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Thermotropic liquid crystals from alkali metal dihexadecylphosphates

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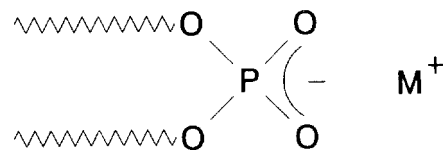
Lithium, sodium, potassium, rubidium, and caesium dihexadecylphosphates were synthesized. Their thermal stability was checked by thermogravimetry. Their ability to show thermotropic mesomorphic behaviour was investigated using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. All these compounds were found to exhibit a lamellar structure in the crystalline state at room temperature and a columnar structure of hexagonal symmetry in the mesomorphic state at high temperature. The potassium, rubidium, and caesium derivatives were found to exhibit an additional $Ia3d$ body-centred cubic structure in the temperature range between the crystal and the columnar phase. Structures and structural parameters are briefly discussed.

1. Introduction

Dialkylphosphoric esters and salts have been widely employed over the past years for the preparation of vesicles. Summarized in two review articles [1, 2], most of the papers published in this connection up to early 1995 deal essentially with questions related to the preparation, the characterization and the properties of such vesicles. In a recent paper, vesicles derived from alkali metal dihexadecylphosphates were studied in some detail, particularly from the point of view of their stability and size as a function of the cation used [3].

Now, many of the amphiphiles that are able to produce vesicles and lyotropic molecular assemblies, when in the presence of a solvent, are also known to form thermotropic liquid crystals when heated in the pure state [4–6]. We hence thought it of interest to try to find if such was also the case for the dialkylphosphoric salts of alkali metals.

In the present paper the thermotropic liquid crystalline behaviour of lithium, sodium, potassium, rubidium, and caesium dihexadecylphosphates is investigated using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction:



$M = \text{Li, Na, K, Rb, Cs}$

2. Synthesis

The synthesis of the alkali metal dihexadecylphosphates was carried out in two steps. First the corresponding dihexadecylphosphoric acid was synthesized following a method analogous to that given in [7], by adding slowly, with stirring, two equivalents of hexadecanol and one equivalent of pyridine dissolved in dry benzene to a solution of phosphorus oxychloride (POCl_3) in dry benzene at 0°C . After heating under reflux for 5 h and cooling to room temperature, the mixture was treated exhaustively with 1 M aqueous HCl to remove pyridine. After evaporation of the organic phase, the residue was recrystallized twice from ethyl acetate. In a second step, the acid was neutralized with stoichiometric amounts of the corresponding metal hydroxides in ethanol. The final products were recrystallized at least twice from ethanol.

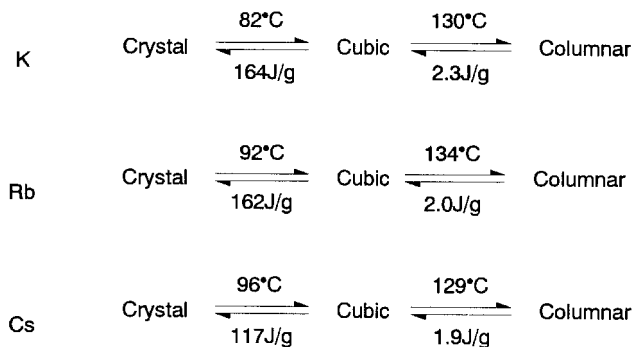
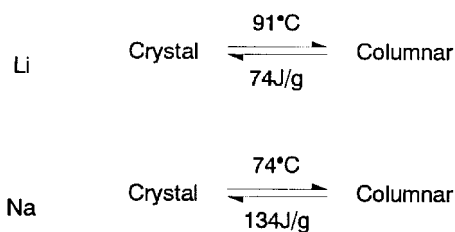
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The purity of the salts was checked by elemental analysis. $C_{32}H_{66}PO_4Li$: calc. C 69.53, H 12.03; found C 69.31, H 12.05. $C_{32}H_{66}PO_4Na$: calc. C 67.57, H 11.69; found C 67.44, H 11.78. $C_{32}H_{66}PO_4K$: calc. C 65.71, H 11.37; found C 65.51, H 11.58. $C_{12}H_{66}PO_4Rb.H_2O$: calc. C 59.19, H 10.56; found: C 59.13, H 10.19. $C_{12}H_{66}PO_4Cs.H_2O$: calc. C 55.16, H 9.84; found: C 55.33, H 9.94.

