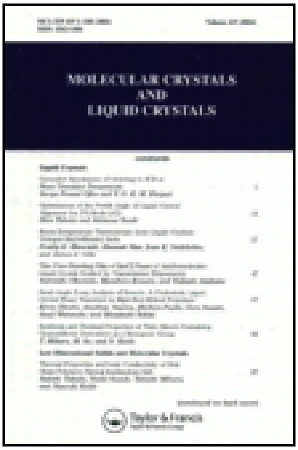

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Phase Transitions in Mesomorphic Benzylideneanilines†

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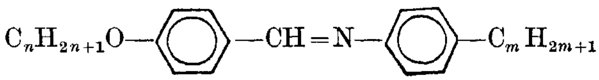
We have synthesized[1] 35 compounds of structural formula



where n and m take on values from 1 to 7 and 4 to 8 respectively.[2] We have studied the phase behavior and identified many of the mesomorphic phases of these compounds by means of differential scanning calorimetry[3] (DSC) and thermal microscopy[4] (TM).

The results of this work are summarized in Table 1 where transition temperatures of the various phases are indicated. The line notation of Verbit[5] is used except that smectic phase classifications are sometimes also shown. In most cases transitions were detected both calorimetrically and microscopically, but the more accurate temperatures from TM are quoted.[6] In certain instances transition temperatures were too low for use of TM; for these DSC temperatures are given. No solid-solid transition data are given.

Although smectic types A, B, and C are indicated in Table 1, the identification of smectic C is only tentative. However, the evidence favoring our assignment of the C classification is considerable: similarity of textures to those of smectic C in the literature,[7] small latent heat L of transition to the A phase,[8] and temperature position between the B and A phases. However, the extreme smallness of L (in some cases essentially undetectable), a few doubts about the textures, and the apparent gradualness of the $C \rightarrow A$ transition

† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

TABLE 1 Mesomorphic Transition Temperatures†

Compound	Transition Temperatures (°C)
10.4	K 20.9 N, 45.9 I
20.4	K 35.3 N, 79.0 I
30.4	K 41.1 N, 55.7 I (23.3 S_1[S_B])
40.4	K 8‡ S_3, 41.0 S_2[S_B], 45.2 S_1[S_A], 45.7 N, 74.7 I
50.4	K 12‡ S_2[S_B], 52.1 S_1[S_A], 52.4 N, 69.0 I
60.4	K 10‡ S_3?, 55.4 S_2[S_B], 58.2 S_1[S_A], 69.2 N, 77.0 I
70.4	K 32.2 S_3[S_B], 63.3 S_2[S_C?], 64.8 S_1[S_A], 74.1 N, 76.2 I
10.5	K 39.7 N, 62.8 I
20.5	K 63.3 N, 90.4 I
30.5	K 32.7 N, 71.1 I (23.6 S_1[S_B])
40.5	K 28 S_2[Mosaic], 41.5 S_1[Mosaic], 44.4 N, 84.6 I (30 S_3?)
50.5	K 29 S_4, 46 S_3[S_B], 48 S_2[S_C?], 52 S_1[S_A], 53.6 N, 77.5 I
60.5	K 40 S_3, 45.2 S_2[S_B], 61.6 S_1[S_A], 75.2 N, 85.2 I
70.5	K 23‡ S_4, 58.0 S_3[S_B], 64.4 S_2[S_C?], 68.3 S_1[S_A], 79.6 N, 83.2 I
10.6	K 35.3 N, 53.7 I
20.6	K 39.6 N, 80.2 I
30.6	K 40.7 N, 62.8 I (19.8 S_1[S_B])
40.6	K 26‡ S_2[S_B], 47.3 S_1[S_A], 54.7 N, 76.9 I
50.6	K 36 S_5, 40.8 S_4, 43.4 S_3[S_B], 51.0 S_2[S_C?], 52.8 S_1[S_A], 61.4 N, 73.0 I
60.6	K 15‡ S_3, 35 S_2[S_B], 62.9 S_1[S_A], 77.0 N, 80.7 I
70.6	K 40.4 S_3[S_B], 66.9 S_2[S_C?], 69.7 S_1[S_A], 80.2 I
10.7	K 27.3 N, 62.8 I
20.7	K 52.5 N, 86.2 I
30.7	K 30.6 N, 70.0 I (20.0 S_1[S_B])
40.7	K 20 S_3, 29 S_2[S_B], 48.8 S_1[S_A], 56.5 N, 83.3 I
50.7	K 29.5 S_4, 37.3 S_3[S_B], 52.1 S_2[S_C?], 55.4 S_1[S_A], 64.0 N, 78.0 I
60.7	K 27 S_2[S_B], 66.0 S_1[S_A], 81.3 N, 85.3 I
70.7	K 33 S_4, 55 S_3[S_B], 69.0 S_2[S_C?], 72.0 S_1[S_A], 83.7 N, 84.0 I
10.8	K 49.3 N, 58.6 I
20.8	K 47.6 N, 80.6 I
30.8	K 38.9 N, 65.1 I (19.4 S_1)
40.8	K 33 S_2[S_B], 49.5 S_1[S_A], 63.7 N, 79.0 I
50.8	K 43.2 S_2[S_B], 53.6 S_1[S_A], 67.2 N, 74.6 I
60.8	K 29 S_2[S_B], 66.3 S_1[S_A], 81.7 N, 82.5 I
70.8	K 48.1 S_2[S_B], 69.7 S_1[S_A], 82.8 I

