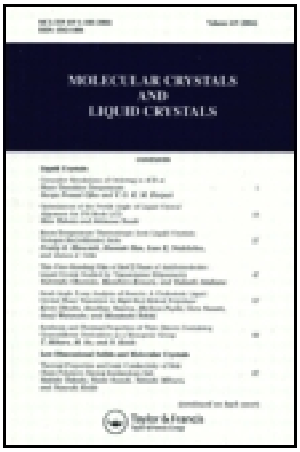

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Structure and Conformation of 2,3,6, 7,10,11 -hexakispentyloxytriphenylene by TEM and Computer Simulation

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Structure and Conformation of 2,3,6, 7,10,11-hexakispentyloxytriphenylene by TEM and Computer Simulation

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Experimental electron diffraction patterns and high resolution images were used to determine the space group and unit cell dimensions of 2,3,6,7,10,11-hexakispentyloxytriphenylene. Subsequently the molecular conformation was calculated by energy minimized package in Cerius2. Using this method, we got the HPT crystal structure: space group: P6/mmm; lattice type: hexogonal; the lattice parameters are $a = b = 20.3$ Å, $c = 3.52$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The core of HPT is not perpendicular to the column. The angle between a axis and HPT core plane is 9° which cannot be seen in b-c projection. The simulated ED patterns and HREM images are good agreement with the experimental ED patterns and HREM images.

Keywords: Triphenylene; electron diffraction; computer simulation; molecular conformation; discotic liquid crystals

1. INTRODUCTION

High Resolution Electron Microscopy(HREM), which is an interesting new kind of experimental method developed in several decades, especially the studies if dislocations in crystal structure [1], the direct imaging if single

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crystals [2] and the structure analysis of biopolymers [3]. Vast meaningful results have been obtained since HREM was applied in organic materials several decades before, but this experimental method was restricted in the field of organic crystals for the reasons as follows. First, the image contrast is very low because organics are generally composed by light elements such as C, H, O, N, etc., which have weak scattering effect for electrons. Second, organic materials, especially those with low Tm (Melting Temperature), are susceptible to electron irradiation damage. At last, due to the variety and uncertainty of the organic crystals, the interpretation of their HREM image is not a routine matter, As the developments of instruments and methods, the first two reasons are already not the key restricted features up to now.

High quality high resolution electron micrographs with high signal-to-noise ratio can be recorded by using highly sensible negatives and MDS. method (Minimum Dose system, i.e. carrying out astigmatism correction and focusing at one field of view, then taking photographs at another field of view which has been radiated.). In some newly developed electron microscope. Image enhancer can take the place of MDS method in the case of irradiation sensible specimens (Tm < 100°C). In the aid of this device, astigmatism correction and focusing can be carried out at high magnification, thus the quality of the images can be greatly improved. The unfavored negatives, i.e. the negatives with low signal-to-noise ratio or low contrast, can also be improved by Fourier transforms via computer or optical devices. Nevertheless, the third problem is still unsolvable. It's well known that X-ray four-circle diffractometer is reliable tool in determing crystal structure. But this method is not practical in the case of organics with small sample amount or poor cultivablity, which means inaccessibility of single crystals with large enough size. The information contained in HREM images of organics with unknown structure parameters is limited. Therefore, up to now, HREM studies of organics are still focused on some high Tm ones with known structure.

Recently, computer simulations have been widely applied in the field of chemistry [4]. Crystal structure can be decided by computer experiments, which is the nickname for computer simulation. For a certain organic, it can gave not only the most energy satisfied 3-D crystal packing under the given force field, but also the corresponding simulation experimental results, such as HREM and ED etc. However, simulation results for a certain material can be significantly varied by the different given force fields and periodic boundary conditions. Reasonable results can only be drawn after verification by comparing simulation with experimental. Generally, molecular simulations provide a effective way to interpret crystal structure.

Discotic liquid crystals have been extensively studied for several decades [5, 6, 7]. In the mesophase, they are stacked together to form a columnar structure. All the promising uses of discotic liquid crystals in molecular energy transition, photoconductivity, etc. [8] are based upon this unique structure. For many years, differential scanning calorimetry (DSC) was applied for detecting their phase transitions: Wide angle X-ray diffraction was used to study the characteristics of structure in different temperature; Polarizing optical microscopy (POM) was carried out to observe their texture. However, all the mentioned methods can only give macro information averaged from vast cells. HREM is a powerful tool to study Discotic liquid crystals at molecular level. Potential projection of atoms or molecular along one given direction can be directly obtained from this experiments.

In this paper, HPT with unknown structure is chosen as sample. Different methods have been applied for preparing specimens with different crystal orientation. All the specimens were studied by HREM and SAED (Selected Area Electron Diffraction). The energetically favorable conformation of HPT is calculated by minimizing under Dreiding II force field. HREM and ED are calculated from this model and compared with experimental ones. The experimental results is in good accordance with the simulation results from Cerius2 1.6.

2. EXPERIMENTAL

1. Sample: 2,3,6,7,10,11-hexakispentyloxytriphenylene (HPT)

This sample was synthesized by Holger Bengs and Helmut Ringsdorf. The synthesis of HPT is described elsewhere [18]. HPT displays two mesophase: Dho and Dhd above 66°C. The phase transitions are K66Dho71Dhd122 I. When the sample is exposed in electron beam, it will suffered from a consistent temperature rising for the enthalpy effect. Phase transitions will occur as the sample temperature is above 60°C and the structure order will be degraded.