3. Thermal behaviour

Before anything else, the compounds were analysed by thermogravimetry (Mettler TC10A, TA processor, M3 balance, nitrogen flux). At a heating rate of $10^\circ C \text{ min}^{-1}$, the compounds were found to degrade readily at temperatures over about $220^\circ C$, the rate increasing slightly with the size of the metal cations (Figure 1). Experiments carried out isothermally as a function of time showed in fact that the samples start degrading slowly below $220^\circ C$ (Figure 2), withstanding however a few hours heating at $150^\circ C$ with weight losses smaller than a few per cent. For this reason our subsequent investigations were restricted to temperatures below $150^\circ C$. On the other hand, special thermogravimetry experiments showed the samples to lose weight at about $80^\circ C$, corresponding exactly to the departure of one molecule of water per molecule of salt; they also showed that the samples rapidly recovered their initial degree of hydration upon cooling back to room temperature in the open air. It thus became clear that samples should be cautiously dried off before use and handled with care.

The thermotropic liquid crystal polymorphism of the materials was then investigated by differential scanning calorimetry (Perkin-Elmer DSC-7, heating and cooling rates of $10^\circ C \text{ min}^{-1}$) and polarizing optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage). Upon heating from room temperature, the DSC traces showed the presence of one (for Li and Na derivatives) or two (for K, Rb, and Cs derivatives) sharp endothermic peaks indicative of first order phase transitions. As shown below, the first, rather strong peak corresponds to the melting of the crystal into a liquid crystalline phase, while the second, very weak peak corresponds to a transition between two liquid crystalline phases. Upon cooling from $150^\circ C$, both transitions take place reversibly, with a hysteresis of about $10\text{--}20^\circ C$. This behaviour is summarized in the following polymorphic schemes:



Visual observation of the compounds by polarizing microscopy fully confirmed the DSC measurements. For the lithium and sodium derivatives, the melting of the crystal upon heating led directly to the formation of a spontaneously birefringent, rather fluid phase, and for

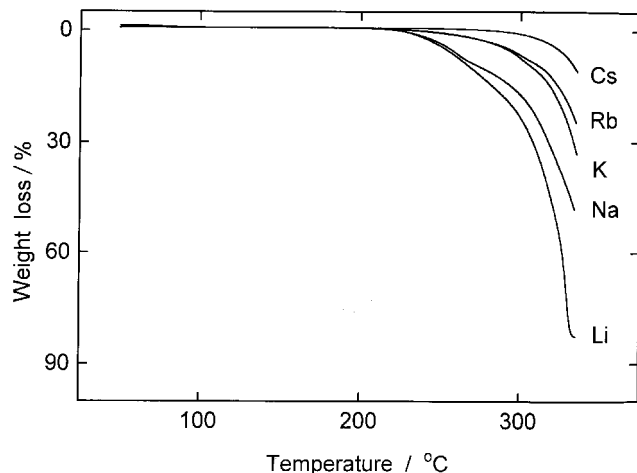


Figure 1. Degradation of alkali-metal dihexadecylphosphates as a function of increasing temperature.

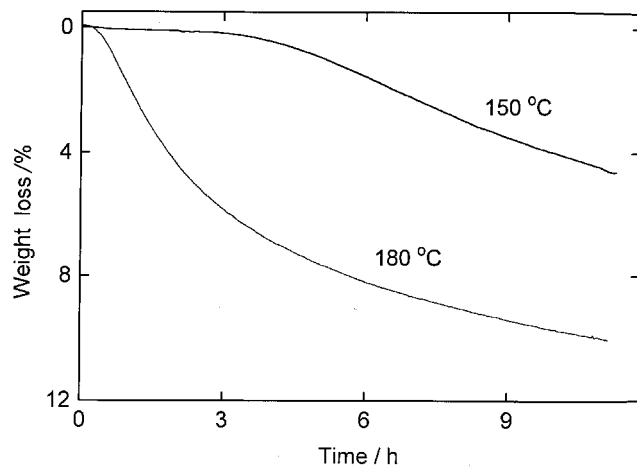


Figure 2. Isothermal degradation of sodium dihexadecylphosphate as a function of time.

the potassium, rubidium and caesium derivatives to the formation of an intermediate isotropic, rather viscous phase (shown below to be a cubic mesophase). The texture of the birefringent fluid phases was not easy to develop satisfactorily in all cases, due to the thermal degradation of the samples at high temperature and the consequent impossibility of developing the textures by slow cooling from the isotropic melt. However, in the case of the most stable caesium salt, it was possible, by prolonged annealing at 140°C, to get well developed textures (Figure 3) indicating a columnar structure beyond any reasonable doubt.

