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J. L. Alabart [a], E. Melendez [a], B. Ros [a] & J. L. Serrano [a]
[a] Departamento de Quimica Organica, Facultad de Ciencias, Universidad de Zaragoza, Spain
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Influence of Changes in Central Core on the Mesomorphic Properties of 4,4′-Dialkoxy-2,2′-Dihydroxybenzalazine and Derivatives

J. L. ALABART, E. MELENDEZ, B. ROS and J. L. SERRANO

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, Spain.

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Two new series of compounds that have mesomorphic properties were synthesized: the 4,4′-dialkoxy-2,2′-dihydroxy-α-methylbenzalazines and the 4,4′-dialkoxy-2,2′-dihydroxybenzalazines. The first series shows crystalline and smectic polymorphism.

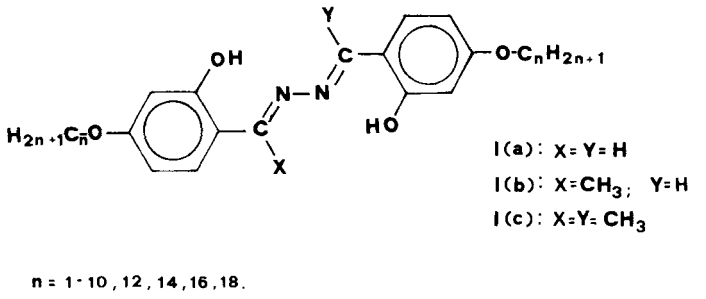
A comparative study of the mesomorphic properties of these series with those of the 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines was carried out to establish the influence of the central groups on the mesomorphic properties.

INTRODUCTION

In the study of liquid crystals it is usual to find that slight modifications in the geometry of a compound cause important variations in their mesomorphic properties.[1,2]

In previous papers we have shown that the introduction of one or two hydroxyl groups at position(s) 2 of the aromatic rings improves ostensibly, the mesomorphism of benzalazine derivatives.[3,4]

Working in this way, a comparative study of the mesomorphic properties of three series of benzalazine derivatives: 4,4′-dialkoxy-2,2′-dihydroxybenzalazines I(a); 4,4′-dialkoxy-2,2′-dihydroxy-α-meth-



Sketch I

ylbenzalazines I(b); and 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines I(c) was made.

Series I(c) has been described in a previous paper[3], while the other series I(a) and I(b) were specially synthesized for this paper. The existence of compounds with benzalazine,[5,6] α-methylbenzalazine,[7] and α,α′-dimethylbenzalazine[8,9] central groups has been known for some time. We observed that the benzalazine central bridge provides the compounds with better mesogenic properties than the α,α′-dimethylbenzalazine bridge. However, the fact that so little has been published about α-methylbenzalazines, makes any comparative study of these central bridges difficult. For this paper, the *ortho*-hydroxylated central cores were chosen for the following reasons.

The compounds of the three series studied show excellent mesomorphic properties and they are more thermally and chemically stable than the analogues without hydroxyl groups.

These hydroxyl groups, by hydrogen-bonding effects,[4] induce near planarity of the molecules in this kind of compounds,[10,11] and this enables us to establish the influence of the substituents CH_3 or H placed in the bridge.

EXPERIMENTAL

Synthesis

The method of synthesis used for these compounds is similar to that described previously.[3] 4,4′-Dialkoxy-2,2′-dihydroxybenzalazines I(a) were prepared using the method used to prepare 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines. The compounds of the asymmetric series of 4,4′-dialkoxy-2,2′-dihydroxy-α-methylbenzalazines I(b)

were prepared as for the 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines. However, it should be pointed out that modifications had to be introduced.

The conditions of alkylation of the OH group in position 4 had to be modified. In the 2,4-dihydroxyacetophenone derivatives, the *ortho*-hydroxyl group does not react in the conditions of Williamson's alkylation described in the previous paper (alkyl bromide, K_2CO_3 and acetone).

However, this hydroxyl group *is* alkylated in the 2,4-dihydroxybenzaldehyde derivatives. In this case, it was necessary to use a weaker base ($KHCO_3$) and very long reaction times (72-120 h.).

Purification of all the compounds required the use of chromatographic techniques (column or P.T.L.C.).

Techniques

The melting points, transitions temperatures and enthalpies were determinated using a PERKIN-ELMER DSC-2 Differential Scanning Calorimeter.

