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X-Ray Diffraction Study on the Reentrant Smectic A Phase in a Binary Liquid Crystal System

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The X-ray investigation of a binary mixture of two homologues of 2-(4-alkoxybenzylideneamino)fluorenones [dodecyloxy and tridecyloxy derivatives, abbreviated as FLNOC12 and FLNOC13, respectively] and pure compounds FLNOC12, FLNOC13 has been carried out. It has been clarified that the reentrant smectic A phase in the mixture has a partially bilayer structure in contrast with the higher temperature smectic A phase, where the layer spacing is nearly equal to the average molecular length. The reentrant smectic A phase is found to be induced by the molecular association and by the destabilization mechanism of the smectic C structure.

Keywords: reentrant smectic phase, x-ray study, binary liquid crystal

1. INTRODUCTION

Since the discovery of the reentrant nematic phase in the liquid crystalline mixture of terminal polar mesogen by P. E. Cladis,[1] the reentrant phonemena have been extensively studied. Several models[2–5] have been proposed to explain the occurrence of the reentrant nematic and smectic A phases in mesogens with a strongly polar substituent such as cyano or nitro groups at the terminal part in the core moiety. In these compounds, the association of molecules with antiparallel dipole moments and the repulsive steric forces are considered to be the main origin of the reentrant behaviour. Therefore, particularly in a reentrant nematic phase, the smectic phase coexists with short range ordering.[6]

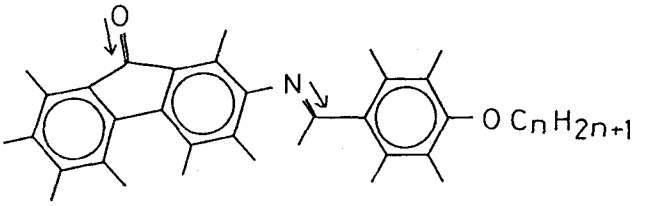
However, a binary mixture of terminal non-polar mesogens also exhibits a reentrant phenomenon.[7] A binary mixture of terminal non-

polar compounds with a new phase sequence of a N—S_A—S_C—S_A has been reported.[8] The detailed structure of the reentrant S_A phase, however, is not clear because of its narrow temperature and concentration range. Recently, a binary mixture of terminal nonpolar compounds, 2(4-alkoxybenzylideneamino)fluorenones) [FLNOCn], with a reentrant S_A phase having a wide temperature and concentration range has been found.[9]

In this paper, we report on the structural properties of pure compounds FLNOC12, FLNOC13 and a mixture of FLNOC 12-13:50mol% in order to clarify the mechanism of the reentrant behaviour.

2. EXPERIMENT

The synthesis of FLNOCn compounds is described in reference 11. The FLNOCn molecules have two strong dipole moments: one is situated at the position of the $\left(O{=}\overset{|}{C}-\right)$ bond (4 Debye) and the other is at that of the $\left(-N{=}\overset{|}{C}-\right)$ bond (1-2 Debye). These are nearly perpendicular to the molecular axis as shown below.



The molecular length l of a mixture is given by

$$l = 0.5\, l(\text{FLNOC12}) + 0.5\, l(\text{FLNOC13}) = 32.1\text{A},$$

where l(FLNOC12) = 31.5A and l(FLNOC13) = 32.7A.

FLNOC12 and FLNOC13 have different phase sequences as follows:

FLNOC12: I→N→S_A→S_C→K

FLNOC13: I→N→S_A⟶K.

The S_C phase does not appear in FLNOC13. When the number of carbon atoms n in the alkyl chain of FLNOCn is between $n = 6$ and $n = 11$, the smectic phases are the S_C phases. At $n = 12$, FLNOCn forms the S_A phase in addition to the S_C phase. However, when n becomes larger than 13, the S_C phase suddenly disappears and only the S_A phase is realized as a layer-structured phase.[10] In these compounds, an acentral transverse dipole moment in core moiety plays an important role for the formation of the S_C phase,[10] while the microscopic mechanism of the stabilization and/or the destabilization of the S_C phase is not fully understood.

