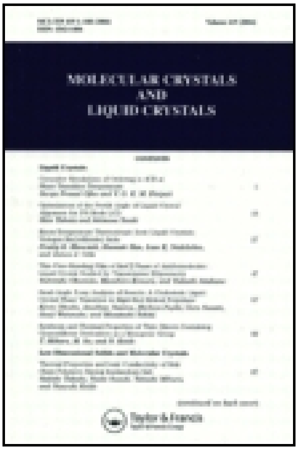

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Orbital Study on the Ferroelectricity of Odd Nylons

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To cite this article: Akira Imamura, Hiroshi Kubota, Yutaka Ogawa & Yuriko Aoki (1996): Molecular Orbital Study on the Ferroelectricity of Odd Nylons, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 278:1, 99-109

To link to this article: http://dx.doi.org/10.1080/10587259608033661

Mol. Cryst. Liq. Cryst., 1996, Vol. 278, pp. 99–109
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MOLECULAR ORBITAL STUDY ON THE FERROELECTRICITY OF ODD NYLONS

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ABSTRACT

Recently, nylon-11 and nylon-7 have been found to be ferroelectric and this ferroelectricity was related to hydrogen bonds between polymer chains. When the crystal structure of nylon-11 is complete and has little disordered structures, the ferroelectricity is difficult to be exhibited because of the fairly strong network of the hydrogen-bonding system. The ferroelectricity is obtained for nylon with the slightly disordered crystal structure. This was confirmed by measuring the vibrational frequency for the N-H bond stretching. For the nylon with the disordered crystal structure, the vibrational frequency was found to shift to the higher wavenumber, indicating the loosening of the hydrogen-bond in question.

In the present paper, we calculate the vibrational frequency for the N-H bond stretching by using ab initio molecular orbital method in order to shed light on the relation between the degree of the disorder of the crystal and the magnitude of the shift of the vibrational frequency. In connection with this research, we had proposed a method, by which we can determine the structure of the molecule in the crystal. In this method, the geometry of the central molecule is optimized under the effect of the environmental molecules with the fixed geometry. After the optimization of the central molecule, the geometry of the environmental molecules is changed to that of the central molecule. This procedure is continued iteratively until the convergence in the geometry is obtained. We refer to this method as S-SCF method(structual SCF method). By using this S-SCF method, we obtained the intimate relation between the shift of the vibrational frequency and the degree of the disorder of the crystal and also the barrier for the polarization reversal in agreement with experimental data.

INTRODUCTION

Nowadays, the progress in the molecular orbital theory together with remarkable increment of the ability of electronic computers make us accessible to the study on physico-chemical properties of polymers from view point of the electronic structure of the polymer[1,2]. The ferroelectricity is also one of these physico-chemical properties of polymers.

Recently, nylon-11 and nylon-7 have been found to be ferroelectric[3,4,5] and this ferroelectricity was related to hydrogen bonds between polymer chains. When the crystal structure of nylon-11 is complete and has little disordered structures, the ferroelectricity is difficult to be exhibited because of the fairly stable network of the hydrogen-bonding system[3,4,5,6]. The ferroelectricity is obtained for nylons with the slightly disordered crystal structure. This was confirmed by measuring the vibrational frequecy for the N-H bond stretching[7]. For the nylon with the disordered crystal structure, the vibrational frequency was found to shift to the higher wavenumber, indicating the loosening of the hydrogen-bond in question.

Although the shift in the vibrational frequency for the N-H bond stretching in hydrogen-bond gives a measure of the degree of the disorder qualitatively, little is known concerning the molecular structural information for the appearence of the ferroelectricity of nylon-11. On the other hand, ab initio molecular orbital theory can predict quantitatively the molecular structure and the frequency analysis for vibrational spectra. In addition to this, we had proposed a novel method[8] , by which we can determine the structure of the molecule in the crystal, that is, S-SCF method which will be explained later. Consequently, in the present article, we study the relationship between the degree of the disorder in a model system and the shift in the frequency of the N-H bond stretching vibration as well as the potential barrier for the rotation of the peptide group in connection with the polarization reversal by using the ab initio S-SCF method.

