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CRYSTAL STRUCTURE OF 11-{[(4′-HEPTOXY-4-BIPHENYLYL) CARBONYL] OXY}-1-UNDECYNE

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The crystal structure of 11-{[(4′-heptoxy-4-biphenylyl) carbonyl] oxy}-1-undecyne (A9EO7), an acetylene with a biphenyl mesogenic moiety, was studied by combination of electron diffraction (ED), wide-angle X-ray diffraction (WAXD), and molecular simulation of ED pattern and molecular packing. A9EO7 was found to adopt an orthorhombic $P2_12_12$ space group with cell parameters of $a = 5.78\,Å$, $b = 7.46\,Å$, and $c = 63.26\,Å$, for which molecular packing calculations were conducted to elucidate the molecular conformation. Its crystal morphology was observed using a transmission electron microscope (TEM) and an atom force microscope (AFM). A9EO7 crystal grew to form step like morphology. Crystallization behavior of A9EO7 in magnetic field was examined. Induced by magnetic field A9EO7 could crystallize in such a way that its molecular long axis was parallel to the substrate.

Keywords: acetylene; structure; morphology; TEM

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INTRODUCTION

Polyacetylene is one of the simplest organic conjugated polymers. However, its insoluble and infusible properties make it difficult to study its chemical structure and to process it in solution or melt. Therefore, the research and application in academic and industrial fields are greatly limited. Introduction of side group to the polyacetylene backbone can not only improve the stability against air and solubility in organic solvent [1] but also endow the resulting polymer with other properties, such as optically active properties [2], permeation [3], and liquid crystalline properties [4].

The polyacetylene substituted by mesogenic moiety is of interest because the resulting polymer possesses both unique liquid crystalline and electro-optical properties [5]. The orientation of polyalkyne backbone accompanying the orientation of side-chain induced by magnetic field in the liquid crystalline phase improves the electric properties of the polymer [6].

In the crystalline state, symmetry operation determines the packing of the molecules in the cell, which is of great help to recognize and understand the arrangement of the molecules in liquid crystalline phase. In this paper, the crystal morphology and structure of an acetylene with a biphenyl mesogenic moiety, 11-{[(4′-heptoxy-4-biphenylyl) carbonyl] oxy}-1-undecyne (A9EO7), was studied in detail. Crystallization behavior of A9EO7 under magnetic field was also examined. Based on the packing of A9EO7 in crystal lattice, the study on molecular arrangement of A9EO7 and its polymer in liquid crystalline phase was performed systemically.

EXPERIMENTS

Specimen Preparation

The synthesis and chemical properties of A9EO7 were already reported in our previous paper [7]. The molecular structure of A9EO7 is given in Figure 1. A9EO7 was dissolved in toluene to make a 0.1 wt% solution. The sample solution was dropped on thin carbon film surface, which was deposited onto the surface of freshly cleaved mica. After the solvent evaporated, microcrystals from solution were obtained. Microcrystals from

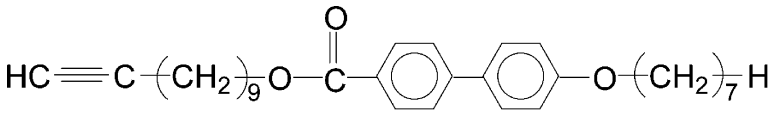

FIGURE 1 Molecular structure of A9EO7.

melt were obtained after the microcrystals from solution were heated up to melting point and then cooled. The carbon film carrying the sample was transferred to Cu grid. The sample on the Cu grid could be observed on its image and electron diffraction (ED) in transmission electron microscope (TEM).

The microcrystals on carbon-coated mica surface from solution were heated up to melting point and then quickly transferred into magnetic field. The carbon-coated mica surface carrying the sample was parallel to the direction of the magnetic field. Magnetic field could affect molecular arrangement during crystallization when A9EO7 was cooled from isotropic melt. After it was cooled to room temperature the carbon film carrying the sample was transferred to Cu grid. Morphology observation and electron diffraction (ED) was carried out using a transmission electron microscope (TEM).

Instruments

Wide angle X-ray diffraction (WAXD) pattern was recorded in a reflection mode with a Rigaku D/max 2500 PC diffractometer using an X-ray beam from Cu $K\alpha$ radiation with a wavelength of 1.54056 Å. The TEM samples were investigated using a JEOL2010 TEM operated at 200 kV. A rotation and tilt holder was used to obtain different crystallographic projections of the unit cell. The sample was exposed in magnetic field of 1 Tesla during cooling from the isotropic melt state to crystal state, to induce the molecular crystallization to make the molecular long axis parallel to substrate. Computer modeling was performed using an Indigo workstation, and the Cerius^2 3.0 package provided by Molecular Simulation Inc. (USA) was used.

