Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Thermotropic liquid crystalline ionic stilbazoles and their miscible mixtures with non-ionic carbazolyl compounds

Yozo Kosaka[a]; Takashi Kato[b]; Toshiyuki Uryu[b]
[a] Central Research Institute, Dai Nippon Printing Co., Ltd., Tokyo, Japan [b] Institute of Industrial Science, University of Tokyo, Tokyo, Japan

To cite this Article Kosaka, Yozo , Kato, Takashi and Uryu, Toshiyuki(1995) 'Thermotropic liquid crystalline ionic stilbazoles and their miscible mixtures with non-ionic carbazolyl compounds', Liquid Crystals, 18: 5, 693 — 698
To link to this Article: DOI: 10.1080/02678299508036678
URL: http://dx.doi.org/10.1080/02678299508036678

LIQUID CRYSTALS, 1995, VOL. 18, NO. 5, 693–698

Thermotropic liquid crystalline ionic stilbazoles and their miscible mixtures with non-ionic carbazolyl compounds

by YOZO KOSAKA*
Central Research Institute, Dai Nippon Printing Co., Ltd.,
Ichigaya-Kagamachi, Shinjuku-ku, Tokyo 162-01, Japan

TAKASHI KATO and TOSHIYUKI URYU
Institute of Industrial Science, University of Tokyo,
Roppongi, Minato-ku, Tokyo 106, Japan

(*Received 22 September 1994; accepted 24 October 1994*)

New thermotropic ionic liquid crystals were prepared from *trans*-4-nitro-4′-stilbazole and alkyl halides. *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium bromides containing alkyl chains with 7 to 10 carbons and the chloride homologues containing alkyl chains with 5 to 10 carbons exhibited smectic phases. For example, *trans*-*N*-decyl-4-nitro-4′-stilbazolium bromide and *trans*-*N*-hexyl-4-nitro-4′-stilbazolium chloride showed smectic phases from 175 to 186°C and from 129 to 190°C, respectively. The temperature range of mesophases increased with decreasing size of the counteranions. The miscibility of *trans*-*N*-alkyl-4-nitro-4′-stilbazolium bromide in Schiff's base compounds having various electronegative groups was examined by differential scanning calorimetry and polarizing microscopy. Miscible binary mixtures were prepared from *trans*-*N*-alkyl-4-nitro-4′-stilbazolium bromides and 4-alkoxy-*N*-(9-methyl-2-carbozolyl-methylene)anilines. The 1:1 (mole ratio) binary mixture of *trans*-*N*-hexyl-4-nitro-4′-stilbazolium bromide with 4-hexyloxy-*N*-(9-methyl-2-carbazolylmethylene)aniline exhibited a stable smectic phase between 83 and 149°C, though a smectic phase is not exhibited by both individual components. The miscibility in the binary mixtures might be caused by a combination of ionic and electron donor–acceptor interactions.

1. Introduction

Typical liquid crystals are usually composed of two major structural portions; a rigid elongated aromatic core and terminal flexible alkyl chains or polar groups [1]. Recently, novel families of liquid crystals have been found in compounds that form a rod-like structure through intermolecular hydrogen bonding [2–6], electron donor–acceptor interactions [7–11], and ionic interactions [12–23].

Hydrogen-bonded liquid crystals have been obtained by the complexation of carboxylic acids as H-bond donors with pyridyl compounds as H-bond acceptors [2, 3]. Stilbazoles serve as one of the key components of these liquid crystals [2, 4]. The complexes exhibit remarkable enhancement of the mesophases. Metal-containing liquid crystals have also been prepared by the complexation of metals with *trans*-4-alkoxy-4′-stilbazoles [20–23]. The mesophase ranges of these complexes are larger in comparison to those of the *trans*-4-alkoxy-4′-stilbazoles [20–24]. Liquid crystalline stilbazole derivatives having a quaternized pyridyl unit also have potential for liquid crystalline materials.

In this paper, we wish to report the liquid crystallinity of ionic *trans*-*N*-alkyl-4-nitro-4′-stilbazoles with counteranions of chloride, bromide, and iodide (see figure 1). The effect of the alkyl chain length on the liquid crystalline behaviour was studied. The halides of these compounds have electron-accepting character. Binary mixtures were prepared from these bromides and non-ionic carbazolylmethyleneanilines (see figure 2). These carbazolyl derivatives have electron-donating properties [25, 26]. The effect of donor–acceptor interactions on phase behaviour was examined for these mixtures. Both the ionic compounds and binary mixtures were characterized by optical polarized microscope observation, differential scanning calorimetry, and X-ray diffractometry.

