

Thermal Study of Some Liquid Crystals

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Liquid crystals of the type *p*-phenylene-di-*p-n*-alkoxy benzoate have been prepared in the laboratory. The thermal study of compounds is done using four function MON-Q-derivatograph. The method suggested by Boerswa and later clarified by Garn was adopted for thermal study. Using the area of DTA peak, the calibration coefficient (g) values have been evaluated and discussed. The transition temperatures of nematogenes having homologues were measured and its correlation with number of carbon atoms in the chain discussed.

INTRODUCTION

The liquid crystals have assumed great importance now-a-days especially because of their anisotropic properties, their subtle response to the minute temperature changes and a certain amount of dichroism. Liquid crystals have immense applicability in the digital watches, optical displays, temperature sensors, television screen and in medicotherapy. "Spin label technique" in which liquid crystals are used is gaining supreme importance for the investigation of artificial or biological membrane.¹ Liquid crystals are used as anisotropic solvents in N.M.R. spectroscopy.²⁻⁴ Mixtures of nematogenes are used in most of LCD devices.^{5,6}

A number of methods are suggested for fabrication of mesophases.⁷⁻¹⁰ Some work was undertaken about the transition temperatures of mesophase and the length of the hydrocarbon chain.^{11,12}

Literature shows that some work was done using phenyl benzoates¹³ or biphenyls¹⁴ but no work is undertaken using the liquid crystals of the type *p*-phenylene-di-*p-n*-alkoxy benzoate. Taking into consideration the importance of liquid crystals, it was thought that to prepare the liquid crystals of the type *p*-phenylene-di-*p-n*-alkoxy benzoate, using DTA peaks of nematogenes evaluate the calibration coefficient and measure transition temperatures of mesophases.

EXPERIMENTAL

30.0 g of *p*-hydroxy benzoic acid (Koch Light Laboratories, England) was mixed with 100 mL of ethyl alcohol and 3-5 mL of conc. sulphuric acid. The mixture was refluxed to get *p*-hydroxy ethyl benzoate. 30.0 g of potassium bromide (BDH) was treated with 25.0 mL of conc. sulphuric acid. The

hydrobromic acid thus obtained was treated with 11 g (*ca.* 11 mL) of *n*-alkyl alcohol (BDH) and 28 g (*ca.* 15 mL) of conc. sulphuric acid to get *n*-alkyl bromide. 6.5 g of sodium (SM Chemicals) in 150 mL of absolute alcohol, 60.0 g of *p*-hydroxy ethyl benzoate in 140 mL of absolute alcohol and 40 g (45–50 mL) of *n*-alkyl bromide were refluxed for 3 h to get an oily mass as *p*-alkoxy ethyl benzoate. 50.0 mL of *p*-alkoxy ethyl benzoate were mixed with 250 mL of 10% alcoholic KOH (BDH) and after refluxing the mixture was acidified with conc. HCl. The precipitate thus obtained *i.e.* *p*-alkoxy benzoic acid (22 g) was treated with 37.0 g (*ca.* 23 mL) of thionyl chloride (Robert Johnson) to get *p*-*n*-alkoxy benzoyl chloride. The product thus obtained was mixed with saturated solution of hydroquinone (May and Baker Ltd.) (0.5 mol) in dry pyridine (BDH) to get *p*-hydroxy phenyl-*p*-*n*-alkoxy benzoate. The unsymmetrical esters *i.e.* *p*-phenylene-di-*p*-*n*-alkoxy benzoates were synthesized from the appropriate reagents. *p*-*n*-alkoxy benzoyl chlorides and *p*-hydroxy phenyl-*p*-*n*-alkoxy benzoates were prepared by the same procedure as used in the preparation of the latter except that, at the start, a solution of the phenol was added to a solution of acid chloride (3 moles per mole of phenol) both in anhydrous pyridine medium.

The products were recrystallized from suitable solvents such as dioxane, alcohol or hexane (any one of the above), dried over silica gel in desiccator and were subjected to elemental analysis. The results of elemental analysis were found approximately equal to calculated values.

