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THERMAL PROPERTIES OF 4-ALKYL-4′-CYANOSTILBENES: A NEW SERIES OF LIQUID CRYSTAL COMPOUNDS*

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ABSTRACT

The transition heats and temperatures of a series of 4-alkyl-4′-cyanostilbenes were measured with the DuPont 990 thermal analyzer. The entropies of both the solid-to-mesophase and the mesophase-to-isotropic liquid was found to be dependent on the number of carbons in the alkyl chain on the molecule. The entropy change in the nematic-to-smectic transition found in the C_7 member of the series was found to be extremely small.

INTRODUCTION

This paper describes some thermodynamic properties of a new series of liquid crystalline compounds which we have recently prepared[1]. The general formula for these compounds, 4-alkyl-4′-cyanostilbenes, is shown in Fig. 1 in which the R group is varied from a normal C_5 alkyl chain to C_{11}.

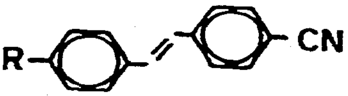

Fig. 1. General formula for stilbenes.

Structural similarities between these compounds and the 4-alkyl-4′-cyanobiphenyls, liquid crystals that have recently been found very useful in the fabrication of electroöptical devices, prompted us to investigate the thermal properties of these new liquid crystals. The single bond which joins the two aromatic rings in the biphenyls is replaced by a *trans* double bond.

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The purity of these materials, a very critical parameter particularly when one is comparing small energy differences in a homologous series of compounds, was determined by thin-layer chromatography, combustion analysis and gas chromatography. The latter could readily detect impurities as low as 0.01 wt. % in which the R group is a different length carbon chain. The conformation of the molecular structure, particularly the absence of *cis* isomers was confirmed by 100 Mz NMR spectrometry.

Preliminary investigation was carried out using polarized light microscopy[1]. We are at present planning to extend this microscopical investigation by means of depolarized light intensity measurements. Differential thermal analysis was performed to complement the microscopic work and is described in this paper. The type of liquid crystal phase present, whether nematic or smectic, can be seen quite readily by inspection of the texture when observed under a polarizing microscope. However, it is much more difficult if one is trying to determine which of the several kinds of smectic is present, and it is often necessary to use the miscibility technique[2] or X-rays. Where a smectic phase is present we have therefore not attempted to identify to which subclass it belongs but have simply labeled it smectic or, if more than one, smectic is observed in a single compound, have arbitrarily labeled them smectic I and II.

EXPERIMENTAL

The instrumentation used in making the DTA measurements was the DuPont 990 thermal analyzer with the DSC cell. The cell was calibrated from −40 to 150°C, and a low temperature dual stage mechanical cooling accessory facilitated the subambient measurements. The transitions were integrated by cutting out and weighing. Three or more repetitive values were measured for each transition.

Weekly calibration runs between −40 and 150°C were made on a sapphire disk. From these runs the cell constant (E) was calculated at each of 6 temperatures from the specific heat of sapphire.

Sample and calibration runs were made at a rate of 5°C min^{-1}. Just prior to the onset of a transition the display was switched to a time base of 0.5 min in.$^{-1}$ to expand the x axis without disturbing the scan rate.

This factor was then used to calculate ΔH in cal g^{-1} for each peak. Individual values were average and conservative confidence limits were constructed for each mean.

Samples were weighed to the nearest 0.02 mg on a Cahn electrobalance and sealed into DuPont hermetic sample pans in air.

Each sample was programmed from −40 to +150°C at a rate of 5°C min^{-1} and then from 150 to −40°C at the same rate. This procedure was repeated after 15 min at −40°C a sufficient number of times to result in 2 similar traces, which were used for calculation of ΔH.

Temperatures were read at the peak of the transition and are in reasonable agreement with results from microscopy. These are shown in Fig. 4.

