CHAPTER 3

FAR-INFRARED ABSORPTION IN A HOMOLOGOUS SERIES OF LIQUID CRYSTALS

3.1 Introduction

There has been considerable interest recently in the far-infrared (submillimetre wave) absorption of polar fluids in the 10 - 210 cm^{-1} range. Based on numerous theoretical[1-5] and experimental[6-12] studies it is now recognised that, in general, the four possible factors that normally contribute to their absorption in this region are:

i) the tail of the microwave Debye absorption, corrected for molecular inertial effects,[13-16]

ii) the Poley resonance due to the librational motion of the molecule as a whole in a temporary cage formed by its neighbours,

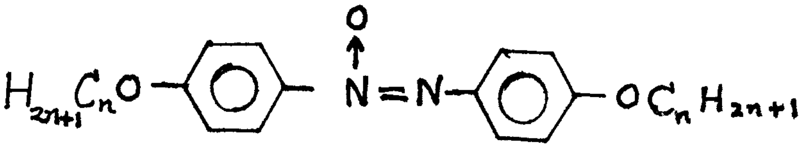
iii) the torsional motion of specific polar groups which are capable of undergoing intramolecular reorientation, and

iv) other possible low frequency deformation modes of the molecule.

The absorption of nonpolar fluids has been accounted for in terms of the transient dipoles induced by the fields from the neighbours.[12]

The rather complex molecular structure of most thermotropic liquid crystals[17] makes it very likely that their far-infrared absorption might arise from overlapping contributions both due to intramolecular motion and the permanent dipole moment of the molecules, if any. Experimentally, it can become quite difficult to discriminate between these factors and assess their relative importance solely from the spectra of unrelated mesogens, as their molecular structure and dipole moments may vary considerably. A systematic study of several homologues within a given series, as a function of the end chain length, is therefore desirable as it can lead to a better understanding of the spectra and their dependence on the molecular structure. While this approach is evident in past studies of several other properties[16,19] of liquid crystals, including their Raman[20,21] and near-infrared[22,23] spectra, the far-infrared studies reported hitherto[24-32] have only dealt with specific mesogens without any attempt to correlate the spectral changes within a series with the corresponding molecular structure.

In this chapter we present the results of a far-infrared investigation of seven members of the well known p,p'-di-n-alkoxyazoxybenzene series,[24] $C_1 - C_7$, the number of carbon atoms in their alkyl chain varying from 1 - 7. Molecules of this series have the structure



Here we discuss the spectra of the different compounds in the fluid phases in relation to their molecular structure. This series of compounds were chosen for the present study as their thermal,[33] optical[34,35] and microwave dielectric[36] properties are all well characterised. Moreover the orientation of their permanent dipole moment, due to the central azoxy group, as also that of their end alkoxy group moments are known to contribute to the du —— dielectric relaxation process rn their fluid phases. One can therefore expect that the short time details of both the rigid molecular motion and the end group motion should be manifested in their far-infrared spectra. Indeed, our results show that the end group motion does make a significant contribution to the absorption, especially in the case of the lower homologues.

3.2 Experimental

C_1 - C_7 obtained from Eastman Kodak Co. were purified, where necessary, by recrystallisation and column chromatography. The nematic-isotropic transition temperatures (T_{NI}) were determined by thermal microscopy and they compared well, to within 0.5°C, with the values reported by Arnold.[33]

The closely related mesomorphic p,p'-azoxytoluene (PAT) was also studied during this investigation. It was synthesised by the oxidation of p-nitrotoluene, following the method used for the preparation of azoxybenzene.[37] Far-infrared absorption spectra in the range 30-210 cm^{-1} were obtained using the Polytec FIR-30 Fourier spectrometer. The spectral resolution was between 5 - 8 cm^{-1}. The sample cell consisted of two wedged α-quartz windows separated by a teflon spacer of ~ 110 μm thickness. The plane of the windows contained the two principal axes. For polarization studies of C_1 (PAA) in the nematic phase, the windows were rubbed parallel to the c axis and the liquid crystal allowed to flow between them along the direction of rubbing. Although the resultant sample was homogeneously aligned, the degree of alignment was not quite uniform over the entire sample. Other experimental details are found in chapter 2 and elsewhere.[24-26]

Though the cell windows were wedged, the parallelism of the liquid films can create interference fringes in the observed spectra. Such fringes were not noticeable in C_1 and C_2. However, weak fringes were seen in C_3 - C_7 and PAT presumably because they all exhibit much lower absorbance. The observed amplitude (typically between 4% - 6%) and spacing ($\sim$30 cm^{-1}) of these fringes were in good agreement with estimates based on the sample film thickness and the available data on the far-infrared refractive indices of α-quartz[38] as also the high frequency dielectric constants of the liquid crystals[36] in the microwave region. The spectra of C_3 - C_7 reported here have been corrected so as to remove these weak interference fringes from the observed spectra. For this purpose, the transmission spectra of two independent measurements were first averaged. The final spectrum was then hand drawn through the mean values between successive maxima and minima. It was found that the numerical fringe removal method described by Clark and Moffatt[39] also yielded results closely similar to that obtained by the above procedure. In view of the low absorbance, the considerable breadth and the absence of any sharp features in the spectra of C_3 - C_7, as will be seen later, subtraction of the fringes from the observed spectra is unlikely to obscure or degrade their spectral content to any significant extent. In all cases, the intensity values of the spectra reported here are estimated to be accurate to within ~5%.

