Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

An Intercomparison of Temperatures and Heats of Transition for Esters of Cholesterol

G. Jerry Davis [a b], Roger S. Porter [a] & Edward M. Barral II [c]

[a] Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, 01002

[b] Stauffer Chemical Company, Dobbs Ferry, New York

[c] IBM Corporation, San Jose, California, 95114

Version of record first published: 28 Mar 2007.

To cite this article: G. Jerry Davis , Roger S. Porter & Edward M. Barral II (1970): An Intercomparison of Temperatures and Heats of Transition for Esters of Cholesterol, Molecular Crystals and Liquid Crystals, 11:4, 319-330

To link to this article: http://dx.doi.org/10.1080/15421407008083524

Molecular Crystals and Liquid Crystals. 1970. Vol. 11, pp. 319–330

Printed in Great Britain

An Intercomparison of Temperatures and Heats of Transition for Esters of Cholesterol

G. JERRY DAVIS† and ROGER S. PORTER

Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

and

EDWARD M. BARRAL II

IBM Corporation
San Jose, California 95114

Received May 8, 1970; *and in revised form September* 21, 1970

Abstract—Thermodynamic information on the aliphatic esters of cholesterol has recently been reported in a number of publications. Because of parallel publication, it has not been possible to develop intercomparisons between sets of data by different workers. In addition, new data are presented here on the temperatures and heats of transition for the odd carbon number aliphatic esters from C_{11} to C_{19}. From this composite information, it has been possible to develop new and more complete correlations for each transition concerning entropy changes and odd–even effects as a function of ester molecular weight from the formate to the C_{20} ester.

1. Introduction

The pure esters of cholesterol represent the fundamental molecular series for evaluation of one of the three major types of liquid crystals, the cholesteric mesophase. The properties of this series are important in a myriad of industrial and biological research areas such as in thermography and the formation in atherosclerosis of arterial deposits which contain cholesterol and its esters.

Thermodynamic information on this series has been reported in a series of recent papers.[1–8] Because several of these papers have been in press at the same time,[2–4,7] unfortunately no intercomparison of data has been previously made. In addition, some previously unpub-

† Present address: Stauffer Chemical Company, Dobbs Ferry, New York.

lished results on the higher esters are compared here with the recently published information. All the methods are basically thermal analysis and most of the samples employed have been relatively pure with results apparently independent of ester origin. The comparisons made here are among sets of data belonging to the modern era and cover the first twenty members of the aliphatic ester series. The variety of older data available is inevitably less reliable because the esters were less satisfactorily recovered from materials found in nature. Most of the early studies on esters of cholesterol involved reports of transitional temperatures only. Reviews on the thermodynamic behavior of mesophase transitions have been recently given.[9,10] Virtually no values for heats of transition have appeared until the last five years. Thus this combined consideration of recent data can help evaluate (1) whether there is a break in the heats of transition curve as a function of molecular weight, as suggested by data of one set of workers; (2) whether there is an odd–even effect in heats and temperatures as a function of molecular weight for the ester series; (3) whether the results from different investigators and techniques provide concordant results, particularly where the heats of transition are inordinantly small, as is generally the case for cholesteric–isotropic transitions.

2. Experimental Methods

Before presenting the intercomparison of results, methods of ester purification and analysis should be stated. The majority of samples by all the workers were obtained from commercial supply houses. The number of esters available and their purity has increased markedly in recent years. The earlier work by Barrall *et al.*[1] and the recent study of Sell and Neumann[2] have involved purification by ethanol recrystallization. The new studies of Barrall reported here utilized vacuum sublimation from the mesophase for purification. Gas chromatography has also been used for ester purity evaluation.[3] Recrystallization from *n*-pentanol, a solvent superior to ethanol, has been used for recrystallization purification in another study.[4] In other research,[2] polarization microscopy and DTA (duPont Model 900) at 10 °C/minute heating rates were used for evaluation of transition temperatures. Ennulat[3] has also used 10 °C/minute in

measuring the temperatures and heats of transition for the esters using a Perkin–Elmer DSC-1. Barrall *et al.*,[1] and Davis *et al.*,[4] have used the DSC-1B with the latter utilizing a lower scanning rate of 1.25 °C/minute. Arnold *et al.*[6,7] mainly used DTA.[7]

