Modeling of structures of poly(oxyhexaorganocyclotetrasiloxy-2,6-diyl) mesophases

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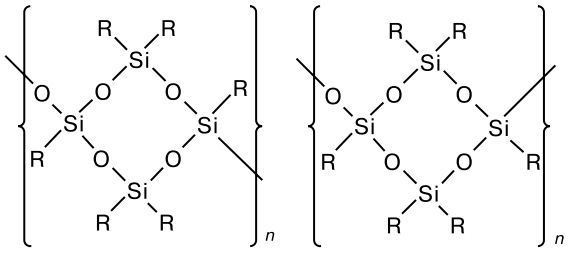
The idealized liquid-crystal structures of two cyclolinear organosilicon polymers, *viz.*, poly(oxyhexaorganocyclotetrasiloxy-2,6-diyls), where the alkyl substituent is Et (**1b**) or Pr (**1c**), were modeled. The columns of monomer units in polymers have different conformations, *viz.*, a distorted long boat in **1b** and a distorted long chair in **1c**. Both polymers have columnar structures with the most probable antiparallel arrangement of the columns.

Key words: molecular modeling, mesomorphic polymers, cyclolinear polyorganosiloxanes.

Cyclolinear polyorganosiloxanes belong to an interesting class of organosilicon polymers exhibiting unexpected physical properties. Several groups of such polymers with different tacticities containing siloxane rings of different sizes, different inter-ring bridges, and various organic substituents have already been synthesized.[1] Numerous studies demonstrated that most of cyclolinear polyorganosiloxanes exhibit mesomorphic properties and form thermotropic mesophases. Rather recently, it has been found that mesomorphic cyclolinear polyorganosiloxanes can form Langmuir mono- and multilayers.[2—4]

The aim of the present study was to reveal the effect of organic substituents in the rings of the chain on the detailed molecular and mesomorphic structure of poly(oxyhexaorganocyclotetrasiloxy-2,6-diyls) (**1**) of the general formula



trans unit *cis* unit

Earlier studies[5,6] have demonstrated that compounds **1** containing the methyl substituents (**1a**) are able to form mesophases when their chains are substantially enriched with *trans* units. According to the data of differential scanning calorimetry (DSC) and results of powder X-ray diffraction study, compound **1a** occurs as two mesomorphs, *viz.*, high-temperature mesophase I (100—110 °C) and low-temperature mesophase II (80—100 °C).[7] Attempts to establish the atactic molecular structures of the mesophases based on experimental data failed, because their X-ray diffraction patterns were poorly informative. Molecular modeling confirmed the assumption that a cylindrical macromolecule serves as a structure-forming element of mesophase **1a**.[7—9] High-temperature mesophase I is characterized by the hexagonal symmetry of the packing of macromolecular columns in the basic plane. As the temperature decreases, the number of molecules per asymmetric unit increases and its symmetry is lowered. Mesophase II is characterized by the orthogonal packing of the macromolecules.

With the aim of studying the effect of the organic substituents in the polymer chain on the properties of **1**, we synthesized compounds **1** with the alkyl substituents R = Et (**1b**) or R = Pr (**1c**) having atactic structures.[10] According to the powder X-ray diffraction data, compounds **1b** and **1c** containing *n*-propyl substituents do not crystallize but occur in the mesomorphic state in the broad temperature range from the glass transition temperature T_g to the isotropization temperature T_i (T_g = –100 °C, T_i = 280 °C for **1b** and T_g = –40 °C, T_i = 340 °C for **1c**). The X-ray diffraction patterns for compounds **1b** and **1c** are qualitatively identical and each have one intense reflection at 2θ = 9.2° for **1b** and 2θ = 8.2° for **1c**. These

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values correspond to d = 9.54 and 10.78 Å, respectively. The structures of ordered phases of these compounds were not unambiguously established for two reasons. First, the experimental data were poorly informative and, second, oriented samples cannot be prepared. To determine the detailed structures of these compounds at the molecular and supermolecular levels, we carried out calculations by molecular mechanics. The results of this modeling are discussed below.

