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Hexagonal columnar mesophases from phthalocyanine

Upright and tilted intracolumnar molecular stacking, herringbone and rotationally disordered columnar packing

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Three series of metal-free phthalocyanines with alkyl, alkoxy, and alkoxymethyl side groups have been studied with X-ray diffraction. The structure of the columnar mesophases was described as a two dimensional (pseudo) hexagonal packing of indefinitely long stacks of phthalocyanine molecules. From the slope of the squared intercolumnar distance as a function of the number of methylene groups in the peripheral chains, and using the known value of the volume of one methylene group in the liquid state, the stacking period of the molecules along the columnar axis was calculated. It was found to be equal to 3·5 Å for the alkoxy and 4·9 Å for the alkyl and alkoxymethyl derivatives. This is interpreted to mean that in the alkoxy series the molecules are oriented upright with respect to the columnar axis, while in the alkyl and alkoxymethyl series the molecules are tilted by an angle of 46°. Taken as circular for the alkoxy, the aromatic cores of the columns may be assumed elliptical in shape for the alkyl and alkoxymethyl series. The lateral packing of the elliptical columns was found to depend upon the length of the side chains. It is achieved with herringbone rectangular symmetry when the chains are short as in the octyloxymethyl derivative, and with complete rotational disorder when the chains are long as in the octadecyloxymethyl derivative. When the side chains are moderately long, as in the dodecyloxymethyl derivative, the packing depends upon the temperature; it is herringbone rectangular at low temperatures and rotationally disordered at high temperatures.

1. Introduction

Phthalocyanine molecules with eight rather long peripheral alkyl chains are well known to produce liquid crystals with columnar symmetry [1–11]. Upon heating, the alkyl chains are disordered at the transition from the crystal to the liquid-crystalline state, and the system adopts a structure corresponding to the stacking of the aromatic cores in columns laterally assembled according to a two dimensional hexagonal lattice. The characteristic features of the phthalocyanine derivatives, as compared to other discotic molecules also found to produce columnar liquid crystals, are manifold. Their flat aromatic core is exceptionally large, offering a possibility for extended π-electron delocalization [12], and also for strong van der Waals interactions thus enhancing the thermal stability of the columnar mesophases. In addition, their chemical architecture offers a possibility to include a variety of metal atoms in the central cavity of the molecules, opening a new way of producing one dimensional metallic systems with potentially interesting conducting properties.

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From a geometrical point of view, the columnar structure is often characterized by two parameters: the intercolumnar distance, D, and the stacking period of the molecules along the columnar axis, h. As a rule, the hexagonal lateral ordering of the columns is developed over large distances and hence is easy to determine experimentally by small angle X-ray diffraction. On the other hand, the internal structure of the columns is more difficult to handle and needs much care to describe with precision. This is particularly true for the columnar mesophases of the metal-free phthalocyanine derivatives. As revealed by the width and the Bragg position of the corresponding wide angle scattering signal (when present in the X-ray patterns), the degree of intracolumnar ordering and the stacking period of the molecules turns out to depend upon the mesogen considered. Thus, according as to whether the molecules carry eight alkoxy [9, 11] or eight dodecyloxymethyl peripheral chains [2], the intracolumnar stacking is described as either regular with a period of only 3·4 Å or else liquid-like in character with a period of as much as 4·6 Å. It is useful to note, incidentally, that in the particular case of dodecyl peripheral chains, the intracolumnar stacking has not as yet been specified in the literature, because of insufficient experimental X-ray diffraction evidence [9]. Following the current nomenclature [13, 14]. the alkoxy phases with the aromatic cores regularly stacked over one another fall into the category of the ordered columnar liquid crystals (D_{ho}); while the dodecyloxymethyl phases with the aromatic cores randomly superposed fall into that of the disordered ones (D_{hd}).

The present paper studies in some detail the intracolumnar stacking of the three series of metal-free phthalocyanines, the chemical structure of which is shown in figure 1. More specifically, it attempts to establish whether their stacking period really depends upon the nature of the flexible peripheral chains as reported in the literature, then to try to connect their measured stacking density with the specific requirements of molecular packing.

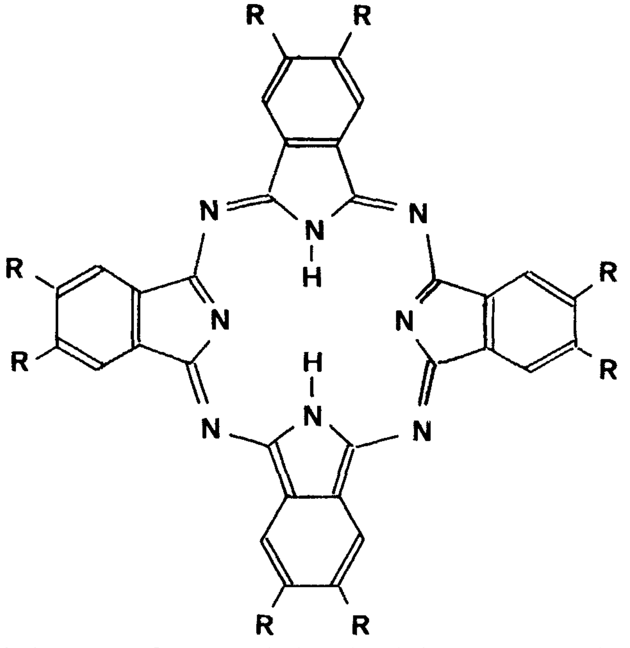

Figure 1. Chemical structure of the octasubstituted phthalocyanine molecules studied: alkoxy: $R = \text{–O–(CH}_2)_n\text{–CH}_3$; alkoxymethyl: $R = \text{–CH}_2\text{–O–(CH}_2)_{n-1}\text{–CH}_3$; alkyl: $R = \text{–CH}_2\text{–(CH}_2)_n\text{–CH}_3$.

