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Relation Between Structure and Mesogenic Activity in α,α'-Dimethylbenzalazines

Influence of Intramolecular H-Bonding (II)

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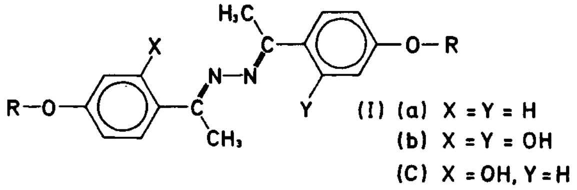
The central molecular geometry of three series of benzalazines: 4,4′-dialkoxy-α,α'-dimethylbenzalazines, 4,4′-dialkoxy-2,2′-dihydroxy-α,α'-dimethylbenzalazines, and 4,4′-dialkoxy-2-hydroxy-α,α'-dimethylbenzalazines was studied by U.V., I.R., and ^{1}H N.M.R. spectroscopy.

All the compounds studied show the E-E configuration. The intramolecular H-bond between the nitrogen of the azine central group and the H of the OH group in position 2 of the aromatic ring is "exceptionally" strong in accordance with the calculations made using Schaefer's equation. This bond conditions the geometry of the molecules, as well as their mesogenic properties. The intramolecular H-bonding favors the formation of mesophases whose properties are also related to the number of bonds of this type which the molecules contain.

INTRODUCTION

In the previous paper,[1] we have described the synthesis and mesomorphic properties of three homologous series of α,α'-dimethylbenzalazines of general formula:

The widely different properties shown by the three types of compound make a study of the influence exercised by the molecular geometry on the mesogenic properties of the compounds both interesting and necessary. We have studied two essential problems: The configuration (E or Z) of the C=N bond, and the effects that one or two intramolecular H-bonds have upon the spatial structure of the central core.



$R = C_nH_{2n+1}$ With $1 \leq n \leq 10, 12, 14, 16, 18$

SKETCH 1

EXPERIMENTAL

Of all products prepared, we have selected the following for this study:

^{1}H N.M.R., I.R., U.V.

(I)(a), R = H: (1-a) 4,4′-dihydroxy-α,α′-dimethylbenzalazine.

(I)(b), R = ethyl: (2-b) 4,4′-diethoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine.

(I)(a), R = octyl: (3-a) 4,4′-dioctyloxy-α,α′-dimethylbenzalazine.

(I)(b), R = octyl: (4-b) 4,4′-dioctyloxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine.

(I)(c), R = octyl: (5-c) 4,4′-dioctyloxy-2-hydroxy-α,α′-dimethylbenzalazine.

U.V.

(I)(a), R = ethyl: (6-a) 4,4′-diethoxy-α,α′-dimethylbenzalazine.

(I)(c), R = ethyl: (7-c) 4,4′-diethoxy-2-hydroxy-α,α′-dimethylbenzalazine.

(I)(b), R = pentyl: (8-b) 4,4′-dipentyloxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine.

(I)(c), R = pentyl: (9-c) 4,4′-dipentyloxy-2-hydroxy-α,α′-dimethylbenzalazine.

These compounds were chosen because of their excellent solubility and stability.

^{1}H N.M.R. spectra were obtained with a PERKIN-ELMER R-12-B using $CDCl_3$ and CCl_4 solutions, with TMS as an internal reference.

U.V. spectra were obtained with a PERKIN-ELMER 200 using *n*-pentane and acetonitrile solutions.

I.R. spectra were obtained with a PERKIN-ELMER 283 using $CHCl_3$ solutions for the 4000–1500 cm^{-1} zone.

