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THE INVESTIGATIONS OF DIFFERENT NPP CRYSTAL SURFACE STRUCTURES BY AFM

DA-WEN WANG, CHENG YE, JIAN-LIANG ZHAO and CHUN-LI BAI*
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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The investigations of nonlinear optical crystal surface structures have been reported in this paper for the first time. The AFM observations for cleavage (101) surface and (001) surface of NPP crystal indicate that the molecular arrangements on both of them are the same with its bulk structure, without any superstructure. And the phenyl and pyrrolidine rings in (001) surface can be distinguished. The angle between the molecular charge transfer axis and the binary axis obtained by AFM is 56°, closed to the optimal angle, which leads to the large nonlinear optical efficiency of NPP crystal.

1. Introduction

The molecular design and crystal engineering of organic second-order nonlinear optical crystal are complicated and eye-catching, more and more work has been found in this field. N-(4-nitrophenyl)-(*L*)-prolinol (NPP) is a successful example of molecular design.[1] As a result of the employment of the chirality and hydrogen-bond, the angle between the molecular charge transfer axis and the binary axis (58.6°) closes to the optimal angle (54.74°), NPP displays a very large nonlinear efficiency, its power SHG intensity is 150 times of that of urea. The crystal growth methods and the physical properties of NPP with its bulk structure have been deeply studied. But there is little knowledge about its surface structures because of its nonconductor property. It is the development of atomic force microscope (AFM) which makes it possible to observe its surface structures directly.

AFM, as a new surface analysis technique, can be used to study the surface structures of different kinds of materials with ultrahigh resolution, which opens a new approach to image organic molecules and to observe the functional parts such as chiral centres and dipoles in organic molecules.[2] It has been a powerful tool for studying organic photo-electronics. The different NPP crystal surface structures have been investigated using our homemade AFM instrument for the first time. The AFM results about cleavage (101) and (001) surfaces have been reported in this paper. On (101) surface, the surface molecular arrangement is a zigzag and on (001) surface is a parallelogram, which are consistent with its bulk structure

*To whom correspondence should be addressed.

without any superstructure. The angle between the molecular charge transfer axis and the binary axis obtained by AFM is 56°, closes to the optimal angle.

2. Experiment

NPP sample was synthesized using a same method with reference.[1] NPP crystal was grown by solution-cooling or solvent evaporation. After improving the solution growth technique, the large NPP crystals with the size up to $20 \times 20 \times 3$ mm^3 and $10 \times 10 \times 8$ mm^3 had been obtained.[3] The bulk structure parameters can be obtained by X-ray diffraction. They are: monoclinic with space group $P2_1$, $a = 0.52601$ nm, $b = 1.49056$ nm, $c = 0.71831$ nm, $\beta = 105.217°$, $V = 0.5434$ nm^3, which is the same with the reference.[1]

The AFM instrument is made by our Lab, which has been used for the successful studies of organic ferromagnetic and other materials.[4] It produces images of the topography of materials by scanning a sharp tip mounted on a cantilever over a sample surface. The lever deflects in response to the tip's interactions with the sample, these deflections are monitored by electron tunnelling to its back, which gives us the topography information of the sample surface. The cantilever and the tunnelling tip are made of tungsten slice and Pt/Ir wire, respectively.

3. Results

First the AFM image of HOPG (0001) surface was obtained with atomic resolution which was used for calibrating observed AFM images of NPP.

The NPP molecular structure and the stereodrawing of the molecular packing in the NPP crystal are shown in Figs. 1 and 2. The crystal structure of NPP is monoclinic and its surface structures are dependent on its orientations, so the AFM observations of different oriented NPP surfaces are different. The results obtained on cleavage (101) and (001) surfaces are shown here.

3.1. *The Cleavage (101) Surface*

(101) surface is a possible cleavage surface. Figures 3 and 4 show the AFM images of this surface with different scanning areas. Figure 3(a) and (b) with the scanning areas of 76 nm × 74 nm and 31 nm × 38 nm respectively indicated a unsmooth streak structure. In Fig. 4(a), the scanning area is so small (4.6 nm × 5.3 nm) that the resolution of this picture is very high which makes it possible to observe the surface molecules. In the image, the zigzags arranged along left bottom to right top can be found. The distance between two neighbouring zigzags is about 0.8 nm and the length between two folded points in one zigzag is about 1.1 nm.