2. Experimental

4-Alkoxy-*N*-(9-methyl-2-carbazolylmethylene)anilines (*m*Cz: $m = 2, 6, 10$) and 4-hexyloxy-*N*-(4′-*R*-substi-

---

* Author for correspondence.

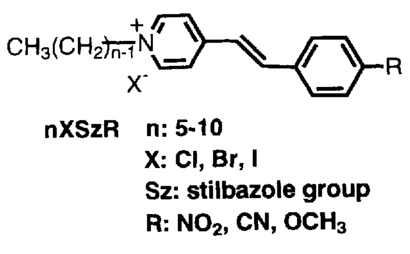

Figure 1. Molecular structures of *trans*-*N*-alkyl-4-substituted-4′-stilbazolium halides (*nXSzR*).

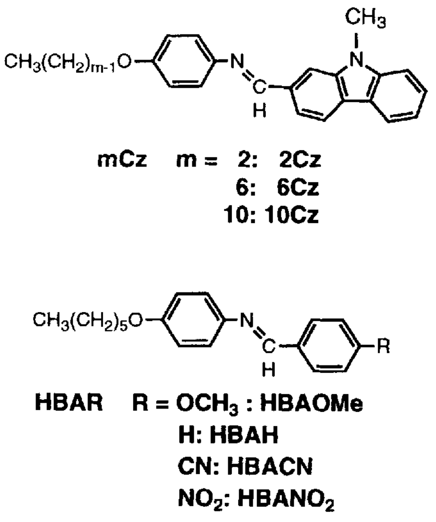

Figure 2. Molecular structures of 4-alkoxy-*N*-(9-methyl-2-carbazolylmethylene)anilines (*m*Cz) and 4-hexyloxy-*N*-(4′-substituted-benzylidene)anilines (HBAR).

tuted-benzylidene)anilines (HBA*R*: *R* = OMe, H, CN, NO_2) were prepared according to the procedure previously described [26].

2.1. trans-*4-Substituted-4′-stilbazoles* (*SzR*)

trans-4-Substituted-4′-stilbazoles (Sz*R*) were prepared according to a modification of the literature method [27, 28]. As a representative case, synthesis of *trans*-4-nitro-4′-stilbazole ($SzNO_2$) is described. A mixture of 4-nitrobenzaldehyde (15·1 g, 0·1 mol), 4-picoline (11·2 g, 0·12 mol) and acetic anhydride (20 ml) was heated at 70°C for 48 h under dry N_2. After cooling, the reaction mixture was poured into cooled water and the precipitate was collected by filtration. The resulting product was purified on a silica gel column using chloroform/methanol (20 : 1) as eluent, followed by recrystallization of the isolated solid from methanol to provide $SzNO_2$. For $SzNO_2$: yield 38 per cent m.p. 171·9°C (lit. [29] m.p.: 171–172°C) and ^1H NMR ($CDCl_3$): 7·18 (1 H, d, J = 16·4 Hz), 7·35 (1 H, d, J = 16·0 Hz), 7·41 (2 H, d, J = 4·4 Hz), 7·67 (2 H, d, J = 8·8 Hz), 8·26 (2 H, d, J = 8·8 Hz), and 8·65 (2 H, d, J = 4·4 Hz). For *trans*-4-cyano-4′-stilbazole (SzCN): yield 47 per cent; m.p., 124·8°C and ^1H NMR ($CDCl_3$): 7·14 (1 H, d, J = 16·0 Hz), 7·30 (1 H, d, J = 16·4 Hz), 7·41 (2 H, d, J = 6·0 Hz), 7·64 (2 H, d, J = 8·4 Hz), 7·69 (2 H, d, J = 8·4 Hz), and 8·64 (2 H, d, J = 6·0 Hz). For *trans*-4-methoxy-4′-stilbazole (SzOMe): yield 15 per cent; m.p., 132·3°C (lit. [29] m.p: 131·5–132·5°C) and ^1H NMR ($CDCl_3$): 6·88 (1 H, d, J = 16·0 Hz), 6·93 (2 H, d, J = 8·8 Hz) 7·26 (1 H, d, J = 16·8 Hz), 7·34 (2 H, d, J = 5·6 Hz), 7·49 (2 H, d, J = 8·8 Hz), and 8·56 (2 H, d, J = 6·0 Hz).

