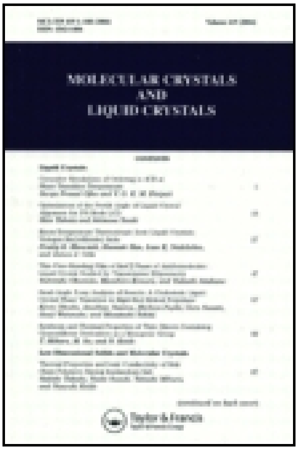

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Solid and Liquid Crystalline Phases of Aliphatic Esters of 4,4′-Dihydroxy-α,α′-Dimethylbenzalazine

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Solid and Liquid Crystalline Phases of Aliphatic Esters of 4,4′-Dihydroxy-α,α'-Dimethylbenzalazine

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INTRODUCTION

We have undertaken a systematic study of polymers whose chains are of such chemical composition and structure that liquid crystalline phases may reasonably be expected. Polyesters of general formula:

$$[\text{—OOC(CH}_2)_n\text{—COO—}\phi\text{—C(CH}_3) = \text{N—N=C(CH}_3)\text{—}\phi\text{—}]_x$$

have been prepared that give anisotropic liquid phases, probably of smectic C type.[1] The characterization of the doubly homologous series of esters of formula:

$$\text{CH}_3(\text{CH}_2)_n\text{—COO—}\phi\text{—C(CH}_3)\text{=N—N=C(CH}_3)\text{—}\phi\text{—OOC(CH}_2)_n\text{CH}_3$$

rose then as a necessary side problem. The calorimetric measurements made on the phase transitions of these compounds and the optical observations of their mesophases are in any case of intrinsic interest.

Experimental

4,4′-Dihydroxy-α,α'-dimethylbenzalazine:

$$(\text{HO—}\phi\text{—C(CH}_3)\text{=N—N=C(CH}_3)\text{—}\phi\text{—OH})$$

was prepared from 4-hydroxy-acetophenone and hydrazine sulphate as reported[2]. Melting point (221°C in ref. 2; 222–223°C in ref. 8; 224.0°C this work) and NMR spectrum (Figure 1a) confirmed the nature and purity of the compound.

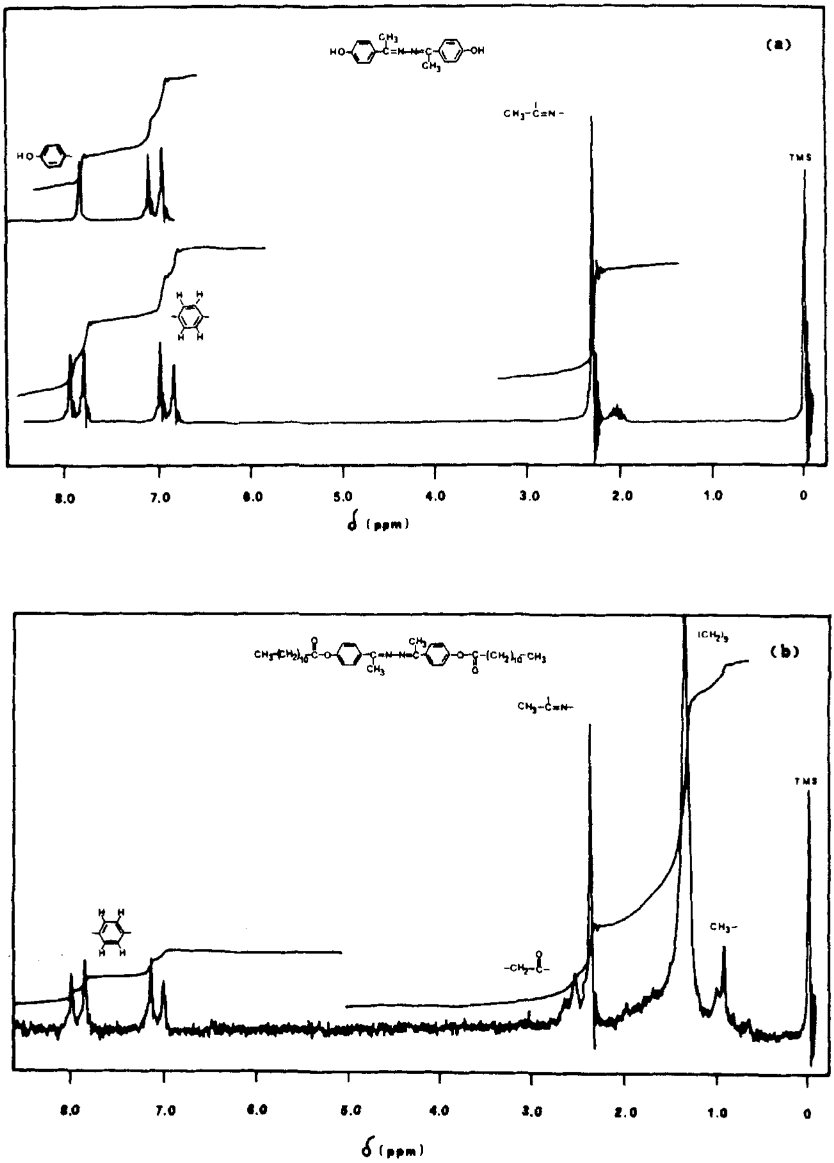


FIGURE 1 a) NMR spectrum of 4,4′-dihydroxy-α.α′-dimethylbenzalazine (solvent: deuterated acetone).
b) NMR spectrum of 4,4′-didodecanoyloxy-α,α′-dimethylbenzalazine (solvent: carbon tetrachloride).