The DTA of the samples were taken on a four function MOM-Q-derivatograph with heating rate (ϕ) $1.25^\circ\text{C min}^{-1}$. The transition temperatures were obtained by scrupulous observations of thermograms and are more or less authenticated by fluorescence intensity study.

RESULTS AND DISCUSSION

The method suggested by Boerswa¹⁵ and later clarified by Garn¹⁶ was used for thermal study. The instrument was standardized with the peaks obtained for KNO_3 and CaCO_3 whose ΔH values are 50.43 J g^{-1} and 174.0 J g^{-1} respectively.¹⁷ Almost identical *g* values were obtained ($8.5 \times 10^{-3} \text{ J m}^{-2}$) in these cases.

Areas of the transition peaks were measured by drawing a line from the point where the thermogram (DTA) departs from the base line to the point where it returns. The results were treated assuming a direct relationship between peak area and ΔH . A calibration coefficient was then calculated as

$$g = \frac{H \times m}{A}$$

where *A* = area of peak in sq. m.

m = weight of the sample in g.

H = heat of fusion or transition (J g^{-1}).

g = calibration coefficient (J m^{-2}).

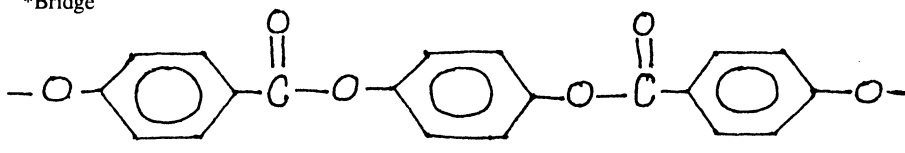
The results obtained for *g* values for the liquid crystals studied are given in

Table-1. Except in C₂H₅—bridge—C₄H₉, ca. 0.9, all other values of g range from 1 to 55.

TABLE-1
CALIBRATION COEFFICIENTS (g) AND NUMBER OF CARBON ATOMS IN THE
CHAIN OF NEMATOGENS (m = 0.050 g)

Mesophase	H J g ⁻¹	Area of peak (A × 10 ⁴) m ²	$g = \frac{H \times m}{A}$ (g × 10 ⁴) J m ⁻²	No. of carbon atoms in the chain
CH ₃ —Bridge*—C ₃ H ₇	169.00	1.60	5.28	18
CH ₃ —Bridge—C ₅ H ₇	204.30	0.50	20.43	20
CH ₃ —Bridge—C ₆ H ₁₃	2980.00	4.40	33.86	21
CH ₃ —Bridge—C ₇ H ₁₅	1187.00	1.90	31.23	22
CH ₃ —Bridge—C ₈ H ₁₇	600.90	5.60	5.27	23
C ₂ H ₅ —Bridge—C ₃ H ₇	2043.00	1.80	56.75	19
C ₂ H ₅ —Bridge—C ₄ H ₉	78.20	4.40	0.88	20
C ₂ H ₅ —Bridge—C ₇ H ₁₅	392.10	1.00	19.60	23
C ₂ H ₅ —Bridge—C ₈ H ₁₇	158.90	2.30	3.45	24
C ₃ H ₇ —Bridge—C ₄ H ₉	333.70	2.30	4.76	21
C ₃ H ₇ —Bridge—C ₆ H ₁₃	180.30	3.20	2.82	23
C ₃ H ₇ —Bridge—C ₇ H ₁₅	1556.00	2.30	33.84	24
C ₃ H ₇ —Bridge—C ₈ H ₁₇	151.40	1.80	4.73	25
C ₄ H ₉ —Bridge—C ₅ H ₁₁	65.07	1.70	1.91	23
C ₄ H ₉ —Bridge—C ₆ H ₁₃	648.60	3.30	9.83	24
C ₄ H ₉ —Bridge—C ₈ H ₁₇	506.00	0.50	50.60	26
C ₅ H ₁₁ —Bridge—C ₅ H ₁₁	972.70	4.00	12.16	24
C ₅ H ₁₁ —Bridge—C ₆ H ₁₃	125.80	1.60	3.84	25
C ₅ H ₁₁ —Bridge—C ₈ H ₁₇	447.90	0.40	56.04	27
C ₆ H ₁₃ —Bridge—C ₆ H ₁₃	169.30	1.20	7.05	26
C ₆ H ₁₃ —Bridge—C ₇ H ₁₅	896.20	1.60	28.00	27
C ₆ H ₁₃ —Bridge—C ₈ H ₁₇	524.00	2.40	10.91	28
C ₇ H ₁₅ —Bridge—C ₈ H ₁₇	433.20	0.90	24.08	29
C ₈ H ₁₇ —Bridge—C ₈ H ₁₇	581.30	0.90	32.30	30