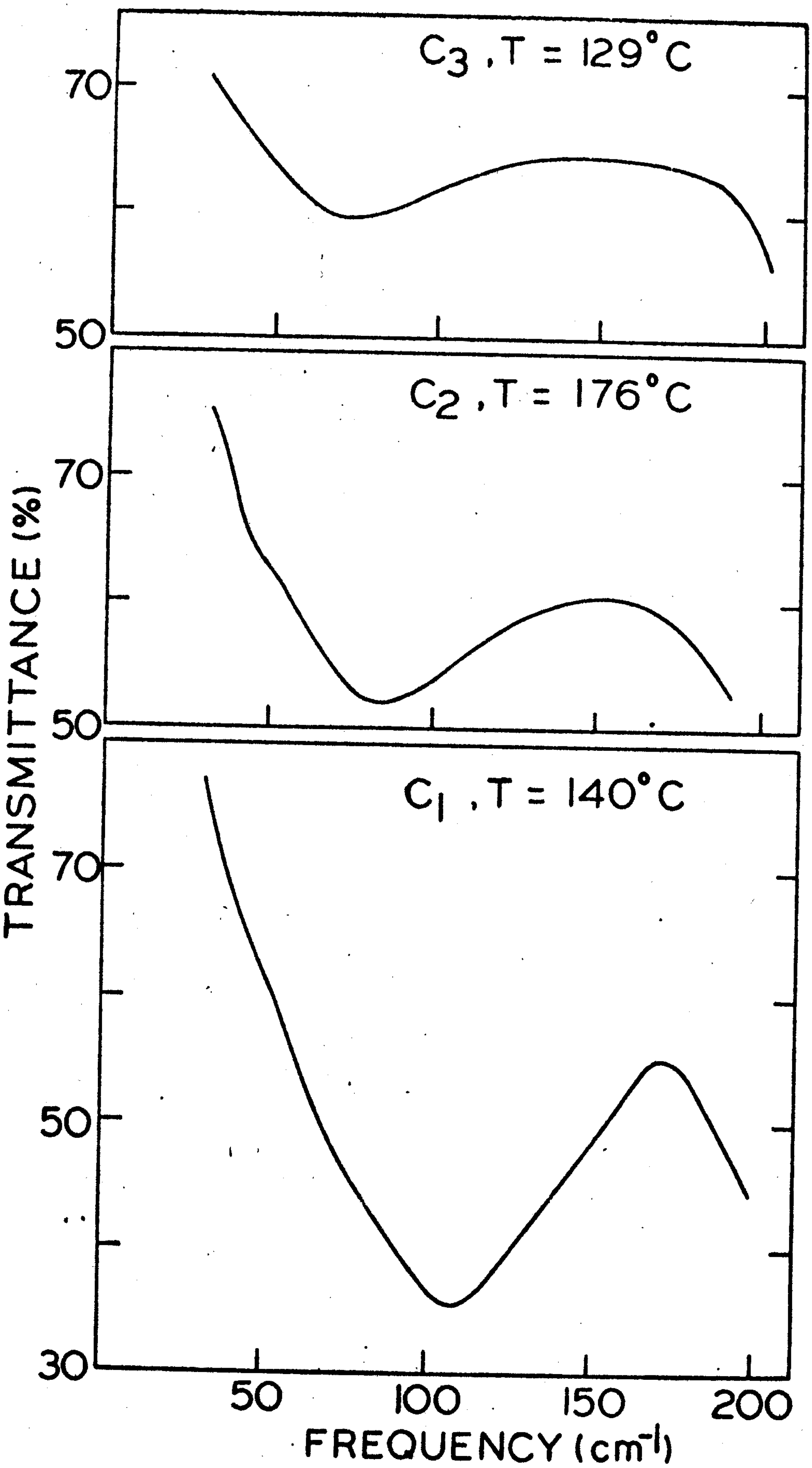
3.3 Results and Discussion

The long range molecular ordering of liquid crystals is generally found to have no pronounced effects on their near- and far-infrared spectra. Rather, the spectra appear to be more sensitive to the molecular structure and short range effects in the fluid phases.[24-32] Thus, the isotropic, the nematic and the smectic A and C phases all yield closely similar spectra. This was found to be the case during the present study also. However, polydomain liquid crystal samples sometimes cause loss of radiation due to scattering and this can lead to minor differences in the intensities and baselines of the spectra, as compared to those of the isotropic phase. Such effects are, of course, wavelength dependent and usually become noticeable at wavelengths shorter than 100 μm. Both to avoid the effects arising from such artifacts and to simplify the task of choosing the dielectric parameters needed for the following discussion, we shall concern ourselves here mainly with the spectra of all the mesogens in the isotropic phase. This however does not limit our main arguments and conclusions strictly to the isotropic phase alone, as the short range molecular order in this phase does not differ appreciably from that of the nematic phase.[31,40]

Figures 3.1 and 3.2 show the spectra of $C_1 - C_7$ in the isotropic phase. The intensity of the absorption is maximum in the case of C_1. A monotonic decrease in the absorption strength is evident on going to C_2 and C_3. A similar trend is seen with regard to the frequency at maximum absorption in the three lowest homologues. To within ± 3 cm^{-1}, the respective values in $C_1 - C_3$ are 105, 84 and 75 cm^{-1}. The spectra of $C_4 - C_7$ appear too broadened to permit a straightforward comparison of their intensities or the positions of

FIGURE 3.1

Far-infrared absorption spectra of $C_1 - C_3$ in the isotropic phase. The respective sample temperatures are also indicated.


