

Novel Thermotropic Liquid Crystals without a Rigid Core Formed by Amphiphiles Having Phosphonium Ions

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Abstract: Thermotropic liquid-crystalline behavior of phosphonium salts, which are structurally simple amphiphiles with positively-charged phosphorus atoms and without rigid cores, was evaluated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffractometry. The phosphonium salts were found to show a smectic A (S_A) phase in which a homeotropic structure was formed spontaneously. It is significant that the phosphonium salts possess an advantageous feature as thermotropic liquid crystals and show a stable liquid-crystalline phase and a simple phase transition behavior in comparison with commonly available ammonium analogs. For example, dimethylditetradecylphosphonium chloride showed the highest S_A to isotropic (I) phase transition temperature (T_{SI} , 187 °C) and the S_A phase in the widest temperature range (119 °C on heating) among the cationic amphiphiles examined in the present study, while dimethylditetradecylammonium chloride with the same structure except the cationic part showed the lowest T_{SI} (70 °C) and the narrowest liquid-crystalline temperature range (22 °C on heating).

Introduction

Thermotropic liquid crystals have been widely used as active media in liquid-crystal display devices and spatial light modulators.¹ Typical thermotropic liquid crystals are usually composed of two major structural parts: an elongated rigid aromatic core and terminal flexible alkyl chains or polar groups.² Recently, novel families of thermotropic liquid crystals have been found in aromatic compounds which are based on strong noncovalent interactions to assemble the parts through a molecular recognition process.³ Several studies have been done on thermotropic liquid-crystalline behavior of aromatic compounds possessing cationic moieties such as quaternary ammonium and pyridinium derivatives.⁴ It has been found that introduction of positively-charged nitrogen atoms into a molecule results in formation and stabilization of the liquid-crystalline phases by the ionic interaction.^{4f,5}

Quaternary ammonium salts without rigid cores have been used extensively as a representative compound in self-assembled

synthetic membranes, which mainly have a hydrophilic part and double long alkyl tails as a hydrophobic part similarly to the phospholipid molecules.⁶ Such synthetic bilayer-forming amphiphiles are known to form spontaneously various aggregates in aqueous dispersion like liposomes from naturally-occurring phospholipids.⁶ In aqueous solutions, their lyotropic liquid-crystalline properties have been investigated in detail such as aggregate morphology and phase transition behavior.⁷ However, very few studies have been performed on the thermotropic liquid-crystalline behavior of cationic amphiphiles without rigid cores except some quaternary ammonium salts.⁸ In particular, lyotropic as well as thermotropic liquid-crystalline behavior of the phosphonium salts with positively-charged phosphorus atoms has not been explored so far.

Study on antimicrobial activity of organic cations has shown that phosphonium salts with double long alkyl chains are more active than quaternary ammonium salts with the same structure.⁹ Furthermore, we proposed a new concept for the mode of action of the cationic biocides. The antimicrobial activity of organic cations is ascribed essentially to the molecular organization of the organic cations within the aggregates in aqueous solution;¹⁰

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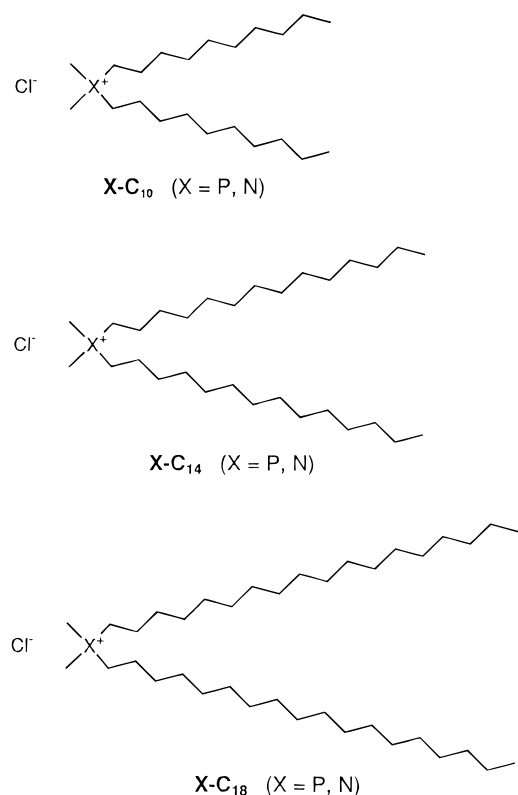
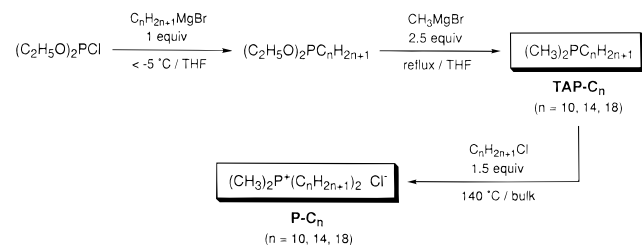


Figure 1. Chemical structures of dimethyl-substituted phosphonium and ammonium salts with double long alkyl chains used in this study.