METHOD OF CALCULATIONS

In order to study the molecular and the electronic structures of a molecule in a crystal, we proposed previously S-SCF method (structural SCF method). The detail of this method was already published in the previous paper[8], and then only this method is briefly described in this article. In this method, the geometry of the central molecule is optimized under the effect of the environmental molecules with the fixed geometry. After the optimization of the central molecule, the geometry of the environmental molecules is changed to that of the optimized central molecule. This procedure is continued iteratively until the convergence in the geometry between the central and the environmental molecules is obtained. By this procedure, we can calculate the molecular and the electronic structures of a molecule in a crystal with relatively small number of the geometrical variables in the optimization procedure. In the present article, we applied ab initio molecular orbital method to the hydrogen bonding network system in odd nylons which have peptide groups. The effect of the neighboing peptide groups in the network system is reasonably taken into account by the above-mentioned S-SCF method. Ab initio molecular orbital calculations were carried out with Gaussian 90 or 92 program package with various types of basis sets.

RESULTS AND DISCUSSION

Molecular Structure of Odd Nylons in a Crystal

In Figure 1, the crystal structure of Nylon 7 is shown, indicating the hydrogen bonding network system through peptide groups. In Figure 2, the structures of the unit for Nylon 5, Nylon 7 and Nylon 11 are shown. First of all, a series of isolated model eompounds for odd nylon shown in Figure 3 were calculated by ab initio molecular orbital method with the basis set of 6-31G$**$. The obtained results are listed in Table I for from n=0 (Nylon 3) to n=4 (Nylon 11). The number n indicates the number of methylene units in a segment of odd nylons (see Figure 3). The bond lengths and bond angles calculated are in good agreement among Nylons 5,7,9 and 11. Moreover, the molecular structure of the model molecule for Nylon 11 obtained by 3-2lG basis set is found to reproduce that by 6-31G$**$ basis set. Accordingly, it may reasonably be expected that the model compound for nylon 5 is a pretty good model for the study of the ferroelectricity of odd nylons, and the ab initio MO calculations with 3-21G basis set is reliable enough.

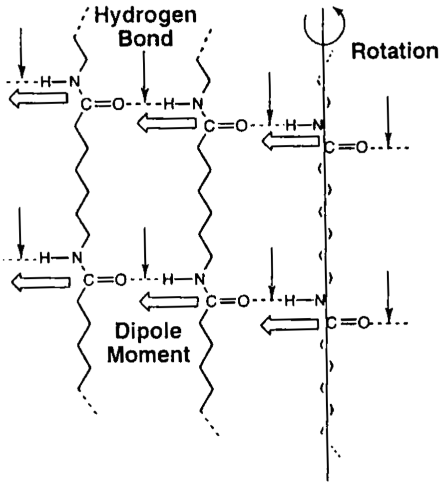
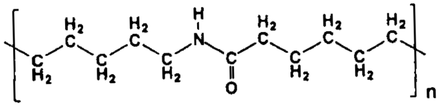
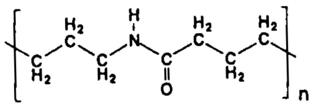


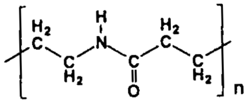
FIGURE 1 Structure of nylon-7 in crystal



nylon 11



nylon 7



nylon 5

FIGURE 2 Structure of odd nylons

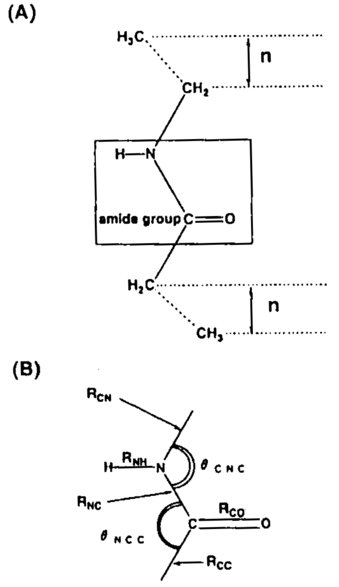


FIGURE 3 Model for the isolated model and geometrical parameters for the optimization

