Cross Over Temperature (T_{co}) in a Number of Symmetric Dimers

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Abstract: Temperature gradient of refractive indices, dn_e/dT and dn_o/dT of a number of symmetric dimeric liquid crystals m.OnO.m compounds namely α,ω-bis(p-n-alkylanilinebenzylidene-p′-oxy) alkanes are estimated using the refractive index data. Most of these materials show nematic phase except very few compounds. All these compounds exhibit more than 100 ^{O}C clearing temperatures due to the presence of second monomer. The T_{CO} exhibits even odd effect with the spacer 'n' and alkyl chain number 'm' values.

Keywords: *Symmetric Dimeric Liquid Crystals, Temperature Gradient of Refractive Indices, Cross Over Temperatures.*

I. INTRODUCTION

The dimeric liquid crystals have their significance when compared to the corresponding monomers. The DLCs are of two types, symmetric and non symmetric depending the monomers present in the DLC material [1,2]. Most of these compounds exhibit nematic phase [1]. However, the corresponding monomers in the symmetric DLCs exhibit smectic phases also. In view of the presence of nematic phase the compounds are suitable for the study of the birefringence and thereby the orientational order parameter. Even though, the synthesis and characterization on the symmetric DLCs with varying space length (n) and the end alkyl chain length (m) are reported earlier by Imrie et al [1], the authors are synthesized and characterized these symmetric DLCs once again in authors experimental work, specially refractive indices using the wedge shaped cell and the modified spectrometer whose particulars are given in the experimental section [3-5].

Further, it is reported in a number compounds and mixture of LC materials [6,7] that temperature gradient of n_e is always negative while the temperature gradient of n_o could change from negative to positive depending on the LC material and the operating temperature. These guidelines can be utilized to prepare LC mixtures with large dn_o/dT at room temperature. In the present manuscript the authors reports the cross over temperature (T_{CO}s) in a number of DLCs and to study their variation with either spacer length (n) or alkyl chain length (m).

A. Experimental

The compounds are synthesized according to the standard procedure reported in the literature [1]. The crude products are repeatedly recrystallized from ethyl acetate until the transition temperatures remain constant. Differential scanning calorimeter (DSC) studies are carried out using a differential scanning calorimeter (Perkin–Elmer, Diamond). Nematic and SmA phases exhibited by the compounds are identified by observing their characteristic optical textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic studies is ±0.1 ^{O}C. The refractive indices of a LC are measured with a wedge-shaped glass cell, similar to the one used to obtain birefringence by Haller et al. [6], using a modified spectrometer [7]. A wedge-shaped glass cell was formed with two optically flat rectangular glass plates (50 mm × 25 mm) sandwiched with glass plate (0.4 mm) which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge to get the alignment of the LC molecule. The cell is filled with the DLC material. The nematic DLC in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block is ±0.1°C.

B. Modified Spectrometer

In order to avoid the difficulty of measuring refractive index of a liquid crystal the author has given up using commercially available refractometers (Abbe and Pulfrich) and instead installed some discrete parts such as an objective with long focal length, an ocular scale etc, for the laboratory spectrometer. Although constructing the telescope part of a spectrometer from discrete parts inevitably sacrifices some features of a usual spectrometer the present modified spectrometer works as far as quantitative observations of liquid crystal are concerned comparable to other methods.

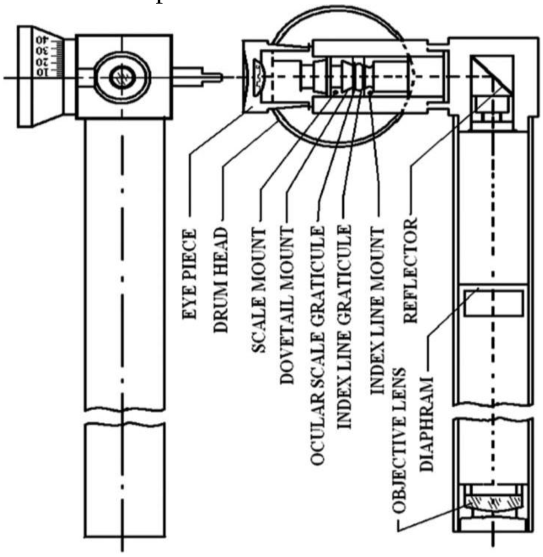

Figure 1: Modified Telescope.

