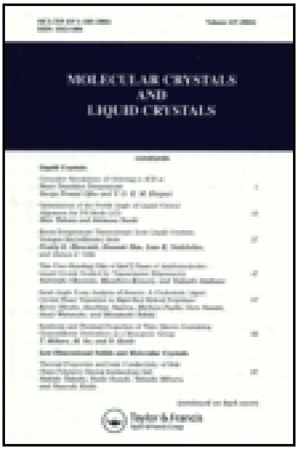

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Thermotropic Liquid-Crystalline Behavior of Alkylammonium X-Substituted Benzenesulfonates

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Thermotropic Liquid-Crystalline Behavior of Alkylammonium X-Substituted Benzenesulfonates

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Five series of smectogenic alkylammonium ($C_nH_{2n+1}NH_3^+$) benzenesulfonates were prepared introducing *p*-chloro, *p*-hydroxy, o-nitro, *m*-nitro, and *p*-nitro substituents to the aromatic nucleus, respectively. All the butyl to octadecylammonium salts exhibit a smectic A phase when $X = Cl$, whereas only the cation carrying a pentadecyl or a longer alkyl group forms a mesogenic salt when $X = OH$ and NO_2. The clearing point depends significantly upon the alkyl chain length when $X = OH$ and NO_2 but not much when $X = Cl$ and $n \geqslant 6$. Combining with the results reported earlier, the following group efficiency order in promoting the thermal stability of smectic A phase was made for the octadecylammonium salts: p-OH > p-Cl > p-NO_2 > m-NO_2 > p-CH_3 > H > p-C_2H_5 > o-NO_2.

Keywords: Smectic, alkylammonium salts, benzenesulfonates, effects of substituents

INTRODUCTION

Alkylammonium benzene-, *p*-toluene-, and *p*-ethylbenzenesulfonates are smectogenic when the cation carries an octyl or a longer alkyl group.[1] The clearing point of the benzenesulfonate is raised by about 20°C by *p*-methyl substitution throughout the series. As for the smectic phase exhibited by non-ionic compounds, the effects of terminal substituents on the mesophase thermal stability have been the subject of great interest,[2–4] whereas, to our knowledge, no systematic work has been done on ionic ones. We reported recently the mesomorphic behavior of the salts formed by the combination of alkyl *p*-aminobenzoates and *p*-ethyl- and *p*-chlorobenzenesulfonic acids, respectively.[5] The smectic phase is significantly stabilized by a *p*-chloro substituent and the incidence of the mesophase is also greatly increased. Even with the butyl ester, the *p*-chlorobenzenesulfonic acid can form a smectogenic salt. Consequently, we planned the present exploratory study in the effects of substituents on the mesomorphic properties of ionic compounds extending our work to five series of alkylammonium X-substituted benzenesulfonates, where $X = p$-Cl, p-OH, o-NO_2, m-NO_2, and p-NO_2. Studying such simple compounds may be profitable to relate the observed changes in mesomorphic behavior to this particular modification of the molecular structure.

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EXPERIMENTAL

All the alkylamines and *p*-chloro-, *p*-hydroxy-, *o*-nitro-, *m*-nitro-, and *p*-nitrobenzenesulfonic acids were commercially available. Equimolar amounts of an alkylamine and an acid dissolved in boiling methanol were mixed. The salt precipitated upon cooling was recovered by filtration and then recrystallized until a sharp mesomorphic-isotropic transition was recorded on the calorimetric curve during the processes of heating and cooling at the same temperature. For example, Found: C, 62.54; H, 9.61; N, 2.95; Cl, 7.67; S, 7.07%. Calcd for $C_{18}H_{37}NH_3^+ \cdot ClC_6H_4SO_3^-$: C, 62.38; H, 9.60; N, 3.03; Cl, 7.67; S, 6.94%. Found: C, 60.96; H, 9.45; N, 5.92; S, 6.59%. Calcd for $C_{18}H_{37}NH_3^+ \cdot p\text{-}NO_2C_6H_4SO_3^-$: C, 60.98; H, 9.38; N, 5.93; S, 6.78%. The calorimetric and X-ray diffraction measurements were carried out as described in our previous paper.[6]

RESULTS AND DISCUSSION

The transition temperatures and the corresponding enthalpy changes of the *p*-chlorobenzenesulfonates are summarized in Table 1. Here, *K*, S_A, and *I* denote crystalline, smectic A, and isotropic liquid phases, respectively. The assignment of the mesophase was made on the basis of a pseudo-isotropic texture with oily-streaks and also an X-ray diffraction pattern consisting of a sharp inner peak and a diffuse outer one. The former peak is accompanied by a weaker one assignable to the second-order reflection. The