C$_3$, T = 129°C
C$_2$, T = 176°C
C$_1$, T = 140°C
70
50
70
50
70
50
30
50
100
150
200
TRANSMITTANCE (%)
FREQUENCY (cm^{-1})

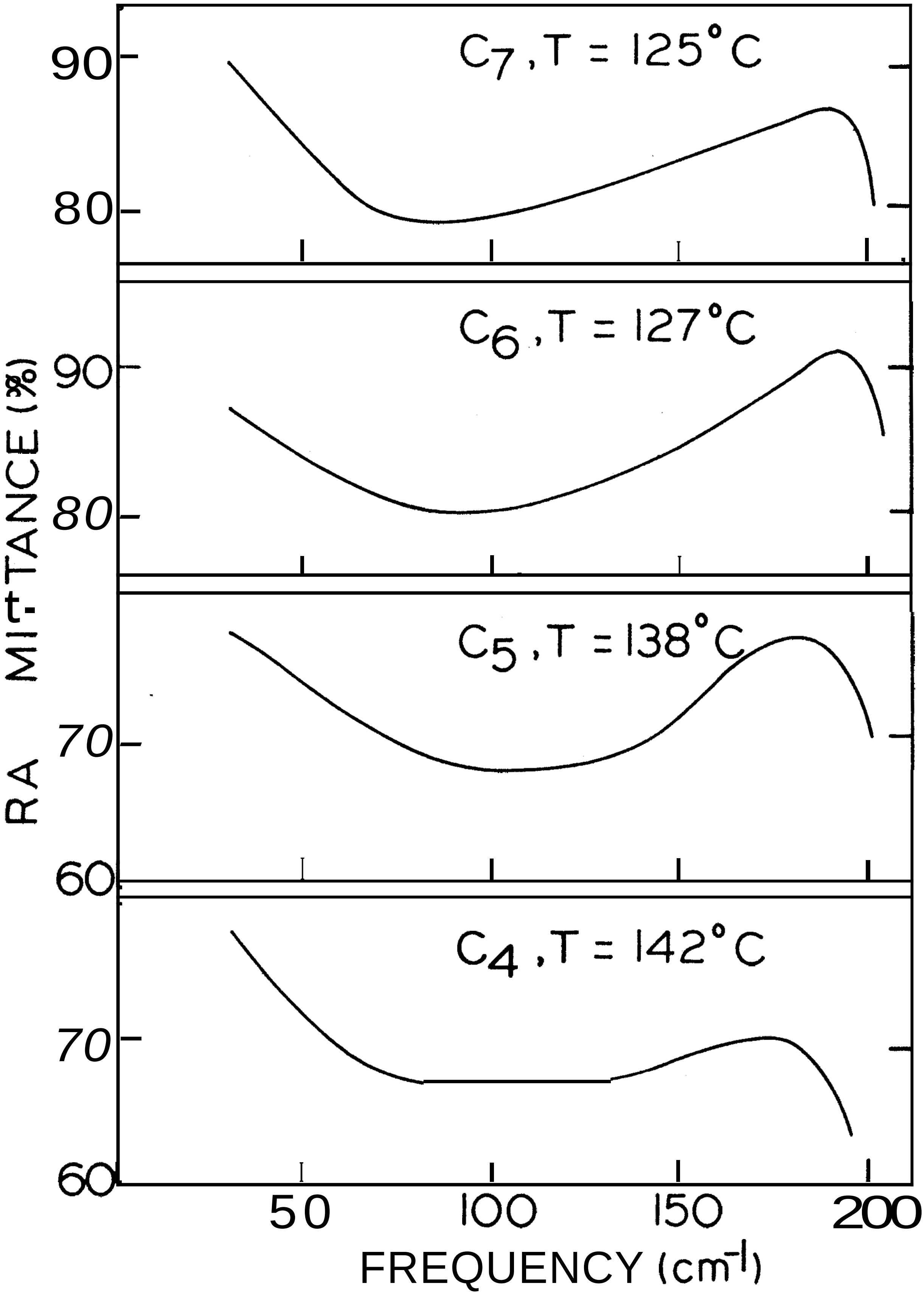


FIGURE 32

absorption spectra of $C_4 - C_7$ in the isotropic phase. The respective sample temperatures are also indicated.

their band maxima. It is however seen that the weak central band still present in C_3 becomes smeared and practically unobservable in $C_4 - C_7$. All the spectra exhibit an increase in the absorption beyond 180 cm^{-1}. This is likely to originate from the intramolecular CH_3 torsion which is expected to occur in the range 190 - 210 cm^{-1}. The width of the bands at half-maximum absorption is ~ 70 cm^{-1} or greater in all cases. This large width is reminiscent of similar behaviour observed in many other polar liquids as well.[7,12]

