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Conformational change of a helical polymer molecule induced by periodic modulation of the internal coordinates

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Conformational change of a helical polymer molecule induced by periodic modulation of the internal coordinates around constant values of a uniform helix was studied by numerical calculation. We paid attention to the ‘spatial resonance’ found by Yamamoto *et al*., who carried out analytical calculation to a linear approximation (Yamamoto, M., Kasai, K. and Hikichi, K., *J. Macromol. Sci. (Phys.)*, 1967, **B1(2)**, 213). The spatial resonance means that when the wavelength of the modulation is equal to one turn of the helix, a finite amplitude of the modulation of the internal coordinates leads to divergence of the fluctuation in the external coordinates. We found that the molecular conformation in the spatial resonance induced by the modulation of the internal rotational angle or the bond angle is not a straight helix but is deformed into a ring-shaped helix, which we call ‘ringed-coil’ conformation. On the other hand, the modulation of the bond length does not give rise to the spatial resonance. When both the internal rotational angle and the bond angle are modulated in a proper way the molecular conformation remains as a straight helix, but the atomic positions are displaced from those of the uniform helix. A few possible applications of the concept of the spatial resonance are proposed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: helix; molecular conformation; internal coordinates)

INTRODUCTION

There are two types of coordinate systems used in the study of the molecular conformation and the molecular motion of helical polymer molecules; one is the external coordinate system composed of the helix radius, the rotational angle between the neighbouring monomers around the helix axis, and the interval of the neighbouring monomers along the helix axis, and the other is the internal coordinate system composed of the chemical bond length, the bond angle and the internal rotational angle. The external coordinate system is suitable to express the intermolecular interaction potential. On the other hand the internal coordinate system is suitable to express the intramolecular interaction potential. Therefore, the interrelationship between the external and internal coordinates has to be considered to study the molecular conformation and the molecular motion.

Yamamoto and co-workers studied the thermal motion in the crystal using the internal coordinate system[1–3]. According to Shimanouchi and Mizushima[4] and Miyazawa[5], Yamamoto *et al.* deduced equations applicable to a non-uniform helix connecting the internal and external coordinates to a linear approximation. Their approximation was based on the assumption that the thermal motion deforms the molecular conformation from the uniform helix but keeps the straight shape of the molecule. Using these equations, they calculated the thermal fluctuation of the external coordinates accompanying thermal motion of the internal coordinates, which can be expressed as

$$h(n,t) = \bar{h} + \Delta h \cos\left(\frac{2\pi(n-n_0)}{\lambda} - \omega t + \alpha\right). \qquad (1)$$

In equation (1) h represents one of the internal coordinates: the bond length r, the bond angle ϕ or the internal rotational angle τ. The atoms are numbered successively along the helix. $r(n,t)$, $\phi(n,t)$ and $\tau(n,t)$ are, respectively, the length of the chemical bond between the nth and $(n+1)$th atoms, which is called the nth bond hereafter, the bond angle between the $(n-1)$th and nth bonds and the rotational angle around the nth bond at a time t. $\bar{h}$, Δh, λ, ω and α are, respectively, the time average of h, amplitude, wavelength, angluar frequency and initial phase of the modulation. The wavelength is expressed in terms of the number of bonds; n_0 is a constant. Yamamoto *et al.* obtained an interesting result in that, when λ is equal to one turn of the helix, the fluctuation of the external coordinates diverges; they called this divergence ‘spatial resonance’.

We carried out numerical calculation of the molecular conformation determined by the internal coordinates given by equation (1) to overcome the limitation of Yamamoto’s linear approximation. As reported in a previous paper[6], we found that modulation of the internal rotational angle to satisfy the spatial resonance condition leads to drastic change in the molecular conformation, from a straight helix to a ring-shaped helix. In this work the molecular conformation induced by the modulation of the bond angle and the bond length, as well as the internal rotational angle, is calculated in detail. The results are compared with the results from the analytical calculation by Yamamoto *et al.*

