ment molecule and a cooperating polypeptide unit remains to be answered.

Torsional deformations resulting in atypical retinal conformations, local charges, alterations in the absorption anisotropy of the pigment chromophore, etc., may produce an equivalent angular displacement in the transition dipole and cannot be discounted in the present studies. That these are not only theoretical possibilities gains support from resonance Raman studies[53,71,72] which report the most dramatic changes in the vibrational properties of retinal in the course of the formation of K_{610}. Moreover, the characteristics of the K_{610} Raman spectra are not directly comparable with that of 13-*cis*-retinal model compounds. In light of these considerations, we can only conclude that, in the course of the $bR_{570} \rightarrow K_{610}$ light-driven reaction, an apparent angular displacement in the K_{610} transition dipole occurs with respect to the nonphotolyzed parent molecule. However, this apparent displacement of the transition dipole is not necessarily indicative of a traditional all-trans → 13-cis isomerization in the retinal chromophore.

Finally, it is important to point out that the above quantitative model is based upon the explicit assumption of a dark back-reaction of type $K_{610}(J_{625}) \rightarrow (bR_{550})bR_{570}$. Alternatively, the possible existence and involvement of a kinetically equivalent pathway can also be proposed. There is not any firm experimental support in favor of any of these possibilities in the bacteriorhodopsin photochemistry at present. A careful inspection of the available kinetic data does not rule out either possibility.

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Thermotropic Liquid-Crystalline Behavior of Some Single- and Double-Chained Pyridinium Amphiphiles

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The present study describes the thermotropic phase transitions in several structurally related amphiphiles containing pyridinium head groups. From the combined results of differential scanning calorimetry (DSC), optical polarization microscopy, and X-ray diffraction, the thermotropic liquid-crystalline phases present in 1-3 and 10 have been characterized. For amphiphiles 1 and 10 a smectic-A phase was observed. The thermotropic liquid-crystalline state of 2 could be identified as a smectic-C phase. The tilt angle of the director was calculated to be ca 58°. The X-ray diffraction pattern of the mesophase of 3 could be best rationalized in terms of a smectic-H phase. The cell constants of the monoclinic lattice are a = 8.63 Å, b = 4.79 Å, c = 51.8 Å, and β = 132.6°, with two molecules per unit cell. The results are discussed in relation to the calculated molecular dimensions obtained from space-filling molecular models. Probable arrangements of the organized amphiphiles in the particular smectic phase are proposed.

Introduction

Amphiphilic molecules often show thermotropic liquid-crystalline phase behavior.[1,2] Reports on thermotropic mesophases of long-chain *N*-alkylated pyridines, pyridinium salts carrying a long hydrocarbon chain at the 2 position,[3] and 1-methyl-3-dodecyloxypyridinium salts and their thio analogues have also been published.[4] However, the nature of these liquid-crystalline phases has not been investigated.

In the course of our studies of the aggregation of 1-methyl-4-*n*-dodecylpyridinium iodide (1), 1-methyl-4-(17-tritriacontyl)pyridinium iodide (2), and 1-methyl-3,5-bis(*n*-hexadecyloxycarbonyl)pyridinium iodide (3) in apolar organic solvents (to form reversed micelles[5]) and in water (to form micelles[6] or vesicles[7]), it was found that these amphiphiles exhibit liquid-crystalline behavior in a distinct temperature range. In this paper we report a study of the thermotropic phases of these amphiphiles and of the structurally related derivatives 4-*n*-nonylpyridinium hydrochloride (4), 4-*n*-dodecylpyridinium hydrochloride (5), hydrobromide (6), and hydroiodide (7), 4-(12-tricosyl)pyridinium hydroiodide (8), 1-methyl-4-*n*-dodecylpyridinium chloride (9) and perchlorate (10), 1-methyl-4-(17-tritriacontyl)pyridinium chloride (11), and 1-methyl-3,5-bis(*n*-hexadecyloxycarbonyl)pyridinium chloride (12). Structural formulas of these compounds are shown in Table I.

The thermotropic phase behavior of these compounds was investigated by using optical polarization microscopy, differential scanning calorimetry (DSC), and X-ray dif-

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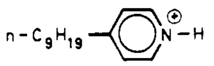
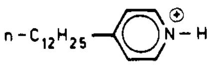
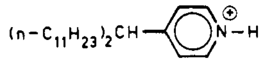
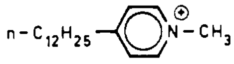
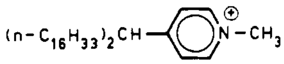
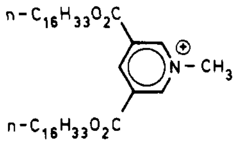
0022-3654/82/2086-1908$01.25/0

TABLE I: Chemical Structures of the Amphiphiles

chemical structure	compd no.
 $Cl^{\ominus}$	4
 $X^{\ominus}$ $X^{\ominus} = Cl^{\ominus}$	5
$Br^{\ominus}$	6
$I^{\ominus}$	7
 $I^{\ominus}$	8
 $X^{\ominus}$ $X^{\ominus} = Cl^{\ominus}$	9
$I^{\ominus}$	1
$ClO_4^{\ominus}$	10
 $X^{\ominus}$ $X^{\ominus} = Cl^{\ominus}$	11
$I^{\ominus}$	2
 $X^{\ominus}$ $X^{\ominus} = Cl^{\ominus}$	12
$I^{\ominus}$	3

fraction on unoriented samples.