The thermal and thermodynamic studies have been described previously.[1] Phase transition temperatures and enthalpies were measured with 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 compounds (1-a) and (2-b) have been the subject of X-ray diffraction studies in collaboration with the Departamento de Cristalografía y mineralogía de la Facultad de Ciencias de la Universidad de Zaragoza. The results of and conclusions drawn from these studies have been published elsewhere.[2,3]

RESULTS AND DISCUSSION

E-Z Isomerism

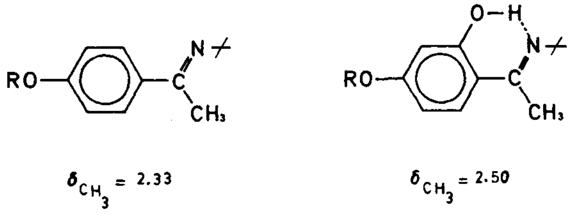
The benzalazines can exist as three types of configurational isomer: E-E, E-Z, and Z-Z. In general, the studies already published on the subject of benzalazines and their derivatives have shown that, by the usual methods of synthesis, the E-E isomer is the only one obtained.[4,5]

However, the two methyl groups in the central core of the present products can affect the isomeric composition. Therefore, to determine the configuration, we carried out the ^{1}H N.M.R. studies, since the signal from the methyl groups is different for each type of isomer.[6]

The N.M.R. signals for the hydroxyl and methyl groups of the central core of the compounds (1-a), (2-b), (3-a), (4-b), and (5-c) are given in Table I.

The existence of just one signal for each type of proton suggests the involvement of a single isomer. By analogy with results obtained by other authors,[7,8] we conclude that our synthetic procedure leads only to the isomer with minor steric hindrance, that is, the E-E isomer.

This configuration was corroborated by the X-ray studies[2,3] on the compounds (1-a) and (2-b).



SKETCH 2

TABLE I

^{1}H NMR data.

	δ (solvent)						
Compounds	R	X	Y	δ 2-OH (CCl_4)	δ 2-OH ($CDCl_3$)	δ CH_3 ($CDCl_3$)	
(1-a)	H	H	H	—	—	2.34 (6H)	
(2-b)	n-C_2H_5	OH	OH		13.79 (2H)		2.51 (6H)
(3-a)	n-C_8H_{17}	H	H	—	—	2.31 (6H)	
(4-b)	n-C_8H_{17}	OH	OH	13.30 (2H)[a]	13.77 (2H)		2.49 (6H)
(5-c)	n-C_8H_{17}	OH	H	13.73 (1H)[a]	14.25 (1H)	2.36 (3H)	2.54 (3H)

[a] These data are used in Schaeffer's equation.

INTRAMOLECULAR H-BONDING

The presence of a hydroxyl group *ortho-* to the azine system suggests that hydrogen bonding may occur and therefore that possible variations in the electronic distribution and the spatial geometry of this part of the molecule may arise.

The intramolecular nature of the H-bonding was shown by the I.R. spectra: low concentration solutions continue to give the associated O—H absorption. The energies of the intramolecular H-bonds were calculated using the method applied by Schaefer[9] to the ^{1}H N.M.R. data (Eq. 1).

$$E = \Delta\delta + 0.4 \pm 0.2 \qquad (1)$$

$$(\Delta\delta = \Delta\delta_{OH} - \Delta\delta_{OH\,phenol} \text{ in } CCl_4)$$

The calculated energy for intramolecular H-bonding in the compounds (4-b) and (5-c) is:

(4-b) $E = 9.4 \pm 0.2$ kcal/mol

(5-c) $E = 9.8 \pm 0.2$ kcal/mol

The hydrogen bonds formed are even stronger than those described[10,11] for similar o-hydroxybenzenes. Moreover, the ν_{OH} data (Table II), which are lower than those reported by Freedman[12] for azomethines derived from salicylaldehide, reflect the increase in bond strength.

These hydrogen bonds play a decisive role in the molecular geometry as demonstrated in the X-ray diffraction study[3] of 4,4′-dihydroxy-α,α′-dimethylbenzalazine[3] (1-a) and 4,4′-diethoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine[2] (2-b). In the former, without hydrogen bonding, the molecule has a marked asymmetry (Figure 1). The torsion angles on the N—N bond of the azine central group are 32°. The plane that defines each N and the next $=C—CH_3$ group is at an angle to the planes of the benzene rings (20° and 13° respectively).