Esters were prepared by standard methods using acyl chlorides (Fluka) which were vacuum distilled three times. (Tridecanoyl- and pentadecanoyl chlorides were prepared from the corresponding carboxylic acids (Fluka)). All the ester compounds were crystallized at least four times and monitored by scanning calorimetry until strictly reproducible behaviour was observed. Final NMR spectra are in accordance with the nature and formula for each compound of the series. The NMR spectrum of 4,4'-Didodecanoyloxy-α,α'-dimethylbenzalazine is shown in Figure 1b as an example.

DSC Analysis Differential scanning calorimetry was performed utilizing a Perkin-Elmer DSC-1 apparatus. The samples were examined under dry nitrogen flow. The phase transition temperatures were taken at the onset of the thermal phenomena. An indium sample of great purity (99.999%, Fluka) was utilized as a reference standard. Scanning rates variable from 0.5 K/min to 16 K/min were used.

Thermal polarizing microscopy The optical observations were made on a Leitz polarizing microscope equipped with heating stage and photographic camera.

Samples were normally kept between holder and cover-glasses previously cleaned with acetone, care being taken not to develop any preferential rubbing. In some cases a rough rubbing of the melted samples was necessary to prevent the complete onset of insignificant homogeneous textures.

Results and discussion

The aliphatic esters of 4,4'-Dihydroxy-α,α'-dimethylbenzalazine (we indicate them with the symbol Cn, $n = 2 \rightarrow 16$ = number of carbon atoms of a single aliphatic group) that have been examined all give rise to liquid crystalline phases with the possible exception for the last compound, C16. All but the first compound, C2, can exist in a second solid phase at high temperatures.

A detailed pattern of the phase transitions is shown by the following schemes: (S = solid phase; Sm = smectic; N = nematic; I = isotropic liquid.)

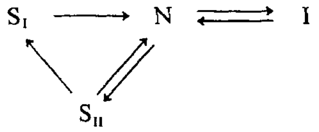
1) C2: A single solid phase, nematic mesophase.

$$\mathrm{S} \rightleftarrows \mathrm{N} \rightleftarrows \mathrm{I}$$

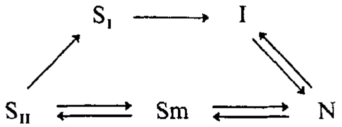
2) C4: Two solid phases related through enantiotropic transformation, nematic mesophase.

$$\mathrm{S_I} \rightleftarrows \mathrm{S_{II}} \rightleftarrows \mathrm{N} \rightleftarrows \mathrm{I}$$

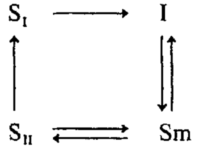
3) C3, C5 → C10: Two solid phases related through monotropic transformation, nematic mesophase.



4) C11: Two solid phases related through monotropic transformation, nematic and smectic mesophases.



5) C12 → C16: Two solid phases related through monotropic transformation, smectic mesophase.



The occurrence of a mesophase is in doubt for C16. Anisotropic nuclei develop from the isotropic liquid one elusive instant before the solid phase S_{II} is formed. No corresponding independent caloric effect is detectable on the DSC apparatus at whatever cooling rate.

Solid–solid transition For all compounds but C4 the solid–solid transition is monotropic. For C4 it is enantiotropic and topotactic: a single crystal can be subjected to many subsequent phase transitions without any detectable damage or permanent modification being caused.

Substantial odd-even effects are observed in the relevant thermodynamic data (Figures 2 and 3; Table I). This implies that the molecular packing of the aliphatic chains is strongly involved in the phase transition. On the other hand, the very low incremental value of transition entropy per aliphatic carbon atom, that is, the average value of $(\Delta S(S_{II} \rightarrow S_I)_n - \Delta S(S_{II} \rightarrow S_I)_{n-2})/4$ which is 0.2 cal mol^{-1} K^{-1}, implies that the aliphatic chain packing in the S_{II} phase is still highly ordered. Some examples of different behaviour are known, like that shown by the series $(CH_3(CH_2)_nNH_3)_2MnCl_4$[3,4] or that discussed by Dvolaitsky *et al.*[5] about the solid–smectic B transition of 4,4′-dioctadecyloxyazoxybenzene.

