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Joaquin Barbera [a] , Mercedes Marcos [a] , Enrique Melendez [a] & Jose Luis Serrano [a]
[a] Departamento de Quimica Orgánica, Facultad de Ciencias, Universidad de Zaragoza, Spain
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4-Alkoxy-4′-(Alkyl or Alkoxy)-2-Hydroxy-α, α'-Dimethylbenzalazines (III); Some Interesting Mesomorphic Compounds

JOAQUIN BARBERA, MERCEDES MARCOS, ENRIQUE MELENDEZ and JOSE LUIS 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-alkoxy-4′-alkyl-2-hydroxy-α, α'-dimethyl-benzalazines and the 4-alkoxy (n)-4′-alkoxy(m)-2-hydroxy-α, α'-dimethylbenzalazines.

Thermodynamic measurements were made, all the compounds gave lower melting points and larger mesophase ranges than the symmetrically substituted compounds.

The dialkoxy (n-m) substituted compounds exhibit polymorphism in the solid state.

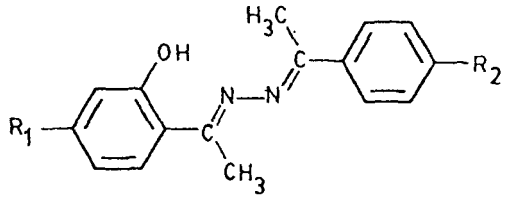
INTRODUCTION

In previous papers[1,2] we have described two series of α, α'-dimethylbenzalazines that have good stability and excellent mesogenic qualities: the 4, 4′-dialkoxy-2-hydroxy-α, α'-dimethylbenzalazines and 4, 4′-dialkoxy-2, 2′-dihydroxy-α, α'-dimethylbenzalazines. However, none of the synthesized compounds melted below 105°C. In order to obtain products of lower melting point and broader mesophase range we have synthesized two new series [1] and [2] of 4, 4′-disubstituted-2-hydroxy-α, α'-dimethylbenzalazines.

In series [1], the 4-substituent (R_1) is an alkoxy group and the 4′-substituent (R_2) is an alkyl group. The n-C_4H_9 group was chosen as one typical terminal alkyl chain to obtain low melting points.[3,4] The n-C_8H_{17} group was also chosen because it was the terminal group that

gave the lower melting points in the previously described series of 4, 4′-dialkoxy derivatives.

In the second series [2], the substituents are alkoxy groups of different lengths



$R_1 = 0.n\text{-}C_nH_{2n+1}$; $R_2 = n\text{-}C_mH_{2m+1}$

$(m = 4{:}n = 1\text{–}10, 12, 14, 16, 18)(m = 8{:}n = 2, 8, 14)$ (1)

$R_1 = 0.n\text{-}C_nH_{2n+1}$; $R_2 = 0.n\text{-}C_mH_{2m+1}$

$(n\text{-}m)$:(1–2, 5, 8),(2–1, 5, 8),(4–2),(5–1, 2, 7),
(8–1, 2),(9–7),(10–8). (2)

RESULTS AND DISCUSSIONS

In series [1] where $R_2 = n\text{-}C_4H_9$, all the compounds have a nematic phase and the melting points are lower than those of the 4, 4′-dialkoxy-2-hydroxy-α, α'-dimethylbenzalazines (see Table I). The minimal melting points for these compounds are obtained when n = 8–10 (Figure 1), i.e., as found for the series of 4, 4′-dialkoxy-2-hydroxy-α, α'-dimethylbenzalazines.

It can be seen that the nematic range (40–60°C) is greater than in the case of the dialkoxy homologues. If the length of the alkoxy chain is increased ($R_1 \geq 0\text{-}C_{14}H_{29}$), an S_A phase appears.

The clearing points show the classical even-odd effect which is also manifested by the N—I transition enthalpies.

For the three compounds of series [1] where $R_2 = n\text{-}C_8H_{17}$, the melting points are also low, but when the alkoxy chain is lengthened, the mesophase changes from nematic to smectic as expected.

It should be pointed out that the influence of the length of the terminal chain on the molecular ordering in the solid states is very small in the latter compounds, and the three compounds with alkoxy chains of very different lengths have closely similar melting points.