The specimens were sealed in a copper cell with mylar windows. The temperature of the sample was controlled automatically by a microcomputer and was stabilized within ± 0.05°C. The samples were cooled from an isotropic liquid phase in a magnetic field of 1 kG to obtain a monodomain sample, which was confirmed by taking Laue photographs at several temperatures.

A position-sensitive proportional counter (PSPC) [Rigaku PSPC-10], with an active area of 10×100 mm^2 and a low flux of a mixture of 90% argon and 10% methane, was used for the X-ray diffraction measurement. As the X-ray source, CuKα radiation, monochromatized by a pyrolytic graphite crystal, was employed (40 kV 80 mA, focus size 1×1 mm^2). The measurements were performed by setting the PSPC horizontal (parallel to the director) and vertical to the scattering plane, as shown in Figure 1.

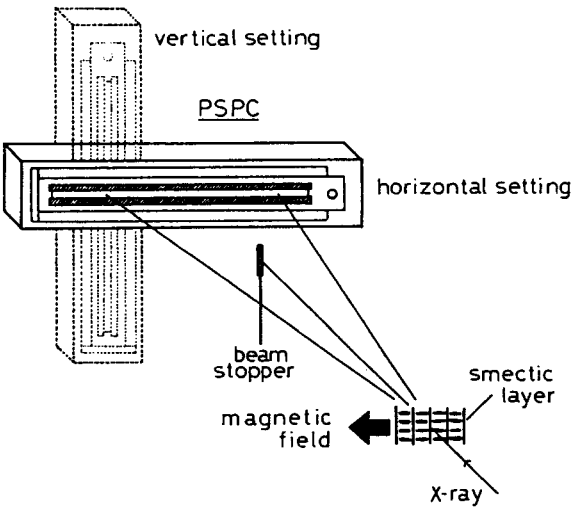


FIGURE 1 Experimental geometries of horizontal and vertical setting.

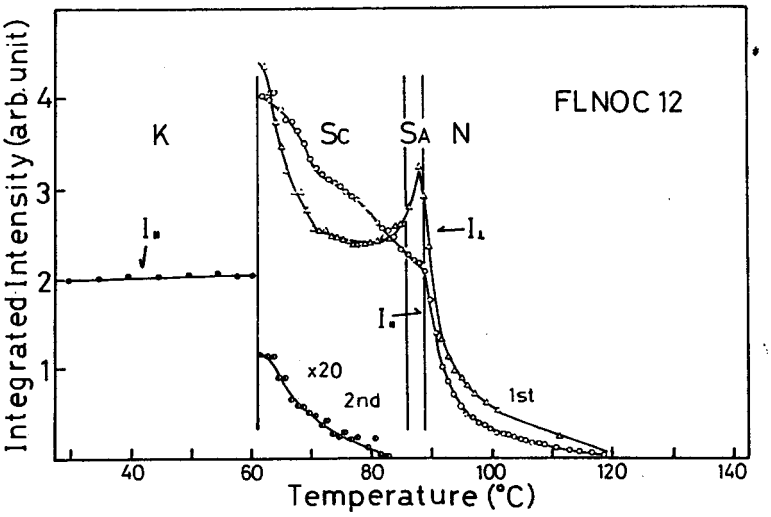


FIGURE 2 Temperature dependence of integrated intensities $I_{\parallel}$, $I_{\perp}$ and $I_{\parallel}$ of 2nd order reflection for FLNOC12.