Scheme 1



the activity is determined primarily by the aggregate morphology and the number of active molecules comprising the aggregates. On the basis of these results, it is assumed that the phosphonium salts possess a high ability of molecular organization in comparison with the quaternary ammonium analogs. Here we report thermotropic liquid-crystalline behavior of phosphonium salts which are structurally simple amphiphiles with positively-charged phosphorus atoms and without rigid aromatic rings.

Experimental Section

General Considerations. The chemical structures of the phosphonium salts (P-C₁₀, P-C₁₄, and P-C₁₈) and the quaternary ammonium salts (N-C₁₀, N-C₁₄, and N-C₁₈) used in the present study are shown in Figure 1. The phosphonium salts (P-C_n) were prepared through trialkylphosphine (TAP-C_n) from diethyl chlorophosphite ((C₂H₅O)₂-PCI) in three steps as shown in Scheme 1. The ammonium salts N-C₁₀ and N-C₁₈ are commercial products (Kei-Ai-Kasei and Tokyo Kasei, respectively), and N-C₁₄ was synthesized by the stepwise alkylation of secondary dimethylamine or the monoalkylation of tertiary alkyl-dimethylamine with primary halides.^{6b,8f,g}

The cationic amphiphiles P-C_n and N-C_n were purified by reprecipitation of the dichloromethane solution into a large excess of diethyl ether and recrystallization from ethyl acetate. The purification was repeated several times. The organic cations prepared were identified

Table 1. Microanalytical Data for the Phosphonium and the Ammonium Salts

compd	calcd (found) ^a (%)				purity (%) ^b
	C	H	N	Cl	
P-C ₁₀	69.71 (69.45)	12.76 (12.85)		9.35 (9.99)	99.5
P-C ₁₄	73.35 (72.98)	13.13 (13.33)		7.22 (7.77)	99.7
P-C ₁₈	75.63 (75.29)	13.36 (13.13)		5.87 (5.44)	99.4
N-C ₁₀	72.98 (72.75)	13.36 (13.55)	3.87 (3.75)	9.79 (9.57)	99.4
N-C ₁₄	75.97 (75.58)	13.60 (13.38)	2.96 (2.78)	7.47 (7.69)	99.5
N-C ₁₈	77.82 (77.60)	13.75 (13.59)	2.39 (2.26)	6.04 (6.39)	99.9

^a Determined by elemental analysis. ^b Estimated by nonsuppressor ion chromatography.

by means of ¹H-NMR spectroscopy (Hitachi R-600, 60 MHz) and fast atom bombardment mass spectrometry (FABMS; JEOL JMS-AX 505W) in which glycerol was used as the FAB matrix and the positive FAB ionization method (PI) was used at an accelerating voltage of 10 kV with Xe atom as the primary ion source. Their purities were examined by elemental analysis and high-performance liquid chromatography (HPLC; Shimadzu HIC-6A). The HPLC instrument operating at 40 °C was equipped with an analytical column for nonsuppressor ion chromatography (Shim-pack IC-C3, 4.6 mm i.d. × 100 mm) which shows superior separation for cations and a conductivity detector (Shimadzu CDD-6A; analytical conditions: polarity, negative; response, standard; gain, 1 μS cm⁻¹). A mixture of acetonitrile (HPLC grade) and 2.0 mM oxalic acid aqueous solution prepared with deionized water (1:1, v/v) was used as a mobile phase at a flow rate of 1.0 mL min⁻¹. Each compound was dissolved in acetonitrile (HPLC grade) so as to give the concentration of 500 μg mL⁻¹, and the sample solution of 20 μL was subjected to the HPLC measurements, in which tetrabutylphosphonium and tetrabutylammonium bromides (Tokyo Kasei; HPLC grade; purity 99.0%) were used as an internal standard substance to determine the purity of P-C_n and N-C_n, respectively. The area of an elution band in comparison with that of the standard was used for quantitative purposes since the conductivity of cationic amphiphiles is dependent only on the concentration of the cationic part, irrespective of the hydrophobic structure. The measurements were done in triplicate for the same sample, and the purity could be determined with an error of only ±0.2%.

The microanalytical data obtained are listed in Table 1. In all the compounds, the found values agreed with the calculated values within the experimental error. As listed in the last column of Table 1, all compounds showed a purity of above 99.4%, indicating that the compounds are of a high purity. Figure 2 shows a typical HPLC chromatogram of P-C₁₄ and N-C₁₄ without the internal standard substance. For each compound, only one peak was observed for the retention time of 8.5 and 8.8 min, which corresponds to the phosphonium and the ammonium ions, respectively. Furthermore, in the mass spectra obtained by the FABMS (PI), the parent cation of P-C_n and N-C_n, which was the highest in relative abundance for each sample, was observed and the other positive ions were absent except their fragment ions. These results demonstrate clearly that the cationic amphiphiles used in this study are free from impurities.

Evaluation of Thermotropic Liquid-Crystalline Behavior. The thermotropic liquid-crystalline behavior of the cationic amphiphiles was evaluated by differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C; heating and cooling rate 1 °C min⁻¹), polarizing optical microscopy (Olympus Model BH-2; Mettler FP82HT hot stage and Mettler FP90 central processor), and X-ray diffractometry (MAC Science MXP³, equipped with a thermal controller, model 5301).