CRYSTAL STRUCTURE STUDIES BY ELECTRON DIFFRACTION

Generally speaking, X-ray diffraction single crystal analysis is a reliable method to determine lattice type, space group, and positions of atoms in a unit cell [8]. However, this method is not appropriate in the case of organic and especially polymeric crystalline materials because it is difficult to prepare so large a single crystal to do X-ray single crystal diffraction experiments for organic material. Selected area electron diffraction is suitable for small and thin crystals.

In recent years, electron crystallography [9–10] and simulation method [11] have been developed both in theory and experimental technique. The procedure of electron crystallographic structure analysis of organic compounds using simulation method is made up of two steps; that is, (1) determination of the cell dimension and space group by electron diffraction

experiments and (2) molecule modeling to the experimentally obtained results by simulation techniques.

ED patterns from different zones and their geometrical relationships are required to determine lattice type and cell parameters. A rotation and tilt specimen holder is used in an electron microscope. By tilting the specimen holder from a zone axis showing an ED pattern, other ED patterns from different crystallographic projections are achieved. The geometric relationship of the tilting ED pattern series and the position of the diffraction maxima in each ED pattern are used to deduce the lattice type and cell parameters.

Finally, the ED patterns and X-ray powder diffraction pattern can be indexed according the structural parameters obtained above. The space group can be determined by considering the extinction principle derived from the indexing results of the diffraction patterns.

The conformation of individual molecules can be calculated using ab inito method or semiempirical method, e.g. a general purpose semiempirical molecular orbital package for the study of chemical structures and reactions (MOPAC), with the availability of a powerful computer resource. Then the obtained molecular conformation is put into the experimental setup cell with the strict restriction of space group symmetry. The molecular packing energy is calculated and minimized by giving appropriate freedom to the molecules and cell parameters. Based on this crystal packing, the ED patterns of different crystallographic projections are calculated and compared to the experimental diffraction patterns. Similarity between the calculated ED patterns and the experimentally obtained ED patterns determines whether the simulative packing can be accepted.

RESULT AND DISCUSSION

Morphology and Structure of A9EO7

The crystal morphology of A9EO7 from solution and melt was observed with TEM. Figure 2 shows the morphology of A9EO7 crystal from solution (2a) and melt (2b). It is obvious that the crystals have steplike and layer morphology. The crystal layer from melt is much smaller than that from solution. This may be the result of the tendency of layer-by-layer rearrangement of molecular orientation when the sample was cooled from melt, during which process A9EO7 underwent a smectic phase. However, the experimental ED patterns of both cases are same, (as Figure 6a shows). And all the ED patterns show the same lattice orientation for different sample regions on a grid. This suggested that the sample film from solution consists of a large single crystal domain with the same orientation. Although the large film separated into small domains when the sample was cooled from melt to crystal state, the small domains kept the same orientation still.

