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The Smectic Dimorphism of Hexadecyloxy- and Octadecyloxyazoxybenzene

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Abstract—4,4'-di-*n*-hexadecyloxy- and octadecyloxyazoxybenzene have been investigated by means of a differential scanning calorimeter and the latter also by density measurement. Both substances exhibit smectic *B* and *C* modifications, which have been proved by miscibility investigation. Under favourable circumstances both types of modifications may exhibit schlieren textures.

1. Introduction

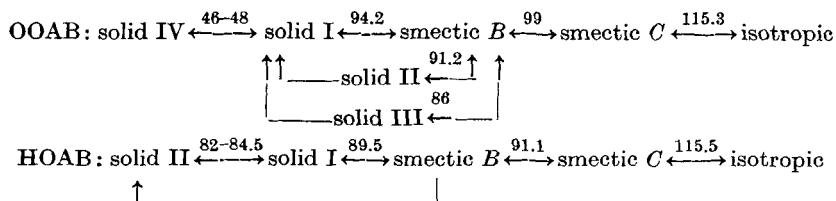
Arnold, Jacobs and Sonntag⁽¹⁾ have published a calorimetric investigation of 4,4'-di-*n*-octadecyloxyazoxybenzene (OOAB). They have attributed to this substance a smectic *B* and a smectic *C* modification. Till now the exact proof of the type of these smectic modifications by means of miscibility and texture investigations has not been established. Now this has been reconsidered and for the purpose of comparison with a related compound we have included 4,4'-di-*n*-hexadecyloxyazoxybenzene (HOAB) into the explorations. Both substances are of special interest because their smectic *B* modifications exhibit schlieren textures similar to those often observed in nematics.⁽²⁾ For a better characterization, measurements of the transition enthalpies of both compounds and the temperature dependence of the density of OOAB have been added.

2. Results

Both substances have been prepared by Arnold and coworkers. In the case of OOAB we used the original substance of Arnold.⁽¹⁾

HOAB has been recrystallized till the transition temperatures remained constant.

The substances have the following transition temperatures:



The transition temperatures have been established by microscopic observation. Starting from the solid state the smectic modifications occur in the form of paramorphoses. With decreasing temperature coming from the isotropic liquid, smectic *C* exhibits a schlieren texture (Fig. 1). At the transition to smectic *B* the schlieren texture is altered considerably, but the smectic *B* modification is able to

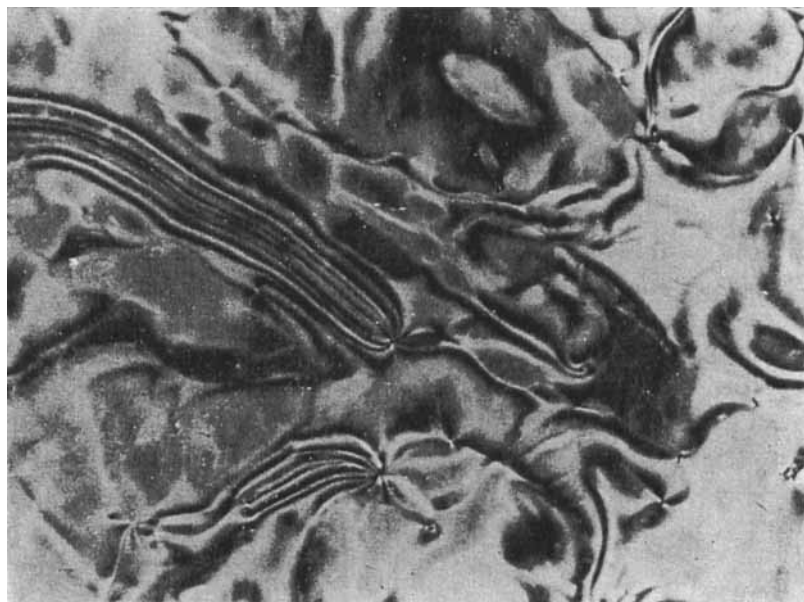


Figure 1. OOAB, schlieren texture of the smectic *C* modification, 105 °C, crossed polarizers, $\times 115$.