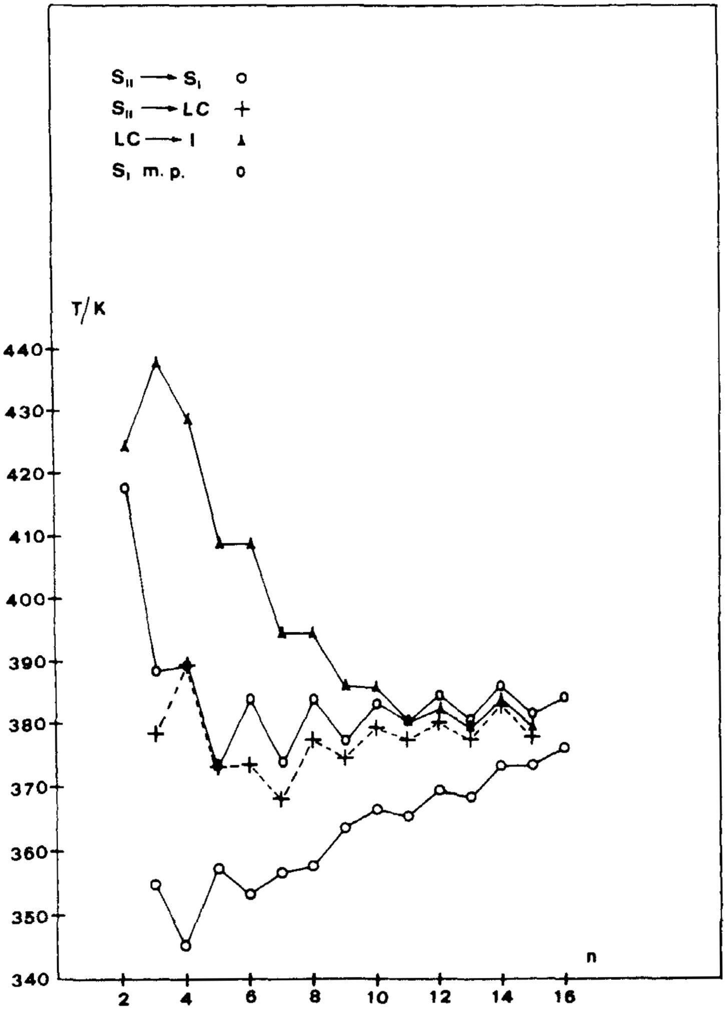


FIGURE 2 Phase transition temperatures. (The lettering is the same as in Table I.)

In that case the solid–solid (or solid–smectic B) phase transition has an entropic effect closely corresponding to a complete disordering (fusion) of the aliphatic chains.

Liquid crystalline phases The occurrence of mesophases is unambiguously observable, with the possible exception for C16, both on the polarizing microscope and on the DSC thermogram. The calorimetric data are by themselves sufficient to indicate the nematic character of the mesophases

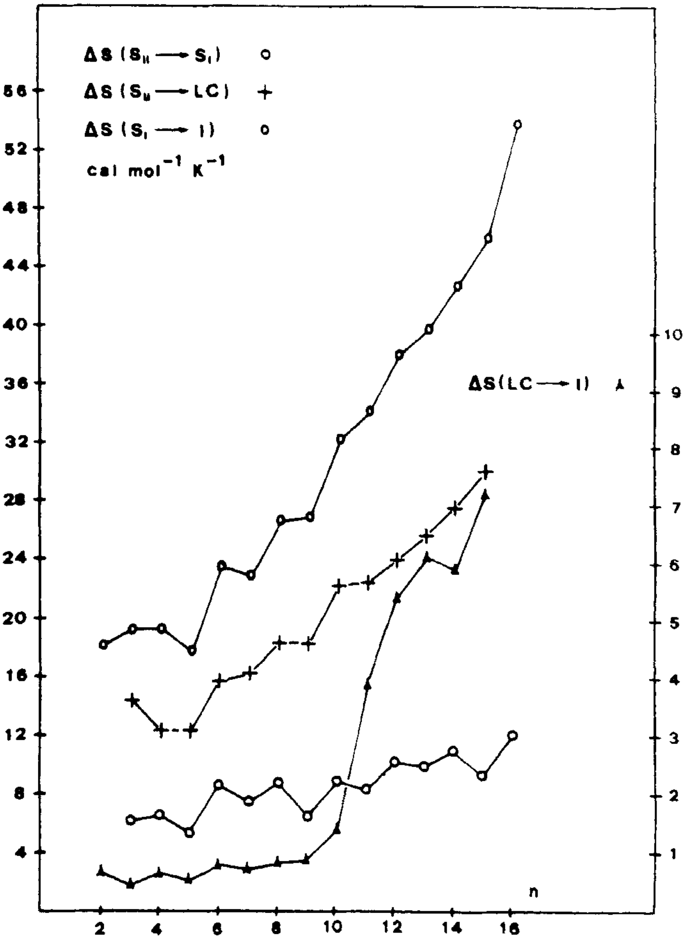


FIGURE 3 Molar transition entropies. The liquid crystal-isotropic liquid transition entropies have been reported on an expanded scale (right side scale). (The lettering is the same as in Table I.)