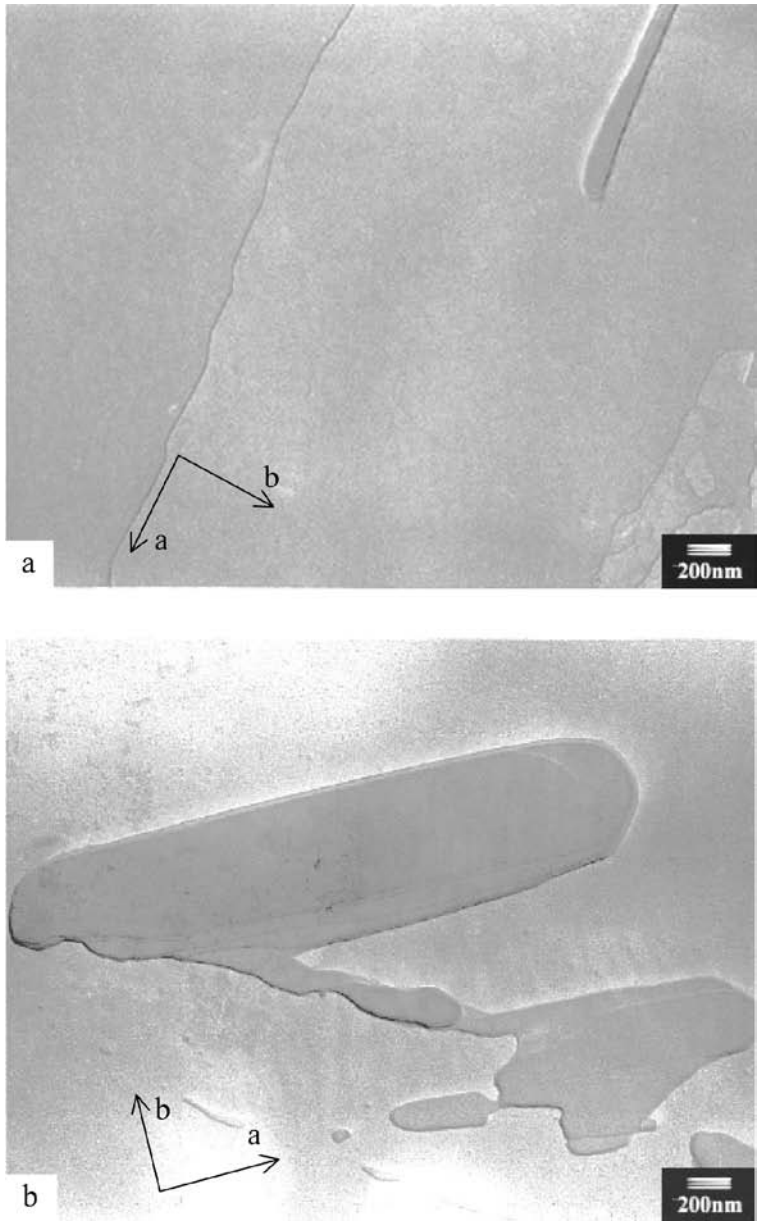

FIGURE 2 Morphology of A9EO7 crystals from (a) solution and (b) melt.

To estimate the thickness of each layer, section analysis was done using AFM, as Figure 3 shows, which confirms the steplike morphology and the thickness of layer. It is obvious that the thickness of different layers is approximately a multiple of 64 Å.

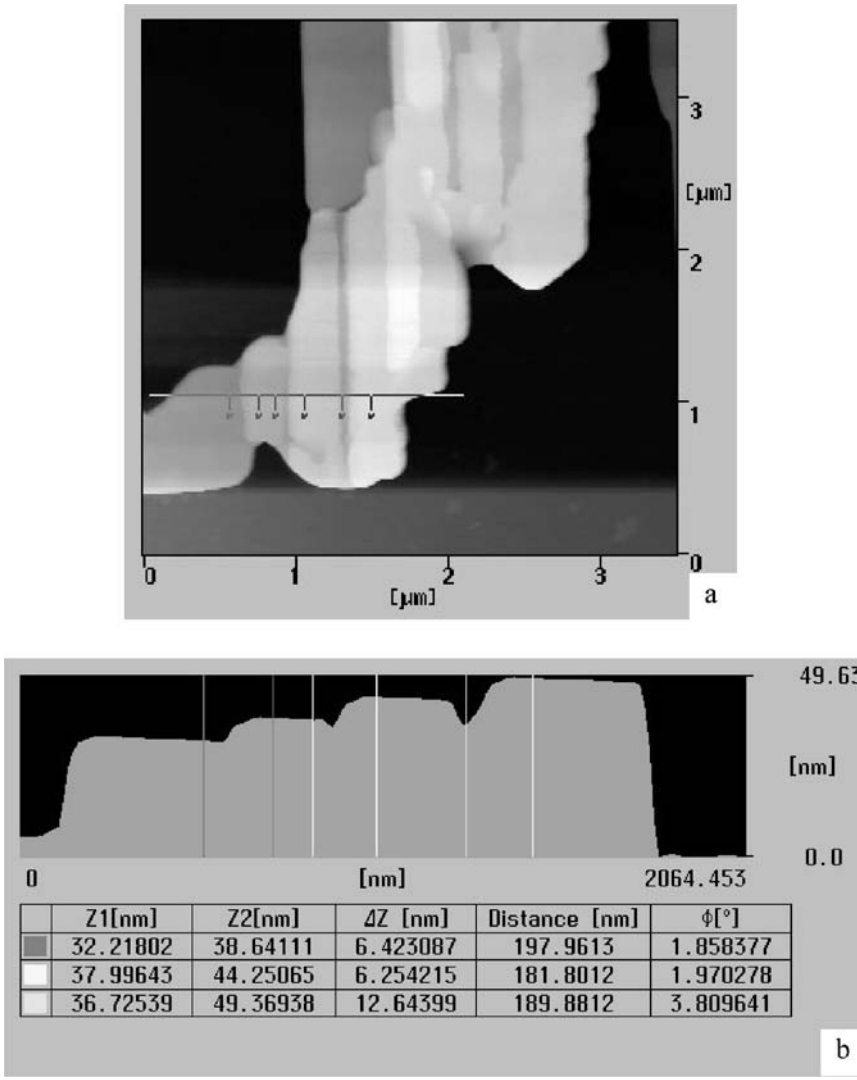

FIGURE 3 AFM section analysis of A9EO7 crystal from solution, (a) morphology of A9EO7 crystal and (b) layer thickness of crystal.

In this study, the molecule of A9EO7 consists of a biphenyl core, carbonyloxy-1-n-undyne at 4 position, and heptoxy at 4′ position, as shown in Figure 1. The length of the molecule is calculated to be about 32 Å. It is hypothesized that the cell parameter c is large, which can be confirmed from pattern of WAXD of A9EO7, as shown in Figure 4. The first peak, $2\theta = 2.791$ degree at small angle area, corresponds to $d = 31.63$ Å. Analyzing the first several peaks of the WAXD pattern, it can be found that $2d_1 = 3d_2 = 6d_3 = 7d_4 = 8d_5 = 63.26$ Å (n in d_n is the sequence number of peak from small angle to wide angle in WAXD pattern of A9EO7). Consequently, a d spacing of $d_{001} = 63.26$ Å is determined, which suggests that cell parameter c is not smaller than 63.26 Å. The diffraction of 001 isn't detected in the WAXD pattern of A9EO7, probably because of some symmetry-related reasons and the reflection beam being close to incident X-ray beam at such a low angle.

