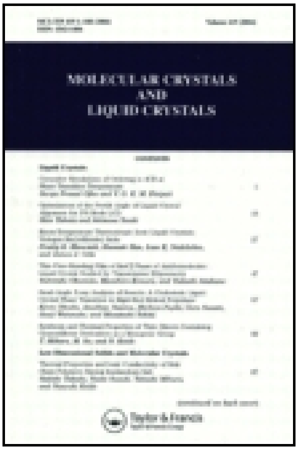

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Solid and Liquid Crystalline Phases of Aliphatic Esters of 4,4′ -dihydroxybenzalazine

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Solid and Liquid Crystalline Phases of Aliphatic Esters of 4,4′-dihydroxybenzalazine

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INTRODUCTION

Polyesters showing thermotropic mesophasic behaviour have been prepared by us by reaction of aliphatic acyl chlorides with some aromatic molecules like 4,4′-dihydroxy-α-methyl stilbene ($HOC_6H_4C(CH_3){=}CHC_6H_4OH$); 4,4′-dihydroxybenzalazine ($HOC_6H_4CH{=}N{-}N{=}CHC_6H_4OH$) and 4,4′-dihydroxy-α,α′-dimethylbenzalazine

$$(HOC_6H_4C(CH_3){=}N{-}N{=}C(CH_3)C_6H_4OH).$$

Work is in progress also to analyse the modifications that small chemical and structural changes may cause to the mesophasic properties of a polymeric material. It is well known that even minor changes in chemical constitution of a mesophase-generating molecule may produce relevant effects on the properties of the liquid phases, modifying the mesophase behaviour or even preventing the very existence of any mesophase. A considerable amount of data is available on low molecular weight compounds[1,2] and some work has been done on lyotropic liquid crystal properties of some polymers[3] while almost nothing is known on thermotropic mesophases of polymers.

This work reports the thermodynamic data relative to the phase transitions in the solid and liquid states of several aliphatic esters of 4,4′-dihydroxybenzalazine and some relevant optical observations on the liquid crystalline phases. A comparison is made with analogous measurements on the α,α′-methylated homologs. A similar comparison of the solid state and mesophasic properties of the polymeric esters containing the benzalazine group and its α,α′-methylated derivative is in progress.

A preliminary note on the properties of the polymers containing the α,α′-dimethylbenzalazine group (—$C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)C_6H_4$—) has been already published[4] and a complete account on the phase transitions and mesophasic behaviour of low molecular weight aliphatic esters containing the same group:

$$CH_3(CH_2)_nCOOC_6H_4C(CH_3){=}N{-}N{=}C(CH_3)C_6H_4OOC(CH_2)_nCH_3$$

is to be published.[5]

EXPERIMENTAL

4,4′-dihydroxybenzalazine ($HOC_6H_4CH{=}N{-}N{=}CHC_6H_4OH$) was prepared from 4-hydroxybenzaldeyd and hydrazine sulphate. The elemental analysis gives the following results:

C % 70.00 calc., 70.08 found;
N % 11.67 calc., 11.79 found;
H % 5.00 calc., 5.07 found.

Because of the incipient decomposition the melting endotherm has a rather broad basis. A clear change of gradient is detectable at 539 K. A melting point of 543 K was reported by Blout and Gofstein.[6] There is a complete agreement between our UV spectrum and that reported by the above authors. Furthermore the NMR spectrum is consistent with the formula (Figure 1a).

Aliphatic esters were prepared by standard methods using acyl chlorides (Fluka) previously three times vacuum distilled. Tridecanoyl- and pentadecanoyl chlorides were prepared from the corresponding dicarboxylic acids (Fluka). All the ester compounds were crystallized at least four times and their purity was monitored by scanning calorimetry until strictly reproducible behaviour was observed. Final NMR spectra are in accordance with the formula for each compound of the series. The NMR spectrum of the didodecanoyl compound is reported in Figure 1b as an example.[13]

DSC Analysis Phase transition temperatures and enthalpies were measured using a Perkin-Elmer DSC-1 Differential Scanning Calorimeter. The samples were examined under dry nitrogen flow. The transition temperatures were taken at the onset of the thermal phenomena. Scanning rates from 0.5 to 16 K/min were used. An indium sample (99.999 %; Fluka) was utilized as reference standard.