All the compounds in series [2] (Table II) melt at around 100°C with the exception of the first two compounds. The mesophase ranges are generally

TABLE I

Transition temperatures and enthalpies for 4-alkoxy-4′-alkyl-2-hydroxy-α, α′-dimethylbenzalazines

n	*m*	Transition	Temperature °C	ΔH kcal/mol	*n*	*m*	Transition	Temperature °C	ΔH kcal/mol
1	4	C—N	78.1	4.64	10	4	C—N	63.9	7.83
		N—I	119.2	0.11			N—I	114.6	0.32
2	4	C—N	93.2	6.22	12	4	C—N	71.6	9.68
		N—I	143.5	0.20			N—I	109.8	0.28
3	4	C—N	96.1	5.18	14	4	C—S_A	76.0	11.15
		N—I	130.4	0.17			S_A—N	80.0*	
4	4	C—C′	81.2	1.54			N—I	105.3	0.44
		C′—N	86.6	4.29	16	4	C—S_A	83.0	13.05
		N—I	134.4	0.25			S_A—N	85.0*	
5	4	C—C′	64.2	3.49			N—I	101.8	0.41
		C′—N	75.8	4.71	18	4	C—S_A	86.1	16.67
		N—I	126.2	0.23			S_A—N	88.0*	
6	4	C—N	71.5	5.60			N—I	98.3	0.44
		N—I	126.9	0.36					
7	4	C—N	67.6	5.60	2	8	C—N	78.4	5.66
		N—I	120.0	0.19			N—I	127.9	0.19
8	4	C—N	65.2	4.83	8	8	C—S_A	77.7	6.53
		N—I	120.0	0.24			S_A—N	111.2	0.55
							N—I	116.6	0.49
9	4	C—N	67.1	9.07	14	8	C—S_A	76.9	11.48
		N—I	115.6	0.28			S_A—I	108.3	1.37

*This temperature was obtained by optical microscopy.

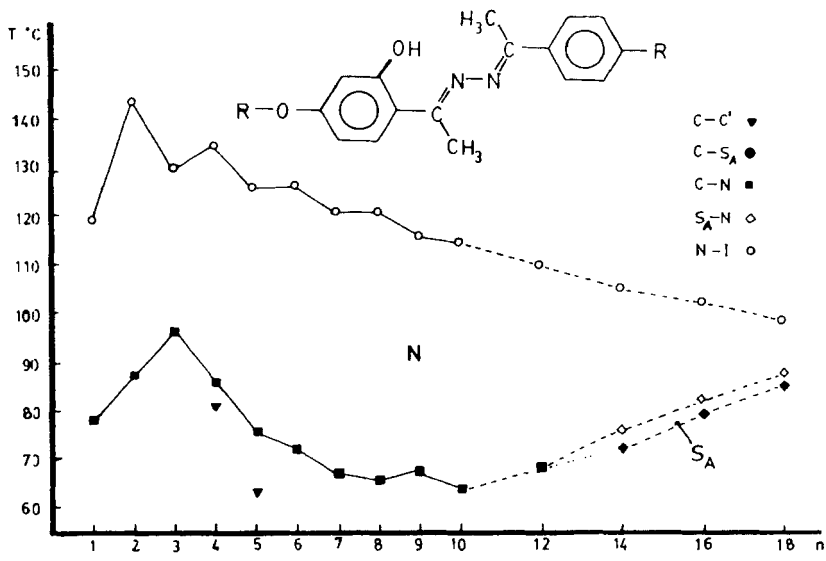


FIGURE 1 Transition temperatures as a function of alkoxy chain length for 4-alkoxy-4'-butyl-2-hydroxy-α, α'-dimethylbenzalazines.

greater than those observed for compounds with symmetrical alkoxy chains representing a similar total complement of carbon atoms.* This increase in the mesophase range is fundamentally caused by the drop in the melting point, as there is in many cases a notable agreement between the nematic-isotropic transition temperatures; this is particularly marked when n and $m \neq 1$. The mesophase ranges are noticeably similar when n and m represent long chains.