4. Structure

The structure of the observed phases was finally investigated using X-ray diffraction (powder samples in Lindemann capillaries, Guinier focusing camera equipped with a bent quartz monochromator, $\text{CuK}\alpha_1$ radiation from an INEL X-ray generator, INSTEC hot stage). Diffraction patterns were recorded photographically or using an INEL CPS-120 curved position-sensitive detector.

The X-ray patterns of the crystal phases contain quite a few equidistant sharp reflections in the small angle region, characteristic of a lamellar arrangement of the molecules, and several reflections in the wide angle region, indicative of a three-dimensional crystal ordering. The lamellar periods measured (see table 1) are very

close to twice the length of the molecules in a hair-pin, fully extended conformation (of about 25 Å as estimated by molecular modelling using Biosym), suggesting that the hexadecyl chains are in all probability standing upright and arranged in double layers.

The X-ray patterns of the fluid, birefringent phases observed at high temperature are typical of a columnar structure of hexagonal symmetry. They contain three to four sharp reflections in the small angle region with reciprocal spacings in the ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$, indicating a two-dimensional hexagonal lattice; a broad band in the wide angle region is related to the disordered conformation of the alkyl chains. The structure involved is therefore similar to that described long ago for the alkaline earth metal alkanooates [8]. The polar heads of the molecules, i.e. the metal phosphate groups, are superposed over one another in columns, surrounded by the alkyl chains in a disordered conformation, and laterally packed according to a two-dimensional hexagonal lattice. The columnar spacings measured are reported in table 1; they are smaller than the periods of the crystal as expected from the two-dimensional spreading of the disordered chains round the columnar cores.

The X-ray patterns of the viscous, isotropic phases of the potassium, rubidium, and caesium derivatives above the melting temperature of the crystal are typical of the well known $Ia3d$ body centred cubic phase described by

