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Multifunctional tetracoordinate phosphorus species with high self-organizing ability

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Contents

Abstract

The unique features of the phosphonium salts as functional materials are reviewed, with emphasis being placed on the comparison between the phosphonium salts and the commonly available quaternary ammonium salts, which have the same structure, differing only in the positively-charged heteroatom. The antimicrobial activity of onium salts with different long-chain segments is described with special reference to structure–activity relationships. The unexpected relationship between the antibacterial activity and the aggregation behavior in aqueous solution (i.e. lyotropic liquid-crystalline properties) was revealed through systematic studies on the antibacterial activity of the phosphonium salts as a novel class of cationic biocides. Furthermore, it is shown that the phosphonium salts can act as thermotropic liquid crystals in spite of the fact that they are amphiphiles without a rigid core. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphonium salts; Cationic amphiphiles; Antimicrobial activity; Self-organizing properties; Lyotropic liquid crystals; Thermotropic liquid crystals

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1. Introduction

Organic cations such as quaternary ammonium and phosphonium salts, which possess tetrahedral coordination about the positively-charged N and P atoms respectively, are used in many fields of science ranging from coordination chemistry to supramolecular chemistry. Use of the amphiphilic ammonium salts as cationic surfactants, having relatively long alkyl segments, is particularly important in practical applications because they can act as phase-transfer catalysts, antistatic agents, ion exchangers, curing agents, detergents and so on. In contrast to the quaternary ammonium salts, very few studies have been performed so far on the functional properties of the phosphonium salts which are another class of cationic amphiphiles. This is probably due to the fact that molecular design of the phosphonium salts is difficult in comparison with nitrogen compounds, because trivalent phosphorus derivatives as starting materials are problomatic to handle and their preparation is difficult. Such problems have evidently depressed the research activity on the phosphonium salts as functionalized materials. In this review, we refer to multifunctional properties of several phosphonium salts with alkyl chains of varying length from the viewpoint of their molecular structure and molecular organization.

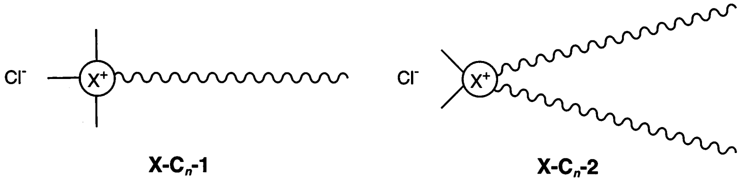
2. Antimicrobial activity of phosphonium amphiphiles

Many studies have been carried out on the antimicrobial activity of cationic biocides. The cationic biocides, whose target sites are the cytoplasmic membranes of microbes, kill microbial cells thus exhibiting bactericidal action [1–4]. They have occupied an important place in the field of external disinfectants as membrane-disrupting antimicrobial agents. In particular, quaternary ammonium salts are representative of this type, and they have been extensively used as potent growth-inhibitors of microorganisms in agriculture, the food processing industry, clinics and so on. Such disinfectants contain common structural features of a positive charge and a fairly hydrophobic section within a single molecule. In most of them, a long alkyl chain is covalently attached to the positively charged nitrogen atom. The structure has a strong effect on the antibacterial activity and the alkyl chain length has been found to significantly influence the antibacterial activity [2,5,6]. In the cationic biocides, the hydrophobic parts of the molecule play a significant role in the interaction with the cytoplasmic membranes, and the longer alkyl tails seem to favor insertion into the hydrophobic region of the membranes and subsequent disruption of the membranes [5].

Recently, the emergence of life-threatening microorganisms, such as HIV and *Mycobacterium tuberculosis*, and drug resistant bacteria (methicillin-resistant) *Staphylococcus aureus* (MRSA) has become a social problem. In an attempt to solve the problems, many new types of antibiotics have been prepared; however, effective means have not yet been established [7–9]. The cationic biocides may be ideal as membrane-disrupting agents, so they need to be insensitive toward enzymatic degradation and export mechanisms of drug resistance, i.e. processes by which the drug is transported out of the microbe [10]. Thus, the cationic biocides would also be expected to be effective against life-threatening microorganisms. Although the existing cationic biocides have a relatively broad antimicrobial spectrum and high activity, they do not have sufficient antimicrobial activity over short periods of exposure to affect microorganisms [7]. Therefore, development of more active cationic biocides is imperative and this has stimulated chemists to devise fundamentally new approaches toward drug design.

Phosphonium salts, possessing positive phosphorus atoms, can be expected to show a high antibacterial activity by strong interaction and high affinity with bacteria, since there are many phosphoric acid derivatives present in tissues such as the cytoplasmic membrane of bacterial cells. As described above, synthesis of the phosphonium salts is difficult in comparison with the ammonium amphiphiles, resulting from less availability of trialkylphosphines with a long alkyl chain as starting materials. Recently however, a simple synthetic route for the dimethyl-substituted tertiary phosphines was established [11], and various types of phosphonium-salt derivatives have been prepared as a novel class of cationic biocides [12,13]. The most typical phosphonium salts with single or two long alkyl tails (carbon number of 10, 14 and 18) and the commonly available quaternary ammonium analogs with the same hydrophobic structure are shown in Fig. 1.