Calculation procedure. To describe the structures of polymers at the atomic level, we used the atom-atom potential method.[11] When constructing the monomer unit of the polymer chain, we used a mechanical model of the molecule, which assumes that the optimum conformation corresponds to the minimum of the conformational energy U

$$U = U_{bond} + U_{ag} + U_{nov} + U_{tor} + U_{H\text{-}bond},$$

where U_{bond} is the bond stretching energy, U_{ag} are the contributions associated with the deviations of the bond angles from equilibrium values, U_{nov} are the contributions of nonvalence interactions, U_{tor} is the energy of internal rotation about the valence bonds, and $U_{H\text{-}bond}$ is the hydrogen bond energy. In calculations, we used the parameters of the potentials determined earlier.[12] The fragment of the polymer chain was constructed by the method of variable virtual bonds.[11] This method enables one to construct a helix with a specified symmetry using two independent variables, *viz.*, the virtual angle δ, which describes the rotation of the monomer unit around the virtual bond passing throughout the unit, and the projection h of the monomer unit onto the axis of the chain, which characterizes its periodicity. These parameters describe the connections between the repeating monomer units.[11] The helix thus constructed has a translational symmetry, which is necessary for calculations of the crystal structure.[11] In this case, the bond angle β at the atom located at the junction of the monomer units is a dependent variable.

The energy of the helix E_{helix} is calculated as the sum

$$E_{helix} = E_{mon} + E_{con},$$

where E_{mon} and E_{con} are the conformational energies of the monomer unit and the connection of the units, respectively. The component E_{mon} is equal for all units of the polymer chain. The energy of connection E_{con} includes the contributions of both nonvalence interactions between the monomer units and deformations of the bond angles and torsion angles to the junction, E_{con} being dependent on the parameters δ and h.

In the first stage of calculations, we revealed stable conformations of polymer chains built from monomer units using a mechanical model of the molecules. For this purpose, we scanned the potential energy of the molecule over the parameters h and δ followed by the minimization with respect to the same parameters and with respect to the torsion angles characterizing the orientation of the methyl groups. The standard reference system was used for all torsion angles.[13]

At the next stage of calculations, the polymer chains were packed in three-dimensional structures using the atom-atom potential method.[11] When modeling the structure, the lattice parameters were not varied; instead, their experimental values were used. Since we failed to determine the space groups from the experimental data, the model of the unit cell was considered within the space group P1 containing two symmetrically independent molecules, the b parameter of the unit cell being doubled. The polymer chains were arranged in the unit cell taking into account the parameter K, which determines the direction of the chains in the cell. For the parallel and antiparallel orientations of the chains, $K = +1$ and $K = -1$, respectively. The chain 1 was placed in the origin of coordinates and the chain 2 was placed in the position with the coordinates $x_2 = 0.0$, $y_2 = 0.5$, $z_2 = 0.0$. When generating trial models, the energy of the molecule in the crystal (U) was scanned over the following parameters: the angles of rotation φ_1 and φ_2 of the molecules 1 and 2 about their molecular axes, the coordinate y_2 determining the arrangement of the chain 2 with respect to the b axis, and the coordinate z_2 determining the arrangement of the chain 2 with respect to the c axis. In the minima of the energy U thus determined, the minimization with respect to the following variables was performed: the helix pitch h, virtual angle δ, coordinates x_2 and z_2, angles φ_1 and φ_2, and torsion angles determining the orientation of the methyl groups.

Results and Discussion

Modeling of the structures of mesophases **1b** and **1c** was carried out using a model of the chain fragment consisting of a sequence of *trans* units, because the polymer chains of **1b** and **1c** consist primarily of the *trans* units (*trans* : *cis* — 70 : 30).

