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Conformational change of a helical polymer molecule induced by periodic modulation of internal rotational angles

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Conformation of a helical polymer molecule with periodic modulation of the internal rotational angle was numerically calculated. It was found that the modulation with wavelength equal to one turn of the helix leads to a 'ringed-coil' conformation. When the amplitude of the modulation was one degree the ring was composed of 956 atoms with a diameter 200 times the bond length. © 1997 Elsevier Science Ltd.

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Introduction

A helix is a typical conformation of polymeric materials. Various synthetic polymers such as polytetrafluoroethylene, polyoxymethylene and poly(ethylene oxide) crystallize in the helical conformation. The helical conformation is also typical in biopolymers, such as proteins. It has been recognized that inter- and intramolecular potential energy is dominant in determining the molecular conformation. Numerical calculations of the potential energy have been carried out for a number of materials. On the other hand, a few authors have studied the potential energy dependence of the molecular conformation from a general viewpoint without specifying a material to find common properties[1–3].

There are a couple of coordinate systems to express the helical conformation. The external coordinate system is composed of the helix radius, the interval between the neighbouring atoms along the helix axis and the rotational angle between the neighbouring atoms around the helix axis, while the internal coordinate system is composed of the chemical bond length, the bond angle and the internal rotational angle. The internal coordinate system is suitable to describe the intramolecular interaction potential. To know the general properties of the conformational change accompanying the change in the internal coordinates will be necessary to study the stability and motion of the helical conformation. For a uniform helix, equations connecting the external and internal coordinate systems were given by Shimanouchi and Mizushima[4] and Miyazawa[5]. Equations connecting the two coordinate systems applicable to a non-uniform helix were deduced by Yamamoto et al.[6–8] in terms of linear approximation. Yamamoto et al. found that the periodic modulation of the internal coordinates with wavelength equal to one turn of the helix leads to an infinite change in the external coordinates. However, they have not obtained the actual conformation for that modulation. In this paper preliminary results of the numerical calculation of conformational change induced by periodic modulation of the internal rotational angles will be reported.

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A model and calculation method

A simple helical molecule composed of one type of atom was considered. Each atom was assumed to have only two chemical bonds; the molecule has neither hydrogen atoms nor side chains surrounding the back bone helix. The molecular conformation determined by the internal rotational angles given by the next equation was calculated.

$$\tau(n) = \bar{\tau} + a\cos\left(2\pi\frac{n-0.5}{\lambda}\right) \quad (1)$$

where $\tau(n)$ is the internal rotational angle around the nth bond which designates the bond between the nth and $(n+1)$th atoms. $\bar{\tau}$, a and λ are the average of τ, amplitude and wavelength of the modulation, respectively. The bond length and the bond angle were fixed at unity and the tetrahedral angle, respectively.

The conformational change from the uniform 18/5 helix (eighteen atoms per five turns of the helix) was studied. The value of $\bar{\tau}$ for the uniform 18/5 helix was calculated using the Shimanouchi–Mizushima equations[4,5]. The amplitude a was assumed to be one degree corresponding to an atomic displacement of only 1.6% of the bond length. Two types of calculations were carried out. Firstly, the positions of 72 atoms were calculated for λ values of $18/m$, where $m = 1, 2, \ldots, 8$. It should be noted that these λ values hold the geometrical equivalence of the unit composed of 18 atoms. Secondly, λ dependence of the molecular conformation was studied in detail around $\lambda = 18/5$ because of the reasons explained in the next section. Studied λ values were $18/m$ with $m = 4.9, 4.95, 4.995, 5, 5.01, 5.05$ and 5.1. Positions of 1000 atoms were calculated in the second type of calculations.