2.2. trans-N-*Alkyl-4-substituted-4′-stilbazolium halides* (nX*Sz*R)

A stirred mixture of Sz*R* (2 mmol), 1-alkyl halide (10 mmol) and DMF (5 ml) was heated at 70°C for 72 h. After cooling, the reaction mixture was poured into ethyl acetate (50 ml). The precipitate was collected by filtration and washed with ethyl acetate. This material was purified by reprecipitation from chloroform using ethyl acetate to provide *nX*Sz*R*. Yield: *n*$ClSzNO_2$, 14–18 per cent; *n*$BrSzNO_2$, 90–95 per cent; *n*$ISzNO_2$, 90–96 per cent. ^1H NMR ($CDCl_3$) for $10BrSzNO_2$: 0·85 (3 H, t, J = 6·9 Hz), 1·30 (14 H, m), 2·00 (2 H, m), 4·88 (2 H, t, J = 6·9 Hz), 7·57 (1 H, d, J = 16·7 Hz), 7·92 (2 H, d, J = 8·3 Hz), 8·03 (1 H, d, J = 16·2 Hz), 8·22 (2 H, d, J = 8·8 Hz), 8·36 (2 H, d, J = 6·9 Hz), and 9·22 (2 H, d, J = 6·4 Hz).

2.3. *Preparation of binary mixtures composed of* n*$BrSzNO_2$ and* m*Cz*

Binary mixtures of *n*$BrSzNO_2$ and *m*Cz were prepared by evaporation of chloroform solutions of these mixtures, followed by drying under vacuum.

2.4. *Characterization*

^1H NMR spectra were recorded ($CDCl_3$) using an OMEGA 400WB (General Electric Co.) NMR spectrometer. A differential scanning calorimeter (Mettler DSC 30) was used to determine phase transition temperatures using heating and cooling rates of 10° min^{-1}. The peak temperature of the endotherm was taken as the transition temperature. An optical polarizing microscope (Olympus BH-2) equipped with a Mettler FP 82 hot stage and a temperature programmer FP 80 was also used to observe phase transitions using heating and cooling rates of 10° min^{-1}. X-ray diffraction data were collected using a Rigaku RINT 1500 X-ray diffractometry.

3. Results and discussion

3.1. *Thermal properties of* trans-N-*alkyl-4-substituted-4′-stilbazolium halides* (nX*Sz*R)

Molecular structures of *trans*-*N*-alkyl-4-substituted-4′-stilbazolium halides denoted as *nX*Sz*R*, in which *n*, *X*, Sz, and *R* are the number of carbon atoms of the alkyl chain, the counteranion, the stilbazole group, and the 4-substi-

Table 1. Thermal properties for *trans*-*N*-alkyl-4-substituted-4′-stilbazolium bromides (*n*BrSz*R*).

n	*R*	Phase transition temperature†/°C
6	NO$_2$	Cr 149 I
6	CN	Cr 250 I‡
6	OCH$_3$	Cr 215 I‡
10	NO$_2$	Cr 175 S 186 I
10	CN	Cr 254 I‡
10	OCH$_3$	Cr 242 I‡

† Transition temperature determined by DSC at 10°/min^{-1} on the first (R = CN, OCH$_3$) and the second (R = NO$_2$) heating runs and by microscopy observation. Cr: crystalline; S: smectic; I: isotropic.

‡ Partial decomposition observed.

Table 2. Thermal properties for *trans*-*N*-alkyl-4-nitro-4′-stilbazolium halides (*nX*SzNO$_2$).

n	*X*	Phase transition temperature†/°C	ΔH_i‡ kJ mol^{-1}
6	Cl	Cr 129 S 190 I	4·8
6	Br	Cr 149 I	
6	I	Cr 193 I§	
10	Cl	Cr 167 S 227 I§	6·2§
10	Br	Cr 175 S 186 I	4·7
10	I	Cr 147 I	

† Transition temperature determined by DSC at 10° min^{-1} on the first (6ISzNO$_2$ and 10ClSzNO$_2$) and the second heating runs and by microscopy observation. Cr: crystalline; S: smectic; I: isotropic.

‡ Measured by DSC. ΔH_i: enthalpy change of clearing.