Table 3.1 lists the molecular and dielectric parameters which are pertinent to the following discussion. Moment of inertia values about the long molecular axis (I) have been calculated for the planar, fully extended, trans conformation of the molecules. The relevant bond lengths and angles of the aromatic and the alkyl parts, respectively, were taken from the crystal structure data[41,42] of C_1 (PAA) and CBOOA. n^2_{IR} is the square of the refractive index of the isotropic phase in the far-infrared at ~ 50 μm. This was estimated by first extrapolating the indices measured in the visible region[34,35] to 2 μm using the empirical relation[43]

$$n^2 - 1 = a + \frac{b}{(\lambda^2 - \lambda_o^2)}, \qquad (1)$$

where a and b are constants to be determined, n^2 is the square of the refractive index at wavelength λ, and λ_o is the resonance wavelength[44] in the ultraviolet region. A 5% increase over the extrapolated value at 2 μm was then assumed to allow for the usually small dispersion effects associated with the infrared active, intramolecular vibrational modes which normally occur within the range 2 - 50 μm. This procedure has previously been used with satisfactory results in the case of other simple polar liquids.[6,12] The n^2_{IR} values so obtained here are also comparable to the experimentally measured indices in several polar liquids.[7,8,11]

ε_∞ is the limiting or high frequency value of the dielectric constant determined by Axmann[36] from Cole-Cole plots of the Debye dispersion data in the microwave region. These values listed in table 3.1 also relate to the isotropic phase, as already noted, close to T_{NI}. The ε_∞ values of C_2, C_3 and C_5 are, to our knowledge, yet to be determined.

Table 3.1

Molecular and dielectric parameters of the homologues studied. I is in units of 10^{-38} g cm^2

Homologue	I	n^2_{IR}	ε^{*}
C_1	4.10	2.65	3.027
C_2	4.25	2.61	-
C_3	5.11	2.53	-
C_4	5.30	2.57	2.680
C_5	6.21	2.45	-
C_6	6.45	2.40	2.569
C_7	7.30	2.40	2.546

*Reference 36; blanks in this column indicate that the corresponding values have not been determined so far.

The asymptotic or limiting value of the absorption coefficient predicted by the Debye theory[45] is given by

$$\alpha_{\infty} = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{c\tau(\varepsilon_{\infty})^{1/2}} \quad , \qquad (2)$$

where c is the velocity of light, ε_0 is the static dielectric constant, and τ is the Debye relaxation time. Using the appropriate dielectric parameters determined by Ammann,[36] we find that the α_{∞} values in the far-infrared are less than 1.6 Np cm^{-1} for all the compounds. Also, the actual values would be even lower if the molecular inertial effects,[13-16] neglected by Debye, are taken into consideration. We note however that even in C_6 or C_7, where the absorption strength is the lowest, the peak absorption coefficient is $\sim$ 20 Np cm^{-1}. Hence the tail of the Debye process can only account for a small fraction of the observed intensities.

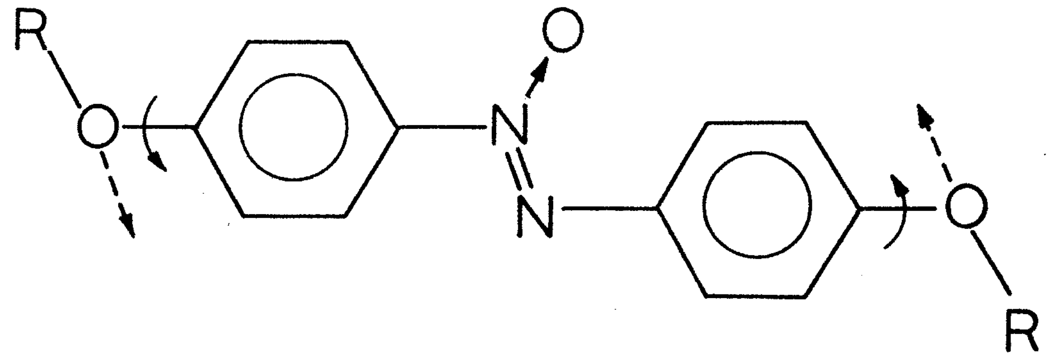
From table 3.1 it is seen that $n_{IR}^2 < \varepsilon_{\infty}$, the difference being the greatest in the case of C_1. This clearly points to the fact that the short time details of the dipolar correlation function are manifested in the far-infrared region. As all these molecules possess a permanent dipole moment, the Poley absorption due to their librational motion about the long axis will necessarily contribute to the far-infrared spectra,[31] provided that the height of the potential barrier which hinders the molecular reorientation is larger than kT. This is generally the case even in the isotropic phase of liquid crystals.[40] However, it seems unlikely that the Poley absorption can completely account for the much stronger absorption of $C_1 - C_3$ as well as the considerable intensity variation that occurs within these three compounds. At $(T_{NI} + 1)$°C, the respective densities[46,47] (ρ) of C_1 and C_2 are 1.143 and 1.060, while their molecular weights (M) are 258 and 286. From table 3.1, the I value of C_3 is $\sim 3\%$ greater than that of C_1. The dipole moments (μ) of the compounds, measured in benzene solutions, are all identical[36,48] to within ~ 3%. We recall[5,49] that the peak position and the total intensity of the librational or Poley absorption should be inversely proportional to $(I)^{1/2}$ and I, respectively; the total intensity of the band should also be directly proportional to μ^2 and N, where N is the molecular number density in the sample volume. If we now make the reasonable assumption that the mean width and depth of the intermolecular potential well[5] within which the molecules librate about their long axes do not differ appreciably between C_1 and C_2, then the peak position of the librational absorption must remain practically unchanged between C_1 and C_2. Also, the above mentioned differences in their ρ, M, I and N values are expected to cause, at the most, a reduction of 20% - 25% in the strength of the librational absorption in C_2 as compared to C_1. In contrast, we note from figure 3.1 that the absorbance of C_2 is smaller by about a factor of 2, while its peak position also shifts down by ~21 cm^{-1}.

