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Structure of the liquid crystalline state in hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazenes

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X-ray measurements on hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazenes $[PN(OC_6H_4C_6H_4OC_nH_{2n+1})_2]_3$ (HACP, $n=7$–9), confirm the previous mesophase identification. The apparent molecular length measured in the mesophase compares to twice the length of an alkyloxybiphenyl side group. Specific features are added to the usual features of the nematic and smectic diffraction patterns which show that the molecular arrays in directions parallel and perpendicular to the director both reflect the peculiar shape of the cyclotriphosphazenes.

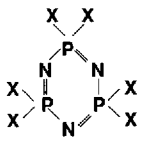
1. Introduction

The molecular organization in the liquid crystalline state is closely related to the chemical structure of the components. The shape of the molecule is generally reflected in the structure and in the physical properties of the liquid crystalline phases [1].

Thermotropic liquid crystals are usually constructed of organic molecules of anisotropic shape [2, 3]. The majority of mesogens have a rod-like or a disc-like shape, bearing in mind that this shape could result from averaging over several conformations (for example, by inversion of conical cores) [4]. In the search for new molecular designs for mesogens of original shapes, one can roughly distinguish two directions. The first idea is to vary the number of alkyl chains grafted around a given core. The mesomorphism is then driven by the relative volume of the paraffinic component in a way similar to that for lyotropic polymorphism, by the lipid/solvent volume ratio. Phasmidic derivatives as well as various thermotropic liquid crystalline salts provide good examples of this case [1, 5]. The second method of shape modification consists in the formation of clusters of a few identical mesogens, generally a twin. Examples of these are found in metallomesogen complexes or in twin discs of different kinds [6, 7]. The flexibility and the direction of the link have a restricted impact upon the mesomorphism which shows some similarities to that of the building units. Mesomorphic hexa-aryloxycyclotriphosphazenes [8–12] can also be considered as 'clusters' and, it is stressed, they are very different from the usual mesomorphic compounds with regard to the shape of the molecules. Six mesogenic side groups are connected in pairs to each P atom of the cyclotriphosphazene ring. Its chemical structure is shown in figure 1. Moreover, from a crystallographic study of hexakis(4-biphenoxy)cyclotriphosphazene [13], the mesogenic side groups are elongated normal to the cyclotriphosphazene ring, forming parallel triplets pointing upwards and downwards. Their architecture compares well with that of cyclic siloxane oligomers with grafted mesogenic side groups [14]. However, the siloxane backbone is highly flexible while, for cyclotriphosphazene derivatives, orientational motion of the mesogens is hindered by the rigidity of the P–O bond. This special molecular form is reflected in the structure and physical properties of their liquid crystalline phases. In this paper, we describe the structure of the cyclotriphosphazene derivatives in the liquid crystalline state as derived from X-ray measurements and discuss its effect on the physical properties.

2. Experimental

The synthesis and the mesomorphic polymorphism of the hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphos-



$X = OC_6H_4C_6H_4OC_nH_{2n+1}(n=7$–$9)$

Figure 1. Molecular structure of hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene $[PN(OC_6H_4C_6H_4OC_nH_{2n+1})_2]_3$ (HACP, $n=7$–9).

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phazenes$[PN(OC_6H_4C_6H_4OC_nH_{2n+1})_2]_3$ (HACP), (figure 1) have been already described [11, 12]. We have studied three homologues ($n=7$–9) with a smectic C-nematic polymorphism. The samples were examined using a previously described X-ray set-up [15]; a point-focused monochromatic X-ray beam ($\lambda(CuK_\alpha)=1{\cdot}541$ Å) was obtained by reflection from a doubly bent graphite monochromator. The sample, stored in a 1·0 mm diameter Lindemann glass capillary tube, is inserted in a cell heated by silicon oil (precision of the temperature regulation is within ±0·5°C). The cell is in the gap of a permanent magnet (0·3 T). Aligned samples could be obtained by slow cooling from the isotropic liquid. The camera is evacuated in order to suppress air scattering. The diffracted X-rays are collected on a flat rectangular film. The temperature was monitored using a chromel–alumel thermocouple.

The microscope observations were performed with a Leitz Orthoplan microscope equipped with a variable temperature stage (Mettler FP 80); samples were examined in polarized light with and without cover glasses.