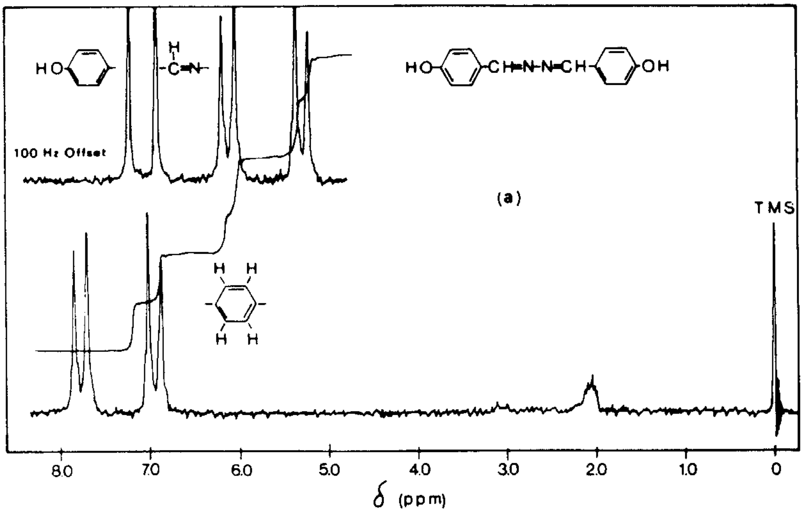

FIGURE 1a NMR spectrum of 4,4′-dihydroxybenzalazine (solvent: deuterated acetone).

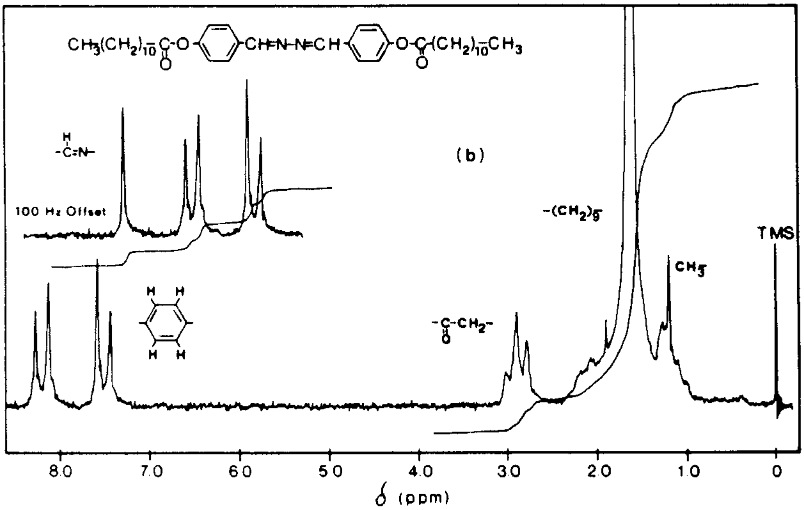

FIGURE 1b NMR spectrum of 4,4′-didodecanoyloxybenzalazine (solvent: deuterated chloroform).

Thermal Polarizing Microscopy The optical observations were made using a Mettler FP5 microfurnace and a Leitz polarizing microscope equipped with photographic camera. The phase transition temperatures measured with the Mettler microfurnace were generally in very good agreement with the corresponding measurement made on the DSC apparatus. Only some of the solid–solid transition with small thermal effect were hardly detectable by optical methods.

RESULTS AND DISCUSSION

All the aliphatic esters (we call them with the symbol Cn, where n is the total number of carbon atoms in a single aliphatic group) of 4,4′-dihydroxybenzalazine show mesophasic behaviour; all but the first two compounds of the series, C_2 and C_3, can exist in different solid phases above room temperature. All the phase transformations are enantiotropic. Compounds $C_2 \rightarrow C_{10}$ show a nematic mesophase, compounds $C_{12} \rightarrow C_{16}$ show a smectic C mesophase, C_{11} shows both smectic C and nematic mesophases. The relevant thermodynamic data relative to the phase transitions are shown in Tables I and II. The dependence of the transition temperatures and entropies on the aliphatic chain length can be more easily seen in Figures 2 and 3 respectively.

Solid–solid phase transitions The initial temperature in the DSC analysis was normally 320°K. Between this temperature and the melting, all the examined compounds, except the first two, show at least one solid phase transition endotherm. Without any information on the crystal structure the entire picture of the solid-phase transitions is not easily rationalizable. It is intriguing, for instance, to note that a total molar entropy change of 5.5 cal $mol^{-1}K^{-1}$ is obtained with four different solid-phase transitions by the exadecanoic ester (C_{16}) while the same amount of entropy change is associated with a single solid-phase transition in the case of C_{15}. Some correlation of data can however be tried.

If the phase transitions occurring at the lowest temperature are considered, it is easily seen that in the range $n = 4 \rightarrow 13$, with the exception of $n = 6$, they constitute an homogeneous class (Figure 2, curve d). (When we say that a set of phase transitions is an homogeneous class, we imply that they correlate two different sets of phases having homologous structure). These phase transitions are also characterized by the fact that they involve the least molar entropic change (Figure 3, curve d; Table I).