2. The EM Specimen Preparation

Two different methods were applied for the purpose to obtain EM specimens with different orientation of crystal.

a. Solution-Casting

A 0.3%(w/w) sample solution was prepared by dissolving the sample in $CHCl_3$. Then, casting the sample solution on the surface of amorphous carbon which was evaporated on the newly split mica. After the sample layer was throughoutly dried, the specimens were annealed to be fully crystallized for 3 hrs, at temperature just below Tm. Sandwiched structure specimens were prepared by evaporating another layer of amorphous carbon on the surface of sample layer, the specimens were ready for EM studies after the specimens were transferred from mica to EM grids and dried.

b. Spin-Coating

A glass substrate which had been evaporated a layer of amorphous carbon was mounted on a spin-coating device rotating at a speed of 1200/min. Sample layer was coated by dropping two drops of sample solution in the center of the substrate. After the specimen was dried and annealed, it was reinforced with another layer of amorphous carbon, then the specimen was transferred onto EM grids for study.

2.2. Electron Diffraction

For many organic crystals, it is extremely difficult or even impossible to obtain the large single crystal necessary for X-ray structural analysis. However, it is possible to obtain single-crystal diffraction patterns from microcrystals by electron diffraction. Their interpretation is very difficult for the following reasons:

(1) The measured intensities are unreliable because dynamic scattering affects the individual reflections independently in a manner depending on the sample thickness, which is usually unknown [9].
(2) Radiation damage may destroy or alter the crystal structure before it can be recorded [10].
(3) Quantitative estimation of electron intensities is uncertain because correct background subtraction is difficult at small and large scattering angles.

However, in recent years, electron crystallography has advanced rapidly, using both direct phase methods [11] and maximum entropy statistics [12], but it is not always possible to obtain a sufficiently large number of accurate intensities required for these methods, so that an alternative approach involving simulation of the diffraction pattern has also been used to analyze this sample. The results obtained by the other methods are in excellent agreement but their analysis is considerably simplified if the results of simulation are available.

Experimentally many crystallographic projections are required in order to obtain a reliable estimate of the cell parameters and space group which are required for the simulation procedure. This is very difficult to achieve because organic molecules are often beam sensitive. Low-dose and cryo-conditions were used but the sample may be destroyed before the series complete.

2.3. High-Resolution Imaging

High-resolution images were obtained by phase contrast imaging with JEM-2000EXII transmission electron microscope, which was equipped with nitrogen cooled cold-finger and Gatan Image Enhancer. This TEM had a spherical aberration of 0.7 mm. The filament was a lanthanum hexaboride electron source. The objective aperture and field limiting aperture used in here were 50 μm and 100 μm respectively.

3. COMPUTATIONAL METHODS

1. Generation of Molecular Model

Semi-empirical calculations based on molecular orbital approximations have been used successfully for many years [13, 14]. The approximations used in such calculations have been described [13]. For this work the results obtained by energy minimizing in the Cerius2 1.6 package.

2. Simulation of Diffraction Pattern

In order to proceed with simulation, the crystal unit cell and space group as determined from the experiment diffraction patterns are required. The energy minimized molecule is placed into the unit cell using Cerius2 such that required symmetry of both molecule and unit cell are satisfied and agree with the observed extinction and symmetry. The major features of the simulated diffraction pattern should agree with the experimental one in all zones. Frequently it is necessary to make conformation adjustments to improve the individual intensities, while, however, still satisfying the required symmetry conditions. In the next step, the density and the packing energy are determined. For organic material the density must be close to one and for all crystals the packing energy should be negative.

When the calculated diffraction pattern is sufficiently similar to the experimental one and the above criteria satisfied, dynamic scattering effects are included. If necessary, the model structure is adjusted.

It is thus possible to obtain a model structure giving good agreement between calculated and experimental diffraction patterns in all projections. The co-ordinates of the atoms in the crystal reference frame are then used as input data for the image simulations.

3. Verification of Model by Simulation of High-Resolution Images

In order to ensure the reliability of the structures obtained by electron diffraction simulations, high-resolution images are also compared with the models obtained from simulations. The experimental difficulties encountered are well known [15,16]. The approach used in this work corresponds to the one described previously [9]. However, in this case, a phase transfer function was chosen such that the spatial frequencies corresponds to 2–5 Å were transferred in the electron microscope. The correct defocus value was obtained on-line from the computed Fourier transform of the image.

The images calculated by Cerius2 are obtained in several stages using the multi-slice technique [17]. The procedure includes the standard steps:

(1) Calculation of projected potential.
(2) Calculation of transmission function.
(3) Propagation of beam through the crystal.
(4) Creation of image.

In the last step, the following parameters are taken into account: spherical aberration, energy of electrons, defocus, defocus spread, beam spread, aperture radius, astigmatism and beam tilt.

4. RESULTS AND DISCUSSION

1. Data Collection

Thin single crystals of HPT were obtained by solution casting and spin coating method. Diffraction patterns and high resolution images were obtained using JEM-2000EXII transmission electron microscope with lose-dose and cryo-facilities.