2. Intracolumnar stacking period

In principle, one of the best adapted methods for determining the stacking period, h, of discotic molecules in a columnar structure, and also for obtaining useful information about the degree of intracolumnar order, consists in analysing directly the wide angle X-ray scattering of preferably oriented samples [14]. However, preparing properly oriented specimens for such a purpose is not always an easy task. In addition, patterns registered do not in all cases contain legible information about the internal structure of the columnar cores, unambiguously distinguished from that concerning the disordered flexible chains. In practice, h can easily, though indirectly, be deduced from the small angle reflections related to the hexagonal lateral packing of the columns. When both the specific volume, v, of the material and the hexagonal unit cell area, $\surd 3D^2/2$, are known, h can indeed be calculated from

$$\surd 3D^2h/2 = vM/N_A,$$

in which M is the molecular weight of the repeat unit [2, 15, 16].

There is an alternative method, also using the lateral packing parameters of the columns, which sometimes can also be successfully applied to determine h. Very conveniently, this method does not entail preliminary measurement of the specific volume of the material; it only requires a systematic X-ray study of homologous series of mesogens, and more specifically an X-ray study of the columnar lateral packing as a function of the length of the peripheral chains. With the reasonable assumption of additivity of the partial molar volumes, the volume of one repeat unit in the columns may indeed by taken as increasing linearly, and interestingly enough in a predictable way, with the number of methylene groups (easily deduced from the known specific volumes of linear paraffins at various temperatures [17], the molecular volume of the methylene groups is readily available [18, 19]). If constant, the stacking period, h, can then be obtained from the linear variation of the squared intercolumnar distance as a function of the number, n, of methylene groups in one alkyl chain [19, 20]. With octasubstituted phthalocyanine derivatives, this linear dependence is described by

$$\begin{aligned}\surd 3D^2h/2 &= vM/N_A\\ &= V_0 + 8nV_m,\end{aligned}$$

where V_m is the volume of one methylene group and V_0 the volume of one substituted phthalocyanine molecule deprived of its methylene groups.

It is this latter method which is used here to study the alkoxy, alkoxymethyl, and alkyl octasubstituted derivatives of metal-free phthalocyanines. Figure 2 shows the variation of the squared intercolumnar distance with the length of the peripheral flexible chains. Clearly, the n dependence of D^2 fits two distinct straight lines: one for the alkoxy, the other for the alkyl and alkoxymethyl derivatives. From a linear least-square fit of the experimental data, we find

$$D^2/\text{Å}^2 = 359{\cdot}2 + 79{\cdot}1n \quad \text{at } 200°\text{C}$$

for the alkoxy derivatives, and $D^2/\text{Å}^2 = 313{\cdot}9 + 53{\cdot}7n$ at 120°C for the alkyl and alkoxymethyl derivatives. The standard deviations are of 12·3 and 38·9 Å^2 for the y intercept, and of 1·5 and 3·1 Å^2 for the slopes of the lines, respectively.

From the slopes of D^2 versus n, $16\,V_m/(\surd 3h) = 79{\cdot}1 \pm 1{\cdot}5$ Å^2 or $53{\cdot}7 \pm 3{\cdot}1$ Å^2, and the value of the volume of one methylene group in a disordered side chain, $V_m = 30{\cdot}1 \pm 0{\cdot}5$ Å^3 at 200°C and $28{\cdot}4 \pm 0{\cdot}5$ Å^3 at 120°C [18], we immediately find: $h = 3{\cdot}5 \pm 0{\cdot}2$ Å

