Glasses of new 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines forming thermotropic and lyotropic discotic mesophases

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Glasses of new 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines forming thermotropic and lyotropic discotic mesophases

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The synthesis and mesogenic properties of a new class of liquid crystalline metal-free and metalated phthalocyanines with different numbers of alkylthio side chains are presented. The effect of the substitution pattern in a series of differently octasubstituted phthalocyanines on the width and order of the thermotropic mesophase is investigated. The exchange of the alkylthio groups from chlorine atoms alters the mesophase width and the melting behaviour. Glassy phthalocyanines, without any tendency to crystallize, can be synthesized in this way. Furthermore, mixtures of differently 4,5-disubstituted benzenedicarbonitriles are tetramerized statistically to the corresponding mixtures of substituted phthalocyanines. The effect of decreasing symmetry at the molecular level on the properties of the liquid crystalline materials has been investigated. Highly oriented columnar systems can be obtained with these mixtures. For all compounds containing less than eight alkylthio groups, lyotropic mesomorphism in hexadecane solution is also found.

1. Introduction

Discotic liquid crystals are of great interest in the field of self-assembling supramolecular systems, because the columnar arrangement of the mesogens is a promising architecture for anisotropic materials and their possible applications as conducting devices (i.e. optical, electrical, photo- and semi-conducting materials) [1–6]. Mesomorphic materials also have the advantages of good solubility and outstanding processability in the bulk or as thin films.

Even if highly oriented domains of macroscopic dimensions have been obtained by the use of an external electrical or magnetic field at high temperatures, a problem may arise at the liquid crystal to crystal transition if the packing situation in the solid phase differs from that in the mesomorphic phase, e.g. for phthalocyanines, a drastic decrease of the orientation is obtained and grain boundaries among the microcrystals appear. However, an optimal intrinsic conductivity in the case of polycrystalline phases is prevented by structural dis-

turbances, as well as by an increasing dynamic disorder within the mesomorphic phase [4]. Therefore it is favourable to realize a glass-like, low temperature phase while maintaining the mesophase structure, but with frozen dynamics of the molecules. One possibility is the incorporation of the disc-shaped mesogens into a polymer environment [7–11]. Other approaches include deviation from planarity of the disc or the use of bulky groups in the vicinity of the disc-shaped core [12–15]. However, these methods will not work in all cases and are not free from disadvantages concerning the possibility of orienting the mesophase in different ways or the degree of intracolumnar order.

Our aim therefore was to synthesize columnar liquid crystalline, glass-forming, low molecular mass materials based on a new approach, using a specific or statistical reduction in the number of alkyl side chains in substituted phthalocyanines in order to suppress recrystallization and control the structure of the columnar mesophase. Phthalocyanines were selected as a disc-shaped moiety as they are one of the most promising classes of compounds for low dimensional conductive devices [1, 4, 16], although recent success has been obtained

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with discotic triphenylenes [17, 18] and mesogenic per-ylene derivatives [19, 20].

Various uniformly substituted mesogenic phthalocy-anines consisting of one pure isomer and related macro-cycles have previously been investigated. Although the central metal ion, the position of substitution and the nature of the side chains were varied, no glassy materials have been reported [1]. For esters of octacarboxy substituted phthalocyanines only a suppressed crystal-lization behaviour has been reported, but no glass trans-ition was observed [21]. Pure isomers of non-uniformly substituted phthalocyanines are much more difficult to prepare. Only a few papers have been presented, based on three different approaches. One possibility utilizes the reaction of a mixture of differently substituted benzenedicarbonitriles followed by chromatographic separation of the different phthalocyanines [16, 22–25]. A second method deals with the reaction of polymer-bound benzenedicarbonitriles with other unbound benzenedicarbonitriles in homogeneous or heterogen-eous solution, followed by cleavage of the polymer bound phthalocyanines formed [16, 26, 27]. As a third method, the ring-enlargement reaction of sub-phthalocyanines with suitably substituted benzenedicar-bonitriles has been investigated [28, 29]. In contrast to the laborious synthesis of pure isomers of non-uniformly substituted phthalocyanines, the easy standard type cyc-lization of benzene-1,2-dicarbonitriles, differently substi-tuted in positions 4 and 5, leads to a mixture of four phthalocyanine constitutional isomers in good yield [30].

However, the effects on the mesophase structure and behaviour of non-uniformly functionalized mesogenic phthalocyanines, as well as of mixtures of these isomers, have still been only scantily investigated. A series of peripherally octasubstituted phthalocyanines containing alkoxy and immiscible methoxy-tri(ethyleneoxy) or -polyoxyethylene side chains [23, 24, 31], as well as non-peripherally octasubstituted phthalocyanines containing a mixture of alkyl and one or two alkoxy or hydroxyalkyl side chains [32] have also been investigated. Significant effects of the substitution pattern on the columnar mesophase width and structure were observed, e.g. poly-morphism of the columnar mesophase. The cyclotetra-merization of different mixtures of 4,5-bis(hexadecyl)- and 4-[3,5-di-t-butyl-4-(1,3,6-trioxaheptyl)phenyl]-phtha-lonitriles in some cases led to glassy mesogens, explained by the bulky nature of the phenyl substituent and the presence of regioisomeric mixtures [25]. The same explanations were used for the formation of stable glasses of regioisomeric mixtures of a phthalocyanine containing four 14,14,14-triphenyl-1,4,7,10,13-pentaoxatetradecyl groups [33]. Closely related tetrabenzotriazaporphyrin

derivatives of drastically diminished symmetry display less ordered mesophases [34].