To compare the antibacterial activity of phosphonium salts with that of their quaternary ammonium analogs, the bactericidal activity of the onium salts with different chain lengths was explored first by the viable cell counting method [13]. Fig. 2 shows plots of logarithmic number of surviving cells versus exposure time for **P–C$_{14}$-1** and **N–C$_{14}$-1** (each with a single tetradecyl group) against *Staphylococcus aureus* (gram-positive strain) and *Escherichia coli* (gram-negative strain). About 10^7 cells ml^{-1} of *S. aureus* were exposed to 280, 28, 2.8, and 0.28 μM solutions (approximately 100, 10, 1, and 0.1 μg ml^{-1}) of the compounds in saline. At a concentration of 280 μM, **P–C$_{14}$-1** was capable of killing all the bacteria within 30 min of contact, and even at 28 μM all of the bacteria were killed within 60 min of contact (Fig. 2(A)). On the other hand, at 28 μM, **N–C$_{14}$-1** killed only > 99.9% of *S. aureus* organisms even at the longest exposure time (Fig. 2(B)). Quite interestingly, the mono-alkyl phosphonium species showed an advantage over the quater-



(X = P, N; n = 10, 14, 18)

Fig. 1. Chemical structures of the phosphonium and quaternary ammonium salts with one and two long alkyl chains. **X–C$_n$-1** and **X–C$_n$-2** are alkyltrimethyl- and dialkyldimethyl-substituted onium salts with decyl, tetradecyl and octadecyl groups, respectively.

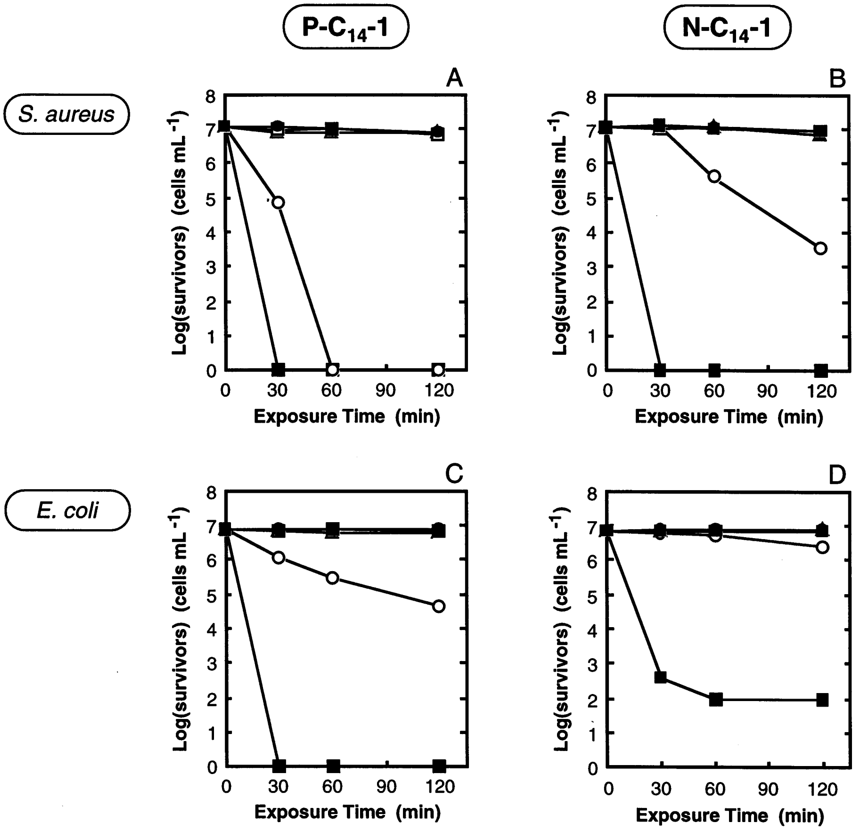


Fig. 2. Plots of the log of number of surviving cells versus exposure time for the phosphonium and the quaternary ammonium salts with the same alkyl substituents against *S. aureus* (A and B) and *E. coli* (C and D): (A) and (C) **P–C$_{14}$-1**; (B) and (D) **N–C$_{14}$-1**. Concentrations: (l) blank, (n) 280 μM, (m) 28 μM, (s) 2.8 μM, (r) 0.28 μM (approximately 100, 10, 1, and 0.1 μg ml^{-1}).

nary ammonium analogs on the bactericidal activity and the kill rate. Similar results were obtained against *E. coli*. The antibacterial activity of the phosphonium salts was much higher than the quaternary ammonium salts and there was a remarkable difference in bactericidal activity between **P–C$_{14}$-1** and **N–C$_{14}$-1** (Fig. 2(C,D)). It is interesting to compare the antibacterial activity of organic cations with two decyl groups (**P–C$_{10}$-2** and **N–C$_{10}$-2**) against *S. aureus*. A difference in antibacterial activity was observed at the lower concentration of 2.8 μM (Fig. 3). **P–C$_{10}$-2** killed all the bacteria within 30 min of exposure, while the corresponding **N–C$_{10}$-2** salt did not kill all the bacteria even at the longest exposure time (120 min). From these results, it may be concluded that the phosphonium salts of the double long-chain type exhibit antibacterial activity superior to the existing quaternary ammonium salts.

