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Structure and order of the discotic compound 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene as revealed by diffraction and molecular simulation studies

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The aggregate structure of the discotic compound 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (HPT) was studied both for the crystalline state and the liquid crystalline state by using electron crystallography and a molecular simulation approach. In the crystalline state, HPT was found to adopt an orthorhombic P_{22_2} space group with cell parameters $a=36.73$ Å, $b=27.99$ Å and $c=4.91$ Å. Molecular packing calculations were conducted to elucidate the molecular conformation and mutual orientational characteristics in the different states. Phase transitions and relationships are discussed from a structural point of view.

1. Introduction

Self-organizing liquid crystalline compounds with disc-shaped molecules are of interest because the columnar phases formed by them give special anisotropic physical properties such as one-dimensional photoconductivity [1, 2] and electron conductivity [3], etc. It is for this reason that molecular engineering, and structural and property studies of discotic compounds, including their low molar mass and polymeric columnar liquid crystals, are currently very active research areas.

Among all columnar liquid crystals, those of triphenylene derivatives have been the most studied, not only because of the flexibility of the molecular engineering that is possible due to their simple molecular structure and symmetry, but also for their stability conferred by the aromatic core. Since the first report on columnar triphenylene liquid crystals in 1978 [4], various liquid crystals based upon this simple aromatic discogen with different substituents and engineered molecular structures have been obtained [5, 6].

Up to now, although the columnar phases formed by triphenylene discogens have been extensively studied and understood to some extent, less attention has been paid to their crystalline phase structures and the conformational changes which accompany the crystalline to liquid crystalline phase transition. However, the latter informa-

tion is indispensable for understanding the packing habit of discogens in different states and how a crystalline phase to mesophase transition occurs. It is of interest, therefore, to study the conformation and molecular packing of discogens in their crystalline states. To some extent, studies of the crystalline phase structure of discogens have been retarded because of the low dimensions of their crystals, which make conventional X-ray single crystal analysis impractical. Fortunately, the availability of recently developed electron crystallographic analytical methods [7-9] based upon powerful computer resources makes the structural analysis of micro-organic crystallites a reality.

In the present work, the aggregate structure of one discotic triphenylene derivative was studied both in the crystalline state and the liquid crystalline state using electron crystallography and a molecular simulation approach. The aggregate structure was manifested in the different phases, and information on molecular conformational characteristics was obtained. Based upon the results, the structural character and phase behaviour of discotic triphenylene analogues can be understood in a new way.

2. Experimental

2.1. Material

2,3,6,7,10,11-Hexakis(pentyloxy)triphenylene (HPT) was synthesized and subsequently purified by flash

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chromatography as described in the literature [10]. The chemical structure of HPT is given in figure 1. HPT is composed of a rigid flat aromatic triphenylene core with six identical flexible alkoxy groups.

2.2. Instruments

Thermograms were obtained using a Perkin-Elmer DSC-2C calibrated with indium at a heating and cooling rate of $10^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere. The optical textures of samples were observed with a Zeiss-Carl Jena polarizing optical microscope equipped with a hot stage. X-ray diagrams (Ni-filtered, CuK_{α} radiation, $\lambda=0.154\text{ nm}$) were recorded in a reflection mode with a Philips PW-1700 automated powder diffractometer. The TEM samples were investigated using a JEOL 2000 EXI electron microscope operated at 100.0 kV. A rotation and tilt holder were used to obtain different crystallographic projections of the unit cell. The tilt angle was adjusted until new zones appeared and until the maximum tilting angle of $\pm 30^{\circ}$ was reached. Computer modelling was performed using an Indigo workstation, and the Cerius² 2.0 package produced by Molecular Simulations Inc. (USA) was used.

2.3. Methodology for structure studies

Generally speaking, although X-ray single crystal analysis is a reliable method to elucidate lattice type, cell dimensions and even atomic positions of appropriate crystals, this method is inappropriate in the case of most organic crystalline materials [11]. This is generally caused by the following shortcomings. First, organic compounds, which are generally composed of light elements with low scattering factors, such as C, H, O and N, etc. cannot give a sufficient number of diffraction maxima; second, most organic compounds are difficult to prepare as large enough single crystals for X-ray single crystal diffraction experiments. However, detailed

knowledge about molecular conformation and packing habits in organic crystals is essential for understanding the relationships between structure and property, and more important, for molecular engineering and design.

Recently, electron crystallography using maximum entropy [8] and simulation methods [9] has been fully developed both in theory and experimental technique and made available to powerful computer resources. Electron crystallographic structure analysis of organic crystallites using simulation methods is suitable for commercially available software and gives good results with acceptable precision [7]. The procedure of electron crystallographic structure analysis using simulation methods is generally composed of two steps. First, determination of the cell dimensions and lowest space group by electron diffraction experiments. Second, molecular modelling to the experimentally obtained cell by simulation techniques.

2.3.1. Cell and space group determination by electron diffraction

To determine a lattice type and cell parameters we need at least three electron diffraction (ED) patterns from different zones and their geometrical relationships, or to obtain ED patterns of basic faces. ED analysis by tilting tiny single crystallites is applicable in most cases, so avoiding the sophisticated techniques demanded in preparation of samples with different basic faces. Crystallite tilting ED experiments can be made by using a rotating-tilting specimen holder in an electron microscope. One initial ED pattern is first finely adjusted, and then two tilting series are achieved based upon the two basic axes in the basic plane found. The geometric relationship of the tilting ED series and the positions of the diffraction maxima in each ED pattern are used as the input to deduce the lattice type and cell parameters. Finally, the corresponding X-ray powder diffraction pattern (XRD) can be indexed according to the above structural parameters. By considering the extinction principle derived from the indexing results of the diffraction pattern, conclusions about a possible space group can be preliminarily drawn.