given by compounds C2 → C10 and the smectic character of those given by compounds C11 → C15 (see ref. 6 for a discussion of thermodynamic data on liquid crystals). In fact, the average value of the ratio $\Delta S(\mathrm{LC} \to \mathrm{I})/\Delta S(\mathrm{S_I} \to \mathrm{I})$ is 0.03 for compounds C2 → C10 and 0.14 for compounds C11 → C15. In the particular case of C11, where two liquid crystalline phases occur, the above ratio is 0.05 for the $\mathrm{LC_{II}} \to \mathrm{I}$ transition and 0.11 for the total $\mathrm{LC_I} \to \mathrm{LC_{II}} \to \mathrm{I}$ transition.

The significant texture that almost exclusively occurs is the Schlieren one. This qualifies the smectic phases as of C type. In one case, C13, no other

TABLE I[a]

Thermodynamic data of phase transitions

	$S_{II} \rightarrow S_I$			$S_{II} \rightarrow LC$			$LC \rightarrow I$			$S_I \rightarrow LC/I$[e]		
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
C2	—	—	—	—	—	—	424.5	0.28	0.66	418.0	7.4	17.7
C3	355.2	2.21	6.2	378.0	5.4	14.3	438.0	0.21	0.48	388.7	7.3	18.8
C4	351.2[b]	2.27	6.5	390.0	4.8	12.3	429.0	0.27	0.63	[f]		
C5	357.5	1.92	5.4	373.5	4.6	12.3	409.0	0.23	0.56	373.3	6.5	17.4
C6	353.5	3.1	8.8	374.0	5.9	15.8	409.0	0.32	0.78	384.4	8.8	22.9
C7	357.0	2.69	7.5	368.5	6.0	16.3	394.7	0.29	0.73	374.5	8.4	22.4
C8	358.0	3.2	8.9	378.0	7.0	18.5	394.5	0.34	0.86	384.5	10.0	26.0
C9	364.2	2.76	7.6	374.7	6.9	18.4	386.6	0.34	0.88	377.7	9.9	26.2
C10	367.0	3.3	9.0	380.0	8.5	22.4	386.5	0.55	1.42	384.0	11.9	31.0
C11	365.8	3.1	8.5	377.8	8.5[c]	22.5	[d]			380.9	13.1	34.4
C12	370.0	3.9	10.5	380.7	9.2	24.2	383.0	2.05	5.4	385.0	14.8	38.4
C13	369.0	3.7	10.0	378.1	9.8	25.9	380.0	2.33	6.1	381.3	15.3	40.1
C14	374.0	4.3	11.5	383.5	10.7	27.9	384.0	2.25	5.9	386.8	16.8	43.4
C15	374.0	3.5	9.4	378.5	11.5	30.4	379.8	2.73	7.2	382.4	17.8	46.5
C16	376.8	4.6	12.2	—	—	—	—	—	—	384.8	20.9	54.3

[a] S_I and S_{II} indicate solid phases at low and high temperature respectively. Temperatures are given in absolute scale (K) and are reproducible within 1 K. Transition enthalpies are given in Kcal mol^{-1}. The relative error is $0.07 \geq \sigma(\Delta H)/\Delta H \geq 0.01$; the maximum error applies to $\Delta H < 1$ Kcal mol^{-1}. The same relative errors affect the entropic data, which are given in cal mol^{-1} K^{-1}. $\sigma(\Delta H)$ is a standard deviation calculated from measurements of ΔH with different samples and in different runs. It may be considered as a measure of the reproducibility of the calorimetric data from sample to sample.

[b] This transition is enantiotropic and the data refer to the $S_I \rightarrow S_{II}$ phase change. The reverse occurs at 346 K.

[c] This value is the difference between the measured values of $\Delta H(S_{II} \rightarrow Sm \rightarrow N)$ and $\Delta H(Sm \rightarrow N)$. The endotherms of subsequent $S_{II} \rightarrow$ Sm and Sm → N transitions are not resolved and the only way to separately measure $\Delta H(Sm \rightarrow N)$ was that of cooling the nematic liquid to let the N → Sm transition occur and then heating to obtain the reverse transition. The same holds, obviously for the entropic datum.

[d] This compounds gives two mesophases:

Sm → N: $T = 378.5$ K, $\Delta H = 0.78$ Kcal mol^{-1}, $\Delta S = 2.1$ cal mol^{-1} K^{-1}.

N → I: $T = 381.0$ K, $\Delta H = 0.66$ Kcal mol^{-1}, $\Delta S = 1.7$ cal mol^{-1} K^{-1}.