We therefore conclude that there must be present an additional, intramolecular contribution which is much more sensitively dependent on the end alkyl group than the Poley absorption. Figure 3.3 shows the two possible conformations of these molecules wherein the alkyl groups (R) are in either the trans or the cis position relative to each other. The end alkoxy groups carry a dipole moment of ~1.3 D. Their directions, indicated by the broken arrows make an angle of ~70° with the para axis of the phenyl rings. The cis-trans isomerism of the molecules is essentially a consequence of the ability of the alkoxy groups to reorient about the phenyl-oxygen bonds. As these internal rotations are sufficiently fast, they also contribute to the overall dielectric relaxation process in the microwave region. It is however to be expected that these intramolecular motions would be hindered by a barrier of considerable height. For example, in both p-dimethoxy benzene (DMB) and anisole, the barrier to methoxy reorientation[9] is found to be ~ 6 kcal/mole. In such cases, the short time behaviour of the internal rotation of the polar group is manifested as a torsional band in their far-infrared spectra. Such a far-infrared active 'echo' of every low frequency dipolar relaxation process is expected on general theoretical grounds[50,51] and experimentally observed in many simpler liquids.[9,10] For instance, while the *cis-trans* isomerism in DMB contributes effectively to the dielectric relaxation process observed in the microwave region, the torsion of the methoxy groups leads to a broad far-infrared absorption band[9] centred at 92 cm^{-1}, with a rather large width of 75 cm^{-1}.

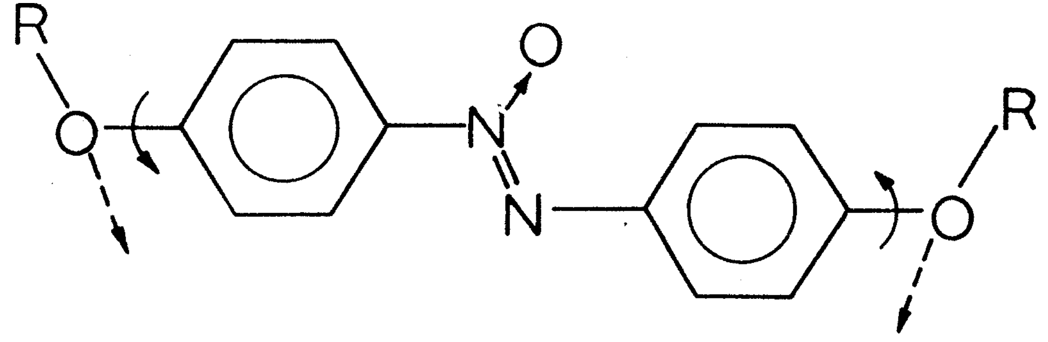
We therefore suggest that the strong absorption in C_1 derives a major part of its intensity from the torsion of the methoxy groups about the phenyl-oxygen bonds, as indicated by the curved arrows in figure 3.3.

FIGURE 3.3

Molecular structure and two possible conformations of the p,p'-di-n-alkoxyazoxybenzene molecules. *trans* and *cis* denote the relative orientation of one end alkyl group ($R = C_mH_{2m+1}$) with respect to the other. Broken arrows indicate the direction of the dipole moment carried by the end alkoxy groups. Curved arrows symbolise the possible reorientation of the alkoxy groups around the phenyl-oxygen bonds.



trans



cis

Quite conceivably, the barrier which hinders this torsional motion could be both narrower and steeper than that in simple liquids such as DMB or anisole, because of the greater anisotropy of the molecular shape as also the short range intermolecular order which persists even in the isotropic phase of mesogens. This might also explain the upward shift in the peak position of the band in C_1, as compared to that in DMB.

The intensity and the peak position of the alkoxy torsional band should be inversely proportional to I' and $(I')^{1/2}$, respectively,[5,49] where I' is the reduced moment of inertia for the rotation of the alkyl group about the phenyl-oxygen bond. For C_1 and C_2, the principal moments of inertia for overall rotation of the molecules are expected to change only slightly with the internal rotation of the end groups. Hence to a satisfactory degree of approximation their I' is given by[52]

$$I' = A\left(1 - \sum_i A\,\beta_i^2 / I_i\right) ; \qquad (5)$$

here A is the moment of inertia of the end alkyl group itself about the phenyl-oxygen bond, β_i is the direction cosine between this bond and the i^{th} principal axis of the whole molecule, and I_i is the moment of inertia of the whole molecule about the latter axis. In the present case, although the two phenyl-oxygen bonds make an angle of ~ 11° with each other,[41] we find that for C_1 and C_2 the resultant difference in the I' value of one end group compared to that of the other is negligible as it is within 1%. We thus estimate the respective average I' values of C_1 and C_2 to be 0.39 and 0.53, in units of 10^{-38} g cm^2. Now, if most of the intensity of the strong band centred at 105 cm^{-1} in C_1 originates from the end group torsion, in C_2 the corresponding peak position must occur at 90 ± 3 cm^{-1}. The intensity of the band in C_2 should also decrease by nearly a factor of 2 as compared to C_1, after the differences in their respective I' and N values are taken into account. The observed peak position of 84 cm^{-1} in C_2 is in fair agreement with that predicted. In as much as the relative shift in the peak positions of C_1 and C_2 is largely determined by their I' values, it follows that in C_2 also, the peak intensity of the torsional band must exceed that of the Poley absorption. Furthermore, it appears that the torsional barrier itself does not change appreciably between C_1 and C_2. The observed decrease in the absorbance of C_2 is also in reasonable agreement with that expected.

