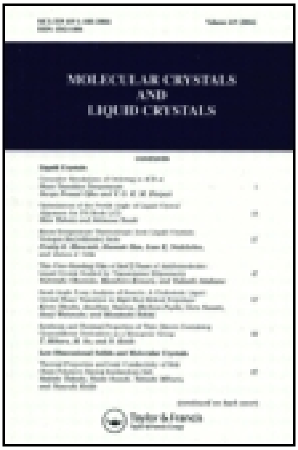

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Thermotropic Mesophases of Benzene Derivatives with Terminally Hydroxylated Groups

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THERMOTROPIC MESOPHASES OF BENZENE DERIVATIVES WITH TERMINALLY HYDROXYLATED GROUPS

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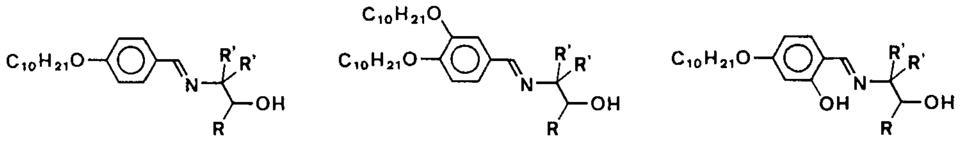
Abstract Nine benzene derivatives substituted with at least one long alkyl chain in common and with various terminally hydroxylated groups have been prepared. Thermotropic mesophases were observed in seven compounds and the hydrogen bonding of the alcoholic OH groups seems to be responsible for this behavior of novel one-ring mesogens. The X-ray diffraction patterns are consistent with a common structural model involving bimolecular layers of hydrogen bonding network separated by fully interdigitated alkyl chains.

INTRODUCTION

Material classes of thermotropic liquid crystals have nowadays become quite diverse.[1] For mesogenic carbohydrates[2] and amphiphilic diols,[3] in particular, the mesophase formation is based on the intermolecular hydrogen bonding interaction and resultant phase segregation (hydrophilic *vs* lipophilic). Thus it is presumably a rather weak interaction, but is sufficiently strong to generate orientational order and further a one- or two-dimensional lattice in the liquid of compounds with appropriate chemical constitution. A question arises as to how the phase transition property is influenced by the cooperative character of the hydrogen bonding system itself. In the hope of sorting out the role of hydrogen bonding interaction in liquid crystals chemistry, we have undertaken a survey of mesomorphism of benzene derivatives carrying terminally hydroxylated groups (FIGURE 1).

RESULTS AND DISCUSSION

The compounds were prepared by condensation of an appropriate benz-



1 **2** **3**

a: R = R'= H; **b**: R = CH_2OH, R'= H; **c**: R = H, R'= CH_2OH

FIGURE 1 Structures of the compounds studied.

aldehyde with an amine containing the 2-aminoethanol backbone. TABLE I summarizes the preliminary results of thermal, structural, and infrared spectral analyses. Here K_1, S_A^+, and I denote crystalline,[4] smectic A, and isotropic liquid phases, respectively. The specific term S_A^+ is after the precedent of diol systems.[5] While the hydroxyethyl derivatives **1a** and **2a** are nonmesogenic, the rest of compounds exhibit mesophases. The orthoscopic textures of the mesophases were largely homeotropic in common and oily streaks and focal conics were observed in some cases.

It can be seen in TABLE I that the thermal stability of the mesophase (T_{SI}) increases as the alkylimino end of the molecule is more heavily hydroxylated (**a** → **b** → **c**). Thus all of the tris(hydroxymethyl)methyl derivatives (**c**) have enantiotropic mesophases. Introduction of an extra hydroxyl group to the central benzene ring (**1** → **3**) is more effective in this regard than that of another alkoxy group (**1** → **2**) and this is most probably due to the intramolecular hydrogen bond leading to an expanded aromatic core and to enhanced structural rigidity.