TABLE II

IR frequencies (cm^{-1}) ($CHCl_3$)

Compounds	R	X	Y	ν_{OH}	$\nu_{C=N}$
(3-a)	n-C_8H_{17}	H	H	—	1612
(4-b)	n-C_8H_{17}	OH	OH	2610	1632
(5-c)	n-C_8H_{17}	OH	H	2610	1628

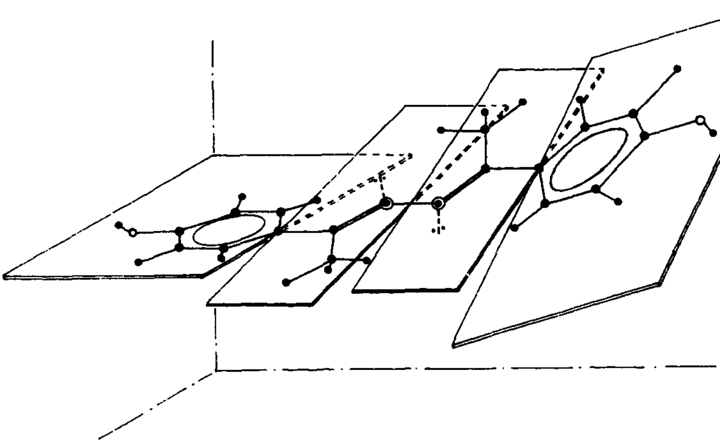


FIGURE 1 Spatial distribution in planes for 4,4'-dihydroxy-α,α'-dimethylbenzalazine.

The aromatic rings are not, therefore, coplanar as two axes defined by the C_1—C_3—C_6 and C'_1—C'_3—C'_6 atoms are plainly visible (Figure 2). The terminal chains (at C_6 and C'_6) are not on a common axis.

The compound (2-b) (with two H-bonds) is a centrosymmetric molecule (Figure 3). The azine group is in a plane at a slight angle to the planes of the benzene rings (4.5° and 4.5°). The terminal chains are contained in the longest axis that passes through the center of symmetry.

The intramolecular hydrogen bonding favors the coplanarity of the aromatic ring and the central azine group.

This structural characteristic and the resulting increase in conjugation is reflected in the U.V. spectra (Table III). A progressive bathochromic

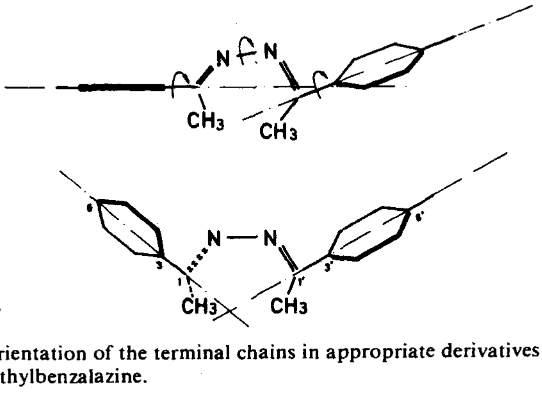


FIGURE 2 Orientation of the terminal chains in appropriate derivatives of 4,4'-dihydroxy-α,α'-dimethylbenzalazine.

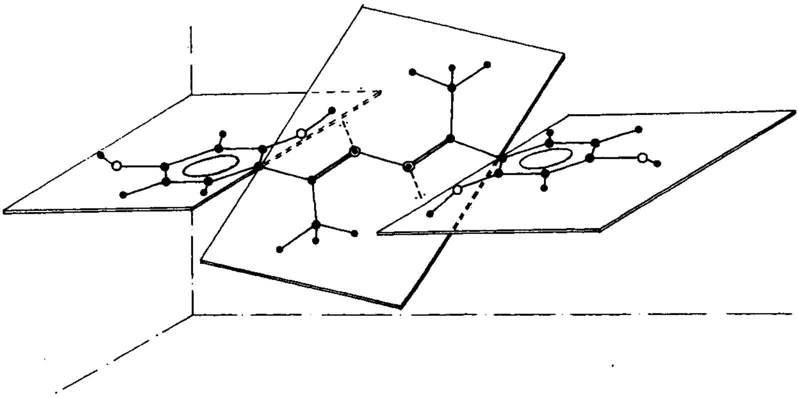


FIGURE 3 Spatial distribution in planes for 4,4'-diethoxy-2,2'-dihydroxy-α,α'-dimethylbenzalazine.

displacement is observed in the B(α) band on going from series I(a) to I(b) to I(c).