2.3.2. Computer molecular modelling and diffraction simulations

In principle, conformations for individual small molecules can be calculated using *ab initio* quantum mechanical methods. For larger molecules, *ab initio* methods become impractical and semi-empirical quantum mechanical methods may be used, e.g. MOPAC. However, while MOPAC calculations can give first estimates of conformational features, the molecular conformation will be affected by the crystal field in a

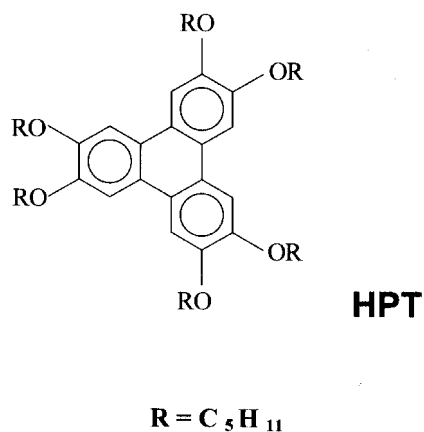


Figure 1. Molecular geometry of 2,3,6,7,10,11-hexakis(pentyl)triphenylene (HPT).

complex manner which will depend on details of the crystal structure and the molecules involved [12].

In this contribution, we adopted a force field approach to obtain the initial molecular conformation. The Dreiding II force field [13] was chosen as the molecular force field throughout the packing calculation. The initial molecular conformation was obtained by energy minimization of HPT with side chains in the all *trans*-conformation as constructed via a 3D sketcher module. Subsequently, this conformation was fully energy minimized using a termination criterion of RMS force $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. Then this initial molecular conformation was put into the experimental set-up cell, with the restrictions decreed by space group symmetry. The molecular packing energy was calculated and minimized by giving appropriate freedom to the molecules and the different side chains.

The potential energy calculation incorporated with CRYSTAL PACKER is determined by superposition of various two-, three- and four-body interactions:

$$E = E_{\text{vdw}} + E_{\text{coul}} + E_{\text{hb}} + E_{\text{tor}}. \quad (1)$$

The Van der Waals term E_{vdw} is calculated using the Lennard–Jones function. The Coulomb energy E_{coul} is treated by means of the Ewald summation technique. The CHARM-like potential is used to calculate the energy term of any hydrogen bonds E_{hb} . The calculation of sub-rotational interactions, E_{tor} , is determined under the Dreiding II force field.

When the packing energy was negative, the ED pattern was calculated and compared qualitatively with the experimental diffraction patterns, in order to select the one which is most similar to the experimental diffraction.

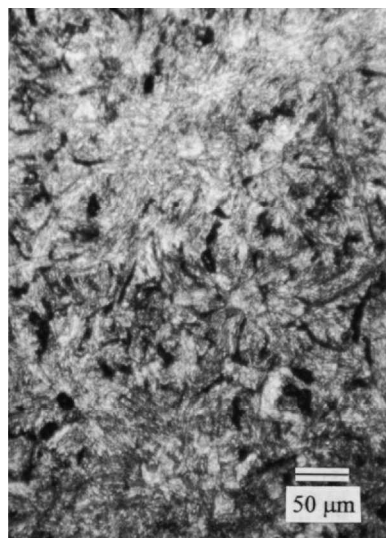
The kinematic intensity for each hkl reflection in Cerius² is calculated using

$$I(hkl) = \left[\sum f_n \cos 2\pi(hx_n + ky_n + lz_n) \right]^2 + \left[\sum f_n \sin 2\pi \sum (hx_n + ky_n + lz_n) \right]^2 \quad (2)$$

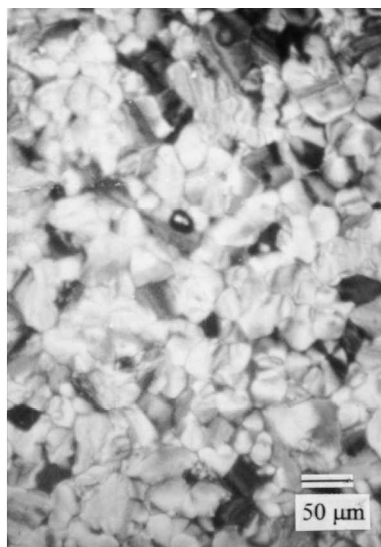
where f_n is the atomic scattering factor for the electrons of atom n , and x_n , y_n , z_n are the fractional coordinates of atom n . The summations are over all atoms in the unit cell.

Table 1. Phase transition behaviour of HPT determined by DSC.

Cycle	Rate	Transitions °C	$\Delta H/\text{Jg}^{-1}$ (T_m)	$\Delta H/\text{Jg}^{-1}$ (T_i)
Heating	$10^\circ\text{C min}^{-1}$	Cr 68.08 Col _{ho} 122.57 I	43.67	11.98
Cooling	$10^\circ\text{C min}^{-1}$	Cr 42.39 Col _{ho} 119.01 I	−45.40	−12.14



(a)



(b)



(c)

Figure 2. Polarized optical micrographs of HPT in the room temperature crystalline state (a), and the LC phases at 73°C observed for HPT by heating the sample from the room temperature crystalline state ($\text{LC}\uparrow$) (b) and by cooling the sample from the isotropic state ($\text{LC}\downarrow$) (c).

