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M. Marcos [a] , E. Melendez [a] & J. L. Serrano [a]
[a] Departamento de Química Orgánica, Universidad de Zaragoza, Spain

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Synthesis and Mesomorphic Properties of Three Homologous Series of 4,4′-Dialkoxy-α,α′-Dimethylbenzalazines

A Comparative Study (I)

M. MARCOS, E. MELENDEZ and J. L. SERRANO
Departamento de Química Orgánica, Universidad de Zaragoza, Spain

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Three homologous series of α,α′-dimethylbenzalazines have been synthesized: 4,4′-dialkoxy-α,α′-dimethylbenzalazines, 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines, and 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines. The influence of molecular structure on the mesomorphic properties was studied.

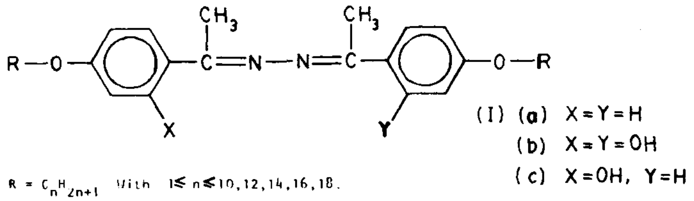
Mesomorphic properties and phase transitions were determined using a polarizing hot-stage microscope and a differential scanning calorimeter. The introduction of one or two hydroxyl groups in position 2- or 2-and 2′- of the aromatic rings (4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines and 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines respectively) gives molecules with an excellent mesogenic quality, and all the prepared compounds of these series exhibit mesomorphism. Compounds of the series with two hydroxyl groups exhibit smectic polymorphism which is not so in the case of the compounds of the other series. The melting temperatures are systematically lower for the 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines than for the other two series.

INTRODUCTION

During the last years, a large number of studies have been made in order to establish relations between molecular structure and mesomorphic properties.[1,2,3] Certain types of compound have been studied in depth, but the aromatic diazines[4,5,6] have received only slight attention.

In our laboratory, three series of substituted aromatic diazines—the

4,4′-dialkoxy-α,α′-dimethylbenzalazines I(a), 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines I(b), and 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines I(c)—were prepared and their mesomorphism studied.



SKETCH 1

In this study our intention is to describe the mesomorphic properties observed in relation to the molecular structures of these diazines, paying special attention to the geometry of the molecular central core. By the introduction of one or two hydroxyl groups in position 2- or 2- and 2′- of the aromatic rings [series I(b) and I(c)], the geometry of the central azine group of series I(a) was modified.

The compounds of series I(a) show monotropic nematic behavior in the compounds where $n = 1,2,3$. The data obtained by us for the compounds of series I(a) when $n = 1$ and 2 differ from those previously reported.[4]

All the prepared compounds of series I(b) and I(c) show mesomorphic behavior. Unlike the compounds of series I(c), the compounds of series I(b) exhibit smectic polymorphism. The type of the mesophase formed depends on the length of the terminal chain.

SYNTHESIS

Preparation of 4,4′-dialkoxy-α,α′-dimethylbenzalazines I(a) and 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines I(b)

The compounds of series I(a) and I(b) were prepared in the same way from 4-hydroxyacetophenone and 2,4-dihydroxyacetophenone respectively. In both cases the synthesis was made in two stages.

(i) The ketone is condensed with hydrazine hydrate to obtain the azines.

(ii) Alkylation of the OH groups in positions 4- and 4′- using the Williamson method.

Experimental conditions, yields and physical constants are given in the experimental part.

Preparation of 4,4'-dialkoxy-2-hydroxy-α,α'-dimethylbenzalazines I(c)

The synthesis of the compounds of series I(c) was effected in three stages. For details of this see the experimental part.

(i) The first step is the preparation of two products: 4-alkoxy-2-hydroxyacetophenone and the hydrazone of 4-hydroxyacetophenone.

(1) Alkylation of the 4- hydroxyl group of 2,4-dihydroxyacetophenone by the Williamson method.

Working with a reduced amount of alkyl halide (ketone/alkyl halide 1/0.9), only the OH group in position 4 is alkylated. The intramolecular H-bond between the oxygen of the carbonyl group and the OH group in position 2 prevents the reaction of the hydroxyl proton under the conditions used.