Figure 5 shows the relationship between real space and reciprocal space. In real space, cell parameter c is much greater than cell parameters a and b. Then, in reciprocal space, cell parameter c* is much smaller relative to cell parameters a^* and b^*. In addition, the film of crystal is too thin. The spots in reciprocal space turn to spikelike spots in c^* direction, as shown schematically in Figure 5b. The reciprocal spots for the neighboring planes, such as (hk0) and (hk1) planes, almost contact each other. Therefore, in

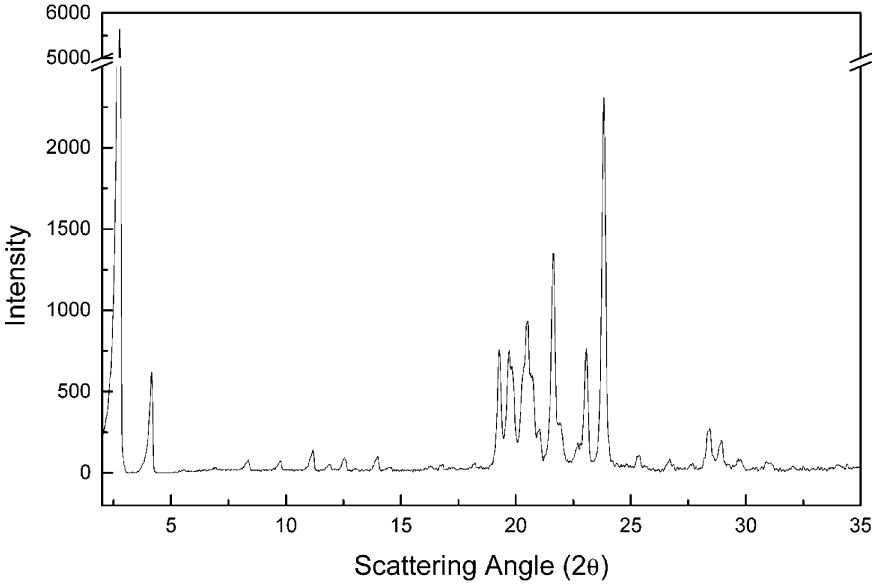

FIGURE 4 WAXD pattern of A9EO7.

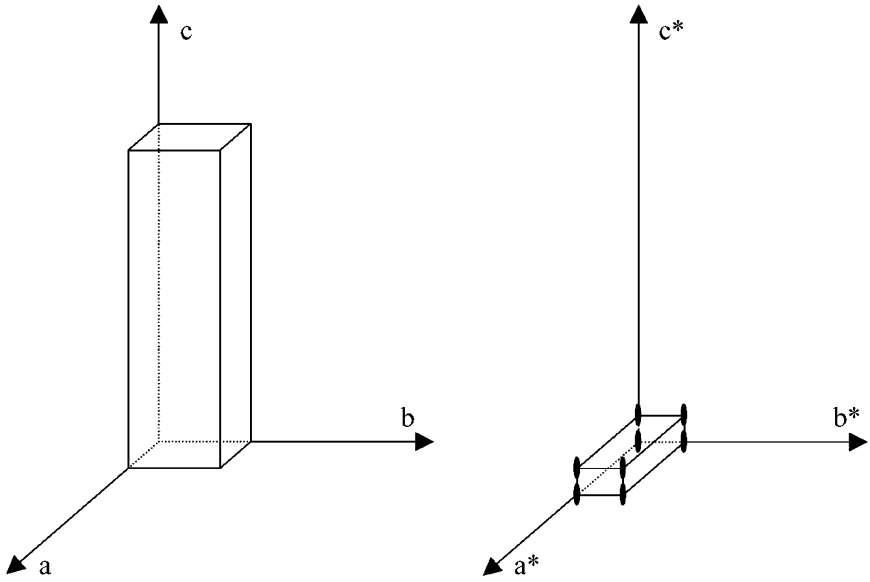

FIGURE 5 Relationship between real space and reciprocal space.

ED experiment it is difficult to notice that the old ED pattern disappears and the new ED pattern appears while tilting the sample.

It's fortunate that a tilting series of two ED patterns was recorded, as shown in Figure 6. The obvious difference between the two patterns is the intensity of the different diffraction spots. Figure 6a is the original ED pattern. It can be characterized as an orthorhombic two-dimensional net. The sample was tilted along the axis defined by horizontal reflection till the new pattern appeared, as shown in Figure 6b, and the tilting angle is about 5.2 degrees. The newly obtained pattern is an orthorhombic two-dimensional net as well. This suggests that A9EO7 gives an orthorhombic unit cell.