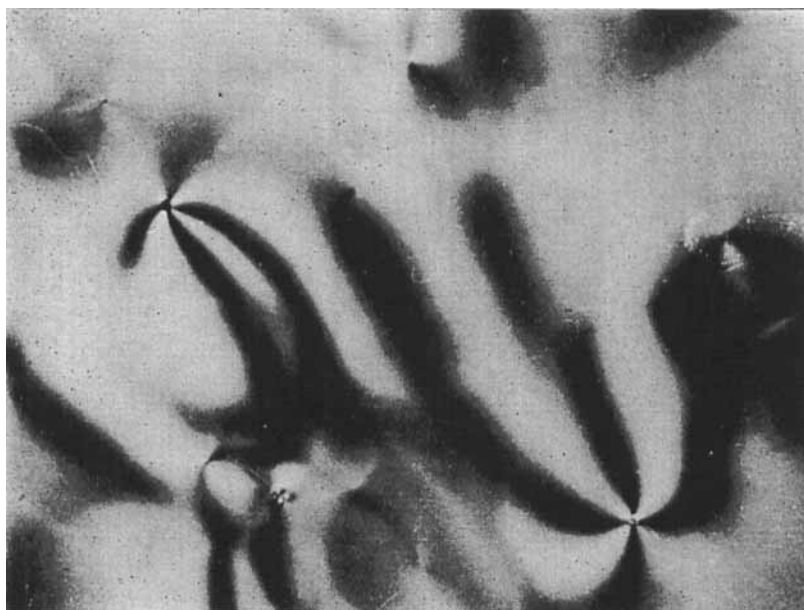


Figure 2. OOAB, schlieren texture of the smectic *B* modification, 97 °C, crossed polarizers, $\times 115$.

exhibit a typical schlieren texture (Fig. 2) or a mosaic texture as is usual for smectic *B* modifications.^(2,3,4) In some former cases, we have found schlieren textures in smectic *B*, but never in such a clear form.

The transitions have been confirmed by means of a Perkin-Elmer Differential Scanning Calorimeter DSC 1 B. The results of the calorimetric investigation are listed in Table 1.

TABLE 1 Transition Enthalpies [cal/mole]

	solid- smectic <i>B</i>	smectic <i>B</i> - smectic <i>C</i>	smectic <i>C</i> - isotropic liquid
OOAB	18950	2530	5280
HOAB	15580	1490	4380

The calorimetric values of OOAB are in good agreement with the study Arnold, Jacobs and Sonntag⁽¹⁾ made in a precision calorimeter.

The phase transitions of OOAB are also visible in the curve of

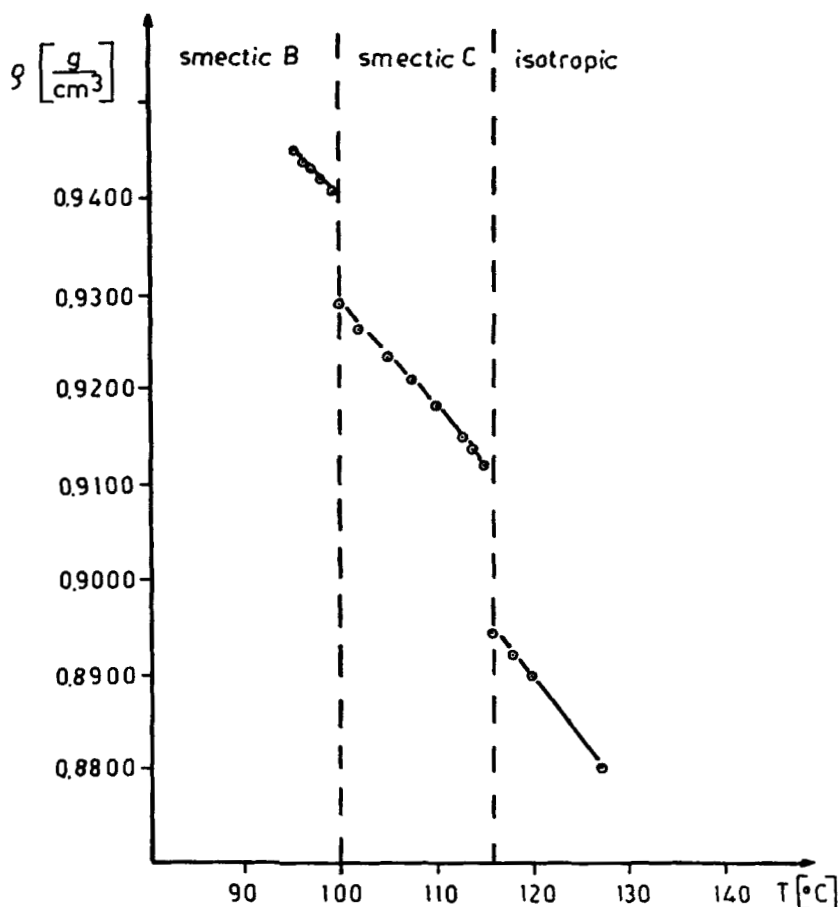


Figure 3. Densities of OOAB plotted against the temperature.

