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THE SYNTHESIS, THERMODYNAMIC AND OPTICAL PROPERTIES OF THE HOMOLOGUS SERIES 4'ALKYLOXY BENZOINILIDENE 4-n-PROPYLOXY ANILINE

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ABSTRACT. The series of 4,4'alkyloxy Benzoinilidene 4-n-propyloxy aniline was synthesized varying the number carbon atoms in the alkyloxy chain. The temperatures and enthalpies of the phase transitions were determined, as were the indices of refraction. Normal nematic phases are found for n = 5 to n = 10, and monotropic nematic phases for c = 4, 11, 12 and 16. For n = 10 to 16 smectic phases were observed which are monotropic and unstable.

INTRODUCTION

One of the areas of interest of the liquid crystal group at the Federal University of Santa Catarina is the synthesis and characterization of new homologus series of thermotropic liquid crystals. For this study we choose the benzylideanilines.

The use of the benzulideanilines in practical applications is somewhat limited by the instability of the imine bond[1,5] however, there are examples of o-hidroxy substituted liquid crystals which are establized by an intramolecular hydrogen bond[6,7]. The compounds we synthesized seem to be more stable than the non-substituted ones[8,9].

The compounds we studied are the 4-alkoxybenzoinilidene-p-propyloxyanilina and are aromatic derivatives of type 1 alkyloxybenzoine. (Other members of our group have studied the -p-ethyl- and -p-decyoxyaniline series and these results will be reported seperately). We will refere to this series by the abreviation ABPA, and to the members of the series by the substitution of the A by the apropriate sufix; for example P for propyl, (PBPA-3) where the number of carbons in the alkoxy chain is also indicated.

These molecules are characterized by a strong inter-molecular hydrogen bond forming a chalate ring which rotates around the C-C bond and thus increases the molecular rigidity.

SYNTHESIS

The synthesis of these componds was carried out by alkylation and condensation reations. The 4-alkoxybenzaldehydes were prepared from 4-hydroxybenzaldehyde and the corresponding alkybromide by the method of Gray and Jones[10]. 4-propylloxyanilina was prepared using the method described by Ban-Hoi, et. al[11]. The 4-alkoxybenzoins were obtained using the technique of Vogel[12].

To obtain 4-alkyloxybenzoinilidene-p-propyloxyanilina, the apropriate 4-n-alkyloxybenzoin (0.01 mol) was disolved in alcohol (20 ml) to which was added an equal-molar quantity of 4-n-propyloxy-aniline followed by one ml of glacial acetic acid. The reaction was refluxed gently on a steam bath for 15-20 minutes then cooled. The precipitate of 2 Hidroxy-1, 2-bis (4-n-alkoxyphenyl)-1-(4-propyloxyphenyl) imenoethane was filtered and recrystalized at least 5 times, or until the transition temperatures were reproducible.

The structure of the final products was confirmed by IR and NMR, for 2-Hidroxy-1,2-Bis (4-n-buthylphenyl)-1-(4-propoxy-phenyl) iminoethane, which gave the following results: IR (KB_R) 3300 cm^{-1} ν_{-OH}; 2950 cm^{-1} ν_{C-H}; 1650 cm^{-1} $\nu_{C=C}$; 1550 cm^{-1} $\nu_{C=N}$. NMR(CDC_3, TMS), 0,8 - 1,2 ppm (m, 9H, 3 CH_3); 1,3-2,1 ppm (m, 10H, 5(CH_2)); 3,8 - 4,2 ppm (m, 6H, 3(CH_2)); 6,8 - 80 ppm (m, 12H, aromatic, 1H, -CH); 8,4 ppm (S, 1H, -OH).

EXPERIMENTAL

All phase transitions were studied with a polarizing microscope and a Mettler hot stage and by diferential scanning calorimetry (DSC). Transition temperatures were reproducible to ± 0,2°C. The textures in the smectic phases were "fan shaped" leading us to believe them to be Sm_A.

The thermodynamic studies were done using a Perkin Elmer DSC-2 calibrated using lead, indium and tin. The transition enthalpies were determined using a heating rate of 2.5 C°/min. The transition temperatures were reproducible to ± 0,2°C and the transition enthalpies to about 3% for the C-I and C-N transitions and about 20% for the N-I transition.