The thermodynamic property for phase transition of P-C_n and N-C_n was explored by means of DSC. About 10 mg of the sample dried completely was placed in an aluminum sample pan and sealed. The sample pan was placed in the DSC cell compartment and cooled to about -20 °C. Measurements were carried out at a heating rate of 1.0 °C min⁻¹ up to 150–220 °C. The phase transition temperature was taken as a peak top, and the enthalpy change was determined from the peak area. To check reproducibility, the measurements were done in quadruplicate for the same sample. The reproducibility of the phase transition temperature and the enthalpy was ±0.3 °C and ±7 %, respectively. The entropy change was calculated by assuming that the

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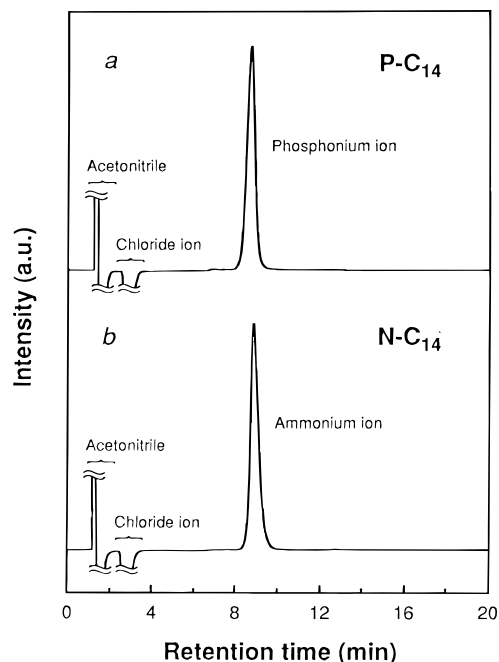


Figure 2. HPLC chromatograms of the phosphonium and the ammonium ions obtained by nonsuppressor ion chromatography: (a) **P-C₁₄**; (b) **N-C₁₄**.

Table 2. Thermodynamic Characterization for Phase Transition of the Phosphonium and the Ammonium Salts^a

compd	K → S _A ^b			S _A → I ^c			T _{decom} ^d (°C)
	T _{KS} (°C)	ΔH _{KS} (kJ mol ⁻¹)	ΔS _{KS} (J K ⁻¹ mol ⁻¹)	T _{SI} (°C)	ΔH _{SI} (kJ mol ⁻¹)	ΔS _{SI} (J K ⁻¹ mol ⁻¹)	
P-C₁₀	38	39	126	155	2.9	6.8	367
P-C₁₄	68	70	205	187	5.6	13	366
P-C₁₈	82	57	160	145	2.4	5.8	362
N-C₁₀	59	9.1	28	94	1.7	4.7	198
N-C₁₄	48	11 ^e	33 ^e	70	4.7 ^f	13 ^f	194
N-C₁₈	85	22	61	122	0.65	1.6	201

^a T_{KS} and T_{SI}, phase transition temperature; ΔH_{KS} and ΔH_{SI}, enthalpy change; ΔS_{KS} and ΔS_{SI}, entropy change. ^b Crystalline (K) to smectic A (S_A) phase transition. ^c Smectic A (S_A) to isotropic (I) phase transition. ^d Decomposition temperature at which 10% weight loss occurred, recorded by TG at a heating rate of 10 °C min⁻¹ in N₂. ^e Estimated from the major peak except the unresolved peak. ^f The base line for calculation of heat of transition was taken as the straight line joining the points of inflexion of both ends of the endothermic peak.

transition is sufficiently reversible. The thermotropic phase transition behavior on heating for each sample is summarized in Table 2.

In addition, to determine the decomposition temperature of the organic cations, thermogravimetry (TG) was conducted with a Seiko I&E TG/DTA220 coupled with a Seiko I&E SDM/5600 thermal analysis station. Experiments were carried out on about 10 mg samples heated in flowing nitrogen (200 mL min⁻¹) at a heating rate of 10 °C min⁻¹. The decomposition temperature was defined as the temperature at which 10% weight loss was recorded by TG. The values estimated are shown in the last column of Table 2.

The X-ray measurements for molecular alignment of the cationic amphiphiles in a liquid-crystalline phase were performed using Cu Kα1 radiation from a 1.6 kW anode X-ray generator at the temperature at which the samples show the liquid-crystalline phase (the series of **P-C_n**, 120 °C; **N-C₁₀**, 70 °C; **N-C₁₄**, 60 °C; **N-C₁₈**, 100 °C). The structural parameters for the liquid-crystalline phase of the samples are listed in Table 3.

