Study of molecular and mesomorphic structure of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)]

E. E. Boda,[a] T. V. Timofeeva,[b] I. V. Razumovskaya,[a] and Yu. T. Struchkov[b†]*

[a]*V. I. Lenin Moscow Pedagogical State University,*
1 ul. Malaya Pirogovskaya, 119882 Moscow, Russian Federation.
Fax: +7 (095) 248 0162
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The molecular and crystal structures of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)] have been modeled. The most probable models of mesomorphic modifications of this compound, which was obtained by minimization of the potential energy of the system, based on experimental data on the unit-cell dimensions have been proposed.

Key words: cyclolinear organopolysiloxanes, liquid crystals, molecular modeling.

Recently, works appeared in which the occurrence of a mesomorphic state of cyclolinear organopolysiloxanes was reported. These partially ordered phases of cyclolinear organosiloxane polymers are assigned to so-called condis crystals, conformationally disordered crystals in which the conformational order is lost to some extent in the packing of parallel molecules.[1] It was established that the formation of a mesophase is affected by the size of the cycloorganosiloxane unit (the number of diorganosiloxane groups included in the cycle),[2] the symmetry of its position in the polymer chain,[2] molecular weight,[3] and "organic environment" (substituents).[4]

With the aim of obtaining data on the effect of the tacticity of the chain on the crystallization process and prerequisites to transformation of cyclolinear organosiloxane polymers to the mesomorphic state, cyclolinear poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)] was synthesized, in which the *trans* to *cis* units ratio is 88 : 12.[5] This polymer attracts particular interest because, unlike other cyclolinear organotetrasiloxanes, this polymer forms two mesomorphic modifications, *i.e.*, orthogonal (I) and hexagonal (II) modifications. The first modification is characterized by two-dimensional rectangular unit cell with the following parameters: a = 17.27, b = 8.43 Å, Z = 2. The parameter of the hexagonal unit cell is a = 9.88 Å, Z = 1.[5]

In this work, we attempt to determine the detailed molecular and crystal structure of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)] minimizing the potential energy of the system taking into account the experimental data on symmetry and unit-cell parameters of the corresponding mesomorphic modifications of this polymer. Analogous calculations have been performed previously for linear polysiloxanes with propyl and ethyl environment,[6] for polydiphenylsiloxane,[7] and for cellulose.[8] When performing calculations of crystal packings, we used a model of a regular molecular chain with a *trans* structure although the real chain contains some number of *cis* units.

Calculation procedure

We used the atom-atom potential method[9] for describing the polymer structure on the atomic level. When constructing the unit of the polymer, we started from a molecular mechanic model assuming that the optimum molecular conformation corresponds to the minimum of the conformation energy U_{conf}, which can be represented as follows:

$$U_{\text{conf}} = U_{\text{a}} + U_{\text{tors}} + U_{\text{b}} + U_{\text{nb}} + U_{\text{q}} + U_{\text{H}},$$

where U_{a} and U_{tors} are the contributions determined by deviations of bond angles and torsion angles from equilibrium values, U_{b} is the energy of stretching of valence bonds, U_{nb} and U_{q} are the contributions of nonbonded and electrostatic interactions, and U_{H} is the energy of hydrogen bonds. The parameters of potentials determined previously[10] were used in calculations. The fragment of the polymer chain was constructed by the method of varying virtual bonds.[9] The advantage of this procedure is that it allows construction of the helix with given symmetry using only two independent variables, which describe conjunction of repeating units. The helix thus obtained has translational symmetry, which is of prime importance in calculations of the crystal structure.[8] In this case, the dependent variable is the bond angle β at the atom, located at the juncture of monomer units.

The energy of the helix E_{hel} was calculated as the following sum:

$$E_{\text{hel}} = E_{\text{mon}} + E_{\text{conj}},$$

where E_{mon} and E_{conj} are conformation energies of the initial unit and conjunction of units, respectively. The term E_{mon} is equal for all monomer units. The energy of conjunction in-

---

[†] Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1470—1476, August, 1995.

cludes contributions of nonbonded interactions of monomer units and deformations of bond angles and torsion angles at the juncture; E_{conj} depends on the parameters δ and h (δ is a virtual angle describing rotation of the monomer unit around the virtual bond, and h is the projection of the monomer unit onto the axis of the chain, which characterizes its tacticity[9]).