3.2. *The (001) Surface*

The same experiments have been done on (001) surface. The AFM results are shown in Figs. 5 and 6(a). The Fig. 5(a) and (b) (scanning areas are 35 nm × 36 nm and

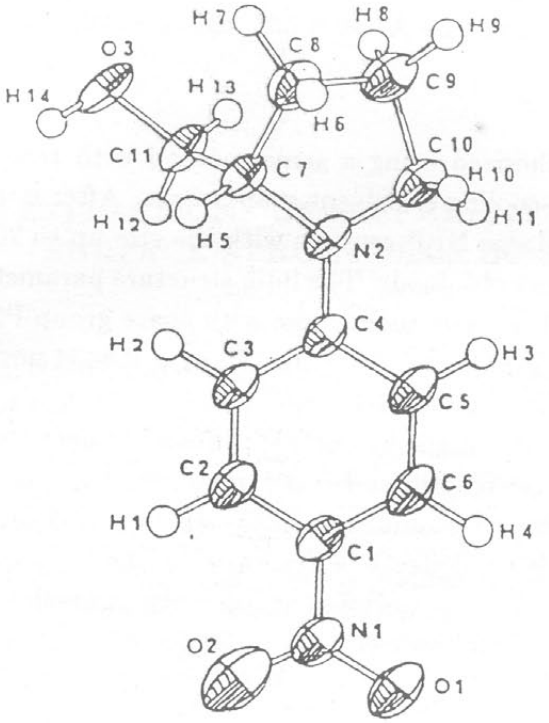


Fig. 1. Molecule of NPP projected on aromatic.