As to C_6, if the phase transition involving the minimum entropic change is considered, it is immediately seen that both the transition temperature

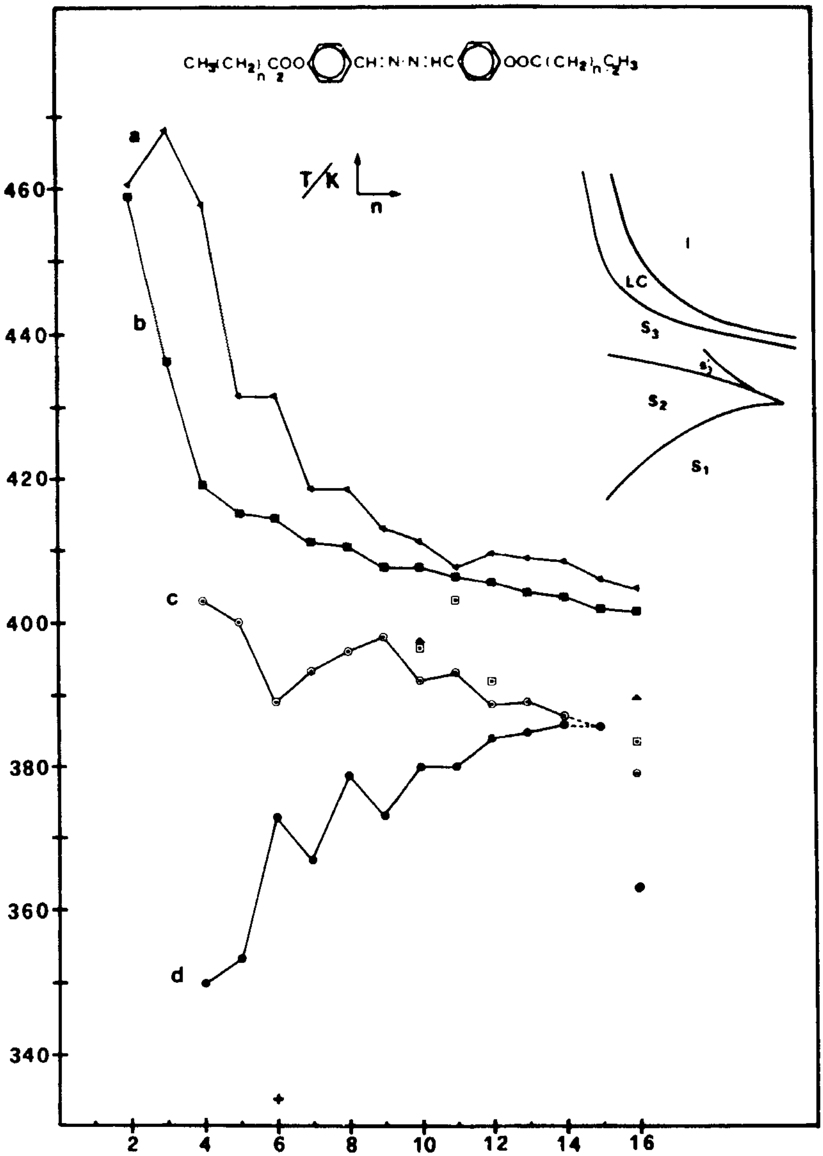

FIGURE 2 Phase transition temperatures.
a: clearing temperature; **b**: melting temperature; **c**, **d**: solid phase transition temperatures (points not connected by lines refer to solid phase transitions).