In the first stage of calculations, stable conformations of the polymer chain built from monomer units were determined; these conformations were calculated with the use of molecular mechanic. For this purpose, we scanned the potential energy of the molecule over h and δ and then minimized the energy with respect to the same parameters as well as the torsion angles characterizing orientation of methyl groups. For all torsion angles, the known system of references was used.[11]

In the second stage of calculations, packing of polymer chains in three-dimensional structures[9] was performed using the atom-atom potential method. When the structure was modeled, the unit-cell parameters were fixed and the experimental data were used.

Scanning of the energy E_{crst} of intermolecular interactions in crystals was performed in the space of parameters x, y, z, and φ, where x, y, and z are coordinates (fractional coordinates) characterizing the location of the polymer axis in the unit cell (x, y) and the center of mass of the monomer on the axis c, and φ is the angle of rotation of the macromolecule around the chain axis. At the points corresponding to the minimum of E_{crst}, the total energy of the molecule in the crystal U_{Σ} was minimized including variation of E_{hel} and E_{crst} respectively to h, δ, x, y, z, and φ with the change in the orientation of methyl groups.

Table 1. Structural parameters of the monomer unit of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)]

Bond	d/Å	Bond angle	β/deg
Si—O	1.64	Si—O—Si	133.2
Si—C	1.88	O—Si—O	107.9
Si—H	1.08	O—Si—C	109.5

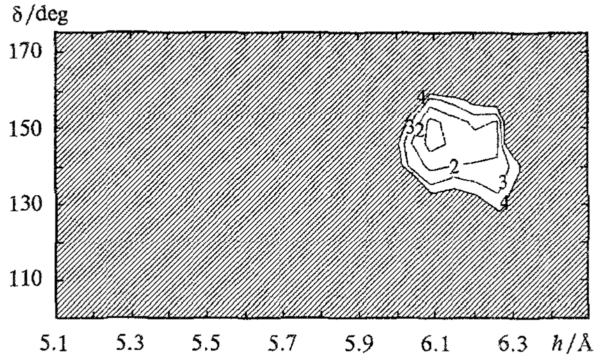
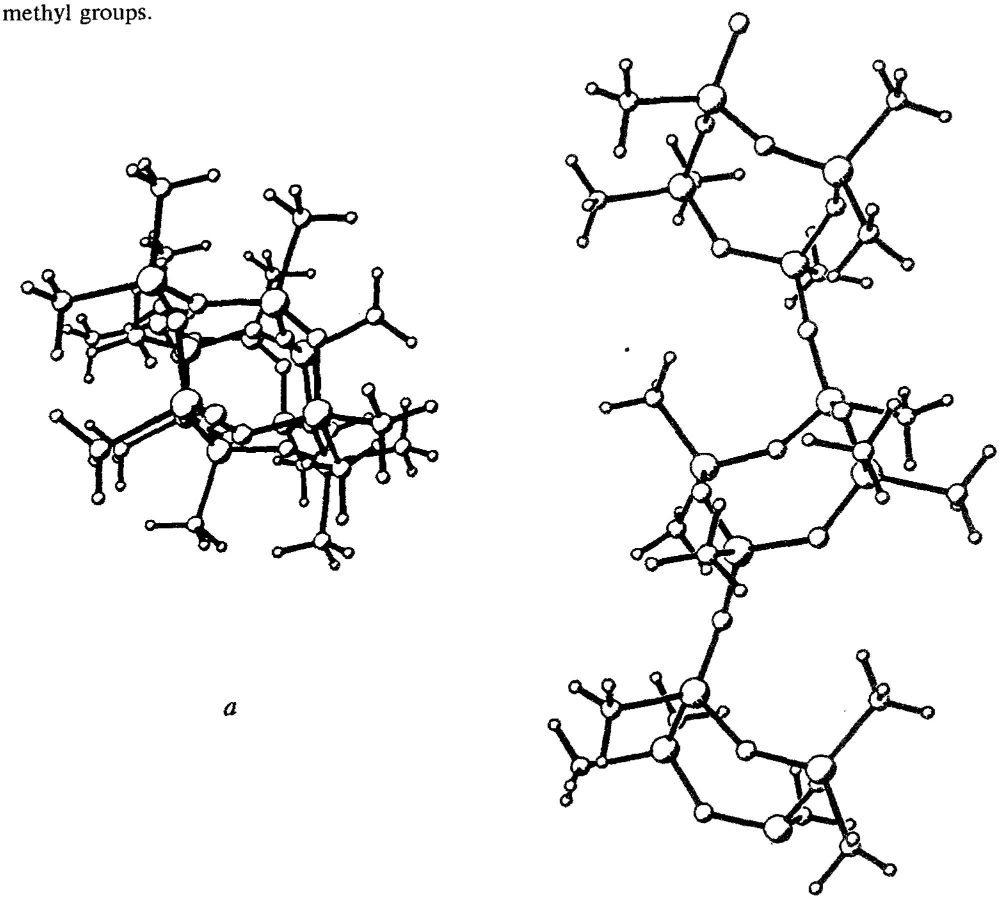