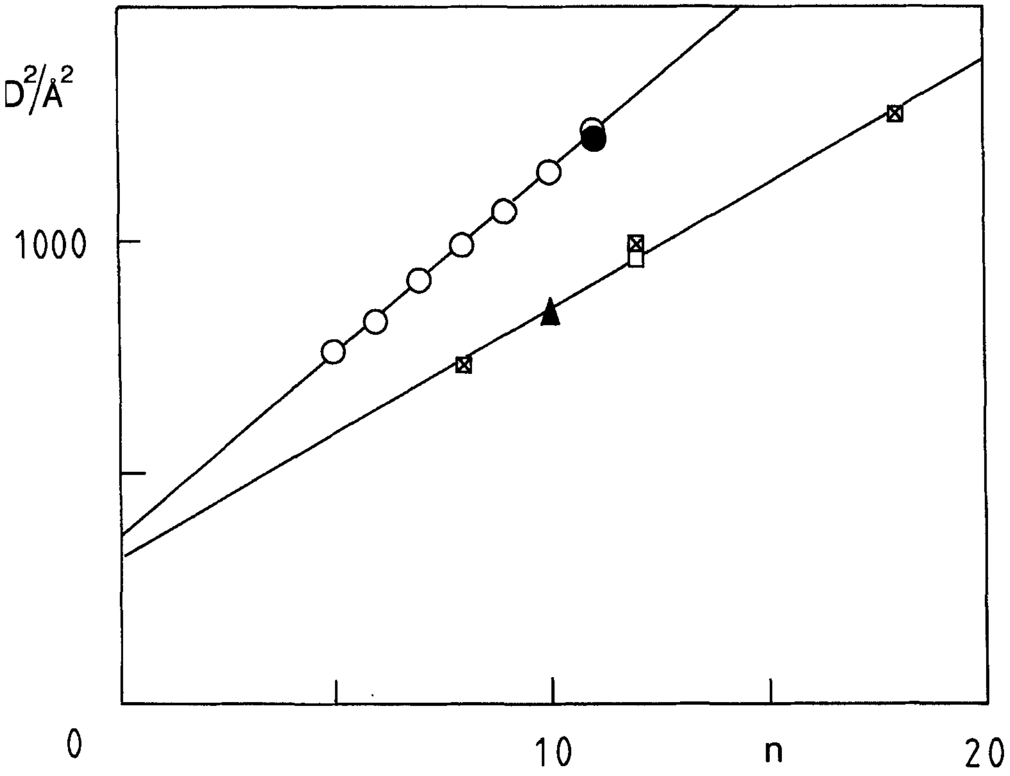

Figure 2. Squared intercolumnar distance as a function of the number of methylene groups of the peripheral chains (for convenience, the methylene groups directly attached to the phthalocyanine moiety in the octaalkyl derivatives are assumed equivalent to ether groups, see figure 1): circles, squares, and triangles represent alkoxy, alkoxymethyl, and alkyl derivatives, respectively; empty and filled signs refer to data borrowed from [11] (measured at 200°C) and [9]; crossed signs refer to data collected in the present work (measured at 120°C).

for the alkoxy series and 4·9 ± 0·4 Å for either the alkyl or the alkoxymethyl series. Within the experimental error, these values compare very well with those previously reported in the literature for the alkoxy series (3·4 Å: determined from the position of a rather sharp wide angle Bragg reflection [11]) and the dodecyloxymethyl derivative (4·6 ± 0·2 Å: deduced from the intercolumnar distance and an estimated value of the specific volume of the material, obtained by extrapolation at high temperature of that measured by flotation with a crystalline sample at 25°C [1, 2]). (It is worthwhile noting that, in [11], the reverse procedure was used to analyse the n dependence of D^2. By assuming that h (deduced from the position of a rather sharp wide angle reflection in the X-ray patterns) is 3·4 Å, a value of 26·4 Å^3 was calculated for the volume of the methylene groups. Clearly, this value is slightly too small. The reason for the discrepancy lies in the molecular model used for the calculations. The intercolumnar distance, D, was indeed taken to give the diameter of the columns supposed to be circular in shape and in close contact with one another. The empty spaces, implicitly supposed to be left among the columns, are of course unrealistic, the peripheral chains being in a disordered state. After correction to the present model by applying the factor $2\sqrt{3}/\pi$, the V_m value of 26·3 Å^3 in [11] increases to 29·1 Å^3 in good agreement with the literature value.)

3. Molecular stacking in the alkoxy derivatives

Given the values of the intracolumnar stacking period, it is of interest to discuss now the molecular packing of the aromatic moieties within the columnar cores. For the alkoxy derivatives, the molecular packing is evident. The observed 3·5 Å stacking period corresponds precisely both to the thickness of the aromatic cores and to the well-known piling distance of aromatic layers in general [21]. The flat phthalocyanine parts of the molecules must, therefore, not only be superposed in close contact with one another, but must also be oriented perpendicular to the column axis (see figure 3).

The perpendicular orientation of the molecules with respect to the column axis is fully confirmed by the value, $2V_0/(\sqrt{3}h) = 359{\cdot}2 \pm 12{\cdot}3\,\text{Å}^2$, of the y intercept of the straight line representing D^2 versus n. The y intercept directly corresponds to the area of the hexagonal unit cell of a fictitious columnar mesophase obtained with the $n=0$ phthalocyanine derivative, i.e. octa(methoxy)phthalocyanine: $(\sqrt{3}/2)D^2_{n=0} = V_0/h = 311 \pm 11\,\text{Å}^2$. This area is closely related to the cross section of the aromatic core of the columns. With the molecules oriented normal to the column axis, it represents the surface of one phthalocyanine molecule, enlarged to include the cross-sectional area of eight peripheral methoxy groups in a liquid-like state. As shown in figure 4, the deduced radius of the aromatic core (assumed circular), $\sqrt{(4V_0/\pi h)} = 9{\cdot}9 \pm 0{\cdot}2\,\text{Å}$, is conclusively consistent with the molecular dimensions. (From the calculated values of $V_0/h = 311\,\text{Å}^2$ and $h = 3{\cdot}5\,\text{Å}$, we can also calculate the volume of one octa(methoxy)phthalocyanine molecule in the columnar state at 200°C. The value found, $V_0 = 1088 \pm 100\,\text{Å}^3$ corresponds to a local density of $\delta_{200°\text{C}} = 1{\cdot}16\,\text{g/cm}^3$, and is perfectly consistent with that ($\simeq 1000\,\text{Å}^3$) calculated from the crystallographic volume ($587\,\text{Å}^3$) of non-substituted phthalocyanine at room temperature [22] by applying to the crystal the commonly accepted relative thermal expansion coefficient of $3 \times 10^{-4}\,\text{K}^{-1}$ and by adding for each peripheral disorded methyl group at 200°C a rough $50\,\text{Å}^3$ (see the Appendix in [19]).)