MODEL AND CALCULATION METHOD

We consider a helical molecule composed of one kind of atom. In this study, deformation from the uniform 18/5 helix is calculated. Atomic positions are calculated along the following procedures. We consider the molecular conformation at a time $t = t_0$, assuming that $-\omega t_0 + \alpha = 0$ in equation (1), except when studying phase dependence. Initially the positions of the zeroth, first and second atoms are calculated according to Shimanouchi, Mizushima and Miyazawa equations[4,5] assuming that $r(0,t_0) = r(1,t_0) = \bar{r}$, $\phi(1,t_0) = \bar{\phi}$ and the rotational angle between the neighbouring atoms around the helix axis is equal to the value of the uniform 18/5 helix. $\bar{r}$ and $\bar{\phi}$ are set to be unity and the tetrahedral angle, respectively. The helix axis is assumed to be identical with the z axis of a Cartesian coordinate system. The first atom is put on the x axis. We consider a plane P containing the above three atoms. The zeroth and second atoms are moved on the plane P symmetrically for the x axis to make $\phi(1,t_0)$ equal to the modulated value determined by equation (1). The value of n_0 in equation (1) is set to be 1 to calculate $\phi(1,t_0)$. For the calculation of r and τ the value n_0 is set to be 0.5. With these values of n_0 the modulated internal coordinates are symmetric for the first atom when $-\omega t_0 + \alpha = 0$. Then $r(0,t_0)$ and $r(1,t_0)$ are adjusted to the modulated values. The position for the nth atom ($n \geq 3$) is calculated referring to the positions of the ($n - 3$)th, ($n - 2$)th and ($n - 1$)th atoms using the next equation.

$$\begin{aligned} \boldsymbol{v}_n = \boldsymbol{v}_{n-1} + r(n-1)\{&-\cos\phi(n-1)\boldsymbol{e}_a \\ &+ \sin\phi(n-1)\sin\tau(n-2)\boldsymbol{e}_b \\ &- \sin\phi(n-1)\cos\tau(n-2)\boldsymbol{e}_c\} \end{aligned} \tag{2}$$

where $\boldsymbol{v}_n$ is the vector designating the position of the nth atom. Geometry of the successive four atoms is shown in *Figure 1*. The a and b directions are, respectively, parallel to the ($n - 2$)th bond and perpendicular to the plane determined by the ($n - 3$)th, ($n - 2$)th and ($n - 1$)th atoms. $\boldsymbol{e}_a$, $\boldsymbol{e}_b$ and $\boldsymbol{e}_c$ are unit vectors along the a, b and c axes, respectively. These three unit vectors are given by the following equations.

$$\boldsymbol{e}_a = \frac{\boldsymbol{r}_{n-2}}{|\boldsymbol{r}_{n-2}|} \tag{3}$$

$$\boldsymbol{e}_b = \frac{\boldsymbol{r}_{n-3} \times \boldsymbol{r}_{n-2}}{|\boldsymbol{r}_{n-3} \times \boldsymbol{r}_{n-2}|} \tag{4}$$

$$\boldsymbol{e}_c = \boldsymbol{e}_a \times \boldsymbol{e}_b \tag{5}$$

where $\boldsymbol{r}_n$ is the vector from the nth atom to the ($n + 1$)th atom, that is,

$$\boldsymbol{r}_n = v_{n+1} - v_n. \tag{6}$$

The value of $\bar{\tau}$, which is necessary to calculate the value of $\tau(n - 2)$ in equation (2), is calculated from Shimanouchi, Mizushima and Miyazawa equations[4,5].

RESULTS

Wavelength dependence

Molecular conformation is calculated for various wavelengths of modulation. The molecular conformations induced by the modulation of the bond angle and the bond length are shown in *Figures 2 and 3*, respectively. The molecular conformations induced by the modulation of the internal rotational angle are almost the same with those shown in *Figures 2 and 3* as reported in a previous paper[6]. *Figure 2* show the projection to the xy plane of 72 atoms (from the first to the 72nd atom). After the atomic positions are calculated according to the method explained in the previous section, the whole molecule is rotated around the x axis to move the vector from the first atom to the 73rd atom onto the yxz plane. The solid circles and the lines show the atoms and the chemical bonds, respectively. The wavelength is (*a*) 18, (*b*) 18/2, (*c*) 18/3, (*d*) 18/4, (*e*) 18/5, (*f*) 18/6, (*g*) 18/7, (*h*) 18/8, (*i*) 18/9; (*i*) is shown in only *Figure 2*. It should be remembered that the value of the internal coordinate determined by equation (1) with each of the above wavelength values has a periodicity of 18 bonds. The amplitude of the modulation is $\Delta\phi = 0.943°$ in *Figure 2* and $\Delta r = 0.0165$ in *Figure 3*. The average of the relative displacement between the nth and ($n + 3$)th atoms corresponding to these values of $\Delta\phi$ and Δr is almost the same as that corresponding to $\Delta\tau = 1°$ used in Ref. [6].