The susceptibility of microorganisms was estimated by the conventional spread plate method (i.e. agar dilution test) [13]. This susceptibility testing provides bacteriostatic activity in the form of the minimum inhibitory concentration (MIC). MIC was taken as the lowest concentration of biocide at which no visible growth could be detected after incubation. The MIC values of the phosphonium salts are summarized in Table 1. The results indicate that phosphonium biocides show a broad antimicrobial spectrum and high activity against most strains tested. It is significant that **P–C$_{10}$-2**, having two decyl groups, exhibited the greatest bacteriostatic activity against MRSA, which is a life-threatening bacteria (MIC = 0.78 μg ml^{-1}). Additionally, it is worth mentioning that the MIC of **P–C$_{10}$-2** for methicillin-susceptible *S. aureus* and that for MRSA are the same.

The overall activity of the phosphonium salts is affected by the hydrophobic structure of the substituents. In a series of **P–C$_n$-1**, containing a single long alkyl chain, the MICs of **P–C$_{14}$-1** and **P–C$_{18}$-1** were lower than those of **P–C$_{10}$-1** with the shortest alkyl chain. In contrast, in the other **P–C$_n$-2** type, the activity increased with decreasing hydrophobicity of the substituents. An optimal hydrophobicity (i.e. total carbon chain length) seems to exist for the bacteriostatic activity. In fact, **P–C$_{18}$-1** and **P–C$_{10}$-2**, which show the highest activities in each of the two structural classes have similar numbers of carbon atoms (21 and 22, respectively).

To obtain more functionalized disinfectants, various polymeric phosphonium salts were also prepared as novel polycationic biocides, and their antimicrobial activities were explored systematically to investigate the correlation between the polymer structure and the antimicrobial activity [14–23]. It has been reported previously that polymeric phosphonium salts exhibit a higher activity by two orders of magnitude than their polymeric quaternary ammonium analogs [14].

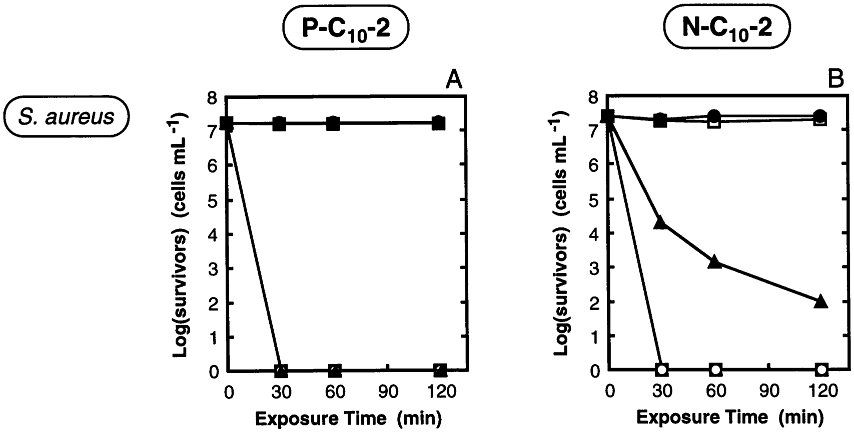


Fig. 3. Plots of log(survivors) versus exposure time for the onium salts with two decyl groups against *S. aureus*: (A) **P–C$_{10}$-2**; (B) **N–C$_{10}$-2**. Concentrations: (l) blank, (n) 280 μM, (m) 28 μM, (s) 2.8 μM, (r) 0.28 μM (100, 10, 1, and 0.1 μg ml^{-1}).

Table 1
Antimicrobial activity of the phosphonium salts with different hydrophobic structures

Compound	MIC (μg ml^{-1})[a]						
	Staphylococcus aureus[b]						
	Methicillin susceptible	Methicillin resistant	*Bacillus subtilis*[b]	*Escherichia coli*[c]	*Enterobacter aerogenes*[c]	*Candida famata*[d]	*Geotrichum candidum*[d]
P–C$_{10}$-1	3.13	50	50	200	>200	>200	>200
P–C$_{14}$-1	0.20	1.56	0.20	12.5	100	200	50
P–C$_{18}$-1	0.78	1.56	3.13	>200	>200	12.5	>200
P–C$_{10}$-2	0.78	0.78	0.78	3.13	3.13	1.56	3.13
P–C$_{14}$-2	12.5	200	100	>200	>200	>200	>200
P–C$_{18}$-2	100	>200	>200	>200	>200	>200	>200

[a] Determined by the spread plate method.

[b] Gram-positive bacteria.

[c] Gram-negative bacteria.

[d] Fungi.