Preparation. Diethyl chlorophosphite as a starting material was supplied by Nippon Kagaku Kogyo and used without further purification. Decyl bromide, tetradecyl bromide, octadecyl bromide, and their chlorides (Tokyo Kasei) were purified by distillation under reduced

Table 3. X-ray Diffraction Data for the Phosphonium and the Ammonium Salts^a

compd	dv (Å) ^b	l (Å) ^c	d ₁ (Å) ^d	a (Å ²) ^e
P-C₁₀	21.2	11.1	4.55	20.7
P-C₁₄	28.1	14.8	4.96	24.6
P-C₁₈	35.6	18.5	4.93	24.3
N-C₁₀	23.7	10.8	4.43	19.7
N-C₁₄	28.0	14.4	4.69	22.0
N-C₁₈	35.3	18.1	4.67	21.8

^a Structural parameters for the S_A phase. Temperature: the series of **P-C_n**, 120 °C; **N-C₁₀**, 70 °C; **N-C₁₄**, 60 °C; **N-C₁₈**, 100 °C. ^b Vertical layer spacing. ^c Molecular length calculated for a completely extended chain. ^d Average lateral distance between the polar headgroups. ^e Average lateral area occupied by a single onium cation.

pressure. Magnesium powder and methylmagnesium bromide (Kodak and Aldrich, respectively) were used without purification. Where possible, all reactions, including oxidations and quaternizations, were carried out under nitrogen in a well-ventilated hood. The trialkylphosphines **TAP-C_n** were characterized by ¹H-NMR spectroscopy (Hitachi R-600, 60 MHz) and electron ionization mass spectrometry (EIMS; JEOL JMS-AX 505W). Elemental analysis of **TAP-C_n** could not be performed using a conventional method because they were oxidized rapidly in air.

Decyldimethylphosphine (TAP-C₁₀). Decyl bromide (44.2 g, 0.20 mol) was slowly added to magnesium powder (4.86 g, 0.20 mol) in 100 mL of tetrahydrofuran (THF) with an iodine crystal under an atmosphere of nitrogen. After 2 h of heating and complete disappearance of magnesium, diethyl chlorophosphite (31.3 g, 0.20 mol) was added to a vigorously stirred reaction mixture below -5 °C. The mixture was warmed immediately to room temperature and stirred for 1 h. Methylmagnesium bromide (59.6 g, 0.50 mol) in THF (250 mL) was added dropwise to the refluxing reaction mixture over a period of 1 h, and then the mixture was refluxed with stirring for 5 h. To complete the reaction, about 200 mL of THF was removed from the reaction mixture, and then the mixture was stirred again under reflux for 2 h. The reaction was quenched by the addition of water (1000 mL), and the precipitated magnesium salt was filtered off. The product was extracted three times with dichloromethane (200 mL) from the filtrate. The extracts were washed several times with water and evaporated to dryness. The crude product was purified by distillation under reduced pressure to give **TAP-C₁₀** (24.6 g) in 61% yield. Bp: 87 °C at 1 mmHg; ¹H-NMR (CDCl₃): δ 0.7–1.1 (m, 9H, (CH₃)₂P(CH₂)₉CH₃), 1.1–1.8 (m, 18H, (CH₃)₂P(CH₂)₉CH₃). EIMS: m/e 202 (M).

Dimethyltetradecylphosphine (TAP-C₁₄). **TAP-C₁₄** was obtained from tetradecyl bromide (55.5 g, 0.20 mol), magnesium powder (4.86 g, 0.20 mol), diethyl chlorophosphite (31.3 g, 0.20 mol), and methylmagnesium bromide (59.6 g, 0.50 mol) similarly to **TAP-C₁₀** (36.2 g) in 70% yield. Bp: 103–105 °C at 0.15 mmHg. ¹H-NMR (CDCl₃): δ 0.7–1.1 (m, 9H, (CH₃)₂P(CH₂)₁₃CH₃), 1.1–1.7 (m, 26H, (CH₃)₂P(CH₂)₁₃CH₃). EIMS: m/e 258 (M).

Dimethyloctadecylphosphine (TAP-C₁₈). The title compound was prepared from octadecyl bromide (66.7 g, 0.20 mol), magnesium powder (4.86 g, 0.20 mol), diethyl chlorophosphite (31.3 g, 0.20 mol), and methylmagnesium bromide (59.6 g, 0.50 mol) similarly to **TAP-C₁₀** (39.0 g) in 62% yield. Bp: 182 °C at 2 mmHg. ¹H-NMR (CDCl₃): δ 0.7–1.1 (m, 9H, (CH₃)₂P(CH₂)₁₇CH₃), 1.1–1.8 (m, 34H, (CH₃)₂P(CH₂)₁₇CH₃). EIMS: m/e 314 (M).

Dicycylmethylphosphonium Chloride (P-C₁₀).⁹ The reaction of decyl chloride (1.53 g, 8.66 mmol) with **TAP-C₁₀** (1.17 g, 5.78 mmol) was carried out in the absence of solvent at 140 °C for 24 h under an atmosphere of nitrogen. The product was dissolved in acetonitrile, washed several times with *n*-hexane, and evaporated to dryness. The product was dried under vacuum and then purified by reprecipitation of the dichloromethane solution into a large excess of diethyl ether and recrystallization from ethyl acetate (1.77 g) in 81% yield. ¹H-NMR (CDCl₃): δ 0.7–1.1 (br, 6H, PCH₂(CH₂)₈CH₃), 1.1–1.7 (m, 32H, PCH₂(CH₂)₈CH₃), 2.18 (d, 6H, J = 14.0 Hz, P(CH₃)₂), 2.4–2.7 (m, 4H, PCH₂(CH₂)₈CH₃). FABMS (PI): m/e 343 (C₂₂H₄₈P⁺).