TABLE I Optimized bond lengs and bond angles with 6-31G**

n=	0	1	2	3	4
Nylon	3	5	7	9	11
Bond Length (Å)					
R_{CN}	1.4497	1.4533	1.4538	1.4538	1.4536
R_{NC}	1.3520	1.3517	1.3515	1.3514	1.3514
R_{CC}	1.5159	1.5207	1.5216	1.5208	1.5206
R_{NH}	0.9915	0.9927	0.9927	0.9927	0.9926
R_{CO}	1.2006	1.2010	1.2013	1.2014	1.2014
Bond Angle (degree)					
θ_{CNC}	121.3789	.9030	.9608	.9613	.9774
θ_{NCC}	115.2993	.0958	.1041	.0824	.0615

Geometry Optimization of the Model Compound for Nylon-5 in the Crystal

In order to carry out the geometry optimization of the model compound for nylon-5 in the crystal, the model for the crystal in Figure 4 was employed. The geometry was determined by using S-SCF method which is described in the previous section. The central model compound is treated as the central molecule and two neighboring molecules as the environmental molecules. The obtained geometry is listed in Table II, indicating that C=O bond length in the peptide group get longer by 0.01 Å and N-H bond length by 0.009 Å. The change in the geometry is due to the formation of the hydrogen bond between C=O and N-H groups.

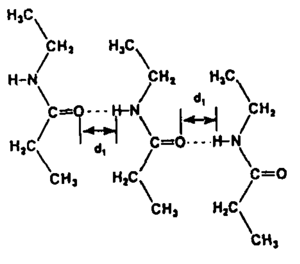


FIGURE 4 Model system for the nylon-5 crystal

TABLE II Optimized geometrical parameter for the molecule in crystal and the isolated molecule

	Molecule in crystal (calculated by S-SCF method)	Isolated molecule ($d_1=\infty$ in Figure 4)
	Å)	
R_{CN}	1.4658	1.4673
R_{NC}	1.3387	1.3539
R_{CC}	1.5190	1.5202
R_{NH}	1.0045	0.9960
R_{CO}	1.2300	1.2192
d_1	1.9530	—
θ_{CNC}	120.5471	120.7687
θ_{NCC}	114.5513	115.0437

The Degree of Disorder, the N-H Stretching Vibration and the Potential Barrier for the Rotation by Polarization Reversal.

In order to study the relation between the degree of the disorder in the crystal of odd nylons and the shift in the wavenumber of the N-H stretching vibration, we carried out the frequency analysis for the model compounds for the nylon shown in Figure 5. In this figure, the model [I-I] is the isolated hydrogen bonding system, while [II-I-I-II] is the hydrogen bonding network system. Consequently, the effect of the network system on the frequency for the N-H stretching vibration is evaluated by comparing these two systems. The obtained wave numbers for the N-H stretching vibration with 3-21G basis set are shown in Figure 6 for [I-I], [II-I-I-II] and the isolated systems. The differences in the wave number between the isolated and the hydrogen bonding molecules are given in the parenthesis. Since the calculated wave number is well known to be generally overestimated by about 10%, the obtained wave number is multiplied by 0.9. Thus, the wave number for the isolated molecule is 3460 cm^{-1} in good agreement with the experimental value of 3400 cm^{-1}. The shift in the wave number due to the formation of the hydrogen bond is calculated to be 145 cm^{-1} corresponding to the experimental value of about 150 cm^{-1}.