DISCUSSION

The characterization of series of liquid crystals and the relation between thermal properties and molecular structure has customarily been carried out using only mesophase transition temperatures. Although this has been very profitable in a number of instances a recent paper by Dewar and Griffin[3] has emphasized the lack of correlation between the transition temperatures and the corresponding heats of transition, and points out the importance of the change in entropy. This homologous series exhibits z similar lack of correlation between ΔH and transition temperature, and therefore the entropy change was used as the principle criterion for the changes of order that are taking place within the system.

The entropy changes that take place in going from the crystal to the mesophase will be discussed first. A plot of the number of carbon atoms in the alkyl chain versus entropy change can show some regularity, or as pointed out by Barrall and Johnson in their review of the thermodynamic properties of liquid crystals[4], can present an extremely scattered picture. These authors are of the opinion that one should expect a regular relationship if one can account for all the crystal forms. Figure 2 shows data in which entropy change is plotted against number of carbon atoms in the alkyl chain. The bold line shows the results of this analysis. A standard least squares or regression analysis was performed and even in the worst case the probability of this association occurring by chance alone is < 0.05.

This relationship, although showing some scatter, shows that the order in the system, even in the crystalline solid is dictated by the length of the alkyl chain, the longer the chain the greater the entropy change to the mesophase, and therefore the more highly ordered the crystalline solid. The existence of this correlation is also a good indication that in this series the crystal structures are all of the same type. This was emphasized by omitting the C_{10} member of the series from the plot. It was the only member whose thermogram was complicated by the simultaneous existence of two solids, both of which melted to the same mesophase. The entropy change calculated from this molecule is quite far from the calculated line.

The entropy change found in the C_7 compound on going from the smectic to the nematic mesophase is extremely small and although clearly discernible in the polarizing microscope would probably remain undetected using a less sensitive instrument than the DuPont 990 thermal analyzer. The estimated value of 0.01 e.u. is an order of magnitude smaller than the smectic → cholesteric transition cited by Barrall et al.[5] as one of the smallest entropy changes ever measured.

The Δs versus carbon number plotted in Fig. 3 for the nematic-to-isotropic liquid transition shows a remarkably smooth relation, as does the smectic-to-nematic or isotropic liquid. The nematic-to-isotropic liquid transitions have a definite minimum at C_6, indicating less order in the nematic phase for this molecule than for others in the series. This is in contrast to other series such as the alkoxybenzoic acids[6] in which the entropy change for this transition is essentially constant indicating that the order involved in the nematic phase is independent of the length of the alkyl chain.

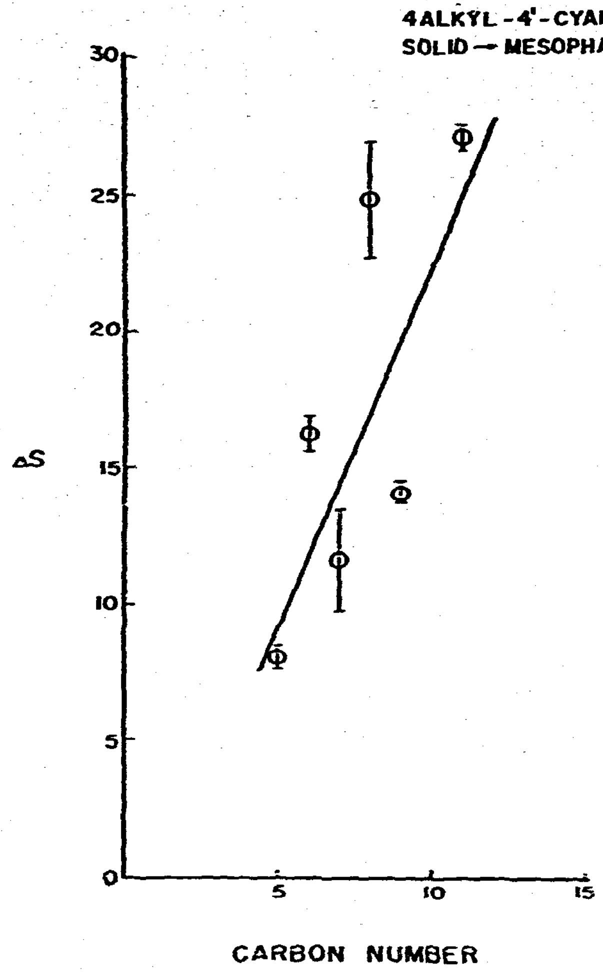


Fig. 2. Carbon number in the alkyl chain vs. Δs for the solid-to-mesophase transition for the stilbenes.