3. Results and discussion

3.1. Phase transitions and polarized optical microscopic observations

The phase transitions obtained by DSC showed that HPT forms an enantiotropic liquid crystal phase (table 1). The phase transitions for HPT are in accordance with the literature [14]. A typical focal-conic texture was observed for the liquid crystalline phase obtained either by cooling the sample from the isotropic state or by heating the sample from the crystalline state (figure 2). However, a difference in order was clearly indicated. The LC phase obtained by cooling from the isotropic state ($LC\downarrow$ state) shows a high degree of regularity. This state has been extensively studied by many authors, and

has been identified as a Col_{ho} phase which possesses a highly ordered hexagonal symmetry. The LC phase obtained by heating HPT from the (poly)crystalline room temperature phase ($LC\uparrow$ state) shows a lower regularity which may result from a lower symmetry. Voigt-Martin *et al.* [15] have reported that only pseudo-hexagonal diffraction can be observed for this state. In this work, we will discuss these two distinct phenomena through the molecular simulation approach.

3.2. The crystalline state structure of HPT

3.2.1. Cell and space group

HPT's cell dimensions were determined using the ED tilting process as described in the experimental section.

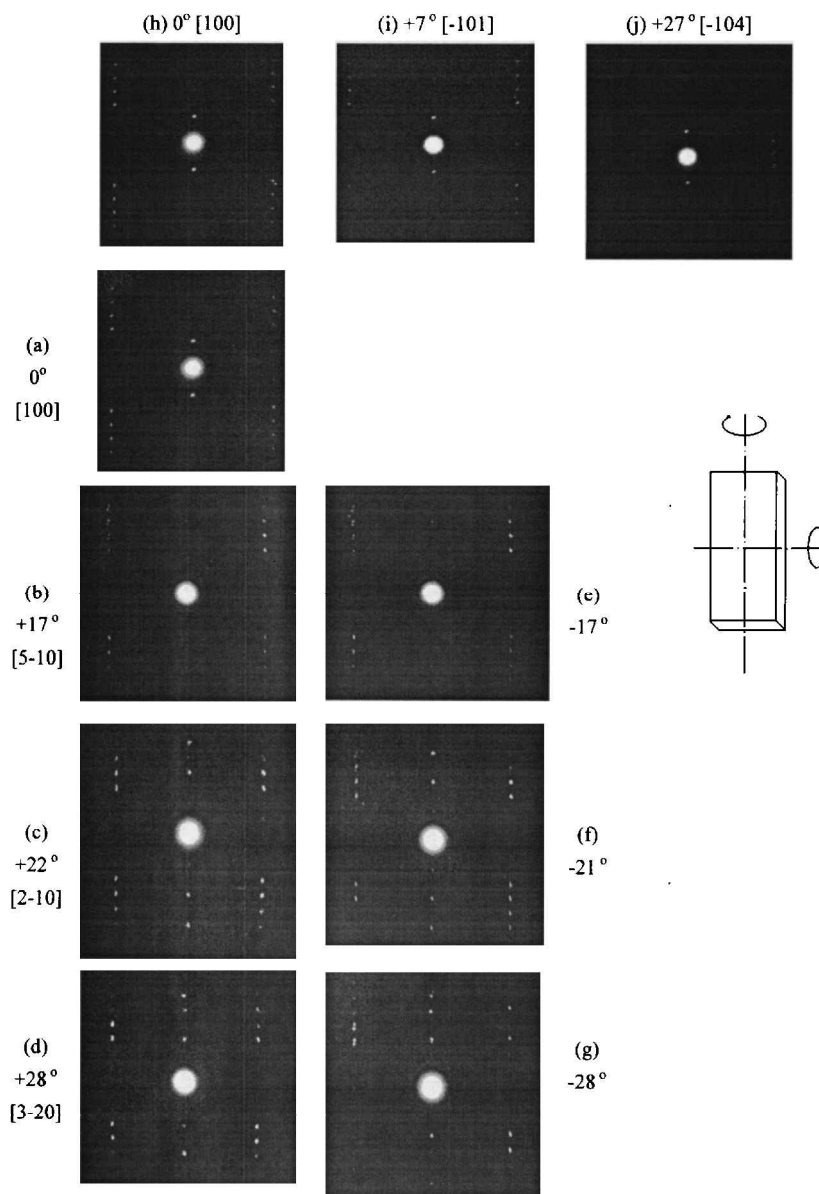


Figure 3. Selected area electron diffraction tilting series for HPT crystallites. The first series (a)–(g) are tilted along the axis defined by the two horizontal reflections. The second series (h)–(j) are obtained by tilting about the axis defined by the two strong vertical reflections. The tilt angles and corresponding zones are indicated together with the series number.

When the tilting axes were carefully chosen from the initial ED pattern, a series of ED patterns from different crystal projections with definite geometrical relationships could be obtained *in situ* from the same single crystallite. Then the cell dimensions were calculated and all the corresponding diffraction patterns were subsequently properly indexed. Symmetry information was obtained from systematic extinctions from the ED series, considering the indexing results of XRD.

Figure 3 shows the ED tilting series. Figure 3(a) is the initial ED pattern [for details see the contrast enhanced pattern in figure 8(a)]. This ED pattern is the only kind of ED pattern obtained by ED from different sample parts. Although all of this kind of ED pattern are oriented in different directions for different sample regions, the film of LC specimen looks uniform and only the contrast varied. This suggests that the sample film consists of single crystalline domains with different orientations, while the crystalline habit is the same. The initial ED pattern can be characterized as an orthorhombic two-dimensional net. The first tilting series is tilted along the axis defined by two horizontal reflections; the specimen is tilted until a new zone is obtained. All the projections obtained are orthorhombic and counterparts with the same degree of tilting in positive and negative directions are identical. This suggests an orthorhombic unit cell. To confirm this deduction another tilting series was obtained by tilting about another axis defined by the two strong vertical reflections of figure 3(a).

