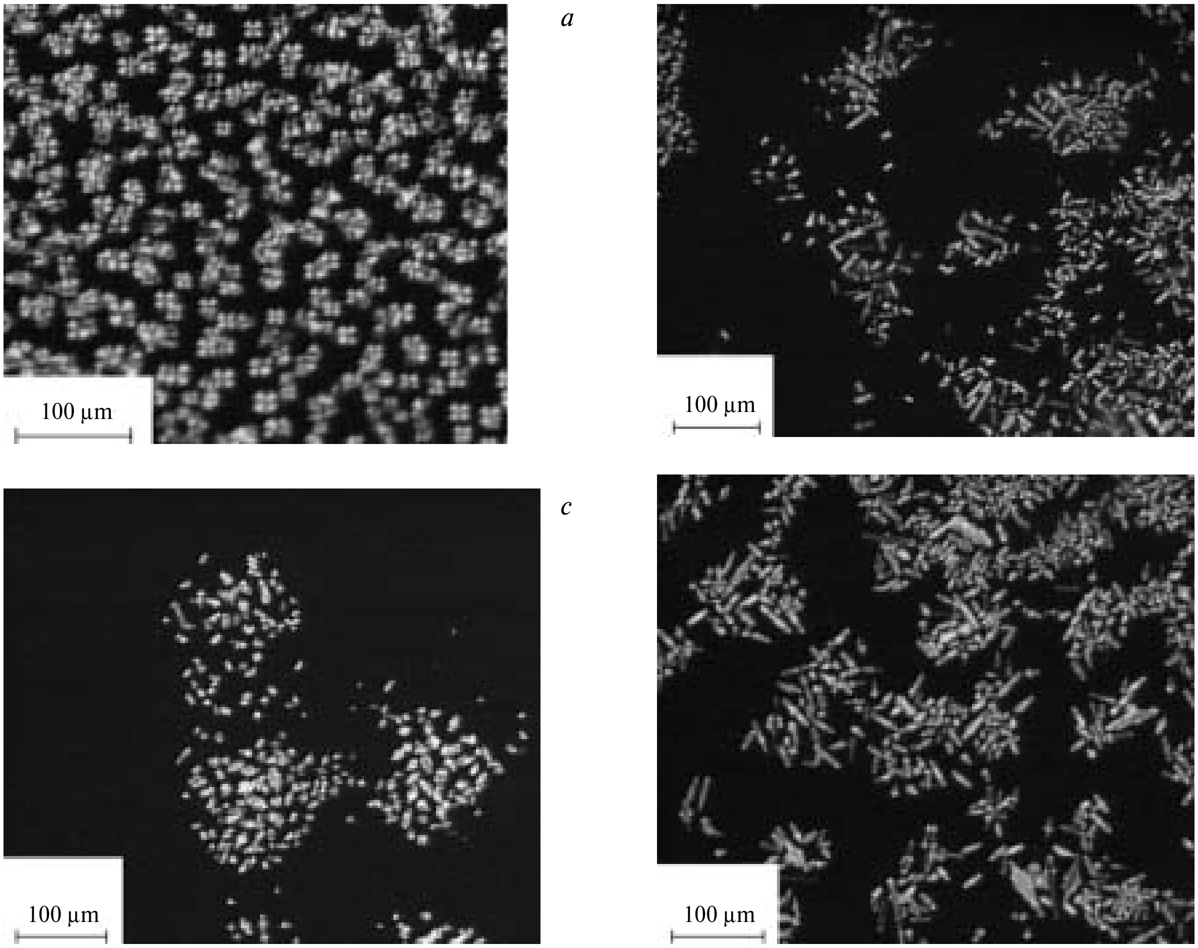


Fig. 2. Optical microphotographs of the textures of compounds **3a**—**d** (cooling rate 1.0 deg min^{-1} from 80 °C): for **3a** at 77.5 °C (*a*), **3b** at 53.05 °C (*b*), **3c** at 78.5 °C (*c*), and **3d** at 78.5 °C (*d*).