At the first stage of calculations, the monomer units of the compounds were modeled. This problem was complicated by the lack of experimental data on the structures of the monomer units, *viz.*, ethylcyclotetrasiloxane and propylcyclotetrasiloxane. We considered the following two initial conformations of the tetrasiloxane ring: a long-chair conformation typical of the low-temperature modification of methylcyclotetrasiloxane[14] and a hypothetical planar conformation. In the search for a stable conformation, we considered the monomer units of **1b** and **1c** as isolated molecules containing two terminal hydroxy groups in the transoid orientation and the corresponding organic substituents. The results of the stochastic search[15] for con-

Table 1. Results of a stochastic search for conformations of the monomer units of **1a**, **1b**, and **1c**

Unit of polymer	Conformation of the ring		*E*/ kcal mol^{-1}
	Starting	Calculated	
1a	Long chair	Boat-chair	−13.7
	Planar	Boat-chair	−13.6
1b	Long chair	Long boat	−8.8
	Planar	Crown	−6.0
1c	Long chair	Long chair	−3.0
	Planar	Crown	−0.3

Table 2. Structural and energy characteristics of the models of isolated polymer chains of **1b** and **1c**

Symmetry of chain	*h*/Å	β	δ	E_{con}	E_{helix}
		deg		kcal mol^{-1}	
		Compound **1b**			
2_1	5.4	167.5	−90.0	214.9	154.4
3_1	5.2	162.5	−53.8	−24.0	−80.8
4_1	4.9	151.7	−55.0	−13.3	−71.0
3_2	4.8	171.3	−127.1	7.8	−47.1
4_3	4.5	160.6	−90.0	−18.3	−71.6
		Compound **1c**			
2_1	6.7	157.9	90.0	68.4	67.7
3_1	6.3	154.6	−119.5	−39.5	−118.6
4_1	6.7	163.3	−129.8	−53.2	−128.9
3_2	6.5	163.8	94.4	−56.8	−149.5
4_3	6.7	161.6	158.9	−18.1	−80.7

formations of monomer units of **1b** and **1c** are presented in Table 1. For comparison, Table 1 gives the results of calculations for **1a**.

The calculations for methylated compound **1** gave only one conformation of the ring, *viz.*, a disotorted boat-chair, regardless of the initial conformation of the tetrasiloxane ring. In the case of the ring containing the bulkiest *n*-propyl substituent, the starting conformation of the ring (long chair, model 1) was only slightly distorted in the course of the stochastic search. Evidently, the models of the monomer units of **1b** and **1c** derived from the starting model 1 are best suited to the further modeling of