It is apparent in *Figure 2e* that the molecular conformation is significantly deformed from the uniform helix when $\lambda = 18/5$. When $\lambda \neq 18/5$ there are 18 solid circles. This means that the molecule has the translational symmetry of the uniform 18/5 helix. In *Figure 2d* and *Figure 2f* the solid circles are notably displaced from the positions of the uniform helix. This suggests that the deformation from the uniform helix becomes significant as the wavelength approaches to 18/5. On the other hand, in *Figure 3* all molecules have the translational symmetry of the uniform 18/5 helix.

Positions up to the 1000th atom are calculated to

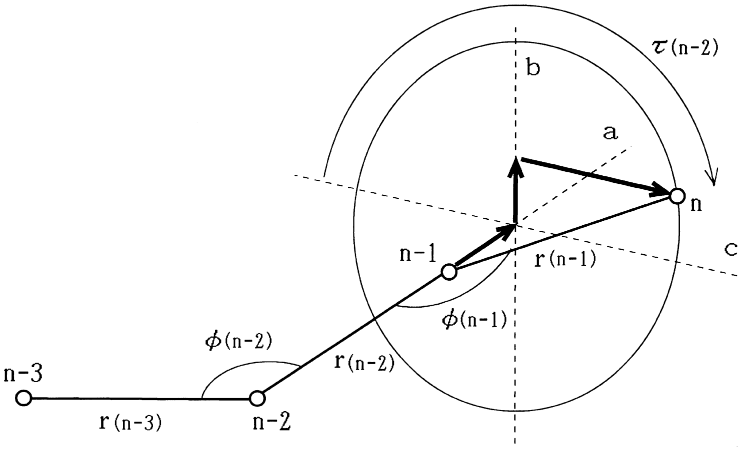

Figure 1 Geometry of the successive four atoms with the structural parameters used in the calculation