Table III shows that this behavior in the three series is independent of the length of the terminal chains. The slight discrepancies are caused by the different solvents.

X-ray studies for the compounds of type I(c) (with one intramolecular H-bond) have not been carried out, but the spectroscopic data suggest a structure intermediate between that of the I(a) and I(b) series. In effect, the ^{1}H N.M.R. spectra (Table I) reveal the presence of two differently situated methyl groups in environments similar to that of series I(a) and I(b). From the U.V. spectra, the bathochromic displacement is found to be proportional to the number of intramolecular H-bonds (approx. 38 nm for one bond and approx. 70 nm for two). Also from the spectra, the vibrational frequencies of the C=N bonds show a gradual variation as a function of the number of hydrogen bonds.

The compounds of series I(b) show luminiscence and thermochromism, and the compounds produce a yellow emission when they are irradiated with U.V. light. Arcorito[5] ascribes a similar phenomenon given by salicylaldazine to the chelate-ring formation which favors electronic conjugation and even the contribution of quinonoid structures to the resonance hybrid:

This hypothesis seems to be corroborated in our ketazines by the differences in the bond lengths that are observed in compounds[3,2] (1-a) and (2-b) (Figure 4).

A significant lengthening of the C_3—C_4, C_3—C_8, and C_1—C_2 bonds

TABLE III

UV absorptions (λ max. nm (log ϵ)).

Compound	R	X	Y	Acetonitrile				*n*-pentane			
(3-a)	*n*-C_8H_{17}	H	H						313	(4.5)	
(5-c)	*n*-C_8H_{17}	OH	H						349	(4.5)	
(4-b)	*n*-C_8H_{17}	OH	OH					363.5^{sh}	378.5	(4.5)	393^{sh}
(6-a)	*n*-C_2H_5	H	H		303.0	(4.4)					
(2-b)	*n*-C_2H_5	OH	H		340.0	(4.4)					
(7-c)	*n*-C_2H_5	OH	OH	360^{sh}	372.6	(4.4)	389^{sh}				
(9-c)	*n*-C_5H_{11}	OH	H		343.2	(4.4)			349.0	(4.4)	
(8-b)	*n*-C_5H_{11}	OH	OH	360^{sh}	372.4	(4.4)	388^{sh}	363^{sh}	378.8	(4.4)	393^{sh}
(1-a)	H	H	H		303.0	(4.3)					

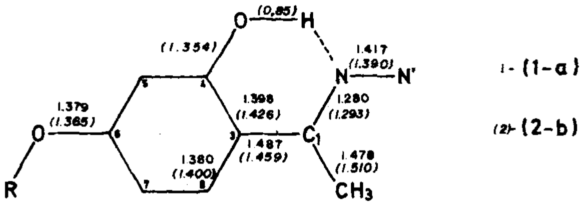
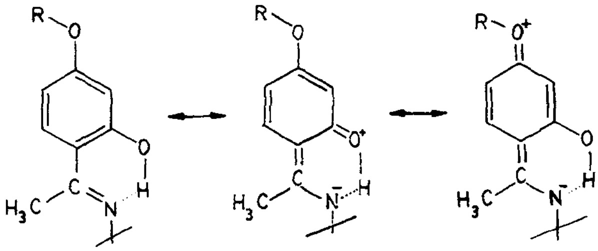


FIGURE 4 Bond lengths for 4,4′-dihydroxy-α,α′-dimethylbenzalazine (1-a) and 4,4′-diethoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazine (2-b).