(2) Formation of the hydrazone of 4-hydroxyacetophenone was effected by the condensation of the ketone with hydrazine hydrate in excess (1 : 4), following the Szmant and McGinnis method.[10] Under these conditions a mixture of hydrazone and azine always appears because the azine is more stable than the hydrazone. After several experiments it was verified that the largest relative proportion of hydrazone was obtained at the end of 24 hours. A white product, in fact a mixture of hydrazone-azine (70%–30% by TLC), is obtained by evaporation of the solvent and the remaining hydrazine hydrate, and crystallization from ethanol. This mixture is then used in step (ii).

It is noted that step (i) could have been carried out in the opposite way: preparation of the 4-alkoxyacetophenone and preparation of the hydrazone of the 2,4-dihydroxyacetophenone.

In this optional method, the alkylation of the 4-hydroxyacetophenone is unambiguous. The method was however ruled out because the 2,4-dihydroxyacetophenone hydrazone, very unstable in solution, tends to bring about the formation of the azine, which is isolated as the major product in the second step. Even though solid hydrazone can be isolated, it decomposes easily.

(ii) The second step is the synthesis of the 4-alkoxy-2,4'-dihydroxy-α,α'-dimethylbenzalazines.

These products are obtained by the condensation of the 4-alkoxy-2-hydroxyacetophenone and the hydrazone of 4-hydroxyacetophenone synthesized in the first step.

The reaction takes place in ethanol under reflux and the hydrazone is added in the form of a mixture of the hydrazone and azine obtained in step i2). The proportion of hydrazone (calculated from the mixture) to ketone is 1 to 1.25. The reaction involves several equilibria (see Scheme 1), and the best results are obtained with long times of reaction. At the end of 100 hours we obtain three major products in similar proportions: 4,4′-dihydroxy-α,α′-dimethylbenzalazine (1), 4-alkoxy-2,4′-dihydroxy-α,α′-dimethylbenzalazine (2) and 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine (3).

4-Alkoxy-2-hydroxyacetophenone (4) is also formed in smaller proportion together with other products (5) (6) and (7) in insignificant amounts.

The different capacity of absorption of the compounds facilitates the separation of the 4-alkoxy-2,4′-dihydroxy-α,α′-dimethylbenzalazine by column chromatography on silica, using benzene as an eluant.

An alternative method involves the condensation of a mixture of 4-alkoxy-2-hydroxyacetophenone and 4-hydroxyacetophenone with hydrazine hydrate. However, this method had to be discarded because the greater stability of the symmetrical azine of the 4-alkoxy-2-hydroxyacetophenone (3, in Scheme 1) makes it the predominant product; the compound required is obtained in a very small proportion.

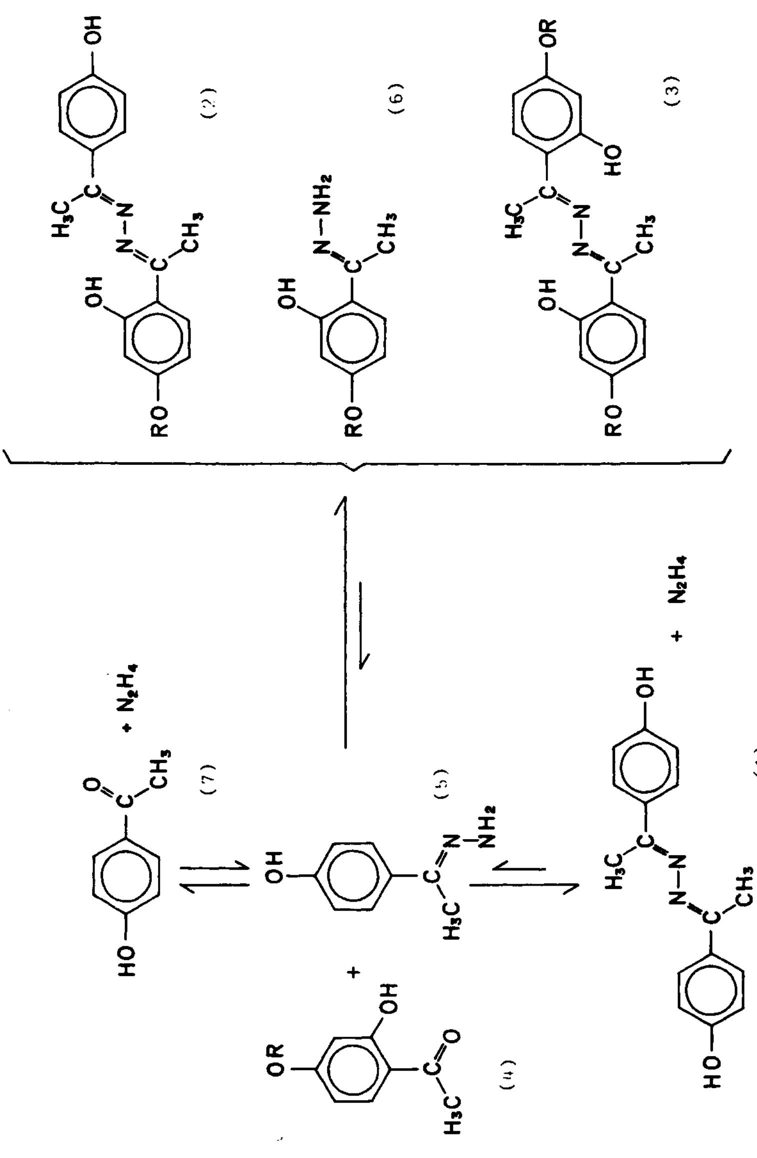
(iii) The third step is the synthesis of the 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines using the Williamson method for alkylation of phenols as for step (i), 1.