X-Ray powder diffraction patterns in the mesophases commonly contained only one Bragg reflection which corresponds to a layer spacing (*d*) of 35 - 38 Å. The values are consistent with a bilayer smectic model as depicted for **3a** in FIGURE 2. The layers of hydrogen bonding network are separated by fully interdigitated alkyl chains. A similar model has been proposed for the S_A^+ phases of the diols.[5] The present systems further involve the intervening aromatic cores, but there is no ordering within the layer; high-angle diffraction was diffuse in all cases but **1c**.[6] Note, however, that the absence of the rigid group from compounds **c** would make the molecular structure analogous to that

TABLE I Physicochemical data for mesogenic benzene derivatives.

Compound	Transition Temperature /°C					d/Å^a	ν_{OH}/cm$^{-1\,b}$
	K_1		S_A^+		I		
1a	•		48		•	-	-
1b	•	84	(•	63)	•	36.8	3380
1c	•	82	•	91	•	38.0	3400
2a	•		50		•	-	-
2b	•	93	(•	78)	•	36.0	3390
2c	•	85	•	94	•	35.2	3420
3a	•	72	(•	69)	•	34.8	3360
3b	•	120	•	132	•	35.6	3390
3c	•	127	•	156	•	34.8	3350-3410

a. Recorded near T_{SI} except for **3c** which was taken just above T_{KS}.
b. Interpolated at T_{SI}.

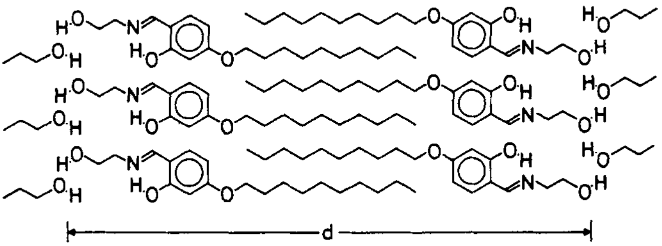


FIGURE 2 A structural model for the S_A^+ phase of **3a**.

of tris(hydroxymethyl)aminomethane, for which a plastic crystalline mesophase has been reported.[7]

It should be added that a nonamphiphilic analogue of **3a** (*n*-propyl in place of the hydroxyethyl group) has no mesophase detectable above room temperature and the mesophase is promoted obviously by the terminal hydroxylation. One should note, however, that the hydrogen bonds do not appear to be very strong. TABLE I quotes peak frequencies of broad absorption bands assignable to the alcoholic OH stretching mode. The values 3360 - 3420 cm^{-1} represent rather weak hydrogen bonds. It should also be added that the frequency shift from the mesophase into the isotropic liquid phase was small and continuous in all cases while a drastic spectral change was often observed upon crystallization. It is also conceivable that the peak frequency is greater in polyols (**a** < **b** < **c**). Since the mesophase stability increases in this order, it does not parallel the average strength of the hydrogen bonds. Perhaps more bifurcated bonds are being formed in polyol derivatives. Therefore, the mesomorphic behavior of the present class of compounds seems to depend more on the dynamic aspect of the hydrogen bonding network, which in turn is determined by the details of molecular constitution.

EXPERIMENTAL

The Schiff base condensation reactions were carried out in boiling benzene (**a** and **b**) or toluene/ethanol (**c**). Purification was effected by repeated recrystallization from hexane (**a**), with either THF (**2b** and **2c**) or ethanol (**3b** and **3c**) added, until sharp and constant phase transition points were obtained. Elemental analyses and ^{1}H-NMR spectra in $CDCl_3$ were consistent with the structures. The mesomorphic transition temperatures were determined by using a Rigaku Thermoflex differential scanning calorimeter. X-Ray powder diffraction in the mesophases was measured with a Rigaku RAD IVB automated diffractometer. Infrared absorption spectra were recorded on a JASCO FT/IR-8000 spectrophotometer modified at IMS for sensitivity enhancement.

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