SKETCH 3

can be observed, whereas the C_1—C_3 and N—N′ bond lengths decrease; this could be attributed to the contribution of quinonoid forms.

A comparison of the data for the N—N′ bond distances for the compounds (1-a)[3] and (2-b)[2] with the distances measured for other compounds (pyrazole,[13] pyridazine[14]) and with the average values for single bonds and double bonds[15] (Table IV) indicates some double bond character for the N—N′ bond in compound (2-b). Compared with Pauling's relation,[16] (2) would suggest a bond order of 1.1.

$$D(n') = D_1 - 0.71\,A \lg n' \tag{2}$$

TABLE IV

Compound	bond-type		distance (Å)
(1-a)	=N—N=		1.417
(2-b)	=N—N=		1.390
Pyrazole	N—N		1.360
Pyridazine	N—N		1.330
	N—N	(sp^3-sp^3)	1.449
Average values	N—N	(sp^2-sp^2)	1.410
	—N=N—		1.240

The C_4—O bond distance (1.354 Å) in compound (2-b) (with respect to the C_6—OH bond distance in (1-a): 1.397 Å) is also significant. This confirms the important participation of quinonoid forms, even though the values are not as small as the values (1.30 Å)[17] for naphthazine.

The compounds of series I(c) (with only one chelate ring) present a pronounced decrease in the intensity of their thermochromism and luminiscence. This could be put down to loss of planarity and electronic conjugation in the molecule.

INFLUENCE OF THE INTRAMOLECULAR H-BONDING ON THE MESOGENIC PROPERTIES

The mesomorphism of a compound is strongly influenced by permanent dipole moments and easily polarizable groups. The chelate rings present in the compounds studied involve the participation of charged quinonoid structures which can be said to influence both the above mentioned factors. For this reason, it is very interesting to relate the intramolecular H-bonding to the mesogenic properties of the benzalazines.

The compounds of series I(b) (two H-bonds) have centrosymmetric and nearly planar molecules arranged in the crystal in a face to face packing. The compounds of series I(a) (without H-bonds) are not arranged in a face to face packing, and the molecules have a V-shape (Figure 3). The higher melting points for series I(b) are a logical consequence of a packing involving larger cohesive forces (Figure 5). After fusion there still remain strong intermolecular forces of attraction between these molecules, with a considerable anisotropy of the electronic polarizability, as a consequence of which the compounds of I(b) series show enantiotropic mesophases.

In series I(a), monotropic mesophases appear only in the three first members (R = $-CH_3$, $-C_2H_5$, n-C_3H_7), in spite of their lower melting points. This behavior is attributed to the low anisotropy of the electronic polarizability and the weak forces of interaction between the non-planar molecules.

In view of the lack of a complete crystallographic study, the behavior of the compounds of series I(c) (with a single H-bond) could be explained by three factors:

—A low lattice energy which brings about a remarkable descent in the melting points of the compounds.

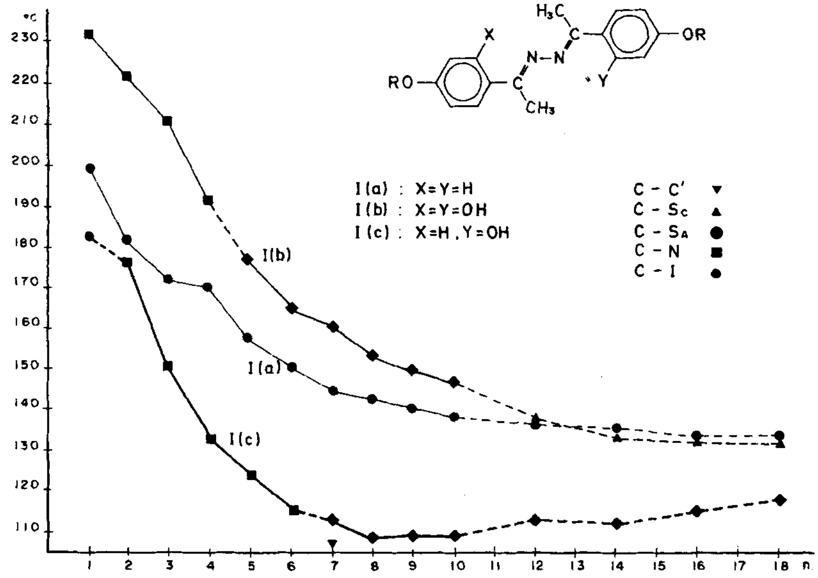


FIGURE 5 Crystal-mesophase transitions as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