EXPERIMENTAL

1. 4,4′-Dialkoxy-α,α′-dimethylbenzalazines

(*a*) *4,4′-Dihydroxy-α,α′-dimethylbenzalazine was prepared following the Szmant and McGinnis method.*[8] 4.08 g. (30 mmole) of 4-hydroxyacetophenone were added to a solution of 0.5 g. (10 mmole) of hydrazine hydrate and 50 ml. of ethanol (96%). The mixture was heated under reflux for 100 hours. The solid was filtered and washed with hot water. The required product was a yellow solid and was purified by crystallization from a water-ethanol mixture (88% yield); m.p. 223°C, (lit[6] m.p. 224°C); i.r. (nujol) cm^{-1}: 3400, 1190 (OH), 1600 (C═N), 1585, 850 (Ar); n.m.r. (CD_3-CO-CD_3) ppm: δ 8.57 (s,1,OH), δ 7.80 (d,2,Ar), δ 6.40 (d,2,Ar), δ 2.35 (s,3,CH_3); u.v. (ethanol) nm: 303 (lg $\epsilon = 4.3$), 217^{sh}; Anal: Calc. for $C_{16}H_{16}O_2N_2$: C 71.6, H 5.8, N 10.4. Found: C 71.7, H 6.2, N 10.4%.

(*b*) *4,4′-Dialkoxy-α,α′-dimethylbenzalazines were prepared from 4,4′-dihydroxy-α,α′-dimethylbenzalazine by the Williamson's reaction as reported by Ching and Galvez.*[9] A mixture of 1.34 g. (5 mmole) of 4,4′-



SCHEME 1

dihydroxy-α,α'-dimethylbenzalazine, 1.45 g. (10.5 mmole) of K_2CO_3, 12 mmole of the appropriate alkyl bromide† and 75 ml. of acetone was heated under reflux for 48 hours. The solvent was removed *in vacuo* and the residue dissolved in benzene. The solution was washed with 5% aqueous sodium hydroxide. The benzene was evaporated and the product crystallized ($n = 1,2,3,4$ from $CHCl_3$, $n = 5,6,7,8,9,10$ from benzene and $n = 12,14,16,18$ from CCl_4). Yields were between 90 and 95%.

2. 4,4'-Dialkoxy-2,2'-dihydroxy-α,α'-dimethylbenzalazines were prepared from 2,4-dihydroxyacetophenone using the same method as for the preceding compounds

(*a*) *2,2',4,4'-Tetrahydroxy-α,α'-dimethylbenzalazine.* A solution of 3.04 g. (20 mmole) of 2,4-dihydroxyacetophenone and 0.5 g. (10 mmole) of hydrazine hydrate in 50 ml. of ethanol (96%) was heated under reflux for 24 hours.

The reaction mixture was cooled. The required product was obtained by filtration, washed with hot ethanol and crystallized from ethanol (80% yield); m.p. 227–230°C (with decomposition); i.r. (KBr) cm^{-1}: 3430, 3280, 1140 (OH), 1600 (C=N), 1600, 845 (Ar); n.m.r. (DMSO) ppm: δ 13.65 (s,1,OH), δ 7.63 (d,1,Ar), δ 6.42 (d,2,Ar), δ 2.47 (s,3,CH_3); u.v. (ethanol) nm: 370 (lg $\epsilon = 4.5$), 303.2^{sh}, 248^{sh}, 222 (lg $\epsilon = 4.5$); Anal: Calc. for $C_{16}H_{16}O_4N_2$: C 64.0, H 5.3, N 9.3. Found: C 63.9, H 5.8, N 8.9%.