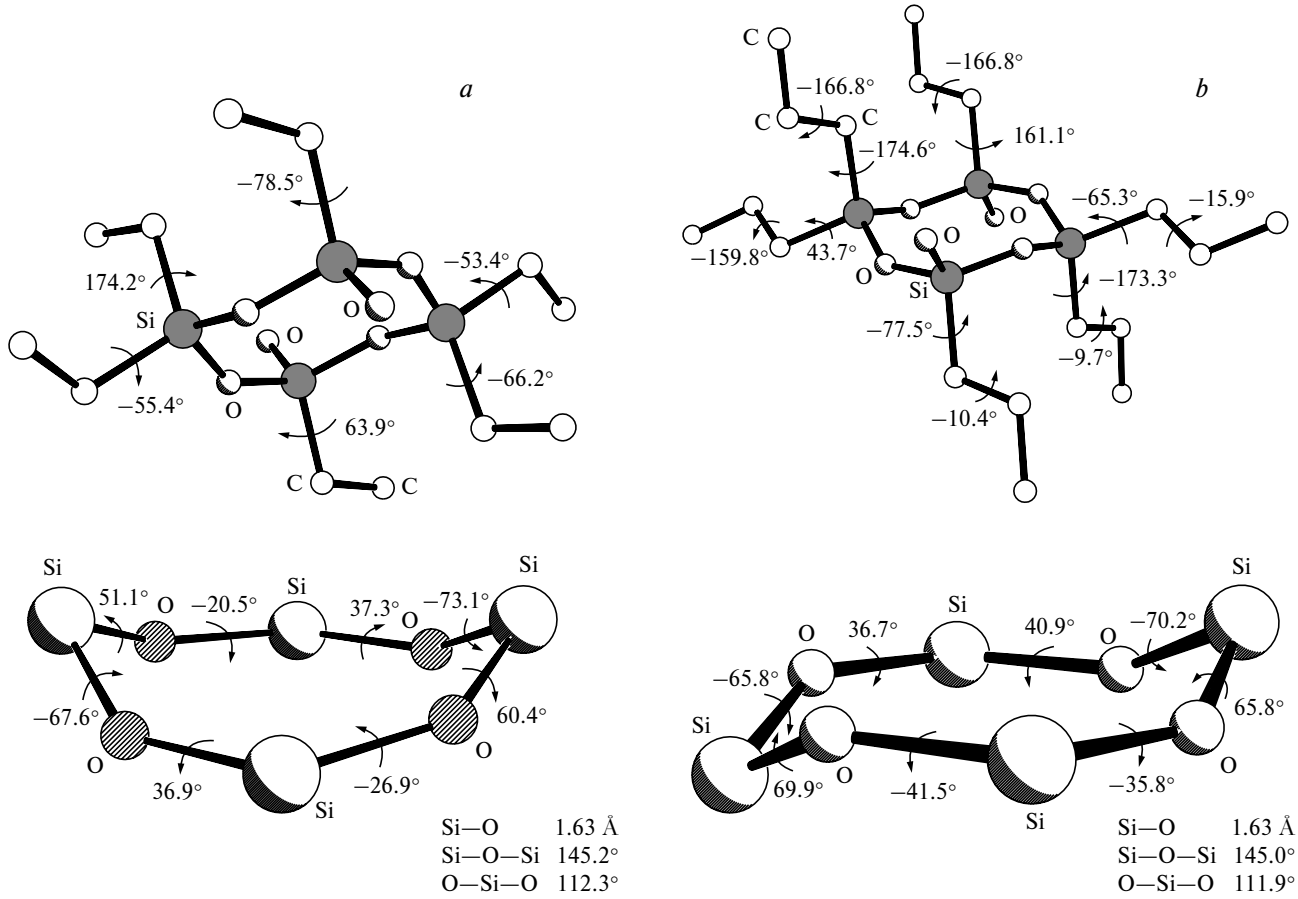

Fig. 1. Models of the monomer units of **1b** (*a*) and **1c** (*b*). The conformational parameters of the tetrasiloxane ring. The units adopt distorted long-boat conformations.

the polymer chain. The results of calculations are in good agreement with the earlier estimates of the possible conformations of the tetrasiloxane ring.[16] The models of the monomer units of **1b** and **1c** and their conformational characteristics are shown in Fig. 1.

At the second stage of calculations, the polymer chain was modeled using the method of variable virtual bonds.[11] Several symmetries of the chain were examined. The results of calculations are presented in Table 2. It is evident that models of the chains with the symmetries 3_1 and 3_2 are energetically favorable for **1b** and **1c**, respectively (Fig. 2). The chain with the symmetry 3_2 is a mirror image of the chain with the symmetry 3_1. Hence, molecules **1b** and **1c** have similar conformations. The molecules tend to adopt a conformation with a minimum number of shortened nonvalence contacts between the adjacent units of the chain, a columnar structure being retained.

At the third (final) stage of modeling, we calculated the packing of the models of the polymer chains for **1b** and **1c** in mesophases. The following experimental unit cell parameters ($Z = 2$) were used:

Compound	*a*	*b*	*T*/°C
	Å		
1b	11.09	22.18	$T_i - 10$
	10.2	20.4	20
1c	12.44	24.88	$T_i - 10$
	11.6	23.2	20