3. STRUCTURAL PROPERTIES

(a) FLNOC12

Figure 2 shows the temperature dependence of integrated intensities $I_{\parallel}$ and $I_{\perp}$ of the FLNOC12, where $I_{\parallel}$ and $I_{\perp}$ represent the integrated intensities along the direction parallel and perpendicular to the director, respectively. Therefore, $I_{\parallel}$ corresponds to the S_A order parameter (amplitude of one-dimensional mass-density wave).[12] In the N phase, $I_{\parallel}$ is small and is the diffuse scattering characteristic of the smectic fluctuation. This diffuse peak grows with decreasing temperature in the N phase and increases further in the S_A and S_C phases. In addition, the second order reflection begins to appear at T_{AC} − 5°C below the S_A–S_C transition temperature T_{AC}. This indicates that the mass density wave changes from a sinusoidal to a square wave. On the other hand, the integrated intensity $I_{\perp}$ increases rapidly in the lower temperature region of the N phase and peaks at T_{NA}. Though it decreases in the S_A and the S_C phases, it again increases before transforming to the crystalline phase. The intensity variation in the S_C phase may be attributed to the spreading of the S_A peak into a ring of scattering due to the tilt of the director. This feature can be seen in the temperature dependence of the full width at half maximum (FWHM) $\Delta q_{\perp}$, which is a measure of the director fluctua-

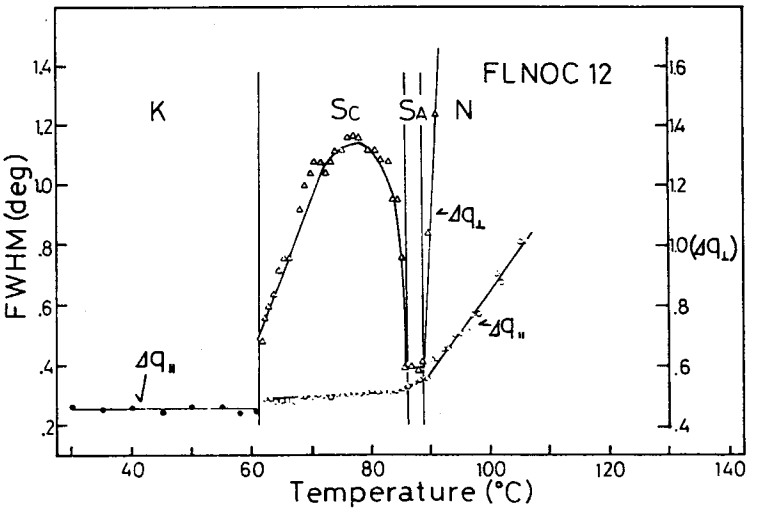


FIGURE 3 Temperature dependence of the full width at half maximum's $\Delta q_{\parallel}$, $\Delta q_{\perp}$ for FLNOC12.

tion, along the direction normal to the director as shown in Figure 3. The $\Delta q_{\perp}$ becomes broad below T_{AC} and then sharp on approaching the crystallization temperature T_{CK}. The tilt angle of the director, the S_C order parameter, determined from the splitting of the peak ($\Delta q_{\perp}$), takes a maximum value 6.8° ± 0.1° around 76°C in the S_C phase. It should be noted that the tilt angle begins to decrease after taking a maximum value with decreasing temperature and does not become zero but takes the value 2° at the T_{CK}. On the contrary, the FWHM $\Delta q_{\parallel}$, a measure of the fluctuation of the layer spacing, shows a monotonical decrease in the N phase and becomes nearly constant in the S_A and S_C phases. The layer structure is much more stabilized in the S_C phase than in the S_A phase because of the narrow temperature range of the S_A phase.

The temperature dependence of the layer spacing d is shown in Figure 4. The spacings are almost constant in the N and the S_A ($d = 1.006l$) phases, and exhibits a small discontinuous change at T_{NA}. In the S_C phases, d changes corresponding to the tilt of the director. The overall feature of the transitions is consistent with that obtained by optical observation.[9] It should be noted that the S_C structure is destablized gradually in the lower temperature region of the S_C phase; this is an intrinsic behaviour and is intimately related with the occurrence of the reentrant phenomenon observed in a mixture of FLNOC12-13:50%.