Samples (2-4 mg) were weighted on a Mettler H-51 balance having a precision of ± 0,05 mg. Peak areas were measured with a Koizumi planometer KP-27 having a precision of 0.05 cm^2. Enthalpy data were obtained from two or three different samples, and each peak measured three times. The enthalpies given are thus the result of 6 to 9 measurements.

The indices of refraction were measured with a microrefractrometer using the Leitz-Jelly principle[13]. Sample alignment was obtained by rubing the prism with lens tissue. Sodium light is seperated by the sample into on ordinary ($n_o=n_\perp$) and an extraordinary ($n_e=n_\parallel$) ray, with the virtual images of these two rays being projected on a scale. An Abbe refratrometer was used to check known substances, showing that our microrefractrometer has a precision of ± 0.002.

The prism with the compound was placed in the Mettler FP-52 for temperature control. The prism was preheated to a temperature well into the nematic range before adding the sample. The temperature was then lowered to the begining of the nematic range and the indices of refraction were measured as a function of temperature. Once the sample is heated above T_{N-I}, a decrease of about 0,2% in the index of refraction is observed, which is taken to imply some sample decomposition. The values given in this article are always those of the first series of measurements.

RESULTS AND DISCUSSION

The temperatures (^{o}C) and enthalpies (cal/g) of transition of the fase transitions as obtained from thermal microscopy and the DSC are presented in Table 1 and Figure 1.

TABLE 1 Transition temperatures (^{o}C) and corresponding enthalpies (cal/g) of disubstituted 4,4'Alkyloxy Benzoinilidene 4-n-propyloxy Anilina (ABPA).

Compounds	T_{C-N}	ΔH_{C-N}	T_{N-I}	ΔH_{N-I}
	T_{C}-I	H_{C}-I		
PBPA-3	133,7^{a}	26,02	-	-
BBPA-4	119,2	21,89	-	-
	111,9^{b}	-	112,3	-
PeBPA-5	103,4	24,17	105,5	0,59
HBPA-6	95,4	24,00	109,3	0,63
HpBPA-7	101,5	27,67	105,9	0,65
OBPA-8	99,4^{a}	26,58	107,9	0,87
DBPA-10	102,36	29,42	105,8	0,93
UDBPA-11	106,3	33,25	-	-
	101,2^{c}	-	103,2	-
DoDeBPA-12	104,2	35,43	-	-
	101,9^{c}	-	103,6	-
HDBPA-16	106,8	36,05	-	-
	99,4^{c}	-	99,9	-

a) These compounds show polymorphism in the solid phase.

b) Monotropic nematic phase.

c) These compounds have both monotropic nematic and smectic phases. The temperatures shown are for the nematic phases.