Fig. 1. Two-parameter dependence of the relative energy E_{conj} on h and δ for the chain with symmetry 2_1; $E_{\text{conj(min)}}$ = 0.0 kcal mol^{-1}. The region of forbidden values of energy is shaded.



a

b

Fig. 2 Projections (*a*) along and (*b*) perpendicular to the axis of the chain with symmetry 2_1.

Results and Discussion

In the first stage of calculations, the monomer unit of the polymer was considered as an isolated molecule with two terminal hydroxyl groups in the transoid orientation. When performing calculations of a monomer unit of the polymer with full geometrical optimization, we used the parameters of potential functions selected previously[10] for octamethylcyclotetrasiloxane $(Me_2SiO)_4$ based on experimental data of X-ray structural analysis and gas phase electron diffraction study. The obtained model of the unit adopts the so-called saddle-like or distorted conformation S_4. This is in good agreement with the results of the studies of possible conformations of the tetrasiloxane cycle, which were performed previously.[12] The structural parameters of the monomer unit are given in Table 1.

When the polymer chain was modeled several alternatives of chain symmetry (2_1, 3_1, 3_2, 4_1, and 4_3) were considered. It was found that a rather low potential energy corresponds only to two of these alternatives: helices 2_1 ($E_{\text{conj}} = -29.14$ kcal mol^{-1}) and 3_1 ($E_{\text{conj}} = -17.98$ kcal mol^{-1}). It is apparent that the helix with 3_1 symmetry is energetically substantially less favorable than the helix with 2_1 symmetry, in which monomer units are packed more closely (with the participation of a greater number of nonbonded contacts, the distances between which are close to the sum of van der Waals radii). The packing of cyclic fragments in this chain is similar in large measure to the packing of disk-like molecules in columnar discotic mesophases.[13]

We constructed the fragment of the 2_1 helix according to the above-mentioned algorithm. First we scanned the potential energy of the molecule varying the step h of the helix from 4.5 to 7 Å with the step of 0.5 Å and a virtual angle δ from 0 to 360° with the step of 10°. Figure 1 shows the two-parameter dependence of the relative energy of the helix on h and δ.

The potential energy of the molecule was minimized by changing the orientations of the methyl groups as well as the h and δ values with the use of parameters corresponding to the minimum of E_{conj}. As a result, we obtained the conformation of an isolated polymer molecule with the following characteristics: $h = 6.3$ Å, $\delta = 146.5°$, $\beta = 163.0°$, $E_{\text{conj}} = -29.14$ kcal mol^{-1} (Fig. 2).

Because it is impossible to establish space groups of mesophases I and II from X-ray structural data, we treated only the space groups, which are consistent with those determined experimentally with respect to symmetry and a number of polymer chains per unit cell. According to the method of potential function symmetry,[14] there is only one such space group, $P2_12_12_1$, in the orthorhombic system (model 1). Two pseudoorthogonal packings in the monoclinic space groups $P2_1$ and Pb with the monoclinic angle equal to 90° and chain symmetry 2_1 (models 2 and 3, respectively) were treated in addition to model 1.