3. Results and discussion

The transition temperatures, determined by microscope observations and by DSC measurements, are summarized in the table for the cyclotriphosphazene compounds [11, 12]. The $n=7$ member showed enantiotropic nematic and smectic C phases and the $n=8$ and 9 members showed only enantiotropic smectic C phases. For these three mesomorphic cyclotriphosphazene derivatives, the following X-ray measurements were performed.

The X-ray photograph of a nematic phase at 182·5°C for the $n=7$ member is shown in figure 2. At small angles, a pair of flat spots are found at $q=2\pi/33{\cdot}2\,\text{Å}^{-1}$ (q is the scattering vector modulus; $q=4\pi\sin\theta/\lambda$) along the magnetic field (meridian). At wide angles, a pair of relatively weak diffuse arcs can be detected around $q=2\pi/4{\cdot}6\,\text{Å}^{-1}$; the maximum intensity is on the equator and the arcs are extended symmetrically on each side of the equatorial plane. This diffuse ring is due to the lateral interferences between mesogenic side groups. Therefore, the X-ray diffraction patterns show no significant difference from those obtained with a nematic phase of the usual rod-like mesogens. The diffraction spots at small angles are rather sharp and characteristic of smectic A type fluctuations [16].

Poymorphism of HACP ($n=7$–9). Transition temperatures (°C); Cr: crystal, S_C: Smectic C, I: Isotropic liquid.

$$n=7\ \mathrm{Cr}\ \xrightleftharpoons[167]{177}\ S_C\ \xrightleftharpoons[182]{182{\cdot}6}\ \mathrm{N}\ \xrightleftharpoons[183]{183{\cdot}4}\ \mathrm{I}$$

$$n=8\ \mathrm{Cr}\ \xrightleftharpoons[159]{167}\ S_C\ \xrightleftharpoons[183]{184}\ \mathrm{I}$$

$$n=9\ \mathrm{Cr}\ \xrightleftharpoons[153]{160}\ S_C\ \xleftrightarrow{184}\ \mathrm{I}$$

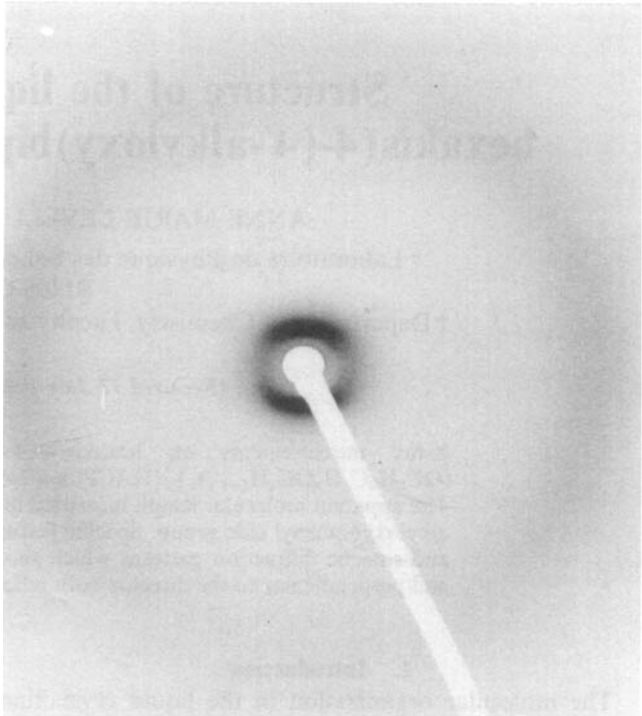


Figure 2. X-ray diffraction pattern of the nematic phase, $n=7$ at 182·5°C.

With slow cooling from the nematic phase, the small angle diffuse spots are transformed into sharp arcs located at $q=2\pi/32{\cdot}8\,\text{Å}^{-1}$; simultaneously the pattern becomes asymmetric with respect to the magnetic field and sharp arcs appear generally at one extremity of the pre-existing nematic inner spot. In fact, it is difficult to obtain either single domains or well oriented fibres of the smectic C phase. This behaviour is not surprising following a nematic to smectic C transition; however, the intensity repartition along the meridional lines of the nematic pattern (reflecting the director repartition) is completely disturbed at the transition, which is rather unexpected.

