Crystal structures of poly(di-n-butyl silane) and poly(di-n-pentyl silane)

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Abstract. The crystal structures of poly(di-n-butyl silane) and poly(di-n-pentyl silane) have been determined by comparing the experimental x-ray diffraction pattern with the theoretical pattern. The side-chain conformation is mostly determined by the intramolecular steric hindrance as well as the van der Waals interaction between the side chains. The Si backbone conformation of both crystals is a $\frac{7}{3}$ helix, which is mainly determined by the intramolecular van der Waals interaction between the nearest-neighbour side chains. On the other hand, the Si backbone conformation of both crystals after a pressure treatment of 1500 MPa is all *trans*, which is caused by the van der Waals interaction between the side chains attached to the second-nearest-neighbour Si atoms. In all cases, one of the two C–Si–C–C groups in Si(C$_4$H$_9$)$_2$ or Si(C$_5$H$_{11}$)$_2$ is an essentially *trans* conformation, whereas the other C–C–Si–C group has a *cis*-like conformation, which is different from that generally accepted.

1. Introduction

Organopolysilanes are one of the candidates for future optical and electronic device materials. They have a one-dimensional silicon backbone, and show an interesting thermochromic behaviour (Kuzmany *et al* 1986, Lovinger *et al* 1986). Such a property has been attributed to the conformational change in the Si backbone. The backbone conformation was examined by the wide-angle x-ray diffraction pattern of the oriented fibres of the materials (Patnaik and Farmer 1992). Up to the present time, the Si backbone conformation of various symmetrically substituted poly(di-n-alkyl silanes) has been reported. For example, poly(di-methyl silane) [Si(CH$_3$)$_2$]$_n$, poly(di-ethyl silane) [Si(C$_2$H$_5$)$_2$]$_n$, poly(di-n-propyl silane) [Si(C$_3$H$_7$)$_2$]$_n$, and poly(di-n-hexyl silane) [Si(C$_6$H$_{13}$)$_2$]$_n$ have an all-*trans* conformation, whereas poly(di-n-butyl silane) [Si(C$_4$H$_9$)$_2$]$_n$ and poly(di-n-pentyl silane) [Si(C$_5$H$_{11}$)$_2$]$_n$ have a $\frac{7}{3}$ helical conformation (KariKari *et al* 1993). However, only a few papers have been published concerning the conformation of the side chains and the packing of the polymer chains (Furukawa and Takeuchi 1993, Furukawa *et al* 1993a, Takeuchi and Furukawa 1993). Moreover, the origin of the variety of the backbone conformation is not known, which is an essentially important problem.

In this paper, the crystal structures of poly(di-n-butyl silane) and poly(di-n-pentyl silane) under an atmospheric pressure as well as a high pressure of 1500 MPa have been examined by comparing the experimental x-ray diffraction pattern with the theoretical pattern. As a result, it is found that the backbone conformation of both crystals under an atmospheric pressure is $\frac{7}{3}$ helix, whereas the conformation after a high-pressure treatment of 1500 MPa is all *trans*, as has been determined previously using oriented fibres. However, the two side chains attached to the same Si atom stretch asymmetrically due to the intramolecular steric

hindrance. This conformation of the side chains as well as the intramolecular van der Waals interaction strongly affects the conformation of the Si backbone. The primitive unit cells have also been determined on the basis of the x-ray diffraction patterns and the reasonable packing of the chains.

2. Theoretical calculation

The computer program to analyse the crystal structure of polysilanes has been developed using conventional diffraction theory (Furukawa *et al* 1992b). A unit cell was first assumed, with the structure factor then calculated for each diffraction index. The Si–Si and C–H bond lengths used in this study were 0.2352 and 0.1090 nm, respectively. The Si–C–C, C–C–H, and H–C–H angles were assumed to be 109.47° (tetrahedral angle).

For the $\frac{7}{3}$ helical conformations under atmospheric pressure, the Si–Si–Si–Si dihedral angle and the Si–Si–Si angle were 149.74 and 117.00°, respectively. The Si–C and C–C bond lengths used for the helical conformations were 0.1946 and 0.1540 nm, respectively. Both the C–Si–C and C–C–C angles were assumed to be 110.00° for the $[Si(C_4H_9)_2]_n$ and $[Si(C_5H_{11})_2]_n$ crystals under an atmospheric pressure.