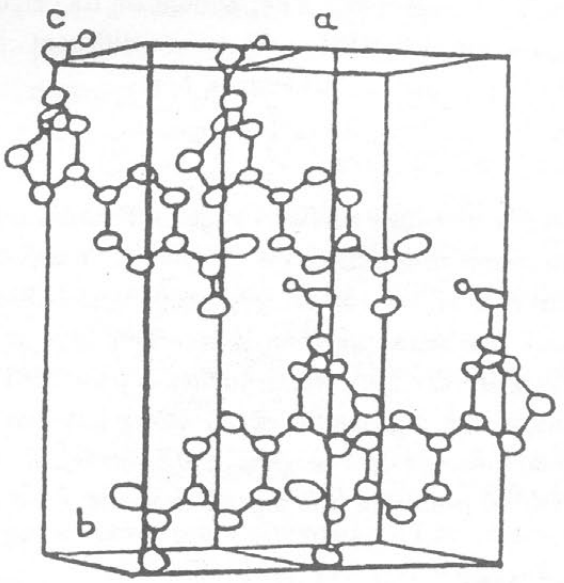
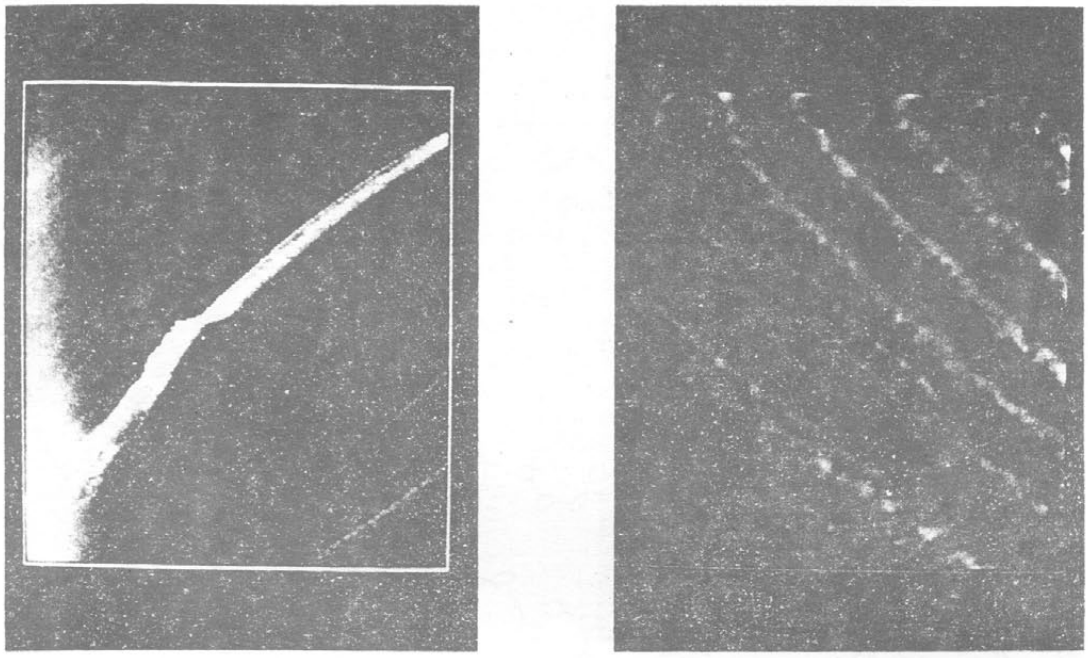
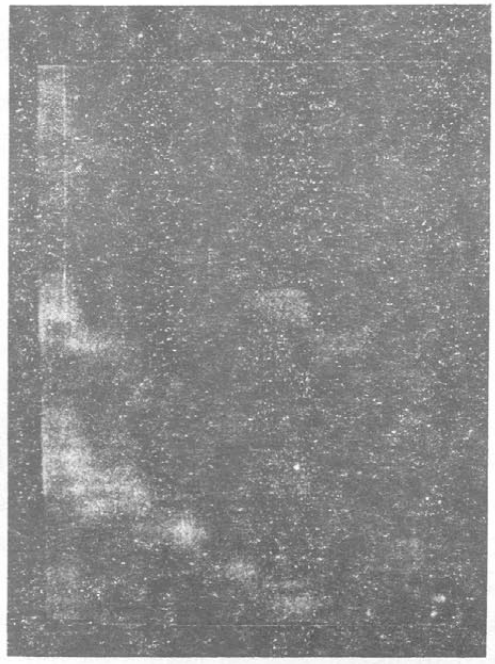


Fig. 2. Stereodrawing of the molecular packing in the NPP crystal.