Figure 1 shows the HREM and corresponding ED pattern from solution casting specimens. From the selected area electron diffraction (SAED) pattern, it can be deduced that this crystal is belong to a hexagonal lattice with

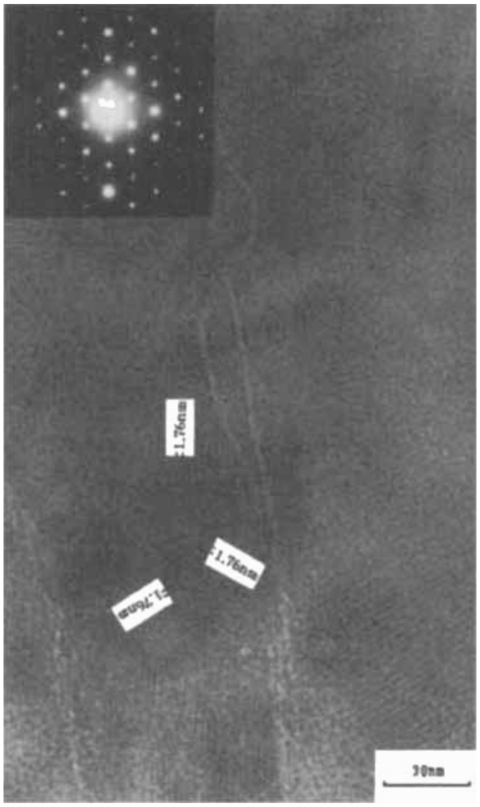


FIGURE 1 High-resolution electron micrograph of HPT in *a-b* project with microdiffraction pattern in correct orientation (inset).

a 6-fold axis. The innermost crystal region measured form HREM image is approximately 50 nm in diameter. The three groups of lattice, found in the center of the image, are encountered with each other at 120°, and the lattice distances of them are 17.6 Å. The white spots in the HREM are corresponded to the channel of electrons and the black spots are related to HPT molecule.

Figure 2 is the HREM and corresponding SAED pattern obtained from spincoating specimens. The crystal orientation here is totally different from that in Figure 1. The innermost diffraction spots in equator in the ED pattern is related to 17.6 Å. And the layer distance, the distance from diffraction center to the first layer, is nearly 3.52 Å. Significant distorted structure is observed in zone A in HREM. In zone B, the wide lattice distance of 17.6 Å is constricted by narrow lattice distance of 3.5 Å, which implies the physical illustration that columns are stacked by discs. In zone C, the lattice

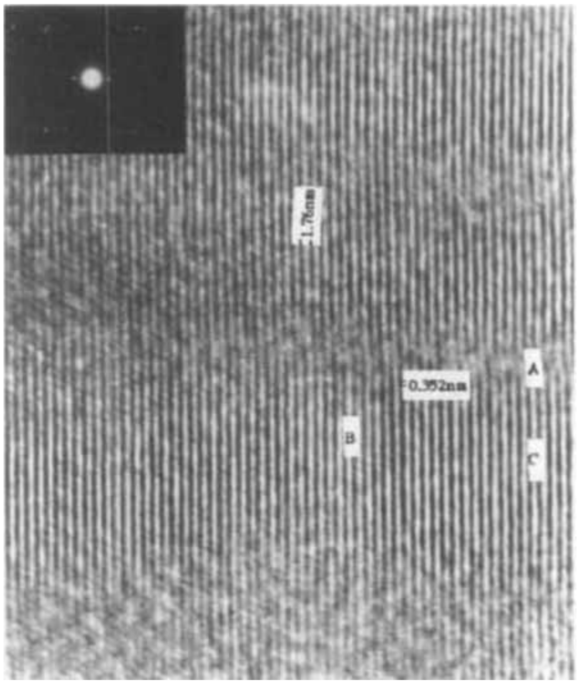


FIGURE 2 High-resolution electron micrograph of HPT in *b-c* project with micro diffraction pattern is correct orientation (inset).

distance of 3.5 Å. can not be illustrated, and only the 17.6 Å. lattice distance exist. This is probably caused by the temperature raising effect of irradiation. When the sample is heated to mesophase, the order of discs are damaged, but the columnar structure are dept. In this case, only the wide lattice distance of 17.6 Å. can be recorded. There is another interesting detail which is that the plane of discs are not perpendicular to the axis of the column, although the discs are parallel to each other. The tilt angle between the center axis of discs and column is 7°. This is a piece of important information to simulate the crystal structure.

2. Molecular Modeling Route

2.1. Conformation of Molecule

One HPT molecular is composed of one rigid core of triphenylene and six flexible pentyloxy-groups (as shown in Fig. 3). The rigid triphenylene core of HPT is trend to stay in a planer style. It's explicit to notice that the energy

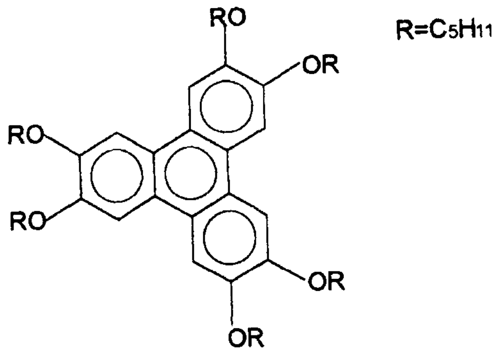


FIGURE 3 The formula of HPT.

satisfied conformation of HPT must have a evenly constructed geometry. Two different conformations of pentyloxy-groups in HPT are suggested by this rule. One is that the pentyloxy-groups with odd position index are above the core plane, while the others with even position index below the plane (The pentyloxy-substitutes with odd and even position indexes are indifferent sides of triphenylene core). The other possible conformation is that all the six substitutes are within the same triphenylene plane. The energy of this two conformation are compared using Cerius2. The first conformation is tend to convert to the second one during energy minimization, which means the all planar conformation is the energy satisfied one. Figure 4 shows the energy curve during minimization. The lowest energy is approximately 4.7×10^2 Kcal/mol. In the final energy satisfied conformation, the six substitutes are evenly attached to the core which introduce on 3-fold axis and three mirror plane (perpendicular to *a*, *b*, *c* respectively) into the HPT molecular structure. All the proceeding simulations are based upon this conformation.