§ Partial decomposition observed.

tuted group in stilbazole unit, respectively are shown in figure 1. *nX*Sz*R* was prepared by reaction of *trans*-4-substituted-4′-stilbazoles (Sz*R*) with alkyl halides. The bromides and iodides were obtained in high yields, while the yield of the chlorides was low. As the ^{1}H NMR spectrum indicated considerable downfield shift of the protons positioned ortho to the pyridinium nitrogen, the ionic bonding of stilbazolium halides was confirmed.

Thermal properties for *trans*-*N*-alkyl-4-substituted-4′-stilbazolium bromides with nitro (*n*BrSzNO$_2$), cyano (*n*BrSzCN), and methoxy (*n*BrSzOMe) terminal groups are summarized in table 1. In the DSC measurement of *trans*-*N*-decyl-4-nitro-4′-stilbazolium bromide (10BrSzNO$_2$), two endothermic peaks corresponding to the crystalline–mesophase and mesophase–isotropic transitions were observed at 175 and 186°C, respectively. Polarized microscopy of this ionic compound exhibited focal-conic fan and homeotropic textures characteristic of a smectic A phase [30]. The enthalpy changes from crystalline to smectic and from smectic to isotropic phase transitions for 10BrSzNO$_2$ were 9·8 and 4·7 kJ mol^{-1}, respectively. The stilbazolium bromides having a *para*-cyano or methoxy group showed partial decomposition above 200°C during both microscope and DSC measurements.

In order to examine the effect of the counteranion and the carbon number of the alkyl chain on the thermal properties, *trans*-4-nitro-4′-stilbazole group was chosen as a mesogenic unit. The thermal properties for *trans*-*N*-alkyl-4-nitro-4′-stilbazolium chlorides (*n*ClSzNO$_2$), bromides, and iodides (*n*ISzNO$_2$) are shown in table 2. The chloride-containing compounds with $n = 6$ (6ClSzNO$_2$) and $n = 10$ (10ClSzNO$_2$) showed smectic phases in the wide temperature range from 129 to 190°C and from 167 to 227°C, respectively. In contrast, 6ISzNO$_2$ and 10ISzNO$_2$ were not mesomorphic, exhibiting melting at 193 and 147°C, respectively. The liquid crystallinity of these ionic compounds increased with decreasing counteranion size, probably because a higher molecular packing was accomplished with the stronger ionic interaction occurring with a smaller halide. A similar tendency was reported for 1-[ω-(4′-methoxy-4-biphenyloyloxy)alkyl]pyridinium halides [15].

The thermal properties for *n*ClSzNO$_2$ and *n*BrSzNO$_2$ having different alkyl lengths are shown in table 3 and figure 3. The stilbazolium chlorides with the alkyl group, from pentyl to decyl, formed smectic phases. In addition, smectic phases were observed for the *n*BrSzNO$_2$ containing the alkyl group from heptyl to decyl. For the

Table 3. Thermal properties for *trans*-*N*-alkyl-4-nitro-4′-stilbazolium chlorides (*n*ClSzNO$_2$) and bromides (*n*BrSzNO$_2$).

Compound	Phase transition temperature†/°C	ΔH_i‡ kJ mol^{-1}
5ClSzNO$_2$	Cr 125 S 184 I	4·2
6ClSzNO$_2$	Cr 129 S 190 I	4·8
7ClSzNO$_2$	Cr 130 S 210 I§	6·3§
8ClSzNO$_2$	Cr 134 S 210 I§	5·1§
9ClSzNO$_2$	Cr 148 S 220 I§	5·1§
10ClSzNO$_2$	Cr 167 S 227 I§	6·2§
5BrSzNO$_2$	Cr 146 I	
6BrSzNO$_2$	Cr 149 I	
7BrSzNO$_2$	Cr 146 S 168 I	6·7
8BrSzNO$_2$	Cr 170 S 175 I	5·8
9BrSzNO$_2$	Cr 154 S 175 I	5·1
10BrSzNO$_2$	Cr 175 S 186 I	4·7

† Transition temperature determined by DSC at 10° min^{-1} on the first (*n*ClSzNO$_2$, $n = 7$–10) and the second (*n*ClSzNO$_2$, $n = 5, 6$; *n*BrSzNO$_2$, $n = 5$–10) heating runs and by microscopy observation. Cr: crystalline; S: smectic; I: isotropic.

‡ Measured by DSC: ΔH_i: enthalpy change of clearing.

§ Partial decomposition observed.