the density plotted against the temperature (Fig. 3, Table 2). The densities were measured by means of a capillary method.⁽⁵⁾

For the purpose of the exact identification of the type of smectic modification, it is necessary to investigate the relations of miscibility in a binary system.⁽²⁾ We have established the diagrams of state by microscopic observation with the method described in a previous paper.^(2,6) As a reference substance we have chosen the *n*-amyl 4-*n*-dodecyloxybenzal-aminocinnamate, a substance which has smectic *A*, *C* and *B* modifications.^(1,7) The diagrams of state of this

TABLE 2 Densities (ρ), molar volumes (V_m) and thermal expansion coefficients (α) of 4,4'-di-*n*-octadecyloxyazoxybenzene

T ($^{\circ}\text{C}$)	ρ (g/cm^3)	V_m (cm^3/mole)	$\alpha \cdot 10^4$ ($^{\circ}\text{C}^{-1}$)
95	0.9448	778.15	
96	0.9440	778.81	8.5
97	0.9430	779.64	10.7
98	0.9422	780.30	8.5
99	0.9407	781.55	16.0
100	0.9292	791.22	123.0
102	0.9262	793.78	16.2
105	0.9238	795.85	8.2
108	0.9212	797.47	9.4
110.5	0.9184	800.52	12.2
113	0.9151	803.41	14.4
114	0.9137	804.64	15.3
115	0.9120	806.14	18.6
116	0.8945	821.91	193.7
118	0.8924	823.85	11.8
120	0.8903	825.79	11.8
127	0.8802	835.26	12.5

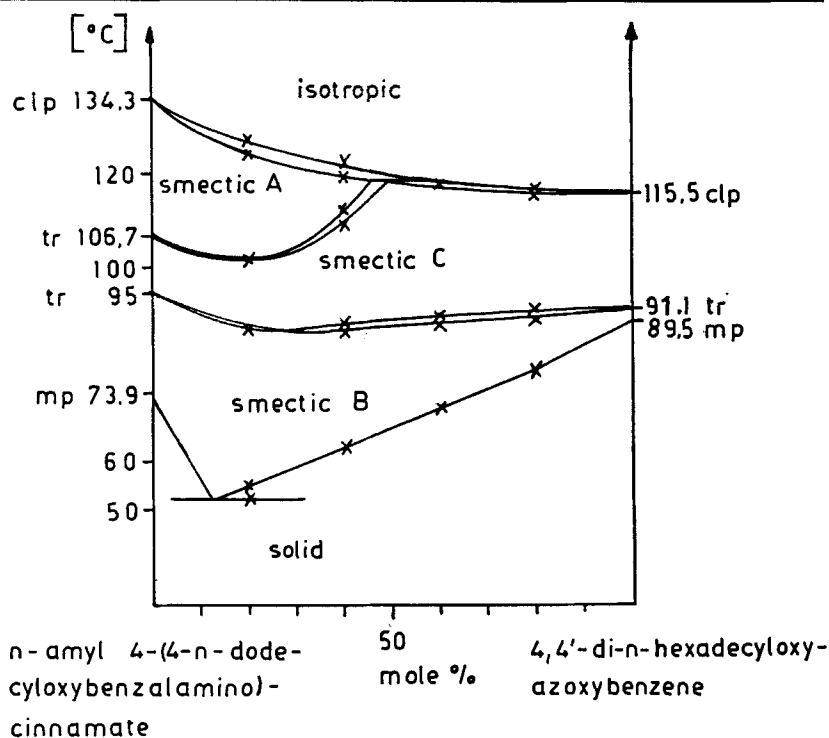


Figure 4. Diagram of state; mp = melting point; tr = transition point; clp = clearing point.