2.2. Simulation of Electron Diffraction Pattern with Cerius2

From two experimental diffraction patterns obtained in different projections the unit cell and possible space groups based on characteristic extinction were determined. Using Cerius2 the energy minimizing molecule was first placed in the cell in such a manner that:

(1) Symmetry requirements were satisfied.
(2) The density was approximately lg/cm^3.

So the minimized HPT molecule was put into a lattice with P6 space group using crystal building in Cerius2. Lattice parameters were set to

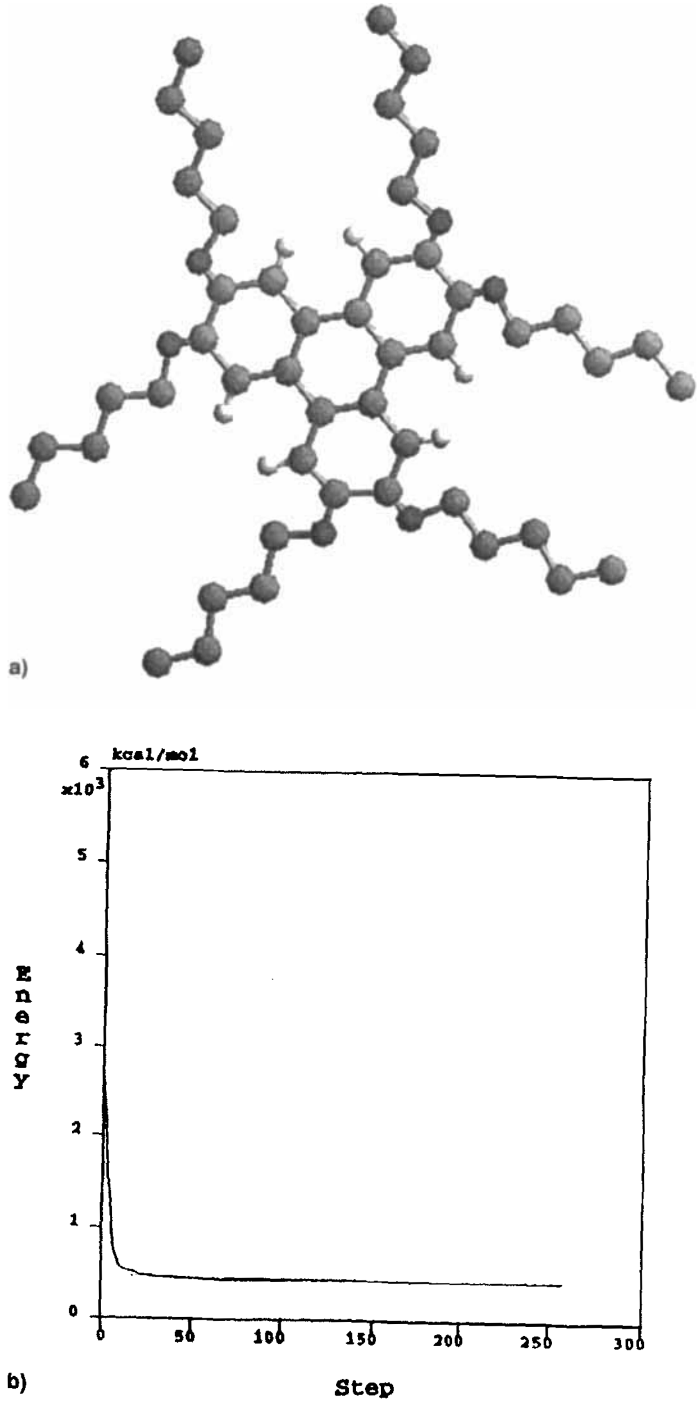


FIGURE 4 (a) Minimized conformation of HPT; (b) The energy minimizing curve.

$a = 30$ Å and $c = 7$ Å respectively. And then using the energy minimizing to minimize the lattice energy, at the meanwhile set the lattice parameter a, b, c variable. The final minimized results are given as $a = 20.3$ Å and $c = 3.5$ Å. D(010) calculated from this structure is 17.58 Å, and this result is in good accordance with that from experimental electron diffraction. Figures 5 and 6 are the simulated electron diffraction pattern which is very similar to the experimental electron pattern.