However, it is difficult to isolate the influence of the symmetry on the mesophase behaviour in all these examples, as this is also affected by steric effects and/or new strong molecular interaction forces. At present, the liquid crystalline behaviour of different isomer mix-tures of phthalocyanines containing less than eight alkyl groups, but no other side chains, has not been investigated.
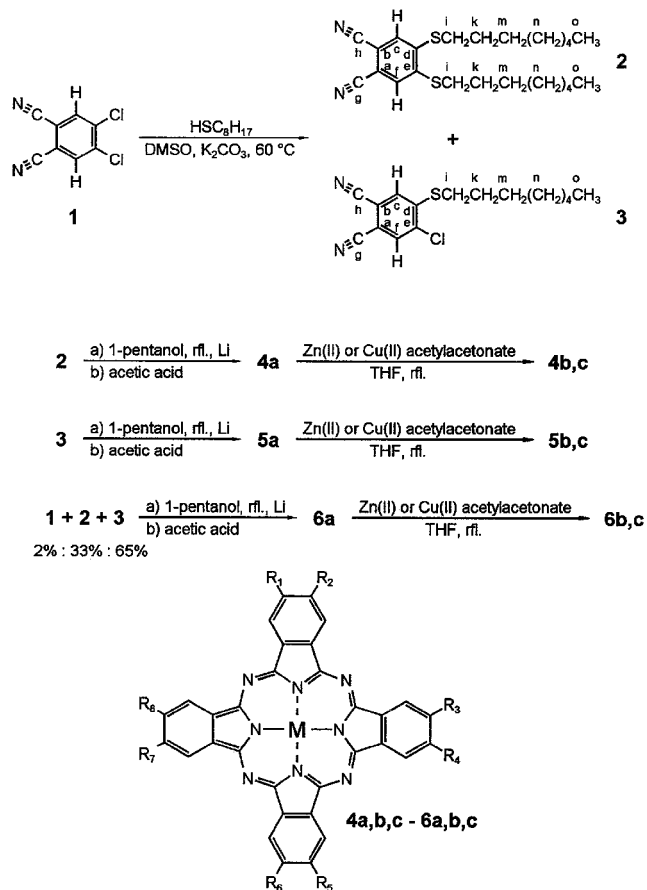
This paper describes the synthesis of 4,5-dioctylthio-(**2**) and 4-octylthio-5-chlorobenzene-1,2-dicarbonitriles (**3**) from 4,5-dichlorobenzene-1,2-dicarbonitrile (**1**) and their cyclization to the analogous octa- or tetra-alkyl substituted phthalocyanines. In order to control the mesogenic properties in an alternative way, physical mixtures of the aforementioned phthalocyanines were also investigated, but without success. The most promis-ing results were obtained by employing a mixture of the three dinitriles **1**, **2**, **3** in the cyclization step. The mixtures obtained of differently substituted phthalocyanines **6a–c** are named 'chemical mixtures'. It will be shown that the copper(II) and metal-free derivatives **6b,c** assemble in a highly oriented columnar structure over a broad temperature range.

2.   Results

2.1. *Synthesis of the substituted phthalocyanines*

Phthalocyanines **4–6** were prepared by the route shown in the scheme. Commercially available 4,5-dichlorophthalic acid was employed as the starting mat-erial for the synthesis of the phthalocyanines. This was converted into 4,5-dichlorobenzene-1,2-dicarbonitrile (**1**) as described previously [35]. Compounds **2** and **3** were statistically synthesized by the reaction of **1** with 1-octanthiol and separated by preparative HPLC. The selective substitution of one chlorine atom by 1-octanethiol for the synthesis of **3** was not practicable without forming **2**, the disubstituted side product.

For the following cyclotetramerization of **2**, **3** or a mixture of **1**, **2** and **3** to the corresponding differently substituted phthalocyanines, the lithium pentoxide cata-lysed reaction [36] was found to give the highest yields of the most pure materials. The metal free phthalocyanines **4a**, **5a**, **6a** were synthesized in yields of *c*. 50 per cent, and subsequent metalations of the metal-free substances by zinc or copper ions led to the phthalocyanines **4b,c**, **5b,c**, **6b,c** in almost quantitative yields. In the case of **2**, the cyclotetramerization led to the phthalocyanines **4a–c**, whereas mixtures of four constitutional isomers **5a–c** were obtained by the cyclization of **3**. The structures of the substances **2–5** were verified by standard analytical methods, e.g. UV-VIS, FTIR, and NMR spectroscopies, MS and elemental analysis (see experimental section). In

Scheme. Synthetic pathways for the substances **2**, **3**, **4a,b,c**, **5a,b,c** and **6a,b,c**; *mixture of the four possible isomers.

Substance	M	$R_{1,2}$	$R_{3,4}$	$R_{5,6}$	$R_{7,8}$
4a	2H	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$
4b	Zn	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$
4c	Cu	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$	$2 \times SC_8H_{17}$
5a*	2H	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl
5b*	Zn	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl
5c*	Cu	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl	SC_8H_{17}, Cl
6a	2H	mixture of derivatives with $R_{1-8} = 8\text{-}n\ SC_8H_{17} + n$ Cl, $n = 1\text{--}7$			
6b	Zn	mixture of derivatives with $R_{1-8} = 8\text{-}n\ SC_8H_{17} + n$ Cl, $n = 1\text{--}7$			
6c	Cu	mixture of derivatives with $R_{1-8} = 8\text{-}n\ SC_8H_{17} + n$ Cl, $n = 1\text{--}7$			

the case of **4** the results are in agreement with published data for octahexylthio substituted phthalocyanines [37].

The 'chemical mixtures' **6a–c** were synthesized by cyclotetramerization of a mixture of **1**, **2** and **3** in a molar ratio of 2%: 33%: 65%. A chromatographic separation of these mixtures of differently substituted phthalocyanines was not successful. However, the employed ratio of the dinitriles in the cyclotetramerization led to the same statistical incorporation into the phthalocyanines. This is indicated by a good agreement between calculated and found values from elemental analysis, as well as with the distribution of the different

compounds in the 'chemical mixture' approximately determined from the mass spectra. It should be mentioned that the relative intensities of the high mass derivatives are too low in comparison with the calculated distribution (see figure 1). Such a deviation was observed for three different ionisation methods: MALDI (matrix assisted laser desorption ionisation), FD (field desorption) and DCI (direct chemical ionisation). However, the spectra with intensity distributions closest to the calculated distribution were found by the MALDI method, and all MS are useful as a 'finger print' of the investigated 'chemical mixture'.
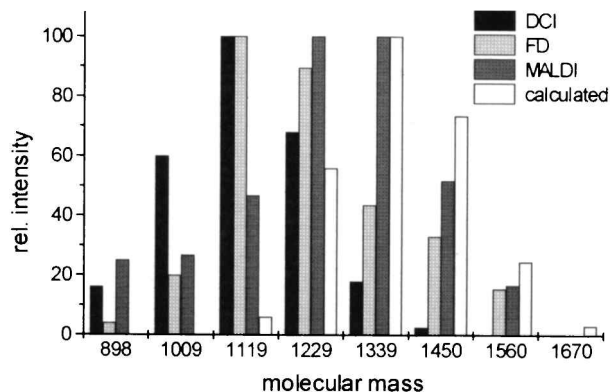
Figure 1. Diagram showing the calculated distributions of the derivatives of the 'chemical mixture' **6a** and the distributions measured by different MS methods. Fragmentation in the case of the DCI measurement is taken into consideration.

Figure 2. UV-VIS spectra of **4b**, **5b** and **6b** in chloroform solution (10^{-6} mol dm^{-3}).