For the all-*trans* conformations after a high-pressure treatment of 1500 MPa, the dihedral angle was 180.00°. The Si–Si–Si angles for the $[Si(C_4H_9)_2]_n$ and $[Si(C_5H_{11})_2]_n$ crystals were 117.00 and 110.04°, respectively. The Si–C and C–C bond lengths for the all-*trans* conformations were 0.1880 and 0.1530 nm, respectively. The C–Si–C and C–C–C angles were assumed to be 108.00 and 111.00°, respectively, for the high-pressured crystals.

In order to compare the theoretical result with the experimental pattern, the appropriate half width and temperature factor were also assumed. The x-ray diffraction patterns of $[Si(C_4H_9)_2]_n$ and $[Si(C_5H_{11})_2]_n$ reported by Schilling *et al* (1989) were used as experimental data. The wavelength of the x-rays used in the theory and experiment was 0.154 nm (Cu Kα radiation).

3. Results and discussion

The dashed line in figure 1(a) shows the experimentally obtained x-ray diffraction pattern for the poly(d–*n*-butyl silane) under atmospheric pressure (Schilling *et al* 1989). The solid line in figure 1(a) is the pattern from which the background has been eliminated. Figure 1(b) shows the corresponding theoretical diffraction pattern.

Figure 1(b) was obtained on the assumption that the molecules are packed as shown in figure 2. In figure 2, the small open and closed circles indicate Si and C atoms, repectively. The envelope shows the van der Waals radii of the CH_2 and CH_3 groups. *a*, *b*, and *c* indicate the primitive translation vectors, whose magnitudes are 1.284, 2.224, and 1.390 nm, respectively. The magnitude of *c* corresponds to the period of the $\frac{7}{3}$ helical backbone. These values are in good agreement with those reported by KariKari *et al* (1993). The crystal has an orthorhombic unit cell with two polymer chains. The centre helix in figure 2(a) rotates inversely with respect to those at the edges of the unit cell, and the two side chains attached to one Si atom stretch asymmetrically due to the intramolecular steric hindrance. That is, one of the two C–Si–C groups in $Si(C_4H_9)_2$ is almost in a *trans* conformation, whereas the other C–C–Si–C group has a *cis*-like conformation. As shown in figure 2(a) and (b), the molecules are closely packed in space, and the intermolecular distance is well explained by considering the van der Waals radii of the CH_2 and CH_3 groups.
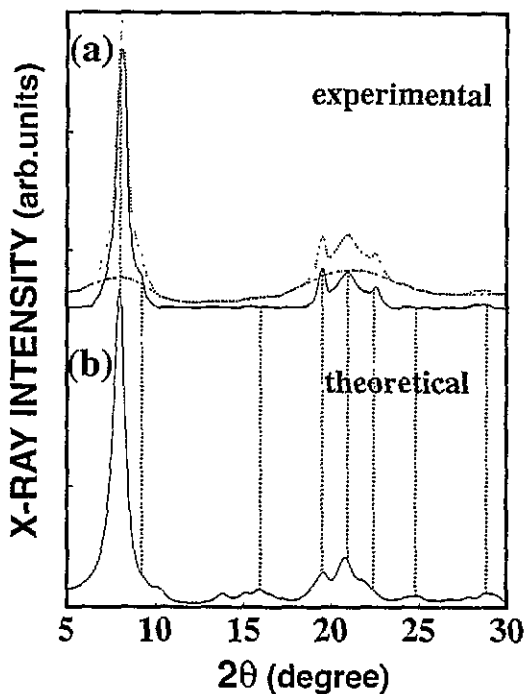
Figure 1. The experimental diffraction pattern (Schilling *et al* 1989) (a) and the present theoretical pattern (b) for the poly(di-*n*-butyl silane) crystal under atmospheric pressure. The solid curve in (a) is the pattern from which the background has been eliminated.
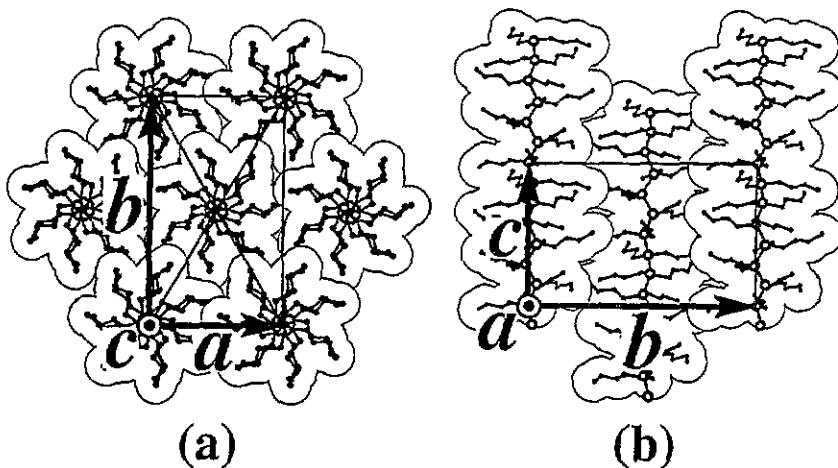

