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# NEW POLYMORPHISM VARIANTS IN BINARY SYSTEMS OF 4,4'-BIS-(n-NONYLAMINO)-BIPHENYL

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**ABSTRACT:** Three diagrams of state with 4,4'-bis-(n-nonylamino)-biphenyl and some cyanoethyl compounds have been studied. In the systems studied the following new phase sequences were found with decreasing temperature:  $S_A N$ ;  $S_A S_C N$ ;  $S_A S_C N S_C$ ; and  $S_A N S_C$ .

As reported in earlier papers the 4-( $\beta$ -cyanoethyl)-phenyl 4-n-alkyloxycinnamates <sup>1,2</sup> and 4-( $\beta$ -cyanoethyl)-phenyl 4-n-alkyloxybenzoates <sup>3</sup> show a strong tendency to form reentrant phases in binary systems. Now the diagrams of state of binary systems with certain cyanoethyl compounds and 4,4'-bis-(n-nonylamino)-biphenyl have been studied by means of the contact method <sup>4</sup> and by the investigations of singular concentrations.

Fig. 1 shows the diagram of 4,4'-bis-(n-nonylamino)-biphenyl <sup>5</sup> and 4-( $\beta$ -cyanoethyl)-phenyl 4-n-dodecyloxycinnamate <sup>1,6</sup>. At small concentrations of the cyanoethyl compound ( $C_{12}$ ) an intermediate  $S_B$  phase is observed. Although both compounds do not

possess a nematic phase, in a limited concentration range (84 - 88 mol%  $C_{12}$ ) an isolated nematic region occurs in the supercooled state within a  $S_C$  region. The peculiar shape of the transition curves gives rise to the following new phase sequences with decreasing temperature:  $S_A S_C N S_C$  (84 mol%  $C_{12}$ );  $S_A N S_C$  (85 mol%  $C_{12}$ ); and  $S_A S_C N$  (87.5 mol%  $C_{12}$ ). The occurrence of a nematic phase below a  $S_A$  phase without a nematic high-temperature phase was already assumed by Heppke et al.<sup>7</sup> from the extrapolation of the transition curve in a binary system.

In the diagram of Fig.2 4,4'-bis(n-nonylamino)-biphenyl is combined with 4-( $\beta$ -cyanoethyl)-phenyl 4-n-decyloxybenzoate exhibiting  $S_A S_C$  polymorphism<sup>3,8</sup>. Similar to the diagram in Fig.1 intermediate regions of the  $S_B$  and the nematic phase occur in the supercooled state. Contrary to diagram 1 an intermediate nematic high-temperature phase appears between 75 and 97 mol% cyanoethyl compound. Because of the curvature of the  $S_A N_{re}$  transition curve a reentrant  $S_A$  phase was observed (80 - 83 mol%  $C_{10}$ ).

When in diagram 2 the  $C_{10}$  cyanoethyl compound is replaced by the  $C_{12}$  homologue<sup>9</sup>, a similar type of diagram is obtained, but the intermediate nematic high-temperature phase disappears and the metastable nematic region below  $S_A$  is limited to a small concentration range (84 - 88 mol%  $C_{12}$ ) (see Fig.3). In this way the new phase sequence  $S_A N$  results with decreasing temperature.

As shown in<sup>10</sup> the alkylamino-biphenyls are strong electron donators and form with liquid-crys-