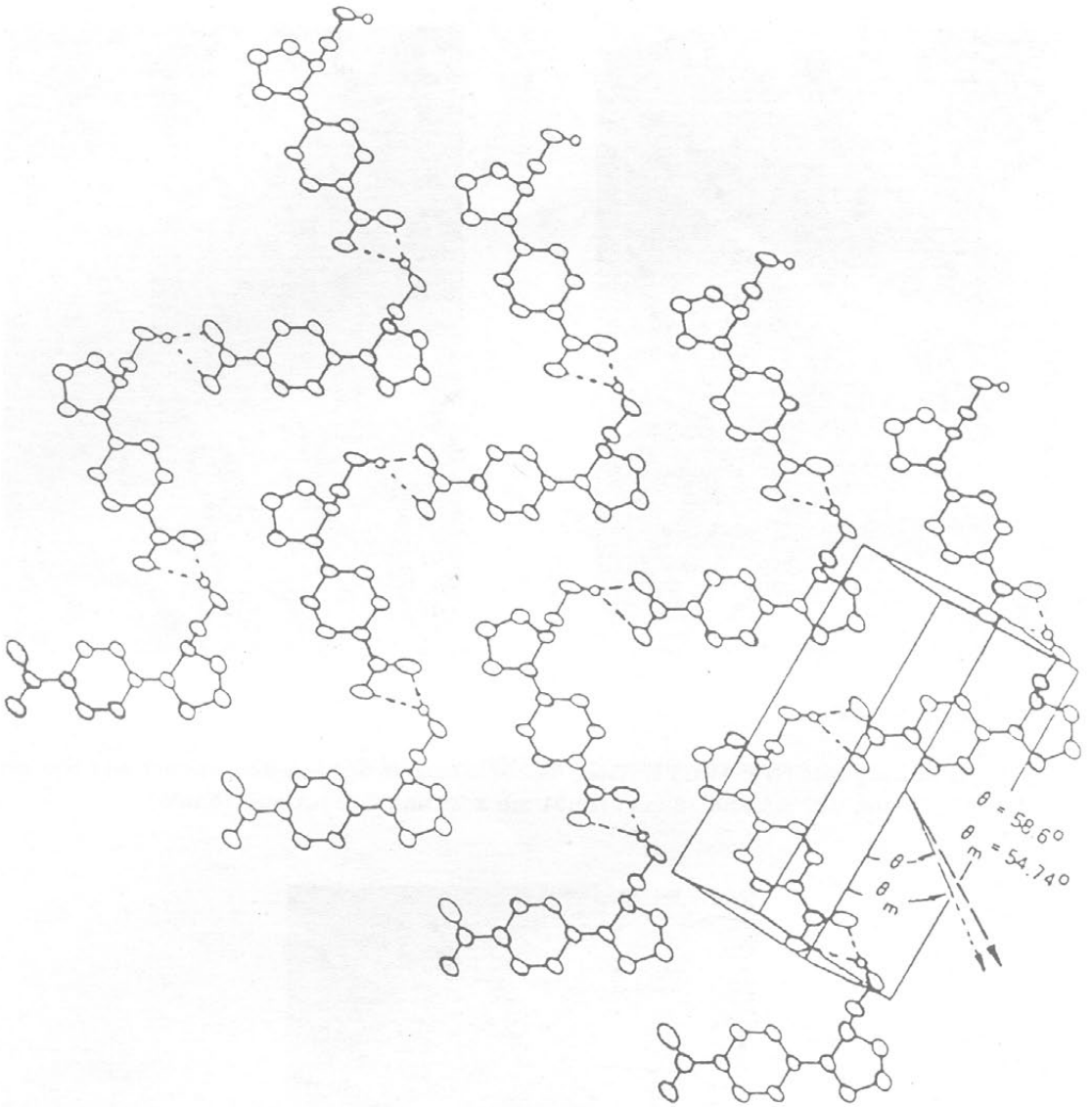
(a) (b)

Fig. 3. AFM images of NPP (101) surface. The scanning area, tunnelling current and bias are: (a) 76 nm x 74 nm, 0.88 nA and 18 mV, (b) 31 nm x 28 nm, 0.88 nA and 18 mV.



(a)

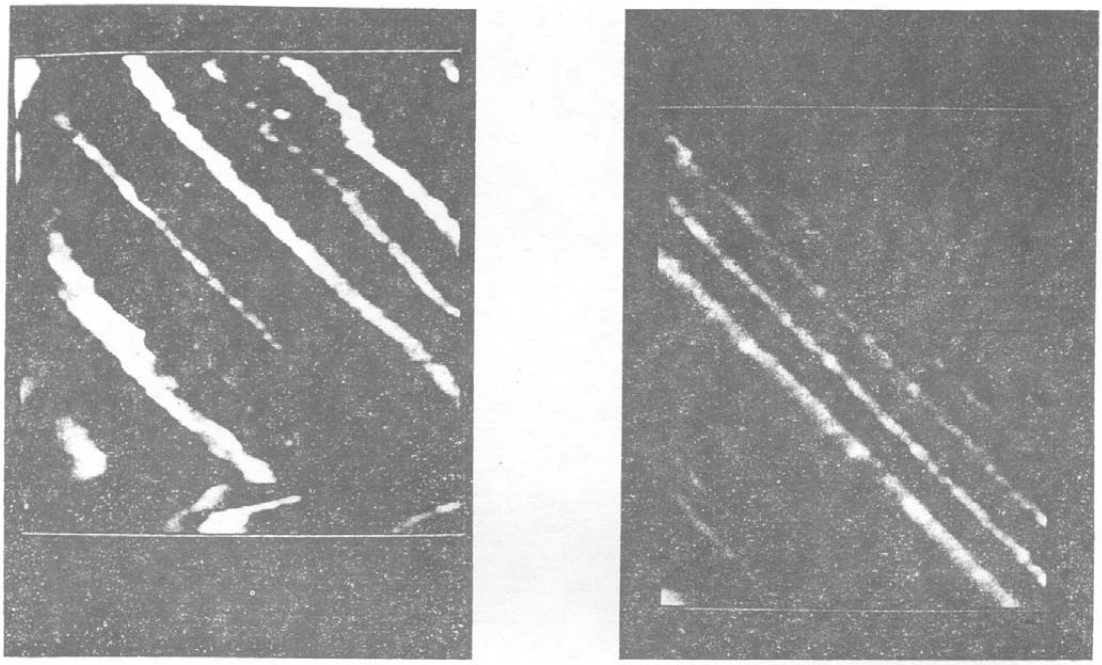
Fig. 4. (a) AFM image of NPP crystal with a small scanning area of 4.6 nm x 5.3 nm, a tunnelling current of 0.88 nA and a bias of 19 mV. (b) (101) surface molecular arrangement of NPP crystal.



