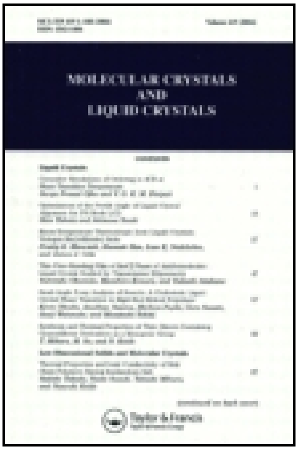

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Properties of a Homologous Series of o-Hydroxy Substituted Anils and Some Binary Mixtures†

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1. Introduction

In an earlier report,[1] an *o*-hydroxy substituted analog (OHMBBA) of the room temperature nematic N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) was prepared, and intramolecular hydrogen bonding was found to stabilize the compound against cleavage of the anil linkage. To examine the properties of this class of compounds, the synthesis of several such *o*-hydroxy substituted compounds was undertaken, and their liquid crystalline properties determined. Two broad temperature range binary systems were also examined consisting of OHMBBA mixed with N-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA), and OHMBBA mixed with N-(*p*-methoxybenzylidene)-*p*-*n*-pentylaniline (MPBA) and their phase diagrams determined. The dynamic scattering behavior of one of these binaries—50–50 OHMBBA–EBBA—was examined.

2. Discussion

Synthesis: The basic synthesis of the 2-hydroxy-4-alkoxybenzaldehydes has been described;[2] 2,4-dihydroxybenzaldehyde is heated with the appropriate alkyl ester of *p*-toluenesulfonic acid. For example, 30 g (0.22 moles) of 2,4-dihydroxybenzaldehyde is dissolved in 150 ml of acetone dried over anhydrous sodium carbonate; 37 g (0.35 moles) of freshly dried sodium carbonate is added and

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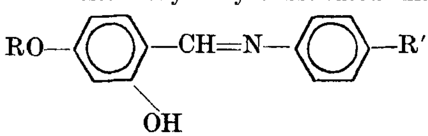
52.7 g (0.26 moles) of ethyl *p*-toluenesulfonate is added dropwise over 2 hours to the stirred refluxing acetone mixture. The reaction mixture is neutralized with hydrochloric acid and the product obtained by steam distillation. The aldehyde thus prepared is condensed with the appropriate *p*-substituted aniline in absolute ethanol which is heated for appr. 1 h, and the resulting product crystallized several times from ethanol.

Melting Behavior: The melting behavior of all compounds was studied on both a Mettler FP-2 hot stage, observing the transition under a microscope, and utilizing a Perkin–Elmer DSC-1B differential scanning calorimeter. For the binary phase diagram determinations, the DSC-1B was operated at a scan speed of 5 °/minute in the low temperature mode of operation.

Compounds Not Showing Mesophase Behavior: The following compounds were prepared by analogous procedure to that described above, and showed no mesophase: N-(*o*-hydroxybenzylidene)-*p*-*n*-butylaniline, m.p. 42.4–42.8°; N-(*m*-ethoxy-*o*-hydroxybenzylidene)-*p*-*n*-butylaniline, m.p. 39.4–39.8°; N-(*m*-ethoxy-*o*-hydroxybenzylidene)-*p*-*n*-pentylaniline, m.p. 32.0–32.4°; and N-(*o*-hydroxybenzylidene)-*p*-*n*-pentylaniline, m.p. 45.4–45.6°.

Compounds Showing Mesophase Behavior: The melting ranges of the *o*-hydroxy substituted anils showing mesophase behavior are listed in Table 1.

TABLE 1 Melting Range of Several Anil-Type Nematic Liquid Crystals and Their *o*-Hydroxy Substituted Analogs



Compound (R)	Compound (R′)	Nematic Range °C	*o*-Hydroxy Substituted Nematic Range °C
Methyl	*n*-Butyl	21–41	44.7–64.5
Ethyl	*n*-Butyl	32.4–79.7	70.4–85.9
Methyl	*n*-Pentyl	39.0–63.2	75.4–79.8
Ethyl	*n*-Pentyl	62.5–89.6	76.0–97.9