DSC-1B measurements[4,5] have a greater precision than the values measured with the DSC-1.[3] Using the DSC-1B, heating rates of 1.25 °C/minute rather than 5 or 10 °C/minute were found advisable for esters exhibiting transitions over narrow temperature ranges. This is because the response of the instrument tends to broaden the apparent endothermic peak and because the transitions themselves extend over several degrees. The lower heating rates, however, reduce the instrument response to calorimetric measurements.

3. Results

Table 1 represents a comparison of temperatures and heats of transition data made on an identical sample of the C_{17} ester. Each set of workers made their own evaluation of purity for the identical sample. One method involves a new interpretation of the complete DSC endothermic trace.[11]

Tables 2, 3 and 4 provide transition temperature data determined by thermoanalytical techniques on samples of comparable and high

TABLE 1 *Studies on Identical Sample of Cholesteryl Heptadecanoate*

	Estimated purity and calorimetric values					
	Davis *et al.*, 98.4%			Barrall *et al.*, 98.2%†		
	T °C	*ΔH* Kcal/m	*ΔS* E.U.	*T* °C	*ΔH* Kcal/m	*ΔS* E.U.
Solid → Cholesteric	75.7	14.63	49.9	77.84	14.38	41.6
Cholesteric → Isotropic Liquid	79.8	0.326	0.93	82.4	0.401	1.13
Cholesteric → Isotropic Liquid (Heating SM)	79.7	0.330	0.93	81.7 82.3	0.403	1.13
Smectic → Cholesteric (Heating SM)	75.4	0.376	1.08	77.9	0.484	1.39
Isotropic Liquid → Cholesteric	79.0	0.326	0.93	80.7	0.338	0.97
Cholesteric → Smectic (Cooling IL)	74.6	0.397	1.15	76.1	0.465	1.33

† An alternate method of determination, used by EMB based on DSC data on the same identical sample, gave a purity of 98.7%.

TABLE 2 Crystal Melting Transition Temperature (°C)

Cholesteryl Normal Ester	Sell and Neumann	Gray	Ennulat†	Barrall *et al.*	Arnold† *et al.*	Davis *et al.*
Formate	96	97.5	98	97.0	- - -	96.6
Acetate	115	116.5	114	110.9	116	114.6
Propionate	96	102	98	101.6	100	97.2
Butyrate	98	102	102.5	98.6	100	- - -
Pentanoate	92	93	99	92.6	88	- - -
Hexanoate	96	99.5	99	120.4	97	- - -
Heptanoate	111	114	113	116.0	107	- - -
Octanoate	106	110	110.5	112.7	103	- - -
Nonanoate	- - -	80.5	80.5	80.7	80	77.8
Decanoate	84	85.5	85.5	87.2	83	- - -
Undecanoate	- - -	- - -	92.5	91.5	85	91.5
Laurate	76	93	92	99.0	91	91.3
Tridecanoate	- - -	- - -	63.5	62.4–68.0	- - -	63.4
Myristate	- - -	71	71.5	73.6	71	70.5
Pentadecanoate	- - -	- - -	70	69.9	- - -	70.3
Palmitate	77	79	77.5	79.6	77	77.3
Heptadecanoate	- - -	- - -	78	78.6	- - -	76.3
Stearate	82	83	82	85.0	82	81.8
Nonadecanoate	- - -	- - -	82	81.3	- - -	80.4
Eicosanoate	- - -	- - -	85	- - -	- - -	83.0

† These data were graphed but not tabulated by Ennulat[3] and by Arnold.[7]
- - - Not measured.

purity. Results are given separately for the crystal melting transition temperature, the smectic–cholesteric transition, and the mesophase–isotropic transition.