2.2. *UV-VIS investigations of the phthalocyanines in solution*

For substances **4–6**, typical absorption spectra of phthalocyanines were observed [38], showing absorption bands in the Soret-band region at 300–400 nm and for the Q-band transitions at 600–700 nm (see table 1). As expected, the Q-bands are split in the case of the metal-free substances due to the lowered symmetry compared with the metalated phthalocyanines. Both the absorption coefficient and wavelength of the maximum of the Q-band are increased with a large number of electron-donating thioether substituents, whereas the position of the Soret-band is unaffected.

For phthalocyanines, the aggregation behaviour in solution is a good indication of interaction between the aromatic macrocycles. Aggregation, even at a low concentration of 10^{-6} mol dm^{-3}, was found for different solvents (CHCl$_3$, CH$_2$Cl$_2$, THF and toluene). The ex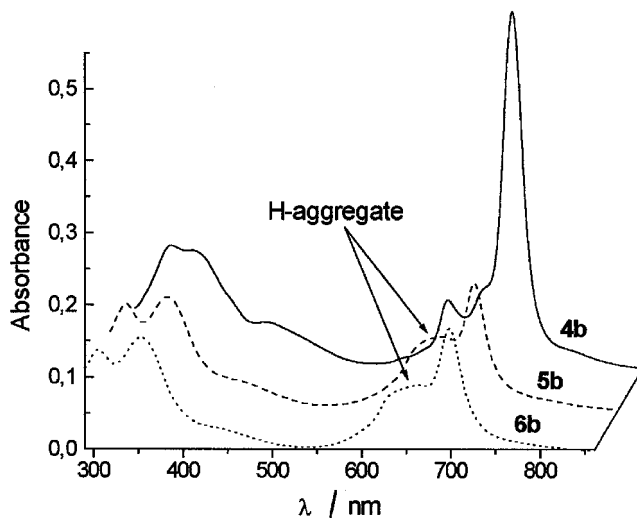tent of aggregation is stronger for substances bearing a low number of alkylthio substituents, as shown for the zinc-containing substances in figure 2. In each case a broadening and a blue-shift of the Q-bands were observed, which is characteristic of exciton coupling between cofacial aggregates (H-aggregates) [39]. Thus, the substances **5** and **6** show a stronger tendency to aggregate into columnar stacks than the derivatives **4**. Spectra of non-aggregated **4–6** were observed for solutions in a mixture of chlorobenzene, containing 0·5 volume percent DMF, at 80°C and at a concentration of 10^{-6} mol dm^{-3}.

2.3. *The mesogenic properties of the phthalocyanines*

The mesomorphic behaviour of the phthalocyanines **4–6** have been investigated by optical polarizing microscopy, DSC and X-ray diffraction.

In polarizing microscopy, birefringent and shearable

Table 1. Absorbance data of the substances **4–6** in a mixture of chlorobenzene and 0·5 volume per cent of DMF at 80°C under inert gas.

Substance	λ_{max}/nm (ε/10^3 dm^3 mol^{-1} cm^{-1})						
	Soret-band region			Q-band region			
4a	334 (58·4)	366 (77·5)	450 (28·9)	637 (28·7)	670 (38·9)	703 (133)	734 (151)
4b		370 (90·2)	440^a	637 (53·9)	678 (41·5)	709 (317)	
4c	328 (64·1)	355^a	442 (22·5)	639 (38·1)	685^a	714 (215)	
5a	309 (45·4)	357 (47·5)	434 (25·6)	627 (25·5)	657 (36·3)	688 (84·4)	721 (90·1)
5b	303 (46·6)	366 (77·5)	430^a	627 (36·9)	667 (35·3)	697 (226)	
5c	308 (54·9)	349 (43·4)	420 (16·8)	631 (32·1)	668 (34·4)	701 (113)	
6a	313 (48·4)	351 (58·9)	437 (26·3)	630 (31·9)	658 (45·4)	689 (89·9)	720 (95·3)
6b	303 (48·2)	366 (74·4)	435^a	628 (31·5)	665^a	697 (172·1)	
6c	309 (76·5)	350 (77·9)	425 (33·6)	630 (51·7)	665^a	699 (161·9)	

^{a} Shoulder.

phases were observed between 10 and ~320°C, indicating a thermotropic liquid crystalline phase for all the phthalocyanines. Clearing of the mesophases was not seen until the substances started to decompose at 320°C, as additionally verified by thermogravimetric analysis. Obtaining obvious textures, for a first classification of the type of mesophase, proved to be difficult; improved preparation techniques for the samples failed due to the very high viscosity and the decomposition at clearing. However, areas of fan-like textures were seen for all compounds, and these are characteristic of columnar mesophases [1, 40].

In the case of compounds **5** and **6**, better results could be obtained by flowing concentrated isotropic solutions in hexadecane between a microscope slide and coverslip and evaporating the solvent at temperatures between 50 and 260°C. In this way a concentration gradient was first created, and lyotropic mesophases could be observed before the thermotropic mesophase was obtained. A schlieren texture, indicative of the formation of a lyotropic columnar nematic (N_C) arrangement [41], was formed at the boundary between the isotropic solution and a mesophase with fan-like texture if the solvent was evaporated at 180°C, see figure 3(a). The fan-like texture presented a probable second lyotropic mesophase, since a transition to a different kind of fan-like texture (pseudo broken focal-conic) was observed for the thermotropic mesophase, see figure 3(b). Rapid cooling from 180 to 35°C ($10°C\,min^{-1}$) of an isotropic solution gave the characteristic dendritic texture of a hexagonal columnar arrangement [33], but in this case of a lyotropic mesophase, see figure 3(c). Evaporation of the solvent at a temperature of 250°C led to a thermotropic mesophase with a schlieren texture, see figure 3(d), which was stable even when annealed at 280°C for two days. This sample provided an impressive example of the very high viscosity of the mesophases of these compounds. A more detailed investigation of the lyotropic mesomorphism of these materials is in progress and will be presented in a separate paper.

The phase transition temperatures were determined by DSC (see table 2). Melting points between 70–80°C and recrystallisation below −10°C were observed for the symmetrically octa-alkyl substituted derivatives **4**, whereas the unsymmetrically substituted substances **5**, **6** do not recrystallize from the mesophase, and only for the zinc-derivatives **5b** and **6b** was a broad melting transition observed in the first heating run. Instead of recrystallization, glass transitions were found between −2 to −12°C, indicating a 'freezing in' of the mesophases. Further transitions could not be detected between −100 and 320°C. Therefore, it is concluded that the phthalocyanines **4–6** are liquid crystalline, even

at room temperature, with an extraordinary phase range of more than 300°C.