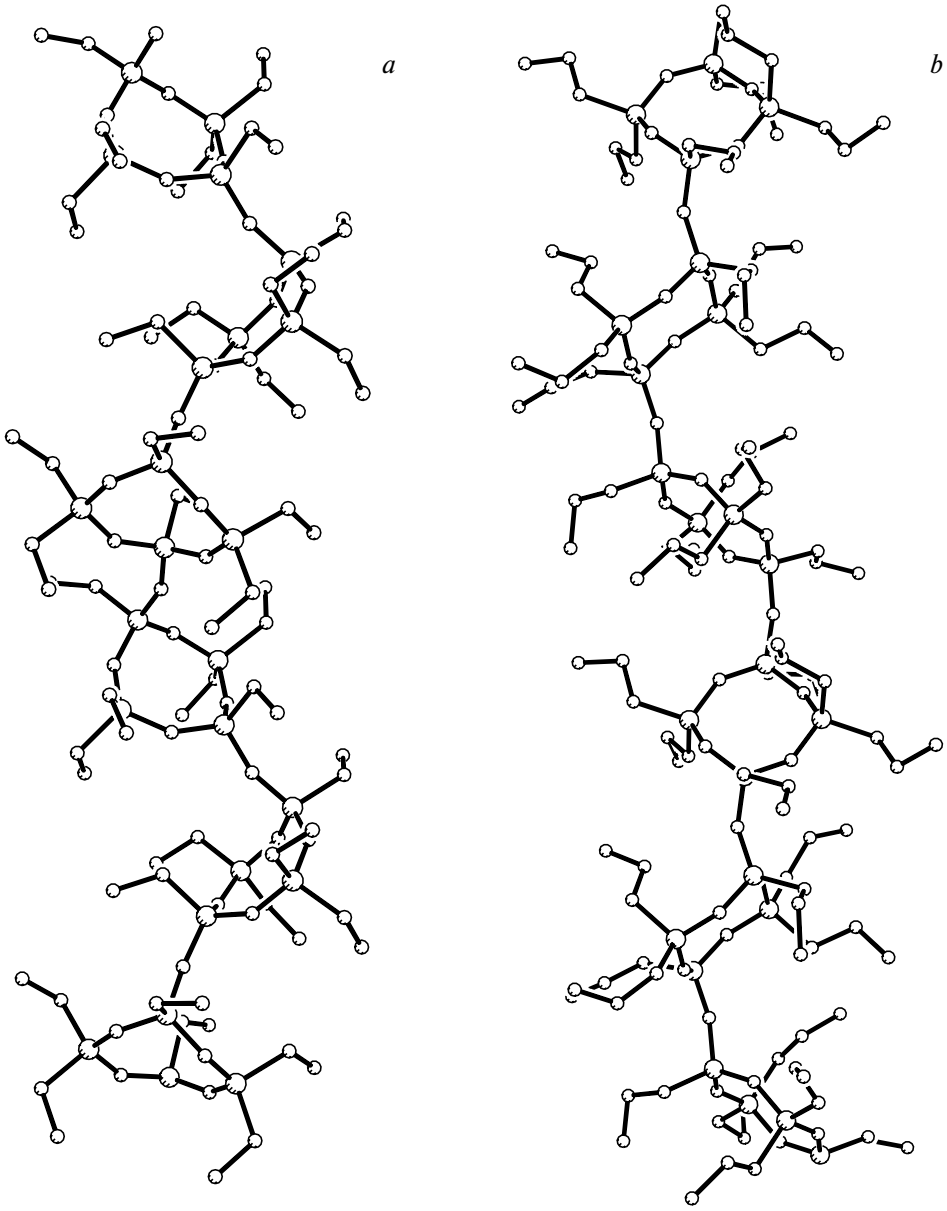

Fig. 2. Models of the helices 3_1 for **1b** (*a*) and 3_2 for **1c** (*b*). Two turns are shown.

