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Syntheses of new ionic liquid crystal materials

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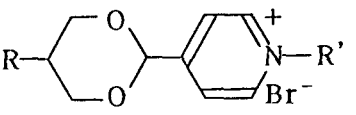
A new pyridinium type thermotropic ionic liquid crystal materials having a 1, 3-dioxane ring in its central core: N-ethyl-4-(5-alkyl-1, 3-dioxane-2-yl) pyridiniumbromides (5) were synthesized. Some of these compounds exhibited liquid crystal phase. Identification of mesophase was carried out. The results of observation of mesophase and X-ray diffraction showed the phase was Smectic A.

1. INTRODUCTION

There are not many reports concerning ionic thermotropic liquid crystal compound having two rings as a core. Some liquid crystal polymers with pyridinium side chain[1] and those with alkyl ammonium salt as a principal chain were reported.[2] And stilbazole type metal-containing liquid crystals were also reported.[3] On the other hand, we have studied 1, 3-dioxane and 1, 3-oxathiane and 1, 3-dithiane type liquid crystal materials.[4]-[8] And ionic liquid crystal materials having these structures in its central core have not been encountered to date and its possibility as a liquid crystal material is interesting. From these points of view, N-ethyl-4-(5-alkyl-1, 3-dioxan-2-yl-)pyridinium bromide 5 was synthesized. In this paper we wish to report the new type of thermotropic ionic liquid crystal material having the two rings in its central core. (Fig. 1)

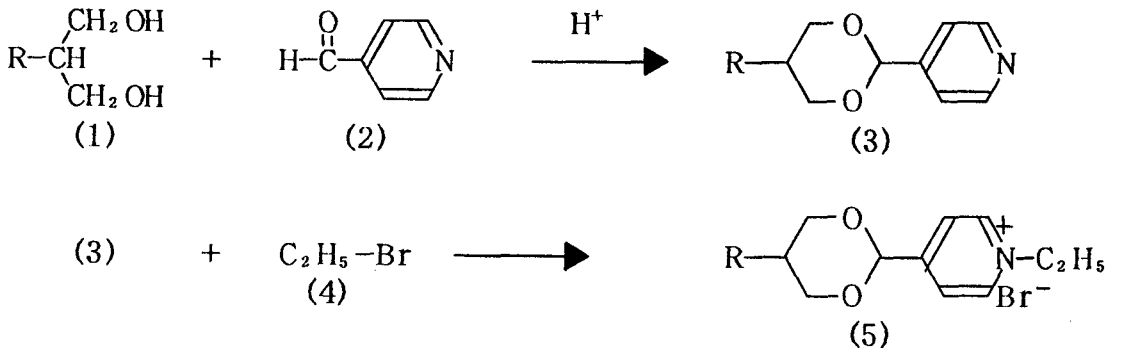


5

Fig. 1. Chemical structure of new ionic liquid crystal compound

2. RESULTS AND DISCUSSION

Compounds 5 were synthesized by the route shown in Fig. 2.



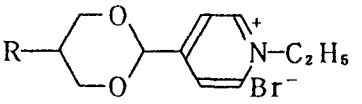
R : C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, $C_{10}H_{21}$, $C_{11}H_{23}$

Fig. 2. Synthetic pathway for the compounds 5.

In the syntheses of compounds 5, both trans and cis isomers were produced which differed at the C-5 position of the 1,3-dioxane ring. Repeated recrystallizations were required to obtain only the trans isomers. In the ^{1}H-NMR spectra for the compounds 5, the C-2 proton signals for the trans and cis isomer are 5.50 and 5.55 ppm, respectively. Therefore, removal of the cis isomer can be checked by the disappearance of its peak in a ^{1}H-NMR spectrum. By the N-alkylation, ^{1}H-NMR signals for pyridinium proton and acetal proton (C-2 proton of the 1,3-dioxane ring) were shifted about 0.8 and 0.3 ppm to the lower magnetic field, respectively. The purity of compounds 5 was checked by the ^{1}H-NMR data and elemental analyses. Good data were obtained for these compounds. To judge the existanse of liquid crystal phases, observation by a micro melting point apparatus equipped with polarizers was made. Compounds 5 exhibited a liquid crystal phase, so that further detailed measurements were made. Measurement of transition temperarures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, a differential scanning calorimeter (DSC), and a X-ray system. Phase transition temperatures for compounds 5 are given in Table 1.