The optical observations were made using a REICHERT-THERMOVAR HT1 B11 polarizing microscope equipped with a heating stage.

The identification of products was carried out by the usual spectroscopic methods: U.V. (PERKIN-ELMER 200), I.R. (PERKIN-ELMER 283), N.M.R. (PERKIN-ELMER R-12-B).

The purity of all products was checked by the above-mentioned techniques and by thin-layer chromatography.

RESULTS AND DISCUSSION

The thermal and thermodynamic data for the mesomorphic transitions of the compounds I(a) and I(b) are listed in Tables I and II.

All liquid crystal phases were characterised simply by the textures observed by optical microscopy.

Series I(a). 4,4′-Dialkoxy-2,2′-dihydroxybenzalazines. As can be seen in Figure 1, the symmetrically substituted compounds of series I(a) show only nematic and smectic C mesophases.

As happens in many other series of homologous mesomorphic compounds,[3] the greater the length of the alkoxy chain, the lower the melting points become, at least initially. The minimum was obtained

TABLE I

Transition temperatures and enthalpies for 4,4′-dialkoxy-2,2′-dihydroxybenzalazines

n	Transition	Temperature °C	ΔH kcal/mol
1	C–I	222.5	10.58
	I–N	202.6	0.15
2	C–N	190.3	10.01
	N–I	217.1	0.32
3	C–N	174.0	12.02
	N–I	185.9	0.14
4	C–N	155.1	9.23
	N–I	192.1	0.31
	I–N	187.9	
	N–S_C[a]	134.7	0.31
5	C–S_C	149.7	9.72
	S_C–N	153.5	0.6
	N–I	180.1	0.37
6	C–S_C	130.8	9.2
	S_C–N	163.9	0.69
	N–I	179.4	0.34
7	C–S_C	123.2	9.34
	S_C–N	165.8	1.15
	N–I	170.9	0.68
8	C–S_C	109.0	8.81
	S_C–N	167.1	1.52
	N–I	168.3	0.56
9	C–S_C	104.9	8.63
	S_C–I	165.6	2.26
10	C–S_C	104.4	9.18
	S_C–I	163.9	2.6
12	C–S_C	109.9	10.09
	S_C–I	157.0	2.55
14	C–S_C	109.1	12.13
	S_C–I	152.6	2.96
16	C–S_C	111.7	15.05
	S_C–I	142.4	3.38
18	C–S_C	107.8	12.77
	S_C–I	135.9	3.32

[a] Monotropic transition.

with the compounds where $n = 9$ and 10; for longer chains a slight increase was found.

The usual odd-even effect in the nematic-isotropic liquid transition can also be seen, and the effect decreases quickly with increasing terminal aliphatic chain length.

For $n = 1$ and $n = 4$, the nematic and smectic C transitions respectively are monotropic. The compounds with short chains ($n = 2$, 3, and 4) show only enantiotropic nematic transitions, while compounds

TABLE II

Transition temperature and enthalpies for 4,4′-dialkoxy-2,2′-dihydroxy-α-methylbenzalazines

n	Transition	Temperature °C	Δ*H* kcal/mol
1	C–N	161.2	8.12
	N–I	186.9	0.12
2	C–N	153.1	7.32
	N–I	221.9	0.22
3	C_1–C_2	137.8	1.51
	C_2–N	151.2	8.73
	N–I	189.8	0.45
4	C_1–C_2	124.2	1.64
	C_2–N	127.8	6.51
	N–I	191.6	0.26
	N–S_C[a]	114.0	
5	C_1–S_C	92.8	2.64
	C_2–S_C	96.7	7.01
	S_C–S_A	144.5	
	S_A–N	145.9	0.15
	N–I	177.4	0.33
6	C_1–S_C	101.3	9.86
	C_2–S_C	82.8	1.09
	C_3–S_C	88.9	0.56
	S_C–S_A	156.0	
	S_A–N	160.3	0.23
	N–I	176.0	0.36
7	C_1–C_3	66.9	3.85
	C_2–S_C	99.3	5.54
	C_3–S_C	81.8	8.20
	S_C–S_A	160.0	
	S_A–N	164.6	1.09
	N–I	168.9	1.20
8	C_1–C_2	70.4	5.10
	C_2–S_C	79.0	6.40
	C_3–S_C	76.1	7.88
	S_C–S_A	160.0	
	S_A–N	166.6	0.71
	N–I	167.2	0.64
9	C_1–C_3	78.6	6.50
	C_2–S_C	81.8	8.45
	C_3–S_C	79.1	6.52
	S_C–I	162.8	1.83
10	C_1–S_C	83.8	10.36
	C_2–S_C	76.0	7.91
	S_C–I	160.0	2.07
12	C_1–C_2	89.8	12.60
	C_2–S_C	90.1	
	S_C–I	153.9	2.47
14	C_1–C_2	61.9	2.06
	C_2–C_3	78.7	3.86
	C_3–S_C	92.8	15.70
	C_4–S_C	90.1	16.25
	S_C–I	148.4	2.48
16	C–S_C	97.1	20.11
	S_C–I	143.0	2.90
18	C_1–C_2	86.7	2.61
	C_2–S_C	101.9	23.01
	S_C–I	137.9	2.61