(*b*) *4,4'-Dialkoxy-2,2'-dihydroxy-α,α'-dimethylbenzalazines.* A mixture of 5 mmole of 2,2',4,4'-tetrahydroxy-α,α'-dimethylbenzalazine, 10 mmole of K_2CO_3, 12 mmole of the appropriate alkyl bromide† and 50 ml. of acetone was heated under reflux for 48 hours. The solvent was removed *in vacuo*. The residue was dissolved in benzene and the solution washed with 5% aqueous sodium hydroxide. The benzene was evaporated and the product purified by crystallization ($n = 1,2,3$ from ethyl acetate, $n = 4,5,6,7,8$ from benzene and $n = 9,10,12,14,16,18$ from CCl_4). Yields were between 70 and 85%.

3. 4,4'-Dialkoxy-2-hydroxy-α,α'-dimethylbenzalazines

(*a*) *4-Alkoxy-2-hydroxyacetophenones were prepared using the Williamson method.*[9] A mixture of 1.52 g. (10 mmole) of 2,4-dihydroxyacetophenone, 1.40 g. (10 mmole) of K_2CO_3, 9 mmole of the appropriate alkyl bromide† and 50 ml. of acetone was heated under reflux for

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† For $n = 1$, methyl iodide was used.

24 hours. The solvent was removed *in vacuo* and the residue dissolved in benzene. The solution was washed with 2% aqueous sodium hydroxide, dried ($MgSO_4$) and the benzene evaporated. The white product obtained (shown to be pure by TLC) in yields between 50 and 80% was utilized in the following step.

(*b*) *Hydrazone of 4-hydroxyacetophenone. This compound was prepared using the Szmant and McGinnis method.*[8] 20 g. of freshly heated calcium oxide, 13.6 g. (100 mmole) of 4-hydroxyacetophenone and 20 g. (400 mmole) of hydrazine hydrate were placed in the extraction thimble of a Soxhlet extractor containing 300 ml. of ethanol (96%) and heated under reflux for 24 hours. The hot solution was filtered and a white product was isolated when the solution was concentrated. This was recrystallized from ethanol and shown by TLC to be a mixture of the hydrazone (7 parts) and the azine (3 parts).

To characterize the hydrazone of 4-hydroxyacetophenone, we obtained the pure hydrazone after several recrystallizations from ethanol of the hydrazone-azine mixture. The yield was 21%, m.p. 154°C, (lit[10] m.p. 155°C); i.r. (nujol) cm^{-1}: 3315, 3280 (NH_2), 3195, 1230 (OH), 1610 (C=N), 1580, 880 (Ar); n.m.r. (CD_3OD) ppm: δ 7.58 (d,2,Ar), δ 6.88 (d,2,Ar), δ 2.15 (s,3,CH_3), δ 4.7 (s,CD_3OD); u.v. (acetonitrile) nm: 270 (lg $\epsilon = 4.24$), 202.7; Anal: Calc. for $C_8H_{10}N_2O$: C 64.0, H 6.7, N 18.7. Found: C 64.1, H 6.8, N 18.1%.

(*c*) *4-Alkoxy-2,4'-dihydroxy-α,α'-dimethylbenzalazines.* A solution of 5 mmole of hydrazone of 4-hydroxyacetophenone (calculated from the hydrazone-azine mixture) and 6.25 mmole of 4-alkoxy-2-hydroxyacetophenone in 50 ml. of ethanol (96%) was heated under reflux for 100 hours. The ethanol was removed and the mixture that remained was separated by column chromatography on silica using benzene as an eluant. The pure product was obtained by evaporation of the middle fraction in yields between 25 and 30%.

(*d*) *4,4'-Dialkoxy-2-hydroxy-α,α'-dimethylbenzalazines.* A mixture of 5 mmole of 4-alkoxy-2,4'-dihydroxy-α,α'-dimethylbenzalazine, 5 mmole of the appropriate alkyl bromide,† 5 mmole of K_2CO_3 and 50 ml. of acetone was heated under reflux for 24 hours. The solvent was removed *in vacuo* and the residue dissolved in benzene. The solution was washed with 5% aqueous sodium hydroxide, dried ($MgSO_4$), the benzene was

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† For $n = 1$, methyl iodide was used.

evaporated and the product purified by crystallization ($n = 1$ from acetone, $n = 2,3,4$ from ethanol, $n = 5,6,7$ from an ethanol-acetone mixture and $n > 8$ from an ethanol-ethyl acetate mixture). Yields were between 85 and 90%.