Observation on these textures indicated that these compounds exhibited a same texture of smectic A phase. To confirm this result, X-ray diffraction were measured for the phase of compound 5-6. (Fig. 3)
This result also support the assignment of the liquid crystal phase as smectic A. That is, the diffraction pattern of the typical smectic A phase was also obtained. The only sharp peak in the small-angle region indicates

Table 1 Phase transition temperatures for compounds 5



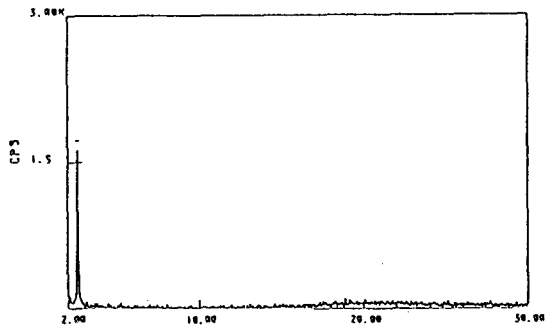
(5)

	R	Phase transition temperatures (°C)
5-1	C_6H_{13}	G $\xrightarrow{-16}$ I
5-2	C_7H_{15}	G $\xrightarrow{-9}$ SmA $\xrightarrow{30}$ I
5-3	C_8H_{17}	G $\xrightarrow{-11}$ SmA $\xrightarrow{53}$ I
5-4	C_9H_{19}	G $\xrightarrow{-1}$ SmA $\xrightarrow{107}$ I
5-5	$C_{10}H_{21}$	G $\xrightarrow{-4}$ SmA $\xrightarrow{152}$ I
5-6	$CH_2=CH(CH_2)_8-$	C $\xrightarrow{58}$ SmA $\xrightarrow{96}$ I
5-7	$C_{11}H_{23}$	G $\xrightarrow{-9}$ SmA $\xrightarrow{181}$ I

* C: Crystal, G: Glass, SmA: Smectic A, I: Isotropic

the layer spacing of this phase is 34.3 A. From the value of layer spacing and the peculiarity as a ionic liquid crystal compound, the molecular arrangement in the smectic A phase seem to be shown in Fig. 4. That is, in this model cationic pyridinium ions and anionic bromonium ions stabilized each other, and long alkyl chains orient to form the smectic phase.

Transition temperatures of isotropic to mesophase for compound 5-6 is lower than those of compounds 5-5 having the saturated long alkyl chain. This seems to originate in the existence of terminal double bond in compounds 5-6.[9),10)]



(2θ /deg.)

Fig. 3. X-ray diffraction pattern of new ionic liquid crystal compound 5-3

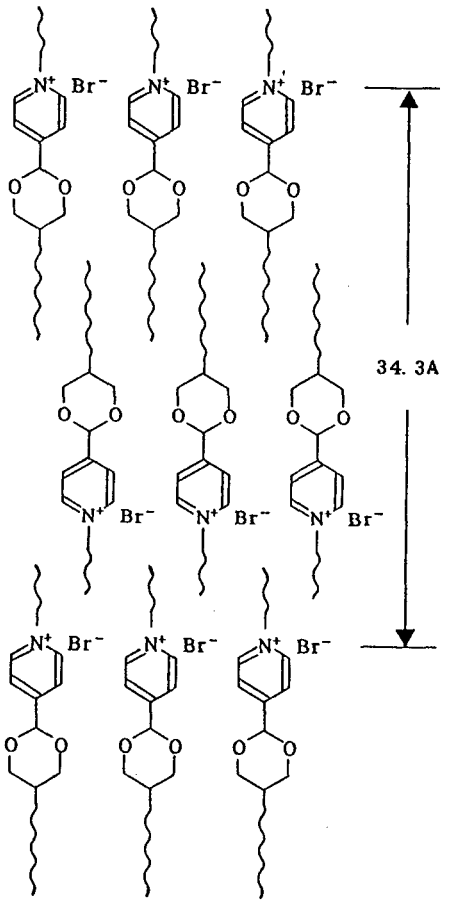


Fig. 4. Molecular arrangement of new ionic liquid crystal compound

The most remarkable feature of these new ionic liquid crystal material is to exhibit liquid crystal phase over a very wide range including ordinary room temperature (e.g. 5-5: C -4 SmA 152 I).

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