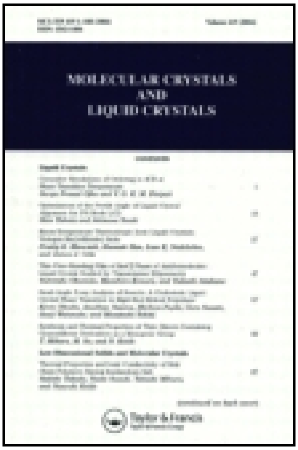

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Effect of Molecular Structure on Mesomorphism. Two Series of Novel Methylene-Bridged Liquid Crystals

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EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM. TWO SERIES OF NOVEL METHYLENE-BRIDGED LIQUID CRYSTALS

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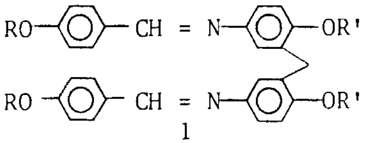
Two series of novel methylene-bridged liquid crystals have been prepared. These molecules are quite wide and as a result only higher homologues exhibit mesomorphism. The enantiotropic mesophases are of the smectic C type. Trends in thermal behavior of these two series indicate that even higher homologues should possess extended smectic ranges.

INTRODUCTION

The length: breadth ratio of most liquid crystalline molecules is quite large. This was recognized some time ago by Vorlander[1] and further delineated by Bernal[2] as a distinguishing structural characteristic of many compounds possessing a mesophase. We wish to report the synthesis and physical properties of a novel class of di-Schiff's base liquid crystals in which two identical molecules (closely related to mesomorphic series described by Weygand[3], van der Veen[4], and Dave[5]) are joined by one saturated carbon atom. The molecular structure is shown below.

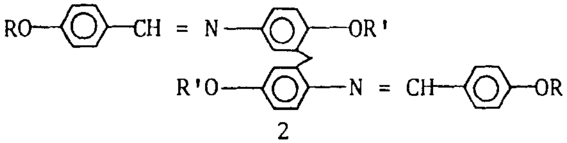


1

R = C_8, C_{10}
R'= C_6, C_7, C_8, C_9, C_{10}

all alkyl chains are unbranched

It is possible to envision a rotation about one of the methano-aryl C-C bonds to produce the conformer 2 below.

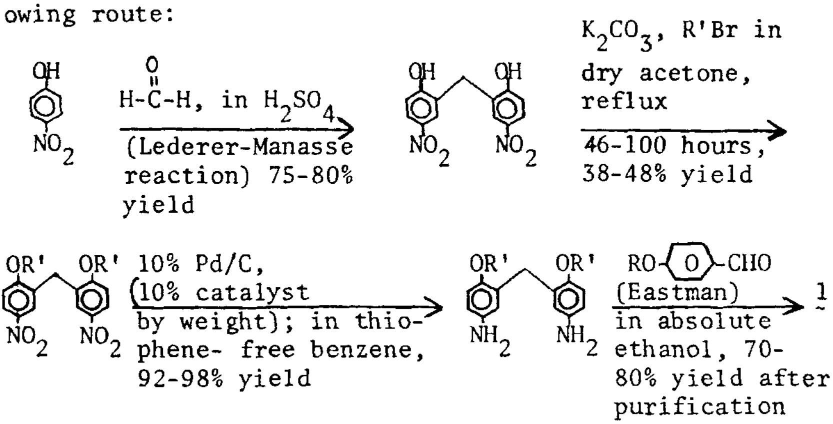


2

In this conformation the molecular dimensions are quite different from those of 1. Examination of Dreiding Stereo-models reveals that conformation 2 is unfavorable due to steric crowding in the center of the molecule. Work is in progress however to determine which conformation is dominant in the mesophase.

EXPERIMENTAL DATA

Compounds for this study were synthesized by the following route:



Structures for the final products, 1, were deduced by method of preparation, elemental analysis (combustion), thin layer chromatography, and spectroscopy. All data are consistent with a highly pure di-Schiff's base product. Each compound was triply recrystallized from a 50-50 mixture of ethanol and chloroform.

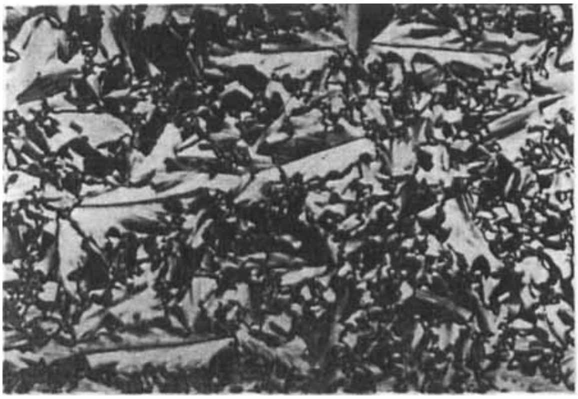
Transition temperatures were obtained by hot stage polarizing microscopy; by heating the sample in a glass capillary in a Thomas-Hoover melting point apparatus; and by Differential Scanning Calorimetry (Perkin-Elmer 1B). Agreement of all three methods was excellent. Transition temperatures from the calibrated DSC instrument are presented in Table 1. The photograph was taken at 200X using a Polaroid camera attached to the polarizing microscope.