3. Relationship between antibacterial activity and lyotropic liquid-crystalline properties

As presented in the previous section, the phosphonium amphiphiles with the shortest alkyl chains (**P–C$_{10}$-2**) among a series of **P–C$_n$-2** exhibited an outstandingly high activity, while the analogous salt with the longest alkyl chains (**P–C$_{18}$-2**) was inactive against all microbes. The cationic biocides of this type are structurally similar to phospholipids in the cytoplasmic membranes of bacteria. The phospholipid molecules possess a hydrophilic part (phosphate, often with other polar residues attached to it) and a hydrophobic part (two long-chain fatty acid tails containing 12–20 carbon atoms) [24]. Although with increasing alkyl chain length **P–C$_n$-2** was expected to interact strongly with the cytoplasmic membranes, the observed activity was opposite to what was anticipated. The inactivation of **P–C$_{18}$-2** cannot be understood on the basis of the basic interpretation for the bactericidal mechanism as described above.

Such effects of alkyl chain length on the antibacterial activity are not confined to the phosphonium salts. In existing disinfectants, it is well known that their antibacterial activities depend strongly on the alkyl chain length, and there is an optimal chain length for the maximum antibacterial activity [25]. Thus, the hydrophilic–lipophilic balance (HLB) of the compounds has frequently been used as a parameter to elucidate their antibacterial activity in a quantitative way. However, HLB theory cannot provide a rational basis for why alkyl chains longer than the optimal length are unfavorable for antibacterial activity. To rationally design more active membrane-disrupting antimicrobial agents, the uncertain effect of alkyl chain length on the antibacterial activity has to be resolved.

In general, active cationic surfactants possess advantageous features as disinfectants. The ability of the surfactant is closely related to the critical micelle concentration (CMC) at which the amphiphiles spontaneously form aggregates in aqueous solution. In other words, they can be regarded as lyotropic liquid crystals. The value of the CMC depends on a large number of parameters, one of which is the length of the alkyl chain attached to the heteropolar heads [26–28]. The longer the alkyl chain length of the surfactant, the lower the CMC becomes, i.e. formation of the aggregates is more readily achieved [26–29]. The aggregation behavior is also affected by the structure of the hydrophobic units of the surfactants. The **N–C$_n$-2** compounds having two long tails have been used extensively as representative compounds in self-assembled synthetic membranes [30–32]. Such synthetic bilayer-forming amphiphiles exhibit much smaller CMC values than the compounds with a single long chain, and they spontaneously form various large-size aggregates in aqueous dispersion similar to liposomes from naturally-occurring phospholipids [30–32]. The lyotropic liquid-crystalline properties of the ammonium amphiphiles in aqueous solutions have been investigated in detail, for example aggregate morphology and phase transition behavior [33–36]. However, very few studies have been done on the correlation between the aggregation behavior and the antibacterial activity.

Table 2
Properties of the phosphonium salts with single and two long-chain segments

Compound	NaCl concentration (M)	Aggregation number	Molecular weight of aggregate[a]	CMC (mM)[b]
P–C$_{14}$-1	0.0	58	18 000	3.9
	0.86	109	33 600	
	1.71	123	38 100	
	2.57	161	49 700	
P–C$_{14}$-2	0.0	189	93 100	0.074
	0.86	–[c]	–	
	1.71	–	–	
	2.57	–	–	

[a] Determined with a low-angle, laser light-scattering photometer (KMX-6) in water.
[b] Critical micelle concentration estimated by electrical conductivity measurement.
[c] Could not be determined precisely because of salting out.

If the size of the aggregates of cationic amphiphiles is enhanced as the alkyl chain length increases, the aggregates which are large enough to be excluded at the cell wall may not reach the target sites (cytoplasmic membranes) through the cell wall, which exists outside the cytoplasmic membranes, and this may result in depression of the activity. In this case the diffusion through the cell wall may play a crucial role in the antibacterial activity, and the activity could be changed by controlling the size of the aggregates. On the basis of such consideration, a new concept was proposed recently for the mode of action of cationic biocides. From the experimental results shown below, it was revealed that the antimicrobial activity of organic cations may be ascribed essentially to the molecular organization of the organic cations within the aggregates in aqueous solution [37]. The activity is determined primarily by the aggregate morphology and the number of active molecules comprising the aggregates.