From these two series of diffraction patterns, an orthorhombic unit cell can be defined without doubt. Figure 3(a) shows a basic zone, which we define as the [100] zone. The b^* and c^* axes are perpendicular to one another and the c^* value is the smallest in this projection among the second tilting series; b^* was constant because it represents the horizontal tilt axis. The a^* axis can be calculated from the first tilting series by comparing the different Laue zones; this is most clearly seen from the 22° and 28° projections in the first tilting series. Therefore, from this series of experiments, the structure of the unit cell could be determined as being an orthorhombic lattice with cell constants: $a=36.73 \text{ \AA}$, $b=27.99 \text{ \AA}$ and $c=4.91 \text{ \AA}$. In order to obtain a density of about 1 g cm^{-3} , there must be four molecules in the unit cell. The final calculated cell density is 0.980 g cm^{-3} .

In the second step of the analysis, the space group can be determined from the systematic absences. Having determined the unit cell, all the ED diffraction patterns and the results from XRD (figure 4) can be indexed. The indexing results of XRD are listed in table 2. The systematic absences are collected as follows: hkl : no conditions; $0k0$: $k=2n$.

By indexing using *International Tables for Crystallography* [16], this orthorhombic lattice gives a

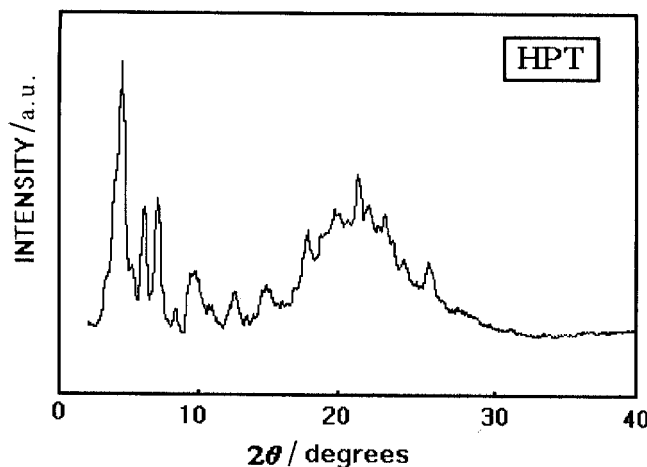


Figure 4. Wide angle X-ray powder diffraction pattern from melt-grown HPT in the crystalline state.

Table 2. The indexing of WAXD peaks of crystalline HPT.

$d/\text{\AA}$		$I/I_{\text{max}}(\%)$	h	k	l
Experimental	Calculated				
21.16	22.16	36.02	1	1	0
18.37	18.37	100.00	2	0	0
16.09	15.36	10.70	2	1	0
14.00	14.00	32.22	0	2	0
12.03	12.24	35.20	3	0	0
10.44	11.13	3.11	2	2	0
9.32	9.18	8.78	4	0	0
8.95	9.04	10.98	1	3	0
8.60	8.73	9.13	4	1	0
8.18	8.32	4.15	2	3	0
7.66	7.68	1.83	4	2	0
7.24	7.35	3.26	5	0	0
6.90	6.87	6.82	1	4	0
6.55	6.55	2.27	4	3	0
6.02	5.98	8.23	6	1	0
5.80	5.77	7.51	5	3	0
5.26	5.25	7.37	7	0	0
4.91	4.91	24.57	0	0	1
4.68	4.68	21.67	2	1	1
4.49	4.49	29.93	2	2	1
4.40	4.36	29.37	3	6	0
4.27	4.28	26.65	4	1	1
4.10	4.10	45.40	3	3	1
3.98	3.98	33.30	1	7	0
3.85	3.83	24.49	6	0	1
3.76	3.74	26.30	5	3	1
3.67	3.67	16.19	1	5	1
3.57	3.56	13.37	7	1	1
3.46	3.47	9.39	7	2	1
3.33	3.33	12.99	2	6	1
3.22	3.19	4.96	7	4	1
3.07	3.06	3.26	2	7	1
3.00	3.01	2.27	3	7	1

lowest space group symmetry of $P_{22,2}$. The symmetry information relating to space group $P_{22,2}$ is as follows:

Laue class mmm ($2/m$ $2/m$ $2/m$);

point group 222 ;

international tables No. 17: bca ;

extinction symbol $P-21-$;

reflection conditions $0k0: k=2n$;

and symmetry operations: (x,y,z) , $(-x,-y,z)$, $(x,-y+1/2,-z)$, $(-x,y+1/2,-z)$.

Formal definition of space group No. 17 is P_{222} , which demands the inter-exchange of a , b , c for the cell. However, to be consistent with the columnar phase, we here still define the shortest axis as the c axis. Finally, it is noted that attempts to fit to other space groups of a related kind ($P_{2,2,2}$) were unsuccessful.

3.2.2. Molecular modelling

Various approaches, including *ab initio* and semi-empirical quantum mechanical methods, have been sug-

gested for calculating the gas phase single molecular conformation which will be chosen as the input or first estimate conformation in the crystal packing calculation. For HPT, a force field approach by molecular mechanical calculation was conducted. The HPT molecule was first constructed with all *trans* side chains. Then proper minimization was carried out to obtain the final, energy stable, gas phase conformation. This conformation (Figure 5) was used as the initial conformation for crystal packing calculation (figure 5). The crystal packing was calculated by giving certain freedoms to the initial molecule and its side chains, with strict restrictions imposed by the unit cell dimensions and space group.

