Chapter 4

4.1 Infrared Measurement of Molecular Order Parameters in a Mixture of Rod-like and Bent-core Molecules :

As mentioned earlier, in a binary mixture the rod-like (R) and bent-core (BC) molecules can be expected to have different order parameters in the nematic phase. The BC molecule which deviates strongly from cylindrical symmetry requires two different order parameters for a full description even in a uniaxial phase. When the molecules are cylindrically symmetric a single order parameter S can describe the orientational order parameter. If it deviates from cylindrical symmetry two order parameters are required.

We have evaluated the order parameters in the nematic phase of mixtures of 8OCB and BC12 compounds by an optical technique in the previous chapter. The optical birefringence reflects only an average orientational order of the medium. The orientational order of the BC molecules
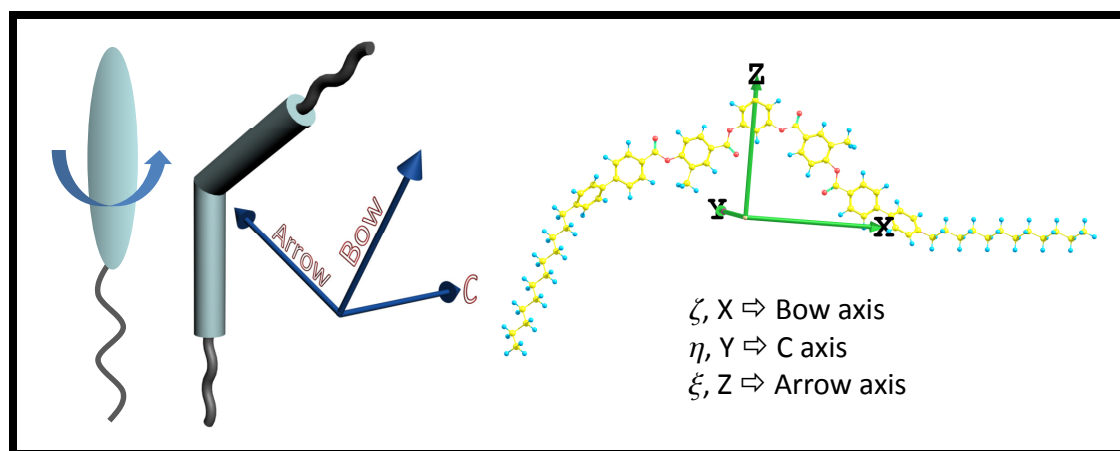
FIGURE 4.1: Rod-like molecules have cylindrical symmetry and bent-core molecules have shape biaxiality. The chains at the two ends of the molecule are not symmetrically oriented in this energy minimized structure of a single molecule. In the condensed nematic and SmA_d phases, a symmetric disposition can be expected to be favoured.

must be described by two order parameters S and D where D is called the *molecular biaxiality order parameter*. A measurement of D using the infrared dichroism technique is possible but would require two independent vibrational modes from the same molecule which can give rise to isolated bands in the IR spectrum[46]. We have used the $C_{Ph} - O$ bonds attached to the phenyl rings and the $C = O$ bonds present in the BC12 molecule to estimate S and D order parameters of the BC12 molecules in a mixture with 11 Mol% of BC12. This method requires a knowledge of the molecular structure. Using a molecular structure which minimizes the energy of single BC molecule the estimated biaxial order parameter D has a relatively large value in the nematic phase of the mixture. This probably shows that the geometrical structure of the molecule in the nematic phase is considerably different from the one which minimizes the single molecule conformational energy. We will first define the relevant order parameters.

4.2 Orientational Order Parameters of A Uniaxial Nematic With Biaxial Molecules

For an arbitrary shaped molecule the tensor order parameter[47] is given by,

$$S_{ij}^{\alpha\beta} = \frac{1}{2} \left\langle 3i_\alpha j_\beta - \delta_{\alpha\beta} \delta_{ij} \right\rangle \tag{4.1}$$

where α, $\beta = x$, y, z is a laboratory fixed coordinate system and i, $j = \xi$, η, ζ is a molecule fixed coordinate system and ζ is along the long axis of the molecule. i_α, j_β are the projections of the unit vectors of i and j along α and β respectively. $\delta_{\alpha\beta}$ and δ_{ij} are Kronecker deltas.
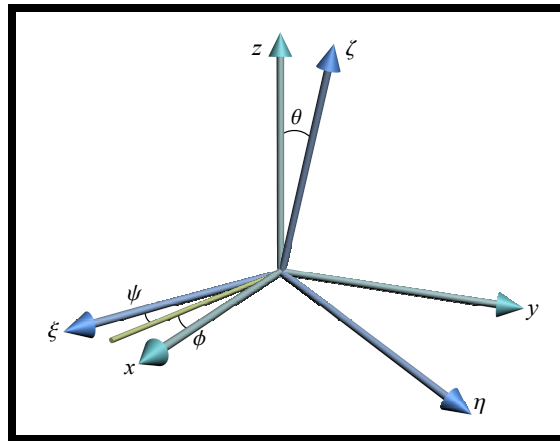

FIGURE 4.2: Eulerian angles between x, y, z and ξ, η and ζ coordinates systems.

The orientation of the molecule can be determined by the three Euler angles θ, ϕ and ψ (see Figure 4.2), where θ is the angle between the ζ and z axes, ψ is the angle between the ξ axis and normal to the $z - \zeta$ plane, and describes a rotation of the molecule around its long axis. ϕ is the angle between the x axis and the normal to the $z - \zeta$ plane. This describes a rotation of the whole molecule around the director (z axis). In the *uniaxial* phase ϕ can take all values (from $0 - 2\pi$) with equal probability and $S_{ij}^{\alpha\beta}$ is a symmetric tensor in i, j, as well as α and β. with zero trace. To describe the average orientation of the molecule with respect to the director, we need the components of ξ, η and ζ along z axis (see Figure 4.2).

$$\begin{aligned}
\xi_z &= \sin\theta \sin\psi \\
\eta_z &= \sin\theta \cos\psi \\
\zeta_z &= \cos\theta
\end{aligned}$$

As the director is along the z axis, the order parameter $S_{ij}^{\alpha\beta}$ (Equation 4.1) can be written as,

$$S_{ij}^{zz} = \frac{1}{2}\left\langle 3\,i_z\,j_z - \delta_{ij}\right\rangle \tag{4.2}$$

putting the values of ξ_z, η_z and ζ_z in Equation (4.2) and omitting the superscript zz we get,

$$\begin{aligned}
S_{\xi\xi} &= \frac{1}{2}\left\langle 3\,\xi_z^2 - 1\right\rangle \\
S_{\eta\eta} &= \frac{1}{2}\left\langle 3\,\eta_z^2 - 1\right\rangle \\
S_{\zeta\zeta} &= \frac{1}{2}\left\langle 3\,\zeta_z^2 - 1\right\rangle
\end{aligned} \tag{4.3}$$

From these we get, two order parameters S and D for a *uniaxial nematic* made of *biaxial molecules*,

$$S = S_{\zeta\zeta} = \frac{1}{2}\left\langle 3\,\zeta_z^2 - 1\right\rangle = \frac{1}{2}\left\langle 3\,\cos^2\theta - 1\right\rangle \tag{4.4}$$

and

$$D = S_{\eta\eta} - S_{\xi\xi} = \frac{1}{2}\left\langle 3(\eta_z^2 - \xi_z^2)\right\rangle = \frac{3}{2}\left\langle \sin^2\theta\,\cos 2\psi\right\rangle \tag{4.5}$$

A finite D means that there is a difference in the tendencies of the two transverse molecular axes to project on the z axis, which is a consequence of the biaxial nature of the molecules. Macroscopic properties like refractive indices (Δn) and dielectric constants ($\Delta\epsilon$) yield only one anisotropy and are hence inadequate to measure both S and D, which reflect two anisotropies. Techniques which depend on the response of individual bonds in the molecules are needed for the purpose of measuring both S and D.