Cell parameters $a = 5.78\,\text{Å}$ and $b = 7.46\,\text{Å}$ were calculated from ED pattern (Figure 6a) which was defined as the [001] zone. Figure 6b was defined as [10-1] zone. Therefore, the structure of the unit cell could be determined as being an orthorhombic lattice with cell constraints: $a = 5.78\,\text{Å}$, $b = 7.46\,\text{Å}$, $c = 63.26\,\text{Å}$ and $\alpha = \beta = \gamma = 90°$. In order to obtain a density of about $1\,\text{g}\cdot\text{cm}^{-3}$, there must be 4 molecules in a unit cell. The final calculated cell density is $1.125\,\text{g}\cdot\text{cm}^{-3}$.

Having determined the unit cell, all the ED patterns and WAXD pattern can be indexed. The indexing result of WAXD (Figure 5) is listed in Table 1. The systematic existence is collected as follows: h00: $h = 2n$; 0k0: $k = 2n$.

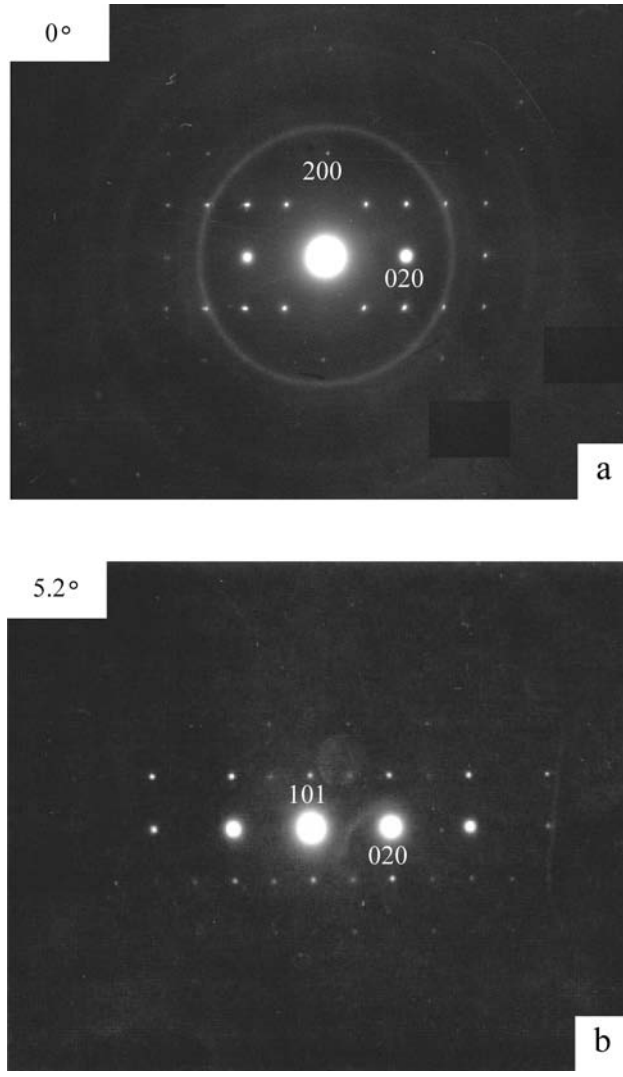

FIGURE 6 ED pattern of (a) [001] zones (b) [10-1] zone.

By indexing using *International Tables for Crystallography* [12], this orthorhombic lattice gives the lowest space-group symmetry of $P2_12_12$. The symmetry information relating to space group $P2_12_12$ is as follows:

Laue class mmm
point group 222

TABLE 1 Result of Powder X-Ray Diffraction

2θ	Index	d
2.79	002	31.63
4.16	003	21.09
8.37	006	10.54
9.76	007	9.04
11.17	008	7.91
11.92	011	7.41
12.56	009	7.04
13.99	0010	6.33
19.28	110	4.57
19.71	112	4.52
19.86	109	4.46
20.52	115	4.30
20.72	1010	4.27
21.03	116	4.19
21.63	117	4.08
23.07	119	3.83
23.83	020	3.73
25.29	026	3.52
26.70	028	3.37
28.41	120	3.13
28.44	121	3.13
28.95	125	3.04
29.79	127	2.96
30.90	200	2.89

international tables No. 18
extinction symbol $P2_12_12$
reflection condition h00: $h = 2n$; 0k0: $k = 2n$
symmetry operations: 1; 2 0,0,z; 2(0,1/2,0) 1/4,y,0; 2(1/2,0,0) x,1/4,0

Crystallization Orientation by Magnetic Field

The sample was placed in magnetic field of 1 Tesla during the crystallization process of A9EO7 when it was cooled from isotropic melt state. The carbon-coated mica surface carrying the sample was parallel to the direction of magnetic field. The electric dipole moment of molecules, the long axis of the molecule, was oriented along the direction of magnetic field, as Figure 7 shows. A9EO7 therefore crystallizes in the mode of the molecular long axis parallel to substrate. Figure 8 shows the morphology and ED pattern of crystal induced by magnetic field. The crystal morphology has striplike features, and crystal is much thicker than noninduced crystal by being deduced from the contrast of picture. The ED pattern, Figure 8b, is