We next scanned the energy over angles of rotation of the polymer molecule about its axis with a fixed position of the chain in the origin of coordinates of the unit cell. All three models have similar dependences $E_{\text{crst}}(\varphi)$ shown in Fig. 3. Calculations of U_Σ for different x and y were performed with the values of φ corresponding to the energy minimum.

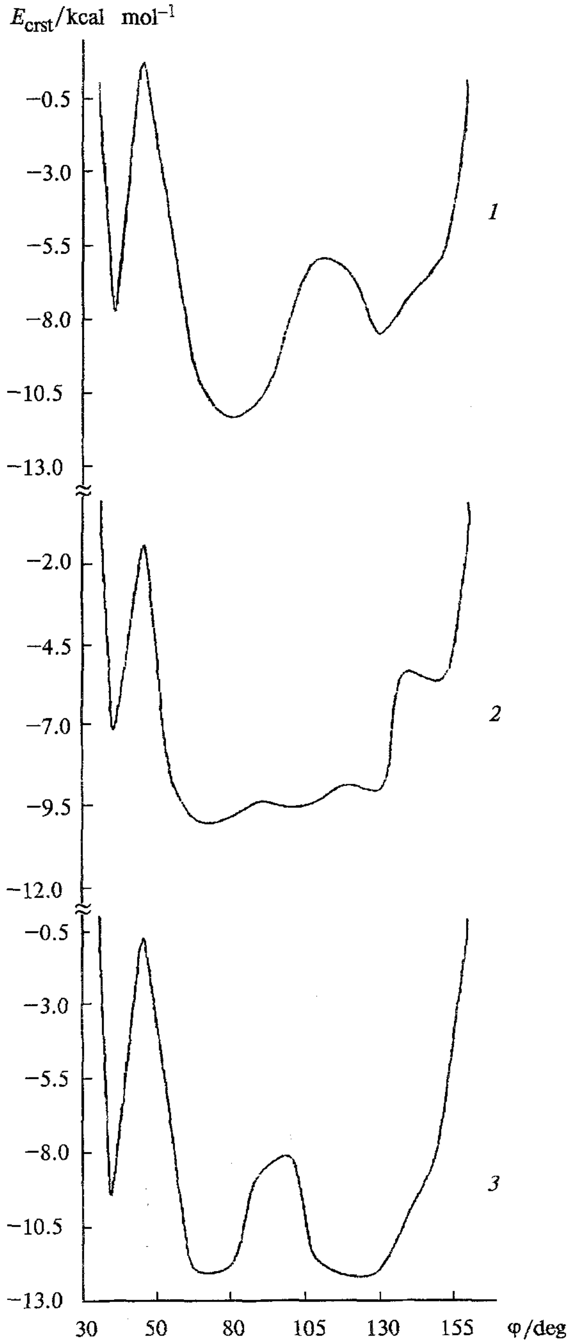


Fig. 3. Dependence of E_{crst} on the angle of rotation of the molecule about its axis φ for models 1 (*1*), 2 (*2*), and 3 (*3*).

The results of subsequent optimization of U_Σ with respect to conformational parameters of the helix, x, y, and φ, are given in Table 2. The packing corresponding to model 3 (Fig. 4) in the space group Pb is energetically most favorable.

Table 2. Structural and energy parameters of the models of orthogonal packing of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)] molecules

Space group	Orientation of the chains	Z	h/Å	x	y	φ/deg	E_{crst}	U_{Σ}
							/kcal mol^{-1}	
$P2_12_12_1$	↑↓	4	6.17	0.0	0.7	80.0	−11.37	−40.52
$P2_1$	↑↑	2	6.17	0.37	0.28	130.0	−10.69	−40.49
Pb	↑↑	2	6.17	0.3	0.25	127.0	−12.92	−42.08

Table 3. Structural and energy parameters of the models of orthogonal packing of symmetrically independent molecules

Orientation of the chains	h/Å	φ_1/deg	x_1	y_1	z_1	φ_2/deg	x_2	y_2	z_2	E_{crst}	U_{Σ}
										/kcal mol^{-1}	
↑↑	6.11	130.0	0.3	0.25	0.0	−50.0	0.1	0.75	0.5	−13.91	−43.04
↑↓	6.11	47.8	0.0	0.7	0.0	80.0	0.5	0.0	0.0	−10.04	−39.43

Analogous calculations were performed for packings with two symmetrically independent molecules in the unit cell. The results of optimization of U_{Σ} with respect to the parameters h, φ_1, φ_2, x_2, y_2, and z_2 for parallel and antiparallel orientations of symmetrically nonequivalent chains in the unit cell are given in Table 3. Calculations demonstrated that the packing with parallel orientation of molecules is energetically more favorable.