Dimethylditetradecylphosphonium Chloride (P-C₁₄).⁹ The title compound was prepared similarly to **P-C₁₀** in 58% yield. ¹H-NMR

(CDCl₃): δ 0.8–1.1 (br, 6H, PCH₂(CH₂)₁₂CH₃), 1.1–1.7 (m, 48H, PCH₂(CH₂)₁₂CH₃), 2.18 (d, 6H, $J = 14.0$ Hz, P(CH₃)₂), 2.4–2.7 (m, 4H, PCH₂(CH₂)₁₂CH₃). FABMS (PI): m/e 455 (C₃₀H₆₄P⁺).

Dimethyloctadecylphosphonium Chloride (P-C₁₈).⁹ P-C₁₈ was synthesized similarly to P-C₁₀ in 12% yield. ¹H-NMR (CDCl₃): δ 0.8–1.1 (br, 6H, PCH₂(CH₂)₁₆CH₃), 1.1–1.7 (m, 64H, PCH₂(CH₂)₁₆CH₃), 2.18 (d, 6H, $J = 14.0$ Hz, P(CH₃)₂), 2.4–2.7 (m, 4H, PCH₂(CH₂)₁₆CH₃). FABMS (PI): m/e 567 (C₃₈H₈₀P⁺).

Results and Discussion

Synthesis of TAP-C_n. In general, the molecular design of phosphonium salts is difficult in comparison with that of quaternary ammonium salts, resulting from much less availability of phosphines as starting materials. To prepare the phosphonium salts with double long alkyl chains which possess the same structure as the common quaternary ammonium salts having the thermotropic liquid-crystalline property, a simple synthetic route of alkyldimethylphosphines (TAP-C_n) with a long alkyl chain as starting materials is to be established. Generally, the trialkylphosphines with different linear alkyl chains can be derived from alkyl-substituted phosphorus chlorides (e.g., R₂PCl₂ and R₂PCl) and phosphine derivatives (e.g., RPH₂ and R₂PH).¹¹ These methods, however, are tedious and result in poor overall yields, or require starting materials that are not readily available or are difficult to handle. Therefore, in this study, we used the diethyl chlorophosphite ((C₂H₅O)₂-PCl) as the starting material which is commercially available and synthesized the alkyldimethylphosphines (TAP-C_n) successfully in two steps by the Grignard method with relatively high yields without side reactions.

In the first step, the intermediates ((C₂H₅O)₂PC_nH_{2n+1}) were prepared from diethyl chlorophosphite with 1 equiv of alkylmagnesium bromide below –5 °C in THF. The overall reaction was rapid and quite exothermic; therefore, freezing the reaction mixture was necessary to maintain a temperature well below –5 °C. It was found by gas chromatographic analysis of the samples which were freed of alkylmagnesium bromide that the reaction was appreciably fast. Furthermore, it was observed by the gas chromatographic analysis that the intermediates ((C₂H₅O)₂PC_nH_{2n+1}) could be obtained quantitatively without side reactions.

In this reaction, the intermediates ((C₂H₅O)₂PC_nH_{2n+1}) could not be isolated from the reaction mixture, being subjected to the second step. Methylmagnesium bromide (2.5 equiv) was used to prepare the dimethyl-substituted tertiary phosphines. This reaction proceeded rather slowly without the occurrence of fast and exothermic processes. The intermediates ((C₂H₅O)₂-PC_nH_{2n+1}) converted to alkyldimethylphosphines (TAP-C_n) where conversion was in the range of 75–85% (estimated by gas chromatographic analysis). The conversion did not depend on the chain length of the substituent. In other words, the steric factor did not disturb the production of the alkyldimethylphosphines. TAP-C_n were finally obtained in 61–70% total yields. Low yields seem to be attributed to isolation and distillation techniques, because TAP-C_n readily converted to phosphine oxides in contact with air and the distillation was difficult because of high boiling points.

Thermodynamic Property of Phosphonium Salts. All the compounds used in this study exhibited the smectic A (S_A) phase. Figures 3 and 4 show typical DSC thermograms observed for the phosphonium salt and the corresponding quaternary ammonium salt, respectively. For the series of the phosphonium salts (P-C_n), we observed clearly two endothermic events on heating (see Figure 3): one is due to melting which

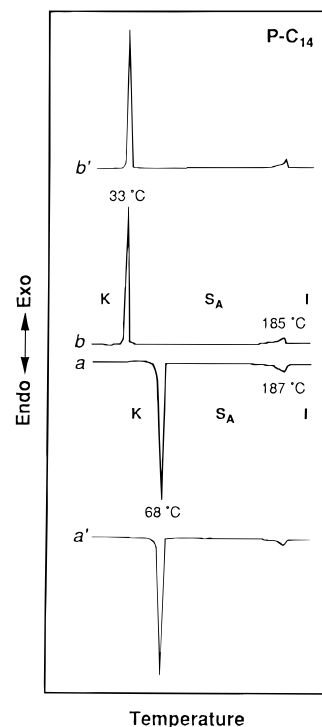


Figure 3. DSC thermograms observed for the phosphonium salt P-C₁₄: (a) second heating scan; (b), second cooling scan; (a') third heating scan; (b') third cooling scan. Abbreviations: K, crystalline; S_A, smectic phase; I, isotropic phase.