[e] Compounds C2 to C10 melt to the nematic liquid; compounds C11 to C16 melt to the isotropic liquid

texture than the insignificant homogeneous one could be obtained. Homogeneous domains formed that persisted even after several passages to the isotropic liquid phase. Figures 4–8 show some relevant morphologies.

In the case of C11 a smectic Schlieren texture changes to a nematic Schlieren one and vice versa (Figure 7*a*, *b*, *c*). The one texture, and phase, converts into the other through an almost continuous change of colour and an intermediate almost isotropic texture is observable. A peculiar aspect is the persistence of most part of the same Schlieren pattern of the smectic phase even through a passage to the nematic phase at higher temperature.

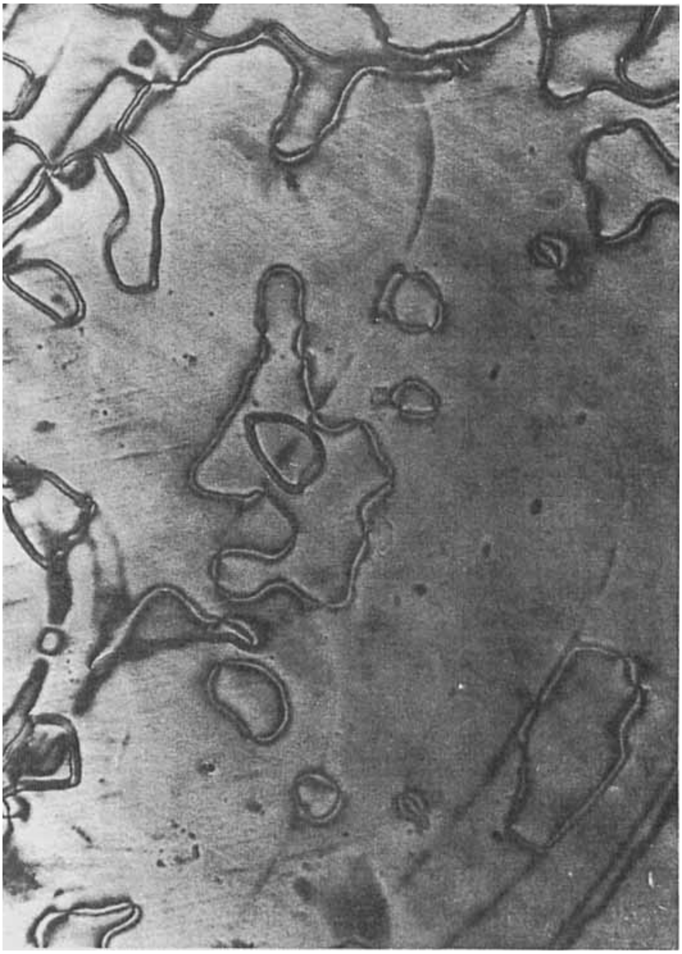


FIGURE 4 4,4′-diacetoxy-α,α′-dimethylbenzalazine (C2), Schlieren pattern in homogeneous texture background. Inversion lines of the first kind. Crossed polarizers. $T = 416$ K on cooling.

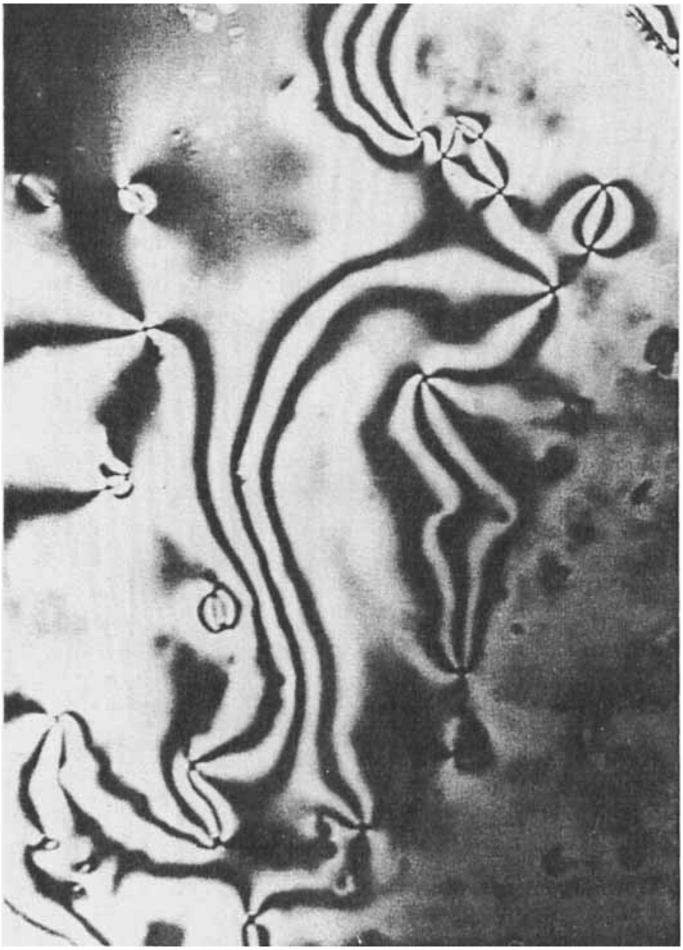


FIGURE 5 4,4'-dipentanoyloxy-α,α'-dimethylbenzalazine (C5).
a) Schlieren pattern with ordinary point singularities with $|s| = 1$, uncovered drop. Crossed polarizers. $T = 401$ K. ($|s|$ = number of brushes/4 has been used by Nehring and Saupe[7] to characterize the different types of singularities in nematic or smectic Schlieren textures.)