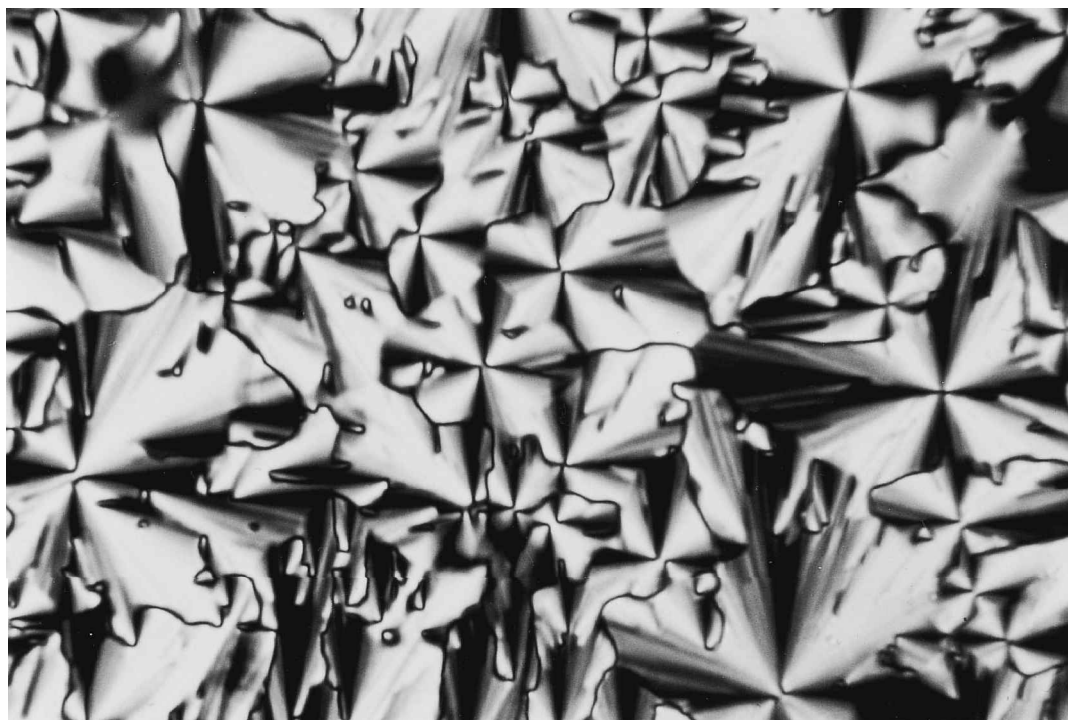


Figure 3. Optical texture of caesium dihexadecylphosphate in the columnar state, observed at 140°C by polarizing microscopy ($\times 300$).

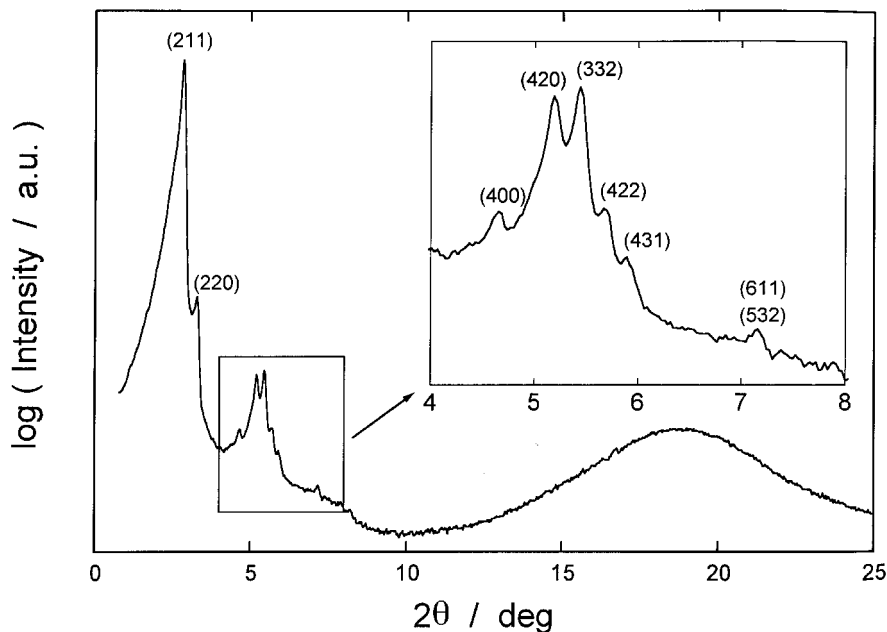


Figure 4. Powder X-ray pattern of potassium dihexadecylphosphate recorded at 120°C. Numerals represent Miller indices of small angle reflections.

Table 2. X-ray diffraction data for potassium, rubidium and caesium dihexadecylphosphates in the $Ia\bar{3}d$ cubic structure at 120°C, d_{obs} and d_{calc} (in Å) are the observed and calculated spacings of the small angle reflections hkl , Int_{obs} are the intensities visually estimated (vs: very strong, s: strong, m: medium, w: weak, vw: very weak), and a is the cubic cell parameter (in Å).

hkl	$(h^2 + k^2 + l^2)^{\frac{1}{2}}$	Potassium $a = 76.1$			Rubidium $a = 71.1$			Caesium $a = 76.7$		
		$d_{\text{calc}}/\text{Å}$	$d_{\text{obs}}/\text{Å}$	Int_{obs}	$d_{\text{calc}}/\text{Å}$	$d_{\text{obs}}/\text{Å}$	Int_{obs}	$d_{\text{calc}}/\text{Å}$	$d_{\text{obs}}/\text{Å}$	Int_{obs}
211	$\sqrt{6}$	31.1	31.1	vs	31.5	31.5	vs	31.3	31.3	vs
220	$\sqrt{8}$	26.9	26.9	s	27.2	27.2	s	27.1	27.1	s
400	$\sqrt{16}$	19.0	19.0	m	19.3	19.2	m	19.2	19.2	m
420	$\sqrt{20}$	17.0	17.0	s	17.2	17.2	s	17.2	17.2	s
332	$\sqrt{22}$	16.2	16.2	s	16.4	16.4	s	16.4	16.3	s
422	$\sqrt{24}$	15.5	15.5	m	15.7	15.8	m	15.7	15.6	m
431	$\sqrt{26}$	14.9	14.9	w	15.1	15.1	w	15.0	15.0	w
611/532	$\sqrt{38}$	12.3	12.3	vw	12.5	—	—	12.4	—	—