The intracolumnar structure just described immediately explains the presence in the X-ray patterns of a narrow wide angle reflection at 3·4 Å. The angular position of the reflection is in agreement with the stacking period mentioned previously within the columns, and its narrowness with the fact that, being superposed in close contact with one another, the molecules should, in addition, be arranged in a fairly regular fashion. However, it must be pointed out that, although narrow, the 3·4 Å reflection is by no means extremely sharp [11], indicating that the intracolumnar ordering does not extend over very large distances. This limitation of the spatial extension of the order is all the more satisfying as the very existence of truly ordered columnar phases (D_{ho} [13, 14]) poses, of course, a serious theoretical problem related to the possible existence at high temperature of long range order in one dimensional physical systems [23].

At this point of the discussion, it is useful to comment briefly on the packing density of the alkoxy chains. Knowing the radial distance ($R = 8{\cdot}0\,\text{Å}$, as obtained by molecular modelling: Sybyl software from Tripos) of the peripheral oxygen atoms from the centre of the aromatic disc, it is possible to calculate the average molecular area available per alkoxy chain on the (cylindrical) surface of the aromatic core. The value found, $S = 2\pi Rh/8 = 22{\cdot}0\,\text{Å}^2$, is consistent with that commonly measured for thermotropic liquid crystals [18]. The average molecular crowding near the aromatic core is therefore, perfectly compatible with a highly disordered conformation of the peripheral chains, as revealed by the presence in the X-ray patterns of a diffuse ring at 4·7 Å [11].

It is also useful to discuss briefly the in-plane rotational ordering of the planar phthalocyanine molecules within the cores about the columnar axis. Simple geometical

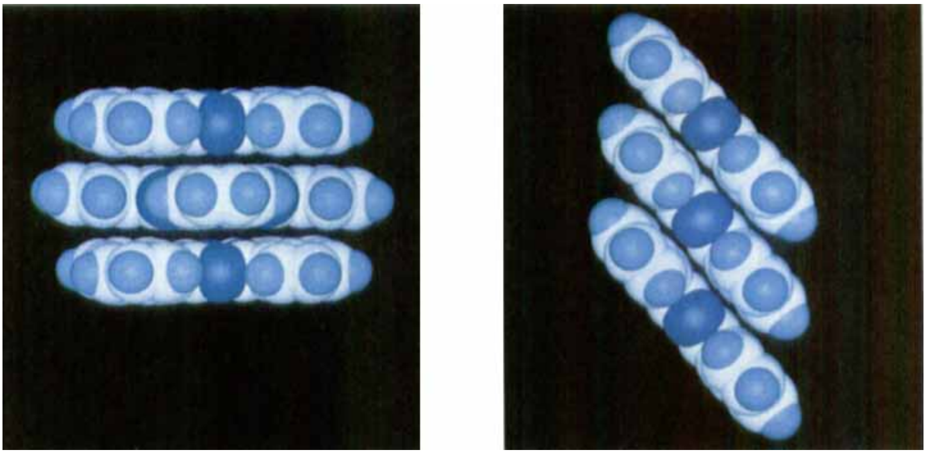

Figure 3. Columnar stacking of phthalocyanine molecules (*a*) oriented perpendicular to the columnar axis with a stacking period of 3·5 Å and (*b*) inclined by 46° with a stacking period of 4·9 Å (Sybyl software from Tripos).

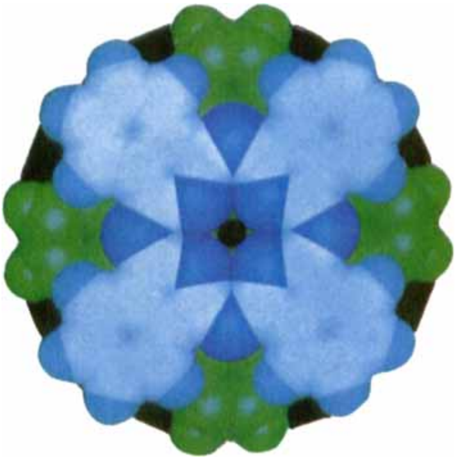

Figure 4. Schematic representation of two octa(methoxy)phthalocyanine molecules axially superposed in a staggered conformation (as obtained by molecular modelling: Sybyl software from Tripos). Black circle 9·9 Å in radius, represents spatial extension of one octa(methoxy)phthalocyanine molecule (cross-sectional area of 311 $Å^2$, shape assumed circular).