2.3. Simulation of HREM Images

In order to begin the simulation procedure, the co-ordinates of all the atoms in the unit cell are required, in this case 126 atoms. These co-ordinates were obtained from the results of the electron diffraction simulation procedure using Cerius2. The images were calculated using multislice method. The results are shown in Figures 7 and 8. Generally, the simulation images are accordance with the experimental images. But in simulation image (⟨1 0 0⟩) the HPT core plane are perpendicular to the column which is not accordance to the experimental images (⟨1 0 0⟩). So the HPT molecule were tilted and rotated in the lattice until both simulated ED patterns

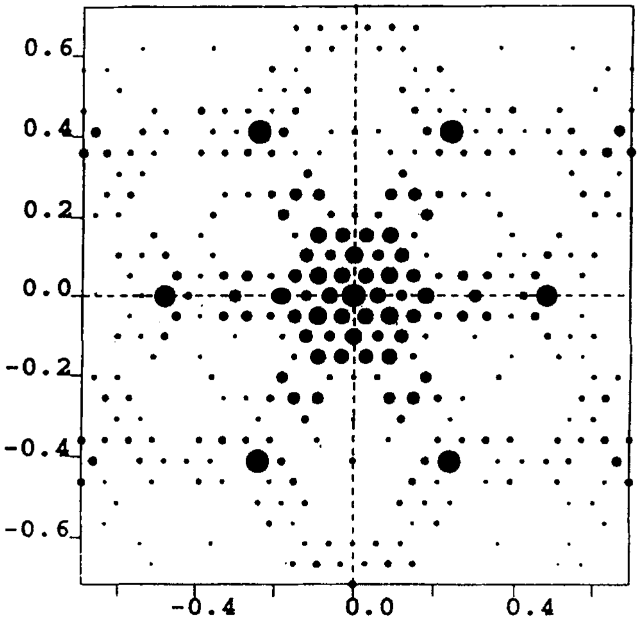


FIGURE 5 Simulated electron diffraction pattern of HPT in a-b projection.

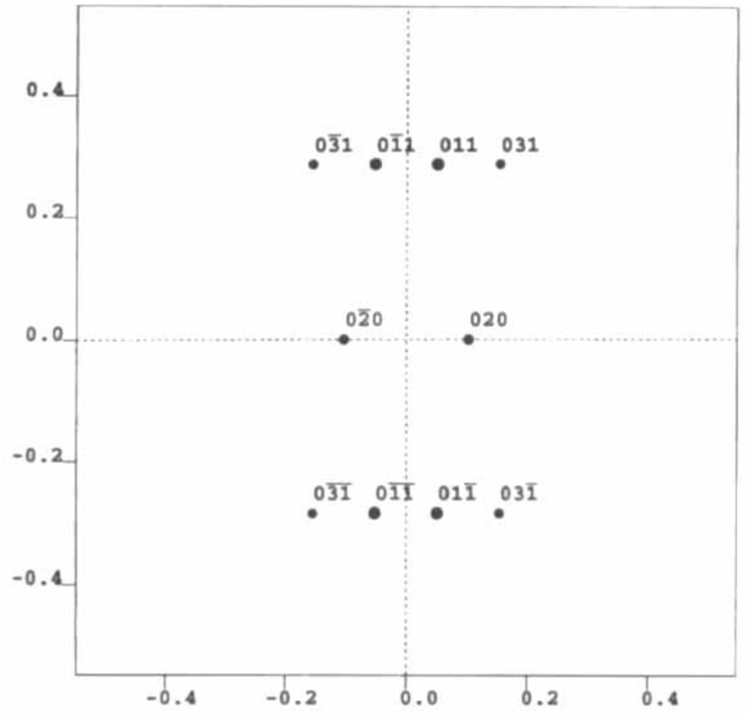


FIGURE 6 Simulated electron diffraction pattern of HPT in *b-c* projection.

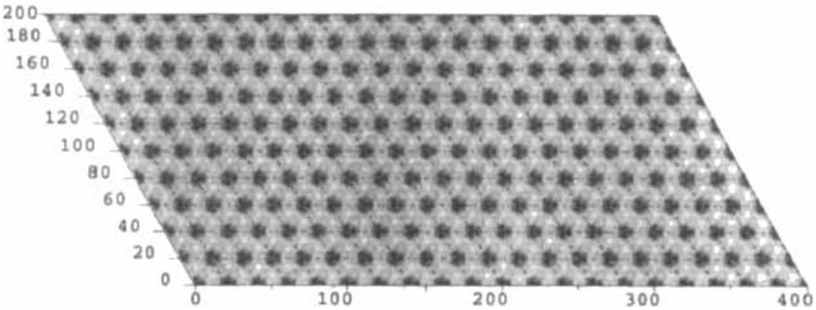


FIGURE 7 Simulated HREM image of HPT in *a-b* projection.

and HREM images were good agreement with experimental ED patterns and HREM images. The results are shown in Figure 9 and Figure 10. The conformations of HPT molecule in lattice are shown from different directions in Figure 11. The angle between *b* axis and HPT core plane is 7°

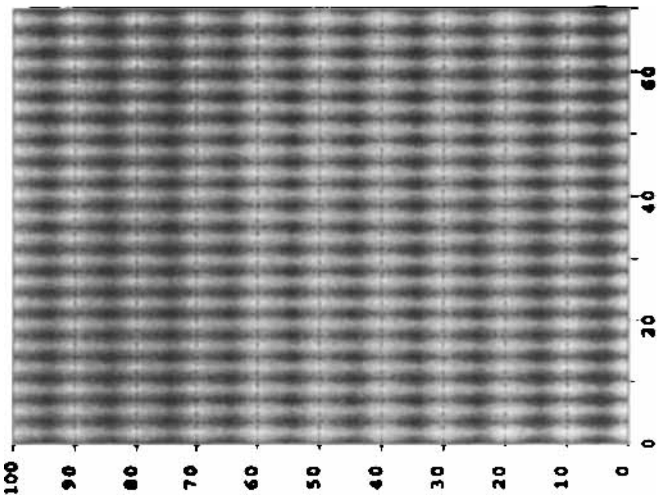


FIGURE 8 Simulated HREM image of HPT in *b-c* projection.