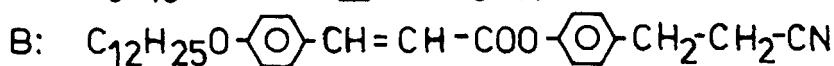
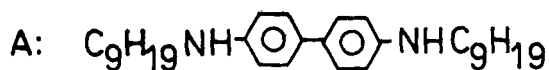
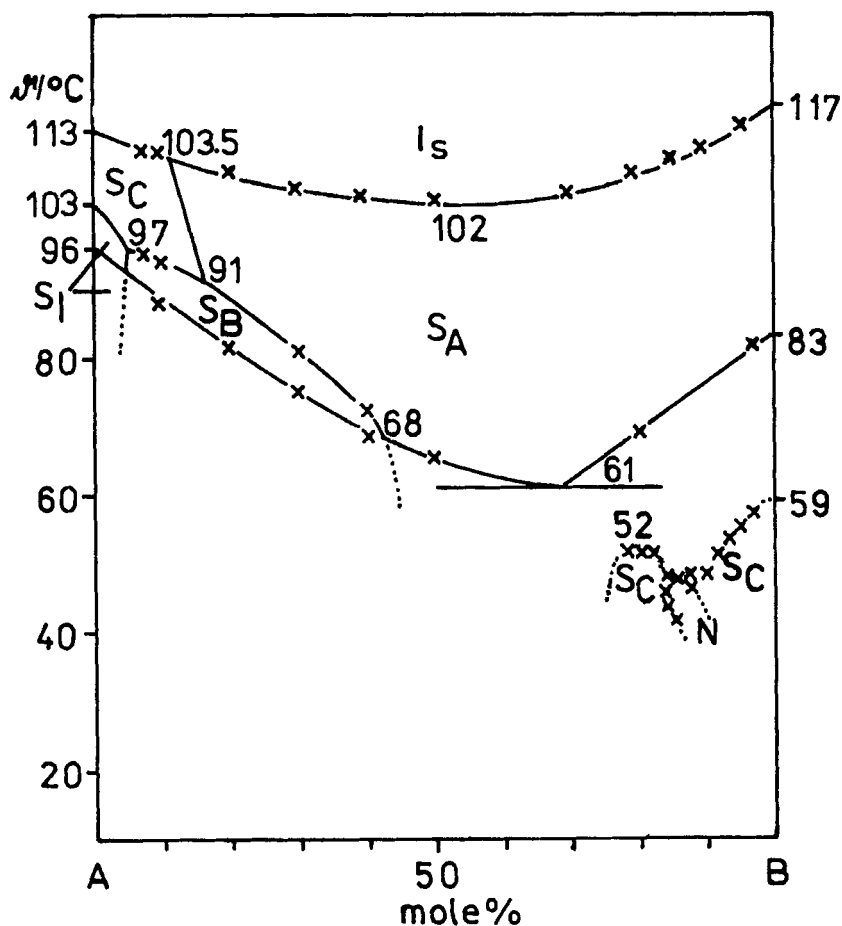