† Linear notation of Verbit (Ref. 5).
‡ Temperature from DSC.
? Questionable phase.
Symbols in [ ] indicate smectic texture from TM.

have led us to make the assignment contingent upon further work we have undertaken.[9] A subsequent paper will deal with this subject, the other smectic and solid phases, and also the latent heats and transition entropies.

A few further comments are in order. Some of the mesomorphic benzylideneanilines of this series have been studied by several other workers.[10–14] Where comparison is possible, agreement of our work with theirs is rather good. However, Flannery and Haas[11] did not detect the smectic phase which we found between 45.2° and 45.7 °C for compound 40·4. Further, Fishel and Hsu[12] report a monotropic smectic phase for 30·5 but not for their other propoxy compounds. Dietrich and Steiger[14] did not report the lower temperature phases observed by us in the series of compounds where the alkyl group was n-butyl.

Some generalizations are apparent from our data. (1) The nematic $\rightarrow$ isotropic transition temperatures show a pronounced even/odd effect with both n and m. (2) The methoxy and ethoxy compounds show only nematic mesophases. (3) The propoxy compounds all show a monotropic smectic phase. (4) The supposed smectic C phase exists only in compounds with $n = 5$ and 7 (but not in all of them). (5) Compounds 70·6 and 70·8 are the only ones lacking a nematic phase. (6) Compound 40·5 shows two mosaic textures. (7) The multiplicity of smectic phases is greatest for $n > 3$ and $m < 8$.

Note added in proof

(1) On the basis of recent work, the assignment of the several smectic C phases may not be regarded as rather firm. (2) The assignment of the smectic B label to the monotropic smectic phases of the propoxy compounds is tentative, being based solely on their mosaic texture. (3) We wish to point out the existence of an interesting phenomenon at the $A \leftrightarrow B$ and $C \leftrightarrow B$ transition temperatures when fan textures are involved in both phases. The phenomenon, which we call "transition bars", consists of alternate bands of A and B or C and B smectic phase material, producing a striped fan appearance *only* at the transition temperature. This phenomenon will be discussed more fully in a subsequent paper.

REFERENCES

1. Preparation and purification methods will be described in a subsequent paper. Purity and structure were verified by gas chromatography, elemental analysis, and nuclear magnetic resonance.

2. In our notation the compounds are designated by nO·m where the symbol "O" is included to differentiate clearly between alkoxy and alkyl groups.
3. DSC was performed on a Perkin–Elmer DSC1B instrument.
4. Liquid crystal textures were observed using a Leitz Wetzlar Dialux–Pol polarizing microscope and a Mettler FP52 micro-furnace for sample temperature control.
5. Verbit, L., *Mol. Cryst. and Liq. Cryst.* **15,** 89 (1971).
6. Temperature accuracy is usually ±0.1 °C from TM, but in a few cases may be ±0.5 °C.
7. Sackmann, H. and Demus, D., *Mol. Cryst.* **2,** 81 (1966). Arnold, H., Demus, D. and Sackmann, H., *Z. Phys. Chem.* (Leipzig) **222,** 15 (1963).
8. Arnold, H., *Mol. Cryst.* **2,** 63 (1966); Demus, D., Diele, S., Klapperstück, M., Link, V. and Zaschke, H., *Mol. Cryst. and Liq. Cryst.* **15,** 161 (1971).
9. Arora, S. L., Taylor, T. R., Fergason, J. L. and Saupe, A., *J. Amer. Chem. Soc.* **91,** 3671 (1969), point out cases of a texture comparable to but perhaps not identical to S_C.
10. Kelker, H. and Scheurle, B., *Angew. Chem. Internat. Ed.* **8,** 884 (1969); Kelker, H., Scheurle, B., Hatz, R. and Bartsch, W., *Angew. Chem. Internat. Ed.* **9,** 962 (1970).
11. Flannery, J. B., Jr. and Haas, W., *J. Phys. Chem.* **74,** 3611 (1970).
12. Fishel, D. L. and Hsu, Y. Y., *J. Chem. Soc.* (D), **1971,** 1157.
13. Knaak, L. E., Rosenberg H. M. and Servé, M. P., *Mol. Cryst. and Liq. Cryst.* (in press).
14. Dietrich, H. J. and Steiger, E. L., *Mol. Cryst. and Liq. Cryst.*, **16,** 263 (1972). This paper was published after the present paper had been submitted for publication. Other benzylideneanilines have been studied by Murase, K., *Bull. Chem. Soc. Japan* **45,** 1772 (1972).