*Bridge



When a graph was plotted with g values as y axis and number of carbon atoms in chain of the liquid crystal as abscissae, some four straight lines were obtained.

The data positively indicates that though homologues have been studied here, the thermal history, characteristics or thermal conductivity of each of the nematogen, is quite distinct and they fall into some four clusters (Fig. 1) as far as their thermal behaviour is concerned.

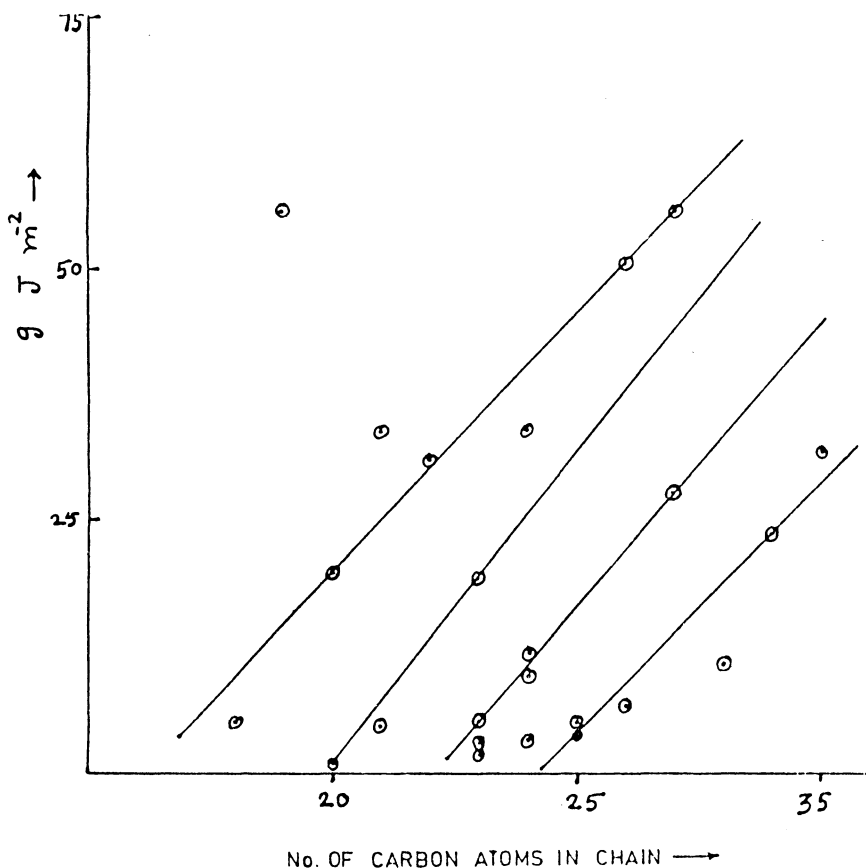


Fig. 1

The usual observation, in the study of nematogens having homologues, was that the specific properties of transformation changes were systematic as the number of carbon atoms increased or decreased. The erratic, but seemingly a disciplined behaviour, is evident from g values obtained.