Experimental Section

Preparation of the Amphiphiles. 1-Methyl-4-n-dodecylpyridinium Iodide (1). To a stirred solution of 13 g (0.14 mol) of freshly distilled 4-methylpyridine (Aldrich) in 100 mL of dry diethyl ether (distilled from P_2O_5 and kept on molecular sieves (4 Å)) was added at −20 °C (under nitrogen) a suspension of 0.14 mol of lithium diisopropylamide in diethyl ether and *n*-hexane. The suspension was first prepared by reaction of 14 g (0.14 mol) of diisopropylamine (BDH) in 100 mL of dry diethyl ether and 100 mL of 15% of *n*-butyllithium in *n*-hexane (Merck) at 0 °C in a nitrogen atmosphere. While the suspension was added, the reaction mixture turned yellow. After the addition of the suspension, the mixture was stirred for another 30 min. Then, 33.5 g (0.14 mol) of pure 1-bromo-*n*-undecane (Merck) was added at the same temperature. The yellow color disappeared. The reaction mixture was stirred for 1 h at −20 °C and subsequently, during the night, at room temperature. After the addition of 200 mL of water and separation of the two solvent layers, the aqueous layer was extracted once with 50 mL and twice with 25 mL of diethyl ether. The combined diethyl ether layers were dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure (water aspirator, 12 mmHg). The crude 4-*n*-dodecylpyridine was treated with 50 mL (0.80 mol) of methyl iodide (Merck) in 100 mL of refluxing acetone in a brown-colored, round-bottom flask for 16 h. The solvent and the excess of methyl iodide were evaporated under reduced pressure (water aspirator, 12 mmHg). The overall yield of 1 was 33.5 g (65%). Crystallization from acetone gave slightly yellow crystals: mp 112.8–113.1 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (3 H, triplet, $J \approx 6$ Hz), 1.25 (20 H, multiplet), 2.88 (2 H, triplet, $J = 8$ Hz), 4.63 (3 H, singlet), 7.8–9.3 (4 H, multiplet). Anal. Calcd for $C_{18}H_{32}NI$ (mol wt 389.36): C, 55.52; H, 8.29; N, 3.59; I, 32.58. Found: C, 55.52; H, 8.32; N, 3.54; I, 32.65.

1-Methyl-4-(17-tritriacontyl)pyridinium Iodide (2). Extension of the 4-methyl substituent in 4-methylpyridine to an *n*-heptadecyl hydrocarbon chain was carried out as described for 1, using 1-iodo-*n*-hexadecane (Merck) as the reagent. Introduction of the second *n*-hexadecyl hydrocarbon chain at the α carbon atom of 4-*n*-heptadecylpyridine also was carried out as described above, except that the temperature was raised to −5 °C to prevent solubility problems. The crude 4-(17-tritriacontyl)pyridine was reacted with a fivefold molar excess of methyl iodide in acetone as described for 1. The reaction was performed on a 0.14-mol scale. The overall yield of 2 was 52.5 g (55%). Crystallization from absolute ethanol gave an almost white solid: mp 72.0 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (6 H, triplet, $J \approx 4$ Hz), 1.28 (60 H, multiplet), 2.80 (1 H, quintet, $J < 2$ Hz, unresolved), 4.75 (3 H, singlet), 7.7–9.5 (4 H, multiplet). Anal. Calcd for $C_{39}H_{74}NI$ (mol wt 683.93): C, 68.49; H, 10.91; N, 2.05; I, 18.55. Found: C, 68.26; H, 10.89; N, 2.08; I, 18.75.