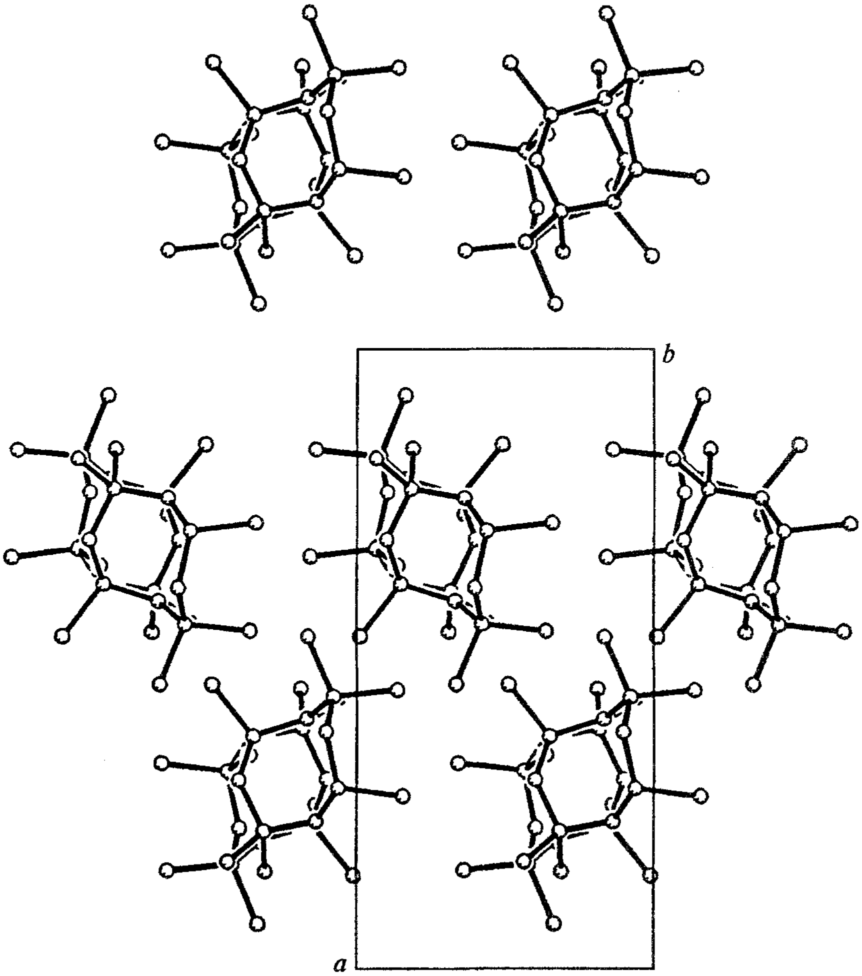


Fig. 4. Model of packing of chains with symmetry 2_1 in the space group *Pb*.

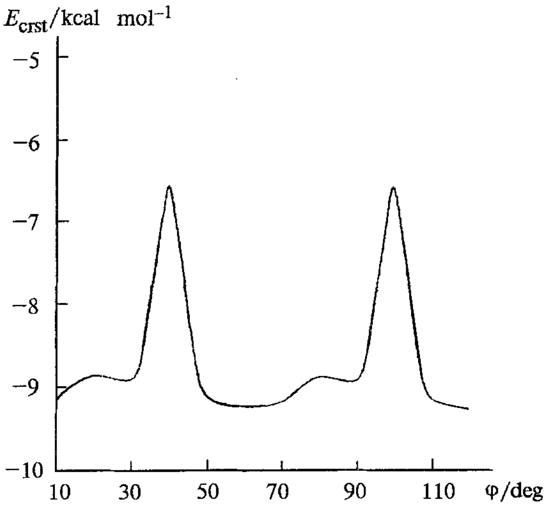


Fig. 5. Dependence of E_{crst} on the angle of rotation φ of the molecule about its axis for the model of hexagonal packing.