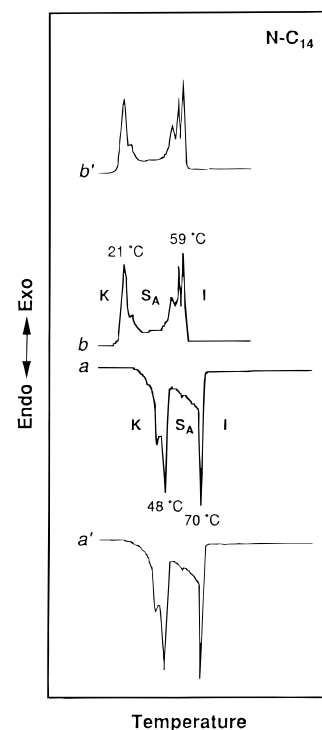


Figure 4. DSC thermograms observed for the ammonium salt N-C₁₄: (a) second heating scan; (b) second cooling scan; (a') third heating scan; (b') third cooling scan. Abbreviations: K, crystalline; S_A, smectic phase; I, isotropic phase.

corresponds to the crystalline (K) to S_A phase transition (T_{KS}), and the other corresponds to the S_A to isotropic (I) phase transition (T_{SI}). As shown in Table 2, in spite of the amphiphiles without rigid cores, the phosphonium salts exhibited a high T_{SI} (145–187 °C). In addition, the phosphonium salt P-C₁₀ showed the S_A phase in the considerably wide temperature range from

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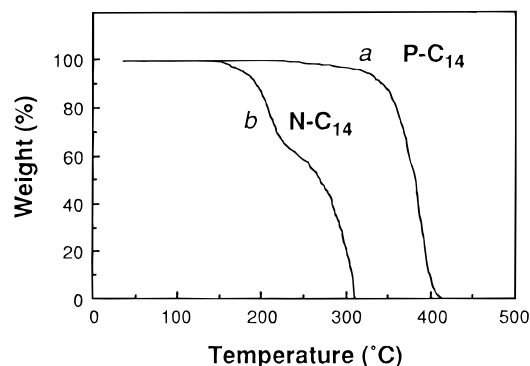


Figure 5. TG thermograms of compounds with different heteroatoms at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere: (a) **P-C₁₄**; (b) **N-C₁₄**.

38 to $155\text{ }^{\circ}\text{C}$. A similar trend was observed for the compounds **P-C₁₄** and **P-C₁₈**. The entropy change (ΔS_{SI}) at the S_{A} to I phase transition for the compounds **P-C₁₀**, **P-C₁₄**, and **P-C₁₈** was 6.8, 13, and $5.8\text{ J K}^{-1}\text{ mol}^{-1}$, respectively. These results clearly indicate that the phosphonium salts show a stable liquid-crystalline phase and a simple phase transition behavior. In particular, the compound **P-C₁₄** with double tetradecyl groups exhibited the most stable liquid-crystalline phases as evidenced by the highest T_{SI} ($187\text{ }^{\circ}\text{C}$), the widest temperature range of S_{A} phases ($119\text{ }^{\circ}\text{C}$), and the highest values of ΔS_{SI} ($13\text{ J K}^{-1}\text{ mol}^{-1}$) among the compounds examined.

In contrast to the phosphonium salts, the ammonium salts with the same hydrophobic structure showed an indistinct or multiple phase transition behavior. For example, in the DSC thermogram obtained for the ammonium salt **N-C₁₄**, both $\text{K} \rightarrow S_{\text{A}}$ and $S_{\text{A}} \rightarrow \text{I}$ phase transitions occurred with a change in baseline which shifted with temperature toward the endothermic direction, indicating a change in the heat capacity (Figure 4). The peak shapes were also more complicated than those of the corresponding phosphonium salt: two endothermic peaks ($\text{K} \rightarrow S_{\text{A}}$, on heating) and three exothermic peaks ($\text{I} \rightarrow S_{\text{A}}$, on cooling) were observed. These DSC peaks except the main peak could be attributed to the $\text{K} \rightarrow \text{K}$ and the $\text{S} \rightarrow \text{S}$ phase transitions. Such complicated phase transition behavior was observed only when the sample was heated slowly ($1.0\text{ }^{\circ}\text{C min}^{-1}$). When the ammonium salt **N-C₁₄** was subjected to the DSC analysis at a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$, DSC thermograms showed only two peaks corresponding to T_{KS} and T_{SI} on heating and cooling, and no multiple phase transition was observed. It was revealed that the phase transition behavior of the ammonium salts is affected by the heating and the cooling rates. In many studies on the phase transition behavior of the ionic thermotropic liquid crystals, the DSC measurements have been performed at a scanning rate of 10 or $5\text{ }^{\circ}\text{C min}^{-1}$. However, to evaluate strictly the thermal property of the ammonium salts, it may be necessary to perform the DSC analysis at a considerably low scanning rate.