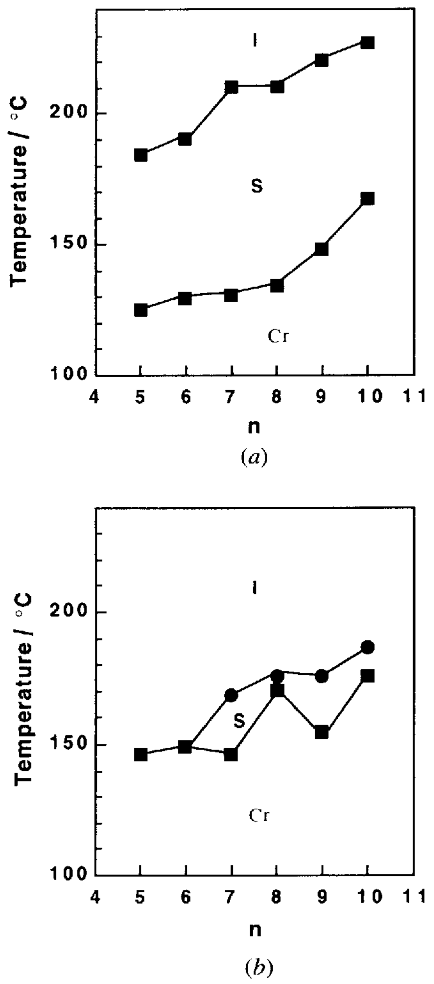

Figure 3. Dependende of the transition temperatures on the carbon number (*n*) of the alkyl chain for (*a*) *trans*-*N*-alkyl-4-nitro-4′-stilbazolium chlorides and (*b*) *trans*-*N*-alkyl-4-nitro-4′-stilbazolium bromides.

*n*BrSzNO_2, the melting temperature showed an odd–even effect in the variation of alkyl chain length from 5 to 10. The melting temperature of the even number of the alkyl group was higher than that of the odd number for the *n*BrSzNO_2. The clearing temperature increased with increasing chain length.

In X-ray diffraction studies, a sharp reflection at 2Θ of 2·90° ($d = 30{\cdot}4$ Å) corresponded to the thickness of the smectic layer. A molecular model of 10BrSzNO_2 in the fully-stretched conformation gave a molecular length of 25·5 Å, 4·9 Å shorter than the layer spacing. The difference might be caused by the existence of a bromide ion (diameter: 3·90 Å) [14, 15]. Like the reported long-chain alkyl pyridinium halides [14], the packing of 10BrSzNO_2 molecules is assumed to be of a sandwich type in which the anion is inserted between the two pyridinium rings.

3.2. *Liquid crystalline properties of the miscible mixtures of* n*BrSzNO*$_2$ *with 4-alkoxy-*N*-(9-methyl-2-carbazolylmethylene)anilines* (m*Cz*)

In this study, it was found that the positively-charged stilbazolium derivatives form electron donor–acceptor mixtures by mixing with electron-donating aromatic compounds, as Schiff's base derivatives, for example, 4-alkoxy-*N*-(9-methyl-2-carbozolylmethylene)anilines (*m*Cz) and 4-hexyloxy-*N*-(4′-*R*-substituted-benzylidene)anilines (HBA*R*: *R* = OMe, H, CN, NO_2) (see figure 2) [26].

After evaporation of the mixture solution, a miscible red-coloured mixture was obtained from 6BrSzNO_2 and 4-hexyloxy-*N*-(9-methyl-2-carbazolylmethylene)aniline (6Cz). In the DSC measurement of this mixture, three endothermic peaks were observed at 67, 83, and 149°C. Microscopy studies revealed that these endothermic peaks correspond to crystalline–crystalline, crystalline–smectic, and smectic–isotropic transitions, respectively. A focal-conic fan texture characteristic of the smectic phase was seen for the 6BrSzNO_2–6Cz mixture, as shown in figure 4 (*a*).

Since the carbazolyl group has a strong electron-donating property, it is assumed that an electron donor–acceptor interaction took place between the carbazolyl group and the electron-deficient nitrostilbazolium group. On the other hand, 1 : 1 binary mixtures between 6BrSzNO_2 and HBA*R* caused phase separation (see figure 4 (*b*)).