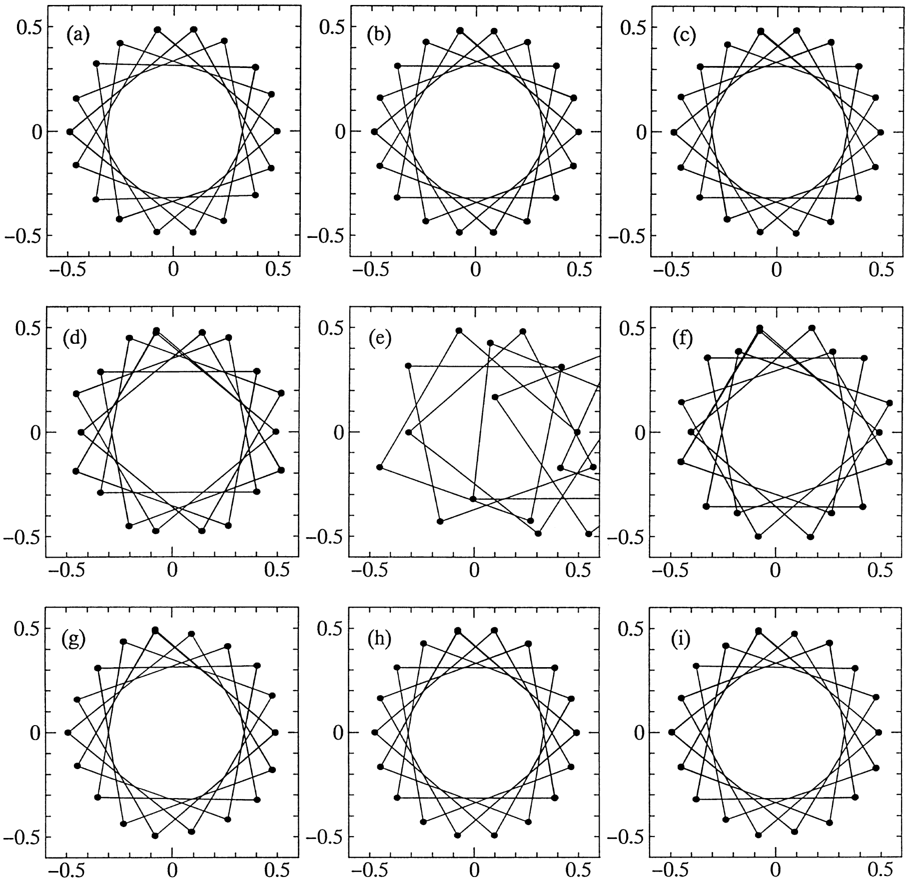

Figure 2 Projection to the *xy* plane of the deformed molecules composed of 72 atoms with the modulation of the bond angle. The wavelength of the modulation is (*a*) 18, (*b*) 18/2, (*c*) 18/3, (*d*) 18/4, (*e*) 18/5, (*f*) 18/6, (*g*) 18/7, (*h*) 18/8 and (*i*) 18/9. The solid circles and the lines show the atoms and the chemical bonds, respectively

investigate the conformation induced by the modulation of the bond angle closely around $\lambda = 18/5$. The amplitude is the same with the above calculation. Results are shown in *Figures 4 and 5*. *Figures 4 and 5* show, respectively, the projections to the *yz* and *xz* planes of the molecule. The conformation with the modulation of the internal rotational angle, which was already reported in a previous paper[8], is almost the same as those shown in *Figures 4 and 5*. Atomic positions are not corrected by rotation around the *x* axis. The molecule is expressed by successive lines connecting every 18 atoms or open circles expressing every 18 atoms. The straight lines (*a*) in each figure show the uniform helix. The wavelength is (*b*) 18/4.9, (*c*) 18/4.95, (*d*) 18/4.995, (*f*) 18/5, (*g*) 18/5.005, (*h*) 18/5.01, (*i*) 18/5.05 and (*j*) 5.1.

Figures 4 and 5 show that significant deformation from the uniform helix occurs in a narrow range of the wavelength around $\lambda = 18/5$. At a wavelength close to 18/5 the helix axis is deformed from a straight line into a helix; the molecular conformation is a coiled-coil. As the wavelength approaches to the 18/5 the radius of the helix becomes larger and the helix pitch of the helix axis becomes smaller. When $\lambda = 18/5$ the helix axis becomes a ring. The conformation at $\lambda = 18/5$ will be called ‘ringed-coil’ conformation hereafter.

It should be noted that $\lambda = 18/5$ is the wavelength equal to one turn of the helix. Conformational change starting from a uniform 19/6 helix was calculated similarly to the case of 18/5 helix, and the ringed-coil conformation was found at $\lambda = 19/6$. This shows that the ringed-coil conformation is not due to the value of 18 or 5. Thus it is confirmed that the ringed-coil conformation occurred when the wavelength was equal to one turn of the helix. This means that the divergence of the external coordinates found by Yamamoto and co-workers[1–3] corresponds to the deformation into the ringed-coil conformation.

Conformational change due to the modulation of the internal rotational angle with a wavelength equal to a multiple of 18/5 is calculated. Two cases such as $\lambda = 2 \times (18/5)$ and $\lambda = 3 \times (18/5)$ are investigated and the ringed-coil conformation is found in both cases. However, the singularity of these two cases is much weaker than the case of $\lambda = 18/5$. The amplitude of the modulation is set to be 5°. The radius of the ring at $\lambda = 2 \times (18/5)$ and $\lambda = 3 \times (18/5)$ is, respectively, 650 and 2×10^4 while it is 100 when $\lambda = 18/5$ with an amplitude of 1°. The singularity at the wavelength equal to multiple turns of the helix was not pointed out be Yamamoto and co-workers[1–3]. The new singularity will be obtained by calculation in higher order approximation.