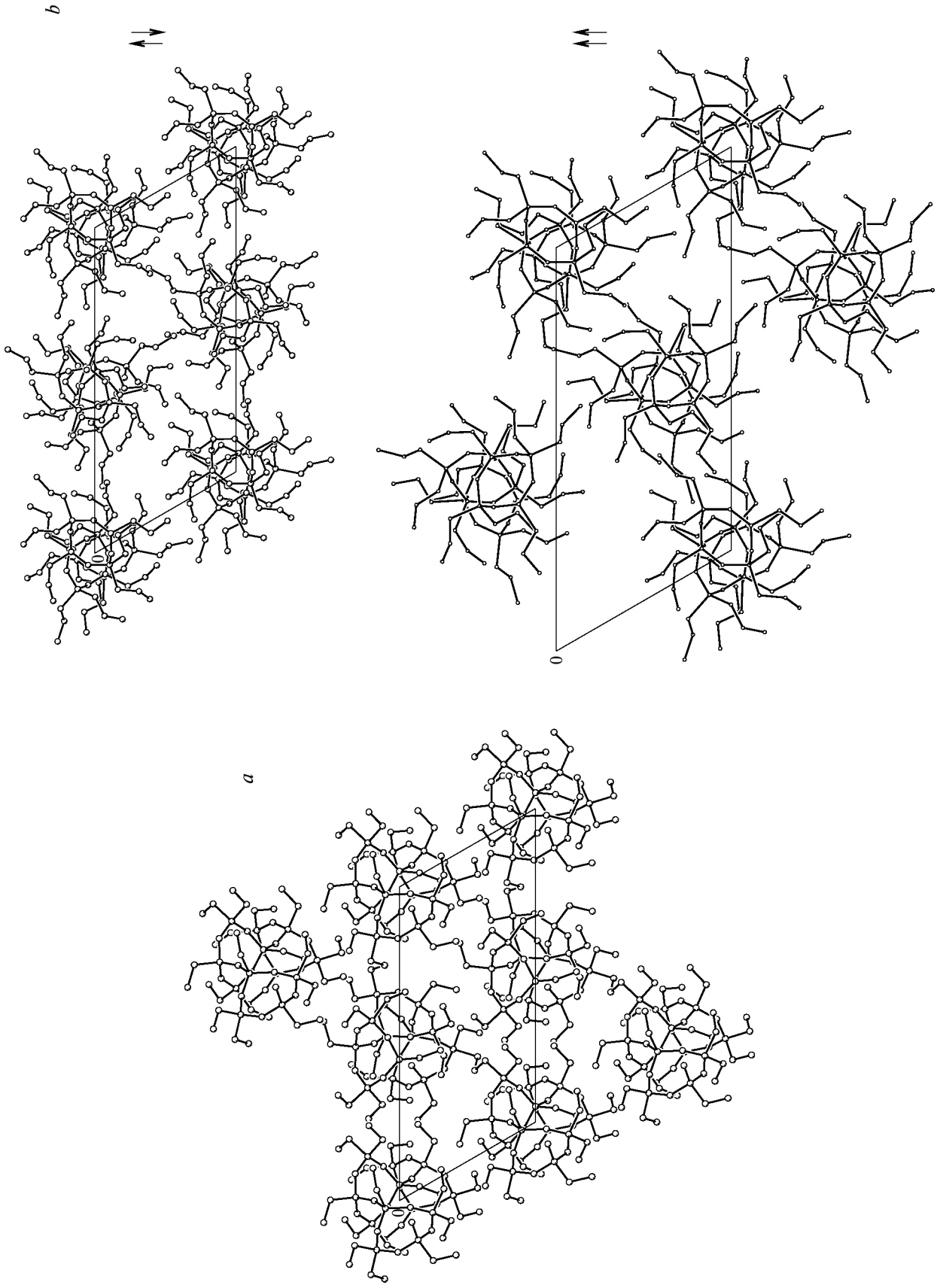

Fig. 3. Models of the packing of molecules **1b** (*a*) and **1c** (*b*) in the mesophases at ~20 °C with the antiparallel orientation of the chains. Projections onto the *xy* plane.

Table 3. Structural and energy characteristics of the models of the pseudohexagonal packing of symmetrically independent molecules **1b** and **1c** at different temperatures

Compound	*T*/°C	Orientation of chain	β	φ_1	x_2	z_2	φ_2/deg	E_{cryst}	*U*
			deg					kcal mol^{-1}	
					Symmetry 3_1				
1b	20	↑↑	157.9	34.9	0.3	0.8	55.0	−14.9	−99.6
		↑↓	157.8	65.0	0.5	0.3	25.0	−15.9	−101.2
	300	↑↑	157.7	0.0	0.4	0.1	65.0	−12.7	−98.2
		↑↓	157.7	145.0	0.5	0.3	65.0	−12.9	−97.9
					Symmetry 3_2				
1c	20	↑↑	164.6	124.9	0.2	0.6	124.9	−12.5	−161.9
		↑↓	165.3	29.8	0.9	0.0	44.8	−12.5	−162.0
	300	↑↑	164.6	135.0	0.8	0.2	135.0	−12.2	−162.0
		↑↓	165.1	4.8	0.6	0.5	114.9	−13.4	−162.9

Note. h = 5.3 (**1b**), 6.5 Å (**1c**), $x_1 = y_1 = z_1 = 0$, $y_2 = 0.5$.