[a]Monotropic transition observed by optical microscopy.

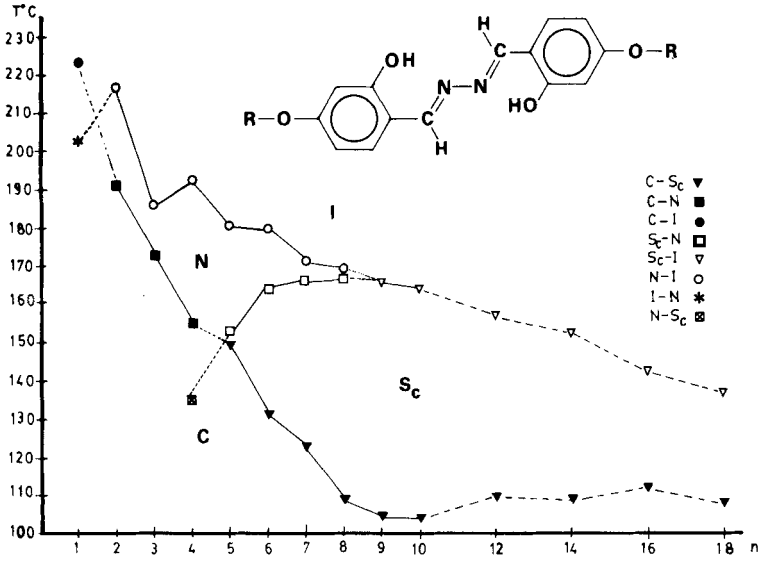


FIGURE 1 Transition temperatures as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxybenzalazines.

with longer chains ($n \geq 9$) show enantiotropic smectic C transitions. For the compounds with intermediate chains, both types of mesophase appear.

Series I(b). 4,4′-Dialkoxy-2,2′-dihydroxy-α-methylbenzalazines. With the appearance of crystalline and smectic polymorphism, it can be seen that the behaviour of the compounds of this asymmetric series I(b) becomes more complex than that of the previous series (Figure 2).

The complexity of the melting cycles—very similar to that observed for other unsymmetrically substituted derivatives described previously (4-alkoxy(n)-4′-alkoxy(m)-2-hydroxy-α,α′-dimethylbenzalazines[12])—stands out.

Two different melting point curves can be distinguished: The curve that appears at the highest temperatures corresponds to the first melting cycle of the products obtained by recrystallization, and the one that appears at the lowest temperatures corresponds to the melting points of the second and later cycles.

Some examples of observed melting cycles are the following:

—For the compounds with n = 3, 4, 12 and 18

$$C_1 \rightarrow C_2 \rightleftharpoons \text{Mesophase} \rightleftharpoons$$

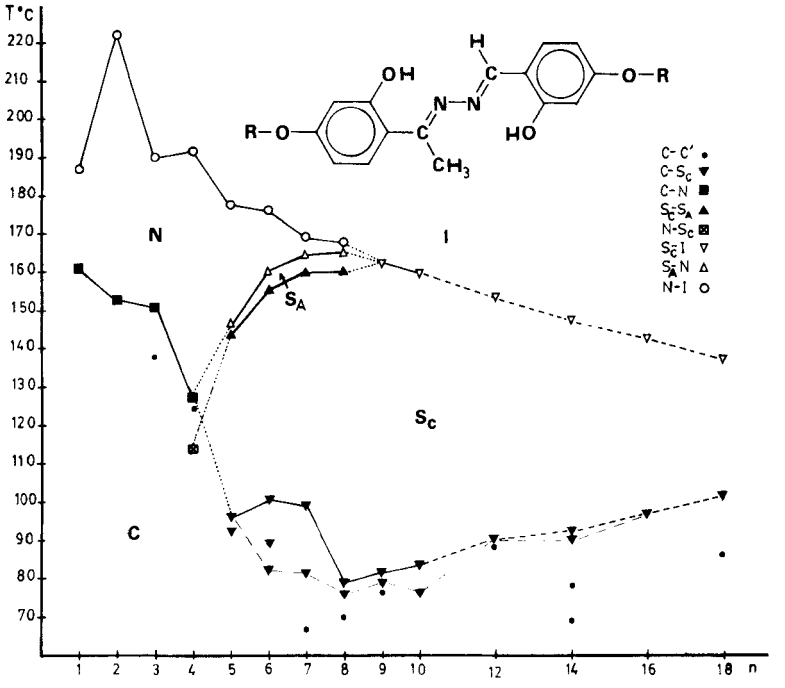


FIGURE 2 Transition temperatures as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxy-α-methylbenzalazines. Continuous line (—): melting points on the first melting cycle. Dashed line (- -): melting points on the second and successive heating cycles.

—For the compound with $n = 5$

$$C_1 + C_2 \rightarrow C_2 + S_C \rightarrow S_C \rightleftharpoons$$
$$\Downarrow\Uparrow$$
$$C_2$$

—For the compound with $n = 6$

$$\begin{array}{ccccc} & & C_2 & & \\ & \swarrow & \Downarrow\Uparrow & & \\ C_1 & \rightleftharpoons & S_C & \rightleftharpoons & \\ & \nwarrow & \Downarrow\Uparrow & & \\ & & C_3 & & \end{array}$$

The curve of the melting points is similar to that described for series I(a), although from $n = 10$ onwards a more pronounced increase is observed.

With the exception of the compound where $n = 4$, for which a monotropic nematic–smectic C transition appears, a direct smectic

C–nematic step is not observed on heating. Instead, an intermediate smectic A mesophase appears for a short interval of temperature.

The nematic–isotropic liquid transitions also show the odd-even effect.

Comparative Study of the Three Series I(a), I(b) and I(c).

Thermal Properties. As can be seen in Figure 3, the symmetrically substituted derivatives of the benzalazines I(a) actually melt at lower temperatures than the homologous α,α'-dimethylbenzalazines I(c).

Notwithstanding, the unsymmetrically substituted series of α-methylbenzalazine derivatives I(b) shows the lowest melting points. This behaviour is similar to that observed previously[4] for derivatives with the unsymmetrically substituted central core 2-hydroxy-α,α'-dimethylbenzalazine. These compounds melt at lower temperatures than the homologues the symmetrically substituted central cores 2,2'-dihydroxy-α,α'-dimethylbenzalazine and α,α'-dimethylbenzalazine.

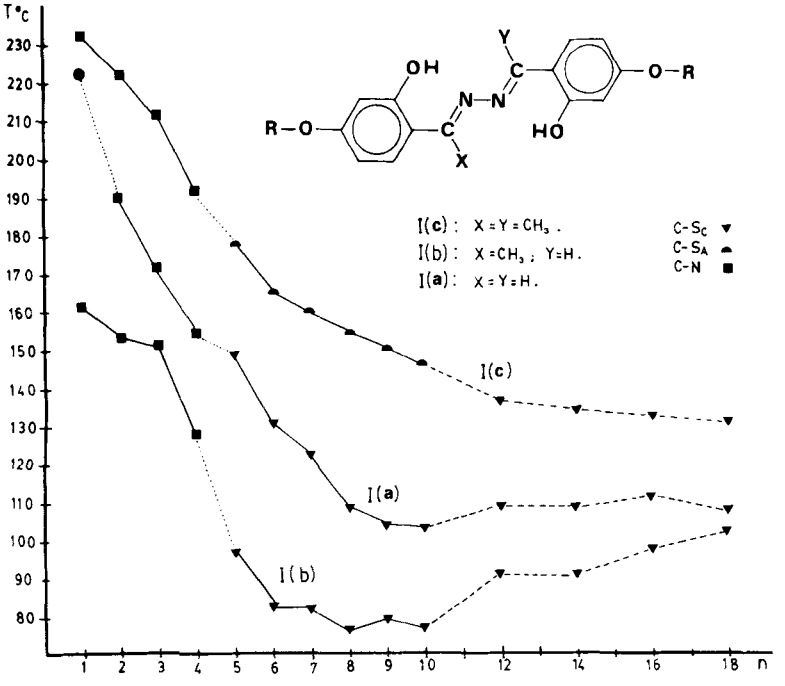


FIGURE 3 Crystal-mesophase transition as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

In the three series described in this paper, crystal-smectic transitions first appear at $n = 5$; whereas the crystal-smectic A transition appears for the α,α-dimethylbenzalazine derivatives, in the other series, the transition observed is crystal-smectic C.