Entropies of transitions data are presented in Figs. 1, 2 and 3. Figure 1 shows the heat of transition as a function of molecular weight for all available data from the formate through C_{20} ester for the transition from the crystal to the mesophase or isotropic liquid, whichever event occurs on direct heating of the sample. The appearance of a measurable smectic mesophase occurs at the C_9 ester with calorimetric results on this mesophase being displayed in Fig. 9. Results from Ref. (3) are taken from a transposition of Figs. 6 and 7 therein (Ennulat private communication). Figure 3 displays the composite data for the mesophase–isotropic transition. This is generally the smallest transition heat and entropy and the greater scatter in this figure is due in part to this feature.

TABLE 3 Smectic–Cholestric Transition Temperatures (°C)

Cholesteryl Normal Ester	Sell and Neumann†	Gray	Ennulat	Barrall *et al.*	Arnold *et al.*	Davis *et al.*
Nonanoate	- - -	77.5	76.3	66.0‡	76	74.6
Decanoate	79	81.5	79.0	68.5	80	- - -
Undecanoate	- - -	- - -	81.9	‖	80	78.9
Laurate	78	83.5	82.1	80.7	81	80.2
Tridecanoate	- - -	- - -	78.8	78.8	- - -	77.5
Myristate	- - -	81	79.9	80.0	79	77.8
Pentadecanoate	- - -	- - -	78.3	77.5	- - -	77.1
Palmitate	75	78.5	78.1	64.0	74	76.5
Heptadecanoate	- - -	- - -	76.5	‖	- - -	74.8
Stearate	74	75.5	75.1	§	72	69.6
Nonadecanoate	- - -	- - -	74.2	‖	- - -	71.8
Eicosanoate	- - -	- - -	74.3	- - -	- - -	—

† By thermal analysis, additional temperatures by a microscopic method were 0–3.5 °C higher for all transitions.

‡ Ennulat comments on this in his paper, Reference 3, p. 256.

§ Not resolved.

‖ Mesophase transition observed from cooling, value not given.

— Mesophase not observed.

- - - Not measured.

4. Discussion of Results

The results in Table 1 indicate a distinct difference in purity evaluation with the value by Davis probably being the highest possible value and the one by Barrall being a lower limit. The table indicates a good agreement between the temperatures and heats of transition for the results on the same ester sample. Transition temperatures reported by Barrall are generally higher than those given by Davis. The difference may be used to calibration differences. Barrall also finds generally higher transition heats with the percent being most for the smallest heats and in the range of 0–25 % A previous comparison on the myristate ester has also confirmed that data in different laboratories can give concordant results within a few percent experimental error in heats and within 3 °C in transition temperature.[1]

The comparison of crystal melting transition temperatures in Table 2 shows that the results of Sell and Neumann generally agree

TABLE 4 Cholesteric–Isotropic Liquid Transition Temperatures (°C)

Cholesteryl Normal Ester	Sell and Neumann	Gray	Ennulat	Barrall *et al.*	Arnold *et al.*	Davis *et al.*
Formate	57	60.5	60.4	57.1	- - -	—
Acetate	92	94.5	95.4	- - -	94	—
Propionate	112	116	114.1	115.2	115	113.0
Butyrate	109	113	111.8	112.5	111	- - -
Pentanoate	107	101.5	109.3	91	97	- - -
Hexanoate	98	101.5	100.4	98.7	99	- - -
Heptanoate	- - -	95.5	92.7	†	92	- - -
Octanoate	- - -	96.5	94.7	92.7	92	- - -
Nonanoate	90	92	92.1	93.0	91	91.7
Decanoate	91	92.5	90.9	91.4	91	- - -
Undecanoate	- - -	- - -	90.0	‡	89	87.9
Laurate	85	90	89.2	87.4	89	87.2
Tridecanoate	- - -	- - -	84.8	83.8	- - -	83.5
Myristate	- - -	86.5	85.2	85.6	84	83.2
Pentadecanoate	- - -	- - -	82.9	81.9	- - -	81.8
Palmitate	80	83	82.6	70.0	79	81.6
Heptadecanoate	- - -	- - -	80.6	82.2	- - -	79.7
Stearate	78	79.5	79.2	71.0	77	74.4
Nonadecanoate	- - -	- - -	77.8	‡	- - -	75.6
Eicosanoate	- - -	- - -	78.1	- - -	—	—