Two methods have been used to measure both the orientational order parameters : (i) NMR spectroscopy where the mesogenic compounds are selectively deuterated. (ii) Infrared (IR) Dichroism technique[46]. We have used the IR technique, using isolated, pronounced and unique bands which are available in the IR spectra. If the orientation of the related transition moments or bonds are known with respect to the molecular geometry, we can calculate S and D order parameters.

Maier and Saupe[48] first derived the relation between the dichroic ratio and the order parameter S assuming cylindrically symmetric molecules. Later Korte[49] and Kocot *et al.* [50] derived the general relation considering both S and D order parameters.

Two sample geometries can be used to measure the order parameters by the IR dichroism technique: (i) One method makes use of polarized IR radiation and planar aligned samples[48, 51]. (ii) The second method is relatively simple and makes use of a homeotropically aligned sample and unpolarized radiation[52, 53]. In our experiment we have used the second method. The liquid crystal cell is made of two CaF$_2$ windows as CaF$_2$ is IR transparent. The two windows are rubbed in a random manner on chamois leather to get polished surfaces. Then they are treated with ODSE (octadecyl triethoxy silane) to obtain a homeotropic alignment (see Subsection 1.6.7 of Chapter 1) and $\sim 25 \mu$m thick mylar spacer is used to get a uniform thickness. The liquid crystal sample is filled in the isotropic phase by capillary flow ensuring that there are no air bubbles. The cell is kept inside a heater which is controlled by a PID algorithm. The heater with the sample cell is placed such that the IR radiation is incident parallel to the director **n**. The sample is heated to the isotropic phase and cooled in small steps. An each temperature the sample is equilibrated for 5 minutes to ($\sim$20 mk accuracy) and the transmission intensity is recorded in the wave number range $1000 - 3200 \, \mathrm{cm}^{-1}$.

4.3 Relation Between The Dichroic Ratio And The Order Parameters

Consider a sample which is aligned homeotropically along the Z direction of a space fixed coordinate system X, Y, Z. Let ξ, η and ζ be the molecule fixed coordinates, such that the long axis of the molecule is along the ζ axis and the director is parallel to the Z axis. The relation between these two coordinates can be described by the Euler angles θ, ψ and ϕ (see Figure 4.3a). Let the long axis (*ie.,* bow axis of BC12 molecule) be along ζ (see Figure 4.3a) and the transition moment related with the chemical bond of interest make an angle α with ζ-axis and its projection on the $\xi - \eta$ plane make an angle β with the ξ axis. The component of the oscillator strength $\mathcal{F}$ which is proportional to the square of the transition moment are given by[49],
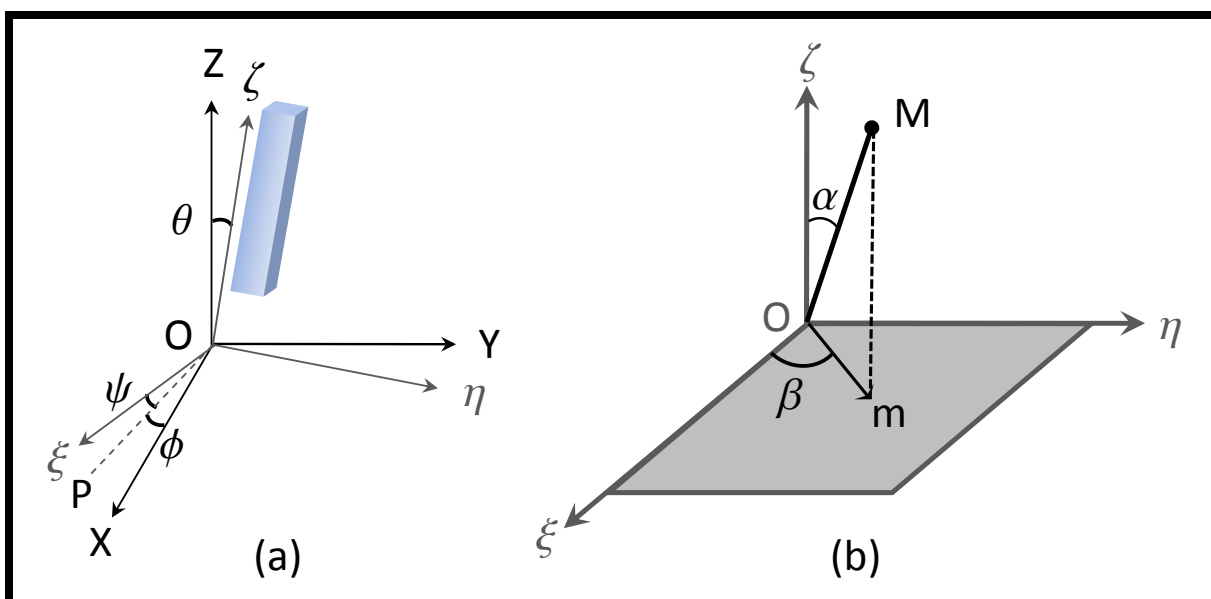
FIGURE 4.3: (a) Eulererian angles (b) the projections of a bond in the biaxial molecule on the molecular axes.

$$\begin{aligned}
\mathcal{F}_\xi &= \mathcal{F}\,\sin^2\alpha\,\cos^2\beta \\
\mathcal{F}_\eta &= \mathcal{F}\,\sin^2\alpha\,\sin^2\beta \\
\mathcal{F}_\zeta &= \mathcal{F}\,\cos^2\alpha
\end{aligned}$$

$$(4.6)$$

By using the the Euler transformations[54] we get the components parallel to the x, y, z axes respectively,

$$\begin{aligned}
\mathcal{F}_x = \mathcal{F}\,\big[&(\cos\phi\cos\psi - \cos\theta\sin\phi\sin\psi)^2\,\sin^2\alpha\cos^2\beta \\
&+(\cos\phi\sin\psi + \cos\theta\sin\phi\cos\psi)^2\,\sin^2\alpha\sin^2\beta \\
&+\sin^2\theta\sin^2\phi\cos^2\alpha\big]
\end{aligned}$$

$$(4.7)$$

$$(4.8)$$

$$\mathcal{F}_y = \mathcal{F}\left[(\sin\phi\cos\psi + \cos\theta\cos\phi\sin\psi)^2\ \sin^2\alpha\cos^2\beta\right.$$
$$+(\sin\phi\sin\psi - \cos\theta\cos\phi\cos\psi)^2\ \sin^2\alpha\sin^2\beta$$
$$\left.+\sin^2\theta\cos^2\phi\cos^2\alpha\right]\quad\text{and}\tag{4.9}$$

$$\mathcal{F}_z = \mathcal{F}\left[\sin^2\theta\sin^2\psi\sin^2\alpha\cos^2\beta + \sin^2\theta\cos^2\psi\sin^2\alpha\sin^2\beta\right.$$
$$\left.+\cos^2\theta\cos^2\alpha\right]\tag{4.10}$$