Surface effects may play their role, presumably, but further investigation is needed to clarify the point.

A regular odd-even effect is detectable for the clearing temperatures, as usual, but only for the nematic compounds is such an effect clearly shown also by the entropy changes.

$S_{II} \rightarrow$ LC *transitions* The average incremental value per aliphatic carbon atom of the transition entropy: $(\Delta S(S_{II} \rightarrow \mathrm{LC})_n - \Delta S(S_{II} \rightarrow \mathrm{LC})_{n-2})/4$ is

FIGURE 5 b) Schlieren texture, domain pattern induced by shearing; covered layer. T = 391 K. Crossed polarizers.

0.8 cal mol^{-1} K^{-1}. No significant difference, in this respect, can be detected between the two classes of compounds (C3 → C10 and C11 → C15).

Although one might see in the entropy diagram a minimum at compounds C4 and C5, nothing like the sharp discontinuity found by Arnold for 4,4′-di(*n*-alkoxy)azoxybenzenes[6] is to be seen. The only evidence distinguishing the nematic compounds from the smectic ones is the absence of odd-even effects in the entropy data of the latter (Figure 3). A parallel dependence of the entropies of the S_{II} crystal phase and of the smectic mesophase on the parity of the term number could be a possible explanation. This is conceivable

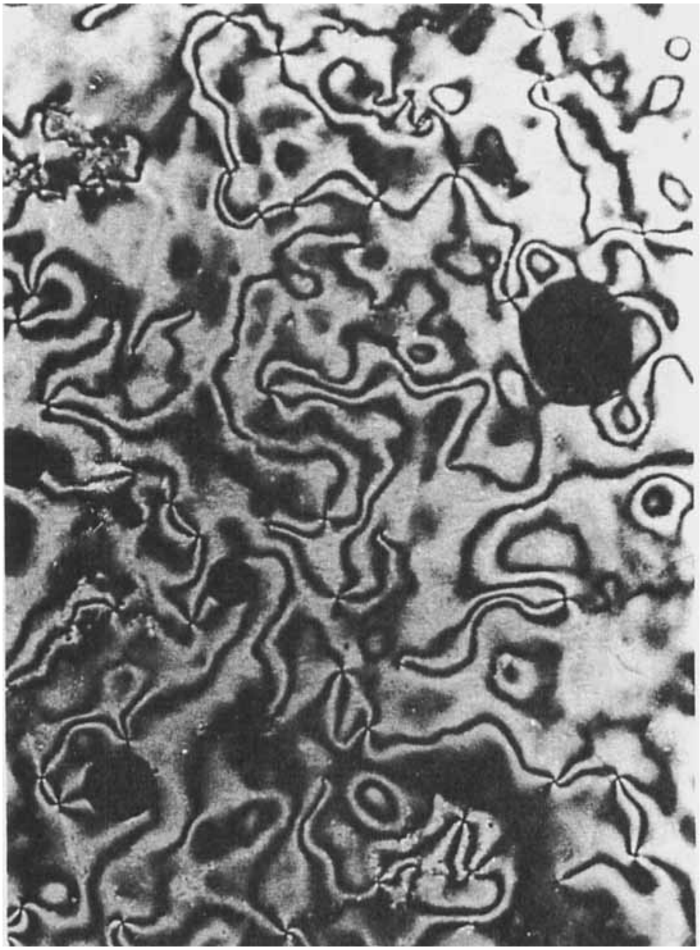


FIGURE 6 4,4′-didecanoyloxy-α,α′-dimethylbenzalazine (C10). $T = 385$ K, crossed polarizers. Point singularities with $|s| = \frac{1}{2}$ characteristic of nematic Schlieren textures are still present.

on account of the considerable structural order still kept by the smectic liquids.

Summary

Aliphatic esters of 4,4′-dihydroxy-α,α′-dimethylbenzalazine with formula:

$$CH_3(CH_2)_n{-}COO{-}\phi{-}C(CH_3){=}N{-}N{=}C(CH_3){-}\phi{-}OOC(CH_2)_nCH_3,$$

$$n = 0 \rightarrow 14,$$

have been prepared and their phase transitions studied by differential scanning calorimetry and optical methods.