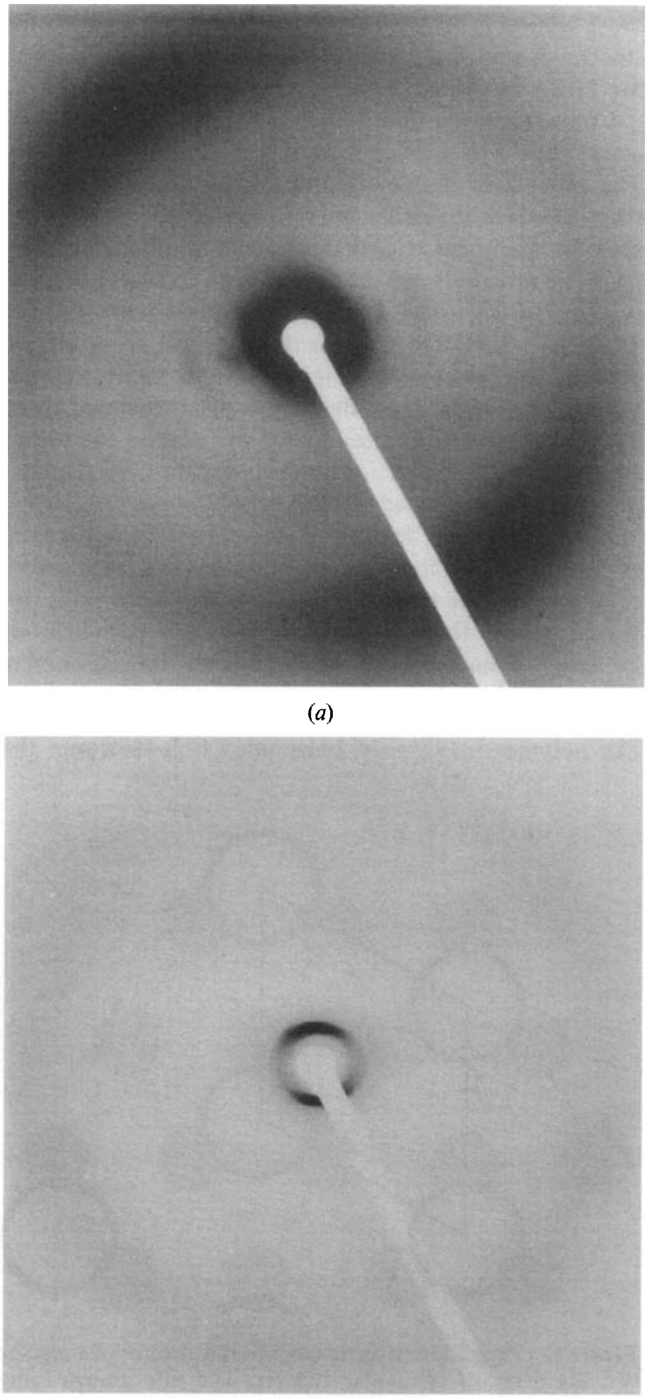
Better patterns for the smectic C phase are obtained for the higher homologues by a slow growing process directly from the isotropic phase, especially for the octyloxy derivative ($n=8$); big single domains of the smectic phase are obtained, but there is no evident relation between the direction of the magnetic field and the director. For $n=8$, just below the clearing point, well localized, round-shaped spots at a small angle—the Bragg peaks—are visible, while the equatorial ring is spread out isotropically, reflecting a wide angular distribution of the molecular axes. In fact, the Bragg spots are probably superimposed over an isotropic diffuse ring which is hardly seen on short exposure patterns.

As shown in figure 3 (*a*), 0·2 K below the I–S_C transition, the mosaic spread-out is increased because the inner reflections form asymmetric arcs around the main spot, while at wide angles, the aspect is almost that of a single domain pattern. The main features are:

(i) a series of Bragg reflections. The intensity is in fact localized on asymmetric arcs of small angular extension. Three orders of reflection can be seen, the intensity decreasing with increasing scattering vector; however, the first peak intensity is several orders of magnitude higher than the intensity of the other two.

(ii) at wide angles the intensity is mainly localized on diffuse arcs with a maximum for $q = 2\pi/4{\cdot}6\,\text{Å}^{-1}$. The two arcs are the section of a torus and we identified the symmetry plane of this torus with the equatorial plane of the pattern. Moreover, a second torus is seen inside the major equatorial ring, with a mean radius $q = 2\pi/8{\cdot}1\,\text{Å}^{-1}$; these two rings characterize the in-plane ordering. The inclination of the row of Bragg peaks with respect to the equatorial plane is specific for a smectic C phase and the corresponding tilt angle is *c.* 20°.