Fig 1 shows construction details of telescope. It consists of long focal length objective (f = 40 cm, aperture = 4.5 cm) and a measuring unit of lateral movements of the transmitted beams.

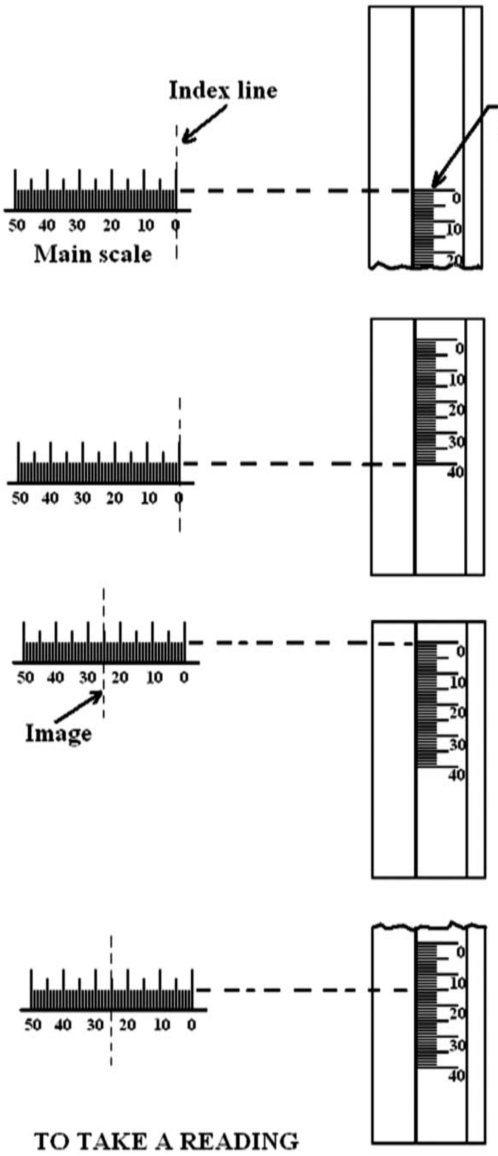

Figure 2: Modified Ocular scale

A reflecting prism is arranged on the optic axis for convenience to observe the images in the horizontal plane instead of vertical plane. The measuring unit for lateral movements of the transmitted beams consists of 1) a cross which is called an index line (thickness = 10 μm) mount to adjust the zero zero coincidence of index line and drum head reading. 2) scale mount carrying calibrated ocular scale (fig 2) of 50 divisions each corresponding to one minute, which can be moved laterally (i.e., horizontal plane of the prism table) over the fixed index line by using drum head and 3) drum head with 40 divisions which is attached to the ocular scale. The 40 divisions on the drum head (fig 2) correspond to one minute (1 Div) in the ocular scale, i.e., each division of drum head it equal to 1.5 seconds of arc. The ocular scale is fixed in a brass block which is machined as a down tail. The scale can be viewed through the eye piece (20X).