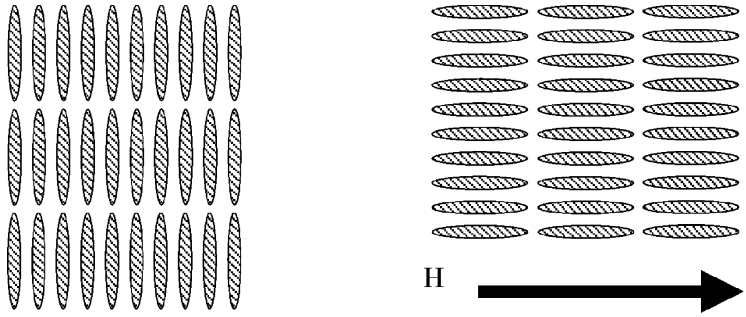

FIGURE 7 Model of molecule orientation induced by magnetic field.

an orthorhombic two-dimensional net also, which confirms that A9EO7 is orthorhombic unit cell, and this pattern is defined as [1—10] zone.

Crystallization process consists of nucleation and growth. Whereas, molecules of A9EO7 array into lattice in a special manner when crystal grows, as shown in Figure 9. After embryo appears, molecules can array into lattice in two manners, i.e., side-by-side and tip-to-tip ways. But the van der Waals forces between forth-coming molecules and in-celled molecules of these two manners are different. Obviously, the van der Waals forces when molecules array into lattice in a side-by-side manner is much larger than in tip-to-tip manner. Therefore, the tendency of crystal growth is in such a way that the nearby molecules adjust their conformation and fit themselves into the lattice parallel to the in-celled molecules. Consequently, the crystals from solution and melt have the same layer morphology. In the other case, the molecules can be induced parallel to substrate to crystallize when exposed in magnetic field, which is equal to the way that the layer-like crystal can be upright to the substrate. Figure 8b shows striplike crystal morphology. This special growth manner is the inevitable result of great ratio of length to diameter of the molecule.

Computational Methods

Conformation of Molecule

The minimum energy gas phase conformation of molecule was calculated by a semiempirical quantum mechanical method incorporated in MOPAC. This method has been established in quantum chemistry for many years [13]. The AM1 method incorporated in the program package MOPAC6.0 was used. The conformation of A9EO7 is shown in Figure 10a. The dihedral angle of two phenyl rings is 40.21 degrees. Zigzag plane conformation of the two tails of heptoxy and carbonyloxy-1-n-undyne, which are nearly on