Figure 6 show the final crystal packing obtained, projected from different directions. The triphenylene molecules are tilted in two directions along the a axis; the angle is 48° . The distance between triphenylene cores is 3.4 \AA , while the c axis distance is increased to 4.9 \AA by the tilting of molecules. All the cores in one cell are oriented in accordance with symmetry operations

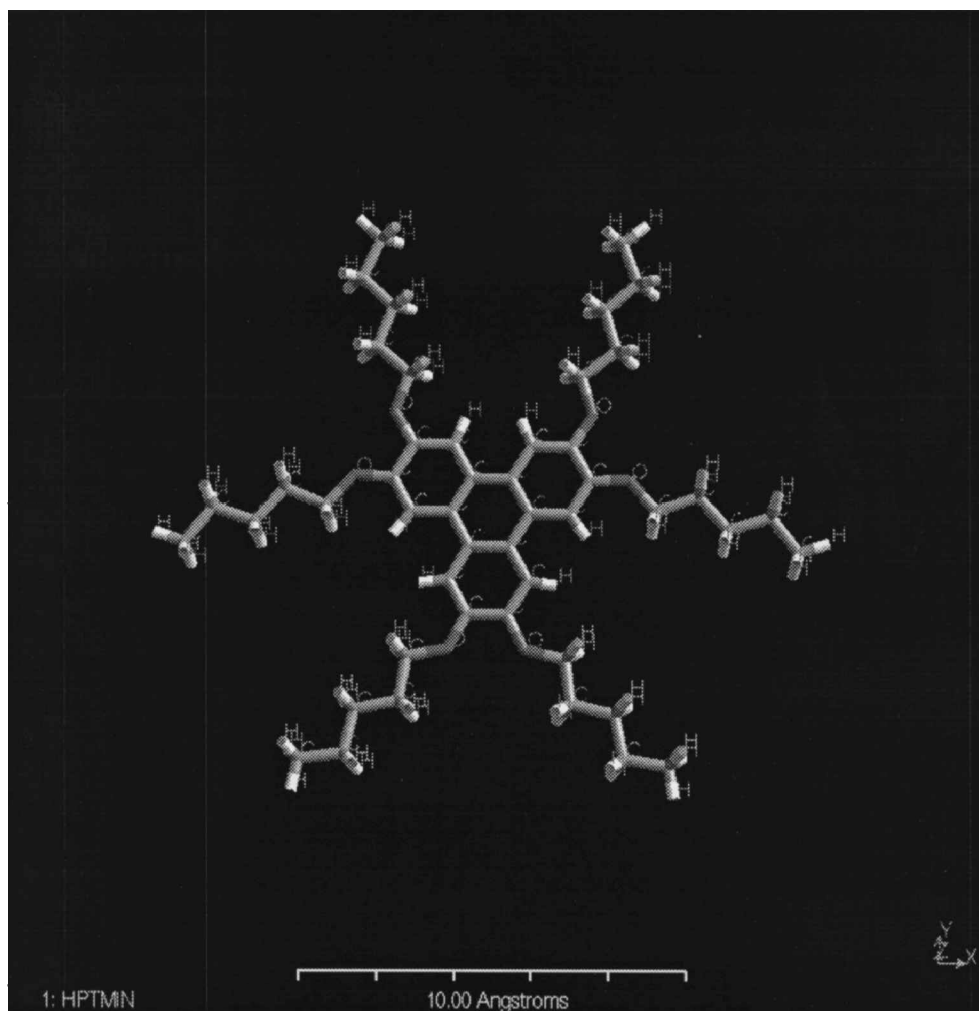


Figure 5. The initial molecular conformation of HPT in the gas phase.