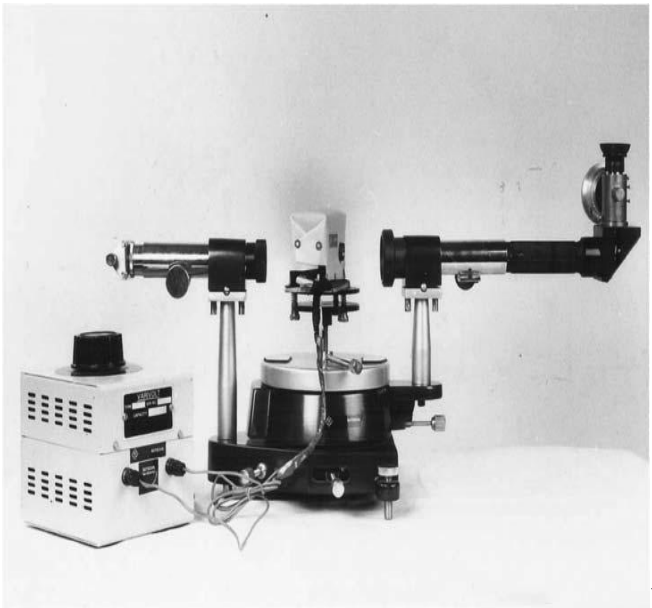

Plate 1: Modified spectrometer.

Using the spectrometer the results obtained in the case of EBBA are in good agreement with the reported data. For cells with wedge angle = 1^0, i.e., the birefringence $\Delta n = 0.8$ can be measured in the field of view of the ocular scale without rotation of the telescope. The absolute accuracy in $n = \pm 0.0004$ for the above cell. The advantage in using ocular scale is to eliminate manual as well as mechanical errors can be eliminated. The refractive index is determined by thin prism formula $n = (1 + D/A)$ where D = deviation = Ocular scale reading + 1/60 x 3/2 x (drum head reading) and A = angle of the wedge shaped cell. The displacement of the scale for the rotation of drum head through one division is clearly visible with reference to the index line. Angular deviation can be estimated to even half the drum divisions corresponding to 0.75 second. The modified spectrometer is shown in plate 1.

The accuracy in the measured refractive indices was ±0.0005. The refractive indices measured in 3.O12O.3, 4.O12O.4, 5.O12O.5, 6.O12O.6 and 7.O12O.7 along with <n> are given in figures 3 to 7.