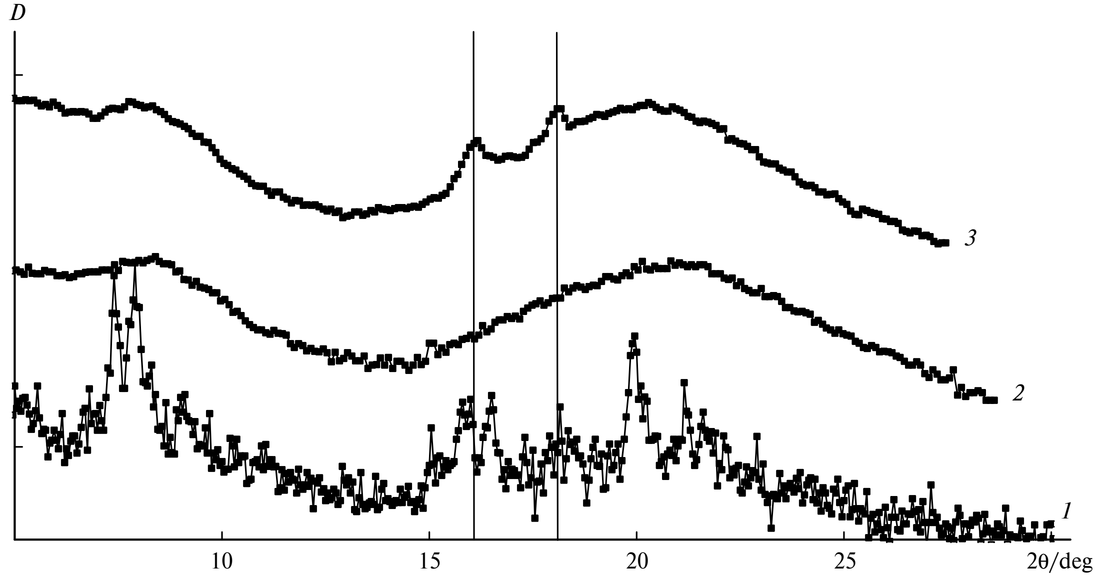


Fig. 3. X-ray diffraction pattern of isomer **3a** (*1*) and the densitograms of isomer **3b** (*2*) and mixture **3a** + **3b** (*3*).

level but their microphase separation occurs. At the same time, several crystalline reflections near the maxima of the amorphous haloes are not observed because of a high intensity of the latter and a nonlinear dependence of the blackening density on the intensity in this region. Meanwhile, a low crystallinity of compound **3a** and its comparatively low fraction in the mixture do not allow one to identify all reflections of the crystalline phase in the X-ray diffraction pattern of the mixture.

For low-angle scattering, two orders of reflections corresponding to a layered structure with a layer size of 50.9 Å were observed for all samples, and only for crystalline sample **3a** both peaks are slightly shifted toward high angles and correspond (at room temperature) to an interplanar distance of 47.7 Å. According to the results of molecular simulation, cyclotetrasiloxane stereoisomers exhibit an almost completely rectified cylindrical conformation of lateral substituents, which form an angle close to 90° with the siloxane ring plane. The length of the lateral substituents is 26.6 Å, which is approximately half an interlayer distance. The mutual ordering of the terminal cyanobiphenyl moieties does not allow the mesogenic groups of one molecule to penetrate into the space occupied by the terminal groups of another molecule. Moreover, an ordered arrangement of the siloxane rings of stereoisomers **3b—d** in a direction perpendicular to their plane is impossible because of the requirement of uniform filling of the space: these rings should be shifted relatively to each other. The layer represents a "double" brush schematically shown in Fig. 4, *b*. Crystallization related to the ordered packing of long substituents is possible only for compound **3a** (see Fig. 4, *a*), which is observed in fact.

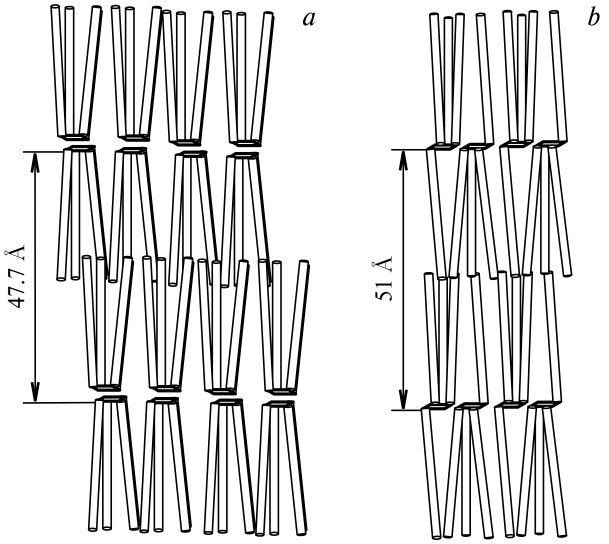


Fig. 4. Scheme of the structures of samples **3a** (*a*) and **3b** (*b*).