TABLE I

Transition Temperatures (t/°C) and Enthalpy Changes (ΔH/kJ mol^{-1})[a] for Alkylammonium *p*-Chlorobenzenesulfonates

n[b]	K_2	K_1	S_A	I
3		· 140(32)		·
4		· 124(24)	[· 112(2.5)][c]	·
5	· 95(6.0)	· 124(21)	· 158(3.2)	·
6	· 66(4.3)	· 106(28)	· 175(3.6)	·
7	· 78(5.9)	· 109(22)	· 170(3.6)	·
8		· 109(25)	· 170(3.5)	·
9	· 110(11)	· 114(17)	· 170(3.3)	·
10		· 104(25)	· 172(3.5)	·
11	· 63(8.3)	· 81(21)	· 175(3.2)	·
12		· 86(26)	· 178(3.4)	·
13	· 80[d]	· 84[d]	· 179(3.7)	·
14	· 78(20)	· 84(23)	· 181(3.5)	·
15	· 76(1.9)	· 85(48)	· 179(4.0)	·
16	· 69(23)	· 91(22)	· 180(3.8)	·
17	· 81(2.5)	· 88(60)	· 179(3.8)	·
18	· 77(22)	· 96(26)	· 180(3.4)	·

[a] Values in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] Monotropic transition.
[d] The sum of enthalpy changes is 39 kJ m·l^{-1}.

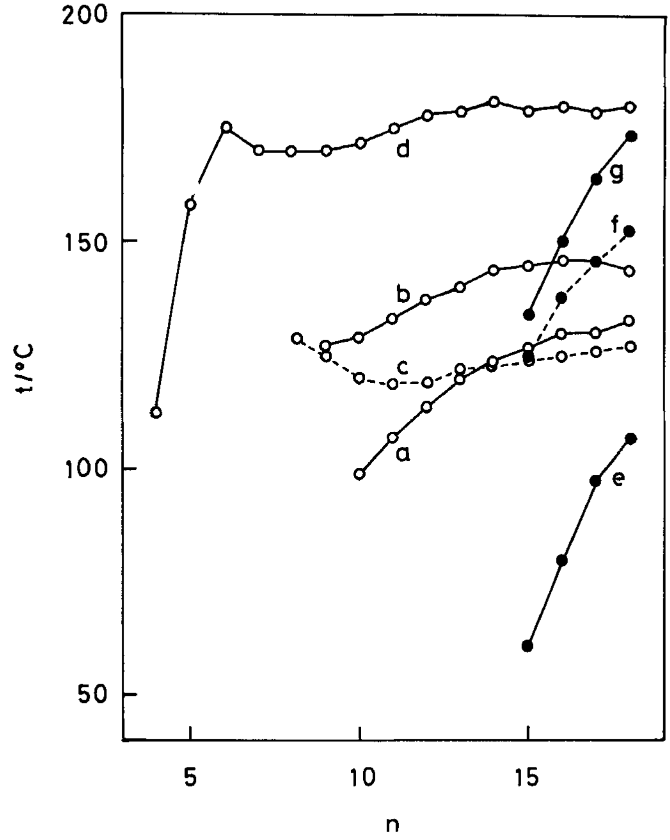

FIGURE 1 Plots of clearing point against the number of carbon atoms in the alkyl group for alkylammonium benzenesulfonates. (a) unsubstituted, (b) *p*-methyl, (c), *p*-ethyl, (d) *p*-chloro, (e) *o*-nitro, (f) *m*-nitro, and (g) *p*-nitro derivatives.