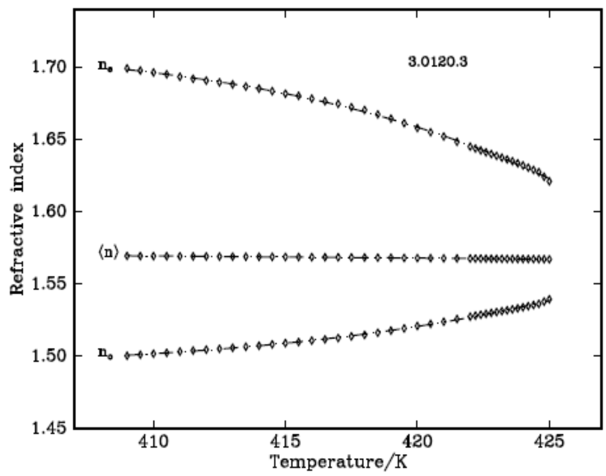

Figure 3: Variation of n_e, n_o and <n> with temperature in 3.O12O.3

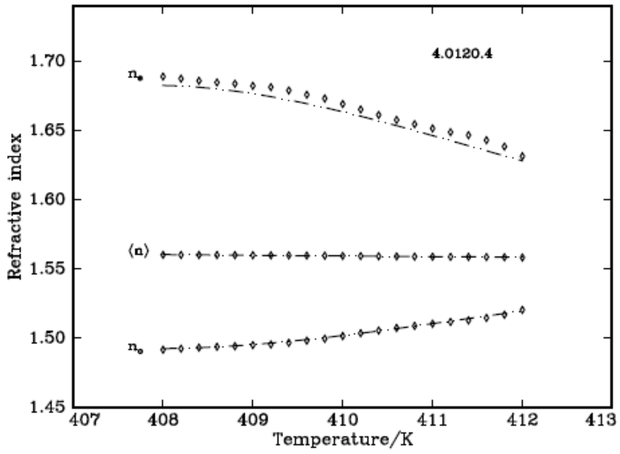

Figure 4: Variation of n_e, n_o and <n> with temperature in 4.O12O.4

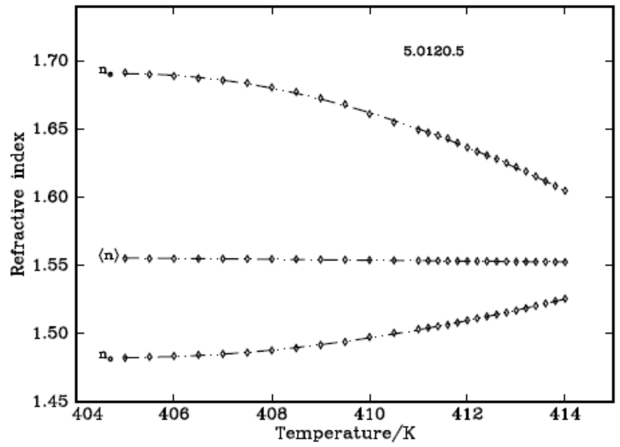

Figure 5 Variation of n_e, n_o and <n> with temperature in 5.O12O.5

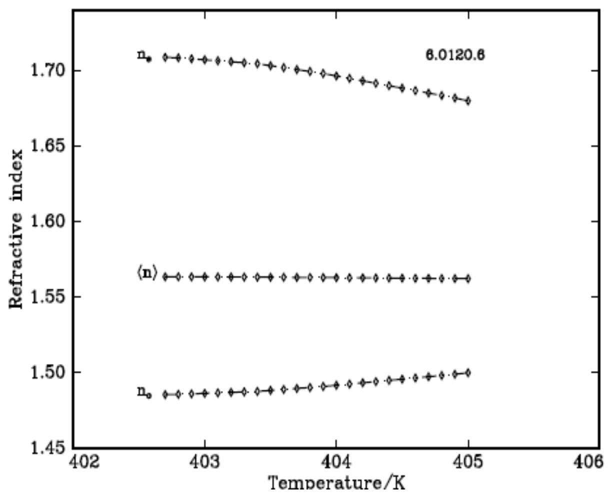

Figure 6: Variation of n_e, n_o and <n> with temperature in 6.O12O.6

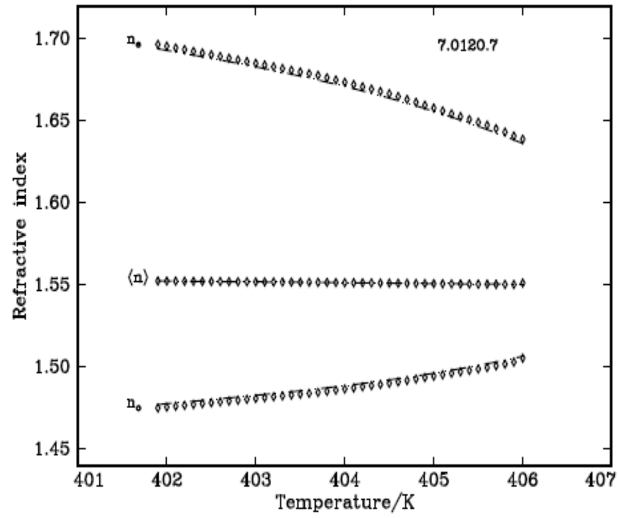

Figure 7 Variation of n_e, n_o and <n> with temperature in 7.O12O.7

II. THEORY

For the sake of completeness and for the ready reference the expressions involved in calculating the gradient of refractive indices and the cross over temperature are given below.

The Lorentz-Lorenz equation for the refractive index is

$$(n^2 - 1)/ (n^2 + 2) = (4\pi/3)\, N\alpha \qquad (1)$$

where N is the molecular packing density, α molecular polarizability. For an anisotropic DLC or LC there are two refractive indices, n_o (ordinary) and n_e (extraordinary). Further, each refractive index is determined by their corresponding molecular polarizabilities, α_o and α_e. Following Vuks isotropic model (which most of the nematic LC compounds follow) and the modified the above equation (1) and obtained the following one as.