A special attention was given to the temperature behavior of the samples of the LC phase (Fig. 5). The temperature increase to the isotropization temperature (and higher than T_i by 10—15 °C) increases both interplanar distances (*d*) due to an increase in the mobility and the energy of the thermal motion of both siloxane rings and lateral substituents with the mesogenic groups. The isotropization region is characterized by a change in the slope of the *d*(*T*) plot. For instance, in sample **3d**, the thermal expansion coefficient for a distance caused by packing of the cyclosiloxane rings is $\sim 1 \cdot 10^{-3}$ K^{-1} in the LC state and $1.8 \cdot 10^{-3}$ K^{-1} in the isotropic state. The thermal expansion coefficient of the second maximum is much lower ($6.5 \cdot 10^{-4}$ K^{-1}) and changes weakly upon isotropization. In compound **3b**, the shift of the diffuse haloes with the temperature increase is much less pro-

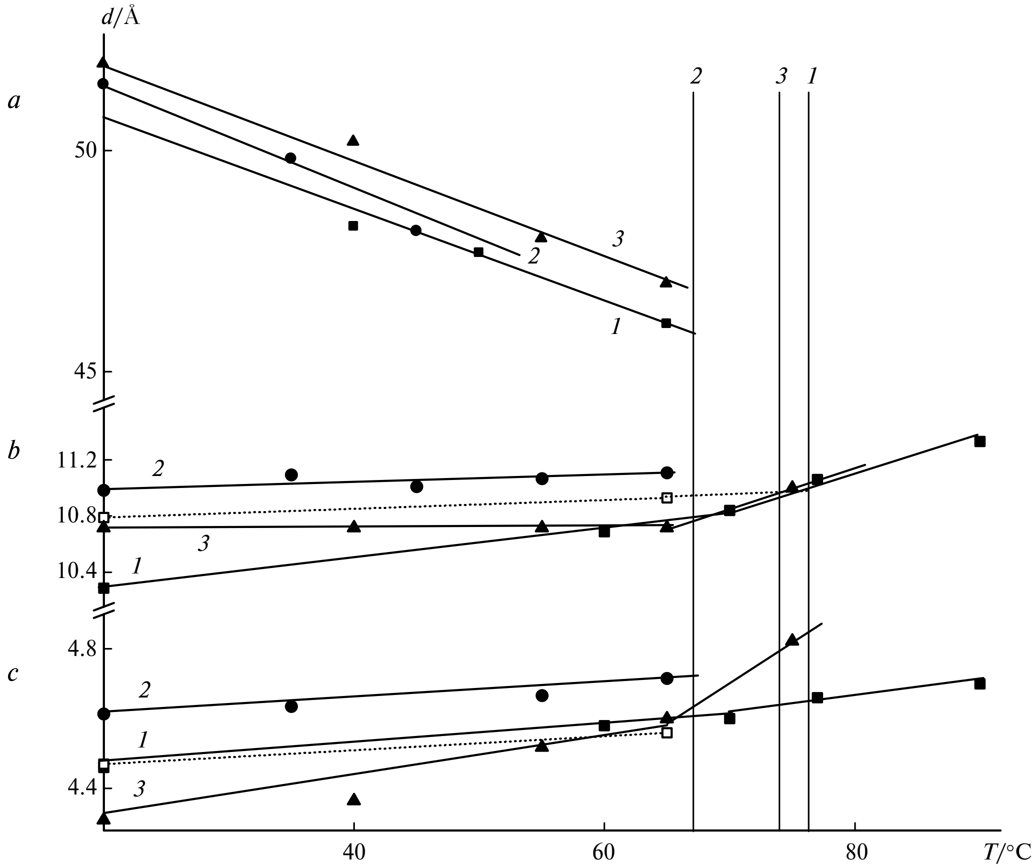


Fig. 5. Temperature dependences of the interplanar distances corresponding to the low-angle peak (*a*) and the first (*b*) and second (*c*) amorphous haloes in the samples of **3a** (*1*), **3b** (*2*), and mixture **3a** + **3b** (*3*). Vertical lines show the isotropization temperatures of the corresponding samples, and the dotted line marks the temperature dependences of the low-angle peak and amorphous haloes for cooling isomer **3d**.

nounced ($d_1 = 2.8 \cdot 10^{-4}$ K^{-1}, $d_2 = 4.8 \cdot 10^{-4}$ K^{-1}). On heating of all compounds, the low-angle maximum shifts toward high angles with a thermal expansion coefficient of ~$2 \cdot 10^{-3}$ K^{-1}, because an increase in the mobility of the siloxane rings and mesogenic groups results in an increase in the free volume accessible for substituents, an increase in the number of *gauche*-conformers in them, and, correspondingly, a decrease in the interlayer distance. Different interactions of the mesogenic groups in isomers **3b—d** and their mixtures result in individual features of the thermal behavior of the layered structure that formed (see Fig. 5). It is of interest that the intensity of the low-angle reflection increases on heating up to 50°C due to annealing and then decreases. The low-angle maximum disappears when the isotropization temperature is achieved.