1-Methyl-3,5-bis(n-hexadecyloxycarbonyl)pyridinium Iodide (3). Following Wang's procedure,[8] 10 g (60 mmol) of 3,5-pyridinedicarboxylic acid (Merck) in 200 mL of methanol and 20 mL of water was titrated with 20% (by weight) aqueous cesium carbonate (Fluka) until pH 7 was reached. The solvent was evaporated under reduced pressure (water aspirator, 12 mmHg), and then the solid residue was suspended in 120 mL of *N*,*N*-dimethylformamide (DMF, Baker). The solvent was evaporated under reduced pressure. This procedure was repeated once. The white dicesium salt was suspended in 120 mL of DMF and was allowed to react with 43 g (120 mmol) of 1-iodo-*n*-hexadecane for 48 h at 70 °C. The solvent was evaporated under reduced pressure (water aspirator, 12 mmHg). The product was solubilized in $CHCl_3$, and the insoluble salts were filtered off. After evaporation of the solvent under reduced pressure (water aspirator, 12 mmHg) the solid was reacted with 5 mL (80 mmol) of methyl iodide (Merck) in 400 mL of refluxing acetone for 60 h in a brown-colored, round-bottom flask. The overall yield of 3 was 32 g (70%). Crystallization from acetone gave yellow crystals: mp 85.0–86.0 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85 (6 H, triplet, $J \approx 5$ Hz), 1.30 (56 H, multiplet), 4.40 (4 H, triplet, $J \approx 7$ Hz), 5.05 (3 H, singlet), 9.20 (1 H, triplet, $J < 2$ Hz), 10.00 (2 H, doublet, $J < 2$ Hz). Anal. Calcd for $C_{40}H_{72}NO_4I$ (mol wt 757.92): C, 63.39; H, 9.58; N, 1.85; I, 16.74. Found: C, 63.50; H, 9.62; N, 1.67; I, 16.41.

4-n-Nonylpyridinium Hydrochloride (4). Extension of the 4-methyl substituent in 4-methylpyridine to an *n*-nonyl hydrocarbon chain was carried out as described for 1 by using 1-bromo-*n*-octane (Merck) as the reagent. The reaction was carried out on a 0.16-mol scale. To a stirred solution of crude 4-*n*-nonylpyridine in 180 mL of diethyl ether was added 32 mL of 32% (by weight) of hydrogen chloride (0.32 mol, Merck). After the addition was complete the solution was stirred for another 15 min. When the solution was cooled to −20 °C, the product precipitated. The overall yield of 4 was 23.2 g (60%). Crystallization from acetone gave white crystals: mp 119.1–119.8 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (3 H, triplet, $J \approx 6$ Hz), 1.30 (14 H, multiplet), 3.00 (2 H, triplet, $J \approx 8$ Hz), 8.0–9.05 (4 H, multiplet), 17.0 (1 H, singlet broad). Anal. Calcd for $C_{14}H_{24}NCl$ (mol wt 241.81): C, 69.54; H, 10.00; N, 5.79; Cl, 14.66. Found: C, 69.21; H, 9.97; N, 5.72; Cl, 14.46.

4-n-Dodecylpyridinium Hydrochloride (5). The preparation of 4-*n*-dodecylpyridine has been described as part

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of the preparation of 1. Acidification of the crude product was carried out as described for 4. The reaction was carried out on a 0.16-mol scale. The overall yield of 5 was 29.5 g (65%). Crystallization from acetone gave white crystals: mp 123.4–124.6 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85 (3 H, triplet, $J \approx 6$ Hz), 1.30 (20 H, multiplet), 2.95 (2 H, triplet, $J \approx 8$ Hz), 7.85–8.95 (4 H, multiplet), >10.0 (1 H, singlet broad). Anal. Calcd for $C_{17}H_{30}NCl$ (mol wt 283.89): C, 71.93; H, 10.65; N, 4.93; Cl, 12.49. Found: C, 71.95; H, 10.39; N, 4.81; Cl, 12.51.

4-n-Dodecylpyridinium Hydrobromide (*6*). The synthesis was carried out as described for 5. Instead of hydrogen chloride, a 47% (by weight) solution of hydrogen bromide in water (Lamers and Indemans) was used. The reaction was carried out on a 0.25-mol scale. The overall yield of 6 was 41.0 g (50%). Crystallization from acetone gave white crystals: mp 137.6–138.9 °C; ^1H NMR ($CDCl_3$, Me_4Si) similar to the ^1H NMR spectrum of 5. Anal. Calcd for $C_{17}H_{30}NBr$ (mol wt 328.34): C, 62.19; H, 9.21; N, 4.26; Br, 24.34. Found: C, 62.17; H, 9.22; N, 4.21; Br, 24.06.

4-n-Dodecylpyridinium Hydroiodide (*7*). The synthesis was carried out as described for 5. Instead of hydrogen chloride, a 67% (by weight) solution of hydrogen iodide in water (Merck) was used. The reaction was carried out on a 0.30-mol scale. The overall yield of 7 was 50 g (44%). Crystallization from acetone gave white crystals: mp 134.1–135.8 °C; ^1H NMR ($CDCl_3$, Me_4Si) similar to the ^1H NMR spectrum of 5. Anal. Calcd for $C_{17}H_{30}NI$ (mol wt 375.33): C, 54.40; H, 8.06; N, 3.73; I, 33.81. Found: C, 54.38; H, 8.14; N, 3.64; I, 33.93.