$$(n^2_{e,\,o} - 1)/(< n^2 > + 2) = (4\pi/3)N\alpha_{e,\,o} \qquad (2)$$

where $< n^2 > = (n^2_e + 2n^2_o)/3$. Based on Vuks isotropic model, the temperature dependent refractive indices can be written in terms of average refractive index < n > and the birefringence $\delta n = (n_e - n_o)$ as [8-10]

$$n_e = < n^2 >^{1/2} + (2/3)(\delta n) \qquad (3)$$

and

$$n_o = < n^2 >^{1/2} - (1/3)(\delta n) \qquad (4)$$

Then, the temperature derivatives of the refractive indices are

$$dn_e/dT = (d<n>)/dT) + (2/3)(d\delta n/dT) \qquad (5)$$

$$dn_o/dT = (d<n>)/dT) + (1/3)(d\delta n/dT) \qquad (6)$$

Further, it is a known fact, experimentally that < n > decreases linearly with the temperature and can be expressed by a linear equation as

$$< n > = A - BT \quad (7)$$

This linear relationship makes the second term in equations becomes a constant for any given LC material. The slope and the intercept values obtained using equation (7) are given in table 1.

Table 1: The intercept and slope values from equation (7)

	intercept	slope
3.O7O.3	1.6429	-0.000146
3.O9O.3	1.6004	-0.00009
3.O10O.3	1.5986	-0.000119
3.O11O.3	1.6026	-0.000097
3.O12O.3	1.6301	-0.000148
4.O7O.4	1.6111	-0.000124
4.O9O.4	1.6135	-0.000129
4.O10O.4	1.6286	-0.00015
4.O12O.4	1.7591	-0.00049
5.O7O.5	1.6214	-0.00015
5.O8O.5	1.6093	-0..0001
5.O9O.5	1.6064	-0.0001
5.O10O.5	1.6184	-.0.000127
5.O11O.5	1.6223	-0.000146
5.O12O.5	1.6880	-0.000329
6.O12O.6	1.7911	-.00056
7.O12O.7	1.5554	-0.0001

Kuczynski et al. [11, 12] proposed a simple relationship between the birefringence $\delta n = (n_e - n_o)$ on its temperature dependence and successfully applied in a number of LC and DLC materials [3, 5, 13, 14] and the relevant expressions are given below

$$\delta n = \Delta n \,.\left(1-\frac{T}{T^*}\right)^{\beta} \quad (8)$$

where T is the absolute temperature, T* and β are constants. ($T^* = T_C+X$) where X is varied from 0.001-4K and the exponent β is close to 0.20 and is not too sensitive to LC structure). This procedure enables one to extrapolate δn to the absolute zero temperature. In practice, the three adjustable parameters T*, Δn and β are obtained by fitting the experimental data for δn to the following equation written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta . \log\left(\frac{T^*-T}{T^*}\right) \quad (9)$$

In the present investigations, the values of log Δn and β are estimated by the linear regression method. The parameter T* is adjusted to get the best correlation coefficient of the linear regression. The data pertinent to all the studied DLCS are shown in table 2.

Table 2: The β, Δn and T_{CO} in all dimers studied

Compound	β	Δn	T_C	T_C+	T_{CO} (K)
3.O7O.3	0.153	0.318	419.1	419.102	332.85
3.O9O.3	0.199	0.316	435.4	435.5	233.00
3.O10O.3	0.170	0.331	425.0	425.011	307.40
3.O11O.3	0.179	0.328	410.9	410.94	238.17
3.O12O.3	0.187	0.344	425.0	425.04	329.24
4.O7O.4	0.207	0.318	403.0	403.007	260.40
4.O8O.4	0.164	0.321	436.8	436.802	322.92
4.O9O.4	0.179	0.320	397.0	397.1	274.54
4.O10O.4	0.184	0.325	421.4	421.44	318.87

Further, in evaluating Δn, (the birefringence in perfect order) only the nematic range is considered. By substituting equations (7) and (8) into equations (3) and (4) the temperature dependent refractive indices will be obtained as

$$n_e(T) = A - BT + (2\Delta n/3)\left(1-\frac{T}{T^*}\right)^{\beta} \quad (10)$$

and

$$n_o(T) = A - BT - (\Delta n/3)\left(1-\frac{T}{T^*}\right)^{\beta} \quad (11)$$