Figure 2. A schematic representation of the structural model for the poly(di-*n*-butyl silane) crystal under atmospheric pressure. (a) and (b) are views from directions parallel and perpendicular to the Si chains, respectively. The small open and closed circles indicate the Si and C atoms, respectively. The envelope shows the van der Waals radii of the CH_2 and CH_3 groups. *a*, *b*, and *c* denote the primitive translation vectors.

From figures 1 and 2, it is concluded that the Si backbone conformation of the poly(di-*n*-butyl silane) crystal under atmospheric pressure is a $\frac{7}{3}$ helix, and the unit cell is orthorhombic ($a = 1.284$ nm, $b = 2.224$ nm, $c = 1.390$ nm). These results are in good agreement with those reported previously. However, the present side-chain conformation

is asymmetric, which is different from those proposed by Walsh *et al* (1990) and Crespo *et al* (1994). In their work, the effect of the intramolecular steric hindrance was not taken into account. Moreover, the present side-chain conformation is supported by the theoretical x-ray diffraction pattern. (The theoretical pattern for the side-chain conformation proposed by Walsh *et al* and Crespo *et al* became quite different from the experimental pattern.) Therefore, the present side-chain conformation is considered to be extremely reliable.
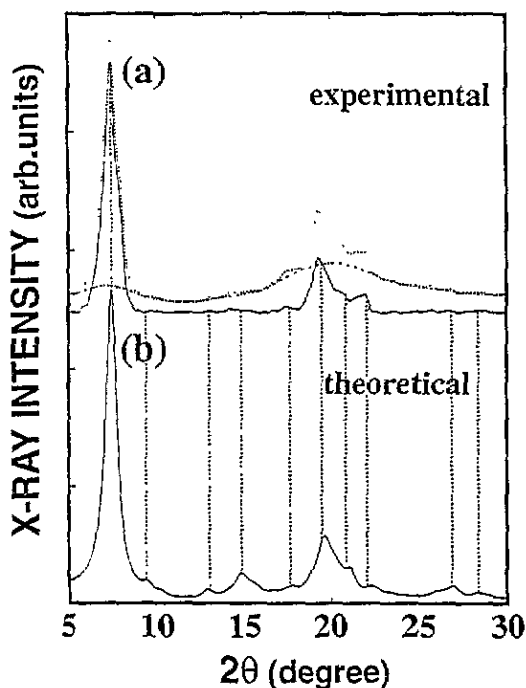

Figure 3. The experimental x-ray diffraction pattern (*Schilling et al* 1989) (a) and the present theoretical pattern (b) for the poly(di-*n*-pentyl silane) crystal under atmospheric pressure. The notations are the same as those of figure 1.

As shown in figure 2(b), each side chain is attached to the nearest-neighbour side chain by the van der Waals force. This result is quite important, because the side-chain configuration determines the position of the Si atom, and hence determines the conformation of the polymer backbone.

Figure 3 shows the x-ray diffraction patterns for poly(di-*n*-pentyl silane) under atmospheric pressure. Similarly to figure 1, the dashed line in figure 3(a) shows the experimental result obtained by Schilling *et al* (1989), and the solid line is the diffraction pattern from which the background has been eliminated. Figure 3(b) shows the corresponding theoretical pattern.