The high melting point of 2,2′-dihydroxy-4,4′-dimethoxybenzalazine is noticeable as it is the only compound from the three series that shows monotropic nematic properties.

In the study of the mesophase-isotropic liquid transitions, the great similarity between the homologous compounds of series I(a) and I(b) is of interest (Figure 4).

When $n = 4$, both compounds show monotropic smectic C phases, and the mesophase-isotropic liquid transition temperatures are very similar. The fact that, in the middle members of series I(a) ($n = 5$–8) the smectic C mesophase turns directly to nematic, whereas a smectic A mesophase appears for a short interval of temperature (1.4–6.6 °C) for the homologous compounds of series I(b) is interesting. However, the derivatives of series I(c) show higher clearing points in all cases than the analogous members of the other two series. In this series, the compounds with intermediate chains ($n = 7$–10, 12, 14) show smectic A–nematic transition.

Generally, speaking the unsymmetrically substituted compounds show much broader mesophase temperature ranges than the symmetri-

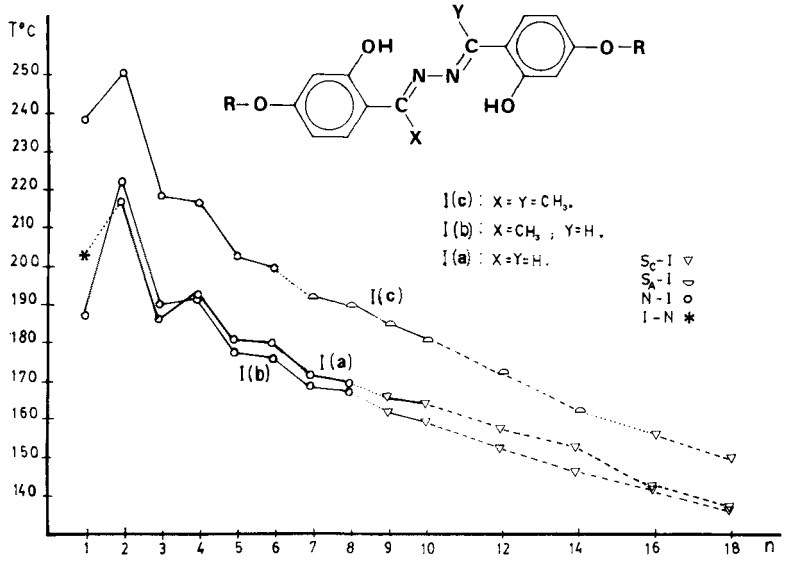


FIGURE 4 Mesophase–Isotropic liquid transition as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

cally substituted derivatives; the α,α'-dimethylbenzalazine derivatives show the smallest mesophase ranges.

Thermodynamic Properties.

As for the thermal properties, the plot of the melting enthalpies for series I(a) (Figure 5) and I(b) (Figure 6) show many similarities.

Series I(c) (Figure 7), with smectic A–isotropic liquid transitions occurring for the compounds with intermediate chain lengths, shows bigger differences, although in the three cases, the differences between the nematic-isotropic liquid and smectic-isotropic liquid transition values are noticeable.