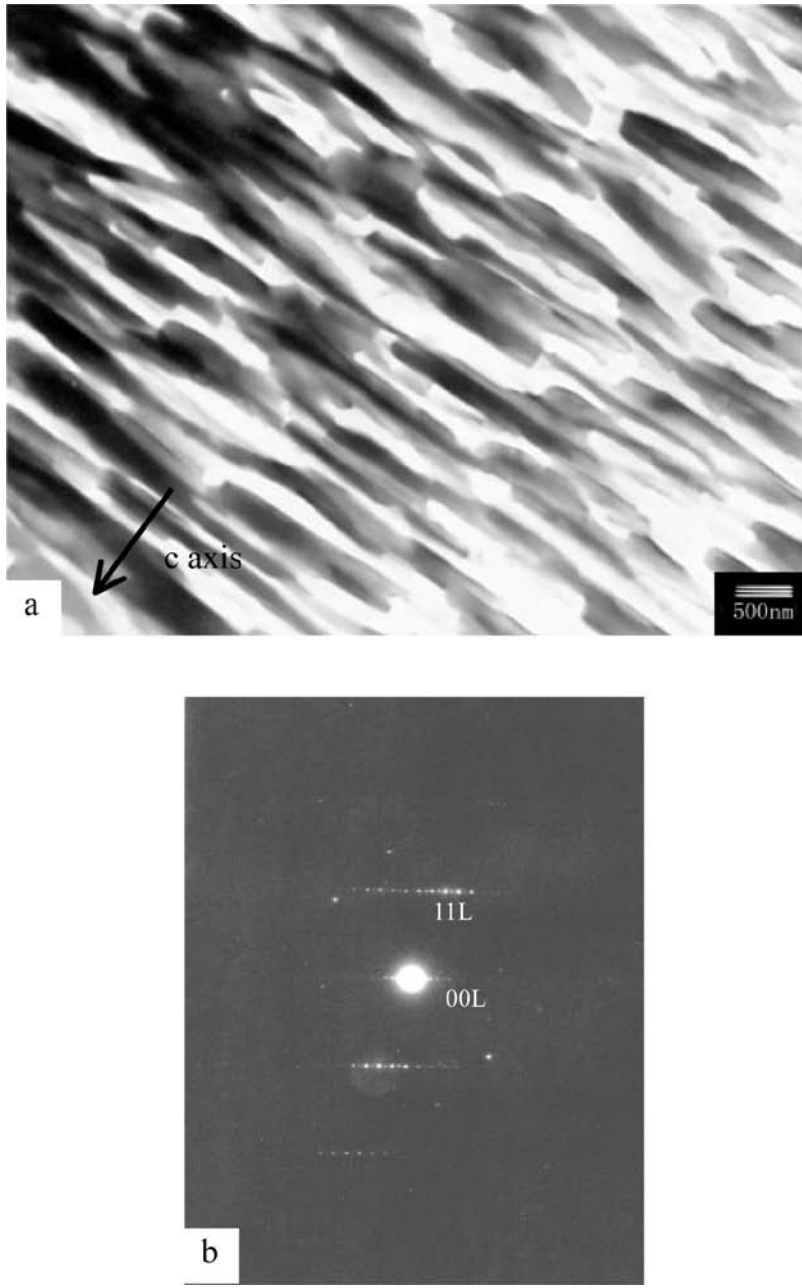

FIGURE 8 (a) Morphology and (b) ED pattern [1-10] zone of crystal induced by magnetic field.

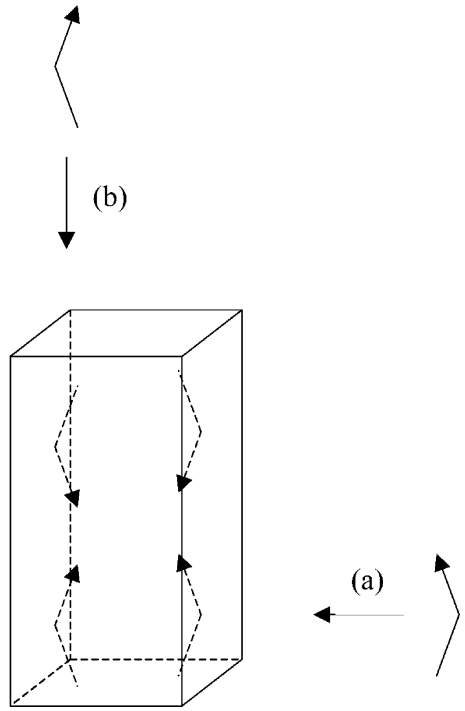

FIGURE 9 Crystal growth manner of A9EO7 (a) side-by-side manner and (b) tip-to-tip manner.

the same planes of neighboring phenyl rings, is found. The direction of molecular electric dipole is nearly parallel to the long axis of the molecule.

Packing of Molecules in Cell

Four molecules were placed into the unit cell using Cerius^2 software with strict restrictions imposed by the unit cell dimensions and space group. Sequentially, it was necessary to make energy minimization so that the crystal energy reached a minimum. The refined packing is shown in Figures 10b to 10d viewed from a different direction, which consists of four independent units in the cell. Each molecule is crystallographically unique.

By using Cerius^2, the simulated ED patterns could be obtained. The major feature of the simulated ED patterns, as shown in Figure 11, coincides with the experimental ones. If there is difference, it is necessary to make conformation adjustment to improve individual intensities, keeping the required symmetry condition satisfied. In the unit cell, with the

