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THERMAL PROPERTIES OF 4-ALKYL-4'-CYANOTOLANES: A NEW SERIES OF LIQUID CRYSTALS*, **

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ABSTRACT

The thermal properties of a new series of liquid crystals, the 4-alkyl-4'-cyanotolanes, were measured. The DuPont 990 thermal analyser was used to measure the temperatures and heats of the transitions. The entropy changes in both the crystal to mesophase and mesophase to isotropic liquid transitions are found to be a function of the length of the alkyl chain on the molecules.

INTRODUCTION

A new series of compounds, the 4-alkyl-4'-cyanotolanes was prepared from the corresponding stilbenes and found to have liquid crystalline properties. The preparative details, and the microscopical investigations of these compounds are to be published[1]. The purity of these compounds was determined by combustion analysis, thin-layer chromatography and gas chromatography. The molecular structure was verified by 100 MHz NMR spectroscopy. This paper presents the thermodynamic properties obtained by differential thermal analysis. The general formula for these molecules is shown in Fig. 1 in which R represents normal alkyl groups from C_5 to C_{11}.

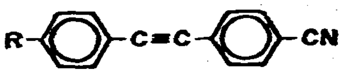

Fig. 1. General formula for tolanes.

EXPERIMENTAL

The measurements were made with a DUPONT 990 thermal analyser equipped with a two-stage mechanical cooling accessory using a DSC cell. The thermograms were run from −40 °C to about 15 °C above the mesophase to the

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isotropic transition temperature of each individual as reported by Cox and Clecak[1]. The DTA had been calibrated from −40 to 150°C using a sapphire standard. Integration of the curves was by cutting and weighing, and three or more repetitive values were measured for each transition.

DISCUSSION

The transitions found in this series are quite different from those which were encountered in the stilbene series[2]. Figure 2 shows that four of the seven members are monotropic, that is they melt directly to an isotropic liquid and the liquid crystal phase is only observable on supercooling. It is also noted that four of the members of the series, the C_7, C_9, C_{10} and C_{11} show polymorphism in the solid phase. These observations were made using the polarizing microscope and due to nucleation of one of the solid phases were not always observed when the sample was run in the DTA. The compounds from C_5 through C_9 all show only one liquid crystal phase, the nematic. The C_{10} has rather complicated thermal

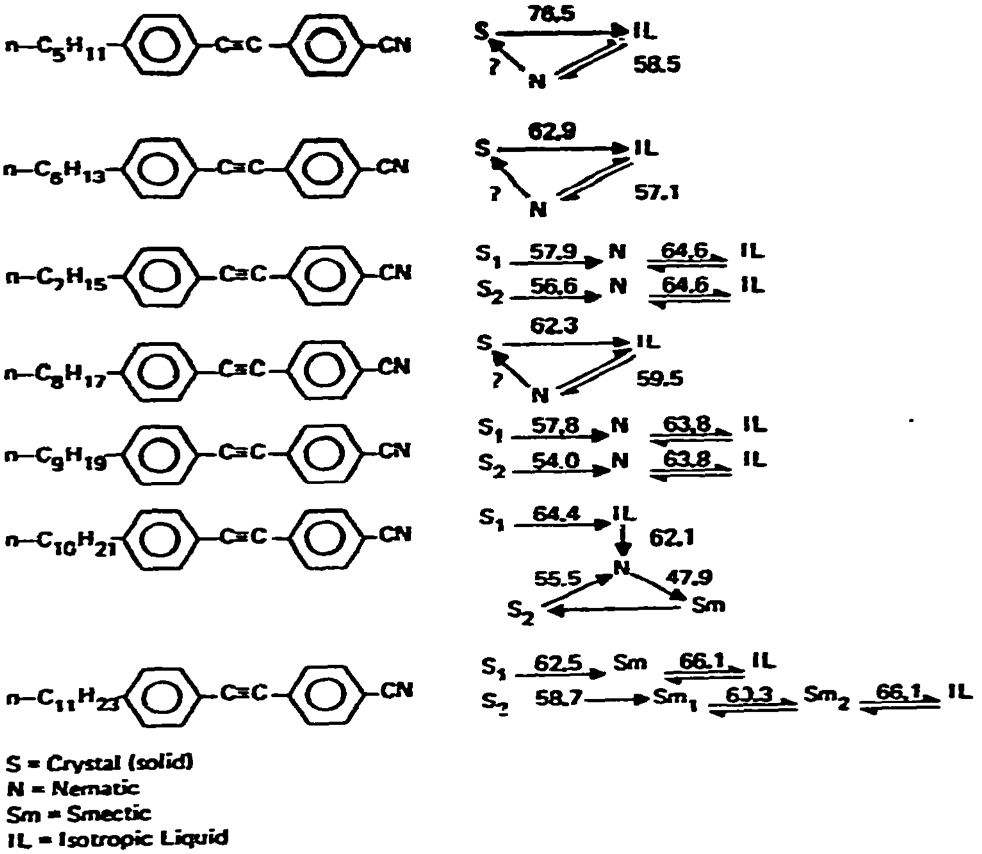

Fig. 2. Transition temperatures for the 4-alkyl-4'-cyanotolanes.