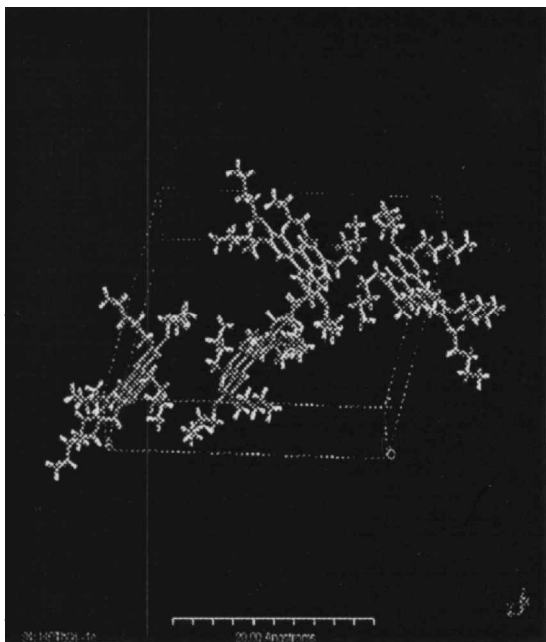
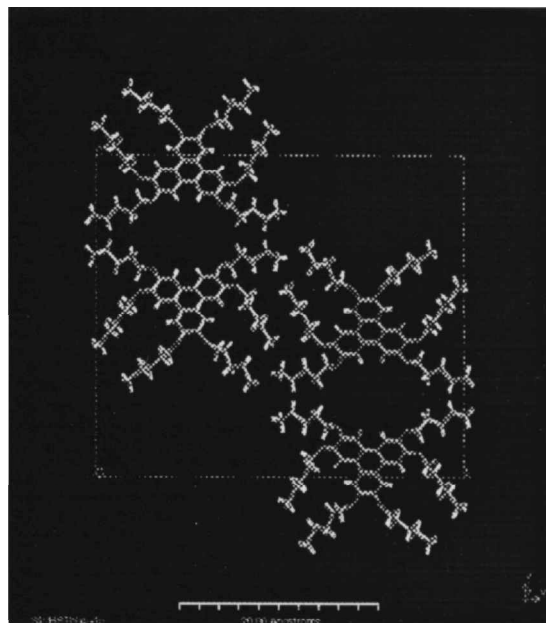
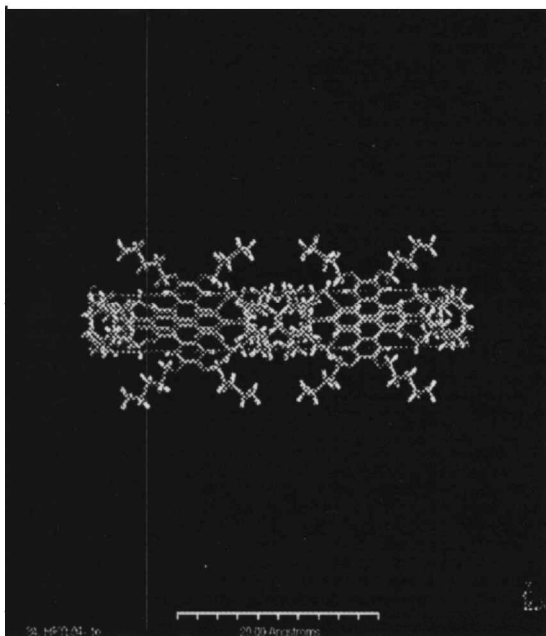
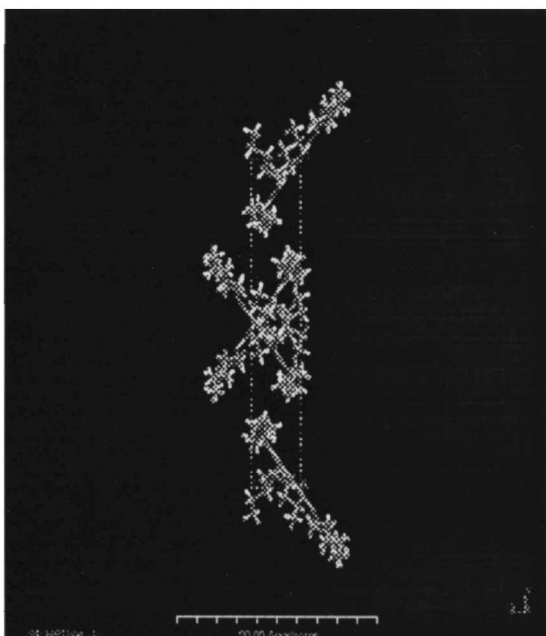
**(a). 3-D view****(b). view along c axis****(c). view along b axis****(d). view along a axis**

Figure 6. Representation of different projections in the $P_{22,2}$ crystal obtained from the CRYSTAL PACKING calculation.

(figure 7). The packing energies (kcal mol^{-1}) per cell are: vdw energy = -233.82 , Coulomb energy = 18.69 and total energy = -215.13 .

These calculated packing results are quite similar to those presented by Voigt-Martin [15], where they used

a simplified short side chain model to simulate a seven-carbon side chain triphenylene crystal by adjusting ED patterns from different zones. This agreement suggests that the crystalline packing character of the discotic triphenylene ether series is similar.

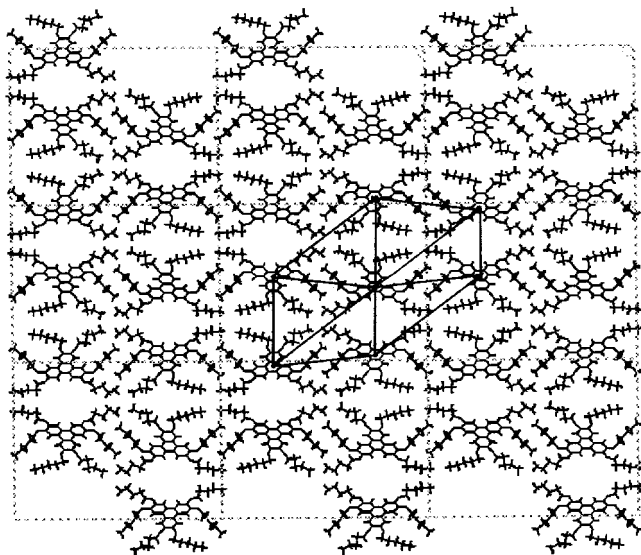
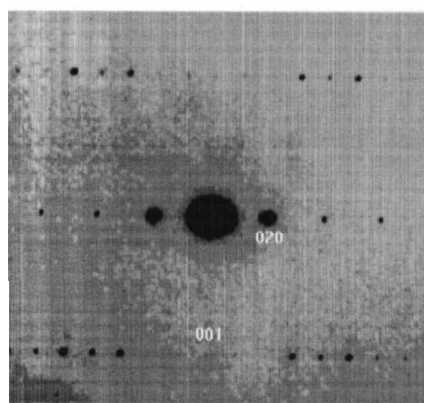
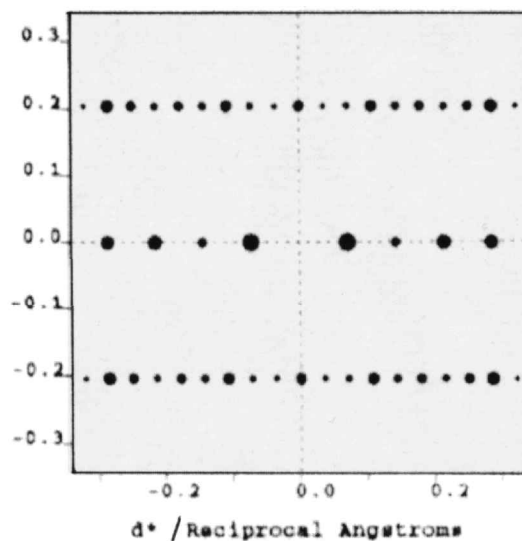


Figure 7. Representation of the *ab* projection in the P_{222} crystal showing multi-unit cells to obtain an over-all impression of the mutual orientation of columns.