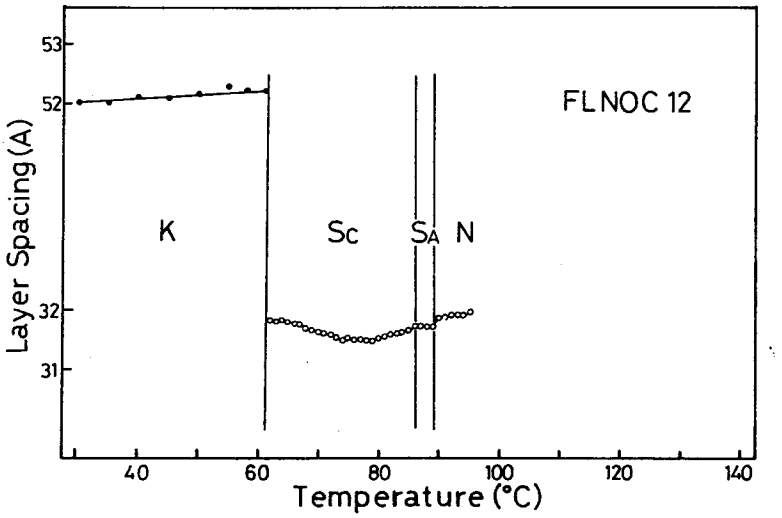


FIGURE 4 Temperature dependence of layer spacings for FLNOC12.

(b) FLNOC13

A pure liquid crystal FLNOC13 has no S_C phase. A simple transition sequence I—N—S_A—K is observed. However, we have found that the S_A phase so far recognized to be a single phase can be distinguished into two phases; i.e., the monolayer structure (A_1) is formed in the high temperature region and the partially bilayer structure (A_d) is constructed in the lower temperature region.

The integrated intensity $I_{\parallel}$ increases continuously from the N to the S_A phase, and the second order reflection appears at 97°C, as shown in Figure 5. The remarkable feature is that $I_{\parallel}$ takes a maximum value around T_{SK} + 10°C. The intensity $I_{\perp}$ also shows a similar temperature dependence. The FWHM $\Delta Q_{\parallel}$ decreases rapidly in the N phase and is temperature-independent in the S_A phase as shown in Figure 6. Anomalous behaviour is not seen at T_{SK} + 10°C. On the other hand, the FWHM $\Delta q_{\perp}$ becomes sharp around T_{NA} and in the temperature region between T_{SK} and T_{SK} + 10°C. A somewhat broad width in the intermediate temperature region in the S_A phase may be caused by a phase modulation of the smectic layer.[12]

The layer spacing d has a weak temperature dependence in the N phase and shows a discontinuous jump at T_{NS}, as shown in Figure 7. In the S_A phase, it is nearly constant but begins to increase around T_{SK} + 10°C. The layer spacing is nearly equal to the molecular length in the temperature independent region (d = 1.018l) and becomes

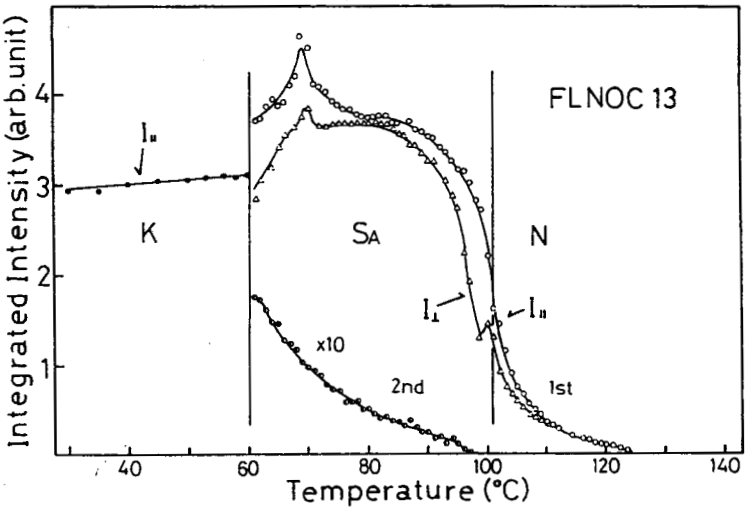


FIGURE 5 Integrated intensities vs. temperature for FLNOC13.