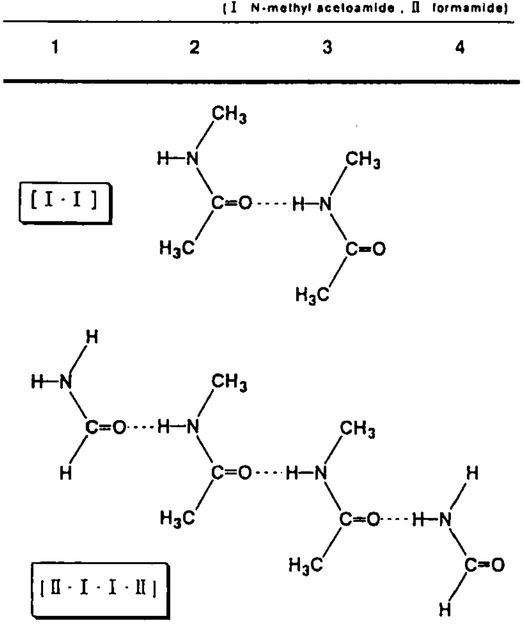


FIGURE 5 Model systems for nylons

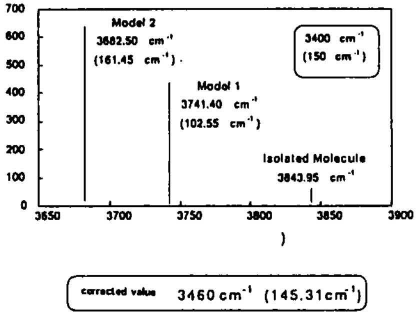


FIGURE 6 Frequency of the N-H bond stretching viblation in the hydrogen bonding system

It is obvious that the ab initio molecular orbital calculations with 3-21G basis set give reliable results for the frequency of the N-H stretching vibration in the hydrogen bonding system. Consequently, by comparing the frequency for the N-H bond for the model [I-I] with that for the model [II-I-I-II], we can evaluate the hydrogen bond network effect on the frequency. The shift in the frequency for [II-I-I-II] is larger than one for [I-I], indicating that the network strengthens the hydrogen bond. In other words, the complete hydrogen bonding network system can reasonably be expected to be stable enough and resistant to the rotation of the peptide group for the polarization reversal. This expectation is corresponding with the fact that the disordered structure in the crystal is required for the appearance of the polarization reversal for odd nylons.

We are now in a position to study the relation between the degree of the disorder in the crystal and the shift in the frequency for the N-H stretching vibration, and also the height of the potential barrier for the rotation of the peptide group which is relevant to the polarization reversal of odd nylons. The degree of disorder is introduced as a model case by the variation in the relative location of the CO and the NH groups in the hydrogen bond as shown as parameters, d_L and d_R in Figure 7. When $d_L=0$ or $d_R=0$, the CO and the N-H groups locate in line to form a complete hydrogen bond. The larger the value of d_L or d_R is, the more the degree of the disorder is. The value of d_L or d_R ranges from 0.0 to 1.0Å. Next, in order to study the interrelation between the degree of the disorder and the polarization reversal, the potential barrier for the rotation of the peptide group have to be calculated for various geometries which correspond to various values of d_L and d_R. The axis for the rotation goes through the middle points of the N-CO and the CO-CH$_3$ bonds as shown in Figure 7. The potential barriers for the rotation were calculated for various types of model systems of the hydrogen bonding network shown in Figure 8 in order to evaluate the effect of the hydrogen bonding network system on the rotational potential barrier.