Luzzati and Spert for the strontium alkanates [9]. In addition to a broad band in the wide angle region, related to the alkyl chains in a disordered conformation, the patterns contain indeed up to eight sharp reflections in the small angle region (figure 4), with reciprocal spacings and intensities (table 2) in perfect compliance with those given in [9]. The parameters a of the cubic lattice are reported in table 1. The structure consists of two interwoven, unconnected networks of 24 short columns, linked by three in a coplanar fashion as shown in figure 5. (As stated in [9], the columns are probably separated by a short gap at the ternary junctions, and their length is therefore slightly shorter than deduced from the distance $a/\sqrt{8} \approx 27.2$ Å of the ternary junctions

in the crystal.) Formed by the polar headgroups of the molecules, the columns are surrounded by the alkyl chains in a disordered conformation.

A detailed structural study of the columnar and cubic phases requires of course a description of the internal structure of the columnar cores, in particular the layout of the phosphate groups within the columnar cores. An experimental method of getting this kind of information, successfully used not very long ago in the study of the columnar phases of several transition metal alkanates [10], is EXAFS spectroscopy, which is a technique leading to a definition of the local environment of metal atoms. Until this method is applied to the present case, the only accessible information on the internal

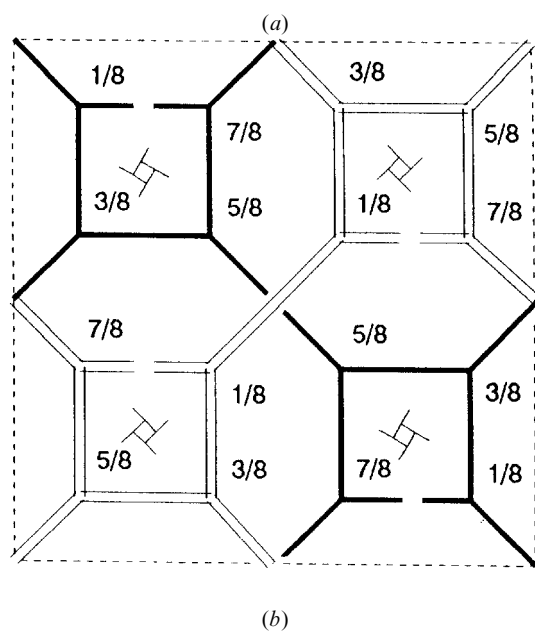
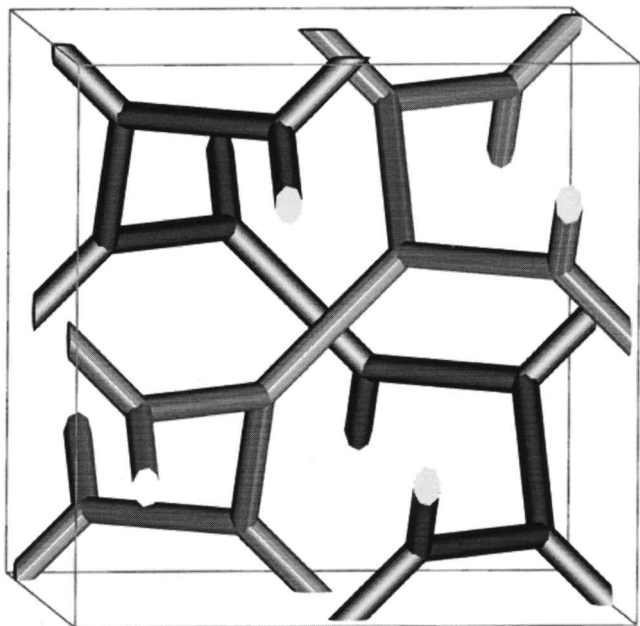


Figure 5. The $Ia3d$ cubic structure of alkali metal dihexadecylphosphates. The structure consists of two interwoven, unconnected networks of short columns (24 columns within each unit cell), linked three by three in a coplanar fashion. (a) Perspective view of one unit cell of the network of columnar cores, (b) crystallographic representation of the structure (fractions represent elevation of junction points within the unit cell).

structure of the columnar cores pertains to the stacking period, h , of the phosphate groups. This parameter may readily be calculated from the molecular volume V and the lattice parameters D and a given by X-ray diffraction

Table 1. Structural parameters (in Å) for the alkali metal dihexadecylphosphates determined by X-ray diffraction: d is the lamellar period of the crystal phases at room temperature, a is the unit cell parameter of the cubic phases at 120°C, and D is the interaxial separation of adjacent columns in the columnar mesophases at the temperatures (°C) shown in parentheses.