To explore the morphological effect of cationic biocides on antibacterial activity, the fundamental aggregation behavior of the phosphonium amphiphiles was investigated at first, and then control of the size of phosphonium aggregates was attempted for **P–C$_{14}$-1** and **P–C$_{14}$-2** containing single and two long-chain segments (carbon number 14), respectively [37]. The values of the CMC for **P–C$_{14}$-1** and **P–C$_{14}$-2** were 3.9 and 0.074 mM, respectively (see Table 2). The CMC of **P–C$_{14}$-2** is smaller by two orders of magnitude than that of the **P–C$_{14}$-1** analog. The results clearly indicate that the phosphonium salt (**P–C$_{14}$-2**) has a high ability to self-associate. This ability was reflected in the aggregation number and the molecular weight of the aggregate as given in Table 2. The aggregation number for **P–C$_{14}$-2** was 189, which was much larger than that for **P–C$_{14}$-1** (58). The compound **P–C$_{14}$-2** can form a larger aggregate than the analog **P–C$_{14}$-1**, which is evident from the molecular weight of the aggregate (18,000 and 93,100 for **P–C$_{14}$-1** and **P–C$_{14}$-2**, respectively). Control of the aggregate size can be achieved readily by changing the ionic strength in aqueous solution [38,39]. As the repulsion between polar head groups is a limiting factor for aggregate formation, increasing counter ion concentration (i.e. ionic strength) results in the lowering of the CMC and an increase in the size of aggregates due to a decrease in the repulsion between ionic head groups [39]. Practically, it was found that the size of aggregates of the phosphonium species could be controlled effectively by the ionic strength without changing the concentration of phosphonium ions. The molecular weight of the aggregate of **P–C_{14}-1** increased as the amount of inorganic electrolyte (sodium chloride) increased, as shown in Table 2. Unfortunately, in the presence of sodium chloride, the molecular weight of the aggregate of **P–C_{14}-2** could not be determined precisely, because **P–C_{14}-2** precipitated.

The antibacterial activity of **P–C_{14}-1** and **P–C_{14}-2** was explored by the viable cell counting method in aqueous solutions of varying ionic strength [37]. Fig. 4 shows plots of log(survivors) versus concentration of sodium chloride for **P–C_{14}-1** and **P–C_{14}-2** against *S. aureus*. Bacterial cells (about 10^7 cells ml^{-1}) were exposed to 28, 14, and 2.8 μM (approximately 10, 5, and 1 μg ml^{-1}) of biocides for 60 min, and the surviving bacteria were counted by the spread plate method. The antibacterial activity of **P–C_{14}-1** was strongly affected by the ionic strength and increased with increasing concentration of sodium chloride (Fig. 4(A)). Although in pure water the phosphonium salt (**P–C_{14}-1**) was inactive at 14 μM, in the presence of 0.86 and 1.71 M sodium chloride, **P–C_{14}-1** killed about 90 and > 99% of *S. aureus*, respectively. It is of interest that in the presence of 2.57 M sodium chloride, **P–C_{14}-1** killed all bacterial cells. A similar phenomenon was also observed at the lowest concentration of **P–C_{14}-1** (2.8 μM). Since the additives do not exert antibacterial activity even at the highest concentration of sodium chloride, it is clear that the state of aggregation due to ionic strength influences the antibacterial activity significantly. Therefore, the morphology is a very important factor affecting the antibacterial activity. Fig. 4(B) indicates the same plots for **P–C_{14}-2** with two long alkyl chains. The original

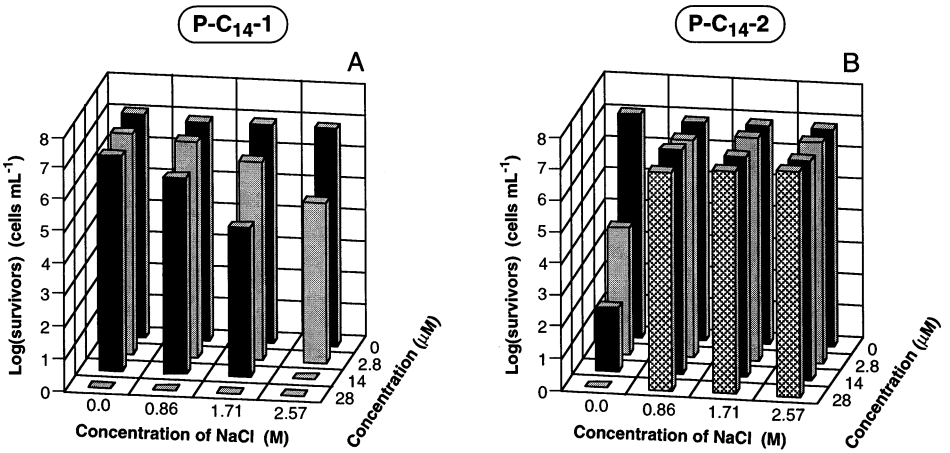


Fig. 4. Plots of log(survivors) versus concentration of NaCl for 28, 14 and 2.8 μM of the phosphonium species and blank against *S. aureus*: (A) **P–C_{14}-1**; (B) **P–C_{14}-2**.

antibacterial activity (evaluated in pure water) of **P–C$_{14}$-2** was much higher than that of **P–C$_{14}$-1**. However, in the presence of sodium chloride, **P–C$_{14}$-2** was much less active irrespective of the concentration of sodium chloride examined. It was confirmed that such depression of the activity was not due to precipitation of the samples resulting from the enhancement of the ionic strength. Thus, it is apparent that the phosphonium ions forming large aggregates are essentially much more active, but that increased size of aggregates is unfavorable for antibacterial activity.