Here, we need discussion if the indistinct phase transition of **N-C₁₄** is ascribed to the intrinsic thermal property. It was assumed that, during repeated heating scans, accumulation of the impurity produced by thermal decomposition resulted in changes in the phase transition behavior. This is unfavorable for the precise evaluation of the phase transition behavior. By comparing the DSC thermograms on the second and the third scans shown in Figure 4, it is apparent that the thermograms on the second heating and cooling are the same as those on the third heating and cooling. In addition, as shown in Figure 5, thermal decomposition of the ammonium salt **N-C₁₄** began at above $155\text{ }^{\circ}\text{C}$ which was higher than the upper temperature limit

($150\text{ }^{\circ}\text{C}$) in the DSC measurements. These results demonstrate that the ammonium salt does not decompose on heating under the present DSC analytical conditions. Although the influence of the impurity contained slightly in the virgin sample ($<0.6\%$) on the thermal property is not understood exactly, it may be concluded at the present stage that the multiple phase transition of the ammonium salts is not due to the thermal decomposition, but due to their intrinsic property. Practically, the similar $\text{K} \rightarrow \text{K}$ phase transition (or solid–solid transition) before melting into the liquid-crystalline phase was observed also for the amphiphilic thermotropic liquid crystals such as quaternary ammonium salts,⁸ pyridinium salts,¹² and sodium salts of carboxylic acids.¹³ Furthermore, it was found that the T_{SI} and the liquid-crystalline temperature range of the ammonium salts was much lower and narrower than those of the phosphonium salts as shown in Table 2. From the TG analyses, the phosphonium salts were found also to be more heat resistant than the ammonium salts (see Table 2 and Figure 5).

It is worth mentioning here that the most significant difference in the thermotropic liquid-crystalline behavior between the phosphonium salts and the quaternary ammonium salts was observed for the analogs **P-C₁₄** and **N-C₁₄** with an alkyl tail of 14 carbon atoms. As described above, the phosphonium salt **P-C₁₄** showed the highest T_{SI} ($187\text{ }^{\circ}\text{C}$) and the widest temperature range of S_{A} phases ($119\text{ }^{\circ}\text{C}$ on heating) among all the compounds examined, while the quaternary ammonium salt **N-C₁₄** showed the lowest T_{SI} ($70\text{ }^{\circ}\text{C}$) and the narrowest liquid-crystalline temperature range ($22\text{ }^{\circ}\text{C}$ on heating). The origin of the superior liquid-crystalline behavior of the phosphonium salts is not well understood at the present stage of research; however, it is at least true that the positively-charged phosphorus atoms play an important role in the formation of the liquid-crystalline phases and enhancement of the thermal stability of the liquid-crystalline phases.

Molecular Alignment Behavior in Liquid-Crystalline Phase. The molecular alignment behavior of the phosphonium salts was explored at first by means of polarizing optical microscopy. Figure 6 shows the optical textures of the compound **P-C₁₄** observed in the sandwiched glass cell. The dark region found in Figure 6a indicates that a homeotropic structure was formed spontaneously. When the sample was heated to a temperature higher than T_{SI} of the sample and then gradually cooled to a temperature below T_{SI} , the uniform homeotropic state was achieved in which the optical texture was not observed. Application of a shearing stress to the glass cell resulted in appearance of the smectic layers in which the conformational freedom of the long alkyl chains is enhanced (Figure 6b). These results indicate that the phosphonium salts show the smectic layers in which homeotropic structures are formed spontaneously.

The quaternary ammonium and the pyridinium amphiphiles are known to show a smectic or smectic-like character which results from the chain-melting of the hydrophobic moieties.^{8a,c,e,12,14} In such liquid-crystalline phases, even after the alkyl chains have melted, the ionic bonding between a polar head and counteranions remains unchanged and free molecular motion of the amphiphiles is prevented by the rigidity of the ionic layers owing

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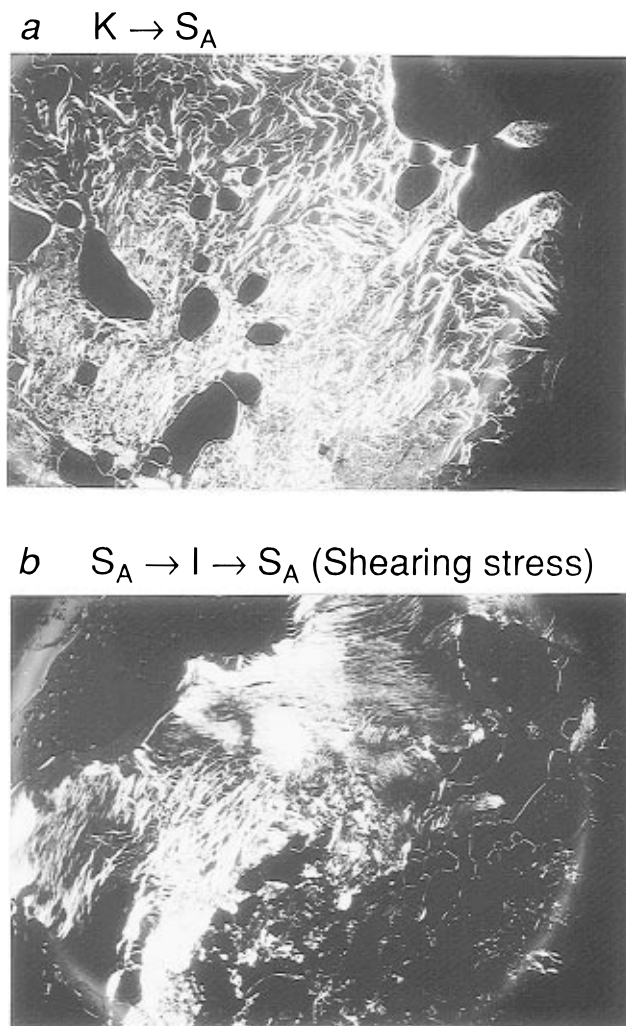