Cation	d^a	a	D
Li ^b	48.0	—	29.6 (110)
Na ^b	48.9	—	30.1 (110)
K	50.8	76.1	32.5 (140)
Rb	51.1	77.1	33.0 (140)
Cs	51.1	76.7	33.7 (150)

^a The lamellar periods d of the crystal phases were measured after cooling from the liquid crystalline phases.

^b The lithium and sodium salts do not recrystallize easily.

(table 1). Elementary geometrical considerations† show indeed that $h_{\text{col}} = 2V/(\sqrt{3} \times D^2)$ and $h_{\text{cub}} \leq 12V/(\sqrt{2} \times a^2)$. Molar volumes of alkali metal dihexadecylphosphates have not yet been measured experimentally (by dilatometry), but h may nevertheless be calculated by taking for the corresponding specific volumes (by analogy with what is known for the alkaline earth alkanooates [8]) a reasonable value of about $1 \pm 0.1 \text{ cm}^3 \text{ g}^{-1}$. The values found are $h_{\text{col}} = 0.7 \pm 0.07$ and $h_{\text{cub}} \leq 0.9 \pm 0.09 \text{ Å}$ for the columnar and cubic phases, respectively. One might be tempted to infer from this result that the packing of the phosphate groups inside the columns of the two phases is different. Such a conclusion is, however, far from being proved. Indeed, the value of $h_{\text{cub}} = 0.9 \text{ Å}$ is probably overestimated and the difference $h_{\text{cub}} - h_{\text{col}} = 0.2 \pm 0.16 \text{ Å}$ might very well be simply attributed to a shortage of about 6 Å ($\approx 0.2 \times 27.2/0.9 \text{ Å}$) in the length of the columns in the cubic structure, which is quite reasonable.

5. Conclusion

The present work shows clearly that the alkali metal dialkylphosphates, which in another connection are known to produce vesicles in the presence of water, are perfectly capable of producing thermotropic liquid crystals as well, when heated in the pure state. The mesophases are only columnar for Li and Na; they are $Ia3d$

† For the columnar structure, the volume of one molecule V equals the area of the hexagonal unit cell $\sqrt{3} D^2/2$ multiplied by the intracolumnar stacking period h . For the cubic phase, the total length of the 24 rods contained in the unit cell ($24 L \leq 24a/\sqrt{8}$; the sign $<$ tells us that the columns are probably separated by a short gap at the ternary junctions, and that their length is therefore slightly shorter than deduced from the distance $a/\sqrt{8}$ of the ternary junctions in the crystal [9]) equals the number of molecules per unit cell a^3/V multiplied by the intracolumnar period h .

cubic and columnar for K, Rb and Cs as a function of increasing temperature. Similar structures were observed for the alkaline earth alkanooates: columnar for Mg [11] and Cd [8], cubic and columnar for Sr alkanooates [9, 12]. The transition from the cubic to the columnar phase takes place at a temperature depending very little on the nature of the alkali metal cation, whereas the transition from the crystal to the liquid crystal occurs (except for the lithium salt) at a temperature increasing appreciably with the size of the cation.

It is of interest to recall that the alkali metal alkanooates [13], the molecules of which contain only one alkyl chain per ionic group, exhibit columnar phases in which the columnar cores, ribbon-like in shape, are arranged according to a two-dimensional centred rectangular lattice. Quite probably, the presence in the alkali metal dihexadecylphosphates of two alkyl chains per ionic group makes the ribbons narrow down, for steric reasons, to a rod-like shape and hence allows them to pack according to a more symmetric, hexagonal two-dimensional lattice, as in the case of the alkaline earth alkanooates [8–11].

A detailed X-ray and dilatometric study of a homologous series of alkali metal dialkylphosphates, presently in progress, will hopefully permit us to discuss more thoroughly the internal structure of the columns in relation to the nature of the cations used.

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