—Enhanced permanent dipole moment produced by the unsymmetric substitution of the benzene rings.

—A high anisotropy of electronic polarizability.

The last two factors would be responsible for the mesomorphism shown by these compounds. However, it is noticeable that the first compound of the series is monotropic in behavior.

The preceding discussion refers to the aromatic central core, but in general increase in the lengths of the terminal chains modifies the thermal and thermodynamic properties of the compounds (Figures 5 and 6) in a regular way.

The range of variations in the thermal properties of the compounds decreases with the increase in chain length, showing a progressive lessening of the influence of the central core of the molecules on these properties. Also, as can be seen in Figure 5, the three curves relating to the melting points tend to join when the chains are sufficiently long.

However, a smaller variation in the data for enthalpy of fusion can be seen for the compounds with two intramolecular H-bonds (series I(b)), suggesting a greater influence of the central group on the crystalline arrangement of the molecules in the solid phase for the compounds

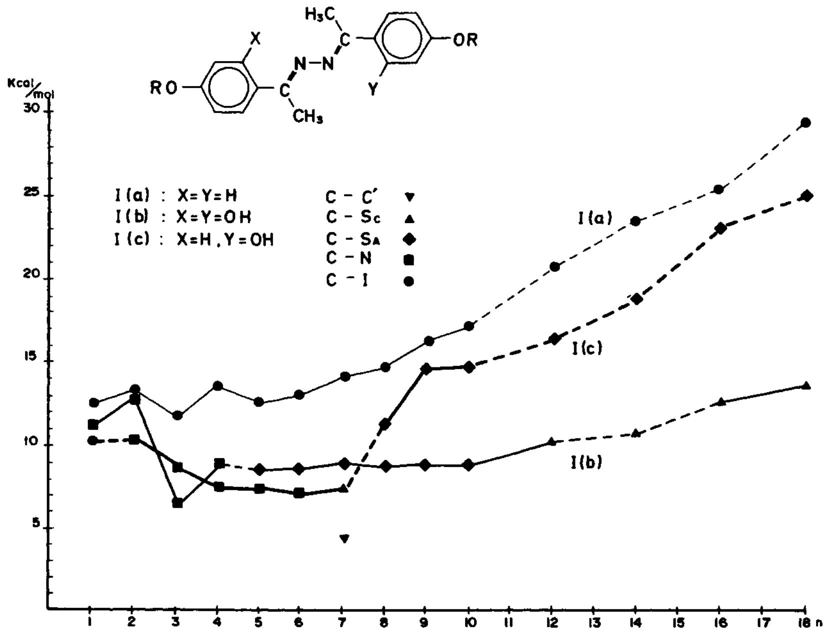


FIGURE 6 Transition enthalpies for the crystal–mesophase changes as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

of this series compared with that for the compounds of series I(a) and I(c), where the influence of the increase of the length of the terminal chains is greater.

CONCLUSION

The intramolecular H-bonding of the 4,4′-dialkoxy-2,2′-dihydroxy-α,α′-dimethylbenzalazines and the 4,4′-dialkoxy-2-hydroxy-α,α′-dimethylbenzalazines is specially strong and produces two fundamental effects in the molecules:

(a) All the molecular elements tend to arrange themsleves in a coplanar way.

(b) The appearance of local permanent dipole moments, and at the same time, enhancement of the anisotropy of the electronic polarizability.

The overall result of these effects is that the mesogenic properties of the molecules are better than those of the analogous compounds without intramolecular H-bonds.

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