Since the bond length and the bond angle were fixed we could determine positions of the first three atoms irrespective of the modulation. We calculated the positions of the first three atoms according to the Shimanouchi–Mizushima equations[4,5]. We assumed that the uniform 18/5 helix is centring around the z axis and an atom is on the positive part of the x axis. The atom on the x axis and the upper (positive z) and lower neighbouring atoms were called the first, the zeroth and the second atoms, respectively. The position of the fourth atom was calculated from the positions of the

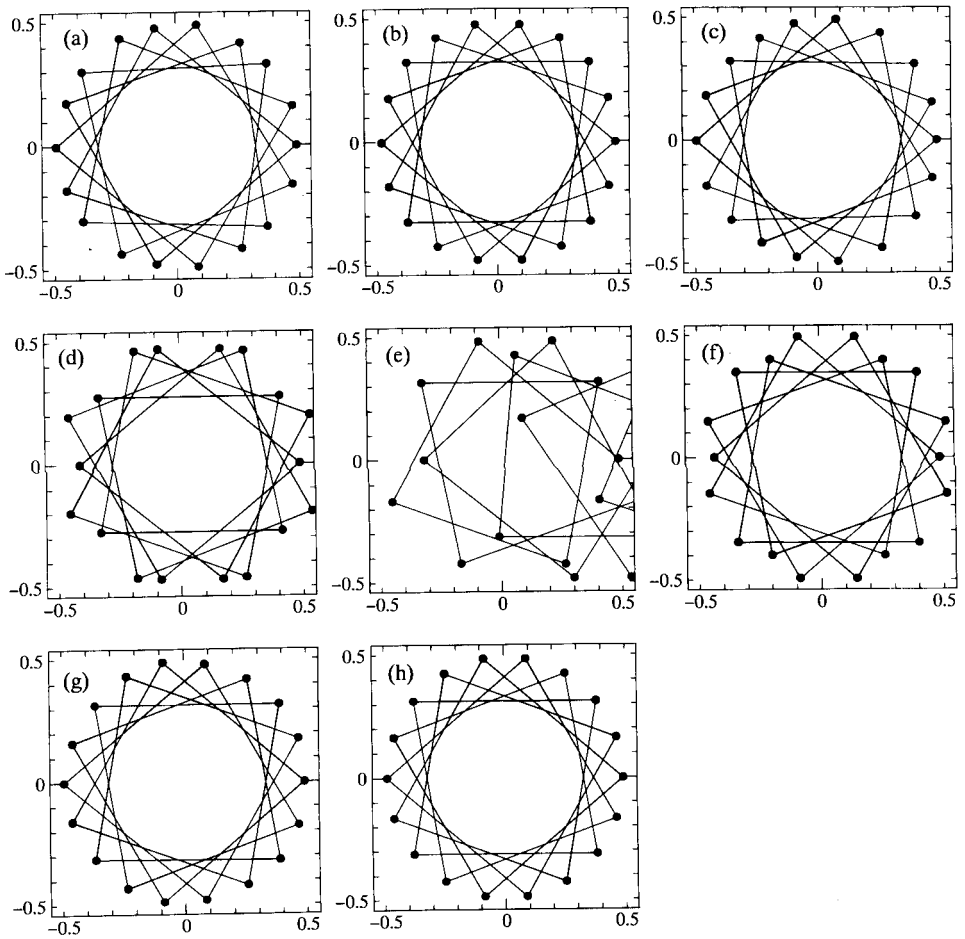

Figure 1 Atoms (solid circles) and chemical bonds (lines) projected to the *xy* plane. The wavelength of the modulation is (a) 18/1, (b) 18/2, (c) 18/3, (d) 18/4, (e) 18/5, (f) 18/6, (g) 18/7 and (h) 18/8

zeroth, first and second atoms and the internal rotational angle of the first bond. Positions of the successive atoms were calculated in the same way. Atomic positions only in the upper direction were calculated, because the molecular conformation determined by equation (1) is axially symmetric around the x axis. In the first type of calculation, positions of the centre of mass were calculated for the first and last 18 atoms, which were not on the z axis when the amplitude a was not zero. The atomic positions were rotated around the x axis in order to move the centre of mass on the xz plane.