We considered two sets of the unit cell parameters for each compound corresponding to room temperature and the temperature near the isotropization point to reveal the possible changes in the conformation of the polymer chain and molecular packing.

The results of minimization of the potential energy *U* of the molecule in the crystal are given in Table 3. Interestingly, the conformational parameters of the symmetrically independent chains are virtually identical with the corresponding parameters of the isolated polymer chains of **1b** and **1c**. This indicates that the crystal field has no effect on the conformation of the chain. The temperature also exerts only a slight effect on the packing parameters of the macromolecules in an ordered structure. However, the antiparallel molecular packing is somewhat more favorable than their parallel packing (see Table 3). The models of the packing of molecules **1b** and **1c** in the mesophases at room temperature are shown in Fig. 3.

To summarize, modeling of the molecular structures of **1b** and **1c** showed that the size of organic substituents affects the conformation of the tetrasiloxane ring. The models of molecules **1b** and **1c** have columnar structures, which confirms the assumption that a cylindrical macromolecule serves as the structural unit of the mesophases of these compounds.[7—9]

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References

1. N. N. Makarova and Yu. K. Godovsky, *Pergamon*, 1997, **22**, 1001.
2. S. I. Belousov, E. Sautter, Yu. K. Godovsky, N. N. Makarova, and W. Pechhold, *Vysokomol. Soedin.,* 1996, **A38**, 1538 [*Russ. Polym. Sci.*, 1996, **A38** (Engl. Transl)].
3. J. Fang, M. Dennin, and C. M. Knobler, *J. Phys. Chem.*, 1997, **101**, 3147.
4. Yu. K. Godovsky, J. Fang, C. M. Knobler, and N. N. Makarova, *Polym. Prep.*, 1998, **39**, 543.
5. N. N. Makarova, I. M. Petrova, and A. A. Zhdanov, *Dokl. Akad. Nauk SSSR,* 1982, **262**, 619 [*Dokl. Chem.*, 1982 (Engl. Transl.)].
6. Yu. K. Godovsky, N. N. Makarova, I. M. Petrova, and A. A. Zhdanov, *Macromol. Chem. Rapid Commun.*, 1984, **5**, 427.
7. T. V. Timofeeva, E. E. Boda, A. P. Polishuk, M. Yu. Antipin, E. V. Matukhina, I. M. Petrova, and Yu. K. Struchkov, *Mol. Cryst. Liq. Cryst.*, 1994, **248**, 125.
8. E. E. Boda, T. V. Timofeeva, Yu. T. Struchkov, and I. V. Razumovskaya, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1470 [*Russ. Chem. Bull.*, 1995, **44**, 1470 (Engl. Transl.)].
9. E. V. Matukhina, E. E. Boda, T. V. Timofeeva, Yu. K. Godovskii, N. N. Makarova, I. M. Petrova, and B. D. Lavrukhin, *Vysokomol. Soedin.,* 1996, **38**, 1545 [*Russ. Polym. Sci.*, 1996, **38**, 1545 (Engl. Transl.)].
10. Yu. K. Godovsky, N. N. Makarova, and N. N. Kuzmin, *Macromol. Chem. Macromol. Symp.*, 1989, **26**, 91.
11. A. J. Pertsin and A. I. Kitaigorodsky, *The Atom-Atom Potential Method*, Springer-Verlag, 1987, 397 pp.
12. T. V. Timofeeva, I. A. Dubchak, V. E. Shklover, and Yu. T. Struchkov, *Teor. Eksp. Khim.*, 1981, **17**, 674 [*Theor. Exp. Chem.*, 1981, **17** (Engl. Transl.)].
13. F. I. Kolpak and J. Blackwell, *Macromolecules*, 1976, **9**, 273.
14. H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, 1955, **8**, 420.
15. M. Saunders, *J. Am. Chem. Soc.*, 1987, **109**, 3150.
16. T. V. Timofeeva, I. L. Dubchak, V. G. Dashevsky, and Yu. T. Struchkov, *Polyhedron*, 1984, **3**, 1109.

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