The parameters A and B are obtained from equation (7) and they are given in table 2 for all the DLCs, while the rest are obtained as stated above. B, β and Δ n have their meaning. The T_{CO} is the cross over temperature. The rate of change of the refractive indices with respect to temperature are obtained as

$$dn_e/dT = -B - (2\beta\Delta n/3)/T^*\left(1-\frac{T}{T^*}\right)^{1-\beta} \quad (12)$$

and

$$dn_o/dT = -B + (\beta\Delta n/3)/T^*\left(1-\frac{T}{T^*}\right)^{1-\beta} \quad (13)$$

Utilizing the equations (12) and (13) the gradient of refractive indices are evaluated in all the DLCs materials and the results are shown in figures 8 to10.

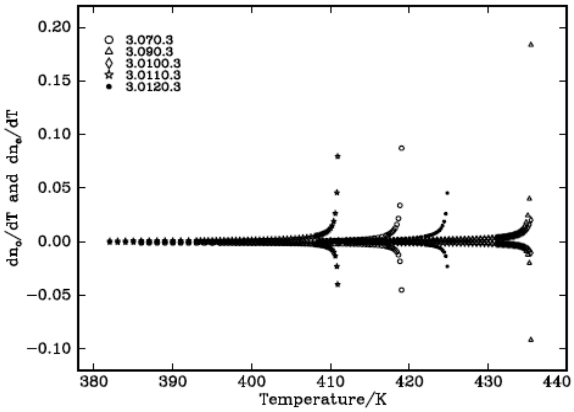

Figure 8 Variation of dn_o/dT and dn_e/dT with temperature in 3.OnO.3 DLCs,

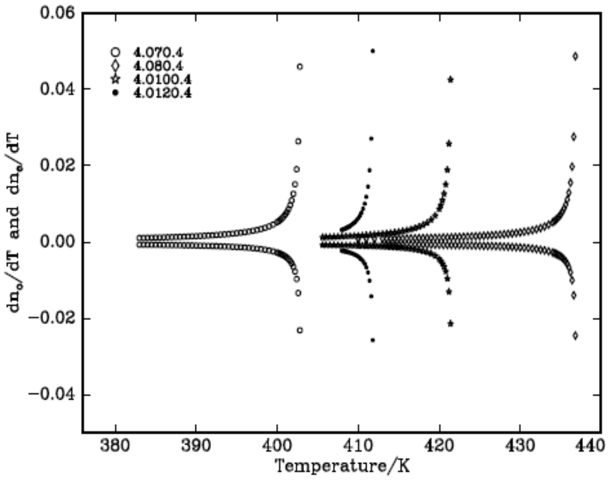

Figure 9 Variation of dn_o/dT and dn_e/dT with temperature in 4.OnO.4 DLCs, F

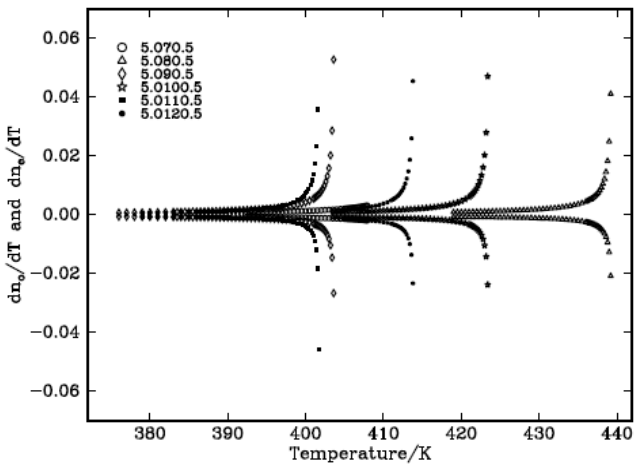

Figure 10: Variation of dn_o/dT and dn_e/dT with temperature in 5.OnO.5 DLCs

In equation (12) the right hand side both the terms are negative and independent of temperature which implies n_e decreases as the temperature increases. However, the equation (13) consists of negative first term and the positive second term which is temperature dependent. At low temperatures ($T << T^*$), the 2nd term is less than the first tem resulting a negative dn_o/dT. With the increase of temperature, the positive term also increases. When $T \cong T^*$, dn_o/dT jumps to a large positive value. However, in the intermediate stage there exists a cross over temperature, T_{CO} where $dn_o/dT = 0$. The expression for T_{CO} is given as [15]