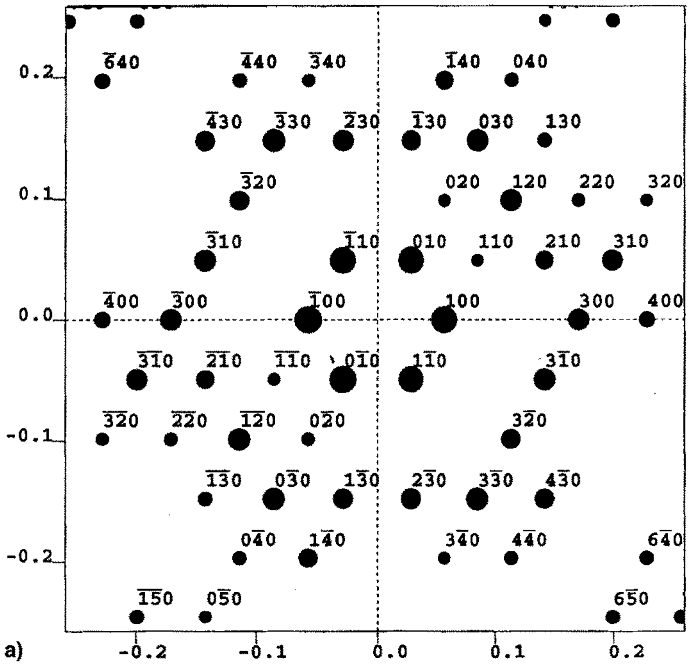


FIGURE 9 (a) Simulated ED pattern; (b) Simulated ED pattern and HREM image of HPT in *a-b*.

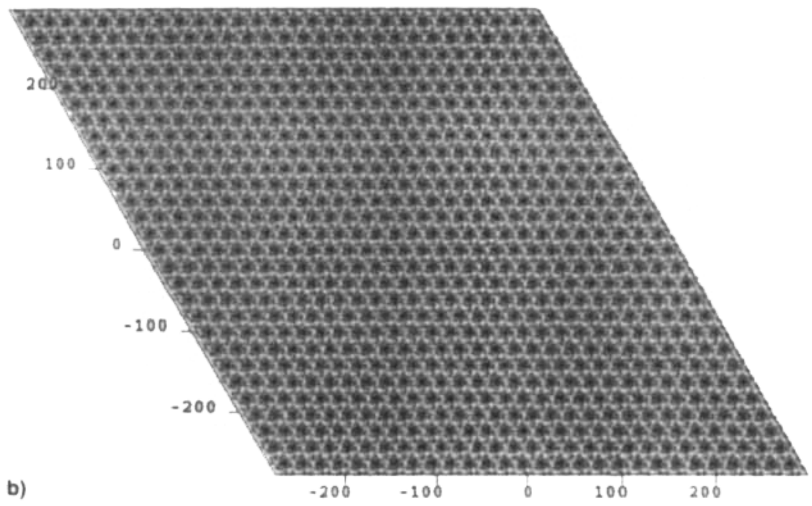


FIGURE 9 (Continued)

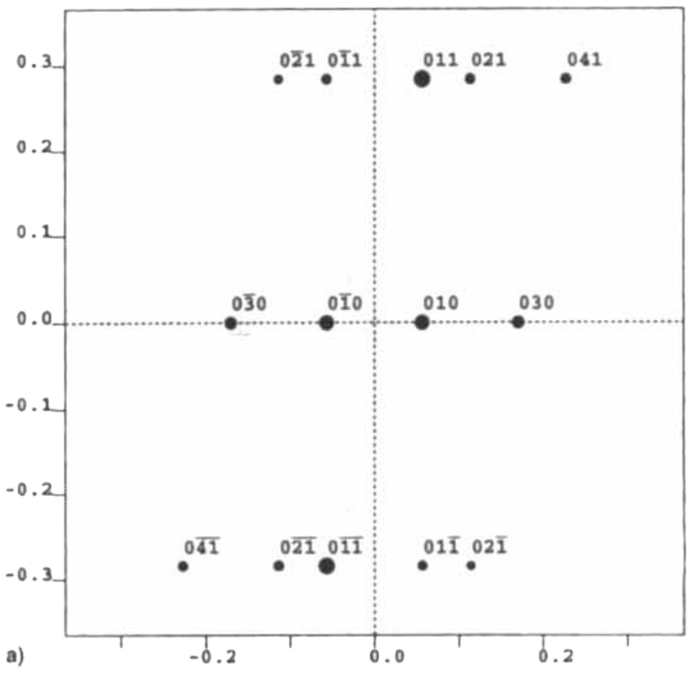


FIGURE 10 (a) Simulated ED pattern; (b) Simulated ED pattern and HREM image of HPT in *b*-*c* projection.