Thus, based on the results of studying the physicochemical behavior of newly synthesized four stereoisomers of phenylcyclotetrasiloxanes with mesogenic groups, we demonstrated the role of the orientation of the mesogenic groups as a decisive factor in the ability of molecules to crystallize and form different types of LC phases. This conclusion is based on the comparison of the low-angle diffraction patterns and optical textures of the stereoisomers and their mixtures, which shows that the type of packing inherent in each isomer is retained during the formation of the LC state.

Experimental

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AMX-400 spectrometer at 20 °C in a solution of $CDCl_3$+CCl_4 or acetone-d_6. IR spectra were obtained on a Specord M-82 spectrometer (KBr pellets served as samples). Temperatures and enthalpies of phase transitions of compounds were determined by differential scanning calorimetry on a Perkin—Elmer DSC-7 instrument with a heating rate of 10 deg min^{-1}.

The structures of samples were studied by the X-ray diffraction method using high- and low-angle procedures. To analyze the general pattern of X-ray scattering, X-ray patterns were obtained on a planar film-holder using an URS-2 setup with point beam collimation (CuKα radiation, Ni filter). Temperature studies were carried out on a DRON-3 instrument using CuKα radiation and a focusing quartz monochromator. Before experiments, the temperature of samples was maintained constant for

20 min with an accuracy of ±0.1 °C. The X-ray low-angle scattering intensity was measured on a KRM-1 setup with slit-like beam collimation and a resolution of 100 nm (CuKα radiation, Ni filter). The phase state of samples was determined by polarization microscopy using an Axiolab Pol microscope (Zeiss) and a heating stage with a Linkam controlling system. Samples were prepared as thin films between two glasses.

Silufol plates (size 20×20 cm) (Kavalier) on sheet aluminum foils covered with Silpearl (broad-pore silica gel according to Pitri) with a UV-254 luminescent indicator were used in TLC. A toluene—hexane—ethyl acetate mixture prepared in different ratios was used as an eluent. Column chromatography was performed on standard Kieselgel 60 phases (0.063—0.100 mm) (Merck).

Karstedt´s catalyst PC072 ((*O*)-1,3-divinyl-1,1,3,3-tetramethyldisiloxaneplatinum complex) (Aldrich) was used in hydrosilylation.

4´-Cyanobiphenyl-4-yl undec-10-enoate (4) was synthesized according to a previously described procedure[12] by the acylation of 4'-cyanobiphenyl-4-ol with undec-10-enoyl chloride in anhydrous THF in the presence of Et_3N. The yield was 80% after double recrystallization from EtOH, m.p. 49.5 °C, T_{N-I} = 75.0 °C (T_{N-I} is the transition temperature of the nematic to isotropic phase).

***cis*-Tetrahydroxy(tetraphenyl)cyclotetrasiloxane (1a)** was synthesized by a previously described procedure,[12] m.p. 178—180 °C. ^{29}Si NMR (acetone-d_6), δ: –69.79 (s).

***r*-2,*t*-4,*t*-6,*t*-8-Tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane (1b)** was synthesized by the fractional recrystallization of a mixture of compounds **1b** + **1c** + **1d** from a toluene—Et_2O (1.0 : 1.0) solution with a purity higher than 87.0%. M.p. 174—176 °C. ^{29}Si NMR (acetone-d_6), δ: –70.05, –70.20, –70.35 (all s, ratio 1 : 1 : 2); the spectrum contained signals assigned to **1a** (~3%), **1d**, and **1c** (7%).

***r*-2,*c*-4,*t*-6,*t*-8-Tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane (1c)** was synthesized by the fractional recrystallization of a mixture of compounds **1b** + **1c** + **1d** in a ratio of 0.15 : 0.50 : 0.35 from a toluene—Et_2O (1.0 : 0.25) solution. M.p. 219—222 °C. ^{29}Si NMR (acetone-d_6), δ: –69.95(s).

***r*-2,*t*-4,*c*-6,*t*-8-Tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane (1d)** was synthesized by the fractional recrystallization of a mixture of compounds **1b** + **1c** + **1d** in a ratio of 0.40 : 0.15 : 0.45 from a toluene—Et_2O (1.0 : 1.0) solution. M.p. 248—250 °C. ^{29}Si NMR (acetone-d_6), δ: –70.51 (s).