The phase diagram for the mixtures of 6BrSzNO_2 with 6Cz is shown in figure 5. Smectic phases were induced in the 6BrSzNO_2–6Cz mixtures containing 25 to 90 mol % of 6BrSzNO_2. In the 1 : 1 mixture of 6BrSzNO_2 and 6Cz, the isotropic temperature (149°C) was 13° higher than the average value based on the compositions, indicating that the electron donor–acceptor interaction between these molecules stabilized the mesophase. The widest mesophase temperature range was observed for the binary mixture of an equimolar composition. On the other hand, binary mixtures with less than 25 mol % of 6BrSzNO_2 showed both smectic and nematic phases from 93 to 122°C, followed by the coexistence of both smectic and isotropic phases which indicated phase separation. The miscible mixtures of 6BrSzNO_2 and 6Cz might simply be formed by the 1 : 1 intermolecular electron donor–acceptor interaction.

The thermal properties of binary mixtures of *n*BrSzNO_2 with *m*Cz having various alkoxy chain lengths are summarized in table 4. Although phase separation was observed for the 1 : 1 mixture of 10BrSzNO_2 with 4-ethoxy-*N*-(9-methyl-2-carbazolylmethylene)aniline (2Cz), other 1 : 1 mixtures showed smectic phases. The mesophase temperature range of the mixtures became wider than that of each individual compound. For example, 1 : 1 mixture of 6BrSzNO_2 with 2Cz exhibited

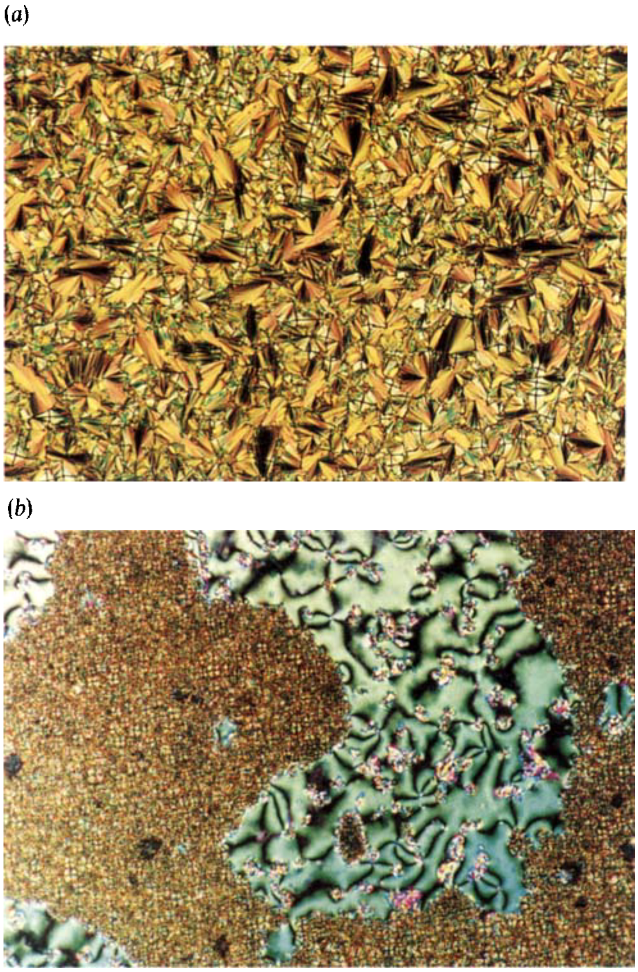

Figure 4. Optical polarized microphotographs of the 1 : 1 binary mixtures of (*a*) *trans*-*N*-hexyl-4-nitro-4′-stilbazolium bromide with 4-hexyloxy-*N*-(9-methyl-2-carbazolylmethylene)aniline at 130°C on the first cooling and (*b*) *trans*-*N*-hexyl-4-nitro-4′-stilbazolium bromide with 4-hexyloxy-*N*-(4′-methoxybenzylidene)aniline at 90°C on the first cooling.

a smectic phase from 86 to 133°C. It is noted that both $6BrSzNO_2$ and 2Cz were not liquid crystalline. The enthalpy changes of clearing for the mixtures were in the range of 2·5 to 4·1 kJ mol^{-1}.