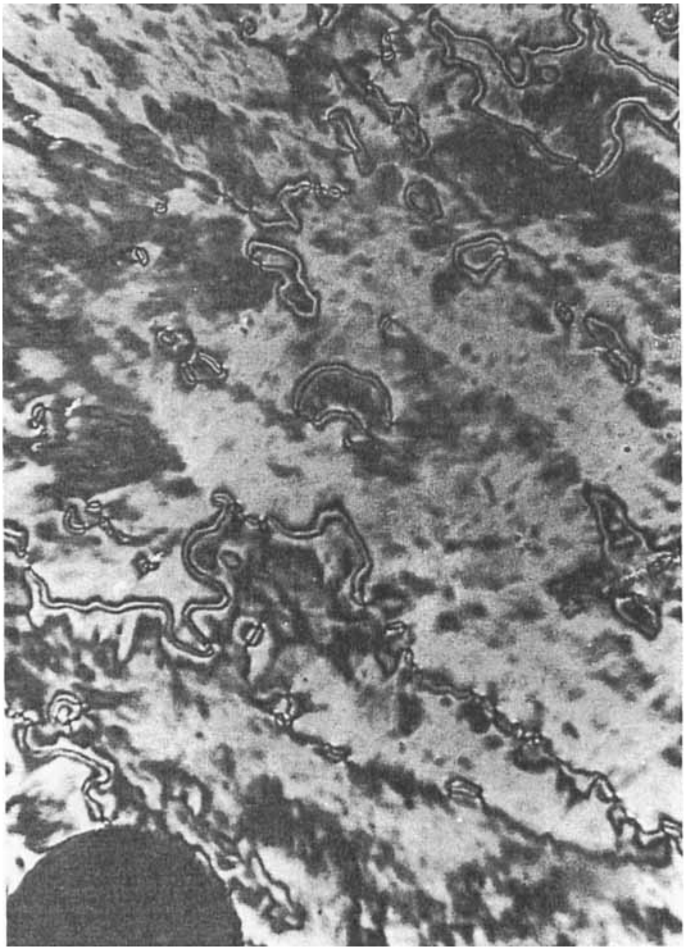


FIGURE 7 4,4′-diundecanoyloxy-α,α'-dimethylbenzalazine (C11). a) Smectic phase, $T = 377$ K on cooling. Crossed polarizers.

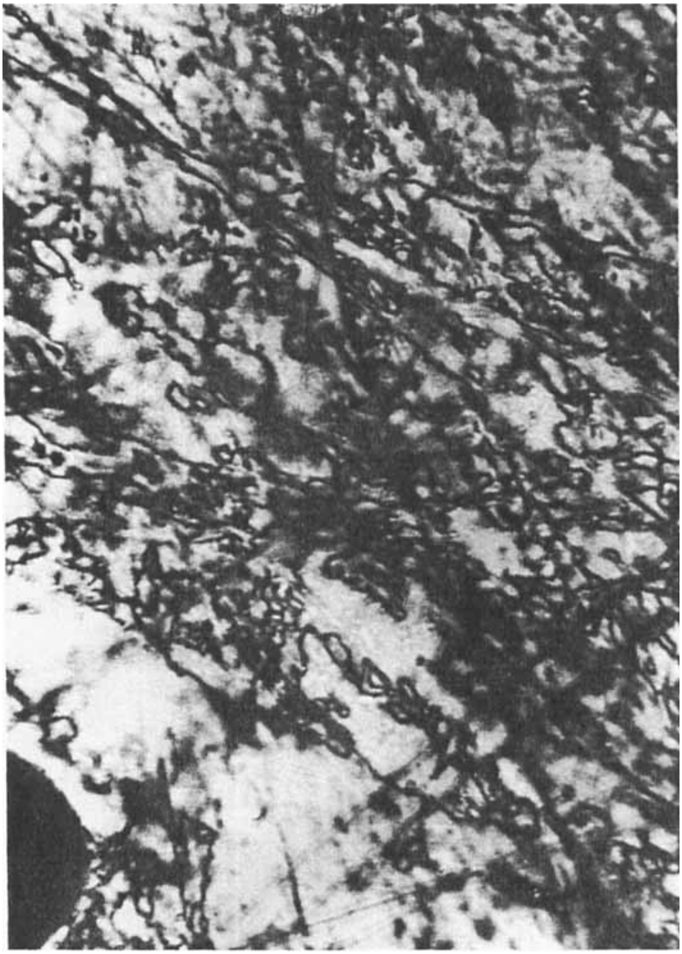


FIGURE 7 b) Nematic phase. $T = 380$ K on cooling. Crossed polarizers.