***cis*-Tetrakis(dimethylsiloxy)tetraphenylcyclotetrasiloxane (2a).** Dimethylchlorosilane (1.50 g, 15.5 mmol) in anhydrous Et_2O (10 mL) was placed in a three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a magnetic stirrer. Compound **1a** (0.92 g, 2.17 mmol) and pyridine (1.02 g, 12.0 mmol) in anhydrous Et_2O (40 mL) were added to the reaction mixture from a dropping funnel. The mixture was stirred for 3 h at 20 °C and for 5 h at 34 °C. In the IR spectrum of the reaction products, the absorption band characteristic of the Si—OH bond at 3400—3700 cm^{-1} was absent. The precipitate was filtered off, Et_2O was distilled off, and fractional distillation gave 0.80 g (61.0%) of compound **2a**, b.p. 175—180 °C ($6 \cdot 10^{-3}$ Torr). Found (%): C, 48.78; H, 6.11; Si, 28.48. $C_{32}H_{48}O_8Si_8$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR (KBr), ν/cm^{-1}: 808, 846 ($SiMe_2$); 909 (Si—Me); 1068 (SiOSi); 1136 (Si—Ph); 1260 (Si—Me); 1430 (Ph—Si); 2143 (Si—H); 2964 (Me); 3050, 3070 (Ph). ^{1}H NMR, δ: 0.32 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 4.91 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 7.13 (t, 2 H, *m*-CH, ^3J = 8.0 Hz); 7.29 (t, 1 H, *p*-CH, ^3J = 8.0 Hz); 7.33 (d, 2 H, *o*-CH, ^3J = 8.0 Hz). ^{29}Si NMR, δ: –3.92 (s, 2 Si, (HMe_2SiO); –78.35 (s, $PhSiO_{3/2}$).

***r*-2,*t*-4,*t*-6,*t*-8-Tetrakis(dimethylsiloxy)-2,4,6,8-tetraphenylcyclotetrasiloxane (2b)** was synthesized according to a procedure similar to that for compound **2a**. Compound **1b** (0.25 g, 0.45 mmol), C_5H_5N (0.45 g, 5.69 mmol), and DMAP (0.003 g) in Et_2O (5.0 mL) were added for 45 min to dimethylchlorosilane Me_2SiHCl (0.49 g, 5.2 mmol). The reaction mixture was stirred for 4 h. Compound **2b** was obtained in 92.0% yield (0.33 g). Found (%): C, 48.98; H, 6.01; Si, 28.20. $C_{32}H_{48}O_8Si_8$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR (KBr), ν/cm^{-1}: 808, 846 ($SiMe_2$); 909 (Si—Me); 1068 (SiOSi); 1136 (Si—Ph); 1260 (Si—Me); 1430 (Ph—Si); 2143 (Si—H); 2964 (Me); 3050, 3070 (Ph). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: –0.07 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 0.16 (d, 12 H, $H(C\underline{H}_3)_2SiO$,^3J = 2.8 Hz); 0.24 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 0.32 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz) (3.0% **1a**); 4.56 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 4.70 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz) (7.0% **2c**); 4.77 (sept, 2 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 4.84 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 4.91 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 7.13 (t, 2 H, *m*-CH, ^3J = 8.0 Hz); 7.29 (t, 1 H, *p*-CH, ^3J = 8.0 Hz); 7.33 (d, 2 H, *o*-CH, ^3J = 8.0 Hz). ^{29}Si NMR ($CDCl_3$ + CCl_4), δ: –3.84 (s, 2 Si, HMe_2SiO); –78.02, –78.20, –78.34 (ratio of intensities 1 : 2 : 1) (s, $PhSiO_{3/2}$).

***r*-2,*c*-4,*t*-6,*t*-8-Tetrakis(dimethylsiloxy)-2,4,6,8-tetraphenylcyclotetrasiloxane (2c)** was synthesized similarly to compound **2a**. A solution of compound **1c** (0.10 g, 0.19 mmol), C_5H_5N (0.08 g, 1.05 mmol), and DMAP (0.003 g) in Et_2O (4.0 mL) was added to dimethylchlorosilane (0.41 g, 4.4 mmol). Compound **2c** was obtained in 93.0% yield (0.11 g). Found (%): C, 48.78; H, 6.01; Si, 28.20. $C_{32}H_{48}O_8Si_8$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR (KBr), ν/cm^{-1}: 808, 846 ($SiMe_2$); 900 (Si—Me); 1070 (SiOSi); 1128 (Si—Ph); 1265 (Si—Me); 1433 (Ph—Si); 2141 (Si—H); 2960 (Me); 3050, 3070 (Ph). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: 0.08 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 4.64 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 7.15 (t, 2 H, *m*-CH, ^3J = 8.0 Hz); 7.33 (t, 1 H, *p*-CH, ^3J = 8.0 Hz); 7.36 (d, 2 H, *o*-CH, ^3J = 8.0 Hz). ^{29}Si NMR ($CDCl_3$ + CCl_4), δ: –3.86 (s, 2 Si, (HMe_2SiO); –78.23 (s, $PhSiO_{3/2}$).

