THERMOTROPIC LIQUID CRYSTALS VI. THE PREPARATION AND MESOPHASE PROPERTIES OF ASYMMETRICALLY 4,4'-DISUBSTITUTED PHENYL BENZOATES

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We have undertaken preparation of complete series of 4,4'-disubstituted phenyl benzoates, 1, and their thermal characterization to test the effect of terminal alkyl group branching at various positions with respect to the aromatic ring. We also wished to establish which of these compounds would be most useful in more detailed physical studies of structure and conformation 1-3. Some members of these series for which substituents are normal alkyl and/or alkoxy groups have been reported by other investigators 4,5.

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1, X = \text{alkyl or alkoxy group}
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2, X = \text{alkyl or alkoxy group}
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Studies of the effect of molecular structure changes on mesomorphic behavior have been inherent in recent synthetic efforts toward low temperature nematic compounds. These have usually been concerned with alteration of the nature of the central group or with control of relative conformation for the two aromatic rings in systems generally represented by 2,6-12.

Changes in the terminal group structure have been usually limited to variation of electrical nature (substitution of nitrile, halogen, alkoxy, acyl, etc.) or homologation within the normal chain series 13-16. Although branched-chain compounds often melt at lower temperatures than the isomeric normal derivatives, few terminally branched compounds of type 2 have been reported to exhibit mesophase properties. Extensive work on such compounds has
probably been inhibited because of the well established generalization that thermotropic liquid crystals have molecules that are long, rigid, rod-shaped and with no protuberances on the major axis. Only the work reported by Gray is a recent exception to this; his studies have involved branching of the alkyl moiety in benzylidene derivatives of alkyl 4-aminocinnamates. Branching in these compounds is significantly removed from the aromatic ring system that delineates the principal molecular dimensions.

RESULTS:

The synthesis of precursor phenols and benzoic acid derivatives for this study followed well documented procedures with the exception of the preparation of 4-alkylbenzoyl chlorides. These latter compounds were obtained in one step from the corresponding alkylbenzenes by modified Friedel-Crafts acylation with oxalyl chloride. A detailed study of this reaction is reported elsewhere.

A two step synthesis of 4-alkoxyphenols by Williamson alkylation of p-benzyloxyphenol, then hydrogenolysis, has been reported by VanMeter and Klandermann. In our hands this technique worked well; typical overall yields were ~70%. We are inclined, however, to favor the one step procedure we have outlined as somewhat less time consuming for small to medium size batches.

Thermal characterization of the 4,4'-disubstituted phenyl benzoates was accomplished by hot-stage microscopy and confirmed by DTA using well-established techniques. Thermal data are listed in Tables 1, 2, and 3 and are illustrated in plots versus carbon number, Figures 1 - 4.

We are in essential agreement with most data previously reported for several of the normal members of these series. Discrepancies are footnoted in Table 1 for 4-methoxylphenyl 4'-n-butylbenzoate (Code: 10-4) and for compounds 40-4, 70-4 and 4-04. Generally the phenyl benzoate esters have relatively low melting points (<100°C) and there is significant occurrence of

We have found it convenient to use a simple alphanumeric code for identification of 4,4'-disubstituted phenyl benzoates with terminal alkoxy and alkyl groups. As an example: 4-n-propylphenyl 4'-sec-butylbenzoate is coded: 3-031(1); the standard script Arabic numerals refer to the length of the longest carbon chain as a 4- or 4'-substituent and superscript numbers refer to position and size (in parentheses) of a branched carbon chain on the main chain of carbon atoms. Oxygen position is indicated by "0"; the dash is the phenyl benzoate moiety.