† Not resolved.
‡ Mesophase temperature obtained from cooling, value not given.
— Mesophase note observed.
- - - Not measured.

with those of Barrall *et al.*, and of Gray with differences generally of several degrees and less except for data on the hexanoate and the laurate ester where a difference of 15° was found from the results of Gray.[12] It may be noted that irregular results on the laurate ester have been found in several of the studies cited herein. Arnold[6] reports that, by the second of his purity determination methods,[13] his cholesteryl laurate contained 8.1% impurity. The temperature of transition presented by H. Arnold for the laurate crystal to isotropic liquid transition is 91.3 °C, exactly the same as that by Davis *et al.*[4] The measurements by Gray[12] were made with a hot stage microscope in contrast to the basically thermoanalytical techniques used by other investigators. Barrall *et al.*[1] used differential thermal analysis rather than DSC, as was incorrectly cited and data given verbatim in Ref. (3).

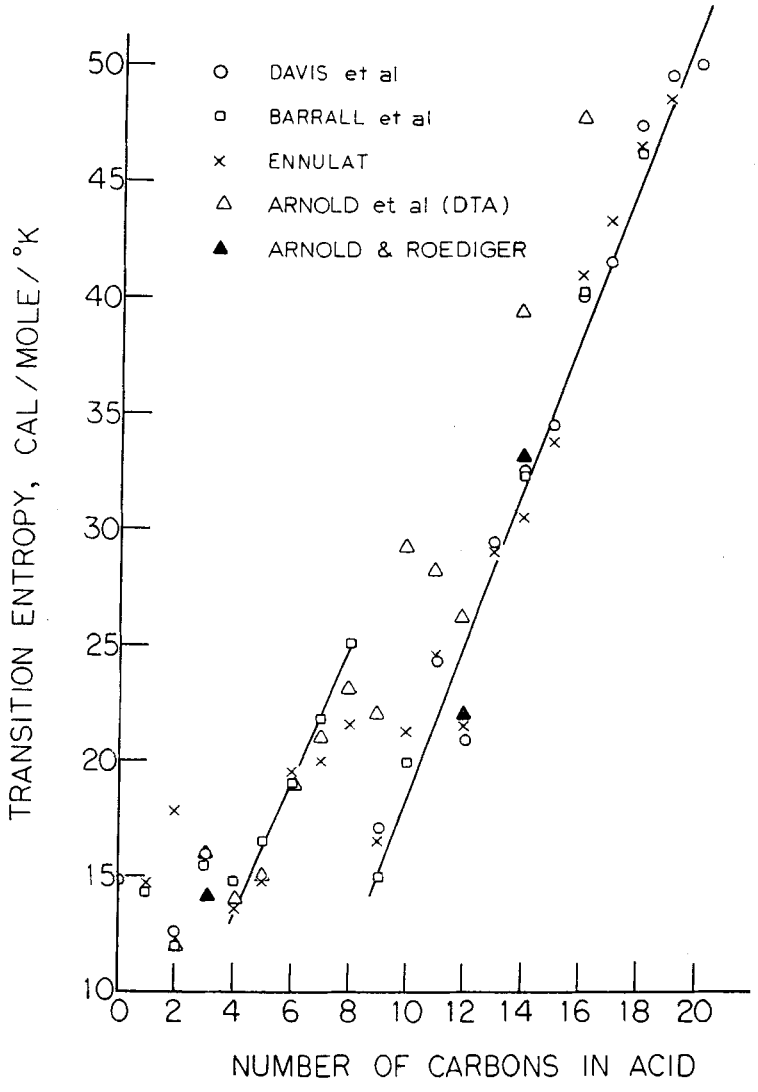

Figure 1. Aliphatic esters of cholesterol: crystalline melting transition entropies.