considerations of steric hindrance show that the aromatic cores can hardly superpose on top of one another in an eclipsed stereochemical conformation, for at least two reasons. The first is related to the packing of the alkoxy side chains. As is well known for the structure of various crystalline forms of paraffins [21], the smallest possible lateral packing distance of linear alkyl chains is about 5 Å, that is much greater than the stacking distance available between two successive aromatic cores in the columns. As a result, despite the sufficient extent of their molecular area at their attachment to the aromatic core, the alkoxy side chains cannot properly locate themselves along the same generatrix, but must have their anchoring sites mutually displaced round the columnar axis. The second reason is connected with the superposition of the aromatic cores themselves. As is also well known for the structure of various non-linear condensed aromatic compounds in the crystalline state (see page 12 in [21]), adjacent parallel aromatic layers generally pile up with an in-plane displacement; atom-on-atom stacking in the crystal is thus seldom seen, the largest possible number of atoms being accommodated between the atoms of the adjacent molecules. The packing density of the layers is thus appreciably increased. A staggered conformation of the phthalocyanine molecules, with a 45° rotation about the columnar axis, seems the most convenient to relax the steric repulsions of the disordered side chains. The oxygen atoms, that is the anchoring sites of the alkoxy chains, are then as uniformly distributed round the aromatic core as possible (see figure 4), and the smallest distance between oxygen atoms of adjacent molecules (≈ 7 Å, calculated using molecular modelling: Sybyl software from Tripos) is of the right order of magnitude. It is clear, however, that, though less probable, staggered conformations with angles not far from 45° might also occur.

The presence in the X-ray patterns of an additional broad and weak reflection at 7·0 Å [11], corresponding to twice the stacking period of the molecules, suggests a weak tendency of the aromatic rings to form dimers. In some respects, this would compare to what has been reported to occur with single layered smectic liquid crystals of highly polar mesogens, containing small fluctuating double-layered smectic (cybotactic) domains [24]. Dimerized structures with unsubstituted metal-free phthalocyanine have already been identified spectroscopically in the so-called *x*-crystalline polymorphic form [25]. But in these, the two coaxially superposed molecules are rotated with respect to one another by an angle of only 20° (see figure 8 (*a*) in [25]). If the dimers in the columnar phase considered were identical to those described for the *x* form, then the steric repulsions of the side chains would be only imperfectly relaxed and the probability of dimerization rather small, explaining why the observed 7·0 Å reflection is very weak and broad.

4. Molecular stacking in the alkyl and alkoxymethyl derivatives

For the alkoxymethyl and alkyl derivatives, in which the stacking period is about 4·9 Å, the description of the molecular packing is not so straightforward as for the alkoxy derivatives. The first natural idea to occur is that the aromatic cores are oriented perpendicular to the column axis, as in the previous section. With such an orientation of the molecules, the packing of the aromatic cores should be liquid-like in character, and the columnar phase should as a result fall into the category of disordered columnar phases (D_{hd}). Indeed, the stacking period measured is much larger than the thickness of the aromatic layers, and hence the molecules have every available space for strong thermal motion. However, such a structural model cannot readily be accepted for at least three reasons. In the first place, the excess of stacking period ($h = 4{\cdot}9$ Å) over that ($\approx 3{\cdot}4$ Å) of a close-packed pile of aromatic molecules is excessively large, corresponding to an intolerable reduction (≈ 36 per cent) of the local density of the aromatic cores. This density reduction is all the less plausible as the rigid and large polarizable aromatic cores are submitted to strong van der Waals attractions. (The strength of these van der Waals interactions is indicated by the fact that phthalocyanine does not melt upon heating, prior to thermal decomposition at 550°C [26].) Next, the cross-sectional area of the aromatic core of the columns—$(\sqrt{3}/2)D^2_{n=0} = V_0/h = 272 \pm 34\ \text{Å}^2$ deduced as previously from the y intercept of D^2 versus n—is significantly smaller than expected ($\approx 311\ \text{Å}^2$). Finally, and quite importantly, a columnar model of the disordered type does not account for the weak and rather narrow X-ray reflection observed experimentally at 3·56 Å for the octyloxymethyl derivative, suggesting that the aromatic cores are on the contrary stacked in close contact with each other.

One other, thoroughly adequate and satisfactory, way of describing the intracolumnar structure is to let the molecules be tilted with respect to the column axis. On the evidence of the close-packed structure suggested by the 3·56 Å reflection the molecular tilt may be calculated by comparing the measured stacking period of the columnar phase ($h = 4{\cdot}9$ Å) with the well-known stacking period of flat aromatic molecules in the crystal. (The aromatic cores being tilted with respect to the columnar axis, the 3·56 Å reflection corresponding to their intracolumnar stacking is out of the reciprocal columnar axis. The diameter of the aromatic core of the columns is rather small, and the spatial extension of the reflection in a direction parallel to the equator is rather large. For simple geometric reasons related to Ewald's construction of the diffraction diagrams, the maximum of the peak registered in powder X-ray patterns leads to a slightly overestimated value of the stacking period.) This calculation gives $\theta \approx \cos^{-1}(3{\cdot}4/4{\cdot}9) = 46°$ (see figure 3(*b*)); quite significantly, this tilt corresponds remarkably well to that ($45° < \theta < 48°$: see [27] or table III.I in [28]) found for the β form of unsubstituted phthalocyanine in the crystalline state. In this form the superposed aromatic molecules are shifted in the molecular plane with respect to each other in a direction parallel to that of two diagonally opposed non-central nitrogen atoms. We also note that the stacking period measured crystallographically for the β form (4·85 Å) is identical to the 4·9 Å stacking period found here. It is important to point out immediately that, with the molecules hydrogen-bonded along the stacking axis [25], the β form is the more stable of the two tilted crystalline structures of phthalocyanine, namely α and β, reported in [28]. In such a structural model for the columnar phase, with the molecules tilted with respect to the columnar axis by an angle $\theta \approx 45°$, the aromatic core of the columns is no longer circular, but elliptical in shape; as a result, its cross-sectional area is reduced with respect to the surface of an octa(methoxy)phthalocyanine molecule ($\approx 311\ \text{Å}^2$), in fair agreement with that deduced from the y intercept of D^2 versus n.