With longer alkyl chains, the intramolecular reorientation will require increasing cooperation between neighbouring molecules. Hence one expects that the torsional barrier should increase in the higher homologues. The different possible chain conformations will also cause a spread in the I' value and this will effectively smear out the band over a wider range of frequencies. Such a broadening due to a multiplicity of chain conformations is of course not possible in the case of C_1 and C_2. Finally, the increasing values of I' in the higher homologues will serve to attenuate Ma torsional band. For these reasons, the task of estimating its peak position and intensity in 4 - C_7 as also the calculation of their I' values becomes more and more complicated. In any case, the Foley absorption will begin to emerge as the more important process among the higher homologues. As it is less sensitive to the increase in chain length, only a gradual decrease in its intensity is expected. This picture is in qualitative agreement with the spectra of C_3 - C_7.

In order to seek further confirmation of the assignment of the strong absorption in C_1 to the methoxy group torsion, we have examined its polarization characteristics in the aligned nematic phase. In addition, we have also studied the absorption of the structurally related mesomorphic compound PAT in its liquid phase at 80°C. The latter spectrum is shown in figure 3.4. The weak structure seen clearly in the interval

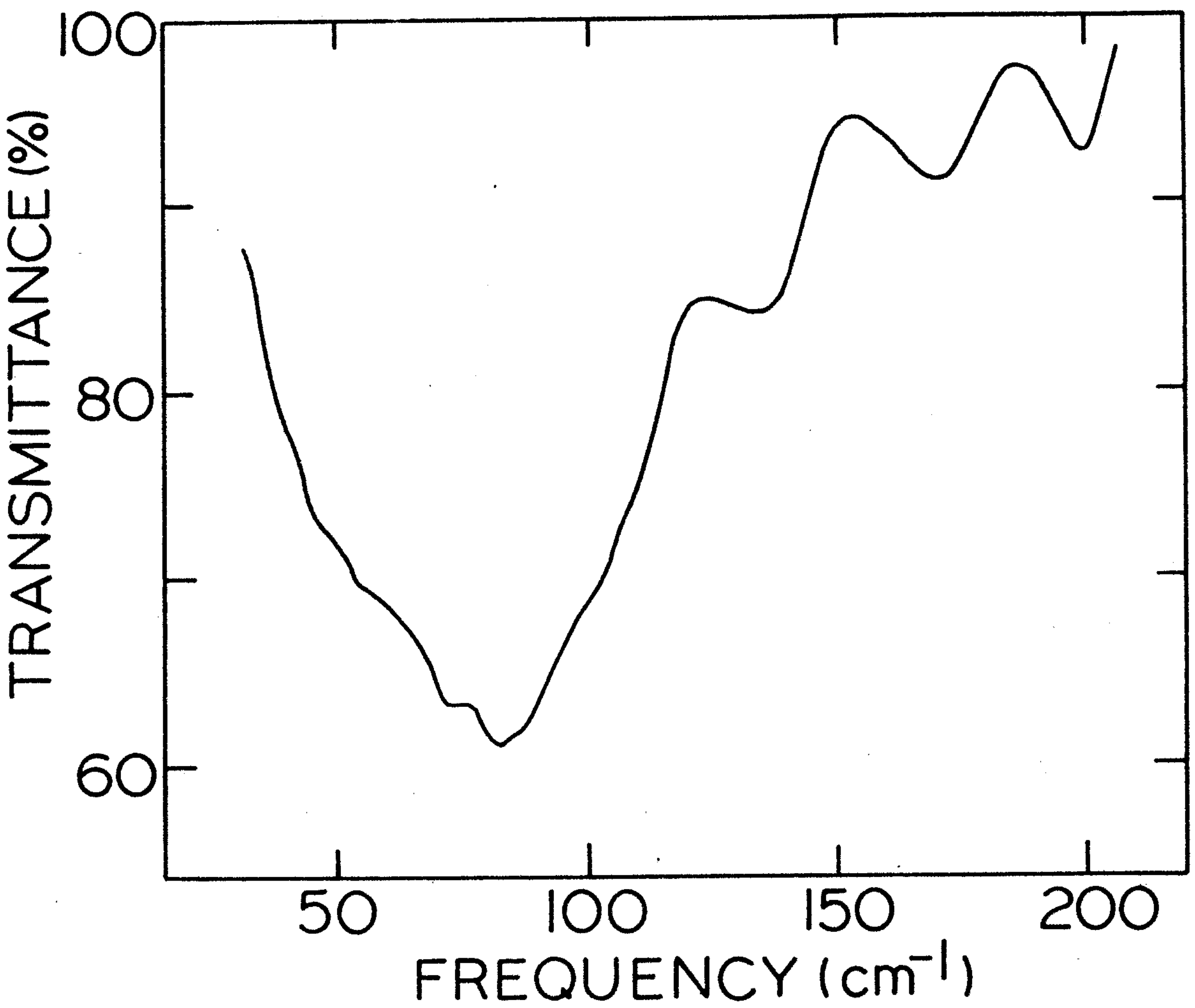


FIGURE 3.4

Far-infrared absorption spectrum of PAT in the liquid phase at 80°C.