mesophase is thermodynamically stable except that exhibited by the butylammonium salt. The clearing point rises rapidly as the alkyl chain length increases and then remains in a range of 170 to 180°C (see plot d in Figure 1). Compared with the other series, the incidence of a mesophase is exceptionally high and the clearing point is promoted by 50 to 70°C by the introduction of a *p*-chloro substituent with respect to the benzenesulfonate (compare with plot a in Figure 1). The enthalpy change at the $S_A - I$ transition is mostly in the range of 3.2 to 4.0 kJ mol^{-1} and is larger by a factor of 1.2 to 1.8 than that given by the unsubstituted benzenesulfonates. The layer spacing (d/nm) is approximated by $d = 0.125n + 1.14$. The increment per methylene group is in good agreement with the value expected for a fully-extended conformation of alkyl chain and indicates that the chains are perpendicular to the smectic layer in conformity with the above-metioned phase assignment. The molecular length of a *p*-chlorobenzenesulfonate ion along the line joining the 1- and 4-positions of the aromatic nucleus was estimated to be about 1.05 nm on the basis of the standard bond lengths, angles, and van der Waals radii.[1] The thermochemical ionic radii of NH_4^+ and SO_4^{2-} were employed for the NH_3^+ and SO_3^- groups respectively. The sum of the former thermochemical radius and the molecular length, 1.19 nm, agrees fairly well with the limiting value for $n = 0$. Therefore, the long axes of the two component ions are almost perpendicular to the smectic layer and in line with each other. It is highly probable that the ion pairs in a smectic layer are alternatively oriented so that the alkyl chains are interdigitated with each other. Such models have been proposed to represent the mesophases of ionic mesogens such as alkylammonium halides and 1-alkyl-4-methylpyridinium halides.[7–9] In contrast to these halides, the molecular length of the present anion is long enough to be comparable with that of the pentylammonium cation.

A terminal hydroxyl group is known to promote markedly the mesophase of ordinary thermotropic liquid-crystalline compounds through intermolecular hydrogen bonding.[10,11] Furthermore, a greatly enhanced mesomorphic temperature range through the formation of intermolecular hydrogen bonds in a number of binary mixtures has been reported.[12,13] So we prepared a series of the *p*-hydroxybenzenesulfonates. Table II presents the results for the six higher members. No mesophase could be observed for the tridecylammonium salt but a metastable mesophase is detectable for the next homologous member. Then, the thermodynamically stable mesophase is obtained. For example, the phase of the pentadecyl homologue is stable over the temperature range of 65°C. The clearing point is considerably raised and the temperature range of stable existence of the mesophase is broadened by ascending the series and the upper limit could not be determined because of the thermal decomposition, for example, wider than 160°C for the octadecyl homologue. It may be noted that the enthalpy change at the clearing point is markedly smaller; that is, 1.1 kJ mol^{-1} compared with 2.2 kJ mol^{-1} reported for the unsubstituted benzenesulfonate.[1] These observations are in good conformity with what we observed for the 1-napthol-4-sulfonates.[14] Namely, a metastable mesophase appears at 95 and 128°C from the supercooled melts of the tridecyl and tetradecylammonium 1-naphthol-4-sulfonates, respectively. In this series too, the $S_A - I$ transition temperature rises rapidly as the series is ascended and a thermodynamically stable mesophase appears in the higher homologous members. The clearing point for the hexadecyl homologue is as high as 225°C. For all the naptholsulfonates, the enthalpy chang at the clearing point was less than 0.1 kJ mol^{-1}. Thus, the thermal stability rapidly enhanced by ascending the

TABLE II

Transition Temperatures (t/°C) and Enthalpy changes (ΔH/kJ mol^{-1})[a] for Alkylammonium *p*-Hydroxybenzenesulfonates

n[b]	K_3	K_2	K_1	S_A	I
13	· 94(5)	· 104(12)	· 115(12)		·
14		· 85(12)	· 119(18)	[· 101(1.1)][c]	·
15	· 80(11)	· 92(5)	· 120(16)	· 185(1.1)	·
16	· 84(15)	· 118(19)	· 125(11)	· > 215 (decomp)	·
17	· 81(13)	· 111(22)	· 124(11)	· > 265 (decomp)	·
18	· 84(13)	· 112(23)	· 123(5)	· > 285(decomp)	·

[a] Values in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] Monotropic transition.

TABLE III

Transition Temperatures (t/°C) and Enthalpy Changes (ΔH/kJ mol^{-1})[a] for Alkylammonium o-, m-, and p-Nitrobenzenesulfonates

n[b]	K_3	K_2	K_1	S_A	I
			Ortho-Substituted		
14			· 56(42)		·
15		· 50(18)	· 68(28)	[· 61(0.4)][c]	·
16			· 68(48)	· 80(0.6)	·
17		· 58(20)	· 73(33)	· 98(0.8)	·
18			· 72(57)	· 107(0.9)	·
			Meta-Substituted		
14	· 69(11)	· 82(14)	· 131(23)		·
15	· 73(14)	· 92(15)	· 130(23)	[· 125(1.2)][c]	·
16	· 70(8)	· 97(17)	· 131(22)	· 138(1.4)	·
17	· 69(21)	· 100(20)	· 129(23)	· 146(1.5)	·
18	· 77(12)	· 104(22)	· 129(23)	· 153(1.5)	·
			Para-Substituted		
14			· 126(22)		·
15	· 49(16)	· 86(0.6)	· 131(25)	· 134(0.9)	·
16		· 47(14)	· 128(26)	· 150(1.3)	·
17		· 59(19)	· 130(28)	· 164(1.4)	·
18		· 52(16)	· 127(28)	· 175(1.6)	·

[a] Values in parentheses.