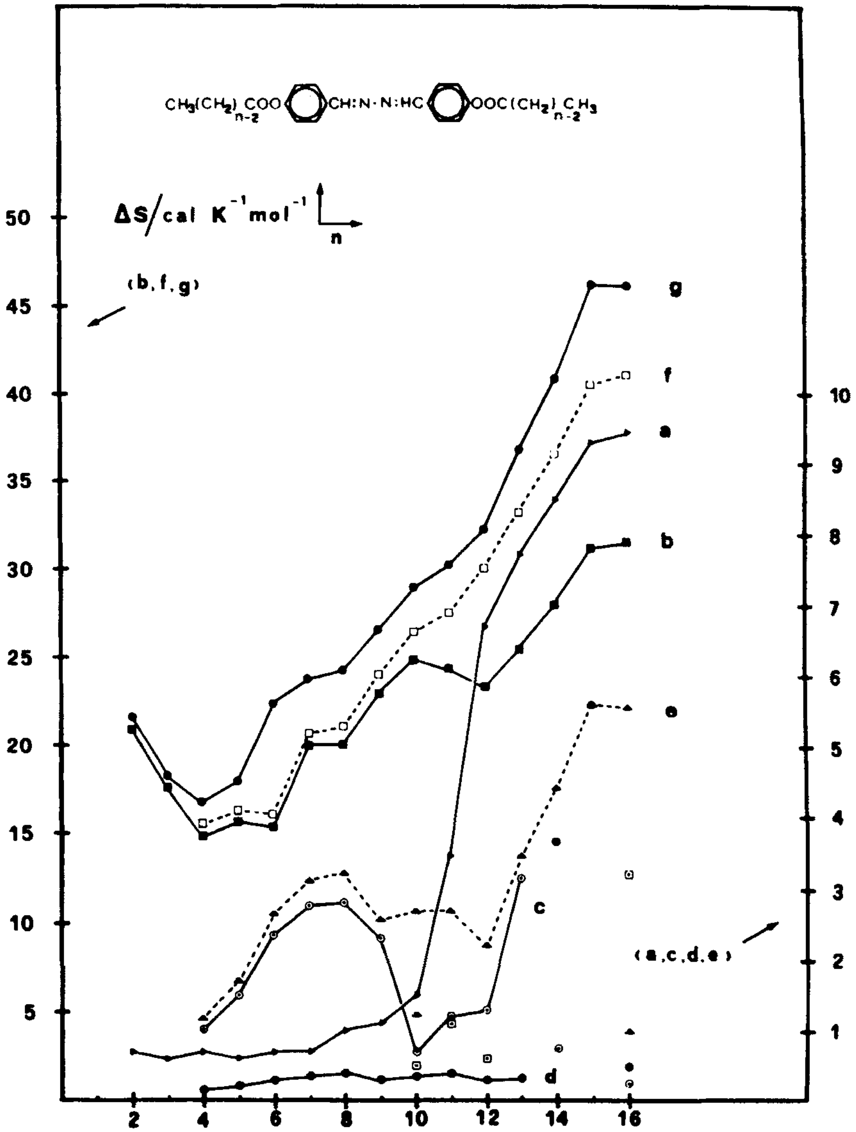

FIGURE 3 Molar phase transition entropies. (**b**, **f**, **g**: left side scale; all others: right side expanded scale).
a: clearing; **b**: melting; **c**, **d** and all other points not connected by lines: solid phase transitions; **e**: total solid phase transition entropy; **f**: melting entropy + clearing entropy; **g**: total (solid – solid + melting + clearing) transition entropy.

TABLE I[a]

Thermodynamic data on solid-phase transitions

	$S_0 \rightarrow S_1$			$S_1 \rightarrow S_2$			$S_2 \rightarrow S_3'$			$S_2(S_3') \rightarrow S_3$		
n	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
2												
3												
4				350.0	0.05	0.14				403.0	0.41	1.02
5				353.5	0.07	0.20				400.3	0.61	1.52
6	334.0	1.23	3.68	373.2	0.12	0.32				389.0	0.91	2.34
7				367.0	0.13	0.35				393.7	1.08	2.74
8				379.0	0.15	0.40				396.0	1.11	2.80
9				373.0	0.10	0.27				397.8	0.91	2.29
10				380.0	0.14	0.35	392.3	0.27	0.69	397.7[b]	0.49	1.23
11				380.0	0.15	0.39	393.0	0.47	1.20	403.0	0.44	1.09
12				384.1	0.11	0.29	388.5	0.50	1.29	391.7	0.24	0.61
13				384.7	0.13	0.33				389.0	1.22	3.14
14							386.0	1.41	3.65	387.1	0.29	0.74
15										385.5	2.15	5.58
16	363.0	0.22	0.61	379.0	0.09	0.24	383.6	1.23	3.21	389.7	0.38	0.98

[a] Symbols and physical units: n = number of carbon atoms in a single aliphatic chain. T (K) transition temperature, reproducible within 1 K. Molar transition enthalpies, ΔH, are given in Kcal mol^{-1}. The relative error is $0.07 \geqslant \sigma(\Delta H)/\Delta H \geqslant 0.01$; the maximum error applies to $\Delta H < 1$ Kcal mol^{-1}. The same relative error affect the entropic data, ΔS, which are given in cal mol^{-1}K^{-1}. $\sigma(\Delta H)$ is a standard deviation calculated from measurements of ΔH in different runs and with different samples. It may be considered as a measure of the reproducibility of the calorimetric data. S_n indicates different solid phases.

[b] This phase transition is preceded by another almost coincident one: $T = 396.6$ K; $\Delta H = 0.16$ Kcal mol^{-1}; $\Delta S = 0.40$ cal mol^{-1}K^{-1}.

(373.2 K) and the amount of entropic change (0.32 cal mol^{-1}K^{-1}) assign this phase transition to the homogenous class previously defined. Within this class, the regular dependence of the transition temperature and entropy change on the chain length, with the usual odd-even effects, is unambiguously shown in Figures 2, 3, curve d.

As to C_{14} and C_{15}, the first (and the only one for C_{15}) phase transition occurs at a temperature (386.0 K, C_{14}; 385.5 K, C_{15}) perfectly compatible with those of the class above defined, but the molar entropic change is by no means comparable. Although only a direct crystal structure analysis could give an unambiguous picture, we could tentatively conclude that compounds $C_4 \rightarrow C_{15}$ have homologous crystal structures at temperatures below the first phase transition, down to 334.0 K for C_6, down at least 320 K for the others. We call this crystal phase with the symbol S_1. The crystal structures of compounds $C_4 \rightarrow C_{13}$ are assumed to be equally homologous in the temperature range between the first and the second solid phase transitions. This second crystal phase is called S_2. As to C_{14} and C_{15}, the second

TABLE II[a]

Thermodynamic data on phase transitions involving liquid phases.