The 1 : 1 mixture of $6BrSzNO_2$ and 6Cz did not show a mesophase–crystalline transition on cooling from the isotropic melt for both DSC and microscopy studies using a cooling rate of 10 ° min^{-1}. The X-ray diffraction pattern of the quenched mixture of $6BrSzNO_2$ and 6Cz showed a sharp reflection at 2Θ of 3·76° (d = 23·5 Å) corresponding to the thickness of the smectic layer and a broad peak reflection at 2Θ of 21·88° (d = 4·06 Å) due to the distance between the mesogenic groups. Polarized microscopy of this mixture showed homeotropic and focal-conic fan textures. These results suggest that this mixture exhibits a smectic A phase. The thickness of the smectic layer (d = 23·5 Å) was close to the calculated molecular length of 24·0 Å for the fully-stretched 6Cz molecule. It is assumed that the miscibility and the induction of the smectic phase are caused by the complex formation of electron donor and acceptor mesogens, as illustrated in figure 6.

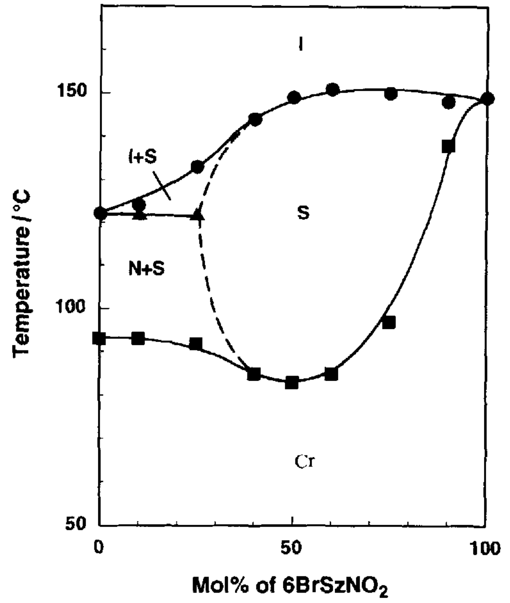

Figure 5. Binary phase diagram for the mixtures of *trans*-*N*-hexyl-4-nitro-4′-stilbazolium bromide with 4-hexyloxy-*N*-(9-methyl-2-carbazolylmethylene)aniline.

Table 4. Thermal properties of 4-alkoxy-*N*-(9-methyl-2-carbazolylmethylene)aniline and their 1 : 1 binary mixtures of *trans*-*N*-alkyl-4-nitro-4′-stilbazolium bromides (nBrSzNO$_2$–mCz).†

Compound and 1 : 1 mixture	Phase transition temperature‡/°C	ΔH_i§ kJ mol^{-1}
2Cz	Cr 142 (N 133) I¶	
6Cz	Cr 93 N 123 I	0·3
10Cz	Cr 107 N 114 I	0·3
$6BrSzNO_2$-2Cz	Cr 86 S 133 I	4·1
$6BrSzNO_2$-6Cz	Cr 83 S 149 I	2·9
$6BrSzNO_2$-10Cz	Cr 109 S 141 I	2·5
$10BrSzNO_2$-2Cz	Phase separation	
$10BrSzNO_2$-6Cz	Cr 88 S 168 I	3·5
$10BrSzNO_2$-10Cz	Cr 106 S 182 I	3·0

† The 1 : 1 binary mixtures were prepared by evaporation of chloroform solutions of these mixtures.

‡ Transition temperature determined by the DSC measurement at a scanning rate of 10° min^{-1} on the second heating and optical polarized microscope observation. Cr: crystalline; S: smectic; N: nematic; I: istropic.

§ Measured by DSC. ΔH_i, enthalpy change of clearing.

¶ Monotropic.

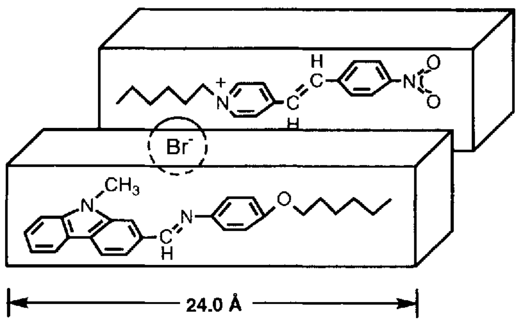

Figure 6. Schematic illustration of a proposed structure for the 1 : 1 complex of *trans-N*-hexyl-4-nitro-4′-stilbazolium bromide with 4-hexyloxy-*N*-(9-methyl-2-carbazolylmethylene)aniline.

4. Conclusions

In conclusion, *trans*-4-nitro-4′-stilbazolium chlorides and bromides exhibited smectic phases. The new miscible complexes of the bromide compounds and non-ionic liquid crystals containing a carbazolyl group exhibited smectic phases in a wide temperature range by the combination of the ionic and electron donor–acceptor interactions.