(iii) a set of equidistant diffuse lines, parallel to the equatorial plane, centred on the meridian and slightly arced, surround the odd order spots. These lines are the intersection by the Ewald sphere of a set of periodic reciprocal planes. The arced shape corresponds to a superposition of slightly disoriented sets of planes.


(*a*)

(*b*)

Figure 3. X-ray diffraction patterns of the smectic C phases, (*a*) $n = 8$ at 182·8°C, and (*b*) $n = 9$ at 183·9°C.

The pattern shows no significant evolution with temperature with respect to the layer spacing and the tilt angle.

For the nonyloxy derivative ($n = 9$), the evolution of the diffraction pattern on cooling is similar: just below the clearing point, the wide angle scattered intensity appears to be isotropically distributed, while at a small angle, arcs of limited angular extension are aligned parallel to the magnetic field (figure 3 (*b*)). Then at a lower temperature, big single domains of the smectic phase grow, and the diffraction pattern is qualitatively similar to figure 3 (*a*). In fact, the major part of the diffracted intensity is localized in the Bragg peaks and in the outer equatorial rings. Moreover, these two components are typical of any smectic C phase, while the additional features originate in the specific local ordering of the cyclotriphosphazene rings. Furthermore, long exposure patterns of the nematic phase of the heptyloxy ($n = 7$) derivative also show the inner equatorial ring and the set of odd order diffuse planes.

The temperature dependence of the estimated interlayer distance when $n = 9$ is shown in figure 4, indicating that in the S_C phase region, the interlayer spacing is almost constant at 35·2 Å. The chain length dependence $L(n)$ (where n is the number of carbon atoms

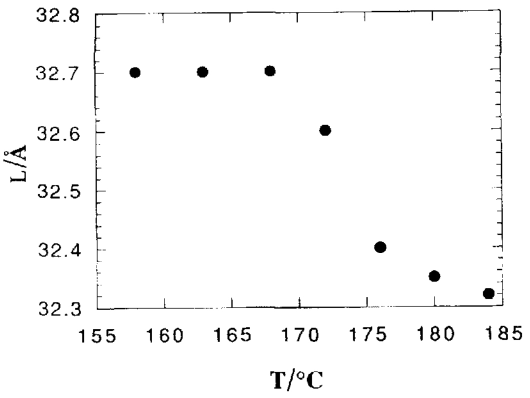


Figure 4. Temperature dependence of the interlayer spacing $L(T)$ of the smectic phase in the $n=9$ derivative.

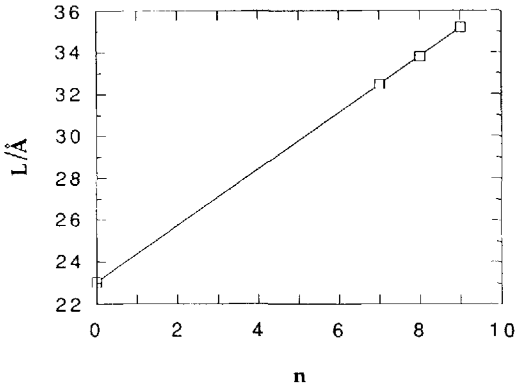


Figure 5. Carbon number dependence of the layer thickness $L(n)$ of smectic C phase in HACP.

of the aliphatic chain and L the layer spacing) is shown in figure 5. The increment per added carbon on each side chain is about 1·3 Å, and the extrapolated length $L(0)$ to $n=0$ is about 23·5 Å. $L(0)$ measures the thickness of the core layer, which is assumed to be independent of the side group length. The core layer contains the cyclotriphosphazene rings and the biphenyl moieties, including the oxygen atoms of the alkyloxy terminal group; moreover, the length increment resulting from the volume difference between the terminal methyls and the methylene groups has to be included. Taking into account these facts, $L(0)$ compares with the length of hexakis(4-biphenoxy)cyclotriphosphazene, (HBP)$\sim$20·6 Å deduced from the crystal structure data [13] (average mean H_{up}–H_{down} distance where H_{up} and H_{down} are the 4′- or *para*-hydrogen atoms of upward and downward pointing biphenyl groups grafted onto the same phosphorus atom). We neglect tilt effects, i.e. on the one hand, the global tilt of the director in the smectic C and, on the other hand, the tilt of the side groups with respect to the cyclotriphosphazene plane for HBP. Therefore, the comparison of the two lengths suggests that the biphenyl skeleton including the cyclotriphosphazene ring is not much changed between the crystalline and liquid crystalline phases. The slope of the layer spacing versus n gives an idea of the side group packing. A methylene unit is confined in a cylindrical segment of length 1·3 Å/(2 cos 20°C) = 0·70 Å. For an estimated density of 1 g cm^{-3}, the corresponding average cross section is 40 Å^2. This chain area is higher than for smectic A and C phases of rod-like mesogens (*c*. 25 Å^2 for TBBA at 180°C [17]).