4-(12-Tricosyl)pyridinium Hydroiodide (*8*). The synthesis has been carried out following the procedure described for 2. Instead of 1-iodo-*n*-hexadecane, 1-bromo-*n*-undecane (Merck) was used as the reagent. The crude pyridine derivative was acidified with 67% (by weight) of an aqueous hydrogen iodide solution (Merck) as described for 4. The reaction was carried out on a 0.04-mol scale, starting from 4-*n*-dodecylpyridine. The overall yield of 8 was 6 g (28%). Crystallization from acetone gave a white crystalline solid: mp 92.0–92.4 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85 (6 H, triplet, $J \approx 6$ Hz), 1.30 (40 H, multiplet), 2.85 (1 H, quintet, $J < 2$ Hz, unresolved), 6.40 (1 H, singlet broad), 7.8–9.1 (4 H, multiplet). Anal. Calcd for $C_{28}H_{52}NI$ (mol wt 529.63): C, 63.49; H, 9.90; N, 2.64; I, 23.96. Found: C, 63.59; H, 9.99; N, 2.34; I, 23.98.

Amphiphiles 9–12 were quantitatively obtained by reaction of the corresponding analytically pure iodides with an excess of silver chloride (silver perchlorate) in 10% (by volume) ethanol–water at 70 °C. The precipitated silver iodide and an excess of silver chloride were filtered off and the solvent was removed under reduced pressure (water aspirator, 12 mmHg).

1-Methyl-4-dodecylpyridinium Chloride (*9*). Crystallization from acetone gave white crystals: mp 50.4–51.1 °C; ^1H NMR ($CDCl_3$, Me_4Si) similar to the spectrum of 1. Anal. Calcd for $C_{18}H_{32}NCl$ (mol wt 297.91): C, 72.57; H, 10.83; N, 4.70; Cl, 11.90. Found: C, 71.79; H, 10.86; N, 4.59; Cl, 11.77. The compound is strongly hygroscopic.

1-Methyl-4-dodecylpyridinium Perchlorate (*10*). Crystallization from acetone gave white crystals: mp 93.0–93.5 °C; ^1H NMR ($CDCl_3$, Me_4Si) similar to the spectrum of 1. Anal. Calcd for $C_{18}H_{32}NClO_4$ (mol wt 361.91): C, 59.74; H, 8.91; N, 3.87; Cl, 9.80. Found: C, 59.87; H, 8.85; N, 3.84; Cl, 9.55.

1-Methyl-4-(17-tritriacontyl)pyridinium Chloride (*11*). Crystallization from acetone afforded colorless crystals (mp 64.0 °C) which contained one molecule of water of crystallization: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (6 H, triplet, $J \approx 4$ Hz), 1.28 (60 H, multiplet), 2.8 (1 H, quintet, $J < 2$ Hz, unresolved), 4.75 (3 H, singlet), 7.7–9.5 (4 H, multiplet). A concentration-dependent water signal was observed at about δ 4.4. Anal. Calcd for $C_{39}H_{74}NCl \cdot H_2O$ (mol wt 610.50): C, 76.72; H, 12.55; Cl, 5.81. Found: C, 76.53; H, 12.42; Cl, 5.78.

TABLE II: Melting Points of Some Long-Chained Pyridinium Derivatives

compd	mp, °C	ΔH, kcal mol^{-1}
4	119.1–119.8	8.0
5	123.4–124.6	7.8
6	137.6–138.9	8.0
7	134.1–135.8	8.5
8	92.0–92.4	

1-Methyl-3,5-bis(n-hexadecyloxycarbonyl)pyridinium Chloride (*12*). Crystallization from acetone gave slightly yellow crystals: mp 102.0–102.5 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85 (6 H, triplet, $J \approx 5$ Hz), 1.30 (56 H, multiplet) 4.40 (4 H, triplet, $J \approx 7$ Hz), 5.03 (3 H, singlet), 9.20 (1 H, triplet, $J < 2$ Hz), 10.00 (2 H, doublet, $J < 2$ Hz). Anal. Calcd for $C_{40}H_{72}NO_4Cl$ (mol wt 666.47): C, 72.10; H, 10.88; Cl, 5.32. Found: C, 71.44; H, 10.84; Cl, 5.23.

Differential Scanning Calorimetry (*DSC*). DSC measurements have been carried out on a Perkin-Elmer DSC-2 apparatus, using sealed aluminum pans. The heating rate was 10 °C min^{-1}. The temperature scale was calibrated by using the known phase-transition temperatures as determined by hot-stage (optical) polarization microscopy. An additional check was carried out by using the melting point of *trans*-azobenzene (mp 68.5 °C). Calibration of the enthalpy change at the transition temperature was carried out according to the manufacturer's instructions. Indium was chosen for calibration ($\Delta H = 6.8$ cal g^{-1}).