In comparison with the analogous oxygen derivatives of **4** [42], the alkylthio substitution results in decreasing melting points and therefore in a broadening of the mesophase range. Substances **5**, containing chlorine in addition to alkylthio substituents, are the first examples of liquid crystalline phthalocyanines surrounded by only four alkyl chains, but mesogenic phthalocyanines containing four oligo(oxyethylene) chains have been previously described [40]. As expected, recrystallization is suppressed in the case of the phthalocyanine mixtures **5** and **6**. It should be noted here, that binary physical mixtures of substances **4** and **5** do not behave as such. The thermograms of these mixtures show separately the thermal transitions of both substances, indicating that the substances do not produce a mixed mesophase. In the case of the mixture of **4c** and **5c**, which surely consist of the same mesophase as determined by X-ray measurements (see below), we have a further example of behaviour contrary to the 'law of miscibility' [43].

The structure of the mesophases was investigated by X-ray diffraction, which clearly proves the liquid crystalline character of the substances **4–6** (see table 3). Powder diffraction patterns of **4b,c** and **5b,c** contain the typical reflections of a columnar mesophase of substituted phthalocyanines [1]: an intercolumnar peak in the small angle region (between 20–24 Å), a broad halo of the alkyl chains at c. 4·6 Å and a more or less intense reflection relating to the intracolumnar stacking at c. 3·5 Å. However, reflections of higher order (1,1 and 2,0), proving a hexagonal columnar arrangement, were observed only for the compounds **4b,c** and **5c**, and a second halo of low intensity was found for substances **5b,c** at 6·5 or 6·9 Å, respectively. The reason for this additional halo and also for the slight splitting of the (1,0) reflection of **4b** (see figure 4), presuming a biaxial phase, must be clarified by further experiments. The intercolumnar distances of the octa-alkylated derivatives **4b,c** of c. 27 Å calculated from the (1,0) reflections (see table 3), are much smaller than the value of 30·5 observed for the analogous oxoether derivatives [42]. This is in contrast to the larger diameter theoretically calculated for the thioether derivatives. This difference cannot be explained by different conformations of the alkyl chains, but perhaps by a more effective inter- or intracolumnar interlacing of the alkyl chains [1]. As expected, the intercolumnar distance of the tetra-alkylated derivatives **5b,c** of c. 24 Å is smaller in comparison with the octa-alkylated derivatives **4b,c**.

The quality of the molecular order can be estimated by analysis of the intensity and the sharpness of the reflections. Comparing **4** and **5**, it is obvious that the intensity (and the values) of the intercolumnar reflection
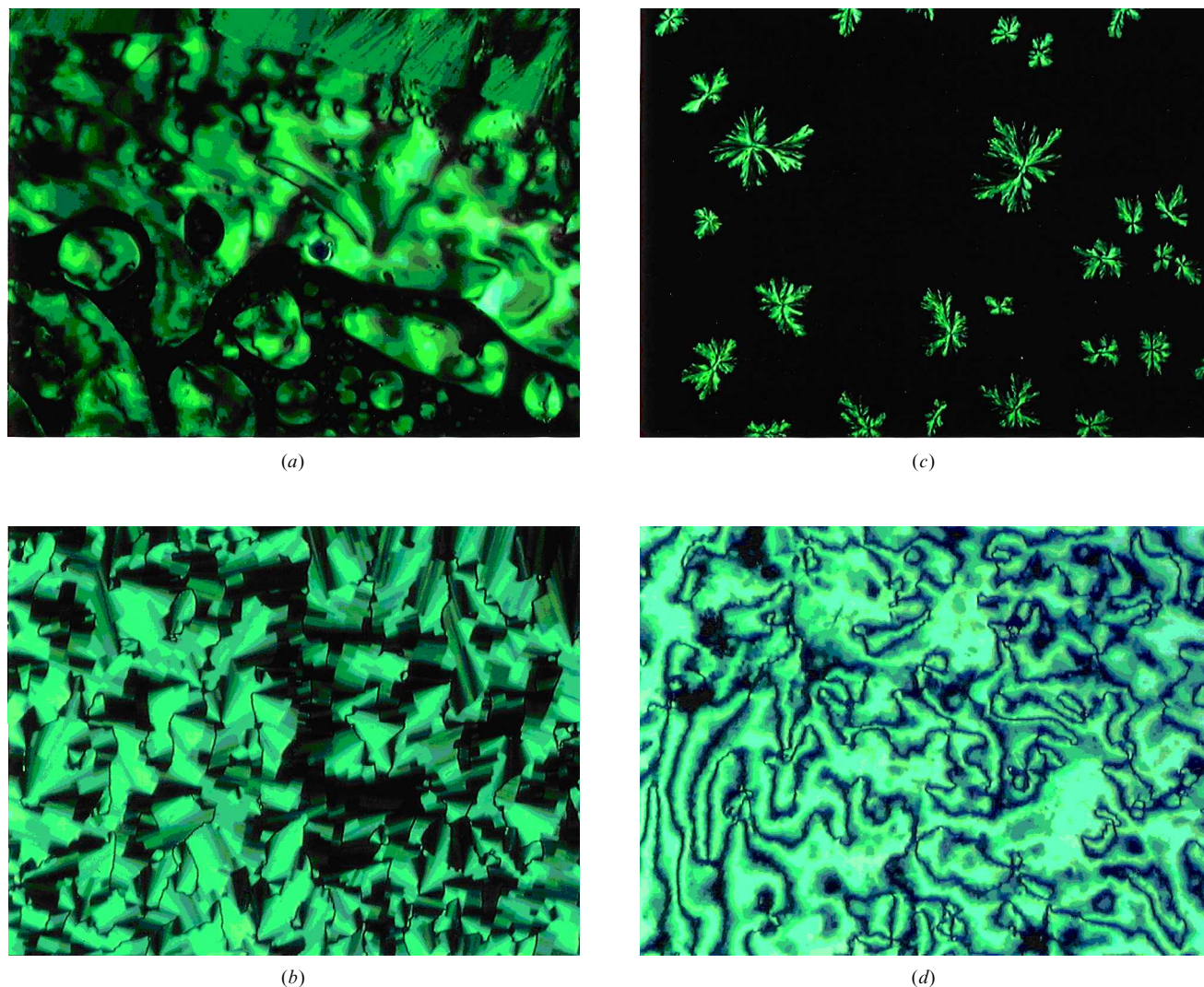
(a)

(c)

(b)

(d)

Figure 3.   Photomicrographs of typical textures of lyotropic and thermotropic mesophases of **5a** and **5c** obtained by evaporation of the solvent from concentrated solutions in hexadecane. (*a*) Lyotropic mesophase of **5c** at 180°C. A schlieren texture has formed at the boundary between the isotropic solution (bottom) and a fan-like texture (92x, crossed polarizers); (*b*) thermotropic mesophase of **5a** after evaporation of hexadecane at 180°C (184x, crossed polarizers); (*c*) dendritic texture of a nucleating lyotropic mesophase of **5c**, obtained by cooling a concentrated solution of the compound in hexadecane from 180–35°C (92x, crossed polarizers); (*d*) schlieren texture of a thermotropic mesophase of **5c** at 35°C, obtained by evaporation of the hexadecane at 250°C (184x, crossed polarizers).