properties, from solid I it melt to the isotropic liquid directly, supercooling reveals first a nematic liquid, then a smectic, which finally solidifies to a solid II. This solid melts to the nematic liquid. Thus it is monotropic only with respect to the smectic mesophase. The C_{11} melts from a solid I to a smectic at 62.5 °C and then to the isotropic liquid at 66.1 °C. On solidification a solid II is formed which melts lower, at 58.7 °C, revealing a smectic I phase which is monotropic to solid I as it has a transition to smectic II at 60.3 °C. The C_7 and C_9 members of the series also show solid polymorphism, solidifying to different solids after melting than those that were obtained on recrystallization of the compound from a solvent. In each of these latter cases solid I and solid II simply melt at different temperatures to identical nematic liquids.

A comparison of these compounds to the corresponding biphenyls and stilbenes is interesting. It would be expected that the transition temperatures and the types of mesophase encountered would be similar for corresponding members within each of these series. They have very close molecular geometries, particularly the biphenyls and tolanes, and if the appearance of the smectic phase is in any sense a function of the length to breadth ratio of the molecules one would expect the tolanes to show a smectic phase somewhat before the biphenyls. It is surprising therefore to see a smectic in the C_8 member of the biphenyl series and not until the C_{10} in the tolanes. It is possible of course that there are smectic

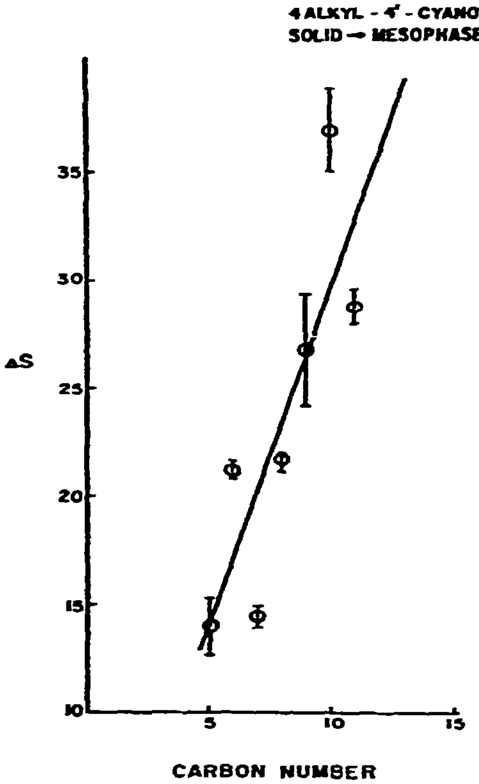

Fig. 3. Carbon number in the alkyl chain vs. ΔS for the solid to mesophase transition.

phases in the C_8 and C_9 tolane compounds which simply are masked by the crystalline solid. These, if they exist, are as yet undetected.

We feel that it is more instructive to compare changes in entropy when investigating the molecular order of a liquid crystal system. Transition temperatures or enthalpies alone have been shown to be potentially misleading[4]. Figure 3 is a plot of the entropy change for the solid to mesophase transition against the number of carbon atoms in the alkyl chain. There is a somewhat scattered but linear relationship, which shows that the magnitude of the change in order is determined by the length of the alkyl chain in the molecule. This relationship is somewhat surprising when one considers the solid polymorphism found in this series of compounds.

An interesting comparison was made in Fig. 4 in which the biphenyls, the stilbenes and the tolanes are on the same graph and we have plotted the carbon number of each versus the entropy change from the crystal to the mesophase. The slope of the best line for each of these series is very close and statistically they are probably identical. The entropy change for each is therefore a function of the length of the hydrocarbon tail. The line for the stilbenes is below that of