	$S_3 \rightarrow LC$			$LC \rightarrow I$			$S_1 \rightarrow I$	
n	T	ΔH	ΔS	T	ΔH	ΔS	ΔH	ΔS
2	458.8	9.60	20.9	460.5[b]	0.32	0.69	9.92	21.6
3	436.3	7.66	17.6	468.0	0.27	0.58	7.93	18.2
4	419.2	6.26	14.9	457.8	0.33	0.72	7.05	16.8
5	415.3	6.54	15.7	431.5	0.25	0.58	7.47	18.0
6	414.6	6.37	15.4	431.7	0.30	0.69	8.93	22.4
7	411.0	8.23	20.0	418.5	0.29	0.69	9.73	23.8
8	410.5	8.27	20.1	418.5	0.41	0.98	9.94	24.3
9	407.7	9.37	23.0	412.8	0.46	1.11	10.8	26.7
10	407.8	10.2	25.0	411.3	0.60	1.47	11.9	29.1
11	406.5	9.82	24.2	[c]			12.3	30.3
12	405.4	9.48	23.4	409.4	2.74	6.69	13.1	32.3
13	404.0	10.4	25.6	408.8	3.16	7.73	14.9	36.8
14	403.5	11.3	28.0	408.3	3.46	8.47	16.5	40.9
15	401.8	12.6	31.3	406.0	3.77	9.28	18.5	46.2
16	401.4	12.7	31.6	404.7	3.83	9.46	18.4	46.1

[a] Symbols and physical units: see note a of Table I. *LC*: liquid crystal phase; *I*: isotropic liquid.

[b] Reference 12 reports a clearing point at 465 K, but we must point out that our transition temperatures are taken at the onset of the thermal phenomenon. With an heating rate of 8 K/min the liquid crystal–isotropic liquid transition of C2 is completed at 464.5 K.

[c] This compound shows two liquid crystal phases:

$Sm \rightarrow N$: $T = 406.9$ K; $\Delta H = 1.05$ Kcal mol^{-1}; $\Delta S = 2.58$ cal mol^{-1}K^{-1}.

$N \rightarrow I$: $T = 407.5$ K; $\Delta H = 0.35$ Kcal mol^{-1}; $\Delta S = 0.86$ cal mol^{-1}K^{-1}.

crystal phase is probably not homologous to S_2 on account of the considerably higher entropic change that corresponds to the first phase transition.

Coming back to C_6 we must add that the S_1 crystal phase occurring at temperatures above 334 K is subject to considerable undercooling. No exothermic peak is detected on cooling the S_1 phase down to 173 K even at low scanning rate. The complete transition from the undercooled S_1 phase to that stable at room temperature needs about ten hours at room temperature.

We take now into account the set of phase changes, that come next as to transition temperature. The roughly linear dependence of the transition temperature on the chain length (Figure 2, curve c) is in no way paralleled by the entropy change function which, on the contrary, shows a rather peculiar shape (Figure 3, curve c). We should conclude that although the S_2 crystal phases are presumably structurally homologous they transform, on heating, into structurally heterogenous crystal phases. This last point should be confirmed by the further behaviour of C_{10}, C_{11} and C_{12}. These compounds, which change, on heating, their S_2 phase with a minimum of entropy increase, show one additional phase change (two almost coincident for C_{10}). For reference sake, the symbol S_3 has been assigned to the crystal phases stable up to the melting point. A sketchy outline of the phase diagram is shown inside Figure 2. As to C_{16}, it is hardly recognizable any correlation of its solid state behaviour with that of the preceding compounds. The examination of higher members of the series could possibly show whether a new set of correlable phase transitions is just starting with C_{16}.

Liquid crystal phases If the total solid–solid transition entropy function is examined (Figure 3, curve e) and the assumption is maintained that the S_1 phases are structurally homogeneous, one should conclude that the S_3 crystal phases are not. On these bases it would have been reasonable to expect that the melting temperature and entropy functions (Figures 2, 3, curve b) showed a somewhat irregular shape. This does not happen. The melting temperature function is strikingly regular and small odd–even effects are still detectable. The melting entropy function consists of two approximately linear and parallel, but not collinear, parts. The first part contains the compounds that melt to a nematic liquid, $C_4 \rightarrow C_{10}$, (C_2 and C_3 having very short aliphatic chains behave differently in accordance to many analogous observations), the second line contains those melting to a smectic liquid $C_{12} \rightarrow C_{16}$. The only compound, C_{11}, that shows both nematic and smectic phases lies between these two lines. The non-collinearity of the latter disappears if we consider the melting + clearing entropy function $\Delta S(S_3 \rightarrow LC) + \Delta S(LC \rightarrow I)$, (Figure 3, curve f). This leads to the conclusion that the non-collinearity of the two portions of the melting entropy function must simply be ascribed to the high residual intermolecular order typical of the smectic phases, as compared to the nematic ones. Finally, the regular dependence of both melting temperature and entropy on the aliphatic chain length suggests that the crystal phases S_3 stable up to the melting point are structurally homogeneous. The opposite conclusion was previously drawn from considerations on solid-phase transitions. It clearly appears that a direct structural analysis is the only way out of this ambiguity.