(in Å) decreases with a lower number of octylthio groups, whereas the intensity of the intracolumnar reflection increases (see table 3 and figure 4). The decreasing intensity is also accompanied by a broadening of the reflection, indicating a decrease in long range order of the molecules. Therefore, the intercolumnar distance and the intracolumnar order can be controlled by varying the number of alkyl side chains. Reducing the number of octylthio groups results in a smaller inter-columnar distance and a loss of long range order of the packing of the columns, due to the diminished symmetry. In contrast, the intracolumnar long range order increases

with the change from eight to four alkyl side chains. This is explainable in terms of the known packing problem of the alkyl chains within the columns [44], which is less effective in the case of only four alkyl side chains.

The 'chemical mixtures' **6a–c** now combine high inter- and intra-columnar order. The material behaviour of these substances is quite different from the brittle consistency of the glassy states and mesophases of **4** and **5**, because **6a–c** are ductile, waxy materials. Therefore, it was easy to produce small sticks of the 'chemical mixtures' (*c*. 10 mm long and 2 mm in diameter) by rolling,

Table 2.   Transition temperatures and enthalpies for the octasubstituted phthalocyanines **4–6** determined by DSC (heating rate $10°C$ min^{-1}, heating range -100 to $320°C$).

Substance	1. Heating run $T_{Cr \to Col}/°C$ (ΔH/kJ mol^{-1})	1. Cooling run $T_{Col \to Cr}/°C$ (ΔH/kJ mol^{-1})	2. Heating run $T_{Cr \to Col}/°C$ (ΔH/kJ mol^{-1})
4a	70 (59)	-21 (-12)	-9 (14)[b]
4b	76 (66)	-11 (-21)	5 (-62)[c,b], 79 (88)[b]
4c	75 (73)	-24 (-14)	-12 (11)[b]
5a	-7[a]	-10[a]	-7[a]
5b	62 (26)[d]	-12[a]	-8[a]
5c	-5[a]	-11[a]	-8[a]
6a	-6[a]	—	-4[a]
6b	66 (31)[d]	-11[a]	-5[a]
6c	-2[a]	-2[a]	-2[a]

[a] Glass transition.
[b] Heating rate $2°C$ min^{-1}.
[c] Cold crystallization.
[d] Very broad.

Table 3.   Bragg-spacings (in Å) of the mesophases of substances **4–6** at $125°C$ and their assignment in terms of a two-dimensional hexagonal lattice. Column diameters D (in Å) were calculated from the (1,0)-reflection, assuming a hexagonal lattice; intracolumnar distances h (in Å) were calculated from the reflection at angles of approx. 26 (in 2Θ). s=strong, m=medium, w=weak, b=broad.

Substance	1,0	1,1	2,0	halo 1	halo 2	h	D
4b	23·16 s + 22·06 s	13·56 w	11·23 w		4·60	3·53 w, b	c·27
4c	23·50 s	13·86 w	11·88 w		4·66	3·51 w, b	27·14
5b	20·53 s			6·5	4·48	3·40 m, b	23·71
5c	20·96 s	12·41 w	10·81 w	6·9	4·70	3·40 w, b	24·20
6a	21·01 s			6·8	4·04	3·40 m	24·26
6b	21·01 s			6·8	4·67	3·49 m	24·26
6c	21·01 s			6·8	4·04	3·41 m	24·46

and to investigate them by X-ray diffraction in the transmission mode. For all three substances, sharp and relatively intense reflections for the inter- and intra-columnar stacking periodicity as well as two halos, as described before for **5**, were observed (see table 3). Reflections of higher order, however, were not seen, but surprisingly compounds **6a** and **6c** show typical diffraction patterns for an oriented sample (see figure 5), whereas **6b** does not. In the case of **6a** and **6c**, simple mechanical forces generated by rolling orient the columnar axis in the mesophase orthogonal to the shearing field. First investigations of copper-containing 'chemical mixtures' of different compositions clearly prove a relationship between the average number of alkylthio groups and the phase behaviour. Mixtures with a higher number of alkylthio groups are less oriented, and a reduction in the number of alkylthio groups (**1**, **2**, **3** in molar ratios of 9:18:73 or 21:9:70) results in more brittle materials and also less oriented columnar mesophases.

3.   Conclusion

It has been shown that phthalocyanines substituted by fewer than eight alkyl side chains melt into a thermotropic columnar mesophase. The inter- and intra-columnar distances, as well as long range orders are controllable by varying the number of alkyl chains. Crystallization or recrystallization from the mesophase is suppressible by the use of mixtures. Finally, the use of easily synthesized and characterized 'chemical mixtures' of phthalocyanines, substituted with different numbers of alkyl side chains and chlorine atoms, results in mechanically oriented columnar mesophases of high inter- and intra-columnar order. The diminution of the number of alkyl side chains also facilitates lyotropic mesomorphism in apolar solvents like hexadecane. Highly oriented thin films should be obtainable from the fluid lyotropic mesophase, overcoming the disadvantage of not being able to use the clearing point of the very viscous thermotropic mesophases to assist in alignment.
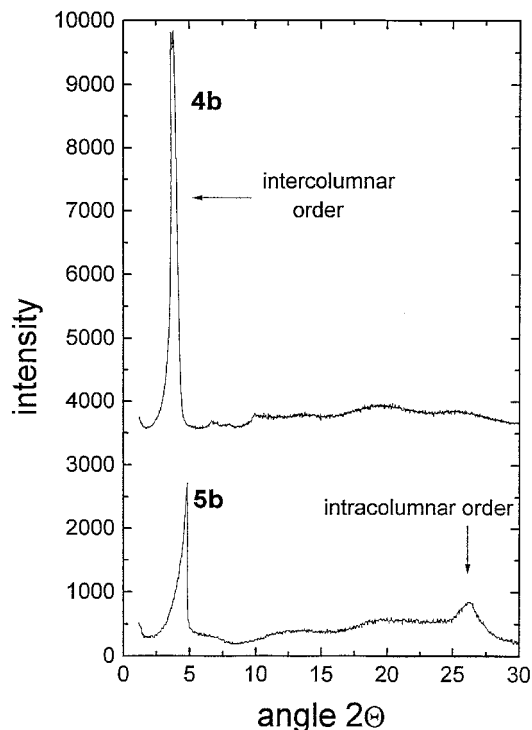
Figure 4.   X-ray diffraction patterns of **4b** and **5b** at 127°C.