TECHNIQUES

The melting points, transition temperatures and enthalpies were determined 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) and mass spectrometry (HEWLETT PACKARD 5943A).

The purity of all products was checked by the above mentioned techniques, by elemental analysis (C, H, N) and by thin-layer chromatography.

RESULTS AND DISCUSSION

The transition temperatures and the mesomorphic phases of the different compounds of series I(a) and I(b) are listed in Tables I and II.

The degree of mesomorphism shown is very different for the two series. In series I(a), only the compounds with $n = 1,2,3$ showed monotropic nematic phases (Table I, Figure 1). In series I(b), however, all the compounds were mesomorphic and the type of mesophase depended on the length of the terminal chain (Table II, Figure 2). A nematic phase was found for the terminal chains $n = 1,2,3,4$. When the terminal chains had $n = 5$ and 6, a smectic A phase and a nematic phase appeared, and when $n = 7,8,9,10$, the compounds presented only smectic A phases. For longer chains ($n = 12, 14$), two smectic phases, C and A, appeared. Finally, for the longest chains ($n = 16, 18$), only smectic C phases were formed.

This type of evolution of the mesomorphism with lengthening of terminal chains has been frequently observed for numerous series and in particular with such symmetric compounds as the 4,4′-dialkoxy derivatives of trans-1,4-diphenylcyclohexane[11] and diphenyldiacetylene.[12]

TABLE I

Transition temperatures, enthalpies and derived entropies for the compounds with structure (I)(a)

n	Transition	Temperature °C	Δ H kcal/mol	Δ S cal/mol °K
1	C → I	199.3	12.55	26.57
	I → N[a]	158.8	0.42	0.97
2	C → I	182.8	13.31	29.19
	I → N[a]	180.3	0.55	1.22
3	C → I	172.1	11.82	26.54
	I → N[a]	142.8	0.30	0.73
4	C → I	170.9	13.18	29.67
5	C → I	157.8	12.38	28.73
6	C → I	150.8	12.90	30.48
7	C → I	145.3	13.92	33.27
8	C → I	142.8	14.79	35.57
9	C → I	140.4	16.49	39.88
10	C → I	137.3	17.26	42.05
12	C → I	136.4	20.99	51.24
14	C → I	135.0	23.84	58.40
16	C → I	132.8	25.86	63.70
18	C → I	132.4	29.66	73.13

[a] Monotropic transition.

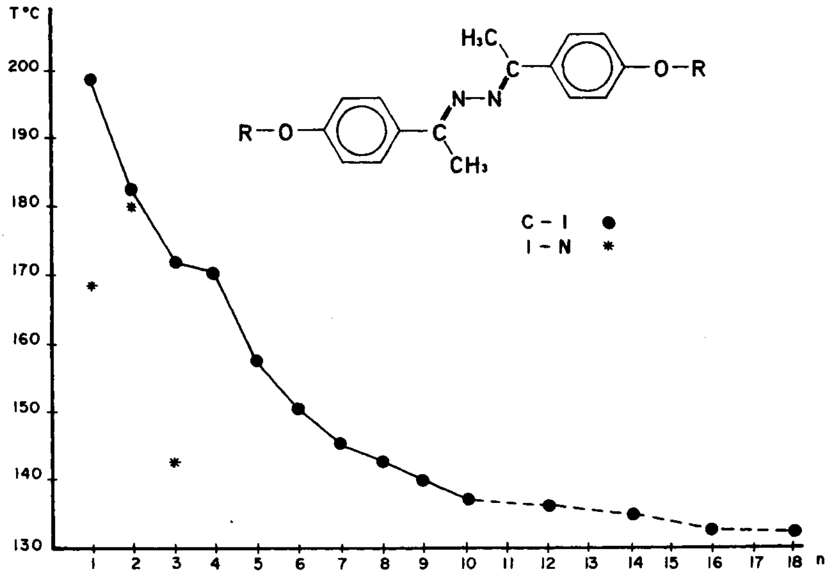

FIGURE 1 Transition temperatures as a function of alkyl chain length for 4,4'-dialkoxy-α,α'-dimethylbenzalazines.

