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Y. Matsunaga [a b], S. Sakamoto [a], A. Togashi [a] & M. Tsujimoto [a]
[a] Department of Chemisty, Faculty of Science, Hokkaido University, Sapporo, 060, Japan
[b] Department of Materials Science, Kanagawa University, Hiratsuka, Kanagawa, 259-12, Japan
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Smectogenic Salts Formed by Combination of Alkyl *p*-Aminobenzoates and *p*-Ethyl- or *p*-Chlorobenzenesulfonic Acid

Y. MATSUNAGA*, S. SAKAMOTO, A. TOGASHI and M. TSUJIMOTO

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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Two series of smectogenic salts were obtained by combining alkyl *p*-aminobenzoates with *p*-ethyl- and *p*-chlorobenzenesulfonic acids, respectively. The shortest ester alkyl chain required to generate a smectic A phase is nonyl when the former sulfonic acid is employed but the chain may be as short as butyl when the latter is employed. The smectic A-isotropic transition temperature in the second series is significantly higher than that in the first series, indicating that the terminal substituent on the anion is as crucial as that in non-ionic mesogens in determining the mesophase stability.

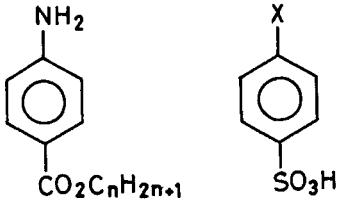
Keywords: Smectic, alkyl p-aminobenzoates, benzenesulfonates

INTRODUCTION

Long-chain alkylammonium salts and *N*-alkylated pyridinium salts have been known to exhibit mesomorphic phases.[1–7] To our knowledge, however, the effects of modification of molecular structure upon the properties of liquid crystals formed by such salts have not received much attention. We reported earlier on the thermotropic liquid-crystalline behavior of alkylammonium benzene-, *p*-toluene-, and *p*-ethylbenzenesulfonates and also picrates.[8] The last-mentioned salts are smectogenic only when the cation carries an alkyl group as long as heptadecyl or octadecyl, whereas the benzenesulfonates can be smectogenic when the cation carries a decyl or longer alkyl group. Thus, a remarkable difference in the chain length required to generate a smectic A phase was found between these two kinds of anion. In addition, we observed a smectic A phase for a number of alkylammonium alkanesulfonates and also naphthalene-1- and 2-sulfonates.[9,10] It seemed interesting to us to extend our work to salts consisting of cation and anion both of which are benzene derivatives. In this way, one would introduce structural parameters to the constituent molecules which influence the liquid crystal properties and develop widely this field. In order to explore such

* Present address: Department of Materials Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan.

molecular correlations, we employed alkyl *p*-aminobenzoates (1) and *p*-ethyl- and *p*-chlorobenzenesulfonic acids (2a and b) as the component compounds.



(1) (2a) $X = C_2H_5$
(2b) $X = Cl$

Alkyl *p*-aminobenzoates are known by our previous work to form not only stable yellow-colored salts but also metastable red-colored charge-transfer complexes when combined with picric acid.[11] However, no mesophase is given either by the salts or by the molecular complexes. Therefore, it is rather striking to see in the present work that the combinations with benzenesulfonic acids can produce a large number of smectogenic salts.

EXPERIMENTAL

Alkyl *p*-aminobenzoates were prepared by reactions between *p*-nitrobenzoyl chloride and appropriate alcohols and then by reduction with zinc dust and calcium chloride in 75% aqueous ethanol.[12] The *p*-ethyl- and *p*-chlorobenzenesulfonic acids were commercially available. Equimolar amounts of an alkyl *p*-aminobenzoate and a benzenesulfonic acid dissolved in benzene or hexane–ethanol mixtures were mixed. The salts which precipitated on cooling from the solution were filtered and then recrystallized from the same solvent until a sharp smectic–isotropic transition was recorded on the calorimetric curve during the processes of heating and cooling at the same temperature. For example, Found: C, 66.40; H, 8.75; N, 2.86; S, 6.35. Calcd for $(C_{13}H_{27}O_2CC_6H_4NH_3^+)(C_2H_5C_6H_4SO_3^-)$: C, 66.50; H, 8.57; N, 2.77; S, 6.34. Found: 52.82; H, 5.21; N, 3.58. Calcd for $(C_4H_9O_2CC_6H_4NH_3^+)(ClC_6H_4SO_3^-)$: C, 52.92; H, 5.22; N, 3.63. Calorimetric and X-ray diffraction measurements were performed as described in our earlier papers.[8–10]