It is useful to close this section with a brief consideration of the molecular area of the peripheral chains near the aromatic cores. The molecules being tilted and the aromatic cores elliptical in shape, the surface available per chain on the surface of the aromatic cores may easily be calculated from

$$S = 2\pi R\sqrt{[(1 + \cos^2\theta)/2]}\,h/8,$$

where R is the major semi- axis of the ellipse. With R equal to the radius of the aromatic core (8·0 Å), the molecular area is about $26{\cdot}5\ \text{Å}^2$. Much larger than in the case of the alkoxy derivatives, the lateral space is amply sufficient for the aliphatic chains to take up a spatially disordered liquid-like conformation. This is all the more so as the linear distance of the anchoring sites of the side chains along the columnar axis (4·9 Å), comparable to the usual lateral packing distances of linear paraffin chains, is also perfectly adequate to avoid steric repulsions in spite of the non-staggered conformation of the adjacent aromatic cores.

5. Columnar packing in the alkoxymethyl derivatives

In a previous paper [2] devoted entirely to the columnar behaviour of the metal-free octa(dodecyloxymethyl)phthalocyanine, a reversible phase transition was reported to occur at about 180°C between two columnar mesophases with exactly the same two dimensional hexagonal lattice. The two mesophases were presented as differing from one another in that the low temperature phase displayed an additional small angle sharp Bragg reflection at 20·5 Å. Considered as unrelated to the hexagonal lattice, this extra peak was tentatively attributed to a periodic variation of the electron density distribution along the columnar axis, rising from a possible periodic distortion of the columns [2]. Such a modulation seemed quite reasonable, as it could formally be compared to what was known to happen with many alkali metal soaps in the mesomorphic state [29]. Owing to the preference of the ionic end groups of the soap molecules to pile up densely in opposition to the paraffin tails tending for their own part to take up disordered conformations at high temperatures, the ionic double layers of the lamellar crystal break upon heating into ribbons periodically arranged in space and surrounded by the aliphatic chains spreading outwards in a fan-shaped configuration (see figure 6 in [30]). Transposed to the columnar case, this idea of fragmentation amounts to describing the modulation as the breaking of the columnar cores into one dimensional periodic sets of discrete regions of densely packed phthalocyanine moieties, standing at a distance to allow the peripheral chains to fan out in a liquid-like conformation. More than simply descriptive, this model proved perfectly predictable from a theoretical point of view. It corresponds, in fact, to one of the possible solutions to the structural problem posed by one dimensional stacks of flat molecules with lateral chains when the optimal spacing of the plates is smaller than the optimal spacing of the chains [31]. Plausible in itself, but nevertheless insufficiently supported by direct experimental evidence [2], this interpretation of the columnar modulation clearly needed further studies in order to be definitely accepted. Additional X-ray diffraction studies were thus carried out in the present work, dealing with the specific series of alkoxymethyl phthalocyanine derivatives in which the modulation have specifically been detected.

Three typical compounds were considered with alkoxymethyl chains of different lengths, namely the octyloxymethyl, dodecyloxymethyl, and octadecyloxymethyl derivatives. The first displayed the modulation over the whole range of thermal stability of the columnar mesophase, that is from 67 to 320°C [2], the second displayed the modulation over the range from 78 to about 180°C and behaved as normal columnar mesophase at higher temperatures; the last did not show the modulation at all, whatever the temperature above the transition temperature from the crystal into the liquid crystal, at 62°C. The modulated columnar phases in question were characterized by the presence in the X-ray patterns of extra low angle Bragg reflections as sharp as those related to the two dimensional packing lattice of the columns. To study these reflections, special powder diffraction diagrams with properly chosen exposure times were carefully registered. Patterns from macroscopically oriented samples would have provided invaluable information in this connection, allowing us to disentangle the intracolumnar and intercolumnar positional interactions; unfortunately, these turned out impossible to obtain in practice due to the high viscosity of the materials. It is useful to state at this point that the intensity of the $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ Bragg reflections related to the hexagonal packing of the columns was steadily decreasing as a function of the scattering angle, as expected from columnar structural elements with finite lateral size. For the dodecyloxymethyl derivative, the presence of the sharp reflection at 20·5 Å reported in [2] was thus fully confirmed; its intensity ranged between that of the $\sqrt{4}$ and $\sqrt{7}$ reflections. For the octyloxymethyl derivative, the X-ray patterns were richer, containing at 120°C two sharp reflections, one at 17·8 Å with an intensity slightly weaker than that of the $\sqrt{3}$ reflection of the hexagonal lattice and a second very weak one at 12·6 Å.