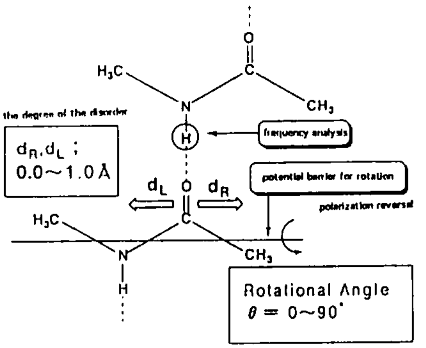
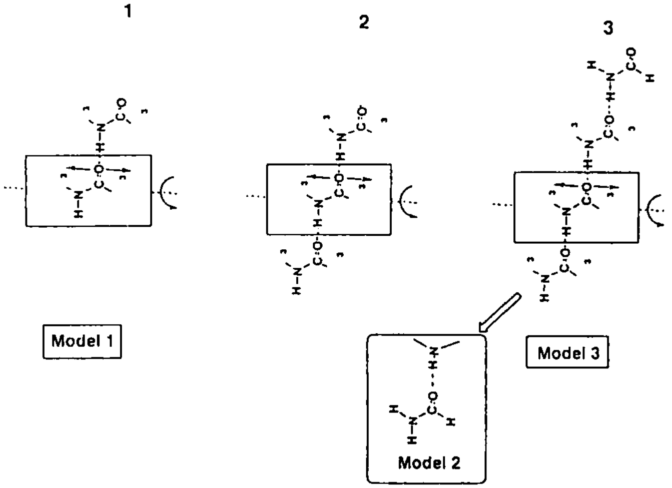


FIGURE 7 schematic illustration for the degree of the disorder, d_L and d_R



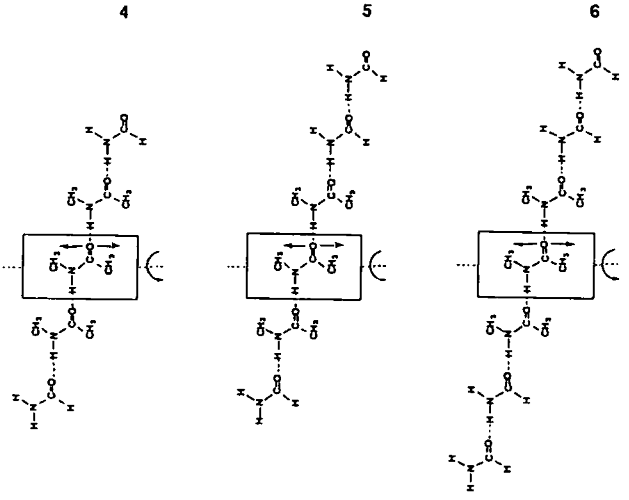


FIGURE 8 Models for the hydrogen bonding network system

In Figure 9, the calculated potential barriers are plotted as the number of hydrogen bonds. In this figure, the value of ΔERot is obtained as the difference between the potential barrier at d_L=0 and that at d_L=1.0Å. From this result, it is obvious that the model system with three hydrogen bonds is adequate to evaluate the difference in the potential barrier with reference to the degree of the disorder. In other words, the effect of the hydrogen bonding network is localized within a few peptide groups with regard to the potential barrier for the rotation. Hereafter, the model 1 and the model 2 in Figure 8 were calculated for the frequency analysis while the model 1 and the model 3 in Figure 8 were used for the calculation of the potential barrier. The model 2 is appropriate for the frequency analysis because of the small size of the system which decreases the computation time of the frequency analysis. The model 3 is appropriate for the calculation of the potential barrier since the lack of the methyl groups in the model 2 should probably be of some effect on the stability of the hydrogen bond, and then on the rotational barrier. In Figure 10, the changes in the rotational barrier as the function of the values of d_L and d_R are plotted against the shift in the frequency of the N-H stretching vibrations as the function of the values of d_L and d_R. We can see from this figure that the degree of the disorder is predicted by the shift in

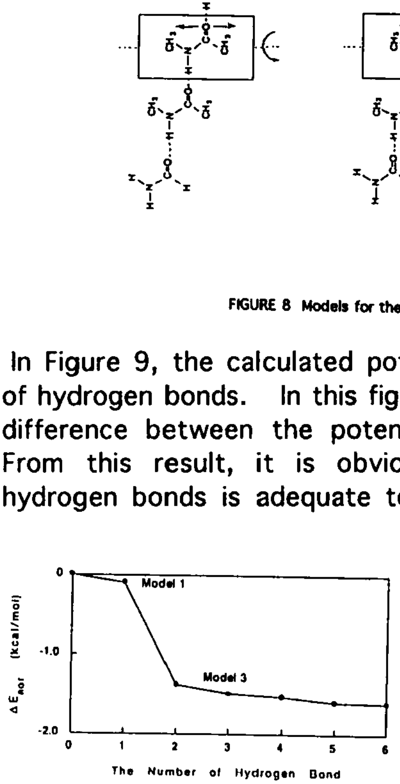


FIGURE 9 Change in the potential barrier for the rotation versus the number of hydrogen bonds