***r*-2,*t*-4,*c*-6,*t*-8-Tetrakis(dimethylsiloxy)-2,4,6,8-tetraphenylcyclotetrasiloxane (2d)** was synthesized similarly to compound **2a**. A solution of compound **1d** (0.30 g, 0.54 mmol), C_5H_5N (0.63 g, 8.00 mmol), and DMAP (0.003 g) in Et_2O (9.0 mL) was added to dimethylchlorosilane (0.51 g, 5.40 mmol). Compound **2d** was obtained in 92.0% yield (0.39 g). Found (%): C, 48.78; H, 6.01; Si, 28.45. $C_{32}H_{48}O_8Si_8$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR (KBr), ν/cm^{-1}: 808, 846 ($SiMe_2$); 909 (Si—Me); 1068 (SiOSi); 1136 (Si—Ph); 1260 (Si—Me); 1430 (Ph—Si); 2143 (Si—H); 2964 (Me); 3050, 3070 (Ph). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: –0.03 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 4.59 (sept, 1 H, $\underline{H}Me_2SiO$, ^3J = 2.8 Hz); 7.13 (t, 2 H, *m*-CH, ^3J = 8.0 Hz); 7.29 (t, 1 H, *p*-CH, ^3J = 8.0 Hz); 7.33 (d, 2 H, *o*-CH, ^3J = 8.0 Hz). ^{29}Si NMR ($CDCl_3$ + CCl_4), δ: –3.78 (s, 2 Si, (HMe_2SiO); –78.23 (s, $PhSiO_{3/2}$).

***cis*-Tetrakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethyl)siloxy}(tetraphenyl)cyclotetrasiloxane (3a).** Compound **2a** (0.42 g, 0.36 mmol) and 4´-cyanobiphenyl-4-yl undec-10-enoate (0.94 g, 2.60 mmol) in toluene (2.7 mL) were placed in a three-necked flask preliminarily filled with argon and equipped with a reflux condenser, a thermometer, a magnetic stirrer, and a dropping funnel. Karstedt´s catalyst PC072 (Aldrich) (5 μL, recalculated to [Pt] = $1.56 \cdot 10^{-6}$ mol L^{-1}) was added with stirring. The reaction mixture was heated for 5 h at 65 °C. The reaction course was monitored by IR spectroscopy: the absorption band characteristic of the Si—H bond at 2138 cm^{-1} disappeared. Platinum was removed from a toluene solution of the reaction products (5%) on a column packed with silica gel (column height 2 cm, diameter 5 mm). The solvent was distilled off. Compound **3a** was purified by precipitation from a benzene—methanol solution. Compound **3a** was obtained in 21.0% yield (0.25 g). Found (%): C, 68.48; H, 7.04; N, 2.23, Si, 10.30. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H, 7.04; N, 2.51; Si, 10.07.

IR (KBr), ν/cm^{-1}: 791, 842 ($SiMe_2$); 915 (Si—Me); 1062 (SiOSi); 1131 (Si—Ph); 1178 $CO(CH_2)$; 1255 (Si—Me); 1379, 1430 (Ph—Si); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C=N); 2851, 2925 (CH_2) 3020, 3050, 3072 (Ph, C_6H_4). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: 0.17 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.57 (m, 2 H, CH_2SiO); 1.29 (quint, 2 H, CH_2—$C\underline{H}_2$—CH_2); 1.41 (m, 6 H, CH_2—$C\underline{H}_2$—CH_2); 1.75 (quint, 2 H, C(O)—CH_2—$C\underline{H}_2$, J = 7.6 Hz); 2.55 (t, 2 H, C(O)—$C\underline{H}_2$, J = 7.6 Hz); 7.04 (t, 2 H, *m*-CH, ^3J = 7.2; 7.6 Hz); 7.16 (d, 2 H, C$\underline{H}$—C—CN, J = 8.6 Hz); 7.23 (t, 1 H, *p*-CH, Ph, J = 7.2 Hz); 7.26 (d, 2 H, *o*-CH, Ph, J = 6.8 Hz); 7.55 (d, 2 H, C$\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 8.6 Hz); 7.63 (d, 2 H, C$\underline{H}$—CH—C—O, ^3J = 8.4 Hz); 7.70 (d, 2 H, CH—C$\underline{H}$—C—O, C_6H_4O, J = 8.4 Hz). ^{29}Si NMR (400 MHz, $CDCl_3$ + CCl_4), δ: 10.72 (s, CH_2Me_2SiO), −79.70 (s, $PhSiO_{3/2}$).