Close inspection of the extra peaks showed that those located at 20·5 and 17·8 Å are exactly in a ratio $\sqrt{4}:\sqrt{7}$ with respect to the first harmonic, d_1, of the hexagonal lattice (calculated value of $(\sqrt{4}/\sqrt{7})d_1$: 20·5 and 17·7 Å for the dodecyloxymethyl and octyloxymethyl derivative), while that located at 12·6 Å is in a ratio $\sqrt{4}:\sqrt{13}$ (calculated value of $(\sqrt{4}/\sqrt{13})d_1$: 13·0 Å for the octyloxymethyl derivative). Though

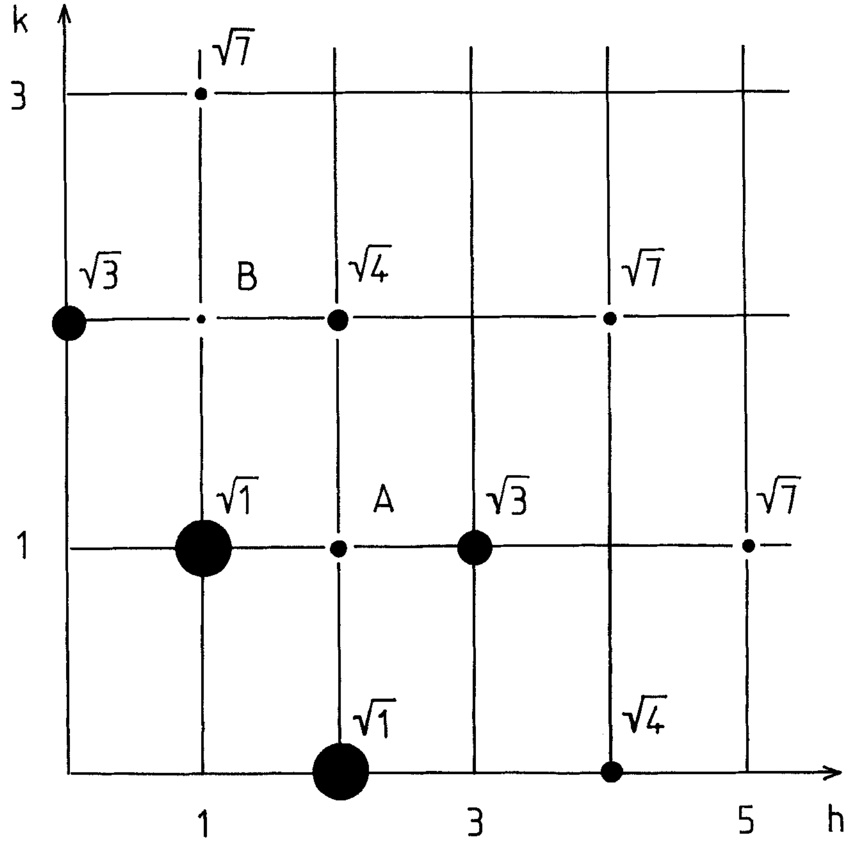

Figure 5. Reciprocal lattice of the columnar mesophase of octa(octyloxymethyl)phthalocyanine: the size of the filled circles simulates the intensity of the observed reflections; $\sqrt{7}/\sqrt{4}$ and $\sqrt{13}/\sqrt{4}$ extra reflections are designated by A and B; reflections 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$ are identical to those observed with the high temperature hexagonal columnar mesophase.

appropriate to describe the positional ordering of the columnar axes, the hexagonal lattice considered up to now accounts therefore only imperfectly for the packing symmetry of the system. In fact, the packing symmetry of the modulated columnar phase is properly analysed using a (pseudohexagonal) rectangular lattice with two columns per unit cell and lattice parameters as follows: $a=46{\cdot}9$, $b=27{\cdot}1$ Å for the octyloxymethyl and $a=54{\cdot}2$, $b=31{\cdot}3$ Å for the dodecyloxy derivative. The $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ reflections, along with the $\sqrt{7}/\sqrt{4}$ and $\sqrt{13}/\sqrt{4}$ extra reflections may thus immediately be indexed as shown in figure 5. Hints of further extra reflections agreeing with the rectangular lattice could also be detected, but were cautiously neglected because of their extreme weakness.

The systematic extinction of the odd $h00$ and $0k0$ reflections alone unequivocally shows that the two dimensional space group which describes the symmetry of the modulated columnar system is p2gg [32]. The two columns in the rectangular unit cell are placed with their axis at the origin and centre of the cell (see figure 6). The packing of the column axes is, therefore, hexagonal as claimed previously [2] and the rectangular symmetry revealed by the extra reflections is related to the orientation of the elliptical columns about their axes in a herringbone configuration. This type of arrangement is very common in the field of organic crystallography. It counts among the lowest free-energy possible arrangements of hard and rigid molecules, leading to closest packed two dimensional crystalline layers [21]. It is frequently observed also in the field of liquid crystals, namely with D_{rd} disordered discotic [33], smectic E [34], and smectic B [35] mesophases. It is worth noting, however, that in opposition to what is described