(b)

Fig. 4. (*Continued*)

20 nm × 21 nm, respectively) show some streaks rise and fall which indicated that the surface is not atomic smooth in large area. In small area of 4.5 nm × 5.7 nm, the typical AFM image indicates the existence of periodical structure in spite that the observed surface is not atomic smooth because of the existence of one high streak rises from right bottom to left top. The surface structure consists of long protrude which arranged in parallelogram with long line of 1.4 nm and short line of 0.4 nm. The length of the long protrude which consists of two small protrudes is about 1.1 nm.



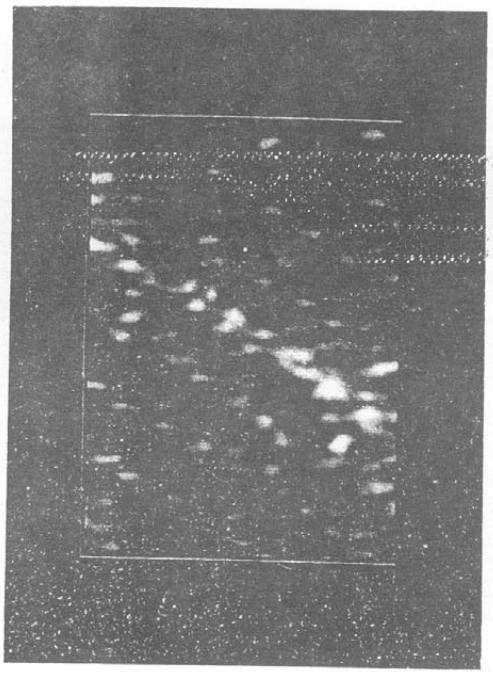
(a) (b)

Fig. 5. AFM images of NPP (001) surface. The scanning area, tunnelling current and bias are: (a) 35 nm x 36 nm, 1.1 nA and 11 mV, (b) 20 nm x 21 nm, 1.1 nA and 11 mV.