Now taking the ensemble average and by trigonometric manipulations we get,

$$\langle\mathcal{F}_x\rangle = \mathcal{F}\left[\frac{1}{2}\sin^2\alpha + \frac{1}{2}\left(1 - \frac{3}{2}\sin^2\alpha\right)\langle\sin^2\theta - t\rangle\right.$$
$$\left.+\frac{1}{4}\sin^2\alpha\cos 2\beta\left\langle\sin^2\theta\cos 2\psi + 2V\right\rangle\right]\tag{4.11}$$

$$\langle\mathcal{F}_y\rangle = \mathcal{F}\left[\frac{1}{2}\sin^2\alpha + \frac{1}{2}\left(1 - \frac{3}{2}\sin^2\alpha\right)\langle\sin^2\theta + t\rangle\right.$$
$$\left.+\frac{1}{4}\sin^2\alpha\cos 2\beta\left\langle\sin^2\theta\cos 2\psi - 2V\right\rangle\right]\tag{4.12}$$

$$\langle\mathcal{F}_z\rangle = \mathcal{F}\left[1 - \sin^2\alpha - \left(1 - \frac{3}{2}\sin^2\alpha\right)\left\langle\sin^2\theta\right\rangle\right.$$
$$\left.-\frac{1}{2}\left\langle\sin^2\theta\cos 2\psi\right\rangle\sin^2\alpha\cos 2\beta\right]\tag{4.13}$$

where,

$$t = \sin^2\theta\cos 2\phi\tag{4.14}$$
$$V = (1 + \cos^2\theta)\cos 2\phi\cos 2\psi - 2\cos\theta\sin 2\phi\sin 2\psi\tag{4.15}$$

In the uniaxial phase, $\langle\mathcal{F}_x\rangle$ and $\langle\mathcal{F}_y\rangle$ are equal. This implies both t and V vanish in Equation (4.11) and Equation (4.12)[55]. Substituting the expression of $S = (3\langle\cos^2\theta\rangle - 1)/2$ and $D = 3\langle\sin^2\theta\cos 2\psi\rangle/2$ we get,

$$\langle \mathcal{F}_x \rangle = \langle \mathcal{F}_y \rangle = \frac{1}{3} \mathcal{F} \left[1 - S(1 - \frac{3}{2} \sin^2 \alpha) + \frac{1}{2} D \sin^2 \alpha \cos 2\beta \right] \quad \text{and} \quad (4.16)$$

$$\langle \mathcal{F}_z \rangle = \frac{1}{3} \mathcal{F} \left[1 + 2S(1 - \frac{3}{2} \sin^2 \alpha) - D \sin^2 \alpha \cos 2\beta \right] \quad (4.17)$$

For a homeotropically aligned sample with the radiation incident along the Z direction (*ie.,* along the director) the absorbance is given by,

$$\begin{aligned} A &= \left[\langle \mathcal{F}_x \rangle + \langle \mathcal{F}_y \rangle \right] \\ &= \frac{2}{3} \mathcal{F} \left[1 - S \left(1 - \frac{3}{2} \sin^2 \alpha \right) + \frac{1}{2} D \sin^2 \alpha \cos 2\beta \right] \\ &= A_{\mathsf{LC}} \end{aligned} \quad (4.18)$$

This is the absorbance in the liquid crystalline phase. In the isotropic phase both S and D are zero giving,

$$A_{\mathsf{iso}} = \frac{2}{3} \mathcal{F} \quad (4.19)$$

The dichroic ratio

$$\boxed{R = \frac{A_{\mathsf{LC}}}{A_{\mathsf{iso}}}} \quad (4.20)$$

Substituting R and Equation (4.19) in Equation (4.18) we get,

$$\boxed{1 - R = S \left(1 - \frac{3}{2} \sin^2 \alpha \right) - \frac{1}{2} D \sin^2 \alpha \cos 2\beta}$$

$$(4.21)$$

It is clear that measurement of dichroic ratios (R) of two different bonds which make different angles α and β with respect to the molecular axes (ξ, η and ζ) can be used to estimate both S and D.
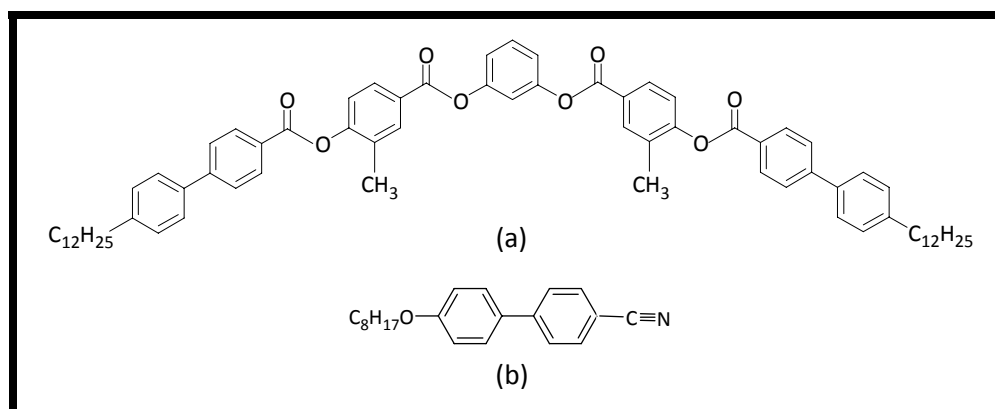
FIGURE 4.4: Molecular structures of (a) 1,3-phenylene bis[4–(3-methylbenzoyloxy)]$4'$-*n*- dodecyl-biphenyl $4'$ -carboxylate (BC12) and (b) 4-*n*-octyloxy $4'$-cyanobiphenyl (8OCB).