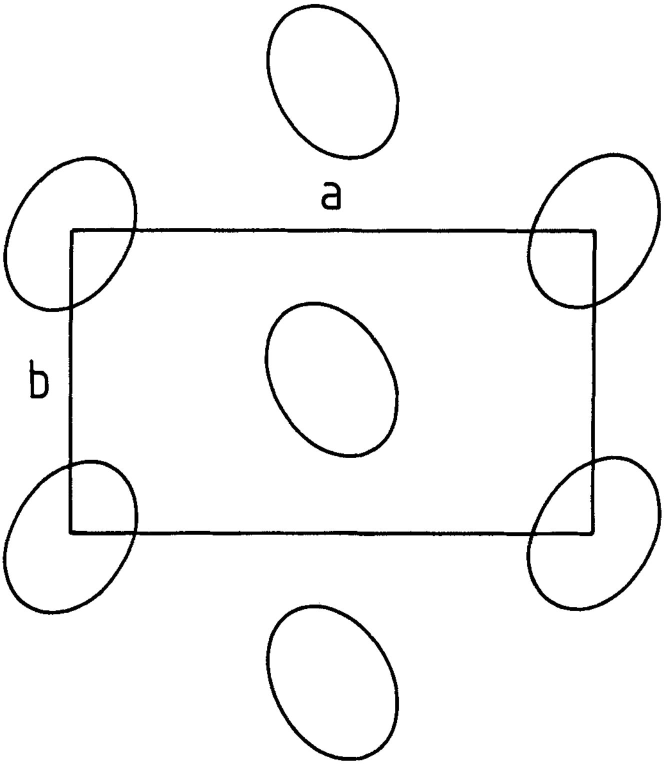

Figure 6. Schematic representation of a herringbone arrangement for the elliptical columns in the low-temperature columnar mesophase of octa(octyloxymethylphthalocyanine.

here for the alkoxymethyl-substituted phthalocyanines, the lateral packing of the molecules in the columnar D_{rd} and smectic E mesophases is not pseudohexagonal ($a=b\sqrt{3}$) but truly rectangular (distorted hexagonal: $a\neq b\sqrt{3}$), and that in the smectic B phases, where the lateral packing is globally hexagonal, the rectangular herringbone ordering develops only locally as smectic E fluctuations. In all of these mesophases, the herringbone arrangement arises from the elongated cross-sectional shape of the molecules and their anisotropic repulsive interactions. For the phthalocyanines, the geometrical anisotropy of the hard columnar cores (the ellipticity of which is rather small: $1/\cos\theta=1/\cos 45^\circ\approx 1{\cdot}4$) is less pronounced than that ($6{\cdot}25/3{\cdot}5\approx 1{\cdot}8$ [36]) of the hard aromatic molecular cores in the smectic phases; furthermore, their steric repulsions are considerably softer due to the screening effect of the liquid-like peripheral alkyl chains between the columns. We can then easily understand why, in the phthalocyanines, the columnar lateral packing is hexagonal and not truly rectangular, and also why the herringbone configuration, which exists for short alkoxymethyl chains, is either totally absent for the long octadecyloxymethyl or vanishes upon heating at high temperatures for the dodecyloxymethyl derivative.

6. Conclusion

In this paper, the hexagonal columnar behaviour of three series of metal-free phthalocyanines with three kinds of peripheral chains has been analysed from a structural point of view. The results obtained may be summarized as follows. As far as the internal structure of the columns is concerned, two stacking modes were established. With alkoxy peripheral chains, the aromatic cores were found [11], to be oriented perpendicular to the columnar axis; on the other hand, with alkyl and alkoxymethyl side chains, they were found to be tilted by an angle of 46°, as in the most stable, hydrogen-bonded β crystalline form of metal-free unsubstituted phthalocyanine. In both cases, the aromatic cores were found to be in close contact with one another, and hence presumably superposed in a fairly regular, though not infinitely extended, fashion. With this consideration, the columnar phases in the present work would all better fit in the category of the so-called ordered columnar phases. The distinction between upright and tilted stacks of molecules within the columns depending upon the chemical nature of the peripheral chains is experimentally well established. It is, furthermore, in perfect compliance with previous observations of aromatic compounds [37], showing that oxygen atoms directly attached to a planar aromatic system exert significant effect in steering from a tilted to an upright stack structure through weak hydrogen bonds.

Regarding finally the lateral arrangement of the columns, which is achieved following a two dimensional hexagonal lattice, three packing modes were established, related to the shape of the columnar cores and their azimuthal orientation about their axis. With alkoxy peripheral chains, the aromatic columnar cores are fairly circular in shape and their rotational orientation in the unit cell is quite immaterial. With alkoxymethyl and alkyl peripheral chains, the aromatic columnar cores are elliptical in shape and their orientation with respect to the hexagonal lattice becomes a matter of great importance. Thus, for short side chains, the cross-sectional anisotropy of the columns is relatively pronounced, their azimuthal orientational ordering is well developed, and their packing results in a herringbone configuration. For long side chains, the cross-sectional anisotropy of the columns is strongly reduced and their hexagonal packing is achieved with complete rotational disorder about the column axis. Finally, for moderately long side chains, the columnar packing develops in a herringbone configuration at low temperatures and in a rotationally disordered configuration at high temperatures. The thermal transition between the two configurations will be discussed in a forthcoming paper [38].

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