The differences in the melting enthalpies of the compounds are highly significant. For the crystal–nematic transition, a close similarity

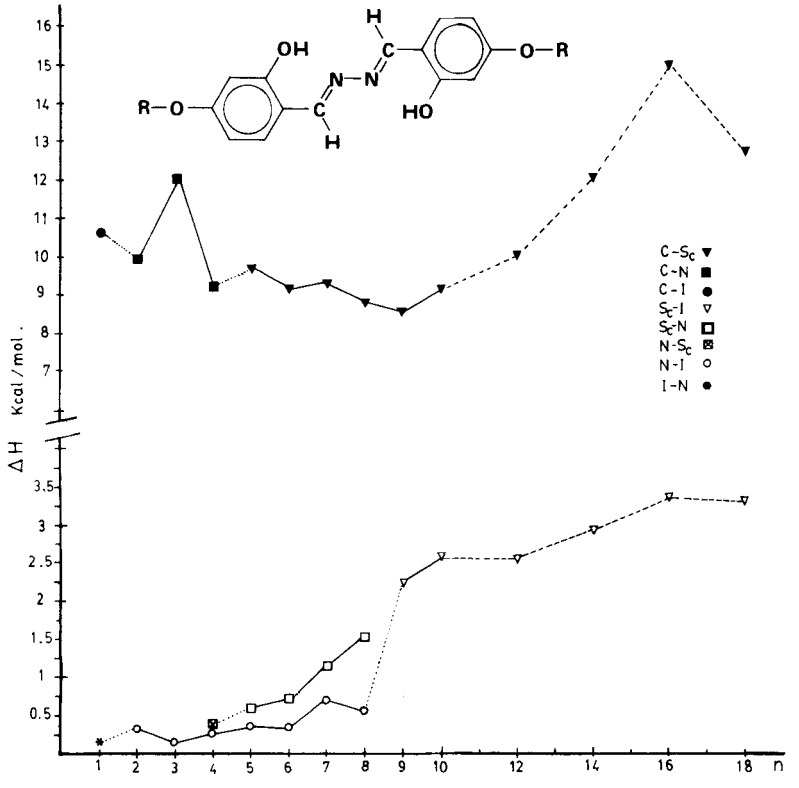


FIGURE 5 Transition enthalpies as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxybenzalazines.

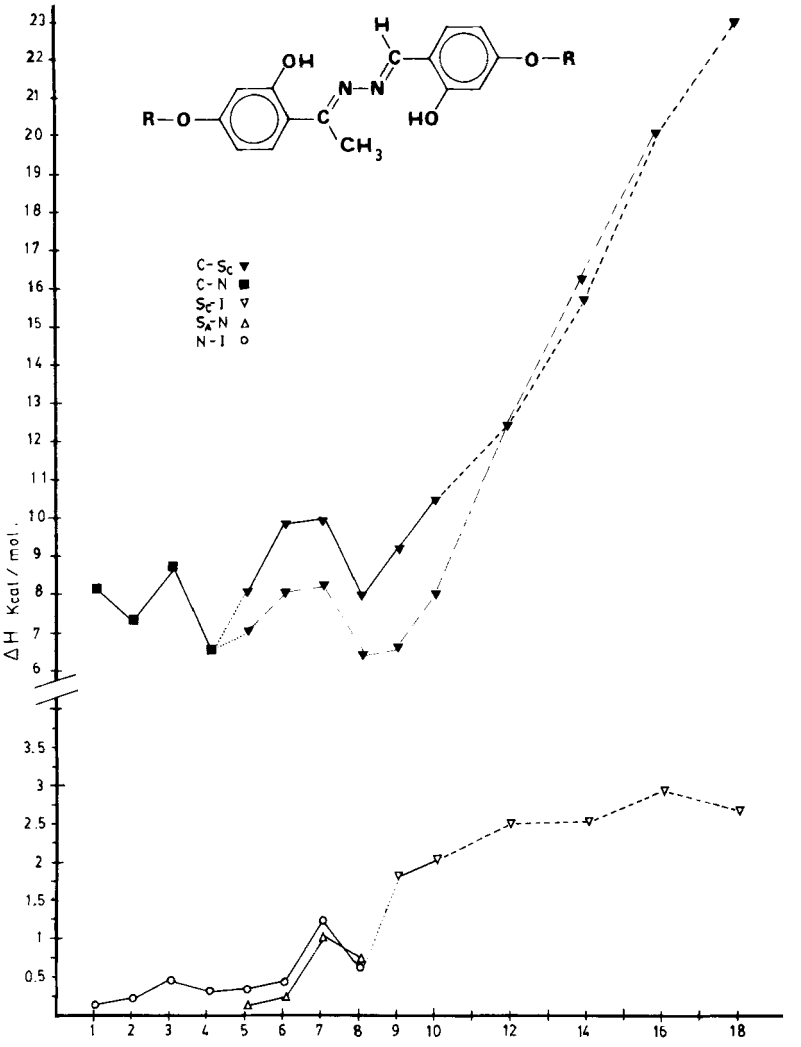


FIGURE 6 Transition enthalpies as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxy-α-methylbenzalazines. Continuous line (—): ΔH measured on the first melting cycle. Dashed line (- -): ΔH measured for second and successive heating cycles.

is observed between the homologous compounds of series I(a) and I(b), where the compounds with $n = 3$ show the highest values. The opposite happens in series I(c), where this compound shows the smallest melting enthalpy.