The hexagonal packing was modeled in the triclinic space group $P1$ with unit-cell parameters corresponding to this packing and helix symmetry 2_1. When minimizing U_Σ, we varied the same parameters as in the case of the orthorhombic packing. The dependence of E_{crst} on φ is shown in Fig. 5. Minimization of U_Σ with respect to h and φ afforded the packing with the following characteristics: h = 6.17 Å, φ = 54.9°, E_{crst} = −9.51 kcal mol^{-1}, U_Σ = −38.46 kcal mol^{-1} (Fig. 6).

For calculations of the packing of two symmetrically independent molecules in the space group $P1$, we used a unit cell with doubled parameters (a = 9.88, b = 19.6 Å, Z = 2). In this case, according to the results of calculations, an antiparallel orientation of chains is energetically most favorable (Table 4).

For elucidating the possible mechanism of the occurrence of the mesomorphic state of poly[oxy(hexamethylcyclotetrasiloxane-2,6-diyl)], we performed scanning of the potential energy of symmetrically independent molecules in crystals over two variables: φ_1 (the angle of rotation of the molecule about its axis) and z_1 (the fractional shift of the molecule along its axis). The results of this scanning for the orthogonal packing are shown in Fig. 7 for antiparallel polymer chains. The relative energies are depicted as isoenergetic contours; the region of forbidden values of energy at the corresponding φ_1 and z_1 is shaded.