Optical Polarization Microscopy. Optical studies of the various phases were carried out on a Leitz Ortho-plan-pol polarizing microscope, equipped with a Mettler FP52 hot stage, connected to a Mettler FP5 melting-point apparatus. The observed textures were photographed by using a Wild Photoautomat MPS 45.

X-Ray Diffraction Measurements. X-Ray diffraction patterns were photographically detected as a function of temperature by using a Guinier-Simon camera (Enraf-Nonius). The temperature was increased at a rate of 2–5 °C h^{-1}. The powdered samples were kept in Lindeman glass tubes of 0.3-mm diameter, while Co Kα1 radiation was used ($\lambda = 1.78892$ Å).

Results

The compounds with an N-protonated pyridinium core show a simple single phase transition from the solid state to an isotropic liquid (see Table II). On the other hand, in the case of an N-methylated pyridinium core, sometimes a rich polymorphism is observed, including solid–solid transitions and smectic phases. The results are summarized in Table III. For 8 no DSC measurements were performed, because no sufficient quantity of the compound was available for an accurate determination. Since from optical polarization microscopy no indication was obtained for liquid-crystalline behavior, no attempt was made to synthesize a new batch. Because perchlorates like 10 can easily explode, no DSC measurements were carried out on that amphiphile.

The identification of the smectic-A phases (L_α phases) in the case of 1 and 10 is already very likely from the simple focal-conic[9] and homeotropic textures (see Figure

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(9) See, for example: Demus, D.; Richter, L. "Textures of Liquid Crystals"; VEB Verlag: Leipzig, 1978.

TABLE III: Melting Points and Some Other Phase Transitions of Some Long-Chained 1-Methylpyridinium Derivatives

compd	mp,[a] °C	ΔH, kcal mol^{-1}	further phase transitions
9	50.4–51.1	10.6	
1	112.8–113.1	5.8	crystalline–crystalline: ~61 °C,[b] $\Delta H = 1.0$ kcal mol^{-1} smectic-A–isotropic: 148–153 °C, $\Delta H = 0.15$ kcal mol^{-1}
10	92.0–93.5		crystalline–crystalline: ~30, ~55, and ~70 °C[b] smectic-A–isotropic: 94.5–95.0 °C
11	64.0	13.6	
2	72.0	10.4	crystalline–crystalline: 66–67 °C,[b] $\Delta H = 0.14$ kcal mol^{-1} smectic-C–isotropic: 82–83 °C, $\Delta H = 0.23$ kcal mol^{-1}
12	102.0–102.5	9.0	
3	85.0–86.0[c]	10.2	crystalline–crystalline: ~53 °C,[b] $\Delta H = 0.35$ kcal mol^{-1} smectic-H–isotropic: 105–106 °C, $\Delta H = 4.4$ kcal mol^{-1}

[a] Temperatures determined by hot-stage optical (polarization) microscopy. [b] Determined from X-ray diffraction experiments. [c] A weak transition was observed at 93 °C ($\Delta H = 1.3$ kcal mol^{-1}) by DSC, which could not be substantiated by the other methods.

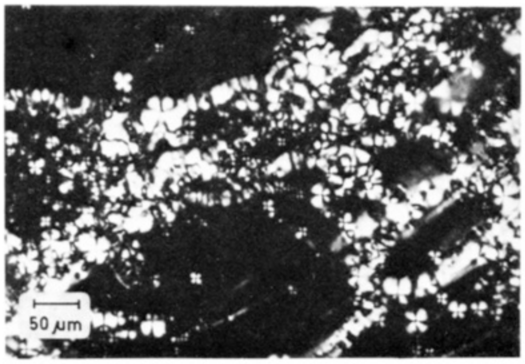

Figure 1. Homeotropic texture with some residual focal conics of a thin layer of **1** at 120 °C (crossed polarizers, initial magnification 100×).

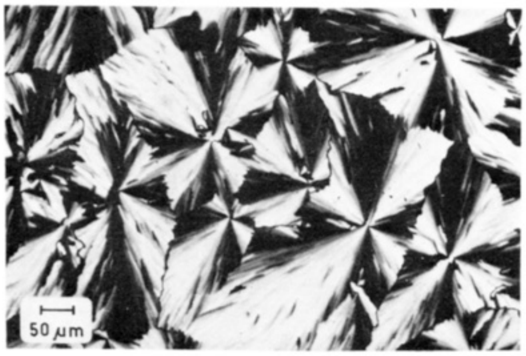

Figure 2. Focal-conic-like texture of a thin layer of **2** at 78 °C (crossed polarizers, initial magnification 70×).

1). In the case of **2** the assignment is slightly more complicated. Focal-conic-like textures are observed (Figure 2), but homeotropic textures are completely absent. In combination with the occurrence of schlierenlike textures,[9] this renders a tilted phase (smectic-C-like) very plausible.