All the examined compounds melt to a mesophasic liquid. The DSC measurements seem sufficient by themselves to define the nature of the mesophases. The $\Delta S(LC \rightarrow I)/\Delta S(S_1 \rightarrow I)$ ratio ranges between the values of 0.03 and 0.05 for compounds $C_2 \rightarrow C_{10}$ which give nematic mesophases. For compounds $C_{12} \rightarrow C_{16}$ the above ratio ranges between 0.20 and 0.23. Such high values are characteristic of smectic phases.[7] For C_{11} we found the value of 0.03 for $\Delta S(N \rightarrow I)/\Delta S(S_1 \rightarrow I)$ and the value of 0.11 for $\Delta S(Sm \rightarrow I)/\Delta S(S_1 \rightarrow I)$, which is considerably lower than the corresponding values found for the higher members of the series, but is still within the range of values found for smectic mesophases. The optical observations indicate that the smectic phases are of C type. Some relevant examples are shown in Figures 4-7. Figure 6, showing a Schlieren pattern of smectic C_{14}, needs a comment. Several points are observable where many brushes of surrounding defects converge, simulating a point defect of very high $|s|$ number ($|s|$ = number of brushes/4 has been used by Nehring and Saupe[8] to classify Schlieren patterns in nematic and smectic C phases). No special surface effect can be claimed to explain their presence since the entire Schlieren pattern and the position of these points does change completely by cyclically heating to the isotropic phase or cooling to the S_3 crystal phase. No relation whatsoever can be found between two successive optical patterns thus obtained. It is observed, on cooling the isotropic liquid, that several neighbouring defect lines that casually form may converge to a single point that ends up to the form shown in Figure 6. These are therefore not the origin where the defects of an ordered structure are irradiated from but the ultimate

TABLE III

Data for comparison between aliphatic esters of 4,4′-dihydroxybenzalazine and their α,α′-methylated homologs.

$CH_3(CH_2)_{n-2}COO\phi CR{=}N{-}N{=}CR\phi OOC(CH_2)_{n-2}CH_3$; R = H, CH_3

	a		**b**		**c**		**d**		**e**	
n	H	CH_3	H	CH_3	H	CH_3	H	CH_3	H	CH_3
2	1	1	458.8	418.0	460.5 N	424.5 N	0.69	0.66	21.6	18.4
3	1	(2)	436.3	388.7	468.0 N	438.0 N	0.58	0.48	18.2	19.3
4	3	2	419.2	390.0	457.8 N	429.0 N	0.72	0.63	16.8	19.4
5	3	(2)	415.3	373.3	431.5 N	409.0 N	0.58	0.56	18.0	18.0
6	4	(2)	414.6	384.4	431.7 N	409.0 N	0.69	0.78	22.4	23.7
7	3	(2)	411.0	374.5	418.5 N	394.7 N	0.69	0.73	23.8	23.1
8	3	(2)	410.5	384.5	418.5 N	394.5 N	0.98	0.86	24.3	26.9
9	3	(2)	407.7	377.7	412.8 N	386.6 N	1.11	0.88	26.7	27.1
10	5	(2)	407.8	384.0	411.3 N	386.5 N	1.47	1.42	29.1	32.4
11	4	(2)	406.5	380.9	407.5 Sm, N	381.0 (Sm, N)	3.44	3.80	30.3	38.2
12	4	(2)	405.4	385.0	409.4 Sm	383.0 (Sm)	6.69	5.4	32.3	38.4
13	3	(2)	404.0	381.3	408.8 Sm	380.0 (Sm)	7.73	6.1	36.8	40.1
14	3	(2)	403.5	386.8	408.3 Sm	384.0 (Sm)	8.47	5.9	40.9	43.4
15	2	(2)	401.8	382.4	406.0 Sm	379.8 (Sm)	9.28	7.2	46.2	46.5
16	5	(2)	401.4	384.8	404.7 Sm	—	9.46	—	46.1	54.3

a Number of solid phases from room temperature to melting point. Parentheses refer to monotropic transformations.

b Melting temperatures (K).

c Clearing temperatures (K) and type of mesophase. In parentheses are the monotropically observable mesophases.

d $LC \rightarrow I$: transition entropy (cal $K^{-1}mol^{-1}$).

e $S_1 \rightarrow I$: total (solid phase + melting + clearing) transition entropy (cal $K^{-1}mol^{-1}$).

place where the isotropic disorder is confined by a convergent onset of molecular ordering. Reversely, on heating, these are the points where the change to the isotropic phase takes the start.