RESULTS AND DISCUSSION

The transition temperatures and associated enthalpy changes are given in Table I for the eleven *p*-ethylbenzenesulfonates. Here, K, S_A and I stand for crystalline, smectic A, and isotropic liquid phases, respectively. The melting point (K–S_A transition temperature) and clearing point (S_A–I transition temperature) are plotted in Figure 1 against the number of carbon atoms (n) in the ester alkyl group. All the *p*-aminobenzoates with nonyl to octadecyl groups form mesogenic salts with this benzenesulfonic acid. The salt

TABLE I

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

n^b	K_2	K_1	S_A	I
8		· 120 (41)		·
9	· 101 (9.4)	· 118 (11)	· 130 (2.1)	·
10	· 109 (17)	· 117 (17)	· 139 (2.2)	·
11	· 110 (17)	· 115 (19)	· 144 (2.3)	·
12		· 144 (34)	· 150 (2.3)	·
13		· 147 (33)	· 152 (2.3)	·
14		· 118 (45)	· 156 (2.2)	·
15		· 116 (50)	· 158 (2.2)	·
16		· 120 (54)	· 160 (2.2)	·
17		· 118 (57)	· 163 (2.2)	·
18		· 123 (55)	· 163 (1.9)	·

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

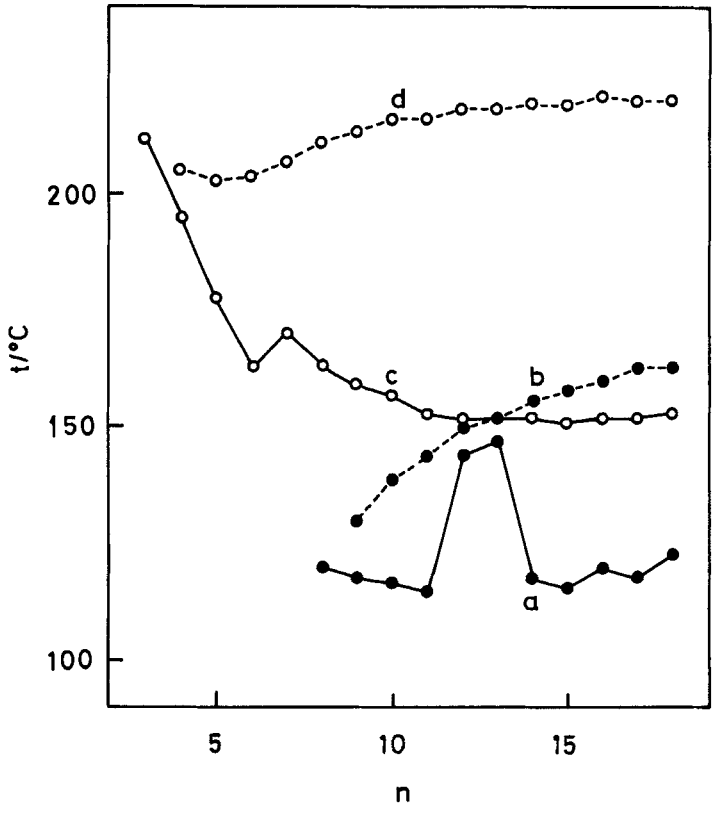


FIGURE 1 Plots of transition temperatures against the number of carbon atoms in the ester alkyl group (*n*) in the cation. (a) Melting point, (b) clearing point of the *p*-ethylbenzenesulfonates, (c) melting point, and (d) clearing point of the *p*-chlorobenzenesulfonates.