The mode of the modulation with a wavelength equal to one turn of the helix was called ‘$E(\theta)$ mode’ by Yamamoto *et al.*[1] accounting for the symmetry of the atomic displacement. However, the symmetry is based on the assumption that the deformed helix is still in a straight shape. This assumption is not correct as shown in *Figures 4 and 5*. Therefore the term ‘$E(\theta)$ mode’ is not proper in this case.

Amplitude and phase dependence

Dependence of the conformational change on the amplitude and the phase is calculated. The wavelength is fixed to be 18/5. The amplitude investigated is 1–5° at 1° intervals for $\Delta\tau$, and 1, 2, 3, 4 and 5 times 0.943° for $\Delta\phi$. The

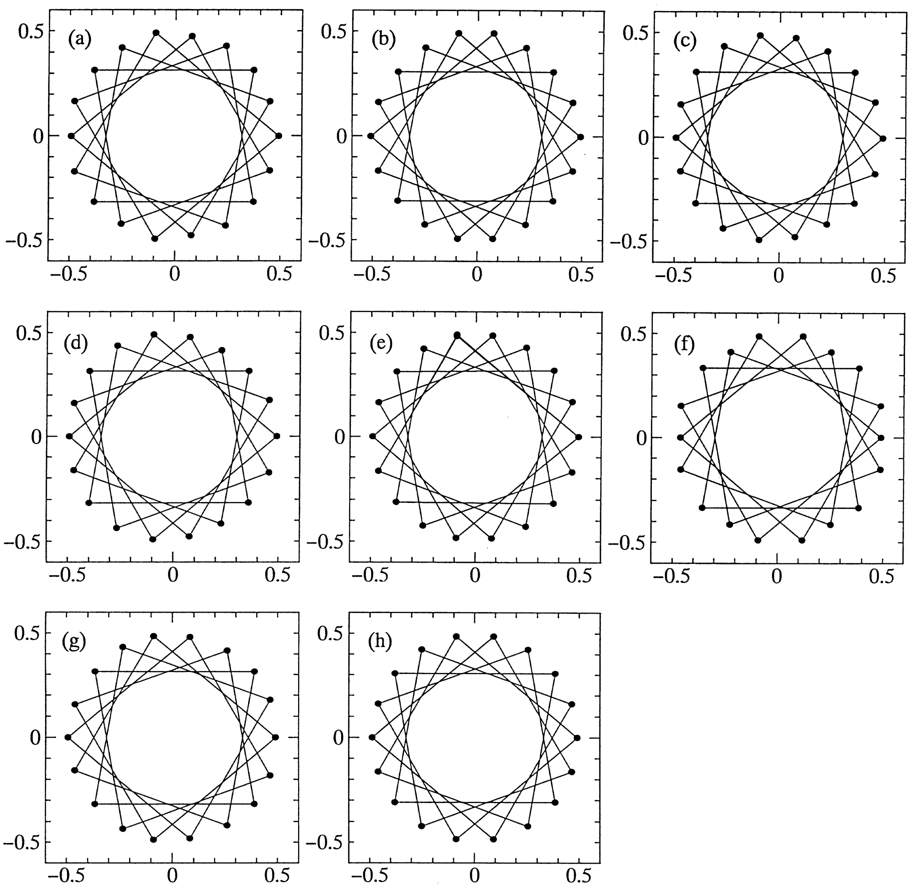

Figure 3 Projection to the *xy* plane of the deformed molecules composed of 72 atoms with the modulation of the bond length. The wavelength of the modulation is (*a*) 18, (*b*) 18/2, (*c*) 18/3, (*d*) 18/4, (*e*) 18/5, (*f*) 18/6, (*g*) 18/7 and (*h*) 18/8. The solid circles and the lines show the atoms and the chemical bonds, respectively