The assignment to the class of smectic phases with liquid layers is confirmed by the X-ray results which show a single sharp reflection at low Bragg angles (001 reflection, corresponding to the layer spacing), and an additional diffuse reflection at larger angles (corresponding to the average lateral distance between the molecules within the smectic layers).[10] The layer distances are compared in Table IV with the length of a stretched molecule, as calculated from space-filling molecular models, not taking the counterion into account. Finally, the relatively small value of ΔH at the transition to the isotropic phase is also in agreement with smectic phases with liquid layers.

TABLE IV: Layer Spacings and Molecular Lengths of 1–3 and 10 in the Smectic State

compd	d_{001},[a] Å	l,[b] Å	compd	d_{001},[a] Å	l,[b] Å
1	29.0	23	2	30.0	28
10	29.5	23	3	38.1	28

[a] Layer spacing. [b] Molecular length as deduced from molecular models.

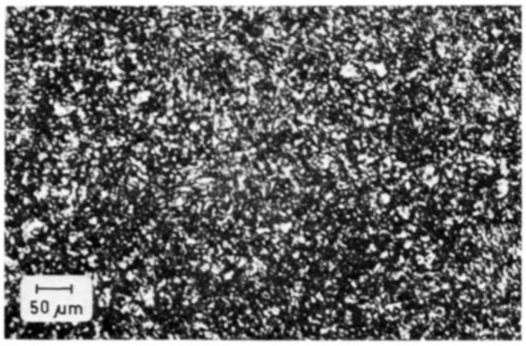

Figure 3. Smectic fine-grain texture of **3** at 100 °C (crossed polarizers, initial magnification 70×).

The high-temperature crystalline phases are rather waxy, and from their appearance under the microscope the presence of smectic phases with ordered layers could be possible. However, the X-ray diffraction patterns show only minor changes at the phase transitions, indicating true crystalline phases. This is in agreement with the relatively small ΔH values as compared with the melting transition.

The situation is rather different for the high-temperature phase of **3**. Here the microscope observation of fine-grain textures typical for a smectic phase with ordered layers (see Figure 3) is supported by the DSC and X-ray results. In the DSC the highest ΔH is found at the melting transition leading to this phase, while ΔH at the transition to the isotropic phase is somewhat higher than for smectics with liquid layers. The X-ray diffraction pattern shows a dramatic change at the transition solid smectic. Besides the 001 and two higher-order reflections, three relatively strong reflections at higher Bragg angles as well as several additional weaker reflections were recorded. It was possible, using a least-squares refinement procedure, to reconcile the positions of these reflections with a monoclinic lattice with the cell constants[11] $a = 8.63$ Å, $b = 4.79$ Å, $c = 51.8$ Å, and $\beta = 132.6°$. Assuming that no hitherto unknown smectic phase is involved, this leaves the possibility of the presence of a smectic-H phase[10,12] (tilted

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(10) Doucet, J. In "The Molecular Physics of Liquid Crystals"; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 14.

(11) A full list of observed and calculated Bragg reflections of **3** is available from the authors.

TABLE V: Lateral Dimensions of 1-3 and 10 in the Smectic State

compd	d', Å	A,[a] Å^2	compd	d', Å	A,[a] Å^2
1	4.15	19.9	2	4.56	24.0
10	4.71	25.6	3		15.2

[a] See text.

phase, but possessing a herringbone-like packing within the layers) or a smectic-G phase (tilted phase, but having a pseudohexagonal packing within the layers). Since several reflections hkl with $h + k = 2n + 1$ (n is integer) were observed, and since these reflections should be absent for a smectic-G phase, it is tentatively concluded that a smectic-H phase is the correct characterization of this liquid-crystalline state.

In the X-ray diffraction patterns of the smectic-A and smectic-C phases, an additional diffuse reflection was observed at larger angles. These angles correspond to the average lateral spacing between the hydrocarbon chains.[13] From the maximum of the reflection, an average repeat distance d' is obtained. Assuming a geometry consisting of close hexagonal packed cylinders, the average molecular spacing within a smectic layer is given by $2d'/\sqrt{3} \approx 1.155d'$. The distance d' and the average area available per alkyl chain are related by $A = 2(d')^2/\sqrt{3} \approx 1.155(d')^2$. For amphiphile **3** the area A was calculated from the cell constants of the monoclinic lattice. The obtained values for d' and A are listed in Table V.

Discussion

From the results listed in Tables II and III, it may be concluded that the structure of the head group plays a crucial role in determining the mesomorphic behavior. When the nitrogen in the pyridine ring is protonated or if the counterion is a chloride anion, no liquid-crystalline phases are observed. Perhaps the relatively high melting points of the protonated pyridinium compounds, as compared with those of the methylated compounds, should be invoked to explain this observation. The chloride anion could be unfavorable for liquid-crystalline behavior, because the smaller ionic radius, with respect to the iodide anion, could well lead to less shielding of the positive charges of the pyridinium rings and, therefore, to an increased electrostatic repulsion between the head groups.