According to Gray,¹⁴ a smooth curve can be drawn through the points, if the temperatures of a mesophase to isotropic transitions were plotted against the length of the hydrocarbon chain being homologued. It was also noted¹⁸ that single smooth curves are usually not obtained to fit all the points but two smooth curves should be obtained for odd and even number of carbon atoms in the chain. It is

curiously noted that odd and even curves frequently converge at chain lengths of 8–10 carbon atoms.^{19, 20}

In the present studies, the author has observed no such simple relationship and does not expect the behaviour as the chains in the terminal group are not expected to behave in a normal manner at least in liquid crystals.

A plot of carbon atoms in a chain vs. the C—N and N—I temperatures resulted in some nine smooth lines, the six lower lines (Fig. 2) naturally representing C → N temperatures while the three upper lines depicting N → I temperatures. It must be admitted that they do not just lie on a straight line but an approximate behaviour comes very near to linearity.

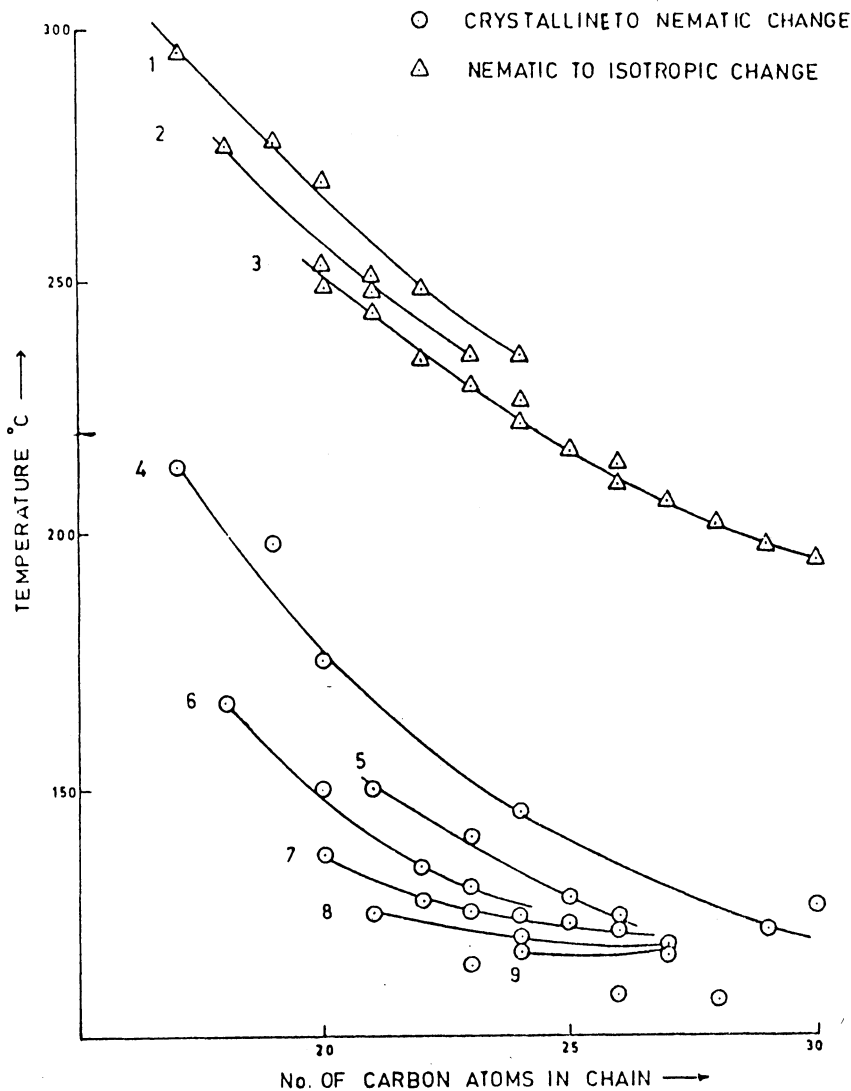


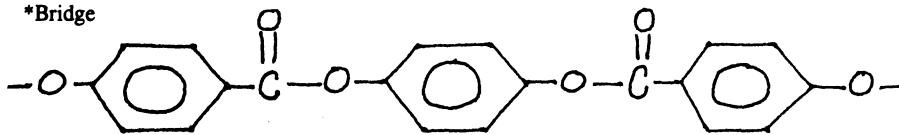
Fig. 2

Table-2 shows that the effects of initial substituents as terminal groups are well marked, the C—N and N—I temperatures being as high as 213°C and 295°C respectively.