TABLE II

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

n[b]	K_3	K_2	K_1	S_A	I
3			· 212 (29)	·	
4		· 86 (12)	· 195 (12)	· 205 (6.0)	·
5		· 77 (10)	· 178 (12)	· 203 (6.0)	·
6		· 113 (7.0)	· 163 (14)	· 204 (6.5)	·
7		· 99 (5.9)	· 170 (14)	· 207 (4.8)	·
8	· 92 (13)	· 103 (4.7)	· 163 (12)	· 211 (5.1)	·
9		· 98 (21)	· 159 (13)	· 213 (5.1)	·
10	· 108 (14)	· 114 (13)	· 157 (12)	· 216 (5.0)	·
11		· 107 (29)	· 153 (11)	· 216 (4.8)	·
12		· 114 (35)	· 152 (12)	· 218 (4.7)	·
13		· 113 (36)	· 152 (13)	· 218 (4.3)	·
14		· 116 (41)	· 152 (12)	· 219 (4.8)	·
15		· 116 (41)	· 151 (11)	· 219 (4.6)	·
16		· 118 (46)	· 152 (12)	· 221 (4.6)	·
17	· 114 (22)	· 118 (27)	· 152 (12)	· 220 (4.0)	·
18		· 121 (52)	· 153 (12)	· 220 (5.0)	·

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

formation is confirmed by the replacemnt of sharp N–H stretching vibrational bands appearing in the region from 3100 to 3400 cm^{-1} with broad N^+–H stretching vibrational ones in the region from 2500 to 3000 cm^{-1}. The salts formed by the nonyl, decyl, and undecyl esters exhibit a solid–solid (K_2–K_1) transition in the temperature range of 101 to 110°C. The appearance of this transition results in a marked decrease of the enthalpy change at the K_1–S_A transition, which is located in a narrow range of 115 to 123°C except for the salts formed by the dodecyl and tridecyl esters. The X-ray diffraction pattern of the unoriented mesophase is characteristic of unstructured smectic phases; namely, it consists of a sharp peak (001 reflection, corresponding to the layer spacing) accompanied by its weak second order reflection at low Bragg angles and a diffuse one at larger angles (corresponding to the average lateral distance between the molecules within the smectic layers, 0.47 nm). The strong tendency to be homeotropic excludes the possibility of a smectic C phase. The clearing point is gradually raised by increasing the chain length of the ester alkyl chain from 130°C for the nonyl homologue to 163°C for the octadecyl homologue (see plot b in Figure 1). The temperature range of stable existence of the mesophase is as narrow as 5 to 6°C for the dodecyl and tridecyl homologues because of anomalously high melting points for these two members. The melting point of the other members changes smoothly with the alkyl chain length and the mesophase of the nonyl homologue is stable over a temperature range of 12°C and that of the heptadecyl homologue over 45°C. The associated enthalpy changes are rather small in agreement with the assignment to the class of a smectic A phase and are practically the same for all of the members.

Table II presents the thermodynamic data for the fifteen *p*-chlorobenzenesulfonates. The chloro substitution is so efficient that the shortest chain for smectic A formation is the butyl group. The salts are rich in polymorphic forms. In addition to the K_2–K_1 transition shown by all the mesogenic salts, a K_3–K_2 transition is detected for the salts

derived from the octyl, decyl, and heptadecyl esters. The enthalpy change at the K_2–K_1 transition is relatively small when the ester alkyl chain is decyl or shorter but it is large with longer alkyl groups. The transition temperature in the higher homologous members are found in the range from 107 to 121°C. The melting point is mostly located at temperatures higher by 30 to 40°C than those of the *p*-ethylbenzenesulfonates (compare plots a and c in Figure 1). The lengthening of the ester alkyl chain decreases the melting point until a limiting value of 152°C is reached by the dodecyl homologue. The enthalpy change is rather small and does not depend much upon the alkyl chain length; namely, 11 to 14 kJ mol^{-1}. As is shown in Figure 1, the mesophases appearing in the second series are thermodynamically more stable compared with those in the first one, indicating that the terminal substituent on the anion plays a very important role in determining the smectic A phase persistence (compare plots b and d). The difference in clearing point between these two series is as large as 60 to 80°C. The clearing point is raised but only slightly by ascending the homologous series. While the mesophase given by the butyl homologue is stable merely in a temperature range of 10°C, those given by the tetradecyl to octadecyl homologues are stable over a range of 67 to 69°C. The enthalpy changes associated with the S_A–I transition are markedly larger than those in the ethylbenzenesulfonate series, resulting in twice as large entropy changes. The smectic A phase in the present series must be less disordered than that in the other one. Higher S_A–I transition temperatures and also a higher incidence of the smectic A phase in the *p*-chlorobenzenesulfonates may be accounted for by this higher degree of ordering.

