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A new ionic liquid crystal compound with viologen group in the principal structure

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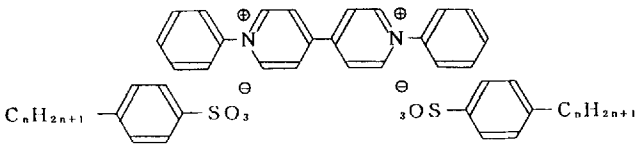
A new ionic liquid crystal system, based on compounds with the viologen group (for example, **1–2**: Cr 190 S_A 280 dec.) has been synthesized, and is found to exhibit the smectic A phase.

1. Introduction

There are only a few reports concerning ionic thermotropic liquid crystals. Some liquid crystal polymers with the pyridinium side chain [1] and those with alkyl ammonium salt as a principal chain have been reported [2]. Hydrogen-bonded liquid crystals have also been reported [3]. In this paper we wish to report the new type of ionic liquid crystal material shown in figure 1.



(**1**)

Figure 1. Chemical structure of the new ionic liquid crystal compound (**1**).

2. Results

Generally, 4,4′-bipyridium salts have been studied as a redox material [4, 5]. However, liquid crystal materials having the 4,4′-bipyridinium salt structure have not been encountered to date but their possibility as liquid crystal materials is interesting. From such a point of view, 1,1′-diphenyl-4,4′-bi-pyridinium bis (*p*-alkylbenzenesulphonate) (**1**) was synthesized by the anion exchange reaction of 1,1′-diphenyl-4,4′-bipyridinium dichloride with an excess of *p*-alkylbenzenesulphonic acid. The purity of the *p*-alkylbenzenesulphonic acid is important. If *p*-alkylbenzenesulphonic acid contains small amounts of sodium *p*-alkylbenzene sulphonate, this salt would remain in the final compounds. The purity of compounds (**1**) were checked by ^{1}H NMR and elemental analyses and good composition data were obtained for these compounds.

Phase transition temperatures for compounds (**1**).

	$R \rightarrow$ Phase transition temperatures†/°C	
1–2	*c*–$C_{10}H_{21}$	Cr 205 S_A 285 dec.
1–2	*n*–$C_{13}H_{27}$	Cr 190 S_A 280 dec.
1–3	*n*–$C_{15}H_{31}$	Cr 168 S_A 290 dec.

† Cr: Crystal, S_A: Smectic A, dec.: decomposed.

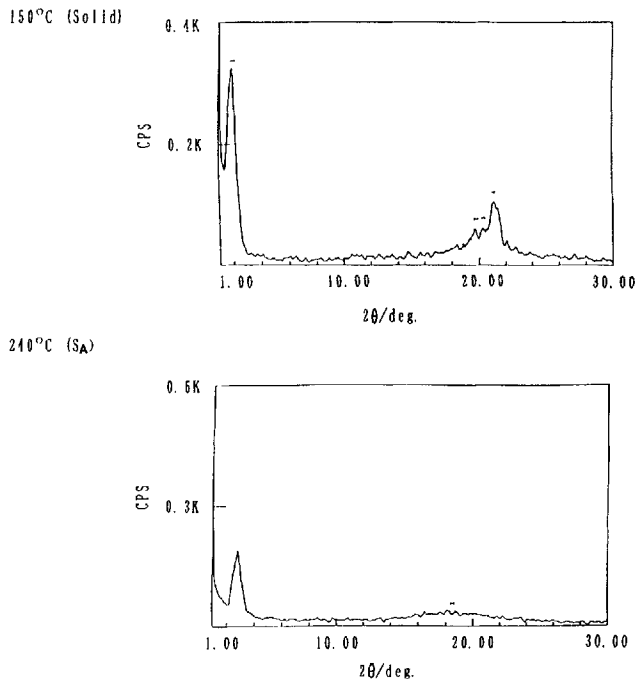


Figure 2. X-ray diffraction pattern of new ionic liquid crystal compound measured with a Rigaku X-ray Rad 2B system using Ni-filtered CuK_α radiation.