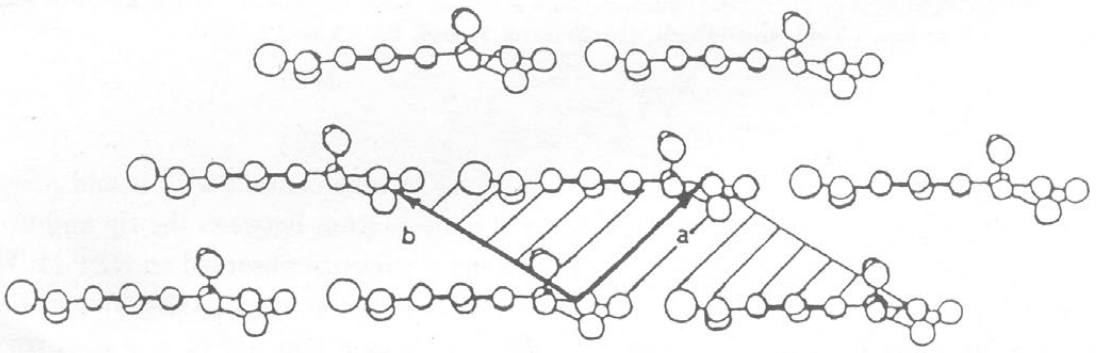
4. Discussion

When scanning a surface, the cantilever tip of AFM may contact with it and move on it, which may create some scratch when the interaction between the tip and the surface is large enough. As the runs of the streak structures observed on NPP (101) and (001) surfaces are different from the tip scanning direction, these structures cannot be caused by tip scanning. The NPP molecule consists of a phenyl ring and pyrrolidine ring, when forming crystal, the molecules are held head to tail by intermolecular hydrogen bonds between the hydroxy group of one molecule and the nitro group of the next to form long chains which stretch along (001) and (101) surfaces, thus it is easy to find streak structures on these surfaces.

On (101) surface, the angle between the mean plane of the molecule and the cleavage plane is about 11°, the molecules zigzag on the surface and are held head to tail by O(3) – H(14)...O(2) intermolecular hydrogen bond, which is shown in Fig. 4(b). This is consistent with AFM result of Fig. 4(a) with zigzag chains stretched from left bottom to right top. There is one NPP molecule between two neighbouring folded points. The theoretical results (calculated from X-ray diffraction) and the AFM measurement results of NPP molecule length and the distance between two neighbouring zigzag chains presented in Table 1, are consistent with each other well, which indicated that the (101) surface structure is the same with its bulk structure without any superstructure.



(a)



(b)

Fig. 6. (a) AFM image of NPP crystal with a small scanning area of 4.5 nm x 5.7 nm, a tunnelling current of 0.94 nA and a bias of 8 mV. (b) (001) surface molecular arrangement of NPP crystal.

According to crystal structure analysis, the molecular arrangements will be a parallelogram if it is viewed from (001) surfaces, which is qualitative consistent with the AFM observed results. The theoretical results of the parallelogram and molecular length close to the observed data by AFM, as shown in Table 1. Some error may be caused from the nonatomic flat of the observed surface. Thus, it can be concluded that the (001) surface is also the same with its bulk structure without any superstructure.

It is also possible for organic crystal to have superstructure surfaces just like semiconductor, such as the experiment results obtained by R. M. Overney *et al.*[5]

Table 1. Parameter table of NPP surface molecular arrangements.

	(101) Surface		(001) Surface	
	Theoretical results	AFM results	Theoretical results	AFM results
Length of molecule (nm)	1.1	1.1	1.1	1.1
Distance between two neighbouring zigzags of (101) surface (nm)	0.9	0.8		
Angle (°)	58.6	56		
Length of long line of the parallelogram on (001) surface (nm)			1.6	1.4
Length of short line			0.5	0.4

Our AFM studies about (001) and (101) surfaces indicated that both of them have not any superstructure and the quality of observed crystals is quite good.

NPP displays a very large nonlinear efficiency. This is because that the angle between the molecular charge transfer axis and the binary axis closes to the optimal angle (54.74°).[1] It is possible to obtain this angle from molecular arrangement of the (101) cleavage surface in the case of without superstructure. The observed angle by AFM is 56°, by X-ray diffraction 58.6°, they are close to the optimal angle, which proves that NPP has a very large nonlinear efficiency.

In brief, AFM is a powerful tool for surface structure investigation. The experiment results show that the molecular arrangements of (101) and (001) surfaces of NPP crystal with good quality are the same with its bulk structure without any superstructure. By AFM, the NPP molecule can be observed, the phenyl ring and the pyrrolidine ring in one molecule can also be distinguished. The observed angle between the molecular charge transfer axis and the binary axis closes to the theoretical results which is consistent with the X-ray diffraction results. These results give us some information about the surface structures of NPP crystal directly in real space for the first time, which is a complement to its bulk structure knowledge.

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