Further investigations will have to show if the use of mixtures of molecules containing a reduced number of side chains is generally favourable or if it depends on the special substitution pattern used here. Trialkoxytriphenylene, for example, does not display a mesophase, whereas the tribromotrialkoxytriphenylene is mesomorphic, but over a much narrower range than the classical hexa-alkoxy derivative [45]. The exact structures and, in particular, the dynamics of these mesophases have also to be studied by further investigations.

4. Experimental
4.1. *Methods*

UV-VIS absorption spectra were recorded using a Perkin Elmer Lamda 9 spectrometer. FTIR spectra of films on KBr pellets were recorded with a Bio-Rad Digilab FTIR FTS7 instrument. ^{1}H and ^{13}C NMR spectra were measured using a Bruker WH 360 employing the deuterium signal of the solvent as the lock and TMS as internal standard. MS investigations were made with a Finnigan MAT 8222 (DCI), Bruker TOF (MALDI) or ZAB2-SE-FDP (FD). HPLC were recorded with a Merck-Hitachi-System (L-3000 Photo Diode Array Detector, L-6200A Intelligent Pump, T-6300 Column Thermostat, AS 2000A Autosampler). As columns, a 250-4 Merck LiChrospher Si-60 (10 μm) or LiChrospher RP-18 (5 μm) was used. For preparative

HPLC the Merck-SepTech instrument Nova Prep 5000 with a 250-25 Merck LiChrosorb RP-18 (7 μm) column was employed. Calorimetric studies were performed using a Polymer Laboratories DSC or a Mettler DSC TA 3000 and thermogravimetric analysis using a Mettler TG50 instrument. Polarizing microscope measurements were made with a Leitz Orthoplan equipped with a Leitz microscope hot stage 1350. X-ray diffractograms in the reflection mode were measured using a Siemens Kristalloflex diffractometer with a collimator width of 0·3 mm, using Ni-filtered Cu K_α-radiation. Scattering patterns in the transmission mode were recorded with a flat camera (2D-Xe-detector, 256×256 cells) equipped with a hot stage, again using Ni-filtered Cu K_α-radiation (rotating anode Rigaku RV-300).

4.2. *Synthesis*
4.2.1. *4,5-Dichlorobenzene-1,2-dicarbonitrile* (**1**)
This compound was synthesized as described previously [35].

4.2.2. *4,5-Dioctylthiobenzene-1,2-dicarbonitrile* (**2**) *and 4-octylthio-5-chlorobenzene-1,2-dicarbonitrile* (**3**)
A solution of 8·38 g (42·8 mmol) of **1** (see Scheme) in 25 ml dry DMSO was heated at 60°C. Then 8·7 ml (50 mmol) of octanthiol and 15 g (107 mmol) of K_2CO_3 were added to the solution with stirring. After 24 h, the resulting suspension was added to 200 ml of 0·1 M aqueous HCl. The precipitate was filtered off, washed with 200 ml of 10% aqueous Na_2CO_3 solution and then with distilled water. The white product mixture was dissolved in a minimum of methanol and purified by preparative HPLC on LiChrosorb RP-18 (7 μm) 25×250 mm using methanol as eluant. As the first fraction, 5·78 g (44%) of **3** and as the second fraction, 1·25 g (7%) of **2** were obtained (flow: 39 cm^3 min^{-1}; concentration: 19·5 g dm^{-3}; injection volume: 39 cm^3).

2: M.p. = 58°C. IR (as a film on KBr): $\nu = 2229$ cm^{-1} (C≡N). ^{1}H NMR (360 MHz, CDCl$_3$) (for numbering see the scheme): δ (ppm) = 7·40 (s, 2H, c,f-H), 3·00 (t, 4H, i-H), 1·75 (m, 4H, k-H), 1·48 (m, 4H, m-H), 1·35–1·25 (m, 16H, n-H), 0·88 (t, 6H, o-H). ^{13}C NMR (360 MHz, CDCl$_3$): δ (ppm) = 144·21 (d,e-C), 128·08 (c,f-C), 115·67 (a,b-C), 111·02 (g,h-C), 32·70, 31·72, 29·06, 29·03, 28·88, 28·03, 22·61 (i,k,m,n-C), 14·07 (o-C). MS (EI): m/e (per cent) = 416(100) M$^+$, 304(67) M$^+$–C$_8$H$_{16}$, 192(21) M$^+$–2(C$_8$H$_{16}$), 112(6) C$_8$H$_{16}$$^+$. UV-VIS (ethanol): λ_{max}/nm (log ε) = 229 (4·0), 250 (3·9), 279 (4·5), 326 (4·0).

3: M.p. = 89°C. IR (as a film on KBr): $\nu = 2231$ cm^{-1} (C≡N). ^{1}H NMR (360 MHz, CDCl$_3$) (for numbering see the scheme): δ (ppm) = 7·72 (s, 1H, f-H), 7·46 (s, 1H, c-H), 3·01 (t, 2H, i-H), 1·77 (m, 2H, k-H), 1·50 (m, 2H, m-H), 1·35–1·25 (m, 8H, n-H), 0·92 (t, 3H, o-H). ^{13}C NMR (360 MHz, CDCl$_3$): δ (ppm) = 147·29 (d-C),

135·99 (e-C), 133·06 (f-C), 128·63 (c-C), 114·83 (a-C), 114·52 (b-C), 114·33 (g-C), 110·88 (h-C), 31·87, 31·66, 28·99, 28·96, 28·82, 27·59, 22·55 (i,k,m,n-C), 14·02 (o-C). MS (EI): m/e (per cent)$=306(100)$ M^+, $271(2)$ M^+–Cl, $194(45)$ M^+–C_8H_{16}, $112(16)$ $C_8H_{16}^+$. UV-VIS (ethanol): λ_{max}/nm (log ε)$=213$ (4·3), 251 (4·4), 301 (4·2).