As can be seen in Tables 2, 3 and 4, the transition temperatures of Ennulat are generally consistent with those earlier reported by Gray,[12] within 3 °C, except for results on the pentanoate ester. Results of Davis *et al.*[4] are also in general accord being in the range

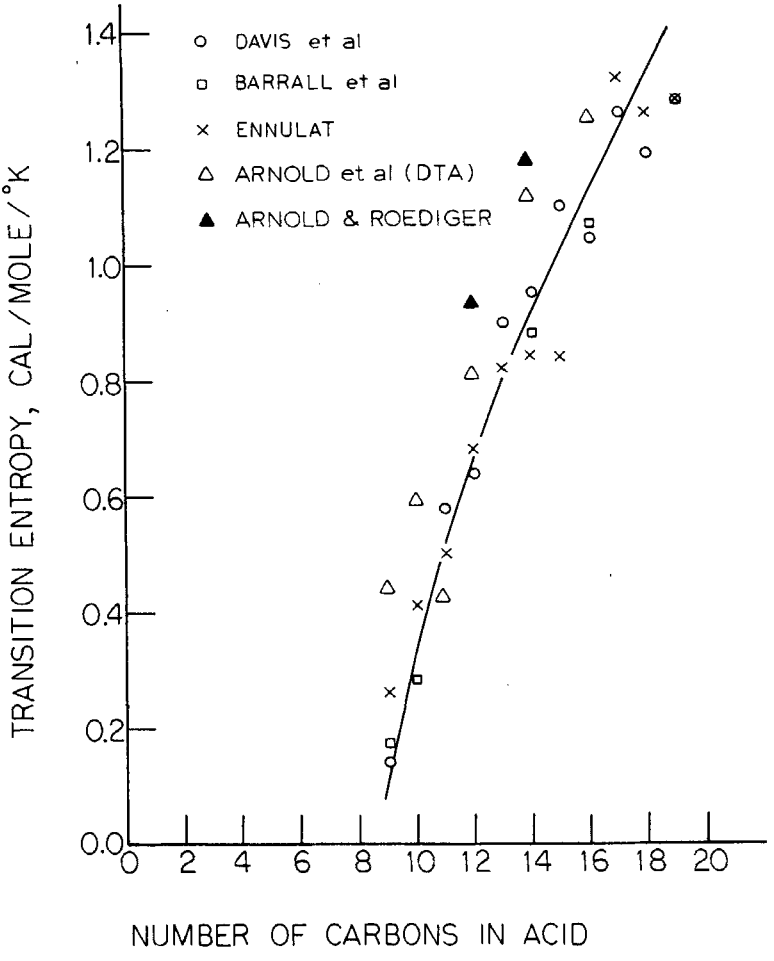

Figure 2. Aliphatic esters of cholesterol: smectic–cholesteric transition entropies.

of 0.4 to 2.1 °C lower than the values of Ennulat except for the stearate ester for which the transition is 5 °C lower for the smectic to cholesteric transition

Odd–even effects in transition temperatures and heats have generally not been found in the evaluation of composite data presented here. Such variations are also generally absent in individual