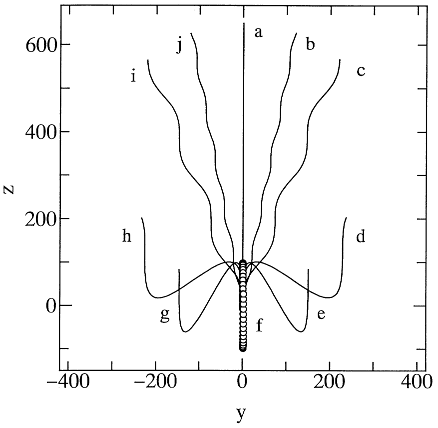

Figure 4 Projection to the *yz* plane of the molecules composed of 1000 atoms. The molecule is expressed by successive lines connecting every 18 atoms ((*a*)–(*e*) and (*g*)–(*j*)) or open circles expressing every 18 atoms (*f*). The straight line (*a*) is the uniform helix. (*b*)–(*j*) show the deformed molecules by modulation with a wavelength of (*b*) 18/4.9, (*c*) 18/4.95, (*d*) 18/4.99, (*e*) 18/4.995, (*f*) 18/5, (*g*) 18/5.005, (*h*) 18/5.01, (*i*) 18/5.05 and (*j*) 5

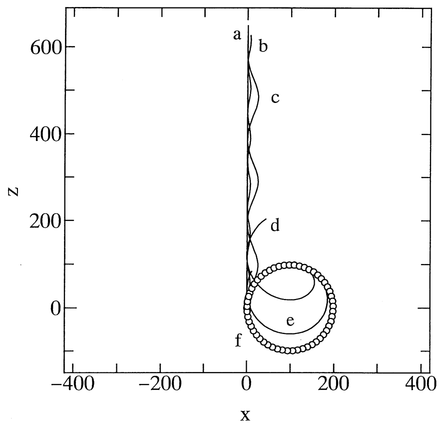

Figure 5 The same molecules with those in *Figure 4* projected to the *xz* plane

calculated radius of the ring is given in *Table 1*. The first column shows the amplitude of the modulation. The second and third columns show the radius of the ring due to the modulation of τ and ϕ, respectively. The radius of the ring is almost linear to the inverse of the amplitude within the amplitude range investigated.

The phase $-\omega t + \alpha$ in equation (1) is changed from 0 to 315° at 45° intervals. Phase dependence in the case of the modulation of the internal rotational angle is the same as that of the bond angle. As the phase $-\omega t + \alpha$ becomes larger the ringed-coil is rotated clockwise around the z axis stepwise at the step of 45°. This result is as expected because the phase of the modulation varies by 360° during one turn of the helix.

Complex mode

As mentioned above, the conformational change induced by the modulation of the internal rotational angle is similar to that of the bond angle. It is expected that a proper superposition of the modulation of the bond angle on the

Table 1 Amplitude of the modulation and radius of the ring of the ringed-coil conformation

Amplitude (°)^a	Modulation of τ	Modulation of ϕ
Δ_0	99.9	99.2
$2 \times \Delta_0$	49.9	49.6
$3 \times \Delta_0$	33.2	33.0
$4 \times \Delta_0$	24.9	24.7
$5 \times \Delta_0$	19.9	19.7

^{a} $\Delta_0 = 1$ for $\Delta\tau$ and $\Delta_0 = 0.943$ for $\Delta\phi$

Table 2 Amplitude of the complex mode of the internal rotational angle and the bond angle with their ratio

$\Delta\tau$ (°)	$\Delta\phi$ (°)	$\Delta\phi/\Delta\tau$
1	0.936	0.936
2	1.872	0.936
3	2.808	0.936
4	3.744	0.936
5	4.679	0.936

modulation of the internal rotational angle will lead to a straight helix because of compensation for tendency to curve the helix axis. Such a type of complex mode is investiagted by a trial and error method. The wavelength and $\Delta\tau$ are set to be 18/5 and 1°, respectively. Then $\Delta\phi$ is changed until the 73rd atom comes to the position right above the first atom. The phase $-\omega t + \alpha$ of τ and ϕ are fixed to be 0 and 180°, respectively. A similar calculation is carried out for $\Delta\tau = 2$, 3, 4 and 5°. The complex mode which keeps the straight shape of the helix is found for each value of $\Delta\tau$. Values of $\Delta\tau$ and $\Delta\phi$ are given in *Table 2* with the ratio of $\Delta\phi$ to $\Delta\tau$. The values of $\Delta\phi/\Delta\tau$ agree very well with each other. *Figure 6* shows the displacement of atoms from the position of the uniform 18/5 helix. $\Delta\tau$ and $\Delta\phi$ are set to be 5° and 5×0.936°, respectively. In *Figure 6* dr, dθ and dz are displacements in the radial direction of the helix, in the rotational direction around the helix axis, and in the z direction, respectively. *Figure 7* shows a projection of the atomic positions to the xy plane. The solid and open circles are the atomic positions of the uniform helix and the same helix with *Figure 6*, respectively.