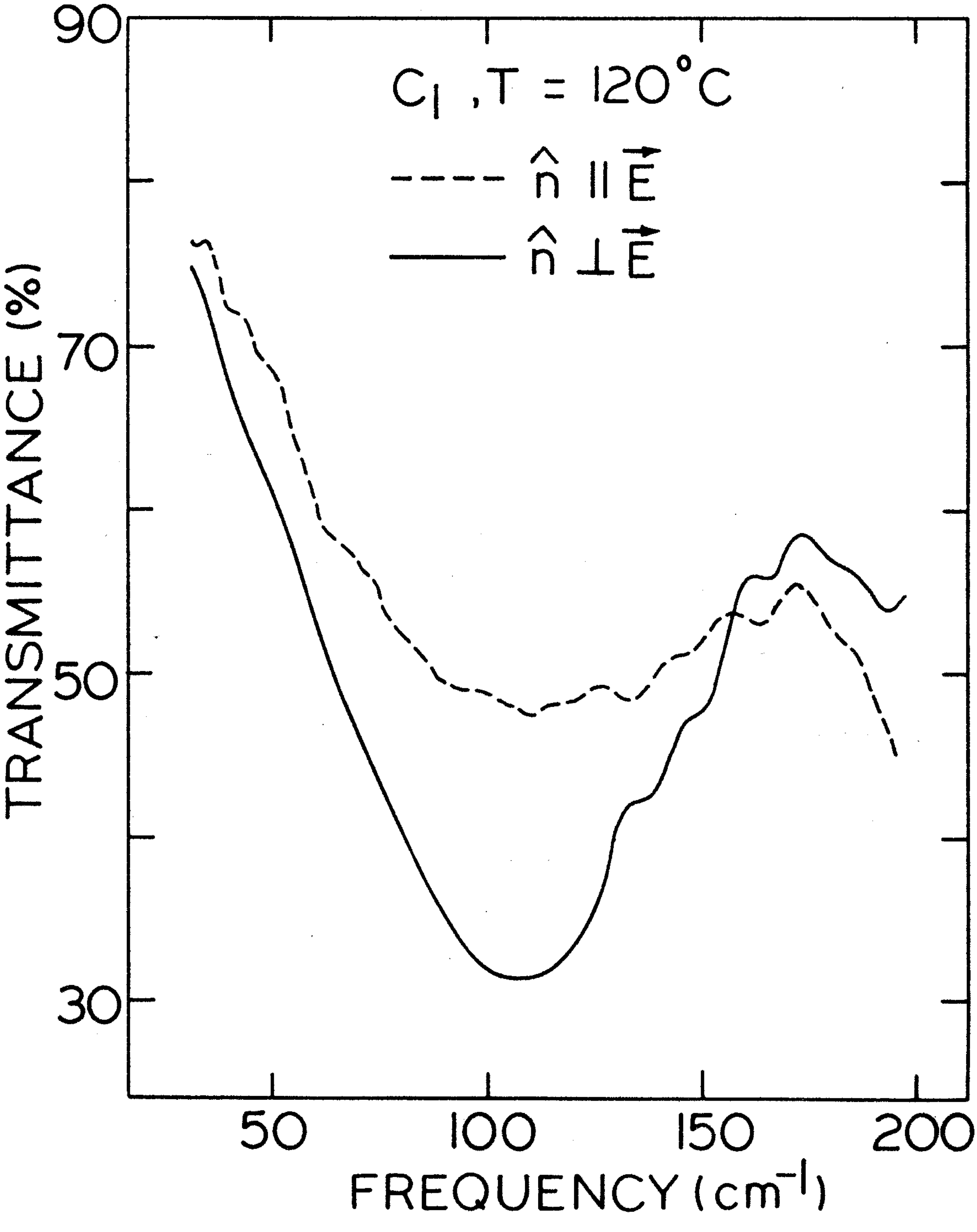
120 - 210 cm^{-1} arises probably due to interference fringe effects. If so, the main band would also be distorted slightly by such fringes. The considerable variation in the absorbance due to the main band would of course limit the validity of a simple fringe subtraction technique in this case over the entire spectral range.[39] In any case, as the possible distortion of the main band should be relatively minor, no attempt was made to eliminate the fringes from this spectrum. The peak position of the band occurs at 83 cm^{-1}. The μ and I values of PAT are almost identical to those of the *trans* form of C_1. Hence the Poley absorption will contribute to its far-infrared spectrum. However, as the methoxy group torsion must be absent now, the overall intensity of the absorption in PAT should be considerably diminished in comparison to C_1. This expectation is clearly borne out by our observations.

The polarization spectra of C_1 in the homogeneously aligned nematic phase are shown in figure 3.5. As noted earlier, the alignment was not quite uniform over the entire sample. Despite this, the spectra do show clear evidence of the dichroic behaviour of the absorption band. From figure 3.3, the methoxy torsional mode should have the major component of its transition moment perpendicular to the long axis of the molecule; this is indeed what is observed.