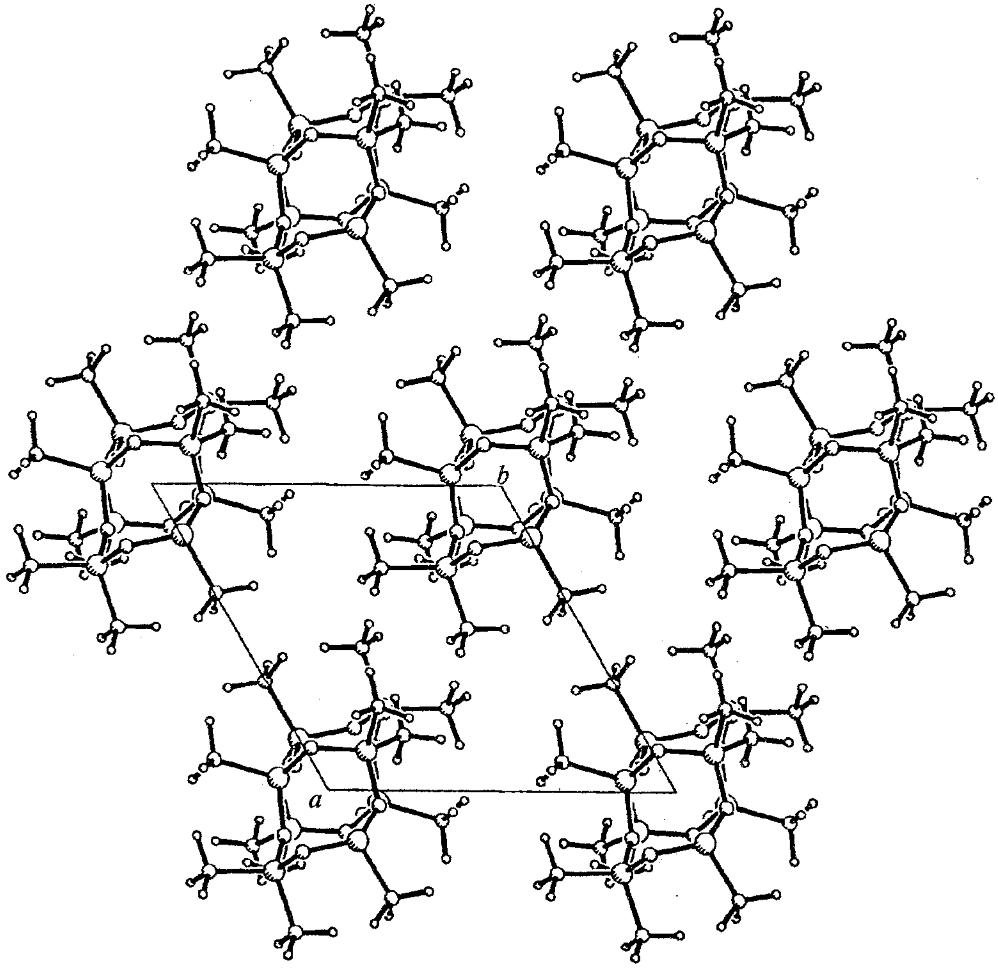


Fig. 6. Model of hexagonal packing of chains with symmetry 2_1.

Table 4. Structural and energy parameters of the models of hexagonal packing of symmetrically independent molecules

Orientation of the chains	h/Å	φ_1/deg	x_1	y_1	z_1	φ_2/deg	x_2	y_2	z_2	E_{crst} /kcal mol^{-1}	U_Σ /kcal mol^{-1}
↑↓	6.17	−60.0	0.0	0.0	0.0	−40.0	0.5	0.0	0.0	−12.3	−41.46
↑↑	6.20	0.0	0.0	0.0	0.0	90.0	0.5	0.7	0.4	−9.74	−39.04

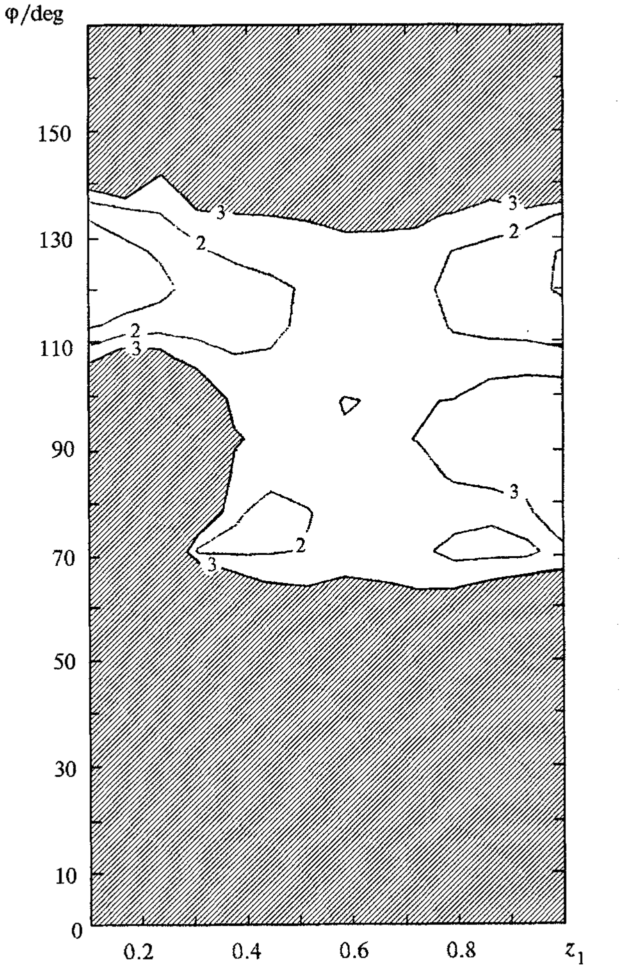


Fig. 7. Two-parameter dependence of E_{crst} on φ_1 and z_1 for the model of orthogonal packing for parallel symmetrically independent chains.

Note that the region, in which the molecule can change its position within this model, is rather wide. This region is normally limited by the range of 3 kcal mol^{-1}.[15] The results of analogous calculations for other models are given in Table 5. Based on these results, it can be proposed that molecules have more freedom when rotating about their axes than when shifting along this axis.