TABLE-2
CHANGE IN TRANSITION TEMPERATURES WITH CHANGES IN LENGTHS IN THE MESOPHASES

Mesophase	No. of carbon atoms in the chain	T _(CN) crystalline-nematic change (°C)	T _(NI) nematic-isotropic change (°C)
CH ₃ —Bridge*—C ₂ H ₅	17	213	295
CH ₃ —Bridge—C ₃ H ₇	18	167	277
CH ₃ —Bridge—C ₅ H ₁₁	20	137	253
CH ₃ —Bridge—C ₆ H ₁₃	21	125	244
CH ₃ —Bridge—C ₇ H ₁₅	22	127	234
CH ₃ —Bridge—C ₈ H ₁₇	23	125	229
C ₂ H ₅ —Bridge—C ₃ H ₇	19	198	278
C ₂ H ₅ —Bridge—C ₄ H ₉	20	150	270
C ₂ H ₅ —Bridge—C ₅ H ₁₁	21	150	251
C ₂ H ₅ —Bridge—C ₆ H ₁₃	22	134	248
C ₂ H ₅ —Bridge—C ₇ H ₁₅	23	130	235
C ₂ H ₅ —Bridge—C ₈ H ₁₇	24	124	235
C ₃ H ₇ —Bridge—C ₃ H ₇	20	175	249
C ₃ H ₇ —Bridge—C ₄ H ₉	21	151	248
C ₃ H ₇ —Bridge—C ₆ H ₁₃	23	114	230
C ₃ H ₇ —Bridge—C ₇ H ₁₅	24	120	222
C ₃ H ₇ —Bridge—C ₈ H ₁₇	25	128	216
C ₄ H ₉ —Bridge—C ₅ H ₁₁	23	140	229
C ₄ H ₉ —Bridge—C ₆ H ₁₃	24	117	226
C ₄ H ₉ —Bridge—C ₈ H ₁₇	26	121	214
C ₅ H ₁₁ —Bridge—C ₅ H ₁₁	24	145	222
C ₅ H ₁₁ —Bridge—C ₆ H ₁₃	25	123	215
C ₅ H ₁₁ —Bridge—C ₇ H ₁₅	26	108	210
C ₅ H ₁₁ —Bridge—C ₈ H ₁₇	27	116	207
C ₆ H ₁₃ —Bridge—C ₆ H ₁₃	26	124	213
C ₆ H ₁₃ —Bridge—C ₇ H ₁₅	27	118	206
C ₆ H ₁₃ —Bridge—C ₈ H ₁₇	28	107	202
C ₇ H ₁₅ —Bridge—C ₈ H ₁₇	29	121	198
C ₈ H ₁₇ —Bridge—C ₈ H ₁₇	30	126	195

*Bridge



As the terminal groups get increased chain length, the N—I and C—N temperatures drop down considerably, say from 295°C for CH₃—Bridge—C₂H₅ to 229°C for CH₃—Bridge—C₈H₁₇ and C—N for these drop from 213°C to just 125°C. But this does not go on down the series. There are periodical jumps and falls.

The only probable or more possible reason for erratic behaviour of liquid crystals (g values and transition temperatures) seems to be that there are considerable internal steric effects as well as external packing effects of these two-dimensional laminar type nematogenes. The chains may be parallel or antiparallel and will certainly offer stiff resistance to C—N or N—I changes according to the way they are oriented. The sandwiched phenyl rings may be flattened, may have enough room to get fully distended. All these factors ultimately contribute to the slightly erratic behaviour of the nematogens studied in the present investigation.

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