$d = 1.031l$ before transforming to the crystalline phase. This indicates that the transition from the monolayer structure (A_1) to the partially bilayer structure (A_d) takes place around T_{SK} + 10°C. The partially bilayer structure may originate in the dimerization of molecules. The association of molecules has a significant effect on the occurrence of the reentrant S_A phase of a mixture. It should be emphasized that

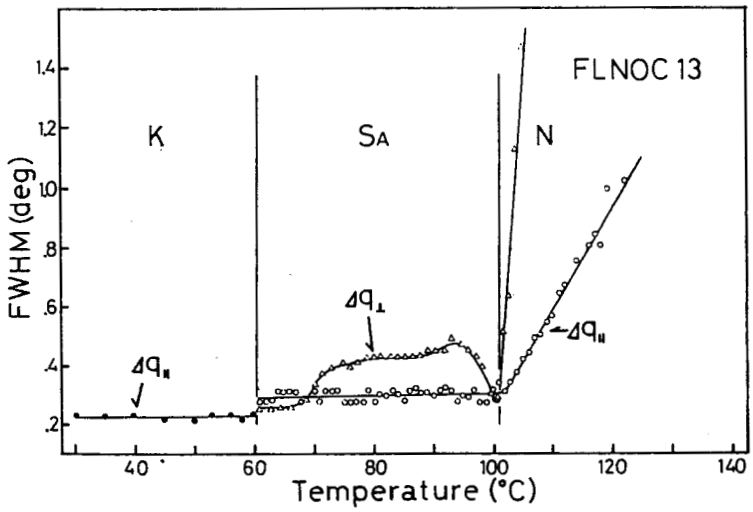


FIGURE 6 FWHM's as a function of temperature for FLNOC13.

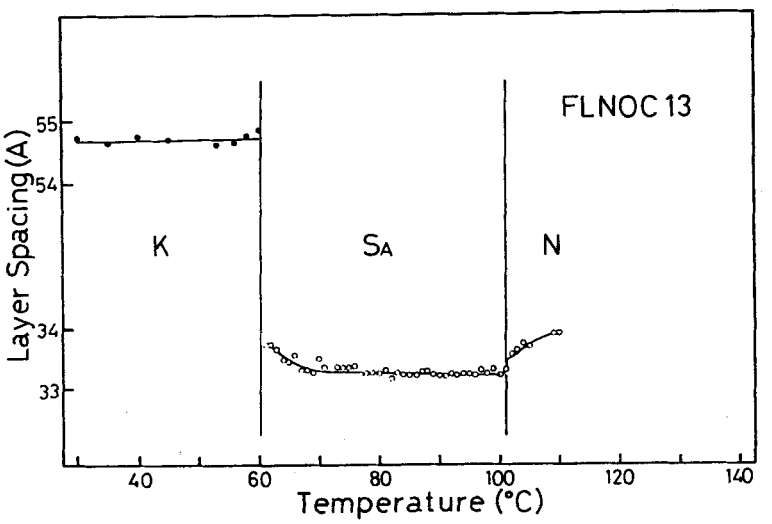


FIGURE 7 Temperature dependence of layer spacings for FLNOC13.

the partially bilayer structure appears as a metastable state. In fact, A_d region depends largely on the cooling rate.

(c) FLNOC12-13:50mol%

The temperature dependence of the integrated intensities $I_{\parallel}$ and $I_{\perp}$ are shown in Figure 8. In the N phase, only a diffuse scattering caused by the cybotactic smectic ordering is observed. This diffuse peak grows with decreasing temperature and becomes more intense in the S_C phase. The intensity $I_{\parallel}$ is proportional to the translational order parameter in the S_A and the S_C phases.[12] The increase in the intensity $I_{\parallel}$ indicates the stabilization of the layer structure. This is consistent with the narrow peak width $\Delta q_{\parallel}$ in the S_A, the S_C and the R—S_A phases, as shown in Figure 9. The second order reflection appears at the intermediate temperature in the S_C phase. The intensity $I_{\parallel}$ and that of the second order reflection show the temperature variation in the R—S_A phase. The peak width $\Delta q_{\parallel}$, however, exhibits no appreciable change. On the other hand, the intensity $I_{\perp}$ shows a similar temperature dependence with $I_{\parallel}$ except around T_{NA}. The peak width $\Delta q_{\perp}$, which reflects the tilt of the director, takes the same value in the S_A and the R—S_A phases, but shows a temperature variation in the S_C phase associated with the splitting of the scattering peak. The S_C order parameter increases initially and then decreases in the S_C phase with decreasing temperature. This behaviour resembles that of