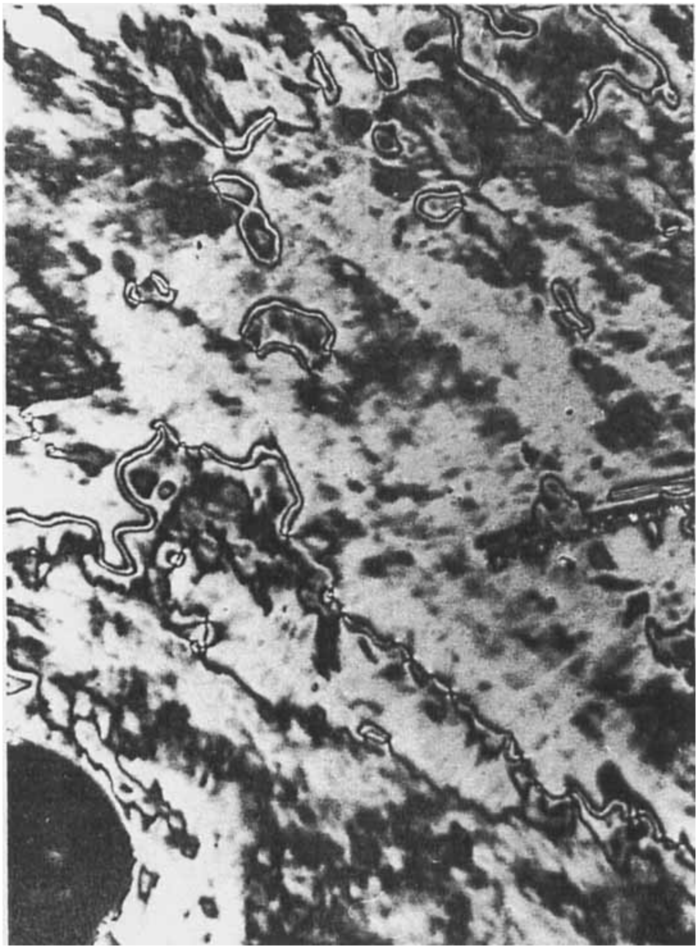


FIGURE 7 c) Smectic phase, $T = 377$ K on cooling. Crossed polarizers. The temporal sequence was $a \rightarrow b \rightarrow c$. Although with some alterations, part of the Schlieren pattern of a appears also in c after a passage to the nematic b.

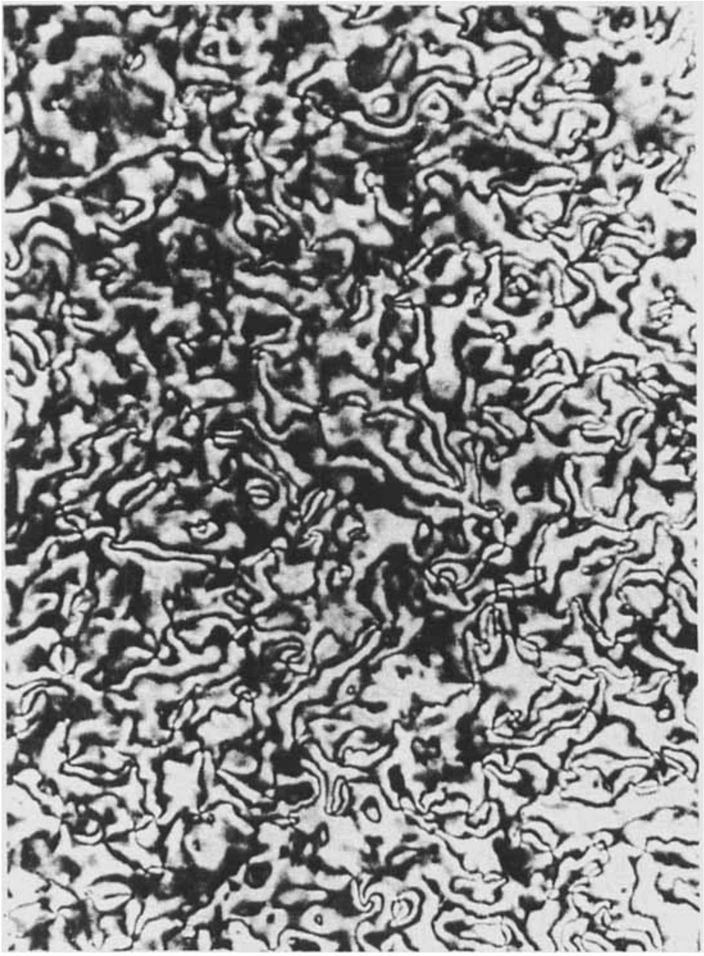


FIGURE 8 4,4′-dipentadecanoyloxy-α,α′-dimethylbenzalazine (C15). Smectic Schlieren texture $T = 379$ K. Crossed polarizers.

Compounds with $n = 0 \rightarrow 8$ give nematic mesophases; those with $n = 10 \rightarrow 13$ give smectic C mesophases and that with $n = 9$ gives both smectic and nematic mesophases while no unambiguous evidence of any mesophase was found for $n = 14$.

All compounds but the first one ($n = 0$), can exist in a second solid phase at high temperature. The two solid phases are monotropically related in all cases except when $n = 2$.

Calorimetric data relative to the phase transitions and optical patterns of liquid crystalline phases are shown.

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