$$T_{CO} = T^* [1 - \{3B\, T^* / (\beta \Delta n)\}^{1/(\beta-1)}] \qquad (14)$$

III. RESULTS AND DISCUSSION

Using the equation (14), the cross over temperatures is calculated for all the symmetric dimmers studied. The particulars are given in the table 2. The figure 11 and 12 show the variation of T_{CO} either with the central linkage or with end alkyl chain number.

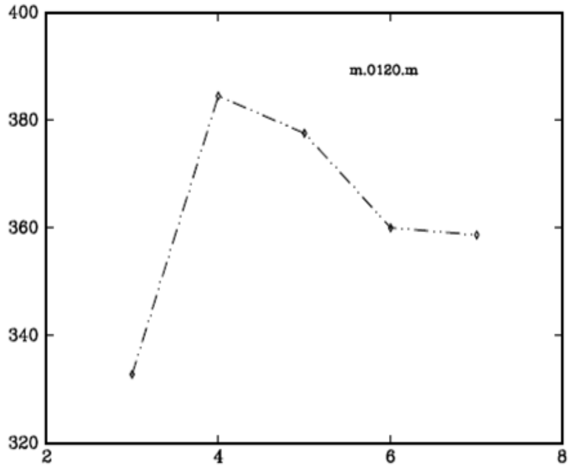

Figure 11: Variation of T_{CO} with m value

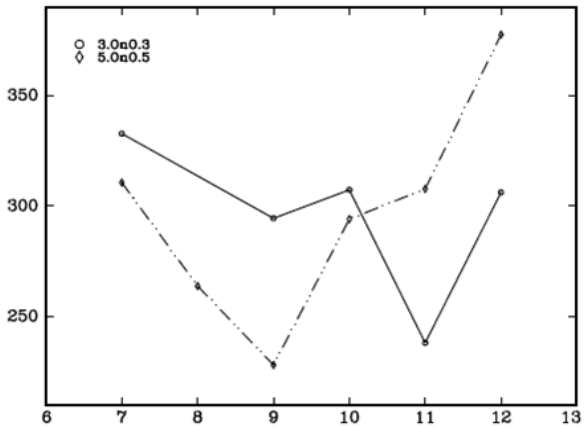

Figure 12: Variation of T_{CO} with n value.

The figures reveal that there is no regular variation of T_{CO} with these numbers and exhibits an odd-even effect with the even numbers showing higher values. Further, it is observed that the T_{CO} values are below that of the clearing temperatures reported for the DLC compounds. It is observed from our study that T_{CO} values are very sensitive to all the three parameters viz., B, β and Δn values. A change of slope (A) value of ± 0.00001 will change T_{CO} value by roughly ± 12 to 13 degrees. Similarly a change in β value by ± 0.01changes T_{CO} value by ± 7 degrees and similarly a change of ± 0.01 in Δn will show a change of ± 3.0 degrees in T_{CO} values. This reveals clearly that any change in these values exhibits a large change in the cross over temperatures which are in fact characteristic of the material under consideration.

The salient features observed from the study are

- The T_{CO} value is always less than the T_{NI} value.
- Lower the value of the slope obtained from equation $\langle n \rangle = A - BT$, the lower the value of T_{CO}. A change of 0.00001 in the slope value will show a change of 12 to 13 degrees in T_{CO}.
- Further, the cross over temperature depends on both β and Δn values also to some extent.
- The T_{CO} exhibits no regular variation with either n or m (figures 11 and 12)

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