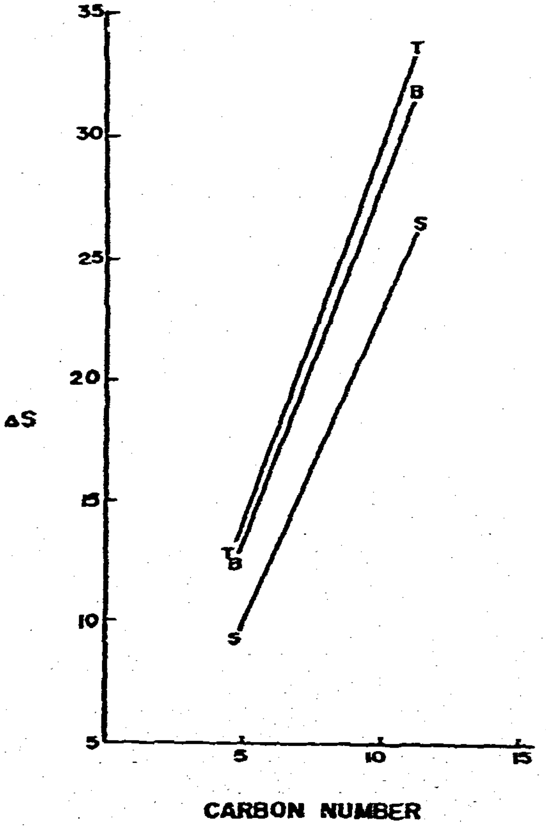

Fig. 4. Carbon number in the alkyl chain vs. ΔS for the solid to mesophase transitions for the biphenyls, stilbenes and tolanes.

the other two indicating a lower overall change for this series. Thus, the slope of the line appears to be determined by the tail while its relative position derives from the central portion of the molecule.

Figures 5, 6, and 7 in which the entropy change versus carbon number in going from the mesophase to the isotropic liquid is plotted for the stilbenes, tolanes and biphenyls all exhibit a minimum at the C_6 compound. This indicates that the order in the nematic system for both cases is governed by the tail length and that the six carbon tail is peculiar in that there is the least order in this member for each series.

It is evident that the entropic changes in the transitions even from the crystalline solid are for the most part governed by the length of the hydrocarbon tail. The magnitude of the entropy changes from the mesophase to the isotropic liquid appears to be about the same for each series. This is a little unexpected when the increased rigidity of the molecules on going from the biphenyl to the tolane is considered. One would expect a greater change in order from the mesophase

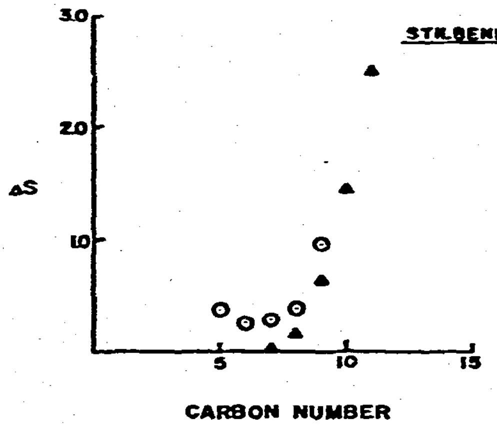

Fig. 5. Carbon number in the alkyl chain vs. ΔS for the mesophase to isotropic transition for the stilbenes.

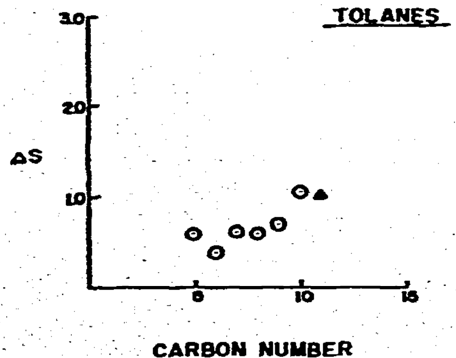

Fig. 6. Carbon number in the alkyl chain vs. ΔS for the mesophase to isotropic transition for the tolanes.

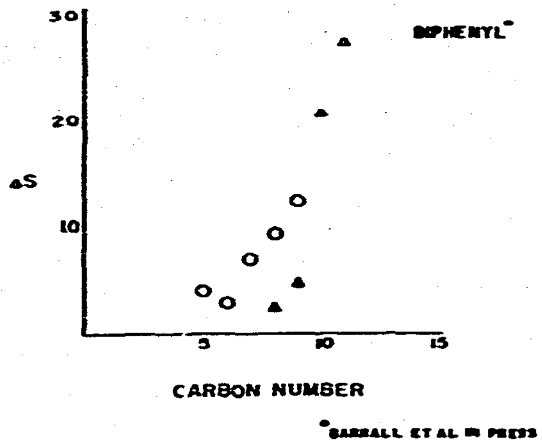

Fig. 7. Carbon number in the alkyl chain vs. ΔS for the mesophase to isotropic transition for the biphenyls.

to isotropic liquid for the tolanes than for the biphenyls. However, this is not observed.

The preparation of these three series of liquid crystals, the biphenyls, the stilbenes and the tolanes has made possible the first study of liquid crystal series in which the structure of the molecules differ only by the multiplicity of the bonds joining the aromatic rings.

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