Figure 6. Optical textures observed for the phosphonium salt **P-C₁₄** under crossed polarizers: (a) homeotropic alignment (dark region) at 120 °C after heating from the crystalline to liquid-crystalline phase; (b) texture obtained on application of shearing stress at 120 °C after cooling from the isotropic to liquid-crystalline phase.

to the ionic interaction between polar heads. The ionic aggregation of the organic cations contributes to the formation of the smectic layer structure. The phosphonium salts as cationic amphiphiles were also assumed to show the smectic character. This prediction was verified by the X-ray diffraction analysis (Table 3). The X-ray diffraction patterns observed for the phosphonium salts are shown in Figure 7. The smectic layer spacing calculated from the diffraction angle was 21.2, 28.1, and 35.6 Å for **P-C₁₀**, **P-C₁₄**, and **P-C₁₈**, respectively. The calculated molecular length in their most extended configuration was 11.1, 14.8, and 18.5 Å for **P-C₁₀**, **P-C₁₄**, and **P-C₁₈**, respectively, when the counteranion was not taken into account. The layer thickness determined by the X-ray measurement corresponds roughly to a 2-fold molecular length of each phosphonium salt. These results, therefore, suggest the packing model proposed in Figure 7, in which the phosphonium salts form a bilayer structure in the S_A phase. A similar result was observed for the ammonium analogs, and there was no difference in the molecular arrangement for the S_A phase between the phosphonium and the ammonium salts (see Table 3). This is evident also from the fact that the values of ΔS_{SI} of the ammonium salts were on the same order as those of the phosphonium salts.

In Figure 7, the broad X-ray diffraction peaks were observed in the high-angle region, which contains information on the

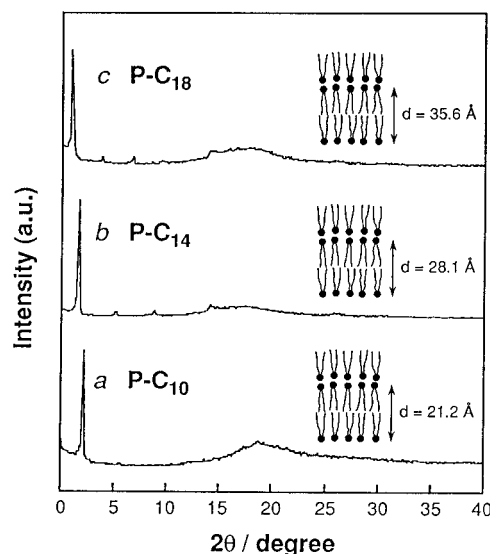


Figure 7. X-ray diffraction pattern measured at 120 °C and schematic illustration of molecular arrangement in the smectic A phase of the phosphonium salts: (a) **P-C₁₀**; (b) **P-C₁₄**; (c) **P-C₁₈**; (●) dimethylphosphonium; (~) alkyl chain.

internal order within a layer. Although the shapes of the broad high-angle diffraction peaks were slightly different among the samples, we estimated the average lateral area occupied by a single phosphonium cation from the diffraction angle which was taken as the peak top. The average distance between the P^+ groups was 4.55, 4.96, and 4.93 Å for **P-C₁₀**, **P-C₁₄**, and **P-C₁₈**, respectively. Thus, the occupied area per polar headgroup was found to be 20.7, 24.6, and 24.3 Å² molecule⁻¹ for **P-C₁₀**, **P-C₁₄**, and **P-C₁₈**, respectively, which was calculated on the basis of the simplest molecular arrangement (square array model). These order-of-magnitude calculations allow us to explore the relationship between the internal structure of the phosphonium ions within a smectic layer and their thermotropic liquid-crystalline behavior. The values of the occupied area or the lateral molecular spacing described above were approximately the same not only as those of **N-C_n**, but also as those of the ionic thermotropic liquid crystals showing smectic character such as quaternary ammonium salts,^{8c} pyridinium salts,^{5a,12a,b} and metal salts of carboxylic acids,¹⁵ as reported previously. Unfortunately, the superior liquid-crystalline property of the phosphonium salts cannot be interpreted in terms of the occupied area of a molecule in the liquid-crystalline phase.

Conclusions

The phosphonium salts, which are structurally simple amphiphiles with positively-charged phosphorus atoms and without rigid cores, showed a stable liquid-crystalline phase and a simple phase transition behavior in comparison with the ammonium analogs. These phase structures are characterized as smectic A in which a homeotropic structure is formed spontaneously. The emergence of phosphonium ions possessing an advantageous feature as thermotropic liquid crystals has generated a considerable interest and stimulated the research on the formation of supramolecular assembly including a liquid crystal.

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