***r*-2,*t*-4,*t*-6,*t*-8-Tetrakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethylsiloxy)}-2,4,6,8-(tetraphenyl)cyclotetrasiloxane (3b).** Compound **3b** was synthesized similarly to compound **3a**. Karstedt´s catalyst (0.4 μL) was added to a mixture of compound **2b** (0.08 g, 0.10 mmol) and 4´-cyanobiphenyl-4-yl undec-10-enoate (0.16 g, 0.45 mmol) in anhydrous toluene (0.60 mL), and the resulting mixture was heated for 1 h at 55 °C. The reaction was not completed, and an additional portion of Karstedt´s catalyst (4.0 μL, calculated to [Pt] = $1.32 \cdot 10^{-6}$ mol L^{-1}) was introduced. After 30 min, the absorption band characteristic of the Si—H bond was absent from the IR spectrum. Compound **3b** was isolated by preparative TLC (eluent toluene—hexane—AcOEt, 0.80 : 0.20 : 0.05) in 18.0% yield (0.04 g). Found (%): C, 68.48; H, 7.04; N, 2.23, Si, 10.30. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H,7.04; N, 2.51; Si, 10.07.

IR (KBr), ν/cm^{-1}: 791, 842 ($SiMe_2$); 915 (Si—Me); 1062 (SiOSi); 1131 (Si—Ph); 1178 $CO(CH_2)$; 1255 (Si—Me); 1379, 1430 (Ph—Si); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C=N); 2851, 2925 (CH_2) 3020, 3050, 3072 (Ph, C_6H_4). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: −0.20 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.008 (dd, 12 H, $(C\underline{H}_3)_2SiO$); 0.08 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.54 (m, 2 H, H_2SiO); 1.20 (quint, 2 H, CH_2—$C\underline{H}_2$—CH_2); 1.39 (m, 6 H, CH_2—$C\underline{H}_2$—CH_2); 1.72 (quint, 2 H, C(O)—CH_2—$C\underline{H}_2$, J = 7.6 Hz); 2.52 (t, 2 H, C(O)—$C\underline{H}_2$, J = 7.6 Hz); 7.10 (t, 1 H, *p*-CH, ^3J = 7.4 Hz); 7.15 (d, 2 H, *m*-CH, Ph)*; 7.16 (d, 2 H, C$\underline{H}$—C—CN, J = 8.8 Hz); 7.44 (d, 2 H, *o*-CH, Ph, ^3J = 7.6 Hz); 7.54 (d, 2 H, C$\underline{H}$—CH—N, C_6H_4CN, ^3J = 8.8 Hz); 7.62 (d, 2 H, C$\underline{H}$—CH—C—O, ^3J = 8.0 Hz); 7.70 (d, 2 H, CH—C$\underline{H}$—C—O, C_6H_4CO, J = 8.0 Hz). ^{29}Si NMR ($CDCl_3$ + CCl_4), δ: 10.27 (s, CH_2Me_2SiO), −79.50, −79.63, −79.70 (all s, $PhSiO_{3/2}$).

***r*-2,c-4,*t*-6,*t*-8-Tetrakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethylsiloxy)-2,4,6,8-(tetraphenyl)cyclotetrasiloxane (3c).** Compound **3c** was synthesized similarly to compound **3a**. Karstedt´s catalyst (0.5 μL) was added to a mixture of compound **2c** (0.11 g, 0.14 mmol) and 4´-cyanobiphenyl-4-yl undec-10-enoate (0.23 g, 0.63 mmol) in anhydrous toluene (0.70 mL), and the resulting mixture was heated for 1 h at 55 °C. The reaction was not completed, and an additional portion of Karstedt´s catalyst (2.0 μL, calculated to [Pt] = $0.6 \cdot 10^{-6}$ mol L^{-1}) was introduced, After 30 min, the absorption band characteristic of the Si—H bond was absent from the IR spectrum. Compound **3c** was isolated by preparative TLC (eluent toluene—hexane—AcOEt, 0.80 : 0.20 : 0.05) in 34.0% yield (0.10 g). Found (%): C, 68.78; H, 6.97; N, 2.34, Si, 10.30. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H, 7.04; N, 2.51; Si, 10.07.