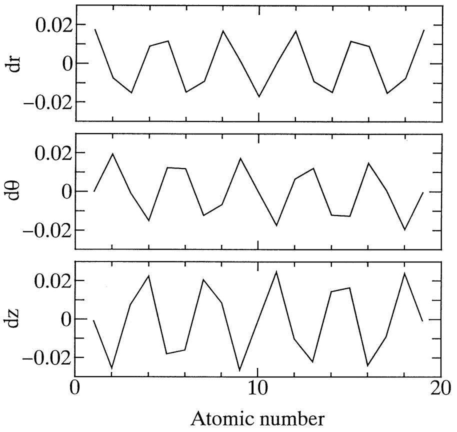

Figure 6 The displacement of atoms due to the modulation of the complex mode from the position of the uniform helix. dr, dθ and dz are displacements in the radial direction of the helix, in the rotational direction around the helix axis, and in the z direction, respectively

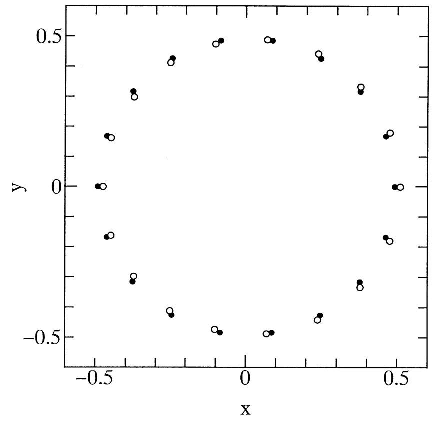

Figure 7 Projection to the xy plane of the atomic positions of the uniform helix (solid circles) and the same molecule with *Figure 6* (open circles)

DISCUSSION

The work by Yamamoto *et al.* was carried out to explain the thermal motion of the rigid helix around the helix axis observed by Chiba *et al.* in the crystal of polyoxymethylene[7]. They suggested that thermal motion satisfying the condition of the spatial resonance is the motion of the rigid helix around the helix axis. Since the molecular conformation in the polyoxymethylene crystal is taken to be an 18/5 helix neglecting the difference between the carbon and oxygen atoms, the results of our calculation can be applied to this case. The thermal motion in the crystal must keep the straight shape of the helix. As shown in *Table 1* the radius of the ring of the ringed-coil conformation is about 100 times the bond length when the amplitude of the modulation is only 1°. The typical thickness of the polymer crystal is similar to the radius of the ring. The spatial resonance mode of only the internal rotational angle or the bond angle give rise to too large curvature of the helix.

The spatial resonance mode which keeps the straight shape of the helix is the complex mode of the internal rotational angle and the bond angle. However, it should be noted that the atomic displacement due to the complex mode is not confined in a plane parallel to the xy plane, as shown in *Figure 6*, and the projection of the atomic displacement is not rotation around the helix axis, as shown in *Figure 7*. Therefore the spatial resonance of the complex mode does not correspond to the thermal motion of the rigid helix around the helix axis in the polyoxymethylene crystal. Molecular motion expressed by a soliton model[8] is another possibility to explain the molecular motion around the helix axis.

It is found that only small modulation of the internal rotational angle or the bond angle around the constant value of a uniform helix can lead to a significant change of the whole conformation. The deformed conformation does not always have the translational symmetry of the original uniform helix if the modulation itself has the periodicity of the original uniform helix. The ringed-coil conformation occurs when the wavelength is equal to one turn of the helix or its multiple. It should be noted that one turn of the helix is not a length equal to a multiple of the interval of neighbouring atoms. The geometric feature of a continuous helix is essential for the occurrence of the ringed-coil conformation. Yamamoto *et al.*[1] pointed out that the spatial resonance occurs due to accumulation of deviation from the uniform helix because the period of the deviation is the same as the turning period of the helix. Occurrence of the spatial resonance when the wavelength is equal to a multiple of the helix turn means that the accumulation effect is not linear to the modulation.