Figure 3(b) was obtained on the assumption that the molecules are arranged as shown in figure 4. In figure 4, the notations are the same as those of figure 2. The magnitudes of the primitive translation vectors, a, b, and c, are 1.385, 2.380, and 1.390 nm, respectively. The magnitude of c corresponds to the period of the $\frac{7}{3}$ helical backbone. The crystal has a monoclinic unit cell ($\beta = 85.00°$) with two polymer chains, and the centre helix rotates inversely with respect to that at the edge of the unit cell. The two side chains attached to one Si atom stretch asymmetrically due to the intramolecular steric hindrance.

The most important point is that the fifth C atom occupies a *gauche*-like position in order to increase the van der Waals interaction between the intramolecular side chains (see
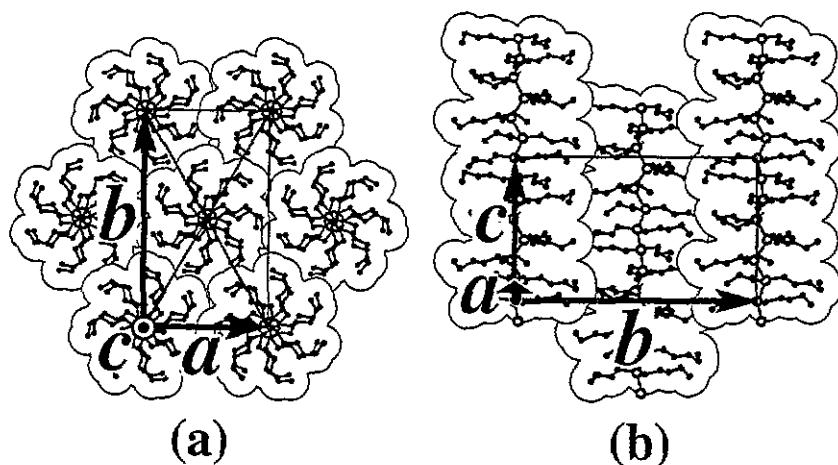
Figure 4. A schematic representation of the structural model for the poly(di-*n*-pentyl silane) crystal under atmospheric pressure. The notations are the same as those of figure 2.
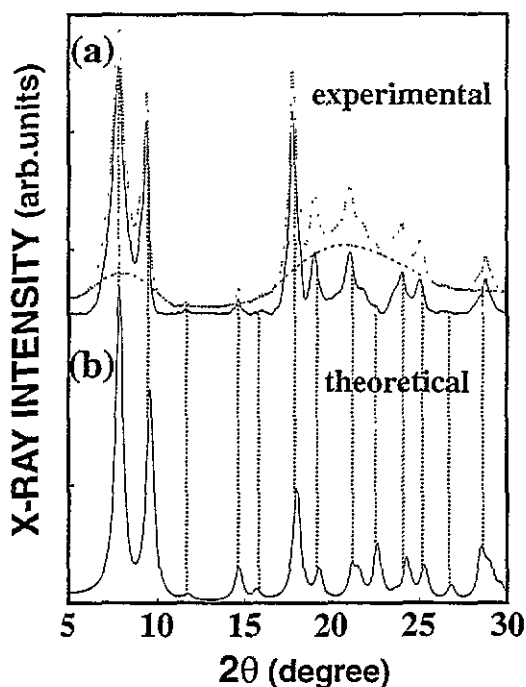

Figure 5. The experimental x-ray diffraction pattern (Schilling *et al* 1989) (a) and the present theoretical pattern (b) for the poly(di-*n*-butyl silane) crystal after a pressure treatment of 1500 MPa. The notations are the same as those of figures 1 and 3.

figure 4(a)). This change in the fifth C atom position from a *trans* one causes a good agreement between the experimental and the theoretical diffraction patterns (see figure 3). This fact strongly supports the above discussion concerning the origin of the $\frac{7}{3}$ helical backbone conformation.