Considering in somewhat more detail the smectic-A phase of **1** and **10**, we note that the observed layer spacing is about 1.25 times the estimated length of a fully stretched molecule (Table IV). Since in a smectic-A phase the director $\vec{n}$ is oriented parallel to the normal of the layer, some kind of bilayer structure must be invoked. From space-filling molecular models a longitudinal length of ca. 7 Å for a 1-methylpyridinium group was estimated. When this value is taken into account, together with the values reported in Table IV, a model with overlapping alkyl chains, as sketched in Figure 4, seems likely. Moreover, in this way a favorable packing is obtained if the counterion is positioned close to the pyridinium ring. From space-filling molecular models the lateral area occupied by a single 1-methylpyridinium head group is estimated to be 24 Å^2. For an iodide anion a value of 14.5 Å^2 was calculated, using a value of 2.15 Å for the van der Waals radius.[14] The total area occupied by head group and counterion (38.5 Å^2) corresponds nicely with the available area for twice a hydrocarbon chain (A = 39.8 Å^2, Table V). For the perchlorate anion an area of 25.6 Å^2 was calculated, using a value of 1.452 Å for the interatomic distance between chlorine and oxygen[15] and a van der Waals radius of 1.40 Å for the oxygen atom.[14] Combination of the areas of the head group and the perchlorate anion results in a value of 49.6 Å^2, which is in good agreement with the available area for twice a hydrocarbon chain area (A = 51.2 Å^2, Table V). As demanded by the symmetry of the smectic-A phase, the proposed structure is uniaxial.

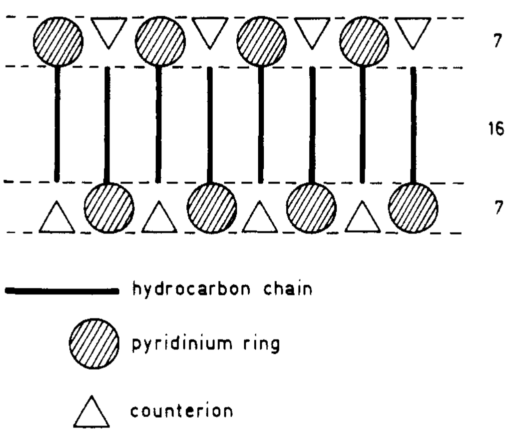

Figure 4. Schematic representation of the proposed bilayer structure of the orthogonal smectic phase of **1** and **10**.

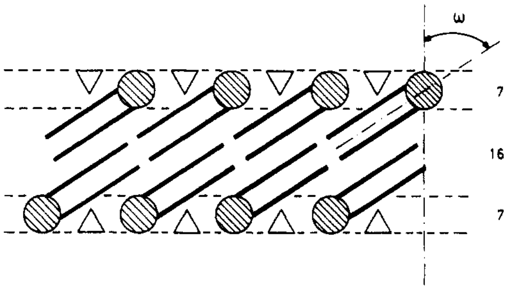

Figure 5. Schematic representation of the proposed bilayer structure for the tilted smectic phase of **2**. See Figure 4 for the meaning of the symbols.

For the tilted smectic phase (tentatively called smectic-C phase) observed for amphiphile **2**, an optimum packing can be obtained by placing the molecules in a bilayer structure without any overlap of the hydrocarbon chains. In this way a region of twice the area per alkyl chain (48.0 Å^2, Table V) is available for the head group and the counterion. As calculated before, the head group and the counterion need at least an area of 38.5 Å^2. When one takes into account the values reported for **2** in Table IV, the tilt angle of the director $\vec{n}$ in this smectic phase is calculated to be $\omega \approx 58°$. In Figure 5 a schematic representation of the proposed structure is given. The macroscopic biaxiality of the smectic-C phase arises from the long-range correlation of the tilt direction in the various layers.

From the cell constants obtained for the smectic-H phase of amphiphile **3**, it is concluded that two molecules are present in the elementary cell, since the observed value for c (51.8 Å) is about twice the estimated molecular length l (28 Å, Table IV). In this respect it is different from the usual smectic-H phases.[10] The proposed molecular ar-

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(12) We follow the nomenclature recommended by: Demus, D.; Goodby, J. W.; Gray, G. W.; Sackmann, H. In "Liquid Crystals of One- and Two-Dimensional Order"; Helfrich, W., Heppke, G., Eds.; Springer: West Berlin, 1980; p 31.

(13) See, for example, Leadbetter, A. J. In "The Molecular Physics of Liquid Crystals", Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 13.