the frequency of the N-H bond, and that the smaller the potential barrier for the rotation is, the larger the shift in the frequency is. That is to say, the easiness of the polarization reversal should be intimately related with the degree of the disorder of the crystal in question, and be predicted from the magnitude of the shift in the frequency for the N-H stretching vibration in good correspondence with the experimental results.

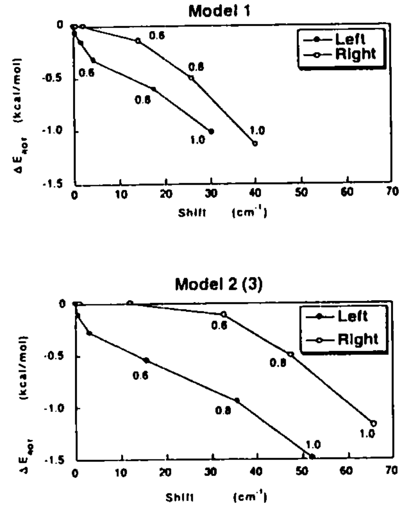


FIGURE 10 Change in the potential barrier versus shift in the frequency for various values of d_L and d_R

However, in Figure 10, for the same values of d_L and d_R, the lines are not identical but different considerably from each other. In order to find the reason why the lines are not identical, we carried out the calculation with the same proceduce as that in Figure 10 for the model system shown in Figure 11. In this model system, the steric hindrance between methyl groups in the different model compounds should be nearly equal for the same values of d_L and d_R. The plottings of the difference in the rotational barrier against the shift in the frequency are given in Figure 12, indicating that the two lines for d_L and d_R are nearly identical with each other. Since odd nylons have long chains with many methylene groups in them, the model system in Figure 11 should be suitable for the real system. Consequently, it can be concluded that the degree of the disorder gives nearly uniquely the magnitude of the shift in the frequency as well as the difference in the potential barrier for the rotation. At the present time, the degree of the disorder is defined only in the same plane as the peptide group. We also carried out the same type of the calculation for the degree of the disorder which is defined not only in the plane but also out of the plane.

In this case, We obtained the similar conclusion about the relation between the degree of the disorder and the shift in the frequency, and also the potential barrier for the rotation.

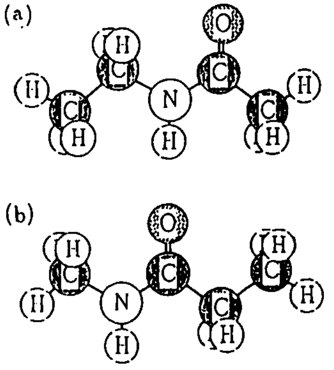


FIGURE 11 Model molecules for the steric hindrance

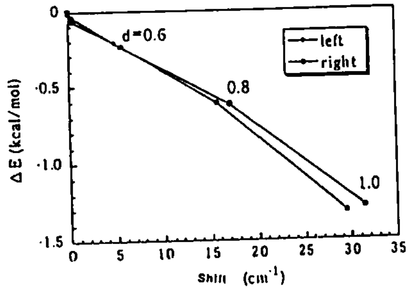


FIGURE 12 Change in the potential barrier versus shift in the frequency

CONCLUSION

By using ab initio molecular orbital method together with S-SCF method, the intimate relation was found between the degree of the disorder and the shift in the frequency of the N-H bond stretching vibration as well as the height of the potential barrier for the rotation in connection with the polarization reversal. Accordingly, we can infer the degree of the disorder from the magnitude of the shift in the frequency and also the height of the potential barrier for the appearence of the polarization reversal through ab initio molecular orbital calculations.

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