The relationship between the layer spacing (d/nm) in the smectic A phase and the number of carbon atoms (n) in the ester alkyl group is approximated by $d = 0.115n + 1.62$ for the *p*-ethylbenzenesulfonates and by $d = 0.132n + 1.75$ ($n \geq 8$) for the *p*-chlorobenzenesulfonates. The increment per methylene group is fairly close to the value expected for a fully-extended conformation of the alkyl chain (0.125 nm), suggesting that the chains are essentially perpendicular to the smectic layer. A smaller value for the *p*-ethylbenzenesulfonates may imply that the chains are conformationally more disordered than those in the *p*-chlorobenzenesulfonates. This proposition is in conformity with the markedly different entropy changes at the S_A–I transition discussed above. The molecular length of a protonated *p*-aminobenzoic acid along the line joining the 1- and 4-positions of the aromatic nucleus is estimated to be 0.94 nm and that of a *p*-chlorobenzenesulfonate ion 1.05 nm on the basis of the standard bond lengths, angles, and van der Waals radii. As to the charged parts (NH_3^+ and SO_3^- groups), the thermochemical ionic radii of NH_4^+ and SO_3^{2-} were employed because a strong electrostatic attraction between these two groups may be assumed.[13] The crystals and smectic layers are supposed to be made of ion pairs which are alternatively oriented with the alkyl chains interdigitated with each other. The length of 1.75 nm for the limiting case of $n = 0$ is shorter than the sum of the above-mentioned molecular lengths (1.99 nm). This disagreement may imply that the two molecular cores arranged in line make fairly large angles with the normal to the smectic layer because of the orientational disorder[14–15] or that the long axes of the two component ions are not quite in line with each other. A mean tilt angle of about 28° suggested by $\cos^{-1}(1.75/1.99)$ is not within the range from 0 to 25° proposed by Leadbetter *et al.*, therefore, these two situations might be considered together in our cases.

It must be emphasized that the length for the limiting case of $n=0$ in the *p*-ethylbenzenesulfonate series is shorter by 0.13 nm than that in the *p*-chlorobenzenesulfonate series in sharp contradiction to a little but definitely longer molecular length of the former anion. Previously, we noted that the layer spacing shrinks by the replacement of a *p*-toluenesulfonate ion with a *p*-ethylbenzenesulfonate ion in the alkylammonium salts.[8] Furthermore, the spacing in the smectic A phase given by alkylammonium alkanesulfonates was found to diminish as the alkyl chain length in the anions is increased.[9] All these observations suggest that the alkyl group attached to the anions is dissolved, to some extent, into the layer formed by the paraffinic parts of the counter ions; that is, the ester alkyl group in the present series.

p-Chloro substitution is often pointed out to encourage smectic A behavior though the reason is not made clear. The following terminal group efficiency order in promoting smectic A phase thermal stability was noted by Gray comparing the S_A–N/I transition temperatures of 4-(4-X-substituted benzylideneamino)-4′-octyloxybiphenyls, $NHCOCH_3 > Br > Cl > F > N(CH_3)_2 > H > CH_3 > NO_2 > CH_3O$.[16] Although the later work by Takenaka *et al.* on three-ring systems carrying two ester linkages revealed that the order varies, to some extent, by the orientation of the linking groups, *p*-halogeno substituents are invariably more favorable to the smectic A stability than alkyl substituents and also that these terminal substituents are capable of promoting the mesophase.[17] The present limited results and the failure to observe a smectic A phase for the unsubstituted benzenesulfonates seem to be in accord with the above-mentioned broad trend.

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