4.2.3. *2,3,9,10,16,17,23,24-Octaoctylthiophthalocyanine (4a) or isomeric mixture of 2,3,9,10,16,17,23,24-tetraoctylthio-tetrachlorophthalocyanines (5a)*

460 mg (1·5 mmol) of **2** or 625 mg (1·5 mmol) of **3** were dissolved in 20 ml of dry 1-pentanol under reflux conditions. Then 10 mg (1·44 mmol) of lithium was added to the stirred solution under inert gas and 5 min later the dark green suspension was cooled to room temperature. The suspension was added to 30 ml of acetic acid and stirred for 10 min at 50°C. The filtered blue product was precipitated twice from diethoxymethane solution, first by adding methanol and then by adding acetone in the second step. This precipitate was further purified by flash chromatography on silica gel using toluene/n-hexane, 8:2 as eluant. Yields: 1·35 g (54%) for **4a** and 1·14 g (62%) for **5a**.

4a: IR (as a film on KBr): $\nu=3290$ cm^{-1} (N–H), 1597 cm^{-1} (C=C$_{arom.}$). $C_{96}H_{146}N_8S_8$ (1668·8): calculated C 69·10, H 8·82, N 6·71, S 15·37; found C 69·20, H 8·87, N 6·64, S 15·45 per cent.

5a: IR (as a film on KBr): $\nu=3291$ cm^{-1} (N–H), 1596 cm^{-1} (C=C$_{arom.}$). MS (DCI, negative, NH$_3$): m/e (rel. intensity)$=1228(100)$ M^+, $1194(7)$ MH^-–Cl, $1116(10)$ M^-–C_8H_{16}, $1084(1·5)$ M^-–SC_8H_{16}. MS (FD+): m/e (rel. intensity)$=1228·8(100)$ M^+, $615·5(27)$ M^{2+}. $C_{64}H_{78}N_8S_4Cl_4$ (1229·5): calculated C 62·53, H 6·39, N 9·11, S 10·43, Cl 11·53; found C 62·37, H 6·73, N 9·01, S 10·38, Cl 11·13 per cent.

4.2.4. *'Chemical mixture' of chloro and octylthio 2,3,9,-10,16,17,23,24-octasubstituted phthalocyanines (6a)*

24 mg (0·12 mmol) of **1**, 0·825 g (1·98 mmol) of **2** and 1·196 g (3·90 mmol) of **3** were dissolved in 25 ml of dry 1-pentanol under reflux. Then 20 mg (2·88 mmol) of lithium was added to the stirred solution under inert gas and 5 min later the dark green suspension was cooled to room temperature. The subsequent work up corresponded to that described for **4a** and **5a**, apart from the use of toluene for the flash chromatography. Yield: 1·44 g (70%).

6a: IR (as a film on KBr): $\nu=3288$ cm^{-1} (N–H), 1601 cm^{-1} (C=C$_{arom.}$). MS (MALDI, DHB-matrix, reflectron, 15 kV): m/e (rel. intensity)$=1559(2·5)$ $M^+[7R=SC_8H_{17}, 1R=Cl]$, $1449(7·8)$ $M^+[6R=SC_8H_{17}, 2R=Cl]$, $1339(15·0)$ $M^+[5R=SC_8H_{17}, 3R=Cl]$, $1229(15·0)$ $M^+[4R=SC_8H_{17}, 4R=Cl]$, $1119(7·0)$ $M^+[3R=SC_8H_{17}, 5R=Cl]$, $1009(4)$ $M^+[2R=SC_8H_{17}, 6R=Cl]$, $899(3·8)$ $M^+[1R=SC_8H_{17}, 7R=Cl]$. $C_{72·96}H_{97·04}N_8S_{5·12}Cl_{2·88}$ (1352·5): statistically calculated C 65·01, H 7·31, N 8·21, S 12·30; found C 64·64, H 7·15, N 7·74, S 11·67 per cent.

4.2.5. *Zinc(II)- or copper(II)-2,3,9,10,16,17,23,24-octa-octylthiophthalocyaninato (4b or 4c respectively), zinc(II)- or copper(II)-2,3,9,10,16,17,23,24-tetra-octylthiophthalocyaninato (5b or 5c respectively) or zinc(II) or copper(II) complexes of the 'Chemical mixture' of chloro and octylthio 2,3,9,10,16,17,-23,24-octasubstituted phthalocyanines (6b or 6c, respectively)*

0·1 mmol of metal free substance **4a**, **5a** or **6a** was dissolved in a solution of 0·3 mmol of metal acetylacetonate in 100 ml of diethoxymethane and heated under reflux for 1 h. The crude products were purified by flash chromatography as described before. Metalations are observed always to be quantitative.

4b: IR (as a film on KBr): $\nu=1595$ cm^{-1} (C=C$_{arom.}$). ^{1}H NMR (360 MHz, C$_2$D$_2$Cl$_4$): δ (ppm)$=7·65$ (s, 8H, H$_{arom.}$), 3·14 (t, 16H, S–CH$_2$), 1·82 (m, 16H, S–CH$_2$–C$\underline{H}_2$), 1·6–1·2 (m, 80H, CH$_2$), 0·93 (t, 24H, CH$_3$). $C_{96}H_{144}N_8S_8Zn$ (1732·1): calculated C 66·57, H 8·38, N 6·47, S 14·81; found C 66·74, H 8·42, N 6·30, S 14·34 per cent.

4c: IR (as a film on KBr): $\nu=1596$ cm^{-1} (C=C$_{arom.}$). $C_{96}H_{144}N_8S_8Cu$ (1730·28): calculated C 66·64, H 8·39, N 6·48, S 14·82; found C 66·52, H 8·51, N 6·33, S 14·50 per cent.

5b: IR (as a film on KBr): $\nu=1596$ cm^{-1} (C=C$_{arom.}$). MS (DCI, negative, NH$_3$): m/e (rel. intensity)$=1292(7)$ M^-, $1258(5)$ MH^-–Cl, $1224(1·5)$ MH^-–2Cl, $1180(2)$ M^-–C_8H_{16}, $159(100)$. MS (FD+): m/e (rel. intensity)$=1293(100)$ M^+, $646(27)$ M^{2+}. $C_{64}H_{76}N_8S_4Cl_4Zn$ (1292·8): calculated C 59·46, H 5·93, N 8·67, S 9·92, Cl 10·97; found C 59·76, H 6·08, N 8·85, S 9·77, Cl 11·25 per cent.