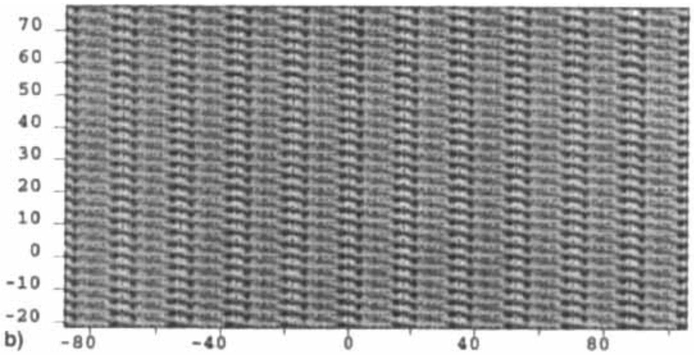
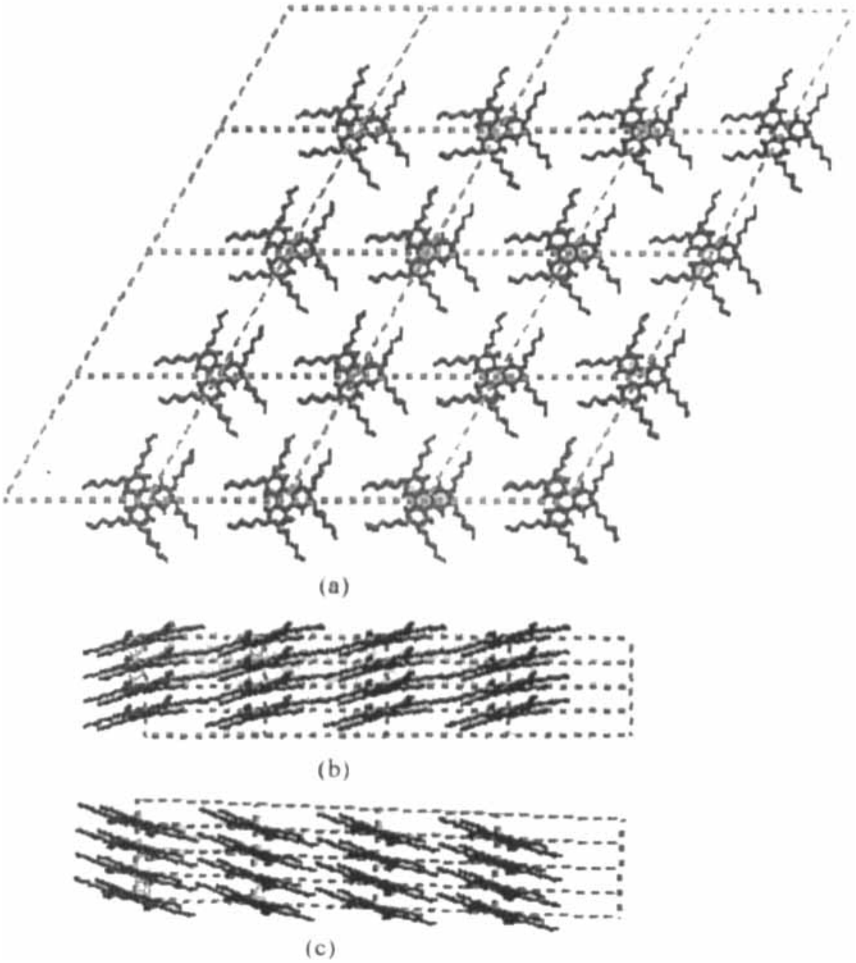


FIGURE 10 (Continued).

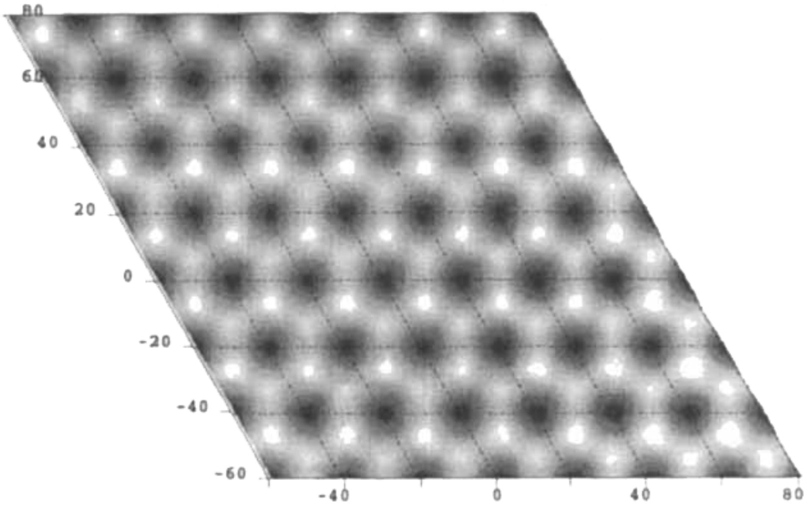

(a)

(b)