FIGURE 1

The dotted curves indicate phase transitions in the supercooled state

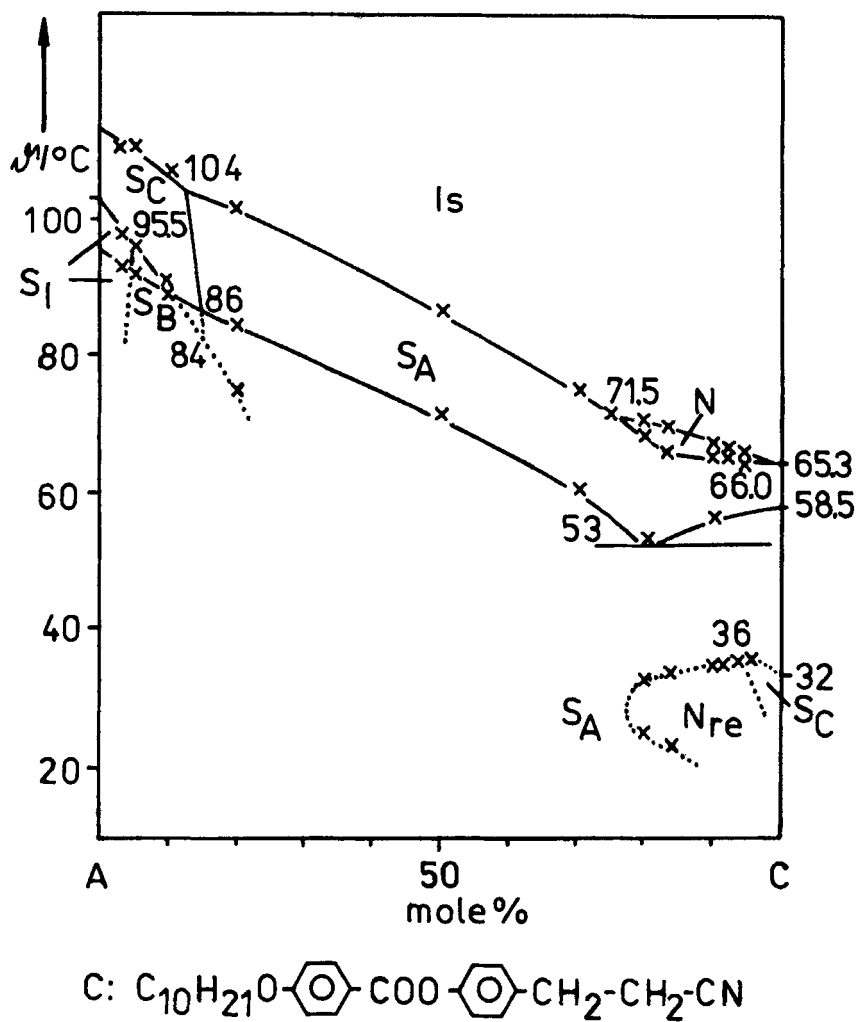


FIGURE 2

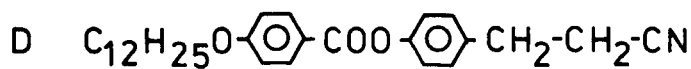
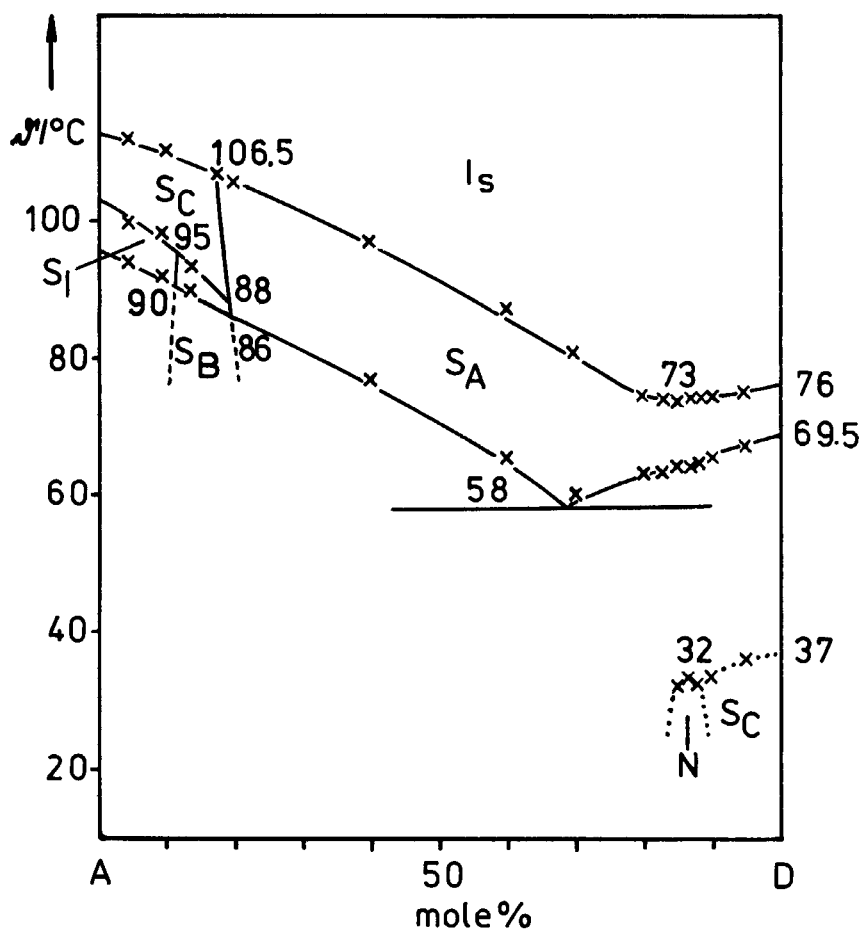


FIGURE 3

talline electron acceptors electron donator acceptor (EDA) complexes in the liquid-crystalline and isotropic state. The EDA interaction could be detected in the binary system of diagram 1, indicated by the yellow colour of the mixtures whereas the pure compounds are colourless. The yellow colour is due to a wide charge transfer band found in a spectrophotometer between 370 and 440 nm. In the systems of diagram 2 and 3, a charge transfer band could not be observed, but probably weak EDA interaction exists also in these mixtures.

In all the three systems the EDA interaction seems to be too weak to cause maxima in the curves of the transition  $S_A/N$  as it has been found in many other cases <sup>10</sup>.

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