[b] The number of carbon atoms in the alkyl group.

[c] Monotropic transition.

homologous series and also the small enthalpy at the clearing point appear to be common to these hydroxy compounds.

The transition temperatures and associated enthalpy changes for three series of the nitrobenzenesulfonates are listed in Table III. When the alkyl group is pentadecyl or longer, a mesophase is observable for these series. While the melting point in the o-nitrobenzenesulfonates is in a rather narrow range of 56 to 73°C, the clearing point is markedly raised by increasing the alkyl chain length (see plot e in Figure 1). The mesophase in the pentadecyl homologue is metastable but the phase in the highest homologous member has a temperature range of stable existence of 35°C. The melting points of the m- and p-nitro derivatives are close to each other but they are much higher than that of the o-nitro derivatives. The clearing point is also appreciably higher than that of the corresponding o-nitro compound and its magnitude depends upon the location of the substituent (compare plots f and g in Figure 1). Thus, we find the order of thermal stability of the smectic A phase in our compounds as follows: p-NO_2 > m-NO_2 > o-NO_2. In addition, it is noted that the enthalpy changes associated with the $S_A - I$ transition in the m- and p-nitro derivatives are larger almost by a factor of two than those in the o-nitro derivatives.

The above-mentioned order of nitro groups in promoting smectic thermal stability agrees with that found for ordinary mesogenic three-benzene systems studied by Sakurai *et al.*[15] They reported the thermal behavior of the smectic A phase exhibited by 4-(4-nonyloxyphenoxycarbonyl)phenyl o-, m-, and p-nitrobenzoates and also o-, m-, and p-nitrophenyl 4-(4-nonyloxyphenoxycarbonyl)benzoates. Contrary to our benzenesulfonates, these non-ionic compounds are not only smectogenic but also nematogenic. The $S_A - N$ transition temperatures of the former three compounds are 84, 115, and 195°C, and those of the latter are 60, 120, and 198°C, respectively.

As for non-ionic mesogens, it is well known that the introduction of a lateral substituent gives rise to a marked depression of S_A-N/I transition temperature because of increased molecular breadth.[2] The relation between transition temperature and molecular diameter for 3'-X-4'-alkoxybiphenyl-4-carboxylic acid carrying a substituent such as F, Cl, Br, and I is nearly rectilinear; however, the point for the nitro group lies well above the line but lower than that for the parent compound. This deviation has been attributed to the importance of dipolar interaction acting across the long axes of the molecules which enhance the lateral attraction retaining the smectic order. Consequently, it is important to compare these transition temperatures with those of the unsubstituted compounds in order to clarify the effects of the substituent. Unfortunately, their parent compounds have no accessible smectic phase. However, Sakurai *et al.* could deduce the latent $S_A - N$ transition temperatures from phase diagrams of some binary systems.[16] The value for 4-(4-nonyloxyphenoxycarbonyl)phenyl benzoate is about 50°C and is lower than even that of the *o*-nitro derivative, indicating the predominance of the dipolar effect over the counteracting breadth effects in the *o*- and *m*-nitro derivatives. On the other hand, the value for phenyl 4-(4-nonyloxyphenoxycarbonyl)benzoate, about 130°C, is located between those for the *m*- and *p*-nitro derivatives, suggesting that the molecular breadth effects are significant.[16] The former situation is rather exceptional for non-ionic mesogens. In our case, the situation is more complex; that is, the $S_A - I$ transition temperatures for most of the *m*-nitro derivatives are higher than those of the unsubstituted ones (compare plots a and f), whereas those of the *o*-nitro derivatives are lower (compare plots a and e in Figure 1).

The present limited observations on the liquid crystal properties of substituted benzenesulfonates seem to be not in disagreement with the effects of substituents reported by earlier workers for non-ionic smectogens.[2–4] The group efficiency order in promoting smectic *A* phase thermal stability in alkylammonium X-substituted benzenesulfonates is not independent of the alkyl chain length, as in depicted in Figure 1. For the octadecylammonium salts, the following order is observed; p-OH $>$ p-Cl $>$ p-NO_2 $>$ m-NO_2 $>$ p-CH_3 $>$ H $>$ p-C_2H_5 $>$ o-NO_2.

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