However, for the crystal–smectic transitions, the symmetrically substituted series I(a) and I(c) behave in a very similar way. For these

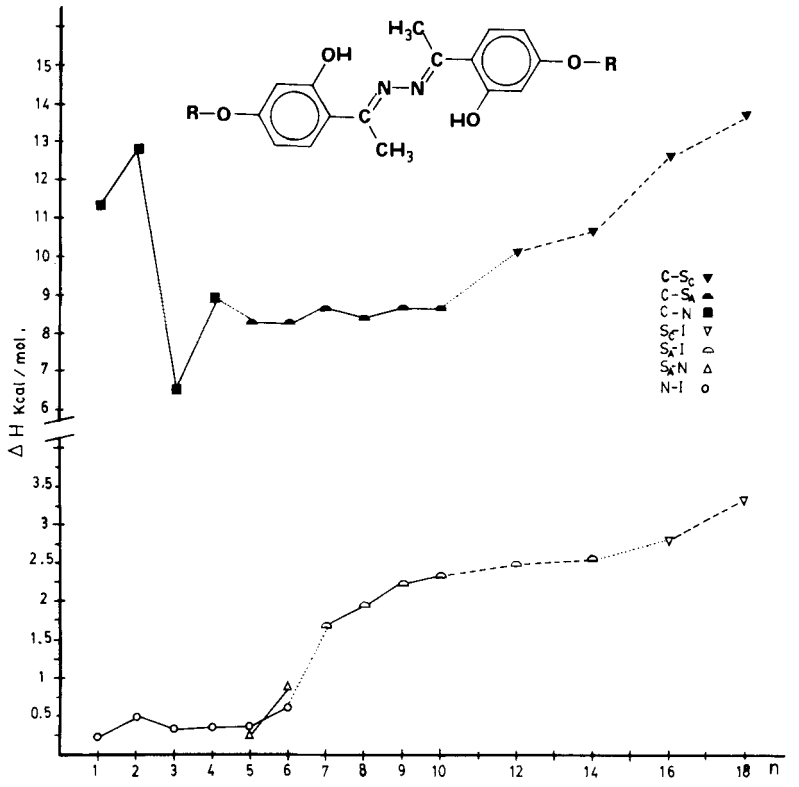


FIGURE 7 Transition enthalpies as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines.

series, the melting enthalpies of the compounds with $n = 5$–10 vary very little. From $n = 10$ onwards there are slight increases in the differences.

However, for the unsymmetrically substituted series a very irregular variation is seen. Two different melting enthalpies (Figure 6) are observed. The continuous line corresponds to the melting enthalpies measured during a first melting cycle, while the dashed curve corresponds to values measured in succeeding melting cycles. In all cases, except when $n = 14$, the melting enthalpies of the first cycle are higher than the others. In these compounds, the melting enthalpies also increase progressively with increasing chain length ($n > 10$), although the effect is now very much greater.

CONCLUSIONS

The melting points of the derivatives involving the α,α-dimethylbenzalazine bridge are higher than those of the homologous derivatives with the benzalazine bridge and, as both are nearly planar, it can be concluded that the methyl groups cause a significant increase in the molecular interactions in the crystal. In the same way, the methyl group confers a greater thermal stability upon the mesophases which have much higher clearing points.

The lack of central symmetry introduced by the α-methylbenzalazine bridge apparently gives rise to smaller interactions in the solid state, giving compounds with low melting points.

However, the greater freedom of the molecules in the mesophases must allow them to reduce the influence of steric hindrance of the methyl group to a minimum, as the mesomorphic properties are very similar to those of the homologous members of the symmetrically substituted series with a benzalazine bridge. The unsymmetrical nature of the central group also causes the appearance of crystalline polymorphism.

The derivatives with the α-methylbenzalazine bridge are the most interesting from a practical standpoint, since they give the lowest melting points and much the greater mesophase temperature ranges.

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