At present, it is believed that the antibacterial activity of cationic agents depends only on the structural feature of the molecules. From the results obtained, however, the antibacterial activity should vary with the morphology (molecular organization) of the aggregates, i.e. the lyotropic liquid-crystalline properties. The proposed new concept may reveal why the antibacterial activity of cationic biocides is suppressed with increasing alkyl chain length above an optimal chain length. The activity is not affected directly by the structure of the substituents attached to the polar heads, but is affected by the size of the aggregates which is enhanced with increasing alkyl chain length. The cations forming aggregates so large as to be excluded at the cell wall show a lower activity.

4. Feature of phosphonium salts as thermotropic liquid crystals

Thermotropic liquid crystals have been widely used as active media in liquid-crystal display devices and spatial light modulators [40–44]. 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 [45]. Recently, novel families of thermotropic liquid crystals have been found amongst aromatic compounds. These have strong noncovalent interactions, which allow assembly of the parts through molecular recognition processes [46–49]. Several studies have been carried out on the thermotropic liquid-crystalline behavior of aromatic compounds possessing cationic moieties such as quaternary ammonium and pyridinium derivatives [50–55]. It has been found that introduction of positively-charged nitrogen atoms into a molecule results in formation and stabilization of the liquid-crystalline phases due to ionic interactions [55–57]. However, very few studies have been performed on the thermotropic liquid-crystalline behavior of cationic amphiphiles without rigid cores, with the exception of some quaternary ammonium salts [58–64].

From the studies on the antimicrobial activity and the lyotropic liquid-crystalline behavior of cationic amphiphiles as described above, it is deduced that the phosphonium salts, particularly the **P–C$_n$-2** salts with two long alkyl segments, exhibit a high degree of molecular organization even in the bulk condition. More recently, the thermodynamic properties of the phosphonium salts were evaluated, and it was revealed that in spite of being structurally simple amphiphiles without rigid aromatic rings, they possess advantageous features as thermotropic liquid crystals, and show a stable liquid-crystalline phase and simple phase transition behavior compared to the classical ammonium analogs [11].

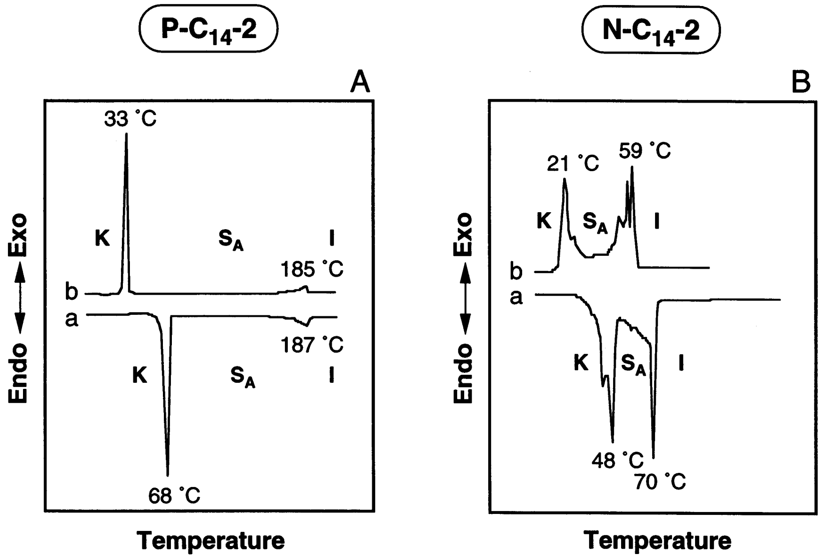


Fig. 5. DSC thermograms observed for compounds with different heteroatoms: (A) **P–C$_{14}$-2**; (B) **N–C$_{14}$-2**; (a), second heating scan; (b), second cooling scan. Abbreviations: K, crystalline; S_A, smectic phase; I, isotropic phase.

The thermotropic liquid-crystalline behavior of **P–C$_n$-2**, and **N–C$_n$-2** as a reference compound, was evaluated by differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffractometry, and it was confirmed that all the amphiphiles exhibited the smectic A (S_A) phase (possessing bilayer structure) in which a homeotropic structure was formed spontaneously. Fig. 5 shows typical DSC thermograms observed for the **P–C$_{14}$-2** salt and the corresponding **N–C$_{14}$-2** salt. For the series of **P–C$_n$-2**, two endothermic events were clearly observed (see Fig. 5(A)); one is due to melting which 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 3, the phosphonium salts exhibit a high T_{SI} (145–187°C) and exist in the S_A phase for a considerable temperature range. In particular, the compound **P–C$_{14}$-2** with two tetradecyl groups exhibited the most stable liquid-crystalline phase as evidenced by the highest T_{SI} (187°C), the widest temperature range for the S_A phase (119°C), and the highest values of ΔS_{SI} (13 J K^{-1} mol^{-1}) among the compounds examined. In contrast to the phosphonium salts, the ammonium salts showed indistinct or multiple phase transition behavior. For example, in the DSC thermogram obtained for **N–C$_{14}$-2**, both K–S_A and S_A–I phase transitions occurred with a change in baseline which shifted with temperature toward the endothermic direction, indicating a change in the heat capacity (Fig. 5(B)). The peak shapes were also more complicated than those of the corresponding phosphonium salt.

