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EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM 8.[1] A NEW SERIES OF TRIFLUOROMETHYL LIQUID CRYSTALS

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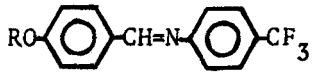
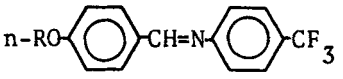
A new series of trifluoromethyl liquid crystals, the 4-n-alkoxybenzylidene-4'-trifluoromethylanilines, has been synthesized. All members of the series with three carbons or more in the alkoxy chain are enantiotropic smectics. There is an odd:even effect in the smectic-isotropic transition temperatures. The smectic phase is of the B type. Members of this series strongly promote enhanced smectic A phases in many binary mesophase systems.

We[2] have recently reported the effectiveness of 4-n-decyloxybenzylidene-4'-trifluoromethylaniline, 1, in promoting enhanced smectic A behavior in binary liquid crystals. This non-linear thermal behavior in mixed systems is quite intriguing in that, 1, possesses no smectic A phase itself. In an effort to further investigate trifluoromethyl as a terminal substituent we have synthesized members of the homologous series 4-n-alkoxybenzylidene-4'-trifluoromethylaniline shown below.



1

These compounds were prepared by condensing 4-trifluoromethylaniline with an equimolar amount of the appropriate 4-n-alkoxybenzaldehyde in absolute ethanol. The amine and aldehydes (C_1-C_8) were purchased commercially. The C_{10} and C_{12} aldehydes were prepared after the method of Gray.[3] The reaction mixture was stirred at room temperature for 24 hours after which the solution was concentrated under reduced pressure. The product was collected as a solid crystalline precipitate. Three or four recrystallizations from absolute ethanol afforded the pure product. Infrared and nuclear magnetic resonance spectra were obtained on all products. Elemental (combustion) analyses were obtained for



R	K↔I	K↔S	S↔I
1	90[a]	-----	-----
2	107	-----	-----
3	---	87.5[b]	90.0
4	---	76.0	89.0
5	---	61.0	84.0
6	---	72.0[c]	84.5[c]
7	---	54.5	81.0
8	---	57.0	81.5
10	---	67.0[d]	77.5[d]
12	---	57.0	75.5

TABLE 1. (a) This compound has also been reported[4] to be non-mesomorphic. (b) Undergoes a solid-solid transition at 34°. (c) This compound has been previously reported[5] to have a K↔I temperature of 84.5°C. (d) reference 2.

several randomly selected members of the series. All methods indicated a highly purified product.

Table 1 contains transition temperatures for this series. Temperatures are in degrees Celsius and were determined using hot-stage, polarized-light microscopy. We used dif-

FIGURE 1. Photomicrograph of 4-hexyloxybenzylidene -4'-trifluoromethylaniline at 76°C.

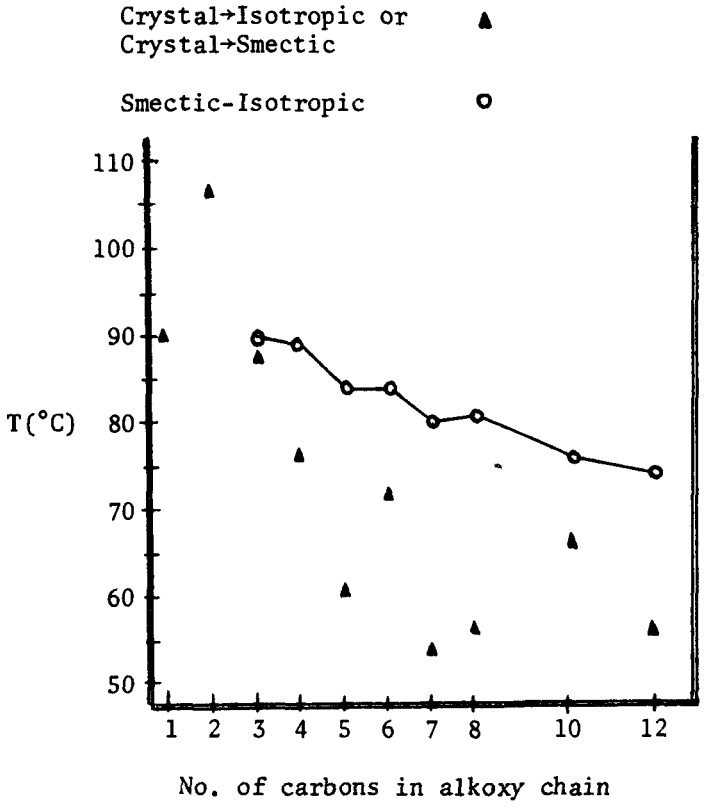


FIGURE 2. Plot of transition temperatures vs. alkoxy chain length.

ferential scanning calorimetry as a check on several of the compounds. The agreement of the two methods was excellent. The optical texture of these compounds seen between crossed polarizers is most unusual. The smectic phase often appears from the isotropic liquid as rods with intermittent homeotropic areas. It can however be made to take on a mosaic pattern. A photomicrograph (100X) of the C_6 compound in its smectic phase at 76° is provided above in Figure 1. The smectic phase is somewhat viscous, but nonetheless fluid. We were for a while uncertain as to the appropriate smectic classification for this series but have recently learned that the C_{10} compound is miscible with an authentic smectic B sample.[6]

Figure 2 shows graphically the relationship between

alkoxy chain length and transition temperatures. A familiar odd-even alternation of mesophase-isotropic temperatures is found in this series. The members of this series often strongly promote enhanced smectic A phases in mixed mesophase systems. This aspect of their behavior is currently under study.

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References

1. For part 7 in this series see A. C. Griffin, R. F. Fisher and Stephen J. Havens, submitted to J. Org. Chem.
2. A. C. Griffin, T. R. Britt, N. W. Buckley, R. F. Fisher, S. J. Havens, and D. W. Goodman, "Liquid Crystals and Ordered Fluids, Vol. 3," J. F. Johnson and R. S. Porter, eds., Plenum Press, N.Y., N.Y., (1978), p. 61.
3. G. W. Gray and B. Jones, J. Chem. Soc., 1467 (1954).
4. P. M. Maginnity and J. L. Eisenmann, J. Amer. Chem. Soc., 74, 6119 (1952).
5 D. Coates and G. W. Gray, J. Chem. Soc., Perkin II, 300 (1976).
6. J.-C. Dubois, private communication.