Examples of other low frequency intramolecular modes that may occur in the region of interest here are: (i) C - X out-of-plane bending modes[53] and (ii) $\angle C - O - C$ bend and CH_2CH_2 torsional modes which are expected[54] when the polymethylene chain becomes sufficiently long. In the present compounds, no distinctly resolvable features are observed that can be attributed to such modes. Between 100 - 150 cm^{-1}, C_4 and C_5 show an augmented absorption as compared to C_6 and C_7. This seems to suggest the presence of a

FIGURE 3.5

Dichroic behaviour of the far-infrared absorption of C_1 in the nematic phase at 120°C. The sample was homogeneously aligned. $\hat{n}$ and $\vec{E}$ denote, respectively, the direction of alignment and the electric vector of the incident radiation.



C_1 , T = 120°C
$\hat{n} \parallel \vec{E}$
$\hat{n} \perp \vec{E}$
TRANSMITTANCE (%)
90
70
50
30
50
100
150
200
FREQUENCY (cm^{-1})

weak feature in this range which is attenuated in C_6 and C_7. It is however clear that these modes are too weak to be distinguished here from the more intense, composite profile of the Poley and torsional absorptions. Such a superposition of the different features discussed above in an unresolved spectrum would also preclude any attempt to evaluate their individual profiles.

Both librational and torsional absorptions should be sensitive to the nature of the intermolecular potential which hinders these motions. Even the slight changes in the near-neighbour environment brought about by the nematic-isotropic transition are generally found to cause a downward shift of 7 - 10 cm^{-1} in the peak position of the absorption bands in the isotropic phase, when compared to the nematic or cholesteric phase.[24,31,32] Bulkin and Lok[28] also noticed that the absorption band of C_1 effectively disappears in dilute solutions of CCl_4, even when the pathlength of the sample is proportionately increased. This again points to the role of the intermolecular potential in determining the character of the far-infrared spectra of these systems.

It is of interest to comment here briefly on the results of some earlier, related studies on liquid crystals. L'vova et al[29] investigated the spectra of C_2 in the different phases using a single beam grating spectrometer. They attributed the central absorption band to the libration of the molecules about the long axis. The contribution from the ethoxy group torsion which is revealed in this study was not considered by them. The peak position of their spectrum in the isotropic phase is nearly 12 cm^{-1} higher than what we have observed. Also, contrary to the above mentioned trend seen at the N-I transition, they have reported a slight increase in the peak position on going from the nematic to the isotropic phase. The reproducible nature of our spectra as also the use of a Fourier transform spectrometer enable us to determine the peak positions with better accuracy. Thus we feel that the differences between our spectrum and that of L'vova et al may reflect their instrumental accuracy.

The far-infrared absorption of N-p-methoxy-benzylidene-p-n-butyl aniline (MBBA)[30,31] and its ethoxy analog (EBBA)[55] have been recently investigated. Vertogen et al[55] who studied EBBA have not published its spectra in the fluid phases. The broad band observed in the nematic and isotropic phases of MBBA has been interpreted by Evans et al[31] as arising entirely from the librational motion of the molecule about the long axis. They applied the Brot-Larkin[5] and Wyllie[3] molecular dynamic models and determined a fit to the experimental absorption profiles in terms of the characteristic parameters of each model. Nonetheless one expects that the methoxy group torsion, which is largely responsible for the intense absorption observed here in C_1, should contribute to the absorption profile in MBBA as well. While the spectra do show a very clear shoulder around 100 cm^{-1} on the low frequency side of the main peak,[30,31] this feature was not discussed by Evans et al. In this context, a careful comparison of the spectra of MBBA and EBBA in the fluid phases might help establish whether the shoulder observed in MBBA originates from the methoxy group torsion.

3.4 Concluding Remarks

The present investigation has shown that in addition to the Poley absorption, the torsional motion of end alkoxy groups can make a significant contribution to the far-infrared absorption of liquid crystals, especially among the lower homologues of a series. The expected trend in the position and the intensity of the torsional band on the specific end group has been confirmed here amongst the first two homologues,

C_1 and C_2. The torsional assignment gains further support from the polarisation spectra of C_1 as also the reduced intensity of the far-infrared absorption in PAT. The mesogenic molecules studied here are all completely asymmetric. The molecular structure[41] of C_1 shows that the torsional motion of the alkoxy groups occurs, strictly speaking around non-parallel axes. Hence the theoretical analysis of these torsional modes will necessarily be a tedious exercise.

The Poley resonance is expected to dominate the far-infrared absorption of $C_4 - C_7$. Compared to the trans form, the cis conformer of the molecules will carry a larger dipole moment because of the additional contribution from the end group moments. However, the cis conformer will become less probable with increasing end chain length and it can lead to a slightly higher Poley intensity only among the lower homologues. As is characteristic of many other polar liquids, the Poley absorption of $C_4 - C_7$ appears considerably broadened. This may well arise from a distribution in the height and width of the potential barrier[5,7] which hinders the librational motion. Collision broadening and the possible spread in I values due to the various conformations adopted by the end chains are other factors that can cause additional broadening.

The molecules we have considered are all of point group symmetry C_1. Hence the librational and torsional bands should, in principle, be observable in the Raman spectra also. However, even in homologue C_1, where the far-infrared absorption is quite intense, there is no direct evidence of a corresponding Raman band in the nematic and isotropic phases.[21,56] Recently Lund et al[57] have shown that in many simple molecular liquids a construction of the 'absorbed energy' profile from the depolarised Rayleigh wing spectra yields information similar to that contained in the far-infrared absorption spectra. It therefore appears that such an analysis applied to the Rayleigh wing spectra of liquid crystals might well prove to be a promising and alternative method of elucidating the molecular motions that are manifested in their far-infrared spectra.

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