Table 3
Thermodynamic data for phase transitions of the phosphonium and ammonium salts[a]

Compound	K–S_A[b]			S_A–I[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})	T_{decom}[d] (°C)
P–C$_{10}$-2	38	39	126	155	2.9	6.8	367
P–C$_{14}$-2	68	70	205	187	5.6	13	366
P–C$_{18}$-2	82	57	160	145	2.4	5.8	362
N–C$_{10}$-2	59	9.1	28	94	1.7	4.7	198
N–C$_{14}$-2	48	11	33	70	4.7	13	194
N–C$_{18}$-2	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 N_2.

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 3. From the results obtained by thermogravimetry (TG), the phosphonium salts were also revealed to be more heat resistant than the ammonium salts (see Table 3). 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–C$_{14}$-2** and **N–C$_{14}$-2** with alkyl tails of 14 carbon atoms. As described above, **P–C$_{14}$-2** showed the highest T_{SI} (187°C) and the widest temperature range for the S_A phase (119°C on heating) among all the compounds examined, while **N–C$_{14}$-2** showed the lowest T_{SI} (70°C) and the narrowest liquid-crystalline temperature range (22°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 phase and in enhancing the thermal stability of the liquid-crystalline phase.

5. Conclusions

The dimethyl- and trimethyl-substituted phosphonium ions with alkyl chains of varying lengths are structurally simple amphiphiles consisting of positive phosphorus atoms and hydrocarbon chains. However, they show advantageous features as cationic biocides, lyotropic liquid crystals, and thermotropic liquid crystals in comparison with the corresponding quaternary ammonium salts. Such tetracoordinate phosphorus species possessing multifunctional properties may be one of the most important groups with potential for applications in new functionalized materials.

References

[1] T. Ikeda, in: M. Szycher (Ed.), High Performance Biomaterials, Technomic, Pennsylvania, USA, 1991, p. 743.

[2] T.J. Franklin, G.A. Snow, Biochemistry of Antimicrobial Action, Chapman and Hall, London, 1981, p. 58.

[3] W.B. Hugo, A.R. Longworth, J. Pharm. Pharmacol. 16 (1964) 655.

[4] W.B. Hugo, A.R. Longworth, J. Pharm. Pharmacol. 18 (1966) 569.

[5] H. Kourai, T. Horie, K. Takeichi, I. Shibasaki, J. Antibact. Antifung. Agents 8 (1980) 9.

[6] R.J. Schaeufele, J. Am. Oil. Chem. Soc. 61 (1984) 387.

[7] Y. Sakagami, H. Yamazaki, H. Yokoyama, H. Masuda, A. Takasaki, M. Tanifuji, T. Yoshinaga, M. Tanaka, K. Matsuo, Chemotherapy 37 (1989) 1342.

[8] M. Limbert, D. Isert, N. Klesel, A. Markus, K. Seeger, G. Seibert, E. Schrinner, Antimicrob. Agents Chemother. 35 (1991) 14.

[9] T. Toyosawa, S. Miyazaki, A. Tsuji, K. Yamaguchi, S. Goto, Antimicrob. Agents Chemother. 37 (1993) 60.

[10] K. Naka, A. Sadownik, S.L. Regen, J. Am. Chem. Soc. 115 (1993) 2278.