TABLE II

Transition temperatures, enthalpies and derived entropies for the compounds with structure (I)(b)

n	Transition	Temperature °C	Δ H kcal/mol	Δ S cal/mol °K
1	C → N	232.2	11.32	22.39
	N → I	237.9	0.23	0.44
2	C → N	222.3	12.84	25.91
	N → I	249.9	0.48	0.93
3	C → N	210.7	6.51	13.45
	N → I	217.8	0.31	0.63
4	C → N	191.8	8.84	19.01
	N → I	216.3	0.36	0.74
5	C → S_A	177.8	8.30	18.40
	S_A → N	190.1	0.27	0.58
	N → I	202.7	0.33	0.69
6	C → S_A	165.2	8.30	18.93
	S_A → N	195.7	0.89	1.90
	N → I	199.5	0.58	1.23
7	C → S_A	160.3	8.69	20.04
	S_A → I	191.9	1.70	3.65
8	C → S_A	153.8	8.43	19.74
	S_A → I	189.8	1.96	4.24
9	C → S_A	149.8	8.71	20.58
	S_A → I	184.8	2.22	4.85
10	C → S_A	146.0	8.68	20.72
	S_A → I	181.3	2.34	5.15
12	C → S_C	136.8	10.18	24.85
	S_C → S_A	165.0	—	—
	S_A → I	172.3	2.50	5.62
14	C → S_C	133.8	10.66	26.75
	S_C → S_A	159.5	—	—
	S_A → I	161.8	2.60	5.99
16	C → S_C	132.0	12.67	31.26
	S_C → I	155.8	2.80	6.52
18	C → S_C	130.5	13.79	34.17
	S_C → I	148.9	3.13	7.41

Examination of the molecular structures of the compounds of series I(a) and I(b), at least qualitatively, permits us to offer an explanation for these differences in the mesomorphic properties. In the paper which follows this, evidence is presented indicating that intramolecular H-bonding between the 2- and 2′- hydroxyl groups and the azine nitrogen atoms gives the molecules a rigid central core with the result that the aromatic rings adopt an almost coplanar orientation and the polarizability of the molecules is increased. The desired and observed consequences are a reinforcement of the mesomorphic properties and an ele-

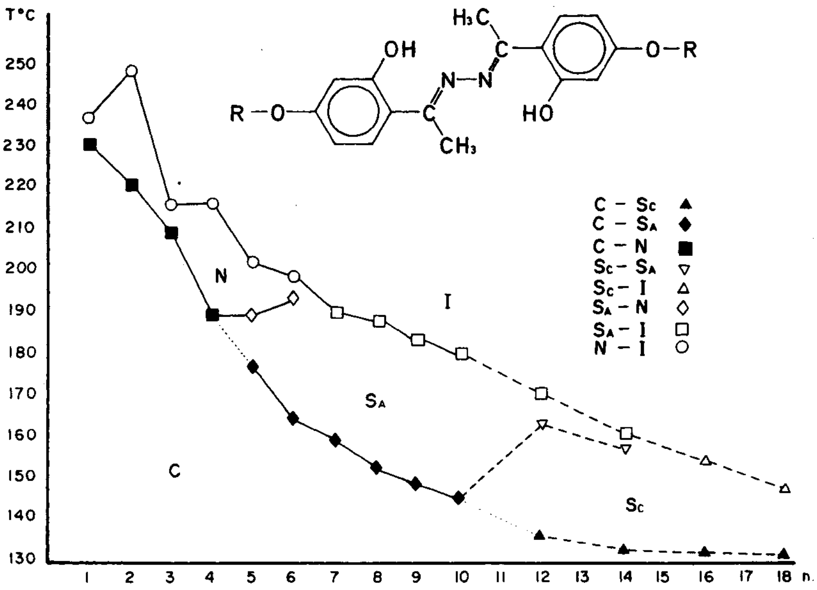

FIGURE 2 Transition temperatures as a function of alkyl chain length for 4,4'-dialkoxy-2,2'-dihydroxy-α,α'-dimethylbenzalazines.

vation of the melting temperatures for the compounds of series I(b) compared with those of the compounds of series I(a).

The transition temperatures and the mesomorphic phases of all the compounds of series I(c) are listed in Table III.

All the prepared compounds show liquid crystalline behavior. The mesophases observed evolve in a systematic way according to the aliphatic chain length.

Compounds with C_1–C_6 show a nematic mesophase; compounds with $C_n \geq 9$ show a smectic A mesophase and with C_7–C_8 both smectic A and nematic mesophases.

This behavior is similar to that found for the compounds of series I(b). However, there are two differences. The melting points are systematically lower for the compounds of series I(c) (Figure 3) than those of series I(b), and whereas there is no smectic polymorphism in series I(c), there is in series I(b).