4.3.1 Different useful Chemical Bonds of 8OCB and BC12 Molecules

The 11M mixture has been used to measure the order parameters using the IR dichroism technique. Figure 4.5 shows the full spectrum of 11M mixture at 75°C (N phase). The structural formulae of the compounds 8OCB and BC12 are shown in Figure 4.4. The $C \equiv N$ bond of 8OCB molecule (Figure 4.4) gives rise to a strong isolated band at 2225 cm^{-1} (Figure 4.6) and it can be used to measure the orientational order parameter of 8OCB molecules. 8OCB molecules rotate practically freely about their long axes. We assume that the molecules are essentially cylindrically symmetric (though in reality there is a small deviation from cylindrical symmetry) and it is enough to measure the order parameter S. BC12 molecule has four $C = O$ bonds, and the stretching vibration of these bonds gives rise to a relatively wide and isolated band along with subsidiary peaks around $1760-1780$ cm^{-1} (see Figure 4.7). In an independent experiment we have seen that the $C_{Ph} - O$ (C stands for the carbon of the aromatic phenyl ring) bond of the 8OCB molecule occurs at 1179 cm^{-1} while that of the BC molecules occurs at a slightly lower frequency of 1165 cm^{-1} (see Figure 4.8). In the mixture the resulting split band corresponding to the $C_{Ph} - O$ bond can be decomposed into two Gaussian peaks. The intensities corresponding to the absorption of $C \equiv N$ bond of 8OCB, and $C = O$ bond of BC12 and $C_{Ph} - O$ of both molecules are plotted in logarithmic scales and the integrated absorptions (A) of all the bands are calculated by measuring the areas between baseline and the absorption profiles. The dichroic
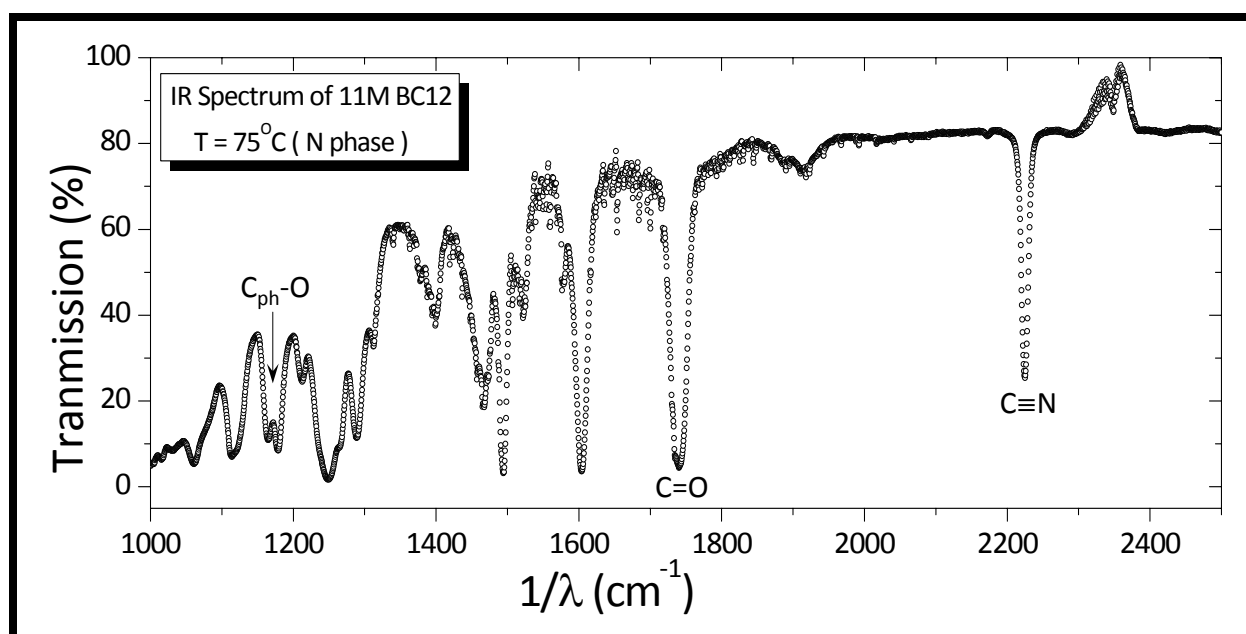
FIGURE 4.5: IR spectrum of 11M mixture in the nematic phase

ratios R $(= A_{\mathsf{LC}}/A_{\mathsf{iso}})$ corresponding to all the bonds are obtained at different temperatures. The table of $(1-R)$ of $C_{\mathsf{Ph}} - O$ and $C = O$ bonds of BC12 are shown in Table 4.1. $(1-R)_{C_{\mathsf{Ph}}-O}$ of BC12 monotonically increases with decrease in temperature. With decrease of temperature, $(1-R)_{C=O}$ of BC12 decreases upto 60°C and increases at 55°C.

We have calculated the S order parameter of 8OCB molecules using the absorption bands of both $C \equiv N$ and $C_{\mathsf{ph}} - O$ bonds for different temperatures. Both the bonds are along the long axes of the 8OCB molecule (see Figure 4.4). These two order parameter values are very close (see Figure 4.9). These numbers are also very similar to, though somewhat smaller than the average order parameter of the mixture estimated from optical birefringence. The difference between the IR data and the optical estimates increases at higher temperatures in the nematic phase(Figure 4.9).

In order to calculate the two order parameters S and D of BC molecules we should know the geometrical structure of the molecule. We have used the *Spartan 04* software to get the minimum energy conformation of a BC12 molecule. This software can be used to perform both molecular mechanics and quantum mechanical calculations. Though different methods give somewhat different molecular structures, the minimum energies are very similar. In the liquid crystalline

Temperature	$(1-R)_{C_{Ph}-O}$
100 (Iso)	0.00
80	0.01
75	0.06
70	0.09
65	0.10
60	0.11
55	0.12

Table 4.1: Temperature variation of $(1-R)_{C_{Ph}-O}$ of BC compound is listed. $(1-R)_{C_{Ph}-O}$ monotonically increases with decrease in temperature in the nematic range.

Temperature	$(1-R)_{C=O}$
100 (Iso)	0.00
80	-0.04
75	-0.07
70	-0.10
65	-0.12
60	-0.13
55	-0.11

Table 4.2: Temperature variation of $(1-R)_{C=O}$ of BC compound is listed. With decrease of temperature, $(1-R)_{C=O}$ decreases upto 60°C and increases at 55°C.

phases we expect that there is a distribution of different molecular structures. We can expect that in the liquid crystal phase where the molecules would like to pack efficiently, a symmetric structure is more likely than a non-symmetric structure. The Hartree-Fock BL3YP calculation gives a somewhat symmetric structure which we have used for further calculations. From the symmetrized molecular structure, we calculate the angles made by all the four $C=O$ bonds and all the four $C_{ph}-O$ bonds with the Bow, Arrow and C axes.

As we discussed in the previous chapter, in the nematic phase the long axes (Bow) of BC molecules are oriented along the long axes of 8OCB molecules. In the nematic phase ζ, ξ, η are taken to be along Bow, Arrow and C axes respectively. Using the angles made by the four $C_{ph}-O$ and $C=O$ bonds with the ζ, ξ and η axes we can calculate the average values of $\sin^2 \alpha$ and $\sin^2 \alpha \cos 2\beta$ for both the bonds. We get two equations of R (Equation (4.21)) for the two bonds $C_{ph}-O$ and $C=O$ and solving these we get S and D order parameters of the BC molecules.

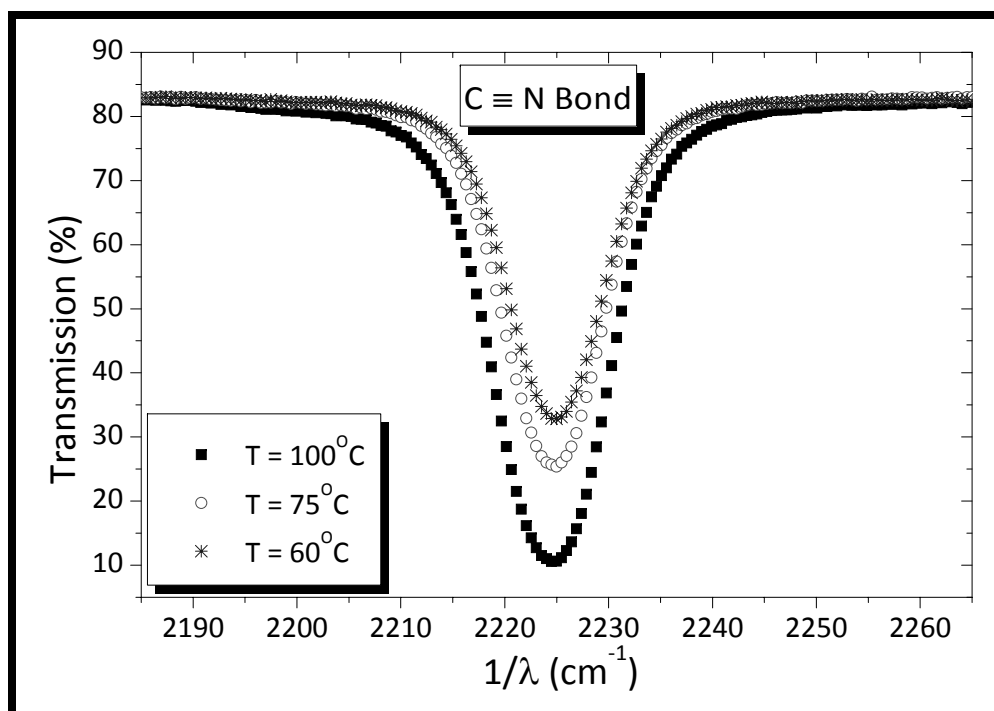Both S and D of BC12 are positive and increase with decreasing temperature in the nematic