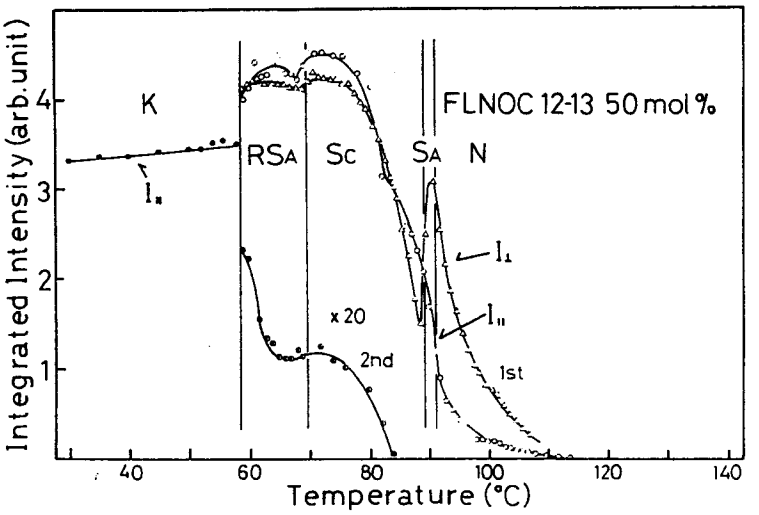


FIGURE 8 Integrated intensities $I_{\parallel}$, $I_{\perp}$, and $I_{\parallel}$ of 2nd order reflection at various temperatures for FLNOC12-13:50mol%.

the pure compound FLNOC12. It should be noted that the S_C order parameter is zero in the R—S_A phase.

The layer spacing d in the R—S_A phase is somewhat larger than that in the S_A phase, as shown in Figure 10. This suggests that the layer structures are different from each other. The values of d are

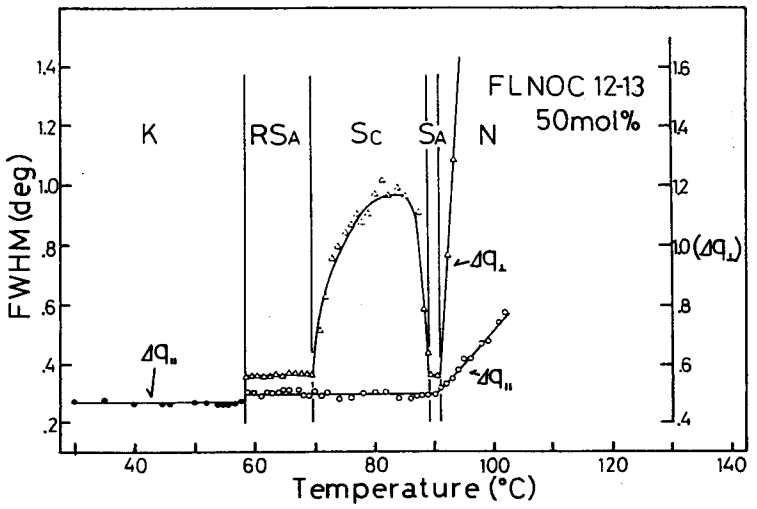


FIGURE 9 Variation of FWHM's vs. temperature for FLNOC12-13:50mol%.