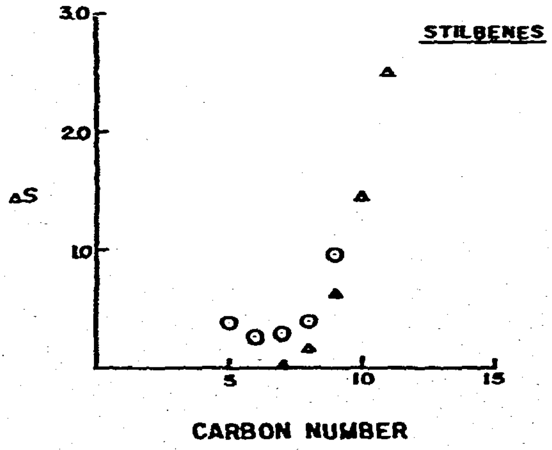
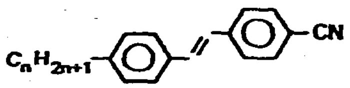


Fig. 3. Carbon number in the alkyl chain vs. Δs for the mesophase to isotropic liquid for the stilbenes. ○, nematic → isotropic liquid; △, smectic → nematic or isotropic liquid.



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5	$S \xrightarrow{55.5°C} N \xrightarrow{101°C} IL$
6	$S \xrightarrow{54.5°C} N \xrightarrow{89.5°C} IL$
8	$S \xrightarrow{61°C} S_m \xrightarrow{62°C} N \xrightarrow{91°C} IL$
8	$S \xrightarrow{52°C} S_{mI} \xrightarrow{57.5°C} S_{mII} \xrightarrow{80°C} N \xrightarrow{89°C} IL$
9	$S \xrightarrow{58°C} S_m \xrightarrow{95°C} N \xrightarrow{96.5°C} IL$
10	$S \xrightarrow{47.8°C} S_m \xrightarrow{95.8°C} IL$

S = Crystal (Solid)
N = Nematic
IL = Isotropic Liquid
Sm = Smectic

Fig. 4. Melting and liquid crystal transition temperatures of *trans*-4-alkyl-4'-cyanostilbenes.

The plot of the Δs versus carbon number in going to the nematic or isotropic liquid from the smectic phase shows relatively small entropy changes when the transition is to the nematic phase. These changes increase rapidly, as would be anticipated, above C_9 where the transition is directly to the isotropic liquid.

In summary, a new series of liquid crystalline compounds were prepared and their heats and transition temperatures measured by DTA. It was shown that the order in the system seems to be a function of the length of the hydrocarbon tail on the molecule. The types of mesophase and the place within the series where they appear are not unusual and correspond to other liquid crystal series which have been studied. The very small entropy change found in the C_7 member of the series for the smectic–nematic transition is intriguing in that it indicates either a more highly structured nematic than is usual or a less ordered smectic.

REFERENCES

1 R. J. Cox and N. J. Clecak, to be published.
2 H. Sackmann and D. Demus, *Mol. Cryst. Liquid Cryst.*, 21 (1973) 239.
3 M. J. S. Dewar and A. C. Griffin, *J. Am. Chem. Soc.*, 97 (1975) 6662.
4 E. M. Barrall II and J. F. Johnson, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Halsted Press, a Division of John Wiley and Son, New York, 1974, p. 260.
5 E. M. Barrall II, R. J. Cox, A. Doelman, N. J. Clecak, J. A. Logan and A. R. Gregges, *I.B.M. Research Report RJ 1781.*
6 E. M. Barrall II and J. F. Johnson, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Halsted Press, a Division of John Wiley and Son, New York, 1974, p. 266.