	R - R'	$T_{C \to S}$[a]	$T_{S \to I}$[a]	$T_{C \to I}$[a]
Series A	8 - 6			137.7
	8 - 7		(114.0)	126.3
	8 - 8	121.0	125.1	
	8 - 9	121.1	130.1	
	8 - 10	117.6	133.3	
Series B	10 - 6			130.3[b]
	10 - 7		(112.0)	119.1
	10 - 8	110.2	123.8	
	10 - 9	112.1	127.9	
	10 - 10	113.5	131.5	

(a) transition temperatures in °C, values in parentheses represent monotropic transitions.

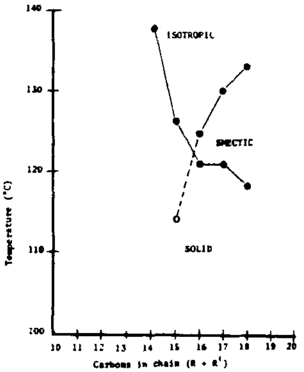
(b) this compound exhibited a crystal-crystal transition at 49.1°.

Textures for all enantiotropic mesophases were of the smectic type. The photograph below shows the texture of compound 10-8 which is characteristic for the enantiotropic smectics.

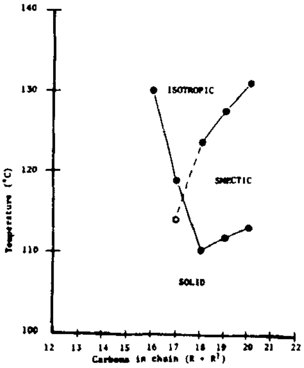


Miscibility studies indicate that these enantiotropic smectics are of the smectic C type. The textures of compounds 8-7 and 10-7 are of the Schlieren type and are identical. It has not yet been ascertained whether these monotropic mesophases are smectic. Enthalpies of mesophase-isotropic transitions are all quite large; in some cases as large as the crystal-mesophase enthalpies. This is taken as additional evidence of smectic mesophases.

Graphs 1 and 2 show plots of transition temperature vs. alkoxyl chain length for 1, Series A and B.



Graph 1. Data depicting transition temperature as a function of chain length in series A compounds. The symbol ● represents enantiotropic transitions; ○ represents a monotropic transition.



Graph 2. Data depicting transition temperature as a function of chain length in series B compounds. The symbol ● represents enantiotropic transitions; ○ represents a monotropic transition.

DISCUSSION

Data in graphs 1 and 2 show similar features for both series A and series B. Melting temperatures, C→S and C→I, decrease (or in some cases increase, but only slightly) with increasing alkoxyl chain length. Smectic→isotropic temperatures on the other hand increase with increasing alkoxyl chain length. The C→S and S→I curves intersect in similar fashion for both series A and B. Each series has one compound with a monotropic mesophase followed by, as one increases molecular length, enantiotropic smectic phases having enhanced temperature existence ranges with increasing alkoxyl chain length. It appears from these data that compounds in both series A and series B which have longer alkoxyl chains than those presented here should have even wider smectic ranges. It is interesting to note that the minimum molecular length required to produce any mesophase for these compounds is quite larger than that for most mesomorphic compounds.[6] We take this as additional evidence of the importance of the length:breadth ratio in mesogenic structures. Our two series of "wide" molecules could not attain a stable mesophase until the molecular structure was sufficiently increased in length by quite long alkoxyl tails. By the time a stable mesophase became possible the alkoxyl chain was long enough to preclude a nematic phase; only the smectic was seen.

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REFERENCES

1. D. Vorlander, "Chemische Kristallographic der Flussigkeiten", Akademische Verlagsgellschaft, Leipzig (1924).
2. J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933).
3. C. Weygand and R. Gabler, *J. Prakt. Chem.*, **151**, 215 (1938).
4. J. van der Veen and A. H. Grobben, *Mol. Cryst. Liq. Cryst.*, **15**, 239 (1971).
5. J. S. Dave and P. R. Patel, *Mol. Cryst.*, **2**, 103 (1966).
6. See for example the compilations of W. Kast in "Landolt-Bornstein", Sixth Edition, Springer, Berlin, 1960, Vol. II, Part 2a, pp. 266-335.