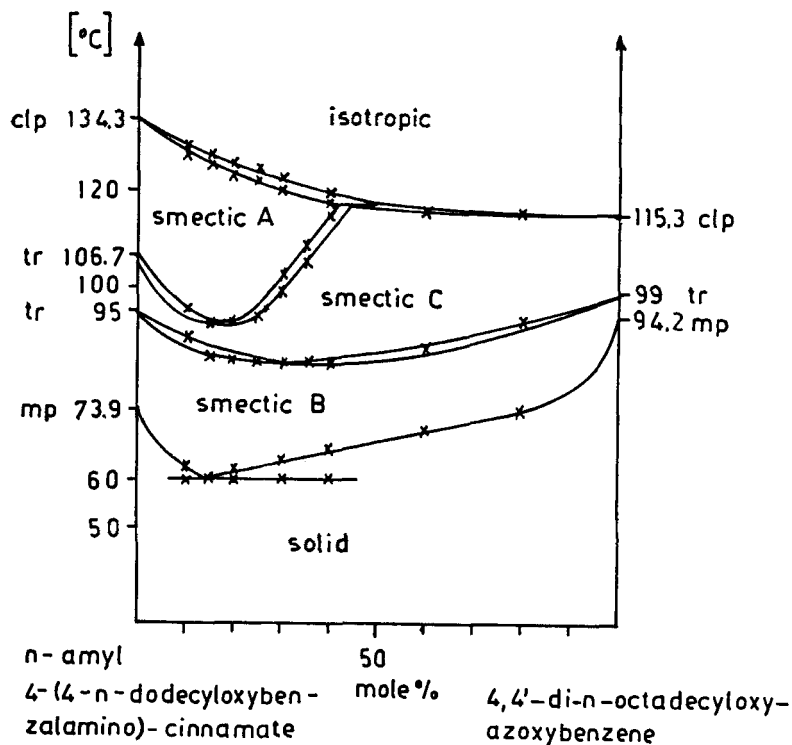


Figure 5. Diagram of state.

substance with HOAB and OOAB are given in Figs. 4 and 5. It is obvious that the two smectic modifications of HOAB and OOAB show an uninterrupted series of mixed liquid crystals with the smectic *C* and *B* modifications. Consequently these modifications in the sense of the rule of selective miscibility can be marked with the symbols *C* and *B*, respectively.

3. Discussion

By investigation of the relations of miscibility with a formerly published substance^(1,7) we were able to confirm the type of the smectic phases of HOAB and OOAB as smectic *C* and *B* modifications, respectively. This fact is of special interest because most of the formerly investigated *B* modifications appear in specific mosaic

textures or in form of unspecific textures (paramorphoses).^(2,4,8) The smectic *B* modifications of HOAB and OOAB also exhibit mosaic textures, but under favourable circumstances appear as characteristic schlieren textures which are very clear and are comparable with schlieren textures of nematics.^(2,8) Schlieren textures in smectic *B* have been found in other substances,⁽²⁾ but only in indistinct forms which did not allow a detailed analysis of these textures.

We know only a few substances which possess the smectic polymorphism *C* and *B*.⁽⁹⁾ It is remarkable that the lower homologues of the series of the di-*n*-alkoxyazoxybenzenes exhibit only nematic and smectic *C* modifications.⁽¹⁰⁾ But the two highest known members of the series, namely HOAB and OOAB, have smectic *B* modifications. Only the 2,5-bis-(4-*n*-alkoxyphenyl)-pyrazines⁽¹¹⁾ show a comparable behaviour. In other cases, for instance alkyl alkoxybenzylideneaminocinnamates, the lower members of the homologous series exhibit *B* modifications⁽¹²⁾ and the higher members additional *C* modifications.⁽⁷⁾

In all cases so far investigated the *C* and *B* modifications show remarkable differences in structure,⁽¹³⁻¹⁶⁾ enthalpy and density.⁽⁵⁾ Also the relative large enthalpy and density changes at the smectic *C/B* transitions of HOAB and OOAB confirm this statement although the size of these changes may be caused in part by the high molecular mass of the substances.

Till now we have no structure determinations of the smectic *C* and *B* modifications of HOAB and OOAB. It would be of special interest to know if the smectic *B* schlieren texture is connected with one of the two possibilities of the smectic *B* structure, namely the tilted or the orthogonal layer structure.⁽¹⁶⁾

From theoretical considerations it has been concluded that the smectic *B* modifications in fact should be a special kind of crystalline structure.⁽¹⁷⁾ With regard to the smectic *B* schlieren texture, a typical liquid crystalline texture, this statement seems doubtful.

Acknowledgement

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