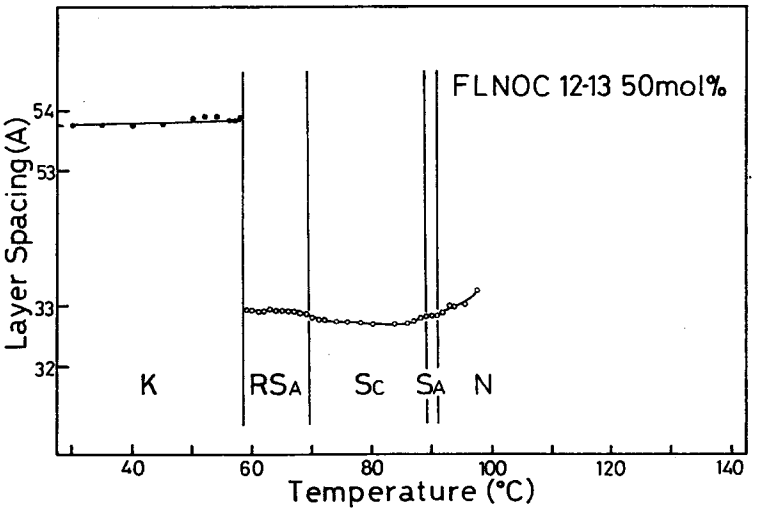


FIGURE 10 Temperature dependence of layer spacings for FLNOC12-13:50mol%.

$d = 1.025l$ in the R—S_A phase and $d = 1.018l$ in the S_A phase, where l is the average molecular length. The relative change in the values of d indicates that the monolayer structure is formed in the S_A phase and the partially bilayer structure is constructed in the R—S_A phase. This dimerization process is very similar to that of pure FLNOC13. The R—S_A phase is in the metastable state and is transformed into the crystalline phase after a long time. The temperature range of this phase also depends on the cooling rate.

4. DISCUSSION

The R—S_A phase with the same phase sequence as a mixture of FLNOCn molecules is observed in a mixture of terminal non-polar compounds 2,5-bisphenyl-1,3,4-thiadiazole added 1.4mol% 2-phenyl-5-(4-n-butyloxyphenyl)-primidine.[8] In these compounds, the layer spacings of the S_A and R—S_A phases are reported to be nearly equivalent to the molecular length, though the numerical value of the ratio is not shown. On the other hand, the reentrant phenomena are observed in materials such as 4-n-octyloxybenzoyloxy-4′-cyanostilbene ("T8" for short)[13] and 4-nonyloxy-benzoyloxy-4′-cyanoazobenzene (9OBCAB).[14] These compounds have the same sequence of phase transition, I—N—S_A—RN—RS_A—K, and the higher temperature S_A phase is partially bilayer while the R—S_A phase has a monolayer

structure. A similar phase sequence (I—N—S_{Ad1}—RN—S_{Ad2}—K) is found in a mixture of liquid crystals:4-cyanophenyl 4-(4-nonyloxy-3-bromobenzoyloxy) benzoate and 4-(4-heptyloxybenzoyloxy) benzylidene-4-cyanoaniline.[6] In this mixture, two S_{Ad} phases are formed by a partially bilayer structure. In these compounds, a highly polar cyano or nitro group attached to one end of the molecule, which results in the strong antiparallel near-neighbour correlations, plays an important role in the reentrant phenomena.

For the case of FLNOCn compounds, the R—S_A phase is induced at least by two mechanisms; one is the association of molecules (dimer formation) and the other is the destabilization process of the S_C structure. We have seen that these mechanisms exist intrinsically in pure compounds. The dipole-induced interactions caused by acentral transverse dipoles are important for the tilt alignment.[14] In addition, other factors such as the length of the terminal alkyl chain and steric repulsive force are essential to the creation and/or destruction of the S_C structure.

5. SUMMARY

We have investigated the structural property of the R—S_A phase in a mixture of terminal non-polar compounds, FLNOC12-13:50mol%, by the X-ray diffraction method. It has been revealed that the layer configuration of the R—S_A phase is the partially bilayer (Ad) and is different from that of the higher temperature S_A phase. The molecular association is caused by the dipole–dipole interactions between molecules. We have shown that the main origins of the formation of the R—S_A phase exist intrinsically in pure compounds. It should be emphasized that the R—S_A phase appears as a metastable state and as a dynamical (time-dependent) phenomenon. We have also found the partially bilayer phase (Ad), which was not observed either optically or by calorimetric measurements, in the pure compounds FLNOC13.

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