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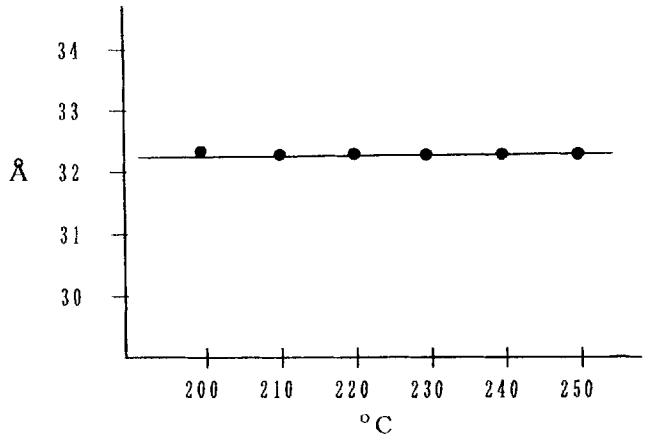

Figure 3. Temperature dependence of the layer spacing for the new ionic liquid crystal material.

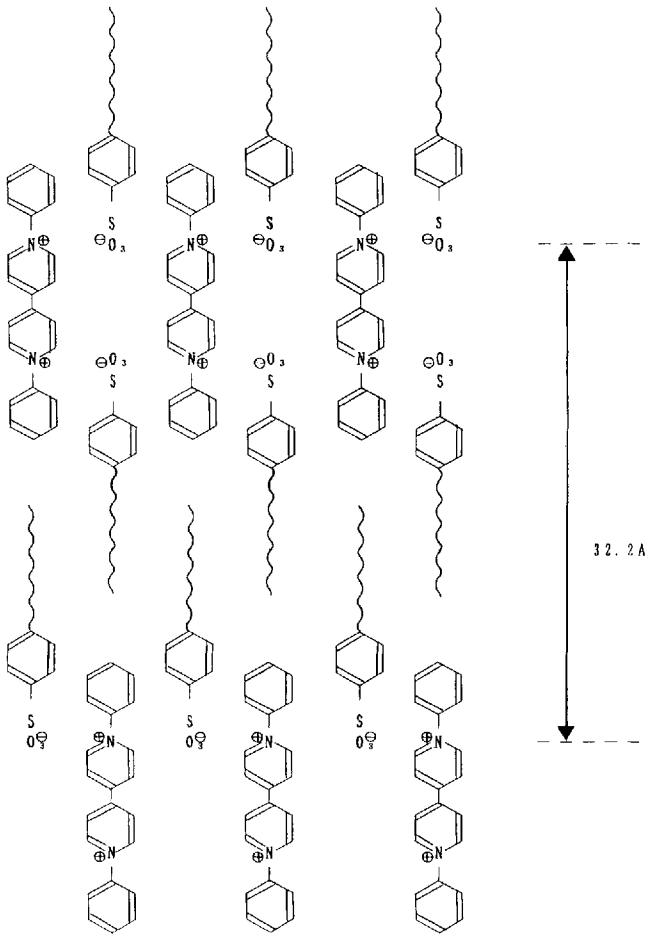

Figure 4. Possible molecular arrangement of new ionic liquid crystal compound.

To judge the existence of liquid crystal phases, observation by a micro-melting point apparatus equipped with polarizers was made. All of these compounds exhibited a liquid crystal phase, so further detailed measurements were made. Measurement of the transition temperatures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, a differential scanning colorimeter (DSC), and an X-ray system.

Mesomorphic transition temperatures for compounds (**1**) are given in the table. Observation of these textures indicated that the type of liquid crystal phase is smectic A. To confirm this result, an X-ray diffraction study was performed for the new phase of compound **1–2** at several temperatures, and supported the assignment of the liquid crystal phase as smectic A (see figure 2).

At 150°C the diffraction pattern indicates the solid state, and at 200, 210, 220, 230, 240, and 250°C, the diffraction patterns indicate the smectic A phase, showing a broad peak at wide angle (see figure 3). The peak shape indicates that this phase may be smectic A or C. However, the layer spacing of 32·2 Å (see figure 3), does not vary with temperature, as would be expected for a smectic C phase [6], indicating that the phase is not smectic C but smectic A. From the value of the layer spacing and the ionic nature of this liquid crystal compound the possible molecular arrangement in the smectic A phase is shown in figure 4. In this model, cationic pyridinium ions and anionic sulphonate ions stabilize each other, and long alkyl chains orient to form the smectic phase. These compounds also showed photochromic behaviour by redox reaction between the pyridinium cations and sulphonate anions. For example, a fine powder of compound **1–2** was heated to 220°C under nitrogen and sandwiched between two glass plates to provide an air-tight thin film free of oxygen. This film was subject to near-UV radiation from a 75 W high-pressure mercury lamp for 30 min. The resulting absorbance at 570 nm increased.

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