Finally, we show a comparison with the aliphatic esters of 4,4′-dihydroxy,α,α'-dimethylbenzalazine.

The replacement of an hydrogen atom in both α positions with a methyl group is sufficient to drastically differentiate the behaviour of these two series of homologous compounds particularly in the solid state. The main differences together with some similar features are shortly summarized in Table III.

The overall pattern of the differences of behaviour between the two classes of compounds is not surprising, apart from the striking differences in the solid state. A considerable amount of data has been collected on the effect of local small chemical changes on the mesophasic properties of particular compounds. The regular observation is made, that is almost a rule, that the substitution of an hydrogen atom with a methyl group lowers the clearing temperature. More recent observations show that in several (*p*,*n*-alcoxy,*p*′,acyloxy-)- or *p*,*n*-alcoxy,*p*′,*n*-alcoxy-*N*-benzylidene anilines, the substitution of an hydrogen atom in orto position with a methyl group lowers melting and clearing points and reduces the range of stability of the mesophases.[9] Similar results are observed in methyl substituted stilbenes.[10,11] On the contrary we must point out that in our case the stability range of the nematic mesophases of the α,α'-methyl substituted compounds is generally widened.

Summary

The phase transitions and the mesophasic behaviour of a series of compounds with formula:

$$CH_3(CH_2)_{n-2}COO\phi CH{=}N{-}N{=}CH\phi OOC(CH_2)_{n-2}CH_3;\ n = 2 \rightarrow 16$$

has been studied by DSC and optical methods.

Compounds with $n = 4 \rightarrow 16$ can exist in several crystal phases and all give enantiotropic mesophase. Compounds with $n = 4 \rightarrow 10$ give a nematic liquid crystal phase, those with $n = 12 \rightarrow 16$ give smectic mesophases. Only the undecanoic ester ($n = 11$) gives both nematic and smectic mesophases. The phase transition entropies have been determined from DSC measurements. A comparison is made with the behaviour of the corresponding α,α'-methylated compounds:

$$CH_3(CH_2)_{n-2}COO\phi C(CH_3){=}N{-}N{=}C(CH_3)\phi OOC(CH_2)_{n-2}CH_3;$$

$$n = 2 \rightarrow 16$$

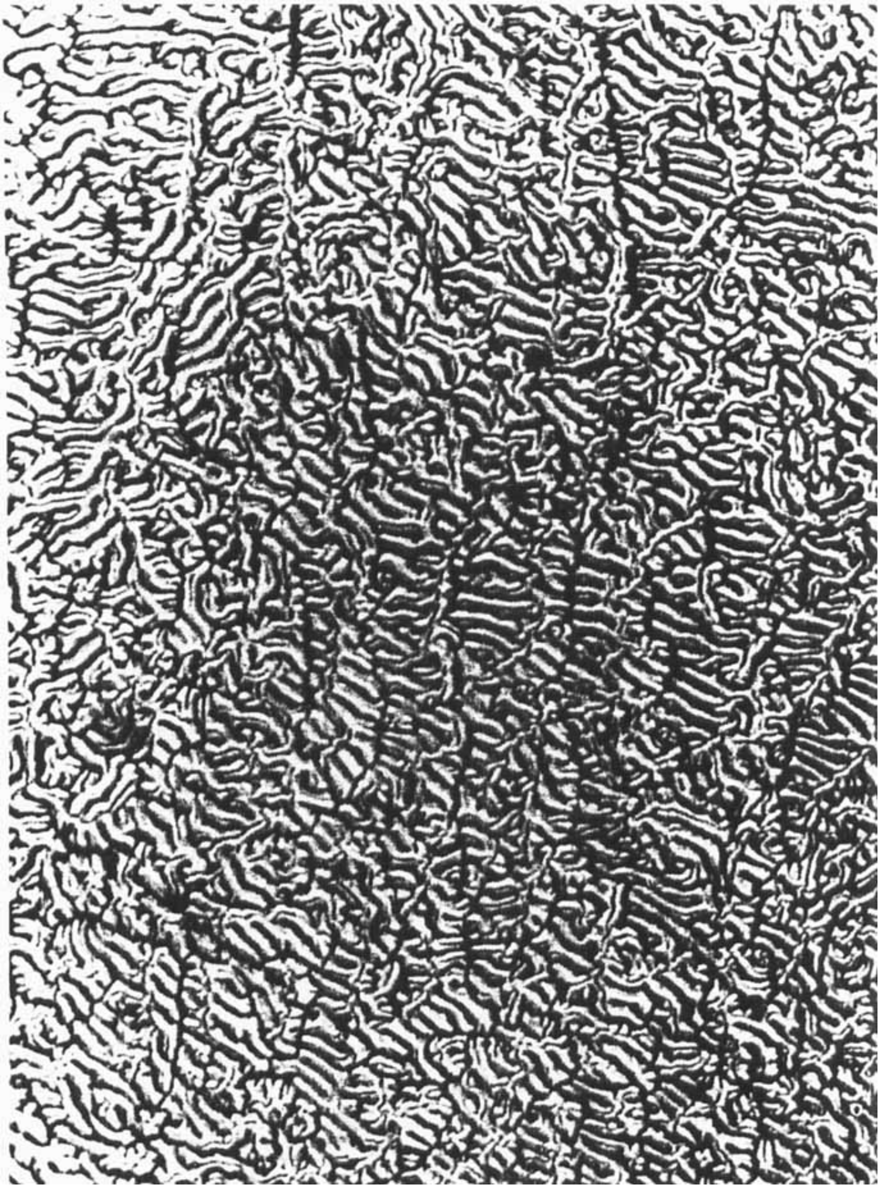

FIGURE 4 4,4′-undecanoyloxybenzalazine. $T = 406.0$ K; smectic liquid; crossed polarizers.

FIGURE 5 4,4′-undecanoyloxybenzalazine. $T = 407.2$ K; nematic liquid; crossed polarizers.

FIGURE 6 4,4′-tetradecanoyloxybenzalazine. T = 407.0 K; smectic liquid; crossed polarizers.

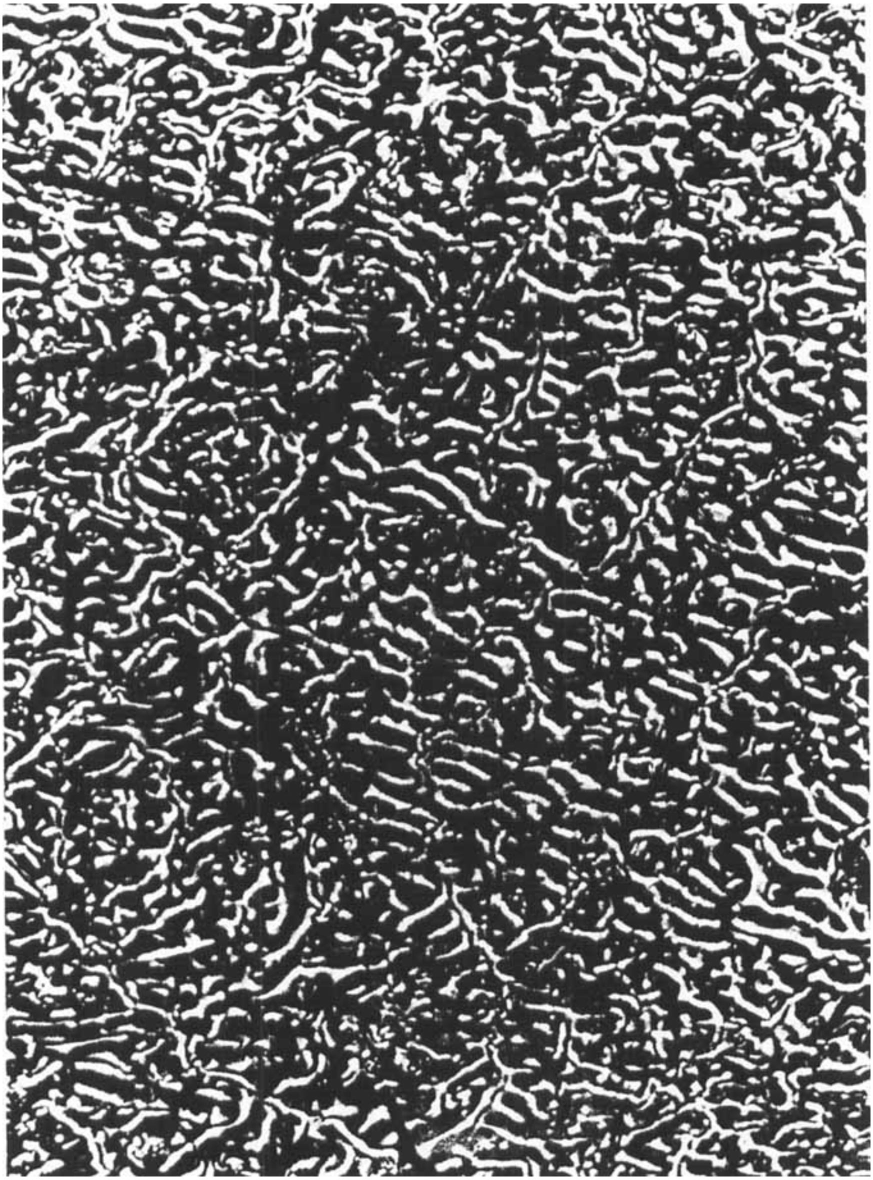

FIGURE 7 4,4′-pentadecanoyloxybenzalazine. $T = 405.0$ K; smectic liquid; crossed polarizers.

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