As regards mesomorphism, the compounds of series I(c) occupy an intermediate position between the non-mesomorphic compounds of series I(a) and the compounds of series I(b) which exhibit smectic polymorphism.

TABLE III

Transition temperatures, enthalpies and derived entropies for the compounds with structure (I)(c)

n	Transition	Temperature °C	Δ H kcal/mol	Δ S cal/mol °K
1	C → I	183.3	10.19	22.32
	I → N[a]	166.8	0.27	0.62
2	C → N	177.3	10.33	22.94
	N → I	196.4	0.47	1.00
3	C → N	150.8	8.67	20.69
	N → I	166.3	0.43	0.98
4	C → N	133.8	7.43	18.24
	N → I	166.4	0.35	1.02
5	C → N	125.3	7.92	19.87
	N → I	153.3	0.43	1.02
6	C → N	114.3	7.37	19.01
	N → I	151.6	0.41	0.98
7	C → C′	106.7	4.72	12.41
	C′ → S_A	112.8	7.36	19.05
	S_A → N	128.7	0.27	0.68
	N → I	143.0	0.51	1.22
8	C → S_A	107.3	11.52	30.28
	S_A → N	137.1	0.68	1.67
	N → I	142.0	0.75	1.81
9	C → S_A	109.8	14.68	38.33
	S_A → I	136.4	1.78	4.35
10	C → S_A	108.8	14.50	37.97
	S_A → I	136.0	2.18	5.32
12	C → S_A	111.8	16.94	44.00
	S_A → I	132.8	2.43	5.99
14	C → S_A	110.9	18.27	47.57
	S_A → I	127.4	2.57	6.41
16	C → S_A	112.7	23.89	61.90
	S_A → I	121.7	2.66	6.75
18	C → S_A	115.8	25.22	64.83
	S_A → I	119.1	2.30	5.87

[a] Monotropic transition.

This result can be attributed to the molecular structure of the compounds. The compounds of series I(c) are structurally intermediate between the compounds of series I(b) and those of series I(a). In effect, the presence of one hydrogen bond between the hydroxyl group in the *ortho*-position and one nitrogen of the azine group in the compounds of series I(c)—as shown in the paper which follows this—gives the molecular central core some rigidity which increases the polarizability of the molecules. This structure tends to favor mesomorphism to a greater degree than the flexible structure of the compounds of series

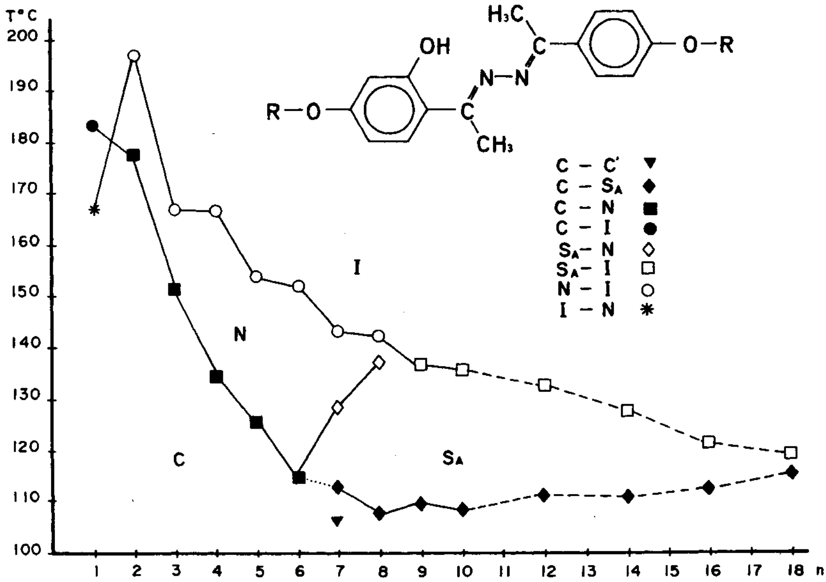

FIGURE 3 Transition temperatures as a function of alkyl chain length for 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines.

