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X-RAY INVESTIGATIONS OF A REENTRANT NEMATIC PHASE FORMED OF TERMINAL-NONPOLAR COMPOUNDS

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(Submitted for publication January 11, 1983)

ABSTRACT: A binary system of terminal-nonpolar compounds is presented in which a stable reentrant nematic phase occurs. X-ray investigations were carried out in the N, S_A , N_{re} , and S_C phase.

Up to now it was believed generally that the reentrant phenomenon is a characteristic feature of the terminal-nonpolar compounds or of their mixtures 1, 2. Recently we could show that a reentrant nematic phase (N_{re}) occurs in a binary system of terminal-nonpolar compounds 3. This case was predicted theoretically by Longa and de Jeu 4. In this system the N_{re} phase was found in the supercooled state and crystallized after formation. Now we present a new binary system of terminal-nonpolar compounds in which a stable N_{re} phase exists in a limited concentration range.

The first component of the binary system is an assymetrically substituted three-ring compound possessing a nematic phase in a large temperature range and additionally a metastable $S_{\rm C}$ phase.

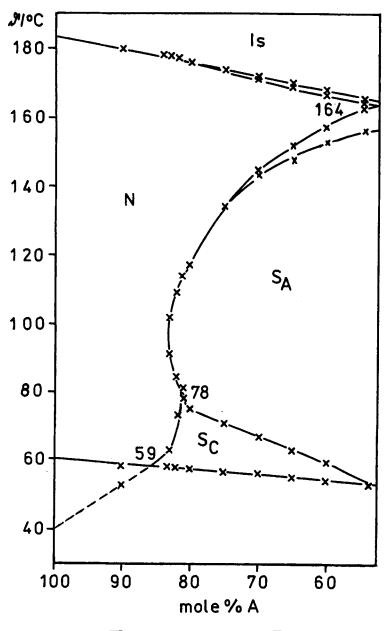
$$C_2H_5$$
 H $-C00$ $-$

The second component is a symmetrically substituted three-ring pyrimidine which exhibit smectic tetramorphism (S_A, S_C, S_F, S_C)

$$c_{10}H_{21}O - \bigcirc - \bigcirc - \bigcirc - \bigcirc - c_{10}H_{21}$$
 (B)
 c_{r} 87.5 s_{g} 117 s_{F} 133.5 s_{c} 179 s_{A} 183 Is ⁵

Fig. 1 shows the part of the diagram of state in which the N_{re} phase appears. This diagram was studied by means of microscopical observations as well as by calorimetric measurements. It is seen from Fig. 1 that between 81 und 84 mole% A a stable N_{re} phase occurs on cooling of the S_A phase. By further cooling the S_C phase is formed.

X-ray investigations were performed at a mixture with $x_B = 0.18$. By means of oriented samples we proved the phase sequence N, S_A , N_{re} , S_C with decreasing temperature (Fig. 2a - d, respectively). To obtain the accurate d-values we used a small-angle equipment in connection with an intensity recording. The scattering regions between $1^{\circ} \le 0 \le 2^{\circ}$ at different temperatures are given in Fig. 3a - d. The intensity of the four examples was recorded with the



A: $C_2H_5 - H C00 - C00 - C00 - OC_7H_{15}$

FIGURE 1

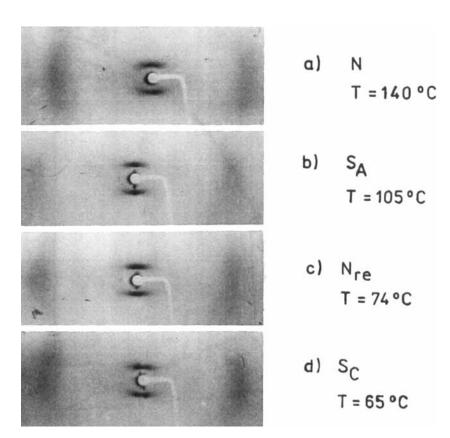


FIGURE 2

same amplification. Therefore only very small and diffuse scattering is visible in the N phase (Fig. 3a). The smectic phases exhibit the strong inner ring (Figs. 3b, 3d) whereas Fig. 3c proves the degeneration of the layer order within the N_{re} phase. However a comparison of the Figures 3a and 3c suggests the existence of cybotactic groups in the N_{re} phase.

Using Bragg's law we calculate the d-value in the S_A , N, and S_C phase, $d_{S_A}=32.7$ Å, $d_{N_{re}}=32.8$ Å, and $d_{S_C}=31.3$ Å, respectively.

The comparison of the d-values with the averaged molecular length ($L_{av} = x_A L_A + x_B L_B = 34$ Å) shows that there is no hint for a kind of dimerization found in reentrant systems with polar substances. Therefore, it must be concluded that the appearance of the N_{re} phase is not connected with the formation of dimers with d > L. The observed difference L - d is in agreement with the results of other high temperature phases and can be explained by the presence of long non-rigid aliphatic chains.

The tilt angle of the S_{C} phase is calculated by

$$\cos \beta = \frac{d_{S_C}}{d_{S_A}}$$

The value $B = 17^{\circ}$ is in agreement with the values estimated from the inner spots of the oriented patterns (Fig. 2d).

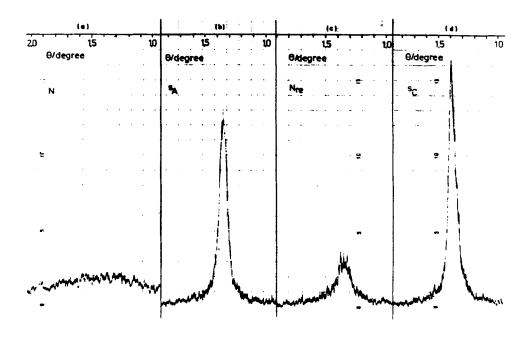


FIGURE 3

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