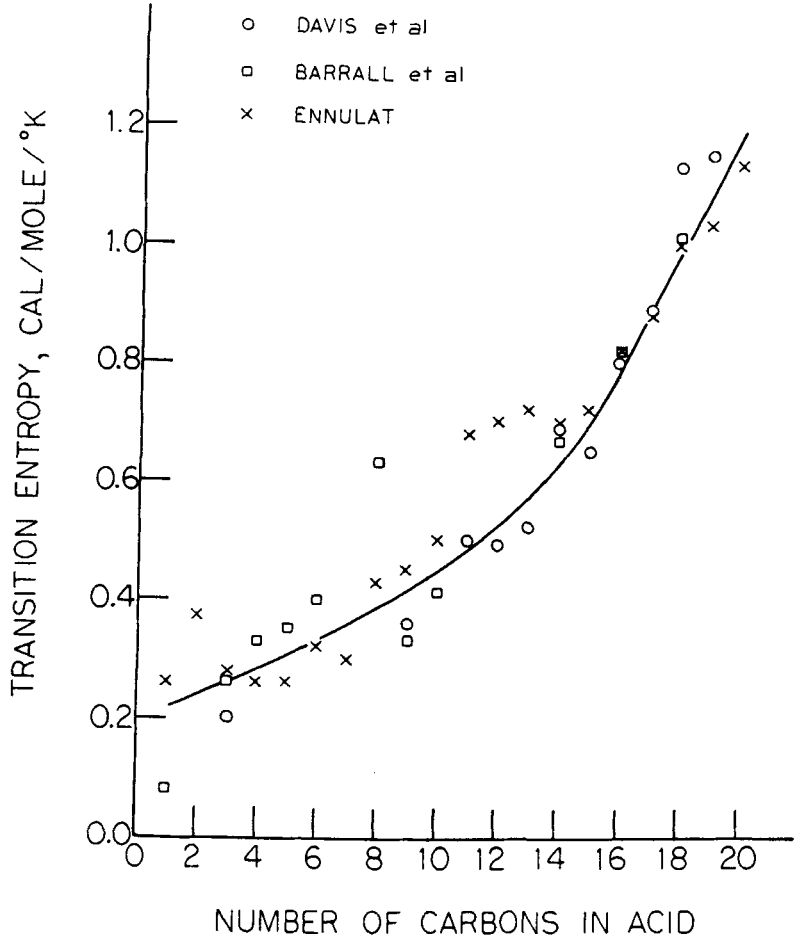

Figure 3. Aliphatic esters of cholesterol: cholesteric–isotropic liquid transition entropies.

sets of data. Gray noticed, however, in his early studies[12] an odd–even effect in transition temperatures that was subsequently not observed in the comparable data.[3] In the work of Davis *et al.*[4] an odd–even effect is seen only with the C_{13} to C_{19} esters for the temperature of the crystal–mesophase transition. When presented separately, the sum of transition entropies for each ester,[4] exhibit a minor but real odd–even effect for esters from the nonanoate to the nonadecanoate, excluding only the laurate.

The data by Barrall in the tables and figures for the odd esters above C_9 represent new and previously unpublished results. Thermal data for these odd esters have not been available until recently[3,4] and intercomparison of this data is being made here for the first time. The solid–mesophase transition heats of Barrall are generally lower than those of Davis although good agreement is generally evident, see Table 1 and the figures.

Extrapolation of the transition temperature data of Davis *et al.* indicates that transition temperature for the C_{20} mesophase is 72 °C which would be 2 °C below the temperature for the isotropic liquid–crystal transition of 74.1 °C. This may be the reason why this ester did not display a mesophase.[4]

Additional heats and temperatures of transition for several cholesteryl esters, viz. C_9 and C_{14} esters, have been given by Leclerq *et al.*[8] The new Arnold temperatures[7] all agree within 1 °C of his earlier values on three esters.[6]

The entropy of transition data of Davis *et al.*,[4] Barrall *et al.*,[5] and Ennulat[3] for all three mesophase transitions appear in Figs. 1, 2 and 3. In Fig. 1, the transition entropies for melting of crystals to the isotropic liquid are shown for the C_4 ester through the C_{20} ester. Almost without exception the data can be represented by two straight lines, particularly on allowance for experimental error. Since the heat of this transition generally represents the total order change from crystal to melt, the entropy changes with molecular weight should be compared to $R \log 3$, the theoretical increase in entropy per added CH_2 unit. For data in the reliable range from acetate to the C_{19} ester, the value is 2.18 kcal/CH_2, identical with the theoretical value. The heats of Arnold *et al.*[6,7] are also given in Figs. 1 and 2. Most of the entropies are in good agreement. Values for the higher esters in Fig. 1 are distinctly high as are, by about 40%, all the cholesteric–isotropic entropies. This is likely because Arnold includes the cholesteric specific heats in these values.[6,7]