Results and discussion

Results of the first type of calculation are shown in *Figure 1*. The atomic positions are projected on the xy plane. Solid circles and lines express the atoms and the chemical bonds, respectively. The wavelength decreases from 18/1 to 18/8 corresponding to *Figure 1a–h*. In *Figure 1a–d* and *Figure 1f–h* there are eighteen solid circles. This means that the molecule has translational symmetry along the z axis with the period of eighteen atoms. On the other hand *Figure 1e* shows a significantly distorted conformation. It can be seen that the atomic positions in *Figure 1d* and *f* are notably displaced from a circle. These results suggest that conformational change becomes more significant as the wavelength approaches to 18/5.

The second type of calculation was carried out to investigate detailed conformational change around $\lambda = 18/5$. Results are shown in *Figure 2*. *Figure 2a* and *b* show

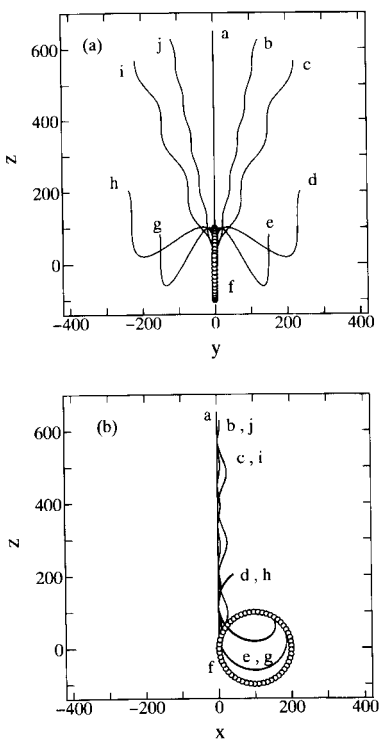

Figure 2 Curves b–j show molecular conformations for the wavelength close to 18/5 and curve a shows the uniform 18/5 helix projected to the (a) *yz* plane and (b) *xz* plane. The wavelength is: b, 4.9; c, 4.95; d, 4.99; e, 4.995; f, 5; g, 5.005; h, 5.01; i, 505; and j, 5.1. The curves, except f, show successive chemical bonds; open circles of f show the $(18p + 1)$th atom ($p + 0, 1, 2, \ldots$)

projections on to the yz and xz planes, respectively. Curve a is the uniform 18/5 helix. Curves b–e and g–j are the results for $\lambda = 18/5/m$ with $m = 4.9, 4.95, 4.99, 5.005, 5.05$ and 5.1, respectively, These curves are composed of successive chemical bonds. Curves b–e and g–j exhibit the coiled-coil conformation. A distinct conformation was found for $\lambda = 18/5$, as shown by open circles designated by *Figure 2f*. Open circles show the positions of the $(18p + 1)$th ($p = 0,1,2,\ldots$) atoms. The open circles are arranged along a ring on the xz plane. This means that the axis of the uniform helix becomes a ring when $\lambda = 18/5$. Such a conformation could be called a 'ringed-coil' conformation. One turn of the ring is composed of 956 atoms although the position of the 957th atom is not identical with the position of the first atom. The diameter of the ring is ca. 200 times the bond length. It can be seen that, as the wavelength approaches 18/5 from smaller values, the helix axis becomes notably distorted from a line to a helix and inclined to the positive y direction. The 'helix of the helix axis' reaches a ring when the wavelength is equal to 18/5. Then the 'helix of the helix axis' is directed to the negative y direction for the wavelength larger than 18/5 and returns to the line of the uniform helix as the wavelength departs from 18/5. This change of the shape of the helix axis occurs in a narrow range of the wavelength.

It should be noted that the wavelength of 18/5 corresponds to one turn of the uniform 18/5 helix. We carried out similar calculations starting from 19/6 helix and found that the wavelength corresponding to one turn of the uniform 19/6 helix was also singular. This result means that the singularity of the molecular conformation is not due to the numbers 18 and 5 but due to the wavelength equal to one turn of the helix. Therefore the results shown in *Figures 1 and 2* agree with the results of Yamamoto et al. It can be seen that the change in external coordinates from the values of the uniform helix becomes infinite in a linear approximation. The molecular conformation with modulation of the bond angle and the bond length will be reported in the near future, with detailed comparison with the results of Yamamoto et al.

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