For this calculated low energy crystalline packing cell containing four triphenylene molecules which are tilted at an angle of 48° to the *ab* plane, while the stacked columns remain perpendicular to this plane, the agreement between theoretical and experimental diffraction is qualitatively good (figure 8). Quantitative comparison of electron intensities is inapplicable here, because of high radiation and dynamic scattering effects on the experimental ED patterns.



(a)



(b)

Figure 8. Comparison of experimental ED pattern (a) and simulated ED pattern (b) in the [100] zone. The experimental ED pattern is inverted to improve the image contrast.

3.3. Columnar phase structure of HPT

Figure 9 compares the X-ray diffraction spectra of the LC phases obtained at 73°C for HPT by heating the sample from room temperature crystalline state ($\text{LC}\uparrow$) and by cooling the sample from the isotropic state ($\text{LC}\downarrow$). In both LC phases, HPT displays a strong reflection at smaller angles, and a halo and an asymmetric reflection on the top of this halo. The scattering maxima are given by the Bragg spacings and can be interpreted by analogy with the values found for triphenylene as follows: 19.3 \AA for $\text{LC}\downarrow$ and 18.4 \AA for $\text{LC}\uparrow$, corresponding to the (10) intercolumnar distance in the hexagonal lattice; 4.5 \AA for both $\text{LC}\downarrow$ and $\text{LC}\uparrow$ corresponding to the non-oriented, liquid-like arrangement of the alkyl chains; 3.6 \AA for both $\text{LC}\downarrow$ and $\text{LC}\uparrow$ corresponding to the constant distance between the triphenylene cores in the column. The hexagonal lattice constant a can be calculated from the (10) diffraction maxima as 22.3 \AA for $\text{LC}\downarrow$ and 21.3 \AA for $\text{LC}\uparrow$. Additional reflections from the hexagonal lattice occur, but are too low in intensity to appear in this plot. These scattering diagrams are characteristic of the hexagonal columnar lattice. However, the symmetry information for individual columns cannot be efficiently drawn from powder diffraction diagrams, although the hexagonal lattice is clearly indicated.

To apply molecular simulation to the hexagonal columnar phase of HPT, some approximations in the molecular modelling route must be introduced. Here, the lattice of this highly ordered columnar phase is treated as a crystalline-like, three-dimensional periodic system. Also, the gas phase single molecular conformation was

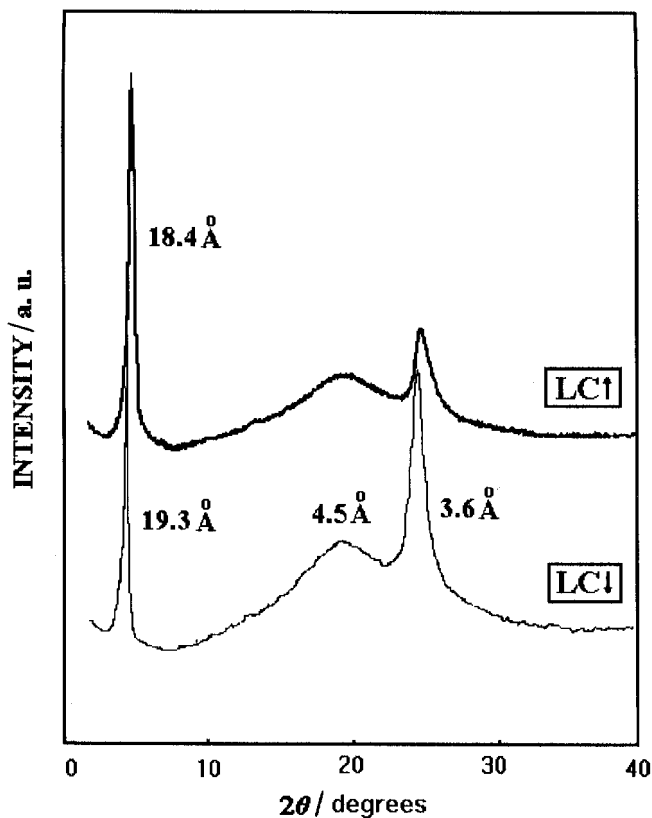


Figure 9. Comparison of X-ray diffraction spectra of LC phases at 73°C observed for HPT by heating the sample from the room temperature crystalline state (LC \uparrow) and by cooling the sample from the isotropic state (LC \downarrow).

chosen as the representative conformation with the highest spatial occupation ratio. HPT with this 'average' conformation was placed at the lattice points of the hexagonal lattice. Although the dynamic properties of HPT have not been directly considered in the modelling process, the above approximation should be efficient to compare mutual orientation and order by adopting the high spatial occupational conformation.