IR (KBr), ν/cm^{-1}: 791, 842 ($SiMe_2$); 915 (Si—Me); 1062 (SiOSi); 1131 (Si—Ph); 1178 ($CO(CH_2)$); 1255 (Si—Me); 1379, 1430 (Ph—Si); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C=N); 2851, 2925 (CH_2) 3020, 3050, 3072 (Ph, C_6H_4). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: −0.07 (d, 6 H, $(C\underline{H}_3)_2SiO$); 0.54 (m, 2 H, $C\underline{H}_2SiO$); 1.25 (quint, 2 H, CH_2—$C\underline{H}_2$—CH_2, J = 7.6 Hz); 1.31 (m, 6 H, CH_2—$C\underline{H}_2$—CH_2); 1.70 (quint, 2 H, C(O)—CH_2—$C\underline{H}_2$, J = 7.6 Hz); 2.45 (t, 2 H, C(O)—$C\underline{H}_2$, J = 7.6 Hz); 7.14 (t, 2 H, *m*-CH, ^3J = 7.2; 7.6 Hz); 7.19 (d, 1 H, *p*-CH, ^3J = 7.2 Hz); 7.16 (d, 2 H, CH—C—CN, J = 8.8 Hz); 7.40 (t, 2 H, *o*-CH, Ph, J = 7.6 Hz); 7.55 (d, 2 H, C$\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 8.8 Hz); 7.62 (d, 2 H, C$\underline{H}$—CH—C—O, ^3J = 8.4 Hz); 7.70 (d, 2 H, CH—C$\underline{H}$—C—O, C_6H_4O, J = 8.4 Hz). ^{29}Si NMR (400 MHz, $CDCl_3$ + CCl_4), δ: 10.50 (s, CH_2Me_2SiO), −79.50 (s, $PhSiO_{3/2}$).

***r*-2,*t*-4,c-6,*t*-8-Tetrakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethylsiloxy)}-2,4,6,8-(tetraphenyl)cyclotetrasiloxane (3d).** Compound **3d** was synthesized using a procedure similar to that for compound **3a**. Karstedt´s catalyst (0.6 μL, calculated to [Pt] = $0.2 \cdot 10^{-6}$ mol L^{-1}) was added to a mixture of compound **2d** (0.08 g, 0.10 mmol) and 4´-cyanobiphenyl-4-yl undec-10-enoate (0.17 g, 0.46 mmol) in anhydrous toluene (0.50 mL), and the resulting mixture was heated for 4 h at 55 °C. The IR spectrum of the reaction mixture contained no absorption band characteristic of the Si—H bond. Platinum was removed from a toluene solution of the reaction products (5%) on a column packed with silica gel (column height 2 cm, diameter 5 mm). The solvent was distilled off, and compound **3d** was purified by precipitation from a benzene—methanol solution. Compound **3d** was obtained in 45.0% yield (0.09 g). Found (%): C, 68.56; H, 7.04; N, 2.20, Si, 10.40. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H, 7.04; N, 2.51; Si, 10.07.

IR (KBr), ν/cm^{-1}: 790, 842 ($SiMe_2$); 915 (Si—Me); 1062 (SiOSi); 1131 (Si—Ph); 1178 $CO(CH_2)$; 1257 (Si—Me); 1380, 1430 (Ph—Si); 1490, 1610 (Ph, C_6H_4); 1770 (C=O); 2257 (C=N); 2851, 2925 (CH_2) 3020, 3050, 3072 (Ph, C_6H_4). ^{1}H NMR ($CDCl_3$ + CCl_4), δ: −0.15 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.32 (m, 2 H, CH_2SiO); 1.27 (quint, 10 H, CH_2—$C\underline{H}_2$—CH_2, J = 7.6 Hz); 1.30 (m, 6 H, CH_2—$C\underline{H}_2$—CH_2); 1.74 (quint, 2 H, C(O)—CH_2—$C\underline{H}_2$, J = 7.6 Hz); 2.55 (t, 2 H, C(O)—$C\underline{H}_2$, J = 7.2); 7.16 (d, 2 H, C$\underline{H}$—C—CN, J = 8.4 Hz); 7.29 (t, 2 H, *m*-CH, Ph, ^3J = 6.4; 6.8 Hz); 7.40 (t, 1 H, *p*-CH, Ph,

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* The triplet is hidden by a more intense doublet signal from the C$\underline{H}$—C—CN proton.

^3J = 6.8 Hz); 7.55 (d, 2 H, C$\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 8.4 Hz); 7.65 (d, 2 H, *o*-CH, Ph, J = 6.4 Hz); 7.71 (d, 2 H, CH—C$\underline{H}$—C—O, C_6H_4CO, ^3J = 8.4 Hz). ^{29}Si NMR (400 MHz, $CDCl_3 + CCl_4$), δ: 10.72 (s, CH_2Me_2SiO); –79.70 (s, $PhSiO_{3/2}$).

Mixtures of compounds: (1) a mixture of compounds **3a** + **3b** was prepared from pure isomers **3a** and **3b** in a solution of $CCl_4 + CDCl_3$ (ratio 1 : 1);

(2) a mixture of compounds **3a** + **3d** was prepared from pure isomers **3a** and **3d** in a solution of $CCl_4 + CDCl_3$ (ratio 0.7 : 0.3);

(3) a mixture of compounds **3a** + **3b** + **3d** was prepared from pure isomers **3a**, **3b**, and **3d** in a solution of $CCl_4 + CDCl_3$ (ratio 1.0 : 0.3 : 1.0).

The data of the ^{1}H and ^{29}Si NMR spectra are presented in Table 3.

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