References

[1] Gray, G. W., 1987, *Thermotropic Liquid Crystals* (Wiley).
[2] Kato, T., and Fréchet, J. M. J., 1989, *J. Am. chem. Soc.*, **111**, 8533.
[3] Kato, T., Fréchet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Fujishima, A., Jin, C., and Kaneuchi, F., 1993, *Chem. Mater.*, **5**, 1094.
[4] Kato, T., Kihara, H., Uryu, T., Fujishima, A., and Fréchet, J. M. J., 1992, *Macromolecules*, **25**, 6836.
[5] Diele, S., Madicke, A., Geißler, E., Meinel, K., Demus, D., and Sackmann, H., 1989, *Molec. Crystals liq. Crystals*, **166**, 131.
[6] Fouquey, C., Lehn, J.-M., and Levelut, A.-M., 1990, *Adv. Mater.*, **2**, 254.
[7] Park, J. W., Bak, C. S., and Labes, M. M., 1975, *J. Am. chem. Soc.*, **96**, 4398.
[8] Araya, K., and Matsunaga, Y., 1981, *Molec. Crystals liq. Crystals*, **67**, 153.
[9] Imrie, C. T., Karasz, F. E., and Attard, G. S., 1991, *Liq. Crystals*, **9**, 47.
[10] Ebert, M., Frick, G., Baehr, C., Wendorff, J. H., Wüstefeld, R., and Ringsdorf, H., 1992, *Liq. Crystals*, **11**, 293.
[11] Praefcke, K., Singer, D., and Eckert, A., 1994, *Liq. Crystals*, **16**, 53.
[12] Busico, V., Ferraro, A., and Vacatello, M., 1985, *Molec. Crystals liq. Crystals*, **128**, 243.
[13] Sodhölter, E. J. R., Engberts, J. B. F. N., and Jeu, W. H., 1982, *J. phys. Chem.*, **86**, 1908.
[14] Bazuin, C. G., Guillon, D., Skoulios, A., and Nicoud, J. F., 1986, *Liq. Crystals*, **1**, 181.
[15] Rodriguez, D. N., Frere, Y., Gramain, P., Guillon, D., and Skoulios, A., 1991, *Liq. Crystals*, **9**, 321.
[16] Yousif, Y. Z., Othman, A. A., Masoudi, W. A. A., and Alapati, P. R., 1992, *Liq. Crystals*, **12**, 363.
[17] Nusselder, J. J. H., Engberts, B. F. N., and Doren, H. A. V., 1993, *Liq. Crystals*, **13**, 213.
[18] Ujiie, S., and Iimura, K., 1992, *Macromolecules*, **25**, 3174.
[19] Ujiie, S., and Iimura, K., 1994, *Chemistry Lett.*, p. 17.
[20] Bruce, D. W., Lalinde, E., Styring, P., Dunmur, D. A., and Maitlis, P. M., 1986, *J. chem. Soc. chem. Commun.*, p. 581.
[21] Rourke, J. P., Fanizzi, F. P., Salt, N. J. S., Bruce, D. W., Dunmur, D. A., and Maitlis, P. M., 1990, *J. chem. Soc. chem. Commun.*, p. 229.
[22] Bruce, D. W., Dunmur, D. A., Lalinde, E., Maitlis, P. M., and Styring, P., 1986, *Nature, Lond.*, **323**, 791.
[23] Bruce, D. W., Dunmur, D. A., Hudson, S. A., Lalinde, E., Maitlis, P. M., McDonald, M. P., Orr, R., and Styring, P., 1991, *Molec. Crystals liq. Crystals*, **206**, 79.
[24] Bruce, D. W., Dunmur, D. A., Lalinde, E., Maitlis, P. M., and Styring, P., 1988, *Liq. Crystals*, **3**, 385.
[25] Kosaka, Y., Kato, T., and Uryu, T., 1994, *Macromolecules*, **27**, 2658.
[26] Kosaka, Y., and Uryu, T., 1994, *Macromolecules*, **27**, 6286.
[27] Shaw, B. D., and Wagstaff, E. A., 1933, *J. chem. Soc.*, p. 77.
[28] Chiang, M. C., and Hartung, W. H., 1945, *J. org. Chem.*, **10**, 21.
[29] Katritzky, A. R., Short, D. J., and Boulton, A. J., 1960, *J. chem. Soc.*, p. 1516.
[30] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals* (Leonard Hill).