Complementary information on the molecular organization could be derived from the single domain pattern. The intra-layer liquid organization produced a double ring interference similar to the double equatorial ring seen for many smectic phases of metallomesogen twins [5]. The ratio between the two average distances, 8·1/4·6, is close to $3^{1/2}$. Therefore, assuming that the ring at $2\pi/4{\cdot}6\,\text{Å}^{-1}$ is related to a local hexagonal array of side groups, the inner ring originates in a local trigonal superlattice, where the side groups are associated three by three (figure 6). Consequently, the double equatorial ring is related to distortions induced by the cyclotriphosphazene ring in the side group organization.

Another unusual feature of the diffraction patterns is the set of diffuse lines. These lines are the intersection of a periodic set of parallel reciprocal planes with the Ewald sphere; thus the scattered intensity derives from an array of uncorrelated periodic rows. Indeed similar diffuse lines have been observed in the diffraction pattern of some nematic and smectic phases, especially in comb-like polymers [18] or in phasmids [19]. However, the

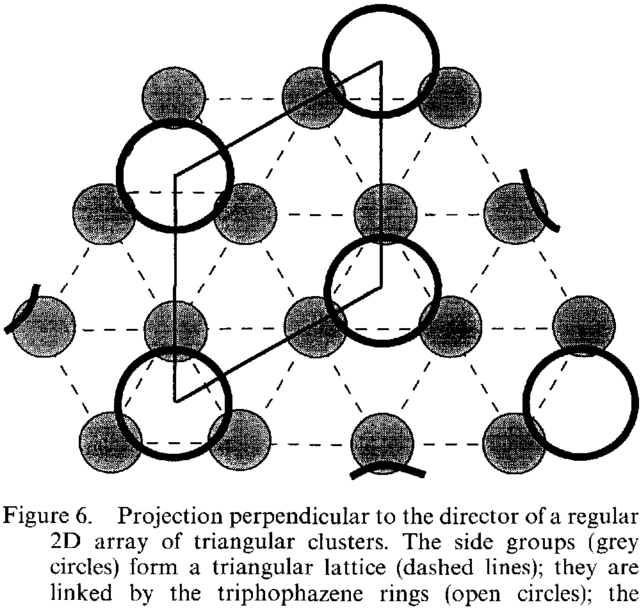
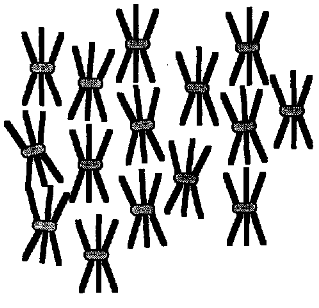


Figure 6. Projection perpendicular to the director of a regular 2D array of triangular clusters. The side groups (grey circles) form a triangular lattice (dashed lines); they are linked by the triphophazene rings (open circles); the superlattice is shown in full line. This molecular organization is locally preserved in the mesophases.

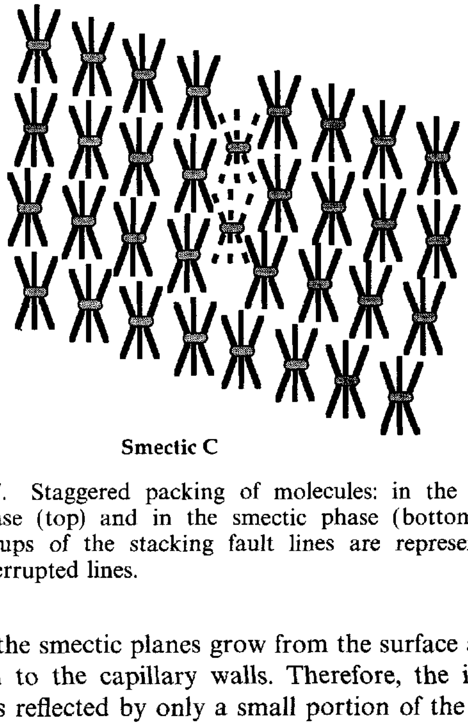
extinction of the intensity in the even order reciprocal planes is specific to the series studied here. The normal to the planes gives the direction of the rows (parallel to the director); the period corresponds to the distance between two adjacent layers along this direction, i.e. the apparent length of the molecules. The lateral extension of the planes measures the diameter of the rows and coresponds to the lateral dimension of a molecule; the thickness of the planes is almost independent of the rank of the plane and measures the length of the row, *c.* 70 Å, i.e. 2 molecular lengths.