Figure 10(a) shows the mutual orientation of HPT molecules in the LC \downarrow phase. The planes of the HPT molecules are marked with circles. The discotic molecules are non-interrelated between columns, so allowing the molecules to rotate around their column axis. By adopting this kind of packing, no restrictions are imposed on the fast free rotation of HPT molecules around the column axis as observed by NMR experiments [17, 18]; the vdw range of the single HPT molecules just satisfies the dimensions of the hexagonal lattice. Highly ordered hexagonal symmetry may be obtained from the fast rotation of HPT along columns on the experimental time scale. The highly ordered hexagonal symmetry from the packing and molecular rotation

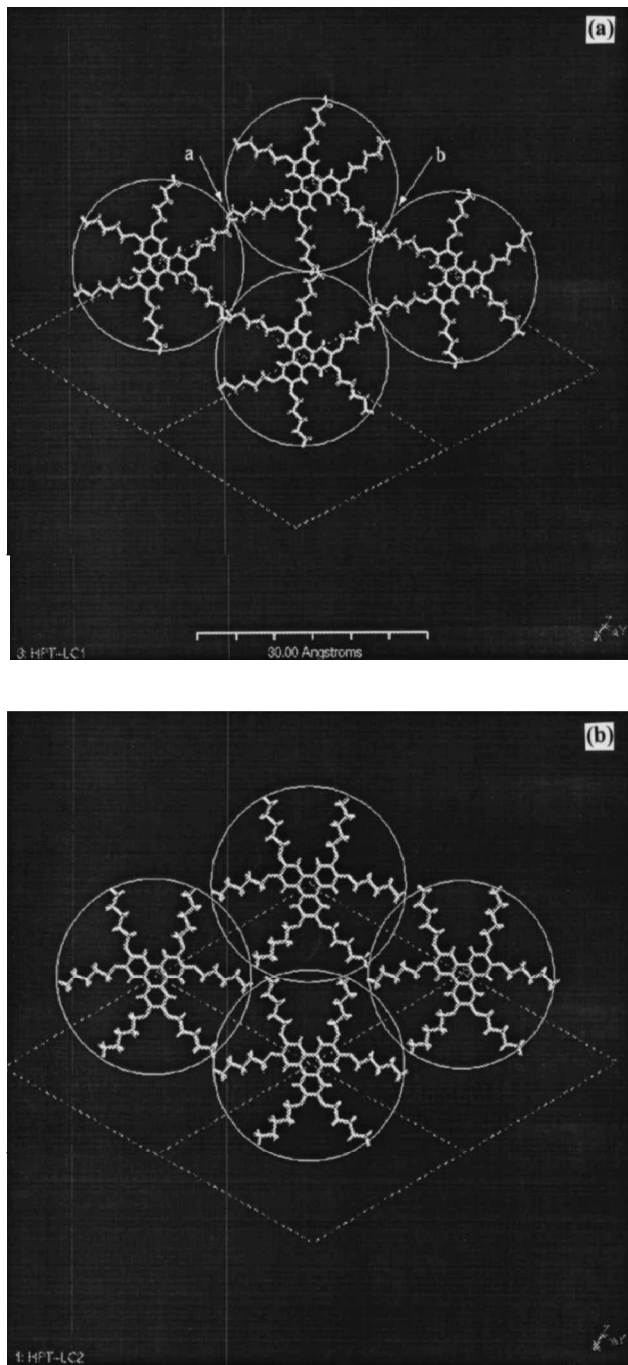


Figure 10. Molecular modelling results of the columnar phase LC \downarrow (a) and LC \uparrow (b).

characteristics of HPT give a Col $_{h0}$ phase in the macro-view.

As to LC \uparrow , a different mutual orientation of the HPT molecules is obtained [figure 10(b)]. To satisfy the vdw interaction, the HPT molecules must have a core oriented packing style which introduces a tightened or shrunk hexagonal columnar packing. This core oriented

packing may be ascribed to that obtained from the crystalline state, where symmetry operations impose a strict core orientation along a column of tilted cores (figure 7). Although when the crystalline to liquid crystalline phase transition occurs, the tilt of the cores will disappear and the molecules will be in a dynamic state, the core orientation is preserved to some extent. In this packing style, the free rotation of HPT in columns will be restricted, and although the LC \uparrow phase still shows a hexagonal lattice, it can only give a pseudo-hexagonal diffraction along the columns, as already found by Voigt-Martin by using ED in conjunction with a heating stage [15].

4. Conclusions

The aggregate structure of the discotic compound 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene was elucidated both in the crystalline state and the liquid crystalline state by using electron crystallography and a molecular simulation approach. In the crystalline state, HPT was found to adopt an orthorhombic $P2_22_1$ space group with cell parameters $a=36.73$ Å, $b=27.99$ Å and $c=4.91$ Å. Molecular packing calculations gave the molecular conformation and mutual orientational characteristics in the different states. The phase transitions and relationships for HPT can thus be understood from a structural point of view.

Generally, whilst intramolecular forces are strong, intermolecular force are weaker and short-range in their effect. Intramolecular forces determine molecular shapes, which in turn play an important role in determining the most effective ways of packing the molecules together in the crystal. If the intermolecular forces are particularly large or strongly dependent on the relative orientation of adjacent molecules, such as the π -electron stacking arrangement of triphenylene discogens, molecular conformational characteristics resulting from intramolecular forces will modify the packing characteristics deriving from the equilibrium intermolecular forces. This has been manifested in the phase transition of HPT from its tilt packing in the crystalline state to the hexagonal packing of the columns.

In the crystalline state, the HPT molecule is restricted to a low energy conformation for the localized energy minima. The HPT molecules are densely packed together while satisfying the intermolecular π - π stacking. The triphenylene cores are oriented with short range order, but the lateral side chains are disordered to some extent. While the triphenylene core's rigid aromatic nature makes the HPT molecules pack in an ordered way, the dynamic nature of the alkoxy chains may introduce

disorder to the system. The columnar phase is formed when the tendency to disorder and order are in equilibrium in the mesophase temperature range. At this stage, the molecules are in a conformationally fluid style. The packing character and dynamic nature of the columnar phase permit molecular movement to a greater or lesser extent, which in turn may result in polymorphy. Systematic studies of polymorphy existing in a columnar system are in progress.

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