5c: IR (as a film on KBr): $\nu=1598$ cm^{-1} (C=C$_{arom.}$). MS (DCI, negative, NH$_3$): m/e (rel. intensity)$=1289(3)$ M^-, $1255(1)$ MH^-–Cl, $1221(0·1)$ MH^-–2Cl, $192(100)$. $C_{64}H_{76}N_8S_4Cl_4Cu$ (1290·9): calculated C 59·55, H 5·93, S 9·93, Cl 10·99; found C 59·48, H 5·89, S 9·80, Cl 10·88 per cent.

6b: IR (as a film on KBr): $\nu=1598$ cm^{-1} (C=C$_{arom.}$). MS (FD+): m/e (rel. intensity)$=1511(19)$ $M^+[6R=SC_8H_{17}, 2R=Cl]$, $1400(43)$ $M^+[5R=SC_8H_{17}, 3R=Cl]$, $1290(91)$ $M^+[4R=SC_8H_{17}, 4R=Cl]$, $1180(100)$ $M^+[3R=SC_8H_{17}, 5R=Cl]$, $1070(26)$ $M^+[2R=SC_8H_{17}, 6R=Cl]$, $961(22)$ $M^+[1R=SC_8H_{17}, 7R=Cl]$ (Ions of fragmentation, always involving elimination of one chlorine atom, are not cited). $C_{72·96}H_{97·04}N_8S_{5·12}Cl_{2·88}Zn$ (1429·0): statistically calculated C
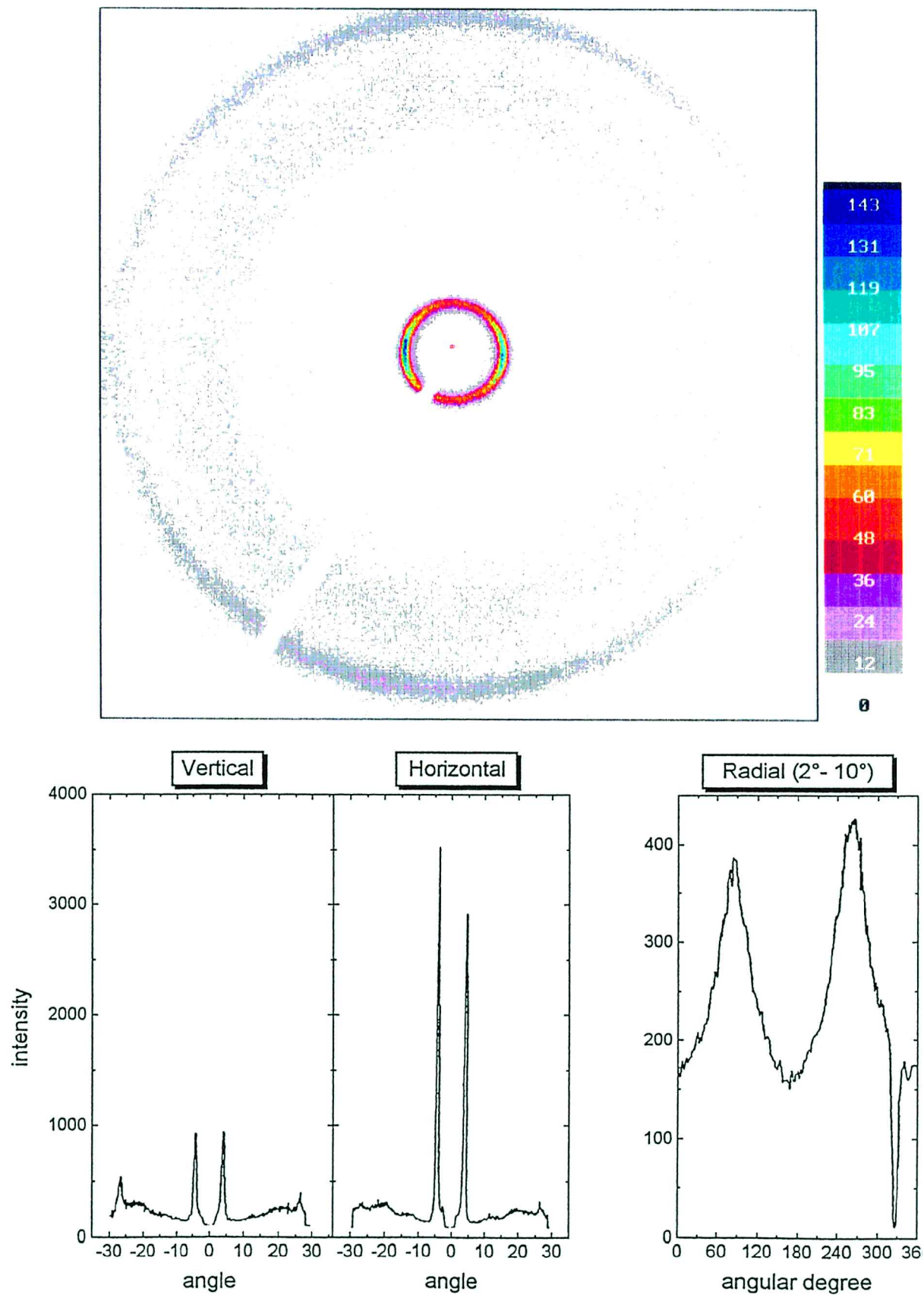
Figure 5. X-ray scattering pattern (transmission mode) obtained for a small stick (10 mm × 2 mm) of **6c** in the mesophase at 127°C; the stick is oriented orthogonal to the beam and vertical in space.

62·13, H 6·85, N 7·84; found C 61·78, H 6·52, N 8·26 per cent.

6c: IR (as a film on KBr): $\nu = 1596\,\mathrm{cm}^{-1}$ ($C = C_{\mathrm{arom.}}$). MS (DCI, negative, NH_3): m/e (rel. intensity) $= 1510(2)$ $M^-[6R = SC_8H_{17}, \quad 2R = Cl]$, $1400(26)$ $M^-[5R = SC_8H_{17}, 3R = Cl]$, $1290(98)$ $M^-[4R = SC_8H_{17}, 4R = Cl]$, $1180(100)$ $M^-[3R = SC_8H_{17}, 5R = Cl]$, $1070(35)$ $M^-[2R = SC_8H_{17}, 6R = Cl]$, $959(6)$ $M^-[1R = SC_8H_{17}, 7R = Cl]$ (Ions of fragmentation, always involving elimination of one chlorine atom, are not cited). $C_{73\cdot92}H_{97\cdot08}N_8S_{5\cdot24}Cl_{2\cdot76}Cu$ ($1427\cdot2$): statistically calculated C 62·21, H 6·86, N 7·85; found C 61·72, H 6·29, N 8·33 per cent.

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