We have previously shown[2] that in this type of compound, the geometry of the central core is clearly asymmetrical; however, in these compounds the effect[5,6] of reversal of terminal chains is insignificant and the inversion of the central core has no noticeable effects on the mesogen properties. The compounds studied for this purpose (Table II: compounds 1–10) have very similar transition temperatures and their transition enthalpies are very close.

In the series referred to with symmetrical terminal chains, a crystal-crystal transition was observed only in the case of the OC_7H_{15} group.

For the compounds described in this paper, we have observed that a large number show polymorphism in the solid state. We have observed three different types of behavior.

*n-m: | 3 | C—N: 150.8, N—I: 166.3; | 4 | C—N: 133.8, N—I: 166.4; | 5 | C—N: 125.3, N—I: 153.3; | 6 | C—N: 114.3, N—I: 151.6.

TABLE II

Transition temperatures and enthalpies for 4-alkoxy(n)-4′-alkoxy(m)-2-hydroxy-α, α′-dimethylbenzalazines

n	m	Transition	Temperature °C	ΔH kcal/mol	n	m	Transition	Temperature °C	ΔH kcal/mol
1	2	C—N	146.7	7.69	2	8	C—N	101.3	8.76
		N—I	181.4	0.42			C′—N	98.3	7.73
2	1	C—N	149.3	7.21			N—I	155.6	0.32
		N—I	180.8	0.50	8	2	C—N	101.5	3.09
1	5	C—C′	99.5	3.71			C′—N	99.7	6.91
		C′—N	116.7	6.37			N—I	155.6	0.48
		C″—N	101.0	9.79	4	2	C—N	117.2	7.72
		N—I	154.1	0.21			C′—N	111.1	6.04
5	1	C—N	105.4	8.75			N—I	178.4	0.53
		C′—N	104.7	8.97	5	7	C—C′	99.3	4.85
		N—I	151.1	0.24			C′—S_A	102.1	6.19
1	8	C—N	104.3	9.91			S_A—N	121.2	0.13
		N—I	144.6	0.38			N—I	147.0	0.33
8	1	C—N	103.9	9.71	9	7	C—S_A	106.9	10.29
		C′—N	99.2	9.42			S_A—N	136.1	0.54
		N—I	143.3	0.43			N—I	139.5	0.74
2	5	C—C′	105.4	0.42	10	8	C—S_A	105.8	13.97
		C′—N	110.4	7.42			S_A—N	135.7	2.69
		N—I	167.9	0.45			N—I	137.2	
5	2	C—N	109.2	9.45					
		C′—N	104.1	7.37					
		N—I	168.8	0.45					

C→N⇌I for the compounds with (*n-m*):(5–1),* (8–1), (5–2),* (2–8), (8–2), (4–2).

This transition type can be seen for compounds with a longer chain in the aromatic ring which carries the hydroxyl group.

C→C′→N⇌I for the compound with (*n-m*):(1–5).

C′⇄

C′⇌N or S⇌I for the compounds with (*n-m*):(2–5), (5–7).

For the compounds with the shortest and the longest terminal chains, this type of behavior was not observed.

EXPERIMENTAL

The preparation of the compounds was carried out following the methods described in a previous paper.[1] The 4-alkylacetophenones used in the synthesis of the compounds of type [1] were prepared as reported Van der Veen[4] and others by Friedel-Crafts acylation.

In the synthesis of the compounds of series [1], two symmetrical azines appeared as secondary products: 4, 4′-dibutyl-α, α'-dimethylbenzalazine [3] and 4, 4′-dioctyl-α, α'-dimethylbenzalazine [4]. The thermodynamic data for these are given below:

C—N 50.6°C(lit[7] 53°C), 5.46 kcal/mol

N—I 68.6°C(lit[7] 67°C), 0.013 kcal/mol (3)

C—C′ 45.4°C, 3.40 kcal/mol

C′—I 63.4°C, 6.24 kcal/mol

I—N 59.7°C, 0.19 kcal/mol (monotropic) (4)

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*The C′→C transition in these cases only takes place when a fresh recrystallization is carried out.

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