Table 5. Regions of changes of the parameters φ_1 and z_1 for the models of the packings of symmetrically independent molecules

Packing	Orientation of the chain	φ_1/deg	z_1
Orthogonal	↑↓	47—140	0.0—0.1
Hexagonal	↑↑	0—10	0.0—0.42
	↑↓	97—170	0.47—0.55
		30—110	0.0
		150—210	0.0
		−50÷−90	0.0

We thank A. I. Pertsin (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) for providing the PLMR program for calculating the packing of polymer molecules and for valuable advice in the course of this study.

The work was supported by the International Science Foundation and the Russian Universities program (Grants PM5000 and M71000).

References

1. Yu. K. Godovskii and V. S. Papkov, *Mezomorfnoe sostoyanie gibkotsepnykh polimerov, ZhK polimery* [*Mesomorphic State of Flexible-Chain Polymers, Liquid-Crystalline Polymers*], Khimiya, Moscow, 1988 (in Russian).
2. N. N. Makarova, I. M. Petrova, and Yu. K. Godovskii, *Dokl. Akad. Nauk SSSR*, 1983, **269**, 1368 [*Dokl. Chem.*, 1983, **269** (Engl. Transl.)].
3. Yu. K. Godovsky, N. N. Makarova, and I. I. Mamayeva, *Macromol. Chem. Rapid Commun.*, 1986, **7**, 32.
4. N. N. Makarova, E. V. Matukhina, and I. M. Petrova, *Vysokomol. Soedin., Ser. B*, 1989, **31**, 708 [*Polym. Sci. USSR*, 1989, **31** (Engl. Transl.)].
5. T. V. Timofeeva, E. E. Boda, A. P. Polishuk, M. Yu. Antipin, E. V. Matuhina, I. M. Petrova, N. N. Makarova, and Yu. T. Struchkov, *Mol. Cryst. Liq. Cryst.*, 1994, **248**, 125.
6. I. L. Dubchak, A. I. Pertsin, and A. A. Zhdanov, *Vysokomol. Soedin., Ser. A*, 1987, **24**, 567 [*Polym. Sci. USSR*, 1987, **24** (Engl. Transl.)].
7. I. L. Dubchak, T. M. Babchinitser, L. G. Kazaryan, L. M. Tartakovskaya, N. G. Vasilenko, and A. A. Zhdanov, *Vysokomol. Soedin., Ser. A*, 1989, **31**, 65 [*Polym. Sci. USSR*, 1989, **31** (Engl. Transl.)].

8. A. I. Pertsin and O. K. Nugmanov, *Vysokomol. Soedin., Ser. A*, 1981, **23**, 2147 [*Polym. Sci. USSR*, 1981, **23** (Engl. Transl.)].
9. A. I. Pertsin and A. I. Kitaigorodsky, *The Atom-Atom Potential Method*, Springer-Verlag, Berlin, Heidelberg, 1987, 1986.
10. T. V. Timofeeva, I. L. Dubchak, V. E. Shklover, and Yu. T. Struchkov, *Teor. Eksp. Khim.*, 1981, **17**, 674 [*Theor. Exp. Chem.*, 1981, **17** (Engl. Transl.)].
11. F. I. Kolpak and J. Blackwell, *Macromolecules*, 1976, **9**, 273.
12. T. V. Timofeeva, I. L. Dubchak, V. G. Dashevsky, and Yu. T. Struchkov, *Polyhedron*, 1984, **3**, 1109.
13. T. V. Timofeeva, P. M. Zorkii, and A. P. Polishchuk, *Strukturnye issledovaniya zhidkikh kristallov novogo tipa. Diskoticheskie mezofazy i zhidkokristallicheskie kolonchatye H-assotsiaty* [*Structural Studies of Liquid Crystals of a New Type: Discotic Mesophases and Liquid-Crystalline Columnar H-Associates*], in *Problemy kristallokhimii* [*Problems of Crystal Chemistry*], Nauka, Moscow, 1990, 149—166 (in Russian).
14. P. M. Zorkii, *Simmetriya molekul i kristallicheskikh struktur* [*Symmetry of Molecules and Crystal Structures*], Moscow State Univ. Publishers, Moscow, 1986 (in Russian).
15. W. C. McCron, in *Polymorphism, Physics, and Chemistry of the Organic Solid State*, Interscience, New York, 1965, **2**, 725—767.

Received November 25, 1994