(14) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 58th ed.; CRC Press: Cleveland, OH, 1977.

(15) Truter, M. R. *Acta Crystallogr.* **1961**, *14*, 318.

rangement in the smectic-H phase is as illustrated in the picture shown in Figure 5, except for the different location of the iodide counterion (vide infra). Combination of the observed layer spacing (d_{001} = 38.1 Å, Table IV) and l results in a calculated tilt angle of the director $\vec{n}$ of ω = 47°. This angle corresponds satisfactorily with the experimental value of $\omega = \beta - 90° = 42.6°$. The small value observed for the lateral area per alkyl chain (A = 15.2 Å^2, Table V) for **3**, as compared with the A values observed for the amphiphiles **1**, **2**, and **10**, is striking. From molecular models a lateral area for the head group of **3** can be estimated as ca. 17 Å^2 (per alkyl chain; the value depends somewhat on the orientation of the 3 and 5 substituents). This leaves no (lateral) area for the iodide counterion. Since the pyridinium nucleus in **3** is very electrophilic,[5] it is suggested that the iodide counterion will be located near the 4 position of the pyridinium ring, embedded in the hydrocarbon chains.

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Determination of Vapor Diffusion Coefficients in Zeolite by the Frequency Response Method

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A new method for determining vapor diffusion coefficients in micropores of zeolites is developed. In this method, the volume of a chamber containing a permeating gas together with the sorbent is varied sinusoidally with an amplitude by a few percent, after an equilibrium state is reached. The phase angle and amplitude of vapor *pressure* change induced are measured as a function of the frequency of the driving oscillations. Characteristic functions representing in-phase and out-of-phase components of the pressure variations are calculated analytically on the basis of Fick's law of diffusion in (i) a plane sheet and (ii) an isotropic sphere as models for one- and three-dimensional channels in zeolites, respectively. In order to confirm the utility of the new method, a krypton-over-sodium mordenite system at -20 °C, perhaps one of the simplest systems of zeolites, is investigated for angular velocities ranging from 1 to 100 rad/min. Results are in good agreement with the theoretical predictions derived from model i; the conclusion is that $(D/L^2) = 5.3 \times 10^{-3}$ s^{-1} at equilibrium pressures around 300 Pa, where D denotes the Fickian diffusivity, and L the length of the main channel of the synthetic mordenite. This method is expected to be of great value especially when different types of diffusion and/or adsorption occur simultaneously or when D is large and the inertia of a microbalance usually used in the standard method prevents reliable results.

Introduction

Molecular shape selective catalysis in intracrystalline space of siliceous zeolites has opened up a spectrum of new opportunities in catalytic science and industry.[1] Diffusional mass transport in zeolites is therefore an important process determining accessibility of reactants to catalyst "internal" surface.[2,3]

Diffusivity has usually been determined from sorption rates measured with a microbalance by matching the experimental data to an appropriate theoretical sorption curve based on Fick's law of diffusion.[4,5]

A frequency response method was applied by Evnochides and Henley[6] to simultaneous determination of the diffusion and solubility coefficients of a pure gas for a thin polymer film. The phase angle and amplitude of the *weight* changes were measured as a function of the frequency of a sinusoidal pressure variation of the gas. An electrobalance and a signal generator for low-frequency pressure variation were employed.

In the present method, the *pressure* response of a sorption system to sinusoidal volume variation is measured. Some theoretical preparation is required to interpret the experimental results.

Diffusion in zeolites with one- and three-dimensional channels is treated mathematically as diffusion in a plane sheet and in an isotropic sphere, respectively. To confirm the utility of the new method, actual data on a krypton-over-mordenite system are analyzed according to the theoretical procedure below.

Theoretical Section

Let us consider a case where a sorption system at equilibrium is perturbed by changing the equilibrium volume sinusoidally. The change may be described, using complex notation, by

$$V = V_e(1 - v e^{i\omega t}) \qquad (1)$$

where V_e denotes the mean volume, or the volume at the equilibrium,[7] v is the relative amplitude of the volume variation, and ω is the angular velocity of the sinusoidal generator. The perturbed vapor pressure P and the concentration c of a diffusing substance in a medium or a pore

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[1] Weisz, P. B. *Proc. Int. Congr. Catal., 7th* **1980**, *A*, 3.
[2] Venuto, P. B.; Landis, P. S. *Adv. Catal.* **1968**, *18*, 259.
[3] Riekert, L. *Adv. Catal.* **1970**, *21*, 281.
[4] Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974.
[5] Rabo, J. A., Ed. *ACS Monogr.* **1976**, *No. 171*.
[6] Evnochides, S. K.; Henley, E. J. *J. Polym. Sci., Part A-2* **1970**, *8*, 1987.

[7] The subscript e will indicate the mean value which is assumed to be identical with that at equilibrium.

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