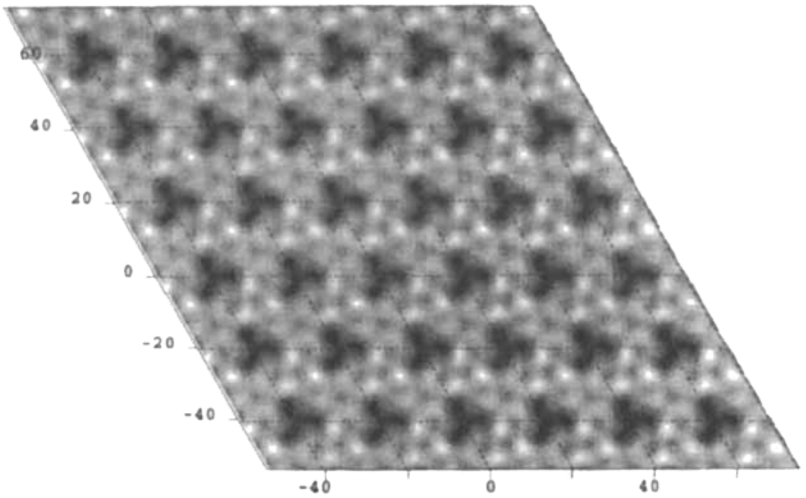
(c)

FIGURE 11 The conformation of HPT (a) from top view, (b) from side view along X-axis, (c) from side view along Y-axis.

which can be seen in *a*-*c* projection. The angle between *a* axis and HPT core plane is 9° which cannot be seen in *b*-*c* projection. Figure 12 shows the contrast change in the image of the HPT crystal for a fixed thickness as

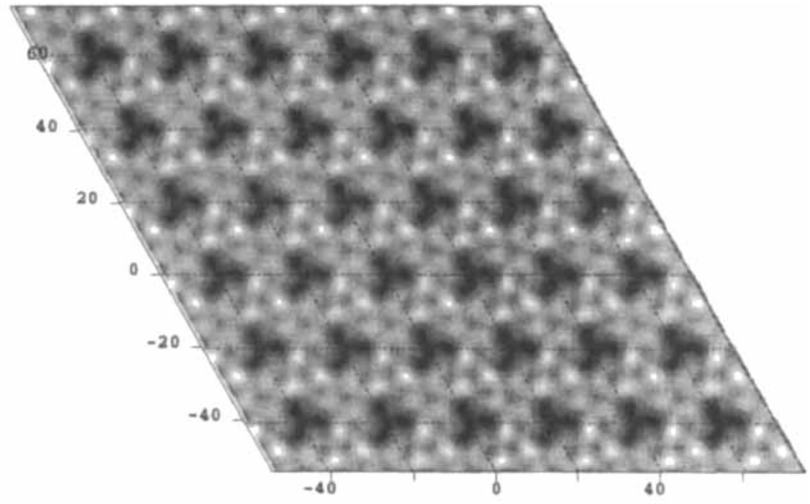


a) (a) Δf= -9000

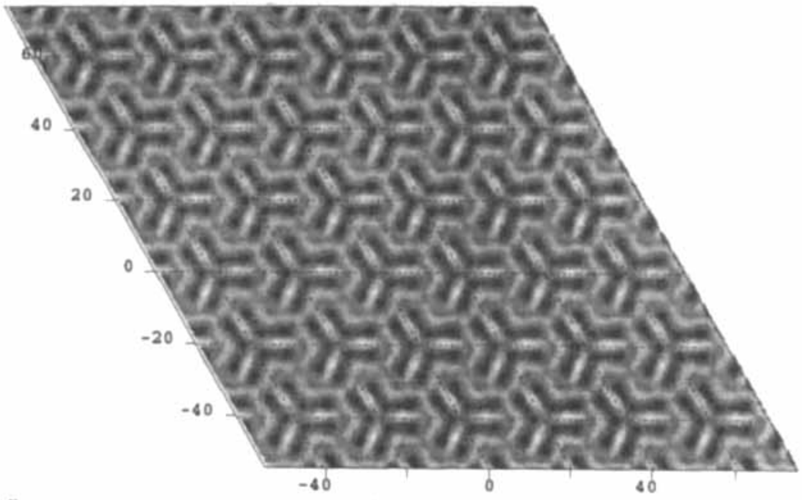


b) (b) Δf= -5000

FIGURE 12 Simulated HREM images obtained from model structures for different defocus (Δf).



c) (c) Δf= -3000



d) (d) Δf= -1000

FIGURE 12 (Continued).

function of defocus. While the whole molecule is imaged at small defocus values, at large defocus values only the repeat period along the chain is observed in the form of a single dot.

CONCLUSION

We have developed procedures enabling decisions to be made regarding suitability of specific organic molecules. The procedure consisted of several parts:

(1) Extimation of cell constants and space group from experimental electron diffraction patterns.
(2) Calculation of minimum energy conformation of the molecule using energy minimize in Cerius2 package.
(3) Calculation and optimisation of simulated diffraction pattern using the conformation calculated in (2) in initial stages and the space group with cell constants obtained from (1).
(4) Determination of atomic structure of crystalline phase from electron diffraction using procedures (1)–(3) above.
(5) Determination of structure from high-resolution images.
(6) Simulation of high-resolution images using the atomic co-ordinates obtained in (4).

Using this method, we got the HPT crystal structure: space group: P6/mmm; lattice type: hexogonal; the lattice parameters are $a = b = 20.3$ Å, $c = 3.52$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$. The core of HPT is not perpendicular to the column. The angle between a axis and HPT core plane is 9° which cannot be seen in b-c projection. The simulated ED patterns and HREM images are good agreement with the experimental ED patterns and HREM images.

Acknowledgment

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