FIGURE 4.6: Absorption band corresponding to the stretching of $C \equiv N$ bond of 8OCB molecules in the mixture

bonds	$(\zeta\angle C_{Ph}\text{-}O)°$	$(\xi\angle C_{Ph}\text{-}O)°$	$(\eta\angle C_{Ph}\text{-}O)°$	$(\zeta\angle C{=}O)°$	$(\xi\angle C{=}O)°$	$(\eta\angle C{=}O)°$
1	50.2	40.0	86.9	13.2	82.9	78.9
2	60.1	30.1	86.7	32.2	85.8	58.2
3	59.4	30.6	89.3	78.0	43.0	49.5
4	57.7	32.5	86.4	3.4	89.1	86.8

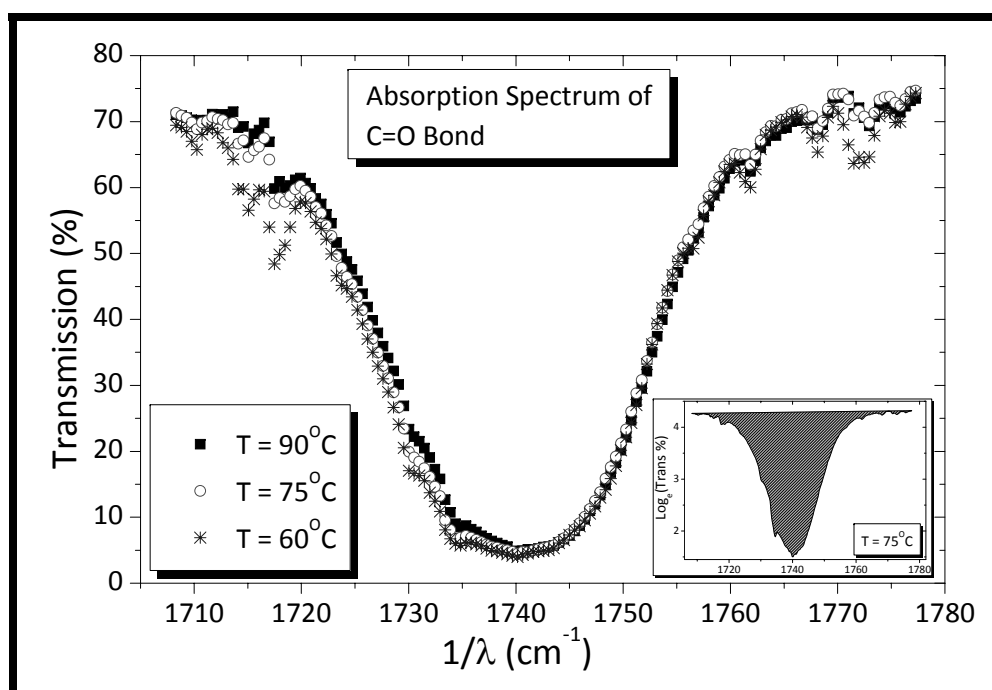Table 4.3: The angles made by the four C_{ph}-O and C=O bonds with ζ, ξ and η axes.

Figure 4.7: Absorption spectrum of C=O bond of the BC12 molecule. The inset shows the detail of measuring the absorption coefficient A using Log_e(Trans %) versus wavenumber plot.

phase (see Figure 4.9). In the smectic phase we could not get any reasonable values for S and D order parameters with the known mutual arrangement *viz.* the arrow axes along the director.

From the NMR studies on a nematic liquid crystal made of only BC molecules, Xu *et al.* [56] have found very low value ($\sim$ 0.025) of the order parameter D. Indeed in order to get reasonable values of the S order parameter, they had to use a molecular geometry which was different from the energy minimized geometry of a single molecule. We believe that the values of S that we have got are clearly underestimated compared to the values obtained from optical measurements and IR data on 8OCB molecules(Figure 4.9). Further, D parameters are also overestimated.