In the linear approximation studied by Yamamoto *et al.* the external coordinates were assumed to change sinusoidally, accompanying the sinusoidal modulation of the internal coordinates. According to their analytical calculation the amplitude of the sinusoidal change in the external coordinates diverges as follows. The following equations are shown in condensed forms to show the essential parts responsible for the divergence; the full forms are given in Ref. [1].

Modulation of τ:

$$\Delta p = f_1(k)(\cos\theta - \cos k)^{-2}\Delta\tau \qquad (7)$$

$$\Delta\theta = f_2(k)(\cos\theta - \cos k)^{-2}\Delta\tau \qquad (8)$$

$$\Delta d = f_3(k)(\cos\theta - \cos k)^{-1}\Delta\tau \qquad (9)$$

Modulation of ϕ:

$$\Delta p = (f_4(k)(\cos\theta - \cos k)^{-2} + f_5(k)(\cos\theta - \cos k)^{-1})\Delta\phi \qquad (10)$$

$$\Delta\theta = (f_6(k)(\cos\theta - \cos k)^{-2} + f_7(k)(\cos\theta - \cos k)^{-1})\Delta\phi \qquad (11)$$

$$\Delta d = f_8(k)(\cos\theta - \cos k)^{-1}\Delta\phi \qquad (12)$$

Modulation of r:

$$\Delta p = f_9(k)(\cos\theta - \cos k)^{-1}\Delta r \qquad (13)$$

$$\Delta\theta = f_{10}(k)(\cos\theta - \cos k)^{-1}\Delta r \qquad (14)$$

$$\Delta d = f_{11}\Delta r \qquad (15)$$

In equations (7)–(15), Δp, $\Delta\phi$ and Δd are the amplitude of the modulation of, respectively, the helix radius, the rotational angle between the neighbouring atoms around the helix axis and the interval of the neighbouring atoms along the helix axis. θ and k are, respectively, the average value of the rotational angle between the neighbouring atoms around the helix axis and the wave number of the modulation. In our present calculation $\theta = 2\pi \times 5/18$. The ringed-coil conformation occurs when $k = 2\pi \times 5/18$. $f_m(k)$ ($m = 1,\ldots,10$) is a continuous function of k and f_{11} is a constant independent of k.

Equation (13) and equation (14) show that the external coordinates diverge due to the modulation of r as well as τ and ϕ. This is inconsistent with the results of our calculation. Paying attention to the order of divergence, however, it can be seen that the ringed-coil conformation occurs only when Δp and $\Delta\theta$ diverge in the second order as $(\cos\theta - \cos k)^{-2}$. It has not yet been explained why the first order divergence is not important for the deformation of the molecule.

The constant value of $\Delta\phi/\Delta\tau$ shown in *Table 2* can be calculated assuming that the sum of the terms of the second order divergence in equation (7) and equation (10) is equal to zero. The obtained value is 0.936 in very good agreement with the values in *Table 2*. The same value can be obtained from equation (8) and equation (11). This is consistent with the above consideration that only the second order divergence is important for the drastic conformational change.

A few possible applications of the concept of the spatial resonance are mentioned below. *Table 1* shows that the radius of the ring of the ringed-coil conformation is less than 20 times bond length when the amplitude is 5°. This suggests the possibility of a rather sharp turn of the molecule in solution or melt without mixing of the *trans* and *gauche* conformations. Such a sharp turn will be able to occur in a hard chain in which conversion from the *trans* to *gauche* or vice versa is difficult.

The spatial resonance may reduce the magnitude of the force constant relevant to the change in the shape of the whole molecule. Large deformation of the whole molecule occurs with only small change of the internal coordinates. The increase of the internal energy due to the deformation will be small because the internal energy mainly depends on the local conformation determined by the internal coordinates. Large deformation with small increase of the internal energy means that the force constant is small.

The small force constant suggests that the molecular motion satisfying the condition of the spatial resonance mode will have a large amplitude and a small frequency. it should be noted that experimental results and computer simulations about various protein molecules showed that the relative motion between the rigid secondary structures connected together by a flexible part is very slow with a large amplitude[9]. Such a mode of molecular motion may correspond to the molecular motion satisfying the condition of spatial resonance.

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