Figure 5(a) shows the experimentally obtained x-ray diffraction pattern for poly(di-*n*-butyl silane) after a pressure treatment of 1500 MPa (Schilling *et al* 1989). Figure 5(b) shows the corresponding theoretical diffraction pattern.
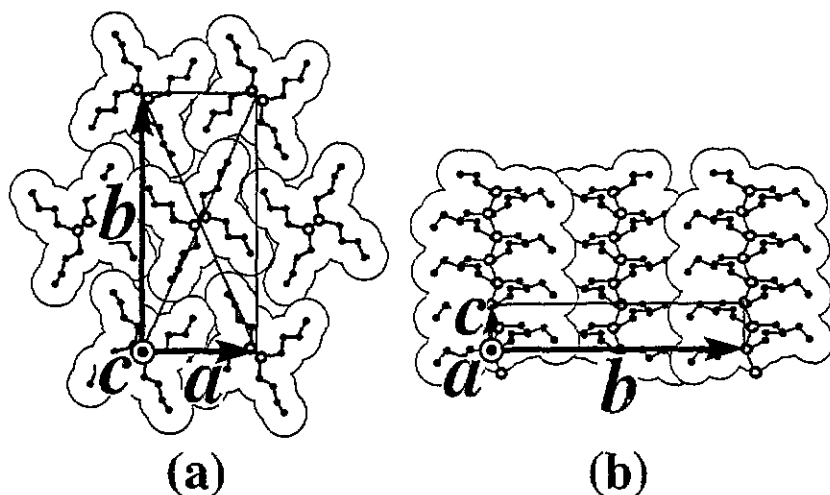
(a)   **(b)**

Figure 6. A schematic representation of the structural model for the poly(di-*n*-butyl silane) crystal after a pressure treatment of 1500 MPa. The notations are the same as those of figures 2 and 4.

Figure 5(b) was obtained on the assumption that the molecules are packed as shown in figure 6. In figure 6, the notations are the same as those of figures 2 and 4. The magnitudes of the primitive translation vectors, a, b, and c, are 1.011, 2.256, and 0.399 nm, respectively. The magnitude of c corresponds to the period of the all-*trans* backbone conformation. The crystal has an orthorhombic unit cell with two polymer chains. Similar to figures 2 and 4, the two side chains attached to one Si atom stretch asymmetrically due to the intramolecular steric hindrance. For the all-*trans* backbone conformation, each side chain interacts with another side chain attached to the second-nearest-neighbour Si atom, as has been reported for poly(dimethyl silane) (Furukawa and Takeuchi 1993), poly(diethyl silane), poly(di-*n*-propyl silane) (Furukawa *et al* 1993a), and poly(di-*n*-hexyl silane) (Takeuchi and Furukawa 1993).

The important point is that the C atoms in a side chain are not in a plane perpendicular to the c axis (see figure 6(b)), probably due to the high pressure of 1500 MPa. Although the side chain has such a complex configuration, the van der Waals interaction between the side chains is well preserved, because the corresponding distance between the two CH_2 or CH_3 groups is almost constant (i.e., the magnitude of the primitive translation vector c, see figure 6(b)).

Figure 7(a) and (b) shows the experimentally obtained x-ray diffraction pattern (Schilling *et al* 1989) and the present theoretical pattern, respectively, for the poly(di-*n*-pentyl silane) crystal after a pressure treatment of 1500 MPa.