The main reason for this result is that the values of S and D are quite sensitive to the assumed molecular structure. Indeed calculation shows that there are many different conformers which have only slightly different energies (conformers 1 to 16 in Figure 4.11). There is considerable flexibility about the four $-$COO$-$ groups. In any case, these energies are for the conformations of *isolated* molecules. In the condensed nematic phase, packing effects which increases the overall entropy will be favoured and is likely to alter the average molecular conformation. Thus the
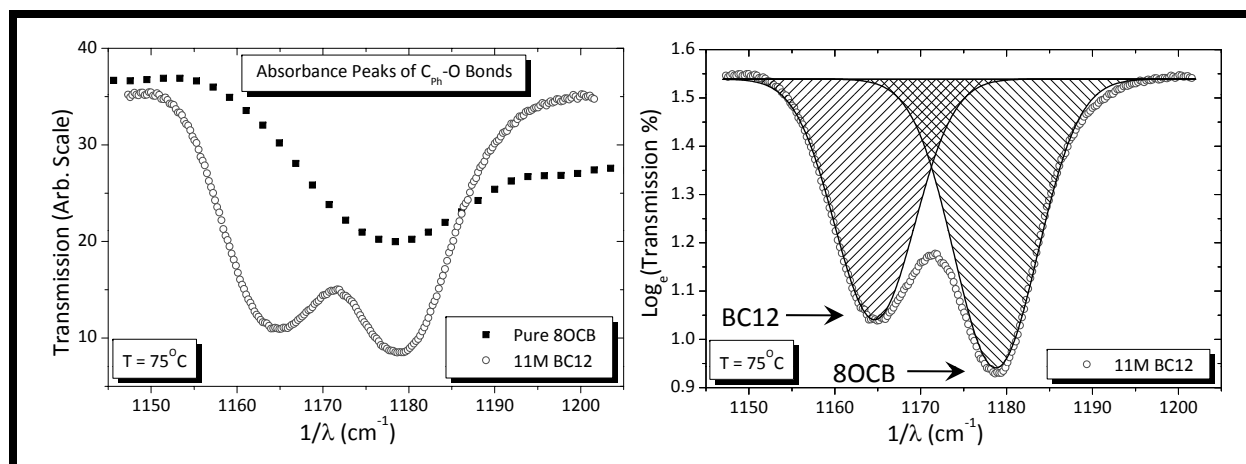
FIGURE 4.8: Absorption spectra corresponding to the $C_{ph} - O$ bond of both the molecules in the mixture and that of pure 8OCB. The Gaussian absorption profiles to separately get the A coefficients of the two types of molecules are shown in the right.
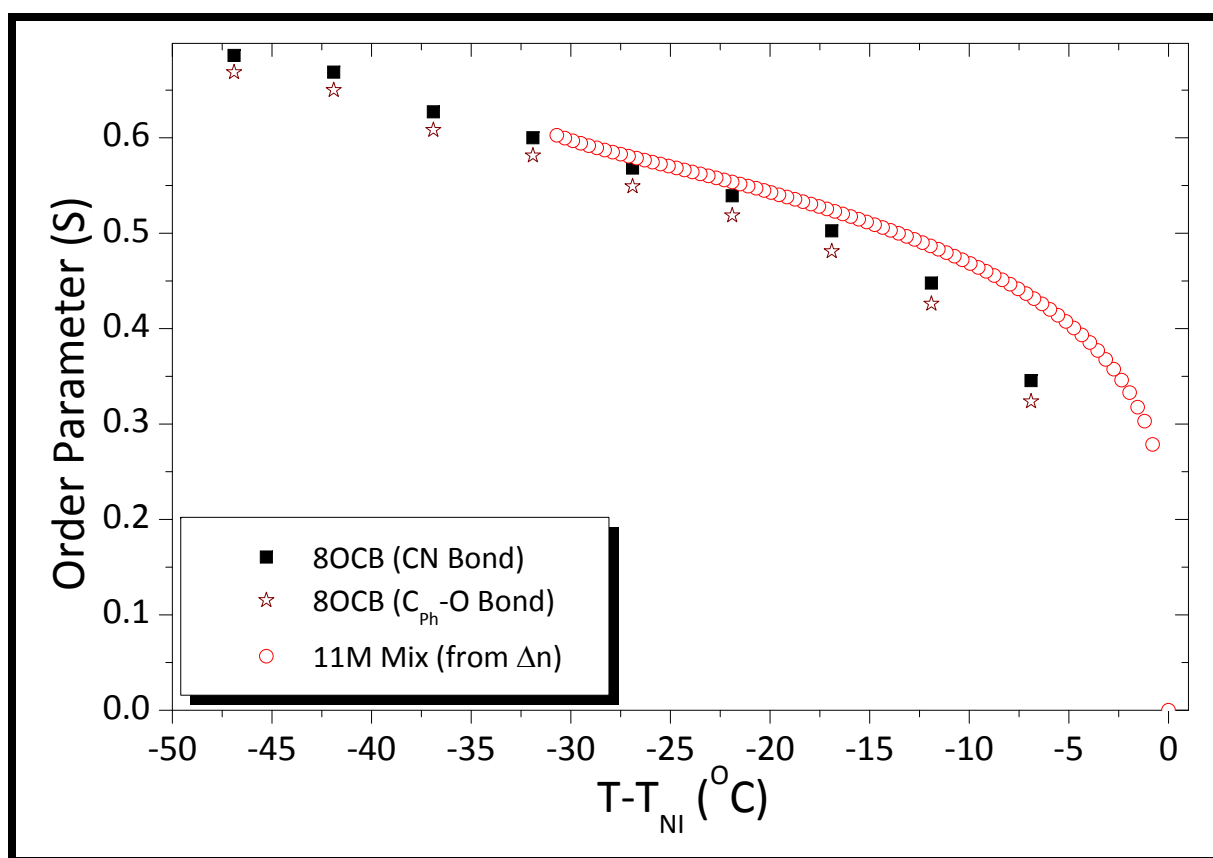

FIGURE 4.9: Order parameter of 8OCB using 2 different bonds compared with the average order parameter of the 11M mixture calculated from optical birefringence.
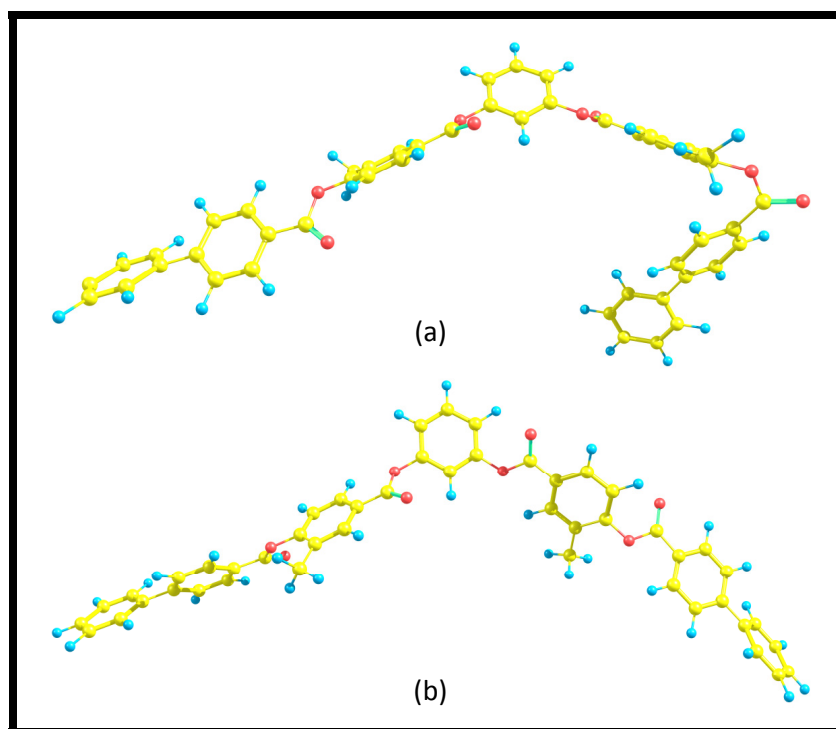
Figure 4.10: (a) One of the molecular structures of a BC12 molecule (only core) which is in the higher energy branch (20-38 conformers) (see Figure 4.11) (b) One of the molecular structures of a BC12 molecule (only core) which is in the lower energy branch (1-16 conformers). The structure having the lowest energy is used to calculate S and D of BC12.
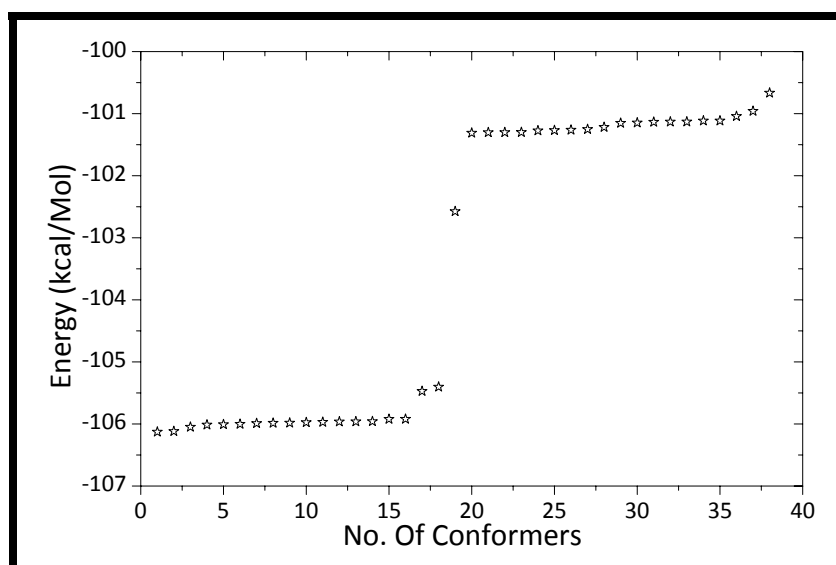