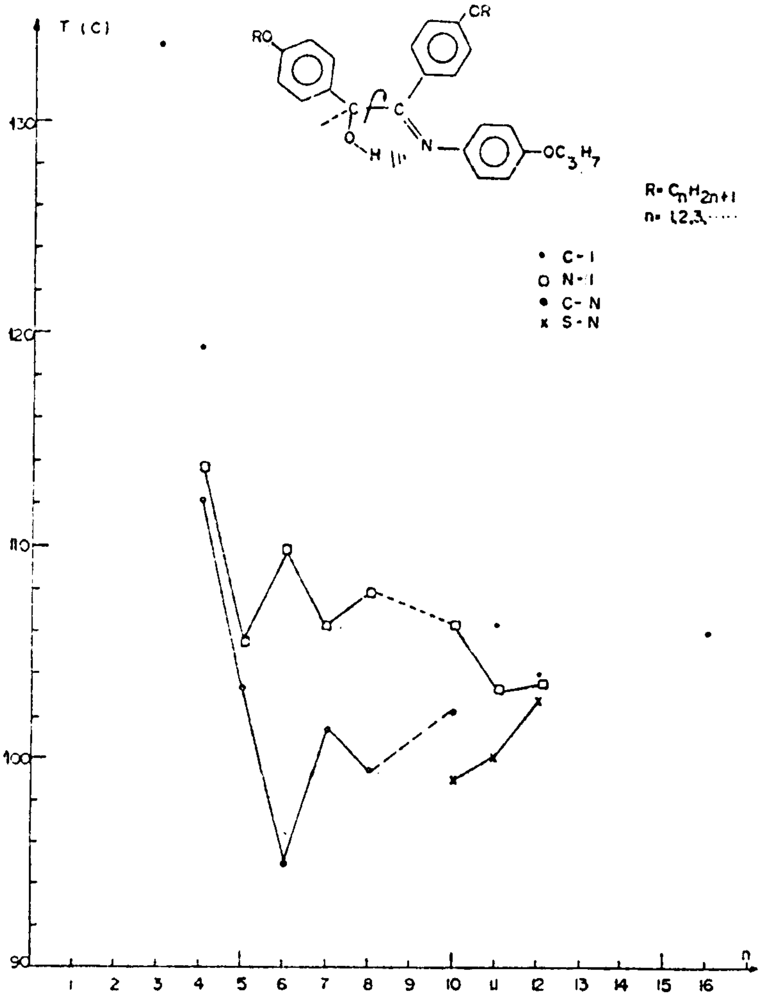

FIGURE 1 Transition temperatures of the ABPA homologes.

The compounds DBPA-10, UDBPA-11, DoDeBPA-12 and HDBPA-16 all presented monotropic phases with a fan shaped texture over a small temperature internal. This phase is quite unstable and rapidly crystalizes. The nematic phases of the last three compounds (BPA-11-12-16) are also monotropic. PBPA-3 and BBPA-4 did not show any mesophases, even monotropic.

The even - odd effect can be seen both in the transition temperatures, where compounds with an even number of carbon atoms in the alkoxy chain tended to be higher than those with an odd member as well as in the enthalpies. In the transition enthalpies the odd numbered compounds have the higher values, especially between n=3 and n=10. Due to the small N-I transition enthalpies, the error for these points is relatively greater, as described in reference[14].

The ordinary (n_o), extraordinary (n_e) and isotropic (n_i) indexes of refraction are shown as a function of reduced temperature ($\tau = T/T_{NI}$) in figure 2. In figure 3, the birrefringence is shown to have the values (0.22 for τ = 0.96 and 0.18 for τ = 0.98) one would expect for molecules containing more than one benzene ring[15,16].

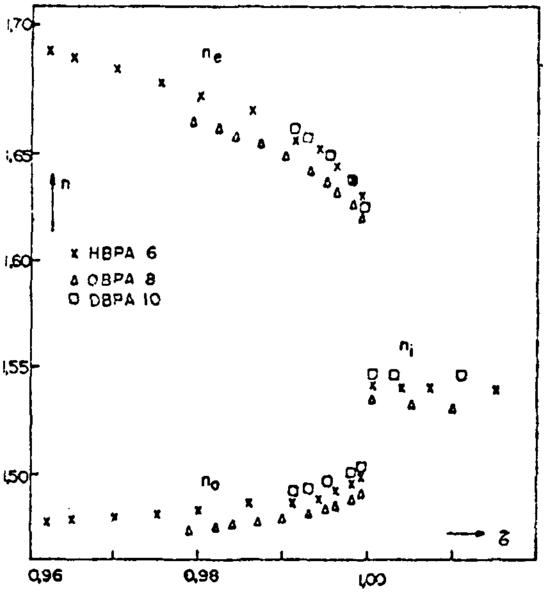

FIGURE 2 Refractive indices as a function of reduced temperature of the ABPA homologes.

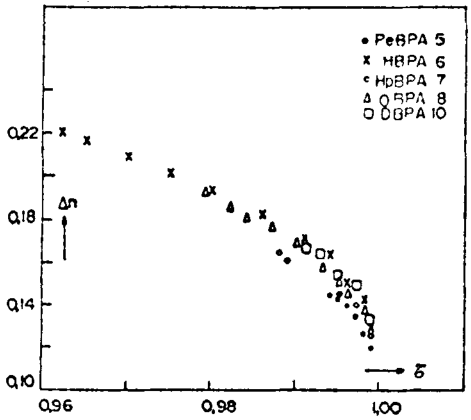

FIGURE 3 Birefringence (Δn) as a function of reduced temperature of the ABPA homologes.

As can be seen in Fig. 2 and 3, the birefringence $\Delta n = n_e - n_o$ and n_e both decrease as the temperature is increased, especially for values chose to T_{NI}, while n_o increases.

With the exception of perhaps HBPA-6, the temperature interval of the nematic phase is too narrow to permit a realistic determination of the order parameter. It is equally difficult to compare the values of the birefringence, as this phase only exists for $\tau = 0.98$.

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