Figure 7(b) was obtained on the assumption that the molecules are packed as shown in figure 8. The magnitudes of the primitive translation vectors, a, b, and c, are 1.269, 2.480, and 0.385 nm, respectively. In this case, the backbone conformation is all *trans*. The crystal has an orthorhombic unit cell with two polymer chains. In contrast to figure 6(b), the side chain has a simple configuration, because the magnitude of the vector c is smaller than that in figure 6(b). However, similar to figure 6(b) as well as conventional all-*trans*-backbone organopolysilanes, each side chain is bonded to another side chain attached to the second-nearest-neighbour Si atom by the van der Waals force, which causes the all-*trans* backbone conformation.
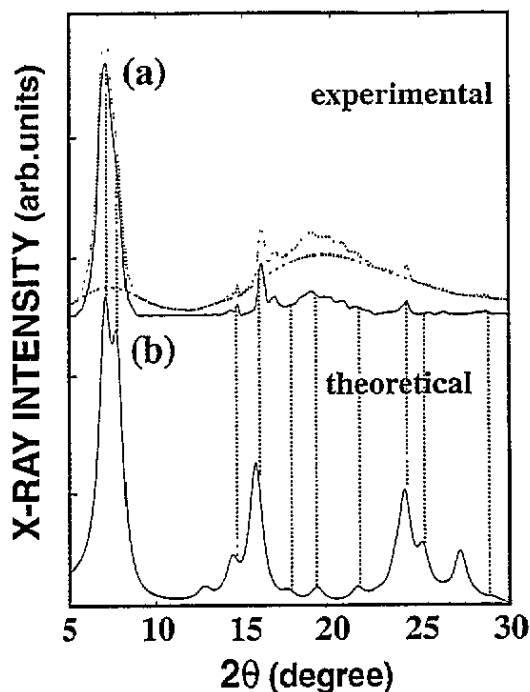
Figure 7. The experimental x-ray diffraction pattern (Schilling *et al* 1989) (a) and the present theoretical pattern (b) for the poly(di-*n*-pentyl silane) crystal after a pressure treatment of 1500 MPa. The notations are the same as those of figures 1, 3, and 5.
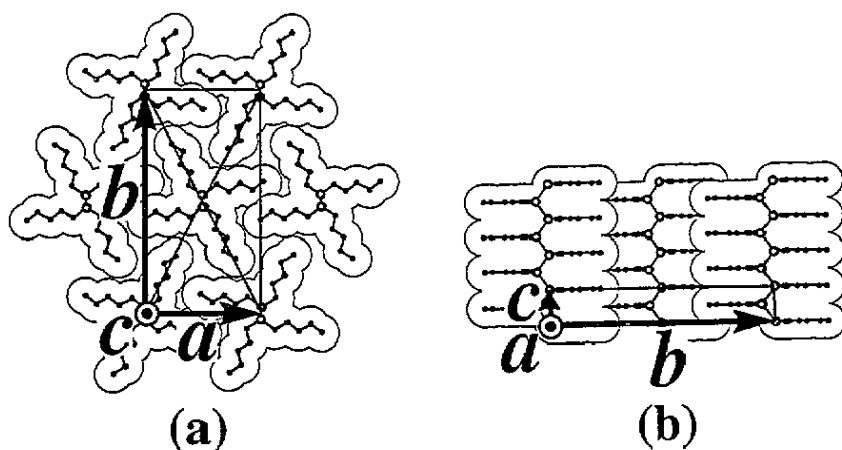

Figure 8. A schematic representation of the structural model for the poly(di-*n*-pentyl silane) crystal after a pressure treatment of 1500 MPa. The notations are the same as those of figures 2, 4, and 6.

4. Summary and conclusion

The structures of the poly(di-*n*-butyl silane) and poly(di-*n*-pentyl silane) crystals have been determined by comparing the experimental x-ray diffraction pattern with the theoretical pattern. The poly(di-*n*-butyl silane) crystal under atmospheric pressure has an orthorhombic unit cell with the values of the lattice parameters $a = 1.284$ nm, $b = 2.224$ nm, and $c = 1.390$ nm. The poly(di-*n*-pentyl silane) crystal has a monoclinic unit cell with

$a = 1.385$ nm, $b = 2.380$ nm, $c = 1.390$ nm, and $\beta = 85.00°$. The Si backbone conformations are both $\frac{7}{3}$ helix.

In contrast to the structures under atmospheric pressure, the backbone conformation is changed to all *trans* after a pressure treatment of 1500 MPa. The poly(di-*n*-butyl silane) crystal has an orthorhombic unit cell with $a = 1.011$ nm, $b = 2.256$ nm, $c = 0.399$ nm. The poly(di-*n*-pentyl silane) crystal also has an orthorhombic unit cell with $a = 1.269$ nm, $b = 2.480$ nm, and $c = 0.385$ nm.

In all cases, the side-chain conformation is asymmetric due to the intramolecular steric hindrance. This result is quite important, because the Si backbone conformation is mainly determined by the side-chain conformation and the van der Waals interaction between the side chains. For the $\frac{7}{3}$ helical backbone, each side chain is bonded to another side chain attached to the nearest-neighbour Si atom by the van der Waals force, whereas it is bonded to another side chain attached to the second-nearest-neighbour Si atom for the all-*trans* backbone. It is considered that the backbone conformation of the poly(di-*n*-hexyl silane) crystal is all *trans* because the intramolecular van der Waals interaction becomes reduced for a $\frac{7}{3}$ helical conformation due to the long side chain of C_6H_{13} (Takeuchi and Furukawa 1993).

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