In the smectic phase, the scattered intensity in a set of parallel equidistant planes is a consequence of a columnar local order: short columns (one molecule in diameter and two in length) are displaced with respect to the mean position defined by the layered structure. Based on the odd/even modulation of the scattered intensity, we derived the displacement amplitude for the rows: half of the layer. Therefore, in the smectic phase some molecules are out of their mean position with a translation of a half-layer thickness; these out of phase molecules form local stacking fault lines (figure 7). The existence of these defect lines can be understood if we consider that the molecule departs from a cylindrical shape and has rather the shape of a diabolo; moreover, the misfit between the chain area (40 Å^2) and the mean side group area deduced from the position of the equatorial rings ($\cong$25 Å^2) could be explained by a conical distribution of the paraffinic chains.

In the nematic phase, the diffraction pattern is similar to that of fibre-like nematics [20]. However the four spots characteristic of smectic C fluctuations (skewed cybotactic groups [16]) are absent, and the intensity vanishes on the second reciprocal plane, but is visible at the third order. Consequently, the molecules form end-to-end files in the nematic phase, and a preferential translation of half a molecular length occurs between neighbouring molecules. In other words, the local order in the nematic phase is a kind of staggered array, which is preserved in the vicinity of a stacking fault line in the smectic C. Moreover, this staggered array of molecules probably hinders the formation of smectic layer undulations as is asserted by the unusual round shape of the Bragg spots.



Nematic



Smectic C

Figure 7. Staggered packing of molecules: in the nematic phase (top) and in the smectic phase (bottom); sides groups of the stacking fault lines are represented by interrupted lines.

Finally, let us discuss the textures: the magnetic field is able to align the nematic phase, but seems to have a weak effect upon the smectic texture. In fact, optical microscopy observations show that, on cooling, the smectic phase appears in two steps: first, the layer planes are parallel to the glass plates and many disclination lines of the azimuthal director are visible; then, in a second step, focal domains grow slowly. This behaviour is reflected in the X-ray diffraction patterns. If one goes directly from the isotropic phase into the smectic C phase, the smectic planes grow from the surface and are parallel to the capillary walls. Therefore, the incident beam is reflected by only a small portion of the sample which corresponds to layer planes correctly oriented considering the Bragg law. The resulting Bragg spots are aligned perpendicularly to the capillary axis, i.e. parallel to the magnetic field. On the contrary, all the irradiated volume contributes to the wide angle diffraction, and taking into account the planar distribution of the layer normals and the conical distribution of the director around each normal, one can easily explain the full circle aspect of the wide angle ring (i.e. for $n=9$ just below the clearing temperature). In a further stage, small smectic C seeds with random orientation grow far away from the walls. The size of a domain is governed by the cooling rate: slow cooling rates correspond to small numbers of seeds and big domains. However, even when we have a pattern which appears to be that of a single domain (figure 3 (*a*)), we cannot assert that a significant part of the irradiated volume actually contributes to the central part of our pattern. For these reasons, we cannot make a quantitative estimation of the number of stacking faults; moreover, a measure of the orientational order parameter is also impossible.

4. Conclusions

The organization of hexa-aryloxyphosphazene molecules in the mesophase is closely related to their peculiar chemical architecture. Accordingly to the structural data, the molecule can be considered as a triangular cluster of rod-like dimers of aryl groups. The apparent length of the molecule is consistent with this scheme, while a double equatorial ring with intensity maxima at $q = 0{\cdot}76\ \mathrm{\AA}^{-1}$ and $q = 1{\cdot}37\ \mathrm{\AA}^{-1}$ is the signature of the triangular cluster structure. In the nematic phase, the molecules have a strong tendency to form a staggered array parallel to the director, and this staggered array subsists in linear stacking faults in the smectic phase. Such an array, destroying the natural segregation between aromatic and paraffinic moieties, must be favoured by geometric parameters which means that the molecule departs slightly from the cylindrical shape. Finally, the textures in the X-ray set-up can be compared to those obtained between glass plates and observed by optical microscopy. However, the origin of the great density of disclination lines observed in a homeotropic geometry is not understood.

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