A question persists concerning a break in the entropy curve in Fig. 1. Although not found by Ennulat,[3] it appears that the data of Barrall *et al.*,[1] and the composite data of several workers[9] both seem to suggest that there is a marked change in total transition entropy between the C_8 and C_9 ester.

In Figs. 2 and 3 are presented the smectic to cholesteric and cholesteric to isotropic liquid transition entropies respectively. The same trend and general curvature of data as a function of molecular weight are observed in the composite and in the individual sets of data. Minor odd–even effects in the heats, even if present, are not likely to be noted in this composite data because the uncertainty in measurements may be as high as 10 to 20%. Temperatures of transition for these individual and composite data likewise do not reveal an odd–even effect.

A major difference in data is that Ennulat[3] reports a cholesteric to isotropic liquid transition for both the formate and acetate and Davis[4] *et al.* report none. These transitions were located upon cooling from the melt. The samples of Davis *et al.*[4] turned crystalline before these temperatures for transition were reached. Since the presence of impurities are known to lower transition temperatures, the samples of Davis *et al.*[4] may have been of a higher purity. Impurities appear to dissolve readily in mesophases. The common impurities are of like composition to the major constituent.

There is disagreement on the ester chain length for which the cholesteric to isotropic liquid transition begins. There is agreement, however, that the smectic to cholesteric transition begins with the nonanoate ester.[3,4] Gray[12] had previously reported that this mesophase began with the C_7 ester. However, the sharp downward slope of data in Fig. 2 at the C_9 ester would predict that C_8 and C_7 smectic transitions, if present, would have extremely small entropies of transition associated with them. On a thermodynamic basis it is thus unlikely that the smectic mesophase forms in pure esters below the C_9 ester.

Acknowledgement

Two of us, GJD and RSP, wish to express appreciation for support by the National Institutes of Health, Grant HE 11342.

REFERENCES

1. Barrall, E. M. II, Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **71**, 1224 (1967).
2. Sell, P. J. and Neumann, A. W., *Z. physik. Chemie Neue Folge* **65**, 13 (1969).
3. Ennulat, R. D., *Mol. Cryst. and Liq. Cryst.* **8**, 247 (1969).
4. Davis, G. J., Porter, R. S. and Barrall, E. M. II, *Mol. Cryst. and Liq. Cryst.* **10**, 1 (1970).
5. Barrall, E. M. II, Johnson, J. F. and Porter, R. S., in *Thermal Analysis*, **1**, Schwekner, R. F., Jr. and Garn, P. D., Eds., Academic Press, p. 555, 1969.
6. Arnold, H. and Roediger, P., *Z. physik. Chem.* (Leipzig) **239**, 283 (1968).
7. Arnold, H., Demus, D., Koch, H.-J., Nelles, A. and Sackmann, H., *Z. physik. Chem.* **240**, 185 (1969).
8. Leclerq, M., Billard, J. and Jacques, J., *Compt. Rend.* **264**, 1789 (1967).
9. Porter, R. S., Barrall, E. M. II and Johnson, J. F., *Accounts Chem. Res.* **2**, 53 (1969).
10. Johnson, J. F., Barrall, E. M. II and Porter, R. S., *Mol. Cryst. and Liq. Cryst.* **8**, 1 (1969).
11. Davis, G. J. and Porter, R. S., *J. Thermal Analysis*, **1**, 449 (1969).
12. Gray, G. W., *J. Chem. Soc.* 3733 (1956).
13. van Wifk, H. J. and Smit, W. M., *Analytica. Chem. Acta.* **24**, 45 (1961).