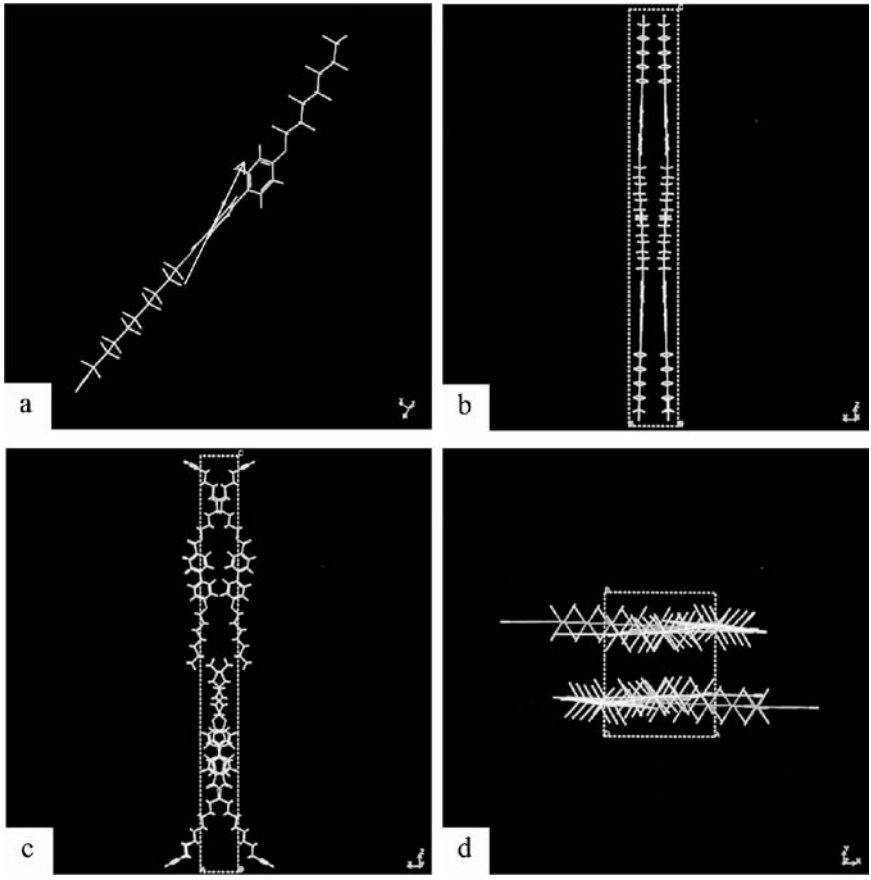

FIGURE 10 (a) The molecular conformation of A9EO7 in gas phase, Representation of different projection in $P2_12_12$ crystal, view along (b) X axis, (c) view along Y axis, and (d) view along Z axis, respectively.

exception of the fact that the two phenyl rings are nearly in the same plane, the calculated ED patterns are similar to the experimentally obtained ones. This singlular discrepancy coincides with the situation where two phenyls of biphenyl are in the same plane in crystal state, but dihedral angel between two phenyls is existent in gas state [14].

CONCLUSIONS

In this paper, the crystal morphology and crystal structure were studied. The crystals have steplike and layer morphology, and the layers grown from

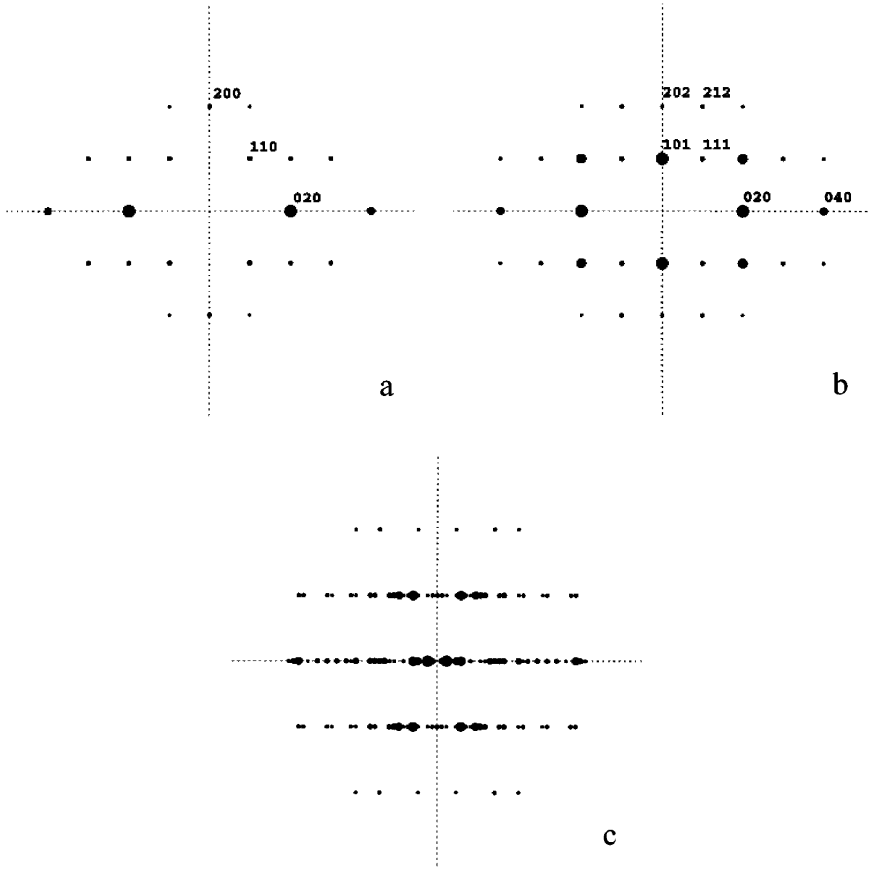

FIGURE 11 Simulated electron diffraction patterns of A9EO7 along (a) [001] zone, (b) [10-1] zone, and (c) [1-10] zone, respectively.

solution are greatly larger than those from melt. A9EO7 crystallizes in the mode of the molecular long axis perpendicular to the substrate. On the other hand, the molecules can crystallize in the manner of the molecular long axis parallel to the substrate when A9EO7 is exposed in a uniaxial magnetic field, and the crystal is much thicker than noninduced one.

The structure was determined to be orthorhombic $P2_12_12$ space group, and the cell parameters were $a = 5.78\,\text{Å}$, $b = 7.46\,\text{Å}$, $c = 63.26\,\text{Å}$, and $\alpha = \beta = \gamma = 90°$.

Molecular packing calculation was conducted using Indigo workstation and Cerius[2] 3.0 package. In gas phase, the dihedral angle between two phenyl rings is 40.21 degrees. Two tails of heptoxy and carbonyloxy-1-n-

undyne are found to have a zigzag plane conformation and are on the same plane of neighboring phenyl rings. In the unit cell, however, the two phenyl rings are nearly in the same plane.

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