Figure 4.11: Calculated energies of different conformers of BC12 molecule. Conformers 1 to 16 have practically similar energies.
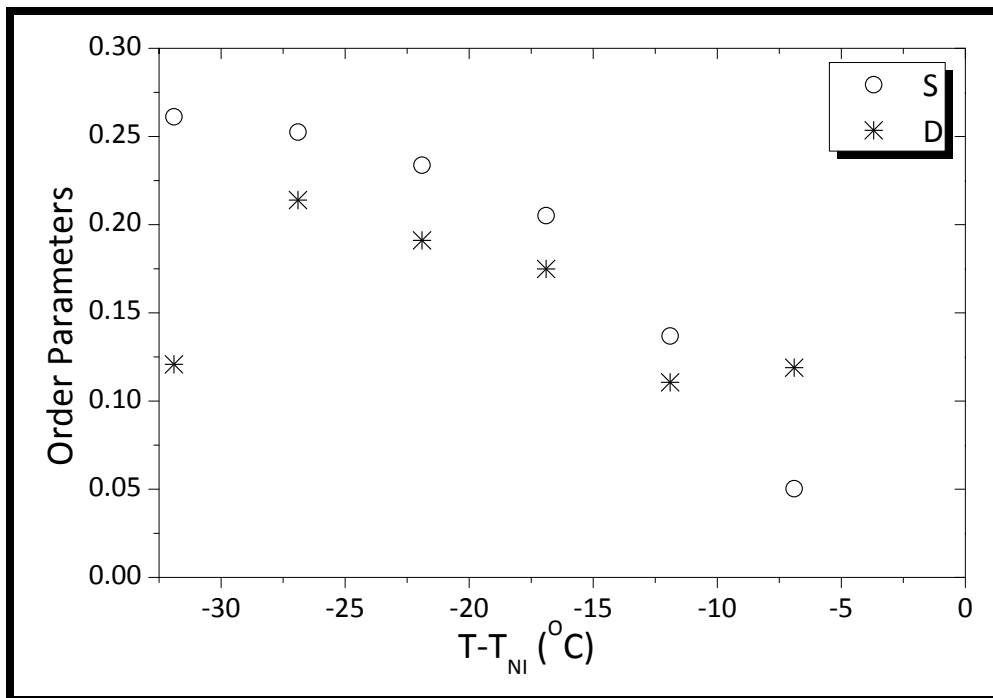
FIGURE 4.12: Uniaxial and biaxial order parameters of BC12, estimated from IR data.

average molecular structure is likely to be different from the one assumed in our calculations. Indeed a similar problem has been noted in calculating the order parameter from the NMR studies on single component nematogenic bent-core compounds[57]. Thus the order parameters S and D that we have estimated are to be taken with caution. The IR method can become useful only if the correct average molecular conformation in the mixture can be independently determined.

The birefringence Δn which measures the macroscopic anisotropy of the medium is also influenced by the biaxiality of the BC molecules. For the sake of completeness, we describe below the influence of the different order parameters of the components, and the biaxiality of the BC molecules on the optical properties.

4.4 Principal Polarizabilities of 8OCB and BC12 Molecules

The order parameter is directly related to polarizability anisotropy of the medium. If α_o and α_e are the polarizabilities of the medium for the ordinary and extraordinary refractive indices (see subsection(1.6.2)),

$$
\begin{aligned}
\alpha_e &= \overline{\alpha} + \frac{2}{3}\Delta\alpha_0\, S \\
\alpha_o &= \overline{\alpha} - \frac{1}{3}\Delta\alpha_0\, S
\end{aligned}
\tag{4.22}
$$

where $\overline{\alpha}$ is the average polarizability and $\Delta\alpha_0$ is the polarizability anisotropy of the molecule in the perfectly oriented medium. From these we get,

$$
S = \frac{\alpha_e - \alpha_o}{\Delta\alpha_0}
\tag{4.23}
$$

The exact relationship between the principal polarizabilities α_e and α_o and the refractive indices n_e and n_o is not known in strongly anisotropic liquid crystal medium. Vuks derived a formula[58] considering an isotropic internal field and this formula over-estimate the anisotropy of polarizability. The Vuks formula is given by, (see 1.6.2)

$$
\frac{4\pi}{3}\,\nu\,\alpha_e = \frac{n_e^2 - 1}{n^2 + 2}
\tag{4.24}
$$

$$
\frac{4\pi}{3}\,\nu\,\alpha_o = \frac{n_o^2 - 1}{n^2 + 2}
\tag{4.25}
$$

where $\nu(=\rho N_a/M)$ is the number of molecules/cc, ρ is the density, N_a is the Avogadro number and M is the molecular weights of the molecule. The order parameter S (Equation (1.14)),

$$
S = \frac{\alpha_e - \alpha_o}{\Delta\alpha_0} = \frac{\overline{\alpha}}{\Delta\alpha_0}\frac{n_e^2 - n_o^2}{n^2 - 1}
\tag{4.26}
$$

In the nematic phase, the Vuks equation can be rewritten as,

$$
\frac{4\pi}{3}\frac{\rho N_a}{M}\,(\alpha_e - \alpha_o) = \frac{n_e^2 - n_o^2}{n^2 + 2}
\tag{4.27}
$$

$$
\text{or,} \quad \frac{4\pi}{3}\frac{\rho N_a}{M}\,(\Delta\alpha_0\, S) = \frac{n_e^2 - n_o^2}{n^2 + 2}
\tag{4.28}
$$

In a mixture with two types of uniaxial molecules the Vuks equation can be written as,

$$\frac{4\pi}{3}\left[\frac{x\rho_1 N_a}{M_1 x + M_2(1-x)}\Delta\alpha_1 S_1 + \frac{(1-x)\rho_2 N_a}{M_1 x + M_2(1-x)}\Delta\alpha_2 S_2\right] = \frac{n_e^2 - n_o^2}{n^2 + 2} \qquad (4.29)$$

where, M_1 and M_2 are the molecular weight of two types of molecules, x is the Mol fraction of 1st type of molecule in the mixture, and $\Delta\alpha_1$, $\Delta\alpha_2$ are polarizability anisotropies and S_1, S_2 are order parameters of the two types of molecules respectively. Let us assume $\rho \approx 1$ for all the liquid crystals. Therefore,

$$\frac{4\pi}{3}\left[\frac{x N_a}{M_1 x + M_2(1-x)}\Delta\alpha_1 S_1 + \frac{(1-x)N_a}{M_1 x + M_2(1-x)}\Delta\alpha_2 S_2\right] = \frac{n_e^2 - n_o^2}{n^2 + 2} \qquad (4.30)$$

Following a procedure similar to that of Section 4.3 for polarizabilities, the optical anisotropy of nematic with biaxial molecules $\Delta\alpha\, S$ is to be replaced by,

$$\Delta\alpha\, S \rightarrow S\left(\alpha_\zeta - \frac{\alpha_\xi + \alpha_\eta}{2}\right) + \frac{D}{2}\left(\alpha_\xi - \alpha_\eta\right) \qquad (4.31)$$

where, α_ζ, α_ξ and α_η are three principal polarizabilities of the biaxial molecule along ζ, ξ and η axes respectively.