[11] A. Kanazawa, O. Tsutsumi, T. Ikeda, Y. Nagase, J. Am. Chem. Soc. 119 (1997) 7670.
[12] A. Kanazawa, T. Ikeda, T. Endo, J. Appl. Polym. Sci. 53 (1994) 1237.
[13] A. Kanazawa, T. Ikeda, T. Endo, Antimicrob. Agents Chemother. 38 (1994) 945.
[14] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A: Polym. Chem. 31 (1993) 335.
[15] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 31 (1993) 1441.
[16] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 31 (1993) 1467.
[17] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 31 (1993) 2873.
[18] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 31 (1993) 3003.
[19] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 31 (1993) 3031.
[20] A. Kanazawa, T. Ikeda, T. Endo, J. Appl. Polym. Sci. 52 (1994) 641.
[21] A. Kanazawa, T. Ikeda, T. Endo, J. Polym. Sci. Part A Polym. Chem. 32 (1994) 1997.
[22] A. Kanazawa, T. Ikeda, T. Endo, J. Appl. Polym. Sci. 53 (1994) 1245.
[23] A. Kanazawa, T. Ikeda, T. Endo, J. Appl. Polym. Sci. 54 (1994) 1305.
[24] R.D. Dyson, Cell Biology, second ed., Allyn and Bacon, Boston, 1978, p. 70.
[25] T.J. Franklin, G.A. Snow (eds.), Biochemistry of Antimicrobial Action, Chapman and Hall, London, 1981, p. 58.
[26] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975, p. 19.
[27] A. Helenius, K. Simons, Biochim. Biophys. Acta 415 (1975) 29.
[28] D. Lichtenberg, R.J. Robson, E.A. Dennis, Biochim. Biophys. Acta 737 (1983) 285.
[29] S. Saito, T. Tsuchiya, Chem. Pharm. Bull. 33 (1985) 503.
[30] T. Kunitake, Y. Okahata, J. Am. Chem. Soc. 99 (1977) 3860.
[31] T. Kunitake, Y. Okahata, K. Tamaki, F. Kumamaru, M. Takayanagi, Chem. Lett. (1977) 387.
[32] T. Kunitake, Bunshi Shuugoutai (Molecular Organization), The Chemical Society of Japan (Ed.), Gakkai Shuppan Center, Tokyo, 1983, p. 122.
[33] K. Deguchi, J. Mino, J. Colloid Interface Sci. 65 (1978) 155.
[34] E.J.R. Sudhölter, J.B.F.N. Engberts, D. Hoekstra, J. Am. Chem. Soc. 102 (1980) 2467.
[35] Y. Okahata, R. Ando, T. Kunitake, Ber. Bunsen-Ges. Phys. Chem. 85 (1981) 789.
[36] S. Kaneshina, Langmuir 5 (1989) 1383.
[37] A. Kanazawa, T. Ikeda, T. Endo, J. Appl. Bacteriol. 78 (1995) 55.
[38] K. Shinoda, T. Yamaguchi, R. Hori, Bull. Chem. Soc. Jpn. 34 (1961) 237.
[39] A. Helenius, D.R. McCaslin, E. Fries, C. Tanford, Methods Enzymol. 56 (1979) 734.
[40] M. Schadt, W.J. Helfrich, Appl. Phys. Lett. 18 (1971) 127.
[41] A. Boller, H. Scherrer, M. Schadt, Proc. IEEE 60 (1972) 1002.
[42] R.D. Sterling, R.D. Te Kolste, J.M. Haggerty, T.C. Borah, W.P. Bleha, SID Dig. 21 (1990) 327.
[43] V.J. Fritz, Proc. SPIE 1255 (1990) 59.
[44] M. Schadt, H. Seiberle, A. Schuster, Nature 381 (1996) 212.
[45] P.G. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford, 1974, p. 1.
[46] C.T. Imrie, F.E. Karasz, G.S. Attard, Liq. Cryst. 9 (1991) 47.
[47] M. Ebert, G. Frick, C.H. Baehr, J.H. Wendorff, R. Wüstefeld, H. Ringsdorf, Liq. Cryst. 11 (1992) 293.
[48] T. Kato, J.M.J. Fréchet, P.G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, F. Kaneuchi, Chem. Mater. 5 (1993) 1094.
[49] C.M. Paleos, D. Tsiourvas, Angew. Chem. Int. Ed. Engl. 34 (1995) 1696.
[50] D.W. Bruce, D.A. Dunmur, E. Lalinde, P.M. Maitlis, P. Styring, Nature 323 (1986) 791.
[51] J.P. Rourke, F.P. Fanizzi, N.J.S. Salt, D.W. Bruce, D.A. Dunmur, P.M.J. Maitlis, Chem. Soc. Chem. Commun. (1990) 229.
[52] D.W. Bruce, D.A. Dunmur, S.A. Hudson, E. Lalinde, P.M. Maitlis, M.P. McDonald, R. Orr, P. Styring, Mol. Cryst. Liq. Cryst. 206 (1991) 79.
[53] D. Navarro-Rodriguez, Y. Frere, P. Gramain, D. Guillon, A. Skoulios, Liq. Cryst. 9 (1991) 321.
[54] Y.Z. Yousif, A.A. Othman, W.A. Al-Masoudi, P.R. Alapati, Liq. Cryst. 12 (1992) 363.
[55] S. Ujiie, K. Iimura, Macromolecules 25 (1992) 3174.
[56] V. Hessel, H. Ringsdorf, F. Reinhard, J.H. Wendorff, Makromol. Chem. Rapid Commun. 14 (1993) 707.

[57] Y. Kosaka, T. Kato, T. Uryu, Liq. Cryst. 18 (1995) 693.
[58] V. Busico, P. Corradini, M. Vacatello, J. Phys. Chem. 86 (1982) 1033.
[59] A. Malliaris, C. Christias, G. Margomenou-Leonidopoulou, C.M. Paleos, Mol. Cryst. Liq. Cryst. 82 (1982) 161.
[60] V. Busico, P. Cernicchlaro, P. Corradini, M. Vacatello, J. Phys. Chem. 87 (1983) 1631.
[61] G. Margomenou-Leonidopoulou, A. Malliaris, C.M. Paleos, Thermochim. Acta 85 (1985) 147.
[62] J.D. Gault, H.A. Gallardo, H.J. Müller, Mol. Cryst. Liq. Cryst. 130 (1985) 163.
[63] C.M. Paleos, G. Margomenou-Leonidopoulou, D. Babilis, C. Christias, Mol. Cryst. Liq. Cryst. 146 (1987) 121.
[64] G. Margomenou-Leonidopoulou, Thermochim. Acta 134 (1988) 49.