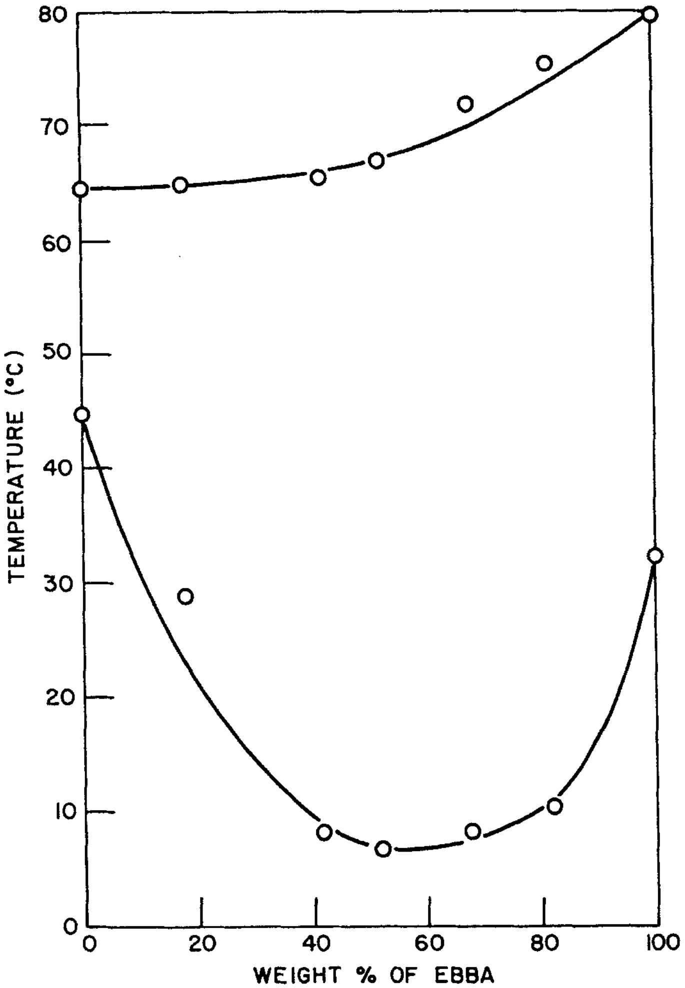


Figure 1. Phase diagram of the system OHMBBA–EBBA. Upper curve, nematic–isotropic transition; lower curve, solid–nematic transition. 100% values by microscopic determination of m.p.; binary values by DSC determination.

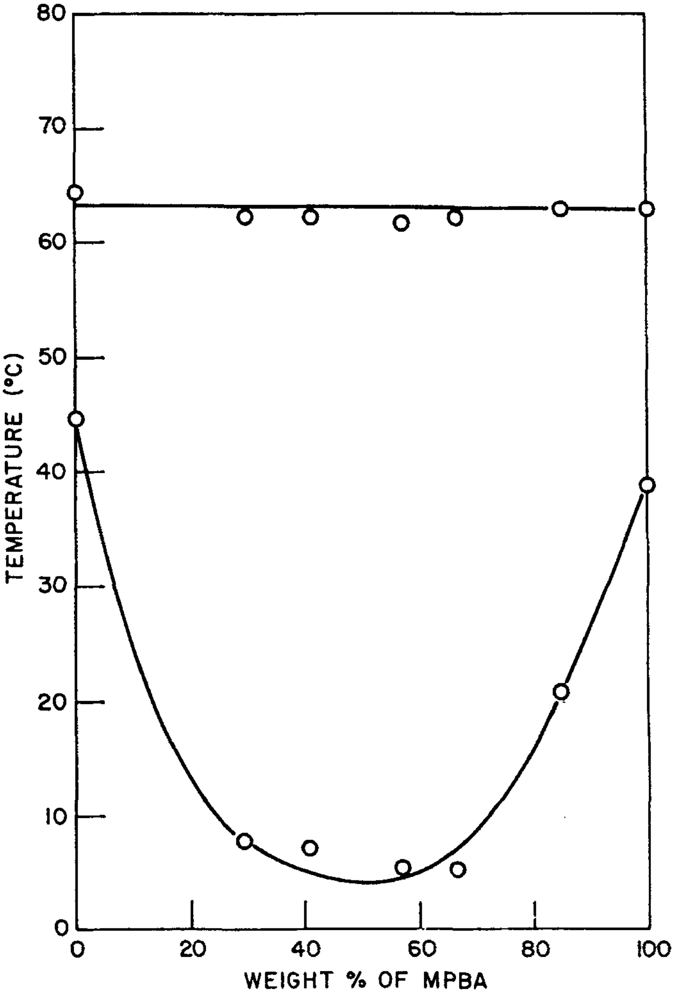


Figure 2. Phase diagram of the system OHMBBA–MPBA. Upper curve, nematic–isotropic transition; lower curve, solid–nematic transition. 100% values by microscopic determination of m.p.; binary values by DSC determination.

Binary Phase Diagrams: The binary phase diagrams of OHMBBA–EBBA is given in Fig. 1, and that of OHMBBA–MPBA in Fig. 2. Both systems show nematic behavior over the entire composition range; the former showing a maximum temperature range of 7–67° at approximately 50/50 wt %; the latter showing a temperature range of 5–62° at approximately 40/60 wt %. A third system examined was a 50/50 wt % mixture of OHMBBA with "Nematic Phase V";[3] this binary has a nematic range of $< -20°$ to 70°, but the complete phase diagram has not as yet been determined.

Electro-optic Effects: The 50–50 binary of OHMBBA and EBBA was studied as described previously[1] for determination of its dynamic scattering characteristics. The stability of this binary is better than that found in ordinary anils; storage in air of an unsealed 12.5 μ sample between tin oxide electrodes for a period of 1 month leads to no change in the electro-optic characteristics. Response to voltage pulses seems to be independent of the history of the sample. Threshold voltages for 60 Hz ac are approximately 9 V, dc approximately 4 V on a 12.5 μ sample. For comparison, MBBA has the same ac threshold, but approximately 6 V dc threshold. dc rise times and decay times are less than 50 msec.

3. Conclusion

The effect of *o*-hydroxy substitution on anil type nematic liquid crystals in general raises the temperatures of both the solid-nematic and nematic–isotropic transitions. *m*-Alkoxy substituted analogs and compounds not containing an alkoxy group do not show a mesophase. Studies on binary systems indicate that broad temperature range systems can be found involving mixtures of the *o*-hydroxy compounds with anils or azoxy compounds. Dynamic scattering studies indicate the system to be potentially useful in display devices. Stability of the mixtures appears greater than those for the non-substituted anils alone; hydrogen bonding both inter- and intramolecularly may be involved.

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REFERENCES

1. Teucher, I., Paleos, C. M., and Labes, M. M., *Mol. Cryst. and Liq. Cryst.* **11**, 187 (1970).
2. Zemplen, G., Farkas, L. and Sattler, T., *Acta Chim. Hung.* **22**, 449 (1960).
3. Nematic Phase V is an azoxybenzene type liquid crystal manufactured by E. Merck, Darmstadt, Germany, having a nematic range of -5 to 75°.