In our mixture of cylindrically symmetric rod-like and biaxial bent-core molecules the Vuks equation can be written as,

$$\frac{4\pi}{3}N_a\left[\frac{(1-x)\Delta\alpha_R}{N_c}S_R + \frac{x}{N_c}\left\{S_{BC}\left(\alpha_\zeta - \frac{\alpha_\xi + \alpha_\eta}{2}\right) + \frac{D_{BC}}{2}\left(\alpha_\xi - \alpha_\eta\right)\right\}\right] = \frac{n_e^2 - n_o^2}{n^2 + 2}$$
$$(4.32)$$

where, $N_c = M_{BC}x + M_R(1-x)$ and x is the Mol fraction of BC molecules in the mixture, $\Delta\alpha_R$, M_R are the polarizability anisotropy and molecular weight of the R molecule, respectively. S_{BC}, D_{BC} and M_{BC} are the molecular uniaxial and biaxial order parameters and molecular weight of the BC molecules respectively.

We have estimated the polarizability anisotropies of 8OCB and BC12 molecules. The main contribution of the molecular polarizability comes from the aromatic parts of the molecules. The aliphatic chain has a much smaller polarizability *anisotropy* compared to the aromatic part. We assume that in the nematic liquid crystal phase where the molecules would pack efficiently, a symmetric structure is more likely than non-symmetric structures. The symmetric structure as
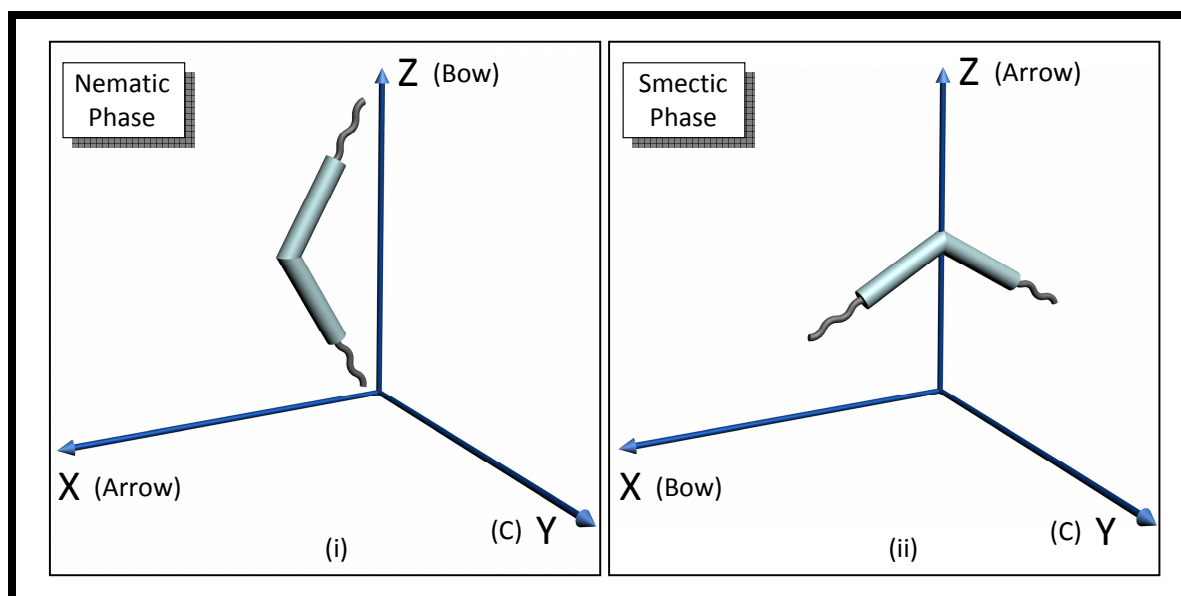
FIGURE 4.13: (i) In the N phase, the Bow axis of BC12 molecule is along the Director (Z) axis and the Arrow axis is along the X axis. (ii) In the Smectic phase, the arrow axis of BC12 molecule is along the Director (Z) axis and the Bow axis is along the X axis. C axis is along the Y axis in both the phase.

given by the Hartree-Fock BL3YP calculation is used for the calculations. We assume that the following three axes are the principal axes of polarizability of the molecule. We consider the line joining the last two carbon atoms of the aromatic core as the *bow* (B or ζ) axis. A line perpendicular to the bow axis and passing through the apex is called the *arrow* (A or ξ) axis. And a line perpendicular to both bow and arrow axes is called the C (η) axis.

The BC molecule is assumed to be made of two *uniaxial* R like molecules, attached at the center at an angle of $\sim 120°$. As both halves are equivalent it is enough to calculate the polarizability of one arm, and the principal polarizabilities of the BC molecule are then calculated using the usual tensorial addition. Each arm consists of one biphenyl unit, one and half benzene rings, two $O-C=O$ groups, one methyl group attached to the side, 11 CH_2 and 1 CH_3 groups in the chain. We use the group polarizability data from two recent references[59, 60]. In these papers the molecular electronic polarizabilities of a few mesogenic molecules have been calculated using *ab initio* quantum-mechanical techniques for different wavelengths, using different software packages. In our experiment we have used He–Ne laser to measure the refractive indices. As such the data closer to 633nm wavelength is used in our calculation. From reference[59] we have estimated the

polarizabilities of the O$-$C$=$O groups. And the polarizabilities of benzene, bi-phenyl rings and chains are taken from reference[60]. Using these we have calculated the polarizabilities along the Bow ($\alpha_B = 1312.9$), Arrow ($\alpha_A = 1182.9$) and C ($\alpha_C = 1038.2$) axes, where the polarizabilities are given in atomic unit (a.u.) for a wavelength of ~ 600nm. In the reference [60] itself the polarizabilities of 8OCB molecule was calculated for a wavelength of 600nm. Again treating the molecule as uniaxial rod, they get, $\alpha_{long} = 417.4$ a.u. and $\alpha_{short} = 191.2$ in a.u., and $\Delta\alpha = 226.2$ a.u. or, 33.5 Å^3

In the uniaxial nematic phase, if the molecules are oriented as in Figure 4.13(i), the polarizability anisotropy of BC12 molecule, $\Delta\alpha = \alpha_B - (\alpha_A + \alpha_C)/2 = 202.4$ a.u. or, 30 Å^3. And in the uniaxial smectic phase as in Figure 4.13(ii), $\Delta\alpha = \alpha_A - (\alpha_B + \alpha_C)/2 = 7.4$ a.u. or, 1.1 Å^3.

From Equation (4.32), it is clear that in the mixture, we have *three* unknown order parameters, *viz.* S_R corresponding to the rod-like molecule, S_{BC} and D_{BC} corresponding to the bent-core molecules. As only one anisotropy, *viz.* $(n_e - n_o)$ is measured, it will be impossible to measure all the order parameters from such a single macroscopic anisotropy. However, as we discussed in the previous chapter, the birefringence data used with the Haller extrapolation procedure gives a reasonable measure of the macroscopic orientational order parameter in the medium.

4.5 Conclusions

The attempt to measure both S and D molecular orientational order parameters of the BC molecules in the 11M mixture shows that the average geometrical conformations of the molecule may be quite different from the one got on the basis of energy minimization of a single BC molecule. The packing effects are likely to change the molecular structure to favour entropic gain in the free energy. Since BC12 has four relatively flexible O$-$C$=$O groups, such a change of structure which may also depend on temperature, is highly likely.