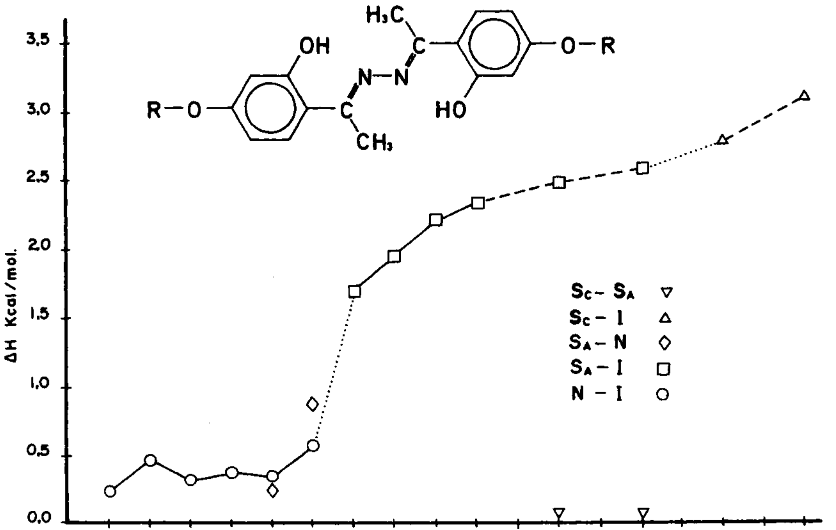

FIGURE 4 Enthalpy change for mesophase transitions as a function of alkyl chain length for 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines.

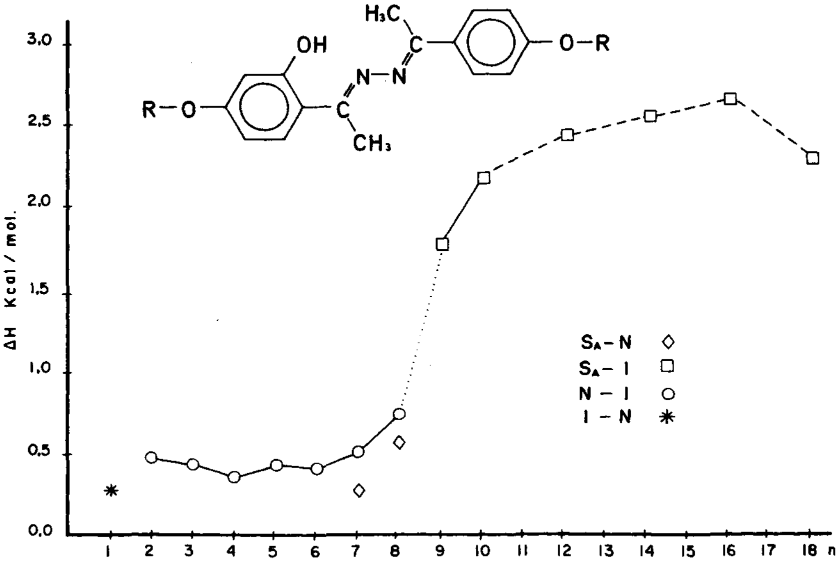

FIGURE 5 Enthalpy change for mesophase transitions as a function of alkyl chain length for 4,4-dialkoxy-2-hydroxy-α,α'-dimethylbenzalazines.

I(a), but is less favorable than the totally rigid structure produced by the two hydrogen bonds found in the compounds of series I(b).

It is further noted that a decrease in the crystal-mesophase transition temperatures (Tables I, II and III) occurs with increasing alkoxy chain length (Figures 1, 2 and 3). We also see the usual odd-even effect in the mesophase-isotropic liquid transitions (Figures 2, 3). As usual this effect is more marked for compounds with short terminal chains and tends to decrease with increasing terminal aliphatic chain length.

The transition enthalpies and entropies are of the same order as those usually found for mesogens (Figures 4, 5).

TEXTURES OBSERVED

The mesophase textures were observed using thin films of the samples mounted between a glass slide and a cover slip, and polarizing microscope.

All the observed mesophase textures were classical. For the nematic mesophase we observed the textures: "schlieren", "marbled", and "homeotropic". For the smectic A phase we observed the textures: "focal-conic", "broken fan", "homeotropic", and the appearance of "smectic bâtonnets" at the isotropic liquid-smectic A transition. The smectic C phase in general showed a "schlieren" texture and in some cases the "broken fan" textures.

CONCLUSIONS

Our study has shown that it is possible to form hydrogen bonds with the nitrogen atom of the central core by the introduction of hydroxyl groups—see the paper which follows this. Aromatic azines forming mesophases and even exhibiting smectic polymorphism have thus been prepared. It has also been shown that by controlling the rigidity of the central core (by the introduction of 1 or 2 hydroxyl groups), the nature of the mesomorphism and the melting points of the compounds can be influenced.

It would be desirable to modify the structures of these compounds so as to obtain transition temperatures nearer room temperature, thus facilitating their practical use. Another solution would be to employ mixtures.

At present we are attempting to obtain better results using both methods.

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